MOLECULAR BREAKDOWN OF DIFFERENT FORMS OF NATURAL RUBBER AND ITS INFLUENCE ON PROPERTIES OF THEIR MIXES AND VULCANIZATES

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CERTIFICATE

Certified that the thesis entitled "Molecular breakdown of different forms of natural rubber and its influence on properties of their mixes and vulcanizates", being submitted by Mr. K.T. Thomas, M.Sc, M.Tech, LPRI, for the degree of **Doctor of Philosophy** to the Cochin University of Science and Technology, is a record of bonafide research work carried out by him under my supervision and guidance.

Mr. Thomas has worked on this research problem for about seven years. The results included in this thesis have not been submitted for the award of any other degree or diploma. It is also certified that Mr. Thomas has fulfilled the necessary requirements for submission and has passed the qualifying examination.

N.M. Mathew.

DECLARATION

I hereby declare that the thesis entitled *"Molecular Breakdown of different forms of Natural Rubber and its influence on Properties of their Mixes and Vulcanizates"* is the original work carried out by me under the supervision of Dr. N.M. Mathew, Joint Director, Rubber Research Institute of India, Kottayam-686009, and no part of this thesis has been presented for any other degree from any other institution.

Kottayam - 686 009 **K.T. Thomas**

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LIST OF ABBREVIATIONS

Rubbers

EBC - Estate brown crepe
ENR - Epoxidised natural rubber
ISNR - Indian standard natural rubber
NR - Natural rubber
PLC - Pale latex crepe
RSS - Ribbed smoked sheet
SMR - Standard Malaysian Rubber
TSR - Technically specified rubber

Additives

CBS - N-Cyclohexyl-2 benzthiazyl sulphenamide
DDDS - 2, 2′ dibenzamido diphenyl disulphide
DPG - Diphenyl guanidine
HAF - High abrasion furnace
MBT - 2-Mercapto benzo thiazole
PCTP - Pentachlorothio phenol
PNP - Para nitro phenol

Other Abbreviations

ASTM - American Society for Testing and Materials
BI - Breakdown index
BIS - Bureau of Indian Standards.
CV - Coefficient of Variation
DC - Dry Coagulum
DRC - Dry Rubber Content
DM - Desirability Measure
d_c - Diameter of the capillary die
d_e - Diameter of the extrudate
E - Energy of activation
EB - Elongation at break
FC - Fresh Coagulum
h - Hour
IR - Infrared
kJ/mol - kilo Joules/mol
M - torque
$\bar{M}_n$ - Number average molecular weight
$\bar{M}_w$ - Weight average molecular weight
MWD - Molecular weight distribution

Nm - Newton meter
Nm-min - Newton meter-minute
phr - parts per hundred rubber
R - Universal gas constant
rpm - revolutions per minute
S - Rotar speed
s^{-1} - per second
T - Temperature (absolute)
T_g - Glass transition temperature
T_m - Melting temperature
TS - Tensile strength
TTQ - Totalised torque
UTM - Universal Testing Machine
W - Energy required for mastication

LIST OF SYMBOLS

$\dot{\gamma}_w$ - True shear rate at the wall
τ_w - True shear stress at the wall
η - Shear viscosity
n' - flow behaviour index
ΔP - Pressure drop
Po - Wallace plasticity
ΔPo - Change in Wallace plasticity
ΔM - Change in torque

CHAPTER I

INTRODUCTION

"No single species of plant has in the short span of hundred years, so utterly altered life styles around the globe as *Hevea brasiliensis*". This statement by Richard. E. Shultz holds its credibility rather by the enormous number of products that are being made out of natural rubber. From 'eraser' to 'giant tyres', the range of products that can be made available from the same is very broad. The history of the survival and domination of natural rubber is an inspiring example of an environmentally desirable material prospering in the face of competition from synthetic counterparts

AN INTRODUCTION TO RUBBER INDUSTRY

The earliest reference about rubber appeared in print in the Spanish book 'De Orbe novo' in 1612. (1) Francois Fresneau and Charles de la Condamine deserve the honour of bringing out the rubber tree, *Hevea brasiliensis* to the attention of the scientific community in Europe. In 1775, Condamine published a paper that was entirely devoted to rubber based on information provided by Fresneau.

The most spectacular event in the history of natural rubber was the successful transfer of *Hevea* from the Brazilian area around the Amazon and the subsequent establishment of commercial plantations in tropical Asia and Africa. Royal Botanical Garden, Kew, England played a decisive role in this complex domestication process. It was from there that the *Hevea* seeds brought from Brazil by Henry Wickham were germinated and the seedlings distributed.

EARLY DEVELOPMENT IN TECHNOLOGY

Rectified turpentine was offered as a satisfactory solvent for rubber in 1763 by French chemists L.A.P. Herissant and P.J. Macquer. (2) This was followed by a patent from Samuel Peal in 1791, for water proofing of fabrics using rubber solution. But the real pioneers of rubber industry were Thomas Hancock and Charles Goodyear. The first major discovery of Hancock in 1819 was the process of mastication of raw rubber. By 1824 he has developed the use of fillers, compression moulding at higher temperature, solution dipping, spreading and impregnation of woven and non-woven fabrics. A wide range of applications were envisaged utilising masticated rubber. But these products proved inadequate and unsatisfactory as the unvulcanised rubber softened in summer and became brittle in winter. This ultimately resulted in loss of confidence in rubber products and the subsequent closure of many factories.

However, the discovery of vulcanisation by Charles Goodyear in 1839 has regenerated the hope and aspirations of those who were interested in rubber as a potential industrial raw material.

The first pneumatic tyre was invented in 1845 by R.W.Thompson, but it never achieved commercial success. It was John Boyd Dunlop, who reinvented the pneumatic tyre in 1885 and patented it. John Perkins (1899) had discovered the process of making smoked sheets, by coagulation of latex with acid.

A number of innovations had been evolved since the beginning of this century which, in turn, had contributed to the upgradation of the quality of rubber products. A few of them are listed below.

1904 - Use of carbon black as a reinforcing filler
1919 - Antioxidants
1937 - Accelerators
1941 - Injection moulding
1946 - Radial tyres
1958 - Antiozonants
1960 - Thermoplastic elastomers
1965 - Technically specified rubber

CULTIVATION OF RUBBER

Natural rubber, has been found in the latex of over 2000 species of plants belonging to 311 genera and 79 families. (3) The *Hevea* family itself contains 11 types of plants yielding latex. However, *Hevea brasiliensis* is the most important commercial source of natural rubber. The latex from other species have higher resin content and different coagulation characteristics. (4)

The rubber tree is sturdy, quick growing and tall. It grows in many types of soils, provided the soils are deep and well drained.

A warm humid equable climate (21°C to 35°C) and a fairly distributed annual rainfall of not less than 200 cms. are necessary for the optimum growth of this plant. Rubber trees have a well developed tap root and laterals. The cambium, in between the wood and the bark is responsible for the increase in girth of the tree, including bark renewal. *Hevea* trees are exploited for a period of 20-23 years from the commencement of tapping. The propagation is carried out either by seeds or by budgrafting, the latter being more popular. Tissue culture propagation of rubber clones is also being attempted.

Latex is obtained from the bark of the tree by tapping. Tapping is a process of controlled wounding, during which thin shavings of bark are removed. The aim of tapping is to cut open the latex vessels in the case of trees tapped for the first time or to remove the coagulum which blocks the cut ends of the latex vessels in case of tree under regular tapping. The tapping cut of the trees should have a slope of about 25°-30°. The latex vessels in the bark run at an angle of 3-5°, to the right and therefore, a cut from high left to low right will open larger number of latex vessels.

When the tree is tapped and the vessel is cut the pressure at the location of the cut is released and the viscous latex exudes. This exudation of latex would result in the displacement of latex along the length of the latex vessel owing to strong forces of cohesion existing in the liquid phase. This would result in fall of pressure in the vessels leading to entry of water from the surrounding tissues which makes the latex more dilute. The dilution would make the latex less viscous resulting in enhanced flow. But subsequently disturbances in osmotic concentration in latex vessel would cause damage of lutoid particles culminating in the plugging process. This ultimately would block the cut ends of the latex vessels and thus the latex flow would cease. (5)

LATEX

Latex is a weak lyophilic colloidal system of spherical or pear shaped rubber globules suspended in an aqueous serum. The rubber globule is surrounded by a protective layer of proteins and phospholipids which impart the lyophylic colloidal nature to latex and the stability of latex is mainly due to the negative charge present on the protective layer. Also it contains a variety of non-rubber constituents both organic and inorganic, in addition to rubber. The proportion of these constituents may vary with clones, nutrition, climate etc. But in general, the composition of latex is as follows.

Rubber - 30-40%
Proteins - 2-2.5%
Ash - 0.7-0.9%
Resins - 1-2.0%
Sugars - 1-1.5%
Water - 55-60%

Fresh latex, as it comes out of the tree, is slightly alkaline or neutral. It becomes acidic rapidly due to bacterial action. The formation of organic acids neutralises the negative charge on rubber particles and the latex gradually gets coagulated on keeping. Intensive tapping reduces the rubber content in latex. It may be as low as 20 or 25 per cent.

CROP COLLECTION

The main crop from rubber plantation consists of latex and field coagulum. The proportion of these materials varies depending on the tapping system followed, climatic conditions, stability of latex, stimulant application, age of the tree etc. On an average it is observed that the proportion of latex and field coagulum is in the range of 80 to 85per cent and 15 to 20per cent respectively. While latex can be processed and marketed in any one of the forms such as latex concentrate, ribbed smoked sheet, technically specified rubber, crepe rubber, or chemically modified rubber, field coagulum is processed and marketed as either technically specified rubber or crepe rubber.

Whichever is the method adopted for processing the latex, it is to be preserved adequately, so as to prevent precoagulation in the field and also during various processing operations. The scrap collected as cup coagulum, (cup lump), tree lace or earth scrap.

DIFFERENT TYPES OF RAW RUBBER

The main marketable forms of dry natural rubber are ribbed smoked sheet (RSS), estate brown crepe (EBC), and technically specified rubber (TSR). However, other forms like skim rubber also find application in the industry especially because of its lower price and better colour.⁽⁶⁾ Chemically modified forms of natural rubber have been introduced to improve the properties of the same. Epoxidised natural rubber (ENR) is one of the most important among them.

RIBBED SMOKED SHEET

Converting natural rubber latex into ribbed smoked sheet (RSS) is the oldest method of processing. This method is widely adopted by rubber growers because of its simplicity, lower cost of processing and the viability even if the quantity of latex is small. Latex intended for processing into RSS is treated with any one of the short term preservatives (anticoagulants) such as sodium sulphite, formalin or ammonia, if it shows a tendency for precoagulation. A combination of formalin and sodium meta silicate is reported to be an ideal anticoagulant system for latex to be processed into RSS.(7) At the collection centre, latex is initially sieved through 40 and 60 mesh sieves to remove suspended impurities. Since the quantity of chemicals required for processing latex into RSS is based on its DRC, a quick estimate of the same is made, usually by the hydrometric method. Latex from different fields is blended to make sheets of uniform quality. The bulked latex is diluted to a DRC of 12.5per cent, by adding water, to improve the quality of the sheets produced. Dilution helps in settling denser and finer impurities at a faster rate and in obtaining a softer coagulum which can be easily sheeted. It also helps faster drying of sheets.(8) On allowing the diluted latex to remain undisturbed for about 10-15 minutes, the denser impurities settle fast and the latex is transferred to another tank, without disturbing the sediments. Sodium bisulphite and paranitrophenol are added to latex at this stage, if found necessary.

Sodium bisulphite is added to prevent discolouration of the coagulum, caused by enzymes of the polyphenol oxidase type. Phenols and aminophenols present in latex combine with oxygen from the air to form orthoquinones, which react with naturally occurring amino acids and proteins in latex, to give coloured products resembling melanin. (9) The enzymes are believed to catalyse the above reactions and sodium bi suphite prevents the discolouration by preferentially getting itself reacted with atmospheric oxygen. About 1.2 g of sodium bisulphite is normally found to give satisfactory protection for latex containing 1kg dry rubber. It is added as 20per cent solution. Use of excess quantity of the above may lead to slow drying of sheets since the excess chemical which remains on the surface of the coagulum gets converted into sodium bisulphate which is hygroscopic in nature. To prevent mould growth on the surface of the sheets, the wet sheets are dipped in a 0.1per cent solution of paranitrophenol for a few minutes before dripping and drying.[10]

The diluted latex is coagulated in pans, troughs or tanks. Coagulation pans are usually made of aluminium, while the tanks may be of aluminium or masonry which is lined inside with aluminium or glazed tiles. Solutions of volatile acids such as acetic and formic acids at low concentrations are used for coagulating latex. Such weak acids provide uniform coagulation and excess acid if any, gets volatilized off during drying. The pH of coagulation is maintained at about 4.6 to get complete recovery of rubber to avoid fermentation of latex and to get a soft coagulum. It was reported that dilute sulphuric acid also can be used as a coagulant in sheet rubber production. However, Neef (1950) reported that rubber coagulated with excess of sulphuric acid showed considerable softening when it was heated at 140°C for 3h More recent studies indicated that sulphuric acid can be used as coagulant for NR latex in sheet rubber production, if all conditions such as dosage, dilution, washing of sheets and machinery are properly taken care of. (11) Another nonvolatile acid that is recommended for latex coagulation is sulphamic acid. Use of optimum dosage and proper washing of the coagulum during sheeting to remove residual acid were reported to yield good quality sheets when this chemical is used. (12)

Latex coagulum is sheeted after maturation. Sheeting operation squeezes out serum present in the coagulum and reduces its thickness to about 3mm. This is done by passing the coagulum through a set of hand operated plane rollers, followed by one pass through a pair of grooved rollers on which the grooves are spirally cut at an angle of 45° and 3 to 5mm width and depth. The ribbed design helps to increase the surface area of the sheet for faster drying and also minimise sticking between the dried sheets. A sheeting battery consists of four or five sets of plane rollers and one set of grooved rollers arranged in a row with their nip gap progressively reduced. Uniformity and softness of the coagulum are the two important parameters that affect the efficiency of the sheeting battery.(13) The rollers are driven by electric motor. The coagulum is washed thoroughly during sheeting to remove the serum and residual chemicals. In case where paranitrophenol has not been added to the latex, the washed sheets are dipped in a 0.1 per cent solution of PNP for about 10-15 minutes.

The sheets can be dried in a smoke house or hot air chamber. Partial drying in sunlight followed by smoke drying is also widely practised. It has been reported that upto a moisture level of 10 per cent, syneresis is the main process of water removal and drying below this level is diffusion controlled. (14) The sheeted coagulum is allowed to drip off the water emerging due to syneresis, before it is fed into a smoke house. Several types of smoke houses such as those with furnace inside or outside the drying chamber, batch or continuous type are in operation. The RRIM tunnel type smoke houses meet almost all the requirements of an ideal smoke house. In this type of smoke house, the furnace is outside the drying chamber and smoke and hot air are led into the chamber through underground flue inlets. The temperature of smoke house is maintained at 50°C - 60°C by adjusting the flue outlets, furnace door apertures, roof ventilators and air inlets on the furnace door. (15)

The sheets are put on reapers placed on trolleys which moved on a central rail track inside the chamber. The dried sheets can be usually taken out after four days.

Use of solar energy to dry sheet rubber has been attempted in many ways. Direct exposure of wet sheets to sunlight did not affect the dynamic properties of dried sheets. However, exposure of dried sheets to sun may adversely affect the properties. (16) Experiments with smoke houses fitted with solar panels showed that there could be a saving of about 50 to 60 per cent firewood by using solar energy .(17) In such smoke houses, the main drying process occurs with the help of hot air generated by flat plate solar collectors and firewood is used only as a back-up heat source to maintain the temperature of the drying chamber during night.

The dried sheets are visually examined and graded, adopting the norms prescribed by the International Rubber Quality and Packing Committee under the secretariat of the Rubber Manufacturers Association Incorporated, USA and which are described in the 'Green Book'. The six grades available are RSSIX, RSS1, RSS2, RSS3, RSS4, and RSS5. The important parameters considered in grading the sheets are degree of dryness, presence of foreign matter, virgin rubber, oxidised spot, blisters, bubbles, resinous matter, transparency, colour, tackiness, over smoking, mould growth, dark or coloured spots etc.

CREPE RUBBERS

When coagulum from latex or any form of field coagulum or RSS cuttings, after necessary preliminary treatments, is passed through a set of creeping machines, crinkly, lace -like rubber is obtained. This, when dried, is called crepe rubber. There are 29 grades of crepe rubber, contained in six different types which are described in the 'Green Book'. However, based on raw material used, crepe rubbers can be grouped into two, namely latex crepes and those produced from field coagulum. The crepes prepared from field coagulum materials fall into five types, estate brown crepe (EBC), thin brown crepes or remilled crepes, thick blanket crepes, flat bark crepes and smoked blanket crepes. For low quality crepes, field coagula such as cup lump, tree lace, shell scrap, earth scrap, bark scrap etc., and cuttings and rejections of pale latex crepe, smoked and unsmoked sheets are made use of. The manufacturing procedure depends on the type of raw material used and the grade of the crepe to be produced. However, for all the grades, steps such as sorting of the coagulum, precleaning, maceration, remilling, refining etc., are involved. The quality of the final product depends to a large extent, on the quality of the raw material, the number of passes through each machine and on the extent of washing given at each stage. The lower grade crepes are dried in drying sheds at ambient temperature. Crepe rubber produced from tree lace is of inferior quality compared with that from cup lump, since tree lace undergoes severe degradation on storage. (18)

With the advent of technically specified rubber, production of lower grade crepes has come down drastically . But the latex grade, namely pale latex crepe (PLC) and sole crepe are preferred to even the best quality TSR, in some applications such as pharmaceutical and food contact products, electrical insulation, rubber solution and cements etc., because of their higher purity and lighter colour. (19)

PALE LATEX CREPE AND SOLE CREPE

These are manufactured from latex under strictly controlled conditions, Morris (20) and Peries (9) described detailed procedure for their manufacture. The ideal latex, for PLC and sole crepe production should have a lower concentration of yellow colouring matter and one which yields rubber having a higher Mooney viscosity. Considering the above factors, latex from the clone PB86 is found to be most suitable for PLC production.

For removing the yellow colouring matter, fractional coagulation or bleaching method or a combination of these two is usually followed. For fractional coagulation, about 20per cent of the acetic acid or oxalic acid required for complete coagulation is stirred well into the latex until small clots of coagulum containing the yellow pigment are formed. After removing the coagulum the remaining latex is coagulated using formic acid or oxalic acid. The bleaching process consists of treating the latex with certain mercaptans which preferentially react with the colouring matter. The bleaching action of the above chemicals is reported to be effected through oxidation of xanthophyll and other oxygenated forms of carotene. (21) The bleached latex is coagulated using formic acid or oxalic acid. The coagulum obtained in either process is passed through a set of machinery consisting of macerators, crepers and smooth rollers. The thickness of crepe coming out from the plane rollers is adjusted between 0.8 to 1.0mm. Drying of the crepe is done in sheds maintained at a temperature of 32-35°C. Dried latex crepes are examined for defects and the selected grades are laminated to produce sole crepe of the required dimensions. Grading of pale latex crepe is done as per the standards specified in the 'Green Book'.

TECHNICALLY SPECIFIED RUBBER

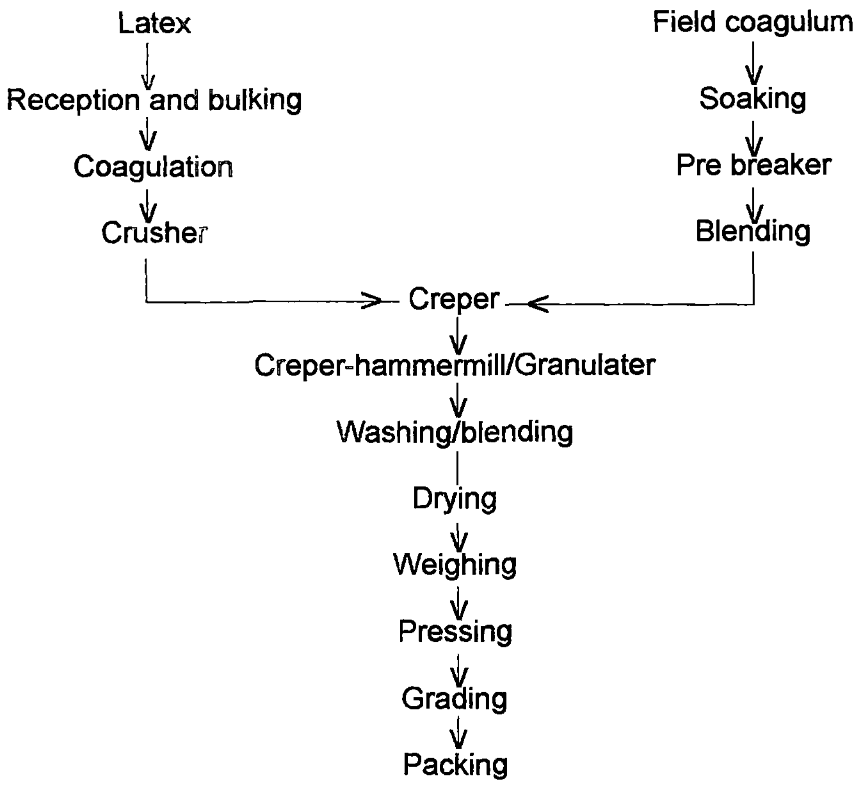
The main shortcomings of the above conventional forms of natural rubber are:

1. Multiplicity of grades, posing problems to the consumer.
2. Non-availability of technical information on quality of rubber.
3. Poor presentation of rubber in large bare back bales prone to contamination.

Hence attempts were made to evolve better methods of processing and grading based on technical parameters.(22) Parameters that could provide a satisfactory indication of the quality of NR were identified.(23) NR in technically specified form was first introduced in 1962 by the *SOCFIN* group of companies in Ivory Coast. But wider consumer acceptance to this new form was received only after the introduction of the Standard Malaysian Rubber (SMR) scheme in 1965.

The major advantages of TSR are claimed to be its improved consistency in properties and the availability of different grades to suit individual requirements of the end user.(24) This new method enabled NR producers to process both latex and field coagulum, using almost the same set of machinery. Also the processing time is reduced to less than 24h The production of TSR involves a series of unit operations which may vary slightly depending upon whether latex or field coagulum is used as the starting material.

The steps involved in the production of TSR can be generalised as given below.



Crumbs of coagulum may be prepared by purely mechanical means(25) or by a mechanochemical process. Among different processes for production of TSR, those which have received commercial acceptance are (i) Dynat process (ii) Decan remill process (iii) Hevea-crumb process.

Dynat process

This method of processing involves four machines i.e., a rotary cutter, pelletiser, drier and baling press. When field coagulum is processed a rotary cutter with a perforated screen is employed for initial size reduction.(26) The pelletiser operates by a process of extrusion and cutting. The washed crumbs are dried in a vertical semi-continuous drier. A lower temperature (60-65°C) with high humidity at the feeding point and a higher temperature (90-93°C) and low humidity at the discharge point of the drier are maintained.

Decan remill process

The above process consists of coagulating latex in cylindrical tubes, veneering, calendering and granulating the coagulum to produce fine crumbs.(27) Coagulation is done by assisted biological method. For processing the field coagulum granulators and hammer-mills are used. Rapid drying is achieved by adjusting flow rate, humidity and temperature of the air passed through a bed of crumbs.

Heaveacrumb process

This process was developed and patented by the Rubber Research Institute of Malaysia and involves addition of a small quantity of castor oil either in latex stage or during processing of the coagulum.(28) The advantage of this method is that even conventional machinery such as creper can be used for producing crumbs. Polypropylene glycol of low molecular weight was reported to be an effective alternative to castor oil.(29)

During the last two decades many processing units have been established in India for the production of TSR, and the total production of the same during 1995-96 was 34650 metric tonnes.

In India TSR is generally marketed in conformity with the specifications laid down by the Bureau of Indian Standards under the general name Indian Standard Natural Rubber (ISNR).

SKIM RUBBER

Skim rubber is obtained by the coagulation of the secondary fraction of natural rubber latex, during centrifugal concentration process. Skim latex has a low DRC (5-10%) and a higher proportion of non-rubber constituents. It is usually coagulated using sulphuric acid. The coagulum is thoroughly washed and processed into crepe rubber. The rubber particles in skim are relatively smaller in size and have most of the proteins adsorbed on to them. The inferior quality of skim rubber could be attributed to many factors. The inconsistency of the material with respect to its raw rubber properties contributed significantly to its poor reputation.(30) It leads to scorchy cure and poor ageing properties.(31)

Many attempts have been made to upgrade the quality of skim rubber. Enzymic deproteinisation of skim latex using trypsin, followed by coagulation was reported to improve its quality.(32)Creaming of skim latex using tamarind seed powder followed by coagulation also improves the quality of skim rubber.(33) Skim rubber obtained by microbial fermentation is having better properties compared to those of rubber recovered by calcium chloride treatment.(34) Rubber having better properties could be produced from skim latex by following the process described by Ong.(35) In this process, skim latex is treated with sodium metabisulphite (0.04% on DRC) before acid coagulation. The coagulum is soaked in 3per cent sodium hydroxide solution, washed and then soaked in dilute sulphuric acid solution. It is then washed and treated with a composite solution consisting of thiourea and oxalic acid.

Despite the potentially adverse features, skim rubber has always been favoured by many consumers. It has a low dirt content, often accompanied by light colour and has a relatively low price. Blending of skim rubber with normal grades of natural rubber is an obvious approach in offsetting the adverse features of skim. However, skim rubber was excluded from the 'Green Book' - the International Standards of Quality and Packing for Natural Rubber Grades.

Skim rubber differs most obviously from normal natural rubber in respect of the levels of fatty acid and protein content. Either or both of these could be responsible for the abnormal cure behaviour of the same. The bound protein may act as a reinforcing agent to produce high modulus vulcanizates from skim rubber.(36)

The composition of skim rubber varies with the type of centrifuge, the speed of centrifuging, the efficiency of the process and estate practices adopted. Many serum materials such as proteins have a higher specific gravity than rubber and migrate to skim fraction during centrifuging.

Because of its low DRC and high ammonia and non-rubber contents, it is difficult to coagulate skim latex into a coherent coagulum. The usual coagulant is sulphuric acid, but calcium chloride, formic acid and spontaneous coagulation are also employed. The coagulum is machined into crepe, and the appearance of the same is similar to that of EBC.

The main characteristics of skim rubber are outlined below. (37)

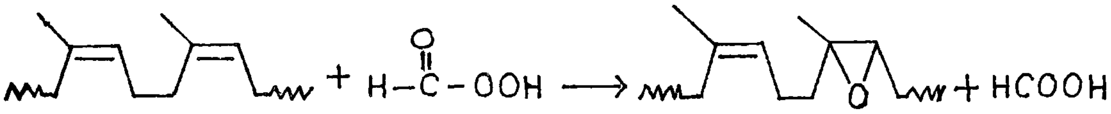
1. Colour : Light
2. Dirt content : Very low
3. Non-rubber content : Up to 30 per cent

4. Copper content : 4-20 ppm
5. Acetone extract : 3-5 per cent
6. Mill breakdown : Normal
7. Power consumption : Slightly higher
8. Mill shrinkage : Less than normal
9. Cure rate : Fast, giving scorchy compounds
10. Hardness of vulcanizate : Higher
11. Modulus : Higher
12. Resilience : Lower
13. Ageing behaviour : Variable

EPOXIDISED NATURAL RUBBER (ENR)

The mechanical properties of natural rubber (NR) are generally superior to those of many synthetic elastomers. However, NR cannot compete with speciality synthetic rubbers such as butyl and nitrile rubbers with regard to gas permeability and oil resistance.

Chemical modification of NR has been studied earlier by many workers. The objectives of modifications were either to change the properties of the polymer or as a route to other useful innovative concepts such as bound antioxidants.(38) The epoxidation reaction was known to be applicable to NR earlier.(39-40) It was chosen as an alternative route for modification which could be carried out at the latex stage.



Epoxidation of natural rubber.

The reaction is to be carried out under suitably controlled conditions. Otherwise, several side reactions could take place which may alter the properties of the rubber drastically.(41) Two reagents that are used for epoxidation of NR latex are peroxy acetic acid and performic acid formed *insitu* by the reaction between formic acid and hydrogen peroxide. Two grades viz, ENR-25 and ENR-50 with 25 and 50 mole per cent epoxidation respectively have assumed commercial importance.

Epoxidation of natural rubber results in a systematic increase in polarity and glass transition temperature which are reflected in the properties of ENR vulcanizates. For every mole per cent epoxidation, the glass transition temperature (Tg) increases by approximately 1°C(42) Thus ENR 25 and ENR 50 exhibit glass transition temperatures of -48°C and -23°C respectively. The stereoregularity of ENR is reflected in the high strength properties of gum vulcanizates. ENR, like natural rubber, undergoes strain crystallization and this has been confirmed by X-ray diffraction studies.(43)

The increase in polarity on epoxidation results in a marked increase in resistance to hydrocarbon oils. Epoxidation also alters the compatibility with other polymers and results in a decrease in the rate of air permeation. It is also reflected in an increase in damping properties at ambient temperature.

However, the relatively high glass transition temperature of ENR-50 can lead to low-temperature stiffening problems, which can be minimised to some extent by addition of plasticisers.

The ageing properties of ENR, as with other unsaturated polymers, are relatively poor where sulphur crosslinking system is employed. The best ageing resistance is obtained with efficient vulcanizing (EV) or sulphur less formulations. On ageing ENR-50 vulcanizates harden with a subsequent increase in modulus, reduction in elongation at break and eventually a loss of tensile strength. This hardening is associated with a different oxidation mechanism to that operating with natural rubber. (44)

With ENR-50 the main site of oxygen attack is the sulphur crosslinks which are oxidised to sulphur acids. These acids attack epoxide groups resulting in ringopening and crosslinking reactions. However, these acids can be neutralised by the inclusion of a base in the formulation.

Wet grip, wear and rolling resistance of ENR suggest that the same could be used in tyre tread. The low air permeability properties of ENR-50 can be utilised in tyre inner tubes. Also blends of ENR-50 and NR were found to give comparable air retention properties to that of chlorobutyl/ENR blends. Apart from tyres, ENR may find application in other fields such as flooring materials and sports shoe soling compounds due to high wet grip properties. ENR-50 is also being utilized as a cover compound for PVC conveyor belting, due to its high adhesion to PVC.

MOLECULAR PARAMETERS OF NR

Molecular weight

The molecular weight of natural rubber can be expressed either as number average molecular weight, $\overline{M}n$ or weight average molecular, $\overline{M}w$. Normally $\overline{M}w > \overline{M}n$. The weight average molecular weight of natural rubber ranges from 300000 to about 10 million. The number average molecular weight $\overline{M}n$ involves measurement of colligative properties like osmotic pressure.(45) Light scattering method is useful for measurement of $\overline{M}w$ and molecular weight distribution. (MWD).(46)

A full characterization of a polymer like natural rubber requires determination of its molecular weight distribution (MWD). It has been proved by gel permeation chromatographic studies that the molecular weight distribution of unmasticated natural rubber is distinctly bimodal.(47) The various grades of NR show differences in molecular weight and its distribution. Clonal variations are also observed to affect the molecular weight distribution of NR though the range of molecular weight is nearly the same for all the clones.(48) However, the mean values and the shapes of the MWD curves are different. Storage hardening tends to change the shape of the molecular weight distribution curve from bimodal to unimodal and $\bar{M}w$ slightly.

Gel content

Gel refers to the proportion that remains undissolved when rubber is immersed in a solvent. The gel structure in natural rubber is complex.(49) It consists of the more highly branched and highly crosslinked components of the rubber closely intertwined with insoluble high molecular non-rubber substances like proteins. The increase in gel content during storage is responsible for hardening of rubber.(50) The gel phase thus observed in solid or latex rubber which underwent prolonged storage is known as macrogel. The crosslinked fraction in *Hevea* latex is termed as microgel. It is formed in the latex present within the vessels of the tree.(51)

Chain branching

The presence of non-isoprene groups leads to formation of branched chains. The existence of the same in natural rubber has been proved through dilute solution viscometry.(52) The rheological properties of NR are strongly influenced by long chain branching. It has been suggested as a factor explaining the slow rate of stress relaxation of *Hevea* rubber compared to guayule and synthetic polyisoprene.(53)

Storage hardening

Natural rubber develops higher hardness during storage. The hardening process is accelerated by low relative humidity and higher temperature of storage. The mechanism of storage hardening is known to involve carbonyl groups in rubber. The amino acids present among the non-rubber constituents are also believed to be playing a role in the hardening reaction.(54)

Low temperature crystallization

The maximum rate of crystallization occurs at about -24°C, and it requires approximately 8 h to complete the process of crystallization. However, natural rubber freezes even at 0°C, if the exposure time is sufficiently long.[55] When natural rubber is stretched beyond 300 per cent, crystallization becomes rapid. This phenomenon, known as strain induced crystallization contribute to the high green strength of NR.

Melting temperature

The temperature at which the last traces of crystallinity disappear is usually described as melting temperature (Tm). The melting temperature depends markedly on the temperature at which crystallization occurs. The melting temperature of NR has been assigned a value of 28°C, though values slightly above the same have been reported. This has been explained in terms of some degree of orientation in amorphous rubber prior to crystallization.(56)

Transition temperature

All polymeric materials at some temperature, undergo a glass transition from a glassy to a rubbery state.The Tg should be below the temperature of application if the rubber is to have any practical utility. The Tg of NR was established as -72°C by specific volume measurements. Many factors have to be considered in association with the transitions which have been reported in detail by Boyer.(57)

Rheological properties

Flow measurements using Wallace rapid plastimeter and Mooney viscometer, suffer from two main disadvantages. They are capable of operating only at one rate of shear. Also the rate of shear imparted by the above items of equipment is far less than those typical of modern rubber processing equipment.(58) This led to the development of capillary rheometers which are being extensively used to extend measurements to higher shear rates (10^3 S^{-1}). There are many reports on the capillary flow behaviour of raw and filled NR stocks.(59-61) It has been shown that samples of different grades with similar Mooney viscosity exhibited significantly different flow behaviour.(62)

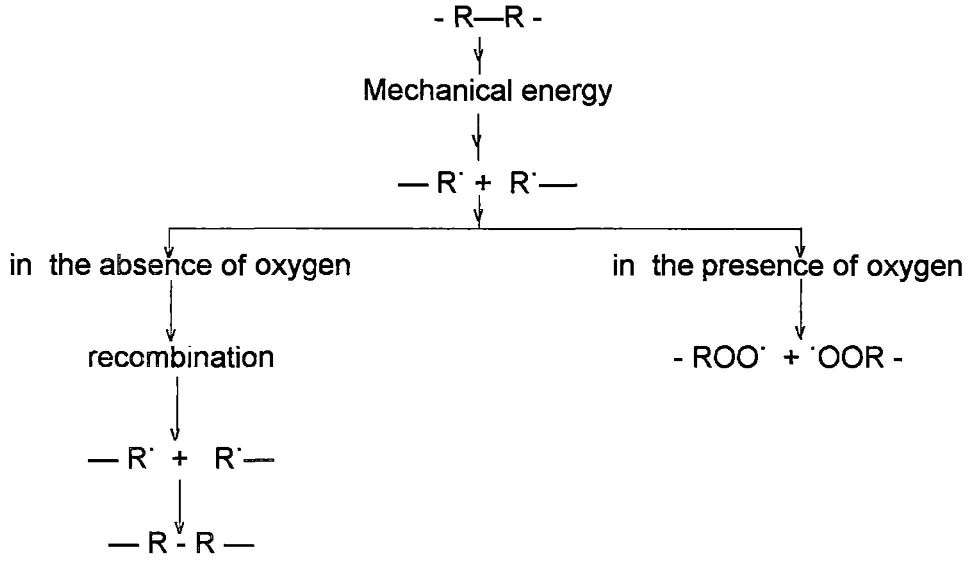
SECONDARY PROCESSING

Appropriate classification of raw materials and prediction of their processability play an important role in the control of any manufacturing process. Rubber being a high polymer, properties of mixes and vulcanizates prepared from it depend very much upon the length of the polymer chain. The extent of molecular breakdown imparted to rubber, during the above manufacturing operations has a significant influence on these properties.

Mastication

Mastication is an important step in the manufacture of natural rubber compounds. It decreases the viscosity of rubber, promotes good dispersion of fillers and chemicals and improves compound plasticity. This facilitates improved processing. Rheological properties such as die swell, shrinkage and building tack are improved by mastication.It was Staudinger who first demonstrated that mastication caused degradation of molecular chains.[63] The dependence of the efficiency of mastication on temperature has been studied by many authors.(64) The significance of the presence of oxygen during mastication was proved by trials conducted in inert atmosphere of nitrogen or carbon dioxide. (65-66)

During mastication at lower temperature, the molecules are being ruptured by shearing forces, which can be represented as



Principle of mastication of rubber.

Pike and Ayrey provided evidence for the mechano-chemical aspect of degradation during cold mastication.(67-68) At lower temperature, the viscosity of the rubber is high and greater work is done on it during mastication. The energy of deformation is distributed unequally among chemical bonds of the polymer chains and could be concentrated locally on a few of them, because of the long chain structure of the rubber molecules.

Mastication at higher temperature, designated as thermo-oxidative mastication is an oxidation reaction and it has a positive temperature coefficient. The mastication effect under such as situation increases with increasing temperature. The energy consumption in this process is relatively low due to the low viscosity of the elastomer.

Peptisers

The thermo-oxidative breakdown of rubber is promoted by certain chemicals known as peptisers. They are effective as radical acceptors at lower temperatures in the absence of oxygen and as promoters of oxidative breakdown through formation of primary radicals at higher temperature. Peptisers also shift the start of the thermo-oxidative reaction to lower temperatures.

Of many substances used as peptising agents, only combinations of activators with thiophenols, aromatic disulphides and mixtures of salts of saturated fatty acids are currently used. Peptisers are reported to be added to natural rubber latex to reduce the viscosity of the rubber dried at temperatures above 100°C.(69)

The efficiency of mastication decreases with increasing temperature, until thermo-oxidative reaction begins above 130°C. For this reason, peptising agents are usually used either at as low a temperature as possible or at a temperature above 130°C in internal mixers. The efficiency of mastication is reported to be minimum around 100°C.[70]

Mastication on a mixing equipment can be integrated with the mixing process, as modern peptising agents do not lose their effect by addition of compounding ingredients such as fillers, plasticisers, zinc oxide, and stearic acid. Accelerators and antioxidants have limited influence on the process of mastication.(71-73)

Mastication in internal mixers is almost exclusively performed with peptising agents. As the temperature inside the mixing chamber may increase up to 160°C, lower levels of peptising agents (about 0.1phr to 0.2phr) are sufficient to bring about the desired degree of degradation.

Peptising agents that contain activators have a slight influence on ageing properties of the vulcanizate.(74) This effect was more pronounced with increased amount of activator present in the peptiser. The antioxidants added during compounding can nullify this effect to a large extent.

Mixing

The important mixing devices used in rubber industry are the two-roll open mill and the internal mixer. Kneaders and continuous mixers also have their share in the industry.

Two-roll mixing mill

For effective mixing and homogenization, a bank of the material must be formed above the nip. This reservoir of material ensures that the nip is adequately fed and effective shearing is done on the material. If the bank of material is too large, stationary volumes of material will form with no shearing action imparted. The rolls of a mill act upon a thin flowing wedge of material which is simultaneously compressed and forced to flow between the rolls.

The important advantages of an open roll mill are low-temperature running characteristics and versatility. It is a better option when the compound to be prepared is temperature-sensitive.

The dust hazards caused by two-roll mills have largely contributed to their disappearance from mixing department of large manufacturing units. However, they are still used as a secondary mixing device for incorporating the curatives.

Internal mixer

The mixing of rubber in an internal mixer is a complex operation, involving a number of different mechanisms and stages. These can be resolved into four basic processes.

1. Viscosity reduction
2. Incorporation
3. Distributive mixing
4. Dispersive mixing

Each of these can occur simultaneously and each can be the main rate determining process which will control the mixing time. The mixing time will depend on the type of the compound being mixed and the mixing condition.

During mastication, the viscosity and elasticity of rubber are reduced and the rubber can be caused to flow around additives, incorporating and encasing them in a matrix of rubber. Rubber can also penetrate the interstices between particles in the agglomerate.(75) Thus it becomes immobilised and is no longer available for flow, reducing the effective rubber content of the mix.(76) This may lead to increase in viscosity of the compound, which permits high forces to be applied to the particle - agglomerates and to cause their fracture. Due to the above phenomenon, the occluded rubber gets released, reducing the applied forces. If a rise in temperature accompanies mixing, the mix viscosity will decrease and the efficiency of dispersive mixing will decrease more rapidly.

The important factors which govern mixing in an internal mixer are the rotor speed, fill factor, ram pressure and batch temperature. Dispersive and distributive mixing generate conflicting requirements with respect to rotor speed. The rate of distributive mixing is a function of rotor speed, proceeding more rapidly as speed is increased. But to retain a high viscosity in rubber for dispersive mixing, it is desirable to run a mixer slowly, to minimise the rise in batch temperature.

Underfilling of the mixing chamber is essential for efficient mixing and fill factor in the range of 0.65-0.85 are generally used.(77) Very low fill factors are obviously uneconomic and excessively high fill factors result in material remaining idle and not taking part in the mixing process. As the fill factor increases the mode of mixing changes from exponential mixing to laminar mixing, with a consequent increase in the mixing time.

The force applied to the ram should ensure that materials charged into the mixer engage rapidly with rotors and be sufficient to prevent the subsequent upthrust of the batch from displacing it upwards. Such an action may produce a stagnant region similar to that resulting from an excessively high fill factor. A substantial reduction in ram pressure causes a radical drop in mixing efficiency.

Extrusion

Extruders are widely used in rubber industry in a variety of applications. It can be used as a shaping machine, as a in the case of dump extruders which accept the material from an internal mixer and give it a shape suitable for further operations. Mixing extruders or continuous mixers are used to incorporate and distribute particulate additives. They are also used to preform the rubber compound for subsequent operations.

Depending on the temperature of the feed stock, extruders may be categorised in two ways. Hot feed extruders have been used by the rubber industry where the feed stock is prewarmed in a prior operation. Usually a two roll mill is used for prewarming. Cold feed extruders handle the rubber compound at ambient temperature.

The major physical difference between hot and cold feed extruders lies in the length to diameter (L/D) ratio of the screw. In the case of hot feed extruders the function of the screw is merely to convey the rubber compound towards the head, because the preplasticisation of the compound is being carried out on a two-roll mill. But in the case of a cold feed extruder, the screw must input to the rubber all the mechanical work necessary to raise it to the desired temperature for smooth flow through the die. This requires screw of large L/D ratio.

Cold feed extruders have largely replaced hot feed types in production lines where good dimensional accuracy is required. But the capital cost and energy consumption of conventional cold feed extruders are very high compared to the hot feed types, which justifies the application of the latter still in the industry. (78)

Another type of extruder is the vented extruder. It is designed to extract trapped air, moisture and other volatile components from a mix, thus reducing the porosity resulting from their expansion during low pressure vulcanization. Vented extruders are also used for improving extrudate quality, even for sponge rubber.(79)

Extruder has the widest application in tyre manufacture, over seventy per cent of the rubber in a tyre being extruded. In twin-head extruders which is used for sheathing cables, the head is usually T-shaped. The wire which is to be sheathed is passed through the head at right angles to the line of the screw. By fitting a special head equipped with fine gauzes, supported by a strong perforated plate, the extruder may be used for straining raw rubber or rubber compound to remove foreign particulate matter from mixes.

Continuous mixers are devices for the incorporation of additives into rubber, followed by distributive and dispersive mixing. The distributive mixing is influenced strongly by the L/D ratio of the screw and the dispersive mixing by the size of the clearances between the dams and barrel.

Calendering

A calender is used for production of rubber sheet or rubber coated fabric of uniform thickness throughout its length and width. Many types of calenders are used. The production of rubber sheet or coated fabric of uniform dimensions both lengthwise and crosswise poses many technical problems. Calender bowls will deflect slightly due to their weight and further deflection results from the action of loading them with rubber compound. The conventional method to rectify the deflection of rolls is to impart a slightly convex profile to the upper roll and concave profile to the lower roll.(80) An improved method is to fit special bearings which permit the axis of the top roll to be moved slightly in relation to that of the middle, giving the effect of opening the nip at the roll ends more than at the centre.

There are two ways of coating fabrics, i.e.,by frictioning or by skim coating. The latter is the term used when a sheet of rubber is applied to a fabric surface by calender. Frictioning applies a film of rubber which penetrates the interstices of the fabric. It is always done on raw fabrics without any previous treatment other than drying. Skim coating is generally applied to fabrics which have been pretreated with a suitable adhesive.

Calender performance is dependent on a number of factors, such as feed stock temperature, size of the rolling bank at the nips, roll temperature, size of the calender and wind-off tension. Two forms of surface faults are generally identified, 'Crows feet', resulting from low temperature of the calender rolls or the feed stock and blisters resulting from excessive temperature of the above.

Moulding

Moulding operations are concerned with the sequential shaping and crosslinking of a rubber mix. Three main techniques adopted for moulding are compression moulding, transfer moulding, and injection moulding. In compression moulding, a rubber blank is made to flow to the shape of the mould cavity by the action of the mould closure. There are three types of compression mould, viz., straight or flash, positive and semi-positive. In straight type moulding the shape, size and positioning of the charge are very important. Positive or plunger type moulds prevent escape of rubber due to the long and narrow flow path and high pressures can be applied effectively to the rubber charge causing it to flow fully and consistently to the form of the mould cavity. Semi-positive moulds incorporate advantages of both straight and positive type moulds.

In transfer moulding, rubber flows from an auxiliary cavity into mould cavity through a narrow channel. It gives better dimensional accuracy. Also new and clean surfaces are generated on rubber, which is important in the case of rubber-to-metal bonded products. Lower unit manufacturing costs are possible with transfer moulding compared to compression moulding.

Injection moulding is best suited for production of thin walled articles with very short cure times. The main advantages of screw injection moulding over transfer moulding are the elimination of thixotropic effect and better control of heat history of the material.

MOLECULAR BREAKDOWN DURING DIFFERENT TYPES OF PROCESSING OPERATIONS

Different forms of natural rubber differ in their processing behaviour as these undergo different levels of physical and chemical treatments during the post-harvest operations and storage. A simple comparison of the mechanical energy input and drying temperature of different forms are given below.

Sl. No	Form of rubber	Starting material	Machinery	Temperature of drying
1.	Ribbed smoked sheet	Latex coagulum	Sheeting roller	50-60°C
2.	Pale latex crepe	Latex coagulum	Macerators and plane rollers	33-35°C
3.	Estate brown crepe	Field coagulum	Macerator, creper	Ambient temperature
4.	TSR	Latex coagulum	Macerator, creper, Hammer mill	100-105°C
	TSR	Field coagulum	Prebreaker, macerator, creper, hammer mill	95-100°C
5.	Skim crepe	Skim latex coagulum	Macerator, creper,	Ambient temperature

During processing, minimum mechanical energy is imparted to sheet rubber as the same is subjected to less number of passes on the sheeting rollers. Crepe rubbers are subjected to more number of passes on the macerator/creper. In the case of TSR, high shearing action of the hammer mills can reduce the plasticity to a greater extent.

The temperature of drying is also different for different forms as shown above. There is a practice among the small growers, to dry their sheets in the open sun. If the sheets are having thickness less than 3mm, drying can be achieved within 7-8 days in open sun alone. However, the thickness of the sheets produced in the small grower sector is usually higher than the above, and hence it may take more time to get them dried. Long exposure time in direct sunlight can cause deterioration of the sheet by ultraviolet rays.

The maximum temperature in the smoke house is around 60°C. If this is exceeded, the quality of the sheets can be affected. The crepe grades are dried usually at ambient temperatures. The inferior quality of certain grades of crepe can be attributed to the poor quality of the raw material. The drying temperature of the technically specified rubber are higher than the other forms, and hence chances for oxidation are higher. This is observed at least in the case of TSR grades which are being produced from field coagulum grades.

The rubber undergoes further breakdown during product manufacturing operations. The rubber industry operates with devices imparting shear stresses and shear rates over a wide range.

INFLUENCE OF MOLECULAR BREAKDOWN ON PROPERTIES

Investigations have already endorsed the fact that processing characteristics vary between different grades of natural rubber.(59,81) The quality and storage history of the raw material and the method of primary processing adopted may affect the rheological properties. (82-83) It can also affect the final properties of the vulcanizate.(84)

The influence of the method of coagulation and time of maturation of the coagulum on plasticity retention index and Mooney viscosity has been reported. (85) The temperature of drying of the rubber can also affect the processing properties. (86-87) Higher temperature of drying can increase the rate of oxidation, leading to chain scission.

Variability can also arise due to a progressive stiffening of raw rubber during storage. The hardening process is accelerated by low relative humidity and high temperature of storage. It involves carbonyl groups present on the main rubber chain and amino acids present among the non-rubber constituents.(88) Storage hardening can contribute to a reasonable extent to the flow properties of raw rubbers.(89,48) It could be prevented by blocking the carbonyl groups using suitable chemicals.

The duration and environment of storage of field coagulum on properties of the rubber, (especially crepe and TSR) is also important. The storage of field coagulum for longer periods in undesirable conditions may affect their properties adversely. Also the higher temperature of drying may affect PRI of field coagulum grades of TSR.

The rate of oxidation may vary depending on the atmosphere in the driers. The electrical driers are having an oxygen rich atmosphere than the diesel driers.

The extent of breakdown is higher during the secondary processing operations such as mastication and mixing, compared to those described above. The effect of variations in mastication and mixing procedure on vulcanizate properties have been reported. (90-91) Vulcanizates prepared from raw rubber subjected to varying degrees of low and high temperature mastication showed no significant effect attributable to the degree of mastication. Though peptisers can increase the rate of breakdown excessive levels of the same can affect the properties of the vulcanizates adversely. (92)

OBJECTIVES AND SCOPE OF THE PRESENT STUDY

Natural rubber is a high polymer. Its properties are highly dependent on its molecular weight and its distribution, gel content etc. Being a natural product these characteristics are highly influenced by factors such as the clone, age of the tree, soil characteristics and seasonal factors, tapping intensity, use of yield stimulants, processing conditions, storage etc. Therefore, the different forms of processed NR are highly variable with respect to its processability as the same is controlled very much by basic molecular parameters.

In order to make raw NR workable its molecular weight and gel content are usually reduced by mastication, a highly energy demanding operation. This operation has to be carefully controlled in order to prepare rubber mixes of improved quality. One of the most important disadvantages of NR is the variability in its mastication behaviour. In a modern rubber product manufacturing unit, where automatic mixing and further processing are being attempted, this becomes a serious shortcoming, especially as synthetic rubbers are much more consistent and dependable in this respect. One of the main objectives of introducing TSR was to make NR more consistent with respect to raw rubber properties. Although this objective has been largely fulfilled, it has not been found to be adequate enough to make the processing characteristics as dependable and predictable as in the case of synthetic polymers. The main characteristics specified for TSR are dirt content, volatile matter, ash, nitrogen, Po and PRI. Except perhaps Po and PRI, the other properties do not influence processablity of the rubber significantly. Even Po and PRI do not correlate well with the mastication behaviour and processablity of rubber. Therefore, in order to make TSR more consistent with respect to processing parameters, detailed studies on mastication and rheological behaviour assume importance.

The problem becomes more complex considering the fact that even now TSR forms only 45 per cent of the total global production of

NR. Conventional forms such as sheet and crepe still account for a major portion of processed NR. The total production of natural rubber in India during 1995-96 was 506910 metric tonnes. It included different forms such as centrifuged latex, ribbed smoked sheet, crepe rubber and technically specified rubber. Sheet rubber holds the predominant share in the market as the proportion of small holdings in the country is comparatively higher than the estate sector. The contribution of TSR to the total production of NR is approximately nine per cent. Though the installation of new crepe rubber processing units are restricted by legislation, they still have a due share in the market.

The tyre sector is the biggest consumer of natural rubber in the country and the consumption pattern varies for different forms of NR. The conventional grades of NR which find extensive use in the above sector are sheet (RSS4, RSS5) and crepe (EBC 1X, 2X). The market trends indicate that among ISNR grades, ISNR 20 is the preferred grade. Variability in processability is likely to be much higher in these forms of NR. In countries such as Thailand and India where the conventional forms predominate, the problem assumes greater significance. Thus in spite of the best efforts by the NR producing countries, even today the conventional forms of NR such as sheet and crepe with wide variability in properties predominate the market. Even in the case of TSR consistency in properties related to processability needs further improvement.

Attempts to make NR more attractive to the consuming industry, especially in comparison with synthetic rubbers, call for improvement in the consistency in processing characteristics. Any attempt to improve consistency in the processability of NR calls for detailed investigations on the mastication behaviour and rheological properties of different forms of NR. However, studies in this area have been very limited. Earlier studies on processability of rubber have been based on measurement of parameters such as Mooney viscosity, plasticity etc. However, in recent years more sophisticated techniques such as capillary rheometry and torque rheometry have become popular. Investigations using these techniques are believed to be highly rewarding.

Skim rubber is a byproduct from the latex concentration process. When natural rubber latex is concentrated by the centrifugal process a small fraction consisting mostly of the smaller particles of rubber is obtained as skim latex, while the major portion is collected as concentrated latex or cream. The rubber content of skim is in the range of 3 to 8 per cent. The nonrubber content of this latex is very high and therefore, the rubber recovered from skim latex is considered to be of poor quality. Properties of skim rubber are different from normal grades of natural rubber. However, if used judiciously, this rubber could be taken advantage of in specific areas of application. As skim rubber is a poor quality rubber, scientific investigations on processability including mastication behaviour etc., on this rubber have been very limited.

There have been attempts to modify natural rubber chemically with the main objective of modifying properties of the same so as to make it usable in areas where it is not used at present. Several modified forms of rubber have been introduced, some of which are still available commercially while some others have become less popular because of the introduction of better synthetic substitutes. Epoxidised natural rubber is perhaps the latest introduction in this area. This rubber possesses special qualities such as oil resistance, low air permeability and the unique combination of low rolling resistance and high wet grip. However, during storage, the viscosity of the rubber and its gel content increases probably owing to side reactions involving epoxide group. As ENR is a newly introduced material, systematic investigations on the processability aspects of this rubber have been very limited.

The present study, therefore, has been undertaken with the following objectives.

1. To investigate the effect of extent of mastication on different grades of natural rubber. The extent of mastication can be controlled by varying the time of mastication, shear rate or by the use of peptisers.
2. To compare the different forms of NR which are widely used in the tyre industry, with regard to their breakdown behaviour, rheology and consistency in properties.
3. To study the consistency in raw rubber properties and breakdown behaviour of skim rubber and the effect of incorporation of the same with the normal grades of NR.

4. To understand the breakdown characteristics of different grades of epoxidised natural rubber.

The thesis is divided into the following chapters

Chapter	**I**	**Introduction**
Chapter	**II**	**Materials and Experimental techniques**
Chapter	**III**	**Mechanical breakdown of natural rubber**
Part	I	Effect of mechanical breakdown on processability and vulcanizate properties of TSR
Part	II	Effect of peptisers on molecular breakdown of TSR
Chapter	**IV**	**Studies on different forms of natural rubber with special reference to rheology and breakdown behaviour**
Part	I	Comparative evaluation of ISNR 20 with conventional forms of natural rubber
	A	Raw rubber properties, processing characteristics and vulcanizate properties
	B	Rheological properties
Part	II	Comparative assessment of breakdown behaviour of ISNR 20 and conventional forms of NR
Chapter	**V**	**Studies on skim rubber**
Part	I	Variability in raw rubber properties and breakdown behaviour of skim rubber
Part	II	Effect of incorporation of skim with TSR
Chapter	**VI**	**Studies on breakdown properties of epoxidised natural rubber**
Part	I	Effect of epoxy content on breakdown properties of epoxidised natural rubber
Part	II	Effect of peptiser on breakdown properties of ENR 50
Chapter	**VII**	**Summary and conclusions**

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CHAPTER II

MATERIALS AND EXPERIMENTAL TECHNIQUES

The details of the materials used and the experimental techniques adopted in the present investigations are given in this chapter.

Natural Rubber

Samples of different forms of natural rubber required for the study were collected from different sources.

Ribbed smoked sheet (RSS): RSS 4 and RSS 5 grades were supplied periodically by the Rubber Marketing Societies at Palai, Trivandrum, Konni and Nilambur.

Estate brown crepe (FC): EBCIX samples processed from fresh field coagulum (FC) were collected periodically from the following estates:-

(i) Kutikal Estate, Mundakayam
(ii) Arasu Rubber Corporation, Keeriparai
(iii) New Ambady Estate, Kulasekharam
(iv) Cheruvally Estate, Manimala

Estate brown crepe (DC): Crepe rubber samples from dry field coagulum were collected from different processing units around Kottayam.

ISNR 20 (FC): ISNR 20 grades processed from fresh field coagulum in the estate sector were collected from the following estates:-

(i) Shaliyacari Estate, Punalur.
(ii) Rehabilitation Plantations Ltd., Punalur.
(iii) TR & T Estate, Mundakayam
(iv) Pullangode Estate, Nilambur.

ISNR 20 (DC): ISNR 20 grades, processed from dry or semi dry field coagulum in the nonestate sector were collected from the following processing units:-

(i) Heveacrumb Rubber Pvt. Ltd., Poovarani
(ii) Corubber Crumb Factory, Thodupuzha
(iii) INDIAR Crumb Rubber Factory, Palai
(iv) Pilot Crumb Rubber Factory (PCRF), Rubber Board, Kottayam.

ISNR 5: The above grade was supplied by the PCRF, Rubber Board. The Bureau of Indian Standards (BIS) specifications (IS: 4588-1986) for ISNR 20 and ISNR 5 grades are given below:

	Parameter	ISNR 5	ISNR 20
1	Dirt content, per cent by mass, Max	0.05	0.20
2	Volatile matter, per cent by mass, max	0.80	0.80
3	Ash, per cent by mass, Max	0.50	1.00
4	Nitrogen, per cent by mass, Max	0.60	0.60
5	Initial plasticity, (Po) Min	30.00	30.00
6	Plasticity retention index, PRI, Max	60.00	40.00

Skim Rubber: Skim crepe samples were collected periodically from the following four latex centrifuging units:

(i) Padinjarekkara Agencies, Kottayam
(ii) Chenappady Estate, Erumeli
(iii) Kuppakayam Estate, Mundakayam
(iv) Meenachil Rubber Growers' Processing and Marketing Society, Palai

The skim block rubber was supplied by the Pilot Crumb Rubber Factory , Rubber Board, Kottayam

Epoxidised natural rubber (ENR): The four grades of ENR, viz, ENR 10, ENR 25, ENR 50 and ENR 60 were prepared at the pilot plant in the Rubber Research Institute of India. Epoxidation of NR was carried out by performic acid formed *insitu* by reaction between formic acid and hydrogen peroxide. The recipe and the reaction conditions applied for the production of different grades of ENR are given in Table 2.1

After attaining the required level of epoxidation, the reaction was arrested by neutralising the acid with ammonia (25%). The epoxidised rubber was separated from the reaction mixture by destabilising with ammonium sulphate. The coagulum was dried at 70°C.

Characterization

IR spectra of ENR samples were recorded using a Shimadzu IR spectrometer (FTIR-8101 M) in the region 4000 cm^{-1} to 600 cm^{-1}. Isoprenic elastomers (natural and synthetic) exhibit characteristic absorption peaks due to the responses of chemical entities such as symmetrical and asymmetrical stretching vibrations of -CH_2 groups in the range of 3000 - 2800 cm^{-1}, of unsaturated CH=CH units at 3025 cm^{-1} and 1660 cm^{-1}, of substituted unsaturated units at 845 cm^{-1} and 840 cm^{-1}, the being assigned for the trans and cis 1,4-isomers, and the absorption at 890 cm^{-1} corresponding to isopropenyl -$C(CH_3)=CH_2$ groups[1-2]. In the IR spectrum of ENR, some of the peaks remain unchanged, but significant modifications also occur. The most affected spectral region as a consequence of epoxidation is that of the backbone unsaturation; An important diminution occurs in the 835 cm^{-1} absorption band (Cis-1,4 units) and the corresponding increase in the 870 cm^{-1} absorption peak which was assigned to the epoxy groups placed on the backbone(3). Modifications in the 900-800 cm^{-1} region of the IR spectra are illustrated in Fig 2.1. Quantitative analysis of the samples was made by a method reported earlier(4). The absorbancy determination of IR spectrum is shown in Fig 2.2. In fact, the width of the 835 cm^{-1} band is so important that the presence of olefin slightly modifies the measurement of the 870 cm^{-1} absorbency. This interference, evaluated at 14 per cent of the absorbence at 835 cm^{-1} has been subtracted. Similarly 1.9 per cent of the absorbence at 1375 cm^{-1}, which is the specific band of methyl group has to be subtracted from A_{3460}.

The epoxy content E can be expressed as

$$E = \frac{100\,K_1 \times A_{(870)}\,\text{corr.}}{A_{(835)}\,K_1 \times A_{870}\,\text{Corr.} + K_2 \times A_{3460}\,\text{corr.}} \quad \text{mol\%}$$

where K_1 and K_2 are measured by a direct method (^{1}HNMR)

Peptisers: The peptisers used were:

1. Pentachlorothiophenol(PCTP) Renacit -7, Bayer (India) Ltd.
2. 2,2' Dibenzamido diphenyl disulphide(2,2'DDDS) Renacit 11, Bayer (India) Ltd.
3. MBT - Accicure MBT, ICI India Ltd. Rubber Chemicals Division

Additives

Carbon Black : The Carbon black used was high abrasion furnace (HAF) black N-330 with surface area 80 M^2/g; pH 7.6 supplied by Phillips Carbon Black Ltd, Durgapur, India.

Stearic acid : Commercial grade, Sp.gr. 0.85

Zinc Oxide : Commercial grade, Sp. gr. 5.55

N-Cyclohexyl-2 benzthiazyl sulphenamide (CBS) : Vulkacit CZsupplied by Bayer (India) Ltd.

Process Oil

Aromatic oil : VGC 0.92, Aniline point (47°C) supplied by Indian Oil Corporation

Sulphur : Commercial grade

Solvents

Toluene : Analytical grade, supplied by Merck.

Other Chemicals :

Formic acid : 98% Commercial grade

Hydrogen peroxide : 30% Commercial grade

Nonionic stabiliser : Vulcastab VL (Ethylene oxide condensate) supplied by ICI (India) Ltd.

EXPERIMENTAL TECHNIQUES

Mastication of rubber

A torque rheometer, Haake Rheocord (Model R-90) was used for the mastication studies. A photograph of the equipment is given in Fig 2.3. Many types of torque rheometers have been widely used for polymer blending, studies on processability of polymers and evaluation of rheological properties of polymer melts[5-7]. The torque rheometer is essentially a device for measuring the torque generated due to the resistance of a material being mixed or flowing under preselected conditions of shear and temperature. The heart of the Rheocord is a mixing chamber whose volume is approximately 370cc. Mixing or shearing of the material in the mixing chamber is done by two horizontal rotors with protrusions. The resistance generated by the material is measured with the help of a dynamometer. A thermocouple protruding into the chamber enables the temperature to be continuously monitored. The speed of the rotors and the temperature of the mixing chamber can be varied. The speed of the rotors can be changed from 0-120 rpm and the temperature from 0-500°C. Different rotors can be employed depending upon the nature of the polymers. The rotors can be easily mounted and dismounted due to the simple design of the fastening and coupling system. Once the test conditions (rotor type, rpm and temperature) are selected, sufficient time should be given for the temperature to attain the set value and become steady. Subsequently the material can be charged into the mixing chamber and the ram closed.

The important parameters that can be derived from the Rheocord are torque (t) at every instant (can be measured with an interval of every 6 secs), totalized torque (TTQ), which is a measure of the work done during mastication or mixing and the temperature ($T^{o}C$) of the rubber under mastication. The data can be obtained either as a graphical plot or digital description from the microprocessor attached to the equipment.

Molecular weight

The weight average molecular weight $\overline{M}w$ was measured as per BS 1673 part 6, 1969. A known quantity of the rubber was dissolved in toluene and different dilutions were prepared from the same. Using an Ostwald viscometer, the flow time of the solutions were calculated from the expression ts/to, where ts is the flow time of rubber solution and to is the flow time of the solvent. The intrinsic viscosity (e) can be obtained as

$$\eta = KM^{a}$$

where M = Average molecular weight

K,a = Constants for the solvent-polymer system

η can be obtained experimentally from

$$\eta = \mathrm{Lim}_{C\to 0} \left[\frac{\eta_{sp}}{C} \right]$$

Where η_{sp} = Specific viscosity.

Gel content

The gel content of the rubber samples was measured as per ASTM D-2765-84 by extracting the soluble component in hot toluene for 12 h using a soxhlet assembly and drying in a vacuum oven set at 70^0c for 24 h. About 0.5 g each of the sample was weighed and placed in a 15x 15 mm envelope made from 120 gauge stainless steel woven mesh. The sample in theenvelope was immersed in refluxing toluene for 12 h, dried in vacuum and the gel fraction was calculated from the initial and final sample weights.

Evaluation of raw rubber properties

Wallace plasticity (Po): Plasticity of the raw rubber sample was measured using a Wallace Rapid Plastimeter as per IS 3660 Part I 1972.

Plasticity retention index(PRI): Plasticity retention index was measured as per IS 3660 Part III 1971. Samples of known initial plasticity were aged at 140 ± 0.50 ° C in an ageing oven for 30 minutes and the final plasticity was measured. PRI was calculated as

$$PRI = P_{30} \times 100/Po$$

Dirt content: The dirt content of the rubber samples was estimated as per the procedure laid out in IS 3660 Part I 1972. Known weight of the rubber was dissolved in mineral turpentine and filtered through a 325 mesh sieve. The percentage of the dried material retained on the sieve was expressed as the dirt content in per cent.

Volatile matter: The percentage of the moisture was determined as per IS 3660 Part I 1972.

Nitrogen : Nitrogen content of the samples was determined as per IS-3660 Part II 1968

Mooney viscosity : Mooney viscosity of the samples was determined using a Mooney Viscometer (Model Shimadzu SMV 202), as per ASTM D1646-87.

Optimum cure time: Optimum cure time was determined using a Monsanto Rheometer - R 100 at 150 °C, as per ASTM. D 2084-93

Scorch time: Scorch time of the samples was measured using a Mooney Viscometer (Model Shimadzu - SMV 202) at 120°C as per ASTM 1646-94

Mechanical properties:

Stress-strain properties were determined according to ASTM D412-87 using dumb-bell test pieces using a Zwick Universal Testing Machine (Model 1474) with a crosshead speed of 500 mm/minute.

Tear resistance: Tear resistance was determined as per ASTM D624-86 using unnicked, 90° angle test pieces, at a crosshead speed of 500 mm/ minute on a Zwick Universal Testing Machine (Model 1474)

Abrasion resistance: Abrasion resistance was determined in a DIN type abrader as per DIN 535516 and expressed as volume loss (mm^3) .

Hardness : Hardness was measured according to ASTM D 2240-86 using a ShoreA durometer.

Compression set : Compression set was determined as per ASTM D 395-89 Method B. The samples compressed to 25 per cent of the original thickness were aged at 70°C for 72 h and the ratio of reduction in thickness to the original thickness of the sample, was expressed as per cent set.

Ageing characteristics : Ageing characteristics were studied by measuring the retention in tensile properties of samples aged at 70°C for 14 days and at 100°C for 96 h.

Dynamic properties : Dynamic properties were evaluated on a Yerzely Oscillograph. Yerzely Resilience, tan δ and dynamic modulus were determined as per ASTM D 945-92

Flexing : The flex characteristics of the vulcanizates were determined using a DeMattia Flexing Machine as per ASTM D 813-95.

Heat buildup : Heat buildup (ΔT°C) of samples were determined using a Goodrich Flexometer, as per ASTM D 623-93

Water absorption : Water absorption was determined by keeping the samples in water for various periods and finding out the increase in weight. (ASTM D 471-95)

Rheological evaluation

Rheological properties were evaluated using a capillary rheometer attached to a Zwick Universal Testing Machine (Model 1474) as per ASTM D 5099-93. A schematic diagram of the capillary rheometer is given in Fig 2.4.

The extrusion assembly consisted of a hardened steel barrel underneath the moving crosshead of the machine. A hardened steel plunger which was accurately ground to fit inside the barrel was held to the load cell by a latch assembly. The barrel was thermally insulated from the rest of the machine. The capillary used was made of tungsten carbide steel. It had a length to diameter (lc/dc) ratio of 40 with an angle of entry of 180°. The temperature inside the barrel and the capillary was varied between 90°C and 120°C with an accuracy of ±1°C. The cross-head speed could be varied in the range of 0.5-500 mm/min.

The samples were uniformly masticated on a two-roll mill. A fixed volume of the sample was put into the barrel and was forced down the capillary by the plunger attached to the moving crosshead. After a warm up period of three minutes, the sample was extruded through the capillary at 10 different speeds. Forces corresponding to the specific plunger speeds could be measured by the pressure transducer attached to the plunger and were recorded using a strip chart recorder assembly.

The force and the crosshead speed were converted into apparent shear stress (τ_w) and shear rate ($\dot{\gamma}_w$) at the wall respectively using the following equations involving the geometry of the capillary and plunger.

$$\tau_w = F/\ 4A_p(l_o/d_c)$$

$$= 3n' + 1/4n' \times 32Q/\pi\ d_o^3$$

where F is the force applied at a particular shear rate, A_p is the crosssectional area of the plunger, l_o is the length of the capillary, d_o the diameter of the capillary, Q the volume flow rate (calculated from the velocity of the crosshead and the diameter of the plunger) and n' the flow behavior index defined as

$$n' = d(\log \tau_w) / d(\log \dot{\gamma}_w)$$

and determined by regression analysis of the values of τ_w and γ_w obtained from the experimental data. γ_w is the apparent wall shear rate calculated as:

$$\gamma_w = 32Q/\pi d^3_o$$

The shear viscosity was calculated as:

$$\eta = \tau_w / \dot{\gamma}_w$$

The temperature dependence of the viscosity was calculated from the activation energy E for viscous flow from an Arrhenius type expression.

$$\eta = Ae^{E/RT}$$

where R is the gas constant, T the absolute temperature and A, a constant.

Corrections employed in capillary rheometer.

For capillary rheometer, a series of corrections is appropriate to determine the true shear viscosity[8]. Generally the most important correction is that due to end effect. This effect is negligible when the die used has a large ratio of length (l) to diameter (d). The end effect can be eliminated by using two or more dies of the same diameter but different lengths(9) if the pressure drop (ΔP) over a finite length is plotted versus l/d for the same shear rate in each die. The Bagley plot so obtained should be linear and intercept at l/d = 0 determines the end correction factor or Bagley correction factor (P_c). The true shear stress at the capillary wall (τ_w) can then be calculated, using the expression.

$$\tau_w = \Delta P - P_c / (2l/R)$$

Polymer melts show non-Newtonian behavior and so the apparent shear rates may be corrected by the degree of non-Newtonian behavior (Rabinowitsch correction) by using the slope of the curve (10). The shear stress at the wall need be corrected as suggested by Bagley (11). But the correction factor diminishes as the length to diameter ratio increases and for a capillary having l/d ratio 40, it is assumed that the correction factor is negligible. The following assumptions were made

1. There is no slip at the capillary wall.
2. The flow pattern is constant along the capillary
3. The flow is isothermal.
4. The material is incompressible.

5. The fluid is time independent.
6. The flow properties are independent of hydrostatic pressure.

Extrudate swelling

The die swell is related to the elasticity and first normal stress difference of polymer melts.(12) The extrudates were collected as they emerged from the capillary, taking care to avoid any deformation. The diameter of the extrudate was measured at several points after 24 h of extrusion using a binocular stereomicroscope. The average value of five readings was taken as the diameter of the extrudate(d_e). The extrudate swelling was calculated as the ratio of the diameter of the extrudate to that of the capillary (d_e/d_c)

Mastication studies using Haake-Rheocord 90.

The Haake-Rheocord, was also used to study the rheological behavior of different forms of natural rubber. The instrument imparts a very complex shearing motion to the polymer and subsequently the data cannot be taken as fundamental rheological properties. However, the design of the mixing head of the Rheocord is similar to that of an internal mixer, and hence the behavior of the rubber in actual processing can be simulated. The relationship obtainable from the rotor torque and rotor speed was shown to be similar to the usual power law expression (13) as:

$$M = C(n)KS^n$$

Where M is the torque, n the power law index, C(n) a function weakly dependent on n, K a constant and S rotor speed.

The slope of the plot log M Vs log S gives the power law index n.The energy of activation (E) can be obtained from the slope of the plot of shear viscosity η against (I/T) using Arrhenius equation.

Different forms of natural rubber were masticated in the Haake-Rheocord under the following conditions :

Specimen volume : 259 cc
Temperature : 80°C
Revolution : 60 min $^{-1}$
Time : 15 min

The following parameters were obtained from the Rheocord data:

M_2(Nm) : The value of the torque at the second minute which is characteristic of the energy required for mastication.

M_{15}(Nm) : The value of the torque at the fifteenth minute is proportional to the viscosity of the rubber at T_F°C

M_{2-15}(Nm) : The reduction in torque at 2 and 15 minutes and is characteristic of the decrease in viscosity of the material during the test

T_F°C : The stabilised temperature of the material which is characteristic of the heat buildup of the rubber under the given conditions.

ΔT(°C) : The difference between the final temperature of the sample and the initial temperature of the mixing chamber wall.

$W_{2\text{-}15}$(Nm-min) : The work done in masticating the sample from t=2 to t=15 min which can be obtained directly as the difference between the totalized torque [TTQ] values at the corresponding time intervals.

The masticated samples were matured for 24 h and remasticated under the same conditions. The above defined parameters were compared in each case.

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Table 2.1
Recipe and reaction conditions for different grades of epoxidised natural rubber.

Ingredients	Concentration moles per litre			
	ENR-10	ENR-25	ENR-50	ENR-60
Rubber hydrocarbon	2.94	3.38	2.94	2.94
Formic acid(98%)	0.5	0.75	0.75	0.75
Hydrogen peroxide (30%)	0.75	1.5	2.6	2.9
Non ionic stabiliser (Ethylene oxide condensate)	4	4	4.5	4.5
Time of reaction(h)	20	18	24	27
Temperature of reaction °C	50±1	50±1	52±1	52±1

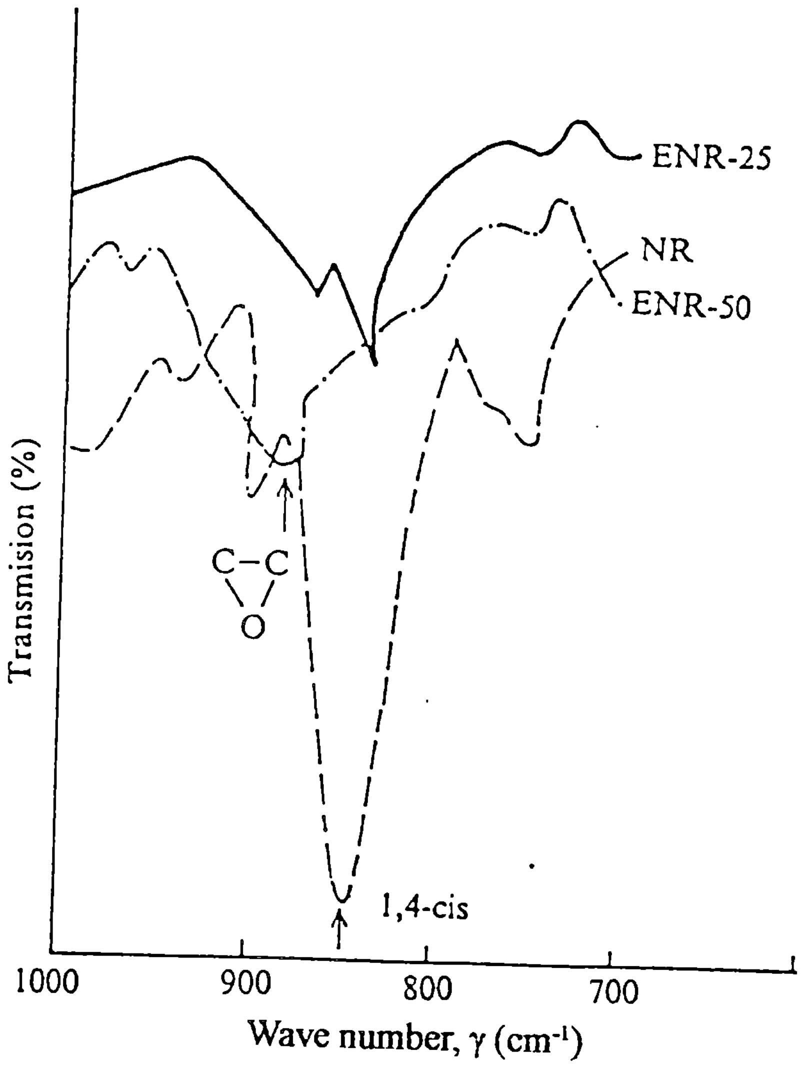


Fig. 2.1 Modifications in 900 - 800 cm^{-1} region of I.R. Spectra of ENR

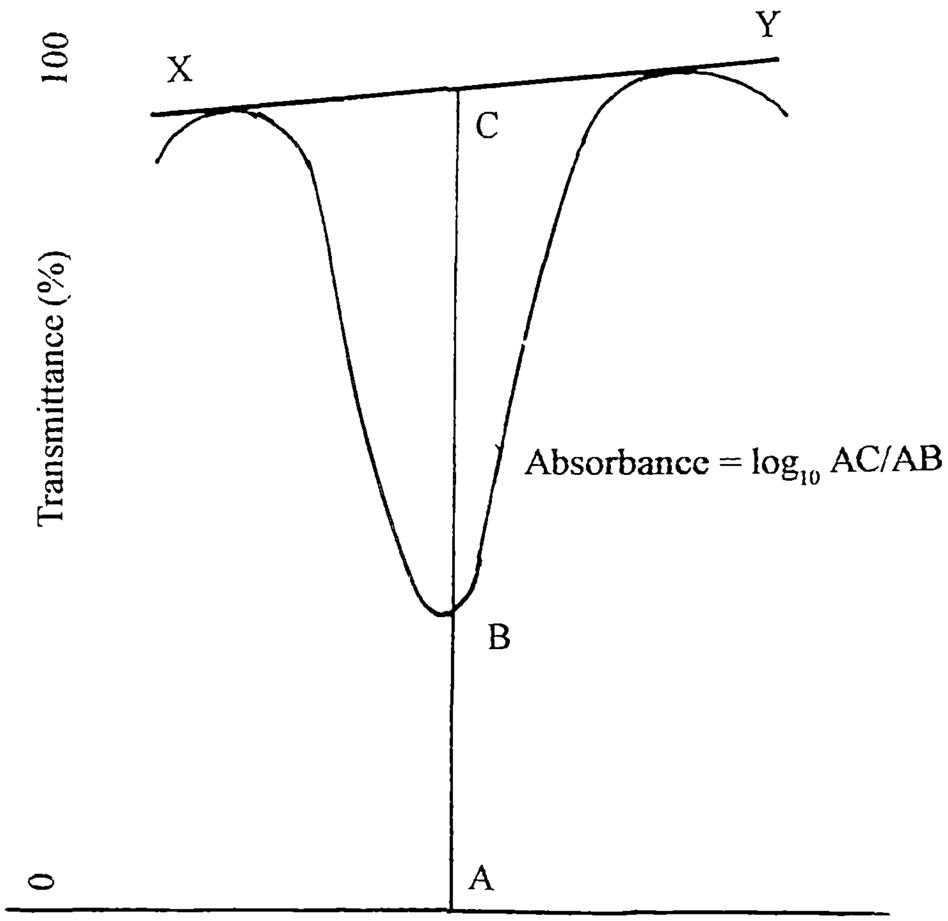


Fig. 2.2 Absorbance determination with I.R. Spectrum

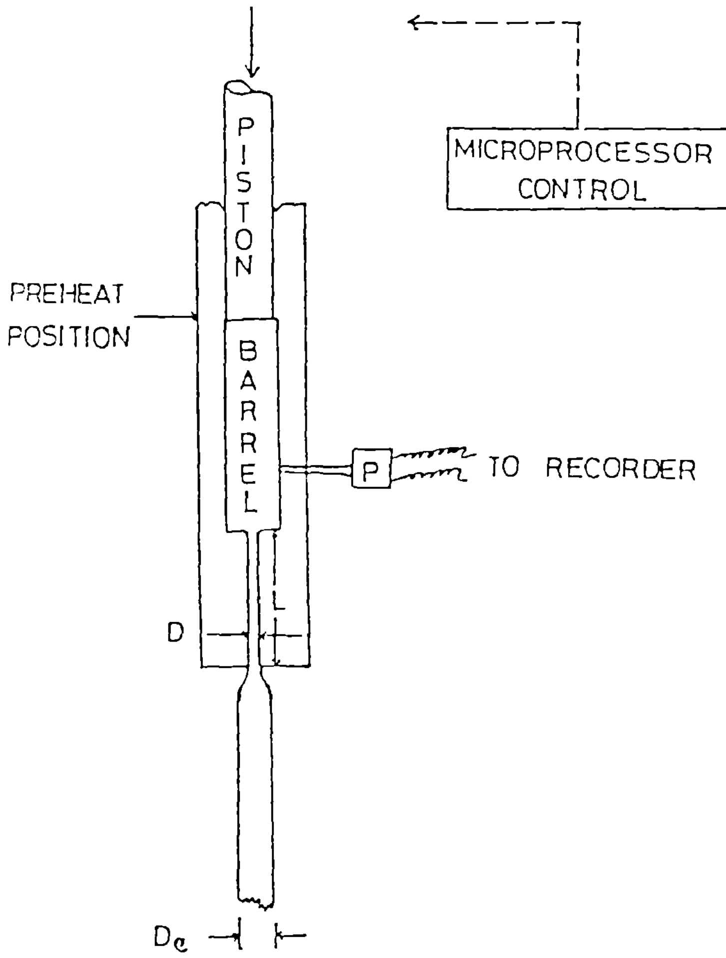


Fig. 2.4 Schematic diagram of a Capillary rheometer

CHAPTER III

MECHANICAL BREAKDOWN OF NATURAL RUBBER

The conversion of any rubber into a fully compounded mix involves mechanical energy being imparted to it through various processing operations. Mastication is essential in the case of natural rubber as its viscosity in the raw stage is not low enough for subsequent processing. During mastication, the long chain elastomer molecules are split by the higher shear forces. Chain fragments are formed with terminal free radicals. If not stabilised, they can recombine into long chain molecules.[1-2] Atmospheric oxygen or chemical peptisers help in stabilising the polymer free radicals generated during mastication.[3-4] The molecular weight is lowered and consequently the viscosity is decreased.

Part I of this chapter is concerned with the extent of breakdown and its effect on processability and vulcunizate properties while Part II deals with the effect of peptisers.

PART 1

EFFECT OF MECHANICAL BREAKDOWN ON PROCESSABILITY AND VULCANIZATE PROPERTIES OF TSR

It is reported that a direct correlation exists between high levels of mechanical working on rubber and reduced service life of products.[5] Among the product manufacturing operations, mastication contributes to maximum breakdown.[6] Studies have been reported correlating the extent of breakdown during processing and properties of the resulting vulcanizates.[7-8] In most of the work done earlier, the effect of mechanical breakdown on a single form of natural rubber was studied. The extent of breakdown was varied mainly by changing the temperature of the mixing chamber or by the duration of mixing. The general conclusion derived from the above studies was that varying levels of breakdown occurring to the elastomer during the mixing process do not alter the properties of the resulting vulcanizates significantly.

However, the quality and storage history of the raw rubber can affect its mastication behaviour and may lead to differences in vulcanizate properties. Hence this part of the study was envisaged to investigate the effect of varying levels of breakdown on the vulcanizate properties of two grades of ISNR, viz, ISNR 5 processed from latex coagulum and ISNR 20 processed from field coagulum.

EXPERIMENTAL

Samples of ISNR 5 and ISNR 20 were masticated on the Haake-Rheocord 90. The extent of mastication was varied by varying the time of mastication, shear rate (rpm) and the temperature of the mixing chamber. The samples were masticated at a fill factor of 0.7 for different time intervals (viz 0,2,5,10,20 and 40 minutes) at 60°C at an rpm of 60. The extent of breakdown occurred to the rubber were measured in terms of the molecular weight $\overline{M}w$, and Wallace plasticity (P_o) of the samples. The gel content and plasticity retention index (PRI) of the samples were also determined. The above parameters were determined by varying the rotor speed viz 50,60,70, 80 and 100 rpm keeping the time of mastication and temperature constant.

The samples masticated to different levels were matured for 24h and then the ingredients added in the Rheocord as per the recipe given in Table 3.1. However, curatives were added in a separate stage on a two-roll mill of size 30 cm x 15 cm. Cure characteristics, strength properties, ageing characteristics, hardness, heat buildup and compression set of the samples were determined as per the relevant ASTM procedures.

RESULTS AND DISCUSSION

Figure 3.1 shows the effect of mastication on molecular weight ($\overline{M}w$). The weight average molecular weight $\overline{M}w$ of the unmasticated rubber was found to be higher for ISNR 5. This was expected as the same was processed from latex. The lower molecular weight of ISNR 20 may be attributed to the chain branching occurring due to prolonged storage and poor storage conditions of field coagulum from which the rubber has been prepared.

However, the rate of reduction in molecular weight was more pronounced in the case of ISNR 5. In both grades, the reduction in molecular weight was found to be higher during the initial period of mastication. The effect of prolonged mastication on molecular weight was found to be less significant especially in the case of ISNR 20. This may be due to the higher temperature attained in the rubber mass during prolonged mastication making it progressively softer, correspondingly reducing the shear forces. This agrees well with the observations reported earlier.[9]

Figure 3.2 shows the reduction in gel content of the samples during mastication. ISNR 20 shows almost twice the gel content of ISNR 5, in the case of unmasticated samples. Though gel content got reduced during the mastication process, it was found to be always higher for the former. It has been observed that the increase in gel content during storage is responsible for the hardening of rubber stored in bulk.[10] The gel phase consists of the more highly branched and lightly crosslinked fractions of rubber closely intertwined with insoluble high molecular nonrubber substances like proteins. Higher gel content of ISNR 20 indicates poor quality of the raw material compared to ISNR 5, which is having a lower gel content. Factors such as mechanical shear or oxidative degradation are known to disaggregate the gel and make it soluble. It is found to be true in the case of both the grades as it reduces substantially with the extent of mastication.

Figure. 3.3 gives the change in plasticity of the rubbers with extent of mechanical breakdown. The decrease in plasticity value (ΔP_o) during mastication is plotted in Figure. 3.4. As in the case of Mw, ISNR 5 showed a higher reduction in Po than ISNR 20. But the rate of reduction in Mw was comparatively lower than the P_o values. (Figure.3.5) This can be attributed to the influence of the microgel on the flow and recovery characteristics of NR.[11] The Mw was determined from the gel free samples whereas P_o was determined on the samples containing the gel.

Figure. 3.6 shows the effect of mastication on Mooney viscosity of the samples. The trend is almost the same as that of Wallace plasticity. However plasticity retention index (PRI) was reduced to the same level for both the grades of rubbers (Figure.3.7), though there was a wider a difference initially. This also support the observation that ISNR 5 degrade at a higher rate during mastication compared to ISNR 20. But this reduction in PRI is drastic only in the case of prolonged mastication.

Effect of shear rate

Shear rate was varied by changing the rotor speed, keeping the time of mastication and initial temperature the same. The effect of varying the shear rate on the molecular weight Mw and gel content are given in Table 3.2.

Compared to time of mastication, the effect of rotor speed on molecular weight was found to be less significant. Observations made earlier,[12] indicated that the speed of rotor had a better influence on the breakdown properties, than the temperature, provided the test was conducted at constant initial viscosity and temperature. In this case the lower rate of reduction in the parameters such as Mw and P_o can be attributed to the higher heat generated at higher speed and subsequent reduction in the viscosity of the stock and hence the shear force. In fact the main influence of temperature is simply the secondary one of altering the viscosity of rubber. If the tests were conducted at isothermal conditions, the influence of speed of the rotors would have been significant.

The reduction in Wallace plasticity during mastication at different speeds is shown in Table 3.3. The rate of reduction in P_o was observed to be lower at higher rpm as in the case of Mw.

Effect of mechanical breakdown on vulcanizate properties

The processing characteristics and vulcanizate properties of gum compounds prepared using both the grades (ISNR 5 and ISNR 20) with different levels of mastication are given in Tables 3.4 and 3.5.

Cure curves of gum mixes of ISNR 5 and ISNR 20 are shown in Figures 3.8 and 3.9 respectively. It could be seen that even the samples which were masticated to the maximum extent showed almost similar cure characteristics compared to that of samples masticated to the minimum level.

In both grades the important vulcanizate characteristics which showed significant difference with the extent of mastication were identified to be the retention in tensile strength after ageing and compression set. Sears (1988) has done earlier work on this aspect and observed that in the case of black filled vulcanizates, the degree of mastication has no significant effect either on the aged or unaged properties. However, in the present study, the lower retention of tensile properties after ageing with higher extent of mastication is supported by the corresponding higher values for compression set. The masking effect of carbon black might have played a role in nullifying the effect of ageing in the former case. At both 70°C and 100°C, a reduction in tensile strength with corresponding increase in mastication level is observed. The other properties showed almost the same trend for all the samples indicating that these properties are not influenced significantly by the extent of breakdown.

However, ISNR 5 shows better performance than ISNR 20, in almost all the properties. This is clear from the initial tensile strength, the retention of the same after ageing and the compression set. This definitely indicates the influence of storage of the raw rubber prior to processing. ISNR 5, being processed from fresh latex coagulum can retain the properties to a higher extent than ISNR 20, where the starting material is field coagulum.

CONCLUSION

1. ISNR 5 was found to have a higher molecular weight than ISNR 20. The rate of reduction of $\bar{M}w$ with the extent of mastication was also found to be higher for the former.
2. It was observed that the maximum reduction in molecular weight and Wallace plasticity was attained during the initial period of mastication. Prolonged mastication was shown to have less effect on these properties.
3. The gel content of ISNR 20 was comparatively higher.
4. Varying the rotor speed of the mixer did not affect the properties of raw rubber significantly.
5. In both the grades, retention in tensile strength after ageing and compression set were identified to be the properties affected mostly by the extent of mastication.

Table 3.1

Formulation of gum mix

Ingradients	phr
NR (ISNR 5/20)	100
Stearic acid	2
Zinc oxide	5
CBS	0.6
Sulphur	2.5

Table 3.2

Effect of rotor speed on mol. wt and gel content

Time 5 (Min); Temp 80°C

	ISNR 5		ISNR 20	
RPM	$\overrightarrow{Mw}$ x 10^5	Gel %	$\overrightarrow{Mw}$ x 10^5	Gel %
0	10.8	9.5	8.4	18.4
50	9.4	4.6	7.9	14.8
60	8.7	2.8	7.6	10.7
80	8.4	2.3	7.2	9.8
100	8.1	2.1	7.0	9.3

Table 3.3

Effect of rotor speed on Wallace plasticity (Po)

Time 5 min; Temp 80°C

	Wallace plasticity (Po)	
(RPM)	ISNR 5	ISNR 20
0	49	37
50	41	34
60	38	31
80	32	29
100	29	28

Table 3.4

Properties of ISNR 5 (gum mix)

Mix No.	Time of mastication (Min)	Optimum cure time at 150°C (Min)	Scorch time at 120°C (Min)	Modulus 300% N/mm^2	Tensile strength N/mm^2	Tear strength N/mm	Compression set %	Heat buildup ΔT°C	Hardness shore A	R*a a TS 70°C 14 days	R*a a TS 100°C 96 h
A	0	9	8	2.5	16.9	44	25	9	45	72	13
B	2	12	9.5	2.8	18.0	44	24	8	44	72	15
C	5	12	8.5	2.8	20.2	42	24	11	46	81	19
D	10	12.5	9.0	2.6	20.0	43	23	11	47	83	22
E	20	11.0	9.0	2.3	19.0	42	28	12	40	76	12
F	40	11.0	8.0	2.3	20.1	42	29	11	40	67	12

R*.a.a retention after ageing.

Table 3.5
Properties of ISNR 20 (gum mix)

Mix No.	Time of mastication (Min)	Optimum cure time 150°C (Min)	Scorch time at 120°C (Min)	Modulus 300% N/mm^2	Tensile strength N/mm^2	Tear strength N/mm	Compression set %	Heat buildup ΔT°C	Hardness shore A	R* a a TS 70°C 14 days	R*a a TS 100°C 96 h
L	0	8	9	2.3	14.8	42	23	8	44	69	11
M	2	11	11	2.3	17.3	42	29	6	43	72	14
N	5	10.5	9.5	2.6	18.8	44	26	6	43	77	15
O	10	10.5	8	2.2	17.5	41	27	6	42	74	11
P	20	11	8	2.4	17.7	41	34	6	41	64	11
Q	40	12	7	2.3	17.0	41	37	5	41	58	8

R*.a.a retention after ageing.

Figure 3.1 Effect of Mastication on Molecular weight

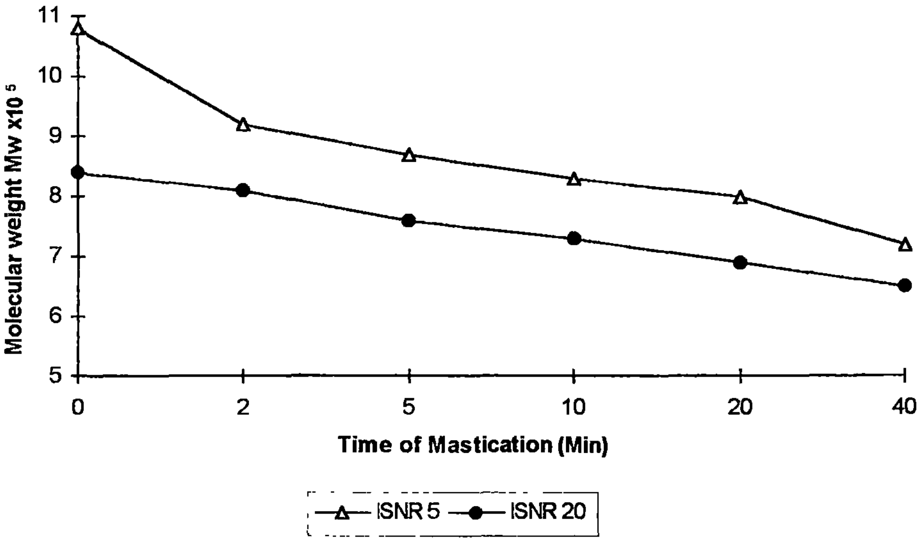


Figure 3.2 Effect of Mastication on Gel content

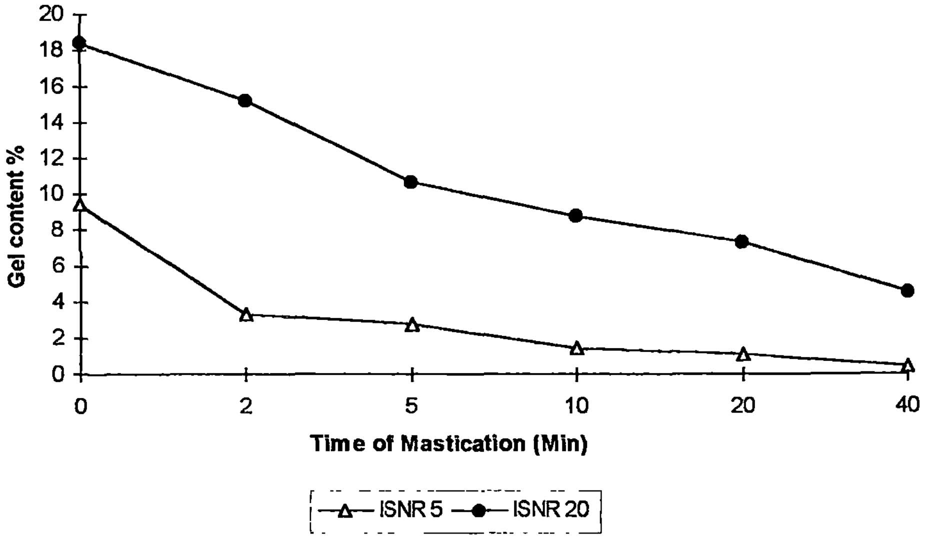


Figure 3.3 Effect of Mastication on Wallace plasticity

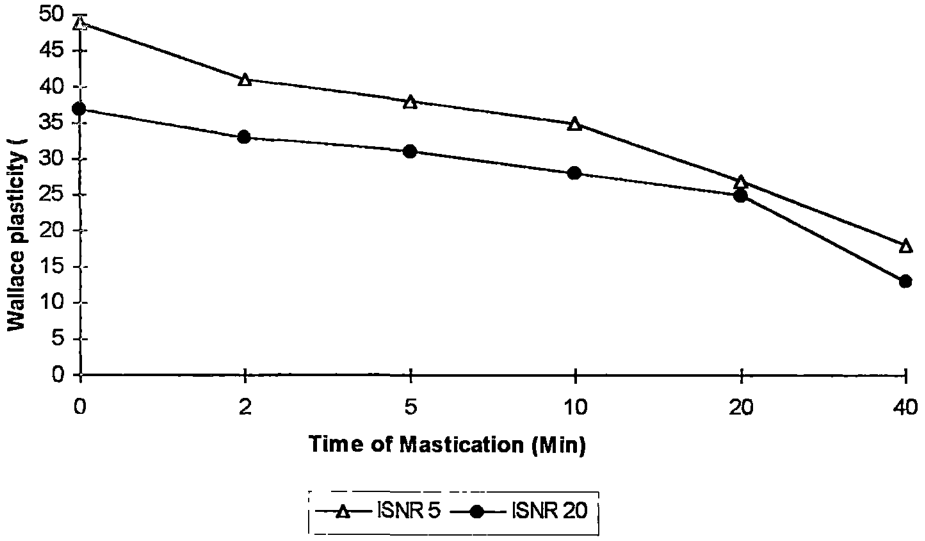


Figure 3.4 Reduction in Wallace plasticity with extent of Mastication

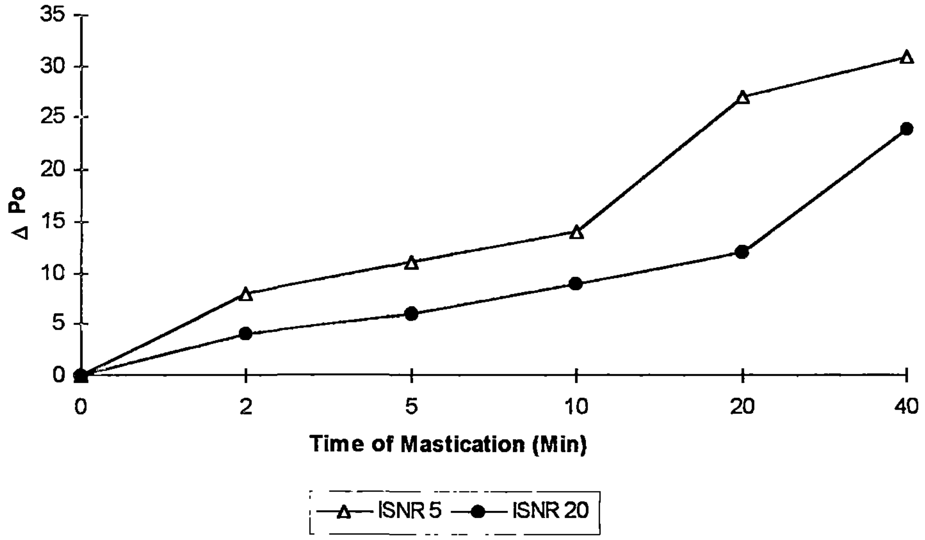


Figure 3.5 Reduction in Molecular weight with extent of Mastication

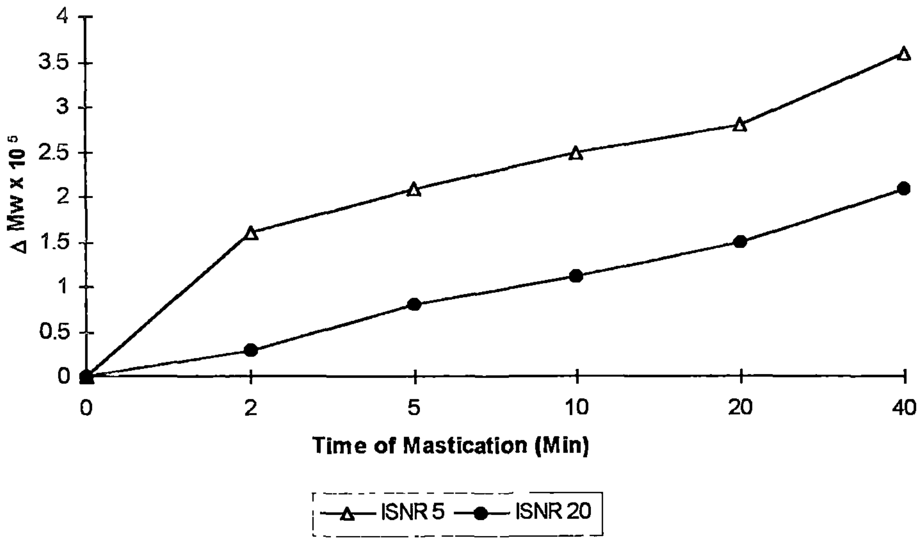


Figure 3.6 Effect of Mastication on Mooney viscosity

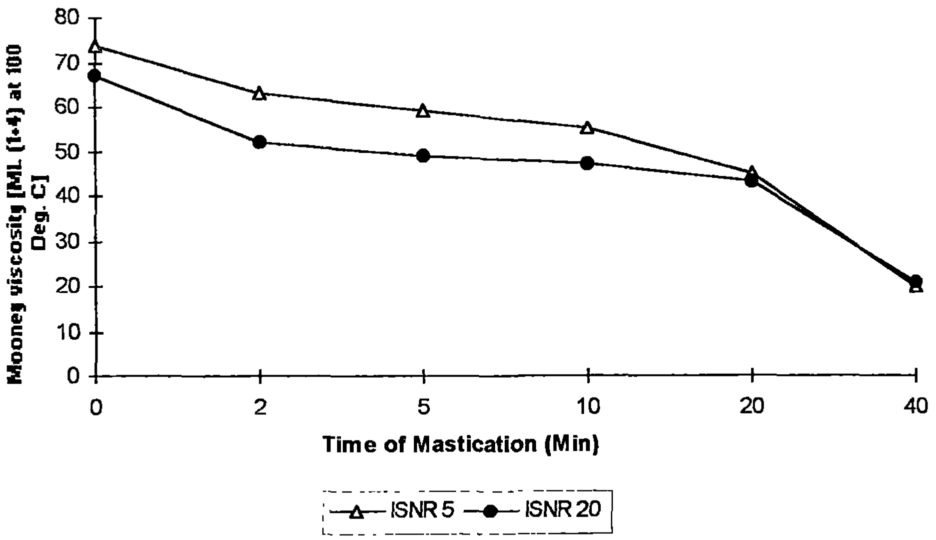
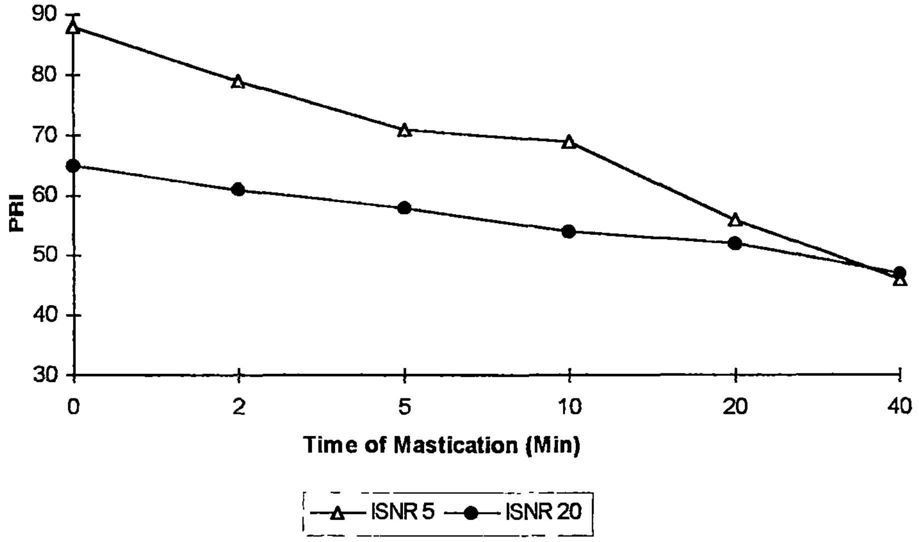


Figure 3.7 Effect of Mastication on Plasticity Retention Index



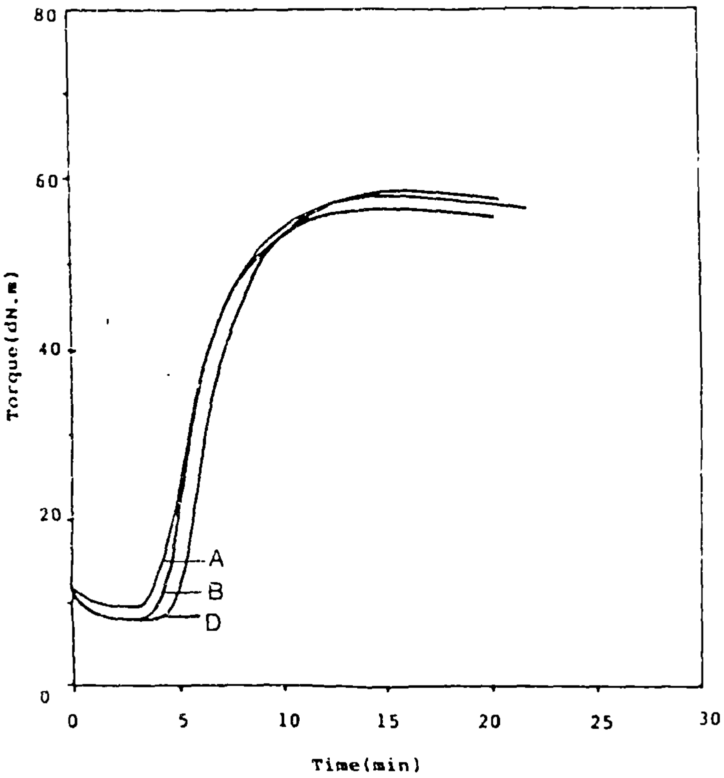


Fig. 3.8 Cure curves for gum mixes of ISNR 5

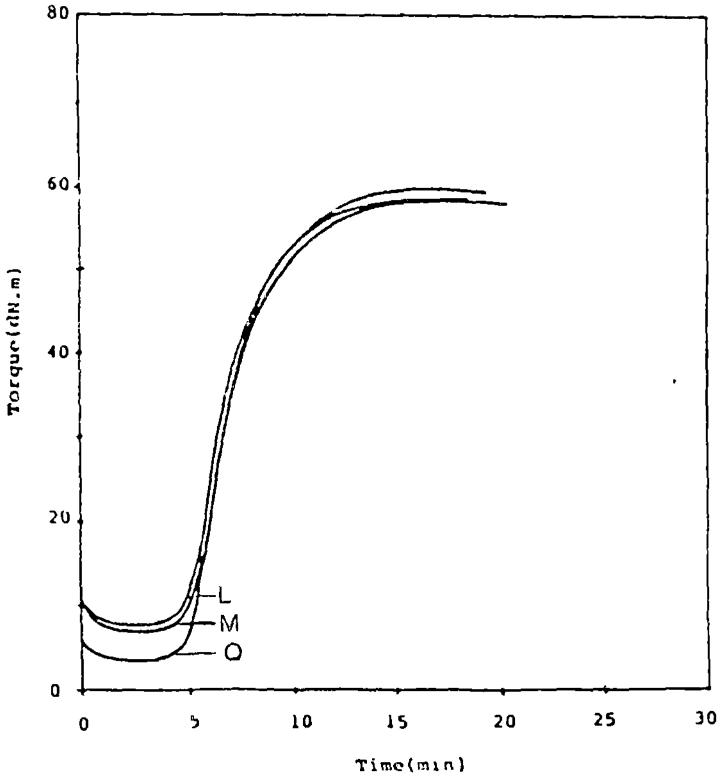


Fig. 3.9 Cure curves for gum mixes of ISNR 20

PART II

EFFECT OF PEPTISERS ON MOLECULAR BREAKDOWN OF TSR

The term ‘peptiser’ is attributed to those chemicals which accelerate the softening of rubber during mastication. More precisely, they can be defined as those which catalyse the thermo-oxidative breakdown of rubber.[2] A peptiser should act as radical acceptor for mechano-chemical scission during cold mastication or promoters of oxidative scission at high temperatures. Most of the commercial peptisers possess both these functions to varying degrees.

Many compounds, including nitroso compounds, mercaptans and their zinc salts, thiocarboxylic acids and their salts, thiazoles, sulphenamides, hydrazines, peroxides and metal complexes are known to have peptising effect.[13] However, combinations of activators with thiophenols, aromatic disulphides and mixtures of salts of saturated fatty acids have essentially remained in use.

The effect of peptisers on mastication of natural rubber has been reported by Fries and Pandit[3]. They have studied the effect of pentachloro thiophenol (PCTP) with accelerators such as DPG, MBT and ZDEC in the mastication of natural rubber in an internal mixer. A definite reduction in Mooney viscosity was observed for the samples containing PCTP. Also it was reported that the vulcanizate properties of the mixes were not affected by the peptisers, if used at an optimum level. However, excessive levels of the same can affect the properties of vulcanizates adversely.[14] Chandra[15] *et.al* studied the effect of PCTP on blends of NR/SBR. The effect of the peptiser was found to be less, when the proportion of SBR was higher in the blend.

Since its introduction in 1949, by Bayer Germany, the pentachloro thiphenol based peptisers have played a major role in the rubber industry. But due to health hazards caused by the same it is now being withdrawn from the market. Recently dibenzamido diphenyl disulphide based peptisers have replaced the former.

The present study is a comparative evaluation of Renacit -11 a new peptising agent from Bayer (India), (which is basically 2,2' dibenzamidodiphenyl disulphide) and PCTP. It was reported that MBT has moderate peptising action, when added in the latex stage.[16] Hence the same has also been included in the study.

EXPERIMENTAL

The required amount of pepstisers were added after charging the rubber (ISNR 5) in the mixing chamber of the Haake Rheocord and prior to the closure of the ram. Parameters such as Wallace plasticity, molecular weight ($\tilde{M}$w), stabilised torque (torque attained after a fixed time), work done in masticating the samples to a fixed torque (measured in terms of totalised torque, TTQ) were evaluated with respect to the dosage of the peptiser, rotor speed, initial temperature of the mixing chamber and duration of mastication.

RESULTS AND DISCUSSION

Effect of dosage of peptiser

Figure 3.10 shows the effect of dosage of peptisers on Wallace plasticity of the samples. It is seen that 2,2' dibenzamido diphenyl disulphide (2,2' DDDS) showed maximum reduction in viscosity at 0.15 phr level and beyond. MBT did not impart much effect. It was observed that no linear relation exists between increase in plasticity and the amount of peptiser used. The most significant effects were observed with the minimum dosage of peptiser used.

The effect of dosage of peptisers on molecular weight of the rubber under mastication is illustrated in Fig. 3.11. Here also the minimum amount of the peptiser used (0.15 phr) brings about a significant change in $\overline{M}w$, the maximum effect being shown by 2,2' DDDS. Increasing the amount of peptiser did not reduce the molecular weight proportionately. The effect of MBT in reducing the molecular weight was found to be insignificant.

As the mastication proceeds, torque reaches a maximum value and then descends. It almost stabilises by half the period of mastication (i.e, 2.5 min), and this torque is taken as the stabilised torque. The values of the stabilised torque attained is plotted against the dosage of the peptiser in Fig.3.12. It can be seen that the stabilised torque reduces with the dosage of the peptiser. 2,2'DDDS and PCTP show the same trend, whereas in the case of MBT, the effect is not pronounced.

The totalised torque (TTQ) can be taken as a measure of the work done during mastication. The TTQ at a fixed torque (t =100Nm) is measured for all the samples. The effect of dosage of peptiser on TTQ is given in Fig.3.13. As in the previous cases the effect is more pronounced with the minimum dosage of the peptiser. MBT does not show much effect. The reduction in mastication energy for 2,2'DDDS and PCTP follows the same pattern.

The peptisers were found to reduce the temperature rise during mastication. Table 3.6 shows the rise in temperature (ΔT)with the corresponding dosage of the peptiser. It can be seen that there is a definite decrease in ΔT, with the incorporation of the peptiser. Here also the minimum dosage of the peptisers viz, 2,2'DDDS and PCTP, reduces ΔT to a significant level, further increase in the dosage bringing out only marginal effect. This agrees with the observations reported earlier. The peptisers can bring down the viscosity of the stock at a faster rate than the mix containing no peptiser, so that shear forces become less. This causes less heat generation during mastication in the presence of peptiser.

Effect of temperature

As the chamber temperature is increased, viscosity showed significant reduction. Fig.3.14 illustrates the same. The ideal temperature for effective functioning of 2,2' DDDS was reported to be in the range of 130-170°C. [17] The higher level of mastication realised in the case of samples peptised with DDDS and PCTP can be attributed to the effect of higher temperature. The control and MBT did not show such an effect since the decrease in viscosity is only due to the effect of temperature.

Effect of speed of rotor

Table 3.7 shows the effect of rotor speed on Wallace plasticity. Even at a low rotor speed, the effect of the peptiser is evident. At 50rpm, difference in Wallace plasticity (ΔPo), with the unmasticated sample is 8, whereas the same for the sample containing 0.15 phr of 2,2' DDDS is 15, almost double that of the former. As the rotor speed increases, Po is getting reduced. However, the effect of increasing the speed of rotor on viscosity is less for the control sample and the sample containing MBT. But the peptised samples show a decreasing trend with increase in speed of rotation. This can be attributed to the higher efficiency of the peptiser at the higher temperature generated by the higher rotor speed.

Effect of time

The effect of time of mastication on Wallace plasticity of the samples containing the peptisers and the control is given in Table 3.8. The effect of peptiser is predominant at 5 minutes of mastication, and the effect continues up to 10 minutes. Beyond 10 minutes, further reduction in plasticity is less and P_0 of all the samples are almost the same after prolonged mastication for 20 minutes. This indicates that beyond an optimum time, mastication does not produce any appreciable effect. This also can be attributed to the low viscosity of rubber attained during continuous mastication, so that slippage of the molecular chains occurs and hence further degradation is very slow.

CONCLUSIONS

1. Among the peptisers studied 2,2' dibenzamido diphenyl disulphide was found to perform better than or equal to pentachloro thiophenol.
2. An optimum dosage of peptiser was found to yield better results. An increase in the peptiser content does not bring about a corresponding reduction in molecular weight and the related properties.
3. MBT does not impart any peptising effect.

Table 3.6

Effect of dosage of peptiser on temperature rise during mastication

Initial Temp. 80°C; RPM 60; Time 5 (min)

	Temperature rise during mastication, ΔT °C		
Dosage	2,2'DDDS	PCTP	MBT
0	51	51	51
0.1	47	48	51
0.25	46	45	50
0.5	45	45	49

Table 3.7
Effect of rotor speed on Wallace plasticity

Temp: 80°C; Time 5 min; Initial Po (UM) = 49*

RPM	Wallace plasticity			
	CONTROL	MBT (0.15phr)	2,2' DDDS (0.15 phr)	PCTP (0.15 phr)
50	41	38	34	34
60	38	36	29	30
80	32	33	24	27
100	29	29	18	20

* Unmasticated.

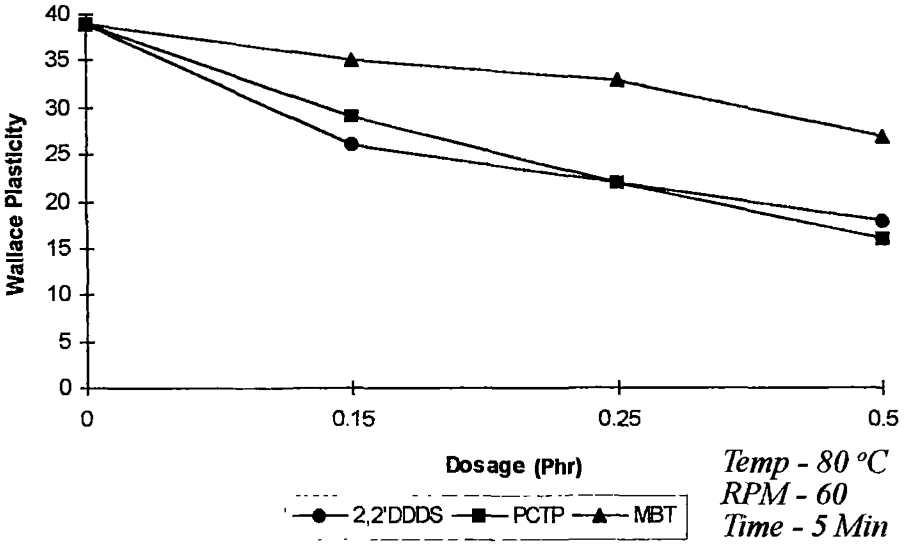
Table 3.8
Effect of time of mastication on Wallace plasticity

RPM. 60; Temp. 80°C; Initial Wallace plasticity (UM) =49*

Time	Wallace plasticity			
	CONTROL	MBT (0.15phr)	2,2' DDDS (0.15 phr)	PCTP (0.15 phr)
5	38	36	29	30
10	27	29	21	24
15	19	18	15	16
20	13	14	12	11

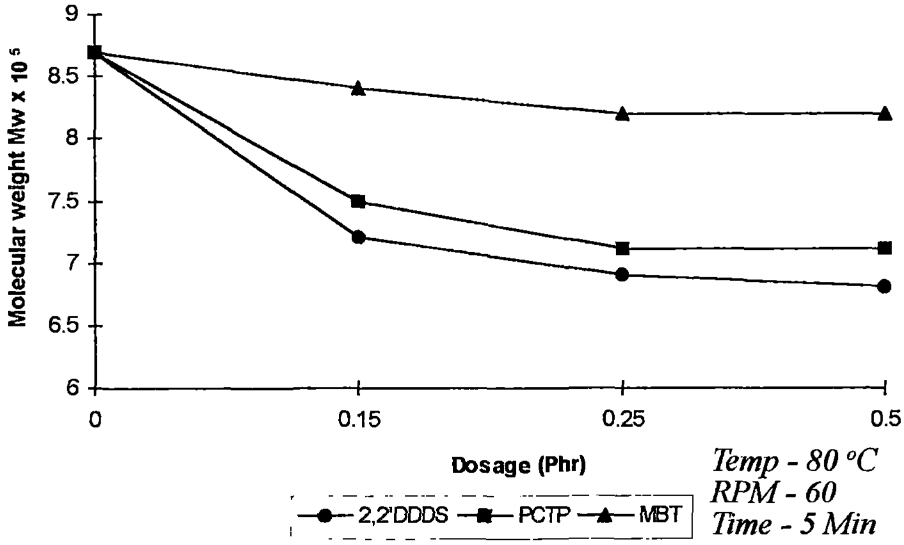
*Unmasaticated.

Figure 3.10 Effect of dosage of peptiser on Wallace Plasticity



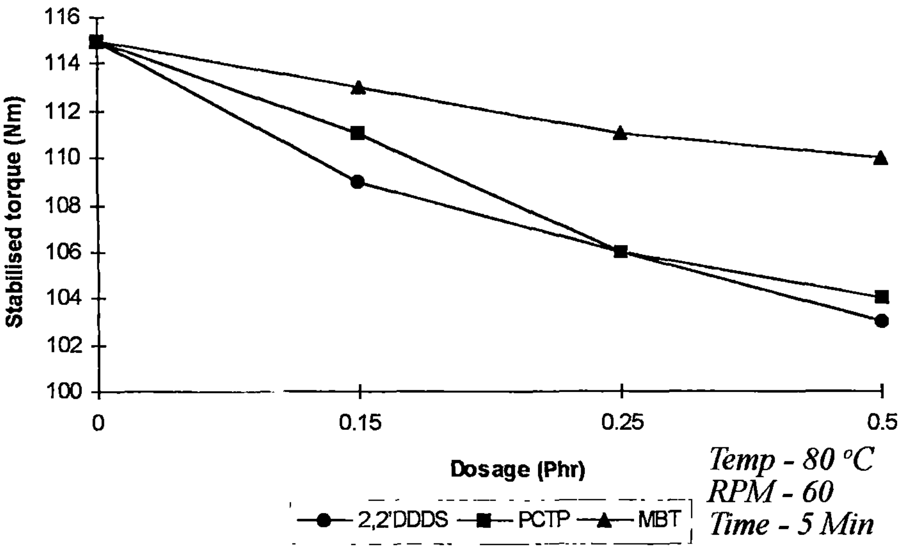
Temp - 80 °C
RPM - 60
Time - 5 Min

Figure 3.11 Effect of dosage of peptiser on Molecular weight



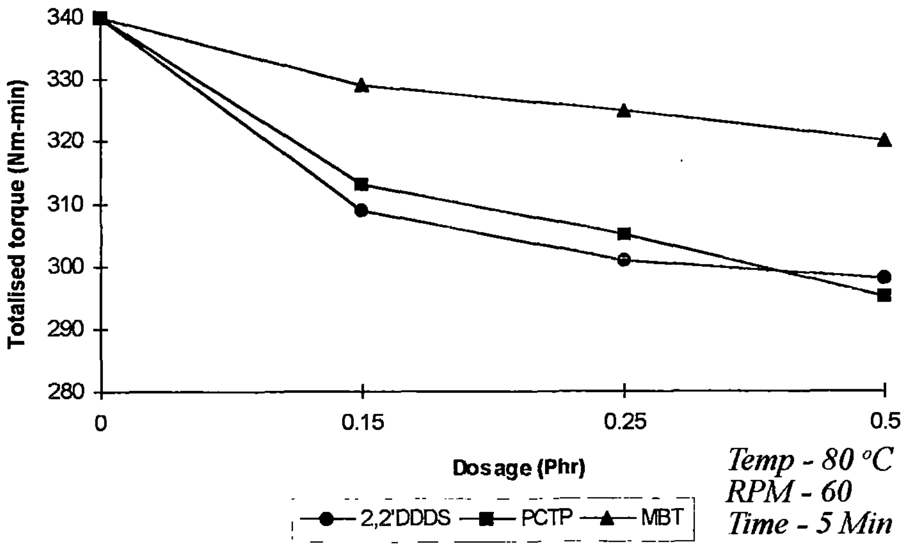
Temp - 80 °C
RPM - 60
Time - 5 Min

Figure 3.12 Effect of dosage of peptiser on stabilised torque



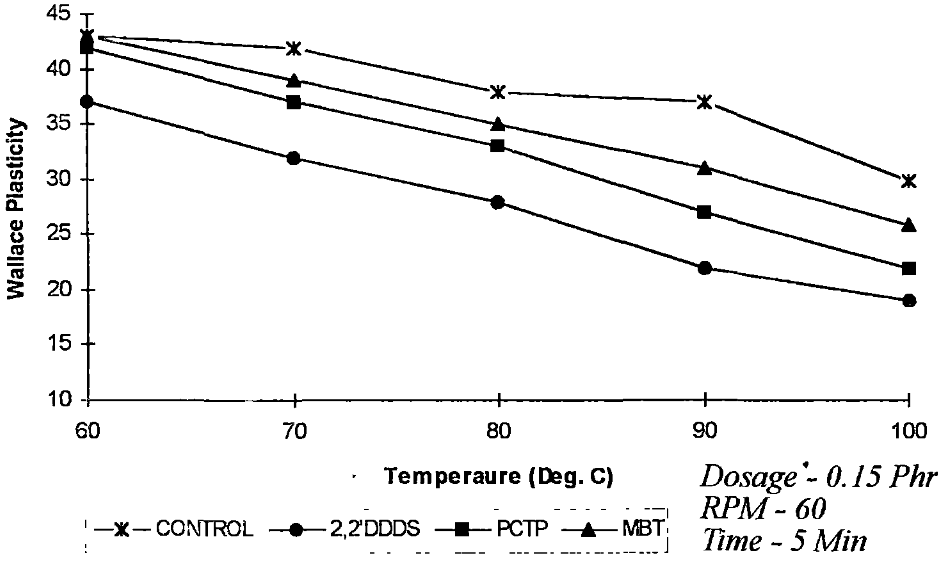
Temp - 80 °C
RPM - 60
Time - 5 Min

Figure 3.13 Effect of dosage of peptiser on totalised torque



Temp - 80 °C
RPM - 60
Time - 5 Min

Figure 3.14 Effect of temperature on Wallace Plasticity



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CHAPTER - IV

STUDIES ON DIFFERENT FORMS OF NATURAL RUBBER WITH SPECIAL REFERENCE TO RHEOLOGY AND BREAKDOWN BEHAVIOUR

PART I

COMPARATIVE EVALUATION OF ISNR 20 WITH CONVENTIONAL FORMS OF NATURAL RUBBER

One of the striking disadvantages of natural rubber is the variability in its properties, particularly its mastication behaviour. The problem assumes greater importance with its conventional forms such as sheet and crepe.

A major share of natural rubber in India, is being consumed by the tyre sector and the consumption pattern varies for different forms of NR. The conventional grades which find extensive use in the above sector are sheet (RSS 4 and RSS 5) and crepe (EBC IX and 2X). The market trends indicate that among the TSR grades, ISNR 20 is the preferred grade for the tyre sector. The contribution of ISNR to the total production of NR in the country is approximately nine per cent.

The major advantages of TSR are claimed to be its improved consistency in properties and the availability of different grades to suit individual requirements of the end user. Automation in processing as being adopted in the industry, especially in the tyre sector, calls for better consistency in the mastication behaviour of rubber so that variation in the compound viscosity is minimum. In spite of the best efforts by the NR producing countries, even today the conventional forms of NR such as sheet and crepe with wide variability in properties predominate.

Any attempt to understand the status of the available forms of raw rubber with respect to its processability and consistency will be highly rewarding as this can lead to innovations to improve the consistency of the same. The present study envisages a comparative evaluation of ISNR 20 with other conventional forms of NR which are being consumed by the tyre sector viz RSS 4, RSS 5 and EBC IX.

PART I A. RAW RUBBER PROPERTIES, PROCESSING CHARACTERISTICS AND VULCANIZATE PROPERTIES

Studies have been made comparing sheet and block grades of rubber processed from latex [1]. Also attempts to study the processabilty and vulcanizate properties of block rubbers, were made in comparison to those of conventional grades processed from the same raw material [2-4]. In most of the studies reported earlier, the number of samples and frequency of collections were limited. In this part the consistency in raw rubber, processing and vulcanizate properties of ISNR 20 has been compared with that of other forms .

EXPERIMENTAL

Samples of RSS 4, RSS 5, EBC IX and ISNR 20 were collected from different regions in the traditional rubber growing areas in Kerala, four times with an interval of three months each. As ISNR 20 and EBC are processed from fresh and semi-dried forms of field coagulum, both the types were included in the study. The samples are designated as fresh field coagulum (FC), and semi-dried field coagulum (DC). The details of the same are given in Table 4.1.

The raw rubber properties specified for ISNR and the acetone extractables were determined according to the respective IS procedures. The processing properties of the ACS-1 mix and the technological properties of the HAF (N330) black filled mixes (formulation given in Table 4.2) were evaluated as per the relevant ASTM test procedures.

The data were statistically analysed and the mean, coefficient of variation (CV) and the desirability measure (DM) were worked out. The mean value explains the average performance of the grade with regard to the parameter and the coefficient of variation estimates the level of consistency. A more consistent distribution has a lower coefficient of variation and vice-versa. In order to determine the desirability of different forms of NR with regard to its properties, a desirability measure (DM) has been worked out. Desirability measure is the sum of the squares of deviations of the observed values from the desired value expressed relative to the desired value.

Coefficient of variation CV = $\sigma / \bar{X} \times 100$

Where σ = standard deviation

$\bar{X}$ = mean

and Desirability measure (DM) = $\Sigma\left[\frac{Y - Y'}{N}\right]$

Where Y = observed value

Y' = desired value

N = No. of samples

Since performance stability and nearness to the desired value are equally important, mean, coefficient of variation and DM should be observed simultaneously for a reliable comparative analysis. A lower value for CV and DM indicates better consistency and performance respectively.

RESULTS AND DISCUSSION

Table 4.3 shows the statistically analysed data for raw rubber properties. As was expected, dirt content was minimum for sheet grades. Compared to estate brown crepe, EBC (DC) from the non-estate sector, absolute values are better for ISNR 20. The value of DM is higher for EBC(DC) grades while it is more or less the same for EBC(FC), ISNR 20 (FC) and ISNR 20 (DC) grades. Superiority of sheet grades is very evident from the significantly lower absolute values.

The more efficient drying methods of ISNR 20 grades impart lower volatile matter as is evident from their DM values. But CV is comparable in all the forms indicating same level of consistency. If field coagulum is processed fresh into crepe, lower volatile matter could be achieved, as is observed for EBC(FC). Processing of fresh field coagulum leads to lower volatile matter in ISNR also. Wrapping of ISNR with polyethylene sheet might also contribute to the lower volatile matter. In the case of sheets, the higher volatile matter may be attributed to the lower temperature in the smoke house and due to the removal of the sheets from the smoke house before complete drying prompted by a visually dry appearance. Storage of bare sheets in humid places also causes moisture absorption.

The field coagulum grades of rubber, viz EBC and ISNR 20, contain higher ash than sheet rubber. The processing of field coagulum in the fresh stage causes reduced ash content. EBC (FC) is close to ISNR 20 grades with respect to ash. EBC (DC) contains maximum ash. The trend is consistent as the CV value is found to be lower. However, DM is found to be the highest for EBC (DC). Sheet rubbers have the lowest ash content. Even the CV is lower compared to ISNR 20. DM also is found to be markedly lower for sheet.

Absolute values indicate that the lowest nitrogen content is for the crepe samples and the highest for the sheet. There is reasonably good consistency in all the samples except for ISNR 20 (FC). DM value is found to be minimum for crepe.

During the formation of field coagulum through spontaneous coagulation and during its storage, considerable bacterial activity takes place leading to decomposition of proteins into soluble products, resulting in lower nitrogen content in crepe as well as ISNR grades, processed from field coagulum.

Wallace plasticity (P_o) is indicative of the processabilty of the rubber and the energy required for mastication. Though the crepe samples show consistency, as is evident from lower CV values, the mean values for Po are higher for the same. This may be attributed to the lower level of thermo-oxidative chain scission taking place in the rubber, probably owing to the lower temperature of drying, compared to that of ISNR 20 and sheet. Mean values for ISNR 20 grades indicate that they are in the processable range of plasticity. It can be seen that consistency in P_o values for ISNR 20 grades and sheet grades are comparable. This agrees with the observations made by Livonniere[5] that the consistency of TSR is to be improved. DM values are minimum for RSS 4 and ISNR 20 (DC).

Plasticity retention index (PRI) is a measure of the resistance to oxidation of raw rubber. As the raw material used in the production of sheet rubber is fresh latex, PRI of the same is higher, as was expected. PRI of crepe rubber processed from dry field coagulum is comparatively lower, indicating the inferior quality of the raw material used. There is not much difference between PRI of the two types of ISNR 20. The CV values are also comparable for the sheet and ISNR 20 grades whereas the same is higher for the EBC grades. DM is minimum for the sheet grades followed by ISNR 20 and EBC (FC) grades.

As expected, acetone extractables are higher for the sheet grades, since the chances of degradation and leaching by water are less. The effect of storage of field coagulum on the acetone extractables is manifested by the lower value of the same by EBC (DC) grades. The CV values are comparable for sheet and ISNR 20 grades.

Processing properties.

Table 4.4 enlists scorch and cure characteristics of the mixes (ACS -1 and HAF -filled mixes). It is seen that for sheet grades, optimum cure time and scorch time are higher probably due to acid retention in the same. But evidently ISNR 20 grades show better consistency in both properties, as is evident from the CV values. This is definitely an advantage of ISNR 20, as it is showing consistent cure characteristics. But DM is minimum for the sheet grades. The above differences in scorch and cure characteristics are not so prominent for the HAF - filled vulcanizates. This could be attributed to the neutralisation of residual acidity by HAF black. CV values are comparatively lower for sheet grades, but differences are less significant, DM being maximum for EBC (DC) grades.

Technological properties.

Tensile properties of the HAF - filled compounds are given in Table 4.5. Modulus at 100 per cent and 300 per cent elongation and tensile strength are higher for sheet rubber. CV values are comparable for all the three forms. However, ISNR 20 processed from fresh field coagulum, evidently shows better consistency than the same from dry field coagulum, as is evident from the lower CV values. DM is minimum for sheet grades followed by EBC (FC) and ISNR 20 (FC) grades. CV is generally comparable and DM is maximum for EBC (DC). Elongation at break is comparable for all the three forms, DM and CV showing similar trends.

Ageing behaviour

Ageing studies of vulcanizates at 100°C show better retention in strength properties for the sheet grades, but better consistency is observed for ISNR 20 grades. CV values are marginally lower for the above. DM is minimum for sheet grades. At 70°C, the differences in ageing properties are observed to be less significant. DM is minimum for the EBC (DC) grades. The concentration of naturally occurring antioxidants is likely to be more in sheet rubber as it has been prepared by coagulation of latex under controlled conditions. Creosotic deposits formed due to smoking enhance the same. Concentration of natural antioxidants is lower in the field coagulum grades as a result of bacterial coagulation. Moreover, field coagulum undergoes degradation to varying levels during storage. This explains the poorer ageing characteristics of EBC and ISNR 20 grades compared to sheet grades.

Table 4.6 summarises the vulcanizate properties of the above compounds. Sheet grades show better wear, set and crack initiation characteristics. This could be explained on the basis of higher molecular chain length in sheets as these are subjected to minimum mechanical work during processing. The lower dirt content contributes to better crack initiation characteristics compared to the field coagulum grades. CV values are almost comparable for all the grades with respect to abrasion and compression set properties. The absolute values of the above indicate the superiority of sheet grades over the field coagulum grades. DM is minimum for sheet grades. ISNR 20 (FC) and EBC(FC) grades show higher values for CV with respect to flex cracking characteristics.

Heat build-up values are marginally lower for ISNR 20 grades and this could be attributed to the fact that the 100% and 300% moduli values are lower for the above. DM is significantly lower for the same. However, CV values are distributed over a narrow range.

CONCLUSIONS

1. Sheet rubber grades (RSS 4 and RSS 5) show better raw rubber properties than crepe and ISNR 20, except for volatile matter and plasticity.
2. Compared to ISNR 20, sheet grades were observed to have almost comparable level of consistency in raw rubber properties.
3. ISNR 20 grades show better consistency in processing properties such as scorch and cure characteristics.
4. Vulcanizate properties such as tensile strength and elongation at break are better for sheet grades compared to all other grades.
5. Significant differences were not observed among ISNR 20 processed from dry or fresh coagulum.

6. EBC processed from fresh field coagulum is superior to EBC from dry field coagulum in raw rubber and vulcanizate properties.
7. All the raw rubber properties are superior for ISNR 20 from dry field coagulum compared to EBC (DC).
8. Although ISNR 20 was expected to be more consistent, at least with respect to raw rubber properties, the level of raw material blending used for making these grades do not bring about this.

Table 4.1
Sources of samples

Form of rubber	Source
RSS 4, RSS 5	Palai, Venjaramood, Konni, Nilambur.
EBC (FC)	Mundakayam, Nagercoil, Kulasekharam, Manimala.
EBC (DC)	Different processing units in and around Kottayam.
ISNR 20(FC)	Punalur, Mundakayam, Nilambur.
ISNR 20(DC)	Palai, Thodupuzha, Poovarani and Kottayam.

Table 4.2
Formulation of HAF- filled mix

Ingredients	Part by weight
Natural rubber	100.0
Stearic acid	2.0
Zinc oxide	5.0
Naphthenic oil	5.0
HAF black (N330)	50.0
N-cyclohexyl-2 benzthiazole sulphenamide	0.7
Sulphur	2.5

Table 4.3

Raw rubber properties

Parameters	RSS 4	RSS 5	EBC (DC)	EBC (FC)	ISNR 20(DC)	ISNR 20(FC)
Dirt, %						
Mean	0.07	0.09	0.32	0.13	0.13	0.13
CV	57.40	47.83	52.28	54.48	42.59	76.08
DM	0.06	0.08	0.31	0.12	0.12	0.12
Volatile matter, %						
Mean	1.03	1.05	1.43	0.90	0.58	0.41
CV	31.41	31.43	34.43	39.36	31.26	41.99
DM	0.89	0.90	1.28	0.75	0.43	0.26
Ash, %						
Mean	0.44	0.45	0.79	0.53	0.63	0.60
CV	27.10	26.30	22.25	34.62	35.56	44.40
DM	0.29	0.30	0.64	0.38	0.48	0.45
Nitrogen, %						
Mean	0.48	0.47	0.40	0.37	0.46	0.45
CV	18.82	17.54	16.68	27.28	23.44	71.38
DM	0.30	0.29	0.22	0.19	0.28	0.27
Po						
Mean	44	46	51	53	40	44
CV	12.30	14.55	8.99	10.39	18.12	19.58
DM	4.9	7.3	11.1	23.6	4.9	8.4
PRI						
Mean	82	80	46	60	62	58
CV	12.43	9.48	34.24	25.8	11.89	19.99
DM	12.44	14.1	48.94	35.00	32.44	36.56
Acetone extract, %						
Mean	3.04	2.94	1.85	2.25	2.52	2.36
CV	13.50	12.21	18.62	22.21	10.93	17.50
DM	1.94	1.84	0.75	1.15	1.42	1.26

Table 4.4

Processing properties

Parameter	RSS 4	RSS 5	EBC (DC)	EBC (FC)	ISNR 20(DC)	ISNR 20(FC)
ACS 1 mix						
Scorch time at 120°C, seconds						
Mean	790	810	491	519	511	448
CV	39.91	32.30	42.12	37.84	20.30	21.47
DM	693	667	991	963	972	1035
Optimum cure time 150°C, seconds						
Mean	921	958	704	738	662	680
CV	23.26	19.11	18.35	18.77	6.17	12.61
DM	518	481	735	702	777	759
HAF - filled mix						
Scorch time at 120°C, seconds						
Mean	1027	1022	935	884	869	933
CV	24.27	14.45	9.34	17.10	13.10	16.08
DM	449	453	540	592	606	543
Optimum cure time at 150°C, seconds						
Mean	590	572	501	613	578	573
CV	9.78	9.46	5.76	14.37	6.80	7.07
DM	130.0	148.0	219.0	107.0	142.5	147.0

Table 4.5

Physical properties

Property	RSS 4	RSS 5	EBC (DC)	EBC (FC)	ISNR 20(DC)	ISNR 20(FC)
100% modulus, N/mm^2						
Mean	3.22	3.09	3.02	3.07	2.92	2.95
CV	12.89	6.0	10.83	7.13	15.32	5.95
DM	0.68	0.81	0.83	0.88	0.98	0.95
300% modulus, N/mm^2						
Mean	11.43	11.23	10.83	10.91	10.32	10.65
CV	9.09	3.23	6.40	3.19	15.44	6.35
DM	1.68	1.88	2.19	2.28	2.78	2.45
Tensile strength, N/mm^2						
Mean	24.43	24.58	23.77	22.80	23.04	23.53
CV	7.73	3.56	7.13	16.82	8.43	5.19
DM	2.57	2.42	4.2	3.23	3.96	3.48
Elongation at break,(%)						
Mean	579	596	607	604	619	602
CV	9.66	8.95	6.80	6.01	12.01	8.10
DM	118.58	120.5	111.83	109.33	107.88	114.33
Retention after ageing at 70°C, 14 days,%						
Mean	59.0	57.30	59.70	63.90	62.30	52.50
CV	9.74	15.03	21.0	17.08	19.6	20.9
DM	23.0	24.7	18.10	22.3	22.5	29.5
Retention after ageing at 100°C, 4 days,%						
Mean	27.18	24.82	22.64	21.0	20.73	17.09
CV	46.8	32.6	37.6	29.1	20.8	26.9
DM	25.82	28.18	32.0	30.36	32.27	35.91

Table 4.6

Technological properties

	Property	RSS 4	RSS 5	EBC (DC)	EBC (FC)	ISNR 20(DC)	ISNR 20(FC)
DIN abrasion loss, mm^3							
	Mean	84.73	83.44	100.22	98.54	95.49	93.70
	CV	15.95	14.55	12.13	16.03	11.23	11.05
	DM	20.38	19.09	35.87	34.19	31.14	29.43
Compression set at 70°C,%							
	Mean	28.87	28.82	36.06	33.81	34.04	34.43
	CV	14.63	11.59	12.86	7.96	15.98	16.83
	DM	4.94	4.89	12.13	9.88	10.11	10.50
Heat build up at 50°C, ΔT,°C							
	Mean	28.03	26.97	27.39	27.27	25.67	26.45
	CV	10.35	9.58	11.04	11.36	16.14	6.14
	DM	11.33	10.27	10.69	10.57	8.91	9.75
Resilience, %							
	Mean	55.04	54.60	55.35	54.51	55.39	54.83
	CV	4.50	5.14	5.90	5.46	5.38	1.72
	DM	6.72	7.13	6.38	7.22	6.34	6.90
Crack initiation, K. cycles							
	Mean	14.54	13.25	11.44	10.82	10.47	10.90
	CV	32.90	24.99	23.32	47.37	32.62	41.33
	DM	9.51	9.73	11.54	13.23	13.58	13.15
Crack failure, K. cycles							
	Mean	65.7	55.5	46.6	48.9	56.5	51.7
	CV	25.0	29.9	23.5	45.5	23.4	28.1
	DM	20.02	30.16	39.07	31.68	29.21	33.97

PART 1 B 1. RHEOLOGICAL PROPERTIES

Rheological behaviour of raw rubber and rubber compounds play an important role in the product manufacturing operations such as mixing, extrusion, calendering and moulding.[6-7] In order to predict the processability of an elastomer, test conditions should simulate the operating conditions as closely as possible. As the above operations involve, very high shear rates, capillary rheometer or torque rheometer can provide more realistic conclusions on the rheological response of rubber during processing.

CAPILLARY RHEOMETRY

Earlier studies on processability of rubber have been based on parameters such as Mooney viscosity and plasticity.[8-9] A few studies on the rheology of raw rubber have also been reported.[10-11] The objectives of such studies were to acquire typical flow data for different grades of natural rubber and to compare the rheological behaviour of these forms.

Different processing conditions are adopted for sheet, crepe, and technically specified rubber. The former two forms are dried at lower temperatures compared to TSR. The mechanical energy input in the production of TSR is also higher. This is reflected in the molecular parameters and plasticity of the different forms of NR.[12]

In the present study rheological and die swell behaviour of the three forms of natural rubber are reported.

EXPERIMENTAL

The various characteristics of different rubbers used in the study are summarised in Table 4.7. The samples were uniformly masticated on a two-roll mill. Eight grams of the test samples was put into the barrel and was forced down the capillary by the plunger attached to the moving crosshead. After a warm-up period of 3 minutes, the sample was extruded through the capillary at 10 different speeds. Forces corresponding to the specific plunger speeds could be measured by the pressure transducer attached to the plunger and were recorded using a strip chart recorder assembly.

The force and the crosshead speed were converted into apparent shear stress (τ_w) and shear rate ($\dot{\gamma}_w$) at the wall respectively using the equations, defined earlier involving the geometry of the capillary and plunger.

RESULTS AND DISCUSSION

For easier interpretation of results the samples have been grouped into two groups; Group I [RSS 4, EBC (FC), ISNR 20 (FC)] and Group II [RSS 4, EBC (DC) and ISNR 20 (DC)]. This grouping has been done mainly based on the starting material from which EBC or ISNR 20 has been prepared. In both cases RSS 4 has been included for comparison. Figure 4.1 shows the variation of shear viscosity of the samples (Group I) with shear rate at 90°C. The same for Group II are given in Fig 4.2. It is seen that the samples behave almost similarly, especially for Group I at higher shear rate. At the higher shear rates, the molecular level differences due to the raw material and mode of processing are getting nullified, that the response of the materials towards flow, becomes almost uniform. Figure 4.3 shows the variation of shear viscosity with shear rate for Group II samples at 120°C. RSS 4 samples show comparatively less viscosity at lower shear rates.

Table 4.8 shows the flow behaviour index (n') of the samples. The value of n' is much below unity indicating the highly non-Newtonian nature of the rubber melts. Further more, n' is not a constant. ISNR 20 and EBC samples processed from dry field coagulum show comparatively lower values for (n') .

Dependence of the melt viscosity on temperature was determined by the Arrhenius type equation

$$\eta = Ae^{E/RT}$$

Where A is a constant, E is the activation energy and R, the universal gas constant. By measuring the slope of a plot of log η Vs 1/T (Fig 4.4), energy of activation E can be found out, at different shear rates. Table 4.9 shows the values for E at 14.53 s^{-1}, 145.3 s^{-1}, 1453 s^{-1} and 14530 s^{-1}.It is found that activation energy decreases at higher shear rates. EBC (DC) samples shows less activation energy than all the other samples at all shear rates. However, the ISNR 20 (DC) samples do not follow this behaviour. Its values are almost close to that other forms.

Higher values of E shows higher dependence of viscosity on temperature. The poor quality of the raw material is manifested by the EBC (DC) sample with lower values of E, indicating the least dependence of viscosity on temperature. Raw rubber properties of EBC(DC) and ISNR 20 (DC) do not vary much except Mooney viscosity. However, the flow behaviour at higher shear rates differentiate these rubbers more distinctly as is shown by the values for E.

Table 4.10 gives the die swell (de/dc) of the raw rubber samples at two shear rates 65.85 s^{-1} and 658.5 s^{-1}. In general, die swell increases with shear rate. Die swell is a relaxation phenomenon. When the molten polymer flows through the capillary, shearing tends to maintain the molecular orientation of the polymer chains and when the melt emerges from the die, the molecules tend to recoil, leading to the phenomenon of die swell [13]. The elastic recovery of the polymer chain is influenced by factors such as stress, relaxation, crosslinking and presence of foreign matter.

It is seen that those forms of NR, which are being processed from dry field coagulum (DC) show lower die swell. This is expected as dry coagulum can undergo molecular chain scission or crosslinking during storage under adverse conditions. Higher gel content of the dry coagulum (DC) samples supports the above observation.

CONCLUSIONS :

1. The rheological behaviour of RSS 4, EBC (FC) and ISNR 20(FC) are almost similar especially at higher shear rates.
2. The value of the flow behaviour index (n') is much below unity for all the samples indicating the highly non-Newtonian nature of the rubber melts.
3. ISNR 20 (DC) and EBC (DC) samples processed from dry or semi dried field coagulum show comparatively lower values for n'.
4. The poor quality of EBC processed from dry field coagulum is manifested by its lower value for energy of activation.
5. The forms of NR, being processed from dry field coagulum show lower die swell, the minimum being for EBC(DC).

Table 4.7
Raw rubber properties

Form of rubber	Wallace plasticity	Plasticity retention Index	ML(1+4) 100°C	Gel content %	Acetone extract %
RSS 4	47	81	74	4.57	2.2
EBC (FC)	43	58	79	7.83	2.4
EBC (DC)	54	54	86	10.02	1.10
ISNR 20(FC)	54	67	67	5.82	2.76
ISNR 20(DC)	46	58	70	9.48	2.63

Table 4.8

Flow behaviour index (n') of different rubbers

Form of rubber	Temperature (°C)			
	90	100	110	120
RSS 4	0.27	0.24	0.21	0.20
EBC (FC)	0.26	0.26	0.23	0.22
EBC (DC)	0.24	0.22	0.21	0.19
ISNR 20 (FC)	0.28	0.25	0.23	0.22
ISNR 20 (DC)	0.25	0.23	0.22	0.21

Table 4.9

Activation energy of flow of different forms of NR (kJ Mol^{-1})

Form of rubber	Shear rate s^{-1}			
	14.53	145.3	1453	14530
RSS 4	4.2	3.6	2.7	2.2
EBC (FC)	4.3	3.5	2.8	2.3
ISNR 20 (FC)	4.3	3.6	2.7	2.3
EBC (DC)	3.9	3.2	2.3	1.9
ISNR 20 (DC)	4.1	3.6	2.6	2.1

Table 4.10

Die swell at 100°C of different forms of NR.

Form of rubber	Shear rate s^{-1}	
	65.8	658
RSS 4	3.8	6.6
EBC (FC)	3.5	7.1
EBC (DC)	2.0	4.9
ISNR 20 (FC)	3.2	7.8
ISNR 20 (DC)	3.0	5.3

Figure 4.1 Variation of shear viscosity with shear rate at 90 deg.C (Group I)

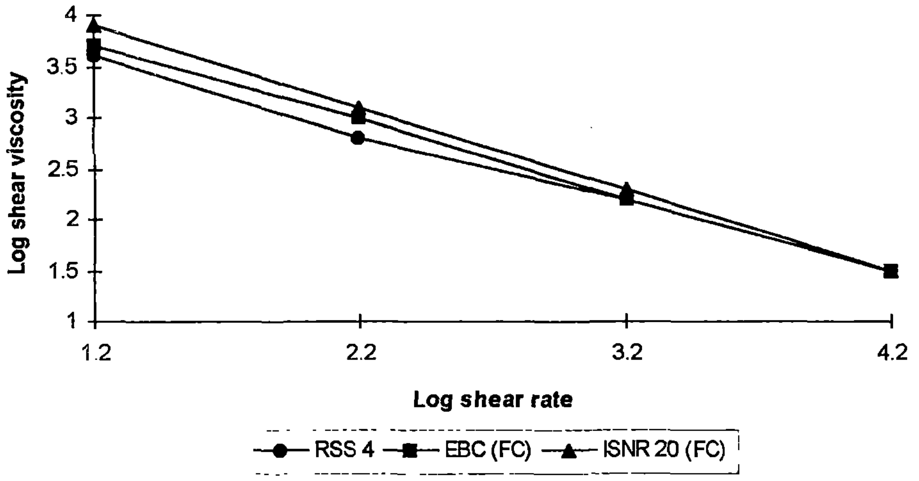


Figure 4.2 Variation of shear viscosity with shear rate at 90 deg.C (Group II)

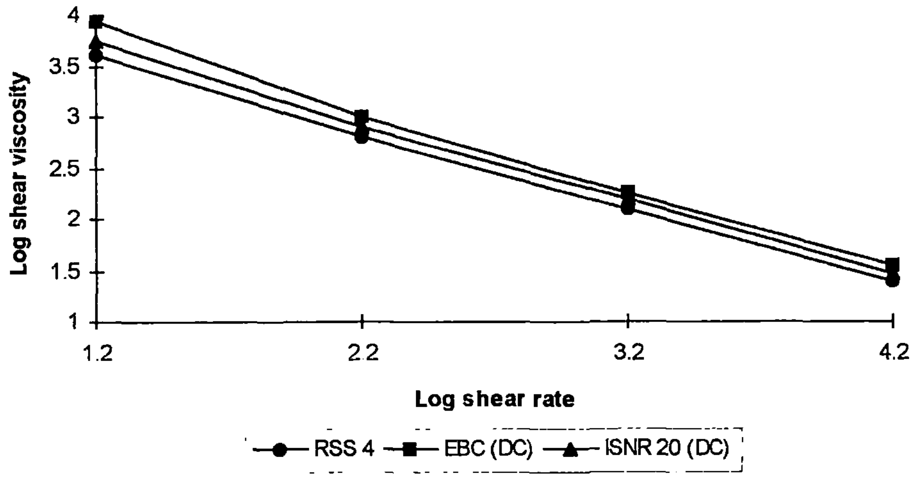


Figure 4.3 Variation of shear viscosity with shear rate at 120 deg.C (Group II)

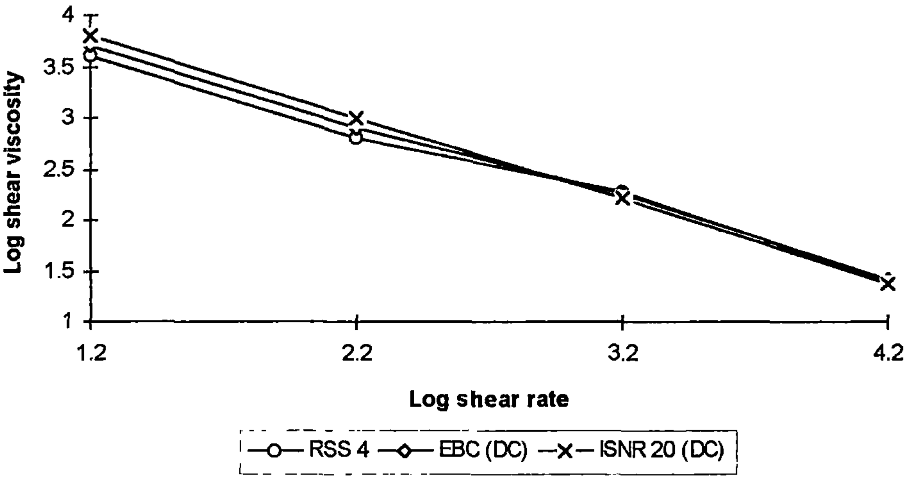
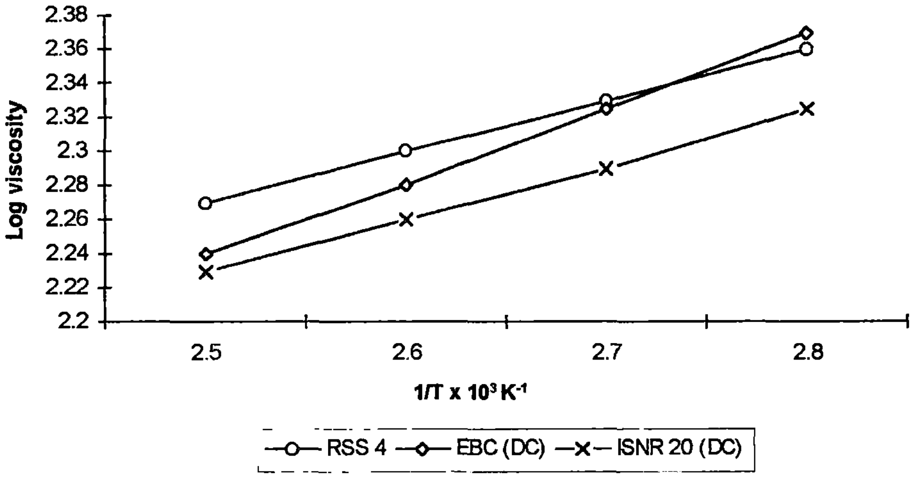


Figure 4.4 Log viscosity vs.1/T curves (Group II) [Shear rate 145.3 S^{-1}]



PART I B 2. MASTICATION STUDIES USING TORQUE RHEOMETER

The Haake-Rheocord 90 has been used to study the rheological behaviour of different forms of natural rubber. The instrument imparts a very complex shearing motion to the polymer and subsequently the data cannot be taken as that of fundamental rheological properties. However, the design of the equipment is similar to that of an internal mixer and hence the behaviour of the rubber in actual processing can be compared. The processability of different elastomers have been studied earlier using a Brabender Plasticorder.[14-16] The present study has been made to characterize the rheological behaviour of different forms of natural rubber using the Haake-Rheocord 90.

EXPERIMENTAL

The different forms of natural rubber studied were the same as in the previous case and were collected from the same sources. The raw rubber properties are given in Table 4.11. The samples were masticated in the Haake-Rheocord under the following conditions.

Specific volume	-	259 cc
Temperature	-	80°C
Revolution	-	60 min^{-1}
Time	-	15 min

The different forms of NR were characterized by the rheogram. The nature of the torque and temperature curves and their changes with time are characteristic of the material. To analyse the changes occurring during mastication, the following parameters, defined earlier, were evaluated.

M_2 (Nm) - The value of the torque at the 2nd minute.

M_{15} (Nm) - The value of the torque at the 15th minute, i.e., the final torque.

$M_{2\text{-}15}$ (Nm) - The reduction in the value of the torque.

T_F (°C) - Final temperature

ΔT°C - Difference between the initial and final temperature

$W_{2\text{-}15}$ (Nm - min) - The energy input from 2 min to 15 min, which can be obtained directly from the difference in the corresponding TTQ values.

The samples were masticated under the specified conditions and the above parameters were measured. The masticated raw rubber samples were matured for 24 h and again subjected to a second cycle of mastication, under the same conditions. Figures 4.5 and 4.6 show typical curves obtained for EBC(DC) and RSS 4 samples respectively for successive mastication tests. Table 4.12 gives the values for the first cycle of mastication. The highest M_2 value is obtained for RSS 4 samples followed by EBC (FC) samples. During the process of mastication, the torque and temperature attains almost a steady state which is characterized by M_{15} and T_F'. It can be seen that the final temperature is directly proportional to M_{15}. The largest reduction in torque i.e., $M_{2\text{-}15}$ was observed for EBC (FC) samples followed by ISNR 20(FC) samples. Increase in temperature i.e. (ΔT) is found to be proportional to the reduction in viscosity. However, in the case of RSS 4 , ΔT is the highest with comparatively lower value for $M_{2\text{-}15}$. This could be attributed to the higher molecular weight of RSS 4 sample, as it undergoes least degradation during processing. Hence the viscosity reduction in this case is less. In the case of field coagulum grades viz, EBC(FC) and ISNR 20 (FC), $M_{2\text{-}15}$ values are higher but ΔT is lower than that for RSS 4. ISNR 20(DC) samples give the lowest value for $M_{2\text{-}15}$. $W_{2\text{-}15}$, i.e. the work done in masticating the samples from the 2nd minute to the 15th minute, as measured by the TTQ, is higher for RSS 4, followed by EBC grades. ISNR 20 samples show lower values.

The values obtained for the defined parameters during the second mastication cycle are given in Table 4.13.

The extent of variation of the values for the said parameters for both cycles can be taken as a measure of the degradation to the sample. A higher difference between the two successive cycles of mastication indicates more degradation of the rubber at the molecular level. Bartha et.al.[14] have studied the degradation behaviour of different rubbers on a Brabender Plasticorder in a similar way. They have reported that butyl rubber showed minimum difference between successive mastications, indicating less degradation .

Table 4.14 gives the differences in the above parameters for the rubbers between the two successive mastication trials. It is seen that RSS 4 obviously, maintains difference for the above values indicating a higher level of degradation compared to the other forms. This is clearly seen from the differences in M_{15},T_F, ΔT and $W_{2\text{-}15}$ values. ΔP_0 i.e. the change in Po values of the same at the 2nd minute and 15th minute of mastication can be correlated with $M_{2\text{-}15}$ values. The EBC (FC) samples show similar behaviour but less significant compared to RSS 4.

The least difference is shown by EBC (DC) samples, as the extent of degradation occurred to the material during the second mastication is minimum. This is because, the material had already degraded to a high level, so that mechanical shearing becomes less effective during mastication to cause further breakdown.

The torque (M) at a particular temperature can be taken as approximately equivalent to viscosity. Hence, Arrhenius equation can be applied and

$$\log M \quad = \quad Ae^{E/RT}$$

Where M is the torque, E is the activation energy, R the universal gas constant and A a constant. A plot of log M vs 1/T can give straight lines, characteristic of each sample. The slope of the same can give a measure of the energy of activation, though the absolute values may be far from the values obtained from capillary rheometry.

The plot of log M vs 1/T made for EBC (DC) samples for the two mastication tests are given in Figure 4.7. The values of $\frac{\Delta \log M}{\Delta 1/T}$ are worked out for each sample for both the mastication tests and are given in Table 4.15. It can be seen that the difference between the gradients are maximum for RSS 4 samples and minimum for EBC (DC) samples. EBC (FC) samples show higher levels of degradation though ISNR 20 samples (both grades) show almost similar values. The lower value for the gradient obtained for EBC (DC) agrees well with the lower values for energy of activation E obtained when the same were evaluated using the capillary rheometer

CONCLUSIONS

1. The torque rheometer can give meaningful conclusions on the rheological behaviour of different forms of natural rubber.
2. The difference in the extent of breakdown parameters of the rubber, during successive mastication can be taken as a measure of the degradation.

3. A plot of log M vs.1/T can give straight lines characteristic of each sample. The slope of the same can give a measure of the energy of activation.
4. RSS 4 gives maximum difference between the slopes for Arrhenius plots and EBC (DC) the minimum, indicating higher extent of degradation for the former.
5. The lower values for the gradient of the Arrhenius plot, obtained for EBC (DC) agrees well with the lower values for energy of activation E, manifested by the same, using a capillary rheometer.

Table 4.11
Raw rubber properties

Form of rubber	Wallace plasticity	PRI	Ash %	Volatile matter %	Dirt %	Nitrogen. %
RSS 4	46	81	0.63	0.92	0.03	0.56
EBC (FC)	53	64	0.57	1.25	0.20	0.48
EBC (DC)	54	56	0.72	1.61	0.60	0.40
ISNR 20(FC)	52	60	0.63	0.46	0.13	0.38
ISNR 20(DC)	41	57	0.71	0.37	0.11	0.45

Table 4.12
Characteristic values for Ist cycle of mastication

Form of rubber	M_2 (Nm)	M_{15} (Nm)	T_F(°C)	M_{2-15}	ΔPo	ΔT(°C)	W_{2-15} (Nm-Min)
RSS 4	128	84	158	44	16	78	1303
EBC (FC)	123	73	148	50	19	68	1240
EBC (DC)	125	79	148	46	15	65	1202
ISNR 20(FC)	123	74	146	49	17	66	1139
ISNR 20(DC)	100	68	142	32	12	62	1150

Table 4.13
Characteristic values for 2nd cycle of mastication

Form of rubber	M_2 (Nm)	M_{15} (Nm)	T_F(°C)	M_{2-15}	ΔPo	ΔT(°C)	W_{2-15} (Nm-Min)
RSS 4	77	55	131	22	10	51	859
EBC (FC)	94	74	141	20	12	58	1064
EBC (DC)	85	63	130	22	13	58	975
ISNR 20(FC)	87	57	130	30	14	50	949
ISNR 20(DC)	71	50	128	21	9	51	939

Table 4.14

Difference in characteristic values during Ist and 2nd mastication cycles.

Form of rubber	M_2 (Nm)	M_{15} (Nm)	TF(°C)	M_{2-15} (Nm)	ΔPo	ΔT(°C)	W_{2-15} (Nm-min)
RSS 4	51	29	27	22	6	27	444
EBC (FC)	38	10	18	28	6	10	265
EBC (DC)	31	5	7	26	3	7	138
ISNR 20(FC)	36	17	16	19	3	16	190
ISNR 20(DC)	29	18	14	11	3	11	211

Table 4.15

$\frac{\Delta \log M}{\Delta 1/T}$ values for different forms during successive mastication cycles x 10^3

Form of rubber	Ist cycle	IInd cycle
RSS 4	0.86	0.54
EBC (FC)	0.74	0.51
EBC (DC)	0.48	0.41
ISNR 20(FC)	0.59	0.47
ISNR 20(DC)	0.53	0.49

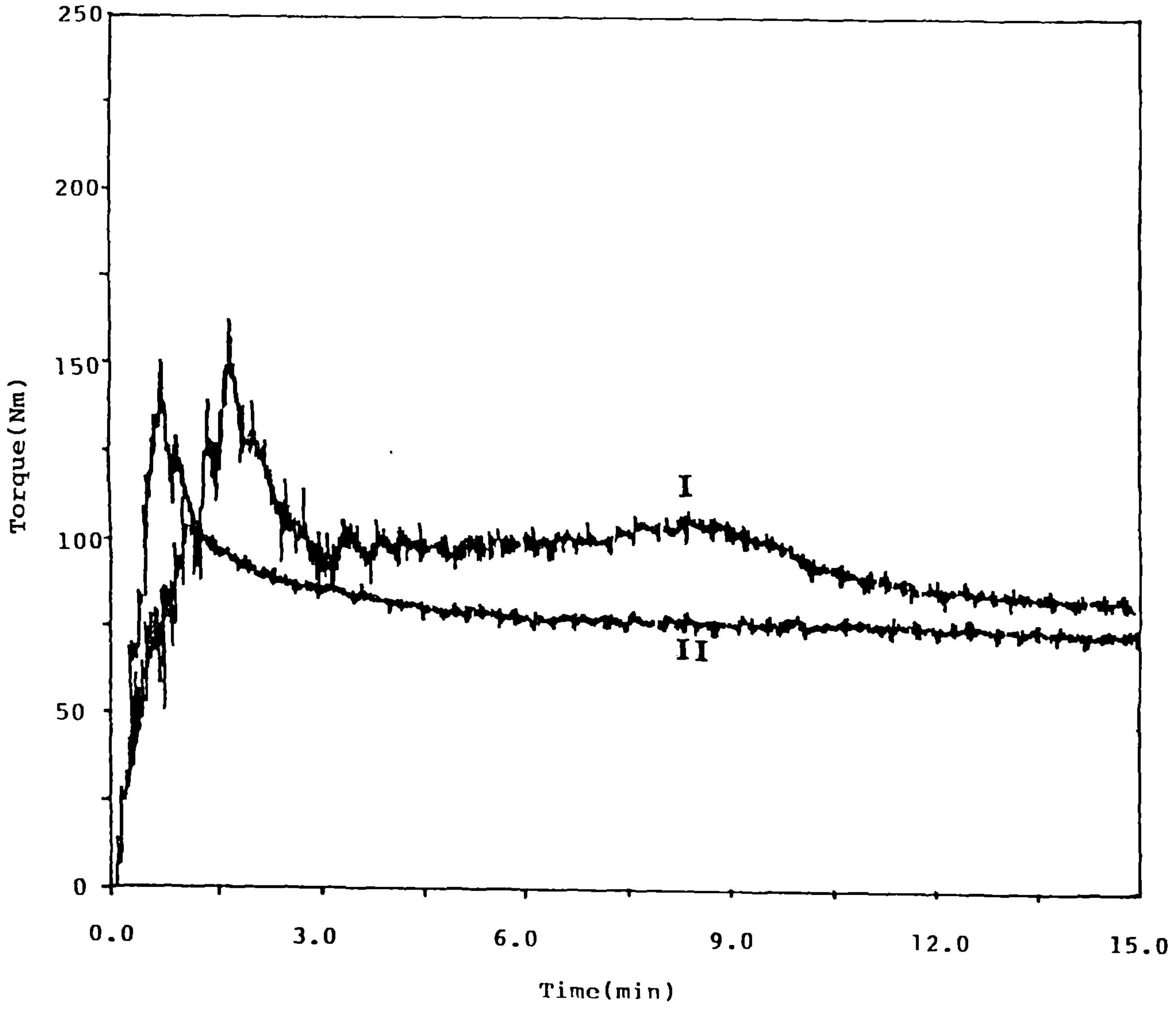


Fig. 4.5 Typical Rheogram obtained for EBC (DC) during successive mastication

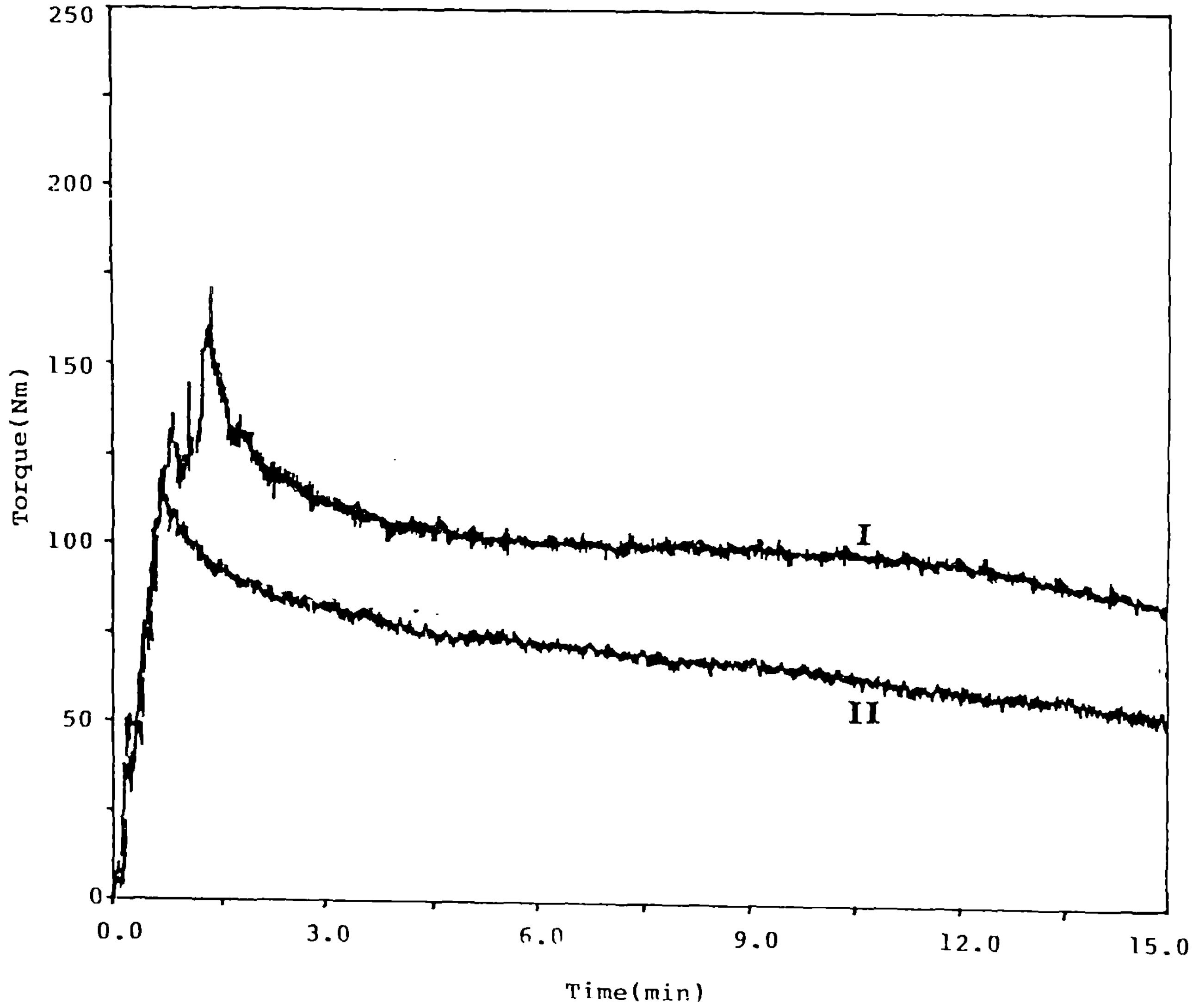
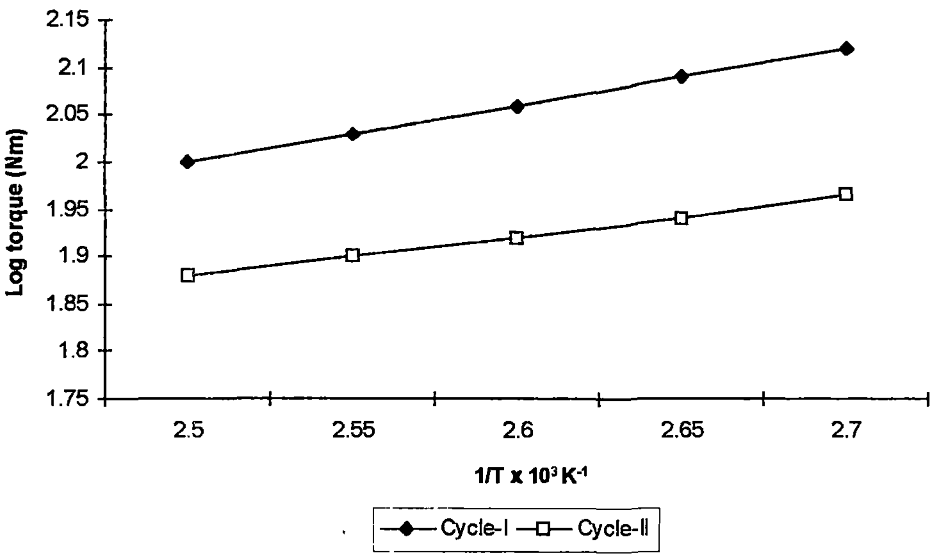


Fig. 4.6 Typical Rheogram obtained for RSS 4 during successive mastication

Figure 4.7 Variation of Log torque with temperature for EBC (DC) sample



PART II

COMPARATIVE ASSESSMENT OF BREAKDOWN BEHAVIOUR OF ISNR 20 AND CONVENTIONAL FORMS OF NATURAL RUBBER

The breakdown behavior of different forms of natural rubber may vary as the source material and the route for processing the same are different. The breakdown behaviour of natural rubber and its influence on processability have been studied using a Brabender Plasticorder and attempts were made to evaluate the suitability of a breakdown index (BI) derived from such measurements.[18,19] As such, there is no fixed definition to describe rubber breakdown. The change in Mooney viscosity or Wallace plasticity before and after mastication may provide some indication of the same. Often, it was found that the BI suggested was not satisfactory in predicting the processing behaviour of mixed compounds. A 'toughness index' was also suggested, but being proprietary the details were not disclosed.[20] Another approach to the problem was to assign a viscosity reduction parameter (VRP), in which a drop in viscosity after a fixed cycle of thermal degradation in a heated press at a fixed temperature was measured[21]. It was reported that, at about 200°C, VRP holds better correlation with breakdown in an internal mixer.

In the present work, different forms of NR have been studied with special reference to the effect of raw rubber properties on breakdown parameters. A comparative evaluation of the rubbers with respect to the above parameters has also been made.

EXPERIMENTAL

The breakdown properties of the following forms of natural rubber were studied.

(i) ISNR 20 (FC)
(ii) EBC (FC)
(iii) ISNR 20(DC)
(iv) EBC (DC)
(v) RSS 4

The samples were collected from four different locations. The mode of collection was described in Chapter II. The total number of samples collected for each form was 16. The raw rubber properties (P_o and PRI) for the samples were determined. Each sample was masticated on the Haake-Rheocord 90 under the following conditions.

RPM	- 40
Time	- 20 min
Initial temperature	- 40°C

From the Rheocord data, the following parameters were evaluated. Figure 4.8 illustrates the same.

t max - Maximum torque attained

$[TTQ]_1$ - Totalized torque at a constant torque value t = 100 Nm, so that the same can give the energy required for mastication of the samples to a fixed viscosity level.

T_1 - Temperature (°C) at t = 100 Nm

$[BI]_1$ - Rate of initial breakdown from t max to the fixed torque t = 100 (Nm), measured from the drop in torque with time.

$[TTQ]_2$ - Final TTQ

$[BI]_2$ - Rate of final breakdown from t = 100 Nm to the final torque.

T_2 - Final temperature(°C).

RESULTS AND DISCUSSION

Table 4.16 gives the mean and CV of the above properties of the different forms of NR. As discussed in the previous section, ISNR 20(DC) samples showed the lowest mean value for P_0, whereas EBC (FC) showed the maximum value. Plasticity retention index (PRI) is maximum for RSS 4 and minimum for EBC (DC). The variation in PRI values is maximum for EBC (DC) and minimum for RSS 4, as is indicated by the CV values. The mean values for energy required to masticate the samples to a fixed torque, i.e., $[TTQ]_1$ is found to be the highest for ISNR 20 (FC) samples. This is unexpected, since RSS 4, which is subjected to minimum mechanical breakdown during processing is expected to consume more energy during mastication. A wide difference in the CV for the above parameter is observed between ISNR 20 (FC) and ISNR 20(DC) samples.

Initial rate of breakdown $[BI]_1$ is the highest for EBC (DC) samples, followed by ISNR 20(DC) samples. Wide variation is shown by ISNR 20(DC) samples. RSS 4 samples give CV almost comparable to that of ISNR 20(FC). Final temperature T_2 (°C) is the lowest for

EBC (DC) samples showing less heat generation during mastication. However, ISNR 20 (FC) and ISNR20 (DC) samples show better consistency with regard to the temperature build-up. RSS 4 also showed a more consistent behaviour than the EBC samples.

The rate of final breakdown is less than that of the initial breakdown. This is because the torque attains almost an equilibrium value at (t = 100 Nm) and further mastication does not change the torque considerably. The higher viscosity attained by the rubber at equilibrium torque reduces the effect of shearing to a lesser extent. The final rate of breakdown is the highest for EBC (DC). This can be attributed to the lower initial plasticity of the above samples. The coefficient of variation for the rate of final breakdown $[BI]_2$ is found to be less for ISNR 20(DC) samples compared to all the other samples.

Effect of breakdown on raw rubber properties.

Attempts were made to correlate the raw rubber properties viz. Po and PRI with the breakdown parameters defined earlier, for each form of rubber.

In the case of RSS 4 a highly significant positive correlation existed between Po and $[TTQ]_1$, i.e. the energy required to masticate the rubber to a fixed viscosity level. The magnitude of the relationship is shown in Table 4.17 Also such a correlation exists between P_o and the final TTQ i.e. $[TTQ]_2$. Being the least degraded rubber during processing, the dependence of mastication energy on Po can be justified since P_o can be taken as a direct measure of molecular weight and gel content . As the Po is high, the molecular chain length is high and hence the work required to shorten the chain length will be proportionately high. A weak correlation has been observed between PRI and the final TTQ.

Table 4.18 gives the correlation analysis for ISNR 20(FC). Here also Po shows a significant correlation between energy of mastication and Po but not to the same magnitude as that for RSS 4. No correlation has been observed between PRI and any other parameter.

However, ISNR 20(DC) gives a different trend. As is evident from Table 4.19, significant positive correlation exists between the following parameters.

Po and $[TTQ]_1$, i.e. TTQ at torque t = 100 Nm
Po and $[TTQ]_2$, i.e. final TTQ
Po and temp T_1(°C) at torque t = 100 Nm
Po and final temp T_2(°C)
PRI and rate of final breakdown, i.e. $[BI]_2$

Also significant negative correlation exists between

PRI and rate of initial breakdown, i.e. $[BI]_1$

Compared to all other forms, ISNR 20(DC) shows a strong dependence of breakdown parameters on the raw rubber properties. So also, it was observed in the previous section, that there was not much difference in the processing and vulcanizate properties of ISNR 20(DC) and ISNR 20(FC) samples. However, the dependence of breakdown parameters on raw rubber properties varies widely for both the forms.

In the case of ISNR 20(FC) the significant correlation is observed only between Wallace plasticity (P_o) and energy of mastication. EBC samples do not show any significant correlation(Table 4.20 & Table 4.21).

Analysis of variance (ANOVA)

To test the equality of means, analysis of variance was tested, and wherever the absolute difference between treatment pairs was lower than CD, it is taken as non-significant, and hence the treatments can be compared statistically and vice-versa.

Table 4.22 (a) and (b) give the analysis of variance for P_o. It can be seen that treatment pairs viz,

RSS 4 and ISNR 20 (FC)
RSS 4 and EBC (DC)
ISNR 20 (FC) and ISNR 20 (DC)
ISNR 20(FC)and EBC (DC)
ISNR 20(DC)and EBC (DC) can be compared.

In the case of PRI less number of treatment pairs are statistically comparable [Table 4.23 (a) and (b)]

ISNR 20 (FC) and ISNR 20 (DC)
ISNR 20 (FC) and EBC (FC)
ISNR 20 (DC) and EBC (DC)

show non-significant difference. It could be noted, except for the first pair, that the raw material used for the preparation of the rubbers were the same.

Table 4.24 (a) and (b) explain the ANOVA for energy of mastication i.e., $[TTQ]_1$ required to masticate the rubber to a fixed torque. The following pairs show behaviour comparable statistically.

RSS 4 and ISNR 20 (FC)
RSS 4 and EBC (FC)
ISNR 20 (DC) and EBC (FC)

The similarity of the first two pairs indicate the better quality of the raw material. As noted earlier the same is high for the above samples. The similarity between ISNR 20 (DC) points out the higher quality of field coagulum being processed by the units which produce ISNR 20 in the non-estate sector.

Table 4.25 (a) and (b) give the result of anova for the rate of initial breakdown, $(BI)_1$. Except for the following pairs the differences are non-significant.

RSS 4 and EBC (DC)
ISNR 20 (FC) and EBC (DC)

ISNR 20 (DC) and EBC (DC)
EBC (DC) and EBC (FC)

It is seen that non-similarity in the rate of breakdown can be due to the difference in the original raw material used. The significant difference between ISNR 20 (DC) and EBC (DC) indicates the poor quality of EBC (DC). This can be justified as ISNR 20 (DC) can be compared with RSS 4, in respect of the rate of initial breakdown.

Table 4.26 (a) and (b) give the ANOVA for final $[TTQ]_2$. Only four pairs holds non-significant difference.

RSS 4 and ISNR 20 (FC)
RSS 4 and ISNR 20 (DC)
RSS 4 and EBC (FC)
ISNR 20 (DC) and EBC (FC)

The ANOVA for this parameter is almost the same as in the case of $[TTQ]_1$. Here also the higher quality of raw material imparts similar behaviour between the pairs.

In the case of final breakdown $(BI)_2$, similar rates are shown between

RSS 4 and ISNR 20 (FC)
ISNR 20 (FC) and ISNR 20 (DC)
ISNR 20 (FC) and EBC (FC).

The results are shown in table 4.27 (a) and (b). The non-inclusion of EBC (DC) in the above pairs shows that the raw material used for the same is totally different from that of the other forms.

Table 4.28 (a) and (b) explain the ANOVA for final temperature. (T_2 °C) The pairs showing similarity are

RSS 4 and ISNR 20 (FC)

RSS 4 and ISNR 20 (DC)

ISNR 20 (FC) and ISNR 20 (DC)

ISNR 20 (DC) and EBC (FC).

This also points out to the better quality of raw material used for the processing of ISNR 20 in the non-estate sector. The absence of EBC (DC) from the above groups shows the inferior quality of the raw material being used for the same.

CONCLUSIONS

1. The easiness of breakdown was found to be maximum for EBC (DC) followed by ISNR 20 (DC).
2. In the case of RSS 4, a highly significant positive correlation existed between Wallace plasticity (P_0) and the energy required for mastication of the same.
3. ISNR 20 (DC) was observed to have maximum dependence of breakdown parameters on raw rubber properties.

4. Analysis of variance test for the breakdown parameters of different forms of NR indicated that comparisons are possible, between the grades, though EBC (DC) showed odd behaviour.

Table 4.16
Mean and CV values for the breakdown characteristics

	FORM OF RUBBER									
Parameter	**ISNR 20(FC)**		**ISNR 20(DC)**		**RSS 4**		**EBC(FC)**		**EBC(DC)**	
	Mean	**CV**	**Mean**	**CV**	**Mean**	**CV**	**Mean**	**CV**	**Mean**	**CV**
Wallace plasticity	49.4	8.6	43.7	22.4	50.8	10.4	57.4	17.9	47.9	18.5
Plasticity rention index	56.7	18.1	52.6	21.5	77.7	6.6	60.3	20.1	47.3	19.3
TTQ at T = 100 Nm (Nm - Min)	1342	14.1	1019	36.3	1239	22.7	1107	24.5	809	14.1
Initial rate of breakdown $[BI]_1$	12.1	18.4	19.4	43.2	11.9	20.2	13.1	24.5	20.4	17.0
Final TTQ (Nm - Min)	2216	4.7	2105	6.3	2179	5.2	2109	9.3	1905	7.9
Final rate of breakdown $[BI]_2$	0.79	36.2	0.94	25.8	0.96	37.9	0.97	31.6	1.57	50.9
Final temp T_2(°C)	112.9	3.6	110.9	4.5	110.8	4.5	107.9	6.9	102.5	6.2

Table 4.17
Correlation analysis for RSS 4 samples

Variables	Correlation coefficient	T value
X_1 & X_3	0.7379	4.09**
X_1 & X_4	0.5964	-2.78*
X_1 & X_5	0.3909	1.59
X_1 & X_6	0.7752	4.59**
X_1 & X_8	-0.1288	-0.49
X_2 & X_3	-0.5750	-2.63
X_2 & X_4	0.3728	1.50
X_2 & X_6	-0.6127	-2.90*
X_2 & X_7	0.1892	0.720

X1 - Po
X2 - PRI
X3 - TTQ at torque t = 100 Nm i.e. $[TTQ]_1$
X4 - Rate of initial breakdown i.e. $[BI]_1$
X5 - Temp. T1 (°C) at t = 100 Nm
X6 - Final TTQ i.e. $[TTQ]_2$
X7 - Rate of final breakdown $[BI]_2$
X8 - Final temp T2(°C)
* - Significant
** - Highly significant

Table 4.18

Correlation analysis for ISNR 20(FC)

Variables	Correlation coefficient	T value
X_1 & X_3	0.6538	3.23**
X_1 & X_4	-0.6538	-0.790
X_1 & X_5	0.3345	1.33
X_1 & X_6	0.5112	2.23*
X_1 & X_8	0.0869	0.33
X_2 & X_3	0.3386	1.35
X_2 & X_4	0.0762	0.29
X_2 & X_6	0.3144	1.24
X_2 & X_7	-0.1409	-0.53

Table 4.19

Correlation analysis for ISNR 20(DC)

Variables	Correlation coefficient	T value
X_1 & X_3	0.8429	5.86**
X_1 & X_4	-0.8577	-6.24**
X_1 & X_5	0.8612	6.34**
X_1 & X_6	0.6679	3.36**
X_1 & X_8	0.8435	5.88**
X_2 & X_3	0.4466	1.87
X_2 & X_4	-0.3174	1.25
X_2 & X_6	0.2320	0.89
X_2 & X_7	-0.5397	2.40*

Table 4.20
Correlatation analysis for EBC(DC)

Variables	Correlation coefficient	T value
X_1 & X_3	0.5094	2.21*
X_1 & X_4	0.1861	0.71
X_1 & X_5	0.0123	0.05
X_1 & X_6	-0.1279	-0.48
X_1 & X_8	-0.0334	-0.13
X_2 & X_3	-0.2863	-1.12
X_2 & X_4	-0.1322	-0.49
X_2 & X_6	0.3058	1.20
X_2 & X_7	-0.3938	-1.60

Table 4.21
Correlation analysis for EBC (FC)

Variables	Correlation coefficient	T value
X_1 & X_3	-0.1969	-0.75
X_1 & X_4	0.1535	0.58
X_1 & X_5	-0.1860	-0.71
X_1 & X_6	-0.3735	-1.15
X_1 & X_8	-0.4436	-1.85
X_2 & X_3	0.2177	0.83
X_2 & X_4	-0.4510	-1.89
X_2 & X_6	-0.5089	-2.21*
X_2 & X_7	-0.1699	-0.65

Analysis of variance for Wallace plasticity

Table 4. 22(a)

Form of rubber	Mean
RSS 4	50.81
ISNR 20(FC)	49.44
ISNR 20(DC)	43.69
EBC (DC)	47.94
EBC (FC)	57.38
	VR**= 4.90 CD=6.34

Table 4. 22(b)

Treatment pairs		Absolute difference	NS/S
RSS 4	ISNR 20(FC)	1.32	NS
RSS 4	ISNR 20(DC)	7.12	S
RSS 4	EBC (DC)	2.87	NS
RSS 4	EBC (FC)	6.57	S
ISNR 20(FC)	ISNR 20(DC)	5.75	NS
ISNR 20(FC)	EBC(DC)	1.50	NS
ISNR 20(FC)	EBC(FC)	7.94	S
ISNR 20(DC)	EBC(DC)	4.25	NS
ISNR 20(DC)	EBC(FC)	13.69	S
EBC (DC)	EBC(FC)	9.40	S

Analysis of variance for plasticity retention index

Table 4.23(a)

Form of rubber	Mean
RSS 4	77.69
ISNR 20(FC)	56.69
ISNR 20(DC)	52.62
EBC (DC)	47.25
EBC (FC)	60.25
	VR**= 21.89 CD = 6.95

Table 4.23(b)

Treatment pairs		Absolute difference	S/NS
RSS 4	ISNR 20(FC)	21.0	S
RSS 4	ISNR 20(DC)	25.07	S
RSS 4	EBC (FC)	30.44	S
RSS 4	EBC (DC)	17.44	S
ISNR 20(FC)	ISNR 20(DC)	4.07	NS
ISNR 20(FC)	EBC (DC)	9.44	S
ISNR 20(FC)	EBC (FC)	3.56	NS
ISNR 20(DC)	EBC (DC)	5.37	NS
ISNR 20(DC)	EBC (FC)	7.63	S
EBC (DC)	EBC (FC)	13.00	S

Analysis of variance for $[TTQ]_1$

Table 4.24(a)

Form of rubber	Mean
RSS 4	1239.1
ISNR 20(FC)	1342.0
ISNR 20(DC)	1018.0
EBC (DC)	809.0
EBC (FC)	1107.0
	VR ** = 9.97 CD = 183.19

Table 4.24(b)

Treatment pairs		Absolute Difference	NS/S
RSS 4	ISNR 20(FC)	103.56	NS
RSS 4	ISNR 20(DC)	220.18	S
RSS 4	EBC (DC)	429.18	S
RSS 4	EBC (FC)	132.12	NS
ISNR 20(FC)	ISNR 20(DC)	323.75	S
ISNR 20(FC)	EBC(DC)	532.75	S
ISNR 20(FC)	EBC(FC)	235.69	S
ISNR 20(DC)	EBC(FC)	209.00	S
ISNR 20(DC)	EBC(FC)	88.06	NS
EBC (DC)	EBC(FC)	297.06	S

Analysis of variance for $[BI]_1$

Table 4.25(a)

Form of rubber	Mean
RSS 4	11.96
ISNR 20(FC)	12.06
ISNR 20(DC)	19.38
EBC (DC)	20.38
EBC (FC)	13.11
	VR ** = 13.05
	CD = 3.23

Table 4.25(b)

Treatment pairs		Absolute difference	S/NS
RSS 4	ISNR 20(FC)	0.10	NS
RSS 4	ISNR 20(DC)	1.42	NS
RSS 4	EBC (DC)	8.40	S
RSS 4	EBC (FC)	1.15	NS
ISNR 20(FC)	ISNR 20(DC)	1.32	NS
ISNR 20(FC)	EBC (DC)	8.31	S
ISNR 20(FC)	EBC (FC)	1.04	NS
ISNR 20(DC)	EBC (DC)	6.99	S
ISNR 20(DC)	EBC (FC)	0.29	NS
EBC (DC)	EBC (FC)	7.29	S

Analysis of variable for $[TTQ]_2$

Table 4.26(a)

Form of Rubber	Mean
RSS 4	2179.8
ISNR 20(FC)	2216.8
ISNR 20(DC)	2105.8
EBC (DC)	1905.2
EBC (FC)	2109.1
	VR = 11.29 CD = 100.89

Table 4.26(b)

Treatment pairs		Absolute difference	S/NS
RSS 4	ISNR 20(FC)	37.03	NS
RSS 4	ISNR 20(DC)	74.00	NS
RSS 4	EBC (DC)	274.62	S
RSS 4	EBC (FC)	70.62	NS
ISNR 20(FC)	ISNR 20(DC)	111.06	S
ISNR 20(FC)	EBC (DC)	311.68	S
ISNR 20(FC)	EBC (FC)	107.68	S
ISNR 20(DC)	EBC (DC)	200.62	S
ISNR 20(DC)	EBC (FC)	3.38	NS
EBC (DC)	EBC (FC)	204.00	S

Analysis of variance for $[BI]_2$

Table 4.27(a)

Form of rubber	Mean
RSS 4	0.96
ISNR 20(FC)	0.79
ISNR 20(DC)	0.94
EBC (DC)	1.57
EBC (FC)	0.97
	VR ** = 8.60 CD = 0.29

Table 4.27(b)

Treatment Pairs		Absolute difference	S/NS
RSS4	ISNR 20(FC)	0.17	NS
RSS4	ISNR 20(DC)	1.99	S
RSS4	EBC (DC)	0.61	S
RSS4	EBC (FC)	1.00	S
ISNR 20(FC)	ISNR 20(DC)	0.15	NS
ISNR 20(FC)	EBC (DC)	0.78	S
ISNR 20(FC)	EBC (FC)	0.18	NS
ISNR 20(DC)	EBC (DC)	0.63	S
ISNR 20(DC)	EBC (FC)	3.00	S
EBC (DC)	EBC (FC)	0.60	S

Analysis of variance for final temp (T_2°C)

Table 4.28(a)

Form of rubber	Mean
RSS 4	112.94
ISNR 20(FC)	110.81
ISNR 20(DC)	110.88
EBC (DC)	102.53
EBC (FC)	107.88
	VR ** = 8.02 CD = 4.03

Table 4.28(b)

Treatment pairs		Absolute difference	S/NS
RSS4	ISNR 20(FC)	2.13	NS
RSS4	ISNR 20(DC)	0.07	NS
RSS4	EBC (DC)	8.30	S
RSS4	EBC (FC)	2.93	NS
ISNR 20(FC)	ISNR 20(DC)	2.06	NS
ISNR 20(FC)	EBC (DC)	10.44	S
ISNR 20(FC)	EBC (FC)	5.06	S
ISNR 20(DC)	EBC (DC)	8.37	S
ISNR 20(DC)	EBC (FC)	3.00	NS
EBC (DC)	EBC (FC)	5.37	S

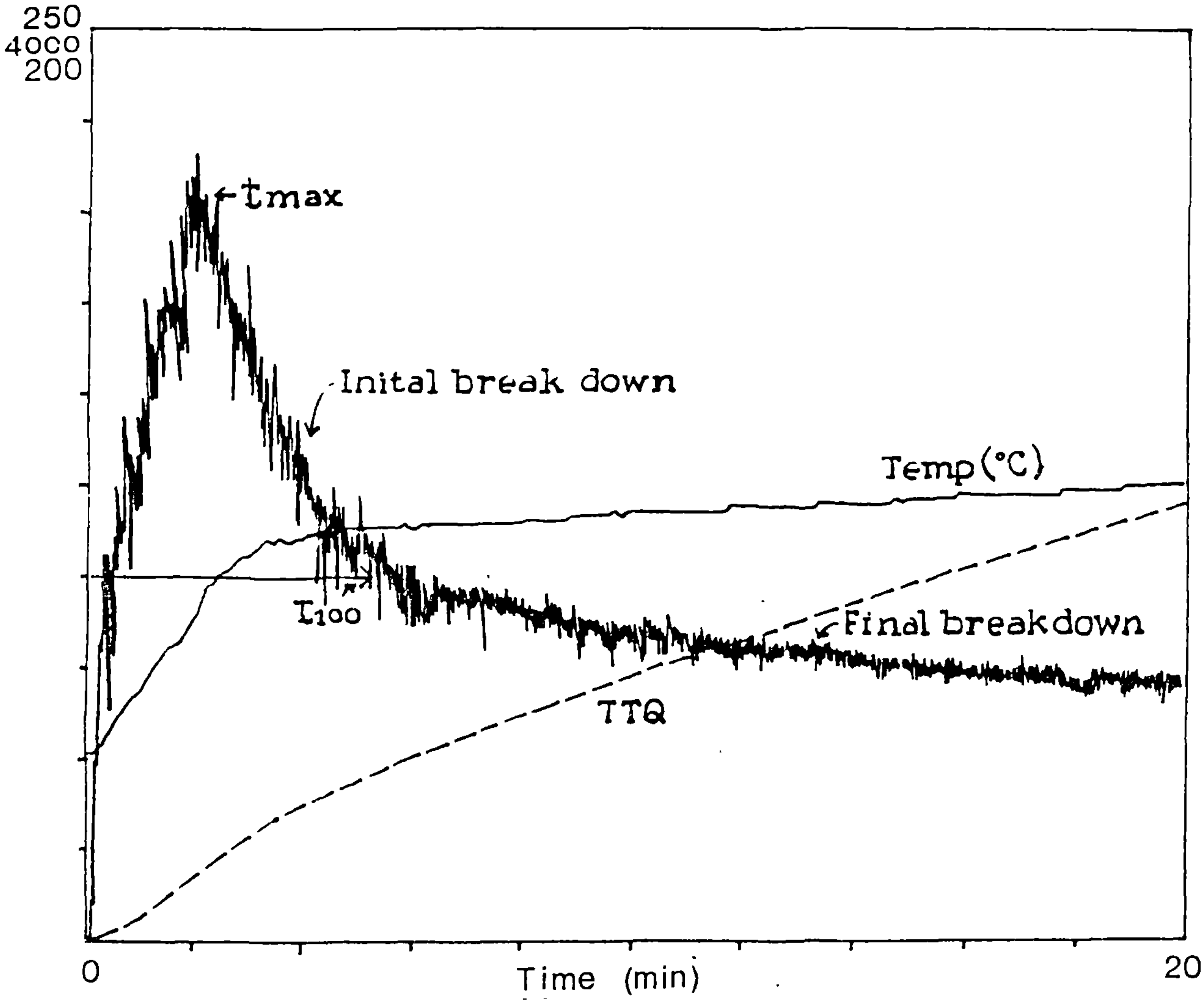


Fig. 4.8 Typical rheogram - Breakdown parameters

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CHAPTER V

STUDIES ON SKIM RUBBER

PART I

VARIABILITY IN RAW RUBBER PROPERTIES AND BREAKDOWN BEHAVIOUR OF SKIM RUBBER.

A. RAW RUBBER PROPERTIES AND BREAKDOWN BEHAVIOUR

In spite of its light colour and lower dirt content, the inconsistency in the properties of skim rubber has been pointed out as a serious shortcoming of the same.[1] Also scientific investigations on processability including mastication behaviour of this rubber have been very limited.

In India, skim rubber is processed and marketed as crepe. But in most other rubber producing countries, the same is processed and marketed as block rubber. The present study is envisaged to explore the extent of variability in raw rubber properties and molecular breakdown characteristics of skim crepe. A comparison of the same with skim block is also made with regard to the above properties. Also the effect of peptiser on the breakdown properties of skim rubber is studied.

EXPERIMENTAL

Skim crepe samples were collected from four different processing units in Kerala, four times with an interval of three months between collections. Skim block rubber was prepared in one of the above units. The raw material was the same as that of crepe. The samples were analysed for raw rubber properties specified for ISNR. (IS 4588-1986).

The molecular breakdown properties were studied using a Haake-Rheocord 90. The mechanical energy input or the work done is obtained by integrating the area under the torque- time curve. [2-4]

$$W = 2\pi n \int_{t_1}^{t_2} M.dt$$

Where M = torque (Nm)

and n = revolutions per minute.

This is directly obtained as totalised torque (TTQ Nm-min) using a microprocessor attached to the machine. When all other factors are kept constant, TTQ can be used to compare the energy required for mastication . At a fill factor of 0.7, a batch of 240 g of the sample was masticated at a fixed rpm of 40, with an initial temperature of 40°C. The samples were masticated for a prolonged period of 20 minutes.

From the Rheocord data the following parameters were evaluated.

t_{max} - Maximum torque attained

$[TTQ]_1$ - Totalised torque at a constant torque value t = 100 Nm so that the same can give the energy required for mastication of the samples to a fixed viscosity level.

T_1 - Temperature (°C) at t = 100 Nm

$[BI]_1$ - Rate of initial breakdown from t_{max} to the fixed torque t = 100 Nm, measured from the drop in torque with time.

$[TTQ]_2$ - Final TTQ, which is a measure of the energy required to masticate the samples for the total period.

$[BI]_2$ - Rate of final breakdown from t = 100 Nm to the final torque.

T_2 - Final temperature(°C).

RESULTS AND DISCUSSION

The raw rubber properties of the samples are given in Table 5.1. Though dirt content is comparatively low, the results show a high level of inconsistency as is evidenced by the high coefficient of variation (CV). The ash content also shows the same trend. However, lower values are obtained for the CV for Wallace plasticity and Mooney viscosity. This indicates a better homogeneity in the plasticity of the samples which definitely is a processing advantage.

The mean and the coefficient of variation (CV) of the different raw rubber properties of skim crepe samples are compared with those of ISNR 20 in Table 5.2. The data for ISNR 20 were obtained from the experiments detailed in the previous chapter. (Chapter-IV) As was expected ash content was comparatively less in the case of skim rubber. Nitrogen content is higher and the level of inconsistency is also much higher. The values for ash content and nitrogen are widely different as is evident from the T values.

Breakdown properties

The parameters selected for the study are the maximum torque (t_{max}), totalised torque, $(TTQ)_1$, obtained at a fixed torque t = 100 (Nm), rate of initial breakdown as measured by the drop in torque with time, from t_{max} to t = 100 Nm, the rate of final breakdown from torque t = 100 Nm to the final torque, temperatures T_1 at t = 100 Nm and T_2 the final temperature [5]. The breakdown characteristics of the samples are given in Table 5.3. CV is minimum for t_{max}.

To correlate the raw rubber properties with breakdown characteristics of the samples, a correlation coefficient has been worked out in each case. The correlation analysis of Wallace plasticity with other variables is given in Table 5.4.

It can be seen that the correlation coefficient for Po and $[TTQ]_1$ at t = 100 Nm is highly significant. As the critical breakdown occurs from t_{max} to t = 100 Nm, it can be concluded that plasticity of skim rubber is the major factor influencing consumption of energy during the initial breakdown period.

Plasticity retention index (PRI) is inversely related to the initial rate of breakdown and is found to be very highly significant. Correlation coefficient for the above variables was found to be $r = -0.8363$. This shows the significant effect of PRI on the initial breakdown of skim rubber. However, the correlation is less significant in the case of extended breakdown. ($r = -0.2383$).

Comparison of skim crepe and skim block

Raw rubber properties of skim crepe and skim block processed from the same raw material are given in Table 5.5. It is seen that PRI is drastically affected in the case of skim block. Po is also much reduced by the higher mechanical energy input and the higher drying temperature used in the production of block rubber. The average molecular weight $\overline{M}$w was also found to be lower. Nitrogen content is much lower in the case of skim block, mainly owing to the more efficient washing employed in the production of block rubber. The volatile matter is also substantially reduced in the case of skim block .

The breakdown characteristics of both the forms are shown in Figure 5.1. A comparative data of the above are given in Table 5.6. The initial breakdown energy is much less for the skim block and the initial breakdown index of the same is double that of skim crepe. However, on prolonged mastication, the values for TTQ comes closer as the time factor also is considered in computing TTQ.

B EFFECT OF PEPTISER.

The viscosity of the skim crepe samples are usually high, as is indicated by the high Po values. This may be due to the higher protein content in skim rubber and lower quantum of energy imparted during the production of crepe. As the plasticity value is higher, there could be a tendency to use peptisers to help the mastication process of this rubber. The effect of the peptiser on the mastication behaviour of skim rubber is therefore investigated.

EXPERIMENTAL

Skim crepe with the following raw rubber properties were used for the study.

Dirt content, %	0.09
Wallace plasticity, (Po)	50
Plasticity retention index (PRI)	34
Ash content, %	0.1
Volatile matter, %	1.13
Nitrogen content, %	1.74
Mooney viscosity, ML (1+4), 100°C	95

The samples were masticated in the Rheocord at prefixed rpm, temperature and time. Different dosages of the peptiser, viz, 2,2' dibenzamido diphenyl disulphide were incorporated and the effect of the same on Wallace plasticity, Mooney viscosity and energy for masticating the rubber to a fixed torque were measured.

RESULTS AND DISCUSSION

Table 5.7 gives the Wallace plasticity (P_o) and Mooney viscosity of the masticated samples of skim with corresponding dosage of the peptiser. The corresponding values obtained for ISNR 5 in the earlier experiment (Chapter-III) are also included in the same for comparison.

It was observed that the reduction in viscosity was not significant with the addition of peptiser, unlike in the case of ISNR 5.

In the case of skim rubber, the addition of peptiser even up to 0.5 phr level does not bring about much saving in energy whereas in the case of ISNR 5 even the lowest dosage of peptiser (0.15 phr) makes a significant drop in the energy for breakdown. The effect of temperature on the mastication behaviour of the samples is given in Table 5.8. The lower effect of peptiser in the mastication of skim rubber is manifested by the lower difference in Wallace plasticity (Po) between the peptised and unpeptised samples.

The same trend is obtained by varying the speed (rpm) of the rotor. The results are shown in Table 5.9. The higher non rubber constituents and lower hydrocarbon content of skim rubber may be attributed to the insignificant effect of peptiser during the mastication of the same. As skim rubber alone is seldom used in rubber products, the mastication of the same is carried out by blending with other grades of NR. Peptisers can contribute to the mastication of these blends depending upon the quantity of the superior grades of NR being used.

CONCLUSIONS

1. Skim rubber shows higher level of inconsistency in raw rubber properties. However, lower coefficient of variation (CV) is observed for Wallace plasticity indicating more consistency in processability.
2. Plasticity of skim rubber is found to be the major factor influencing consumption of energy during initial breakdown. The rate of breakdown of skim block is higher than that of skim crepe.

3. Plasticity retention index is found to be inversely related to the initial rate of breakdown and is found to be very highly significant.
4. The effect of peptiser was found to be less in skim rubber compared to the ISNR 5.

Table 5.1

Raw Rubber Properties of skim crepe samples

Sl No.	Sample No.	Dirt %	Wallace Plasticity	PRI	Ash %	Volatile matter %	Nitrogen %	MLI+4 at 100°C
1	S1	0.09	60	55	0.55	1.72	2.96	95
2	S2	0.06	62	65	0.36	1.48	3.12	97
3	S3	0.02	61	44	0.18	2.28	2.17	99
4	S4	0.04	61	41	0.18	2.10	2.57	100
5	S5	0.02	44	20	0.08	1.04	1.50	88
6	S6	0.09	50	34	0.10	1.13	1.74	95
7	S7	0.18	48	69	0.59	4.68	2.57	89
8	S8	0.07	42	64	0.48	3.50	2.72	87
9	S9	0.12	55	67	0.67	2.97	2.91	91
10	S10	0.15	43	74	0.53	2.97	2.77	81
11	S11	0.22	58	43	0.32	2.18	1.90	91
12	S12	0.13	56	43	0.43	2.19	1.87	89
13	S13	0.20	57	49	0.32	2.34	1.96	91
14	S14	0.11	53	40	0.24	2.07	1.72	91
15	S15	0.07	50	66	0.49	3.73	0.83	91
16	S16	0.11	59	59	0.21	3.38	2.09	93
Mean		0.1371	53.29	51.0	0.3488	2.5540	2.1600	91.41
SD		0.1444	6.74	15.25	0.1811	1.001	0.6493	4.82
CV		105.32	12.65	29.90	51.92	39.19	30.06	5.27

Table 5.2
Comparison of raw rubber properties of skim crepe and ISNR 20

Property	ISNR 20			Skim crepe		
	Mean	CV	Specification limit	Mean	CV	T value
Dirt content, %	0.13	76	0.2 (Max)	0.14	105.3	-1.80
Wallace plasticity	45	19.5	30 (Min)	53	12.6	14.24
Plasticity retention index	58	19.6	40 (Min)	51	29.9	2.98
Ash content, %	0.60	44.4	1.0 (Max)	0.35	51.9	-14.83
Volatile matter, %	0.41	42.0	0.80 (Max)	2.55	39.2	7.22
Nitrogen content, %	0.45	71.4	0.60 (Max)	2.16	30.1	9.38

Table 5.3
Breakdown properties of skim crepe samples

Sl No.	Sample No.	Po	PRI	t_{max} (Nm)	$[TTQ]_1$ Nm-Min	$[BI]_1$ Nm/min	T_1(°C)	T_2(°C)	$[TTQ]_2$ Nm-Min	$[BI]_2$ Nm/min
1	S1	60	55	200	545	17.4	92	102	1660	1.8
2	S2	62	65	205	570	12.5	94	108	1735	1.3
3	S3	61	44	155	584	18.6	102	113	1885	1.9
4	S4	61	41	190	585	22.1	90	100	1720	2.4
5	S5	44	20	130	426	23.3	96	108	1470	2.5
6	S6	50	34	190	447	16.6	89	104	1464	2.6
7	S7	48	69	165	480	13.5	83	98	1480	2.1
8	S8	42	64	185	317	11.8	88	101	1653	1.5
9	S9	55	67	180	590	11.5	99	107	1535	0.9
10	S10	43	74	150	405	9.5	92	105	1280	2.3
11	S11	58	43	155	490	19.5	104	115	1320	1.2
12	S12	56	43	192	525	15.1	97	108	1135	1.0
13	S13	57	49	200	705	14.1	101	112	1910	0.6
14	S14	53	40	190	520	18.5	91	103	1490	1.3
15	S15	50	66	165	354	15.5	98	109	1598	1.5
16	S16	59	59	120	496	16.6	102	115	1719	1.1
	Mean	53.69	52.06	182.00	500.56	16.00	94.88	106.75	1568.88	1.63
	SD	6.76	15.00	15.00	96.88	3.84	5.97	5.26	212.14	0.62
	CV	12.59	28.97	8.78	19.35	24.00	6.29	4.93	13.55	38.04

Table 5.4
Correlation analysis of Wallace plasticity with other variables.

Sl.No.	Variable	Correlation coefficient
1.	$(TTQ)_1$, at t = 100 Nm	0.7511 **
2.	Initial rate of breakdown $(BI)_1$	0.2753
3.	Final TTQ, $(TTQ)_2$	0.4221
4.	Final temperature (T_2°C)	0.3839

Table 5.5
Raw rubber properties of skim crepe and skim block rubber

Parameter	Crepe	Block
Dirt content, %	0.13	0.11
Wallace plasticity	56	30
Plasticity retention index	49	Melted
Ash content, %	0.43	0.41
Nitrogen content, %	1.87	1.01
Volatile matter %	2.19	0.93
Mooney viscosity, ML (1+4) 100°C	89	56
Molecular weight Mw x 10^5	9.7	7.3

Table 5.6
Breakdown properties of skim crepe and skim block

Sl. No.	Parameter	Crepe	Block
1.	Maximum torque, t_{max} (Nm)	200	125
2.	$(TTQ)_1$ at t = 100 Nm (Nm-min)	797	244
3.	Initial rate of breakdown $(BI)_1$	20	40
4.	$(TTQ)_2$ Nm - min	1910	1720

Table 5.7
Effect of dosage of peptiser on Wallace plasticity of skim crepe and ISNR 5 samples

RPM 60, Temperature 80°C, Time: 5 Min

Dosage (Phr)	Skim crepe: (Initial Po = 50)		ISNR 5 (Initial Po = 49)	
	Wallace plasticity	ML (1+4) at 100°C	Wallace plasticity	ML (1+4) at 100°C
0	34	73	38	79
0.15	34	70	26	66
0.25	32	68	21	62
0.5	31	69	18	57
0.75	29	67	16	51
1.0	27	65	15	51

Table 5.8
Effect of temperature on Wallace plasticity of skim crepe rubber

RPM 60, Time 5 Min

Temperature °C	Wallace plasticity	
	Control	With peptiser (0.25 phr)
50	45	42
60	39	37
70	35	35
80	34	31
100	21	18

Table 5.9

Effect of rotor speed on Wallace plasticity of skim rubber

Initial Po = 50; Time 5 min, Temp 80° C

RPM	Wallace plasticity	
	Without peptiser	With peptiser (0.25 phr)
50	44	41
60	34	31
80	27	29
100	18	21

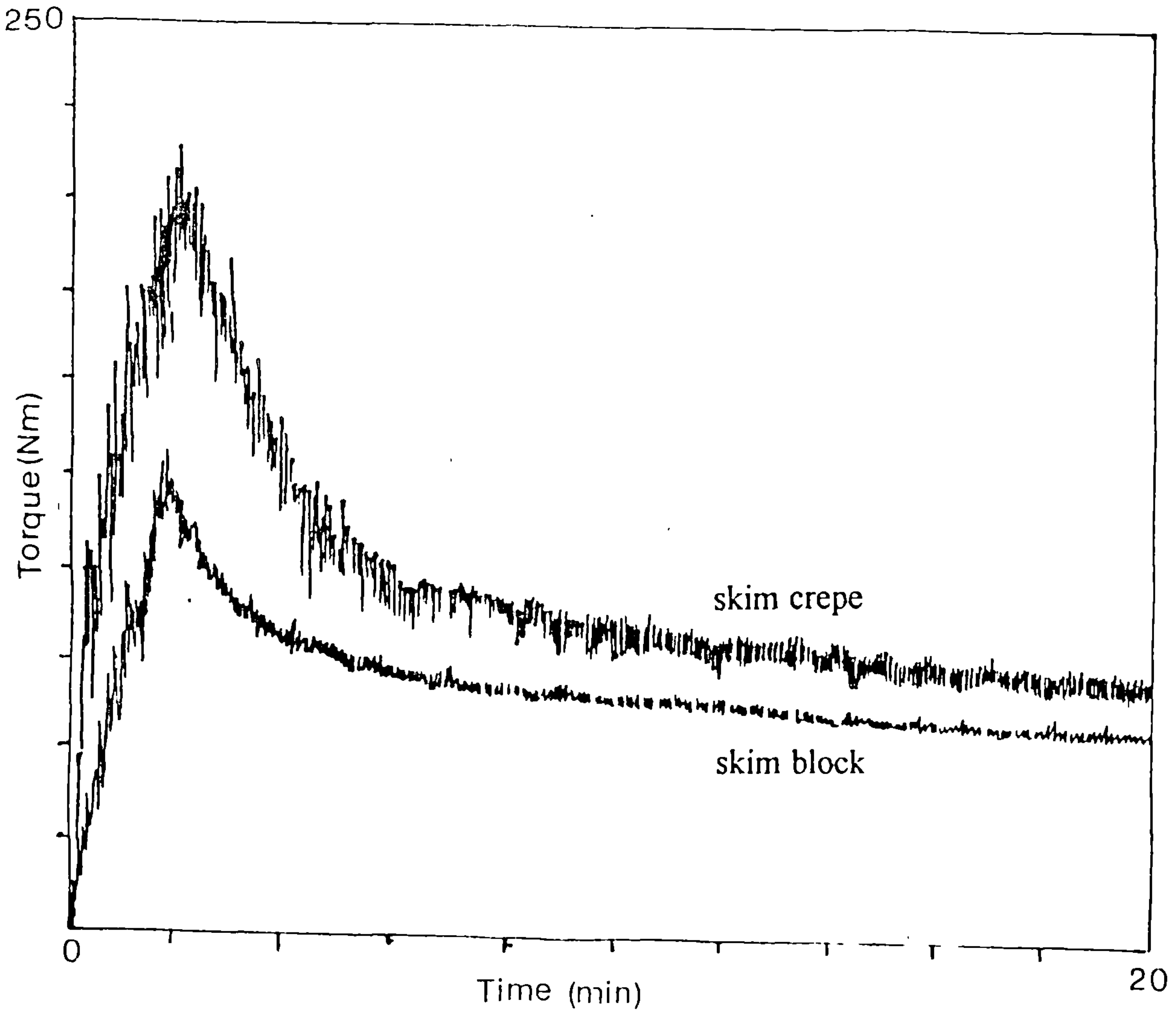

Fig. 5.1. Rheogram obtained for skim crepe and skim block rubbers

PART II

EFFECT OF INCORPORATION OF SKIM RUBBER WITH TSR

Properties of skim rubber are different from normal grades of natural rubber. The relatively high non-rubber constituents, especially the 'bound protein' in skim may act as a reinforcing agent to produce high modulus vulcanizates. [6] It may also affect the cure characteristics of the same.[7] Hence, skim rubber is seldom used alone in rubber products. The practice adopted is to substitute a part of the natural rubber by skim, so that the properties are not affected to a great extent, and the cost is optimised. In this study, the effect of incorporation of skim rubber, with a general purpose grade of natural rubber (ISNR 20), at different proportions, is investigated.

EXPERIMENTAL

To address the problem of variability, one typical sample of skim block is used in the study. The raw rubber properties of the skim block and ISNR 20 used for the study are given in Table 5.10.

Different blends of skim with ISNR 20 were prepared on a two roll mill. (15cm x 30cm) The proportion of the blends are given in Table 5.11.

Gum compounds were prepared using the ACS-1 formulation for all the above blends and their cure and scorch characteristics studied. Filled compounds from the above blends using HAF black were prepared as per the formulation given in Table 5.12.

Cure and vulcanizate properties of the mixes were measured. Dynamic properties were evaluated using a Yerzely Oscillograph. The effect of skim on the water absorption characteristics of the vulcanizates was also assessed.

RESULTS AND DISCUSSION

Cure characteristics of the ACS-1 compounds are given in Table 5.13. Optimum cure time at 150°C, steadily increases with the skim content. The cure rate index shows a steady decline with increased proportion of skim. Scorch time however decreases with increase in skim content. This can be attributed to the presence of decomposition products of proteins present in skim which can function as accelerators for vulcanization. Its effect will be more pronounced in the initial stages of vulcanization, by increasing the rate of formation of the activator complex.

Cure characteristics of the HAF- filled compounds are given in Table 5.14. The acid content of the skim contributes to its low vulcanization rate as is evident from the lower cure rate index of samples containing higher proportions of skim. The skim samples show an acidic pH.

The contribution of 'bound protein' on the vulcanizate modulus can be understood from the observation that a correlation exists between the nitrogen content of the samples and the increase in torque MHR – ML on the rheograph of the corresponding ACS-1 mix.

Table 5.15 illustrates the same. The relation holds better, at higher proportions of skim.

Vaulcanizate properties

Table 5.16 gives the tensile properties of the filled vulcanizates. Modulus at 200 per cent increases with skim content, as is indicated by the data on Table 5.15. However, tensile strength shows a declining trend. Though the tear values show a scatter, it is evident that the same is not affected significantly by the incorporation of skim.

One of the major reasons for the poor reputation of skim rubber is the inferior ageing properties of its vulcanizates.[6] The retention in tensile properties of the same are given in Table 5.17. It can be seen that the properties are not deteriorated significantly, even up to 50 parts of skim. Elongation at break gives a better indication of ageing, than tensile strength.

The other relevant technological properties of the vulcanizates are summerised in Table 5.18. Heat buildup decrease initially and then increases. Resilience also decreases, compression set at room temperature and at 70°C increases. Flex crack resistance decreases with incorporation of skim. Both crack initiation and failure are faster when skim rubber is added. The higher modulus imparted by skim could be one of the reasons.

The dynamic properties obtained from the Yerzely Oscillograph are given in Table 5.19.

The results endorses the earlier suggestion[8] that addition of skim rubber to conventional grades of natural rubber improves its dynamic properties. Tan δ steadily increases, with a corresponding decrease in Yerzely resilience. This indicates a better area of application for skim rubber where damping characteristics are required.

Data on the water absorption of the vulcanizates are give in Table 5.20. Water absorption increases with increased skim content. The increase is linear with time of immersion. This can be directly correlated with the nitrogen content of the above samples. It has already been reported[9] that skim rubber vulcanizates absorb more water especially when the filler (HAF black) content is less than 30phr. The differences are less, at higher filler loadings. This may be attributed to the influence of the increased modulus restricting the ability of the protein to take up water and to swell.

CONCLUSIONS

1. Optimum cure time is increased and scorch time reduced with progressive addition of skim rubber. The differences are less significant in the case of filled vulcanizates.
2. Technological properties are affected adversely at higher concentration of skim. Maximum deterioration is observed in the case of flex characteristics.

3. Dynamic properties, especially tan δ are increased by the addition of skim rubber.
4. In general, a blend proportion of 70/30 with ISNR 20 and skim was found to give satisfactory results for general purpose rubber formulations.

Table 5.10
Raw rubber properties of skim block and ISNR 20

Parameter	Skim block	ISNR 20
Dirt content, %	0.11	0.02
Ash content, %	0.41	0.24
Volatile matter, %	1.58	0.29
Nitrogen content, %	1.30	0.25
Acetone extract, %	4.64	1.84
Wallace plasticity	30.00	42.00
pH	6.20	7.10

Table 5.11
Blend ratios of skim block rubber and ISNR 20

	A	B	C	D	E	F	G
ISNR 20	100	90	80	70	60	50	0
Skim block	0	10	20	30	40	50	100

Table 5.12
Formulation of filled mixes

Ingredient	MIX No. A1	B1	C1	D1	E1	F1	G1
ISNR 20	100	90	80	70	60	50	0
Skim	0	10	20	30	40	50	100
Stearic acid	2	2	2	2	2	2	2
Zinc oxide	5	5	5	5	5	5	5
HAF black	40	40	40	40	40	40	40
Aromatic oil	4	4	4	4	4	4	4
CBS	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5

Table 5.13
Cure characteristics of ACS-1 mixes

Property	MIX No. A	B	C	D	E	F	G
Optimum cure time at 150°C (Min)	9.25	10.50	12.00	14.00	14.75	16.00	20.00
Scorch time at 120°C (Min)	10.50	10.00	9.50	9.50	8.00	8.00	5.50
Cure rate index	14.20	12.50	10.00	8.30	8.70	7.10	5.90

Table 5.14
Cure characteristics of HAF filled mixes

Property	MIX No. A1	B1	C1	D1	E1	F1	G1
Optimum cure time at 150°C (Min)	8.5	8.5	10.0	10.0	10.5	11.0	13.0
Scorch time at 120°C (Min)	12.0	12.0	11.0	11.5	11.0	10 .0	9.0
Cure rate index	15.4	15	12.5	13.0	11.8	11.0	9.1

Table 5.15
Influence of nitrogen content on rheometric torque of blends

Sample No.	Nitrogen %	(MHR - ML)
A	0.25	36
B	0.32	35
C	0.53	42
D	0.72	41
E	0.75	44
F	0.88	48
G	1.30	61

Table 5.16
Tensile properties of the vulcanizates containing different proportions of skim

	MIX No.						
Property	A1	B1	C1	D1	E1	F1	G1
Modulus 200%, N/mm^2	3.80	3.50	3.60	3.80	4.4	4.3	5.3
Tensile strength, N/mm^2	29.1	28.7	27.1	25.8	25.5	25.3	22.6
Tear strength, N/mm	102	101	98.4	101	108	111	105

Table 5.17
Percentage retention in tensile properties after ageing

		MIX No.						
		A1	B1	C1	D1	E1	F1	G1
Tensile strength	After 14 days at 70°C	45	47	43	43	41	39	36.6
	After 72 h at 100°C	11.8	13.1	12.2	10.6	10.4	10.0	10.2
Elongation at break	After 14 days at 70°C	48.6	47	49	46	41	39	31
	After 72h at 100°C	25	25	23	19	18	18	16

Table 5.18
Technologicial properties of the vulcanizates

	MIX No.						
Property	A1	B1	C1	D1	E1	F1	G1
DIN abrasion loss, mm^3	101.0	103.0	102.9	98.6	96.5	95.0	94.1
Heat buildup, ΔT,°C	28.0	23.0	24.0	25.0	29.0	31.0	39.0
Rebound resilience, %	61	63	59	57	54	53	47
Hardness Shore A	53	53	55	56	59	62	66
Compression set (22h, 70°C), %	45	51	55	58	59	61	62
Compression set (72h ambient temp.),%	8.3	8.9	10.6	11.2	11.5	11.5	15.3
DeMattia flexing; Crack initiation (K.cycles)	44.6	37.0	42.67	26.87	24.67	18.57	11.50
Crack failure (K. cycles)	136.9	87.6	85.2	73.4	69.5	61.7	21.8
Dynamic set from heat buildup measurements %	5.1	3.6	3.2	3.7	4.4	4.9	7.6

Table 5.19
Dynamic properties

	MIX No.						
Property	A1	B1	C1	D1	E1	F1	G1
Yerzely resilience (%)	79.8	77.6	76.9	75.5	70.6	68.4	58.9
Dynamic modulus (MPa)	7.46	7.54	7.58	8.12	9.34	9.63	16.0
Tan δ	0.1439	0.1616	0.1667	0.1793	0.2221	0.2471	0.3371

Table 5.20

Water absorption at room temperature

	Change in mass, %						
Time (h)	A1	B1	C1	D1	E1	F1	G1
22	0.26	0.30	0.32	0.32	0.32	0.29	0.47
46	0.31	0.4242	0.45	0.50	0.55	0.51	0.88
70	0.48	0.49	0.58	0.62	0.61	0.55	0.91
166	0.77	0.96	0.92	0.97	0.95	1.10	1.57
670	1.15	1.57	1.69	1.72	1.78	2.11	2.93

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CHAPTER VI

STUDIES ON BREAKDOWN PROPERTIES OF EPOXIDISED NATURAL RUBBER

Epoxidation of natural rubber results in a systematic increase in polarity and glass transition temperature which are reflected in the properties of ENR vulcanizates.[1] The increase in polarity results in a marked increase in resistance to hydrocarbon oils and a decrease in the rate of air permeation. It also alters the compatibility with other polymers.[2] The degree of improvement in these properties depends on the extent of epoxidation.[3]

NR latex could be epoxidised to any desired level and when performed under carefully controlled conditions the primarily formed epoxide ring could be preserved.[4] However, only two grades viz., ENR 25 and ENR 50 have assumed commercial importance. As ENR is an elastomer having high viscosity, the same has to be masticated before incorporation of fillers and other ingredients.

Oxidation behaviour of epoxidised natural rubber has been reported by Ivan *et.al.*[5] It was found that the oxidation rate depends on the degree of epoxidation. Epoxidised rubber was found to be less prone to oxidation compared to unmodified rubber. However, the loss of natural antioxidants from NR during the production of ENR is to be considered and the stability of ENR to thermo-oxidative degradation results from a balance of these factors.

The effect of epoxy content on vulcanizate properties of ENR has been reported.[6-8] The studies have been restricted to ENR 25 and ENR 50. The degradation of vulcanized ENR was found to be influenced by the curing system used. The mechanism of degradation was reported to be different from that of NR vulcanizates.[3] IR analysis of aged ENR 50 vulcanizates showed a reduction in the number of epoxide groups indicating the formation of ring opened products. Crosslinked sulphur in ENR can get oxidised to sulphur containing acids which react with epoxy groups yielding ring opened products.

Aspects of processing and ageing of ENR 50 has been studied in comparison with those or NR and NBR.[9-10] It was observed that the degree of breakdown of the former was higher on a two roll mill. The processing behaviour of ENR 50 and ENR 25 were studied and a destruction index was arrived at.[5] It was reported that the destruction index was higher for ENR 50, indicating a higher rate of breakdown. Its gel content was found to be increasing after thermo-oxidative destruction, suggesting that reactions involved in mechanical processing of ENR were different in some aspects from those of isoprenic rubbers. Compared to chain scission, crosslinking predominates in the case of ENR.

PART I

EFFECT OF EPOXY CONTENT ON BREAKDOWN PROPERTIES OF EPOXIDIZED NATURAL RUBBER

In this part, an attempt is made to correlate breakdown properties of different grades of ENR with the extent of epoxidation.

EXPERIMENTAL

Epoxidised natural rubber with 10, 25, 50 and 60 mole per cent epoxidation were prepared. The recipe and the conditions for the same were discussed earlier (Chapter II). After the epoxidation, the latex was coagulated and the coagulum processed as block rubber.

CHARACTERIZATION

IR spectra were recorded using a Shimadzu Fourier Transform Infrared Spectrophotometer (FTIR - 8101M). Lightly masticated ENR was dissolved in spectroscopically pure chloroform and a thin film was cast on NaCl disc. Quantitative analysis was made by the method reported earlier[11] which gives in addition to epoxide and olefinic levels, the mole percentage of the ring opened products. The method is based on the comparison of absorption intensities of epoxide ring at 870 cm^{-1}, the hydroxyl group at 3460 cm^{-1} and unmodified olefinic absorption at 835 cm^{-1}. Figure 2.2 gives the method for absorbance determination from IR spectrum.

Breakdown characteristics

Breakdown characteristics were studied using the torque rheometer (Haake-Rheocord 90). The breakdown properties of different grades of

ENR were studied with respect to temperature, time of mastication and speed of rotor. The following parameters were used to evaluate the breakdown characteristics.

1. Wallace plasticity
2. Gel content
3. M_1 - torque at the first minute
4. M_5 - torque at the fifth minute
5. M_f - Final torque when mastication exceeds 5 minutes
6. T_F - Final temperature (°C)
7. $M_1 - M_5 - \Delta M$
8. $[TTQ]_1$ - Energy required to masticate the sample to a fixed torque.
9. $[BI]_1$ - Rate of breakdown measured as change in torque with respect to time.
10. $[TTQ]_2$ - Energy required to masticate the samples for 5 minutes.

The samples were masticated in the torque rheometer (Haake - Rheocord) at 80°C, at an rpm of 60, for 5 minutes, and the IR spectra of the masticated samples were recorded in order to check if the chemical structure of the materials changed with mastication.

RESULTS AND DISCUSSION

Figures 6.1 to 6.4 give IR spectra of ENR 10, 25, 50 and 60 samples respectively. Table 6.2 gives the epoxy content, olefinic content and percentage of side reactions. It could be seen that the actual epoxy content of the samples prior to mastication were well within the limits of the expected values for the grades. The IR spectra of the above samples masticated at specified conditions are given in Figures 6.5 to 6.8 respectively. Table 6.3 gives the data of analysis of the above spectra. The percentage change in epoxide content during mastication was not much different for all the grades. This could be attributed to the fact that the initial samples were also masticated to a lower level for enabling the dissolution of the same in the solvent. The same has to be viewed in comparison with changes in properties such as Wallace plasticity and gel content of the respective grades, after mastication.

Effect of Temperature

Table 6.4 illustrates the effect of temperature on the Wallace plasticity and gel content of the above grades during mastication. In the case of natural rubber, as the temperature of mastication increases, Wallace plasticity decreases. However, ENR samples showed a different trend. In the case of ENR 10, Wallace plasticity decreases as observed in the case of NR. ENR 25, attains almost a steady value at higher temperature. But ENR 50 and ENR 60 showed a definite increase in Wallace plasticity at higher temperatures. This can be explained in terms of the crosslinking reactions predominating in these rubbers during mastication compared to chain scission, as in the case of NR. This is further supported by the increase in gel content at higher temperature in the case of samples having high epoxy content. At 100°C ENR 25, 50 and 60 show higher gel content than at lower temperatures. At lower temperatures of mastication, the gel content is lower than the initial values showing chain scission to be the predominant mechanism. But at higher temperature crosslinking predominates. The acidic pH might also have contributed to the same.[12] Acid catalysed crosslinking occurs through the opening of the epoxide ring, followed by crosslinking through the ether groups. The crosslinking reactions can be enhanced by the presence of smaller amount of other groups apart from the oxirane group. It was reported that an increase in gel content of ENR 25 and ENR 50 samples occurs during thermo-oxidative degradation.[5] However, values of gel content after degradation were even higher than the original values reported. The initial gel content of the samples used in their study were comparatively lower.

The effect of temperature on the rate of breakdown of different grades of ENR are shown in Table 6.5. It is seen that the rate increases with epoxy content. However, within a particular grade the rate decreases as the temperature is raised. The torque difference ΔM, at the initial and final stages of mastication shows a steady decrease with temperature unlike ΔPo. In the case of ΔPo, it increases initially with temperature and subsequently decreases. It could be attributed to the fact that Wallace plasticity is being measured after mastication of the samples so that the effect of crosslinking is manifested in a better way than by the torque values, which are being measured instantaneously.

The energy required to masticate the samples to a fixed torque level is also given in Table 6.5. It is found that TTQ is mainly dependent on the initial plasticity of the sample. ENR 50 and ENR 60 requires more energy for mastication and the same decreases with increase in temperature.

Effect of rotor speed

Table 6.6 gives the values for the breakdown parameters when the speed is increased. Unlike in the case of temperature, an increase in rotor speed did not cause any increase in Po. Instead, Wallace plasticity eventually decreases indicating that the crosslinking phenomenon present in the former case is not taking place. At higher shear rates, chain scission seems to be the main operating mechanism in the case of ENR, similar to that of NR.

Here also, the rate of breakdown increases with epoxy content. Thus ENR 60 showed maximum extent of breakdown followed by ENR 50. But within the same grade, the rate of breakdown decreases with increase in rotor speed. As the speed of the rotor increases, viscosity reduces substantially. This is clearly observed from the torque values (M_1) of samples having higher epoxy content.

The $[TTQ]_2$ values, after 5 minutes mastication shows that grades with higher epoxy content require higher energy for mastication which initially increases as rotor speed increases and then decreases. At lower rpm, the increase in temperature is less and hence the reduction in viscosity is lower. Hence, more energy is consumed for mastication. But when the speed is increased to 100 rpm, the temperature rise and the corresponding reduction in viscosity is higher, so that the resistance offered by the rubber is lower, thus reducing the energy required for mastication.

Effect of time of mastication

Table 6.7 shows the effect of prolonged mastication of the samples. As the time of mastication is increased, the rate of breakdown becomes less. Wallace plasticity is also found to be decreasing as time increases.

CONCLUSIONS

1. ENR 50 and ENR 60 exhibits an increase in Wallace plasticity and gel content, when masticated at high temperature possibly due to the predominance of crosslinking reactions.
2. The rate of breakdown increases with epoxy content. But within a particular grade, the rate decreased as the temperature increased.
3. At higher rotor speeds, chain scission seems to be the predominant mechanism during mastication and hence no increase in Wallace plasticity was observed.
4. The energy of mastication depends mainly on the initial plasticity of the rubber.

Table 6.1
Raw rubber properties of ENR grades

Grade	Wallace plasticity	ML(1+4) at 100°C	Gel content(%)	pH
ENR - 10	18	47	11.4	5.1
ENR - 25	31	75	22.3	6.0
ENR - 50	64	114	67.6	5.8
ENR - 60	50	93	60.5	6.0

Table 6.2
Data from Infrared spectra of samples prior to mastication.

Sample	Epoxy content(%)	Olefinic content(%)	Side reactions(%)
ENR - 10	12.36	87.22	0.42
ENR - 25	25.32	74.62	0.06
ENR - 50	51.18	46.81	2.01
ENR - 60	60.29	36.41	3.30

Table 6.3
Data from Infrared spectra of samples after mastication

Sample	Epoxy content(%)	Olefinic content(%)	Side reactions(%)
ENR - 10	11.50	78.09	10.41
ENR - 25	23.09	76.68	0.23
ENR - 50	47.33	49.40	3.27
ENR - 60	54.80	39.50	5.70

Table 6.4
Effect of temperature of mastication on Wallace plasticity and gel content

	Wallace Plasticity				Gel content (%)			
Temp(°C)	ENR 10	ENR 25	ENR 50	ENR 60	ENR 10	ENR 25	ENR 50	ENR 60
Control	20	31	64	50	11.4	22.3	67.6	60.5
40	15	20	41	29	10.6	14.3	40.2	35.2
60	16	22	40	28	10.8	14.3	41.5	34.0
80	16	21	42	30	9.2	15.1	42.4	37.4
100	13	20	45	34	9.2	16.6	47.3	41.8

Table 6.5
Effect of temperature on breakdown parameters of different ENR grades

RPM 60; Time 5 Min

Grade	Temp. (°C)	M_1 (Nm)	M_5 (Nm)	ΔM(Nm)	BI Nm/Min	T_F (°C)	$[TTQ]_1$ (Nm-Min)
ENR 10	40	125	67	58	14.5	82	240
	60	107	68	39	9.7	94	222
	100	95	62	33	8.1	129	208
ENR 25	40	110	63	47	11.7	82	247
	60	120	86	34	8.5	94	229
	100	90	78	22	5.5	129	241
ENR 50	40	180	120	60	15.0	116	400
	60	168	111	57	14.3	128	360
	100	150	117	33	8.3	150	305
ENR 60	40	175	103	72	18.0	110	371
	60	170	106	64	16.0	121	369
	100	127	83	44	11.0	147	309

Table 6.6

Effect rotor speed on the breakdown properties of different grades of ENR

Grade	Rotor speed (RPM)	M_1 (Nm)	M_5 (Nm)	ΔM(Nm)	BI Nm/Min	ΔPo	T_F (°C)	$[TTQ]_1$ (Nm-Min)
ENR 10	60	125	71	54	13.5	3	85	396
	60	125	73	52	12.8	4	94	351
	100	125	84	41	10.3	6	120	404
ENR 25	40	125	60	65	16.3	9	87	353
	60	120	95	34	8.5	11	100	402
	100	100	80	20	5.0	14	117	378
ENR 50	40	200	119	81	20.2	14	105	620
	60	175	110	65	16.3	16	127	647
	100	155	100	55	13.8	26	158	627
ENR 60	40	200	105	95	23.8	13	105	694
	60	170	111	99	18.8	20	131	640
	100	140	82	58	14.5	28	159	521

Table 6.7

Effect of time of mastication on breakdown properties of different grades of ENR

RPM 60; Temp. 80°C

Sample	Time of mastication (Min)	ΔPo	BI Nm/Min	T_F (°C)
ENR 10	5	6	5.5	101
	10	6	3.8	112
	20	7	2.6	121
ENR 25	5	9	8.8	96
	10	13	3.7	105
	20	15	2.3	124
ENR 50	5	22	10.7	129
	10	33	7.8	143
	20	45	5.5	150
ENR 60	5	20	18.8	150
	10	20	12.0	125
	20	36	7.8	146

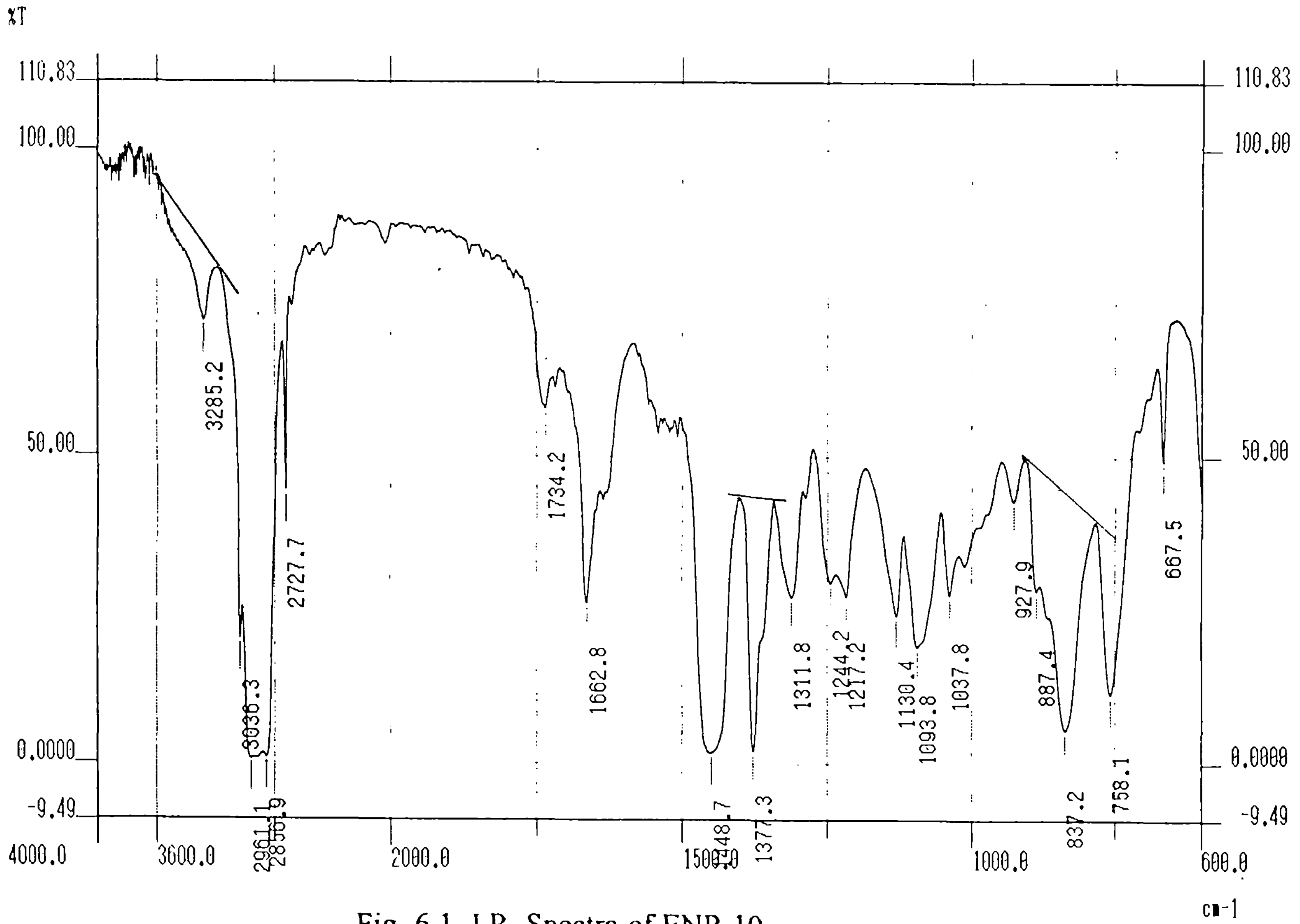

Fig. 6.1 I.R. Spectra of ENR 10

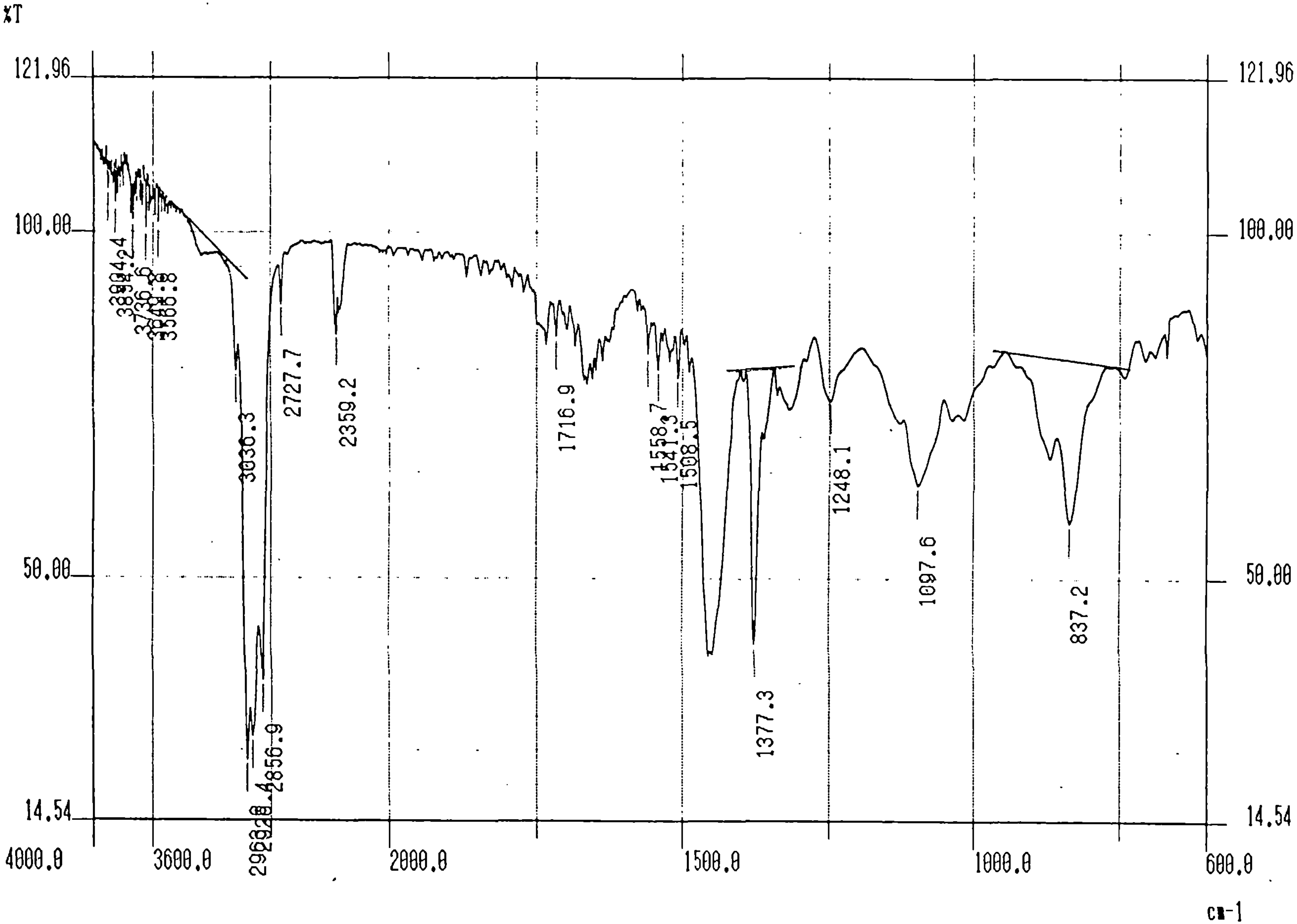

Fig. 6.2 I.R. Spectra of ENR 25

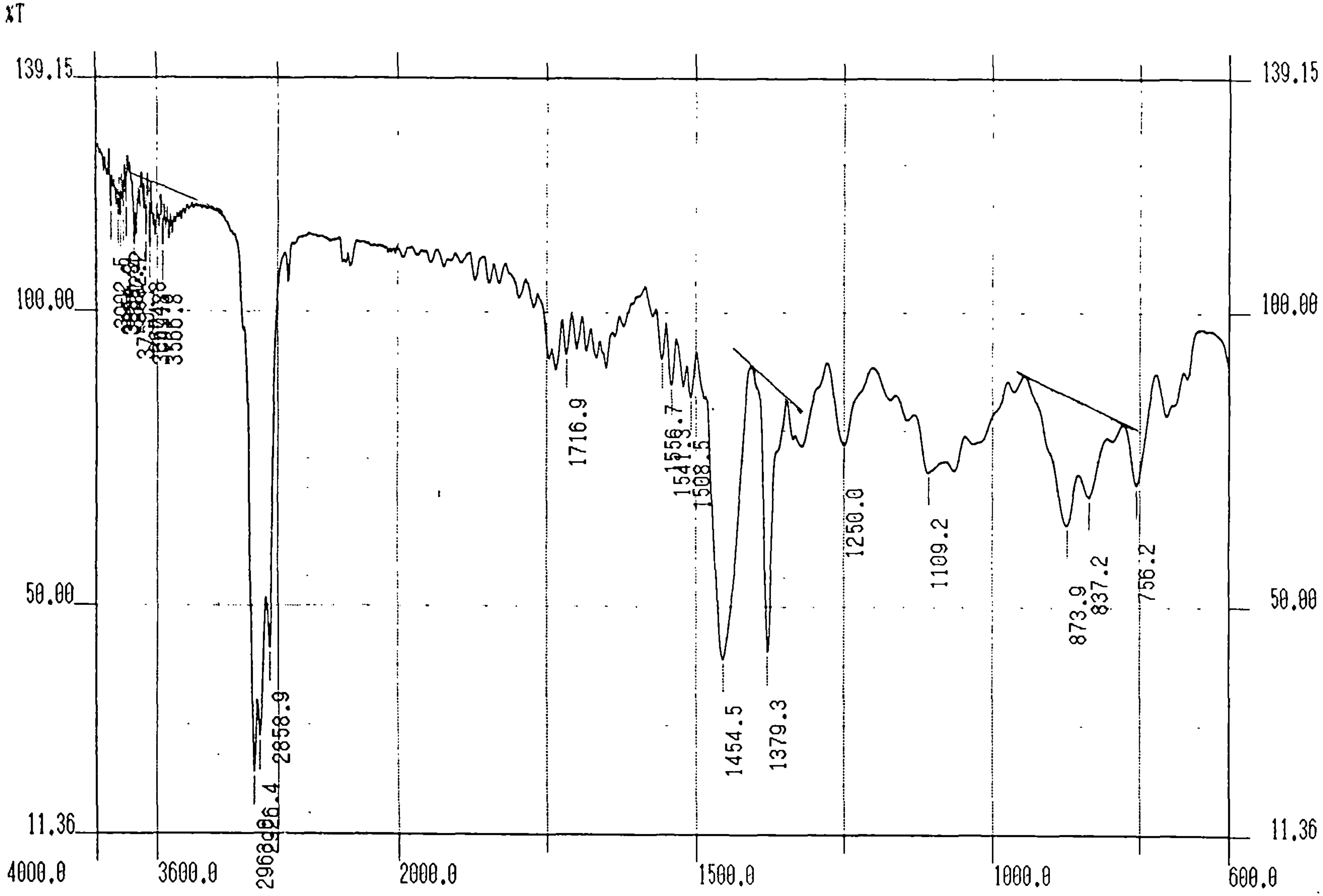

Fig. 6.3 I.R. Spectra of ENR 50

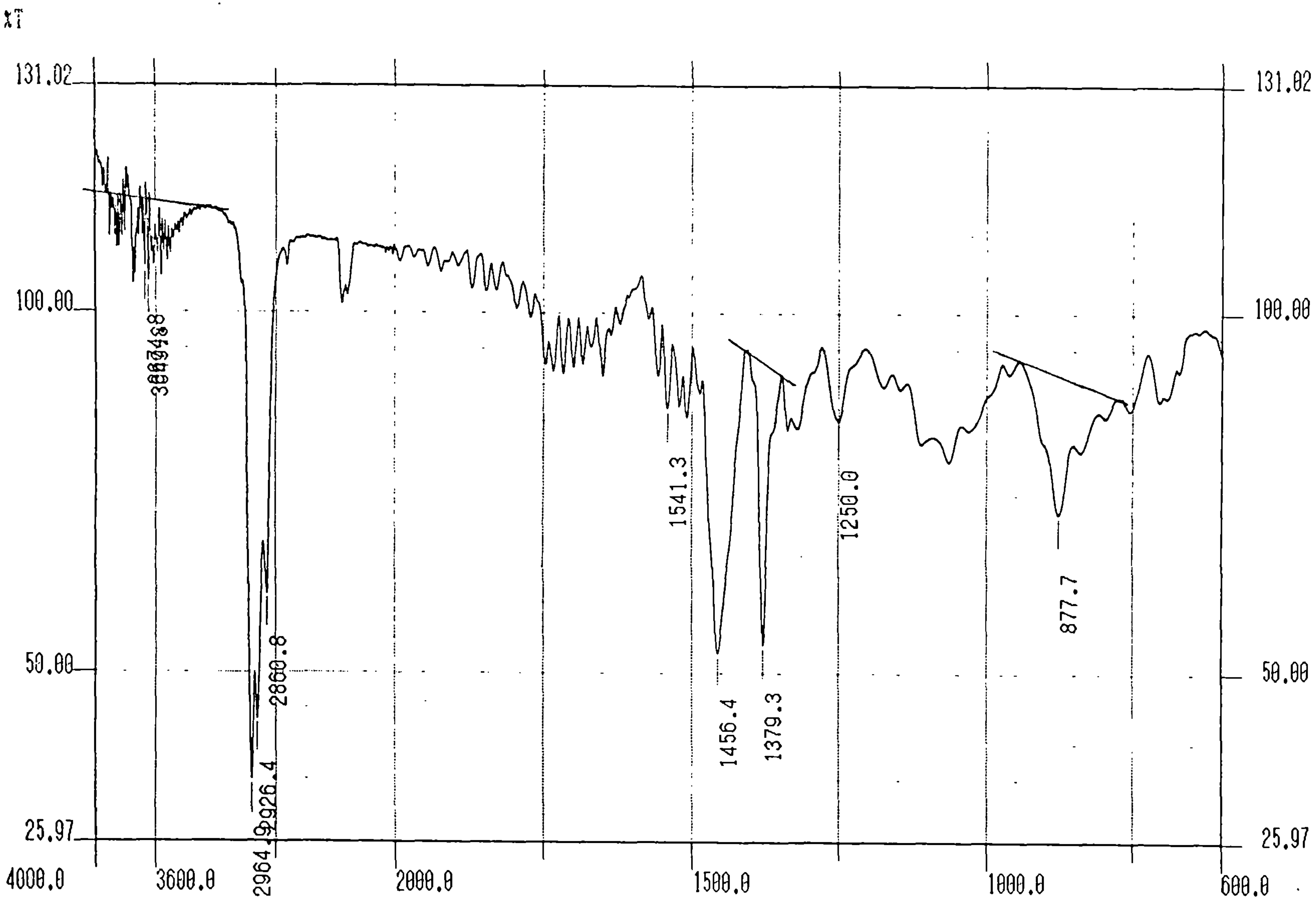

Fig. 6.4 I.R. Spectra of ENR 60

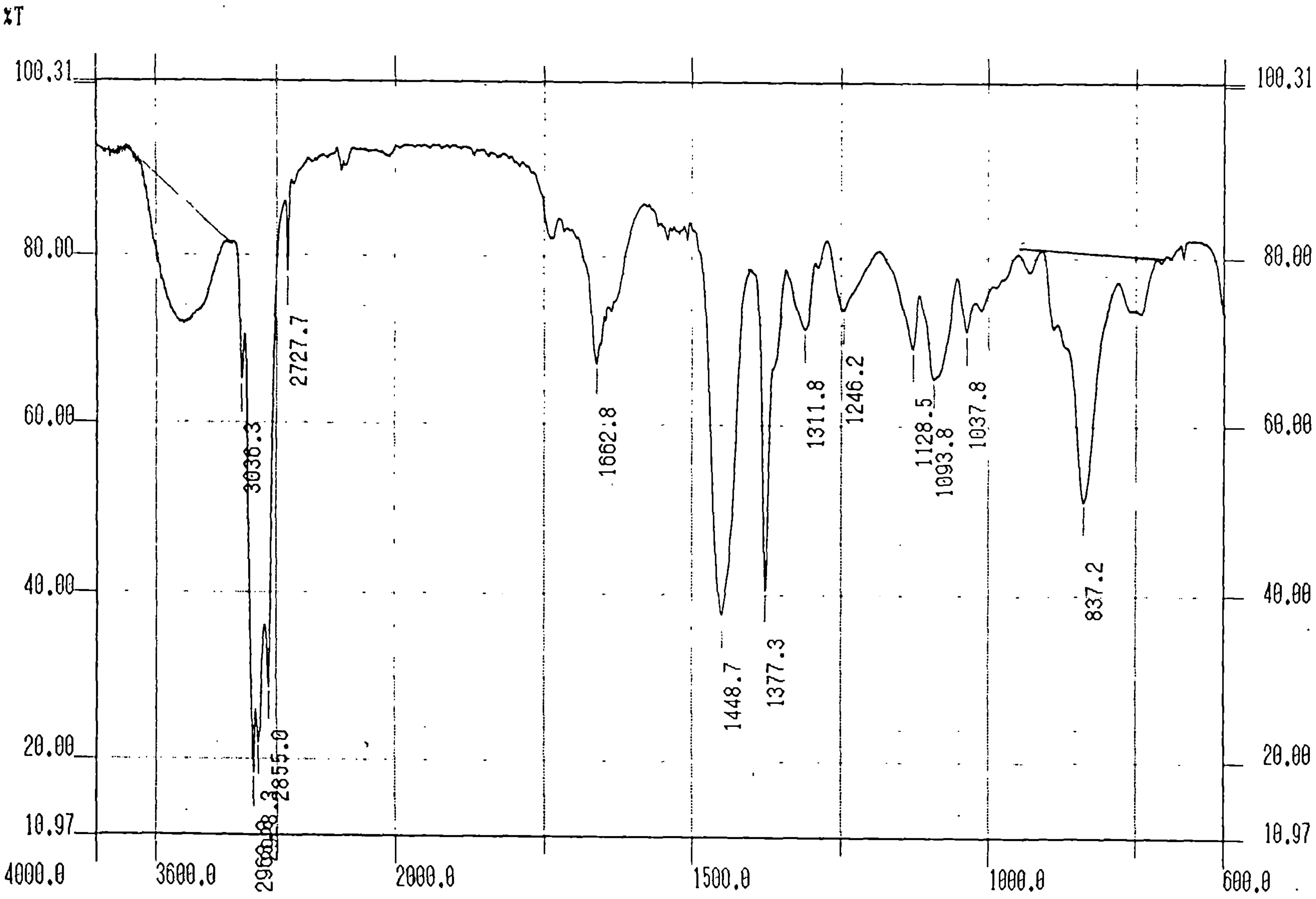

Fig. 6.5 I.R. Spectra of ENR 10 after mastication

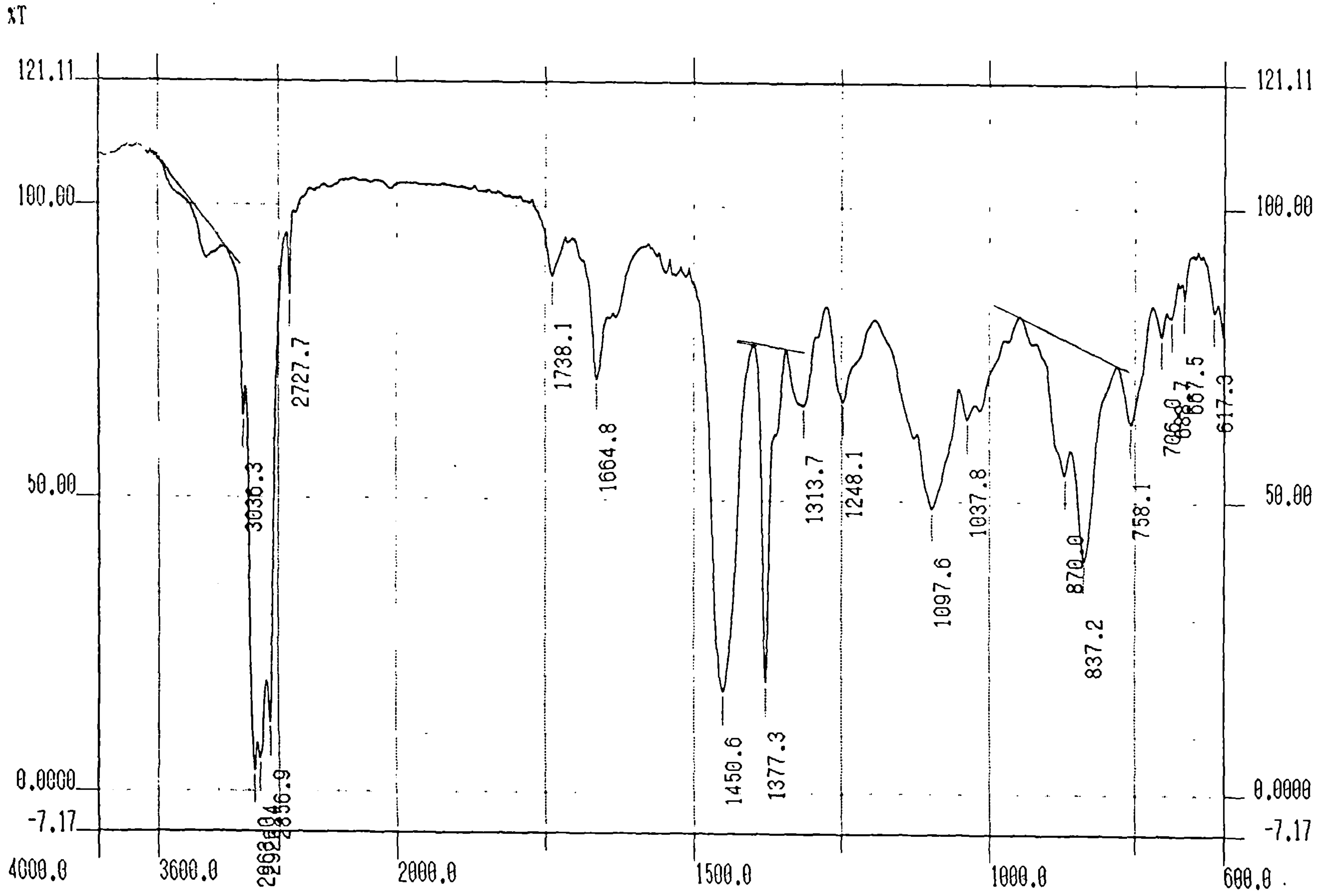

Fig. 6.6 I.R. Spectra of ENR 25 after mastication

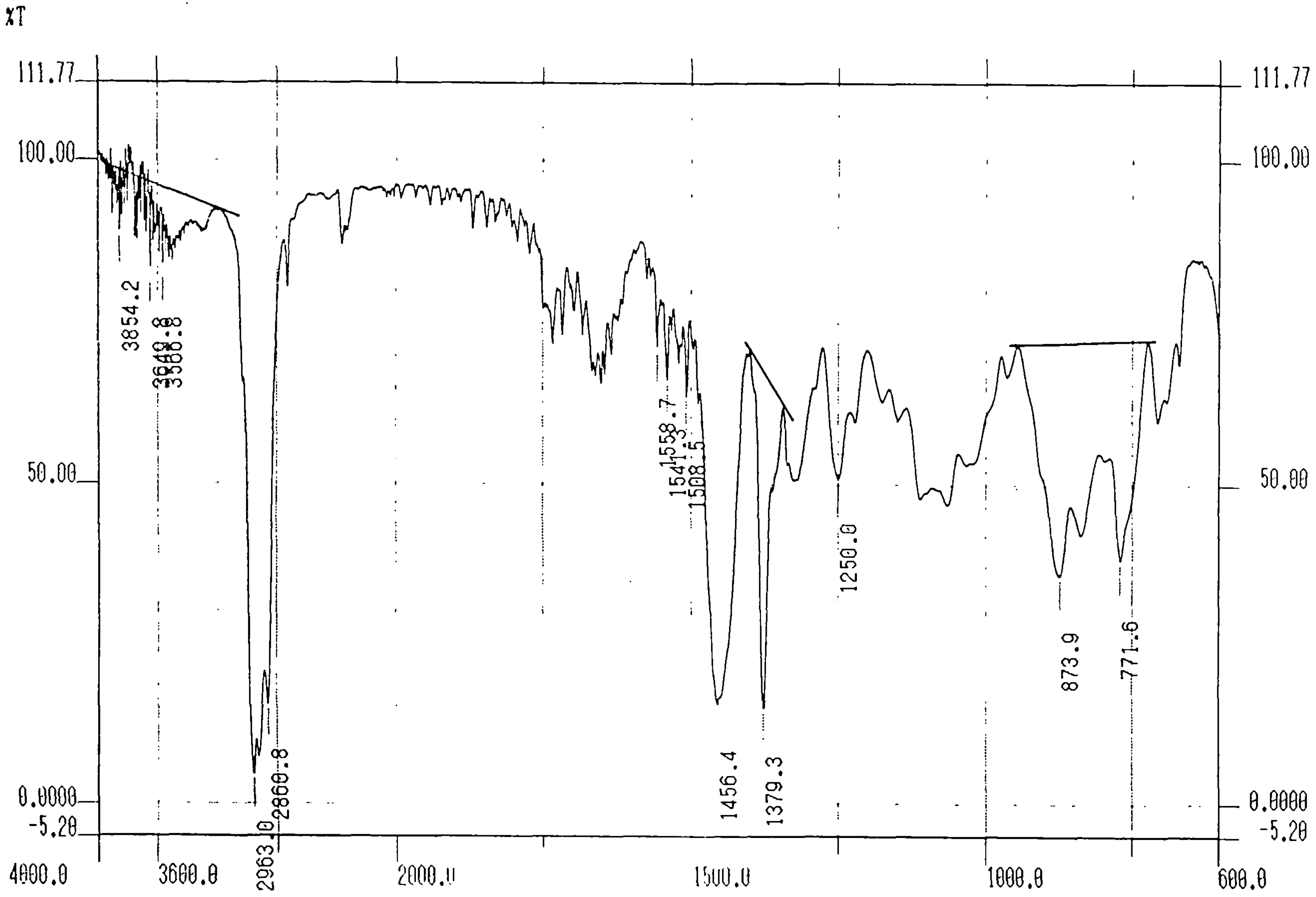

Fig. 6.7 I.R. Spectra of ENR 50 after mastication

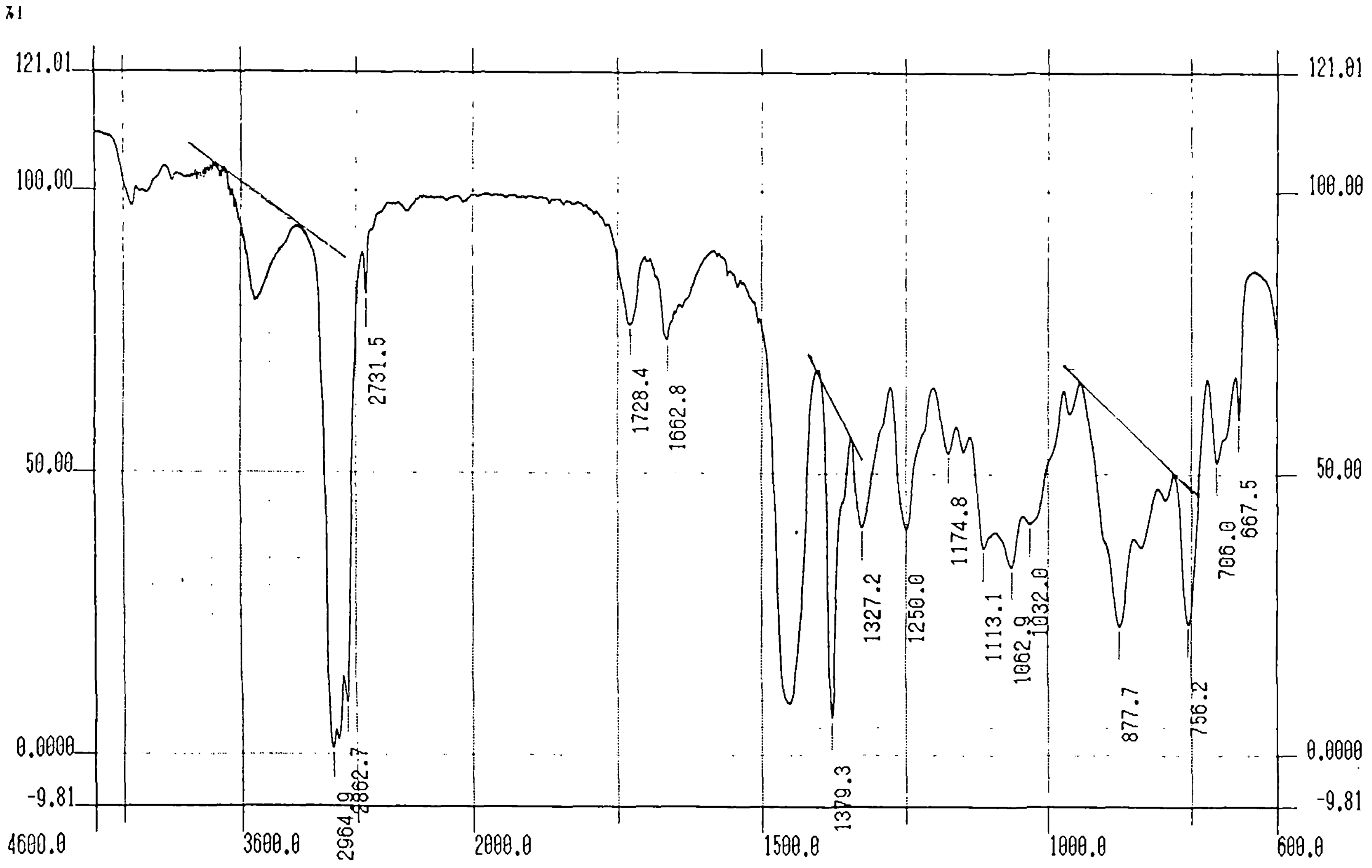

Fig. 6.8 I.R. Spectra of ENR 60 after mastication

PART II

EFFECT OF PEPTISER ON THE BREAKDOWN PROPERTIES OF ENR 50

The Mooney viscosity of the epoxidised rubber samples with higher epoxy content was observed to be higher. Consequently the energy required for mastication of the above is high. The mastication behaviour of ENR samples was found to be slightly different from that of NR. Hence the effect of a peptiser viz., 2,2' dibenzamidodiphenyl disulphide (Renacit -11) on the breakdown properties of ENR 50 have been evaluated.

Effect of dosage

Different dosage of the peptiser (0.15 phr to 1 phr) were added to ENR 50 during mastication. The effect of the same on the breakdown of the rubber was studied. Table 6.8 gives the values of the same. As in the case of NR, significant changes in plasticity and other properties were caused by the initial addition of the peptiser. It is seen that 0.25 phr of the peptiser at 80°C and at an rpm of 60 reduces the plasticity more than half the initial value. A control sample masticated without the peptiser was found to reduce Po only by about 35per cent.

The rate of breakdown was found to increase with the addition of the peptiser. The dump temperature showed a declining trend with the addition of the same. Also the TTQ to attain a fixed torque level was found to decrease with the addition of the peptiser. However, dosages above 0.25 phr did not produce much effect.

Effect of temperature

As it was found that 0.25 phr of the peptiser brings about optimum effect on mastication, the dosage of the same was fixed as 0.25 phr for further trials. Table 6.9 gives the changes in breakdown parameters with the change of temperature for ENR 50 samples to which 0.25 phr of 2,2' dibenzamido diphenyl disulphide was added. Each sample is compared with a control sample without the peptiser. At all the temperatures studied, the peptiser increases the rate of breakdown. Also it reduces the energy of mastication as measured by TTQ . The final temperature was found to be decreasing.

In the case of ENR 50, at 100°C Wallace plasticity was found to be higher than that masticated at lower temperatures without the peptiser. In the presence of the peptiser, no such effect exists. P_o reduces ($P_o = 26$) compared to ($P_o = 45$) the control sample showing that, the peptiser promotes chain scission to a higher extent with little indication of crosslinking as in the case of samples masticated without peptiser at higher temperature.

The speed of rotor was not found to have much effect on the breakdown. However, the rate of breakdown decreases with increase in speed. The difference in Wallace plasticity of the samples subjected to increased shear rate was found to be marginal.

CONCLUSIONS

1. The behaviour of ENR 50 in the presence of the peptiser 2,2' dibenzamido diphenyl disulphide was almost similar to that of NR. A dosage of 0.25 phr of the same could reduce viscosity to the optimum level.

2. The peptiser promotes chain scission to a higher extent with little indication of crosslinking taking place, as in the of samples masticated without peptiser at higher temperature.

Table 6.8

Effect of peptiser on breakdown characteristics of ENR 50

Temp.: 80°C; RPM 60 ; 5 Min Initial Po = 64

Dosage	Wallace plasticity (Po)	Initial torque M_1 Nm	Final torque M_5 Nm	[BI] Nm/min	T_F °C	$[TTQ]_1$ Nm-min
Control	40	175	111	16.0	140	370
0.15	35	172	94	19.5	136	342
0.25	29	174	87	21.8	137	318
0.50	26	168	78	22.5	135	324
1.00	25	170	87	21.6	136	327

Table 6.9

Effect of temperature on breakdown characteristics of ENR 50 with peptiser

Dosage of peptiser 0.25; RPM 60; Time 5 Min Initial Po = 64

Temp (°C)	Wallace plasticity	Initial torque M_1 Nm	Final torque M_5 Nm	[BI] Nm/min	T_F °C	$[TTQ]_1$ Nm-min
60 (control)	40	168	11	14.3	128	360
60 (0.25phr)	33	166	98	17.1	126	346
80 (control)	36	179	118	15.2	143	348
80 (0.25phr)	29	174	87	21.8	137	318
100 (control)	45	150	117	14.3	150	297
100 (0.25phr)	26	152	58	23.5	146	243

Table 6.10

Effect of rotor speed on breakdown properties of ENR 50 with peptiser

Dosage 0.25 phr ; Time 5 min; Temp.80 (°C)

Rotor speed(rpm)	Po	M_1Nm	M_5Nm	[BI] Nm/min	T_F(°C)	TTQ (Nm-Min)
60	29	174	87	21.8	137	318
80	27	166	97	17.3	141	304
100	23	148	93	13.8	157	268

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CHAPTER - VII

SUMMARY AND CONCLUSIONS

Detailed investigations on different forms of natural rubber with regard to their breakdown behaviour, rheology and consistency in properties were carried out. The forms of natural rubber studied were sheet [RSS 4 and RSS 5], ISNR 20 and EBC. In the case of the latter two forms samples from estate and nonestate sectors were included. The samples were collected from different locations at specified intervals, for a particular period. The effect of the extent of mastication on raw rubber properties as well as the properties of the compounds and vulcanizates was also studied.

The consistency in raw rubber properties and breakdown behaviour of skim rubber were studied by collecting samples periodically from selected processing units. The effect of incorporation of skim with ISNR 20 has also been investigated.

Epoxidised natural rubber samples with different levels of epoxidation viz ENR 10, ENR 25, ENR 50 and ENR 60 were prepared. The effect of epoxy content on breakdown behaviour was studied. The performance of the peptiser 2,2' dibenzamido diphenyl disulphide during the mastication of ENR 50 was also investigated.

The effect of extent of mastication on raw rubber and vulcanizate properties of ISNR 5 and ISNR 20 are described in Chapter III. ISNR 5 was found to have a higher molecular weight. The rate of reduction of

$\bar{M}$w with the extent of mastication was also found to be higher for ISNR 5. It was observed that the maximum reduction in molecular weight and Wallace plasticity was achieved during the initial period of mastication. Prolonged mastication was shown to have less effect on these properties. The gel content of ISNR 20 was comparatively higher. However, the decrease of the same at higher levels of mastication is more prominent in the case of ISNR 5. Varying the rotor speed of the mixer did not affect the properties of the raw rubber significantly.

The processing and vulcanizate properties of ISNR 5 and ISNR 20, masticated to different periods and subsequently compounded were studied. The extent of breakdown was found to have less influence on the cure characteristics. In both the grades, retention in tensile strength after ageing and compression set were identified to be the properties that were affected by the extent of mastication. Compression set showed sharp increase with higher levels of mastication, especially in the case of ISNR 20. The other properties were not affected much.

Among the three chemicals which have been evaluated for their peptising action, 2,2' dibenzamido diphenyl disulphide was found to perform better. An optimum dosage (0.15 phr) of the same was found to give better results. An increase in the peptiser content did not bring about a corresponding reduction in molecular weight and related properties. MBT was not found to impart significant peptising effect.

Chapter IV, describes the results of studies on different forms of NR, with special reference to rheology and breakdown behaviour. A comparative evaluation of ISNR 20, was made with the conventional forms being used in the tyre sector. It was found that sheet rubber grades (RSS 4 and RSS 5) show better raw rubber properties than the crepe and ISNR 20 except for volatile matter and plasticity. They also showed the same level of consistency in raw rubber properties compared to ISNR 20. The sheet grades were found to have higher vulcanizate tensile strength and elongation at break. The processing properties were more consistent with ISNR 20. Significant differences in properties were not observed for ISNR 20 grades processed from fresh and dry field coagulum. EBC processed from fresh field coagulum is superior to that from dry field coagulum. However, ISNR 20(DC), processed in the non-estate sector have better properties than EBC (DC).

The rheological behaviour of the above forms were studied using the capillary rheometer. At higher shear rates, RSS 4, ISNR 20(FC) and EBC (FC) behaved similarly. The flow behaviour index n' for all the forms of rubber studied were found to be much below unity indicating the highly non-Newtonian nature of the NR melts. ISNR 20(DC) and EBC (DC) samples which were processed from dry or semi-dry field coagulum showed comparatively lower values for n'. The energy of activation E was found to be less in the case of EBC (DC) manifesting the poor quality of the raw material. Die swell was also found to be minimum for the same.

The torque-rheometer also gave meaningful conclusions on the rheological behaviour of the above forms of NR. It was found that the difference in the breakdown parameters of the rubber during successive mastication can be taken as a measure of the degradation occurring. The slope of the plot of the Arrhenius type equation using torque and temperature, can give a measure of the energy of activation. RSS 4 was found to give maximum difference between gradients (slopes) of the Arrhenius plots for successive mastication trials, indicating higher extent of degradation. EBC (DC) showed minimum difference for the above.

Comparative assessment of breakdown behaviour of ISNR 20 with the conventional forms showed that the ease of breakdown was found to be maximum for EBC (DC). The attempts to correlate statistically the properties such as Po and PRI of the rubbers with their breakdown characteristics showed that, in the case of RSS 4, a highly significant correlation existed between Wallace plasticity and the energy required for mastication. ISNR 20(DC) showed maximum dependence of breakdown parameters on Po. Analysis of variance (ANOVA) for breakdown parameters of different forms indicated that comparisons were possible between grades, though EBC (DC) showed an odd behaviour.

The studies on skim rubber are summarised in Chapter V. The skim crepe showed higher level of inconsistency in raw rubber properties. The major factor influencing the mastication behaviour of skim rubber was found to be its initial plasticity. Comparison of skim block and skim crepe processed from the same raw material showed that the rate of breakdown of the former was higher during mastication. The rate of initial breakdown of skim crepe was found to be inversely related to the plasticity retention index. Peptiser was observed to have less effect in the mastication of skim rubber compared to other forms of NR.

Incorporation of skim with ISNR 20 showed that optimum cure time increased and scorch time reduced with progressive addition of skim rubber. Technological properties are affected adversely at higher concentrations of skim. Maximum degradation is observed in the case of flex characteristics. Dynamic properties were found to be improved by the addition of skim. Tan δ values showed an increasing trend with corresponding increase in skim content. The vulcanizates containing higher proportion of skim absorbed more water, when immersed in the same for a prolonged period.

Chapter VI gives the results of the breakdown properties of different grades of ENR. ENR grades having high epoxy content, viz., ENR 50 and ENR 60 exhibited an increase in Wallace plasticity and gel content, when the same were masticated at higher temperature. This could be attributed to the opening of the epoxide groups followed by crosslinking through the ether groups. However, IR spectra of the different grades prior to and after mastication were only marginally different.

A comparison of the rate of breakdown evaluated on the torque-rheometer showed that ENR grades with higher epoxy content had a higher rate of breakdown. But within a particular grade the rate decreased as the temperature was increased. At higher rotor speeds, chain scission seems to be the predominant mechanism during mastication as is evident from the lower Po values. The energy of mastication of different grades was mainly depending on the initial plasticity.

Mastication of ENR, in the presence of 2,2' D D D S showed similar behaviour as that in ISNR 5 samples. A dosage of 0.25 phr of the same could reduce the viscosity of the rubber to the optimum level.

List of Publications from this work

1. Thomas, K.T., Verghese, L., Joseph,T., Madhusoodanan, K.N. and Mathew, N.M. (1995). "A comparative evaluation of ISNR 20 with conventional forms of natural rubber". Indian Journal of Natural Rubber Research 8(2) : 123-129.

2. Thomas, K.T., Mathew, N.M., Joseph, S. and Premalatha, C.K. "Different forms of natural rubber-comparative rheology". Journal of Elastomers and Plastics (Communicated).

3. Thomas, K.T., Mathew, N.M. and Joy Jacob. "Studies on variability in properties and molecular breakdown behaviour of skim rubber". Indian Journal of Natural Rubber Reserach (Communicated).

4. Thomas, K.T., Mathew, N.M. and Joseph, R. "Studies on the processability of different forms of natural rubber using Torque- rheometer". International Journal of Polymeric Materials (Communicated). ✓

5. Thomas, K.T., Mathew, N.M. and George, M. "Effect of peptisers on molecular breakdown of natural rubber - a comparative evaluation". Die Angewandte Makromolekulare Chemie (Communicated).