STUDIES ON
APPLICATIONS OF RUBBER SEED OIL
IN ELASTOMERS AND PLASTICS

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BY
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..... dedicated to my husband Sabu and

daughters Reemy and Riya

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Ref. No. JD/RT/MGU/2004/RES

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CERTIFICATE

This is to certify that the thesis titled **'Studies on Applications of Rubber Seed Oil in Elastomers and Plastics'** is a bona fide record of the research work carried out by Mrs. Reethamma Joseph under our joint supervision and guidance, in partial fulfilment of the requirements for the award of the degree of **Doctor of Philosophy** in chemistry, under the faculty of science of the Mahatma Gandhi University, Kottayam. The work presented in this thesis has not been submitted for the award of any other degree or diploma earlier. It is also certified that Mrs. Reethamma Joseph has fulfilled the course requirements and passed the qualifying examination for the Ph.D degree of the Mahatma Gandhi University.

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Declaration

I hereby declare that the thesis entitled **'Studies on Applications of Rubber Seed Oil in Elastomers and Plastics'** is an authentic record of the research work carried out by me under the joint supervision of Dr. Baby Kuriakose and Dr. Rosamma Alex of Rubber Research Institute of India, Kottayam. The work presented in this thesis has not been submitted for any other degree or diploma earlier.

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Preface

Hevea brasiliensis is the most important commercial source of natural rubber (NR). The three important by-products and ancillary sources of income from rubber plantation are rubber wood, rubber honey and rubber seed. The fresh seed contain 35% shell and 65% kernel. Dried seed contains about 42% oil. It is extracted by expulsion process. The rubber seed oil (RSO) is semidrying. Fresh oil is pale yellow, but the commercial oil obtained are dark in colour. It can be refined. Although 85% of the area under rubber cultivation in India is in Kerala, the rubber seed processing industry is concentrated in Virudhunagar district of Tamil Nadu, mainly due to favourable weather condition and availability of unutilised capacity in the groundnut oil processing industry.

RSO has been reported to be suitable for soap making, in the manufacture of paints, fatliquor for leather industry, grease and in the preparation of factice. It has been evaluated as an alternative to diesel. However, the full potential of this oil has not been utilized by the industry due to lack of technology and related information in this field. Hence, a detailed investigation has been carried out on the application of RSO and its chemically modified form, epoxidised rubber seed oil (ERSO) in elastomers and plastics.

This thesis is presented in eight chapters. The first chapter consists of a detailed review of the earlier work in this field, especially extraction of RSO, refining, use of oil and its chemically modified forms. The first chapter also explains about vegetable oils, its industrial application/polymer processing, plasticizer and softners, polyvinyl chloride, peptizers, latex compounding and role of coupling agent in silica filled compounds. Review of the work in these areas has become necessary since the work presented in this thesis consisted of use of RSO or ERSO in these areas.

The experimental techniques and details of the equipment used for the study are described in chapter two. Chapters three to eight describe application of rubber seed oil and its chemically modified form in natural rubber, latex foam, various synthetic rubbers and polyvinyl chloride. Chapter three explains the use of epoxidised rubber seed oil as a plasticizer in acrylonitrile butadiene rubber.

The chapter four discusses the effect of RSO as acid acceptor cum plasticizer in polychloroprene compound. Soap prepared from rubber seed oil is used as a foaming agent in natural rubber latex and blends of natural rubber and styrene butadiene rubber latices and the results of the study are presented in chapter V. Chapter VI explains the effect of copper salt prepared from higher fatty acids of rubber seed oil as a peptizer for dirt content estimation of ISNR-5 and ISNR-20. The effect of epoxidised rubber seed oil as a coupling agent and plasticizer in silica filled natural rubber compounds is explained in seventh chapter. The eighth chapter contains the results of the study on the effect of ERSO as a secondary plasticizer/stabilizer in polyvinyl chloride. The summary of the work done and conclusions of the study are given separately towards the end of the thesis.

Contents

Symbols and Abbreviations

AOAC	-	Association of official analytical chemists
ASTM	-	American society for testing and materials
AV	-	Acid value
BIS	-	Bureau of Indian standard
BR	-	Polybutadiene rubber (PB)
CBS	-	N-cyclohexyl 2-benzothiazyl sulphenamide
CCl_4	-	Carbon tetrachloride
CI	-	Compression ignition
CR	-	Polychloroprene rubber
CRI	-	Cure rate index
CS_2	-	Carbon disulphide
CTAB	-	Cetyltrimethylammonium bromide
D		Diffusivity constant
DAE	-	Distillate aromatic extract
DBP	-	Dibutyl phthalate
DEG	-	Diethylene glycol
DINP	-	Diisononyl phthalate
DIOP	-	Diisooctyl phthalate
DMTA	-	Dynamic mechanical thermal analyser
DOA	-	Dioctyl adipate
DOP	-	Dioctyl phthalate
DOS	-	Dioctyl sebacate
DPG	-	Diphenyl guanidine
DRC	-	Dry rubber content
ELO	-	Epoxidised linseed oil
EPDM	-	Ethylene propylene diene monomer
ERSO	-	Epoxidised rubber seed oil
ESO	-	Epoxidised soybean oil
FFA	-	Free fatty acid

FTIR	-	Fourier transform infrared spectrophotometer
GC	-	Gas chromatograph
GLC	-	Gas liquid chromatography
GPF Black	-	General purpose furnace black
HDTES	-	Hexadecyltriethoxysilane
HSL	-	Polymerised 2,2,4-trimethyl 1,2-dihydroquinoline (TDQ)
I V	-	Iodine value
IC	-	Internal combustian
IIR	-	Isobutylene-isoprene rubber
IPPD	-	N-isopropyl-N'-phenyl-P-phenylenadiamene
ISNR	-	Indian standard natural rubber
KOH No.	-	Potassium hydroxide number
LC	-	Liquid chromatograph
LO	-	Linseed oil
LOI	-	Limiting oxygen index
m Pas	-	Milli pascal second
M.T.	-	Metric tonne
MBTS	-	2,2'-dibenzothiazyl disulphide
MgO	-	Magnesium oxide
M_H	-	Maximum torque
M_L	-	Minimum torque
MPa	-	Mega pascal
MPS	-	γ- mercaptopropyltrimethoxysilane
MST	-	Mechanical stability time
MT Black	-	Medium thermal black
mv	-	Millivolts
NA-22	-	Ethylene thiourea (2-imidazolidinethione)
NBR	-	Acrylonitrile butadiene rubber (Nitrile rubber)
Nm	-	Newton meter
NR	-	Natural rubber
OCT	-	Optimum cure time

OTES	-	Octyltriethoxysilane (VP Si 208)
phr	-	Parts per hundred rubber
PRI	-	Plasticity retention index
psi	-	pounds per square inch
PTES	-	Propyltriethoxysilane
PVC	-	Polyvinyl chloride
rev/min	-	revolution per minute
RI	-	Refractive index
rpm	-	Rotation per minute
RSO	-	Rubber seed oil
SBO	-	Soybean oil
SBR	-	Styrene butadiene rubber
SI	-	Spark ignition
Si 69	-	Bis-(triethoxysilylpropyl) tetrasulphide (TESPT)
SP	-	Styrenated phenol
SR	-	Synthetic rubber
SRF Black	-	Semi reinforcing furnace black
SSF	-	Sodium silicofluoride
SV	-	Saponification value
TBLS	-	Tribasic lead sulphate
TCPTS	-	Thiocyanatopropyltriethoxysilane
TDQ	-	Polymerised 2,2,4-trimethyl 1,2-dihydroquinoline (HSL)
TESPD	-	Bis-(triethoxysilylpropyl) disulphide
TESPM	-	Bis-(triethoxysilylpropyl) monosulphide
TESPT	-	Bis-(triethoxysilylpropyl) tetrasulphide
TGA	-	Thermogravimetric analyser
TMTD	-	Trimethylthiuram disulphide
TSC	-	Total solids content
TSR	-	Technically specified rubber
UTM	-	Universal testing machine
UV	-	Ultra violet

VCM	-	Vinyl chloride monomer
VFA No.	-	Volatile fatty acid number
VGC	-	Visocity gravity constant
ZDC	-	Zinc diethyldithiocarbamate
ZMBT	-	Zinc 2-mercaptobenzothiazole
ZnO	-	Zinc oxide
ZST	-	Zinc oxide stability time

%	-	Per cent
ρ	-	Density
δ	-	Delta
η	-	Viscosity
γ	-	Shear rate
τ	-	Shear stress
^0C	-	Degree celcius
dN m	-	Deci Newton meter
E	-	Young's modulus
E'	-	Elastic modulus
E"	-	Loss modulus
g	-	Gram
G'	-	Shear modulus
h	-	Hour
ha	-	Hectare
P_0	-	Initial plasticity
Tg	-	Glass transition temperature
Vr	-	Volume fraction of rubber
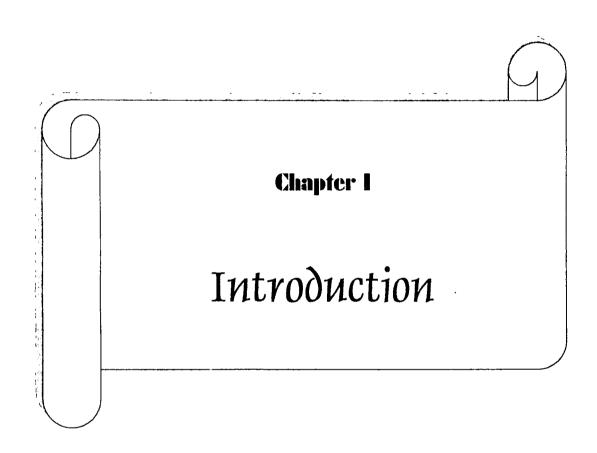
Chapter 1

Introduction

I.1. Rubber Plantation in India

I.1.1. Brief History

Hevea brasiliensis is the most important commercial source of natural rubber (NR). It is a native of the Amazon river basin of South America. It is one of the most recently domesticated crop species in the world and was introduced to tropical Asia through Kew Gardens in the UK, with the seeds brought from Brazil by Sir Henry Wickham. The tree is now grown in the tropical regions of Asia, Africa and America. Commercial cultivation of NR actually started during the 1870's when the British successfully transported Hevea seeds from Brazil for planting in the British India[1,2]. The domestication history of Hevea was chronicled, analysed and reviewed by many[3-8]. The growth of the Indian rubber plantation industry has been mainly through the expansion of rubber cultivation in Kerala. The geographical and agro-climatic suitability proved congenial for rubber cultivation in Kerala.

Natural rubber

Natural rubber (cis-1,4 polyisoprene), has been found in the latex of over 2000 species of plants belonging to 311 genera of 79 families. The minor sources of NR are Manihot glaziovii (Euphorbiaceae), Ficus elastica (Moraceae), Parthenium argentatum and Taraxacum koksaghyz (Compositae). In addition, many other species like Euphorbia intisy (Euphorbiaceae), Cryptostegia grandiflora, C. madagascariensis (Asclepiadaceae), Funtumia elastica and Landolphia sp. (Apocynaceae) have been experimented as possible minor sources of natural rubber. However, Hevea braziliensis is the most important commercial source of natural rubber.

Hevea brasiliensis

The rubber tree is sturdy, quick growing and tall. It grows on many types of soils, provided they are deep and well drained. A warm humid equable climate (21 to 35 °C) and a fairly distributed annual rainfall of not less than 200 mm are necessary for the optimum growth. It however grows successfully under slightly varying conditions also. Rubber trees have a well-developed taproot and laterals.

The bark on tapping yields latex. The cambium, in between the wood and the bark, is responsible for the increase in girth of tree including bark renewal.

The young plants show characteristic growth pattern of alternating period of rapid elongation and consolidated development. The leaves are trifoliate with long stalks. Normal annual leaf fall of mature trees, known as wintering, occurs during the period of December to February in South India. Refoliation and flowering follow wintering. Some trees may occasionally show off-seasonal flowering during September-October also. Pollination is by insects. The fruits mature in about five months after pollination. They are three seeded and burst when mature, scattering the seeds 15 to 18 metres.

I.1.2. Present Status

Since the introduction of the rubber tree in 1878, the rubber plantation sector in India has grown manifold in area of planting, rubber production and productivity.

Table I.1. Total area, tappable area, production, average yield per hectare and consumption of natural rubber

Year	Total area (ha)	Tapped area (ha)	Production (M.T.)	Average yield per hectare (kg)	Consumption (M.T.)
1990-91	475083	306413	329615	1076	364310
1991-92	488514	324540	366745	1130	380150
1992-93	499374	330500	393490	1191	414105
1993-94	508420	338550	435160	1285	450480
1994-95	515547	346270	471815	1362	485850
1995-96	524075	356444	506910	1422	525465
1996-97	533246	365580	549425	1503	561765
1997-98	544534	376970	583830	1549	571820
1998-99	553041	387100	605045	1563	591545
1999-00	558584	394800	622265	1576	628110
2000-01	562670	399901	630405	1576	631475
2001-02	566555	400713	631400	1576	638210
2002-03	569670	407953	649435	1592	695425*

Source : Rubber Board (2003)[9]
* Provisional

Table I.1 gives the details of growth in these areas during the current decade. India is the third largest producer and the fourth largest consumer of NR in the world.

I.2. Ancillary Products From Rubber Plantation
I.2.1. Rubber Wood

The three important by-products and ancillary sources of income from rubber plantations are rubber wood, rubber honey and rubber seed. Among the three by-products, the extent of commercial exploitation of rubber wood is relatively higher, compared to the other two, across the major NR producing countries especially, Malaysia, Thailand, Indonesia, Sri Lanka and India, mainly due to the potential value addition and size of the world market for the rubber wood based finished products. The major products from processed rubber wood are furniture, panel product and household articles. The current estimated value of rubber wood based products is more than U S $ 1 billion.

I.2.1.1. Rubber wood production

The NR plantation area in India is around 0.56 million ha. The annual gross availability of rubber wood was 1.27 million m^3 during 1997-98 and the projected estimate for 2010 is 4.24 million m^3 [10]. The stem wood constitutes 60 per cent of the total timber yield. The remaining 40% is branch wood. Sawn timber suitable for secondary processing amounts to 35% of the stem wood. The current estimated production of rubber wood per ha is 150 and 180 m^3 in smallholdings and estates respectively. At present there are about 100 registered units in the country for processing rubber wood. Some of these units use imported technology and some units are exporting their products. The processing of rubber wood essentially involves a chemical treatment followed by seasoning (drying)[8]. The gross value of processed rubber wood was Rs. 150 million during 2000-01, of which the value of export was only 22% (Rs. 32.91 million)[11].

I.2.2. Rubber Honey

I.2.2.1. Production of rubber honey

The rubber tree is a prolific source of honey, which is obtained from the extra floral nectars at the tip of the petiole and the honey flow period is between the months of January and March. According to BIS specifications, honey is classified into three grades based on the moisture content. It prescribes less than 20 per cent moisture for 'special grade', 20-22 per cent for 'grade A' and 22-25 per cent for 'standard grade'. Rubber honey belongs to medium grade (Grade A) with an average moisture content of 22%.

Organised commercial exploitation of honey from rubber plantation in India is a relatively recent development under the auspices of Khadi and Village Industries Commission (KVIC). The estimates on the production of apiary honey provided by KVIC underline the importance of rubber plantations as a source of honey. In the 1980's the estimated relative share of rubber honey in total apiary honey production in India was about 40%. The sustained decline in the production of rubber honey since 1990-91 was due to the outbreak of Thai sac brood disease and in 1993-94 the production declined to 550 M.T. from the peak level of 2750 M.T. in 1990-91[12]. As a result of the rehabilitation measures, the industry showed signs of revival and the production of rubber honey increased to 4500 M.T. in 2001-2002. The mature rubber plantation in India has the potential to produce 48085 M.T. of rubber honey annually, though the extent of exploitation was less than two per cent of the potential over the years.

I.2.3. Rubber Seed

Rubber seed is an important ancilliary product of the rubber tree having various industrial uses[13]. Rubber (*Hevea brasiliensis*) seeds are light in weight, ovoid shaped and flattened on one side. The seed consists of a hard, brittle shell loosely enveloping a cream coloured kernel. The weight of a seed varies from three to six grams and this variability is due to clonal characteristics, age of the seed and moisture content[13]. Several attempts have been made during the last few decades to exploit thousands of tonnes of rubber seeds, which were allowed to go as waste in rubber estate[13-15].

4

The productivity of rubber seed is 150 kg/ha[16]. The estimated production potential of rubber seed in Indian rubber plantations is given in Table I.2.

Table I.2. Production potential of rubber seed in India

Year	Area under mature rubber (ha)	Production * potential (M.T.)
1900-91	306413	45962
1991-92	324540	48681
1992-93	330500	49575
1993-94	338550	50783
1994-95	346270	51941
1995-96	356444	53467
1996-97	365580	54837
1997-98	376970	56546
1998-99	387100	58065
1999-2000	394800	59220
2000-01	400000	60000
2001-02	400713	60107
2002-03	407953	61193

* Estimated

The seed is used for production of oil and cake and also for raising plant nursery.

I.2.3.1. Composition of fresh seed and kernel

Reports by different authors show wide variations in the composition of rubber seed and dried kernel. The compositions of fresh seed and dried kernel are given in Tables I.3 and I.4 respectively [13,17-27].

Table I.3. Composition of fresh seed

Constituent	Quantity (%)
Shell	35
Kernel	40
Moisture	25

Table I.4. Composition of dried kernel

Constituent	Quantity (%)
Oil	42
Moisture	5
Cake	53

I.2.3.2. Primary processing of rubber seeds

The monopoly of Tamil Nadu in rubber seed processing is due to (1) the coincidence of the seed falling season in Kerala with heavy and continuous rainfall, which necessitates expensive kiln drying; (2) favourable weather conditions; (3) locational advantage of Virudhunagar being a traditional oil seeds processing centre; (4) excess capacity existing in the oil processing mills as rubber seed falling season approximates the slack season of other major oil seeds; and (5) relatively low wage rates. In contrast to expellers, molasses are used in rotaries, which give sour/sweet taste to the processed cake. The processors prefer rotaries to expellers as the profit in rubber seed processing is mainly derived from the sale of cake[28].

The dried kernel contains a small quantity of hydrogen cyanide, which can be lessened by reducing its moisture content and by increasing the period of storage[29] (Table I.5).

Table I.5. Variation of HCN and moisture contents with storage of dried kernel

Period of storage (weeks)	Moisture (%)	HCN content on moisture free basis (%)
0	35.9	0.120
1	29.0	0.023
3	12.7	0.017
4	11.4	0.013
14	8.1	0.006
20	6.5	0.006

Initial studies on commercial utilization of rubber seed revealed that the seed is highly susceptible to damage on storage[30]. The extent to which the quality of the oil contained in the seed is affected, gives an insight into the proper mode of storage and eventually the prospect of industrial utilization of rubber seed oil.

I.2.3.3. Collection and storage of seeds

The seeds start falling from August to October[13,31-33]. This is the seed collection season. However, certain factors have to be controlled while collecting the rubber seeds. Areas where there is rain during the seed falling season would also be unsuitable for seed collection[13]. Rubber seed is susceptible to biological deterioration particularly if left on the ground for more than three days before collection and may yield poor quality oil. Fungal infection and lipase activity increase with time during which the seed remained on the ground[32,34]. Storage of dry seed is necessary for subsequent processing.

Rubber seed has a fat splitting enzyme, which splits rubber seed oil into glycerine and free fatty acids. This makes the oil rancid and unsuitable for industrial use. However, if the seeds are collected within two to three days after falling from the tree and heat treated immediately at over 50 ^{0}C, the enzyme would be destroyed thereby giving a good quality oil of low acidity (not exceeding 2% fatty acid)[31,35]. Free fatty acid (FFA) content of the oil from freshly harvested seed is less than 0.5% (as oleic acid) but increases to almost 27% in two months as a result of storing unsterilised kernel.

It is essential to dry the rubber seeds to the equilibrium moisture content before storage. Drying to the correct level of moisture content slows down the metabolism of the seeds and so makes them to keep longer. It also prevents the growth of fungi and bacteria and considerably retards the activities of insects, pests and mites[36].

Storage is necessary on account of the seasonal nature of the harvest. The storage of moist oil seeds, especially under local conditions, results in mould growth, which in turn causes decomposition of the oil. The kernel cannot be stored for any length of time as it is very prone to attack by insects and worms. Hence, kernel is prepared as and when required. Muralidhara and Madhusudana

Rao[37] recommend DDT spraying on layers of seed to prevent fungal attack on seeds.

The heating of decorticated seeds to a temperature of 120 ^{0}C for over an hour or at 50 ^{0}C for about 48 h may destroy the fat splitting enzyme and the seeds can be stored with no undue increase in free fatty acid content. Hilditch[38] has shown that the oil in the unruptured cell tissues of the kernel is able to withstand, without detriment, the temperature necessary to affect destruction of all enzymes present. It is easier to refine the oil if the FFA content is less than 5%. If a heat-treated seed is decorticated, a pinkish colour can be seen in the inside. This method of storing appears to be satisfactory. Experiments have shown that adequately dried kernel could be kept for 4 months without an appreciable deterioration, even upto 6 months if the humidity during storage was kept under control [31].

Most of the collecting agents decorticate the seeds manually. The seeds when partially dried in the sun, shrink the kernel inside the shell. This facilitated separation of the kernel from the shell without damaging the kernel. The partially dried seeds are placed flat on the ground and cracked with a wooden mallet. Damaged and discoloured kernels are discarded at this stage.

Fresh seed and its kernel contain about 638 and 749mg hydrogen cyanide (HCN) per kg. It is reported that storage at room temperature for a minimum period of 2 months is effective in reducing the HCN content[13,39].

It has been recommended to give a sufficient heat treatment to the rubber seed to inactivate the lipase, soon after collection for storage so as to get a low free fatty acid oil when expelled/extracted.

I.2.3.4. Processing of the seed

85% of the area under rubber cultivation in India is in Kerala, But the rubber seed processing industry is concentrated in places such as Aruppukottai, Thengasi and Nagarcoil of Tamil Nadu. This is mainly due to favourable weather conditions and availability of unutilised capacity in the groundnut oil processing industry[16,40]. A recent development in the mode of procurement of rubber seed is collecting the raw material in the form of kernel. The shell is a good source of fuel. At present, about 65 per cent of the raw material is transported to Tamil

Nadu in the form of kernel and sun dried to reduce the moisture content. Although there are three methods (solvent extraction, expeller and rotary) for extracting rubber seed oil, the rotary method is more common. In India, the preliminary attempts for commercial exploitation of rubber seed was initiated by the KVIC in the late 1960's. The two major products processed from rubber seed are rubber seed oil and rubber seed cake. The production of rubber seed oil and cake for 1997-1998 were 2890 and 4710 tonnes. The production of rubber seed oil and cake for 2002-03 were only 1100 tonnes and 1700 tonnes respectively (estimated).

I.3. Rubber Seed Cake

The main commercial product obtainable from the rubber seed is its oil. The most important by-product after oil extraction or oil expulsion is the rubber seed cake or meal. Though this meal could be used as a fertilizer, the commercial exploitation of rubber seed may in fact be feasible only if this by-product could be sold as animal meal at a reasonably good price[13]. Rubber seed cake contains about 26 to 29% protein[31], compared with 10% protein in coconut cake. If the seeds are not decorticated, then the cake can only be used for manure and could fetch a price of Rs. 140/- per tonne, which is approximately 33% of that obtained if it is sold as animal food. The pressed cake or extracted meal of rubber seed is used as a fertilizer or feed for stock. The meal may be used as a medium protein concentrate in rations for dairy cows and is equal to linseed meal for supporting milk production. Experiment conducted by Talpada et al., show that there was no adverse effect on digestibility of rubber seed oil cake on calves and it can be incorporated in the concentrate mixture of growing calves upto 30% level [41]. Long term tirals with rubber seed cakes on cows show that it can be incorporated in the cattle feed without producing any deleterious effect either on the quality or quantity of the milk or butter produced[42]. Rattnanupong found that rubber seed cake can be used as a feed for goat[43].

Rubber seed cake was formerly used only as a manure. At that time there was some misconception regarding the quality of rubber seed cake as an ingredient of livestock feed[16]. Decorticated seed cake is claimed to be one of the

most digestible concentrated cake foods available and the manurial value of cake is equal to that of linseed cake[35]. The nutritive value of rubber seed cake (Table I.6) is comparable to that of linseed cake and cotton seed cake . But in the case of rubber seed cake, there is a danger in that it contains a cyanogenetic glucoside, which under certain conditions may be converted to the toxic hydrocyanic acid by enzymatic action.

According to Amrithakumar et al.[44] rubber seed cake can safely replace cotton seed cake in the concentrate mixture of cow without affecting milk yield. Rubber seed cake has been evaluated as a source for poultry feeds. The small quantity of HCN present in the cake does not cause any danger to livestock. In India, 50 per cent of the seed cake is used by the cattle and poultry feed manufacturing industries while the remaining is directly used without blending or mixing.

When seed and kernel are pressed in a rotary press, 10% molassess (w/w) was added as a binding material in order to facilitate easy extraction of oil as suggested by Ananthasubramaniam[45].

Table I.6. Chemical composition and nutritive values of rubber seed cake

Component	Nutritive value (%)
Crude protein	29.40
Ether extract	4.88
Crude fibre	7.05
Total carbohydrate	58.33
Calcium	0.22
Phosphorous	0.76

Fermentative modification of protein-rich oil seeds is a traditional practice in Nigeria[46-48]. According to Obeta Ugwuaniyi et al.[49] fermentation improve the acceptability of the seed and oil for industrial, agricultural or human use by changing its chemical composition.

Bhannasiri[50] reported that undecorticated RSO meal contained very high fibre (46 6%) and low crude protein (14.40%). Decortication had reduced the crude fibre content with proportionate increment in the protein content. Buvanendran and Siriwardene[51] and Oluyemi et al.[52] reported that the chemical

composition of decorticated RSO meal varied widely from batch to batch especially in their crude protein and crude fibre content.

I.4. Rubber Seed Oil

Even though Kerala and the North Eastern states are the important areas of rubber cultivation, rubber seed oil production is concentrated in Virudhunagar of Tamil Nadu[53-54]. Nearly 1200 fresh seeds weigh about 5.7 kg from which 4.2 kg dry seed, 2.4 kg dry kernel and 920 g (1 litre) of oil can be extracted[55].

For the production of rubber seed oil having low free fatty acid content, the following precautions must be taken:-

(a)   Early collection of fresh seeds.

(b)   Decortication of seeds to remove the shell, which contains no oil.

(c)   Sterilization of the kernels:-This is necessary to destroy the fat splitting enzymes present in the seed. The kernels are placed in a steam steriliser and heated at atmospheric pressure for a short period [55].

(d)   Drying the kernels in kilns (or in the sun). The ordinary type of copra kiln with a reinforced concrete floor, on which the kernels are spread with a fire at one end below the floor and flue at the other end, is quite suitable[15].

(e)   Storage in a warm dry place.

I.4.1. Extraction of Oil

Different extraction processes, adopted for rubber seed oil production are rendering, pressing and solvent extraction. The extraction of vegetable oils is a difficult matter. Vegetable materials, and in particular some of the oil seeds, contain a large proportion of solid materials associated with the oil. The chief disadvantages of solvent extraction are the high initial cost of the equipment and the fact that some oil seeds   disintegrate under the influence of the solvent and consequently are difficult to handle. However, extraction with solvents constitutes the most efficient method for the recovery of oil from any oil-bearing material. The minimum oil content to which oil cake can be reduced by mechanical expression is approximately the same for all oil seeds, ie. about 2-

3%. Consequently, the oil unrecoverable by mechanical expression, in terms of percentage of the total oil, increases progressively as the oil content of the seed decreases. Substitution of solvent extraction for pressing methods increases the yield of oil[56].

Preparation of rubber seeds

Cleaning

The first step in processing is cleaning to separate foreign materials. The cleaning of seeds is preferably carried out before the seeds are placed in storage.

Dehulling and separation of hulls

Oil seeds are preferably decorticated before they are extracted[35]. Azeemoddin and Rao[18] used rollers to crack the seed and screens to separate hulls and kernels. The hulls of oil-bearing seeds are low in oil content, usually containing not more than 1%. If the hulls are not removed from the seeds before the kernels are extracted, they reduce the total yield of oil by absorbing and retaining oil in the press cake and, in addition, reduce the capacity of the extraction equipment.

Size reduction of oil seeds

The extraction of oil from rubber seeds, either by mechanical expression or by means of solvents, is facilitated by reduction of seed into small particles. A factory pressing rubber seed would consist of the following[34] :

1. Decorticator
2. Roller crusher
3. Heating kettles (steam jacketed)
4. Expeller machines
5. Hydraulic presses (cage type)
6. Filter presses
7. Storage tanks, pumps, boiler etc.

Mechanical pressing may involve decortication and crushing of the seeds and finally, the oil is pressure expelled, filtered and refined. It is presumed that

some amount of remnants may be present in the seed and this would contaminate the oil that comes out from the expeller. It is also suspected that the presence of this small amount of remnants in the oil may make alkali refining and bleaching difficult because of the possible formation of stable emulsion.

Pretreatment of seed and oil recovery

The fresh seed containing high moisture has to be dried in sun or in kiln type dryers to bring moisture to 15 per cent. The seed has to be cracked in rolls and the cracked seed screened to separate hulls and kernels. A two stage crushing of kernels in expellers is reported to produce a cake of 6-7 per cent oil from kernels of 42 per cent oil content.
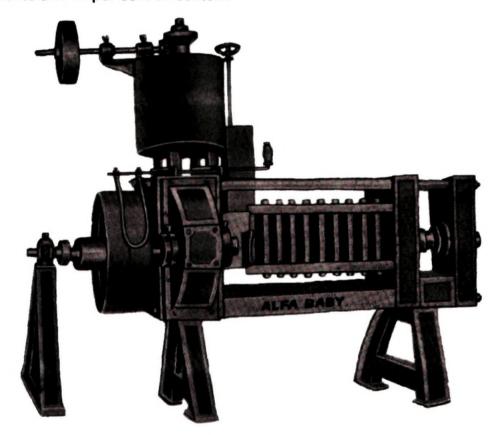
Figure I.1. Oil expeller

The Sri Lankan estimates of oil and cake by expeller method of extraction are as follows [57].

Oil	-	16.7 per cent
Cake	-	69.4 ,,
Residue and other losses	-	13.9 ''

Malaysia used to export rubber seed oil to England, USA, *etc.* during the years 1928 and 1929. Multiple expelling of kernels gave the following results[58].

Oil	-	29.4 per cent
Cake	-	43.5 ,,
Residues other losses	-	27.1 ''

Solvent extraction

The second alternative may be the use of solvents such as petroleum ether, trichloroethylene, hexane and naphtha. Solvent extraction would obviously give a better oil yield than the pressure pressing method.

Extraction trials of whole seed by solvents gave the following yields[59].

Oil	-	19.30 per cent
Meal	-	76.60 ,,
Foots	-	2.93 ,,
Losses	-	1.17 ,,

Attah *et al.*[23] examined the effect of solvent polarity on oil yield and oil properties of rubber seed and found that the equilibrium extracting capacity of each solvent was found to depend on two factors, *viz.*, the nature of the oil and the polarity of the solvent.

Ibemesi *et al.*[60] studied extraction efficiency of different solvents at varying temperatures using rubber seed oil to determine temperature coefficients for enhanced oil removal and the enthalpy changes accompanying the extractions process. Their studies revealed that among all solvents dichloromethane was the most effective solvent in the extraction of rubber seed oil.

The oil obtained by expression has an odour similar to that of linseed oil and is pale yellow in colour. It can be decolourised completely by the use of dilute sulphuric acid followed by filtration with suitable adsorbant[13].

Azeemoddin *et al.*[61] conducted experiments on processing of rubber seed i) decortication, ii) recovery of oil by adapting different methods, *viz.*, hydraulic pressing, expelling and solvent extraction. It was observed that the shells and kernels of rubber seed showed equal bulk density, hence it hampered an effective separation of shells from kernels after decortication by conventional

14

methods. The kernels have a tendency to brown with age and the yield of oil diminishes with increasing brownness of the kernel. Cold hydraulic pressing of rubber seed kernel gave higher oil yield than expeller crushing. Adoption of cold crushing technique in expeller was not successful.

I.4.2. Refining and Bleaching of RSO

Removal of non-glyceride components of oils are called refining. The simplest method is to store the oil for a long time in the cold, when a portion of the contaminants is frozen out and sinks to the bottom (caked foots). In heat refining, the oil is rapidly heated to 250-300 $^\circ$C, precipitation of protein and phosphatides occurs and the insolubilized matter can be removed by filtration or sedimentation. A more effective method consists of treating the oil with hot water or live steam, the oil being kept at a temperature of 55 to 70 $^\circ$C. The greater part of the phosphatides were precipitated as coarse aggregates and may be removed by centrifuging or filtration. The residual water is removed by heating the oil in vacuum.

The raw oil could also be refined by acid or alkali treatment. Acid refining is accomplished by carefully mixing the raw oils to 2% sulphuric acid. Sulphuric acid has the effect of charring and flocculating the mucilaginous matter.

Table I.7. General characteristics of refined RSO

Parameter	Value
Specific gravity	0.9012
Refractive Index, 40 $^\circ$C	1.4656
Viscosity (cps)	38.05
Acid value	9
Saponification value	182
Iodine value	144
FFA (as oleic acid %)	9
Unsaponifiable matter (%)	0.14
Peroxide value (milliequivalent/kg)	0.2

A new possible method for removing the oil soluble proteins from vegetable oil consists in treating them with water and hydrolysing using a proteolytic enzyme eg. Papain. This has the effect of converting the protein to a gelatinous flocculation, which can be readily removed.

According to Njoku and Ononogbu[62] the process of refining improved the quality of the oil. The acid and saponification value of the crude RSO were reported to be high[33]. The lower value after refining is due to the saponification of the FFA during the alkaline treatment in the refining process. Iodine value is higher than reported by Aigbodion[24]. This is due to the fact that the unsaturation level of vegetable oil was found to be affected by many factors including the method of extraction, age of oil and storage. The physical properties show that refining of the oil improved its viscosity and the colour.

I.4.3. Physical Properties and Chemical Composition of Rubber Seed Oil

The rubber seed kernels contain about 42 per cent oil, which is semi-drying type. Fresh oil is pale yellow, but the commercial oil obtained from seeds either by expression or by extraction is dark in colour. The commercial oil contains high FFA. This is because, the seeds deteriorate very rapidly due to high moisture and an endogenous lipase contributes to a rapid rise in FFA.

The properties and composition of the oil have been reported by the Dawson and Messenger[29] and by Azeemoddin and Rao[18]. There is considerable variation in the FFA content of the oil according to the period and condition of storage of seed prior to extraction. Physical constants and fatty acid composition of fatty acids determined by different persons and different methods are given in Tables I.8[20,25,34,63-65] and I.9[21 33,34,63,64,66-70]. This shows that the composition and the quantity of free fatty acids in rubber seed oil can vary considerably. Experiments have shown that while oil extracted from fresh seed is nearly non acidic, the FFA content could rise upto 15-18%[29], if expression has been delayed, permitting fat splitting enzymes to act in the kernel. Enzymatic action could be reduced considerably by drying freshly collected seed so that the moisture is reduced to below 5%. Such dried seed could be stored for over 4 months without a significant increase in its FFA content[13].

The colour of the oil extracted from fresh seed is brighter than that extracted from stored seed. This difference in colour of the oil samples could be attributed to degradation of the oil upon storage of seed since damage of oil is manifested as off-colour, off-odour and increase in free fatty acid. Enzymatic breakdown of rubber seed oil during storage of seeds is accounting for these high level of acidity in oil extracted from stored seeds[31]. Peroxide value, which is a measure of deterioration, also shows that the oil deteriorates in quality during storage of the seed. The oil prepared from fresh seed is inferior in drying properties compared to linseed oil. It is, however, a good substitute for linseed oil in paints.

Methods used for the estimation of fatty acids are gas chromatography, gas-liquid chromatography and urea inclusion process. Rubber seed oil has been reported to have as its constituents, 30-35% of linoleic acid and 21-24% of linolenic acid, giving a property similar to a semi-drying oil such as soybean oil. Rubber seed oil, when alkali refined, could therefore be used in the preparation of air-drying oil modified alkyd. Air-drying alkyds occupy an important place in the paint industry and the demand is estimated at about 16,000 MT (50% solid resin) of which approximately 2,5000 MT of vegetable oil would be needed for the poly-condensation reaction. Rubber seed oil could, therefore, be adopted as a total or partial replacement for the currently used traditional edible oils such as soybean oil or linseed oil in this industry[71].

Storage of RSO

According to Aigbodion[72] RSO stored in metal container with coating inside showed the lowest value of both FFA and peroxide and highest iodine value after 24 weeks of storage.

Table I.8. Physical properties of RSO

Property	1	2	3	4	5	6	7
Specific gravity	-	0.9185	0.9201	0.922	0.920-0.923	0.924-0.93	-
Refractive index	1.4730	1.4	1.4656	1.4703	1.4703	1.466-1.469	-
Iodine value	135.28	145.80	140	131.18	120-124	132-141	137.7
Saponification value	186.0	192.20	192.6	226.35	199	190-195	194.7
Unsaponifiable matter	0.63	1.14	1.2	0.89	0.89	0.5-1	0.7
Free fatty acid (%)	10.93	15.45	4	39-43	19.18	4-40	5.2

Table I.9. Fatty acid composition of RSO (%/weight)

No of c:=bond	Acids	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
14:0	Myristic	-	0.1	0.15	-	1.0	2.2	-	0.2	0.1	0.1	-	0.2	-	0.08	-
16:0	Palmitic	11	8.0	8.7	10.7	9.07	7.6	15	11.36	9.4	10.02	11.02	10.1	7.08	5.9	8.9
18:0	Stearic	12	8.2	9.9	23.8	10.1	10.7	15	8.2	9.3	5.8	9.4	0.3	10.6	5.8	8.5
20:0	Arachidic	1	0.3	-	-	-	-	-	-	-	-	-	-	-	-	-
18:1	Oleic	17	24.8	23.3	47.2	23.5	20.0	58.0	21.4	27.1	27.5	22.95	24.6	25.5	20.1	25.0
18:2	Linoleic	35	36.7	37.1	13.1	39.5	36.0	27.0	37.6	38.9	41.6	40.98	38.9	38.3	32.2	35.2
18:3	Linolenic	24	20.9	20.4	5.4	16.2	23.5	-	20.1	14.95	15.04	14.6	17.1	17.4	35.8	22.4
16:1	Palmitoleic	-	0.3	-	-	-	-	-	-	-	-	-	8.8	-	0.2	-
20:1	Arachidoleic	-	0.2	-	-	-	-	-	-	-	-	-	-	-	-	-
22:0	Behenic	-	0.1	0.09	-	-	-	-	-	-	-	-	-	-	-	-

18

I.4.4. Industrial Applications of Rubber Seed Oil

Rubber seed oil resembles linseed oil in its physico-chemical properties[73]. The suitability of various oils as drying oils for the manufacture of alkyds could be assessed based on the proportions of linoleic (diene acids) and linolenic (triene acids) acids present. Available evidence indicates that oils containing triene acids (eg. glycerol ethers) such as linseed, tung, and perrila oils are yellowing oils, while oils containing diene acids such as rubber seeds, tobacco and soya oils are non-yellowing oils. Although both classes are drying oils, the non-yellowing oils have superior properties for manufacture of alkyd resins. A screening of the oils numerated above reveals that rubber seed, tobacco and conophor oils could be wholly or partially substituted for linseed and soybean oils as drying oils for manufacture of alkyd resins.

Studies on practical utilization of RSO revealed that it has strong potential to substitute linseed oil in alkyd production[74-76]. Generally, rubber seed oil was used in soap making[77,78]. Gandhi *et al.*[67] reported that the rubber seed oil does not contain any unusual fatty acids and it was a rich source of essential fatty acids. Moreover, it's digestibility was found to be 97 per cent as compared to 94 per cent for groundnut oil. From the nutritional and toxicological aspects, the rubber seed oil could be considered for edible use. The oil has found uses in soap, alkyd resin and lubricating oil industries[19,60,64,79]. Several nutritional studies have advocated its use as an edible oil[22,23,73,80-82]. But high lipase activity and residual cyanide, which is common in most plant (oil) in the Euphorbiaceae family, have been limiting factors for their use in nutrition[83]. According to Dayaratne[84] rubber seed contains 25% oil. So it can be used in the preparation of alkyd resin, soap and paint.

An important use of rubber seed oil is in alkyd resins, which are used in large amounts in paint manufacture. Alkyd resins can be made by cooking rubber seed oil with the calculated amount of glycerol and phthalic anhydride.

Rubber seed oil could replace linseed oil in the manufacture of rubber substitutes, paint, linoleum and varnish[77]. It is also suitable for production of fatliquor for leather industry[85]. RSO can be used as a multipurpose ingredient for NR and SBR compounds[86]. RSO imparts excellent mechanical properties to NR and SBR vulcanizates when substituted for conventional plasticizer. It also

improves ageing resistance, abrasion resistance and flex resistance and reduces cure time and blooming. Factice prepared from RSO functions as processing aid in rubber goods manufacture with equal results as those obtained with commercial factice.

I.4.4.1 Soap manufacture

M/s. Lever Brothers (Ceylon) Ltd., have carried out trials with a view to determining the viability of rubber seed oil as an ingredient in laundry/washing soap[13]. This soap compared favourably with the standard product. It is reported that about 300 to 500 tonnes of rubber seed oil blended with coconut oil, can be annually used in soap manufacture in Sri Lanka.

I.4.4.2. Rubber seed oil for paints manufacture

A drying oil suitable for replacement of linseed oil in paints should contain mixed fatty acids with not less than 70% of polyethenoid (linolenic+linoleic) acids, of which linolenic acid should form at least 50% of the total fatty acids of the oil[19]. Rubber seed oil has about 36% of linoleic acid and 24 % of linolenic acid[17]. A mixture of one part of rubber seed oil and three parts of linseed oil has been reported to give a film, which is equal or only slightly inferior to linseed oil itself[13]. A mixture of one part of rubber seed oil and three parts of linseed oil would have 79% of polyethenoid (linolenic+linoleic) acids of which linolenic acid is about 48%[87]. Thus a promising outlet for rubber seed oil is its use as a diluent or extender for linseed oil.

. The drying properties of rubber seed oil could be improved by treating with maleic anhydride. Since maleic anhydride has two carbonyl positions in the α positions in the double bond, it takes part in diene synthesis with conjugated compounds. Maleic anhydride also adds easily to compounds containing isolated double bonds at the α methylene positions. The maleinisation of an unsatrurated oil is a very simple process[31].

Refined rubber seed oil is mixed with 2 to 10% of maleic anhydride and heated in a closed kettle for 2 h at 230 $^\circ$C. The progress of the reaction may be followed by extracting a sample with hot water and titrating to determine the unreacted maleic anhydride. Alternatively, the disappearance of all the maleic

anhydride is indicated when a sample no longer gives a reddish yellow colour with dimethylaniline. The product contains an anhydride group with latent acidic properties. In general, if the treated oil is to be used as a binder, this acidity is neutralised by reaction with an alcohol such as glycerol or pentaerythritol. It is estimated that 16% of maleic anhydride produced is used in alkyd resins and in drying oil[13].

The function of the binder in paint is to bind together the pigment particles and to hold them on to the surface. If the pigment is left out, the binder covers and protects the gloss. Binder in a paint is a polymeric substance or a prepolymer which polymerizes into a 2 dimensional polymeric net work at the surface after applications. RSO is suitable as binder for paints. The binder is either dissolved in a solvent or dispersed in the form of emulsion in the liquid phase.

The presence of the rubber seed oil gives to the synthetic polyesters obtained in this way, the property of "drying" in the air; that means they transform to an insoluble film as a result of polymerisation processes in the unsaturated fatty acid chains. Hence, this oil can be used in the production of paint and lacquers. The outdoor durability, quick drying, inherent flexibility and water re-sistance of alkyd resins make them ideally suited for many surface coating applications such as high grade architectural enamels, primers and undercoaters; interior and exterior enamels, marine paints, house paints; industrial finishes, baking enamels, automotive finishes, plasticizers for nitrocellulose, high temperature baking white enamels in combination with urea formaldehyde resins and emulsion paints.

Alkyds cannot be used successfully where resistance to alkali or other strong chemicals is required. Since alkyd resins are essentially esterification products, alkalis will cause saponification, with resultant disintegration of the film[31]. The evaluation of alkyd resins in emulsion paints has been carried out by Mc Leen[88]. He concluded that they yielded paints of superior adhesion and washability although there was some evidence that washability decreased with storage. The time for drying was longer than with synthetic resin emulsion paints, the brushes could not be cleaned with water since the emulsions broke and solvents had to be used and the whites were just off colour. The basic paint formulations used for the comparisons was one with a low pigment loading-

namely a pigment binder ratio 1:1 equivalent to a pigment volume concentration of 20%. Stress was thus. placed on the emulsions.

The drying properties of rubber seed oil can be regarded as being intermediate between those of soybean and linseed oil[87]. The immediate potential of the use of rubber seed oil in paints could be 400 tonnes to be used instead of linseed oil and 375 tonnes to be used in alkyd resin manufacture. This means that in the paint industry alone 775 tonnes of rubber seed oil can be used annually.

I.4.4.3. In leather industry

The role of oil and oil based fatliquors in leather manufacture is to prevent the adhesion of leather fibres and to impart certain essential characteristics like softness, smoothness and desired strength properties in order to meet the end use. Rubber seed oil has been successfully utilised for the preparation of sulphated oil and the product is found to be satisfactory in its application in the leather production. Experiments on the use of sulphated rubber seed oil as a fatliquor during the fatliquoring process and as a plasticizer in the finishing operation for both the cow hides and goat skins were found to produce satisfactory results. The rubber seed oil was subjected to sulphation by concentrated sulphuric acid at a controlled temperature of 25 ^{0}C . The resultant product was treated with saline water and after allowing to settle, the bottom aqueous layer was discarded by siphoning; the top layer was neutralised with caustic soda solution.

The sulphated rubber seed oil was found to provide clear and stable emulsion with water and complete exhaustion of the fatliquor was observed during the fatliquoring process. The rubber seed oil, as plasticizer, behaved quite well during finishing in respect of easiness of glazing, plate-release and tackiness characteristics.

Leathers treated with sulphited rubber seed oil were softer than those treated with sulphited cotton seed oil A study of the rubber seed oil viz, chemical analysis, preparation of fatliquor and application has proved its viability in the production of highly soft leathers with grain tightness[89].

I.4.4.4. Preparation of grease from rubber seed oil

Grease was produced using the method of Ononoghu *et al.*[90] by a three step process.

(a) Saponification of the oil using sodium hydroxide.

(b) Double decomposition of sodium soap using calcium chloride

(c) Production of grease from calcium soap by adding excess bleached oil.

The colour of the grease produced using oils from the different clones were comparable although storage period has a marked effect on the texture of the grease produced Lubricants produced have good qualities such as brighter colour, higher flash and fire point, lower oxidation value and good saponification values. These qualities confer important characteristics such as resistance to oxidation, tendency to form less carbon during friction and high temperature resistance for improving the operational efficiency of the machine. Rubber seed oil has been found to be potential raw material for grease production[62].

I.4.4.5. Rubber seed oil as a fuel for diesel engines

Rubber seed oil has been evaluated as an alternative to diesel fuel by different research groups. Tests conducted on fuel related properties and engine performance evaluation indicated that the cetane rating of RSO is close to ASTM specified minimum value of 40 for No. 2 diesel oil, which is actually encouraging.

Test conducted on specific fuel consumption, brake power, brake thermal efficiency and exhaust temperature with brake mean effective pressure for the fuels at 2600 rev/min. indicated that RSO shows a considerable similarity to those of diesel oil. In all engine performance tests methyl ester of rubber seed oil (MRSO) also behaved very much similar to diesel oil.

RSO has fuel properties very similar to other vegetable oils. Comparisons with fuel properties of diesel oil indicate that crude RSO meets ASTM limits for cetane number, flash point, total and active sulphur, and water and sediment. However it fails to meat the ASTM limits for viscosity, ash content, carbon residue, cloud and pour points, some of which could be improved by refining the oil.

Amongst the fuel properties of RSO tested, the crucial factors must be high viscosity and distillation characteristics. The high viscosity is found to affect

the charactristics of the fuel spray and thereby causes a number of detrimental effects. The higher distillation temperature (i.e. low volatility) might have an effect on vaporization and combustion characteristics. Fuel properties of MRSO were found to be much more closer to those of diesel oil.·

Short-term engine performance tests indicate that RSO, MRSO and blends of RSO and diesel fuel are very much similar to diesel oil in terms of power productivity, thermal efficiency and specific fuel consumption[91].

Spray penetration, cone angle and droplet size measurements show that RSO sprays are markedly different from those of diesel oil. RSO was bleached and methyl ester was prepared by trans esterification with 6 molar excess of methanol using sodium hydroxide as catalyst[92]. Another work based on rubber seed oil was done by Takeda[93].

I.4.4.6. Preparation of stearic acid

In Sri Lanka a source of stearic acid is RSO. Hydrogenation of the fatty acid from RSO yields about 80% (w/w) of stearic acid[94].

I.4.4.7. In spray oil

Rubber seed oil is used in spray oil in the ratio 3:1[95], for aerial spraying of fungicides.

I.4.5. Chemical Modification of Rubber Seed Oil
I.4.5.1. Epoxidation

Epoxidation of vegetable oil is conveniently effected by a wide range of peracids such as peracetic acid, performic acid, perbenzoic acid etc. usually generated by reacting hydrogen peroxide with the relevant organic acid catalysed by a mineral acid like sulphuric acid. The role of the organic acid is to transfer the active oxygen atom from the aqueous phase to the oil phase, as the hydrogen peroxide and the unsaturated oil alone do not react to any significant extent[96].

The two routes of epoxidising vegetable oils are the following

1. The method in which the peracid is preformed and then used for epoxidation.

2. The procedure in which the peracid is generated 'in situ' in the reaction vessel. The 2nd method is preferable for safety reason.

Extensive works on the 'in situ' epoxidation of rubber seed oil (RSO) by peracetic acid have been carried out in the laboratory[97]. These studies show that the 'in situ' technique of epoxidising RSO can be modified advantageously for optimum yield of epoxide.

Factors affecting epoxidation

In addition to the mole ratios of acetic acid and hydrogen peroxide to the oil, reaction temperature and the concentration of the catalyst are critical to get epoxidised products with the desired oxirane oxygen content. According to Nagiah et al.[98] the optimum amount of sulphuric acid catalyst (2-2.2% on the weight of hydrogen peroxide and acetic acid) must be employed to get the maximum oxirane oxygen content of the epoxidised oil. With lower amount of catalyst less amount of oil is epoxidised even in longer time. Higher dosage of the catalyst appears to lead to partial opening of the oxirane ring.

For example, linseed oil has been epoxidised to high oxirane oxygen contents using sulphuric acid and a cation exchange resin (Amberlite resin CG-120) as catalyst. Sardine oil, when epoxidised under the same condition as linseed oil gives a product with lower oxirane oxygen content. The product obtained from castor oil or dehydrated castor oil (DCO) has very low oxirane oxygen content. This may be due to the presence of hydroxyl group in these oils and the existance of conjugated unsturation in DCO. Both these oils became very viscous after the epoxidation reaction.

Mechanism

Peracid oxidation of C=C bond in a non-polar solvent like dichloromethane gives excellent yield of corresponding epoxidation. The reaction is first order in nature with respect to the olefin and the peracid and it is a bimolecular process.

$$R-\underset{\underset{OH}{|}}{\overset{\overset{O}{\parallel}}{C}} + H_2O_2 \longrightarrow R-\underset{\underset{O-O}{|}}{\overset{\overset{O}{\parallel}}{C}} \diagdown_H + H_2O \qquad \text{---- I (1)}$$

$$R-\underset{\underset{O-O}{|}}{\overset{\overset{O}{\parallel}}{C}} \diagdown_H + \diagup^{\diagdown}C=C^{\diagup}_{\diagdown} \longrightarrow \underset{\diagdown}{C}\overset{O}{\underset{\diagup}{——}}C + R-\underset{\underset{OH}{|}}{\overset{\overset{O}{\parallel}}{C}} \qquad \text{---- I (2)}$$

The product analysis shows that the reaction is stereospecific. ie, cis-olefin yields the cis epoxide and trans olefin give trans epoxide[99].

Numerous methods are available for carrying out the epoxidation reaction, but the most widely used and general method by far is the direct single step epoxidation of unsaturated compounds with organic peroxy acids.

$$R\text{-}CH=CH\text{-}R'+R''\text{-}CO_3H \longrightarrow R-\underset{\underset{O}{\diagdown\diagup}}{CH-CH}-R' + R'' \ CO_2H \qquad \text{---- I (3)}$$

Peroxy benzoic acid is used as the oxidising agent to prepare several epoxides from unsaturated compounds. Since then, hundreds of unsaturated compounds have been successfully epoxidised in yields that are usually high and often quantitative. Numerous inert solvents have been investigated, most widely used are benzene, chloroform and ethyl acetate. Monoperoxy phthalic acid is frequently used for preparation of acid labile epoxides because the peroxy acid reduction product, phthalic acid, is insoluble in chloroform, the usual solvent for the reaction and epoxide ring opening by the carboxylic acid is thereby avoided or minimized.

Although earlier work indicated that peroxy acetic acid could not be used for epoxidation, it has become the most widely used peroxy acid since 1945 because conditions for obtaining high yields of epoxides with a minimum of side reactions were developed and it has been commercially available since 1947 as a 40% solution in acetic acid. Other advantages are that it has a low equivalent weight, a high epoxidation efficiency and a reasonable level of stability at ordinary temperature. Epoxidation of unsaturated compounds with peroxy acetic

26

acid can be conducted in aqueous, non aqueous, homogeneous and hetergeneous media, thus boardly extending the range of epoxidation.

Meta chloroperoxy benzoic acid (85% purity) a stable solid became available commercially in 1962. The rate of epoxidation is higher with this peroxy acid than with peroxy benzoic acid and peroxy acetic acid.

Trifluoro peroxy acetic and peroxy formic acid are also high-speed epoxidising agents but the reaction conditions must be more carefully controlled to avoid lose of epoxide by ring opening with the strong acids formed (trifluoro acetic acid and formic acid respectively).

Effect of solvent

Solvents also affect the rate of epoxidation but the mechanism of their action is not clear. Attempts to correlate solvent effects with dielectric constants have not been too successful. Those solvents, however, which can form intermolecular hydrogen bonds with peroxy acids may reduce their effective concentration by solvation and thereby lower the epoxidation rate. Thus rates are generally lowest in ethyl ether, t-butyl alcohol and acetic acid and fastest in chlorinated solvent and in benzene. The enthalpy and free energy of activation increase and the entropy of activation decreases when a solvent is employed that slows the rate. These results are consistant with the conclusion that the more effective the solvating effect of the solvent for peroxy acid, the lower the rate.

The use of preformed peracetic acid is less applicable to the use of the peracetic acid formed *in situ* since the same byproducts will be present. The side reaction of these byproducts with epoxy group may be minimised by conducting the synthesis in such a way as to maintain phase separation between the epoxy compound and the peracetic acid reactants. This can be accomplished by the use of a large excess of water, when the material being epoxidised is substantially water-insoluble as with natural oil or alternatively, anion or cation exchange resins may be used. If sufonated polystyrene is used, the bulk of the ion exchange resin contains the majority of acetic acid, H_2O_2 and sulfonic acid catalyst, while excluding the higher weight molecules being epoxidised. The ion-exchange catalyst is pre-treated to rid it of metal and a metal sequestering agent

is used during the reaction. The ion exchange resin may be recovered at the end of synthesis.

In synthesising water-sensitive epoxy molecules, it is advantageous to use dehydrated form of the carbon exchange resin, the exchange resin additionally preventing emulsifications by acting as a desiccant.

The *in situ* process may be improved by the addition of a small amount of acid anhydride to the acetic acid/H_2O_2 mixture. Improved yields are obtained from the epoxidation if the initial reaction is conducted at 20 to 25 $^\circ$C for few hours, followed by ½ to 2 hours at 50 to 60 $^\circ$C. 80% of the epoxidation is accomplished at the lower temperature the higher temperature is required only for the last 10-15% of the reaction.

Different methods of epoxidation

Method 1

Rubber seed oil mixed with benzene, acetic acid and sulphuric acid were taken in a round-bottomed flask. Hydrogen peroxide (30%) was added slowly over a period of 2h. The reaction mixture was then maintained at 60 $^\circ$C for 14h. The product was poured in water and the oil layer was washed free of acid[100]. Coomarasamy and Kandasamy[101], epoxidised rubber seed oil and this product could be used as a plasticizer/stabilizer for chlorinated polymers and as a plasticizer in certain alkyd resin formulations.

Method 2

The *in situ* epoxidation of rubber seed oil by peracetic acid had been carried out in laboratory scale by Aigbodion *et al*,[97]. Their studies showed that the *in situ* technique of epoxidising RSO can be modified advantageously for optimum yield of epoxide. Such modifications include use of acetic acid to oil mole ratio >/= 4 and reaction temperature of about 333K (60 $^\circ$C) resulting in minimum oxirane ring opening thereby yielding a product of high % oxirane suitable as plasticizer/stabilizer.

Method 3

Epoxidisation reactions were carried out at 333K (60 $^\circ$C) using performic acid generated *in situ* by the reaction of 30% hydrogen peroxide and formic acid.

In the experiment, RSO (0.14mole), formic acid (0.09 mole) and 30% hydrogen peroxide (0.44 mole) were used[96]. Calculated amounts of RSO and formic acid were placed in 500 ml round bottom flask fitted with a reflux condenser, magnetic stirrer and thermometer. The required amount of 30% hydrogen peroxide was added to the oil dropwise over a two-hour period with constant stirring at predetermined temperature. Progress of reaction was monitored by measurement of the oxirane content of the reaction.

The time of attaining the maximum epoxide content decreased as the reaction temperature increased and was much shorter for epoxidation with performic acid. Therefore epoxidation of RSO with performic acid is more economical.

I.4.5.2. Maleinization and production of alkyd emulsion

Maleinized rubber seed oil (MRSO) was prepared by heating RSO with maleic anhydride under reflux at temperature between 200 and 230 °C for about 90 min[102]. Rubber seed oil was used in the production of alkyd emulsion. Malenized rubber seed oil is used to formulate water-soluble alkyd sample. Acid, saponification and iodine value were affected by malenization. The MRSO samples were of relatively lower volatile organic compounds compared to their corresponding alkyd derivative. While MRSO samples exhibited poor chemical resistance, the alkyd exhibited excellent resistance to acid, water and fair resistance to alkali.

I.4.5.3. Preparation of factice

Factice is recognised as a valuable processing aid and is classed among the compounding ingredients of the rubber technologists. This material possesses certain intrinsic properties, which make it indispensable in mixes during milling, calendaring, extrusion and injection moulding[103,104]. In SBR compounds, factice at the level of 5 phr exhibits accelerating powers and permits low accelerator levels without affecting tensile and modulus of the stock. In neoprene compounds, 10 phr of factice improves the processing behaviour of the elastomer. In butyl tubes the use of factice imparts good extrusion

characteristics, ageing properties to the stock and helps easy black incorporation[105-107]

A wide range of vegetable oil is employed for factice preparation. Linseed, rapeseed, cottonseed, soybean and fish oils are some of the widely used glyceride oils[108] There is indigenous production of factice from linseed oil and rapeseed oil[109]. India produces 400 tonnes of factice annually and approximately the same is the consumption.

Crude RSO (A.V. = 9.79, I.V. = 138.1, S.V=194.1) was heated to 170-175 ^{0}C and powdered sulphur was mixed in. At first, sulphur dissolved in the oil, forming a colloidal dispersion. The viscosity of the mixture gradually increased and finally instantaneous gelling occurred. The colour of the reaction mixture also changed during the progress of the reaction. It was light yellow initially and dark brown towards the final stages. The product was cooled, leached with water and dried[110].

Based on the factice production economy, rubber seed oil may be an ideal substitute for other factice making oils. The cost of raw materials (oil and sulphur) for making factice from RSO will be less than that of other oils.

I.4.5.4. Manufacture of alkyd

A coating is basically composed of binders (film formers), pigments and solvents. Volatile organic solvent is injurious to human health and it is also perceived to be a contributory factor to global warming and depletion of the ozone layer[111]. Alkyd resins are widely used as binders in surface coating due to their unique properties such as colour and gloss retention, film flexibility and durability and compatibility with other resin system. Their peculiar property of compatibility with binders such as acrylics and urethanes has facilitated their use in formulating environment friendly coating in recent times[111-118]. Alkyd resins are defined as products of condensation between polyol, usually having an average functionality equal to or greater than 3 and a polybasic acid, usually dibasic acid or its anhydride modified with monofunctional acid most commonly C_{18} fatty acid or triglyceride[119,120] Such a reaction involving the reactants of average functionality equal to or greater than 3 are prone to net work formation arising from the possibility of a 3-dimensional reaction. The performance quality of alkyd

30

resins as binders becomes optimum at a point during the synthesis when molecules of appreciable sizes are formed[121,122]. Previous researchers[24,62,71,123,124] showed that RSO is a potential raw material in the production of alkyd resin. According to Aigbodion and Pillai[125] properties such as rate of drying and resistance of the alkyds are optimum at 50% oil length.

Oxygen absorption constitutes the initiation stage of autoxidative polymerisation of unsaturated oil, leading to hardening on exposure to air. This phenomenon is known as drying in coating industry. Researchers form Scotland, UK,[126] studied oxygen induced polymerisation of blends of fatty acid from seed oils of rubber, watermelon, soybean and linseed for optimizing the drying performance of the semidrying ones for development of alkyd resin paint binders. For oils of the same geometry of unsaturation, oxygen absorption correlates well with the degree of unsaturation and thus gives a good indication of the drying characteristics expected of such oils [127-129]. A fatty acid of an oil exhibits higher oxygen absorption than the parent oil. This effect arises from the participation of carboxyl group in the decomposition of peroxide formed during the autoxidation process [130,131].

According to Aigbodion and Okieimen[132] the complexity of side reactions like unequal reactivity of the functional groups and the varying degrees of olefinic polymerisation make it difficult to apply theoretical concept in predicting the gel point (beginning of cross linking of molecule).

Raw materials for manufacture of alkyds

The main ingredients in the manufacture of alkyd resins are:
    i)   Rubber seed oil
    ii)   Polyhydric alcohol eg. glycerol.
    iii) Polybasic acid in form of phthalic anhydride - the aromatic ring imparting hardness and toughness to the resin.

Properties of refined rubber seed oil required for alkyd production are the following
    a.   Density: 0.92-0.93 (15 ^{0}C)
    b.   Refractive index 1.474 (25 ^{0}C)
    c.   Iodine value: 134

d. Free fatty acid : 0.3%

e. Acid value: 2

Glycerol, which is required for the reaction could be obtained locally after refining and purification of spent lye (a byproduct of soap manufacture, which contains 18% glycerine).

The basic ingredient of polybasic acid is phthalic anhydride, which is a petroleum-derived material. Phthalic anhydride could be produced either from naphthalene, by vapour phase oxidation of naphthalene using air in presence of a catalyst, usually vanadium pentoxide, or by catalytic oxidation of orthoxylene using vanadium pentoxide as well.

Alkyd preparation

There are two main methods in the manufacture of alkyds:

i)   The alcoholysis process

ii) The fatty acid process

The alcoholysis process is used in preference to the fatty acid process because it is more economical.

Alkyd resin is made by esterification in which phthalic anhydride; refined rubber seed oil and glycerine are reacted together under application of heat and catalyst with elimination of water. Alkyd resins could be classified into the following groups:

(a)   According to the content of the fatty acid or oil.

Short oil alkyd resins: less than 40% oil/fatty acid

Medium oil alkyd resins: 40-60% oil/fatty acid

Long oil alkyd resins: above 60% oil/fatty acid

The oil content is calculated as the triglyceride portion of the non-volatile matter.

(b)   According to the modifying component

Alkyds could be modified in order to obtain specific application properties for example, with benzoic acid, phenolic resins, vinyl toluene, styrene, isocyanates and acrylic, to mention a few.

I.5. Vegetable Oils in Industrial Application/ Polymer Processing

I.5.1. Definition and Classification of Oil

Oils

There are 4 types of oils occurring in nature.

1. Mineral Oil

Mineral oils are mixtures of various hydrocarbons occurring under the earth's crust. Important ones are petroleum, kerosene oil, paraffin oil etc. They have generally unpleasant odour.

2. Essential Oil

These are pleasant smelling liquids occurring in plants. eg. Lemon oil, sandal wood oil, rose oil, clove oil. They mainly consist of terpenes along with aldehyde, ketone, esters, alcohols etc.

3. Waxes

Waxes in general are the mixtures of esters of higher fatty acids with higher monohydric alcohol such as cetyl, myricyl etc. They usually contain higher acids and alcohols in the free state (Paraffin wax is a mixture of higher alkanes).

4. Oils and Fats

They are generally the glycerides of stearic, palmitic and oleic acids. The important difference between oils and fats is that oils are liquids at ordinary temperature and fats are solids. The glycerides constituting the oils contain large proportions of unsaturated acids such as oleic acid, linoleic acid and linolenic acid while glycerides constituting fat contain larger proportions of saturated acids such as lauric acid, myristic acid or stearic acid[133].

Oils and fats are the major component of a class of organic compounds called lipids. The source of oils and fats are plants and animals. Vegetable oils and fats are obtained from the fruits and seeds of plants. They are esters of long chain fatty acids with trihydric alcohol – mixed triglycerides and are non-volatile.

Unlike mineral oils, vegetable oils are commonly referred to as fixed oils or fats because these oils have a fixed composition and boiling point. These oils are inherently less stable than mineral oils because of high degree of

unsaturation and consequent susceptibility to polymerization or gum formation. Both thermal degradation and oxidation of vegetable oils result in the formation of polymeric materials.

I.5.2. Type of Vegetable Oil
Edible and non-edible

This difference depends either on the composition or on the purity. Those fats and oils, such as wool fat and castor oil, which are non-edible due to their composition, can not be converted into edible fats by processing, whereas those which are inedible because of the presence of unpleasant impurities can usually be made into edible products by purification. Oils like cotton seed oil, rubber seed oil, calophyllum oil, kusum oil etc. are non-edible due to the presence of small amounts of toxic components like cyanolipids or cyanoglucoside or small amount of coumarins. Castor oil contains major percentage of ricinoleic acid. It causes stomach disorder and hence are non-edible. Though linseed oil contains no toxic components it is not used for edible purpose due to the presence of large amount of linoleic and linolenic acid, which are precursor of cholestrol[134].

I.5.3. Structure and Composition
a. Triglycerides

They are formed by the reaction of the trihydric alcohol, glycerol (glycerine) and fatty acids – predominantly straight chain containing 12 to 18 carbon atom (rarely 20, 22 carbon atom also). In addition to the chain length of the acid, an important characteristic of oil is the degree of unsaturation. The fatty acids present in oils and fats contain even number of carbon atom. This is because of the particular structure and nature of common biosynthetic mechanism by which the acid grows by the addition of two-carbon atoms at a time. As the proportion of fatty acids in fat is about 95% of the total weight of the molecule, the chemical performance depends on the fatty acid present in the triglycerides.

Structure of simple triglyceride and mixed triglycerides are as shown below.

$$CH_2 - OOC - R$$
$$CH_2 - OOC - R$$
$$CH_2 - OOC - R$$

Simple triglyceride

$$CH_2 - OOC - R$$
$$CH - OOC - R'$$
$$CH_2 - OOC - R''$$

$$CH_2 - OOC - R'$$
$$CH - OOC - R''$$
$$CH_2 - OOC - R'''$$

mixed triglyceride

The acids from six carbon atoms onwards are generally called fatty acids, because no lower acid is usually seen in fats and oils.

The major components of almost all fats and oils are the C_{18} saturated and unsaturated acids, the exception being coconut oil and palm kernel oil where the main fatty acid present is lauric acid with a good quantity of myristic and palmitic acids.

Table I. 10. Saturated fatty acids present in fats/oils

No	Name	Molecular formula	Structure
1.	Caproic acid	$C_6 H_{12} O_2$	$CH_3 - (CH_2)_4 - COOH$
2.	Caprilic acid	$C_8 H_{16} O_2$	$CH_3 - (CH_2)_6 - COOH$
3.	Capric acid	$C_{10} H_{20} O_2$	$CH_3 - (CH_2)_8 - COOH$
4.	Lauric acid	$C_{12} H_{24} O_2$	$CH_3 - (CH_2)_{10} - COOH$
5.	Myristic acid	$C_{14} H_{28} O_2$	$CH_3 - (CH_2)_{12} - COOH$
6.	Palmitic acid	$C_{16} H_{32} O_2$	$CH_3 - (CH_2)_{14} - COOH$
7.	Stearic acid	$C_{18} H_{36} O_2$	$CH_3 - (CH_2)_{16} - COOH$
8.	Arachidic acid	$C_{20} H_{40} O_2$	$CH_3 - (CH_2)_{18} - COOH$
9.	Behenic acid	$C_{22} H_{44} O_2$	$CH_3 - (CH_2)_{20} - COOH$

Table I.11. Unsaturated fatty acids present in fats/oils

No	Name	Molecular formula	Structure
1.	Oleic acid (Mono-unsaturated)	$C_{18} H_{34} O_2$	$CH_3 - (CH_2)_7 - CH = CH - (CH_2)_7 - COOH$
2.	Linoleic acid (Di-unsaturated)	$C_{18} H_{32} O_2$	$CH_3 - (CH_2)_4 - CH = CH - CH_2 - CH = CH - (CH_2)_7 - COOH$
3.	Linolenic acid (Tri-unsaturated)	$C_{18} H_{30} O_2$	$CH_3 - (CH_2)_2 - CH = CH - CH_2 - CH = CH - CH_2 - CH = CH - (CH_2)_6 - COOH$
4.	Palmitoleic acid (Mono-unsaturated)	$C_{16} H_{30} O_2$	$CH_3 - (CH_2)_5 - CH = CH - (CH_2)_7 - COOH$

I.5.4. General Characteristics of Vegetable Oils

The properties of oils and fats are generally those of the compound glycerides. These are greatly influenced by the fatty acid components.

Physical properties

Specific gravity

It is the ratio of the weight of a unit volume of the sample at 25 ^0C to the weight of a unit volume of water at 25 ^0C.

Refractive index

The index of refraction is the degree of deflection caused in a ray of light in passing from one transparent medium into another. Refractive index is measured by the angle through which beam of light is bent when passing through a thin film of oil.

Iodine value

It is a measure of the proportion of unsaturated acids present and gives an idea of the drying character. Iodine value will give a figure of the total degree of unsaturation, number of grams of iodine absorbed by 100 g of oil.

Saponification value (Koettstorfer number)

It is the number of milligrams of KOH required to saponify 1 g of the sample. It is a measure of mean molecular weight of the fatty acids present in the fat.

Unsaponifiable matter

It is a measure of the water insoluble components produced after heating the fat with potassium hydroxide. During this process all the triglycerides are broken down to form glycerol and potassium salt of fatty acid (soap). Both of these are water-soluble. The insoluble hydrocarbons, sterols and fatty alcohol do not dissolve. High value indicates contamination or adulteration.

Acid value

It is a measure of free fatty acid present in a fat. It is the number of milligram of potassium hydroxide required to neutralise the free fatty acid in one gram of oil.

Peroxide value

It is an indication of deterioration of fats. As oxidation takes place, the double bond in the unsaturated fatty acids are attacked, forming peroxide. These break down to produce secondary oxidation products, which indicate a condition known as rancidity.

Titre

Solidifying temperature of the fatty acids prepared from fats and oils.

Smoke point

The temperature (under standard test conditions) at which, continuous smoke stream is observed.

Flash point

The temperature at which, flash appears when a test flame is applied under standard condition.

Fire point

The temperature at which, the flame continues to burn for 5 seconds after the application of the test flame.

Pour point

It is the lowest temperature at which oil can flow. The more straight the chain, the molecular structure, the higher the pour point. Higher the molecular weight, higher the pour point.

Aniline point

It is the temperature at which equal portions of oil and aniline are miscible. Aniline point tends to increase with molecular weight or viscosity and decreases with increase in aromatic content. Oils having low aniline point tend to be compatible with most rubbers.

I.5.5. Vegetable Oils of Commercial Importance[135]

The search for alternative sources for hydrocarbons has been stimulated in recent years due to the depletion of petroleum reserves on one side and the increasing demand for petroleum products on the other[136] Information on commercial aspects related to the availability of oil seeds, yield, extraction and general properties are covered by several investigators[137-139].

Castor oil

Two grades of castor oil arc generally produced, one for medicinal purposes and the other for industrial applications[140].

Castor oil is more viscous than other vegetable oils. It is due to the high content of ricinoleic acid, $CH_3(CH_2)_5CH(OH)CH_2 CH = CH(CH_2)_7 COOH$, present in it which readily forms intermolecular hydrogen bonds. Its viscosity changes only slightly with temperature. It has a low pour point and a low coefficient of friction and with the result that castor oil is considered suitable for lubricating fairly heavy machinery. It has also been used as a component in lubricants of aero engines[141]. It is one of the few vegetable oils with functional acids.

Castor oil like linseed oil and soybean oil, is subjected to various

modifications like epoxidation, blowing, acetylations etc., along with dehydration to give dehydrated castor oil (DCO). All these derivatives and the raw oil seem to be used widely in plastics and rubbers more. Acetylated castor oil imparts better tensile strength and modulus to EVA copolymer film. If dehydrated castor oil is substituted for DBP in nitrile rubber, plasticizing effect is increased, maintaining physicochemical properties and ageing resistance at an equal level.

Linseed oil

Linseed oil is widely used among drying oils, especially in the field of paints, varnishes and other coatings. Epoxidised linseed oil (ELO) is a generally accepted plasticizer for PVC. One to five per cent loading in PVC imparts good heat stability. It is also used in pressure sensitive PVC adhesive tapes. As in the case of plastics it can impart heat stability, low temperature flexibility etc. to elastomer also. Reaction product of ELO with alpha or beta naphthylamines can be used in NR as a plasticizer and antioxidant. It decreases the viscosity, causes no blooming and disperses well in NR. Dynamically crosslinked thermoplastics and nitrile rubber blends with good processability and physical properties are prepared by the addition of about 2 phr of ELO. Aniline and phenyl hydrazine modified ELO is used as multipurpose ingredients in NR and SBR. They act as plasticizer, accelerators and antioxidants. There are a few examples where the derivatives other than epoxide are also used as plasticizer. Acetoxy methyl derivative of linseed oil as plasticizer in PVC can give equal or superior properties compared to conventional diester plasticizer.

Linseed oil as such is used as plasticizer in a few elastomers. Ten to fifteen phr loading of linseed oil in vulcanizates of neoprene rubbers, imparts a heat resistance of >500 h at 120 °C and >50 h at 150 °C. Soybean oil and rapeseed oil also have this property. Vulcanizate properties of neoprene and 1:1 blend of cis-polyisoprene with 1,4 cis butadiene with linseed and other oils were evaluated by Velchewa et al.[142]. Heat and ozone resistance of chloroprene rubber compounds can be modified with 3 to 3.5 phr linseed oil.

Soybean oil

It is one of the most widely used edible oils and comes under the category of semidrying oils. soybean oil (SBO) like linseed oil is also subjected to various

modifications like epoxidation, blowing etc. and the products are being used in plastics and rubbers. Epoxidised soybean oil (ESO) can also impart, low temperature flexibility and heat resistance, to vinyl chloride polymers. Light resistance is also imparted to vinyl chloride polymers by epoxidised soybean oil. Plasticizers of high stability and compatibility are prepared by epoxidising acetylated monoglyceryl acetates of soybean oil, cottonseed oil etc. The storage stability of EPDM and the heat stability of its vulcanizates are increased by incorporating ESO. Two per cent ESO in chlorinated rubber film can increase its heat stability, whereas DOP has little effect. Lockshow and Colin[143] patented a process for preparing hard, strong and abrasion resistant vulcanizates from carboxylated nitrile rubber with ESO as plasticizer. It also imparts good mouldability and release properties to acrylonitrile-styrene polymer.

Rapeseed oil

Rapeseed oil contains traces of sulphur compounds. It has a lower saponification value (higher molecular weight) than other vegetable oils because of its high content of erucic acid (40-55%) and about 10% of other acids with more than 18 carbon atoms. It is more viscous than ordinary oils, except castor oil. It remains fluid at low temperature due to high content of erucic acid and consequently higher degree of unsaturation. Indian rape oil is used extensively in lubrication, especially in machinery where pressures and speeds are quite high[144-146].

Cottonseed oil

Cottonseed oil contains more saturated fatty acids than most oils of equivalent iodine number. This oil generally contains saturated acids 25%, oleic 25% and linoleic acids 50% approximately. It has a higher pour point than castor and rapeseed oils. Due to the presence of significant quantities of saturated acids, which are likely to be deposited in cold weather, the oil is less suitable for lubrication. Refined cottonseed oil has been used for lubrication under conditions of light load and high speed[144, 146].

Coconut oil

Most of the characteristics distinguishing coconut oil from other oils may be traced to a high content of high molecular weight fatty acids. Although coconut oil solidifies at ordinary atmospheric temperatures, its low melting point (24-27 ^{0}C) is due to low molecular weight of its glycerides. It contains a variety of fatty acids, which differ mainly in molecular weights rather than degree of unsaturation. About 90% of the fatty acids in coconut oil are saturated, the prominent being lauric acid. Since its unsaturation is low, coconut oil is extremely resistant to the development of rancidity. As the pour point of the oil is quite high, its utilization for lubrication purposes is limited[146].

Palm oil

Iodine value of palm oil is higher than that of coconut oil because of high content of unsaturated acids in it. However, palm kernel oil has lesser quantity of the short chain, low melting saturated fatty acids, namely caproic and caprylic acids. This oil contains 63% trisaturated, 26% disaturated monounsaturated and 11% monosaturated diunsaturated glycerides. The free fatty acid content of palm oil, like coconut oil, is ordinarily quite high. These oils are used in metal working operations involving high pressures and low speeds[144, 146].

Mahua oil

Mahua oil is similar to tallow and is non-edible oil. Its fatty acid composition is oleic acid 43.3%, linoleic acid 13.7% and lignoceric acid. 1.0%. The only known utilization of mahua oil is, as a lubricant in wool processing and its sulphurized derivatives are reported to have good extreme pressure characteristics[137,139,147].

Karanja oil

In karanja oil, oleic acid is the principal unsaturated fatty acid averaging to about 50 to 60%. Other acids present are, linoleic 9.7%, palmitic 6.06%, dihydroxy stearic 4.36%, arachidic 4.3%, lignoceric 3.2%, stearic 2.2% and myristic 0.23%. Fresh extracted oil is yellowish orange to brown and darkens rapidly on storage. Raw karanja oil has not been used for lubrication purposes but the sulphurized product has good extreme pressure characteristics[137,139,147].

I.5.6. Chemical Modification of Vegetable Oils

I.5.6.1. Epoxidation

Epoxidation is a chemical reaction by which an olefinic double bond is converted by an active oxygen agent, peroxy acid or peracid, to a cyclic three membered ring structure containing oxygen commonly called oxirane or epoxide[148-150]. Epoxidised vegetable oils find wide applications as plasticizer/ stabilizer for vinyl polymers and in organic synthesis[151,152]. Vegetable oils such as vernonia oil naturally containing epoxy (oxirane) groups are well known[153,154].

Current commercial requirements for epoxidised vegetable oils as plasticizer/stabilizer suggest that they should have oxirane content of at least 5% and low iodine value[155]. Epoxidised products also find their use in the formulation of anticorrosive coatings, adhesives and in alkyd resin. Kuddus *et al.* have reported the epoxidation of cottonseed, safflower and tobacco seed oils[156].

Methods for Epoxidation

Epoxidation by inorganic peracids

Use of a tungstic acid catalyst deposited on an inert solid support permits the direct epoxidation of olefin by H_2O_2. Pertungstic acid is the intermediate. The peracids are electrophilic, consequently they react readily if substituents have electron-donating properties (alkyl group). Whereas if the substituents have electron withdrawing property (eg carboxyl group) the epoxidation is retarded. Alkyl ethers, because of the electron attracting properties of the ethereal oxygen atom, are not readily epoxidised by peracetic acid. Hence, glycidyl ethers are not often produced by this method.

Epoxidation of linseed oil using Zeo-karb 225

Linseed oil was epoxidised *in situ* with hydrogen peroxide and acetic acid using Zeo-carb 225(a crosslinked polystyrene sulphonic acid) as catalyst[157].

Epoxidation of oleic acid using Dowex 50W-8X

Oleic acid was epoxidised by preparing peracetic acid *in situ* using Dowex 50 W-8X as catalyst [157].

Epoxidation of linseed oil by H_2SO_4 (50%) catalyst

In a typical reaction, 100g linseed oil (0.689mole of ethylenic unsaturation), 20 g.benzene, 23 g glacial acetic acid(0.38mole) and 50%, sulphuric acid (2.2% on hydrogen peroxide and acetic acid) were used. Hydrogen peroxide (31%, 109g, 1mole) was added slowly over a period of 2 h at 50 °C. The reaction mixture was then maintained at 60-65 °C for 14h. The product was poured in water and the oil layer was washed with water until free of acid. The product had 7.3% oxirane oxygen.

Epoxidation of linseed oil using hydrofluoric acid as catalyst

A maximum oxirane oxygen content of 6.8% was obtained when 0.55 mole of glacial acetic acid and 1.4 moles hydrogen peroxide (30-32%) per mole of ethylenic unsaturation of the oil in the presence of 2% hydrofluoric acid (40%) on the weight of glacial acetic acid and hydrogen peroxide were reacted under conditions given above.

Epoxidation of linseed oil using phthalic anhydride

A mixture of 100g linseed oil (0.689 mole of ethylenic unsaturation), 100g benzene and 148 g (1 mole) phthalic anhydride was heated to 50 °C and 109 g (1mole) hydrogen peroxide (31%) was added over a period of 2 h with continuous stirring. The temperature was raised to 60-65 °C and maintained at that level for 6 h. The product had only 6% oxirane oxygen content.

Epoxidation of maize oil using acetic acid

Xanthium strumarium and maize oils were epoxidised in situ using 30% hydrogen peroxide, glacial acetic acid and concentrated sulphuric acid (diluted to 50% solution) as catalyst. The residual unsaturation, percentage oxirane oxygen, refractive index, number average molecular weight and viscosity were determined. The oils were epoxidised to satisfactory oxirane oxygen content with 30% hydrogen peroxide at 65 °C in 10 h[158].

According to Gall and Greenspan[159] and Nagiah et al.[98] use of 0.5-0.55 mole of acetic acid per mole of ethylenic unsaturation of the oil yields products of higher oxirane content. It was also reported by Greenspan and Gall[160] that acetic acid higher than 0.5 mole leads to a product with low oxirane content due to

catalytic effect of excess acetic acid in oxirane ring opening. 2 to 2.2% of sulphuric catalyst (based on the total amount of hydrogen peroxide and acetic acid) is reported to be the optimum amount for epoxidation reaction. More of the catalyst appears to lead to part opening of the oxirane ring.

Determination of oxirane oxygen percentage

Several methods have been used to determine the oxirane content of epoxidised oils. Volumetric[161-164], NMR[165], thin layer chromatography[166,167], gas liquid chromatography[168,169], colorimetric[170-172], viscosity measurements[173-174] were reported to be useful tools for this.

To study the effect of epoxidation reaction on the structure of the oil, the infra-red spectra of the oil samples (oil sample and epoxidised oil) were found to be useful. The normal characteristic band frequencies of the oil in the case of both sample and epoxidised oils were seen clearly. As epoxidation progressed, new medium intensity band due to formation of epoxy groups appeared at 893, 847 and 820 cm^{-1}. The intensity of these bands increased progressively as the epoxidation period increased. The shoulder at 3077 cm^{-1} disappeared due to epoxidation of the ethylene double bond. The strong band at 3554 cm^{-1} indicated the formation of hydroxyl groups as epoxidation progressed. The intensity of the band increased gradually as epoxidation period increased, thereby showing the possible ring opening reaction of epoxide group and formation of newer hydroxyl groups.

The chromatographic techniques are not accurate, gas chromatography gives too low results owing to the partial decomposition of the labile epoxy esters on the column and the thin layer chromatography gives high results. The colorimetric methods are simple and reproducible but diepoxy fatty acids could not be detected. In some volumetric methods (the indirect methods) the presence of carboxylic acids may interfere and thus a correction for the amount of acid present in the sample has to be made. In general, these methods require an appreciable greater time, especially in the preparation of the standard solutions.

I.5.6.2. Modification of epoxidised oil with amines

Epoxidised oleic acid can be modified with naphthyl amine to produce antioxidant and antirads used in rubber mixes. Thus they can be used as multi functional additives in NR[175].

CH₃-(CH₂)₇-CH=CH-(CH₂)₇-COOH +CH₃-COOOH ------------→   ---- I (4)

CH₃-(CH₂)₇-CH-CH-(CH₂)₇-COOH
                \ /
                 O   (1)

epoxidized oleic acid

CH₃ ~~~~~ HC·CH ~~~~~ COOH +   [naphthalene with NH₂] ----------→   ---- I (5)
            \ /
             O

CH₃ ~~~~~ HC-CH ~~~~~ COOH
            | |
           HO NH—[naphthalene]   (2)

CH₃ —————— HC-CH ——————— C – NH—[naphthalene]   (3)   ---- I (6)
            \ /   ‖
             O   O

Oleic acid was epoxidised by preparing per acetic acid *in situ* using Dowex 50 W-8x as catalyst. The oxirane oxygen content of the epoxidised oleic acid was found to be 4.5%. The reaction of epoxidised oleic acid with naphthylamine was carried out in sealed tube at 130 °C under inert atmosphere for 2 hours[176].

Thus, the reactive functional –NH– group is attached to the backbone of the fatty chain and this exhibits the function of a typical amino-antioxidant, depending on the fact that the reactivity of a functional group in the polymeric chain is practically the same as in the simple organic molecule.

Epoxidised oleic acid modified with p-phenylene diamine can be used as effective antioxidant in rubber vulcanizate, in the absence of stearic acid. The

45

use of high molecular weight or polymeric antioxidant for rubber formulations is a very useful trend to avoid the drawbacks of simple organic compounds[177].

$CH_3-(CH_2)_7-HC-CH-(CH_2)_x-COOH$ + $H_2N-\langle\rangle-NH_2$ ---→
                    $\overset{\backslash}{O}{}^{\prime}$

CH_3-------HC-CH--------COOH
            HO NH

            $\langle\rangle$

            HO NH
CH_3-- ---HC CH------COOH

---- I (7)

CH_3------HC-CH------C-NH-$\langle\rangle$-NH-C------HC-CH------CH_3
            HC NH   O   O   HO NH
            $\langle\rangle$ $\langle\rangle$
            HO NH   O   O   HO NH   (Form I)
CH_3------CH-CH------C-NH-$\langle\rangle$-NH-C------HC-CH------CH_3

---- I (8)

                         HC – CH
                         HO NH
            NH_2
HC – CH + $\langle\rangle$ ——— $\langle\rangle$
   \O/   R   R

Where – R = –H, –OCH3 or –CH3

---- I (9)

                         HC – CH
                         HO NH
            NH_2
HC – CH + $\langle\langle\rangle\rangle$ ——— $\langle\langle\rangle\rangle$
   \O/

---- I (10)

Linseed oil and dehydrated castor oil[178] were epoxidised with hydrogen peroxide and acetic acid using Zeo-Karb 225 as catalyst. The epoxidised oil was then modified with aromatic amine. The reaction product is a good antioxidant for rubber vulcanizates and also markedly affect the Mooney viscosity of the compound during processing. Thus, it can be used as bifunctional

46

(antioxidant/plasticizer) additive for natural rubber compounds. This product also is less volatile, does not bloom to the surface and disperse well in NR mixes owing to the high molecular weight. The labile nature of the -NH- group hydrogen atom affects markedly the efficiency of the antioxidant[179].

Simple organic compounds such as aromatic amine derivatives, phenolic compounds and phosphorous containing compounds are well known antioxidants. However, as their molecular weights are relatively low, they become volatile and may bloom to the surface and they cannot be homogenously dispersed during mixing in the rubber matrix. Thus, the use of polymeric or high molecular weight antioxidants is very useful trend to avoid the above-mentioned drawbacks.

Theoretically, each primary amino group is capable of reacting with two epoxy groups under normal conditions. The formation of tertiary amine is difficult because of steric hindrance. Hence, each primary amino group reacts only with one epoxy group. ie. the reaction usually stops at the stage of secondary amino group formation. Thus, the reactive functional -NH- group is attached to the backbone of the oil chain (long fatty chain) and this may exhibit the function of a typical amino-antioxidant in addition to the plasticizing effect of the oil.

I.5.6.3. Preparation of factice

Factice is essentially, vulcanized vegetable oil and it is prepared by heating finely powdered sulphur with vegetable oils at selected temperatures. The colour of the factice is directly connected with the iodine value of the oil used. Higher the iodine value, darker will be the colour of the factice obtained. Good quality factice is usually produced from oils having iodine value in the range 80-160. Other oils such as rapeseed oil, linseed and castor oil can also be used for the manufacture of factice. The oils used in the manufacture of factice have saturated and unsaturated fatty acids in the form of triglycerides. The greater the content of unsaturated fatty acids the better the factice will be, as the reaction of vulcanization with sulphur or sulphur chloride is a reaction of crosslinking of the double bonds present in the acid chain. The mechanism of the reaction of sulphur with oil is polar in nature and not a free radical one[180,181].

Brown factice

Dark types are prepared by heating some vegetable oils, most commonly rapeseed oil with sulphur at 140-160 ^{0}C. Lighter types, also called golden factice, are prepared at lower temperatures after addition of accelerators. Cheaper types are sometimes extended by addition of unsaponifiable oils. eg., paraffin oil, or bitumens.

White factice

This factice is produced by mixing a sufficient amount of sulphur monochloride into rapeseed oil. In order to prevent too violent a reaction, the oil or the sulphur monochloride is diluted with an inert diluent, which evaporates under the heat of the reaction. In order to neutralize hydrogen chloride developed during storage, a small amount of calcium or magnesium oxide is added.

White factice is a yellowish-white crumbly mass with a characteristic smell. Its acetone extract is up to 50% and its acidity (calculated as hydrochloric acid) is less than 0.I5%. White factice retards vulcanization owing to its acidity and therefore it is seldom used for hot air vulcanization. Only in rubbers for erasers and at a sufficient dosage of sulphur and strongly basic accelerators can the required course of vulcanization be achieved. The retarding effect of white factice on vulcanization is sometimes made use of for compounds with a tendency to scorch. The addition of several phr of white factice eliminates this difficulty and improves the processability at the same time.

Special factices

In addition to the ordinary types, special factices, for CR, NBR and butyl are also produced. The special factices for CR and NBR do not affect the swelling of vulcanizates. A factice free of sulphur and chlorine is used for heat resistant butyl compounds. Specially treated factices for the cable industry are also available.

Application of factice

Factice is a rubber substitute, which is essentially added to rubber, in preparing compounds of different composition for the manufacture of certain rubber articles, like erasers, tubes and tyres.

Table I.12. Application of factice in rubber products

Product	Dosage of factice (phr)
Shoe upper stock	5-10
Cable insulation and ebonite	10-15
Cycle tube	15-20
Extruded articles	20-30
Roller cover stocks	30-40
Eraser	300-500

Factice gives to moulded, calendered and extruded goods a smooth finish, which cannot be obtained by any other compounding ingredient. The surface finish of rubber goods is also improved because factice restrains the blooming of sulphur and oil. Factice imparts resistance to surface oxidation and to ozone and improves resistance to moisture.

I.5.6.4. Fatliquors

Fatliquors are sulphated or sulphited oils. These are prepared by the following methods and used for tanning leather.

Sulphated oil:- It is prepared by reacting the oil with 25-30% sulphuric acid (99.5% purity) at 25 ± 2 ^{0}C followed by washing with brine and neutralisation to pH 6.5 using 35% NaOH solution.

Sulphited oil:- Sulphited oil is prepared by subjecting the oil to oxidative sulphitation using 25-30% solution of sodium bisulphite at 70 ± 5 ^{0}C for a period of 10-15 h. The final pH of the product is adjusted to pH 6.5, if necessary, with a suitable base like ammonia or triethonolamine.

The sulphation can be effectively carried out at low temperature 25 ± 2 ^{0}C. The sulphated oil is very clear and forms a stable emulsion in water. The presence of highly unsaturated acids makes it amenable for oxidative sulphitation to produce sulphited oil. Use of sulphated/sulphited oils as fatliquor helped to introduce fat in the tanning step itself with the simultaneous uniform

uptake of fat chrome in single operation. Sulphited fatliquor is more stable than the sulphated one.

I.5.6.5. Alkyds

The methods of manufacture of alkyd resin have been described in section 1.4.5.4.

In esterification reaction the rate of change in acid value depends on the following factors; different reactivities of primary and secondary hydroxyls of glycerol with carboxyls of phthalic anhydride, proportions of hydroxyl and caboxyls, changes in temperature and removal of water of condensation[182].

Estimation of extent of polyesterification and degree of polymerisation (which is a measure of sizes of molecules) could be done empirically through end group analysis like determination of acid value of the in process samples[183]. Similarly, Kienle et al.[184] also reported the study of polycondensation reaction by determining acid value of reaction mixture at different stages of reaction and calculating extent of reaction thereof.

Application of alkyds

Alkyds are used mainly as binders in paints and coatings. In coating applications of alkyds, it is required that the alkyds be capable of forming hard and durable film after application on the substrate. Such alkyds have been found to be composed of fairly large molecules[185].

I.5.7. Uses of Vegetable Oil
I.5.7.1. Soap

Soaps are salts of the fatty acids, and they are usually prepared either by neutralizing the pre-formed fatty acids with an alkali, or by direct saponification of a fat or mixture of fats or oils by treatment with an alkali, according to the equation shown below:

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$$
\begin{array}{lll}
CH_2\,OOCR & & CH_2\,OH \\
| & & | \\
CHOOCR + 3NaOH \longrightarrow & 3RCOONa + CHOH & \quad ---- \text{ I (11)} \\
| & & | \\
CH_2\,OOCR & & CH_2\,OH
\end{array}
$$

Fat   Sodium   Soap Glycerine
hydroxide

Manufacture of soap from oils and fats

The conversion of fat into soap proceeds according to the above equation:

Pre-mixed fat charge (fat, water, lye and brine) are heated to about $100\,^{\circ}C$ by means of open steam. Simultaneously, caustic soda solution is added in small amounts and the whole mass is kept thoroughly agitated by the passage of steam. By gradual addition of the caustic liquor and careful control of the current of steam, saponification takes place rapidly and the addition of caustic liquor can be completed in a few hours. The content is thoroughly agitated with open steam and brine is added cautiously until the soap separates in the form of a thick curd. Settling is allowed to take place for a few hours. The lower layer of aqueous liquid is then withdrawn. It is 'lye'and contains most of the glycerine originally present in the fat.

The crude curd soap is washed in order to remove alkali and more glycerine, by reboiling it with just sufficient water to form a homogeneous liquid and adding sufficient brine to induce the reformation of curd, which is again allowed to settle. The lye is removed.

Properties of soap

The properties of the soaps are governed by the nature of the fatty acids from which they are derived and, to a lesser extent, by the nature of the cation with which the fatty acids are combined. The typical soap-like characteristics are exhibited by the salts of the fatly acids ranging from about C_8 to C_{20}. Within this range, the corresponding salts of the saturated fatty acids show a regular gradation in such physical properties as rate of solution, foaming characteristics, and tendency to form gels; for example, sodium laurate (C_{12}) is rapidly soluble and the solution yields a profuse, open-textured lather. Whereas sodium stearate (C_{18}) is less readily soluble, its solutions have a greater tendency to gel, and they

yield a less voluminous, close-textured, more stable lather. The soaps derived from the unsaturated acids such as oleic acid are softer, more readily soluble, and have less tendency to form gels than the soaps derived from the saturated acids containing a similar number of carbon atoms. Commercial soaps usually consist predominantly of the salts derived from the saturated acids lauric (C_{12}), myristic (C_{14}), palmitic (C_{16}) and stearic (C_{18}) and the unsaturated acids palmitoleic (C_{16}) and oleic (C_{18}). By a fortunate coincidence, these acids occur abundantly in fats and oils readily available to the soapmaker. Vegetable oils are used for soap manufacture since they are readily available at a lower cost. They are very rich in fatty acid content also.

I.5.7.2. Paints

Some oils when coated to surfaces exposed to atmosphere sets to a thin film forming a dry protective coating. This property is used in the industrial production of oil based coating materials like paints and varnishes. The drying of oils is related to the unsaturation in the oil[186], which is represented by its iodine value. Hence, oils are conventionally classified based on their iodine values in to 3 groups, drying, semidrying and non-drying (Iodine value is >140, 140-125 and <125 respectively). When oil contains conjugated double bonds, the iodine value determined is usually low due to incomplete halogen absorption such a classification can only be used for a rough guidance.

The Von Eyk brother is said to be the first to use linseed oil as a binder[187] whereas Chinatung oil has been used for centuries as a coating for wood objects including, boat, house and furniture.

In the case of fast drying oil with conjugated double bond, such as tung oil and dehydrated castor oil, heat treatment is necessary to gas proof them, so that the oil does not dry to form undesirable wrinkled film.

The oils are not often used in its original form of triglycerides for coating application. It has become a common practice to hydrolyse them first and the free fatty acids are then used to synthesize coating resins with certain advantages. Through trials, it was found that some mixtures of different oils could be used with greater advantage and that natural gums could be added.

I.5.7.3. As a fuel

Recent concern over the price and availability of liquid petroleum fuels has created substantial interest in alternative sources of fuel for internal combustion (IC) engines. In this context, materials such as alcohols, biogas, producer gas and vegetable oils have been identified as suitable fuels. Fuel properties such an octane and cetane number, self-ignition temperature and calorific value are the most important criteria that influence the choice of fuel for spark ignition (SI) or petrol engines and compression ignition (CI) or diesel engines. These fuel properties of some of these materials are compared in the Table I.13.

Table I.13. Important fuel properties for choice of fuel

Fuel	Octane Number	Cetane Number	Calorific Value (MJ/Kg)	Ignition Temperature	Type of Engine Preferred
Petrol	79-98	5-10	45.0	high	SI
Diesel	-	45-55	45.0	low	CI
Ethanol	106-111	0-5	26.7	high	SI
Methanol	106-I 15	-	20.0	high	SI/CI
Biogas	-	-	25.0 MJ/m3	high	SI/CI
Producer gas	-	-	45-5.0 MJ/m3	high	SI/CI
Vegetable oil	-	35-40	39.0	low	CI

While alcohol fuels have been found to be more suitable for SI engines, vegetable oils fuels have been proven to be and appropriate fuel for CI engines. Engine modifications to a greater or lesser extent would be required for use of these fuels.

Vegetable oils have been used as fuels especially during petroleum shortages. In most cases, however, the interest failed due to increased availability of more economical petroleum derived fuels. The very large increase in oil price during 1973 signalled renewed interest in the use of vegetable oils such as sunflower, corn, soybean, coconut etc. as a diesel fuel substitute. Engine tests performed included measurement of power output torque, brake thermal efficiency, exhaust temperature, exhaust emissions, etc. and this results indicated that vegetable oils give performance comparable to diesel fuel in the short-term. But long-term tests showed some or all of the following problems.

The more severe problems such as rapid build up of carbon deposits, gumming up of piston rings, lubrication oil contaminating, etc., are believed to be caused by the high viscosity of the vegetable oils which leads to poor atomization (brake up of fuel into fine droplets) of the fuel which in turn leads to inefficient combustion.

General approach to the solution of these problems included:

Modification of the vegetable oils in order to reduce viscosity and modification of the engine to improve spray atomization and thereby combustion.

The differences in the spray characteristics (spray angle, penetration and droplet sizes) of vegetable oil and diesel oil are attributed to their differences in the physical properties, particularly the viscosity. In addition, differences in some of the chemical properties such as unsaturation, are responsible for problems arising from incomplete combustion after the fuel injection. However, only limited work has been carried out to investigate how the differences between the properties of diesel oil and vegetable oil influence the spray characteristics. RSO has fuel properties very similar to other vegetable oils.

I.5.7.4. Leather industry

Oil and oil based fatliquors are used to prevent the adhesion of leather fiber and to impart certain essential characteristics like softness, smoothness, stretchiness and desired strength properties. The extent of modification of these characteristics is chiefly governed by the nature of the oil, its fatty acid composition, reactive sites and the level of unsaturation. eg. Castor oil based

fatliquors confer dry and soft feel, fish oil based product imparts high degree of softness.

India is rich in castor oil, deficient in neatsfoot oil and does not have cod and sperm oil. Hence functional substitute for cod, neatsfoot and sperm oil based fatliquors[188-193] were developed based on indigenous marine oil like sardina fish oil and vegetable oils such as cotton seed oil, ground nut oil, rice bran oil, pong oil, neem oil and animal oil like fallow, frog oil and dog fat either alone or blended in suitable proportions. Recently there is scarcity of oils and is not available in adequate measure to meet the requirements of the leather industry. Hence there is scope for trying rubber seed oil in this area also.

I.5.7.5. Applications as components

Inspite of various limitations in using vegetable oils as lubricating oils, they impart certain essential characteristics to lubricating oils based on mineral oils. These are viscosity index, oiliness and anti-wear properties and in some applications emulsification property. Animal and vegetable oils have been widely used as oiliness agents to increase the load carrying capacity. Oiliness agents are effective under boundary lubrication condition up to the point when it is displaced from the surface being lubricated[194]. Most commonly used fatty oils as oiliness-imparting agents are lard oil, tallo oil, neatsfoot oil and sperm oil because these are readily available at cheaper cost. For this purpose these oils have to be of the non-drying type and compatible with mineral oils. Oils such as groundnut, cottonseed, mustard, coconut, karanja, and rice bran having various degrees of refinements, can be used depending on the nature of applications. Many compounded oils are formulated using vegetable oil as a blending component[195]. Products such as cutting oils, quenching oils, hydraulic brake fluids, gear oils and rolling oils invariably contain small portions of vegetable oils[196-201].

1. Cutting oil

For neat cutting oils, intended for general machining of mild steel, brass and light alloys, a blend of mineral oils and fatty oils has been recommended[202,203]. The function of fatty oils is to cling tenaciously to the metal surface like the bristles of a brush. This is because of the polar nature of the fatty

oils having long chain molecules. Under boundary lubrication conditions, the presence of such polar molecules reduces the coefficient of friction, thereby conserving energy and ensuring a smoother surface of the work piece. Because of the polarity, a thin film of the fatty oil retained over the surface of the work piece can ensure better protection against rust. In cutting operation, cooling of the work piece is also quite important and in this respect also fatty oils are superior to mineral oils. The percentage of fatty oil content varies between 10 and 30. Another application of cutting oils in metalworking is grinding where cooling and emulsification are important requirements. For these applications also vegetable oils can be used as a blending component.

2. Quenching oils

For quenching oils metal wetting property is very important so that oil comes in intimate contact with the metal being quenched, for effective quenching and tempering. To improve the wettability, compounded quenching oils are produced from fatty oils, which are of either animal or vegetable origin[204]. Rapeseed oil is one of the vegetable oils generally used. The amount of vegetable oils added is limited to 5-10% in compounded oils because when the oil comes in contact with hot metal surface it is burnt or cracked and leaves carbonaceous deposits over the metal, thereby impairing the quenching processes. Also, due to poor stability of the vegetable oil the degradation of the quenching oil can become very fast, specially with respect to increase in viscosity and acid value.

3. Hydraulic brake fluid

Brake fluids are generally formulated with proper additives to impart oxidation stability, corrosion inhibition and anti-wear properties[145,196]. It must provide good lubrication to both metal and rubber. To meet these requirements the mineral oils as a base stock are not considered satisfactory, as the oil could affect the quality of rubber over a period of time. So conventional formulations are based on castor oil. Castor oil alone had certain advantages such as solubility in a wide range of solvents, low pour point, high viscosity index and good lubricity property[146]. Castor oil did not have any deleterious effect on

rubber, and this property could be due to the presence of hydroxy oleic acid (ricinoleic acid).

4. Gear oils

Vegetable oils are also used for gear lubrication as compounded oils. These oils are used in the enclosed and semi-enclosed gears where tooth pressure and rubbing velocities are so high that gear lubricant regular (straight mineral oil) is not suitable. Compounded oil consists of a refined mineral lubricating oil compounded with 5-10% of rapeseed oil or any other suitable fatty oil ingredient with or without a pour point depressant and/or viscosity improvers[205].

5. Rolling oils

Palm oil was originally the vegetable oil used for cold rolling. Compounded oil with sulphur, chlorine and fat are also used as rolling oils. Rapeseed oil, mixture of rapeseed oil and tallow, tallow and palm oil are being used as cold rolling lubricants that ensure low coefficient of friction between the rolls and deforming strips[206].

I.5.8. Limitations of Vegetable Oils
Rancidity

On long storage in contact with air and moisture, oils and fats undergo slow decomposition and develop unpleasant smell. The process is known as rancidification[133]. During rancidification the chemical changes taking place are

1. Enzymatic hydrolysis due to microorganisms and enzymes, producing bad smelling lower fatty acids.

2. Bacterial oxidation of unsaturated acids, produced during hydrolysis forming aldehydes and ketones having unpleasant odour.

3. β-oxidation of unsaturated acids, produced as a result of hydrolysis, followed by decarboxylation forming ketones possessing unpleasant flavour.

Hence it is necessary to protect oils and fats from air and moisture during storage.

Mechanism of rancidification

Polyunsaturated components of vegetable oils are oxidised much more rapidly than are mono unsaturated and saturated components. Polyunsaturated components are the points in autooxidation of oils. Since, linoleic acid is the main polyunsaturated component, autooxidation of this acid is of major importance in oxidative rancidity. The more highly unsaturated acids, although they auto-oxidise more rapidly than linoleic acid does, are present in only minor proportion.

During the initial stages of auto oxidation of linoleates at least 90% of the product formed consist of conjugated mono hydroperoxides, in which the double bond that has shifted its position and is converted to the trans configuration.

$$— CH = CH — CH_2 - CH = CH \longrightarrow — CH = CH- \quad CH = CH- \underset{\underset{OOH}{|}}{CH-} \quad ---- \; I \,(12)$$

| Cis | Cis | Cis | trans |

The rate of autooxidation of linoleates and other methylene interrupted polyunsaturated system is much quicker than that of mono unsaturated system because methylene group is activated by surrounding double bonds.

The autooxidation of the unsaturated components proceeds by a free radical chain mechanism in which hydroperoxides formation and decomposition are the main reactions.

As oxidation continues, further oxidation of the conjugated hydroperoxide occurs and the decomposition products such as low and medium molecular weight (C_3 - C_{11}) saturated and unsaturated aldehydes, ketones and acids are formed. These have strong unpleasant odors and account for the typical "rancid" or "reverted" odors and flavours of auto oxidised fats.

Stability

Vegetable oils being triglycerides of unsaturated acids are more prone to chemical changes such as oxidation, hydrolysis, condensation, etc. When used as engine oil at high temperatures (e.g. ring grooves), vegetable oils crack easily as compared to mineral oils; caster oil decomposes at about 250 ^0C, olive oil at 310 ^0C and mineral oil at 380 ^0C. This leads to heavy carbon deposits on the

piston top, crown, ring grooves and other parts, impairing the performance of the engines. In the crankcase also the vegetable oil deteriorate at a faster rate due to the higher degree of unsaturation resulting in the formation of organic acid and sludge. Some of the organic acids can corrode heating materials. In the presence of moisture, stable emulsions are also formed. All these factors reduce life of the oil thereby increasing the operational cost.

Viscosity

A vegetable oil usually has a single viscosity value, which is quite high and beyond acceptable limits for most of the lubrication purposes, whereas from mineral oils a suitable oil can be selected from a wide range of viscosity grades. In use, due to poor stability and polymerization, the viscosity of vegetable oils increases at a very fast rate. This can adversely affect the performance due to higher fluid friction.

Pour point

The pour point of vegetable oils is quite high and some of the oils such as coconut oil, palm oil, groundnut oil, etc. are solid at low ambient temperatures due to a high degree of saturation. For lubrication purposes high pour point is not desirable because a lubricant has to flow to the mechanism being lubricated.

Corrosion

All vegetable oils contain free fatty acids, some of which are corrosive. Even under ambient conditions the acidity or rancidity can increase over a period of time due to poor stability. Under operating conditions on exposure to higher temperatures, moisture and air or oxygen, deterioration is very fast leading to formation of corrosive acids.

Fungal attack

Rubber compounds that serve in moist, warm areas like the tropics can be impaired or even made useless by fungal attack. A prime source of nutrient for the fungi appears to be in the softener or plasticizer of rubber and plastic compounds. As such, unsaturated oils like linseed are not used in rubber products, which are operated under such service conditions.

I.6. Plasticizers and Softeners

I.6.1. Plasticizers

Plasticizer is a 'compounding material used to enhance the deformability of a polymeric compound'[207]. Softener is 'a compounding ingredient used in small proportions to soften a vulcanizate, facilitate processing or incorporation of filler'.

I.6.2. Use of Plasticizers

Besides fillers, plasticizers play the biggest quantitative role in building a rubber compound. The reasons for the use of plasticizers are manifold[208].

❖ Improvement in flow of rubber compound and energy savings during processing, especially reduced energy peaks.

❖ Better filler dispersion in the rubber compound.

❖ Improvement in processing and tackiness of the rubber compounds.

❖ Influence on the physical properties of the vulcanizates, especially its elongation and elasticity, at low temperatures, lowering of the glass transition temperature, elevating the electrical conductivity, increasing of flame protection etc.

❖ Decrease of elastomer content by using high dosages of carbon black and plasticizer to lower the price of the blend, ie extending the rubber.

Synthetic rubber (SR) is usually harder to process and less tacky than NR and needs larger additions of plasticizers. In comparison to NR, the larger amounts added to SR have less influence on the properties of the vulcanizates.

I.6.3. Theories of Plasticization

The prominent three theories are the lubricity theory, the gel theory, and the free-volume theory. In lubricity theory the polymer might be visualized as non-woven fabric. The individual fibers are like the polymer chains. Although randomly oriented, they are so entwined that moving them is difficult. When a plasticizer is introduced between the chains, they become physically separated and can slide past one another more easily; consequently the whole mass is more deformable.

In the gel theory, the stiffness of the polymer chain is due to a three-

dimensional structure or gel-like network, active sites along the chains serving as hooks as they were between chains. Adding a plasticizer serves to mask these points of attraction and there is a swelling of the gel, so deforming is made easier[207].

The free-volume theory holds that the purpose of the plasticizer is to lower the glass transition temperature (Tg) of the polymer, they increase the concentration of chain ends resulting in greater flexibility.

I.6.4. Requirements for a Plasticizer

In order for a material to behave effectively as a softener or extender, the following requirements are desirable:

❖ The material should not be too volatile under service conditions, as a loss of material through volatility may cause hardening of any given product.

❖ The material should have some physical integrity and therefore not be subject to changes during exposure to oxygen or high temperatures. Physical changes may lead to hardening.

❖ In light or coloured products, it is essential that material should not darken when exposed to UV light.

❖ The material must show good compatibility with rubber, maximum at the concentration used. Poor compatibility can lead to egression of the material from the vulcanizate resulting in loss of properties during service.

I.6.5. Classification

The plasticizers and softeners are classified into

1. Petroleum products.
2. Pine tar and pine products
3. Synthetic resins
4. Esters
5. Natural fats and oils

Fundamentally, rubber-processing oils are high boiling fractions obtained in refining after gasoline, fuel oil, and other low boilers are removed by distillation.

I.6.5.1. Petroleum based oils

These are made up largely of ring structures, with an oil molecule probably containing saturated rings (naphthenes), unsaturated rings (aromatics), and rings with saturated side chains (paraffins). If by indirect analytical means the major portion of the rings appears to be unsaturated, it is classified as an aromatic oil; if saturated rings prevail, it is called naphthenic; but if the naphthenic rings are fewer and a large number of saturated side chains exist, the oil is classified as paraffinic[207].

The viscosity-gravity constant (VGC) is calculated from the specific gravity of the oil at 60 ^{0}F and the Saybolt viscosity at 100 ^{0}F and is used as a way of measuring the aromaticity of an oil and is calculated as follows:

$$VGC = \frac{10G-1.0752 \log(V-38)}{10 - \log (V - 38)} \qquad ---- \ I \ (13)$$

where G is specific gravity at 60 °F and V is Saybolt viscosity at 100°F. The oils with VGC > 0.95 is termed aromatic, 0.85-0.95 is naphthenic and < 0.85 is paraffinic.

Selection of oil for a particular rubber is made after considering different factors involved and a guideline for this is given in Table I.14.

Table I.14. Petroleum oil selection chart for polymers

Polymer	Oil suitability		
	Paraffinic	Naphthenic	Aromatic
Natural rubber	Fair	Excellent	Fair
SBR	Fair	Good	Excellent
Butyl	Excellent	Good	Poor
Polybutadiene	Fair	Good	Excellent
Neoprene	Poor	Good	Excellent
Nitrile	Poor	Fair	Excellent
EPDM	Excellent	Good	Good

Recently, there has been concern about the medical acceptability of some rubber process oils. The International Agency for Research on Cancer classifies

untreated naphthenic oils as carcinogenic. All these oils are generally called distillate aromatic extracts (DAE) and several studies have indicated that DAE are potential carcinogens.

The European Union Dangerous Substance Directive classified DAEs as carcinogenic due to high level of polycyclic aromatic compounds present and requires them to be labelled with skull and cross bones, plus the phrase R 45 may cause cancer. By the beginning of 1990's industries were in search of a proper alternative to DAEs. The major concern being the availability of appropriate oils in the necessary quantities to meet the industry demands.

Properties and compounding

There are two main considerations in choosing a petroleum oil as a softener or plasticizer: (1) its effect on processing behavior and (2) its effect on vulcanizate properties.

Properties of plasticizer
Viscosity

With highly viscous oils handling becomes difficult for accurate and quick addition to the batch. If viscosity is high, molecular weight is generally high and compatibility with the polymer is less. This means that more mixing time is required for full dispersion of ingredients.

Specific gravity

Paraffinic oils have the lowest specific gravity, followed by the naphthenic and then the arormatics.

Pour point

Pour point values of petroleum oils are most often considered in relation to an oil's ability to lubricate well under low temperature conditions. But they are also another guide to the compounder in selecting an oil to give low temperature flexibility. The lower the pour point, the more suitable the oil.

Aniline point

The aniline point of an oil, is the temperature at which aniline and the oil becomes miscible. It is inversely related to VGC value. Low aniline points indicate high aromaticity, and oils with low aniline points are thought to be more compatible with polymers like SBR and neoprene or nitrile.

Volatility

The volatility of an oil is usually measured by the loss in weight after 22 h at 225 ^{0}F. This test is conducted at 225 ^{0}F, since rubber compounds are mixed, cured, and sometimes tested at higher temperatures.

Colour and staining

Aromatic oils are usually dark in colour and so are rarely used in white stocks. In oils, polar compounds are heterocyclic compounds containing nitrogen and sulphur.

Table I.15. General properties of mineral oils

	Density	Storage Stability	Temp. Viscosity Relation	Aniline Point	Low Temp. Properties	Colouration/ Discolour- ation	Peroxide Cure
Paraffinic	Low	Good	Low	High	Good	Good	Good
Rel. naphthenic	↑	↑	↑	↑	↑	↑	↑
Naphthenic							
Rel. aromatic							
Aromatic	↓	↓	↓	↓	↓	↓	↓
Highly aromatic	High	Poor	High	Low	Poor	Strong	Poor

Polar compounds tend to concentrate in the aromatic oils during refining because of similarity to structure. However, these polar compounds reduce the oxidation stability of oil and therefore cause it to discolour during the action of UV light. The lower the aromatics, the lower the staining.

The general properties of the mineral oils are given in Table I.15.

Effect of oil content on properties of mixes/vulcanizates

With increasing oil loading, the compound becomes softer and more easy to prepare. If high volumes of oil are added at the start of the mix, dispersion of carbon blacks or other reinforcing fillers will be poor and vulcanizate properties mediocre. To avoid problems associated with poor dispersion, oils are added part way through the mix, often in increments. An exception occurs in so-called upside-down mixing: that is, mixing in an internal mixer, where the fillers and oils are added first, then the rubber-opposite to conventional mixing techniques. As oil is increased in the vulcanizate, tensile strength, hardness and modulus are lowered and elongation increased. There is a definite limit on the amount of oil that can be compatible with an elastomer. If this limit is exceeded, the oil will sweat out, probably making the vulcanizate unfit for use. Table I.16 gives the level of compatibility of different oils with various type of elastomers.

The oil component that has the most effect on rubber is the aromatic content. In preparing a compound, the oil take up time increases with increasing aromaticity of the oil. Also, the ability to disperse carbon black follows the order aromatic>naphthenic>paraffinic oil. At least in the early stages, highly aromatic oils give faster rates of cure, and this result has been attributed to the heterocyclic sulphur and nitrogen compounds they contain. Tensile strength and tear resistance increase with aromatic content; this may well be due to-better dispersion of the carbon black. Rebound resilience is inferior to that of paraffin oils, but crack resistance is better. Again the hetereocyclic sulphur and nitrogen compounds are subject to stain and discolouring problems.

Generally, one can assume that polar plasticizers are compatible with polar rubbers and non-polar plasticizers with non-polar rubbers and that they should be applied correspondingly.

The amounts in which, mineral oils are used in rubber compounds range between approximately 5-30 phr. In some cases, for example EPDM, larger amounts up to 100 phr are being used.

Table I.16. Compatibility of mineral oils with different types of rubber

	NR	SBR	BR	NBR	CR	CSM	EPDM	IIR
Paraffinic	+	+	+	-	-	-	+	+
Rel.naphthenic	+	+	+	-	-	-	+	+
Naphthenic	+	+	+	O	O	O	+	O
Rel.aromatic	+	+	+	O	+	+	+	-
Aromatic	+	+	+	+	+	+	O	-
Highly aromatic	+	+	+	+	+	+	O	-

+ Compatibility good, O conditionally compatible, - incompatible

I.6.5.2. Pine products

Pine products start with the fractional distillation of pine tree tappings to give turpentine. This is gum turpentine; if pine tree wood stumps are steam-distilled, the product is wood turpentine. Both turpentines contain appreciable quantities of terpenes, which are oligomers of isoprene and have the general formula $(C_5H_8)_n$.

Pine tar, a residue from the distillation of pine gum, is an efficient softener, especially for natural rubber. It is rarely used at levels higher than 5 parts. Besides its softening action it helps in the dispersion of carbon black, has age-resistant qualities and enhances the property known as building tack. With good building tack, hand-made built-up items such as expansion joints hold their shape well before curing. Because of its dark color, pine tar cannot be used for white or light-colored goods. It does have a slight retarding effect on cure.

I.6.5.3. Synthetic plasticizers

Because of their clearly higher prices, synthetic plasticizers are quantitatively less used than mineral oils. Because of the possible variations of their compositions and manifold specific activities, their number is very large. They are more important qualitatively to achieve certain properties in the vulcanizates that have increased with the requirements of modern technology: They are furthermore necessary, for certain types of rubber that are not compatible with mineral oils. This plays an important role in polar rubbers like NBR and CR that are barely compatible with low, or non-polar mineral oils.

Synthetic plasticizers are in most cases the primary platicizers for such rubbers.

The addition of synthetic plasticizers on the two-roll mill or in the internal mixer does not present any difficulty: to the contrary, they act as quasidispersing agents for the incorporation of the fillers and at the same time soften the compounds. Compounds that contain plasticizers show frequently improved tackiness because of their lower viscosity, improved extrusion behaviour, whereby large temperature increases are avoided.

Generally, synthetic plasticizers do not influence the storage stability or scorchiness of the compounds. However, in the vulcanizate a lower Shore hardness and poor tensile properties are observed, depending on the amounts used with otherwise constant compound composition. Frequently, rebound and low temperature flexibility are improved, especially when using monomeric ester and ether types. To achieve good high temperature stability, a careful selection of the plasticizer type is necessary, since especially low molecular products with high volatility are detrimental. For that purpose, higher molecular weight products with low volatility are preferable.

No generalizations can be made about swelling stability of plasticizer containing vulcanizates, since organic solvents extract more or less plasticizers from the vulcanizate, by which a lower swelling appears to take place. Swelling and extraction act therefore in opposite directions. Only polymeric plasticizers migrate less from the vulcanizate.

The synthetic plasticizers do not generally have any effect on discoloration of the vulcanizate. Comparison of a multitude of plasticizers for NBR can be made from ether plasticizers.

Ether plasticizer

Ethers or thioethers are especially well suited for NBR. Dibenzyl ether used to be applied in larger amounts to improve processing of synthetic rubber but has lost its importance today largely because of its volatility.

Polyether and polyether-thioethers play today, depending on the type used, a role as antistatic agents or as very effective plasticizers for achieving highest elasticity and low temperature flexibility in rubber products made of NBR and CR. Examples are methylene-bis-thioglycolic acid, thiobutyric acid butylesters, etc. Quantities used are between 5-30 phr. The optimum on

elastification is reached at the highest dosage mentioned. These products are rather volatile and cannot be applied where very high heat stability is called for.

Ester plasticizers

Phthalic acid esters are frequently used as cheap plasticizers to improve elasticity and low temperature flexibility, particularly for NBR and CR vulcanizates. The following are mainly considered: dibutyl phthalate (DBP), dioctyl phthalate (DOP) and diisooctyl phthalate (DIOP) and diisononyl phthalate (DINP).

Higher molecular weight products are less interesting since low temperature flexibility becomes poorer with long chain phthalates. Quantities added are between 5-30 phr.

Adipic acid and sebacic acid esters

For adipic acid esters e.g. dioctyl adipate (DOA) the same considerations hold as for phthalic acid esters. However, because of their price, use is only justified, if extreme improvement of elastic properties has to be achieved, for example for NBR vulcanizates. Sebacic acid esters play a small role for the production of rubber articles because of price and technological reasons, in spite of the fact that dioctyl sebacate (DOS) gives very good low temperature behavior. The same goes for ester plasticizers based on azelaic acid. To achieve the best heat resistance, sebacates are preferred. Trimellitates - e.g. tri isooctyl - trimellitate (TIOTM) are plasticizers with extremely low volatility. They influence good low temperature behaviour.

Phosphoric acid esters

Corresponding to their use in plastics, phosphoric acid esters are also used in rubber because of their low flammability. They are primarily used in SR types that by themselves exhibit low flammability like CR and require addition of low flammability plasticizers. Primarily considered are tricresyl- and diphenylcresyl phosphate, rarely also esters or mixed esters of xylol or trioctylphosphate. Dosage lies between 5-15 phr. Because chlorine containing plasticizers have become less important as protectants against combustion, the use of phosphoric acid esters has also increased.

Other ester plasticizers

Because of the increasing importance of heat resistant NBR formulations less and less volatile products are utilized. However, their application involves compromises as far as low temperature flexibility is concerned. Because of reasons to obtain simultaneously high temperature performance and low temperature flexibility these plasticizers are often combined with volatile ones, which have a stronger influence to lower the low temperature flexibility. As plasticizers with especially low volatily the following ones are used:

Polyester with different degrees of condensation of which, the ones with higher degree of condensation exhibit the lowest volatility but adversely affect desirable low temperature flexibility, citrates (eg. tributyl acetyl citrate), ricinoleates (eg. butyl acetyl ricinoleate), octyl-iso-butyrate, triglycol dioctylate, tetrahydrofuryloctoate, butyl carbitol-formaldehyde, pentaerythritol-ester etc. are some examples.

I.6.5.4. Vegetable oils

Several vegetable oils reduce the processing viscosity of the rubber compound and improve filler uptake. eg. Palm oil. The influence of the unsaturation on aging of the vulcanizate must be considered. Palm oil melts at 30-40 ^{0}C and softens the rubber greatly. The same considerations apply to soybean oil. When soybeans are processed, a yellowish brown, pasty material is obtained.

I.6.5.5. Factice

Factice is vulcanized vegetable oil. Various factice-types serve various demands. They specifically serve the following purposes:

During processing of rubber compounds

> ➢ improvements of the green strength and dimensional stability during extrusion
> ➢ reduction of the calandering effect
> ➢ improvement of surface smoothness
> ➢ increasing plasticizer absorption

> improvement of handling of very soft compounds with high plasticizer content (for example printing roller covers, closed cell sponge-rubber compounds etc.)

In vulcanizates

> gives a good feel (textile character)
> improves grinding (for example with rolls)
> improves fatigue crack resistance

In the cost analysis:

> saves energy during milling and mixing
> saves labour time by shortening mixing time
> increases extrusion speed
> increases calandering speed
> reduces the cost per volume by lowering the density

I.7. Polyvinyl Chloride: Its Plasticization and Stabilization

Polyvinyl chloride has the general structure $-\left[\begin{array}{c} CH_2-CH \\ | \\ Cl \end{array}\right]_n-$

The monomer, vinyl chloride boils at -14 °C. There are two methods for the production of vinyl chloride: one is by cracking ethylene dichloride in vapour phase and the other is by reacting acetylene with hydrogen chloride, in the presence of a catalyst (the well known addition reaction of acetylene):

$$CH_2Cl - CH_2Cl \xrightarrow[\text{Pressure}]{500\ ^0C} CH_2 = CHCl + HCl \qquad ---- \text{I (14)}$$

$$CH = CH + HCl \xrightarrow[\text{Pressure}]{150\ ^0C} CH_2 = CH\ Cl \qquad ---- \text{I (15)}$$

Industrial polymerisation of vinyl chloride is carried out either in suspension or emulsion. Limited quantities of PVC are also made by bulk polymerisation.

70

Structurally, the PVC molecule is partially syndiotactic and does not have a completely regular structure. PVC has low crystallinity. The polymer molecules are either linear or only slightly branched. PVC is insoluble in vinyl chloride, alcohols, water and hydrocarbons. Acids and alkalis have practically no effect on PVC, at least up to 20 °C. PVC, however, dissolves in ketones, chlorinated hydrocarbons and the like. A mixture of acetone and carbon disulphide is found to be an excellent solvent for PVC. PVC is one of the cheapest and most widely used plastics globally. It is used for the large-scale production of cable insulations, equipment parts, pipes, laminated materials and in fibre manufacture. PVC is thermally not very stable and, beyond 200 °C, it degrades with the evolution of HCl. This is further accelerated by the formation of conjugated double bonds along the chain, which will result in the discolouration of the polymer. To avoid such discolouration a suitable stabilizer is added to the polymer.

PVC, as such is a horn-like material and difficult to process. It is, therefore, compounded with plasticizers. Depending on the plasticizer percentage, fully rigid to highly flexible finished products can be obtained. In many cases, the plasticizer content may be up to 30% by weight of the polymer[208].

Polyvinyl chloride finds extensive use in certain formulations called plastisols and organosols. These are paste-like compositions and are produced from emulsion-polymerised PVC resin particles. The plastisols are produced by dispersing PVC particles into plasticizers. The organosols, on the other hand, are produced by dispersing PVC particles in a suitable mixture of volatile organic liquid and plasticizers. Plastisols and organosols also contain other compounds such as colourants, fillers, blowing agents and stabilizers. At ordinary temperatures, the PVC particles present in plastisols or organosols do not dissolve in the liquid medium, but only remain as a dispersed system. When the temperature is raised to 150-200 °C; PVC fuses with the plasticizer and forms a physically cross linked structure in the shape of the ultimate plastic article.

The total chlorine content in PVC is around 56.8% and can be further increased to 60-65% by dissolving it in a suitable solvent such as chlorobenzene and chlorinating at 100 °C. The polymer thus formed is called chlorinated PVC. It

is assumed that, during chlorination, the chlorine replaces the hydrogen atoms in the $-CH_2-$ units rather than in the $-CH-Cl-$ units of the molecule. The principal advantage of chlorination is that the polymer becomes more resistant to acids and bases. However, the stability towards heat and light is found to decrease. The main use of chlorinated PVC is in the manufacture of adhesives, coatings and fibres.

Polymer Degradation

PVC has high melt viscosity. The viscosity can be reduced by the use of higher processing temperature, but because of the limited heat stability, thermal degradation of PVC begins with the evolution of HCl at approximate temperature of 200 ^{0}C. The rate of degradation increases sharply with increase in temperature. The colour changes from white to yellow, brown, dark brown and then black.

$\qquad$ I (16)

PVC, which is basically colourless, turns deep yellow, orange, brown or black, depending on the concentration of the conjugated double bonds, which in turn, depends on the degree of degradation. The role of HCl in this reaction is catalytic since the degradation becomes faster as soon as HCl is evolved. Any material, which can take away HCl from the reaction sphere can, therefore, arrest the degradation and stabilize the polymer. It is for this reason that PVC available in market contains certain additives called stabilizers, which react with HCl and remove it from the system. Zinc octoate, sodium carbonate, certain salts of calcium or barium or lead, many amines, certain organo-tin compounds and also some epoxidised vegetable oils are used as stabilizers for PVC. The mechanism of their action can be depicted as follows[209] .

$$R - \underset{\underset{O}{\diagdown \diagup}}{CH} - CH - R' + HCl \longrightarrow R - \underset{\underset{OH}{|}}{CH} - \underset{\underset{Cl}{|}}{CH} - R' \qquad \text{---- I (17)}$$

Epoxidised oil

$$M^{++} [R - \underset{\underset{O}{||}}{C} - O]_2^- + 2\,HCl \longrightarrow M^{++}Cl_2^- + 2R - \underset{\underset{O}{||}}{C} - OH \qquad \text{---- I (18)}$$

Metal salts

Although PVC has a tendency to degrade around 200 °C, it is still the world's most widely used plastic.

I.7.1. Manufacture of PVC

All four basic polymerisation processes[209] are followed for the manufacture of PVC and other vinyl chloride monomer copolymers, *viz.* suspension, emulsion, mass and solution.

Suspension process is the most favoured technique with nearly 75% of PVC being produced using it. Emulsion and Mass polymerisation are used to the extent of 20-25%. The solution technique is used only for speciality vinyl coatings, which are generally vinyl chloride monomer (VCM) copolymers and terpolymers with vinyl acetate and acrylates.

Suspension polymerization process

Suspension polymerisation requires suspension of VCM, a low boiling monomer with structure $CH_2= CH- Cl$. It is easy to liquify under pressure for ready suspension and emulsion polymerisation. VCM is an active monomer and undergoes facile polymerisation with free radical initiators. It can also be polymerised using amino initiator droplets in water under agitation. To prevent the droplets from coalescing, suspending agents are added. Typically these are one or more grades of polyvinyl alcohol and tricalcium phosphate salt. Buffer salts like sodium bicarbonate are added to maintain pH as well as the polymerisation rates. Initiators like lauryl peroxide and peroxy dicarbonates are added in proportions that again help maintain a constant initiation rate. The trick here is to see that while lauryl peroxide is used up in the first half of reaction

time, the peroxy dicarbonate remains dormant. There after it becomes active. This is possible due to their half-life for decomposition being different. The constant rate of polymerisation helps to maintain a constant heat load, which needs to be removed by cooling. This not only reduces the cost of cooling and cooling equipments but also allows for shorter cycle time, one time loading and more uniform product.

Other additives like surfactants are also added to increase the porosity of resin. Chain transfer agents are sometimes added to regulate the molecular weights and molecular weight distribution.

In general, suspension polymerisation is carried out at temperature between 60 to 85 ^{0}C under pressue of upto 250 psi. When the VCM conversion reaches about 95%, the pressure inside the reactor starts to drop. Polymerization is then stopped by adding an inhibitor and unreacted monomer is flashed off with vacuum. The PVC beads are then filtered in centrifuge, washed and dried in a flash dryer. The control of polymerisation temperature generally plays a vital role in determining the molecular weight (K-value). For free radical polymerisation, higher polymerisation temperature means lower molecular weight and lower K-value.

Thus PVC of K-value 55-60 is made at temperatures like 80-85 ^{0}C, while PVC of K-value 70-75 is made at temperatures like 65 ^{0}C. Thus, different packages of initiators are generally needed for making PVC of different K-values.

Large growth of PVC over the decades coupled with its safety aspects has necessitated several innovations in PVC manufacturing technology. The three most important areas are: clean reactor technology, large reactor technology and VCM containment.

Mass polymerization process

VCM polymerisation in bulk, without solvent or water or any suspending agent is popularly known as mass polymerisation process. It was commercially developed first in France by Pechiney St. Gobain. Mass polymerisation technology gives resin of highest purity, which is also very porous and hence excellent for plasticization, thus having better clarity and overall electrical properties.

74

Mass polymerisation is carried out in two steps. In the first stage, 50-60% of the total VCM along with the initiators, generally a peroxy dicarbonate type and particle size regulators are added to a smaller vertical reactor. Here first phase of reaction occurs giving about 10% conversion of VCM. The agitation employed during this stage is useful in determining both particle size and resin morphology. This is because of the fact that at this conversion the liquid phase disappears as VCM gets completely absorbed by PVC particles. In this stage, polymerisation is carried out at higher temperatures like 69-70 °C and for about 1-1.5 h. Thereafter, the reactants are pumped into second stage reactors.

Generally a series of large horizontal or as in more modern process vertical reactors are used in the second stage. More VCM (50-40%) along with initiator, other ingredients and content of the first stage reaction are charged into the reactor. Typical, polymerisation temperature here is 55-60 ^{0}C and time 8-10 h. It is in this stage that molecular weight of the resin is determined along with its final morphology. The molecular weight can be controlled by polymerisation temperature and/or chain transfer agents.

Emulsion polymerisation process

PVC produced by emulsion process differs significantly in several important aspects from that produced by either suspension or bulk process. PVC produced by emulsion process is of very fine uniform particle size and the particles are non-porous. They also carry with them large quantity of surfactants, salts etc. as impurity and thus show least purity.

Emulsion polymerisation process is quite similar to suspension process in being one-step process. The polymerisation reactor is followed by a stripper to recover VCM followed by spray drying of the latex.

A typical emulsion polymerisation recipe is as follows. Demineralised water 120 parts, VCM 100 parts, emulsifier, sodium lauryl sulphate 4-5 parts, initiator potassium persulphate 1 part and other additives as buffers and emulsion stabilizers 1 part. Since requirement of emulsion polymer is not large, smaller reactors are used. Otherwise reaction time and temperature are similar compared to suspension being respectively 7-9 hours and 55-70 °C. Reaction kinetics are quite different from the first two processes. The molecular weight is

profoundly affected not only by temperature and any addition of chain transfer agent, but also by quantity of emulsifier used. Higher emulsifier amount and lower initiator concentration yield higher molecular weight resin. Type and amount of emulsifier also determine particle size, higher amount leading to lower particle sizes.

The major usage of emulsion PVC is in plastisol and organosol preparations, mainly due to its non-porous nature with very fine particle size. The resin quickly and irreversibly absorb plasticizer once it is heated to higher than 80 °C temperature and thus finds usage in coating and slush moulding.

I.7.2. Physical Properties

Glass transition temperature

The temperature at which an amorphous polymer changes from its hard or glassy state to a soft or rubbery material is known as the glass transition temperature (Tg). Tg of unmodified commercial grade PVC is between 70 and 80 °C.

Effect of concentration of plasticizer

Small amount of DOP imparts an increase in strength, hardness and modulus to PVC contrary to the general expectation of a plasticizer addition. Thus rather than softening suspension-polymerised PVC, DOP at concentrations of about 15% or less, actually make it stiffer and more brittle. Amount of crystallinity increases on addition of low concentration of DOP.

The low temperature dynamic mechanical properties exhibited similar behaviour. Elastic component of the complex shear modulus G′ below Tg is higher at low concentration of DOP. Point of steep modulus decrease, which is the region for the glass-to-rubber transition, occurs at lower temperature as DOP is added. Thus, even though DOP might appear to behave as an antiplasticizer by making the polymer stiffer, when it is present in even small amounts, Tg is effectively decreased and the polymer is plasticized.

The decrease in Tg with increasing DOP content is also apparent in the mechanical loss curve. The point of maximum loss or Tg decreases and breadth of the mechanical loss spectrum widens with increasing amount of DOP.

Effect of pressure

An increase of pressure causes an increase in Tg. When the chains are under pressure, more thermal energy is required to activate the energy loss mechanism or motion.

I.7.3. Additives for PVC

PVC cannot be processed without the use of additives at high temperature. Plasticization of PVC makes it more akin to rubber rather than plastics with the result that additives that were used in rubber compounding can now be considered for PVC compounding. eg. Oils, wax stearates and metal oxides [210].

The following additives were used in PVC to a small or large extent before it could be processed under high shear at temperature higher than 140-150 ^{0}C. Plasticizers, heat stbilizers, lubricants, flow promoting agents, fillers, impact modifiers, colorants, flame retardants, miscellaneous chemicals (foaming agents, UV stabilizers, etc.). Rigid PVC compounds can be prepared only using heat stabilizers, lubricants and flow promoters with optional addition of impact modifiers, UV stabilizers and fillers for opacity. Thus, in addition to PVC the compound may have no less than 6-7 other additives to the extent of 3-10% by weight. Out of these, the most important ones are plasticizers and stabilizers

I.7.3.1. Plasticizers for PVC

Plasticizer makes PVC softer and makes it more processible by reducing viscosity and by acting as lubricants, allowing it to remain flexible in higher range of temperature. Thus, proper choice of plasticizers becomes an important part of PVC compounding. 40-45% of suspension PVC and 95% of emulsion PVC produced find usage in plasticized application. 80-85% of all plasticizers produced worldwide are used in PVC compounding.

For a given plasticizer, two parameters are important.

1. Its efficiency ie. changing PVC properties to the desired extent with use of little plasticizer as possible.

2. Its effectiveness ie. how much can it affect the desired property and for how long in the usage condition.

Thus, for example, to prepare a PVC compound of 70 Shore A hardness, different plasticizers will be required to be added at different levels. This reflects their efficiency, lower the quantity required of a given plasticizer, higher is its efficiency. But having obtained it, how long the compound remains at 70 Shore A without plasticizer getting migrated or degraded determines its effectiveness.

The effectiveness is also gauged in terms of other specific property required like low temperature flexibility, high temperature resistance, non-flammability etc.

Plasticizer efficiency

For the measurement of plasticizer efficiency hardness test is more prevalent. Plasticizer efficienty can also be judged from the time taken for plasticizer absorption by PVC, at a given temperature for constant plasticizer level. This depends on compatibility and molecular weight. More compatible plasticizer is not only absorbed faster but also requires a slightly lower temperature as compared to a less compatible plasticizer, for a given PVC resin.

For a given series of plasticizers differing in molecular weights only, low molecular weight plasticizers generally are absorbed faster. This is due to the fact that they can migrate into the pores of PVC particle faster than their higher molecular weight counter parts. Thus dry blending is kinetically and thermodynamically controlled process, where a plasticizer first gets adsorbed on the surface then migrates into the pores and finally gets absorbed by PVC. Both solvating power and viscosity of plasticizer play important roles.

Dry blending is a process by which the powder absorbs large part of plasticizer without becoming a paste, slurry or plastic and remains free flowing dry powder only. The general relationship between structure of plasticizers and their behaviour in PVC are shown in Table I.17.
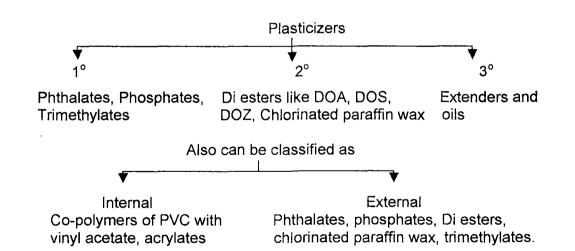
Plasticizers for vinyl resin can be divided into seven chemical classes
    (1) Phthalates (2) Epoxides (3) Aliphatic Diesters (4) Phosphates
    (5) Polyesters (6) Speciality types (7) Extenders
Vinyl plasticizers are primarily esters. Out of these, the first three are the commonly used plasticizers.

Table I.17. General relationships between the structure of plasticizers and their behaviour in PVC

Characteristic/Parameters	Effect
Molecular weight	Increasing molecular weight reduces migration, softening efficiency and volatility
Polarity	Incorporation of extra polar groups such as ester groups in diesters substituting halogens into the benzene ring of phthalate or substituting aryl groups for alkyl ones, reduce softening efficiency worsens low temperature properties, improve solvation and reduces extraction by aliphatic solvents.
Alkyl chain length	Increasing alkyl chain length improves the efficiency of aliphatic and phthalate diesters at equimolecular concentration.
Alkyl chain linearity	This improves low temperature flexibility and efficiency and reduces electrical resistivity.
Separation of ester grouping	Increasing the distance between ester groups, increases solvation, softening efficiency and effectiveness.
Reversal of ester grouping	A change from dibasic acid ester to a dihydric alcoholester of similar chain length leads to a decrease in solution efficiency.

Plasticizers

1°	2°	3°
Phthalates, Phosphates, Trimethylates	Di esters like DOA, DOS, DOZ, Chlorinated paraffin wax	Extenders and oils

Also can be classified as

Internal	External
Co-polymers of PVC with vinyl acetate, acrylates	Phthalates, phosphates, Di esters, chlorinated paraffin wax, trimethylates.

Scheme I.1. Classification of Plasticizers

Phthalates

The phthalates provide the most desirable combination of performance characteristics and low cost of all plasticizer's family used in vinyl resins and thus have become the most widely used. About one-third of plasticizers marketed is DOP and diisooctyl phthalate (DIOP)

Dibutyl phthalate (DBP) is the lowest-molecular weight phthalate can be used in PVC. Even though its boiling point is 340 ^{0}C at atmospheric pressure, it is much too volatile to be used in so called hot processing (calendaring, molding and extrusion) operation, where temperatures of 160-170 ^{0}C are normally used.

It has also been found that vinyl films containing butyl phthalate undergo significant changes in mechanical properties as a result of plasticizer loss that occurs at ambient conditions. Hence dibutyl phthalate is seldom used as the sole plasticizer for polyvinyl chloride.

Epoxy Plasticizers

Epoxy plasticizers are those plasticizers that contain the three-membered epoxide ring.

Epoxy plasticizers represent 7% of the plasticizer industry. Epoxides are primarily used as heat stabilizers. They also enhance light stability in vinyl compositions. As compatible liquids they also contribute plasticizing action to the vinyl composition. The oxirane structure is prepared by adding oxygen across double bond linkage.

Natural oils are commonly used as starting materials for producing epoxy plasticizers. Soybean and linseed oils are two of the most common, since they are readily available and have a high degree of unsaturation. These oils have a chemical structure typical of natural oils and can be represented as the (tri fatty acid) esters of glycerol. The 18- carbon atom fatty acid predominates, as indicated by the molecular weight of about 900. When the epoxidised oils are evaluated for plasticizing characteristics, they show the performance similar to typical of low-molecular weight polyester plasticizers.

Compatibility of epoxy plasticizers varied inversely with the hydroxy and polyether content in addition to the poor compatibility attributed to residual unsaturatuion[211].

Epoxidised oils that had been produced in the absence of aqueous media were found to have a very low hydroxyl – to – oxirane ratio and exhibited good compatibility when employed as primary plasticizer use level in PVC. The presence of oxirane can be detected by infrared spectroscopy if the epoxide constitutes a major portion of the plasticizer sample.

The epoxidised oils have a long chain, flexible structure containing one or more reactive epoxy group. In PVC, the long oil chain contributes flexibility and the reactive epoxy group acts as acid scavenger, preventing degradation of vinyl and providing long term ageing resistance. Thus an epoxidised oil which is usually referred to as an epoxy plasticizer acts both as a plasticizer and acid scavenger in PVC compounds to improve the resistance to ageing or embrittlement.

The oxirane oxygen ring acts synergistically with metallic stabilizers, especially those based on barium, cadmium, calcium and zinc. This co-stabilizing function imparts increased heat and UV light stability to PVC compounds or makes possible the use of reduced levels of the relatively expensive metallic stabilizers while still providing adequate stabilization. As plasticizers, certain epoxides impart polymeric like permanence while others impart good low-temperature properties and low plastisole viscosity, or a balance of permanence and low-temperature performance. Thus, the epoxides are valuable "double duty" products, serving both as plasticizers and as a part of the stabilizer system.

Although epoxy plasticizers have good initial compatibility, one must be aware of the potential for oxidation in certain environments. This can cause loss of compatibility, manifested in the development of an oily, waxy or tacky film on the vinyl article. Thus, total use of levels of these plasticizers are generally restricted and they are considered to be secondary plasticizers.

Epoxy palsticizers are classified as

1. Epoxidised vegetable oil
2. Epoxidised alkyl esters
3. Other epoxy plasicizers

Linseed oil and soybean oil are common vegetable oil bases, which yield higher oxirane oxygen content. Epoxidised oils from these are in certain applications such as blood bags and intravenous tubing. This class of epoxy plasticizers possesses the best combination of economy and stabilizing performance. From a plasticizer performance stand point, epoxidised oils are almost equal to DOP for plasticizing efficiency, but are far more permanent. Except for lower volatility and superior soapy water extraction resistance, the oil epoxides otherwise are similar to typical medium low-molecular weight polymeric plasticizers for low temperature and permanence properties.

Aliphatic diesters are referred to as low temperature plasticizers because they impart improved low temperature flexibility and impact resistance to vinyl position.

Detrimental effects of plasticizers

Special properties that are altered by the plasticizers are:

A. Chemical resistance

The chemical resistance of polyvinyl chloride is very good. However, vinyl compositions are susceptible to attack by certain organic solvents such as tetrahydrofuran, lower molecular weight ketones and esters and chlorinated solvents. Increased plasticizer concentration significantly reduces resistance of flexible vinyls to chemical attack, while the interchange of various types of plasticizer shows only a minor effect.

B. Inflammability

Polyvinyl chloride contains approximately 57% chlorine by weight and supports cumbustion only under unusual conditions. Copolymers of polyvinyl chloride demonstrate some loss of flame resistance as a function of increased level of comonomers (when the comonomers do not contain chlorine). Plasticized vinyls demonstrate a significant level of combustibility. Film thickness, filler level and other formulating additives, which may act as flame-retardants, significantly alter the degree of flammability or burning rate. Increased plasticizer concentration promotes higher flammability. Polymeric plasticizers and epoxidised vegetable oils, such as epoxidised soybean oil,

cause slow-to-medium burning rates. This is apparently due to the low vapour pressure of the high molecular weight plasticizers. All the phosphate plasticizers produced self-extinguishing films when they were used as the sole plasticizer in flexible vinyl compositions.

C. Dielectric properties

The most commonly known applications of PVC are in building and appliance-type wires and electrical insulating tape. The plasticizer used in these cases has significant effect on the dielectric characteristics of the product.

D. Stain resistance

Certain applications of plasticized PVC require resistance to staining. In all cases, the more highly plasticized vinyl compositions are more susceptible to any given staining reagent than the semi rigid vinyl materials. Sulphide staining, which results from the formation of coloured sulphide salts when certain metallic stabilizers are used, is altered in severity by the plasticizer level in the vinyl product, even though the plasticizer itself does not enter into the reaction wherein the sulphide salts are formed. Plasticizers that contain the sulphur atom promote severe sulphide staining, in the presence of stabilizers, fillers or pigments containing heavy metals capable of forming coloured sulphides. Hence sulphur-containing plasticizers never gained wide commercial significance. The most common type of staining results from the absorption of a staining reagent that may come in contact with the surface of the vinyl product. Vinyl covering for floors, countertops, upholstery and other vinyl coatings are typical applications that require resistance to staining.[212,213] Practically all the commonly used plasticizers for vinyls are susceptible to oil based stains.

I.7.3.2. Heat stabilizers for PVC

PVC is required to be stabilized during high temperature processing on three counts.
1. Discoloration of compounds
2. Evolution of HCl
3. Development of unsaturation followed by severe crosslinking.

Once evolution of HCl was understood, several metal oxides, carbonates, hydroxides and bases that can quickly react with it were used as stabilizers. Strong bases like MgO, NaOH etc. catalysed the dehydrochlorination leading to more destabilization, while a mildly basic PbO was more suitable for stabilization. Thus came the development of lead, barium/cadmium, zinc and tribasic compounds as suitable stabilizes for PVC. In PVC, 1-3% of chlorine is allylic or tertiary, while the remaining of 56% chlorine is secondary. Only secondary chlorine atoms show high stability towards heat and chemicals. However, both allylic and tertiary chlorine are labile and reactive and come out as chlorine radical or chloride ion, upon treatment with heat and or chemicals.

The radical or cation on the backbone is stabilized by allylic delocalisation or by tertiary groups making chlorine so labile. Once it comes off, H^+ also comes off eventually leading to dehydrochlorination. One HCl thus introduces allylic group, which accelerates further HCl loss leading to polyene structure, which is what makes PVC colored. The unsaturation thus produced undergoes crosslinking rapidly.

Important factors contributing to PVC instability are the various chemicals used for its production including initiators, emulsifiers, suspension stabilizers, chain transfer agents etc. That is why PVC of similar molecular weight, but from different sources, show different thermal stability.

The thermal history that a PVC resin has acquired is also important. The polymerisation temperature, drying time and temperature, and mode of drying as well as time and temperature of storage all affect the stability of PVC.

Classification of stabilizers:

Stabilizers are classified according to

1. Chemical composition of the stabilizers.
2. Their functional requirements.
3. The type of polymers/plasticizers/fillers with which the stabilizers are employed.
4. The demands of the compounding and processing operations.
5. Requirements of the end use application of the vinyl object or part needing stabilization.

84

According to chemical compositions the stabilizers are divided into

1. Inorganic compounds.
2. Metallo-organic salts or soap.
3. True organometallic containing a carbon-to-metal bond.
4. Pure organic compound.

Stabilizers for PVC can be grouped into four:

1. Lead based stabilizers
2. Tin based stabilizers
3. Mixed metal based stabilizers
4. Non-metal based stabilizers

Stabilizers function in the following ways:

1. HCl absorption

   Nearly all heat stabilizers, being organometal salts, can react with HCl to form metal salts.

   $$Pb(OCOC_{17}H_{32}) + 2HCl \longrightarrow PbCl_2 + 2C_{17}H_{32}COOH \qquad ---- I (19)$$

2. Elimination of labile chlorine

   A labile chlorine, like allylic chlorine, can react directly with the stabilizer thereby eliminating formation of polyene sequence.

   Here though double bond shifts, but remains otherwise intact, the introduction of mercapto group stops the further dehydrochlorination. Such reactions take place not only with tin but also with lead, cadmium and zinc stabilizers.

3. Prevention of autooxidation

   Elimination of HCl from PVC in air is known to be higher as compared to that in nitrogen. This is not only because of autocatalysis by HCl but also due to peroxide formation taking place in air or oxygen. Thus addition of phenolic antioxidants can help to reduce destabilization process. Tin stabilizers, in addition have the ability to breakdown the peroxides.

85

$$R_2Sn \ (S \ CH_2\text{-}COO\text{-}C_8 \ H_{17})_2 + R\text{-}O\text{-}OH \longrightarrow$$

$$R_2SnO + R\text{-}OH + (C_8 \ H_{17} \ COO\text{-}CH_2\text{-}S)_2 \text{ ---- I (20)}$$

Lead based stabilizers for PVC

It is not only the oldest but also the most important of all PVC stabilizers. The most important lead compounds are

1. TBLS – Tribasic lead sulphate – $3PbO. \ Pb \ SO_4. \ H_2O$
2. DBLS – Dibasic lead stearate – $2PbO.Pb \ (OCOC_{17}H_{35})_2$
3. DBLPH – Dibasic lead phthalate – $2 \ PbO. \ Pb(OOC)_2 \ C_6H_4. \ ½ \ H_2O$
4. DBLP – Dibasic lead phosphite – $2 \ PbO. \ PbHPO_3. \ ½ \ H_2O$
5. Dibasic lead carbonate – $2PbO. \ PbCO_3$
6. Lead stearate – $Pb \ (OCO \ C_{17} \ H_{35})_2$

Lead stabilizers are powerful stabilizers for PVC. Though TBLS/DBLS synergy is used most often, the addition of other secondary stabilizers generally does not add to their efficiency. Lead stearate, on the other hand, is also a powerful lubricant, in addition to being a stabilizer. In fact, it needs to be used only at 0.5% level and the usual dosage is 0.2-0.3% only as otherwise that PVC compounds get over lubricated and does not gel well. This results in rough surface of the extrudate.

Lead compounds are now used principally in stabilizing plasticized PVC used for electrical wire insulation and in polyvinyl chloride–acetate copolymer used for phonograph record compositions. It can be also used in the stabilization of extruded rigid PVC compounds for certain types of piping applications, industrial profile etc. Lead salts are among the earliest of PVC stabilizers. Their acid-accepting ability and the fact that the chlorides of lead are insoluble and non-ionisable, therefore inert and do not conduct electricity, account for their great use in electrical insulating materials. eg. Tribasic lead sulphate (3 PbO. $PbSO_4. \ H_2O$).

Epoxy based stabilizers

Epoxidised soybean oil, epoxidised oleic acid esters and other fatty acid oils are extensively used as secondary stabilizers to improve the high temperature heat stability of PVC compounds. They are quite compatible with

PVC and can be used without migration problems at low levels, as they are rarely used at more than 5-7% level mainly due to cost and physical property considerations.

They have at least one epoxy group per molecule and even 2 or 3 depending on the oil used. The major epoxies used are epoxidised soybean oil, epoxidised linseed oil, isooctyl epoxy phthalate, 1,2–epoxydodecane and the epoxy resin of epichlorohydrin/bisphenol A.

Since, zinc and cadmium have particularly pronounced catalytic effect, epoxidised stabilizers find more usage with mixed metal stabilizers. With tin stabilizer, the effect is not so apparent.

It should be noted that apart from long-term thermal stability, epoxies contribute to clarity and high stability too, depending on the stabilizer used. Epoxies along with phosphates help to reduce yellowness of PVC on processing even more efficiently.

Theory of stabilization by epoxides

The oxirane oxygen ring (epoxy group) is a well-known acid acceptor. In PVC stabilization in the absence of metallic stabilizers, HCl from initial degradation is scavenged by the epoxide, converting the epoxy group to chlorohydrins or the epoxy ring opens to react with the free radical at a labile hydrogen site in the PVC, thereby forming an ether linkage with the chlorinated epoxy.

The synergistic stabilizing action of the epoxy group with metallic stabilizers (especially Ba/Cd and Ba/Cd/Zn type) has been exploited for many years. This synergism combines the HCl scavenging effects of the epoxy previously noted and an improvement in the regeneration of the metallic ion by attracting the chlorine of the metallic chloride. The latter reaction is doubly important because it reduces the concentration of metallic chlorides that are catalysts for dehydrohalogenations (decomposition) of PVC.

Evidence of the synergism is the slow deviation of the colour and stiffening (due to cross linking of degraded PVC) in PVC compounds containing epoxides. Epoxidised oil and epoxidised esters of unsaturated fatty acids are widely used in polyvinyl chloride and its copolymers at 1-5 % level in conjunction with other substances for heat and light stabilization.

Although, an effective stabilizer, epoxidised soybean oil has only limited compatibility with PVC and its plasticizing efficiency is only fair. For these reasons, epoxidised esters of unsaturated fatty acids, which are efficient plasticizers as well as stabilizers are sometimes used instead, even though they are more expensive.

Epoxidised soybean oil contains about 4-5 per cent oxirane rings and may be represented by

$$
\begin{array}{l}
\underset{\text{C-O-C-C-C-C-C-C -C -C }}{\overset{\overset{\text{O}}{\parallel}}{}} \quad \underset{\text{-C -C -C -C -C -C -C -C -C -C}}{\overset{\overset{\text{O}}{/\backslash}}{}} \\[4pt]
\underset{\text{C- O- C- C-C- C- C-C-C -C-C-C -C }}{\overset{\text{O}}{\overset{\parallel}{}}} \quad \underset{\text{-C -C -C -C -C -C -C -C}}{\overset{\overset{\text{O}}{/\backslash}\;\;\overset{\text{O}}{/\backslash}}{}} \\[4pt]
\underset{\text{C - O- C- C- C- C- C-C -C -C-C-C }}{\overset{\text{O}}{\overset{\parallel}{}}} \quad \underset{\text{-C -C -C -C -C -C -C}}{\overset{\overset{\text{O}}{/\backslash}\;\;\overset{\text{O}}{/\backslash}}{}}
\end{array}
$$

Stabilization Mechanism

1) Hydrogen Chloride Neutralization

The effectiveness of the stabilizer depends on many factors such as concentration and state of compatibility (solubility) in the polymer system. Ordinarily stabilizers are incorporated, as part of the compounding operations, at the time of addition of plasticizers, colorants, lubricants etc. to the polymer. Since, PVC degradation commences at a much earlier state, the stabilizers are introduced at an earlier stage.

To be effective as an acid acceptor, the stabilizer must be able to react with hydrogen chloride quickly and efficiently, but it must not be too strongly alkaline or else it will actively dehydrochlorinate and thus degrade the resin itself. (eg. Sodium hydroxide, can strip a considerable quantity of hydrogen chloride from PVC, leading to a long conjugated polyene structure of deep red colour).

Other hydrogen chloride acceptors are also used with varying degrees of success, such as epoxides, amine, metallic alkoxides and phenoxide and metallic mercaptides, which neutralize the acid as given below.

$$-\overset{\displaystyle O}{\overset{\displaystyle \diagup \diagdown}{CH - CH}} - + HCl \longrightarrow -\overset{\underset{\displaystyle |}{OH}}{CH} - \overset{\underset{\displaystyle |}{Cl}}{CH} - \qquad\qquad --- I\ (21)$$

$$R\ NH_2 + HCl \longrightarrow RNH_3Cl\ \text{(also secondary and tertiary. amines)} \ --- I\ (22)$$

$$R\ OM + HCl \longrightarrow R - OH + MCl \qquad\qquad --- I\ (23)$$

$$R - SM + HCl \longrightarrow RSH + MCl \qquad\qquad --- I\ (24)$$

2) Displacement of Labile Chlorines

Among the most effective stabilizers are those that have been shown to function by actively attacking weakly held labile chlorine atoms on PVC and replacing them with other groups of inherently greater stability. The progressive zipper like dehydrohalogenation is thereby thwarted before it commences by replacing the initiating labile chlorines with other, more thermally stable groups that require higher energy levels before they are ruptured from the PVC chain. This is the Frey-Horst hypothesis, which has gradually come to be the accepted mechanism by which heavy metal carboxylates and mercaptides function as colour-inhibiting stabilizers.

The soaps of cadmium and zinc, the dialkyl tin carboxylates and mercaptides stabilize PVC by exchanging their ligand for the labile chlorines on the PVC molecules as shown below.

$$M\ (OCR)_2 + \sim\sim -\overset{\underset{\displaystyle \xi}{\overset{\displaystyle |}{C}}}{\underset{}{Cl}} - \sim\sim \longrightarrow M\overset{\diagup Cl}{\diagdown OOCR} + \sim\sim -\overset{\underset{\displaystyle \xi}{\overset{\displaystyle OOCR}{|}}}{C} \sim\sim \longrightarrow \qquad --- I\ (25)$$

$$M(SR)_2 + \sim\sim -CHCl - CH = CH\sim\sim \longrightarrow \qquad\qquad --- I\ (26)$$

$$M\overset{\diagup Cl}{\diagdown SR} + \sim\sim -\overset{\underset{\displaystyle SR}{|}}{CH} - CH = CH \sim\sim \longrightarrow \qquad --- I\ (27)$$

When much hydrogen chloride is present in the partially degraded polymer before the stabilizer has been introduced, or before the stabilizer has been intimately mixed with the polymer by hot shear melt processing, the hydrogen chloride will react with the stabilizer and reduce the amount available to react directly with the polymer in the Frye-Horst displacement reaction, which

introduces stable pendent ester or thioether groups onto the resin. The heavy metal chlorides that are formed and remain in the system as by-product of the desired displacement reaction, are then capable of initiating pronounced cross-linking and further hydrogen chloride evolution via.the Friedel-Crafts mechanism.

I.8. Peptizers

The peptizers are materials included in a mix primarily to reduce the time and energy required in breaking down the polymer. However, at the same time they help with dispersion of dry materials, give smoother stocks, improve extrusion rates, and in some instances increase the homogeneity of blended rubbers. They are generally added in small quantities, usually less than 0.5 parts per hundred rubber (phr), and the effect on vulcanizate properties is minimum.

By using a mixing mill, Banbury, or other plasticating device, the rubber could be masticated to perhaps 60-75 Mooney viscosity, at which point incorporation of fillers would be more easy. The process requires considerable energy, and any material that shortens the time or energy cost, is certainly a process aid. If this breakdown is accelerated by a process aid that works more in a chemical way than a physical way, the agent is called a peptizer.

Peptizers such as Renacit VII from Mobay Corporation, Pepton 44 from American Cyanamid, and Struktol A82 from the Struktol Company of America are very commonly used by the rubber industry. These have been identified as pentachlorothiophenol with activator and dispersing additives, activated dithio-bisbenzaniline on an inert carrier, and a blend of high molecular weight acid ester and active chemical peptizer respectively.

The Mooney viscosity, which is originally high can be almost linearly brought down by mastication alone to 62 after 10 minutes of processing. For many purposes a Mooney viscosity of 60 ±5 would be appropriate before adding other ingredients.

The softening action of the peptizers is readily apparent. Use of any one of the above three peptizers can reduce the higher viscosity rubber to the 60 ± 5 Mooney range within 6-7 minutes of mixing. This was accomplished at levels as low as 0.1 phr for the Renacit VII- and Pepton 44-treated rubbers and at 0.4 phr

level for Struktol A82. Selection of a peptizer would not of course be made solely on effectiveness in reducing viscosity; cost and other technical properties would be considered as well.

Peptizer used is mainly confined to natural rubber compounds. Aromatic mercaptans, formerly the main agents used, have been replaced by other chemicals largely for safety considerations in the workplace. Chelate complexes of iron, cobalt, and manganese accelerate the breakdown of natural and some types of synthetic rubber by thermal oxidation. Peptizer dosages of 0.1-0.5 phr are usually sufficient. The use of peptizers for the mastication of rubber is well outlined by Fries and Pandit [214]. The main factors that determine the peptizing action of the chemicals are time, temperature of mixing and concentration of the chemical [215].

Peptizers in natural rubber

The function of a peptizer is to reduce the viscosity of rubber to make it processable. Reducing viscosity strictly by mechanical means has an inherent limitation. When the rubber is cold, the mixer provides high shear and polymer breakdown occurs rapidly. However, mixing creates heat. As the mix warms, thermal softening provides less shear and the breakdown of molecules becomes slower. Chemical additives called peptizers have been developed to hasten this molecular cleavage. The internal mixers are very sensitive to changes in mixing time or rotor speed. High speed mixing reduces viscosity quite rapidly, but the batches may dump in a very sticky and non-uniform state. This problem may be partly due to inadequate dispersion of the peptizer. To maximize dispersion, the addition of extra plasticizers or process aids has also been suggested [216].

Peptizers are also used in the preparation of rubber solutions and in reclaiming the rubber. Use of chemicals such as xylyl mercaptane and copper oleate is recommended for easy dissolution of raw natural rubber for evaluation of its dirt content as per the Bureau of Indian Standard test procedures.

I.9. Latex Compounding

Rubber products are manufactured from concentrated latex by mixing it with various compounding ingredients. Some of these ingredients like stabilizers, vulcanizing agents, accelerators, antioxidants etc are necessary in manufacture of almost all latex products. Whereas, viscosity modifiers, fillers, plasticizers, etc are selective and used only in certain latex products. The art of mixing various compounding ingredients with latex is known as compounding. All ingredients for latex compounding should be brought to a physical state comparable to latex, before they are admixed.

Addition of water-soluble organic liquids, salt of polyvalent metals, acidic materials etc bring about coagulation of latex. Such ingredients should not be added to latex. Compounding ingredients added to latex may be water-soluble or water insoluble. Water-soluble ingredients can be added into latex as solutions in water. But water insoluble/immiscible ingredients must be added as dispersions/emulsions. During the addition of the compounding ingredients, the mix should be stirred slowly but thoroughly. It is important to avoid contact between the stirrer and the container since latex is readily coagulated by friction. The purposes of adding individual ingredient, their dosage and their effect on different service requirements are briefly discussed.

I.9.1. Compounding Ingredients

The compounding ingredients for natural rubber latex can be broadly classified into eight groups.
1. Surface active agents
2. Vulcanizing agents
3. Accelerators
4. Activators
5. Antioxidants
6. Fillers and pigments
7. Plasticizers
8. Special additives

Surface active agents

All chemicals that are used as stabilizers, dispersing agents, emulsifiers, wetting agents, foam promoters, foam stabilizers, viscosity modifiers, etc come under this class.

Stabilizers are first added into latex during compounding to maintain the latex in the colloidal condition ie. to prevent coagulation of latex compound while adding chemicals, stirring or on storage. They are classified as cationic, anionic and non-ionic according to the chemical nature. For preparation of dipped and extruded products, anionic soaps are generally used.

Examples for anionic stabilizers are Vulcastab D paste (sodium salt of cetyl/oleyl sulphate) ammonium laurate, potassium oleate, etc. Vulcastab D paste is soluble in hot water and it is added at the rate of 0.1 to 1 part for 100 parts of latex depending on the extent of stabilization required. Ammonium laurate is added as a main stabilizer for the preparation of latex thread and gloves; its dosage varies from 0.2-0.5 parts per 100 parts of latex. Addition of potassium oleate to latex causes much bubbles during stirring and it is used as a stabilizer and foam producer in the manufacture of latex foam (0.5 to 1.25 parts per 100 parts of latex).

Curing agents (vulcanizing agents)

Except its use as adhesives, the full potentialities of rubber latex are realized only after vulcanization. On vulcanization, properties such as tensile strength, modulus, elasticity and resistance to ageing of rubber are improved. The normal vulcanizing agent for natural rubber latex is sulphur. Depending on the particular property required for the product, sulphur is added at different levels ranging from 0.3-2.5 phr. Sulphur at 2.5 phr level gives good tensile properties. But heat resistance of the product would be low. Sulphur at 0.3 phr level along with 3 phr TMTD and 1phr thiourea gives products having good heat resistance. In sulphurless cure, TMTD is used as vulcanizing agent.

Accelerators

Accelerators are chemicals added into latex to reduce the vulcanization time and also to increase the technological properties of the vulcanized product. ZDC, ZMBT and TMTD are the main accelerators used in latex compounding.

The common accelerators used with rubber bands, elastic thread, gloves and foam rubber is ZDC and its dosage ranges from 0.5 to 1.3 phr. ZMBT is used in addition to ZDC in latex compounds where increased modulus for the product is required. Its dosage also ranges 0.5 to 1.5 phr. TMTD is required where high heat resistance of the product is needed. Its dosage varies from 2-3 phr and it is used in low sulphur formulations.

Activators

Zinc oxide is the activator used in latex compounds to boost up the cure rate and also to impart additional heat resistance, to the product. The dosage is very low with rubber bands say 0.1 phr and may be as high as 2-3 part with elastic thread. Usage of higher dosage of ZnO should be made with caution, since it has a tendency to destabilize latex, especially if higher level of ammonia is present in latex.

Antioxidants

The antioxidants protect rubber from deterioration by other agencies such as oxygen, heat, light, ozone, trace metals etc. Phenolic type of antioxidants are generally used in latex because they are nondiscolouring, Antioxidant SP (styrenated phenol) at 1 phr level is usually employed in latex compounds. Antioxidant HS or Flectol H (1,2 dihihydro–2,2,4 trimethyl quinoline) is another antioxidant that can be used in latex compounds at low dosages of 0.25 to 0.5 phr. It gives good heat resistance, but it should not be used at a level more than 0.5 phr as at higher levels, it will cause staining and also discolour the product.

Fillers and pigments

Inorganic fillers and pigments are added in latex compounds to cheapen and stiffen the product or to colour it. Clays, whiting, mica powder etc are used as fillers. About 5-10 phr clay or whiting is added in the production of rubber bands. They have to be ball milled for 12-24 hours or made into thick slurry with water using a small quantity of dispersing agent before addition into latex. Large quantity of filler is added to latex foam compounds and also in formulations for latex carpet backing. Colours are available as dispersions and they can be directly added into latex.

94

Plasticizers

Plasticizers are used in latex compounds to reduce the modulus of the products. In gloves, balloons *etc.* mineral oils of the paraffinic and napththanic types are commonly used. These oils are added into latex as emulsions.

Special additives

Depending on the application of the latex compound, certain special ingredients are also added to the latex. Phenol formaldehyde resins, rosin esters, sodium silicate, solvents, starch etc are added to get special characteristics. Use of zinc stearate in place of zinc oxide gives good transparency for the product. Use of trichlorobromo methane in latex compounds imparts flame resistance to the product.

I.10. Role of Coupling Agents in Silica Filled Compounds
I.10.1. Coupling Agent

Coupling agents are defined primarily as materials that improve the adhesive bond of dissimilar surfaces. These involve an increase in true adhesion between the filler and polymer, better wetting, rheology and other handling properties. Better adhesion strength in these cases has been explained by a coupling mechanism through interfacial diffusion and interpenetrating crosslinking networks. The coupling agent creates a strong bond between the two at their interface and modifies the interface region   on the organic and inorganic boundary layers[217]. Surface-active agents can be used to favour interactions between hydrophilic filler and a hydrophobic polymer but this type of coupling is not very effective. Stearic acid and its metallic salts are good examples of surface-active agents. Their effect may be simply described as an increase in the wetting of filler particle surfaces by polymer molecules. Even though the properties of polymers are improved by the addition of surface-active agents their effect does not last long in humid atmosphere or for a long storage period and the physical properties deteriorate.

Surface treatment of fillers to improve polymer-filler interaction has become common during the last decade and a number of publications in this

regard, are available[218-225] dealing with the effect of surface modifiers on the rheological and mechanical properties of composites. Improvement in dispersion level and processability can be attained through the use of surface treatment of fillers. Coupling agents may be fixed to fillers prior to their addition to polymers or they may be added directly to polymers. The problem of compatibility between the filler and polymer matrix can be overcome by modifying the filler-matrix interface [226,227].

Coupling agents, usually have dual reactivity since they are capable of reacting both with polymer and with the filler surfaces. The stability of polymer-filler attachment appears to be related to the strength of the covalent bonds between the polymer and the filler via the coupling agents. Although the exact mechanism of bonding may still be controversial, it is believed that the organo functional portion of the coupling agent reacts with the polymer and becomes covalently bonded to the matrix. There exist many coupling agents for these applications and among these, silane[228] and titanate-coupling agents[229], phosphorous esters[217] and chromium-acid complexes[230], etc. have been found to form strong assemblies.

Marked increase in reinforcement is observed with silane coupling agents in silica filled rubber vulcanizates. Wang and Wolf[231] showed that silane modified silica increases its compatibility with hydrocarbon elastomers, hence, improves filler dispersion, compound processability and certain vulcanizate properties. Now, a series of silane coupling agents are available with general formula $YRSiX_3$, in which Y is the organo functional radical, R represents the alkyl group and X are hydrolysable groups, such as chloro, alkoxy or acetoxy groups. The hydrolysable groups allow them to form strong bonds with the polymer matrix and with the filler particles. Plueddmann[228] gives a detailed account of silanes, in bonding thermoplastic polymers to mineral surfaces. The silane by co-reacting with the polymers modifies the polymer morphology at the interface to improve stress-transfer at the interface. The silane-triol formed by hydrolysis of trialkoxy silane coupling agents has unique bonding capability with silica, glass and some other mineral surfaces. Pickwell[232] studied the use of the bis [triethoxysilyl toluene] polysulphide as a scorch resistant silane coupling agent for mineral-filled elastomers.

Organo titanate coupling agents are unique in that their reaction with the free protons at the inorganic interface, results in the formation of organic monomolecular layers on the inorganic surface. The absence of polymolecular layers at the interface together with the chemical structure of the titanates create novel substrate surface energy modifications and polymer phase interactions, often resulting in viscosity reductions in unfilled, as well as filled polymer composites. Titanate-treated inorganics are hydrophobic, organofunctionals. When incorporated into polymer systems, they often promote adhesion, improve dispersion, rheology, impact strength and mechanical properties. Titanate coupling agents react with the filler surface resulting in the formation of non-extractable organic monomolecular layers providing compatibilization and a molecular bridge between the interface of the inorganic filler and the organic matrix. Several reports are available regarding the use of these types of coupling agents[233,234].

Yamaguchi et al.[235,236] developed some non-nitroso coupling agents and claimed improved dynamic properties in natural rubber, synthetic polyisoprene, styrene butadiene rubber and poly butadiene rubber. Furukawa et al.[237] claimed that modification of carbon black with ethylene glycol, ethanolamine, hexa methylene diamine, 1,2-dimercapto propyl alcohol or phenyl isocynate improved SBR vulcanizate properties as a function of active hydrogen content of carbon black.

I.10.2. Reinforcement by Silica Filler

Maximum reinforcement effect of a filler can be achieved through good dispersion and better chemical or physical interaction with the polymer. Since rubber and carbon black are both hydrophobic substances, there is no problem arises when the two are mixed. When silica is mixed with the commonly used non-polar, olefinic hydrocarbon rubbers, there will be a greater occurrence of hydrogen bond interaction between surface silanol groups in agglomerates than its interaction between polar siloxane or silanol and the rubber, leading to mixing problems[238]. For enhancing the compatibility of hydrocarbon rubber, surface of the silica is to be modified. Bifunctional organo silanes are commonly used to chemically modify the silica surface in order to promote interactions with

hydrocarbon rubbers. Silica, a coupling agent and rubber are usually simultaneously introduced into internal mixers. The chemical reactions occurring during mixing are (1) bonding of the organosilane to the silica surfaces (2) a reaction between the organosilane and the rubber molecules.

Scheme I.2. Mechanism of the silanization reaction

The coupling agent is added to improve the mechanical properties such as tensile, tear and heat build-up of silica-filled rubber vulcanizate. The coupling agent leads to lowering of young modulus, suggesting a better hydrophobation reaction[219,239]. The improvement in heat build-up has been correlated to lower tan δ at 60 °C. When combined with accelerators such as TMTD and CBS, bis - (triethoxy silylpropyl) tetrasulphide (TESPT) causes rubbers having silica filler to crosslink, without any need for sulphur and without the mixing problem normally encountered with silica.

According to Hunsche et al.[240] and Gorl and Parkhouse[241] initially a single bond with the silica surface is formed between one ethoxy silyl group of the coupling agent and a silanol group of the silica (primary reaction). This is followed by the secondary reaction (condensation reaction between pairs of neighbouring silane molecule, which are already bonded to the silica surface) as shown in Scheme I.2. During vulcanization, TESPT may react as an accelerator or it may donate sulphur to the rubber compound.

In the case of carbon black, filler-polymer interaction is mainly of a physical nature, whereas in the case of bifunctional silane as coupling agent, a chemical bond between the silica and the rubber is established.

I.10.3. Silanisation of Silica

The surface energy of silica can be reduced by addition of glycols or amines in rubber compounds. Chemical treatments such as esterification with the polar silane, the so-called silanization reaction takes place which leads to hydrophobation of the surface. The hydrophobation of the silane with a monofunctional alkyl silane reduces the filler network strongly and makes the silica compatible with the rubber matrix. This reduction depends not only on the degree of hydrophobation (eg. amount of silane) but also on the kind of silane.

An increase in the alkyl chain length leads to a lower Payne effect as the hydrophobation improves. The addition of HDTES (Hexadecyl triethoxy silane) that contain long chain alkyl groups to a silica compound results in an outstanding low Payne effect, which makes this alkyl silane useful as a very efficient processing aid. Two explanations for the loss of silica to silica contacts may be stated. (a) Long alkyl chains cover the silica surface very efficiently, or

(b) the long alkyl chain form self oriented layers that shield the surface. All other silanes show a significantly higher filler networking at this dosage. Functionally active polymers containing polar or chemically reactive alkoxysilane groups have been used to interact with silanol groups. Sequence of the Payne effect of these samples is principally not changed after curing, but absolute values differ.

I.10.4. Rubber to Rubber and Filler to Rubber Crosslinking

The crosslinking of the matrix results in a constant increase of the modulus G at all strains and the decrease of tan δ. The degree of matrix cross linkage can also be assessed by the torque developed in a curometer at a particular temperature.

Types of coupling agent

There are different types of coupling agents

(1) Bifunctional silanes, (2) Monofunctional silanes and (3) Non sulphur bearing silanes. Some silanes of commercial importance are the following:

1. TESPT – Bis-(triethoxysilylpropyl) tetrasulphide (Si 69)
2. TESPD – Bis-(triethoxysilylpropyl) disulphide (Si 266).
3. TESPM – Bis-(triethoxysilylpropyl) monosulphide.
4. PTES   – Propyl triethoxysilane
5. OTES   – Octyl triethoxysilane (VP Si 208)
6. HDTES – Hexadecyl triethoxysilane
7. TCPTS – Thiocyanato propyl triethoxysilane

Payne effect

Compounds containing carbon black or silica reinforcing fillers show a high shear modulus (G') at low strain compared to G' at higher dynamic strain. This strain amplitude dependence is referred to as the 'Payne effect'.

The substitution of low levels of (5 to 20 phr) of silica for carbon black can enhance tear resistance, cut growth and adhesion properties. The reinforcement levels and performance properties of carbon black can be obtained with silica and proper use of silane coupling agents, but at a higher cost. In tire treads, silica yields a higher wear resistance and better wet grip in combination with a

100

lower rolling resistance than carbon black[242] especially when highly dispersible silica is used[243].

According to Payne[244], the strain amplitude dependence of a vulcanizate is due to 'filler–filler linkage' of a physical nature which are broken down by straining.

The breakdown and reformation of the network linkages during dynamic deformation consumes energy (hysteresis loss), which is reflected in the variation of tan δ with increasing dynamic strain. The energy that is consumed with each revolution of a tyre through its road contact footprint is the rolling resistance of the tyre. The contribution from the tread compound towards the energy consumed is directly related to its hysteresis losses under tyre operating conditions. Minimising the rolling resistance contributed by the tread compounds reduces the work that must be done by the engine and thus reduces the fuel consumption and the amount of combustion gases that are emitted into the air.

Traction characteristics involve the deformation of a smaller portion of the tread in the immediate vicinity of the road surface contact area. This is very high frequency deformation applied to a much smaller segment of the tread compound. The desired response is for the tread to absorb as much energy as possible to maintain a good grip on the road surface during stopping, starting and cornering - the exact opposite of the response that is targeted in reducing rolling resistance.

I.10.5. Carbon Black versus Silica

The concept of 'magic triangle' is low rolling resistance, traction and tread wear resistance. Use of lower surface area carbon black can improve rolling resistance but results in poor tread wear and traction performance.

Using a high structure black, at a reduced loading can also lower rolling resistance, but traction characteristics is decreased. A variety of approaches to lower rolling resistance have been pursued with conventional carbon black and all have had limited success because of reduction in tread wear and/or traction performance. The interaction of a filler in a polymer system is dependent upon the surface energy resultant from two opposing energy components, a dispersive component γ_s^d and a specific component γ_s^{sp}

101

The dispersive component relates to a strong filler-polymer interaction. A high specific component relates to a strong filler-filler interaction, or leads to the formation of a filler network. Silica has low dispersive component and higher specific component compared to a carbon black of comparable surface area [245].

The difference between carbon black and silica significantly alter their contribution to dynamic performance in the lower strain region associated with rolling resistance. As the dynamic strain is varied, the trends that are observed are primarily due to difference in the amount as well as the strength of networks that are formed by filler aggregates.

Silica has a higher elastic modulus (E') than N-110 carbon black at low strain, but only slightly higher E' at 100% strain. This is attributed from the silica-filler-filler network at low strain, and that this networks breakdown at the high strain levels.

The N-110 carbon black shows the highest tan δ in the 1% to 10% strain region that is associated with rolling resistance. Carbon blacks have less tendency to form a filler-filler network than silicas, but the agglomerates that do form are relatively weak and breakdown in this low strain region. The silica forms more networks, but they are stronger and do not break until higher strains are applied. The silane modified silica shows very little effect from filler-filler network breakdown and reformation and thus less energy consumption than carbon black in the low strain region associated with rolling resistance.

Traction is a very high frequency phenomenon that is beyond the normal dynamic measurement capabilities. 0 °C measurement of tan δ as well as several other dynamic functions have been used as indicators of wet traction, but have not correlated well with tyre performance when comparing carbon black to silica filler systems.

Freund and coworkers[246] presented a potential alternative approach using new carbon blacks, called "Inversion Blacks" with different surface microstructure. It enhanced the interaction with polymer and contributed to lower rolling resistance while maintaining the tread wear, traction and other properties.

Another grade 'Nano Structure' black [247,248] was introduced and featured a narrowed aggregate size distribution for improved tread wear in high severity operating condition. The higher degree of disorder enhances the interaction with

the polymer, giving improved rolling resistance performance[249,250]. Non-structure black gave 10% to 15% lower tan δ at 60 °C, improved tread wear and equal or slightly improved wet traction[248].

I.10.6. Silica Development Activities

In the case of carbon black filled tyre treads, static electric discharge was developed. Besides the aggrevation of a shock from the static charge, it affects the electrical components of vehicles (auto). The silica/silane treads were less conductive than carbon black filled treads. The tyre producers have developed methods to dissipate the static charge. The abrasion resistance imparted by the carbon black is difficult to obtain, even with the use of a coupling agent and a higher surface area for the silica compared to carbon black that is being replaced[251]. Silica aggregates normally have less permanent structure than the high structure carbon blacks typically used in tyre tread compounds. Thus 'occlusion of rubber' effect that occurs with high structure carbon blacks is diminished when silica is substituted and its surface modified with silane coupling agent. The silane modification reduces agglomeration and enables a reasonably good dispersion to occur during mixing, but it also reduces silica's ability to physically trap polymer chains.

This occlusion is an additional restriction of polymer chain mobility imparted by carbon black that must be overcome with the silica/silane system via the covalent bonding of the sulfur functional group of the silane.

A silica labeled as "high dispersibility" or "highly dispersible" silica (HD silica) showed 8% to 10% improvement in tire wear life when compared to standard silica in the same polymer or polymer blend. This is proved to be an important factor in obtaining tread wear performance with new silica/silane system that was comparable to tread containing carbon black.

I.10.7. Silane Coupling and Mixing/processing Options

Bi-functional organosilanes with a sulphur-containing functional group have been used as coupling agents in rubber compounds. The first commercial product was γ-mercaptopropyl-trimethoxy silane (MPS). Despite its disagreeable odor and its effect in reducing scorch time, it has been used extensively in non-

tire rubber applications and to produce treated mineral fillers. The short scorch time severely limited its use in tyres. A world oil shortage in the 1970s generated R&D efforts to find alternate filler choices that were not petroleum based. This created enough interest in the silica/silane filler system that it was evaluated in several tyre programs[252,253]. TESPT was introduced during this period and promoted for use in dynamic rubber applications[242]. Compared to MPS, it gave better scorch delay, very little odor and produced longer, more flexible, sulfur linkages during vulcanization.

The mixing and processing of silica/silane tread compounds is considerably more difficult. The usual method is to react the silica and TESPT silane *in situ* during the mixing of the compound. The attachment occurs via a reaction between the silanol groups of the silica and the ethoxy groups of TESPT and ethanol is released (Scheme I.2). Studies of the silanization reaction indicate that only one of the three ethoxy groups reacts initially to form a single siloxane bond to the silica surface. That is followed by a secondary condensation reaction between adjacent silane molecules that are already bound to the silica surface[254].

The reaction to couple the sulfur functional group to the polymer matrix should occur during vulcanization[255,256]. If the mixing temperature gets too high, the tetrasulfide group of TESPT may split prematurely, giving undesirable pre-crosslinking[257]. This upper limit on mixing temperature is about 160 °C when using TESPT[258]. The precrosslinking can increase the compound viscosity and give processing difficulties. Good control of temperature and mixing time is a necessity. An additional mixing step is usually required to obtain sufficient reaction time at elevated mixing temperatures. The mixing procedure is critical for obtaining good processing and performance with a silica/silane filler system. Contrary to the usual procedures for mixing carbon black filled tread compounds, there is the added burden of carrying out an *in situ* chemical reaction to attach the silane to the silica without exceeding the upper temperature limit where the sulfur chain of the TESPT starts to decompose and generate unwanted crosslinks. The silane attachment is a chemical reaction that requires a fairly high activation temperature as well as sufficient time to proceed to completion.

TESPD, bis-(triethoxysilyl propyl) disulfide, was introduced and shown to give more processing safety when mixing at higher temperatures[258]. The

disulfane group is more stable than the tetrasulfane of TESPT[259]. The additional sulfur required can be added in a later mixing step to achieve a polysulfide distribution similar to that obtained with TESPT[260-264]. When mixed at higher temperatures (160-171 ^{0}C), the data for the TESPD compound did not change significantly, but some of the properties of the TESPT compound were altered– indicating some pre-crosslinking had occurred[258]. The silica / silane gives a lower rolling resistance, an improvement in wet and ice grip, but not good abrasion resistance.

Colvin and Henning[265] gave a good overview of the trade-offs that result from altering the polymer architecture (microstructure and macrostructure). The most important variable influencing the dynamic performance of compounds is the glass transition temperature (Tg) of the polymer and it can be altered by various means. Tg also correlates with treadwear with lower Tg compounds giving improved wear performance.

Nakamura and Takagishi[266], evaluated emulsion SBR modified with amino or hydroxyl groups. They reported that the amino group modification gave enhanced affinity and better dispersion of silica in a silica/silane compound. Rebound at 60 ^{0}C increased in proportion to the degree of modification and increased further when the amino compound was more basic. The chemical modification of emulsion SBR was considered to be a reasonable cost option for further improvement of rolling resistance.

Saito and co-workers[267] reported on evaluations of solution SBR modified with various functional groups. Comparisons were made in a silica/silane compound with the objective of finding a modification that would allow a reduction of the silane coupling agent level. Polymers modified with amino, glycidyl and alkoxy groups all showed encouraging results for dynamic properties and abrasion resistance. Modification with a diglycidylamino group was felt to be the most promising.

Rothon[268] discussed the potential use of functionalised low molecular weight polymers as coupling agents. The addition of silinated polybutadiene at 10% by weight of silica was shown to reduce viscosity, improve stress-strain properties and abrasion resistance and reduce heat build-up. Low molecular weight carboxylated polymers are used commercially to modify basic fillers such as precipitated calcium carbonate. They were not expected to enhance

105

properties with acidic fillers, such as silica or clay, but evidence of some coupling was found.

The use of silicas in combination with bi functional organo silanes, particularly TESPT is becoming more and more important in rubber applications[269]. In passenger tread compounds; it is increasingly being used to reduce rolling resistance[270,271]. Two factors responsible for the properties are the reaction of triethoxysilyl group of TESPT with silanol group of the silica during compounding with loss of ethanol and the reaction of rubber with the silane (eg. tetrasulphide) during curing of the rubber compound[272].

Amount of silane and sulfur influence the vulcanizate properties strongly. Both the silica-silane-rubber and the rubber-rubber (matrix) crosslinking are responsible for the reinforcement. An increase in the amount of silane leads to an increase of the amount of silica to rubber bond, resulting in higher modulus and a strongly reduced elongation at break. The silica to rubber coupling consumes free sulphur resulting in a lower matrix cross link density[273]. During vulcanization with sulphur and accelerators, the rubber is crosslinked by sulfur bridges, resulting in a sulphur network structure depending on the type of accelerator and the ratio of the sulphur and accelerator. With the addition of silica and the sulphur functional silane, silica-silane-rubber bonds are also formed[274]. Both crosslinking reaction of the matrix and silane–rubber coupling take place at the same time, during vulcanization.

In order to activate the di and short chain polysulfanes in the Si 69 for the coupling reaction, the addition of sulphur and accelerators is needed[258]. According to Wolff[275], if free sulphur is not added during mixing, only (in presence of Si 69) pure silica-rubber reinforcement takes place in the compound (ie. there is no matrix crosslinks).

The presence of sulphur and accelerator however favours both the matrix crosslinking and the silane coupling. Recent investigations[276] have demonstrated that the silane-rubber coupling contributes strongly to the delta torque and that TESPD and Si 69 consume free sulphur for the coupling reaction, which reduces the degree of the matrix network. Silanes need to incorporate sulphur for the activation and following coupling reaction, the matrix and silica-rubber coupling compete for the added sulphur in the compound. Once the free sulphur is consumed for both crosslinking reations, no further bonds are built-up. Increase

of the amount of sulphur leads to higher coupling efficiencies as well as an increased crosslink density of the matrix, which result in much higher moduli and reduced elongation.

The ratio, modulus 300% / 50% correlates with the reinforcement and therefore indicates the degree of the silica-rubber coupling.

Relatively high amounts of Si 266 with moderate levels of sulphur are needed to achieve a high degree of silica-rubber coupling without a too strong matrix network resulting in a further reduced elongation at break. Too high amounts of coupling agents reduce the degree of matrix cross linking because a high portion the sulphur is consumed to build up the silica-rubber coupling.

Model of silica/silane reinforcement

Figure I. 2 shows the vulcanizate reinforcement in the case of silica modified with the bifunctional silane TESPT. The silica aggregates form a network, which raises the static modulus and the modulus at low strains, through strong hydrogen bonding[277]. Due to this silica-silica network, part of the matrix rubber is immobilized and become occluded in this network, which also contributes to the modulus at low strains. Additionally, there is a layer of bound rubber chemically bound to the silica surface by the organosilane. Some rubber is probably also loosely adsorbed on the modified surface which also contributes to the bound rubber, but silica-rubber interaction is very weak[278].

Under high deformation, the silica-silica network breaks partly down, according to the stress applied and modulus decreases. With this destruction of the filler network, the occluded rubber is reduced/lost and participates in the matrix deformation, which also leads to a decrease of the modulus. But due to the chemical bond of the silane, the rubber on the silica surface and in its structure remains immobilized and therefore contributes to the modulus even under high strains – "in-rubber structure". Therefore, the Payne-effect is caused by the break-down of the filler network and the loss of occluded as well as loosely adsorbed rubber. This explanation is supported with the findings regarding the reinforcement of carbon black and silica published by Medalia[279].
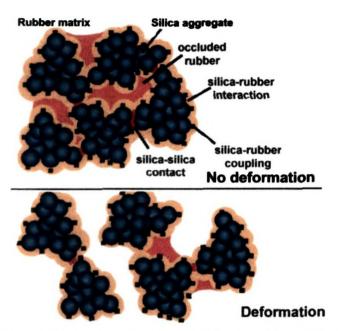
Figure I.2. Model of the reinforcement (Payne-effect) for a silica/TESPT-filled rubber compound
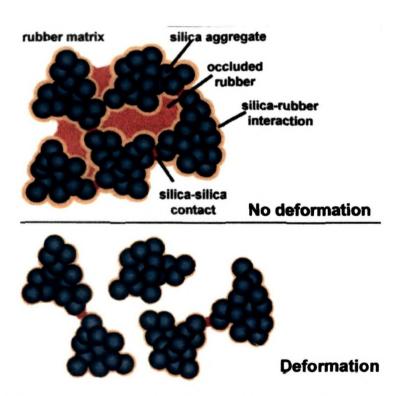

Figure I.3. Model of the reinforcement (Payne-effect) for a silica/short chain alkylsilane-filled rubber compound

If short chain alkylsilane (eg. propyltriethoxysilane, PTES) is used instead of TESPT, the kind of reinforcement changes (Figure I.3). Due to the short alkyl

chain, there is still the possibility to form a silica-silica network, but depending on the degree of hydrophobation the strength of the network decreases. As in the case of TESPT, the network breaks partly down according to the deformation and occluded rubber is lost as well. But contrary to the TESPT modification, the bound rubber on the silica surface is not chemically bond and therefore is lost under stress - the "in rubber structure" is very low. This leads to a lower modulus under high strains.

Scope of the Work

Natural rubber is a versatile polymer, which forms the base material for the manufacture of thousands of rubber products. World production of NR during 2002- 2003 was 72.7 lakh M.T. from a planted area of 93.45 lakh ha. Rubber seed oil is an important by-product from the rubber plantations and it is estimated that there is a world wide potential for the production of 102574– 117227 M.T. per annum of this oil. In India the total area under rubber plantation is 5.69 lakh ha. (mature area is 4.07 lakh ha) It is estimated that there is a potential for the production of 6300-7200 M.T. per annum of rubber seed oil in this country, if the collection and processing of the seed are done in a properly organized manner. Collection of rubber seeds and extraction of the oil can generate employment and also fetch additional income to the farmers. However, farmers do not show much interest in this area because of the un-remunerative price obtained for the seeds collected by them. Renewed interest in this area can be generated if value addition of the oil is effected and new applications are found out, which can be commercialized.

From the review presented in Section I.4 it can be seen that the current areas of application of rubber seed oil are low quality washing soap, paints, alkyd resin, factice etc. It is also seen that other vegetable oils such as linseed oil and soybean oil are used as additives for both rubber and plastics compounding (Section I.5). Since the basic components of rubber seed oil and most of the other vegetable oils are esters of saturated and unsaturated higher fatty acids, it is reasonable to think that the rubber seed oil can also find application as a polymer additive, if suitably modified by appropriate chemical

reaction. Presence of a higher concentration of unsaturated fatty acids in rubber seed oil is helpful in carrying out reactions such as epoxidation to produce epoxidised rubber seed oil. Thus, there is great scope for a detailed examination of the possibilities of making use of rubber seed oil, either as such or as a chemically modified form, in rubber and plastics fields, as a compounding ingredient. Production of value added industrial raw material from rubber seed oil would be helpful in getting a remunerative price for this by-product, obtained from a renewable natural source.

Objectives of the Work

As discussed in the previous sections, vegetable oils have been successfully used in many applications in polymer field. Rubber seed oil (RSO) being a by-product can have economic advantages also in its use. At present, rubber seed oil finds industrial application in limited fields only. In order to widen its field of application, a detailed study was planned with the following specific objectives.

1. Evaluation of rubber seed oil as a plasticizer for arylonitrile butadiene rubber compounds

Esters such as dioctyl phthalate (DOP) and dibutyl phthalate (DBP) are used as palsticizer for nitrile rubber due to their highly polar nature. However, in applications such as oil seals and o-rings, which come into contact with oil or which are used at a higher temperature, plasticizers like DOP and DBP are lost from the product due to leaching or volatilization, causing failure of the product. This happens due to low molecular weight of the DOP / DBP. Rubber seed oil as such is less compatible with nitrile rubber due to its low polarity. But introducing epoxy groups in the unsaturated higher fatty acids present in the oil can enhance the polarity of RSO. Since epoxidised rubber seed oil (ERSO) is more polar and has a higher molecular weight than DOP it is expected to function as a good plasticizer for nitrile rubber. Hence a detailed evaluation of ERSO as a plasticizer for nitrile rubber was undertaken in comparison with dioctyl phthalate.

2. Evaluation of rubber seed oil as an acid accepter cum plasticizer in polychloroprene rubber compounds.

Vulcanization of polychloroprene rubber (CR) is effected by oxides of metals such as zinc and lead through the 1,2 addition units of the monomer present in small quantities in the polymer. Zinc chloride, which is formed in the reaction, acts as an active catalyst of the vulcanization reaction, causing severe scorching of the compound. Converting the zinc chloride to magnesium chloride by reaction with magnesium oxide usually controls this problem. Magnesium oxide acts as an acid scavenger also, by reacting with the hydrochloric acid (HCl), which is formed as a by-product of the reaction between zinc chloride and traces of moisture that may be present in the compound or formed by thermal decomposition / dehydrochlorination of the polymer.

Rubber seed oil contains about 78% of unsaturated higher fatty acids. These fatty acids are expected to react with the HCl to form the corresponding hydrochloride by a simple addition reaction thereby neutralizing the effect of HCl. It is also possible that the zinc chloride / zinc hydrochloride reacts with the higher fatty acids of the RSO to form the corresponding zinc soap, which could act as a plasticizer in CR compounds. Thus a detailed study on the use of RSO in CR compounds was undertaken to evaluate its role as an acid accepter cum plasticizer in polychloroprene rubber.

3. Evaluation of rubber seed oil soap as a foaming agent for latex foam.

Latex foam is manufactured by frothing the latex compound using foaming agents and then stabilizing the foamed structure through controlled destabilization of the serum- rubber and serum – air interfaces, by a process called delayed gelling. Potassium oleate is the common foaming agent used in latex foam production. For economic reasons, use of castor oil soap in combination with potassium oleate soap is practiced by the foam industry. Castor oil and rubber seed oil contain saturated and unsaturated higher fatty acids, in which oleic acid and linoleic acid form a major portion. Hence it is expected that the RSO soap could function as a substitute for oleic acid / castor oil soaps in latex foam production. A comparative evaluation of potassium

oleate, castor oil soap and rubber seed oil soap in latex foam production was made with the above objective.

4. Evaluation of copper salt of rubber seed oil as a peptizer for natural rubber

Natural rubber is marketed in different forms such as sheet, crepe, block and concentrated latex. Out of the dry forms of NR, the block form is graded by assessing the range of values of certain quality parameters like dirt, nitrogen, volatile matter, plasticity and plasticity retention index. The dirt content of block rubber is estimated by dissolving the rubber in a solvent, filtering the solution through a standard sieve and then weighing the dried matter retained in the sieve. For facilitating faster dissolution, easy filtration and reducing the viscosity of the solution, a peptizer like copper oleate or xylyl mercaptan is used. Rubber seed oil is a good source of higher fatty acids such as oleic and linoleic acids and is cheaper compared to oleic acid. To assess the effectiveness of copper salts of mixed fatty acids prepared from RSO in peptizing natural rubber, a detailed evaluation was conducted on its use for dirt content estimation of block rubber in comparison with copper oleate.

5. Evaluation of rubber seed oil as a reinforcement modifier for silica filled natural rubber compounds.

Highly polar and reinforcing filler like silica is very difficult to be dispersed in a non-polar rubber like NR and polybutadiene. For achieving easy dispersion and enhancement of the reinforcing effect, coupling agents like triethoxysiliyl propyl terasulphide (Si 69) is used in silica filled NR compounds. The action of Si-69 is multifold, namely, interaction with the silanol groups of silica, crosslinking with the rubber hydrocarbon and acting as a compatibilizer. However, to achieve the full benefit of using Si69, special mixing techniques are to be followed at a higher temperature. This chemical is very costly also. It is expected that the epoxy group of the ERSO can interact with the silanol groups of the silica and the long chain hydrocarbon part of the fatty acid can easily interact with the non-polar rubber hydrocarbon, so that it could function as a reinforcement modifier in silica filled NR compounds. Since RSO contains unsaturated higher fatty acids, some of these could crosslink with the rubber through sulphur. To assess the role of epoxidised rubber seed oil as a

reinforcement modifier and plasticizer, a detailed evaluation of this material was made in silica filled NR compounds, in comparison with Si 69 and naphthenic oil.

6. Evaluation of epoxidised rubber seed oil as a plasticizer cum stabilizer for polyvinyl chloride.

Polyvinyl chloride (PVC) is one of the most common thermoplastics used in a variety applications. It can be made flexible or rigid by proper selection of the plasticizer and its dosage. Since PVC is polar in nature, ester type plasticizer like DOP and DBP are commonly used. PVC undergoes thermal decomposition with the evolution of hydrochloric acid during heating. For neutralizing the HCl evolved, a stabilizer like calcium stearate is used in PVC compounds. There are several reports, which indicate that epoxidised vegetable oils such as soybean and linseed oils exhibit synergistic effect of a stabilizer and plasticizer in PVC compounds. Hence a detailed study was conducted to evaluate the effect of epoxidised rubber seed oil as a plasticizer cum stabilizer in polyvinyl chloride.

As detailed above, the primary objective of this work is to examine the possibility of widening the area of application of rubber seed oil by exploring its utilization in new fields of rubber and thermoplastics.

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Chapter II

Experimental Techniques

II.1. Materials Used

II.1.1. Concentrated Natural Rubber Latex

Concentrated natural rubber latex conforming to BIS: 5430-1981 used in this study was obtained from the Pilot Latex Processing Centre of the Rubber Board.

The properties of latex used are given in Table II.1.

Table II.1. Properties of NR latex used

Sl. No.	Parameters	Value
1.	DRC (%)	60.1
2.	TSC (%)	61.6
3.	Ammonia (%)	0.22
4.	VFA No.	0.03
5.	KOH No.	0.60
6.	MST (sec.)	1227
7.	Sludge content (%)	Trace
8.	Coagulum content (%)	0.004
9.	Copper (ppm)	Trace
10.	Manganese (ppm)	Trace
11.	Iron (ppm)	-
12.	Magnesium (ppm)	-
13.	ZST (sec.)	166

II.1.2. Styrene-butadiene latex

SBR latex used for the study was obtained from M /s Apar Ltd., Mumbai. The properties of the latex are given in Table II.2.

Table II.2. Properties of SBR latex used

Properties	Value
Dry rubber content (%)	41.98
pH	10.80
Brookfield viscosity (cps)	35
Mechanical stability	Good

II.1.3. Polyvinyl Chloride Resin

PVC resin (powder, emulsion grade, K-value 65) used for the study was supplied by M/s Chemplast, Chennai. In this thesis work, two types of PVC were used. 103 EP Grade and 103 EPM 7 Grade. These are medium molecular weight, general-purpose resin, ideally suited for wire and cable, other flexibles, semi rigid as well as rigid application. These are white, free flowing powder. 103 EPM has faster plasticizer absorption.

Table II.3. Properties of PVC resins used

Properties / Grade	K-value *	Inherent viscosity ASTM D 1243-66	Apparent density (g/ml)	Particle size (% retained)	Specific gravity	Heat loss (% max)
103 EP	64-67	0.90-0.98	0.55	40 mesh nil	1.4	0.7
103 EPM 7	64-67	0.90-0.98	0.50	200 mesh-85	1.4	0.7

* 1% Cyclohexanone

$$K \text{ value} = 1000 \times \frac{1.5 \log z\text{-}1 + \sqrt{1+ 200/c} +1+ .5 \log Z) \, 1.5 \log Z}{150 + 3C} \text{---- II (1)}$$

Where Z = Relative viscosity, C = Concentration in g /100 ml [1].

II.1.4. Polychloroprene

Polychloroprene rubber used for this study was Neoprene W grade, purchased from local sources. It contained no staining stabilizer, elemental sulphur, thiuram disulphide or other chemicals capable of decomposing to yield either free sulphur or a vulcanizing accelerator. Polychloroprene consists mainly (88-92%) of trans 1,4-chloro-2-butylene units. The cis 1,4 addition accounts for 7-12%, the 1,2 around 1.5% and the remainder is 3,4 addition. With the 1,2 addition there is a possibility of the chlorine atom remaining in the allylic form. This chlorine is reactive and permits neoprene to vulcanize under a variety of conditions without the use of sulphur or sulphur bearing compounds.

II.1.5. Acrylonitrile-butadiene Rubber

Nitrile rubber (NBR) used for the study was Aparene N-553. It had 33% acrylonitrile content and was manufactured by M/s Apar, Ltd. Mumbai.

It is a copolymer of butadiene and acrylonitrile, made by an emulsion process. It has good resistance to a wide variety of non-polar oils, fats and solvents. Mooney viscosity ML (1+4) at 100 ^{0}C was 42.

II.1.6. Technically Specified Natural Rubber (ISNR 5)

Block rubbers are technically specified natural rubber, in which the grading is done based on parameters that are evaluated by scientific tests. In this work, ISNR 5 was used. The ISNR-5 (Indian Standard Natural Rubber-5) grade rubber was supplied by the Pilot Crumb Rubber Factory of the Rubber Research Institute of India, Kottayam. Kerala. The specifications of ISNR-5 grade NR and their limits are given in Table II.4. The rubber from the same lot has been used in a particular experiment, since the basic properties such as molecular weight, molecular weight distribution and the contents of non-rubber constituents of NR are affected by clonal variation, season, use of yield stimulants and methods of preparation.

139

Table II.4. Specification of ISNR-5 grade natural rubber[2]

Parameter	Limiting value for ISNR-5	Actual value of sample used
Dirt content (% by mass, max)	0.05	0.03
Volatile matter (% by mass, max)	0.80	0.60
Nitrogen (% by mass, max)	0.60	0.30
Ash (% by mass, max)	0.50	0.40
Initial plasticity (Po, min)	30	42
Plasticity retention index (PRI, min)	60	78

II.1.7. Rubber Seed Oil (RSO)

Rubber seed oil used for the study was obtained from M/s Kathirvel, Virudhunagar. The oil was having light yellow colour, free of bad odour and sediments. The physical properties and chemical composition of the oil used are given in Tables II.5 and II.6 respectively.

Table II.5. Physical properties of rubber seed oil used

Parameters	Values
Acid value	36
Saponification value	191
Iodine value	132
Unsaponifiables (%)	0.80
Refractive index	1.47
Specific gravity, 30 ^0C	0.92
Titre (^0C)	28

Table II.6. Fatty acid composition of rubber seed oil

Fatty acid	Content (%)
Palmitic acid	10.8
Stearic acid	10.0
Oleic acid	23.5
Linoleic acid	38.5
Linolenic acid	16.2
Unidentified portion	1.0

II.1.8. Epoxidised Rubber Seed Oil (ERSO)

Epoxidised rubber seed oil required for the study was prepared fron rubber seed oil using formic acid and hydrogen peroxide. Method of preparatior is given in section II.3.2. Epoxidised rubber seed oils having different levels c epoxidation were prepared by adjusting the time of reaction. The levels of epox content in ERSO varied from 0.5 to 5%.

II.1.9. Fillers

II.1.9.1. Carbon black

The following types of furnace blacks used for this study were supplied b M/s Philips Carbon Black Ltd, Durgapur. The medium thermal black wa purchased from local sources. The properties of these carbon blacks are given ii Table II.7.

Table II.7. Properties of carbon blacks

Properties	SRF	GPF	MT black
DBP absorption number	70	90	33
Iodine Number	26	35	--
Particle size (nm)	83	70	300
Specific gravity	1.81	1.81	1.81
pH	7.0	7.0	7.0

SRF - ASTM N 550   GPF - ASTM N 660   MT - ASTM N 990

II.1.9.2. Non- black fillers

Commercial grade china clay and precipitated silica (Ultrasil VN3) were the non-black fillers used for this study. The china clay was obtained from M/s English India Clays, Thiruvananthapuram and Ultrasil VN3 from M/s Degussa A G, Germany. The properties of these materials are given in Table II.8.

Table II.8. Properties of non-black fillers

Properties	Ultrasil VN3	China clay
Specific gravity	2.00	2.62
Particle size (nm)	40-60	300-325
pH	6.7	5.2
Physical form	Fine white granules	Off-white powder
Staining or discolouring	Non-staining	Non-staining

II.2. Rubber Chemicals[3]

The rubber chemicals used for the study were of commercial grade.

II.2.1. Zinc oxide

Purity (%)	99.6
Specific gravity, 25 ^{0}C	5.6
Melting point (^{0}C)	197.5 ^{0}C
Solubility	Soluble in acids and alkalies

II.2.2. Stearic acid

Specific gravity, 25 ^{0}C	0.85
Melting point (^{0}C)	70
Solubility	Soluble in alcohol, chloroform, CS_2, CCl_4, acetone and benzene

II.2.3. Sulphur

Purity (%)	> 99
Specific gravity, 25 ^{0}C	2 07
Melting point (^{0}C)	114
Solubility	Soluble in CS_2, CCl_4 and benzene

II.2.4. Diethylene glycol (DEG)

$$HO-H_2C - CH_2 - O - CH_2 - CH_2-OH$$

Specific gravity, 25 ^0C	1.12
Boiling point (^0C)	245 .
Solubility	Miscible with water, alcohol and acetone

II.2.5. Magnesium oxide (MgO)

Specific gravity, 25 ^0C	3.6
Melting point (^0C)	288
Solubility	Soluble in acids and ammonium salt solution
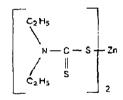
II.2.6. Accelerators

Zinc diethyl dithiocarbamate (ZDC), zinc mercaptobenozthiazole (ZMBT), 2,2'– dibenzothiazyl disulphide (MBTS), tetramethylthiuram disulphide (TMT), N,N'- diphenyl guanidine (DPG) and ethylene thiourea (NA-22) were the accelerators used in the study[4].

II.2.6.1. Zinc diethyl dithiocarbamate

Chemical structure of ZDC is

Melting point	178.0 ^0C
Specific gravity	1.47
Solubility	Soluble in chloroform and benzene
Supplier	Bayer (India) Ltd.. Mumbai

II.2.6.2. Zinc mercaptobenzothiazole

Chemical structure of ZMBT is

Melting point	Decomposes before melting
Specific gravity	1.64
Solubility	Soluble in benzene alcohol and chloroform
Supplier	Bayer (India) Ltd.. Mumbai
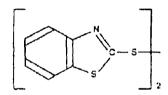
II.2.6.3. 2,2' – Dibenzothiazyl disulphide

Chemical structure of MBTS is

Melting point	175 ^{0}C
Specific gravity	1.54
Solubility	Slightly soluble in benzene and chloroform
Supplier	Bayer (India) Ltd., Mumbai.

II.2.6.4. Tetramethylthiuram disulphide

Chemical structure of TMTD is

Melting point	138 ^{0}C (approx.)
Specific gravity	1.42
Solubility	Soluble in chloroform
Supplier	Bayer (India) Ltd.. Mumbai
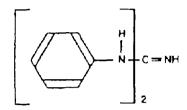
II.2.6.5. N,N'- Diphenyl guanidine

Chemical structure of DPG is

Melting point	145 °C (approx.) decomposed at 170 °C
Specific gravity	1.19 approx.
Solubility	Soluble in alcohol, benzene and CS_2
Supplier	Bayer (India) Ltd., Mumbai
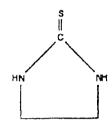
II.2.6.6. Ethylene thiourea (NA-22)

Chemical structure of NA-22 is

Melting point	199-204 °C (approx.)
Specific gravity	1.42
Solubility	Soluble in hot water, methanol, ethanol and acetic acid
Supplier	Bayer (India) Ltd., Mumbai
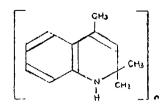
II.2.7. Antioxidants

Polymerised 2,2,4-trimethyl 1,2-dihydroquinoline (TDQ). N- isopropyl N'-phenyl p-phenylenediamine (IPPD), styrenated phenol (SP) were used as antioxidants in the study.

II.2.7.1. Polymerised 2,2,4-trimethyl 1,2-dihydroquinoline

Chemical structure of TDQ is

Melting point	75-90 ^{0}C
Specific gravity	1.08
Staining/discolouring	Staining
Solubility	Soluble in benzene
Supplier	Bayer (India) Ltd., Mumbai

II.2.7.2. N-isopropyl-N'-phenyl-p-phenylenediamine

Chemical structure of IPPD is

Melting point	73 ^{0}C (approx.)
Specific gravity	1.1
Staining/ discolouring	Staining
Solubility	Soluble in oils and hydrocarbons
Supplier	Bayer (India) Ltd., Mumbai
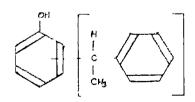
II.2.7.3. Styrenated phenol

Chemical structure of SP is

Boiling point	200-250 ^{0}C
Specific gravity	1.1
Staining/ discolouring	Non-Staining

Solubility	Soluble in alcohol, acetone, hydrocarbons
	and trichloroethylene
Supplier	Bayer (India) Ltd., Mumbai

II.2.8. Plasticizers

Naphthenic oil, dioctyl phthalate(DOP), RSO and ERSO having different percentage of oxirane content were used as plasticizers for this study.

II.2.8.1. Naphthenic oil

Specific gravity	0.9 at 25 ^{0}C
Aniline point	77.8 ^{0}C
Pour point	6 ^{0}C
Flash point	180 ^{0}C
Supplier	Indian Oil Corporation, Cochin.

II.2.8.2. Dioctyl phthalate

Chemical structure of DOP is

Refractive index	1 484
Specific gravity, 23 ^{0}C	0. 986
Viscosity (cps at 30 ^{0}C)	60
Pour point (^{0}C)	46
Vapour pressure (mmHg at 200 ^{0}C)	1.3
Boiling point (^{0}C at 5mmHg)	231
Flash point (^{0}C)	218
Miscibility	Miscible with mineral oil

II.2.9. Special Chemicals

II.2.9.1. Coupling agent (TESPT)

Bis-[triethoxysilylpropyl] tetrasulphide (Si 69) used for the study was supplied by the Degussa Chemical Co., Germany.

Chemical structure of Si 69 is

$$H_5 C_2 O$$
$$H_5 C_2 O \quad Si - (CH_2)_3 - S_4 - (CH_2)_3 - Si \quad O C_2 H_5$$
$$H_5 C_2 O \qquad\qquad\qquad\qquad\qquad\qquad\qquad O C_2 H_5$$
$$\qquad\qquad O C_2 H_5$$

F₁'   F₂'

pH	6.5
Moisture/water content	0 55
Specific gravity at 25 °C	1.095

II.2.9.2 Stabilizer/lubricant

Tribasic lead sulphate (TBLS) and calcium stearate were used as stabilizer and lubricant respectively for the study.

Chemical formula – 3 PbO PbSO₄ H₂O.

Molecular weight	991
Specific gravity	6.4
Refractive index	2 1

Chemical structure of calcium stearate is

$$(C_{17} H_{35} COO)_2 Ca$$

Specific gravity	1.04
Melting point, °C	150-155
Solubility	Slightly soluble in hot alcohol

II.2.9.3. Foam stabilizer (secondary gelling agent)

Cetyltrimethylammonium bromide (CTAB)

$$\left[\begin{array}{c} CH_3 \\ | \\ R - N - CH_3 \\ | \\ CH_3 \end{array} \right]^{+} \quad Br^{-}$$

II.2.9.4. Gelling agent – sodium silicofluoride

Na$_2$ Si F$_6$

Specific gravity	2.7
Solubility	Soluble in hot water
Melting point (^{0}C)	Decomposes at red heat

II.2.9.5. Solvents

The solvents used for this work were supplied by Nice India Ltd., Cochin and their characteristics are given in Table II.9. Both the solvents were redistilled before use

Table II.9. Characteristics of solvents

Solvent	Purity (%)	Specific gravity at (25 ^{0}C)	Boiling point (^{0}C)
Benzene	99.7	0.878	80
Toluene	99.6	0.867	110
THF (HPLC grade)	99.7	0.886-0.888	65-67
Acetonitrile (HPLC grade)	99.8	0.780-0.783	81-83
Diethyl ether	98	0.713-0.717	34-35

Mineral turpentine used for evaluation of dirt content of ISNR 20 and ISNR 5 was of commercial grade, having a boiling point 140 ^{0}C.

Formulations used for preparing the compounds for the study are given in respective chapters. The codes used to distinguish the compounds are also given along with the formulation.

II.3. Experimental Techniques

II.3.1. Composition Analysis of RSO Using GPC

Liquid chromatography

The separation and estimation of fatty acids were done using the Water s free fatty acid HP column. The equipment consists of a constant flow rate pump injector, column and a differential refractometer. The free fatty acid column is a 4

micron bonded spherical silica column providing separations of fatty acids with carbon chain length between 8 and 20 carbons based on carbon chain length and degree of saturation. The elution is in the order of increasing carbon number and the unsaturated acids before saturated for fatty acids of same number of carbon atoms. The free fatty acid column is designed for biological, pharmaceutical materials, typical applications include free fatty acids, fatty acid derivatives, saponified oils, fatty alcohols and fatty acid resins.
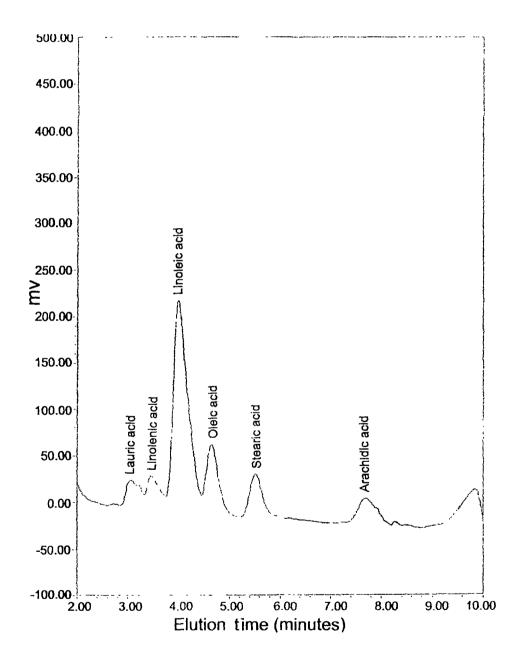
Figure II.1. **Liquid chromatogram of standard fatty acids obtained using 'Waters' free fatty acid column**

The differential refractometer continuously monitors the difference in refractive indices between the pure mobile phase and the mobile phase containing the sample. Snell's law can be used to calculate the refractive index (RI) of a sample solution/solvent from the angle of incidence and the angle of refraction.

The refractometer detects the position of the deflected light beam creating a signal that differs from the baseline signal. By keeping the wavelength, temperature and pressure constant, the refractometer measures the RI with respect to the changes in sample concentration only. The refractometer measures small differences in the RI between a reference solvent and a sample solution; the difference is referred to as Δn, measured in RI units. The detector measures the differences in refractive indices even as low as 5×10^{-8} refractive index (RI) units. Depending on the difference between the RI of the sample and reference, an electrical signal is obtained which is amplified in millivolt recorder.

The continuous mobile phase used is the tetrahydrofuran (THF): water: acetonitrile mixture in the ratio 25:35:45. The samples were dissolved in the solvent mixture-concentration around 0.1% and was injected into the mobile phase.

From the graph, elution time versus millivolts (mv), we can get the peak area of the samples. Using standard fatty acid samples, calibration curves were drawn and the concentration of unknown samples can be estimated using the peak area and concentration of these standard samples.

A typical graph of standard samples is shown in Figure II.1.

Advantages of LC

In all other methods such as GLC, GC etc. methyl ester of the oil is produced first and then converted to corresponding methyl esters of fatty acids. This is a tedious and time-consuming process. In the method followed for the analysis reported here, there is no need to prepare the methyl ester of the material. The soap is directly hydrolysed to fatty acid mixture and is therefore an easier method. The results were comparable with the fatty acid composition obtained by Bressani et al.,[5] using Association of Official Analytical Chemists (AOAC) Official Method.
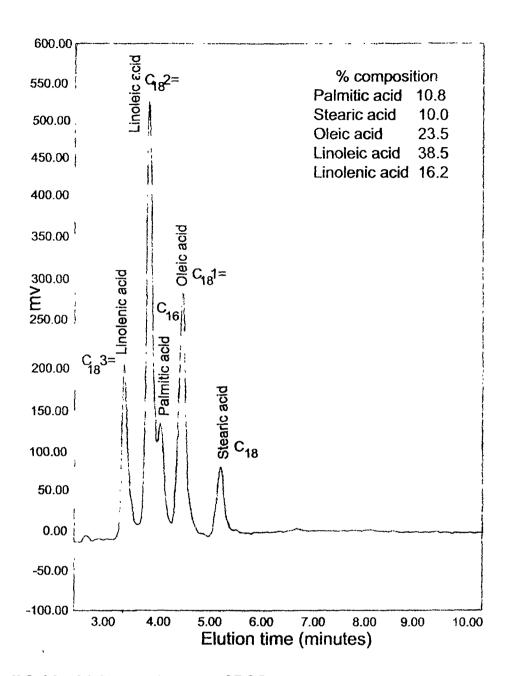
% composition
Palmitic acid 10.8
Stearic acid   10.0
Oleic acid   23.5
Linoleic acid 38.5
Linolenic acid 16.2

Figure II.2. Liquid Chromatogram of RSO

10 g of rubber seed oil was heated in a water bath at 80 ^{0}C. 2.5 g of g of
potassium hydroxide was dissolved in 40 ml water and added to the hot rubber
seed oil and stirred well. The rubber seed oil soap formed was acidified to a pH
2 with dil. HCl. The acidified aqueous solution was then extracted with 50 ml of
ether by shaking vigorously in a separating funnel. The mixture was allowed to
separate into two distinct layers. The lower aqueous layer was drained out into a
beaker, while the other phase was collected. The aqueous phase was poured

back into a separating funnel and extracted with 30 ml of ether each time. The ether extracts were combined and evaporated on a water bath. The residue was dissolved in 20 ml of solvent mixture having the ratio 45:35:25 acetonitrile: water: tetrahydrofuran. HPLC grade solvents were used for preparing the solvent mixture.

Standard graphs were drawn using pure acids by preparing a 0.1% solution in the solvent mixture and using the calibration curve, the unknown samples were estimated by comparing the peak area and corresponding concentration using the LC programme.

II.3.2. Preparation of Epoxidised Rubber Seed Oil

Rubber seed oil was mixed with the required amount of benzene and formic acid as given in Table II.10. Benzene served as the reaction medium. Continuous moderate stirring of the mixture was given throughout the reaction time. The reaction mixture was maintained at 58-60 ^0C and hydrogen peroxide was added drop wise within a period of 2 hours. At the end of the experiment, the mixture was poured into ice. Then it was transferred to a separating funnel, the water layer was separated and the oily layer was washed with warm distilled water until acid free, and then centrifuged and finally dried under vacuum at 40 ^0C.

The same method was followed by the other researchers in this field[6].

Table II.10. Composition of reaction mixture for epoxidation of RSO

RSO	100 g
Benzene	25 ml
Formic acid	10 ml
Hydrogen peroxide (30%)	80 ml

The ERSO having different epoxy content was prepared by varying the reaction time. The epoxidised rubber seed oil was stored at 10 ^0C in a refrigerator. The decrease in epoxy content with time of storage was found to be negligible under the above conditions.

II.3.3. Preparation of 20% Rubber Seed Oil/Potassium Oleate Soap

Soaps are generally prepared by reacting equimolecular quantities of a higher fatty acid and a fixed alkali at the appropriate temperature. The quantities of RSO/oleic acid, potassium hydroxide and water required for preparing 20% solution of soap are shown in Table II.11.

$$C_{17}H_{33}COOH + KOH \longrightarrow C_{17}H_{33}COOK + H_2O \qquad --- \text{ II (2)}$$

Oleic acid   Potassium oleate

Table II.11. Chemicals for preparing 20% soap solution

Parts by weight			
Part A		**Part B**	
Rubber seed oil/ Oleic acid	100	Potassium hydroxide	19.8
Water	400	Water	50

Parts A and B were warmed to 75 °C and B was added to A in small quantities with efficient stirring. The stirring was continued till the solution attained room temperature. 1-2 g more of alkali was needed to get a clear solution in some cases.

II.3.4. Preparation of Copper Oleate from Oleic Acid and Mixture of Copper Salts from Rubber Seed Oil[7]

For preparing copper oleate from oleic acid and mixture of copper salts from rubber seed oil, 6.58 g of sodium hydroxide was dissolved in 65 ml water and 46.38 g oleic acid/rubber seed oil was mixed with it under stirring. The solution was filtered through 'Whatman' filter paper (No. 41). The precipitate obtained was washed 2 to 3 times with distilled water so as to remove the excess sodium hydroxide. It was taken in a clean beaker and dissolved in 500 ml water by heating. A concentrated solution of copper sulphate, prepared by dissolving 25 g of copper sulphate in water was added to this and heated to 90-95 °C. The mixture was stirred for one hour. The top layer of copper oleate/copper fatty acid salt was washed with water in a separating funnel and

purified using diethyl ether as solvent. The copper oleate/fatty acid salt obtained was diluted to 25 per cent solution using pure mineral turpentine.

The average yield of copper salt from oleic acid and rubber seed oil was 80 gms and 70 gms respectively when the reactants were taken in the proportions given above. The reactions involved are given below.

$$C_{17} H_{33} COOH + NaOH \longrightarrow C_{17} H_{33} COONa + H_2O \qquad\qquad — \text{II (3)}$$

Oleic acid   Sodium Oleate

$$2C_{17} H_{33} COONa + Cu SO4 5H_2O \longrightarrow$$
Copper Sulphate
$$(C_{17} H_{33} COO)_2 Cu + Na_2 SO_4 + 5 H_2O (2) \quad — \text{II (4)}$$
Copper Oleate

II.3.5. Preparation of aqueous dispersions

Most of the solid ingredients of the latex compound are insoluble in water and hence the particle size of the ingredients should be reduced to that of the rubber particle in latex for getting their uniform distribution in latex.

The solid material is made to disperse in water, by grinding action in presence of a dispersing agent (dispersol F). Dispersing agent prevents the dispersed particles from re-aggregation. For very fine particle size ingredients like zinc oxide the quantity of dispersing agent required is 1 % by weight whereas for materials like sulphur, 2-3% by weight is required. There are different types of grinding equipments for the preparation of dispersions.

Eg:- Ball mill, Ultrasonic mill, Attrition mill, Colloid mills etc.

Out of these, the most widely used equipment is the ball mill. It consists of a cylindrical container 1/2 to 2/3rd of which is filled with the dispersion slurry and balls and then securely sealed. The container is rotated about its cylindrical axis in a horizontal plane at such a speed that the charge is tumbled. When the mill is working, the balls are carried with the container a short way and then cascade. It is this process of cascading, which cause the particles of the slurry to be comminute. The efficiency of the ball mill depends on the following factors.

(a) Speed of rotation of the jar

There is a critical speed of rotation of the jars at which the grinding action by the balls is maximum. This critical speed (S) in rpm is dependent on the radius of the jars in feet (R) by the equation

$$S = \frac{56.2}{\sqrt{R}} \qquad\qquad - \text{II (5)}$$

Table II.12 gives the required speed of rotation of the jars having different diameters.

Table II.12. Size of the jar and speed of ball mill

Radius of jar (inch)	Ideal speed of container (rpm)
4	93
6	76
8	66
10	59
12	53
15	48
18	44
21	41
24	38

(b) Size of the balls

Generally smaller balls give better action but they may create difficulty in discharging the jar and separating the balls from the dispersion. Large diameter balls damage the container. Normally balls of 1/2" to 3/4" diameter size are preferred.

(c) Material of the balls

Steel balls grind faster due to density of the balls. They are more resistant to self-abrasion of the balls. But steel balls are costly and also require steel jar. Hence porcelain balls are normally used.

(d) Viscosity of the slurry

If the slurry is highly viscous the balls stick together and rotate as a single mass and no grinding action occurs. The viscosity of the slurry should be adjusted without affecting the free cascading of the balls. Too dilute slurry decreases the total solid content of the latex compound.

(e) Ratio between the volume of the charge and of the balls

Ball mills should not be overloaded. The container should not be more than three quarter full and roughly half this volume should be filled with balls.

Period of ball milling

Every fine particle solids need be ball milled only for a period of 24 hours. Eg:- Zinc oxide. But ingredients like sulphur, should be ball milled for 48 to 72 hours. In case of mixture of ingredients including sulphur, the period of ball milling is 48-72 hours.

Ball mills produce very good dispersions. After grinding, the dispersion may be conveniently discharged by covering the mouth of the jar with a piece of wire gauge or even with lid to retain the balls in the jar.

Dispersing agents

The selection and amount of dispersing agent are determined by the physical properties of the chemical to be dispersed. The functions of these agents are to wet the powder, to prevent or reduce frothing and avoid re-aggregation of the particles. The concentration of the dispersing agent should be maintained at the minimum to produce the desired effect and need rarely exceed 2% except in case of sulphur.

Sodium salt of naphthalene sulphonate (Dispersol F)

Manufactured by ICI Ltd., is the dispersing agent used for the preparation of dispersions. Table II.13 gives the formulations for preparing dispersions of the chemicals used in the work connected with latex foam presented in this thesis.

Table II.13 Formulations for preparing dispersions

	Parts by weight
1. Sulphur dispersion (50%)	
Sulphur	100
Dispersol F	3
Water	97
Ball milled for 48 hours	
2. Accelerator ZDC dispersion (50%)	
ZDC	100
Dispersol F	2
Water	98
Ball milled for 24 hours	
3. Zinc oxide dispersion (50%)	
Zinc oxide	100
Dispersol F	2
Water	98
Ball milled for 24 hours	
4. ZMBT Dispersion (50%)	
ZMBT	100
Dispersol F	2
Water	98
Ball milled for 24 hours	

Clay is used as powder and SSF as 20% slurry

Quality of Dispersions

Consistency in the quality of dispersions is highly desirable and hence the quality of the dispersions was tested just before addition to the latex, in each case, by adding a drop of the dispersion into water taken in a tall glass jar. A cloudy appearance indicated good dispersion whereas rapid settling of the ingredient to the bottom of the jar showed poor dispersion

II.3.6. Preparation of Emulsions

Compounding ingredients, which are water immiscible liquids should be emulsified in water before addition into the latex. Examples for these types of compounding ingredients are antioxidant SP, oil etc. The emulsifying agents generally used are fatty acid soaps. The most stable emulsions are formed when emulsions are prepared in which the soap is formed *in situ*. The following recipe

(Table II.14) was used for preparing 50% antioxidant SP emulsion used in the work presented in this thesis.

Parts A and B were separately warmed to about 50 ^{0}C and Part B was then added to A in small quantities under high-speed stirring. Emulsion was prepared as and when it was required. An efficient stirrer was used for preparation of emulsion.

Table II.14. Recipe for preparing SP emulsion

ingredient	Parts by weight
Part A	
Antioxidant SP	100
Oleic acid	3
Part B	
25 % Ammonia solution	4
Water	93

II.4. Analysis of NR Latex for Quality Parameters

The following tests were conducted on the centrifuged NR latex used in the study to ensure its quality[8].

II.4.1. Dry Rubber Content (DRC)

Weighed about 10g of the well-mixed latex sample into a beaker. Added water to get a total solids content of about 20 per cent. Added 8 ml of 2% of acetic acid per gram sample, stirred and the solution was kept undisturbed for about 15 minutes on a water bath. If the serum was milky, added 0.5 ml of rectified spirit per gram of sample and gently stirred. When the serum was clear, collected any small particles of coagulum by rubbing with the main bulk, filtered and washed the coagulum and reduced its thickness to less than 2 mm. Dried the coagulum at a temperature 70 ± 2 ^{0}C. Cooled in a desiccator and weighed.

$$DRC\ (\%) = \frac{W_1}{W_2}\ X\ 100 \qquad\qquad — II\ (6)$$

W_1 = Weight of dry coagulum

W_2 = Weight of latex sample taken

II.4.2. Total Solids Content (TSC)

Weighed accurately about 2 g of the well-mixed latex sample into a previously dried and weighed petridish. Dried it in an air oven at 70 ^{0}C for 16 hours. The dried film was cooled in a desiccator and weighed.

$$\text{TSC (\%)} = \frac{W_1}{W_2} \times 100 \qquad\qquad — \text{II (7)}$$

W_1 = Weight of dried film

W_2 = Weight of sample taken

II.4.3. Mechanical Stability Time (MST)

Weighed out {(100/TS) x 55} = Wg of latex (for adjusting TSC to 55%), added (100-W) ml 0.6% NH₃. Warmed to 35 ^{0}C. Weighed 80g latex into MST container. Placed the container in position and stirred the content at 14000 ± 200 rev/min. until end point was reached. Noted the end point when floculations were first readily seen in the thin film of liquid formed, when a glass rod was dipped into the latex and lightly drawn over the palm of the hand. The MST is expressed in seconds.

II.4.4. Ammonia Content (Alkalinity)

About 2g of the latex was poured it into a 600 ml beaker containing 300 ml of distilled water and 5 drops of methyl red indicator. Immediately titrated against 0.1N hydrochloric acid till yellow colour changed to pink.

$$\text{Ammonia (\%)} = \frac{1.7 \times V \times N}{W} \qquad\qquad — \text{II (8)}$$

V = Volume of HCl   N = Normality of HCl   W = Weight of latex

II.4.5. Volatile Fatty Acid (VFA) Number

Weighed about 50g of latex of known DRC and TSC into a beaker. Added 50 ml, 30% ammonium sulphate ((NH₄)₂ SO₄) solution and stirred the mixture, warming over a water bath until the latex thickened and coagulated. Pressed the

serum out of the coagulum. 25 ml of the filtered serum was taken and acidified with 5 ml dilute sulphuric acid. Pipetted out 10 ml of the acidified serum into the inner tube of the Markham still (steam outlet open) and added 5 drops of silicone antifoaming agent. Washed with distilled water and closed.

Placed a 250 ml conical flask under the tip of the condenser to receive the distillate. Closed the steam outlet partially to divert the steam into the inner tube. Passed the steam gently at first, then closed the steam outlet fully and continued distillation until 100 ml distillate was collected. Titrated the distillate with carbonate free 0.02 N barium hydroxide solution (Ba (OH)$_2$) using phenolphthalein as indicator till pink colour was obtained. A blank test was conducted by substituting 20 ml of water for the 50g of concentrated latex. Titrated the distillate against standard 0.02N Ba(OH)$_2$ using phenolphthalein as indicator. The VFA number is calculated using the equation.

$$\text{VFA Number} = \frac{561 \text{ NV} [50 + ((100\text{-DRC}) \times 50/102)]}{50 \times 10 \times \text{TSC}} \qquad \text{—— II (9)}$$

Where DRC is dry rubber content, TSC is total solid, N and V are the normality and volume of Barium hydroxide solution respectively.

II.4.6. Zinc oxide Stability Time (ZST)

Weighed out a sample of latex containing 100g of TSC (w=100 x 100/TSC). 1 phr (parts per hundred rubber) of potassium oleate was first added as an aqueous solution to natural rubber latex. The pH of the latex was then adjusted to 9.75 by addition of aqueous formaldehyde. The total solids content was reduced to 55.0% m/m by addition of water, the temperature was adjusted to and maintained at 30 ^{0}C and 5 phr of zinc oxide gradually added as a dry, free-flowing powder with mechanical stirring over a period of 10 minutes. One hour after the commencement of zinc oxide addition, the latex was decanted from any sedimented zinc oxide, filtered through a gauze and then immediately subjected to a conventional latex mechanical stability test. The end point was taken as the first definite sign of gross colloidal destabilization as revealed by the presence of flocks in the latex surface[9].

II.4.7. Potassium Hydroxide (KOH) Number

Calibrated the pH meter using standard buffer solution at room temperature (Buffer tablet pH 9.2 /0.06 N sodium borate)

Lowered the clean electrode into the buffer solution, making sure that it does not touch the beaker. Turned knob of pH meter from 'zero' to 'read' and note the pH reading (adjusting to 9.2).

Weighed out 'W' g of latex to give 50 g TSC into 250 ml beaker.

$$W = 50 \times 100/TSC \qquad\qquad \text{—— II (10)}$$

Added a calculated amount of 5% formalin to reduce the NH_3 content of the latex to 0.5% on water phase followed by sufficient water to reduce the TSC to 30%.

The quantity of formalin (F) and water (H) are calculated as

$$F = W(100\text{-}TSC)(A\text{-}0.5)/189 \qquad\qquad \text{—— II (11)}$$
$$H = 166.7 - W - F \qquad\qquad \text{—— II (12)}$$

A is the % of NH_3 in water phase = NH_3 % x 100/100-TSC

Added 0.5 N KOH solution from a burette in 1 ml increment and measured the pH of the latex after each addition (washed the glass electrode each time before the addition of KOH solution). Stopped the addition of KOH solution when the pH increased above 11.5.

The end point of the titration was the point of inflection of the pH – ml KOH titration curve. At the end point, the slope of the curve, that is, the first differential reached the maximum and the second differential changed from a positive to a negative value. The end point was calculated from the second differential change from the positive to negative value.

$$KOH \text{ No.} = (561 \times NV)/(W \times TSC) \qquad\qquad \text{—— II (13)}$$

W – weight of latex, V - Volume of KOH, N - Normality of KOH, TSC - Total solids.

II.4.8. Coagulum Content

Cleaned the wire gauze (180 micron IS sieve) by immersing it in boiling concentrated HNO_3 for 2 minutes. Washed thoroughly with water and dried in the oven before weighing.

Poured 200 gm of latex into a 600 ml beaker and added 200 ml 20% potassium oleate solution. Stirred well with a glass rod. Filtered the mixture through the sieve. Washed the residue with potassium oleate solution until it is free from latex. Dried the sieve in air oven at 70 ^{0}C and weighed.

$$\text{Coagulum content (\%)} = \frac{W_1}{W_2} \times 100 \qquad\qquad \text{—— II (14)}$$

W_1 – weight of dry coagulum, W_2 – Weight of latex sample taken

II.5. Testing of Rubber Seed Oil[10]

II.5.1. Specific Gravity

Weighed the empty specific gravity bottle. Filled it with distilled water (cooled to 20-23 ^{0}C) to overflowing, holding the bottle on its side in such a manner as to prevent the entrapment of air in it. Immersed the bulb in water bath maintained at 25 ± 0.2 ^{0}C for 30 minutes. Carefully removed any water, which has oozed out from the side opening, put the stopper, removed from water bath, wiped, dried and weighed.

Emptied the bottle, rinsed with alcohol, then with ether and dried. Cooled the RSO sample to 20-23 ^{0}C and filled the bottle to overflowing with the oil, holding the bottle on its side in such a manner as to prevent the entrapment of air bubbles. Immersed the bulb of the bottle in bath at 25 ± 0.2 ^{0}C for 30 minutes. Carefully wiped off any oil, which has come through the side tube, inserted the stopper, wiped, dried and weighed.

$$\text{Specific gravity at 25 }^{0}\text{C} = \frac{\text{Mass of oil}}{\text{Mass of water}} \qquad\qquad \text{—— II (15)}$$

II.5.2. Refractive Index

Placed the instrument in such a position that daylight can readily be obtained for illumination of the refractometer prisms. Opened the prisms by means of the head screw and placed two drops of rubber seed oil in the centre of the lower prism. Brought the prisms together and fastened with head screw. The method of measurement is based upon the observation of the position of the borderline of total refraction in relation to faces of the flint glass prism. Brought the borderline into the field of vision of the telescope by rotating double prism in the following manner. Held the sector firmly, moved the alidade forward or backward until the field of vision was divided into bright and dark portions. The line dividing these portions was borderline. This usually would not be a sharp line but a band of colour. Eliminated the colours by slowly turning the screw head of the compensator until a sharp line was obtained. Then adjusted the borderline so that it fell on the point of intersection of the cross wires. Read the refractive index of the substance on the scale of the sector. Repeated and took the average.

Express the refractive index at 25 ^{0}C by the following formula.

$$R= R' + 0.000385 (T'-T)$$ 　　　　 — II (16)

Where, R is the reading reduced to temperature T, R' = the reading at temperature T', T' = the temperature (lab temperature) at which the reading was taken and T the standard temperature (25 ^{0}C).

II.5.3. Acid Value (Free Fatty Acids)

Weighed 10 g of the sample into a 250 ml conical flask; added 100ml of the alcohol ether mixture, warmed, added 1ml of phenolphthalein solution and with constant shaking titrated the mixture with 0.1N alcoholic sodium hydroxide solution until the pink colour persists for a minute.

$$\text{Acid Value} = \frac{56.1 \times 0.1 \times V}{W}$$ 　　　 --- II (17)

where, V is the volume of 0.1N NaOH used in the titration and W is the weight in gram of the sample taken. Also calculated the free fatty acid as oleic acid.

$$\text{Oleic acid \%} = \frac{\text{Acid value} \times 282}{561}$$ 　　　 --- II (18)

164

II.5.4. Saponification Value

Weighed accurately about 2 gms of the rubber seed oil into a conical flask, added 25 ml of the alcoholic potash (40 g KOH in 1 litre of alcohol), attached air condenser and boiled gently for 30 minutes. Blank is done without oil simultaneously. Added a few drops of phenolphthalein indicator and titrated with standard HCl, until the pink colour has just disappeared.

$$\text{Saponification Value} = \frac{56.1 \times N \times V}{W} \qquad \text{— II (19)}$$

Where, N is the normality of the HCl, V is the volume of the acid for the sample-volume of the acid for blank and W is the weight of the sample taken.

II.5.5. Iodine Value

Hanus method was used for the determination of iodine value. Hanus solution was prepared by dissolving 13.62 g of powdered iodine in 825 ml of glacial acetic acid (free of reducing agents) in a dry flask, by gently heating over a water bath. The solution was cooled to room temperature, pipetted out 25ml, added 50ml of water, 10ml of 15% KI solution and titrated with 0.1N thiosulphate. 200ml of glacial acetic acid was taken in a dry glass stoppered bottle and added 3ml of liquid bromine and mixed well. 5ml of this solution was taken, added 10ml of the 15 % KI solution and 50 ml of water. Titrated with 0.1 N thiosulphaté. Calculated the quantity of bromine solution required exactly to double the halogen content of the remaining 800 ml of the iodine solution as follows: A=B/C where A= volume of bromine solution required, B=800 x thiosulphate equivalent of 1ml of iodine solution and C = the thiosulphate equivalent of 1 ml of bromine solution. The final solution should contain 13.2 gms of iodine per 1000 ml (if it contains more; added the calculated quantity of acetic acid). Kept the Hanus solution in a glass stoppered, amber coloured bottle, in a dark place.

Weighed accurately 0.15 to 0.2 g of the rubber seed oil into a 300ml glass stoppered bottle. Added 10 ml of dry CHCl$_3$, or CCl$_4$ and was shaken gently so as to dissolve the oil. Added from a burette exactly 25ml of the Hanus solution, moistened the stopper with the KI solution taking care not to use a quantity sufficient to run down inside the bottle and stoppered the bottle. Started a duplicate and a blank (ie, without oil) exactly as above. Allowed the bottle to

remain in a dark place for 30 min. Added 10 ml of the KI solution and washed down the stopper and neck with about 100 ml of water. Mixed and titrated the iodine solution with the thiosulphate solution, with constant rotation of the contents. When most of the brown colour has disappeared and when the aqueous solution has become yellow, added 1 ml of starch solution and continued the titration until the blue colour has disappeared. Sometimes the lower layer of $CHCl_3$ or CCl_4 will retain some of the iodine and to get this to the aqueous layer, the bottle was shaken well after stoppering it.

$$\text{Iodine value} = \frac{V \times N \times 126.9}{10 \times W} \qquad \text{---- II (20)}$$

where, V is the titre value for blank - titre value for the sample

N = normality of sodium thiosulphate solution and

W = weight of sample.

II.5.6. Un-saponifiable Matter

Accurately weighed 5 gm of the sample into a conical flask. Added 50 ml of alcohol and 10 ml of con. KOH solution (60 g KOH dissolved in 40 ml water). Rotated the flask and refluxed for 60 minutes on a water bath. Cooled to room temperature. A blank was also done. Added 50 ml of petroleum ether, mixed and carefully transferred to a 500 ml separating funnel. Rinsed the flask with two successive 50 ml portions of ether, added to the separating funnel and mixed the contents. Washed the saponification flask with 100 ml of dilute alkali and poured into the separating funnel in slow, steady stream. Rotated the funnel gently to secure better contact of solutions, but do not shake. Allowed the liquids to separate, and then slowly drew off as much of soap solution as possible. Kept the volume of ether at about 150 ml by replacing that dissolved by the wash solutions. Combined the petroleum ether extracts. Further treated the ether solution with two successive 100 ml portions of dilute alcohol drawing off after each treatment. Added 30 ml of distilled water to the ether and mixed by rapid rotation of the separating funnel. When the layers have separated, the water layer was withdrawn. Repeated this treatment until the washings were free from alkali as shown by test in with phenolphthalein solution. Three washings were usually sufficient. Transferred the ether quantitatively to a weighed conical flask,

166

washing the separator with a small quantity of ether. Distilled off the ether carefully from a water bath, dried the flask and residue to constant weight at 100-105 °C.

$$\text{Non-saponifiable matter \%} = \frac{\text{weight of residue}}{\text{weight of sample}} \times 100 \qquad \text{—— II (21)}$$

II.5.7. Titre

When melted fats are allowed to cool and solidify, the temperature at first drops and then, when crystals of solid fat or fatty acids begin to separate, it rises owing to the effect of latent heat liberated during solidification. The highest temperature, reached by a given fat is characteristic of a sample, gives an idea of the hardness and is known as the solidifying point or titre.

A known weight of the sample is treated with caustic glycerine solution and heated until complete saponification has taken place, then washed it free of alkali. Removed any trace of moisture present by slight heating. Then the sample is taken in a titre tube fitted with a stirrer and thermometer and kept in a water bath approximately 15-20 °C below the titre point. Stirring is continued till the temperature remains constant for about 30 seconds. Stirring is stopped and increase in temperature is observed and the highest temperature is reached is expressed as titre.

II.5.8. Determination of Oxirane Percentage

The epoxy content (oxirane content) of the ERSO was determined by the acidimetric method as well as by FTIR method.

II.5.8.1. Acidimetric method[11]

Pipetted 25ml of the hydrochloric acid- dioxan reagent into 500ml glass stoppered flask (Iodine flask). Weighed accurately 0.1 gram of the epoxidised rubber seed oil into the flask. Stoppered the flask and swirled well. Allowed the reaction mixture to stand at room temperature for 15 minutes. Added 25 ml of neutral ethyl alcohol and titrated the excess of acid with the standard 0.1N methanolic sodium hydroxide (Neutral ethyl alcohol is prepared by adding cresol red indicator to the alcohol followed by methanolic sodium hydroxide solution till

its colour became violet). The colour of the indicator (cresol red) changed from pink to yellow just before the end point and from yellow to violet at the end point (V_2).

Performed a blank titration with 25 ml of the hydrochloric acid-dioxane reagent, the difference between the titration of the blank and of the sample was the volume of sodium hydroxide solution equivalent to acid consumed by the epoxide (V_1).

Determination of free acid

Weighed 0.2 gram of the sample into 50 ml of neutral ethyl alcohol and titrated against standared 0.1N methanolic sodium hydroxide (V_3).

$$\text{Oxirane Oxygen (\%)} = \frac{V_1 - (V_2 - V_3) \times N_1 \times 16 \times 100}{W \times 1000} \quad \text{—— II (22)}$$

W – weight (gram) of the sample

V_1 – volume of sodium hydroxide for blank

V_2 – volume of sodium hydroxide for sample

V_3 – volume of sodium hydroxide for free acid

N_1 – normality of sodium hydroxide

II.5.8.2. FTIR method

A 'Shimadzu' make FTIR, Model No. 8101 M was used for estimating the epoxy content of ERSO. In the model FTIR-8000 series, the 'Michelson' Interferometer is used. The principle of the Fourier Transform Spectrophotometer using the 'Michelson' interferometer is briefly described below.

The light emitted from the light source, which is an electrically heated solid eg. Nichrome wire produces a beam of infrared radiation, which is divided (by a system of mirrors) into two parallel beams of equal intensity radiation. The sample is placed in the path of one of the beams and the other is used as a reference beam when a solution is analysed. A slowly rotating diffraction grating or prism varies the wavelength of the radiation reaching the sample and then the

detector. The detector records the difference in intensity between the two beams on a chart as percentage transmittance, called a peak.
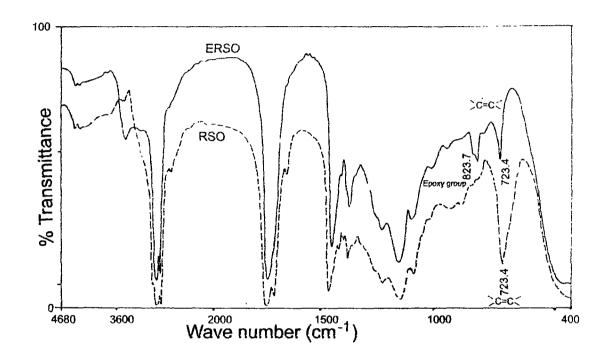
Figure II.3. IR Spectrograph of RSO and ERSO

Operating procedure - One drop of the epoxidised rubber seed oil was placed in between two sodium chloride cells and was mounted on a clamp thereby forming a film of liquid on the window. It was then placed in a demountable cell mount, and placed in the path of IR radiation. From the spectra obtained which is a plot of % transmittance versus wavelength, the epoxidation level, of various samples of ERSO, was measured. Using the peak heights of epoxy group and cis C=C, the level of epoxidation was assessed.

II.6. Raw Rubber Tests

I.6.1. Composite Sample Preparation[12]

About 800 g of rubber sample was cut from the opposite corners of the selected bales of ISNR 5 and ISNR 20 grades of block rubber. The two pieces from each bale were cut into pieces and passed through the laboratory-mixing mill set at a nip gap of 1.65 mm. The blanket obtained was rolled and passed vertically after each pass. 6 passes were given for each sample and finally sheeted out. About 100 g of this composite sample was taken and passed through the mixing mill twice, at a nip setting of 2 mm. The sample for dirt content estimation was taken from this composite sample.

II.6.1.1. Estimation of dirt content[13]

About 10 g of rubber from the composite sample was accurately weighed. Cut into small strips and soaked in 200 ml of mineral turpentine to which 1 ml of copper oleate as peptizer was added. The experiment was repeated using 0.5, 1 and 1.5 ml copper salt of higher fatty acids prepared from RSO as peptizer. The sample was allowed to swell overnight. The solution was heated to 125-130 ^{0}C for 5 h on the next day. The flask was shaken occasionally during the experiment. Infrared lamp was used for heating. Care was taken to minimise local overheating, to avoid formation of gel, which would create difficulties during filtration. When the rubber was completely dissolved, the solution was filtered through previously weighed clean and dry (325 mesh) sieve. The flask containing dirt was washed three times with 20-30 ml of hot mineral turpentine (low aromatic petroleum hydrocarbon solvent) and transferred completely to the sieve washed, dried and weighed.

$$\text{Dirt content} = \frac{W_1}{W_2} \times 100 \qquad \text{---- II (23)}$$

where W_1 = Weight of residue obtained and W_2 = Weight of sample taken

II.6.2. Viscosity of Rubber Solutions

The viscosity of rubber solutions prepared by dissolving ISNR 5 and ISNR 20 using copper oleate and copper salts of higher fatty acids from rubber seed oil as peptizers was tested using 'Haake' Viscotester VT 550, which is generally

used to examine the rheological/physical material parameters of liquid or semisolid substances.

The equipment consists of a cup attached to a temperature-controlled system, which can be maintained at any desired temperature, sensor system and a rotor, which can be rotated at any preset speed. The sensor NV is primarily used for viscosity measurement of low viscosity liquids such as oils, dilute solutions, fruit juices etc. working in the medium shear rate range. The sensor system NV consists of the cup and a bell-shaped rotor. It consists of a coaxial cylinder sensor system with two gaps for shearing the samples on the inside and on the outside of the rotor. This sensor system is used with the temperature vessel, which is connected to an accurate thermal liquid circulator. The amount of sample should be adjusted so that during operation the top surface of the inner cylinder is just covered.
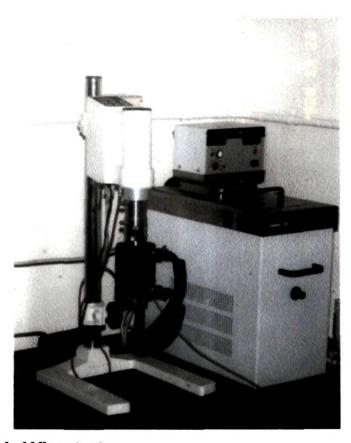
Figure II.4. 'Haake' Viscotester

The substance to be measured (about 9g) is placed in the measuring gap of the sensor system. The rotor is rotated at a preset speed. The sample exerts a resistance to this rotational movement (due to its viscosity), which become apparent as a (braking) torque value applied on the measuring shaft of the VT 550. The torque required to maintain the set speed is proportional to the viscosity. From the torque required, the set speed and the geometry factors of the sensor, information on viscosity, shear stress and the shear rate is calculated. The built-in computer calculates the relevant measuring values for the following factors from the measured variables of speed, torque and sensor geometry. Testing can be done at any desired temperature.

$$\text{Viscosity} = \frac{\text{Shear stress}}{\text{Shear rate}} \qquad\qquad \text{—— II (24)}$$

Viscosity η - m Pa, Shear rate γ - s^{-1} and Shear stress τ - Pa

This equipment was used for assessing the viscosity of rubber solutions prepared by using copper oleate and copper salt of rubber seed oil fatty acids as peptisers. The experiment was conducted at 50, 60 and 70°C and shear rates ranging from 1 s^{-1} to 200 s^{-1}.

10 gram of rubber samples were dissolved in 200 ml of mineral turpentine using the peptizers, copper oleate/copper salt of rubber seed oil fatty acid at different concentrations at 130 °C. When the dissolution was complete, the solution was filtered through previously washed, dried and weighed (325 mesh) sieve and the filtrate were used for viscosity determination at different temperatures and shear rates. The copper oleate was used as peptizer for control sample.

II.7. Preparation and Testing of PVC Compounds

PVC undergoes thermal degradation when kept at higher temperature. For minimising the degradation, stabilizers such as tribasic lead salts and calcium stearate are used. For assessing the effect of ERSO as a stabilizer for PVC, thermogravimetric method was also tried.

172

II.7.1. Preparation of PVC Compounds

The PVC compounds were prepared by melt blending of the polymer with the other ingredients in 'Haake' Rheocord 90 mixing equipment. This torque rheometer is essentially a device for measuring the torque generated due to the resistance of a material to mastication or flow, under preselected conditions of shear and temperature. The heart of the torque rheometer is a jacketed mixing chamber whose volume is approximately 300 ml. Mixing and shearing of the material inside the mixing chamber is done by horizontal Banbury type rotors (with protrusions). The resistance put up by the test material against rotating rotors in the mixing chamber is indicated with the help of a dynamometer attached to a mechanical measuring system, which records the torque. Rotor speed can be controlled from 1-150 rpm. The temperature can be varied up to 300 ^{0}C. The rotors can be easily mounted using the simple fastening and coupling system. The materials are charged into the mixing chamber after setting the test conditions and the final torque shown by the mixture after homogenisation is measured. The experiment can be performed at different rpm and also at different temperatures. The flow curves of the compounds are obtained by plotting torque versus time.

The model of the machine used in this work was Rheomix 3000/3010. The Banbury type rotor was used for preparing the PVC compounds for the study in this experiment. Sample weight is determined using the equation

Sample weight = Bulk density x Net chamber volume x filling percentage
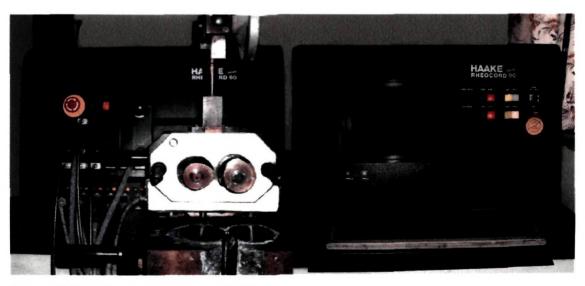
Figure II.5. 'Haake' Rheocord 90

173

The mixing was done at 170 °C at 60 rpm for 50 minutes to study the processability of the PVC compounds. The PVC compounds for physical tests were prepared by mixing the ingredients for 6 minutes at 170 °C and 60 rpm. The mixed material was sheeted out in the mixing mill and then compression moulded in an electrically heated hydraulic press at 160 °C for 3 minutes to get sheets of 150 x 150 x 2 mm size. Aluminium foils were used in between the mould surface and the sample to reduce shrink marks on the sheets.

II.7.2. Dynamic Heat Stability

The dynamic heat stability, static heat stability and colour tests were conducted using PVC samples. The ability of PVC to absorb plasticizer while remaining as a free flowing powder, can be measured by mixing it with the liquid plasticizer in a mixer at high temperature and continuously recording the torque by a torque rheometer. The mix passes through a sticky state before becoming dry, as plasticizer is absorbed. The change in torque with time is used to measure the time taken for the absorption. A typical rheocord trace is given in Figure II.6[14].
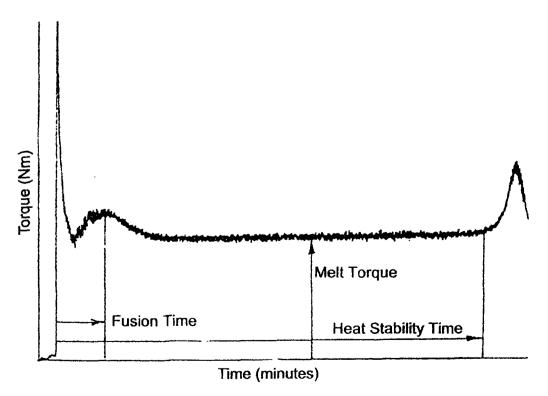
Figure II.6. Typical torque rheometer trace for an unplasticized PVC powder compounds

PVC compounds have a finite heat stability time during processing depending on the temperature, the final limit being decomposition accompanied by a rapid release of HCl. There are two methods for the evaluation of heat stability. In one method, the torque rheometer is run until the melt torque suddenly rises and the time from the maximum fusion torque to a sudden rise at decomposition is recorded. In the second method, small samples are removed from the mixing head at regular intervals, pressed into small plates and the time measured to reach a coloured endpoint is noted. Colour changes through pink, amber, brown and finally black, as the PVC thermally degrades.

For testing dynamic heat stability of the compound, the mixing in the 'Haake' rheocord 90 was continued for 50 minutes and the changes in the stabilized torque were observed.

II.7.3. Tensile Strength, Elongation at Break and Modulus

Dumb-bell shaped test pieces were punched out from the sheets and tested for tensile properties as per ASTM D 638-1999[15] using 'Zwick' 1474 model Universal Testing Machine. Five specimens were tested and the mean of these values were reported. Ageing resistance of the sample was determined by testing the tensile properties of the sample before and after ageing at 100 ^{0}C for 48 h.

II.7.4. Dynamic Mechanical Thermal Analyser

The Dynamic Mechanical Thermal Analyser (DMTA) spectra were recorded on rectangular specimens (length x width x thickness = 6 x 1 x 0.25 cm^3) in tensile mode at a frequency of 10 Hz using a Eplexor 150 N device of Gabo Qualimeter, Testanlagen GmbH, Germany. DMTA spectra, viz. storage, loss moduli and mechanical loss factor (tan δ) were recorded in the temperature range from −100 to 100 ^{0}C at a heating rate of 2 ^{0}C/min.

II.7.5. Static Thermal Stability of PVC Compounds

Thermogravimetric Analysis (TGA)- TGA measures weight changes associated with thermal events. It is commonly used for composition analysis, for determining thermal stability and for the evaluation of thermal decomposition kinetics in order to predict long-term as well as short-term thermal stability. Usual working temperature range is from ambient to 1000 °C.

TGA is used to record a change in mass of a sample under isothermal or dynamic conditions of heating. The sample is subjected to a heating programme, which consists of a heating rate, holding temperature or holding time. Usually a rate of heating of 5 °C/minute is used. In isothermal test, the sample is brought to the test temperature at a faster rate and is allowed to remain at that temperature for the desired time interval. The stability of the polymer is deduced from the weight loss curve, where the decomposition or volatilization of the sample against temperature is quantitatively measured.

A typical thermogram is given in figure II.7. The sample (about 10-15 mg) was taken and heated at a rate of 5 °C/minute from 30 °C to 800 °C. Using programmed heating and a change in atmosphere (purge gas) over the sample, it is possible to determine the weight losses associated with plasticizers or in general acetone extractables (from 100-300 °C), polymer content (300-550 °C) and carbon black or inorganic fillers from 550-800 °C.
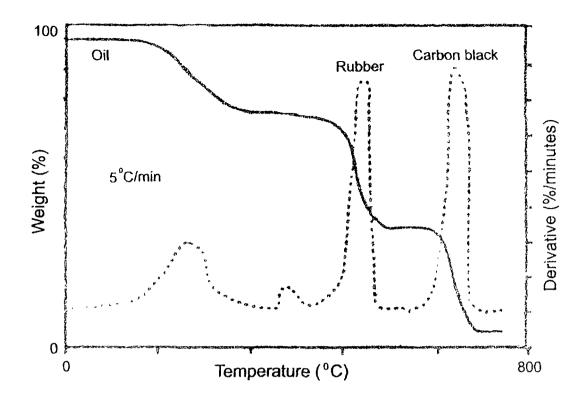
Figure II.7. Typical thermogram from thermogravimetric analyzer

In this thesis work, TGA used for evaluating the thermal stability of RSO/ERSO in PVC compounds and nitrile compounds in comparison with that of DOP at isothermal and dynamic heating conditions.

II.7.6. Colour Test

For colour test, the samples were mixed in the rheocord at 170 °C at 60 rpm, samples were withdrawn at definite intervals and pressed at 170 °C to get uniform thickness. Optical photographs were taken for comparing the colour of the samples.

II.8. Limiting Oxygen Index

The above test was carried out using a Limiting Oxygen Index (LOI) apparatus manufactured by Appareillage Industrialet Scientifique Company, France, according to ASTM - D-2863-77[16]. Both oxygen and nitrogen were

connected to the equipment through pressure regulations (about 2 bars). The flow of gases was regulated at 17 litres per minute.

The specimens of 70 to 150 mm long, 6.5 mm wide and 3 mm thick were cut from vulcanized sheets and clamped vertically in the specimen holder at centre of the column with the top of the specimen at least 100 mm below the top of the open column.

A definite concentration of oxygen for the gas mixture was selected and the flow valves were adjusted so as to read the set oxygen concentration. The test chamber was purged with the mixture for 30 seconds and the specimen was ignited so that it was well lit and the entire top was burning. Subsequent trials were carried out with new specimens and changed concentrations of oxygen. The level of oxygen flow was adjusted to the minimum at which the specimen burned for 3 minutes or more than 30 mm length whichever is earlier. The test specimen was changed after each trial and the test continued until reaching the minimum oxygen concentration with a precision of at least 0.2 %.

II.9. Production of Latex Foam

Latex foam was prepared by the Dunlop process[17]. Steps involved in the production of foam are:

1. Initial compounding with soap, vulcanizing agent and antioxidant
2. Maturation
3. Further compounding with vulcanizing agent, soap and fillers
4. Foaming
5. Foam refining (large air bubbles are eliminated and the cell size become more uniform)
6. Addition of foam stabilizer, cetyl trimethyl ammonium bromide
7. Addition of zinc oxide
8. Addition of delayed action gelling agent, sodium silico fluoride
9. Moulding and gelation
10. Vulcanizing
11. Washing and drying
12. Quality testing

NR latex concentrate was initially compounded with the soap (0.2 phr), sulphur, ZDC, ZMBT (dispersions) and antioxidant SP (emulsion) and kept for maturation for about 16 hours. The matured latex compound, mixed with an additional quantity (1 phr) of soap, was taken in a Hobart planetary mixer and run at high speed (150 rpm) to expand the latex by the frothing action of soap to 7 times the original volume, which was kept the same for all the batches prepared in this experiment. Time taken for 7 times expansion of compounded latex was noted in all cases. At this stage the foam was refined under slow speed stirring. During refining, all the large air bubbles were eliminated and the cell size in the resultant foam should thereby become more uniform. At this point, the foam stabilizer (cetyltrimethylammonium bromide) was added. After one minute, zinc oxide (50% dispersion) and delayed action gelling agent sodium silico fluoride (20%) were added. The pH of sodium silico fluoride was adjusted to between 6-7 units, prior to its addition into the foam. Then it was transferred to the mould, which had already been treated with a mould-release agent and warmed to 40 ^{0}C. The lids were placed in position on the mould after the latter had been filled. The moulds were left to stand for 10 minutes to allow gelation to be completed. The foam in the mould was steam vulcanized at 120 ^{0}C for 45 minutes. The foam was washed, pressed and dried at 70 ^{0}C for 4 h. Both filled and unfilled compounds were used for the study. The properties of vulcanized latex foam were determined as per IS: 1741-1999[18], after 48 hours of preparation of the foam.

Trials were also conducted with SBR latex in the present study. A 50:50 blend of NR and SBR latice was used to achieve the desired properties and reduce cost. Synthetic rubber latice generally require less foam promoter than does NR latex to achieve a given expansion. This is because, the latex itself contains relatively large amount of carboxylate soap and hence, the level of foam promoter is lower for the formulation based upon the blend with natural rubber latex.

II.10. Preparation of Dry Rubber Compounds

All the rubber compounds required for the thesis work were prepared in a two-roll laboratory model-mixing mill (300 x 150 mm) at a nip gap of 1.3 mm and at a friction ratio 1:1.25. Nip gap, mill roll speed ratio, time of mixing and temperature of the rolls were kept at the same for all mixes. All the chemicals were finely powdered for the purpose of homogeneous mixing.

Compounding was done according to ASTM D-3184-89 method B[19]. The elastomer was first passed through the tight nip of the rolls, 0.2 mm twice. A blanket of the rubber obtained was then passed through the rolls set at 1.4 mm nip gap and allowed to form a band around the front slow roll. This started with many holes and after continued passing, the band became smooth. The nip gap was increased to 1.7 mm and all dry ingredients except the fillers and the cure system were then added to the nip. The elastomer was then cut back and forth twice to ensure proper blending and to allow the elastomer in the bank to go through the nip. It is important for efficient mixing to maintain a rolling bank on the mill during the incorporation of ingredients. Carefully collected the materials falling through the nip, from the tray and returned to the mix. The compound was then cut back and forth twice to ensure good dispersion of these dry ingredients throughout the batch. The mill was then slightly opened to increase the nip to 1.9 mm and the fillers along with the liquid plasticizer were added slowly, evenly and alternately to the batch. To prevent excessive loading of fillers at the centre of the mill, strips of compound were cut from the ends of roll several times during this operation and thrown back into the bank. When most of the fillers were incorporated into the compound, the remaining fillers and liquid plasticizer were added to the batch. When no loose filler was visible, the batch was cut back and forth twice more to assure good dispersion. Added the accelerator taking care to avoid any loss. Sulphur was then added to the batch. When it was well dispersed, the entire batch was cut back and forth at least 4 times to assure thorough cross blending. The mixing cycle was concluded by passing the rolled batch endwise through the mill six times with a nip opening of 0.8 mm to improve the dispersion. Finally, the compound was sheeted out to get 6 mm thickness.

II.11. Testing of Unvulcanized Compounds

II.11.1. Time of Optimum Cure

Optimum cure time was measured using an oscillating disc rheometer, 'Monsanto' Rheometer R-100, having oscillation 100 cycles per minute at 3^0 arc, according to ASTM D-2084-93 test method[20]. The optimum cure time corresponds to the time to achieve 90% of the cure, calculated using the formula,

Optimum cure time = $[0.9 (M_H - M_L) + M_L]$ ---- II (25)

where, M_H and M_L are the maximum and minimum torque respectively for the rheograph. A typical rheograph is shown in Figure II.8.
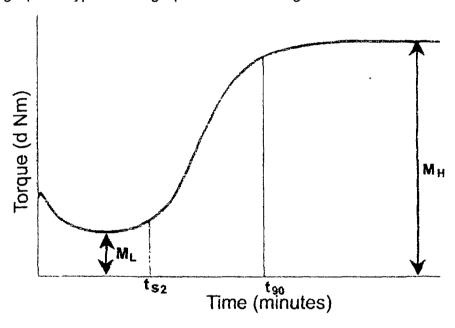
Figure II.8. Rheograph from 'Monsanto' Rheometer, R-100

The temperature of the platens was preset at 150 ^0C. About 15 g of the rubber compound was placed on the rotor. The platens were closed, immediately started the motor for oscillation of the rotor. The viscosity or torque of the sample will get reduced to a minimum value and after sometime increases as the vulcanization starts and reaches a maximum. The rotor was stopped after maximum torque was attained. The platens were opened, the test piece removed and the cavity was cleaned. In this study, the optimum cure time was determined at 150 ^0C, at a chart speed of 60 min. The optimum cure time, scorch time (ts2), minimum torque and maximum torque were noted from the rheograph.

181

II.11.2. Cure Rate Index

Cure rate index is an approximate rate of cure parameter, proportional to the average slope of the cure rate curve in the steep region and is calculated as follows

$$\text{Cure rate index} = \frac{100}{(\text{cure time} - \text{scorch time})} \qquad \text{---- II (26)}$$

where, scorch time is the total time from the start to get 2 units rise from the minimum torque, cure time is the time for optimum cure.

II.11.3. Determination of Mooney Scorch Time

The Mooney viscometer consists of a heated cavity and a rotor, which rotates at 2 rpm. The resistance to rotation of the rotor, exerted by the rubber inside the cavity is measured in Mooney units with the help of a calibrated spring. The platens are closed or opened by a suitable pneumatic system.

A typical trace of Mooney viscosity versus time plot is given in Figure II.9.

The die cavity and rotor were heated to the test temperature of 120 ^{0}C and allowed to stabilize. The cavity was opened, the rotor, with the test sample kept on both sides, was placed in the die cavity, the cavity was closed as quickly as possible and a stopwatch was started. The pressure was maintained at 50 psi. One minute after the die closure, the rotor was started and reading was taken at the desired time intervals. Scorch time, determined at 120 ^{0}C, is the total time from the start in minutes for the viscosity to rise 5 Mooney units (t_5) from the minimum value.
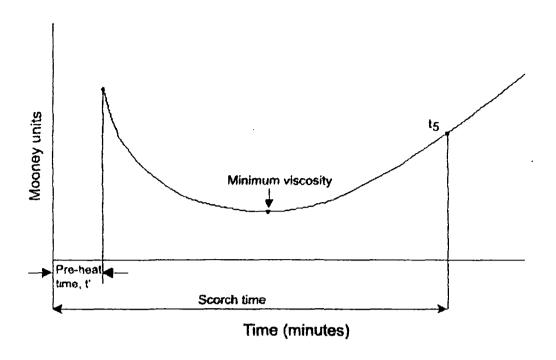
Figure II.9. Scorch graph of Mooney viscometer

II.12. Moulding of Test Samples

Test pieces were compression moulded at 150 °C by placing 5% excess of the uncured stock in the cavity of a suitable mould and curing in a hydraulic press having electrically heated platens, to their respective optimum cure times as obtained from 'Monsanto' Rheometer.

The temperature of the platens was controlled by thermostats and kept within ±1 °C of the set temperature. The test samples were introduced into the mould, which was heated to the moulding temperature of 150 °C, platens were closed and a pressure of 200 kg/cm² was applied. The pressure was quickly released and two or three bumping given to allow entrapped air to escape. The moulding pressure of 200 kg/cm² was then maintained. After the opimum cure time, the pressure was released, the mould opened and the samples were taken out. A marking was given on the moulded samples for tensile tests to indicate the mill grain direction. The moulded samples were immediately cooled after taking out from the mould. For test specimens of thickness greater than 3 mm, additional time was given to the optimum cure time, wherever necessary.

II.12.1. Test Specimen Preparation

For tensile and tear tests, specimens were punched out from the moulde
sheets along the direction of grain using appropriate dies.

II.13. Testing for Vulcanizate Properties

At least five specimens per sample were tested for each property and th
mean of these values was reported. All the physical tests using vulcanized tes
specimens were performed only after a minimum conditioning period of 24 h c
moulding the samples.

II.13.1. Modulus, Tensile Strength and Elongation at Break

These three parameters were determined according to ASTM D-412
98a[21] test method, using dumb-bell shaped test pieces. The test pieces wer
punched out from the moulded sheets using C-type die, along the mill grai
direction of the vulcanized sheets. The thickness of the narrow portion of th
specimen was measured using a dial gauge. The specimens were tested in
Universal Testing Machine (UTM model-1474 supplied by 'Zwick', Germany) a
25 ± 2 ^{0}C with a crosshead speed of 500 mm per minute. The elongation a
break was measured using an extensometer. The elongation at break, modulu
and tensile strength were recorded from stress-strain curve on a strip cha
recorder. The machine has a sensitivity of 0.05 per cent of full-scale loac
Tensile strength is the force per unit area of original cross section to break th
specimen. Modulus is the force per unit area of original cross section to stretc
the specimen to a particular elongation. The modulus and tensile strength ar
reported in MPa and the elongation at break in percentage of original lengt
Five test pieces per sample were used for each test.

II.13.2. Tear Strength

Tear strength is the force required to break the angular test specimen, based on the thickness of the sample. This property was tested as per ASTM D 624-00[22] test method, using unnicked 90° angle test specimens, which were punched out from the moulded sheets, along the mill grain direction. Five test pieces per sample were used for this test. This test was also carried out in a 'Zwick' UTM, at a crosshead speed of 500 mm per minute and at a temperature $25 \pm 2\ {}^{0}C$. The tear strength values are reported in kN/m.

II.13.3. Hardness

Hardness refers to the resistance of the sample towards indentation by a pointer of definite shape, under the application of a load using a calibrated spring.

The hardness of the samples was measured as per ASTM D-2240-00[23] test method using a Shore A - type Durometer, which employs a calibrated spring to provide the indenting force. Since the hardness reading decreased with time after firm contact between the indenter and the sample, the reading was taken immediately after the establishment of firm contact.

II.13.4. Heat Build-up

Heat build-up of the samples was measured as per ASTM D-623-99[24] test method. The test specimen used was cylindrical in shape with a diameter of 17.8 ± 0.1 mm and a height of 25 ± 0.15 mm. It was subjected to rapid cyclic compressive stresses in 'Goodrich' Flexometer at 1800 rpm. Test was conducted at 50 ${}^{0}C$. A constant initial compressive load was applied to the specimen through a lever having high inertia and imposing on the specimen an additional high frequency cyclic compression of definite amplitude. The stroke given was 4.45 mm. The increase in temperature at the base of the test specimen was measured with a thermocouple, which provided indication of the heat generated in flexing the specimen.

Dynamic set

The thickness of the samples was measured before and after the test.

$$\text{Dynamic set } (\%) = \frac{T_1 - T_2}{T_1} \times 100 \qquad\qquad ---- \text{ II (27)}$$

where, T_1 and T_2 are the thickness of the specimen before and after testing

II.13.5. Abrasion Resistance

The abrasion resistance of the samples was tested using a DIN abrader as per DIN 53516[25] specifications. It consists of a drum on to which a standard abrasive cloth is fixed. The drum is rotated at a speed of 40 ± 1 rpm and the total abrasion length is 42 m. Sample having a diameter of 16 ± 0.2 mm and a thickness of 7 mm, was kept on a rotating sample holder. 10 N load was applied. Initially a pre-run was given for the sample and then its weight was taken. The sample was allowed to run over the abrasive surface and the weight after the run was noted. The difference in weights was the abrasion loss. It is expressed as the volume of the test piece getting abraded away by its travel through 40 m. on a standard abrasive surface. The abrasive loss was calculated as follows:

$$V = \frac{\Delta m}{\rho} \qquad\qquad --- \text{ II (28)}$$

where, Δm = Mass loss, ρ = Density, V = Abrasion loss in mm^3

To ensure the consistent uniformity of the abrasive surface of the equipment, standard test pieces were prepared and tested in the abrader. The loss of the standard sample was ensured to be in the range of 170-220 mg, as prescribed for the test.

II.13.6. Rebound Resilience

The rebound resilience of the vulcanizate was measured using Dunlop Tripsometer[26]. The sample was held in position by applying vacuum. It was conditioned by striking it with the indenter six times. A freely falling hammer was dropped from a given height against the specimen at a known angle (45) The pendulum rebounded and the rebound angle was noted. The temperature of the

specimen holder and the sample was kept constant at 30 ^{0}C. Rebound resilience was calculated as,

$$\text{Rebound resilience (\%)} = \frac{1-\cos \theta_2}{1-\cos \theta_1} \times 100 \qquad\qquad \text{— II (29)}$$

where, θ_1 and θ_2 are the initial and rebound angles respectively, θ_1 was 45° in all cases.

II.13.7. Compression Set

The initial thickness of the moulded test samples (12.5 mm thickness and 29 mm diameter) was accurately measured and then compressed to give 25 per cent deflection between two parallel plates provided with spacers and kept in an air oven at 70 ^{0}C for 22 h[27]. After the heating period, the deflection was released, the sample was cooled to room temperature for half an hour and final thickness was measured. The compression set was calculated as follows.

$$\text{Compression set (\%)} = \frac{t_0 - t_1}{t_0 - t_s} \times 100 \qquad\qquad \text{— II (30)}$$

where, t_0 and t_1 are the initial and final thickness of the specimen and t_s is the thickness of the spacer bar used.

II.13.8. Testing for Fungal Growth

Moulded samples were inoculated and incubated for 1 week. There is no fungal attack on the sample.

II.13.9. Determination of Crosslinking Density / Volume Fraction of Rubber

The extent of crosslinking of the vulcanizates was determined through swelling studies by keeping sample in the appropriate solvent for 48 h at 25 ^{0}C as per the method reported by Ellis and Welding[28].

Samples of approximate 10 mm diameter 2.5 mm thickness and weighing approximately 0.3 g were punched from the central portion of the vulcanized film and allowed to swell in toluene at 25 ^{0}C. The swollen samples were taken after the equilibrium swelling period, blotted with filter paper and weighed quickly in a

stoppered weighing bottle. Samples were dried in an oven for 24 h at 70 ^{0}C and then in vacuum and finally weighed after allowing them to cool in a desciccator. Duplicate readings were taken for each sample. The volume fraction of rubber, Vr, in the swollen sample was calculated by the method reported by Ellis and Welding, which takes into account the correction of swelling increment with duration of immersion after the equilibrium is attained.

$$Vr = \frac{(D - FT)\,\rho_r^{-1}}{(D - FT)\,\rho_r^{-1} + A_0\,\rho_s^{-1}} \qquad\text{---- II (31)}$$

where, T - Weight of test specimen

D - Deswollen weight.

F - The weight fraction of the insoluble components

A_0 - Weight of the absorbed solvent, corrected for the swelling increment. (S-T), where S is the swollen weight.

ρ_r and ρ_s – Densities of the rubber and solvent

ρ_r - NR = 0.92 ρ_s - Toluene = 0.86

The value of Vr can be taken as a measure of crosslink density.

II.13.9.1. Swelling over ammonia[29]

A modified pre swelling procedure, which was designed to chemically break polymer-filler bonds, was also used in order to determine the effect of polymer-filler attachment on the effective number of network chains. Swelling the sample for 48h in uncapped bottles in toluene in an ammoniacal atmosphere (in a desciccator, the bottom of which contained concentrated ammonia) was done. Vr' was calculated using the equation II (31) and the difference between Vr and Vr' gives an account of the rubber-filler attachment.

II.14. Measurement of Resistance to Degradation

II.14.1. Measurement of Oil Resistance[30]

Oil resistance and leachability of the sample were studied by keeping the sample in ASTM oil No 3, for 168 h, at room temperature. Specimen having rectangular dimensions of 25 x 50 x 2 mm was used for this study. Initial weight

of the sample was taken as M_1 and it was immersed in 100 ml ASTM No.3 oil at room temperature for 168 h. After this period, the specimen was removed, dipped in acetone, blotted lightly with filter paper and placed immediately in a tared, stoppered weighing bottle and determined the mass M_2 of each of the swollen sample. The extent of swelling, as indicated by the mass of oil absorbed by the sample, was calculated using the equation,

$$\text{Oil absorption (\%)} = \frac{(M_2 - M_1)}{M_1} \times 100 \qquad\qquad \text{---- II (32)}$$

M_1 - Initial mass of the specimen and M_2 - Mass of specimen after swelling in oil

II.14.2. Leaching Loss

To assess the leaching loss, the oil-swollen samples were dried at 70 ^{0}C for 48 h, cooled in a desiccator and weighed (M_3). The leaching loss was calculated as,

$$\text{Leaching loss (\%)} = \frac{(M_1 - M_3)}{M_1} \times 100 \qquad\qquad \text{--- II (33)}$$

II.14.3. Volatilization Loss

Volatilization loss of plasticizer was determined by heating the weighed sample in an air-circulated oven at 100 ^{0}C for 7 days and also by thermogravimetric analysis. Initial weight was taken as M_1 and the final weight as M_4.

$$\text{Volatilization loss (\%)} = \frac{(M_1 - M_4)}{M_1} \times 100 \qquad\qquad \text{--- II (34)}$$

II.14.4. Hot Air Ageing

Dumb-bell shaped tensile test samples (2 ± 0.2 mm thick) were aged at 70 ^{0}C and 100 ^{0}C for 7 days and 3 days respectively in an air circulated oven. The tensile strength was measured before and after ageing. The percentage retention of tensile strength after ageing was calculated as

$$\text{Tensile strength retention (\%)} = \frac{\text{Tensile strength after ageing}}{\text{Tensile strength before ageing}} \times 100 \qquad \text{--- II (35)}$$

The percentage retention of modulus and elongation at break was also measured.

II.15. Testing of Latex Foam[18]

II.15.1. Hardness of Foam

The indentation hardness index of foam is the load in kilograms required to give an indentation in the sample equivalent to 40 per cent of the original thickness of the sample under specified conditions.

The size of the test sample was such that a margin of not less than 5 cm remained outside the area immediately below the indentor. The apparatus capable of applying an indentor to the sample at a uniform speed of about 14 mm per second, having a means of measuring the load required to produce the specified indentation was used. The depth of indentation was measured by means of a graduated scale mounted on the main framework between guide rods. The scale was arranged in such a way that it measured the distance between the base plate on which the test sample is placed and the base of the indentor. The diameter of the indentor was 305 ± 0.25 mm with a 25 ± 0.1 mm radius at the outer edge. The test was carried out at room temperature. The sample was placed on the perforated plate with the cavities downwards.

Before testing, the test area was mechanically conditioned, ie. the area of the sample, which during test will be compressed by the indentor, by applying the indentor with a load at least 50 per cent greater than the load, which will be required in the test. After release of mechanical conditioning load, the test was carried out within 5 minutes. Measured the initial thickness of the test area under a load of 2 kg applied by the indenter. Then carried out the test by lowering the indenter on to the sample at a specified rate and when the specified degree of compression was reached, the load was noted. The indentation hardness index is the load in kg applied to produce the specified indentation of 40 per cent of the original thickness of the sample.

II.15.2. Flexing Test

The test involves submitting a sample of foam to a continued flexing with an indenter for 250,000 cycles at 4 cycles per second and measuring the loss in hardness and thickness.

The samples were tested only after 48h of vulcanization. When a foam sample is submitted to the flexing test, its indentation hardness shall not reduce by more than 20 per cent and its thickness by more than 5 per cent of the original hardness and thickness respectively. The indentor is adjusted to move up to a distance of 40 per cent of the measured height of the sample for 1 complete revolution. Measured the indentation hardness index of the foam after flexing the sample for one minute, ie. 240 flexes. Then continued flexing upto 250,000 cycles, allowed the sample to stand for 30 minutes and then measured the change in thickness as well as hardness of the sample.

II.15.3. Compression Set

The test consists of maintaining the test piece under specified conditions of time, temperature and constant deflection and noting the effect on the height of the released test piece.

The device for measuring the set consists of two flat plates larger in dimensions than the test pieces with spacers and clamp, such that the plates are held parallel to each other and the space between the plates is adjustable to the required deflected height. The thickness of the sample was measured, kept in the compression device and was compressed to 50 per cent to its initial thickness between the parallel steel plates. It was then placed in an oven at 70 ^{0}C for 22 h. Then the test pieces were removed from the oven and released from the compression. A 30-minute recovery time was allowed at room temperature and then the thickness was measured. Compression set is calculated as the difference in thickness on original, expressed as percentage.

II.15.4. Whole Sample Compression

Original thickness of the sample was measured, placed a circular indentor weighing 25 kg on the sample and was allowed to remain for 168 h at room temperature. After this period, the load was removed and the sample was

191

allowed to recover for 30 minutes and thickness was again measured. Compression set is expressed as change in thickness on initial, expressed as percentage.

II.15.5. Ageing

The test consists of subjecting the samples to controlled deterioration by air at an elevated temperature and atmospheric pressure after which, the physical properties were measured and compared with those of unaged samples. The deterioration is measured by the observed change in the physical properties.

The test pieces were kept in an air-circulated oven at 70 ^0C for 168 h. After ageing, the samples were removed from the oven and cooled to room temperature. The aged sample was tested for properties such as hardness within 16-96 h after ageing and the change from the corresponding original values was expressed as percentage.

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Chapter III

Studies on Epoxidised Rubber Seed Oil as a Plasticizer for Acrylonitrile Butadiene Rubber

NITRILE rubber (NBR) is a copolymer of butadiene and acrylonitrile. In NBR the acrylonitrile content may vary from 20 to 45 per cent. With levels under 25% classified as low, 25-35% as medium and 35-45% as high. Major properties are dependent on the acrylonitrile content. It has good resistance to a wide variety of oils and solvents. Hence it is widely used in products like oil seals, pipe protectors, gasket, O-rings etc. NBR shows no self reinforcing effect as there is no crystallinity. The maximum service temperature in presence of oxygen is estimated to be 130 $^0C^1$. When acrylonitrile content increases tensile strength, oil resistance, hardness, modulus, compression set, brittleness temperature, abrasion resistance and heat resistance increase. But resilience and low temperature flexibility decrease[2].

The polarities of acrylonitrile and butadiene are very different and the polarity of the copolymer becomes greater with increasing amount of acrylonitrile. The percentage of the acrylonitrile content in the copolymer has considerable influence on the swell resistance of the vulcanizates in non-polar solvents. The greater the acrylonitrile content, the less the swell in motor fuels, oils, fats etc. However, the elasticity and low temperature flexibility also become poorer. For the same reason, the compatibility with polar plasticizers (eg. those based on esters or ethers) and polar plastics (PVC) improves with increasing acrylonitrile concentrations in the NBR[3].

Temperature of the emulsion polymerization has an effect on curing behaviour and final properties of NBR. Nitrile rubbers are, therefore, designated "hot" and "cold" polymers depending on the polymerisation temperature. "Cold" gums, readily soluble in ketones, are used in solvent-based adhesives. Some formulations may include ester-type plasticizers such as di-2-ethylhexyl phthalate.

As with many elastomers, the presence of oxygen compounds in certain types of carbon blacks reduces their heat-ageing performance. This usually results in the selection of a thermal black for the best heat-ageing NBR compounds.

Basically nitrile rubbers are compounded much like natural rubber. Since, it does not crystallise, reinforcing fillers are necessary to obtain reasonable tensile, tear and abrasion levels. In black compounds reinforcement is proportional to the fineness of the black. Non-black fillers give best heat resistance[4] and also be used with compound that might be in contact with the food products. Fine particle silica is the most reinforcing among the non-black fillers.

Nitrile rubbers are noteworthy because of their resistance to petroleum-based materials. They are not as good as neoprene in their resistance to oxidation and weathering. Low cost makes NBR attractive for applications requiring oil or gasoline resistance such as hose, processing rolls, liners, seals, hydraulic components and refrigerant lines.

Nitrile rubber requires antioxidant to produce products having ageing resistance and long-term service. Where staining is not a problem, amine type antioxidants may be used. If staining is objectionable then phosphates or hindered phenol antioxidants will serve better.

Vulcanization of nitrile rubber is usually accomplished with sulphur, accelerator and zinc oxide and fatty acid as activator. In special cases peroxide may also be used. NBR cures relatively fast, the higher ACN content rubbers curing faster than lower ACN content ones. The amount of sulphur used is based on butadiene content and is generally lower than that used for natural rubber and ranges from 0.7 to 2.3 phr. The solubility of sulphur is considerably less than in NR and hinders its uniform dispersion, for this reason sulphur is added early in the mix.

Because of the relatively fast rate of cure, NBR is usually compounded with only one accelerator, often of the sulphenamide class. If accelerators of the thiazole type are used, a secondary accelerator likes tetramethylthiuram monosulphide (TMTM) or tetramethylthiuram disulphide (TMTD) might also be used. Activating system would be 5 phr zinc oxide and 1-2 parts stearic acid.

Plasticizers are used in almost all nitrile compounds first to aid processing and then to improve low temperature flexibility, resistance to flexing, or to reduce

hardness. Plasticizer level will ordinarily vary from 5-50 phr. Processing can be difficult below 5 phr level, and over 50 phr the material may bleed out and physical properties may deteriorate unacceptably. Three types of plasticizers are generally used[4]. Organic esters to get the best low temperature flexibility, coal tar resins like coumarone indene resin to maintain the tensile properties and to improve building tack, and polymeric esters to obtain high temperature ageing resistance. Some suppliers offer integral stabilizers where the stabilizer is bound chemically into the polymer backbone to improve ageing characteristics[5].

Plastizisers generally used in nitrile rubber are dioctyl phthalate (DOP) and dibutylphthalate (DBP). Vegetable oils are esters and have a higher molecular weight compared to the conventional synthetic esters. Moreover they contain free fatty acids, which can function as a coactivator. Almost all vegetable oils contain phenolic compounds like tocopherol, which are potential antioxidants and can protect the elastomers from oxidation.

In application such as oil seals and O-rings, nitrile rubber vulcanizates lose most of the plasticizers through leaching and volatilisation, causing failure of the product. Epoxidised rubber seed oil, being polar in nature and having higher molecular weight components than DOP/DBP, is expected to be compatible with nitrile rubber and may function as a good plasticizer for nitrile rubber. In this chapter the results of evaluation of epoxidised rubber seed oil in nitrile rubber compounds in comparison with dioctyl phthalate are presented.

The formulations of compounds used are given in Table III.1. The base formulation is typical of an oil seal compound having 65-70 Shore A hardness. Detailed procedures for preparation of compounds, determination of cure characteristics, physical properties, ageing resistance and swelling/ leaching studies are given in Chapter II. The compounds evaluated contained rubber seed oil and epoxidised rubber seed oil of different epoxidation levels. For comparison, dioctyl phthalate was used in the control compound.

199

III.1. Results and Discussion

III.1.1. Effect of ERSO on Cure Characteristics of NBR Compounds

Figure III.1 shows the rheographs of the compound containing DOP, RSO and ERSO (5.2%). It is evident from the figure that both the compounds N7 and N2 have lower value of maximum rheometric torque, compared with compound N1, indicating better plasticizing action of RSO and ERSO (5.2%). Compound N2 showed the lowest value of maximum rheometric torque, probably because of the combined effect of higher plasticizing action and lower extent of crosslinking. Cure characteristics of compounds given in Table III.2 indicate that the compound containing RSO (N2) and those containing ERSO (N3 to N7) have higher cure time than the control compound containing DOP (N1). Different levels of epoxidation of the RSO did not show proportional change in cure time. All the 7 compounds were having the same scorch time (ts_2) from the rheograph. Mooney scorch value (t_5) at 120 ^{0}C is also comparable for the 7 compounds. The increase in cure time of the compounds containing RSO and ERSO may be due to partial utilization of sulphur for reacting with the unsaturated fatty acids present in these materials.

III.1.2. Effect of ERSO on Physical and Mechanical Properties of NBR Vulcanizate

From Table III.3, it is seen that vulcanizates containing ERSO showed comparable tensile strength and modulus with that containing DOP. The tear strength values were marginally higher for compounds N2 and N3. Compounds N2 to N5 have lower extent of epoxidation (< 2%) and these compounds in general showed higher compression set and heat build up, and lower hardness and rebound resilience compared with the control compound N1 which contained DOP as the plasticizer. Among these, the compound N2 that contained RSO, showed lower tensile strength, modulus and rebound resilience and higher elongation at break and compression set. A possible explanation for this observation is that rubber seed oil contains about 78-82 % of unsaturated fatty acids (Table II.2), which can compete with the polymer for reacting with sulphur. As the dosage of sulphur in the

200

formulation is low, there is a chance that presence of unsaturated fatty acids affects the extent of crosslinking of the rubber phase. This argument is further supported by the fact that at higher levels of epoxidation of the rubber seed oil (eg. compounds N6 and N7) some of these properties, which are more dependent on extent of crosslinking showed some improvement. The Vr values given in Table III.5 further support this view. At higher levels of epoxidation, properties such as compression set and heat build up were lower and, rebound resilience higher compared with those of the other compounds. The physical and mechanical properties of the compounds N2 to N5 did not show a regular change with epoxy content of the oil. This is expected to be due to the fact that the level of epoxidation of the oil used in these compounds is rather low. However, use of epoxidised rubber seed oil in place of DOP is not going to adversely affect the properties, which are more relevant to applications such as oil seals and O-rings.

The DIN abrasion resistance of the compounds N2 to N7 was better than the control compound, N1. It has been shown that use of a higher dosage of stearic acid (6phr) in tread formulations enhanced the abrasion resistance[6]. The higher fatty acid soap formed during vulcanization was believed to act as a better lubricant, facilitating slippage of the molecular chains past each other under an applied load in such cases. In the present case also, a similar mechanism is expected to operate in compounds containing RSO and ERSO, resulting in better abrasion resistance.

III.1.3. Effect of ERSO on Ageing Resistance of NBR Vulcanizate

Use of vegetable oils such as linseed oil is reported to enhance the ageing/ozone resistance in polychloroprene based vulcanizates[7,8]. Similar observation in nitrile rubber was reported by Nandanan et al^9. Even though the exact mechanism of action of these oils for such observation, is not fully understood, it is possible that the oil acts as a carrier for the antioxidants in the compound, helping them to be brought to the surface where the oxidation mostly sets off. From Table III.4 it can be seen that the ageing resistance of the compounds containing RSO and ERSO is comparatively better than that containing DOP, as indicated by both better mechanical properties (tensile strength, elongation

at break and modulus 300%) and higher retention of these properties of the vulcanizates after ageing at 70 °C for 7 days.

III.1.4. Effect of ERSO on Swelling and Leaching Behaviour of NBR Vulcanizate

Change in dimension of vulcanized rubber when it comes in contact with oil is a matter of high concern in designing compounds for products such as oil seals. Vulcanized rubber swells in oil by absorbing it. At the same time, certain ingredients such as plasticizers and antioxidants get leached out of the vulcanizates during the swelling process. Data given in Table III.5 indicate that vulcanizates N2 to N7 swell more than the control sample N1, in ASTM No. 3 oil by absorbing the oil. However, as the level of epoxidation of the rubber seed oil increased, the extent of swelling decreases. The higher level of swelling of samples N2 to N7 compared to the control sample N1 is due to lower extent of crosslinking of their vulcanizates, as evident from the lower Vr values of these samples given in Table III.5. The leaching loss, as indicated by the weight loss of the samples swollen in ASTM No 3 oil, was considerably lower for the vulcanizates N2 to N7 compared to the sample N1 that contained DOP as plasticizer. The lower leaching loss of samples N2 to N7 is expected to be due to higher molecular weight of rubber seed oil and epoxidised rubber seed oil, which are in the range of 877 and 960 respectively, compared with that of DOP which is 390[10].

III.1.5. Effect of ERSO on Volatilization Loss and Thermal Stability of NBR Vulcanizate

The use of softeners with very low molecular weight is limited by their high volatility. During vulcanization or service of the product, loss of softener takes place[11]. During heating at a higher temperature, the lower molecular weight plasticizer gets volatilized and escapes from the vulcanizate leading to shrinkage and failure of the products such as O-rings. Volatalization loss from vulcanizates N2 to N7, when heated at 100 °C for 168 h. is much lower than that from the control sample N1 (Table III.5). This is further evident from the thermogram given in Figure

III.2. The weight of the sample retained upto 450 ^{0}C in a heating cycle of 5 ^{0}C per minute is more for the vulcanizate containing 2.7% ERSO than that containing RSO or DOP. The thermograms at isothermal condition (Figure III.3) also show lower heating loss for the sample containing 2.7% ERSO at 250 ^{0}C. These observations indicate that RSO and ERSO impart better thermal stability to NBR vulcanizates compared to DOP.

III.2. Conclusions

The results of the present study indicated that RSO and ERSO could be used as less leachable and low volatile plasticizer for nitrile rubber. Use of ERSO in nitrile rubber gave better abrasion resistance whereas; tensile strength and tear strength were comparable to those vulcanizates, which contained DOP as plasticizer. Lower hardness and slightly higher compression set resulting from lower crosslink density/better plasticizing effect due to the epoxidised rubber seed oil may be corrected by a small increase in sulphur content in the compound.

Table III.1. Formulation of compounds

Ingredients	Formulations						
	N1	N2	N3	N4	N5	N6	N7
Nitrile rubber	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5
MBTS	1	1	1	1	1	1	1
TMTD	2	2	2	2	2	2	2
Sulphur	0.5	0.5	0.5	0.5	0.5	0.5	0.5
TDQ	1.5	1.5	1.5	1.5	1.5	1.5	1.5
IPPD	1	1	1	1	1	1	1
MT Black	50	50	50	50	50	50	50
SRF Black	30	30	30	30	30	30	30
DOP	7	—	—	—	—	—	—
RSO	—	7	—	—	—	—	—
ERSO 1 (0.4%)	—	—	7	—	—	—	—
ERSO 2 (0.9%)	—	—	—	7	—	—	—
ERSO 3 (1.75%)	—	—	—	—	7	—	—
ERSO 4 (2.7 %)	—	—	—	—	—	7	—
ERSO 5 (5.2 %)	—	—	—	—	—	—	7

204

Table III.2. Cure characteristics

Properties	N1	N2	N3	N4	N5	N6	N7
Optimum cure time (t_{90}) at 150 °C (minutes)	6.5	9.5	7.0	9.0	7.5	8.0	8.0
Minimum rheometric torque (dN m)	10	10	11	10	12	10.5	10.5
Scorch time (t_{S2}) from rheograph (minutes)	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Mooney scorch time (t_5) at 120 °C (minutes)	15.5	15.0	14.8	13.8	13.5	14.4	13.8

Table III.3. Physical and mechanical properties of vulcanizates

Properties	N1	N2	N3	N4	N5	N6	N7
Tensile strength (MPa)	10.6	10.3	10.8	10.86	10.9	10.6	10.5
Elongation at break (%)	425	491	454	406	447	449	426
Modulus 100% (MPa)	3.6	2.9	3.5	4.2	3.8	3.3	3.3
Modulus 300% (MPa)	9.2	8.1	9.2	9.6	9.7	8.9	9.0
Tear strength (kN/m)	47.2	49.8	49.2	46.4	47.8	48.4	46.8
Compression set (%)	8.2	10.5	10.3	10.1	10.4	8.1	8.4
DIN abrasion loss (mm^3)	102	93	98	97	95	94	98
Heat build up (ΔT ^{0}C)	45	51	49	47	47	45	43
Hardness (Shore A)	68	66	66	67	67	66	66
Rebound resilience (%)	45.7	42.8	43.4	44.0	44.2	45.9	46.5

Table III.4. Tensile properties after ageing at 70 °C for 168 h

Properties	N1	N2	N3	N4	N5	N6	N7
Tensile strength (MPa)	11.1	10.8	11.4	11.	12.1	11.3	11.6
Retention (%)	104.2	104.7	104.8	101.3	110.2	107.1	110.5
Elongation at break (%)	323	431	347	330	375	393	377
Retention (%)	76.0	87.8	76.4	81.3	83.9	87.5	88.5
Modulus 100% (MPa)	4.8	3.5	4.5	4.9	4.6	3.5	4.2
Retention (%)	134.1	117.6	130.1	116.4	120.3	105.5	127.9
Modulus 300 % (MPa)	10.3	9.4	10.8	10.0	11.2	9.3	10.6
Retention (%)	111.5	116.1	118.0	104.3	115.8	104.5	117.8

Table III.5. Swelling, leaching and volatilisation behaviour of vulcanizate

Parameter	N1	N2	N3	N4	N5	N6	N7
Mass of ASTM No. 3 oil absorbed (%)	1.73	2.00	1.90	1.82	1.82	1.83	1.78
Leaching loss (%)	0.62	0.29	0.27	0.29	0.19	0.18	0.18
Volatilisation loss (%)	1.71	1.58	1.58	1.58	1.55	1.48	1.40
Vr value	0.186	0.167	0.180	0.180	0.183	0.185	0.185
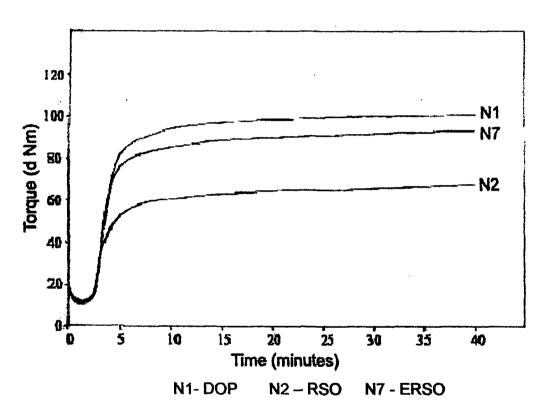
Figure III.1. Rheographs of the compounds N1, N2 and N7
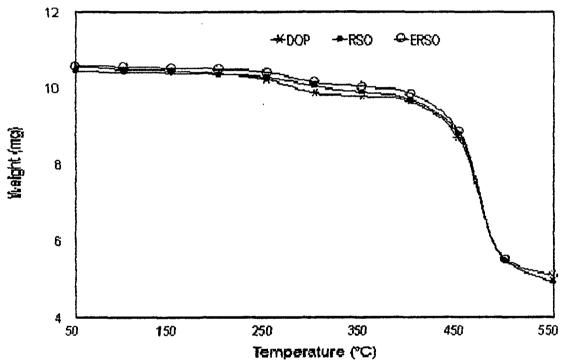
Figure III.2. Thermogram of NBR vulcanizates containing DOP, RSO and ERSO as plasticizers

210
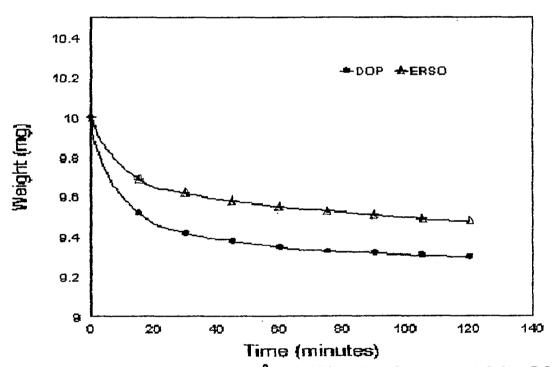
Figure III.3. Thermogram at 250 °C of NBR vulcanizates containing DOP and ERSO as plasticizers

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Chapter IV

Use of Rubber Seed Oil in Polychloroprene Rubber Compound

Polychloroprene rubber (CR) is an all purpose elastomer with a nearly ideal balance properties. It has got very good resistance to weather, ozone and natural ageing. The inherent tackiness and flame resistance of this polymer makes it the ideal choice for many industrial adhesives, coated fabrics and moulded goods.

The molecular structure of polychloroprene rubber primarily consists of trans-chloro-2-butylene units, but three other configurations also occur[1].

Type of addition	Configuration	Approximate %

Trans1,4	H_2 H
	  | |
	—C C
	  \\ $_{/}$ $^{\diagup}$
	    C=C
	       \\
	        C—
	  | |
	  Cl H_2
		88-92

Cis 1,4	H_2 H
	  | |
	—C C
	  \\ $_{/}$
	   C = C
	   | |
	   Cl H
		7-12

1,2	H2 Cl
	  | |
	—C—C—
	      |
	      CH
	      ||
	      CH_2
		1-5

3,4	H_2 H
	  | |
	—C — C —
	      |
	      C—Cl
	      ||
	      CH_2
		1

214

The 1,2 addition of 2-chloro-1,3-butadiene results in polymer having some chlorine available in allylic form. This is a labile form and is the principal site of vulcanization. The degree of crystallinity in CR is largely dependent upon the amount of trans configuration in the polymer. Increasing amounts increase the degree of crystallinity. The CR manufactured by the Du Pont Company is known as Neoprene rubber.

The Neoprenes are classified as general purpose or adhesive types. General purpose types are used in a variety of elastomeric applications, particularly moulded and extruded goods, hose, belts, wire and cable, heels and soles, tires, coated fabrics and gaskets. Compounds prepared from Neoprene GN, cure rapidly and develop highly resilient vulcanizate with good tear resistance. As uncompounded Neoprene GN polymer ages, its viscosity declines; at the same time the polymer become nervier, faster curing and more prone to scorch.

The Neoprene W type has excellent uncompounded stability. Like natural rubber, it can be milled without sticking over a wide temperature range. Neoprene W contains no staining stabilizer.

IV.1. Compounding and Curing of Polychloroprene Rubber

The vulcanization of CR compositions is achieved through metallic oxide. Zinc oxide and magnesium oxide are used in most CR formulations. These two oxides are sufficient to effect cure in the absence of any organic accelerators. However, an accelerator such as NA-22 (ethylene thiourea) accelerates the vulcanization process when very fast cures are required. Since the cure rate with metallic oxides alone is slow, an organic accelerator such as NA-22 is always included in Neoprene W formulations. But it is often very difficult to balance the required cure rate and scorch safety of the compounds when such accelerators are used.

In the vulcanization of CR, magnesium oxide serves as an acid acceptor, preventing premature crosslinking and cyclisation of polychloroprene and it also helps to enhance the properties of the vulcanizate. Proportion of magnesium oxide and zinc oxide is 4 and 5 parts by weight respectively on 100 parts by weight of polychloroprene[2].

IV.2. Chemical Mechanism of Crosslinking of Polychloroprene Rubber

Crosslinking of polychloroprene is primarily due to a continuation of the polymerization assisted by bivalent metallic oxides, which takes place very fast at elevated temperature and correspondingly slower at lower temperature. In polychloroprene, the double bond in the main chain is deactivated for electrophillic reaction by the presence of chlorine atom in the adjacent carbon atom. So vulcanization with sulphur is not possible. Vulcanization of polychloroprene by zinc oxide is due to the presence of the occasional 1, 2 units, which react after an allylic shift of the chlorine atom in the following way[3].

Allylic shift of chlorine atom in 1, 2 additon units

$$
\sim\!\!- CH_2 - \underset{\underset{Cl}{|}}{C} = CH - CH_2 -\!\!\sim \longrightarrow \sim\!\!- CH_2 - \underset{\underset{\underset{CH_2Cl}{|}}{\overset{\|}{CH}}}{C} -\!\!\sim \longrightarrow \qquad \text{-----IV (1)}
$$

Crosslinking in the presence of zinc oxide

$$
\text{-------- IV (2)}
$$

In the presence of organic accelerators such as ethylene thiourea, the following reactions also lead to crosslinking of the polychloroprene rubber[4].

$$\overset{\displaystyle |}{C} = CH - CH_2 - Cl + S = \overset{\displaystyle HN - CH = CH_2}{\underset{\displaystyle HN - CH = CH_2}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}} \longrightarrow$$

$$\overset{\displaystyle |}{\underset{\displaystyle |}{C}} = CH - CH_2 - S - \overset{\displaystyle HN - CH = CH_2}{\underset{\displaystyle HN - CH = CH_2}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}} - Cl \qquad \text{------ IV (3)}$$

$$\overset{\displaystyle |}{\underset{\displaystyle |}{C}} = CH - CH_2 - S - \overset{\displaystyle HN - CH = CH_2}{\underset{\displaystyle HN - CH = CH_2}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}} - Cl \quad + \quad ZnO \longrightarrow$$

$$\overset{\displaystyle |}{\underset{\displaystyle |}{C}} = CH - CH_2 - S - \overset{\displaystyle HN - CH = CH_2}{\underset{\displaystyle HN - CH = CH_2}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}} - O - Zn^+Cl^- \qquad \text{------ IV (4)}$$

$$\downarrow$$

$$\overset{\displaystyle |}{\underset{\displaystyle |}{C}} = CH - CH_2 - S - Zn^+Cl^- + O = \overset{\displaystyle HN - CH = CH_2}{\underset{\displaystyle HN - CH = CH_2}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}} \qquad \text{------- IV (5)}$$

217

$$\overset{\displaystyle |}{\underset{\displaystyle |}{C}} = CH - CH_2 - S - Zn^+Cl^- + Cl - CH_2 - CH = \overset{\displaystyle |}{\underset{\displaystyle |}{C}} \quad\longrightarrow$$

$$\overset{\displaystyle |}{\underset{\displaystyle |}{C}} = CH - CH_2 - S - CH_2 - CH = \overset{\displaystyle |}{\underset{\displaystyle |}{C}} + ZnCl_2 \qquad \text{------- IV (6)}$$

The zinc chloride formed in equations IV(2) & IV(6) is an active catalyst of vulcanization and unless it can be scavenged, its presence during processing operation can cause scorching problem. Magnesium oxide reacts with zinc chloride and thereby enhances the scorch safety and physical properties of the vulcanizate.

$$2\,ZnCl_2 + MgO \xrightarrow{\;H_2O\;} 2\,Zn \Big\langle \begin{array}{c} OH \\ Cl \end{array} + MgCl_2 \qquad \text{----- IV (7)}$$

It is expected that epoxidised rubber seed oil/rubber seed oil could act as an acid acceptor, since it contains above 75% unsaturated higher fatty acids. The epoxide group could also react with the acid easily.

In the work reported in this Chapter, magnesium oxide is replaced by rubber seed oil and epoxidised rubber seed oil. The compounds were prepared by using the formulations given in Tables IV.1. and IV.3. The gum compounds are designated as C1, C2 and C3. In compound C1, ZnO / MgO combination is used as vulcanizing system along with ethylene thiourea as accelerator. In compound C2 and C3 ethylene thiourea (NA-22) is used as accelerator, but magnesium oxide is replaced with, RSO and ERSO respectively. The properties of the gum compounds are given in Table IV.2. The detailed procedures for the preparation of the compounds and testing of the compounds/vulcanizates are given in Chapter II.

IV.3. Results and Discussion

IV.3.1. Effect of RSO on Properties of the Gum Compounds

The rheographs in Figure IV.1 and the cure characteristics given in Table IV.2 indicate that the gum compounds containing rubber seed oil or epoxidised rubber seed oil have better scorch safety, lower cure time and faster cure rate compared with the compound containing magnesium oxide as acid acceptor.

The above combination of cure parameters is very much desirable in rubber compounds for better process safety and fast production rate. The lower values of maximum rheometric torque (Figure IV.1) for the compounds containing RSO and ERSO is due to the plasticizing effect of these materials or that of the higher fatty acids/their zinc soaps. The vulcanizates from these compounds have lower tensile and tear strength compared with that containing magnesium oxide. However these vulcanizates show much better retention of tensile properties after ageing at 100 °C for 72 hours. Rubber seed oil is an ester of higher fatty acids (Table II.2), which may undergo acidic hydrolysis to form higher fatty acids. These can react with zinc hydroxy chloride formed by reaction of zinc chloride with water, to form the corresponding zinc soap, thereby nullifying the effect of zinc chloride on premature vulcanization.

$$ZnCl_2 + H_2O \longrightarrow Zn \Big\langle \begin{smallmatrix} OH \\ Cl \end{smallmatrix} + HCl \qquad \text{------ IV (8)}$$

$$Zn \Big\langle \begin{smallmatrix} OH \\ Cl \end{smallmatrix} + 2RCOOH \longrightarrow (RCOO)_2 Zn + HCl + H_2O \quad \text{----- IV (9)}$$

The HCl produced by reactions involved in equations IV (8) and IV (9) above, can react with the unsaturated higher fatty acids formed by the acid hydrolysis of the rubber seed oil[5,6], according to the general equation given below.

$$R - CH = CH - CH_2 - COOH + HCl \longrightarrow R - CH_2 - CHCl - CH_2 - COOH \quad \text{---- IV (10)}$$

Reduction in tensile properties is expected to be due to the plasticizing effect of rubber seed oil, which may cause a reduction in the extent of crystallization of the polymer. This effect is further evident from the other physical properties of the filled compounds, discussed later. Better ageing resistance of the vulcanizates containing a higher dosage of higher fatty acids in NR compounds is already reported[7]. Since the properties of the gum compounds containing rubber seed oil and epoxidised rubber seed oil are almost similar, the epoxy group does not seem to have any specific role in neutralising the effect of

zinc chloride or HCl and hence in carbon black filled compounds only rubber seed oil was evaluated.

IV.3.2. Effect of RSO on Properties of GPF Black Filled Compounds

The cure characteristics of the GPF black filled compounds C4 to C11 and physical properties of their vulcanizates are given in Table IV.4. As in the case of gum compounds, the compounds containing rubber seed oil have better scorch safety, lower cure time and faster cure rate as indicated by higher mooney scorch time, lower optimum cure time and higher cure rate index values compared with the corresponding values of the compound containing naphthenic oil. Lower values of maximum rheometric torque indicate better plasticizing effect of the rubber seed oil than naphthenic oil. Even though the Vr values of the vulcanizates C8 to C11 are slightly lower than those of the vulcanizates C4 to C7, they show comparable tensile and tear strength values probably due to enhanced dispersion of filler in presence of RSO. The higher plasticizing effect of rubber seed oil over naphthenic oil is indicated by lower hardness, modulus and resilience and higher elongation at break and compression set of the vulcanizates containing rubber seed oil compared with those containing naphthenic oil. This effect may be due to the better lubricating action between the polymer chains caused by the zinc soap of the fatty acid formed during the vulcanization reaction, as described in the previous section. The vulcanizates containing RSO as plasticizer show excellent resistant to abrasion as compared to naphthenic oil. Improvement in DIN abrasion loss of NR and SBR vulcanizates by incorporation of RSO, as compared with aromatic oil has been noted earlier[8]. RSO being a better plasticizer gives more uniform distribution of filler and hence imparts better abrasion resistance to the vulcanizates. The higher fatty acid soaps formed from RSO during the vulcanization reaction also may be contributing to the higher abrasion resistance. This reasoning is supported by appreciably lower DIN abrasion values reported for the vulcanizates containing higher dosage of higher fatty acids[9].

The ageing resistance of the GPF filled vulcanizates containing rubber seed oil is much better than those containing naphthenic oil, as indicated by both better aged mechanical properties and higher retention of tensile properties of their vulcanizates after heat ageing at 100 °C for 120 h. Other vegetable oils

such as linseed oil are also reported to enhance the oxidative ageing/ozone resistance of polychloroprene vulcanizates[10]. Even though the exact reason for this behaviour is yet to be known it is possible that these oils act as carriers for the antioxidant added to the compound, helping them to be transported to the surface of the vulcanizate where the action of the degrading agents is more severe. The limiting oxygen index (LOI) values of compound containing rubber seed oil and naphthenic oil were determined. The LOI is defined as the volume fraction of oxygen in an oxygen-nitrogen atmosphere that will just support steady candle like burning of a material. It has been widely applied as a measure of the polymer flammability. The value obtained for both the compounds were same. Flash point of RSO is also higher than that of naphthanic oil. From these points we can conclude that RSO cannot adversely affect the inflammability of CR.
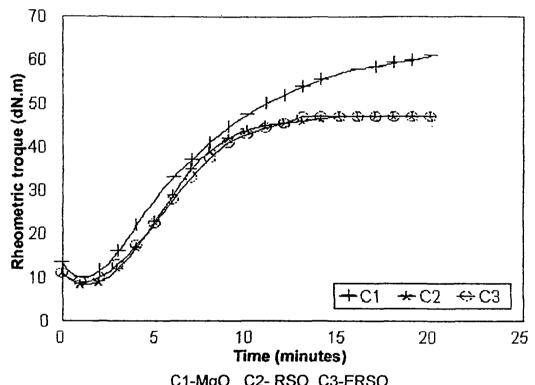
Most of the unsaturated vegetable oils are very compatible with polychloroprene. A disadvantage of unsaturated oil is that fungus may grow on the surface of vulcanizates. Sheets moulded from compounds C8, C9, C10 and C11 were inoculated and incubated at high humidity for a week. These sheets did not show any fungal growth on the surface, which indicated that rubber seed oil can be used in polychloroprene compounds without any fear of fungal attack.

IV.4. Conclusion

The results of the present study indicated that rubber seed oil could be used as an acid acceptor and plasticizer in polychloroprene compounds. Use of rubber seed oil helps to achieve better scorch safety, fast cure rate and better ageing resistance in polychloroprene compounds. It can replace magnesium oxide and process oil together in carbon black filled polychloroprene compounds. Use of rubber seed oil gives comparable tensile and tear strength and better abrasion resistance for the carbon black filled polychloroprene vulcanizates. There was no fungal growth on the surface of the vulcanizates containing rubber seed oil.

Table IV.1. Formulation of polychloroprene gum compounds

Ingredients	C1	C2	C3
Polychloroprene (Neoprene W-Type)	100	100	100
Stearic acid	0.5	0.5	0.5
Antioxident TDQ	1.0	1.0	1.0
Zinc oxide	5.0	5.0	5.0
Magnesium oxide	4.0	-	-
Rubber seed oil	-	4.0	-
Epoxidised rubber seed oil (2% epoxy content)	-	-	4.0
Accelerator NA-22	0.4	0.4	0.4

C1-MgO   C2- RSO   C3-ERSO

Figure IV.1. Rheographs of gum compounds

Table IV.2. Properties of polychloroprene gum compounds

Properties	C1	C2	C3
Maximum Rheometric torque (dN m)	61	47	47
M_H -M_L	51	38.5	38
Optimum cure time t_{90} at 150 ^{0}C (min)	13.0	8.8	9.4
Cure rate index	9.25	15.9	14.5
Scorch time (ts_2) at 150 ^{0}C (min)	2.2	2.5	2.5
Before Ageing			
Tensile strength (MPa)	12.3	8.9	7.6
Modulus 300 % (MPa)	1.9	1.2	1.2
Elongation at break (%)	782	789	781
Tear strength (kN/m)	26.1	17.8	19.5
After Ageing at 100 ^{0}C for 72 h			
Tensile strength (MPa)	10.3	8.9	7.9
Modulus 300 % (MPa)	2.3	1.4	1.5
Elongation at break (%)	682	763	697
Retention of tensile strength (%)	83.7	100	103.9
Retention of 300% modulus (%)	121	116.6	125.0
Retention of elongation at break (%)	87.2	96.7	89.2

Table IV.3. Formulation of GPF black filled polychloroprene compounds

Ingredients	C4	C5	C6	C7	C8	C9	C10	C11
Polychloroprene (Neoprene W - type)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Stearic acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Antioxidant TDQ	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Accelerator NA-22	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Magnesium oxide	4.0	4.0	4.0	4.0	-	-	-	-
GPF Black	10	20	30	40	10	20	30	40
Naphthenic oil	1.0	2.0	3.0	4.0	-	-	-	-
Rubber seed oil	-	-	-	-	1.0	2.0	3.0	4.0

Table IV.4. Properties of GPF black filled polychloroprene compounds

Properties	C4	C5	C6	C7	C8	C 9	C10	C11
Max. Rheometric torque (dN m)	73	78	85	87	61	70	75	81
M_H-M_L	61	65	73	74	50	57	62	67
Optimum cure time, t_{90} at 150 $^{\circ}$C (min)	14.2	14.4	14.0	14.5	9.3	8.4	8.8	8.5
Cure rate index	8.2	8.1	8.3	7.9	13.3	15.8	14.7	14.7
Mooney scorch time at 120 $^{\circ}$C (min)	6.3	6.2	5.4	5.0	7.3	7.4	6.2	6.4
Vr value of swollen sample	0.223	0.242	0.255	0.264	0.222	0.221	0.240	0.255
Before ageing								
Tensile strength (MPa)	19.6	20.6	21.5	20.9	21.1	22.1	22.2	20.9
Modulus 300% (MPa)	4.1	7.1	11.4	14.5	3.2	6.2	9.7	13.1
Elongation at break (%)	750	700	594	482	780	775	650	511
Tear strength (kN/m)	40.3	48.7	53.8	52.4	41.9	51.5	59.0	58.0
Hardness (Shore A)	47	49	55	59	46	50	54	60
Rebound resilience (%)	61	60	57	55	57	56	55	53
DIN abrasion loss (mm^3)	130	109	103	103	135	81	68	65
Compression set (%)	5.3	5.9	7.2	7.5	7.9	7.7	8.7	8.9
After ageing at 100 $^{\circ}$C, 120h.								
Properties	C4	C5	C6	C7	C8	C9	C10	C11
Tensile strength (MPa)	14.1	17.3	18.7	19.9	15.9	20.6	19.6	20.6
Modulus 300% (MPa)	4.7	8.4	13.2	16.6	3.9	7.0	11.6	15.6
Elongation at break (%)	544	474	415	360	655	644	484	397
Retention of tensile strength (%)	71.9	84	87	95.2	75.4	93.2	88.3	98.5
Retention of 300% modulus (%)	114.6	118.3	115.8	114.5	121.9	112.9	119.6	119.1
Retention of elongation at break (%)	72.5	67.7	69.9	74.7	84	83	74.5	77.7

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Chapter V

Studies on Use of Rubber Seed Oil Soap in Natural Rubber and Blend of Natural Rubber and Styrene Butadiene Rubber Latex Foam Production

Natural rubber is used for making a variety of rubber products, both starting from dry rubber and latex. The latex products consume about 11.5% of the rubber used by the industry in India. Foam is one of the important latex products. Chemicals used as foam promoters for the gel process are usually carboxylate soaps, of which the most widely used are resinoleate, castor oil soap and oleates, either alone or in combination. Potassium oleate is commonly used as the foaming agent in latex foam production. Mixture of carboxylate soaps promotes foaming more effectively than do the separate components[1].

According to Murphy et al.[2] latices gel in the neighbourhood of pH 8 when sodium silicofluoride (SSF) was used alone. The gelling pH was unchanged when sodium castor oil soap only was added, but raised to approximately 8.9 when both sodium castor oil soap and ZnO were present.

The rate of zinc soap formation naturally varies to a certain extent with the soap used, leading to some variation in the gelling pH, particularly when the ZnO has only been present in the latex for a short time. Newnham[3] has observed that unless a quantity of zinc oxide much in excess of the soap present is used, all the soap is not converted to zinc soap as the pH is reduced with addition of sodium silicofluoride. This was attributed to a partial adsorption of zinc amine ions by the colloidal silica formed in the hydrolysis of the sodium silicofluoride.

Since, RSO contains higher fatty acids, it can be used for the preparation of soap[4]. Rubber seed oil and castor oil contain saturated and unsaturated higher fatty acids such as stearic acid, oleic acid, linoleic acid etc. Hence in this study, attempts were made to use combinations of RSO soap/potassium oleate and castor oil soap/potassium oleate as a substitute for potassium oleate in latex foam production.

Foamed latex is a three phase colloidal system, which comprises of two disperse phases, rubber particles and air bubbles, and a single continuous phase, a modified latex serum (Figure V.1). Two principal interfaces are present in foamed

latex: serum-rubber interface and serum-air interface. The successful manufacture of latex foam depends upon the proper manipulation of these two interfaces. The gelation of foamed latex involves the destabilization of the serum-rubber interface, so that the rubber particles come together to form a uniform structure in a predetermined and controllable time interval after the addition of the gelling agent, which rigidifies the foam[5].

Latex gelling may be described as a homogeneous coagulation. The important characteristic of a delayed action gelling agent like the SSF is that it can be readily introduced into the latex during mixing. For a standard 60% ammonia preserved centrifuged latex concentrate, thickening does not normally set in until the pH has fallen to about 9.2. The gelling pH is an important characteristic of the latex compound. At the same time, the physical nature of the gel is also important[6].

The hydrolysis of sodium silicofluoride can be represented as

$$Na_2 SiF_6 \rightleftharpoons 2 Na^+ + SiF_6^{--} \qquad\qquad \text{----} \quad V(1)$$

$$Si F_6^{--} + 4H_2O \rightleftharpoons Si(OH)_4 + 4H^+ + 6F^- \qquad \text{-----} \quad V(2)$$

Hydrofluoric acid is liberated by this hydrolysis, but if the gelling was solely due to the acidity developed, the gelling pH would be expected to be on the acid side, which is not the case. The gelling is found to occur at an alkaline pH about 8.2-8.5[7]. It has been suggested that apart from the destabilizing action of the hydrofluoric acid, the powerful adsorptive effect of the silicic acid, on the stabilizers of the colloidal system plays a part in the gelation and this occurs at an alkaline pH[8].

When zinc oxide is present together with soap, it also has a destabilizing effect due to the formation of zinc ammine complex. The complex dissociates to give Zn^{++} ions, which react with the soap causing destabilization of the latex by forming insoluble zinc soap as given below.

$$H_2O$$
$$ZnO \rightleftharpoons Zn(OH)_2 \rightleftharpoons Zn^{++} + 2HO^- \qquad\text{----- V (3)}$$

$$\Big\downarrow NH_3$$

$$\overset{\text{heat}}{Zn^{++} + nNH_3 \longleftarrow Zn(NH_3)_n{}^{++}} \qquad\text{----- V (4)}$$
$$1 \le n \le 4$$

$$Zn^{++} + 2\,RCOO^- \longrightarrow (R\,COO)_2\,Zn \qquad\text{----- V (5)}$$
$$\text{(insoluble zinc soap)}$$

Insoluble zinc carboxylate (eg. soap or proteinate) gets precipitated on the surface of the latex particle, with consequent colloidal destabilization.

Thus gelation of the latex foam occurs in 3 ways

1. The fall of pH due to the presence of hydrofluoric acid
2. The adsorptive effect of the silicic acid
3. The removal of soap by the formation of insoluble zinc soap.

For getting good quality foam, the serum-air interface should get destabilized after the onset of the destabilization of the serum-rubber interface. The way in which these two processes take place, also depends on the quality of soap used. Thus, the soap has an important role in deciding the quality of the foam.

Properties of the latex used in this work are given in Table II.1. Procedure for the preparation of latex foam and the test methods followed are described in sections II.9 and section II.14 of chapter II respectively. Table V.2. shows the time required for 7 times expansion of the latex compounds.

The details of the formulation used for the production of latex foam as per the Dunlop process are given in Table V.1. Compound containing 1.2 phr potassium oleate as foaming agent is taken as the control. In RSOS, potassium oleate is replaced with rubber seed oil soap. POEF and RSOSF are 20 phr clay filled compounds.

231

POCO and PORO are compounds containing 50/50 mixture of potassium oleate /castor oil soap and potassium oleate/rubber seed oil soap respectively. POROF contains 20 phr clay also. In PORO1, the quantity of potassium oleate is only 0.2 phr and that of rubber seed oil soap is 1.0 phr. In RSOS1, only 1.0 phr rubber seed oil soap is used as the foaming agent. All these combinations were evaluated in this study and the results obtained are given in Table V.3. Trials were also conducted with blends of NR and SBR latices in this study. The formulation used for this study is given in Table V.4. A 50:50 blend of NR and SBR latices is used to achieve the desired properties and to reduce cost. Synthetic rubber latex generally requires less foam promoter than NR latex to achieve a given expansion. This is because, the latex itself contains relatively large amount of carboxylate soap. The results are given in Table V.5.

V.1. Results and Discussion

V.1.1. Effect of Soap on Time for Expansion of Latex Compound

Table V.2 shows the time for 7 times volume expansion of latex compounds. It is evident from the results that the time required to get the desired expansion was lower for the compounds, which contained the soap from rubber seed oil or combinatios containing rubber seed oil soap compared with potassium oleate. This indicated better foaming efficiency of the soap from rubber seed oil.

V.1.2. Effect of Soap on Hardness of Latex Foam

Hardness of latex foam, as measured by the weight in kilograms required to reduce the thickness of the sample by 40%, is a measure of its load bearing capacity. Hardness of foam basically depends on expansion given for the latex compound and in this study; the expansion was kept constant (7 times the original volume) in all the trials. When potassium oleate was completely replaced with equal quantity of soap prepared from rubber seed oil or where 1 phr of the soap was used in place of 1.2 phr of potassium oleatè, almost the same hardness was obtained for the foam (Table V.3.). In industry either oleic acid soap or a mixture of soaps of oleic acid and castor oil is normally used. Hence in this study combinations of mixtures of

232

soaps from oleic acid, rubber seed oil and castor oil were also evaluated. The results indicated that use of a 50:50 mixture of oleic acid and rubber seed oil soaps yielded foam having higher hardness (39.5) compared to a 50:50 mixture of oleic acid and castor oil soaps (31.5). Mixtures of soaps of castor oil and rubber seed oil or that of oleic acid and castor oil produced foams of much lower hardness compared with soaps of oleic acid, rubber seed oil or an equivalent mixture of these two, indicating low load bearing capacity of the foam from castor oil soap. The hardness of the foams containing 20 phr china clay was independent of the type of soap used. However the hardness was lower than that of the unfilled compounds. The reduction in hardness of the clay filled foam from compounds POEF, RSOSF, POROF and those containing mixtures of soaps CORO, PORO1 and POCO is expected to be due to the difference in the structure of the foams obtained.

V.1.3. Effect of Soap on Compression Set and Whole Sample Compression of Latex Foam

Compression set is a measure of the capability of the product to retain its original dimensions after the application of a load under compression for a specified time. Lower the set, better the product. Latex foam made by using rubber seed oil soap showed lower set values compared with those made by using oleate soap, both in unfilled and china clay filled samples. In the case of foams prepared by using mixtures of soaps also the same trend was noticed (compound CORO better than compound POCO). The change in thickness under the whole sample compression was almost the same for compounds POE, RSOS and RSOS1. In the case of china clay filled sample, a higher change in thickness was noticed for the sample RSOSF compared with POEF. However, when mixed soaps were used, the change in thickness was least for compound PORO.

V.1.4. Effect of Soap on Flexing Resistance of Latex Foam

In flexing test, the foam is subjected to cyclic loading for 250 kilocycles at 240 cycles per minute. Minimum change in hardness and thickness is an indication of better resistance to flexing. The reduction in thickness was almost the same for the foam samples prepared by using potassium oleate and rubber seed oil soap.

However, foam prepared using rubber seed oil soap showed higher change in hardness except when a mixture of potassium oleate and rubber seed oil soap was used. Potassium oleate and castor oil soap had no significant effect on the modulus of the foam rubber. Treatment of latex with additional soap such as potassium soap of saturated fatty acid, can bring about changes in the properties of the foam such as enhancement of compression modulus and reduced foam shrinkage. Foam prepared using soap from palm oil was reported to give satisfactory foaming and good structure in the vulcanized foam[9]. Palm oil contains about 42% palmitic acid and 4% stearic acid. In both the unfilled and clay filled foam some enhancement in the compression modulus was reported[9]. The change in modulus after flexing or ageing did not show any deleterious effects of the soap. These values were well within acceptable levels and much less than the maximum allowed values (20%) as per the BIS specification.

V.1.5. Effect of Soap on Ageing Resistance of Latex Foam

Change in hardness after ageing at 70°C for 168 hours gives an indication about the long-term performance of the product. In this case also, samples prepared by using rubber seed oil soap showed higher increase in hardness compared with that made by using potassium oleate. This may be due to further crosslinking of the foam during ageing (vulcanization modification). However, the change in hardness was well within the allowed limits.

V.1.6. Effect of Soap on Mould Shrinkage of Latex Foam

Knowledge on mould shrinkage of the products helps to give proper allowance in the size of the mould so that product of exact dimensions can be prepared. The mould shrinkage of the foam prepared by using potassium oleate and rubber seed oil soap was about 11% and there was not much difference between the two samples in this respect.

The properties of the foam prepared using a blend of NR and SBR latices also showed similar hardness values when potassium oleate (NSPOF) or rubber seed oil

soaps (NSROF) were used (Table V.5.). Other properties showed marginal differences but were within the limits of such parameters specified for latex foam.

V.1.7. Effect of Soap on Structure of Latex Foam

Figures V.2 and V.3 are photographs of samples POE and RSOS. Both the compounds had uniform distribution of the cells and cell size and same hardness also. A more close examination of the enlarged views showed that RSOS had more uniform cells and fine structure than POE (Figures V.4 and V.5), which may be the reason for the lower compression set of the foam from RSOS.

V.2. Conclusion

Rubber seed oil can be used for latex foam production using NR or blend of NR/SBR latices. The quality of foam was comparable to that prepared by using commercially available oleic acid soap. The properties of the foam prepared by using the rubber seed oil soap or mixtures of rubber seed oil and potassium oleate soaps were conforming to BIS specification. As price of rubber seed oil is less by Rs. 50/- per kilogram compared with that of oleic acid, use of rubber seed oil for latex foam will be economically advantageous. There is no fungal growth on foam on storage. The properties of the foam prepared from a 50:50 blend of NR and SBR latices also indicated that rubber seed oil soap could be used in such cases also.

Table V.1. Formulations of latex foam

Ingredients	Compound number.									
	POE	RSOS	POCO	PORO	CORO	POEF	RSOSF	PORO1	POROF	RSOS1
NR latex (60%)	100	100	100	100	100	100	100	100	100	100
Potassium oleate (20%)	0.2	-	0.2	0.2	-	0.2	-	0.2	0.2	-
Castor oil soap (30%)	-	-	-	-	0.2	-	-	-	-	-
Rubber seed oil soap (10%)	-	0.2	-	-	-	-	0.2	-	-	0.2
Sulphur dispersion (50%)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
ZDC dispersion (50%)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	2.0
ZMBT dispersion (50%)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
SP emulsion (50%)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Maturation 16 Hrs										
Potassium oleate (20%)	1.0	-	0.4	0.4	-	1.0	-	-	-	-
Castor oil soap (30%)	-	-	0.6	-	0.4	-	-	-	-	-
Rubber seed oil soap (10%)	-	1.0	-	0.6	0.6	-	1.0	1.0	1.0	0.8
China clay (as powder)	-	-	-	-		20	20	-	20	-
Cetyltrimethyl ammonium bromide (30%)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Zinc oxide dispersion (50%)	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Sodium silicofluoride solution (20%)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0

POE - 1.2 phr potassium oleate soap
POCO - 0.6 phr potassium Oleate + 0.6 caster oil soap
POEF - 1.2 phr potassium oleate + 20 clay (filler)
POROF - 0.2 oleate + 1 rubber seed oil soap + 20 clay
RSOS1 - 1 phr rubber seed oil soap

RSOS - 1.2 phr rubber seed oil soap
PORO - 0.6 phr oleate + 0.6 phr rubber seed oil soap
RSOSF - 1.2 phr rubber seed oil soap + 20 clay
PORO1 - 0.2 phr oleate + 1 rubber seed oil soap
CORO - 0.6 phr castor oil soap + 0.6 phr rubber seed oil soap

236

Table V.2. Time for 7 times expansion of latex compound

Compound No.	Time (min)
POE	8
RSOS	6
RSOS1	7
POCO	5
PORO	7
PORO1	7
CORO	5
POEF	8
RSOSF	6
POROF	7

Table V.3. Physical properties of latex foam (tested as per BIS 1741-1999)

Compound number	Initial hardness (kg)	Compression set (%)	Flexing		Whole sample compression	Ageing	Mould shrinkage (after 15 days)
			Increase in hardness (%)	Reduction in thickness (%)	Change in thickness (%)	Increase in hardness (%)	Reduction in diameter (%)
POE	38.0	6.0	5.0	3.8	4.7	9.5	11.0
RSOS	38.0	5.0	15.0	3.8	4.8	14.3	11.4
POCO	31.5	5.6	4.5	2.5	3.5	8.0	8.2
PORO	39.5	5.0	1.0	2.4	1.2	11.1	11.0
CORO	33.0	4.0	3.2	2.4	4.1	6.6	8.7
POEF	35.0	6.0	5.7	2.4	2.3	11.8	9.9
RSOSF	35.0	5.0	14.2	3.8	3.6	15.9	11.6
RSOS1	38.5	5.0	15.0	1.2	4.7	13.5	11.0
PORO1	34.0	5.0	5.9	4.8	3.6	14.6	10.6
POROF	35.0	5.5	1.7	3.8	5.0	13.3	11.2
Max. values as per BIS 1741-1960 (%)	-	20.0	20.0	5.0	5.0	20.0	NA

238,

Table V.4. Formulation for latex foam from NR and SBR latex blend

Ingredients	A Dry weight	B Dry weight	Mix A & B
NR latex (60%)	100	-	-
SBR latex (40%)	-	100	-
Soap (20%) (POE/RSOS)	0.2	0.1	-
Sulphur (50%)	2	2	-
ZMBT(50%)	1	1	-
ZDC (50%)	1	1	-
Styrenated phenol (50%)	1	1	-
Kept for maturation (16 h)			
Soap (20%) (POE/RSOS)	-	-	1
CTAB (30%)	-	-	1
ZnO (50%)	-	-	5
SSF (20%)	-	-	5
Clay (as powder)	-	-	20

Table V.5. Physical properties of latex foam from NR/SBR blends, as per BIS 1741-1999

| Sample number | Initial hardness (kg) | Compr-ession set (%) | Flexing | | Whole sample compression | Ageing |
			Increase in hardness (%)	Reduction in thickness (%)	Change in thickness (%)	Increase in hardness (%)
NSROF (with RSO)	25	6	12	2.43	4.9	13.6
NSPOF (with POE)	26	8	7.7	1.28	4.59	6.0
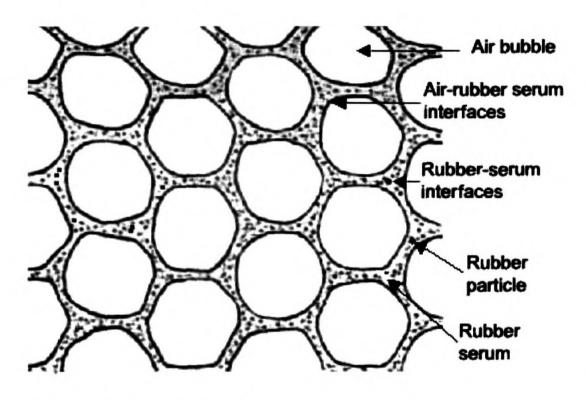
Figure V.1. Foamed latex serum interfaces   (Source[5])

Labels in figure:
- Air bubble
- Air-rubber serum interfaces
- Rubber-serum interfaces
- Rubber particle
- Rubber serum
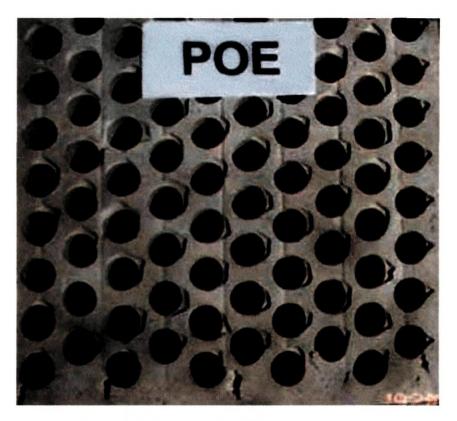
Figure V.2. Photograph of POE
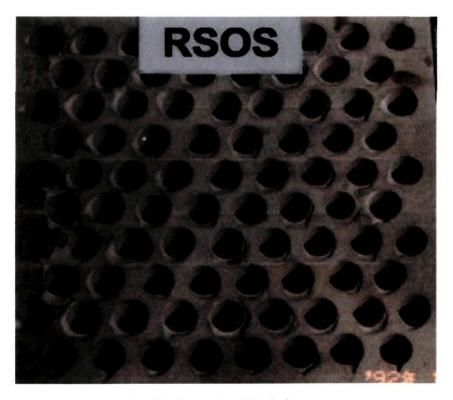
Figure V.3. Photograph of RSOS

242
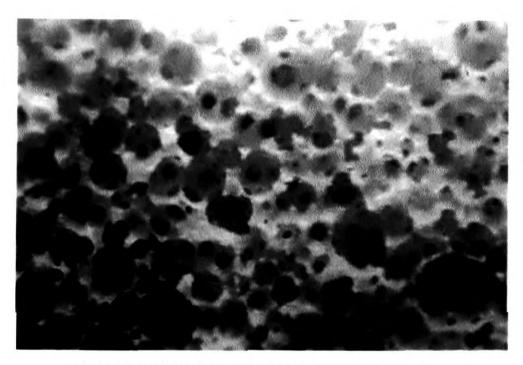
Figure V.4. Photomicrograph of foam sample POE
(magnification 10 X)
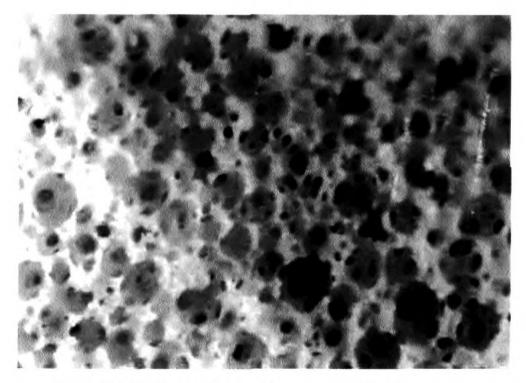
Figure V.5. Photomicrograph of foam sample RSOS
(magnification 10 X)

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Chapter VI

Studies on Copper Salt of Fatty Acids From Rubber Seed Oil as Peptizer for Estimation of Dirt Content in Technically Specified Natural Rubber

Marketable forms of natural rubber are sheet, crepe, block and concentrated latex. Ribbed smoked sheets and various types of crepe rubbers are graded and classified by visual comparison method. The visual classification system provides ample room for malpractice. Besides, this unscientific system is not helpful to the consumer in assessing the quality of raw rubber. However, block rubbers are technically specified natural rubber in which the grading is done based on parameters that are scientifically evaluated.

Dirt content in natural rubber has been found to be very important from the point of view of the rubber manufacturing industry. Quality parameters of technically specified rubber are related to both processing and technical parameters of rubber. P_0 and PRI are related to compound viscosity and ageing resistance respectively. Another important parameter is dirt, which affect the technological properties such as tensile strength, tear strength DIN abrasion and flexing. The dirt present in NR act as initiation points of cracks which grow during repeated stressing in tension, compression etc. leading to catastrophic failure of the material.

Wide variations have been observed in dirt content values from identical raw rubber samples when tested in different laboratories, using similar test procedures[1]. For grading of technically specified rubber (TSR), plasticity retention index and dirt content are the most important primary parameters. Unlike the other specification parameters, considerable variability in dirt level is common for similar sample tested in different laboratories, which might even be following similar analytical techniques[2].

Martin[3] mentioned visual examination of sheet under polarised light. Many dirt particles, which do not appear in normal light, do show up in polarised light. Different procedures for estimating the dirt content of raw rubber have evolved over the years. One method is based on ash content determination, which reflects the quantity of inorganic matter. This method is unreliable for estimating

246

dirt content, since no fixed relationship exists between insoluble dirt and ash content. Furthermore, inorganic substances included in ash determination form only one type of insoluble dirt[4].

In washing method, according to Frank[5], a large sample is divided into small pieces and boiled for a few times with water until the water remained colourless and odourless. The soaked rubber is subsequently milled vigorously on a laboratory mill into a porous crepe, immediately dried at a moderate temperature in vacuum or in a dark room and finally weighed.

American Chemical Society (1940) described a method, according to which the crude rubber is vigorously washed on crepe rolls and the dirt, determined by separating it from the collected washing water (screening, filtering). This method is unsuitable for use in laboratories and is to be considered only as an approximative industrial test. It is impossible to obtain absolute values by the washing method, since even after vigorous washing fine particles of sand, wood, bark and fibres will always be left in the rubber[6].

The straining method involves straining plasticized rubber and estimating the dirt after dissolving the retained rubber in a suitable organic solvent. The most exploited method of all (the dissolution method) involves dissolving raw rubber in a hydrocarbon solvent to obtain a homogeneous and low viscosity solution. The solution is sieved and the retained dirt dried and weighed. This process is normally accelerated by oxygen-carriers that reduce the dissolution temperature[4]. Free radicals formed by mechanical, thermal and chemical bond scission of crude rubber in solution are stabilized by recombining in pairs, or on sites along the rubber chain to give branched species. The presence of a peptizer (eg. xylyl mercaptane) or an oxidation activator (like cobalt naphthenate) in the solution inhibits the recombination process by reacting rapidly with the free radicals. Addition of hydrogen peroxide to mercaptane solution also slightly inhibits recombination.

A sufficiently accurate gravimetric estimation of harmful dirt can be done quickly by the dissolution method. In this method much depends on obtaining a rubber solution with a very low viscosity from which the insoluble part may be easily separated by a suitable process (filtering, centrifuging). These methods were often identical with those used for the determination of filler in vulcanized rubber.

The method proposed by the American Chemical Society (1941) consisted of dissolving rubber in para-cymene to which an oxidising agent (H_2O_2) was added. Hublin[7] studied the use of other materials like naphthalene, α-nitronaphthalene, nitrobenzene, anisole and ortho-nitroanisole. Of these, ortho-nitroanisole was found to be the best since it dissolved the rubber in 20-60 minutes at 100-200 °C.

Bekkedahl[6] recommended a method according to which the rubber is dissolved in toluene to which 1% trichloro acetic acid was added. Van Essen[8] used copper oleate instead of trichloro acetic acid. Kahn[9] of Goodrich Company reported that stannous chloride ($SnCl_4$) could bring down viscosity of rubber solution. Heinish and Van der Bie (1951) studied the use of different peptizers for reducing the viscosity of rubber solutions. These included copper acetate, cobalt naphthanate, RPA-2, RPA-3 and RPA-5 using xylene as a solvent. He found RPA-3 as the most effective one. It was also observed that the addition of a small quantity of a strong electrolyte like HCl reduced the viscosity of the solution further. According to Kuriakose et al[10] kerosene could successfully replace mineral turpentine as a solvent and copper oleate could reduce the viscosity of rubber solution to the same level as obtained by using RPA-3, for the estimation of the harmful dirt gravimetrically.

Dirt content in rubber is defined as particles of foreign matter other than rubber hydrocarbon and the natural serum substances, which can be separated from rubber by physical methods. Harmful dirt is defined as that which is retained on a 325-mesh sieve[11], on sieving the rubber solution. Dirt content in the processed rubber is currently estimated by dissolving rubber in a solvent with the aid of a peptizer, such as copper oleate and then filtering the solution through a standard stainless steel sieve[12,13]

For getting a clear homogeneous solution, the latex grade TSR and sheet rubber as against those of TSR prepared from cup lump and field coagulum and estate brown crepe, required longer time of heating. After a critical duration of dissolution, prolonged heating leads to the formation of macrogel that remained insoluble in most of the non-polar hydrocarbon solvents. This macrogel was reported to be responsible for the poor repeatability of dirt values[1]

The role of copper oleate in the estimation of dirt content is to peptize the rubber so that its dissolution becomes easy and complete within a short time[10]. Copper acts as a pro-oxidant to break the double bond in NR. With the main chain scission, the molecular weight decreases, and dissolution becomes easy.

Rubber seed oil contains about 24% oleic acid. As rubber seed oil is a cheap source of higher fatty acids, this study was undertaken to evaluate its performance as a substitute for oleic acid by preparing the copper salt for estimating dirt content. Since ISNR 5 and ISNR 20 grades are the most common TSR processed in India from latex and field coagulum materials respectively, the effect of the peptizer was evaluated using these grades only. The experiment was done based on a statistical design using 20 samples of ISNR 5 and ISNR 20 each collected from different sources. Three concentrations (0.5, 1.0 & 1.5 ml of 25% solution) of copper salts of mixed fatty acids from rubber seed oil were compared with the standard (1.0 ml of 25% solution) copper oleate solution for the estimation of dirt content. Each dirt content value reported was the average of five determinations.

VI.1. Results and Discussion

Figure VI.1 shows viscosity versus shear rate plots for the rubber solutions containing 1.0 ml of 25% solution of copper oleate (control) and 1.0 ml and 1.5 ml of 25% solutions of copper salt of RSO, at 70 ^{0}C. From Figure VI.1, it is evident that the viscosity of the solution containing 1.0 ml of copper salt solution from RSO is comparable to that of the control, which contained 1.0 ml copper oleate solution at all shear rates. However, the solution, which contained a higher concentration of the copper salt (1.5 ml) showed higher viscosity values, compared with the control. This may be due to the formation of macrogel in the solution. It has been reported that a higher concentration of peptizer or prolonged heating at a higher temperature leads to macrogel formation[1].

Figure VI.2 shows the effect of temperature on the viscosity of the solutions containing 1.0 ml of copper oleate and 1.0 ml of copper salt of RSO, at a shear rate of 20 s^{-1}. The viscosity decreased with increase in temperature. At 70 ^{0}C, the viscosity values of the control and that of the sample containing 1 ml

of copper salt of RSO were the same. But at lower than 70 °C, the solution containing the copper salt of RSO had lower viscosity values. This is advantageous in dirt estimation for quick filtration of the solution through the sieve, even if the temperature is slightly lower.

Figure VI.3 shows the viscosity Vs concentration of peptizer plots, at 20 s^{-1} shear rate and at 70 °C. It was observed that higher concentrations of either copper oleate or copper salt of RSO increased the viscosity at a shear rate of 20 s^{-1} and that both the solutions have the same viscosity when the dosage of peptizer was 1.0 ml. This may be due to the formation of macrogel, which increases the viscosity of the rubber solution when higher concentration (> 1.0 ml) of peptizer was used. Solutions of both ISNR 5 and ISNR 20 showed the same trend in these evaluations.

Tables VI.1 and VI.2 contain the actual dirt content values obtained for 20 different samples of ISNR 20 and ISNR 5 type TSR respectively. These values are the average values of five replications. Tables VI.3 andVI.4 show the statistical analysis results of these values.

From Tables VI.3 and VI.4 it could be seen that the percentage dirt content values obtained for ISNR 20 and ISNR 5 using copper salt of RSO at concentration of 0.5 ml, 1 ml and 1.5 ml of 25% solution, were comparable with that of control (ie. 1 ml of 25% copper oleate solution) as indicated by the mean, standard deviation and t values (It is used to find the significant difference between two treatments). The deviation in the values of dirt content of the experimental samples from those of the control was not significant statistically. This indicated that 0.5 ml, 1 ml or 1.5 ml of 25% solution of copper salt obtained from RSO could be used for the determination of dirt content without affecting the accuracy of the test result. However, from the practical point of view 1.0 ml of 25% copper salt of mixed fatty acids appears to be the ideal concentration of this peptizer, as higher concentration can lead to the formation of macrogel.

VI.2. Conclusion

Copper salts of fatty acids prepared from rubber seed oil was found to be an effective peptizer for dissolving technically specified rubber for estimation of the dirt content. Rubber solution containing 1 ml of 25% solution of peptizer prepared from RSO, per 10 g of rubber has the same viscosity as that prepared using copper oleate. The variation in values of the dirt content of ISNR 5 and ISNR 20 estimated by using copper oleate and copper salt of rubber seed oil as peptizer was not statistically significant.

Table VI.1. Dirt content (%) of ISNR 20 samples

Sl. No.	Control	M1	M2	M3
1	0.198	0.195	0.196	0.200
2	0.096	0.098	0.096	0.099
3	0.095	0.092	0.094	0.099
4	0.093	0.092	0.093	0.097
5	0.099	0.093	0.098	0.095
6	0.092	0.094	0.093	0.095
7	0.118	0.116	0.118	0.120
8	0.088	0.092	0.089	0.113
9	0.125	0.122	0.125	0.126
10	0.111	0.107	0.111	0.108
11	0.083	0.082	0.083	0.084
12	0.155	0.155	0.155	0.157
13	0.199	0.195	0.198	0.195
14	0.127	0.124	0.127	0.128
15	0.110	0.111	0.110	0.111
16	0.099	0.101	0.099	0.098
17	0.122	0.123	0.122	0.121
18	0.150	0.151	0.150	0.151
19	0.183	0.185	0.183	0.183
20	0.139	0.142	0.139	0.138

Control - 1 ml of copper oleate (25%)
M1   - 0.5 ml of copper salt of mixed fatty acid from RSO (25%)
M2   - 1.0 ml of copper salt of mixed fatty acid from RSO (25%)
M3   - 1.5 ml of copper salt of mixed fatty acid from RSO (25%)

Table VI.2. Dirt content (%) of ISNR 5 samples

SI. No.	Control	M1	M2	M3
1	0.031	0.029	0.032	0.040
2	0.042	0.028	0.042	0.041
3	0.010	0.011	0.010	0.011
4	0.015	0.014	0.016	0.015
5	0.034	0.035	0.035	0.034
6	0.016	0.017	0.016	0.018
7	0.030	0.028	0.030	0.030
8	0.028	0.029	0.027	0.028
9	0.023	0.022	0.023	0.023
10	0.029	0.028	0.029	0.031
11	0.013	0.012	0.013	0.013
12	0.011	0.015	0.011	0.011
13	0.048	0.049	0.048	0.049
14	0.025	0.026	0.025	0.027
15	0.024	0.025	0.024	0.027
16	0.009	0.009	0.010	0.111
17	0.020	0.020	0.020	0.020
18	0.024	0.023	0.024	0.024
19	0.030	0.031	0.030	0.031
20	0.018	0.018	0.018	0.018

Control - 1 ml of copper oleate (25%)
M1   - 0.5 ml of copper salt of mixed fatty acid from RSO (25%)
M2   - 1.0 ml of copper salt of mixed fatty acid from RSO (25%)
M3   - 1.5 ml of copper salt of mixed fatty acid from RSO (25%)

253

Table VI.3. Statistical significance of dirt content values in ISNR 20

	Differences		
	Mean	SD	t value
Standard vs M1	0.00055	0.00346	0.71169 NS
Standard vs M2	-0.00015	0.00049	0.02267 NS
Standard vs M3	-0.00610	-1.37081	-1.20328 NS

Standard method is at par with M1, M2 and M3

Table VI.4. Statistical significance of dirt content values in ISNR 5

	Differences		
	Mean	SD	t value
Standard Vs M1	0.00060	0.00278	0.96534 NS
Standard Vs M2	0.00015	0.00067	1 NS
Standard Vs M3	-0.00018	0.00594	-1.35437 NS

Standard method is at par with M1, M2 and M3

254
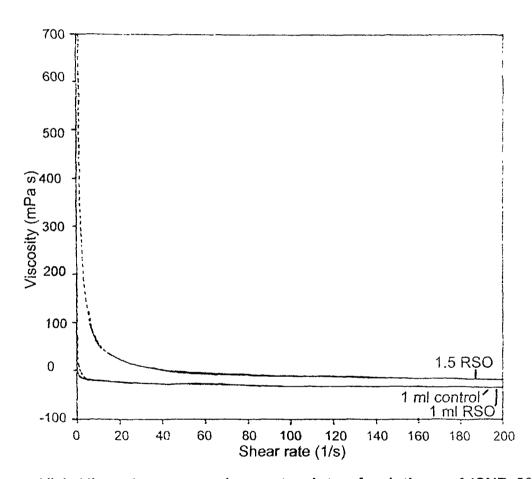
Figure VI.1. Viscosity versus shear rate plots of solutions of ISNR 20 containing peptizer at 70 °C
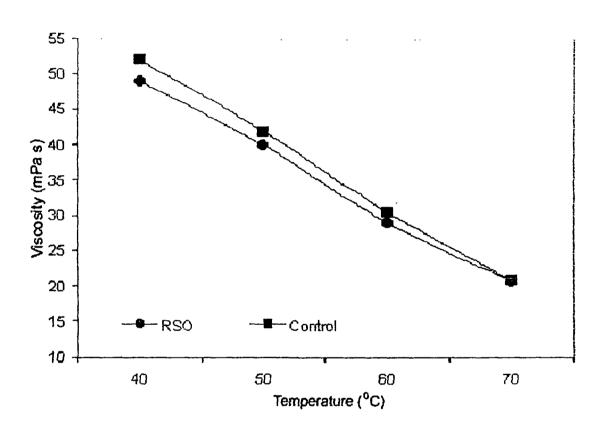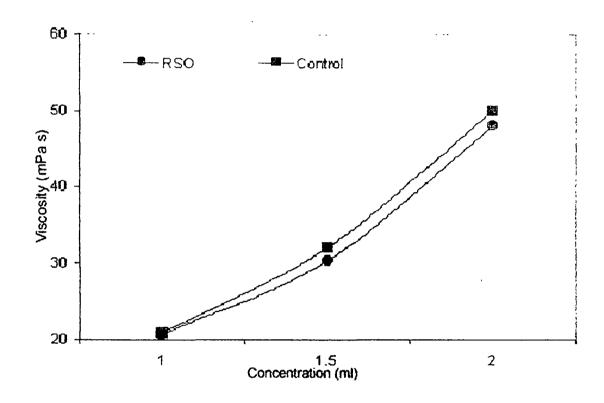
Figure VI.2. Viscosity versus temperature plots for solutions ISNR 20 containing 1.0 ml peptizer at a shear rate of 20 s^{-1}

FigureVI.3. Viscosity versus concentration of peptizer plots of solutions
of ISNR 20 at 20 s^{-1} at 70 ^{0}C

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Chapter VII

Use of Epoxidised Rubber Seed Oil as a Coupling Agent and Plasticizer in Silica Filled Natural Rubber Compounds

Precipitated or fumed silica, having very low particle size, has been used in white/coloured rubber compounds due to its high reinforcing effect, similar to that of carbon blacks. Due to the presence of functional groups such as –OH attached to the silica particle, it forms strong agglomerates through hydrogen bonding. Highly polar nature and high structure of silica make it very difficult to mix with non-polar rubbers[1]. Additionally, fine particle silica has a tendency to adsorb the accelerators, causing to increase the cure time of the compound. Because of these difficulties, use of silica in rubber compounds was limited to certain products like shoe soles, hot water bottles, rice polisher brake/rolls etc. Modification of silica surface with bifunctional organosilanes was helpful in overcoming many of the above problems. Such modified silica could be easily dispersed in rubber and showed the maximum reinforcement effect[2,3]. Subsequently several organosilanes have been developed and evaluated in rubber compounding along with silica[4]. Among these, bis-(triethoxysilylpropyl) tetrasulphide (TESPT) became the most widely used one. The action of TESPT (Si 69) in enhancing the silica reinforcement is explained as follows.

During mixing one of the ethoxysilyl groups of the coupling agent reacts with the silanol group of the silica. This is followed by a condensation reaction between pairs of neighbouring silane molecules[5], as shown in Section 1.10.2 (Scheme I.2). At a higher temperature during vulcanization, a third reaction between the coupling agent and the rubber takes place through added sulphur in the compound or that generated by disproportionation of TESPT. Thus, during mixing hydrophobation of the silica surface takes place, which reduces the silica-silica network and makes the polar silica more compatible with the non-polar rubber. The reaction between the silane and rubber that takes place during vulcanization, completes the silica-silane-rubber coupling leading to better polymer-filler interaction and resulting in maximum reinforcement without

affecting the processing safety[6]. The silica filled compounds prepared by using the organosilane coupling agents showed improvement in properties such as tensile and tear strengths, reduced heat build up, rolling resistance and improved wet skid resistance. The observation that compounds having low rolling resistance, better wet traction and improved wear resistance could be developed through a combination of carbon black and silica along with organosilane coupling agents, generated renewed interest to use silica in tyre tread compounds[7].

Vegetable oils such as rubber seed oil are composed of triglycerides of saturated and unsaturated higher fatty acids. The unsaturated acids may be mono (eg. oleic), di (eg. linoleic) or tri (eg. linolenic) unsaturated carboxylic acids. They can be easily epoxidised by reacting with performic acid[8]. It is expected that the epoxidised rubber seed oil could act as a bifunctional coupling agent for silica reinforcement since the epoxy group can react with the silanol group of the silica and the double bond of the higher fatty acid could be utilized to link it with rubber hydrocarbon by reacting with sulphur added in the compound, during vulcanization. In this chapter the results of the experiments conducted using ERSO of 5% epoxy content as a coupling agent and plasticizer in silica filled natural rubber compounds are presented. For comparison, compounds containing TESPT and naphthenic oil were also used. Details of the materials used and those of the experimental techniques are given in Chapter II. Tables VII.1, VII.2 and VII.3 give the formulation used, cure characteristics of the compounds and physical and mechanical properties of the vulcanizates respectively. Figures VII.1 and VII.2 show the rheographs of the compounds at 150 °C.

S1 was taken as the control compound, in which 3 phr Si 69 was used as d as coupling agent. In S2 and S3 TESPT was replaced by naphthenic oil and ERSO respectively. The silica used was Ultrasil VN3. All other ingradients were same. Compound S4 contained 50 phr silica and 6 phr Si 69. In S5 and S6, 3 phr TESPT was replaced with 3 phr naphthenic oil and ERSO respectively.

VII.1. Results and Discussion

VII.1.1. Effect of ERSO on Cure Characteristics of Silica Filled NR Compounds

From the rheographs (Figure VII.1), it is seen that the compound S1, which contained TESPT has maximum rheometric torque value compared to S2 and S3, which contained naphthenic oil and epoxidised rubber seed oil respectively. Compound S1 had lower cure and scorch times compared with those of S2 and S3. Between S2 and S3, the latter showed slightly lower (M_H-M_L) value and a slightly higher scorch time. The reduced cure time and Mooney scorch time of compound S1 results from the fact that, TESPT can act also as an accelerator[9] and a curing agent[2,9], besides its role as a coupling agent. This is evident from the fast cure rate (Figure VII.1) and higher Vr value (Table VII.3) of the compound S1 compared to S2 and S3. The lower (M_H-M_L) value and higher scorch time of the compound S3 compared to S2 may be due to utilization of part of the sulphur by the unsaturated fatty acids (about 76%) present in ERSO. This argument is supported by the lower Vr value of S3 compared with that of S2 and S1. However, in the case of compounds S4, S5 and S6 (Figure VII.2), which contained a higher dosage (50 phr) of silica, the compound S5 showed higher M_L, M_H, M_H-M_L values and a reduced cure time. At higher loading of silica (50 phr) the chance for the formation of silica-silica network structure through hydrogen bonding of the silanol groups is more. In the presence of a higher dosage (6 phr) of TESPT, the silanol groups of silica react with ethoxysilyl groups of the TESPT[5] resulting in hydrophobation of silica, which prevents the formation of silica-silica network structure. This leads to better dispersion of silica and reduction in viscosity[10,11]. The observed lower values of M_L, M_H and M_H-M_L of S4 compared to those of S5 are due to this reason, since S5 contained 3 phr naphthenic oil and 3 phr TESPT in place of 6 phr of TESPT in S4. Compound S4 showed lower scorch time and a higher Vr value (Table VII.3) indicating participation of TESPT in the vulcanization process. Compound S6 contained 3 phr of ERSO and 3 phr of TESPT and it showed lower M_L, M_H and M_H-M_L values compared to those of S5, indicating involvement of ERSO in hydrophobation of silica through the reaction between the epoxy group and the silanol group of

silica[12,13]. Among the three, compound S6 showed the longest scorch and cure times. This is due to the competition by the unsaturated fatty acids for sulphur during vulcanization, as evidenced by a lower Vr value for S6.

VII.1.2. Effect of ERSO on Physical and mechanical properties of Silica Filled NR Vulcanizates

It has been established that TESPT enhances the reinforcement activity of silica in non-polar rubbers through hydrophobation of silica by reaction of the silanol group of silica with ethoxysilyl group of the silane during mixing and also by forming a crosslink with the rubber hydrocarbon during vulcanization[14,15]. It was also proved that depending on the availability of sulphur in the compound, TESPT can act as a sulphur donor and increase the crosslink density of the matrix[16]. The net result of these reactions is high improvement in physical properties when such compounds are mixed and vulcanized under suitable conditions. The results presented in Table VII.3 are in line with these findings.

Among S1 to S3, and S4 to S6, the compounds which contained TESPT (S1 and S4) showed higher tensile strength and modulus and lower elongation at break values. These two compounds also showed higher Vr values indicating higher levels of crosslinking. Between the compounds, which contained naphthenic oil and ERSO (ie. S2 and S3; S5 and S6), the compounds S3 and S6 showed higher tensile strength, lower modulus and higher elongation compared with those of S2 and S5 respectively. The lower modulus and higher elongation might be the result of better hydrophobation of silica by the epoxy group of the ERSO and lower crosslinking density of the rubber matrix repectively, in S3 and S6. The higher tensile strength of the compounds S3 and S6 over S2 and S5 might be the result of better dispersion of silica achieved through the hydrophobation. It is possible that zinc soap formed by the reaction of zinc oxide and the higher fatty acids present in ERSO might also have helped in achieving a better dispersion of silica in these compounds. It is reported that the ratio of modulus 300% to modulus 100% (M_{300}/M_{100}) is a good indication of reinforcement by filler in a vulcanizate[17]. The M_{300}/M_{100} values given in Table VII.3 clearly show that TESPT+ERSO combination is helpful to achieve better reinforcement by silica than the TESPT+ naphthenic oil combination. This is

further supported by the higher Vr-Vr' values for S3 and S6 compared to those of S2 and S5 respectively. However, compounds, which contained TESPT alone, were superior to those containing ERSO or combination of ERSO+TESPT. The reason for this could be the lower level of matrix crosslinking achieved in vulcanizates containing ERSO and could be corrected by extra sulphur addition.

The hardness of the vulcanizates containing ERSO was lower compared to that of the other vulcanizates, which may be due to lower level of crosslink density as indicated by the Vr values. But the tear strength of the vulcanizates, which contained TESPT/ERSO or combination of ERSO+TESPT was much better than that containing naphthenic oil or naphthenic oil +TESPT respectively. This observation is again the result of better dispersion of silica achieved in the former compounds through hydrophobation of silica by TESPT or ERSO+TESPT combination.

Compression set of the vulcanizate depends on crosslink density and reinforcement levels. Whereas higher level of reinforcement increases the set, a reverse trend is true with increase in crosslink density. Compounds S1 and S4 showed lower set values in the respective groups, even though the levels of reinforcement in these were higher. This is because of the higher level of crosslink density of these vulcanizates, as indicated by the higher Vr values, compared with that of the other vulcanizates. The compression set values of S2 and S3 and those of S5 and S6 were comparable. This observation could be the net result of a combination of effects due to levels of hydrophobation and dispersion of silica and the level of crosslinking in the matrix. As in the case of compression set, lower heat build up was recorded for the vulcanizates containing TESPT alone, compared to the other vulcanizates. Among S1, S2 and S3, the compound containing ERSO+TESPT combination showed higher heat build up, probably due to lower level of crosslinking of the matrix. But at higher silica loading the difference is less noticeable. The reduction in filler-filler interaction through hydrophobation of silica by TESPT and combination of ERSO+TESPT becomes evident when the dynamic set values of the compounds are compared. The vulcanizates S2 and S5 which contained naphthenic oil and combination of naphthenic oil and TESPT respectively, showed much higher dynamic set values compared with the vulcanizates, which contained TESPT alone (S1, S4) and combination of ERSO+TESPT (S3, S6).

265

This observation is not in line with the trend seen in compression set of the vulcanizates, which may be due to the differences in mode and extent of deformation occurring in these two types of tests. In dynamic set measurement, the sample is subjected to high frequency cyclic loading and thereby the broken agglomerates/ networks of silica do not get enough time to recombine, resulting in a higher permanent set. Since the possibility of existence of silica network is more in compounds containing naphthenic oil compared with that of TESPT or ERSO, compounds S2 and S5 undergo higher set under cyclic loading. Since the deformation level in rebound resilience test is low, no wide difference in resilience of vulcanizates S1, S2, S3 and those of S4, S5 and S6 is observed.

The abrasion resistance of the compounds S1 and S4, which contained TESPT was excellent compared with that for the other compounds. There was no appreciable difference in abrasion resistance of vulcanizates, which contained naphthenic oil and ERSO. The tensile strength and elongation at break values of the vulcanizates after ageing at 70°C for 7 days indicate lower retention of these properties for the vulcanizates S1 and S4 which contained TESPT compared with the other compounds. This could be due to a total higher amount of sulphur (added sulphur + that liberated from TESPT) in these compounds, which could produce preferentially polysulphidic crosslinks of poor thermal stability. No appreciable difference, was noted in ageing resistance of compounds, which contained naphthenic oil and ERSO.

VII.2. Conclusion

Evaluation of TESPT, naphthenic oil and ERSO in silica filled natural rubber compounds showed very good improvement in physical properties of the vulcanizates containing TESPT and ERSO compared to that containing naphthenic oil. The action of ERSO in enhancing the properties is expected to be bifunctional and similar to that of TESPT, ie. hydrophobation of silica, which increases its degree of dispersion and formation of a chemical bond with the rubber, thereby ensuring strong polymer-filler interaction.

Table VII.1. Formulation of compounds

Ingredients	S1	S2	S3	S4	S5	S6
Natural rubber	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
Ultrasil VN3	30	30	30	50	50	50
TESPT	3	-	-	6	3	3
Naphthenic oil	-	3	-	-	3	-
ERSO	-	-	3	-	-	3
HSL	1	1	1	1	1	1
MBTS	1	1	1	1	1	1
DPG	0.75	0.75	0.75	0.75	0.75	0.75
DEG	1.5	1.5	1.5	1.5	1.5	1.5
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5

Table VII.2. Cure characteristics of compounds

No.	Rheometric torque (dN m)			Cure time t $_{90}$ at 150 ^{0}C, (min)	Mooney scorch time at 120 ^{0}C, (min)
	Minimum (M$_L$)	Maximum (M$_H$)	Increase (M$_H$-M$_L$)		
S1	3.6	21.4	17.8	7.0	11.4
S2	3.7	14.7	11.0	9.5	13.2
S3	3.7	14.2	10.5	9.7	13.8
S4	8.7	32.0	23.3	16.0	20.8
S5	11.2	36.2	25.0	15.0	31.6
S6	10.8	30.9	20.1	18.0	39.8

Table VII.3. Physical and mechanical properties of vulcanizates

Parameters	S1	S2	S3	S4	S5	S6
Hardness (Shore A)	57	57	56	73	73	72
Tear strength (kN/m)	89.8	61.6	71.2	111.9	98.7	102.3
Compression set (%)	33.1	36.0	36.5	36.0	39.0	39.0
Heat build up (°C)	11	14	15	23	24	24
Dynamic set (%)	.088	2.20	1.72	1.12	2.39	1.65
Rebound resilience (%)	60.0	60.0	60.0	55.0	55.0	56.0
Din abrasion loss (mm^3)	123.6	154.0	153.9	126.9	135.6	136.0
Tensile properties						
Modulus 100 % (MPa)	2.30	2.00	1.80	4.30	3.49	3.30
Modulus 300 % (MPa)	6.70	4.50	4.30	11.99	8.99	8.80
Tensile strength (MPa)	35.5	27.2	29.5	28.3	26.4	28.0
AA*	24.5	26.5	27.9	25.1	25.1	26.6
Elongation at break (%)	705	713	768	568	619	642
AA*	505	631	719	458	538	546
Modulus 300% / Modulus100%	2.91	2.25	2.39	2.79	2.57	2.67
Vr	0.2229	0.1820	0.1778	0.2854	0.2696	0.2669
Vr-Vr'	0.0808	0.0590	0.0638	0.1261	0.1144	0.1164

*   Values after ageing at 70 °C for 96 h

269
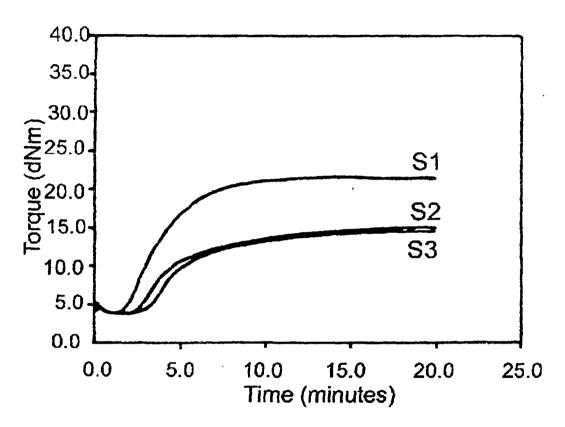
Figure VII.1. Rheographs of compounds S1, S2 and S3 at 150 ^{0}C
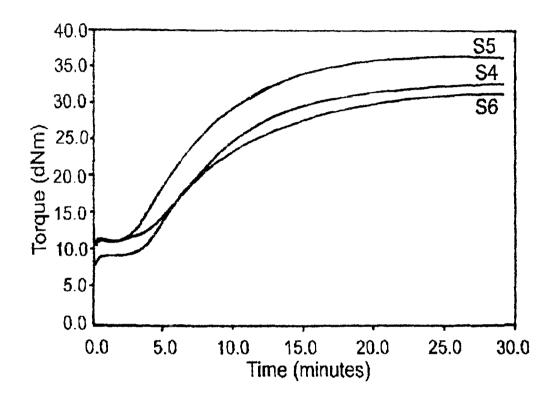
Figure VII.2. Rheographs of compounds S4, S5 and S6 at 150 °C

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Chapter VIII

Studies on Epoxidised Rubber Seed Oil as a Secondary Plasticizer/Stabilizer for Polyvinyl Chloride

Polyvinyl chloride (PVC) is not thermally stable and beyond 100 ^{0}C it degrades with the evolution of hydrochloric acid[1]. This process is further extended by the formation of conjugated and easily oxidisable double bonds along the chain, which will result in the discoloration of the polymer[2]. The reactions involved in this process are shown below.

--- VIII (1)

The rate of degradation increases sharply with increase in temperature and the colour changes from white to yellow, brown and finally black. To avoid such discoloration a suitable stabilizer is added to the polymer. Stabilizers such as tribasic lead sulphate (TBLS) are widely used for PVC. Heat stabilizers for PVC have the ability to react with HCl as it is liberated from the polymer during degradation.

$$Pb\,(OOCC_{17}H_{32})_2 + 2HCl \rightarrow PbCl_2 + 2C_{17}H_{32}COOH \qquad --- VIII\ (2)$$

Epoxidized soybean oil, epoxidized oleic acid ester and other fatty acid oils are extensively used as stabilizers to improve the high temperature heat stability of PVC compound[3]. Use of RSO, ERSO and its lead and barium salts as heat stabilizers for PVC has been attempted by E. Okieimen and E. Ebhoaye[4-6]. In their trials, PVC was mixed with RSO, ERSO and its lead and barium salts and heated the compound in nitrogen atmosphere. The polymer got degraded and the HCl evolved was absorbed in standard sodium hydroxide solution. The

residual concentration of sodium hydroxide was then determined by titration with standard hydrochloric acid. Epoxides can be used as HCl scavenger and the neutralization reaction proceeds as per the following equation.

$$R' - \underset{\underset{O}{\diagdown\diagup}}{CH - CH} - R'' + HCl \rightarrow R' - \underset{\underset{OH}{|}}{CH} - \underset{\underset{Cl}{|}}{CH} - R'' \qquad ---- \quad VIII\ (3)$$

Plasticizers are organic substances added to polymers to improve their flexibility and processability[7]. It increases the softness, elongation and low temperature flexibility and decreases the accumulation of intermolecular forces and the glass transition temperature (Tg) of polymers. They are classified into primary, secondary and extenders[8]. Esters, phosphates and epoxides are the most suitable plasticizers for PVC. Since PVC is polar in nature, mostly ester type plasticizers such as dioctyl phthalate (DOP) and dibutyl phthalate (DBP) are used for its compound. Epoxidized vegetable oil is used both as a plasticizer and acid scavenger in PVC compounds to improve the resistance to thermal ageing.

This chapter contains the results of a detailed study on the use of ERSO as a secondary plasticizer/stabilizer for PVC. Details of the materials used and the experimental techniques followed are given in chapter II, section II.7. The formulations used for preparing the compounds are given in Tables VIII.1 and VIII.2. The processing characteristics of the compounds are given in Table VIII.3.

All the compounds were prepared using 'Haake' Rheocord '90' at 170 ^{0}C and 60 rpm and the ERSO used in these compounds was of 5% epoxy content. For assessing the effectiveness of ERSO and RSO as secondary plasticizers, formulations 1 to 5 were used. Compound 1 containing 60 parts of DOP as plasticizer is taken as the control. In compounds 2, 3 and 4; 10, 20 and 25 parts of DOP respectively were replaced with ERSO. In compound 5, 10 parts of DOP was replaced with RSO. In all these compounds 3 parts tribasic lead sulphate (TBLS) was used as stabilizer. Graphs showing torque versus mixing time were drawn and these are given in Figures VIII.1 and VIII.2.

For assessing the role of ERSO as a stabilizer, compounds 6 to 9 were prepared. In compounds 6 and 7, 10 and 20 parts of DOP were replaced with

276

ERSO respectively and only 2 parts of TBLS was used instead of 3 (ie. one part of stabilizer less than the control). The mixing torque versus time plots are shown in Figure VIII.6. There is no difference in stabilizing torque of these compounds for 50 minutes mixing. So, compounds 8 and 9 were prepared in which 10 and 20 parts of DOP respectively were replaced with ERSO and TBLS was avoided. The torque versus time plots obtained are shown in Figure VIII.7.

Geroge *et al.* had developed a new stabilizer system containing magnesium oxide/zinc oxide combination for PVC (compound B, Table VIII.2). In the work reported here, partial replacement of zinc oxide, magnesium oxide and stearic acid with ERSO was attempted because ERSO could act as a secondary plasticizer/stabilizer (HCl scavenger). Compound A which contained TBLS /calcium stearate combination was used as the control. In compound C, 10 parts of DOP was replaced with ERSO. Compound D contained only 2 parts of magnesium oxide and one part stearic acid, instead of 4 parts magnesium oxide and 2 parts stearic acid respectively. In compound E only half the quantity of zinc oxide, stearic acid and magnesium oxide was used and 20 parts of the DOP was replaced with ERSO. Graphs showing torque versus mixing time (up to 50 minutes) were drawn and are given in Figure VIII. 5. The stabilizing torque and degradation time were noted and given in Table VIII. 3.

The samples used for dynamic mechanical analysis were from compounds 1 to 3 and A to E. The tan δ versus temperature and E' versus temperature plots are given in Figures VIII. 3 and VIII. 4 respectively.

VIII.1. Results and Discussion

VIII.1.1. Effect of ERSO as a Secondary Plasticizer in Polyvinyl Chloride

Figure VIII.1 shows the mixing torque versus time plots of compounds 1 to 3. Compound 1 is the control. It has a stabilizing torque 14 dN.m till 50 minutes mixing. In compound 2 in which 10 parts of DOP was replaced with 10 parts of ERSO, the torque value is the same as that of compound 1 up to 15minutes. After this, it showed 1 unit increase in torque. For compound 3, only 2 units rise in stabilization torque than the control was noticed up to 50 minutes mixing.

From these observations, it can be concluded that compounds 1, 2 and 3 have similar mixing behaviour and the stabilized torque values of compounds in which a part of DOP has been replaced by ERSO are only marginally higher than that containing DOP alone.

Figure VIII.3 shows the tan δ versus temperature plots of samples 1 to 3 and A to E. Compounds 1, A and B have the same Tg value. Compounds 2, C and D have almost comparable Tg values with that of the control compound. In these cases 10 parts of DOP was replaced with ERSO. But in the case of samples 3 and E in which 20 parts of DOP was replaced by ERSO an increase in Tg value was noticed.

Figure VIII.4 shows the elastic modulus versus temperature plots of samples. In this case also samples containing 50 DOP/10 ERSO showed comparable elastic modulus (E') values with that containing 60 parts DOP, whereas samples 3 and E had higher modulus values. These observations further confirmed that 10 parts of ERSO is the safe limit for replacing DOP in PVC compounds. These results also indicated that partial replacement of DOP by ERSO at lower dosage (10 parts) does not affect the processing behaviour of PVC. However, higher dosage of ERSO can adversely affect the processing characteristics. The tensile properties of compounds 1, 2 and 3 given in Table VIII.4 indicated that compounds 2 and 3, which contained combinations of DOP and ERSO, had almost the same tensile strength as that for the control compound 1, which contained DOP alone. Modulus showed regular increase from compound 1 to 3. This coupled with lower elongation at break values of compounds 2 and 3 indicated that the addition of ERSO as secondary plasticizer could be done only at lower level of 10 to 15 parts per 100 PVC. The tensile properties of the samples after ageing at 100 ^{0}C for 48 h showed no appreciable change from the original tensile strength or modulus values of the sample before ageing. These results indicated that ERSO could be used as a secondary plasticizer for PVC at lower level without any adverse effect on processing characteristics and degradation of the sample. Compounds 6 and 7 which contained a lower dosage of stabilizer TBLS (Figure VIII.6) and the compounds 8 and 9 which contained no TBLS (Figure VIII.7), also showed mixing characteristics similar to that of compound 1. Compound 6, which contained a

lower dosage of TBLS and 50 DOP/10 ERSO, had the same stabilizing torque as that of the control. Compound 7, which contained a lower dosage of TBLS and 40 DOP/20 ERSO also showed almost same torque as that of compound 1. This indicated that ERSO could act as a stabilizer in PVC compounds. Mixing curves of compounds shown in Figure VIII.5 indicated that the compound B has a lower stabilizing torque compared to the control compound A. But it has very low degradation stability time (35 minutes only) compared with other compounds. On partial replacement of DOP in compound B, with ERSO (compounds C, D and E), the nature of the mixing curve becomes similar to that of the control, even though these compounds showed a marginal increase in stabilizing torque. There was no sign of degradation of these compounds even after 50 minutes of mixing at 170 ^{0}C. Thus partial replacement of DOP with ERSO in compound B is helpful to enhance the overall performance of the compound B. In the case of B, after 35 minutes the torque increased, to maximum and then deceased. This is because the material breaks down to a powder under shear, after crosslinking[2]. The increase in toque at 35th minute is due to the crosslinking of the resin followed by thermal degradation to black powdery material. Compound C contained stabilizing system zinc oxide/ magnesium oxide and stearic acid. But in compound D, the dosages of stabilizers magnesium oxide and stearic acid were lower than that in compound C. In compound E, magnesium oxide, zinc oxide and stearic acid dosages were only half of those in compounds B and C. Even then, these two compounds showed tensile properties similar to those of A, B and C, before and after aging at 100 ^{0}C for 48 h (Table VIII.4). In the case of compound D a slightly higher tensile strength was obtained, which may be due to the presence of a higher dosage of zinc oxide, which is capable of reacting with the HCl eliminated during degradation of PVC. This indicated that use of ERSO in PVC compounds stabilized with the zinc oxide/magnesium oxide/ stearic acid system, is helpful to enhance its thermal stability without adversely affecting the tensile properties. Compounds 1 and A are of the same composition, but showed difference in tensile strength values. This is because a different grade (103 EP) of PVC was used for compounds A to E.

VIII.1.2. Effect of ERSO as a Heat Stabilizerin Polyvinyl Chloride

Figure VIII.7 shows that for compounds 8 and 9, there is no change in stabilized torque for 50 minutes. Thus, it became evident that ERSO is useful to impart heat stability. From Table VIII.3, it can be seen that for compounds A, C, D and E there is no degradation for 50 minutes. But, for compound B degradation started at the 35th minute. These results indicated that ERSO could be used as a heat stabilizer for PVC, both in conventional type and modified compounds containing MgO/ZnO/stearic acid combination. Since MgO and ZnO are rubber compounding ingredients, ERSO may be a useful additive in blends of PVC with elastomers.

Figures VIII.8 and VIII.9 show the thermograms of compounds 1 and 2. For compound 2 the initial weight loss at a lower temperature is less compared to compound 1. This is because of the higher molecular weight of ERSO, which is in the range of 960, compared with that of DOP, which is 390^{10}. Degradation started first for compound containing DOP alone.

From Figure VIII.10, it could be seen that the compound 10, which did not contain TBLS showed regular change of colour from yellow to brown at an early time compared with the compound 8 that contained 50 parts DOP and 10 parts ERSO. Colour of the sample from compound 8 at 60th minute is almost the same as that of the 25th minute sample of the compound containing DOP alone (Compound 10). From this it is evident that 50 DOP/10ERSO combination gives more stabilizing effect than 60 parts DOP alone. The light yellow colour of the compound 8 at the 3rd minute is due to yellow colour of the ERSO. It is evident from Figure VIII.11, that colour of compound B changed from white to brown within 35 minutes of mixing whereas compounds A, C, D and E did not change to brown even after 60 minutes mixing at 170 °C. The light yellow shade of sample E is due to a higher dosage of ERSO, which is light yellow. These observations further supported the fact that ERSO can be used as a heat stabilizer for PVC.

VIII.2. Conclusion

The study showed that ERSO could be used as a secondary plasticizer for PVC. It gives heat stability for PVC and is less volatile. Compounds containing mixtures of ERSO and DOP had tensile properties comparable to that containing DOP alone. Reduction in dosage of zinc oxide, magnesium oxide and stearic acid in the stabilizer system did not affect the thermal stability of PVC when a combination of DOP and ERSO was used as the plasticizer. DOP/ERSO system works very well with ZnO/MgO in imparting thermal stability to PVC.

Table VIII.1. Formulations for compounding

Ingredients	1	2	3	4	5	6	7	8	9	10
Polyvinyl chloride	100	100	100	100	100	100	100	100	100	100
Tribasic lead sulphate	3	3	3	3	3	2	2	-	-	-
Calcium stearate	1	1	1	1	1	1	1	1	1	1
Dioctyl phthalate	60	50	40	35	50	50	40	50	40	60
ERSO	-	10	20	25	-	10	20	10	20	-
RSO	-	-	-	-	10	-	-	-	-	-

Table VIII.2. Formulations (Series II)

Ingredients	A	B	C	D	E
Polyvinyl chloride	100	100	100	100	100
Tribasic lead sulphate	3	-	-	-	-
Calcium stearate	1	-	-	-	-
Magnesium oxide	-	4	4	2	2
Zinc oxide	-	4	4	4	2
Stearic acid	-	2	2	1	1
Dioctyl phthalate	60	60	50	50	40
ERSO	-	-	10	10	20

Table VIII.3. Mixing characteristics of compounds

Compound number	Stabilizing torque (Nm)	Degradation time (minutes)
1	14	>50
2	15	>50
3	16	>50
4	17.5	>50
5	20	>50
6	14	>50
7	15	>50
8	15.5	>50
9	17.5	>50
A	18	>50
B	14	35
C	18	>50
D	19	>50
E	18	>50

Table VIII.4. Tensile properties of compounds

Compound number	Tensile strength (MPa)	Elongation at break (%)	Modulus 100% (MPa)	Modulus 200% (MPa)
1	18.1 (19.6)	343 (385)	8.6 (7.6)	12.5 (12.1)
2	19.6 (20.5)	322 (356)	10.1 (9.1)	14.3 (14.0)
3	19.0 (20.4)	295 (317)	11.0 (11.1)	15.1 (15.8)
A	15.8 (15.9)	244 (250)	8.4 (7.9)	13.9 (13.6)
B	15.8 (15.4)	258 (264)	8.1 (7.5)	13.1 (12.5)
C	15.6 (15.6)	252 (232)	8.8 (9.3)	13.5 (14.6)
D	16.8 (16.9)	251 (238)	9.1 (9.3)	14.2 (14.4)
E	15.6 (15.7)	261 (236)	9.6 (11.0)	13.7 (15.3)

Values in brackets – after ageing at 100 ^{0}C for 48 h.
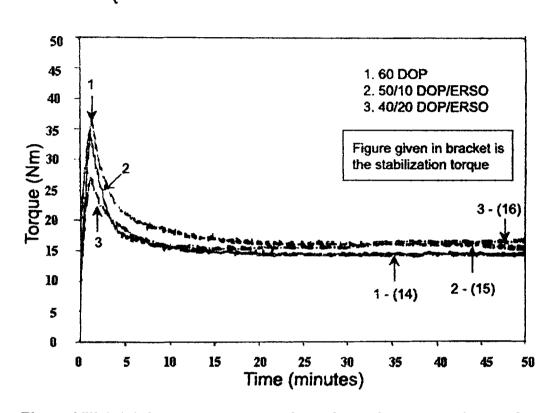
Figure VIII.1. Mixing torque versus time plots of compounds 1 to 3
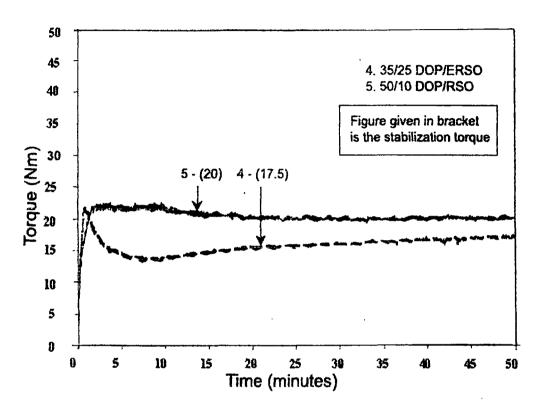
Figure VIII.2. Mixing torque versus time plots of compounds 4 and 5
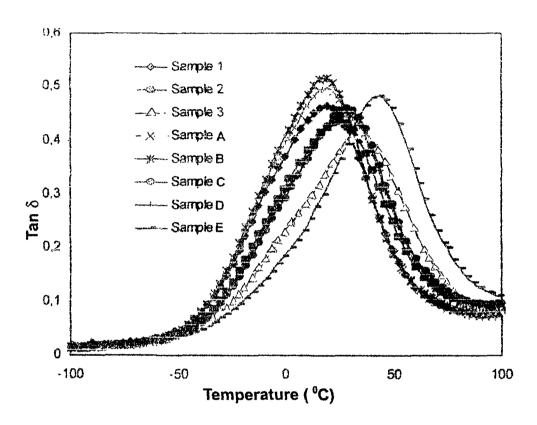
Figure VIII.3. Plots of tan δ versus temperature
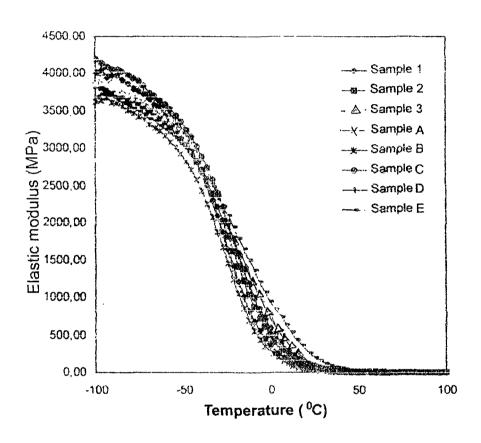
Figure VIII.4. Elastic modulus versus temperature plots
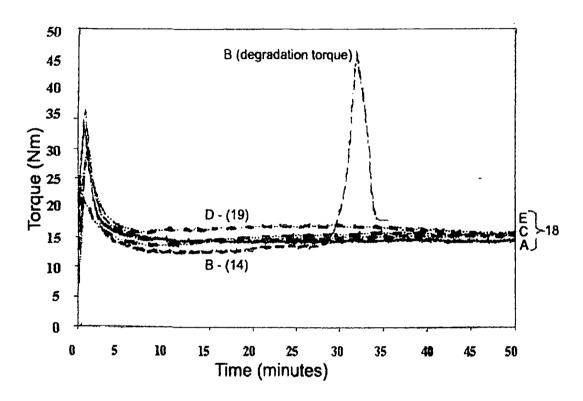
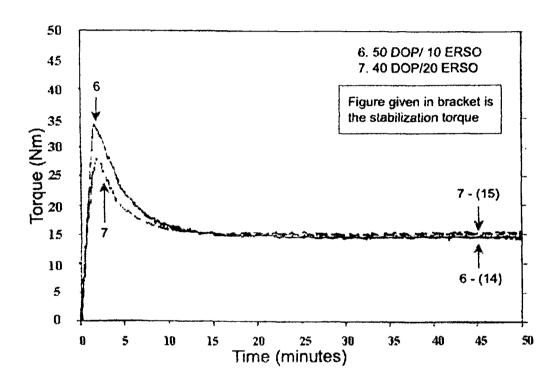Figure VIII.5. Mixing torque versus time plots of compounds A to E

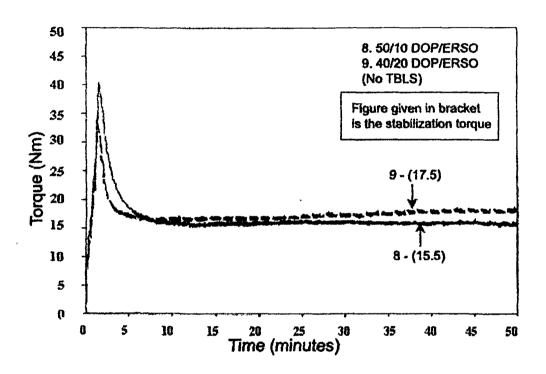Figure VIII.6. Mixing torque versus time plots of compounds 6 and 7

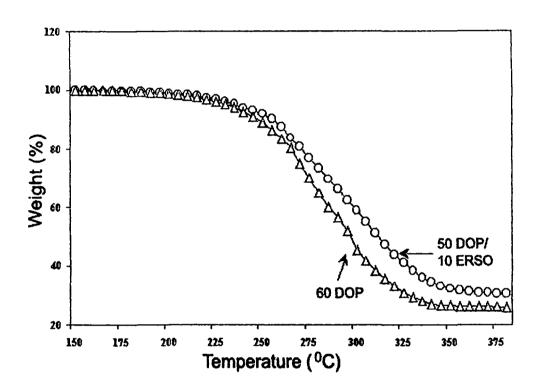Figure VIII.7. Mixing torque versus time plots of compounds 8 and 9

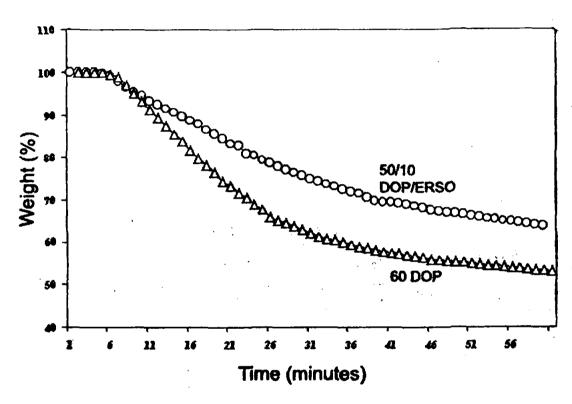Figure VIII.8. Mass retained versus temperature plots of compounds 1 and 2

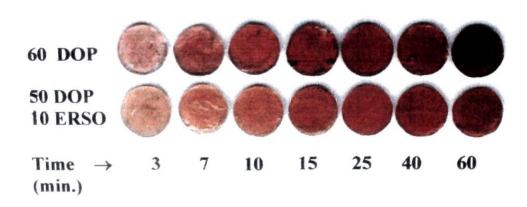Figure VIII.9. Mass retained versus time plots of compounds 1 and 2 at 250 ^{0}C

60 DOP						
50 DOP 10 ERSO						
Time → (min.)	3	7	10	15	25	40	60

Colour change during mixing

Figure VIII.10. Photograph showing change of colour with time of mixing of compounds 8 and 10
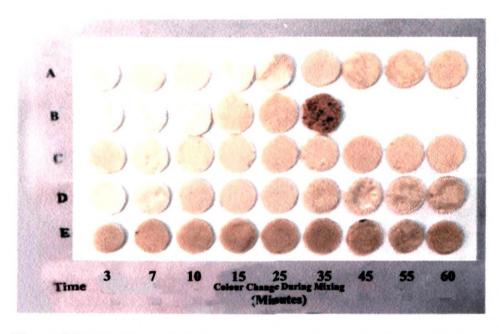

Figure VIII.11. Photograph showing change of colour with time of mixing of compounds A to E

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Summary and Conclusion

Different experiments were conducted to assess the suitability of rubber seed oil/epoxidized rubber seed oil in compounds for acrylonitrile-butadiene rubber, polychloroprene rubber, latex foam, silica reinforcement of natural rubber and in PVC. Use of copper salts of fatty acids from RSO as a peptizer for dissolving natural rubber was also evaluated. The main observations of these experiments are summarised below.

Rubber seed oil contains 80% unsaturated higher fatty acids. When it is epoxidised its polarity is enhanced. Since epoxidised rubber seed oil (ERSO) is more polar and has a higher molecular weight than DOP it is expected to function as a good plasticizer, for polar rubbers like the NBR. Hence, a comparative evaluation of RSO, ERSO and DOP as plasticizer in nitrile rubber compound was made.

Nitrile rubber vulcanizate containing ERSO as plasticizer showed comparable tensile strength and modulus with that containing DOP. At a higher level of epoxidation (5% epoxy content) all the physical and mechanical properties were similar to that of vulcanizate containing DOP. DIN abrasion resistance was better for compound containing RSO and ERSO than that of control. The ageing resistance of the vulcanizates containing RSO and ERSO was comparatively better than that containing DOP, as indicated by both better mechanical properties (tensile strength, elongation at break and modulus 300%) and higher retention of these properties of the vulcanizates after ageing at 70 ^{0}C for 7 days.

The leaching loss, as indicated by the weight loss of the sample swollen in ASTM No. 3 oil, was considerably lower for vulcanizate containing RSO/ERSO compared to that containing DOP as plasticizer. The lower leaching loss of sample is due to higher molecular weight of RSO and ERSO compared to that of DOP. The volatilization loss from vulcanizate containing RSO and ERSO heated at 100 ^{0}C for 168h was much lower than that from the control. These observations indicated that RSO and ERSO impart better thermal stability to NBR vulcanizate compared to DOP. Thus the present study revealed that RSO and ERSO can be used as a less leachable and low volatile plasticizer for nitrile

rubber and that use of these materials in compounds for oil seals and O-rings was expected not to adversely affect their properties/performance.

RSO/ERSO could act as an acid acceptor, as it contains about 80% unsaturated higher fatty acids. The HCl produced during vulcanization/ degradation of polychloroprene rubber can react with the unsaturated higher fatty acids formed by the acid hydrolysis of the rubber seed oil. It is also possible that the zinc chloride/zinc hydrochloride reacts with higher fatty acid of the RSO to form corresponding zinc soap, which could act also as a plasticizer in compound of polychloroprene rubber.

In the work reported in the thesis, magnesium oxide was replaced by rubber seed oil and ERSO in gum compounds of CR. The rheograph and cure characteristic indicated that compounds containing RSO/ERSO have better scorch safety, lower cure time and faster cure rate compared with the compound containing magnesium oxide as acid acceptor. Compound containing RSO/ERSO had maximum plasticizing action, as indicated by lower value of rheometric torque. In carbon black filled polychloroprene compounds, RSO was used instead of napththenic oil and magnesium oxide. Here also compounds containing RSO showed comparable physical properties and better retention in tensile properties after ageing at 100 ^{0}C for 72 h. Due to its higher plasticizing effect than naphthenic oil, better dispersion of carbon black was achieved in compounds containing RSO, as indicated by better abrasion resistance of the vulcanizates, compared to those containing naphthenic oil. Compounds prepared using RSO did not show any fungal growth as in the case of other vegetable oil. Thus it became evident that RSO could be used as an acid acceptor cum plasticizer in polychloroprene compounds.

The soap has an important role in deciding the quality of latex foam. Castor oil and rubber seed oil contain mixtures of higher fatty acids, the potassium salts of which have very good frothing action. Hence, attempts were made to replace potassium oleate soap with that of rubber seed oil in latex foam production. The quality of foam obtained was assessed by performing the tests described in IS 1741-1999.

Hardness of foam basically depends on expansion given for the latex compound and in this study, the expansion was kept constant (7 times the original volume) in all the trials. However, the time required to get the desired

expansion was lower for the compounds, which contained the soap from rubber seed oil or combinations containing rubber seed oil soap, compared with potassium oleate soap. This indicated better foaming efficiency of the soap from rubber seed oil. When potassium oleate is completely replaced with equal quantity of soap prepared from rubber seed oil or where 1 phr RSO is used in place of 1.2 phr of potassium oleate, almost the same hardness was obtained for the foam. Latex foam made by using rubber seed oil soap showed lower set values compared with those made by using oleate soap, both in unfilled and china clay filled samples. In the case of foams prepared by using mixtures of soaps also the same trend was noticed.

In flexing test, the reduction in thickness was almost the same for the foam samples prepared by using potassium oleate and rubber seed oil soap. The mould shrinkage of the foam prepared by using potassium oleate and rubber oil soap was about 11% and there was not much difference between the two samples. All the samples of foam prepared using RSO soap or mixture of potassium oleate and RSO soap met the specifications as per IS 1741-1999. The properties of the foam prepared using a blend of NR and SBR latices also showed similar hardness values when potassium oleate or rubber seed oil soaps were used. There was no fungal growth on storage of foam. As price of RSO is less by Rs 50/- per kilogram compared with that of oleic acid, use of RSO soap for NR latex foam will be economically advantageous.

The dirt content of block rubber is estimated by dissolving the rubber in a solvent, filtering the solution through a standard sieve and then weighing the dried matter retained in the sieve. For facilitating faster dissolution, easy filtration and reducing the viscosity of the solution, a peptizer like copper oleate or xylyl mercaptan is used. RSO is a good source of higher fatty acids such as oleic and linoleic acid. To assess the effectiveness of copper salt of mixed fatty acids prepared from RSO in peptizing NR, it was used for the dirt content estimation of block rubber in comparison with copper oleate.

Rubber solutions were prepared by dissolving 10g rubber in 200 ml mineral terpentine using 1 ml of 25% copper oleate (control) and 1.0 and 1.5 ml of 25% solution of copper salt of RSO. Viscosity versus shear rate plots for the rubber solutions were drawn at 70 °C. The results indicated that the viscosity of the solution containing 1.0 ml of copper salt solution form RSO was comparable

to that of the control, which contained 1.0 ml copper oleate solution at all shear rates.

Viscosity versus temperature plots of the solutions containing 1.0 ml of copper oleate and 1.0 ml of copper salt of RSO, at a shear rate of 20 s^{-1} were also drawn. The viscosity decreased with increase in temperature. At 70 ^{0}C, the viscosity of the control and that of the sample containing 1 ml of copper salt of RSO were the same. But at lower than 70 ^{0}C, the solution containing the copper salt of RSO had lower viscosity values. This is advantageous in dirt estimation for quick filtration of the solution through the sieve, even if the temperature is slightly lower.

Graphs showing viscosity Vs concentration of peptizer plots, at 20 s^{-1} shear rate and at 70 ^{0}C indicated that higher concentrations of either copper oleate or copper salt of RSO increased the viscosity at a particular shear rate and that both the solutions had the same viscosity when the dosage of peptizer was 1.0 ml. Solutions of both ISNR 5 and ISNR 20 showed the same trend in these evaluations.

From the results it could be seen that the percentage dirt content values obtained for samples of ISNR 20 and ISNR 5 using copper salt of RSO at concentrations of 0.5 ml, 1 ml and 1.5 ml of 25% solution, were comparable with that of control (ie. 1 ml of 25% copper oleate solution). The deviation in the values of dirt content of the experimental samples from those of the control was not significant statistically. This indicated that 0.5 ml, 1 ml or 1.5 ml of 25% solution of copper salt obtained from RSO could be used for the determination of dirt content without affecting the accuracy of the test result. However, from the practical point of view 1.0 ml of 25% solution of copper salt of mixed fatty acids from RSO appeared to be the ideal concentration of this peptizer, as higher concentration can lead to the formation of macrogel. It was found to be economically advantageous also.

The epoxy group of the ERSO can interact with the silanol groups of the silica and the long chain hydrocarbon part of the fatty acid can easily interact with the non-polar rubber hydrocarbon, so that it could function as a reinforcement modifier in silica filled NR compounds.

Silica filled natural rubber compounds were prepared using TESPT, ERSO and naphthenic oil and tested for various processing and technological

300

properties. Compounds containing TESPT and naphthenic oil had higher rheometric torque and reduced cure time. In the presence of higher dosage of TESPT, the silanol groups of silica react with ethoxy silyl group of TESPT resulting in hydrophobation of silica, which prevented the formation of silica-silica network structure. This leads to better dispersion of silica and reduction in viscosity. The low Rheometric torque of compound containing TESPT alone, than that of a mixture of naphthenic oil and TESPT is due to this effect. Compound containing mixtures of epoxidised rubber seed oil and TESPT showed lower torque value compared to compound containing naphthenic oil and TESPT, indicating involvement of ERSO in hydrophobation of silica through the reaction between the epoxy group and silanol group of silica.

Compound containing TESPT had higher tensile strength, modulus and lower elongation at break. But in the case of compounds containing TESPT/naphthenic oil and TESPT/ERSO the latter one showed lower modulus and higher elongation. This was due to better hydrophobation of silica by the epoxy group of the ERSO. The higher tensile strength was due to better dispersion of silica achieved through the hydrophobation. Zinc soap formed by the reaction of zinc oxide and the higher fatty acids present in ERSO might also have helped in achieving a better dispersion of silica in the compound. Ratio of modulus 300% to modulus 100% (M_{300}/M_{100}) is a good indication of reinforcement by filler in a vulcanizate. The result indicated that TESPT/ERSO combination was helpful to achieve better reinforcement by silica than the TESPT/naphthenic oil combination. This was further supported by the higher V_r-V_r' value of vulcanizates containing TESPT/ERSO combination than that of vulcanizates containing TESPT/naphthenic oil combination. Tear strength of the vulcanizates containing TESPT, ERSO or combination of ERSO/TESPT was also higher. This was also due to better dispersion of silica through hydrophobation.

The action of ERSO in enhancing the properties through hydrophobation of silica was expected to be bifunctional and similar to that of TESPT. The epoxy group reacts with the silanol groups on silica, which increases its degree of dispersion. Formation of a chemical bond with the rubber through the reaction with sulphur, making use of the unsaturated bonds present in the higher fatty acid chain ensures strong polymer-filler interaction.

Epoxidised linseed oil and soyabean oil are already used commercially for PVC compounding. Hence, a detailed study was conducted to evaluate the effect of ERSO as a plasticzer cum stabilizer in PVC.

Compounds were prepared using 60 parts DOP as control and replacing 10 and 20 parts of DOP with ERSO. Mixing torque versus time plots were drawn using Rheocord 90. The results indicated that all the compounds had similar mixing behaviour. The stabilized torque values of compounds in which a part of DOP was replaced by ERSO, were only marginally higher than that of containing DOP alone. Compound prepared by replacing 10 parts of DOP by 10 parts of RSO showed higher stabilizing torque value and was found to be incompatible also. But in the case of ERSO, upto 20 parts the compatibility problem was less. Beyond 20 parts of ERSO, the increase in stabilized mixing torque was much higher. This indicated that 10 parts was the safe limit for ERSO for replacing DOP.

From tan δ versus temperature plots also it could be seen that replacement of 10 parts DOP with ERSO gave almost comparable Tg value with that of sample containing DOP alone. Elastic modulus Vs temperature plots of samples also showed the same trend. Both the above results indicated that partial replacement of DOP by ERSO at a lower dosage of 10 parts does not affect the processing behaviour of PVC. However, higher dosage of ERSO can adversely affect the processing characteristics.

The tensile properties of the PVC compounds containing 50/10 and 40/20 DOP/ERSO were almost same as that containing DOP alone. The tensile properties of the samples after ageing at 100 ^{0}C for 48 h showed no appreciable change from the original tensile strength or modulus values of the sample. These results indicated that ERSO could be used as a secondary plasticizer for PVC at lower level without any adverse effect on processing characteristics, physical properties and degradation resistance of the sample.

Compounds containing a lower dosage of TBLS as stabilizer and that having no TBLS also showed mixing characteristics similar to that of control when part of the DOP was replaced by ERSO. This indicated that ERSO could act as a stabilizer also in PVC compounds.

Compounds that contained zinc oxide, magnesium oxide (MgO) and stearic acid as stabilizer system and control compound containing TBLS and calcium stearate with 60 phr DOP were prepared. Compounds in which DOP was replaced with 10 and 20 parts of ERSO were also prepared with lower quantity of MgO. In all these cases, there was no sign of degradation even after 50 minutes of mixing at 170 ^{0}C, except in the case of sample containing only ZnO, MgO, stearic acid and DOP. For this particular sample at the 35th minute, degradation occurred and torque increased. The increase in torque at 35 minute was due to the crosslinking of the resin followed by thermal degradation. Even when the dosage of ZnO and MgO was lowered, the compounds, which contained ERSO showed almost the same tensile properties. This observation indicated that use of ERSO in PVC compounds stabilized with ZnO/MgO/stearic acid system is helpful to further enhance its thermal stability without adversely affecting the tensile properties. From thermogravimetric analysis and colour stability test also it could be concluded that ERSO worked as a heat stabilizer for PVC.
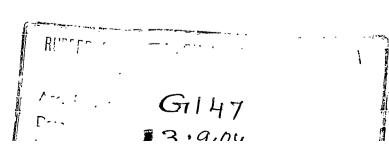
As discussed in the previous pages, it became evident that either RSO or its chemically modified form, epoxidised rubber seed oil, can be used as

1. a plasticizer for acrylonitrile butadiene rubber
2. an acid accepter cum plasticizer in polychloroprene rubber compounds
3. a foaming agent (higher fatty acid soap) for latex foam
4. as a peptizer (copper salts) for natural rubber dissolution
5. as a reinforcement modifier for silica filled natural rubber compound

and

6. as a plasticizer cum heat stabilizer for poly vinyl chloride.

The above findings can open up new areas of application of rubber seed oil.

List of Publications from this Thesis

1. Joseph, R., Premalatha, C. K. and Kuriakose, B. (1997). Studies on use of rubber seed oil in natural rubber latex foam production. *Proceedings of the Ninth Kerala Science Congress*, 27-29 January 1997 Thiruvanathapuram, pp.1-2.

2. Joseph, R., Alex, R., Vinod, V. S., Premalatha, C. K. and Kuriakose, B. (2003). Studies on epoxidised rubber seed oil as plasticizer for acrylonitrile butadiene rubber. *Journal of Applied Polymer Science*, 89: 668-673.

3. Joseph, R., Alex, R., Premalatha, C. K. and Kuriakose, B. (2002). Use of rubber seed oil in polychloroprene rubber compound. *Indian Journal of Natural Rubber Research*, 15(2) : 143-149

4. Joseph, R; Alex, R. Premalatha, C. K. and Kuriakose, B. Studies on use of rubber seed oil soap in natural rubber and blends of natural rubber/styrene butadiene rubber latex foam production. *Indian Journal of Natural Rubber Research*, (In Press).

5. Joseph, R; Alex, R., Nair, R. B., Premalatha, C. K. and Kuriakose, B. Studies on copper salt of higher fatty acids from rubber seed oil as a peptizer for estimation of dirt content in technically specified natural rubber. *Indian Journal of Natural Rubber Research*, (In Press).

6. Joseph, R., Alex, R., Premalatha, C. K. and Kuriakose, B. Use of epoxidised rubber seed oil as a coupling agent and plasticizer in silica filled natural rubber compounds. *Journal of Applied Polymer Science*, (In Press).

7. Joseph, R, Madhusoodhanan, K. N., Alex, R., Varghese,S., George, K. E., and Kuriakose, B. Studies on epoxidized rubber seed oil as a secondary plasticizer/stabilizer for polyvinyl chloride. *Plastics, Rubber and Composites*, (communicated).

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