CURE CHARACTERISTICS AND VULCANIZATE PROPERTIES OF NR/NBR BLENDS

THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE
IN
APPLIED CHEMISTRY

SUBMITTED
BY

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2009

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CERTIFICATE

Certified that this **Project Report** entitled "**Cure characteristics and vulcanizate properties of NR/NBR blends**" is the bonafide record of work done by **Sajini A.P** in partial fulfilment of the requirements for the award of the degree of **Master of Science in Applied Chemistry, Department of Chemistry, University of Calicut, Calicut.**

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The Rubber Research Institute of India
Rubber Board, Ministry of Commerce and Industry, Govt. of India

11-06-09

CERTIFICATE

This is to certify that the thesis titled *"Cure characteristics and vulcanizate properties of NR/NBR blends"* being submitted by Kum. Sajini A.P. to the Department of Chemistry, University of Calicut for the award of the degree of Master of Science in Applied Chemistry is a record of bonafide research work carried out by her. Kum. Sajini A.P. has worked on her research topic from April to June 2009, under my supervision. The results included in this report have not been submitted for the award of any other degree.

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Acknowledgement

I express my deep sense of gratitude to Dr. Benny George, Scientist, Rubber Technology Division, Rubber Research Institute of India, Kottayam for his guidance and valuable suggestions during the course of this work.

I am grateful to Dr. James Jacob, Director of Research and also to Dr. K.T. Thomas, Deputy Director, Rubber Technology Division, Rubber Research Institute of India, Kottayam for allowing me to do the project at RRII and also providing me the necessary facilities for the completion of the work.

I gratefully acknowledge to Prof. P. Mohammad Shafi, Head of the department of chemistry, University of Calicut, Calicut for the support and encouragement for doing this work at RRII, Kottayam. I also gratefully acknowledge the valuable support rendered by Dr.M.T. Ramesh for successful completion of the work.

I express my sincere thanks to all the staff of RT Division especially to Mr. S.N. Sajeev, Mrs. Susamma Joseph, Mrs. Valsa George and Dr. M.L. Geethakumari for their assistance at various stages of the project. I would also acknowledge with thanks the service rendered by the RRII Library.

SAJINI A.P

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CHAPTER 1

Introduction

1. Natural Rubber

Natural Rubber is extracted by the controlled wounding known as tapping of the bark of the trunk of Hevea Brasiliensis[1] trees. The modern age of natural rubber started during the 1870's, when the British transported *Hevea* seeds from Brazil to India for planting[2]. Rubber is cultivated in India in an area of about 6 lakh hectares by about 10 lakh growers with a total production of 8 lakh tones per annum.

Natural Rubber from the rubber tree is collected in to forms viz, liquid latex (75-85%), which contains about (30-40%) dry rubber and the rest (15-25%) of the crop in the form of field coagulum. Field coagulum includes cup lumps, tree lace, shell scrap, pre-coagulated lumps, etc. They are commonly termed as scrap rubber in India. Latex can be processed into 1. Ribbed Sheets, 2. Pale Latex Crepe (PLC) or Sole Crepe, 3.Technically Specified Rubber (TSR) or Specialty Rubbers and 4. Preserved Field Latex and Latex Concentrate. Field coagulum is processed into crepe rubbers or TSR. Latex is considered to be more valuable whereas field coagulum is considered as a secondary product.

1.1 Different marketable forms of natural rubber

1.1.1 Sheet Rubber

Sheet rubber holds the predominant share in the Indian natural rubber market. Raw rubber sheet are of various types like ribbed smoked sheets (RSS) air dried sheets (ADS) and sun dried sheets, depending on the method adopted for drying.

The processing procedure for making sheet rubber includes sieving, bulking, and standardization of latex, addition of chemicals, coagulation, sheeting, dripping and drying.

After drying sheets in smoke houses, they are visually examined by holding them against clear light to see any speck or impurity remaining inside. The grading and packing of smoked sheet rubber is carried out as described in the Inter National Standards of quality and packing for natural rubber grades -The Green Book. According to the green book specification there are 6 grades of sheets. They are RSS 1X, RSS 1, RSS2, RSS3, RSS4 and RSS5. All ribbed smoked sheets shall be packed in rubber covered bales of about 50kg.

1.1.2 Crepe rubbers

When coagulum from latex or any other forms of field coagulum or RSS cuttings, after preliminary treatment is passed through a set of crepe making machines, crinkly, lace-like rubber is obtained. This, when dried is called crepe rubbers. Based on the raw materials used crepe rubbers are classified into two. They are crepes produced from latex, i.e. pale latex crepe (PLC) and sole crepe and those produced from field coagulum. The latex crepe is of better quality when compared to that of field coagulum. Different grades of PLC are used for high quality products like pharmaceutical articles, light coloured and transparent goods, adhesives, tapes, tubings and derivatives such as chlorinated rubber. Sole crepe is used primarily for the production of translucent shoe soling material. Process involved in the production of latex crepes includes sieving, and bulking, standardization of latex, addition of chemicals, removal of pigments, coagulation, crepe making and drying. The grading pale latex crepe and sole crepe is done by examining factors like colour, presence of dirt and variation from thickness and weight specified.

The crepes prepared from field coagulum materials fall into 5 types-thin estate brown crepe, thin brown crepe, thick blanket crepe, flat bark crepe and pure smoked blanket crepe. Processing into crepe rubber was one of the method to upgrade low quality field coagulum such as earth scrap, shell scrap, tree lace etc. Through soaking, agitation, cleaning, creping operation and drying are required to produce good quality field coagulum materials. Crepes are graded by examining parameters like colour, strength and thickness. There are three grades 1X, 2X and 3X. The field coagulum crepes are used for the manufacture of tires, footwears, retreading materials etc.

1.1.3 Technically Specified Rubber (TSR)

TSR is a modern form of marketable rubber and can be produced from latex, field coagulum or blend of both. The production of TSR started during 1960's. Natural rubber marketed as RSS or crepe form, is graded only by visual methods. The inadequacies of the visual grading system made gradual reduction in the marketing of NR. Consequently new methods of processing and presentation were developed to attain the market for NR in compact, medium sized blocks wrapped in polyethylene and adopting a grading system on specifications. These are called technically specified rubbers. In India it is known with general name Indian Standard Natural Rubber (ISNR).

Both latex and field coagulum is used for the production of TSR. The former offers greater uniformity of the raw material and consequently higher grade product. When field latex is used as the raw material, the processing includes operations like bulking, preservation, sieving, coagulation, dewatering, size reduction, drying, bailing, and grading.

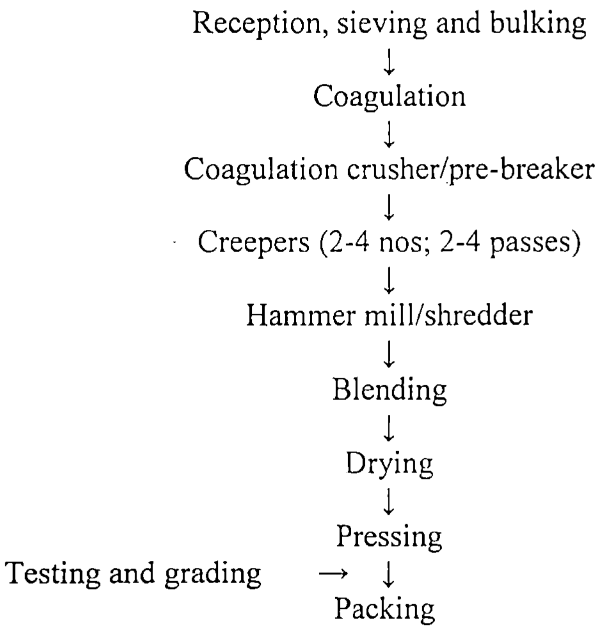


Figure 1.1 Flow diagram for preparation of TSR from Latex

When field coagulum is used the essential unit operations for processing them include dry blending, soaking, pre cleaning, macro blending(creping) and dirt removal, size reduction and dirt removal, drying, bailing and grading. Flow diagram for processing latex into technically specified rubber is shown in Figure.1.1 Flow diagram for processing field coagulum into technically specified rubber is shown in Figure 1.2.

Field coagulum
↓
Sorting and blending
↓
Soaking
↓
Slab cutter/pre-breaker
↓
Blending
↓
Creepers (2-3 nos., 2-4 passes)
↓
Hammer mill
↓
Blending
↓
Creepers (3-4 no.s, 6-8 passes)
↓
Hammer mill/shredder
↓
Blending
↓
Drying
↓
Pressing
Testing and grading → ↓
Packing

Figure 1.2 Flow diagram for preparation of TSR from field coagulum

The major rubber producing countries like Thailand, Indonesia, and Malaysia export block rubber. Each block weighing 33.33kg after marking the grade, is put in LDPE bag and then packed in wooden pallet crates. Each pallet contains 30 blocks. In India ISNR is graded to ISNR 3L, ISNR 3CV, ISNR 5, 10 and 20.

The specifications as per the latest revisions adopted by American Society for Testing and Materials (ASTM) and BIS[3]are given in tables 1.1 and 1.2 respectively.

Table 1.1 Specification for NR technical grades

Property	Rubber grade*				
	L	CV**	5	10	20
Dirt retained on 45-micron sieve (%max)	0.05	0.05	0.05	0.10	0.20
Ash(%max)	0.60	0.60	0.60	0.75	1.00
Nitrogen(%max)	0.60	0.60	0.60	0.60	0.60
Volatile matter(%max)	0.80	0.80	0.80	0.80	0.80
Initial plasticity,P0(min)	30	-	30	30	30
Plasticity retention index, PRI(%min)	60	60	60	50	40
Colour (*Lovibond* scale, max)	6.0	-	-	-	-
Mooney viscosity, ML(1+4)100°C	-	60±5	-	-	-

*Skim is not permitted in any grade .Grades of L, CV, and 5 must be produced from intentionally coagulated latex.

**Other Mooney viscosity range grades of rubber are available in CV50±5, CV70±5, according to customer requirements. CV without suffix is the CV60±5 as shown in the table.

Source: ASTM, 1996 [4]

Table 1.2 Specification for raw natural rubber

Property	ISNR 3CV	ISNR 3L	ISNR 5	ISNR 10	ISNR 20	ISNR 20
Dirt retained on 44-micron aperture(%max)	0.03	0.03	0.05	0.10	0.20	0.50
Ash(%max)	0.50	0.50	0.60	0.75	1.00	1.50
Nitrogen(%max)	0.60	0.60	0.60	0.60	0.60	0.60
Volatile matter(%max)	0.80	0.80	0.80	0.80	0.80	0.80
Initial plasticity,P0(min)	**	30	30	30	30	30
Plasticity retention index, PRI(%min)	60	60	60	50	40	30
Colour (*Lovibond* scale, max)	-	6.0	-	-	-	
Mooney viscosity, ML(1+4)100°C	60±5	-	-	-	-	
Accelerated storage hardening(max)	8	-	-	-	-	-
Colour code	black	black	green	brown	red	yellow

Source: BIS, 1992 **As agreed by purchaser and supplier.

Advantages

Advantages of TSR are quality assurance with respect to important technical parameters, consistency in quality, clean and easy to handle packing, minimum storage space and reduction in processing time[5].

The main advantages of TSR are that, (1)it is available in 6 different grades with technical specifications and consumer can choose the grades according to requirements, (2) as it is processed in bulk quantities adopting latest technology, variations in properties within the same grade is minimum, (3) impurities in the rubber can be assessed as the content of foreign material and volatile matter and (4) being marketed in compact PE wrapped bales, contamination on storage, handling and transportation is avoided.

Grades

1. ISNR 3CV

This grade is produced from good quality field latex and is viscosity stabilized at a narrow range (60±5). This is mainly used in the manufacture of tires, engineering components, extruded and calendered products, etc. Where physical properties of the final product are very critical and consistency in processing behaviour is highly desirable.

2. ISNR 3L

This is also produced from good quality field latex and the maximum colour of this rubber as per the Lovibond scale shall be six units. ISNR 3L is mainly used for light coloured products, pharmaceutical products, feeding bottle teats and large industrial rollers for paper and printing industry, which require high purity . It is a possible substitute for PLC.

3. ISNR 5

This is processed using field latex or high quality field coagulum as the main raw material and is widely used in the manufacture of high quality products like conveyor belts, cycle tubes, engine mountings, foot wear etc. ISNR 5 is a possible alternative to higher quality sheets.

4. ISNR 10, ISNR 20 and ISNR 50

These grades of TSR are processed from quality field coagulum materials and can be used for the manufacture of rubber products according to the quality requirements in place of conventional lower grades of sheet rubber and crepe. Generally ISNR 10 and ISNR 20 grades are used by the tire manufacturers in bulk. ISNR 50 grade is used for the production of cheap products like handmade hoses, foot wear, mats and moulded goods.

1.2 Acrylo nitrile butadiene rubber (NBR)

Nitrile rubber is a copolymer of a diene and an unsaturated nitrile .The majority of the nitrile elastomers produced today are copolymers of acrylo nitrile and butadiene .

Acrylo nitrile content (ACN) is one of the primary criteria for defining every NBR. ACN level due to polarity determines several basic properties such as oil and solvent resistance,low temperature flexibility ,glass transition temperature and abrasion resistance . Typical acrylo nitril content ranges between 18 and 45%

1.2.1 . Manufacture of nitrile rubber

1. Preparation of monomer

Butadiene monomer:- Ethyl alcohol is dehydrogenated to acetaldehyde

$$CH_3\text{-}CH_2\text{-}OH \longrightarrow CH_3CHO+H_2$$

Acetaldehyde and ethyl alcohol are passed over dehydrating catalyst to produce butadiene monomer.

$$CH_3CHO + CH_3CH_2OH \longrightarrow CH_2{=}CH\text{-}CH{=}CH_2 + H_2O$$

2.Polymerisation

Acrylo nitrile and butadiene monomers are made to copolymerize under strictly controlled conditions of pressure and temperature using emulsion polymerization. The polymerization temperature which is very critical during the process is controlled at approximately 50^0 C for cold rubbers. The conversion of monomer is not carried out to completion and the reaction is stopped at predetermined intermediate stage to obtain the desired properties in the finished rubbers.

1.2.2 Properties of NBR

1. Oil, fuel and grease resistance
2. Good abrasion resistance
3. Good hot air resistance
4. Good processing characteristics
5. Low gas permeability
6. Moderate ozone resistance

1.2.3 Uses

1.In rubber goods as moulded technical goods, hoses and tubes

2.In printing rollers, brake linings and clutches, cellular goods coated fabrics, special foot wear rollings,cables and wires and sealing materials.

1.3 Compounding of rubber

The art of making a compound by mixing rubber and compounding ingredients inorder to make a product is known as compounding of rubber. When designing a mixing formulation for a specific end use the compounder takes into account two factors 1.vulcanizate properties, and 2.cost of raw materials involved in the production process which transforms these raw materials into product. The principal task of compounding is to acquire a balance between the final vulcanizate properties, price and processability.

In a rubber product number of ingredients other than the rubber may be present. They are usually,

1. Polymer or rubber(blend of rubber)
2. Cross linking agents, usually sulphur
3. Accelerators for crosslinking reaction
4. Accelerator modifiers
5. Aids to processing(chemical peptizers for polymers, sotteners, plasticizers, dispersing acids, tackifiers, and lubricants)
6. Reinforcing fillers(Black, mineral and organic)
7. Antidegradants (Antioxidants, antiozonant, inhibitors of mineral catalyzed oxidation, protective waxes)
8. Diluents(Inter mineral fillers, organic materials and extending oils)
9. Special additives(Blowing agent)

1.4 Selection of ingredients

1.4.1 Polymer or rubber (blend of polymer)

Most important component of a rubber compound is the polymer. It may be natural, synthetic or reclaimed rubber, mixture of these or a mixture of rubber and a thermoplastic material. This polymer should be of lowest price and should have required properties to provide adequate service, and also it should offer ease of mixing.

1.4.2 Cross linking agent

Sulphur is the most popular crosslinking agent used by the industry. By the use of crosslinking agent the rubber becomes less plastic, resistant to swelling in organic liquids and at the same time the elastic properties are improved. The crosslinking agent reacts with active sites in the polymer to form crosslinks between the chains. Vulcanization system without the involvement of sulphur or sulphur donors are less commonly used and are peroxides, urethanes, metal oxides, resins, electron beams and γ- radiation.

1.4.3 Accelerators for crosslinking reaction

Accelerators are materials added to make a rubber compound to increase the rate of vulcanization and to permit vulcanization to proceed at lower temperature and with greater efficiencies. They can also decrease the quantity of sulphur necessary for vulcanization and considerably improve the physical and technological properties of the vulcanizate.

Accelerators have been classified arbitrarily as low, medium-fast, fast, semi-ultra and as having direct or delayed action accelerators. Again it is classified into organic and inorganic. Organic in turn is divided into two, acidic and basic.

1.4.4 Acceleration modifiers (activators or retardant)

They are materials or mixture of materials to an accelerated vulcanizing system to realize its full potential. The activators used most commonly are ZnO and stearic acid. Increase in fatty acid usually shows the rate of cure increase but result in a higher concentration of more tightly cured and thermally stable network. The additions of ZnO produce a significant change and produce a well cured stock.

1.4.5 Reinforcing fillers

Reinforcing fillers are most particulate constituent of a compound added in large quantities to the rubber to improve the physical properties or to decrease the volume cost. According to their effectiveness they are graded as reinforcing and non-reinforcing. Reinforcing fillers include carbon blacks, silica, fine light coloured fillers, and synthetic reinforcing resins. Non-reinforcing fillers include diluents, coloured pigments, white pigments.

Reinforcing fillers enhance compound properties like hardness tensile strength, modulus, tearstrength and abrasion resistance of a compound. They are sub divided into black and non black fillers. Black fillers are various grades of carbon black and non black fillers include silica, clay, talc etc.

1.4.6 Antidegradants

They are substances when added to rubber in a small quantity retards ageing and protect rubber from internal and external influences in deterioration. These are classified according to the type of protection.

1. Retard to prevent atmospheric oxidation and its effects(oxidation)
2. Retard or prevent the formation of tears caused by ozone attack, under static or dynamic stress (antiozonents)
3. Protect against special type of ageing(special additives)

Antioxidants are of two types, chain breaking and preventive antioxidants according to their function. Some of the commonly used oxidants are 2,2,4-trimethyl-1,2-dihydroquinoline (TDQ), substituted phenols etc.

1.4.7 Antiozonants

They are amorphous and microcrystalline waxes which migrate to the surface and form a physical protective surface layer. E.g.; N,N-Diphenyl-p-phenylenediamines.

1.4.8 Processing aids

A. Softeners or processing oils

Mineral oils are used to increase the plasticity of the compounds, facilitates the dispersion of fillers, improve processability and act as diluents. These are called processing oils. These are classified according to their chemical composition into three main groups. Paraffinic, naphthenic, and aromatic oil gives the best low temperature properties and good ageing and low hysterisis.

B. Chemical peptizers

Chemicals which act as mastication aids, enabling mixing time to be reduced, plasticity increased, and the viscosity of the rubber reduced. They act as oxygen carriers and thus increase the oxidative decomposition of gel structure of rubber.

Egs: Xylyl mercaptian.

C. Plasticizers

A material which may be added to rubber to improve flexibility, particularly at low temperature.

D. Diluents

They include inert mineral fillers, extending oils, etc

E. Coloring agents and pigments

They are dye stuffs for colouring the rubber to the required shade. These can be grouped into inorganic dyes, organic dyes and lacquers. Inorganic dyes include lithophone, titanium dioxide, iron oxide, chromium etc. Organic dyes include a vast range of shades. Many fillers, among them carbon black act as a powerful pigments.

Egs:

White pigments - Lithophone, ZnO, and $TiO2$.
Red pigments - Iron oxide
Yellow pigments - Cadmium lithophone
Green pigment - Chromium oxide
Blue pigment - Ultra marine

1.4.9 Special additives

These are substances which decompose into gaseous products at high temperature or which evolve gases and thus causes rubber compounds to expand before vulcanization, used for the production of cellular rubber articles and hollow articles. They must be well dispersed to obtain an even cell structure, they should not produce any toxic products on decomposition and should have a minimal effect on vulcanization. Blowing agent today in use Dinitrosopentamethylinetetraamine, benzenesulphonehydroxide, azo nitrates etc.

1.5 Mastication and mixing

The raw rubber natural and synthetic can be sottened either by mechanical work termed mastication or by heat or peptizers. Mixing mill is a machine having two hollow rolls which contain cooling or heating systems and are placed in a frame in horizontal for diagonal positions. The rolls move in opposite directions at different speeds in the ratio1:1.1to1:1.5 the second roll is the one moves at a faster speed. The gap between the rolls may be altered. The raw rubber is processed between the rolls by mechanical friction and plasticized. The degree of mastication is greater on cold rolls than warm rolls. The rubber is formed as a band around the front roll, thickness of the band depending on the gap between the rolls while superfluous rubber lies between the rolls as a bank when degree of mastication is reached. The fillers and vulcanizing agents are added on the rolls and the compounded rubber is taken out the rolls by cutting.

1.6 Vulcanization

Vulcanization is a chemical process of inter linking of rubber molecules to change the predominantly plastic properties to elastic properties. Vulcanization is the conversion of rubber molecules into a network by the formation of cross links. These vulcanizing agents are mostly sulphur, peroxide, other special vulcanizing agents or high energy irradiation. Vulcanization is an intermolecular reaction which increases the reactive force and reduces the amount of permanent deformation remaining after removal of the deforming force. According to the theory of rubber elasticity the reactive force resulting from a deformation is proportional to the number of network supporting polymer chains per unit volume of elastomer[6]. Vulcanization usually produces network junctures by the insertion of chemical cross links between polymer chains. The cross links may be formed *through chains of sulphur atoms, single sulphur atoms or carbon-carbon bonds. The* vulcanizate properties are not functions of cross link density only they are affected by the type of cross link, nature of polymer, type and amount of fillers etc[7]. The most widely used vulcanization procedure even today is merely elaborations of the original method of heating rubber with sulphur discovered by Charles Goodyear in 1839 and by Thomas Hancock in 1843[8]. The introduction of organic accelerator in the vulcanization of rubber which began more than 75 years ago led to revolutionary changes in the manufacturing of rubber products. The accelerators enabled vulcanization time to be reduced. The proportion of sulphur required for optimum physical properties could be reduced thus improving the resistance of rubber goods to ageing and preventing blooming of sulphur[9].

1.6.1 Sulphur vulcanization[10]

Sulphur vulcanizing systems usually contained sulphur in amounts of 2.5 to 3 pphr and accelerator in amounts of 0.5 to 1.0 pphr. The accelerated sulphur vulcanization system can be classified into 3 types.

1. Conventional system (CV) containing high sulphur /accelerator ratios.
2. Efficient systems (EV) containing high accelerator/sulphur ratios.
3. Semi EV systems that is intermediate between 1 and 2.

Conventional systems give vulcanizates which possesses excellent initial properties like strength, resilience and resistance to fatigue and abrasion and are satisfactory for many applications. However their heat ageing resistance, creep and stress relaxation properties are less satisfactory. For good ageing resistance and low compression set an EV system is essential or a semi EV system may be chosen as a compromise between cost/performance.

Soluble EV and semi EV systems are zinc-2-ethyl hexanote rather than stearic acid, the latter leading to insoluble zinc stearate formation in the vulcanizates and affects properties. Sulphur is limited to 0.8 phr. Soluble EV system overcomes some of the problems of EV systems such as high physical creep and low resilience. They are ideal for use in engineering components that require low compression set, low creep, low stress relaxation and high reproducibility in modulus and strength.

The chemistry of sulphur vulcanization is so complex[11] In sulphur vulcanization sulphur is combined in the vulcanization network in a number of ways. As cross links it may be present as monosulphide, disulphide or polysulphide, but it may also be present as pendent sulphides or cyclic monosulphides and disulphides.

A diagrammatic representation of the network structure is given in Figure.3

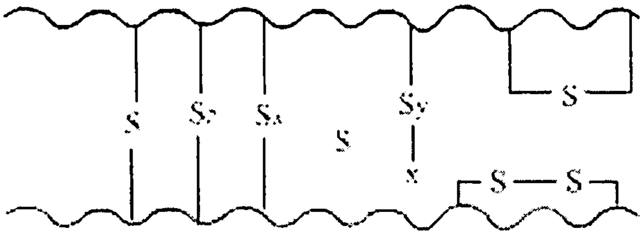


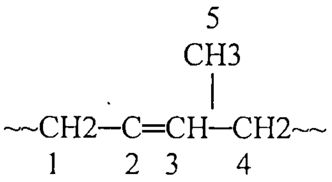
Figure.1.3

An estimate of the no. of sulphur atoms for each crosslink formed has been made. An unaccelerated rubber sulphur vulcanizate may give a figure of 40-45 whilst in conventional accelerated sulphur vulcanizates this "inefficiency" figure may drop to 10-15, special efficient vulcanizing systems can reduce it still further to 4or 5 but for even lower values the so called nonsulphur vulcanizing systems must be used.

The initial step in vulcanization is the reaction of sulphur with the zinc perthiosalt Xsx ZnSxX, where X is a group derived from the accelerator (eg.thio carbomate or benzthiozyl groups). This salt reacts with the rubber hydrocarbon RH to give a rubber bound intermediate.

$$X\,S_xZn\,S_xX \;+\; RH \rightarrow X\,S_x\,R \;+\; ZnS \;+\; HS_{x-1}X$$

And a perthio-accelerator group which with further ZnO will form a zinc perthio-salt of lower sulphur content this may again be an active sulphurating agent forming intermediates Xsx-1R. The hydrogen atom which is removed is likely to be attached to a methylene group in the X-position to the double bond, i.e., in natural rubber the hydrogen atoms at positions 4 and 5 the most liable in this type of reaction.

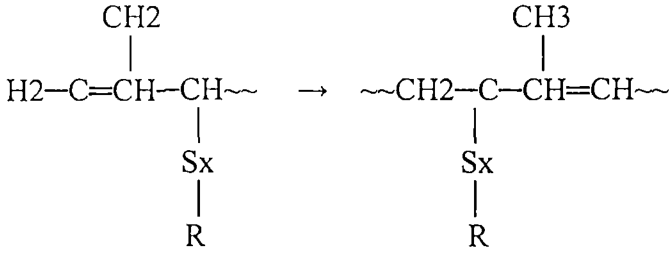


$$\sim\sim\underset{1}{CH_2}-\underset{2}{C}=\underset{3}{\overset{\substack{5\\CH_3\\|}}{CH}}-\underset{4}{CH_2}\sim\sim$$

The intermediate XSxR then react with a molecule of rubber hydrocarbons RH to give a crosslink and more accelerators is regenerated.

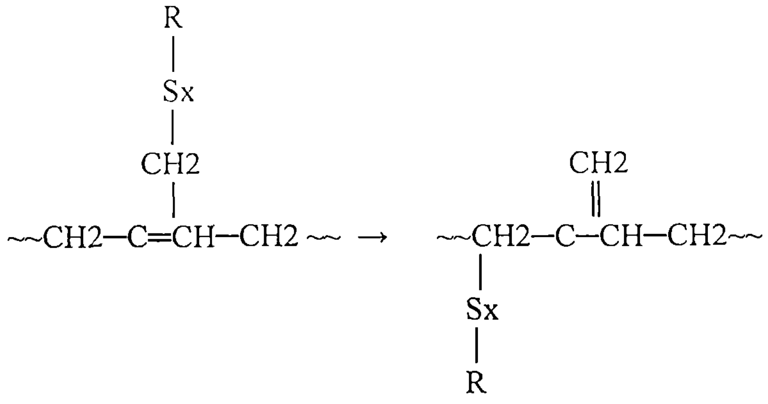
$$XSxR + RH \rightarrow RSx\text{-}1R + XSH$$

It is evident that the cross links which were initially at positions 4 and 5 undergo an allylic shift, with the result that new configuration appear.



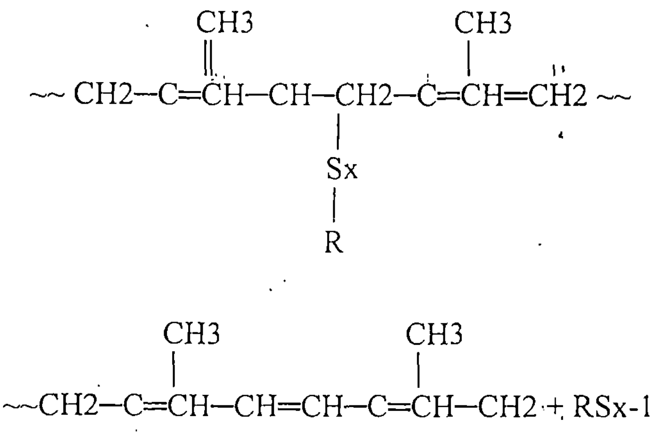
$$H_2-C=\overset{\substack{CH_2\\|}}{CH}-\underset{\substack{|\\Sx\\|\\R}}{CH}\sim\sim \rightarrow \sim\sim CH_2-\underset{\substack{|\\Sx\\|\\R}}{C}-\overset{\substack{CH_3\\|}}{CH}=CH\sim\sim$$

and



$$\sim\sim CH_2-C=\overset{\substack{R\\|\\Sx\\|\\CH_2\\|}}{CH}-CH_2\sim\sim \rightarrow \sim\sim\underset{\substack{|\\Sx\\|\\R}}{CH_2}-\overset{\substack{CH_2\\\|}}{C}-CH-CH_2\sim\sim$$

At the same time, disappearance of crosslinks of the disulphide and polysulphide type occurs with formations of conjugated trienes.



$$\sim\sim CH2{-}\overset{CH3}{C}{=}CH{-}CH{-}\underset{\underset{R}{Sx}}{CH2}{-}\overset{CH3}{C}{=}CH{=}CH2 \sim\sim$$

$$\sim\sim CH2{-}\overset{CH3}{C}{=}CH{-}CH{=}CH{-}\overset{CH3}{C}{=}CH{-}CH2 + RSx\text{-}1$$

A consideration of above reaction leads to the conclusion that, if proceeds as in the case of the final network will be highly crosslinked with mainly monosulphidic bonds, and there will be relatively few modifications of the cyclic sulphide or conjugated such a network is termed efficiently crosslinked.

1.6.2 Peroxide vulcanization

In peroxide vulcanization, direct carbon-carbon crosslinks are formed between elastomer molecules.

The peroxide decomposes under vulcanization conditions forming free radicals on the polymer chains, leading to direct crosslink formation. Peroxides can be used to crosslink a wide variety of both saturated and unsaturated elastomers where as sulphur vulcanization will occur only in unsaturated species.

1.7 Rubber Blends

Development of polymeric materials has largely driven by the desire to make better products at minimum cost. Since synthesizing new polymeric materials is cost intensive ,polymers are often blended to optimum properties. Polymer blends are capable to achieve a desirable combination of properties that are often absent in single component polymer. Polymer blends are attractive due to their properties-processing – cost –performance relationship. Polymer blends often show additivity of properties, that is the result properties of the blend.is a weighted average of its constituents. Moreover blends can show synergism of properties, where a properties like tensile strength of a blend depends on several factors such as combination of properties and cost dilution. Thus blending is an attractive means to design and develop a material with superior performance at low cost.

Elastomeric blends have been used for long time, as rubber products have to meet a set of performance and process requirements that could often be contradictory in nature. The majority of the rubbers are used in the form of blends. The use of elastomeric blends are almost as old as synthetic rubber industry .n some cases, this desirable out come was attained with relative ease, as in the case of blends of general purpose rubber for tyre treads. But in most cases, considerable effort was involved to produce a successful blend of rubbers.

1.7.1 Preparation of Rubber blends

Essentially ,there are two approaches for development of polymer blends. The first approach is physical blending of two or more different polymers. The second approach is chemical blending. Elastomeric blends are prepared by there different techniques

(1) Latex blending– In this blending particle in the latex are very fine and they are dispersed well with help of surfactants. Coagulation is carried out by decreasing the soap concentration.

(2) Solution blending– In this blending individual solutions of the rubber will be prepared in a common solvent and mixed together. The blend is formed by allowing the solvent to evaporate off.

(3) Dry blending– Most elastomer blends are prepared by dry blending in a mill. This is because the process is economical and facilitates the incorporation of compounding ingredients in one operation. The high shearing forces required to blend high molecular weight elastomers are provided only by open roll mills, internal mixes and extruders.

1.7.2 Problems faced during Blending of Rubber

- Incompatibility between the two elastomers
- Unequal distribution of curatives in the blends and hence unequal distribution of cross links in the blends
- Unequal distribution of fillers in the blends

1.7.3 Characteristic features of Rubber Blends

- Polymer ratio
- Phase morphology
- Interfacial adhesion/ cross linking
- Cure characteristic of the blends
- Distribution of cross linking between the elastomers
- Distribution of plasticizer between the elastomers
- Melt flow behavior
- Method of blend preparation

The mechanical properties of blends depend on the concentration of blend components at close to additive effect. Phase morphology of lower particle size of the blend components is obtained when the interfacial tension between the polymer is low. A cross link density ratio close to one along with sufficient interfacial cross links leads to the formation of satisfactory rubber blends.

In rubber blends, it is imperative that both component rubbers are vulcanized almost to the same extent and are almost vulcanized to one another across the interface to obtain acceptable physical properties. Since the level of sulphur and accelerators typically used in rubber are above their solubility limit, curative migration can occur .due to higher solubility of sulphur in unsaturated rubbers and the greater affinity of many accelerators for more polar rubbers, there can be a significant difference in cross link density of the phases of rubber blends. More over the rate of vulcanization varies considerably between the elastomers, leads to less than optimum properties of blend.

1.7.4 Co- vulcanization

The properties of two phase blends are rarely equal to or better than those predicted from the properties of individual polymers. Similar rubbers may show additive properties but dissimilar rubbers give poor blends. This is due to a lack of co-vulcanization. The degree of co-vulcanization depends on the cure rate of individual polymer and distribution of the accelerators between the two polymers.

1.7.5 Compatibilization of polymer blends

There is an increased technological interest in the use of dissimilar rubbers .but these blends results in certain technological problems, primarily due to mutual incompatibility .three types of incompatibilities are observed

(1)Incompatibility due to viscosity mismatch, which prevents
the formation of intimate blends

(2)Thermodynamic incompatibility, which prevents mixing on the molecular scale

(3)Incompatibility due to cure rate mismatch

Most polymers are mutually immiscible or only partially miscible. This is due to the wide difference in their solubility parameter. So when they are blended, they form two phase systems. Lack of effective stress transfer causes failure of the blend. For mutual solubility or miscibility, the difference between the solubility parameter values of polymer 1 and 2 must be less than 1 unit.

At the same time, it is desirable to combine properties of two or more elastomers to develop high performance products. This is accomplished by compatibilizing the blends, either by adding a third component called compatibilizer. Usually block or graft copolymers are used. They have segments with chemistry similar to each of the blended components. They act as polymeric surfactants to reduce interfacial tension between the two phases and promote interfacial adhesion.

Eg :Methylmethacrylate grafted NR in blends of NR and NBR. The chemical modification of one or both of the components of the blend by introducing groups into the chain that is attracted to groups present or introduced into the other type. By this means the enthalpy of mixing is reduced which may result in the increase of compatibility of the components or even in their miscibility.

1.8 Objective

It is reported that the NR –g-PMMA copolymer in an effective compatibilizer for NR /NBR blends[12]. The presence of graft copolymer reduces the phase size and improve cure compatibility leading to better vulcanizate properties. In the present study the vulcanizate properties of NR /NBR 39 blends and PDNR /NBR blends were compared. PDNR is a blend of NR and NR – g -PMMA copolymer at 85/15 blend ratio.

Both NR/NBR and PDNR/NBR blends were prepared at 75/25, 50/50 and 25/75 blend ratios and the cure characteristics, vulcanizate properties and swelling behaviour were studied.

CHAPTER 2

Experimental Techniques

2.1 Materials

(1) Nitrile Rubber (NBR): Aparene N 0684 (39% CAN content) supplied by Apar Industries Limited, Bharuch, Gujarat.

(2) N-heptane: Supplied by Sisco Chem Industries, Mumbai.

(3) PDNR: Prepared at RRII

The compounding ingredients used in this project such as Zinc oxide, Stearic acid, CBS (N-cyclohexyl-2-benzothiazolesulphonamide), sulphur, Mernox 6C (Antioxidant) etc were of commercial grades and used as procured without further purification.

2.2 Methods

2.2.1 Preparation of blends

NR/NBR blends were prepared on a two-roll mixing mill with a different blend ratios 75/25, 50/50, 25/75. Similarly PDNR blended with NBR in the same ratio as mentioned above. The individual rubbers were blended together first and other ingredients were added to the blend. Since the viscosity of NBR39 was high, it was first masticated to lower the viscosity and then NR was added.

Table 2.1 Formulation

Ingredients	Amount, phr
NR	75
NBR39	25
Stearic acid	2
Zinc oxide	3
Antioxidant	1.5
CBS	1.8
Sulphur	1.8

Table 2.2 Designation of various blends

	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S9
NR	75	50	25	-	-	-	100	-	-
PDNR	-	-	-	75	50	25	-	100	-
NBR	25	50	75	25	50	75	-	-	100
All other ingredients are same as above									

2.2.2 Determination of cure characteristics (ASTM D 5289-96)

Cure time is the time for the torque to reach a given percentage of full cure. The most commonly used percentage is 50 and 90. Cure characteristics of the compounds were determined using rheo TECH MD+ Moving die Rheometer at 150 °C according to ASTM D 5289 procedure.

The *rheometer test can be tested where a rubber specimen is stretched to a given* distance (strain) then relaxed by oscillation of the lower die at a specified speed. The test is performed while the specimen is confined in a heat chamber at curing temperature under pressure. The stiffness of the sample increases as vulcanization proceeds and reaches maximum and remains same. The force required to stretch the rubber (stress) is directly proportional to stiffness of the rubber.

The optimum cure time corresponds to the time to achieve 90 % of the cure was represented by the torque attained. It was calculated from the equation optimum cure time.

$$t_{90} = 90/100 \times (M_{max}-M_{min}) + Mmin$$

Where M_{max} = Maximum torque

M_{min} = Minimum torque

2.2.3 Moulding

Test samples were prepared by compression moulding method. The compounded rubber was placed between the cavities of the mould heated to 150 °C and pressure of about 1600 Psi was applied by a hydraulic press by placing this mould between the heated platens of the press. To ensure complete filling a slight excess of compounded rubber was placed in the mould. After curing the pressure was released, the mould was taken out from it and the sample was cooled.

2.3 Testing for vulcanizate properties

2.3.1 Tensile properties (modulus, tensile strength and elongation) ASTM D 412-06)

The three parameters were determined according to the ASTM standards, using dumb bell shaped test pieces. The test pieces were punched out from the moulded sheets using C-type die, along the mill grain direction of the vulcanized sheets. The thickness was measured using a dial gauge. The tests were carried out in a Zwick Universal Testing Machine (UTM) model 1474 at 25±2 °C. The dumb bell specimen was placed in the grip of the testing machine taking care to adjust the specimen symmetrically to distribute tension uniformly over the cross-section. The rate of the grip separator shall be 500 mm/min. The force at the elongation specified for the test and at the time of rupture was recorded to the nearest 10%. Tensile stress at any specified elongation be given as,

$$T= F/A$$

Where T = Tensile stress at % elongation, MPa
F = Force at specified elongation, MN
A = Cross section area of specimen, m^2

The modulus at 100%, 200%, 300% and elongation at break were also noted.

2.3.2 Tear Resistance (ASTM D 624-02)

The test was carried out as per ASTM standards. Samples were punched out from the sheets parallel to the grain direction. This test was carried out on the tensile testing machine. The test sample was mounted on the testing machine. A steadily increasing traction force was applied at 500±50 mm/min until the test piece was completely ruptured. The tear strength values are reported in N/mm.

2.3.3 Sorption Experiment

Rubber sheets, approximately 2mm thick were cut into circular pieces of approximately 2cm dia with a circular cutting die. The thickness of the cut sample were measured. Dry weight of the cut sample were taken before immersion, into airtight, capped test bottles containing 20ml of the solvent. Swelling of the blend was measured in n-heptane. After immersion of the sample in the solvent, the bottle were maintained at room temperature.

The liquid uptake was monitored gravimetrically by weighing the sample at regular intervals. The samples were taken out, wiped with a filter paper and weighed in a tared Petri dish. Weighing is done in a balance, which gives the weight accurately to 0 .0001g. The samples were then placed back into the test bottles immediately.

A possible source of error in these measurements is that arising during weighing, since the sample has to be taken out from the solvent for weighing. However, since the weighing is completed within 20 -30 s, the error can be neglected since the time taken for weighing the sample compared to the time the sample is kept in the solvent between consecutive weighings is negligible. The percentage mass uptake of the liquid was determined till equilibrium is reached. The results of diffusion experiments were expressed as moles of solvent uptake by 100g of polymer sample, Q_t (wt %).

$$Q_t\ (\text{wt }\%) = \frac{\text{Mass of solvent sorbed}}{\text{Mass of polymer}} \times 100$$

CHAPTER 3

Results and Discussion

3.1 Introduction

NR is a general purpose rubber which find major consumption in tyre manufacturing. Nitrile rubber which is a specialty synthetic rubber used mainly in areas where hydrocarbon oil or solvent resistance is required. It is manufactured mainly in three different grades varying in acrylonitrile content . NBR with 28 ,34 and 39 weight percent acrylonitrile is available in the market. NR/NBR blend is used in the industry producing various products. The widely different polarities of these two rubbers leading to incompatibility between the phases in the blend which in turn can leads to inferior vulcanizate properties. The difference in polarities can also leads to the uneven distribution of curatives in these blends during compounding and subsequent vulcanization process. This will results in uneven cross linking density distribution in the two phases of the blend . Since many of the accelerators are polar in nature, it is likely that much part of the added accelerators will be residing in the polar NBR phase leading to higher cross link density in the NBR phase compared to that in NR phase. This may leads to inferior vulcanizate properties. It is reported that the property of NR/NBR blends are highly influenced by the primary, secondary accelerators used for vulcanization[13]. It is also reported that reducing the phases in these blends by the addition of compatibilizers like chloroprene rubber, natural grafted PMMA (NR-g- PMMA) copolymer which significantly reduce the influence of cure system on the vulcanizate properties of NR/NBR blends.

The present study describes the cure characteristics and vulcanizate properties of NR/NBR blends and PDNR/NBR blends. PDNR is a blend of NR and NR-g-PMMA copolymer at 85:50 ratio. PDNR is prepared by blending of NR latex and NR-g-PMMA(containing 30 weight% PMMA) latex and co-coagulating the latex blend using formic acid. The coagulated latex blend is processed in a manner similar to technically specified rubber. This rubber is designated as PDNR.

Blends of NR/NBR as well as PDNR/NBR were prepared at a blend ratio of 75/25, 50/50 and 25/75 as shown in table 2.1&2.2 . A cure system involving CBS(N-cyclohexyl-2-benzothiazole sulfonamide) and sulphur were used to vulcanize these blends. Blending and compounding were carried out in a two roller mill. Two rubbers were blended together as then other ingredients were added.

3.2 Cure characteristics

Cure characteristics of all the compounds prepared were determined in a Moving Die Rheometer at 150^0C. The cure graph of these blends along with NR, PDNR and NBR are given in Figures 3.1 to 3.9. Cure characteristics are summarized in table 3.1.

It can be seen from the table that the cure time of NR and PDNR are same which shows that the presence of graft copolymer does not influence the cure characteristics of NR. The cure rate of NR is 10.50 min and that of PDNR is 10.56 min. Scorch time and cure rate index also follow the same pattern. NBR shows the highest cure time of 13.25 min. Blending of NR as well as PDNR with NBR lead to faster curing in comparison with the individual rubbers. Thus the cure time of NR is reduced from 10.58 min. to 8.61min. in NR/NBR 75/25 blend. The cure time is 8.32 min. when the blend ratio is 50/50, it is increased marginally to 9.61min in NR/NBR 25/75 blend .The cure time was further reduced in all PDNR /NBR blends. Thus the cure time was 6.64min for PDNR /NBR 75/25 blends, 7.87min for 50/50 blends and 8.81 min. for 25/75 blends Similar trends were observed in the case of scorch time and CRI (Cure rate index) also.

3.3 Vulcanizate properties

The vulcanizate properties of blends and the individual rubbers are given in Table3.2&3.3. As expected from a strain crystallizing rubber like NR gum tensile strength is very high which is 30.8 MPa.The blending of NR with 15% of NR –g-PMMA copolymer has not reduced the gum strength of NR.The tensile strength of PDNR obtained is 29.1MPa which is close to the value of NR. It may be noted that the gum tensile strength of NBR is 10 times less than that of NR and has a value of 3.6MPa. The blending of these two rubbers will definitely affect the tensile strength of the blend vulcanizate. It was the objective of this work to determine the tensile and tear properties of NR/NBR blend using CBS(N-cyclohexyl-2-benzothiazoles sulfonamide),sulphur cure system in a comparitabilized or noncomparitabilized the system. It can be seen from the Table compatibilization of NR with NR-g-PMMA graft copolymer marginally increased the tensile strength of this blend. Thus the tensile strength of NR/NBR 75/25 blend is 24.8MPa while that of PDNR/NBR blend is 26.5MPa. Similar trend is observed for 50/50 and 25/75 blend vulcanisates. It may also be noted that in both these type of blends, the tensile strength decreased with increase in NBR content. Modulus also shows similar trend.

In the case of tear strength PDNR shows highest tear strength of 38.5 N/mm.Tear strength of NR is 33.9N/mm and that of NBR is 12.96N/mm. However the blend vulcanisates having similar blend ratios, the tear strength does not show any significant difference. Thus the tear strength for NR/NBR blend at 75/25 ratio is 31.64 and that of PDNR/NBR is 34.35 N/mm. In the case of 50/50 blend, NR/NBR blends shows the value of 31.3 N/mm while that of PDNR/NBR is 30.21N/mm.However considerable reduction in tear strength of NR/NBR blend and PDNR/NBR blend at a blend ratios 25/75 were observed. Thus the tear strength of NR/NBR blend at 25/75 ratio was 22.3 N/mm and that of PDNR/NBR blend was 22.49 N/mm.

Table3.4. shows the tensile properties of blends and the individual rubbers vulcanized to $T_{max.}$ It was observed that tensile strength of both the individual rubbers and the blends were lower than that cured at $T_{90.}$ It was also observed that when cured toT_{max} PDNR/NBR blends in the three blend ratios showed lower values compaired to NR/NBR blends. Elongation at break also showed similar trend. Modulus showed only marginal increase when compared to that of the blends cure at T_{90} at similar blend ratios. This shows that it is preferable to mould the NR/NBR blends at T_{90}.

3.4 Swelling behavior

The swelling behavior of NR, PDNR, NBR39 and their blends in n-heptane were studied at room temperature. Percentage weight increase of individual rubber and their blends are given in Table 3.5 and in Figures 3.10 &3.11

The percentage weight increases with time is plotted in these figures. It is obvious from the tables and figures that both NR and PDNR absorbs large quantity of heptane into its matrix and the weight of the solvent absorbed becomes more than the sample weight in one hour. Thus the percentage weight increase 117 and 101 for NR and PDNR respectively. Both these rubbers reaches equilibrium swelling almost within 5 hours. Due to the presence of PMMA graft copolymer, the swelling of PDNR gum vulcanizate is around 25% less than that of the NR.Thus the equilibrium swelling of NR is 225% while that of PDNR is 197%.In sharp contrast, the rate of swelling and the amount of uptake of the solvent are significantly lower for NBR39. Thus the equilibrium percentage weight increase was only 4.5% for NBR.Comparing the blends, as expected the rate of intake of the solvent as well as the equilibrium uptake reduced with increase in NBR content in these blends. Thus the equilibrium uptake was 151% for NR/NBR blend at 75/25 blend ratio, 92% for 50/50 blend and 44% for 25/75 blend. PDNR/NBR blend showed a marginal decrease in equilibrium uptake of n-heptane.Thus the values are 139%, 83%, 42% at 75/25,50/50 and 25/75 blend ratios respectively.

CHAPTER 4

Conclusion

The following conclusion were made from the present study

1. The tensile properties of NR/NBR and PDNR/NBR were comparable and the improvement in tensile properties of PDNR/NBR were marginal when compared with that of NR/NBR blend at equivalent blend ratios. This shows that the graft copolymer added did not substantially influence the tensile properties of the blend vulcanisates.

2. Swelling resistance of both NR and PDNR increased with increase in NBR content. PDNR/NBR blends showed better solvent resistance at similar blend ratio.

Table 3.1 Cure characteristics at 150^0 C

	MH, dN.m	**ML**	**CRI, m/min**	**Tc 100, min**	**Tc 90, min**	**Ts2, min**
NR	7.17	0.22	40.50	15.31	10.58	8.11
PDNR	7.79	0.37	41.83	17.24	10.56	8.17
NBR	13.37	0.68	10.69	35.12	13.25	3.90
NR/NBR(75/25)	10.53	0.32	29.20	14.92	8.61	5.18
NR/NBR(50/50)	11.00	0.53	31.64	18.16	8.32	5.16
NR/NBR(25/75)	11.69	0.57	22.82	19.37	9.31	4.93
PDNR/NBR(75/25)	9.38	0.19	44.75	13.90	6.64	4.40
PDNR/NBR(50/50)	10.57	0.30	30.74	19.30	7.87	4.62
PDNR/NBR(25/75)	11.59	0.46	25.75	20.42	8.81	4.92

Table 3.3 Tear properties

Blends	Tear strength, (N/mm)
NR	31.64
PDNR	31.31
NBR	12.96
NR/NBR(75/25)	34.35
NR/NBR(50/50)	30.21
NR/NBR(25/75)	22.49
PDNR/NBR(75/25)	33.92
PDNR/NBR(50/50)	38.46
PDNR/NBR(25/75)	22.27

Table 3.4 Tensile properties (cured at T_{max})

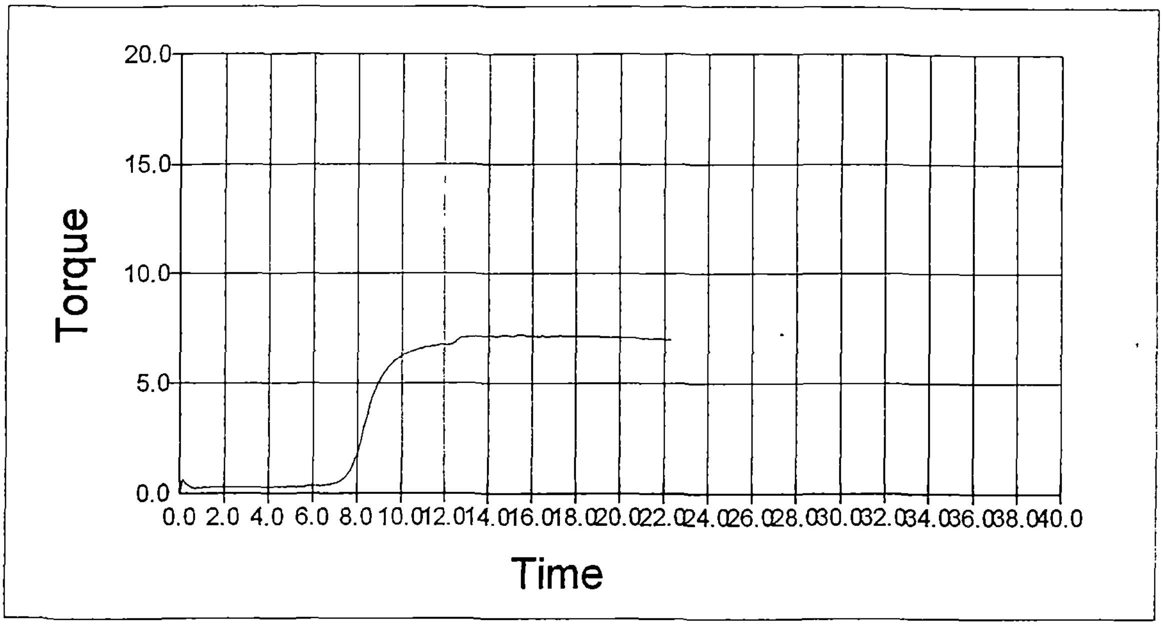
	Tensile Strength, MPa	Elongation at break, %	100% modulus, MPa	200% modulus, MPa	300% modulus, MPa
NR	27.23	693.17	0.90	1.48	2.24
PDNR	26.56	809.37	1.14	2.04	3.45
NBR	4.22	405.41	1.22	1.73	2.49
NR/NBR(75/25)	23.40	631.18	0.95	1.52	2.27
NR/NBR(50/50)	21.7	597.23	1.02	1.55	2.29
NR/NBR(25/75)	11.83	536.54	1.11	1.74	2.61
PDNR/NBR(75/25)	22.46	599.98	1.17	2.02	3.28
PDNR/NBR(50/50)	20.62	584.61	1.18	1.91	3.01
PDNR/NBR(25/75)	10.16	512.93	1.18	1.83	2.80

Table 3.5 Swelling of NR/NBR & PDNR/NBR blends in n-heptane at 28^0C

Time, h	**% weight increase**								
	NR	PDNR	NBR	NR/NBR (75/25)	NR/NBR (50/50)	NR/NBR (25/75)	PDNR/NBR (75/25)	PDNR/NBR (50/50)	PDNR/NBR (25/75)
0.5	76.3	64.8	1.35	51.4	35.2	12.3	56.6	34.8	10.5
1	117.2	100.6	1.5	78.1	52.7	16.8	84.3	49.6	14.1
1.5	149.9	125.5	1.7	101.4	65.1	19.7	106.7	61.4	17.1
2	171.1	145.8	1.85	115.2	73.8	22.6	118.9	69.9	18.3
2.5	187.1	156.8	1.9	125.6	80.2	25.1	126.4	74.2	20.1
3	195	167.95	2.1	133.5	83.2	27.4	129.2	77.8	21.9
3.5	201.7	175.5	2.2	139.3	85.95	30.3	132	79	22.6
4	208.9	182.2	2.35	140.3	86.3	31.6	132.9	81.6	24.7
4.5	220.5	186.5	2.5	141.1	87.69	33.3	134.9	82	26.7
5.5	222.5	192.5	2.65	143.4	88.6	36.1	136.1	83	28.3
6.5	224.6	195.5	3.5	146.7	89.6	38.4	138.1	83.8	30.7
8.15	225.7	195.7	4.3	149.9	90.7	41.95	138.2	83.6	41.9
23	229.2	196.5	4.4	150	91.3	44.06	138.2	83.8	42.5
25	229.2	197	4.5	150.1	91.6	44.08	138.1	83.6	42.6
27	229.3	197.1	4.56	150.1	91.3	44.08	138.6	83.4	42.7

Rheometer Test Report

Report Date : Tuesday, May 19, 2009 11:09:07 AM
Compound ID : TC
Mix Date : Thursday, May 22, 2008
Test Condition : RCPT(150)
OPERATOR : TC
Upper Die Temperature Setpoint : 150.0 C
Lower Die Temperature Setpoint : 150.0 C



Test ID.	CRI(90/2)	MH	ML	Tc100	Tc90	Ts1	Ts2
sa7	40.50	7.17	0.22	15.31	10.58	7.78	8.11

Fig. 3.1 Cure characteristics of NR at 150^{0}C

Rheometer Test Report

Report Date : Tuesday, May 19, 2009 11:33:36 AM
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Mix Date : Thursday, May 22, 2008
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OPERATOR : TC
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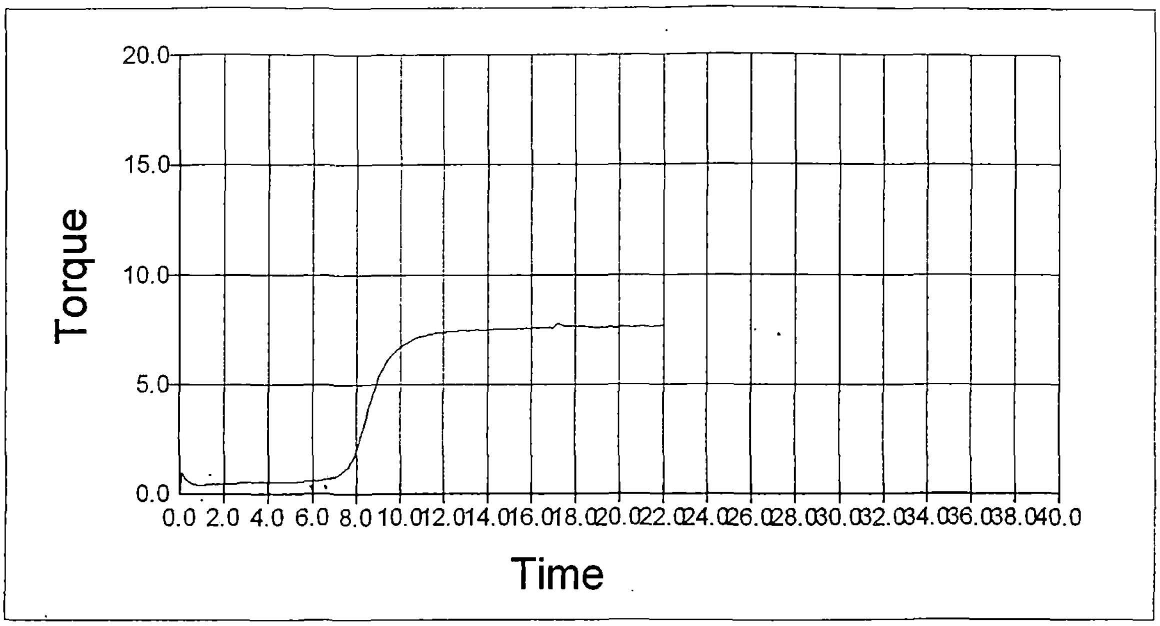

Test ID.	CRI(90/2)	MH	ML	Tc100	Tc90	Ts1	Ts2
sa8	41.83	7.79	0.37	17.24	10.56	7.71	8.17

Fig. 3.2 Cure characteristics of PDNR at 150^{0}C

Rheometer Test Report

Report Date : Friday, May 22, 2009 10:30:51 AM
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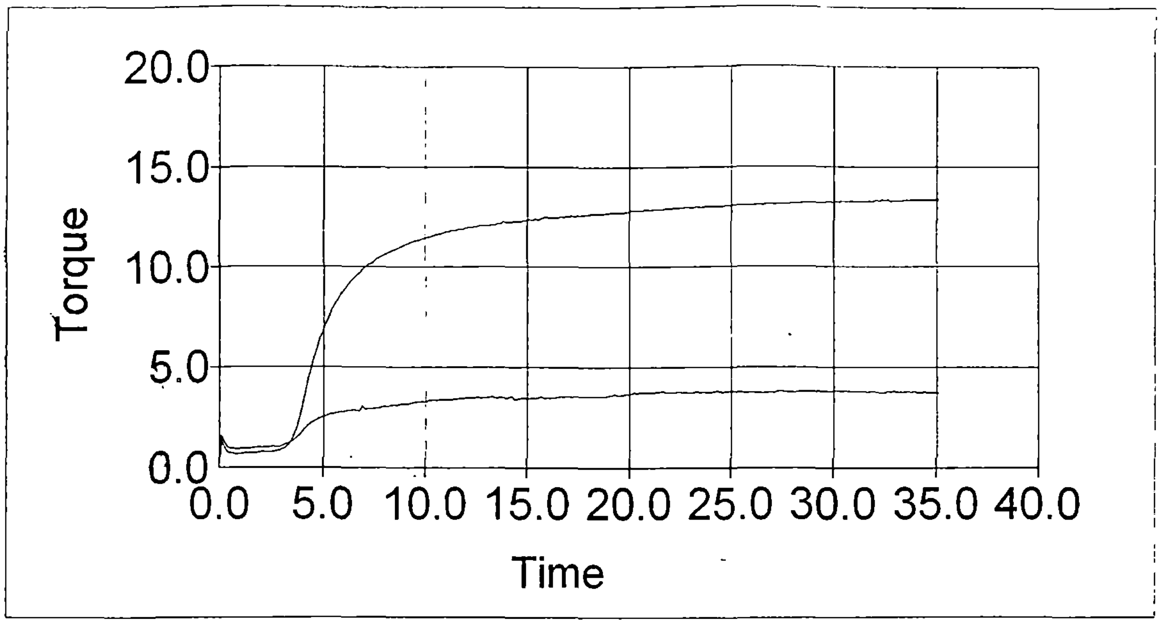
Mix Date : Thursday, May 22, 2008
Test Condition : RCPT(150)
OPERATOR : TC
Upper Die Temperature Setpoint : 150.0 C
Lower Die Temperature Setpoint : 150.0 C



Test ID.	CRI(90/2)	MH	ML	Tc100	Tc90	Ts1	Ts2
Saj 9	10.69	13.37	0.68	35.12	13.25	3.61	3.90

Fig. 3.3 Cure characteristics of NBR at 150^0C

Rheometer Test Report

Report Date : Wednesday, May 13, 2009 12:13:20 PM
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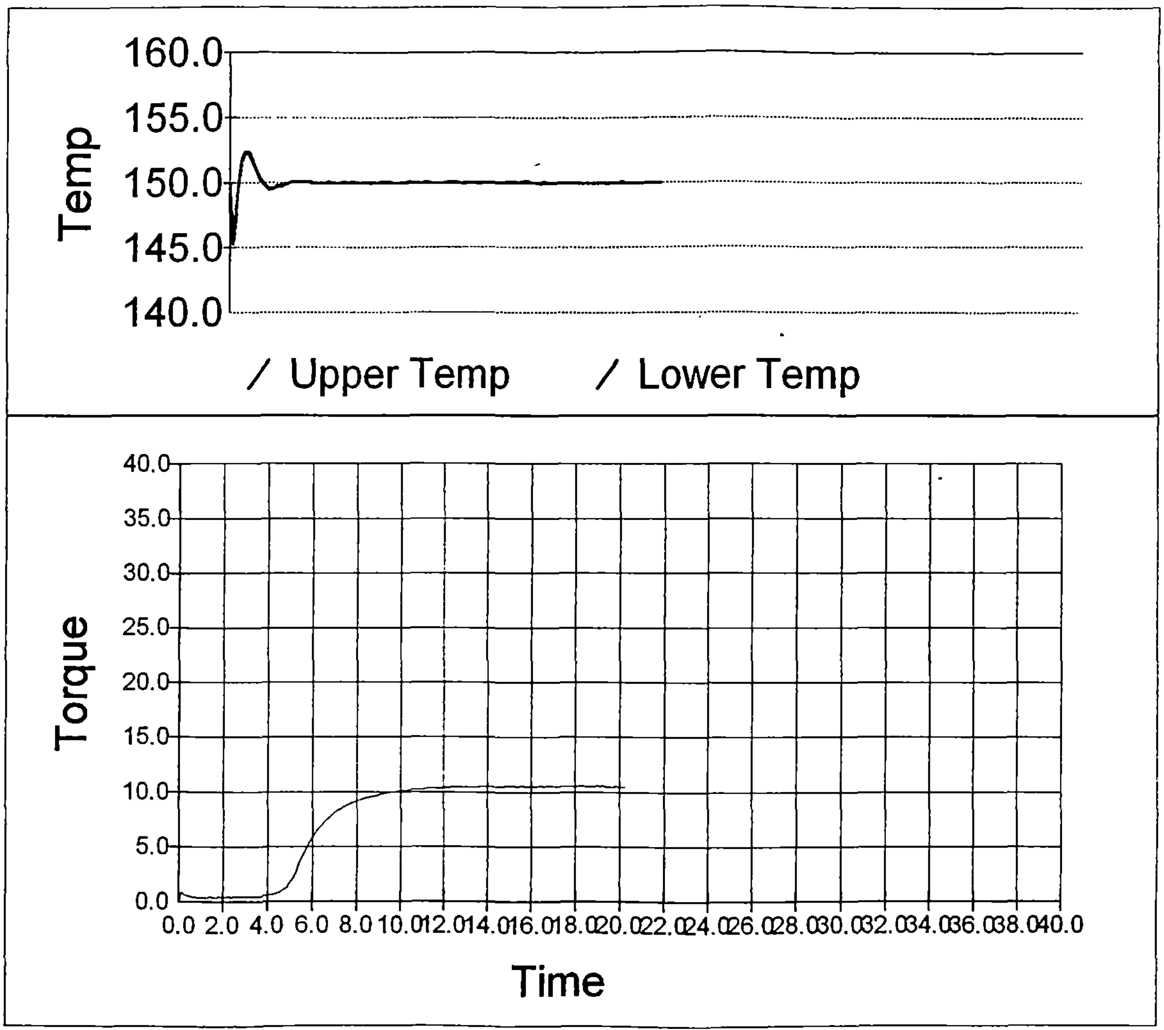
Mix Date : Thursday, May 22, 2008
Test Condition : RCPT(150)
OPERATOR : TC
Upper Die Temperature Setpoint : 150.0 C
Lower Die Temperature Setpoint : 150.0 C

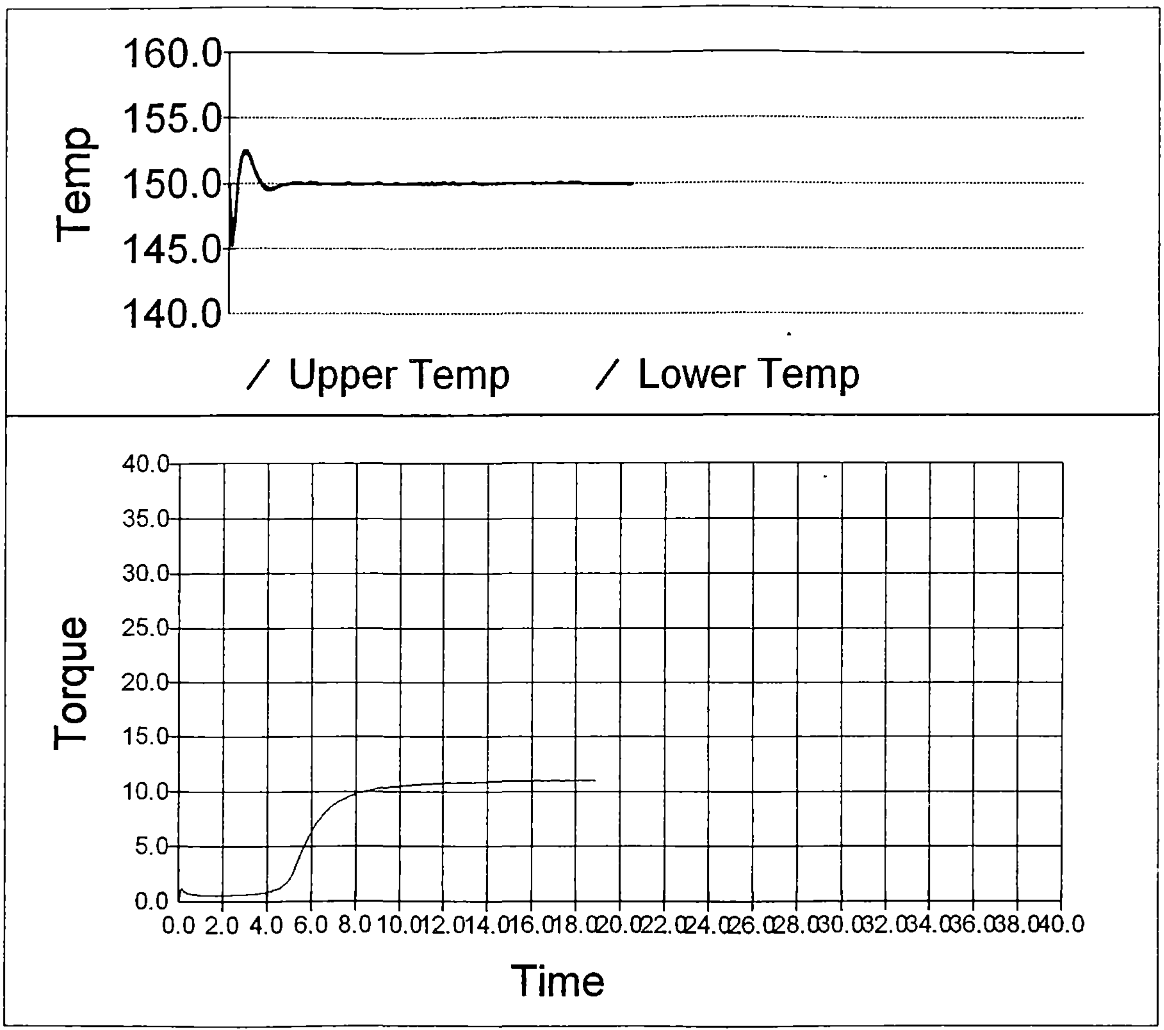


Test ID.	CRI(90/2)	MH	ML	Tc100	Tc90	Ts1	Ts2
sa1	29.20	10.53	0.32	14.92	8.61	4.87	5.18

Fig. 3.4 Cure characteristics of NR/NBR(75/25) at 150^{0}C

Rheometer Test Report

Report Date : Wednesday, May 13, 2009 10:28:42 AM
Compound ID : TC
Mix Date : Thursday, May 22, 2008
Test Condition : RCPT(150)
OPERATOR : TC
Upper Die Temperature Setpoint : 150.0 C
Lower Die Temperature Setpoint : 150.0 C

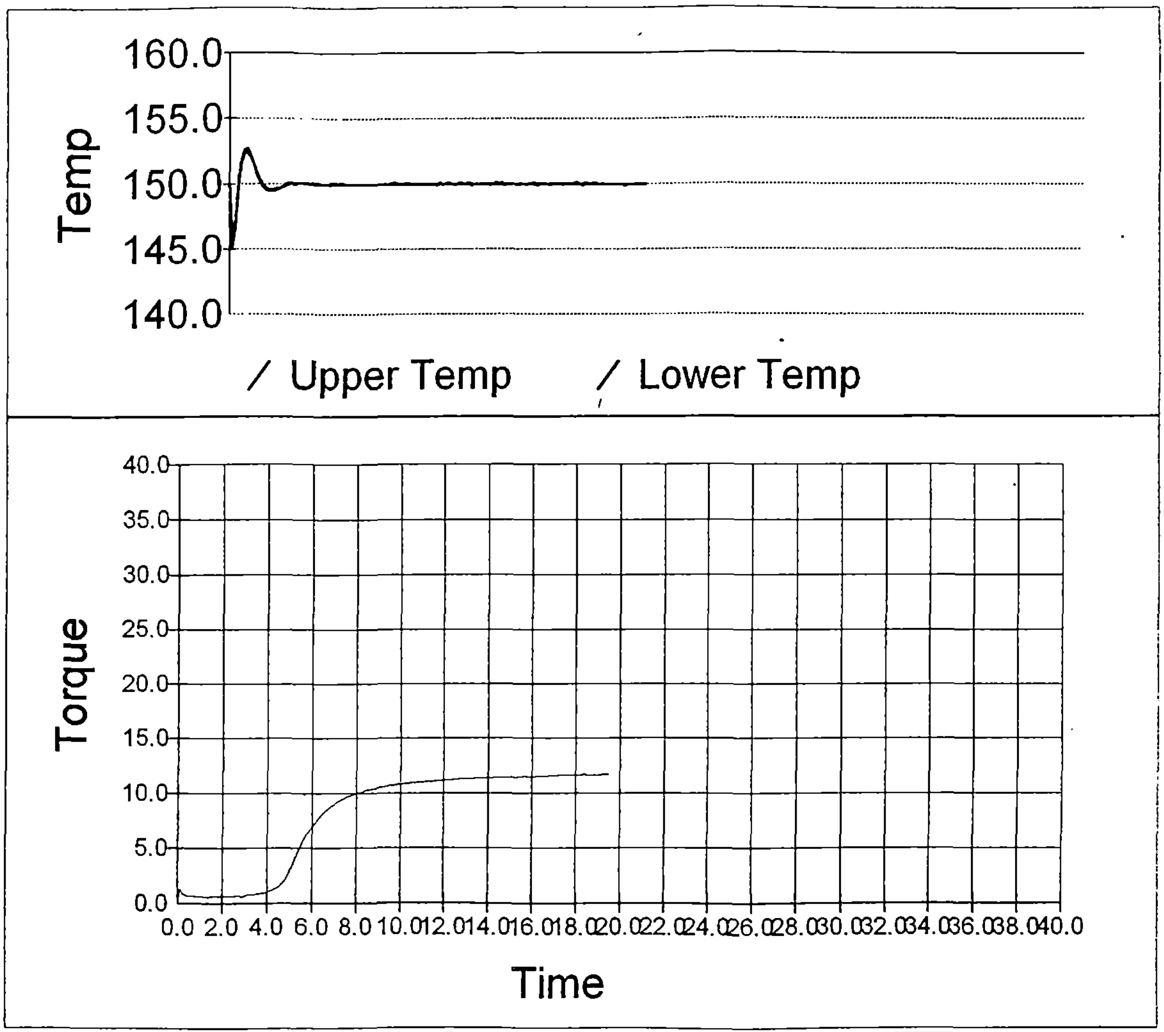


Test ID.	CRI(90/2)	MH	ML	Tc100	Tc90	Ts1	Ts2
SA2	31.64	11.00	0.53	18.16	8.32	4.80	5.16

Fig. 3.5 Cure characteristics of NR/NBR(50/50) at 150^{0}C

Rheometer Test Report

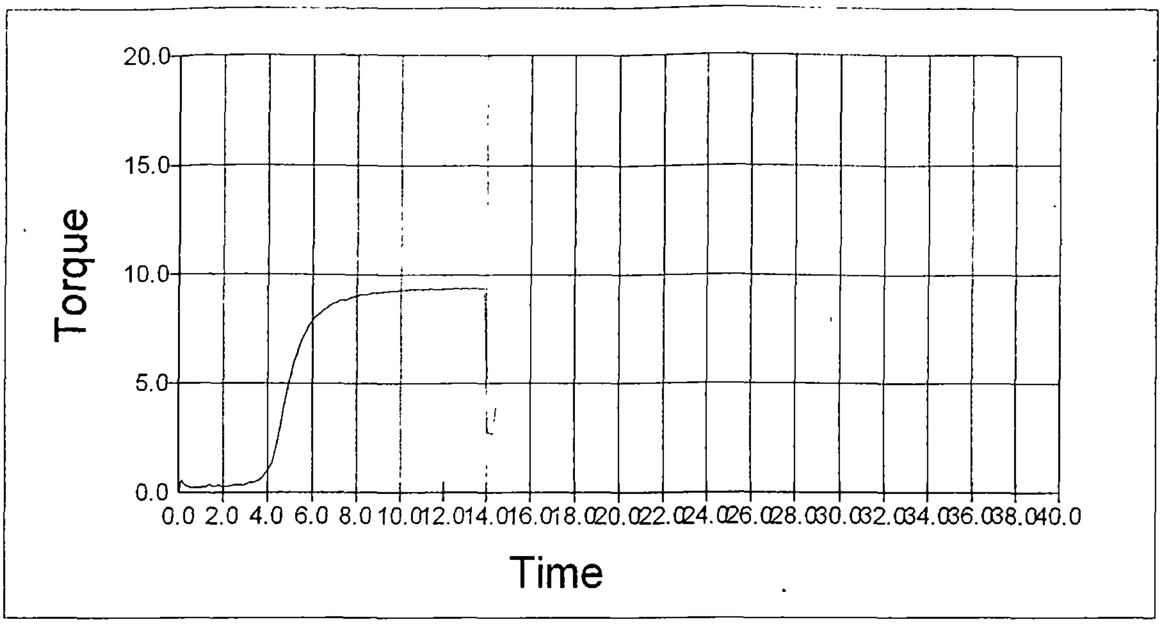
Report Date : Wednesday, May 13, 2009 10:51:05 AM
Compound ID : TC
Mix Date : Thursday, May 22, 2008
Test Condition : RCPT(150)
OPERATOR : TC
Upper Die Temperature Setpoint : 150.0 C
Lower Die Temperature Setpoint : 150.0 C



Test ID.	CRI(90/2)	MH	ML	Tc100	Tc90	Ts1	Ts2
SA3	22.82	11.69	0.57	19.37	9.31	4.57	4.93

Fig. 3.6 Cure characteristics of NR/NBR(25/75) at 150^{0}C

Upper Die Temperature Setpoint : 150.0 C
Lower Die Temperature Setpoint : 150.0 C

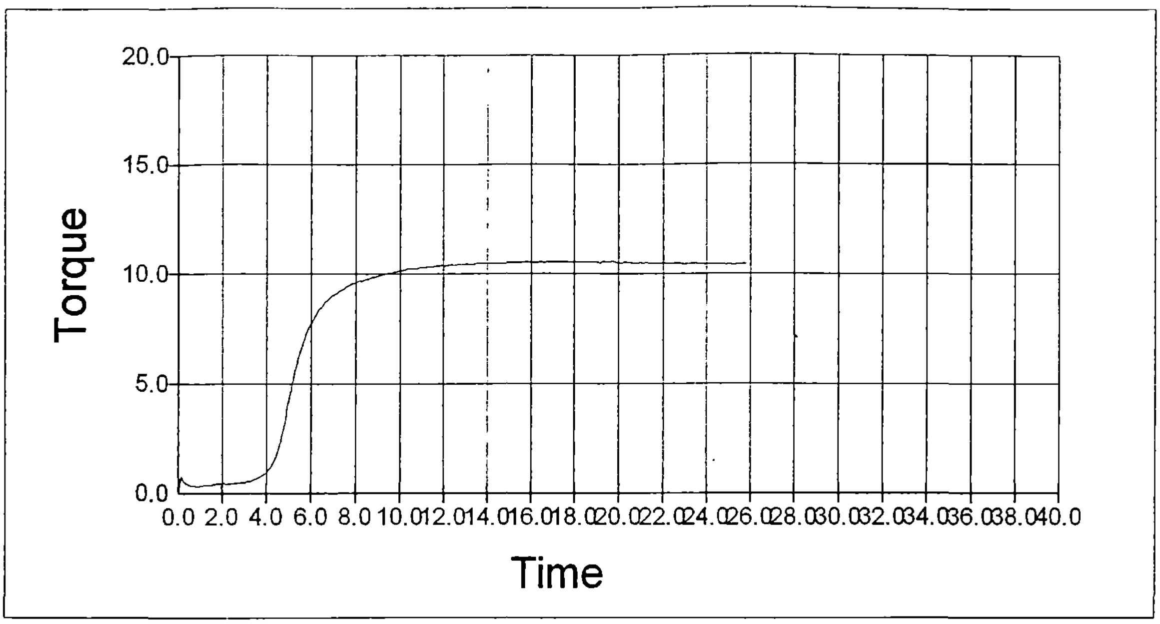


Test ID.	CRI(90/2)	MH	ML	Tc100	Tc90	Ts1	Ts2
sa4	44.75	9.38	0.19	13.90	6.64	4.10	4.40

Fig. 3.7 Cure characteristics of PDNR/NBR(75/25) at 150^{0}C

Rheometer Test Report

Report Date : Tuesday, May 19, 2009 10:18:54 AM
Compound ID : TC
Mix Date : Thursday, May 22, 2008
Test Condition : RCPT(150)
OPERATOR : TC
Upper Die Temperature Setpoint : 150.0 C
Lower Die Temperature Setpoint : 150.0 C

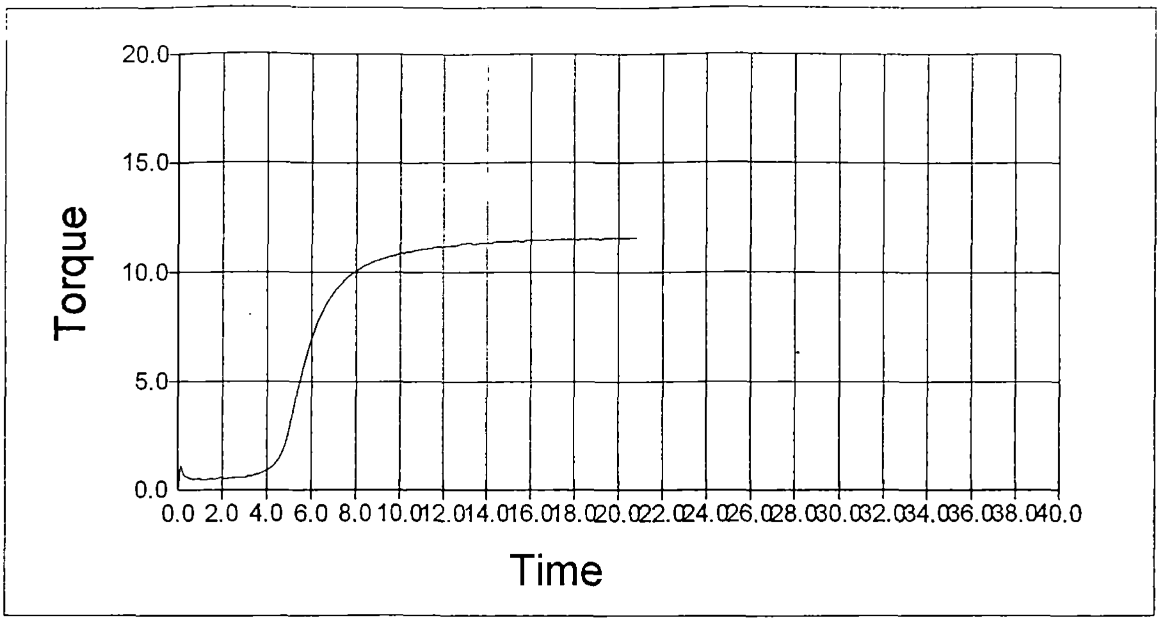


Test ID.	CRI(90/2)	MH	ML	Tc100	Tc90	Ts1	Ts2
sa5	30.74	10.57	0.30	19.30	7.87	4.26	4.62

Fig. 3.8 Cure characteristics of PDNR/NBR(50/50) at 150^{0}C

Rheometer Test Report

Report Date : Tuesday, May 19, 2009 10:43:14 AM
Compound ID : TC
Mix Date : Thursday, May 22, 2008
Test Condition : RCPT(150)
OPERATOR : TC
Upper Die Temperature Setpoint : 150.0 C
Lower Die Temperature Setpoint : 150.0 C



est ID.	CRI(90/2)	MH	ML	Tc100	Tc90	Ts1	Ts2
sa6	25.71	11.59	0.46	20.42	8.81	4.56	4.92

Fig. 3.9 Cure characteristics of PDNR/NBR(25/75) at 150^0C

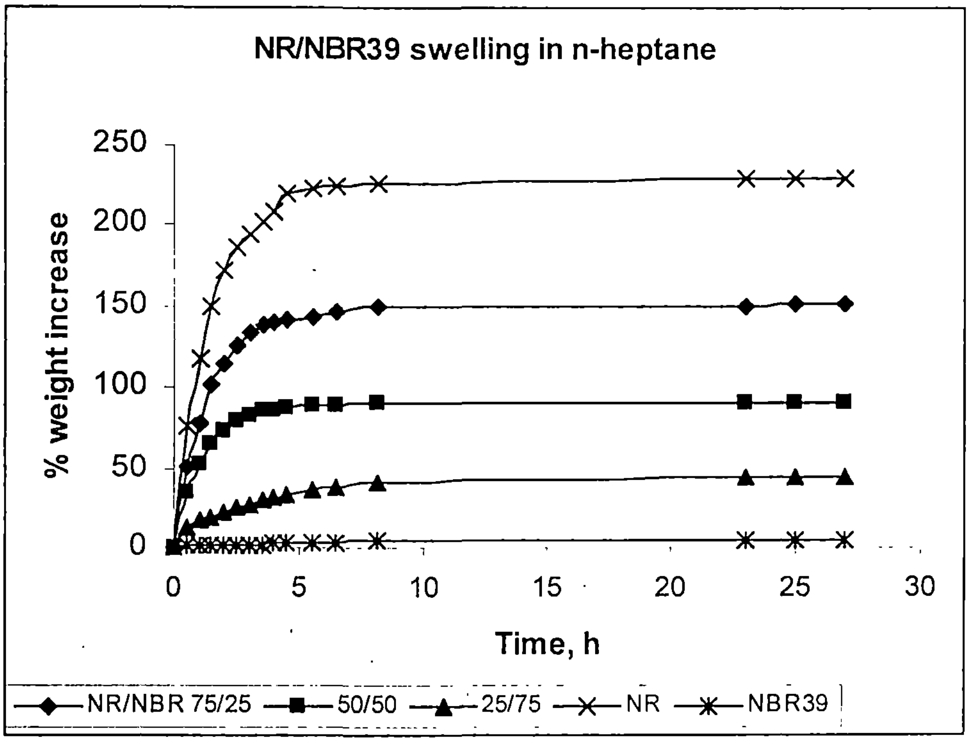


Fig 3.10 . Swelling of NR/NBR blends in n-heptane

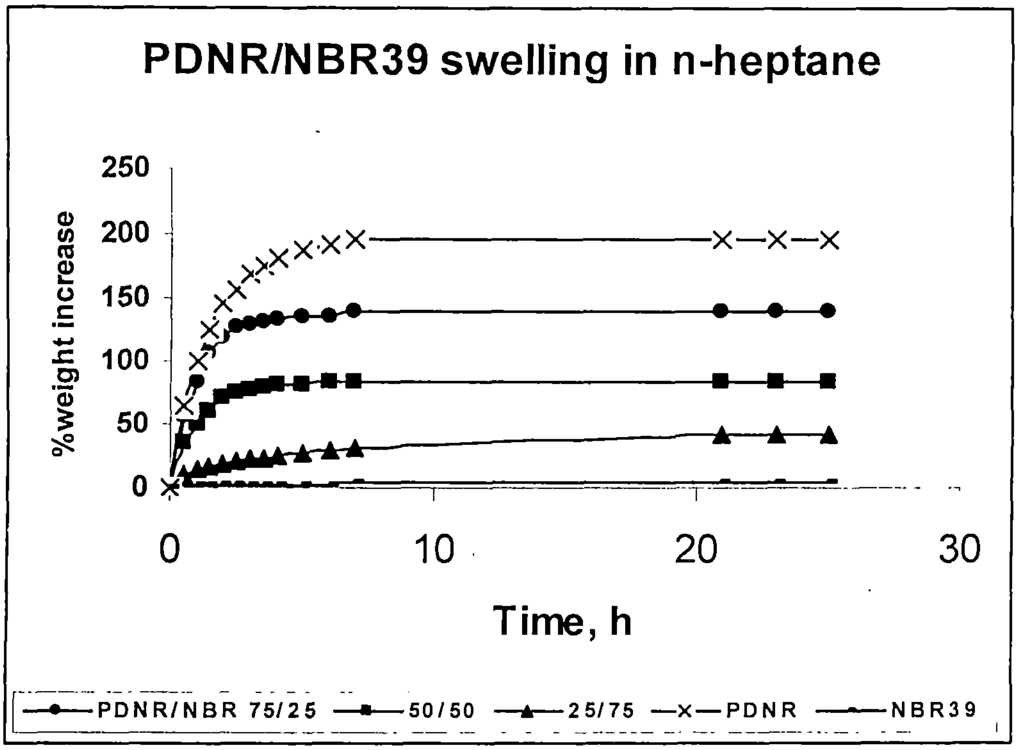


Fig 3.11 . Swelling of PDNR/NBR blends in n-heptane

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