Modification of Natural Rubber using Thermoset Resins

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by

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Certificate

This is to certify that the thesis entitled **"Modification of Natural Rubber using Thermoset Resins"** which is being submitted by Bhuvaneswary M.G. in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy, to the Cochin University of Science and Technology, Kochi-22 is a record of the bonafide research work carried out by her under my guidance and supervision, in the Department of Polymer Science and Rubber Technology, Cochin-682 022, and no part of the work reported in the thesis has been presented for the award of any degree from any other institution.

Dr. Eby Thomas Thachil
(Supervising Teacher)

Declaration

I hereby declare that the work presented in this thesis entitled **"Modification of Natural Rubber using Thermoset Resins"** is based on the original research work carried out by me under the guidance and supervision of Dr. Eby Thomas Thachil, Professor, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin-682 022 and no part of the work reported in this thesis has been presented for the award of any degree from any other institution.

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PREFACE

Natural rubber is an important elastomer with the unique attribute of being a renewable agricultural product. The study was undertaken to investigate the extent to which the drawbacks of natural rubber, especially its poor thermal and oil resistance properties could be nullified by blending with common thermoset resins.

This thesis consists of six chapters. The first chapter consists of introduction and literature survey. Synthesis of epoxy resins and effects of these resins on the properties of NR are covered in the second chapter. Preparation and study the effects of phenolic novolacs are included in the third chapter. The fourth chapter consists of preparation of various novolacs and effects of these resins on the properties of NR. In the fifth chapter preparation of unsaturated polyester resins and their effects are investigated. Major conclusions are summarized in the sixth chapter.

The successful completion of the present research endeavour is made possible by the generous, enthusiastic and inspiring guidance of my dear supervising teacher Dr. Eby Thomas Thachil, Professor and Head, Dept. of Polymer Science and Rubber Technology, CUSAT. With great pleasure, I express my heart-felt gratitude for his professional guidance and competent advice.

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I gratefully acknowledge the support and encouragement received from the Management, HMDP Sabha, former Principal Sri. P.M Suresh, S.N.M. College, Maliankara, Dr. B.Sleema, Head of the department, all the teaching and non-teaching members of the Dept. of Chemistry, S.N.M. College, Maliankara.

I wish to thank the University Grants Commission for the award of Teacher Fellowship for the completion of the research work.

At this moment I remember with love and thanks, the inspiration, love and the blessings of my parents and relatives. Finally I thank my husband Mr. Venu and my daughter Vishnupriya for the understanding and patience and the spirit of accommodation they have rendered at all times.

Above all, I thank God Almighty for bestowing upon me His choicest blessing for the completion of the research work.

Bhuvaneswary M.G

Abstract

This thesis presents the findings of a study on incorporating various thermoset resins into natural rubber for property improvement. Natural rubber is an important elastomer with the unique attribute of being a renewable agricultural product. The study was undertaken to investigate the extent to which the drawbacks of natural rubber, especially its poor thermal and oil resistance properties could be nullified by blending with common thermoset resins. A thorough and comparative understanding of the performance of different resins from this viewpoint will be beneficial for both natural rubber processors and consumers. In this study the thermoset resins used were epoxy resin, phenolics, epoxidised phenolics and unsaturated polyester resin.

The resins were incorporated into NR during compounding and their effects on the properties of NR were studied after vulcanization. Properties were studied for both gum and filled NR compounds. The important properties studied are cure characteristics, mechanical properties, ageing properties, thermal properties, crosslink density and extractability. Characterization studies were also conducted using FTIR, TGA and DSC.

Improvement in mechanical properties was noticed in many cases. The results show that most resins lead to a reduction in the cure time of NR. The performance of epoxy resin is most noticeable in this respect. Mechanical properties of the modified rubber show maximum improvement in the case of epoxidised novolacs. Most resins are seen to improve the thermal and oil resistance properties of NR. Epoxy novolacs show maximum effect in this respect also. However the presence of fillers is found to moderate the positive effects of the thermoset resins considerably.

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INTRODUCTION AND LITERATURE SURVEY

1.1 Introduction

This thesis presents the findings of a study on incorporating various thermoset resins into natural rubber for property improvement. Natural rubber is an important elastomer with the unique attribute of being a renewable agricultural product. The study was undertaken to investigate the extent to which the drawbacks of natural rubber, especially its poor thermal properties could be nullified by blending with common thermoset resins. A thorough and comparative understanding of the performance of different resins from this viewpoint will be beneficial for both natural rubber processors and consumers. The following discussion starts with the general field of elastomers before presenting various aspects of natural rubber processing and modification. A discussion of common thermoset resins is also included. Relevant literatures have been cited wherever necessary.

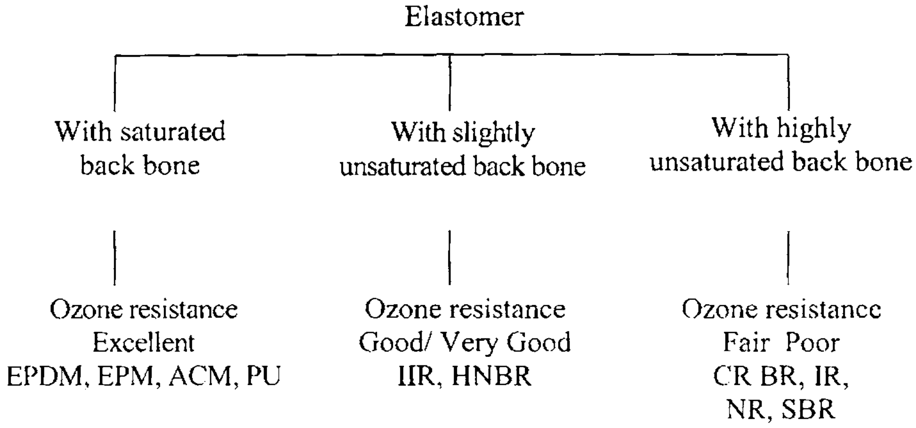
1.2 Elastomers

Elastomers form a special class of polymeric materials characterized by a unique combination of useful properties such as elasticity, flexibility, toughness and impermeability. They are popularly known as rubbers and invariably show a large elongation-at-break. They are macromolecular substances capable of passing, under the effect of vulcanization, from a predominantly plastic state to a predominantly elastic state [1-3].

Generally elastomers are classified as a) commodity or general purpose elastomers such as NR, styrene butadiene rubber (SBR), isoprene rubber (IR) etc. b) high volume speciality elastomers such as ethylene propylene rubber, chloroprene rubber (CR), acrylonitrile butadiene rubber (NBR) and c) low volume speciality elastomers such as polyurethane, silicone, fluorocarbon, polyacrylate, epichlorohydrin, chlorosulphonated elastomer etc.

Elastomers may also be classified in groups, according to different characteristic features including extend of saturation of the polymer chain, oil resistance, flame resistance and service performance [4]. The classification given in Table1.1 is based on the chemical saturation of the backbone polymer chain.

Table 1.1 Classification of elastomers



Elastomers that exhibit high resistance to ozone and weather are characterized by a saturated backbone. Elastomers with a highly unsaturated backbone like NR and polybutadiene (BR) are not inherently ozone resistant. Therefore antiozonants and protective waxes are added during compounding to improve the ozone resistance. CR, though highly unsaturated like NR, shows fair ozone resistance due to the presence of the chlorine atom which reduces the reactivity of double bonds towards oxidizing agents like oxygen and ozone.

Halogen containing polymers like perfluorocarbon rubbers, fluorocarbon rubbers, chloroprene rubber, chlorosulphonated rubber, and epichorohydrin rubber are inherently flame resistant and the flame resistance improves as the polymer halogen content increases. Halogen-free elastomers are not flame resistant unless they contain a high concentration of flame resistant additives.

The following are the important elastomers in use today based on chemical structure.

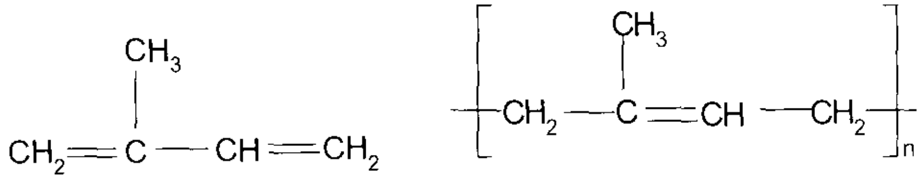
1.2.1 Natural rubber [5, 6]

NR remains the best choice of elastomer for many applications that require low heat build up such as large tires, carcasses of passenger car tires, vibration dampers, springs, engine mountings and bearings. Other products like hoses, conveyer belts, gaskets, seals, rollers, rubberized fabrics, elastic bands, latex foams, adhesives, pharmaceutical and medical products also consume a major part of NR.

It is the most widely used naturally occurring elastomer and is a homopolymer of isoprene having a cis 1,4 configuration as in Fig.1.1 and available in a variety of types and grades including latex, technically specified grades, sheets, crepes, etc.[7].

As indicated earlier, almost all of the NR structure consists of a string of long and uninterrupted cis-1, 4-polyisoprene units. Due to its high structural regularity, NR tends to crystallize spontaneously at low temperature or when it is stretched. Low temperature crystallization causes stiffening, but it is easily reversed by warming. The strain induced crystallization results in the polymer gaining high tensile strength and resistance to cutting, tearing and abrasion [8]. It is also found that both saturated and unsaturated fatty acids found in NR have a synergistic effect on the acceleration of the rate of crystallization of NR [9].

It has the highest resilience (except BR) which is responsible for its very low heat build up. It shows very low compression set and stress relaxation, good electrical insulation and good resistance to abrasion, tear and fatigue.



$CH_2{=}C(CH_3){-}CH{=}CH_2$

$\left[-CH_2-C(CH_3){=}CH-CH_2-\right]_n$

(a) **(b)**

Fig. 1.1 Structures of **(a)** isoprene and **(b)** NR

As in any unsaturated elastomer, NR vulcanizates are susceptible to attack by atmospheric oxygen and ozone and hence its heat and weather resistance are poor. It is not resistant to petroleum based oils and fuels as it contains no polar groups, but can be used with a wide range of organic and inorganic chemicals such as non petroleum based automotive break fluids, silicone oils and greases, glycols, alcohols, water and non oxidising aqueous solutions of acids, alkalis and salts.

Further details of processing and properties of NR will be dealt with in a subsequent Section (1.3).

1.2.2 Styrene butadiene rubber (SBR) [10]

Styrene –butadiene rubbers (SBR) are the general purpose synthetic rubbers. They are copolymers of butadiene and styrene. The polymeric chains contain random sequences of these two monomers which lead to rubber like behavior but render them too irregular to crystallize on stretching. Hence these rubbers do not develop high tensile strengths without the aid of reinforcing fillers. They are manufactured by the copolymerization of butadiene and styrene under controlled conditions using different polymerization techniques. Depending on the method of manufacture, SBR is divided into different grades like emulsion, solution, cold process or hot process etc. The basic structure of SBR is shown in Fig. 1.2

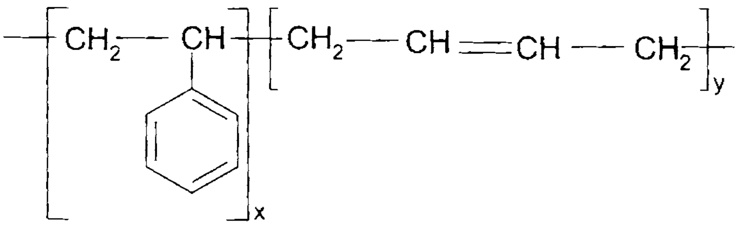


Fig. 1.2 Styrene-butadiene rubber

Of all the SBR made, about 75% goes into tyres [11]. The rest goes into shoes and other footwear, mechanical goods, sponge and foamed products, water proof materials, hose, belting, adhesives and other miscellaneous applications.

The compounding of SBR is similar to that of NR and other unsaturated hydrocarbon rubbers. Sulphur vulcanization is the most convenient method for curing SBR.

1.2.3 Nitrile rubber (NBR) [12, 13]

Nitrile rubber is a copolymer of acrylonitrile (ACN) and butadiene. It has good resistance to various oils and solvents and is widely used in products like oil seals, pipe protectors and blowout preventors [14]. Nitrile rubbers are manufactured by emulsion copolymerization of butadiene and acrylonitrile. Major properties of NBR depend on the acrylonitrile content. Like SBR, it also has an irregular chain structure and will not crystallize on stretching. Hence nitrile rubber requires reinforcing fillers for high strength.

Specialty NBR polymers contain a third monomer (divinyl benzene, methacrylic acid etc.) [15,16]. Some NBR elastomers are hydrogenated [17] to reduce the chemical reactivity of the polymer backbone, significantly improving the heat resistance.

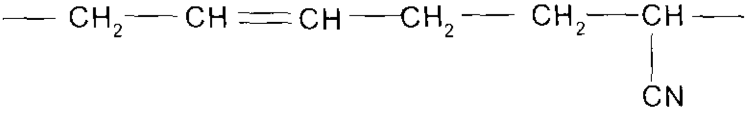
The ACN content is one of two primary criteria defining each NBR grade. The ACN level, by reason of polarity, determines several basic properties, such as oil and solvent resistance [18.19], low temperature flexibility, glass transition temperature and abrasion resistance. Vulcanization can be achieved with sulphur, sulphur donor or peroxide systems. These systems are dealt with in more detail is subsequent sections (Section 1.2.7).

$$CH_2{=}CH{-}CN$$

(a)

$$CH_2{=}CH{-}CH{=}CH_2$$

(b)



$$-CH_2-CH=CH-CH_2-CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}-$$

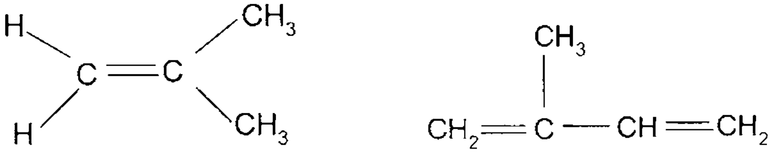
(c)

Fig.1.3 Structure of **(a)** acrylonitrile **(b)** butadiene **(c)** NBR

1.2.4 Butyl rubber (IIR) [20]

Butyl rubber is a copolymer containing mostly isobutylene units with just a few percent of isoprene units. Hence this polymer has only a limited number of double bonds. This small extent of unsaturation is deliberately introduced to provide necessary sites for sulphur vulcanization employed for crosslinking of the rubber. Butyl rubber is commercially vulcanized by three basic methods. These are 1) accelerated sulphur vulcanization, 2) crosslinking with dioxime and related dinitroso compounds, and 3) the polymethylol-phenol resin cure. The good regularity of the polymer chains makes it possible for this elastomer to crystallize on stretching, resulting in high gum tensile strengths. Since it is a soft polymer it is compounded with carbon black to increase the modulus. This material has a low T_g but has a high bounce. The viscoelastic properties of butyl rubber are a reflection of the molecular structure of the polyisobutylene chain. The damping and shock absorption properties of this rubber have found wide application in automotive suspension bumpers [21].

It has excellent ageing properties and very low permeability to gases [20]. So it is often used for tubeless tyre liner, as well as reservoir linings and other barrier applications. Chemically modified forms are frequently used. Figs. 1.4 (a) and (b) give the structures of isobutylene and isoprene.



(a) **(b)**

Fig. 1.4 (a) Isobutylene **(b)** Isoprene

1.2.5 Ethylene-propylene rubbers [22-24]

Ethylene-propylene rubbers (also called EPDM and EPM) continue to be one of the most widely used and fastest growing synthetic rubbers having both

Ethylene-propylene rubbers are valuable for their excellent resistance to heat, oxidation, ozone and weather ageing by virtue of a stable, saturated polymer backbone structure. As non-polar elastomers they have good electrical resistivity as well as resistance to polar solvents such as water, acids, alkalies, many ketones and alcohols.

Because the various chain units are randomly arranged in the chain, these elastomers do not crystallize on stretching and require a reinforcing filler to develop high strength. A third, non-conjugated diene monomer can be terpolymerised in a controlled manner to maintain a saturated backbone and place the reactive unsaturation in a side chain available for vulcanization or polymer modification reactions. The terpolymers are referred to as EPDM (or ethylene propylene-diene with 'M' referring to the saturated backbone structure). An EPDM structure is illustrated in Fig. 1.5.

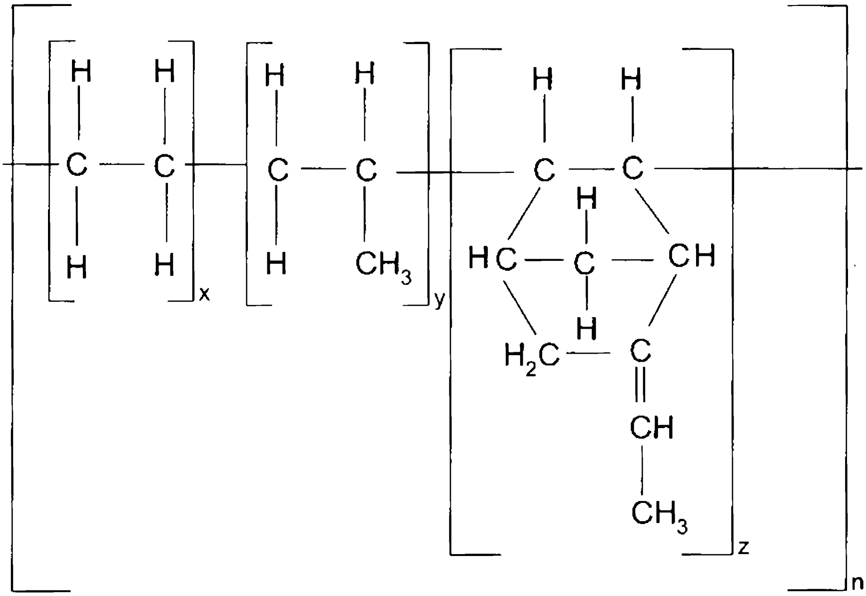
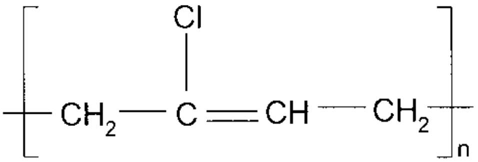


Fig.1.5 Structure of EPDM containing ethylidene norbornene

1.2.6 Chloroprene rubber (CR)

Polychloroprene or Neoprene is the polymer of 2- chlorobutadiene. Since the polymer consists almost entirely of trans-1, 4 units, the chains are sufficiently regular in structure to crystallize on stretching. Hence Neoprene exhibits high gum tensile strengths and is used in the pure gum form in many applications. Crystallinity is a property of all polychloroprene rubbers [25]. But the degree of crystallinity is largely dependent upon the amount of trans configurations in the polymer [26]. Metal oxides are an essential part of the curing system. They regulate scorch, cure rate, and cure state.

CR is important as a raw material for adhesives (solvent based and water based) and has different latex applications such as dipped articles (gloves) and molded foam. It is also employed for improvement of bitumen. Application areas in the elastomer field are numerous such as moulded goods, cables, transmission belts, conveyor belts, profiles etc. This multipurpose synthetic rubber has over half a century of proven performance in thousands of applications [27]. It will continue to be one of the most important synthetic speciality elastomers because of its unique properties.



$$\left[-CH_2-\overset{Cl}{\overset{|}{C}}=CH-CH_2- \right]_n$$

Fig. 1.6 Chloroprene rubber

1.2.7 Butadiene rubber (BR) [28]

It is a non-polar rubber like NR and SBR with a very low T_g. BR is a very high resilience rubber commonly used in combination with NR and SBR in long life rubber tyre treads. It is difficult to process unless blended with another elastomer. Polybutadienes are cured employing conventional sulphur recipes or peroxide systems. For curing, thiazoles and sulphenamides are generally employed alone or in combination with secondary accelerators. The structure is given in Fig. 1.7

$$CH_2{=}CH{-}CH{=}CH_2$$

(a)

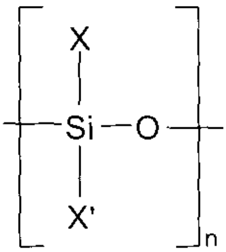
$$\left[-CH_2{-}CH{=}CH{-}CH_2- \right]_n$$

(b)

Fig. 1.7 **(a)** Butadiene **(b)** Butadiene rubber

1.2.8 Silicone rubber [29]

Silicone rubber is unique in not having a carbon back bone. Being –Si-O-Si-O- the useful temperature range is extended considerably for this rubber. It has a T_g as low as -127°C depending on type and can be used at service temperatures of 200°C or more for several years. The siloxane structure results in a very flexible chain with extremely weak interchain forces. Hence, silicone rubbers are noted for exhibiting very little change in physical properties over a range of temperature. They show no tendency to crystallize on stretching and must be reinforced usually with a fine silica powder. Silicone rubbers can be used for making gaskets, tubing, tape, wire, cable, seals, rods, channels and hose apart from other applications like adhesives and sealants.



$$\left[-\overset{X}{\underset{X'}{Si}}-O- \right]_n$$

Fig. 1.8 Silicone rubbers

1.2.9 Urethane rubber [30]

Urethanes are formed by a chain extension reaction rather than the usual polymerization reaction. i.e. these systems are able to make big macromolecules from small macromolecules, rather than the monomer itself. These systems have special advantages, since the properties of the final polymer depend both on the type of original short chain polymers used as well as on their chain length. Hence a wide variety of polymers can be synthesized ranging from rigid to elastic types.

The short chain polymers used are generally two types, polyethers and polyesters. The chain extension reaction whereby these short chains are linked is accomplished by the use of a reactive agent, a diisocynate. For this reaction, the short chain polymers must have terminal hydroxyl groups. In addition to this chain extension reaction, the diisocynate can also react with some of the active hydrogen atoms attached to the polymer chain leading to crosslinking. Another reaction of diisocynate involves water which reacts vigorously to form carbon dioxide gas. Hence, when a little water is mixed with the short chain polymer and diisocynate, a process of simultaneous foaming, polymerization, and vulcanization results, leading to a rapid formation of foamed elastomers or plastics. As elastomers, the urethane polymers show some outstanding physical properties, including high gum tensile strength. The polyurethane reaction is shown in Fig.1.9

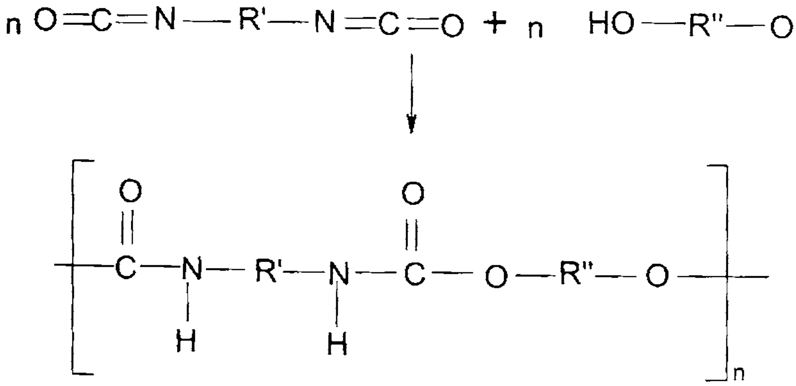


Fig.1.9 Urethane reaction

The versatility of rigid polyurethane foam makes it suitable for an extensive range of thermal insulation applications like refrigerators and freezers for domestic use. Flexible polyurethane is employed in applications like apparel lining, upholstery etc.

Since this work is about the modification of natural rubber the following sections are devoted to its processing and properties and finally various thermoset resins which are potential modifiers.

1.3 Natural rubber – processing and properties [31]

Natural rubber has rightfully been called "the supreme agricultural colonist of all times." Although indigenous to forests in the Amazon Valley, natural rubber has been cultivated principally in South East Asia, especially the countries of Malaysia, Indonesia, Thailand, India and China.

Natural rubber can be isolated from more than 200 different species of plants, *Hevea Brasiliensis* being commercially significant [32]. Rubber trees normally grow to a height of 60 feet. They grow on 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 cm are necessary for the optimum growth of this plant. The tree however grows successfully under slightly varying conditions also. Rubber trees have well-developed tap roots and laterals.

The bark of the tree on cutting yields latex which is the real crop. It is a milky white dispersion of rubber in water. The latex that flows out is channeled into a container or cup attached to the trunk of the tree. Latex collected is transferred to clean buckets. Around eighty percent of the crop from the plantation is in the form of latex.

Premature coagulation of the latex is prevented by the addition of small amounts of stabilizers, such as ammonia (0.01%), sodium sulphite (0.05%), or formaldehyde (0.02%) . Fresh latex from the tree has a normal pH of 7.

1.3.1 Dry rubber production [33]

Depending on the producing country, 10-20% of the latex is concentrated by creaming or centrifuging and shipped to consumer countries where it is used as such to make finished articles including foam for upholstery and bedding, tubing and dipped goods, etc. The remainder is processed into dry rubber, as sheets, crepes etc. These are graded according to International Standards of Quality and Packing.

The conventional forms of NR are graded according to the International Standards of Quality and Packing for Natural Grades. Grading is by visual examination and is based on the presence of dirt, bubbles, uniformity and intensity of colour. Conventional forms are classified into 8 types made up of a total of 35 different grades. Different grades of Natural rubber according to Bureau of Indian Standards are ISNR 3CV, ISNR 5, ISNR 10, ISNR 20 and ISNR 50. BIS specifications of different grades are given in Table 1.2

Table1.2 BIS specifications of Indian Standard NR (as per IS: 4588:1986)

Characteristic	**ISNR 3CV**	**ISNR 5**	**ISNR 10**	**ISNR 20**	**ISNR50**
Dirt content (% by mass)	0.03	0.05	0.1	0.2	0.5
Volatile matter (% by mass)	0.80	0.80	0.80	0.80	0.80
Ash (% by mass)	0.50	0.60	0.75	1.00	1.50
Nitrogen (% by mass)	0.6	0.6	0.6	0.6	0.6

1.3.2 Rubber sheet production

Latex is coagulated in suitable containers into thin slabs of coagulum and sheeted through a pair of smooth rollers followed by a grooved pair and dried to obtain sheet rubber. Depending on the drying method, sheet rubbers are classified into two: ribbed smoked sheets and air dried sheets. After coagulation the coagulum is removed from the pans and thoroughly washed with running water. They are sheeted either in a sheeting battery or smooth rollers to a thickness of 3mm and finally passed through the grooved roller. While sheeting, the coagula are continuously washed and the sheets are later washed in running water in a tank. The wet sheets are allowed to drip on reapers arranged in a well-ventilated dripping shed.

The sheets, after two or three hours of dripping in shade, are put in the smoke house where the temperature is maintained between 40°C and 60°C. The completely dried sheets are removed to the packing shed where they are carefully inspected and graded according to various national standards. The sheets are packed in bales of 50kg weight after grading.

1.3.3 Crepe rubbers

When coagulated latex or any form of field coagulum is passed several times through a minimum of 3 mills with heavy rolls, a crinkly lace-like rubber will be obtained. This lace like rubber when air dried is called crepe rubber. The different types of crepe rubbers are pale crepe, sole crepe, brown and blanket crepes

1.3.4 Special grades of NR [33]

a) Oil-extended natural rubber (OENR)

OENR is a rubber containing 20% to 30% of aromatic or naphthenic process oil. Oil is added to the latex as an emulsion and then coagulated with acid in the usual manner. The coagulum so obtained is then processed as block rubber.

b) Purified rubber

Partially purified crepe prepared by centrifuging the latex prior to coagulation contains less than half the amount of protein and mineral matter normally present in pale crepe. Large proportions of protein can also be removed by treatment of the latex with soaps or other surface active agents and especially with enzymes to give deproteinised rubber

c) Powdered rubber

Powdered rubbers either lightly vulcanized or if unvulcanized, containing large proportions of anti-agglomeration agents, found early application as improvers for road surfacing. More recently, with the increasing interest in potentially easy processing rubbers, particulate NR has been prepared by spray drying latex, by surface bromination of rubber crumbs and by granulation of bale rubber.

d) Skim rubber

When latex is concentrated by centrifuging, the by-product skim latex is coagulated and made into smoked sheet, thick crepe, or granulated rubber. It contains a higher proportion of non-rubbers than ordinary sheet or crepe and is rapid curing, but can sometimes be used with advantage where a clean low-priced rubber is needed.

e) Peptized rubber

Peptized rubber is prepared by adding a small amount of peptizer either to latex prior to coagulation and sheeting or crumbing or to comminuted field coagulum. Depending on the activity of the peptizer and the drying temperature, the rubber has a relatively low viscosity or easily breaks down on mastication.

f) Superior processing (SP) rubber

SP rubbers are prepared by coagulating a mixture of vulcanized and unvulcanized latex and processing and drying to smoked sheet, air-dried sheet or heveacrumb. The proportion of vulcanized latex may range from 20-50%. A concentrated form, 80%, is also produced and an easier processing grade consists of 30 parts of non-staining oil and 70 parts of concentrated form. The special value of SP rubbers either used alone or blended with normal rubbers lies in their ability to confer improved moulding, extrusion and calendaring performance.

1.3.5 Properties and uses of natural rubber

Natural rubber is a high molecular weight polymeric substance with viscoelastic properties. Structurally it is cis1, 4-polyisoprene. Isoprene is a diene and 1, 4 addition leaves a double bond in each of the isoprene units in the polymer. Because of this, natural rubber shows all the reactions of an unsaturated polymer. It gives addition compounds with halogens, ozone, hydrogen chloride etc. The best known reaction of natural rubber is its combination with sulphur. This is known as vulcanization. This reaction converts the plastic nature of raw rubber into an elastic one. Vulcanized rubber will have a high tensile strength and a comparatively low elongation. Its hardness and abrasion resistance are also high when compared to raw rubber. Because of the unique combination of these properties, natural rubber finds application in the manufacture of a variety of products.

The elastic nature of NR also accounts for the resilience of NR products. This resilience implies that less kinetic energy is lost as heat during repeated deformation under stress. Resilience and hysteresis go hand in hand. In a highly resilient rubber little of the energy of deformation is lost resulting in low hysteresis. Little heat is developed as a result of deformation.

The processibility of a compound depends on two properties. One is its viscosity (or plasticity) and other is the time to the onset of crosslinking. Mooney viscometer is widely used to determine the viscosity and the scorch characteristics of fully compounded rubber which operates at an average shear rate of about 2 s^{-1}. The torque required to rotate the disc at 2 rpm at a fixed temperature is defined as the Mooney viscosity.

Table 1.3 Physical properties of natural rubber (ISNR) [34]

Specific gravity	0.92
Refractive index	1.52
Coefficient of cubical expansion	0.00062/°C
Cohesive energy density	63.7 Cal/cc
Heat of combustion	10547.084 Cal/g
Thermal conductivity	0.00032 Cal/s/cm/°C
Dielectric constant	2.37
Power factor (at 1000 cycles)	0.15-0.2
Volume resistivity	10^{15} ohm.cm
Dielectric strength	3937V/mm

Mechanical properties

a) *Hardness*

NR vulcanizates can be produced in a wide range of hardnesses, from very soft (Shore A 30 to 50) to ebonite hardness. This can be done by changing the amount of fillers and softners in the compound as well as the extent of crosslinking

b) *Tensile strength*

Due to the strain crystallization of NR, a high tensile strength of 20MPa or more is observed even in gum vulcanizates. By adding reinforcing fillers to compounds, the tensile strength can rise up to 30MPa.

c) *Elongation at break*

The ultimate elongation depends on the nature and amount of fillers in the compound, and on the degree of vulcanization. It generally is about 500-1000%, or even greater.

d) *Tear resistance*

The tear resistance is also influenced by the strain crystallization [35,36], and it is therefore very good. Highly reinforcing fillers in NR compounds give a much better tear resistance than non-reinforcing fillers.

e) *Age resistance* [37-40]

NR vulcanizates can be given adequate heat ageing resistance by a suitable choice of vulcanization systems and the use of amine or phenolic antioxidants.

f) *Ozone resistance*

The poor ozone resistance under both static and dynamic conditions can be improved with waxes and antiozonants of the p-phenylenediamine type.

The main use of natural rubber is in automobiles. In developed countries, nearly sixty percent of all natural rubber consumed is for automobile tyres and tubes. In heavy duty tyres, the major portion of the rubber used is NR. In addition to tyres, a modern automobile has more than 300 components made up of rubber. Many of these are processed from NR. Uses of NR in hoses, footwear, battery boxes, foam mattresses, balloons, toys etc. are well known. In addition to this, NR now finds extensive use in soil stabilization, vibration absorption and road making. A variety of NR based engineering products have been developed for use in these fields.

1.3.6 Compounding

Compounding is the process of incorporation of various ingredients into the virgin polymer. It is a necessary part of any rubber product manufacturing process. Compounding of elastomers involves milling down the raw rubber into pliable sheets and then incorporating compounding ingredients into it one by one. The properties displayed by a particular rubber vulcanizate are determined to a large extent by the compound composition. The main objectives of compounding are to facilitate processing and fabrication to ensure the required vulcanizate properties and to provide durability at the lowest possible cost [41].

Compounding of dry elastomers is done either on a two roll mill or in a Banbury type internal mixing mill. The two roll mill has a pair of rolls typically 160mm diameter and 330mm length. The ratio of the speed of the front roll to back roll can be say, 1:1.25. The gap between the rolls is adjustable from 0.2 to 8mm and the temperature can be maintained at 70°C or less. Rubber is initially masticated on a cold mill and the compounding ingredients are then incorporated. The mixing procedure is described in ASTM D 3182-3189 [42]. Milling time varies from 10 to 20 minutes.

The Banbury internal mixer was originally manufactured to replace the two roll mill. The basic design of the machine includes two rotors that operate at a slight speed differential. The rotors are non-interlocking. Mixing or shearing action occurs between the rotors and the sides of the mixer and between the rotors themselves. The mixer is top loaded through an opening large enough to accommodate elastomers as well as other ingredients. Pressure is exerted on the batch using a ram which closes the feed opening. Typically Banbury mixing times are less. The Banbury is generally employed for large scale mixing.

Both natural and synthetic rubbers require mastication before compounding, but a longer mastication time is required for the former. For synthetic rubbers there is no need of viscosity reduction by mastication as they are tailor-made for processing. But in the case of NR, which has a high molecular weight, high temperature is produced during mixing due to chain scission. Scorch or premature vulcanization may occur during the processing of a compound due to the accumulated effects of heat and time. Natural rubber has relatively lower scorch safety. The viscosity of a fully compounded stock held at elevated temperature will increase with time as a result of crosslinking [43]. Hence, scorch safety is a major consideration in NR compounding.

1.3.7 Curing

For rubber to become truly useful, its chains must be permanently linked together for improving the strength and other properties. Vulcanization involves the conversion of linear raw rubber molecules into a network by the formation of crosslinks. By this process the rubber is transformed from a plastic substance of very low strength to a resilient highly elastic material of considerable strength, less sensitive to temperature changes [44]. As more crosslinks are formed, the network becomes tighter and the forces necessary to achieve a given deformation increase. The discovery that rubber can be vulcanized or cured by heating with sulphur was a technological accomplishment of great importance [45]. A wide range of chemical reactions take place more or less simultaneously during the vulcanization process.

Many articles on different aspects of vulcanization have been published over the years [46-52]. Curing systems can be classified as sulphur, sulphur donor or sulphurated systems. Sulphur vulcanization can only be applied to rubbers with unsaturation in the backbone or rubbers with unsaturated side groups. The type of crosslinks formed during sulphur vulcanization largely depends on the vulcanization system. Although the most common vulcanizing agent for diene rubbers is sulphur, natural rubber and most of the unsaturated synthetic rubbers can be vulcanized by a wide variety of non-sulphurated agents including organic peroxides, quinones and their oximes and imines, poly nitro benzenes, bis-azo dicarboxylic esters and high energy radiations [53]. Sulphur donor systems consist accelerators containing sulphur but no elemental sulphur. Polychloroprene rubbers are usually vulcanized by metallic oxides [54] like MgO along with other ingredients. Non-olefenic elastomers are generally cured by peroxides or high energy radiations.

1.3.8 Compounding ingredients

a) Vulcanizing agents

Substances that bring about the actual crosslinking process are called vulcanizing agents. Numerous and varied vulcanizing agents are now used in the rubber industry in addition to sulphur, viz. various organic peroxides, quinines, metal oxides, bifunctional oligomers, resins, amine derivatives etc. Vulcanization can also be achieved by using high energy radiation without any vulcanization chemicals.

Sulphur and nonsulphur systems have advantages and disadvantages of their own, but sulphur systems are more versatile. There are several advantages for sulphur as the vulcanizing agent [55-56] viz. (1) higher flexibility during compounding, (2) easier adjustment of the balance between vulcanizing stages, (3) possibility to control the length of crosslinks, (4) better mechanical properties of the vulcanizates and (5) economic viability. Vulcanization reaction is determined by the type of vulcanizing agents, the type of process, temperature and the time of cure. The type and degree of crosslinking are determined by the vulcanization method. The degree of crosslinking, on the other hand, influences the elastic and other properties of the vulcanizate. Therefore, the type of vulcanization is the important connecting link between the raw materials and finished product.

b) Accelerators

Substances that are added in small amounts during compounding to speed up the vulcanization reaction and to improve the physical and service properties of the finished products are called accelerators [57]. These substances can reduce the cure time from days or hours to minutes or seconds at the vulcanization temperature. The decrease in vulcanization time is of tremendous economic importance because of increased turnover and consequent reduction in cost of production. Further, the amount of sulphur required can be reduced considerably in the presence of an accelerator. The first accelerators used in rubber vulcanization were inorganic compounds [58]. Magnesium oxide, litharge and zinc oxide were the most widely used inorganic accelerators of those days.

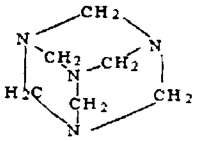
Around 1920 it was discovered that thiuram disulphides enable vulcanization to proceed without sulphur. Later, more delayed action and yet fast-curing vulcanization systems were made possible using thiazole derivatives of sulphenamides. With the discovery of ultra accelerators vulcanization could be achieved even at room temperature [59]. Table 1.4 and Fig.1.10 give commonly used accelerators and their structures respectively.

Table 1.4 Chemical classifications of accelerators [60]

Type	**Example**	**Typical use**
Aldehyde-amine reaction products	Butyraldehyde-aniline condensation product	Self curing
Amines	Hexamethylene tetramine (HMT)	Delayed action for NR
Guanidines	Diphenyl guanidine (DPG)	Secondary accelerator
Thioureas	Ethylene thiourea	Fast curing for CR
Thiazoles	2-mercaptobenzothiazole (MBT)	Fast curing, general purpose, broad curing range
	MercaptoBenzothiozole disulphide (MBTS)	Safe processing, general purpose, moderate cure rate
Thiurams	Tetramethylthiuram monosulphide(TMTM) tetramethylthiuram disulphide (TMTD)	Safe, fast curing
Sulphenamides	N-cyclohexyl 2-benzothiazyl sulphenamide (CBS)	Safe processing, delayed action
Dithiocarbamates	Zinc diethyl dithiocarbamate (ZDEC)	Fast, low temperature use
Xanthates	Dibutyl xanthogen disulphide	General purpose, low temperature use
	Zinc isopropyl xanthate	Latex and adhesives room temperature curing

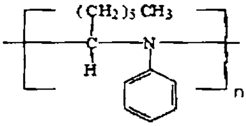
ACCELERATORS

AMINES



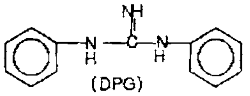
Hexamethylenetetramine (HMT)

ALDEHYDE-AMINE CONDENSATION PRODUCT

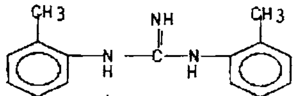


Heptaldehyde - Aniline Condensation Product
(Hepteen Base)

Guanidines



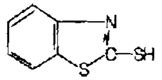
(DPG)
1,3-Diphenylguanidine



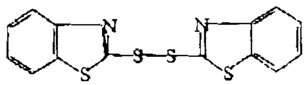
(DOTG)
Di-O-tolylguanidine

ACCELERATORS

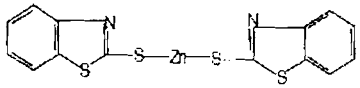
Thiazole Accelerators



MBT

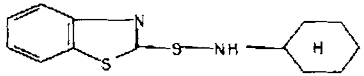


MBTS

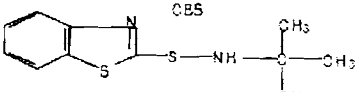


ZMBT

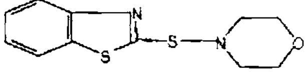
Sulphenamide Accelerators



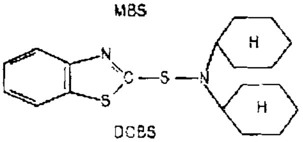
CBS



TBBS



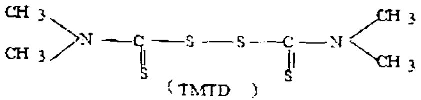
MBS



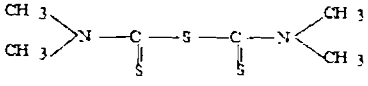
DCBS

ACCELERATORS

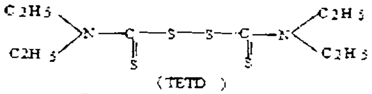
Thiurams



(TMTD)
Tetramethylthiuram disulphide

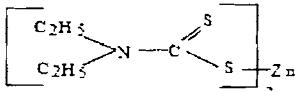


(TMTM)
Tetramethylthiuram monosulphide

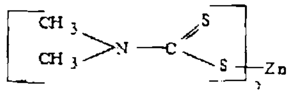


(TETD)
Tetraethylthiuram disulphide

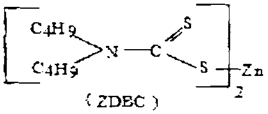
Dithiocarbamates



(ZDEC)
Zinc diethyl dithiocarbamate



(ZDMC)
Zinc dimethyl dithiocarbamate



(ZDBC)
Zinc dibutyl dithiocarbamate

c) Accelerator activators

The rate of vulcanization can be increased by the addition of activators which are often metal complexes. Activators enable an accelerator to exercise maximum effect. Organic accelerators usually require the presence of organic acid or inorganic activators. ZnO is probably the most important inorganic activator but magnesium and lead oxides also find use. Fatty acids (e.g. stearic acid) are used as co-activators. Polyalcohols (e.g. ethylene glycol) and amino alcohols are used to counteract the retarding effect of white fillers.

A combination of ZnO and a long chain fatty acid like stearic acid used as co-activator forms an ideal activator system [61]. Apart from reducing the curing time [62], ZnO also functions as a filler to reduce cost and has some reinforcing effect. The zinc cations from ZnO and / or zinc compounds react with organic accelerators to give an active zinc-accelerator complex, which is one of the main steps in the vulcanization scheme [63].

The complexes react with sulphur, a sulphur donor and other activators to generate the active sulphurating agent. It has been suggested in many studies that these active complexes of zinc ions with accelerators are more reactive than the free accelerator [64]. This active sulphurating agent reacts at the allylic sites of the rubber polymer unsaturations to form a rubber-bound intermediate which reacts with another rubber-bound intermediate or with another polymer chain to generate a crosslink.

d) Fillers

Fillers are usually inorganic powders of small particle size incorporated during compounding for various purposes like improvement of strength and modulus or other properties, cost reduction etc. Choice of the type and amount of the filler to be used depends on the hardness, tensile strength and other properties required in the product. Some fillers are incorporated primarily to reinforce the product and they are termed as reinforcing fillers. Carbon blacks, silicas, silicates etc. are in this class. Others are included mainly to cheapen and stiffen the final product. China clay, barites etc. come under this type. Reinforcement by filler leads to the enhancement of one or more properties of an elastomer by making it more suitable for a given application [65,66]. It is generally agreed that strong links exist between rubber chain and reinforcing filler particles [67-69].

The effect of filler on rubber vulcanizates depends on its physical properties such as particle size, surface area, surface reactivity, electrical charge on the particle and chemical properties such as pH and reactivity towards accelerators. Reinforcing fillers substantially improve the mechanical and dynamic properties of the rubber. As the filler dose increases the properties increase progressively and then decrease. This phenomenon also depends on the type of filler and rubber used.

The most common and effective reinforcing filler is carbon black. There are varieties of blacks characterized by the particle size, method of manufacture etc. A standard classification system for carbon blacks used in rubber is described in ASTM D1765. Some examples are given in Table 1.5. They are essentially elemental carbon and are composed of aggregated particles. During vulcanization carbon blacks enter into chemical reaction with sulphur, accelerator etc. participating in the formation of a vulcanized network. The modification of an elastomer by carbon black reinforcement and vulcanization generates a unique three dimensional visco-elastic network that transforms the soft elastomer into a strong, elastic product [70]. Thus the filler influences the degree of crosslinking also. Carbon black also interacts with unsaturated hydrocarbon rubbers during milling and the rubber is adsorbed on to the filler. This alters the stress-strain properties and reduces the extent of swelling of the product in solvents [71].

Porter [72] has reported that the crosslink density of a black reinforced vulcanization system increased by about 25% compared to the corresponding unfilled ones. Carbon black generally increases the rate of vulcanization and improves the reversion resistance [73]. However they can be used in dark coloured etc. are in this class. Others are included mainly to cheapen and stiffen the final product. China clay, barites etc. come under this type. Reinforcement by filler leads to the enhancement of one or more properties of an elastomer by making it more suitable for a given application [65,66]. It is generally agreed that strong links exist between rubber chain and reinforcing filler particles [67-69].

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Porter [72] has reported that the crosslink density of a black reinforced vulcanization system increased by about 25% compared to the corresponding unfilled ones. Carbon black generally increases the rate of vulcanization and improves the reversion resistance [73]. However they can be used in dark coloured products only.

Table 1.5 Current vs. previous nomenclature of carbon black [74]

ASTM D1765	Old name
N110	SAF (super-abrasion furnace)
N220	ISAF (intermediate super-abrasion furnace)
N330	HAF (high-abrasion furnace)
N358	SPF (super processing furnace)
N660	GPF (general purpose furnace)
N762	SRF (semi reinforcing furnace)

Precipitated silica is the best non-black reinforcing filler so far developed and comes close to carbon black in reinforcing effect. They have particle size as fine as that of carbon black and have an extremely active surface. They are noted for their unique combination of tear strength, adhesion, abrasion resistance, age resistance, colour and economics in many applications. A comprehensive review of precipitated silicas and silicates in rubber has been published [75]. These fillers are manufactured by controlled precipitation from sodium silicate. The ultimate particle size is controlled closely by the conditions of precipitation.

Precipitated silica is highly adsorptive and hence in formulations containing them, it is necessary to use more than the normal quantity of accelerator or a combination of accelerators which is more reactive. Proper choice of the accelerator and activator are essential to obtain appropriate scorch and cure times in silica filled mixes. Diethylene glycol (DEG) is added along with silica during compounding to prevent the adsorption of curatives by silica.

e) Plasticizers

Besides fillers, plasticizers play the biggest quantitative role in building a rubber compound. The reasons for the use of plasticizers are manifold: 1) To facilitate reduction of elastomer content by using high dosages of carbon black and plasticizer to lower the price of the blend, i.e. extending the rubber 2) To improve mechanical properties by incorporation of reinforcing fillers whose dispersion requires a plasticizer 3) To improve the flow of the rubber compound and make energy savings during processing 4) To improve tackiness of the rubber compounds 5) To influence the physical properties of the vulcanizate, especially its elongation and elasticity at low temperatures, lowering the glass transition temperature, elevating the electrical conductivity, increasing flame protection etc.[76]

Plasticizers are generally classified into mineral oils, natural products and synthetic plasticizers. To extend, particularly the non-polar rubbers, relatively cheap mineral oils are used. The choice of mineral oil type depends on its price, polymer type, and compatibility and has relatively little influence on the property spectrum of the vulcanizate. Beyond that, a multitude of natural products can be used, like fatty acids, vegetable oils, glue, rosin, as well as modified natural products like factice, in order to improve the processing properties, tackiness or filler dispersion of the rubber compound [77]. Phosphatic plasticizers hold a place of great significance as they are flame retardants [78,79].

Physical modification of polymers with plasticizers has long been practiced as a means to improve the processability of the compounds and the physico-mechanical properties of the final products. Various organic esters, phosphates etc. are most often used as plasticizers for elastomers capable of polar interactions while natural rubber is plasticized by oils of petroleum origin like paraffinic oil, naphthenic oil and aromatic oil [77]. These are crude oils which are complex mixtures containing thousands of different molecules. Since these complex mixtures are difficult to classify chemically, they are grouped according to the predominant type of hydrocarbon: paraffinic, naphthenic and aromatic.

Even small quantities of plasticizer markedly reduce the T_g of the polymer. This effect is due to the reduction in cohesive forces of attraction between polymer chains. Plasticizer molecules penetrate the polymer matrix and reduce the cohesive forces between the polymer chains and increase the segmental mobility [80,81]. This results in greater processability and reduced chances of degradation.

f) Antioxidants

These substances improve the resistance of elastomers to oxidative reactions which limit their use at higher temperatures and in oxygen and ozone environments. Hydroquinone and pyrogallol were patented as antioxidants in 1901 [82], resorcinol and 2-naphthol in 1920 [83], 1-naphthol in 1922 [84] and mercaptobenzimidazole in 1931 [85]. Currently, bound antioxidants, i.e. antioxidants bonded to polymers are being developed to give maximum resistance to losses by extraction and volatilization [86,87].

All hydrocarbons are vulnerable to deterioration by exposure to heat, light and oxygen. Polymers vary widely in their susceptibility to oxidative degradation. It is well known that the relationship between polymer structure and susceptibility to oxidation depends primarily on the C-H bond dissociation energies of various polymers. Polymers with C-H bonds of low dissociation energies are more readily oxidized than polymers with higher C-H bond dissociation energies. Similarly, a rubber with low olefin content such as EPDM, is more resistant to oxidation than highly unsaturated rubbers such as SBR and NR [88].

Trimethyl dihydroquinolines are materials primarily used to protect rubber articles from degradation by atmospheric oxygen at higher temperatures. They are moderately staining. Phenolic antidegradants represent a group of non-staining non-discolouring additives used primarily in light coloured mechanical goods and tyres. They are weaker antioxidants than amine types. Commonly used example for amine and phenol type antioxidants are trimethyl dihydroquinoline and styrenated phenol respectively.

Table 1.6 Chemical classification of antioxidants [89]

Chemical type	**Example**
Hindered phenol	Styrenated phenol
Amino phenol	2,6-di-t-butyl-dimethyl amino-p-cresol
Hydroquinone	2,5-di-t-amyl hydroquinone
Diphenylamine	Octylated diphenylamine
Alkyl diamine	N,N-diphenyl ethylene diamine
Aldehyde-amine condensation product	Acetone-diphenylamine reaction product
Quinoline	2,2,4-trimethyl 1,2-dihydroquinoline
Phenylene diamine	N,N-diphenyl-p-phenylene diamine

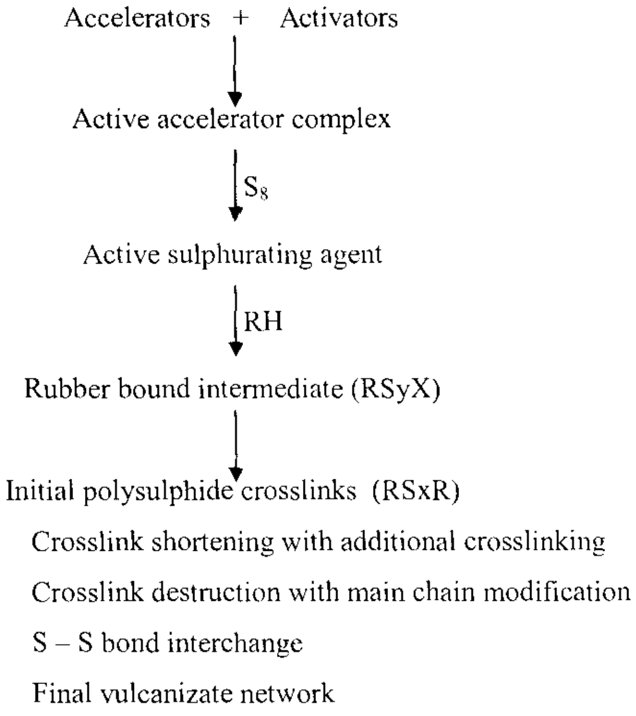
1.3.9 Mechanism of rubber vulcanization [90]

Complex mechanisms are involved in the vulcanization process. A series of consecutive and competing reactions occurs during sulphuration of rubber under vulcanizing conditions and no single mechanism can be proposed.

Sulphur may be incorporated into the vulcanization network in a number of ways. As crosslinks it may be present as monosulphide, disulphide or polysulphide moieties. It may also be present as pendant sulphides or cyclic monosulphides and disulphides. For the study of reaction mechanism, sulphur vulcanization reactions can be broadly classified into two, the unaccelerated and accelerated types. Unaccelerated sulphur formulation consists of rubber and sulphur while the accelerated systems contain rubber, accelerator and sulphur. In addition to this, both types include a zinc oxide – stearic acid activator system. There are also accelerator systems in which elemental sulphur is not present. Instead, the accelerator provides sulphur for vulcanization. These are referred to as sulphur donor systems. The most widely used accelerator of this type is tetramethyl thiuram disulphide (TMTD) [91]

Vulcanization with sulphur in the absence of an accelerator is an extremely slow process. Relatively large amounts of sulphur and long vulcanization times are necessary and the vulcanizates are not of high quality. They have a strong tendency to revert under heat and their resistance to ageing is poor. A problem of sulphur blooming is also noticed. Moreover, the yield of crosslinked polymer is low. This may be due to the formation of multivalent polysulphidic bridges and cyclic sulphidic bridge links.

It is known that several reactions based on different mechanisms may take place simultaneously or consecutively during vulcanization. These reactions range from double bond migration, isomerisation, chain cleavage, cyclisation and formation of vicinal crosslinks [92-98]. The unaccelerated sulphur vulcanization follows a polar mechanism [99,100].



(R represents the rubber chain, X, the accelerator residue)

Fig.1.11 Outline of reaction scheme for the sulphur vulcanization of rubbers

The basic steps in accelerated sulphur vulcanization, proposed by Morrison and Porter [101] are illustrated in Fig.1.11. Accelerator, activators and sulphur interact in the presence of heat to form the active sulphurating agent. Polymer chains (RH) interact with the active sulphurating agent to form polysulphidic pendant groups terminated by accelerator groups (polymer bound intermediate). Pendant sulphurating agent interacts with another polymer chain (RH) to form cross links. Types of sulphur crosslinks possible in vulcanized rubber are shown in Fig.1.12.

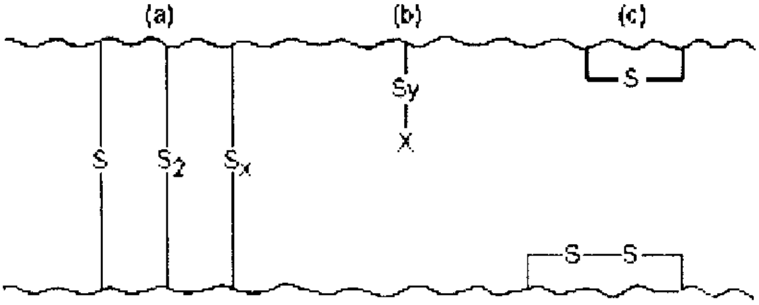


Fig. 1.12 Types of sulphide crosslinks formed in vulcanized rubber [102]

Vulcanization can be characterized relatively easily by measuring the evolution of crosslinks as a function of time using an oscillating disc rheometer (ODR), moving die rheometer (MDR) or rubber process analyzer (RPA). The result graphically expressed is commonly called the cure curve. With these torsional (dynamic) rheometers the torque or shear modulus as a function of time at a certain temperature is measured. It is assumed that the modulus is proportional to the evolving concentration of crosslinks.

Curing occurs in three stages, (1) an induction period, (2) a curing or crosslinking stage and (3) a reversion or overcure stage. The induction period represents the time at vulcanization temperature during which no measurable crosslinking occurs. Following the induction period, crosslinking proceeds at a rate dependent on the temperature, the type of rubber and the curative system. As the curatives and crosslink sites become depleted, the crosslinking reactions slow down until an optimum stiffness is achieved. This represents full cure. Further heating may result in a very slow increase in stiffness (marching modulus) or stock softening (reversion), depending on the type of rubber. These changes are generally reffered to as overcure. A typical cure graph is shown in Fig 1.13.

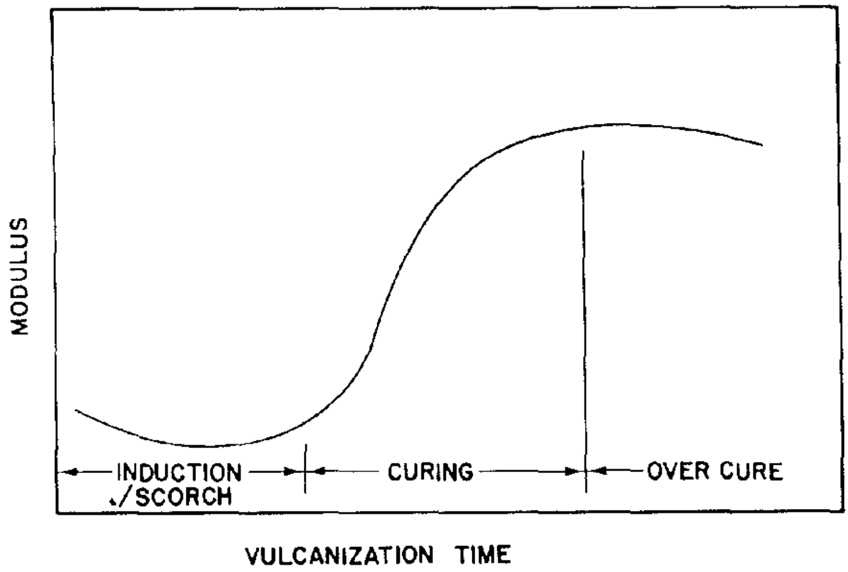


Fig.1.13 Typical cure curve [103]

1.3.10 Moulding [104]

The techniques adopted to make dry rubber products after the compounding step are mainly compression moulding, extrusion, calendaring and transfer moulding.

a) Compression moulding [105]

Compression moulding is the operation of shaping and vulcanizing the rubber compound by means of heat and pressure in a mould of appropriate form. It is the oldest and still the most universally used technique for rubber processing because of suitability for short runs and low mould costs.

During compression moulding heat and pressure are applied to the rubber compound obtained from a milling operation after placing it between the two halves of a mould. Compression moulding most often employs a hydraulic press to apply heat and pressure.. There are two types of compression presses in general use, the conventional parallel platen press using loose moulds and the automated hinged–platen type. The latter uses fixed moulds and because of reduced heat loss, curtails cure times by as much as 50% of that obtained in a press with loose moulds.

The conventional press used for compression moulding is substantially constructed and has two or more platens which are heated either electrically or by saturated steam under pressure. The platens are brought together by pressure applied hydraulically, either by water or oil, to give a loading of 7.5 to 15MPa. Mould designs are generally based on the availability of such pressures which are necessary to achieve closure with an acceptably thin flash. Fundamentally, all processes of moulding are similar, the ways of introducing the material into the mould being different. With compression moulding, to ensure dimensional stability, it is necessary to allow the excess material to move away from the edge of the cavity so that the lands can contact with minimum thickness of rubber between them. Sprue grooves and channels are provided with sufficient dimensions to accommodate this excess and also to allow the escape of air from the mould cavity. Compression moulding has been employed in the present investigation to prepare vulcanized samples.

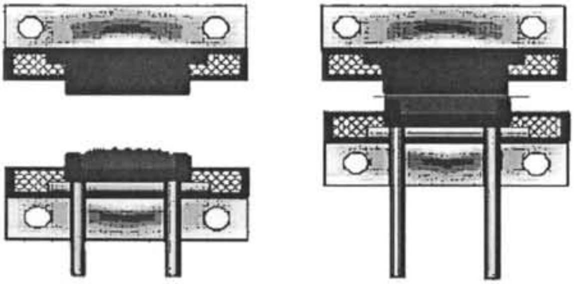


Fig.1.14 Compression moulding [105]

b) Extrusion [106]

Rubber is extruded to make solid or sponge tubing, rods, gaskets, seals, wire insulation and preforms used in compression moulding. With this process, the rubber is continuously forced in the heated condition through a die that gives it the desired cross-sectional size and shape before curing. The extruded compound is finally vulcanized continuously by liquid curing method [107]. Formerly extrudates were nearly exclusively vulcanized in autoclaves, hot air or steam.

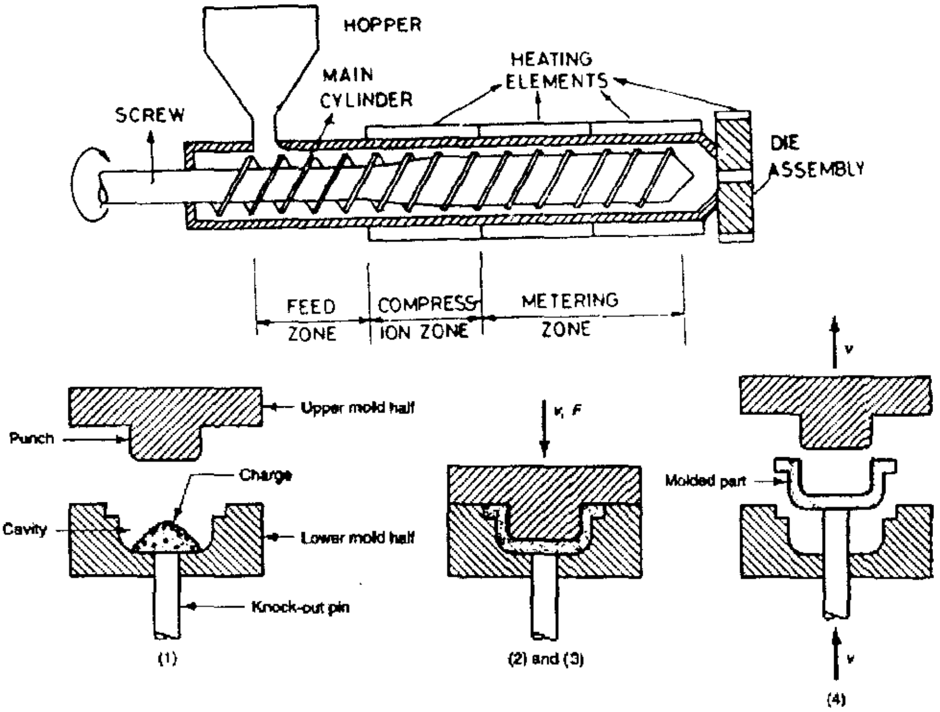


Fig.1.15 Extrusion [105]

c) **Calendering** [108]

Rubbers are calendered by compression in a multi-roll process to produce continuous solid or sponge sheets of uniform thickness. These sheets can be further fabricated into hoses, ducts and die cut seals. Calenders are used to manufacture sheets of varying thickness, to incorporate technical fabrics with rubber and to coat fabrics with rubber.

In most cases, calendaring gives intermediate unvulcanized products. They are then finished and finally vulcanized. In some cases calendered sheets, impregnations or coatings are accelerated so rapidly that they vulcanize at ambient temperature. Most of the sheet products such as roof coverings, rain coat fabrics etc. are vulcanized by pressure-less hot air in heating chambers at 60-70°C.[109]

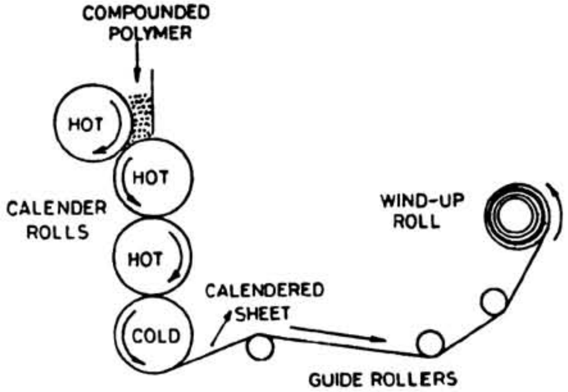
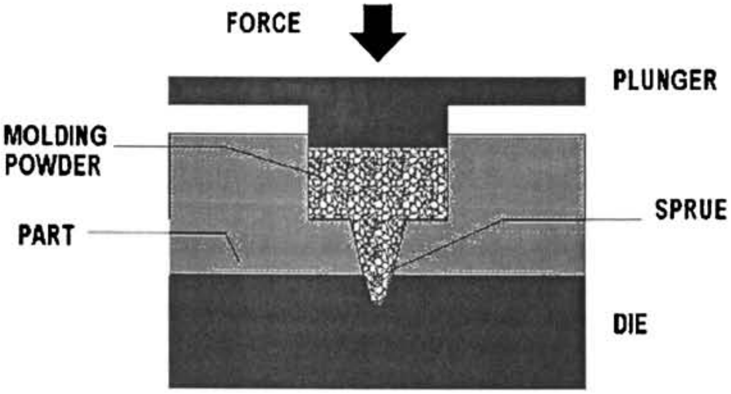


Fig.1.16 Calendering [105]

d) Transfer moulding [110]

Transfer moulding involves the distribution of the uncured stock from one part of the mould to the actual mould cavity. This process permits the moulding of complicated shapes or the embedding of inserts in many products which are difficult with the usual compression moulds. Although the moulds are relatively more expensive than compression moulds, the actual process permits shorter cure times through the use of higher temperatures and better heat transfer obtained by the high pressure applied to force the compound into the mould.



e) Injection moulding [110]

In recent years, injection moulding processes which are normally used for the production of plastics, have been developed for moulding and vulcanization of rubber compounds. By careful temperature control of the feed stock, items can be vulcanized in less than several minutes. This method can be completely controlled by programmed feed, injection and demoulding cycles resulting in low rejection rates and lower finishing costs. The initial cost of both the moulds and equipment has hindered the wider adoption of this type of moulding.

Injection and transfer moulds do not require any provision for excess material flowing out of the mould, simply an escape route for air is sufficient. The mould is closed under pressure and held so while the rubber is forced into the cavities. Any problems of air entrapment in the mould arising from the product design can be overcome by applying a vacuum to the closed mould. These two methods give parts which carry little or no flash adhering to them at the parting lines of the mould.

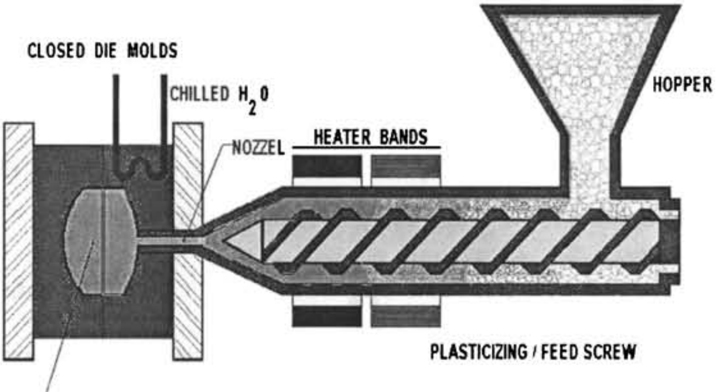


Fig.1.18 Injection Molding [105]

1.3.11 Mechanism of polymer degradation and action of antioxidants

Oxidation of polymers can lead to chain scission, crosslinking or formation of oxygen-containing functional groups in the polymer or its degradation products. All polymers undergo degradation in the presence of oxygen. Oxidation of a hydrocarbon is auto accelerating. In the presence of an impurity or at higher temperature a polymer produces a free radical site which is attacked by oxygen. The peroxide radical so formed attacks another hydrocarbon molecule and new free radicals are formed. In the termination step free radicals combine and stable products are formed. In order to understand the antioxidant inhibition mechanisms, a brief outline of the oxidation process is given below [111].

Initiation

$$\begin{array}{lcl} RH + O_2 & \rightarrow & R^{\cdot} + HOO^{\cdot} \\ AH + O_2 & \rightarrow & A^{\cdot} + HOO^{\cdot} \\ R. + O_2 & \rightarrow & ROO. \end{array}$$

Propagation

$$\begin{array}{lcl} ROO. + RH & \rightarrow & R. + ROOH \\ ROOH & \rightarrow & RO^{\cdot} + OH^{\cdot} \\ ROOH + RH & \rightarrow & RO^{\cdot} + R^{\cdot} + H_2O \\ 2ROOH & \rightarrow & RO^{\cdot} + ROO^{\cdot} + H_2O \end{array}$$

Chain transfer

$$\begin{array}{lcl} ROO^{\cdot} + AH & \rightarrow & A^{\cdot} + ROOH \\ A^{\cdot} + RH & \rightarrow & R^{\cdot} + AH \end{array}$$

Termination

$$\begin{array}{lcl} ROO^{\cdot} + RO^{\cdot} & \rightarrow & \text{Stable products} \\ ROO^{\cdot} + 2A^{\cdot} & \rightarrow & \text{Stable products} \\ A^{\cdot} + ROO^{\cdot} & \rightarrow & \text{Stable products} \end{array}$$

RH - Polymer molecule, AH - Anioxidant, $ROO^{\cdot}$ - polymer peroxy radical, and ROOH - polymer peroxide

1.3.12 Modification of natural rubber

NR can be modified by physical or chemical means. In some cases it is modified by a combination of the two [112]. Physical methods involve incorporation of additives that do not chemically react with rubber. Examples are oil extension, blending with other inert polymers, deproteinisation, prevulcanization, addition of fillers etc. NR is deproteinised to reduce water absorption and protein allergy by enzymatic hydrolysis and radiation processes [113-114]. Deproteinised rubber is used in electrical and medical applications. Prevulcanization is usually done at the latex stage [115]. Prevulcanised latex is used for the production of cast or dipped articles. Superior processing natural rubber is prepared by blending vulcanized and unvulcanized lattices in 80:20 ratios before coagulation [116]. The following sections describe predominantly chemical methods of modification with physical methods limited to filler addition in view of its widespread application.

A) Chemical modification of NR

Chemical modification depends on the chemical reactivity of the NR molecule. Being unsaturated, NR is highly reactive and several chemical reactions can be carried out resulting in materials having entirely different properties.

Chemical modifications can be broadly grouped into 1) attachment of a pendant functional group 2) grafting of a different polymer at one or more points along the NR molecule and 3) intermolecular changes without the introduction of a new chemical group.

a) Chlorinated rubber

Chlorinated natural rubber is one of the first forms of chemically modified NR which finds use in many commercial applications [117]. Chlorination is carried out either in solution or latex [118] condition and the reaction involves substitution and cyclization along with addition of chlorine [119].

b) Epoxidised NR

Latex stage epoxidation of NR under controlled conditions gives epoxidised NR with improved resistance to hydrocarbons and oils, low air permeability, increased damping and good bonding properties which retains the high strength properties of NR [120-124]. Improvement of these properties depends on the degree of epoxidation. Two grades of epoxidised NR, ENR 25 and ENR 50 with 25 and 50 mole percentage epoxidation respectively have attained commercial importance. It is reported that the volume swelling value of ENR 50 in ASTM oils approaches that of medium acrylonitrile NBR and is superior to that of polychloroprene rubber. Another distinctive feature of ENR is the high degree of reinforcement achieved with silica fillers without the addition of silane coupling agent [125].

c) Constant viscosity and low viscosity NR

Increase in viscosity of NR during storage under ambient conditions known as storage hardening is caused by the crosslinking reaction involving the randomly distributed carbonyl groups present on the main rubber chain and the aminoacids present among the non-rubber constituents [126]. This can be inhibited by the addition of small amounts of hydroxyl amine hydrochloride to the latex before coagulation. These chemicals effectively block the carbonyl groups and preserve the Mooney viscosity of the rubber.

d) Addition of fillers

Fillers are one of the major additives used in natural rubber compounds and have a marked effect on rubber properties. Filler functions to modify the physical and to some extent, the chemical properties of vulcanizate [127] The mechanism of reinforcement of elastomers by fillers has been reviewed by several workers [128].They considered that the effect of filler is to increase the number of chains which share the load of a broken polymer chain. It is known that in the case of filled vulcanizates, the efficiency of reinforcement depends on a complex interaction of several filler related parameters. These include particle size, particle shape, particle dispersion, surface area, surface reactivity, structure of the filler and the bonding quality between the filler and the rubber matrix. In rubber industry, fillers in common use are carbon black, china clay, silica and calcium carbonate.

Contrary to the behaviour of most synthetic rubbers, natural rubber (NR) does not require the use of fillers to obtain high tensile strength. This is by virtue of its higher stress crystallization. However the use of fillers is necessary in order to achieve the level and range of properties that are required for technical reasons.

Reinforcing fillers enhance the already high tensile properties of gum natural rubber and they improve in particular the abrasion and tear resistances. The choice of the reinforcing filler as well as the dosage required could be quite different for different elastomers. The activity of fillers in NBR, SBR, BR and EPDM is often more pronounced because of their lack of strain crystallization and partially so in CR [129]. The variation in the effectiveness of fillers in NR and synthetic rubbers can be explained by the theory of over stressed molecules [130-131].

e) Grafting

NR can be modified to graft copolymers by polymerizing vinyl monomers either in latex or solution. Methylmethacrylate (MMA) [132], styrene [133] and acrylonitrile [134] are the prominent monomers used for grafting to NR. Among these, polymethyl methacrylate-grafted NR is the most popular and has been commercialized since mid 1950's in Malaysia under the trade name Heveaplus MG. Generally grafting can be achieved by two methods viz., by the use of chemicals or by irradiation with Gamma rays [135-136]. The developments in this topic during the period of 1950-1990 have been reviewed by Blackly [137]. In later years, considerable efforts have been made to achieve thermoplastic elastomer characteristics to these graft polymers by controlling the polymerization conditions [138-139]. Recently Schneider, et.al. reported that styrene and methylmethacrylate can be graft polymerized on NR latex in two step emulsion polymerization and can be used as toughening agent for SAN and polystyrene [140-141].

Poly (methylmethacrylate) is a hard plastic and when grafted on to NR, it increases the modulus of rubber depending on the percentage of poly (methylmethacrylate) grafted to it. The major use of Heveaplus MG is in adhesives [142]. In the automobile industry, for applications such as light shield, soft fronts, rear ends, rubbing strips and bumpers, blends of Heveaplus MG with NR can be used. It can also function as a compatibilizer in rubber/plastic blends [143]. Styrene grafted NR can find application in microcellular shoe soles in place of high styrene resin grade

Attempts to modify NR latex particles to produce NR interpenetrating networks was made by Hoursten, et.al.[145-146]. Recently Subramanian, et.al.[147] reported NR latex seeded emulsion polymerization of a highly hydrophobic monomer, vinyl neodeconates, under carefully controlled conditions. The DSC studies of the particles so formed shows a 5^0C rise in T_g of the NR indicating the formation of a relatively homogeneous semiinterpenetrating network or graft microphase.

f) Liquid NR (LNR)

Liquid NR is prepared by either thermal or chemical depolymerisation of NR. In thermal depolymerisation, rubber with 0.2 to 0.6 phr peptiser is first masticated to a Mooney viscosity of 25-30 and depolymerised by heating to 220°C-240°C under stirring for 3-7 hrs. LNR with viscosity average molecular weight in the range of 5000-20000 is reported to be produced by this method [148]. Chemical depolymerisation is carried out in the latex stage by a redox reaction involving phenylhydrazene and air [149]. The mechanism of depolymerisation involves the oxidation of phenyl hydrazine by air to give phenyl radical which through addition or transfer reaction initiates the formation of hydroperoxides. These peroxides lead by chain breakage to liquid NR with molecular weight range 6000-20000 depending on the quantity of reagent used. The low molecular weight NR has been found to have similar properties with NR, for example, affinity for ingredients during compounding, chemical behaviour and service life performance [150].

Liquid NR is used in elastic moulds, printing industry, as binder in grinding wheels, as reactive plasticizer [151] and as bulk viscosity modifier [152] in rubber compounds. Carboxy terminated liquid NR (CTNR) is reported as an adhesive in bonding rubber to rigid and non-rigid substrates [153].

g) Cyclised NR

Cyclised NR is a resinous material, obtained by treating NR with acidic reagents like sulphuric acid, p-toluene sulphonic acid and by Lewis acids like, $SnCl_4$, $TiCl_4$, BF_3 and $FeCl_3$. Cyclisation can be done in solid, solution or latex stages [154]. Cyclised NR is found to have increased softening point, density and refractive index of NR. The preparation of cyclised NR latex on commercial scale was well established as early as 1947 [155]. It is used in soleing compounds as on heating it changes to a hard thermoplastic material.

h) Elastomer blends

Normal methods of obtaining polymer blends are dry blending, solution blending, latex blending, etc. In these cases, no chemical bonds exist between the component polymers forming the blends. The flexibility associated with blending of elastomers is such that it can be carried out to suit the requirements of both producer and user.

Corish [156] has reviewed the general techniques for preparing elastomer blends namely, latex, solution and dry blending. Angrove [157] has reviewed latex blending giving particular attention to processing, properties and economics. Blends of NR/BR have been investigated by Blackly [158]. Blends of BR/SBR and BR/NR prepared by latex blending are reported to give a homogeneous dispersion of carbon black [159].

Walters and Keyte [160] indicate greater heterogeneity (NR/SBR blend) in solution mixed blends as did Livingstone and Rongone [161]. Shunda, et al. [162] prepared a satisfactory blend of NR/BR.

Combination of solution and latex blending is also used for master batching [158]. In the Columbian Hydrodispersion process, the elastomer blend is kept in solution and the black is dispersed in solution which transfers into the solution quite rapidly and produces a master batch. In the reverse process, the black dispersed in solvent is blended with latex so as to provide a good dispersion.

Dry blending is applied for the preparation of most of the elastomer blends and uses a mill, Banbury or extruder. This is because the process is economical and facilitates the incorporation of compounding ingredients in one operation. Again, blending is facilitated by mastication which not only reduces viscosity but under proper conditions provides opportunity for reaction (block or graft polymerization) and covulcanization. While Evans and Patridge [163] suggest that incorporation of all the ingredients in a single step is desirable, Shunda [162] suggests that mill mixing provides better dispersion. Avgeropolos, et al carried out extensive mixing studies on EPDM/BR blends [164].

These methods may be further divided into general categories as preblending [165] and phase mixing [166-167]. In the first case, the compounding ingredients are generally added to the premixed elastomers. In the phase mix, an attempt is made to control the specific location of filler and curing agents. This is generally accomplished by the preparation of separate master batches which are then blended mechanically [168-169]. Coran and coworkers [170-171] have applied dynamic vulcanization technique to enhance properties of EPDM/NR and ACR/NBR blends.

An important method for modification of natural rubber is the incorporation of various thermoset resins. These resins and published information on the use of each resin are discussed in subsequent sections.

1.4 Thermoset resins [172]

Thermoset resins change irreversibly under the influence of heat and/or catalysts into an infusible and insoluble material by the formation of covalently crosslinked, thermally stable networks. Important thermosetting resins are epoxy resins, unsaturated polyesters, phenolics, alkyds, vinyl esters, aminoplasts, urethanes etc. [173].

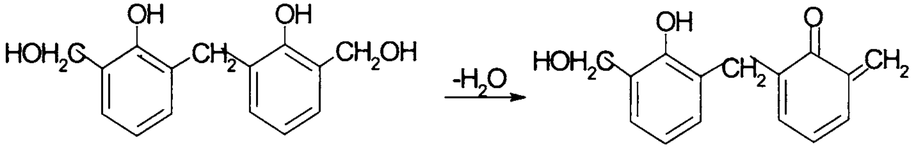
Phenol formaldehyde resins are used to vulcanize olefin rubbers, but again practical use is confined to butyls, halogenated butyls and EPDM, stannous chloride being used as an accelerator. Halogenated resins can also be used. If halogenated phenolic resins are used, the presence of reactive accelerators may not be required.

There are two possible mechanisms for resin cure of unsaturated rubbers. The Chroman mechanism and allyl hydrogen mechanism [174].

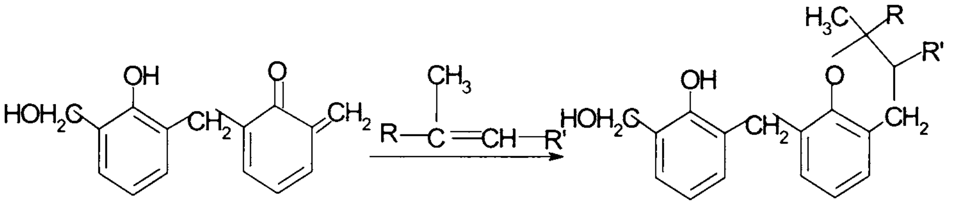
A) Chroman mechanism

a) Formation of quinone methide

At high temperature water is eliminated from the resin leading to the formation of a quinone methide.

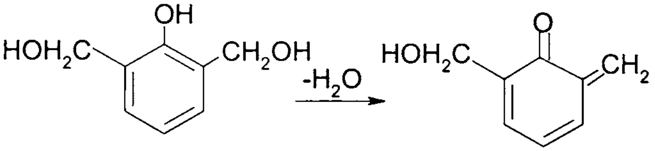


b) Reaction between quinone intermediate and rubber



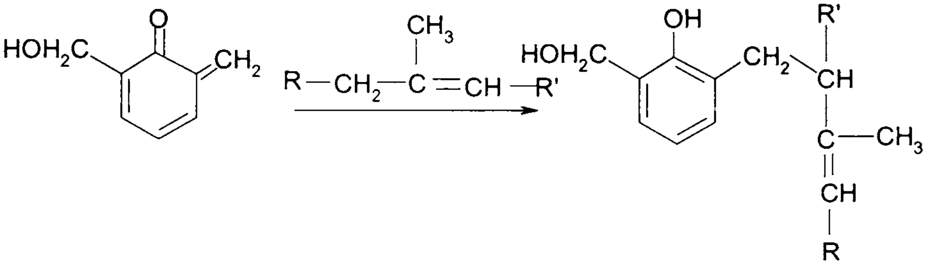
B) The allyl hydrogen mechanism

a) Formation of quinone methide



b) Reaction of quinone intermediate and rubber

Quinone methide abstracts an allyl hydrogen from the unsaturated rubber.



But a systematic study of the effect of various thermosets has not been

1.4.1 Epoxy resins

Epoxy resins are characterized by the presence of more than one 1, 2 epoxide groups per molecule. The three membered ring structure is also known as the epoxide, oxirane, or ethoxyline group (Fig.1.17). This group may lie within the body of the molecule but is usually terminal. The three membered epoxy ring is highly strained and is reactive to many substances, particularly proton donors.

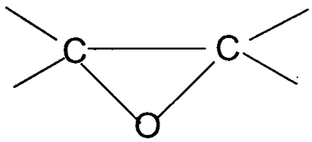
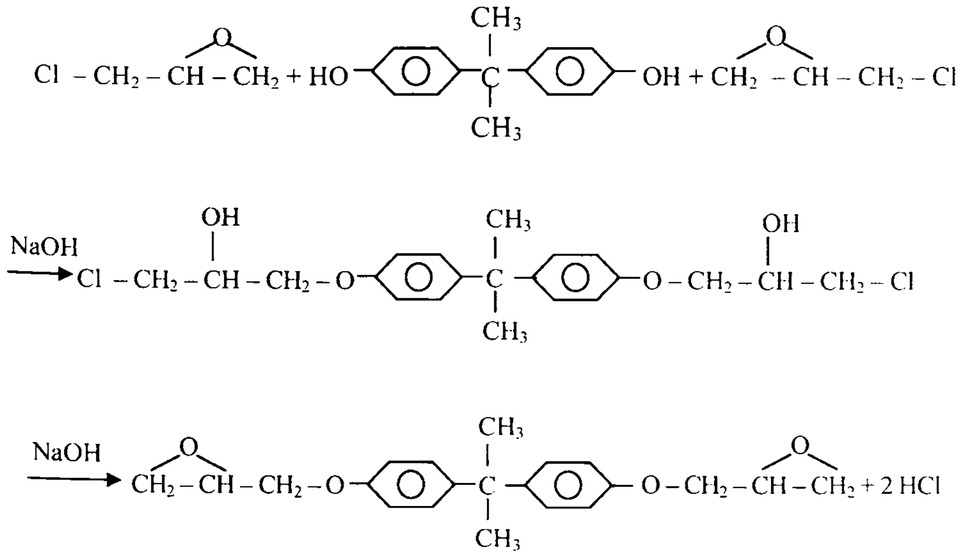


Fig.1.19 Epoxy ring

The first and still the most important class of commercial epoxy resins is the reaction product of bis-phenol A (BPA) and epichlorohydrin in the presence of sodium hydroxide. It is called the diglycidyl ether of bis-phenol A (DGEBA). The reactions involved in its preparation are shown below.



There are a large number of epoxy resins in use. High molecular weight resins are prepared by reducing the excess of epichlorohydrin and reacting under strongly alkaline conditions. The nonepoxy part of the molecule may be aliphatic, cyclo-aliphatic or aromatic hydrocarbon. It may be non-hydrocarbon and polar also. Treatment with curing agents gives insoluble and intractable thermosets. Epoxy resins can be cured at room temperature but quite often heat is applied to accelerate and improve curing. Hardeners include anhydrides, amines, polyamides etc.

The resin is mixed with a curing agent or hardener, its choice depending upon the processing methods, conditions and the properties required. The reactivity of the epoxy ring is enhanced by the presence of the ether linkage separated from it by a methylene unit.

In general, primary and secondary amines act as reactive hardeners whereas tertiary amines are catalytic [173]. Diethylene triamine (DETA) and triethylene tetramine (TETA) are highly reactive primary aliphatic amines used for room temperature cure of epoxy resins.

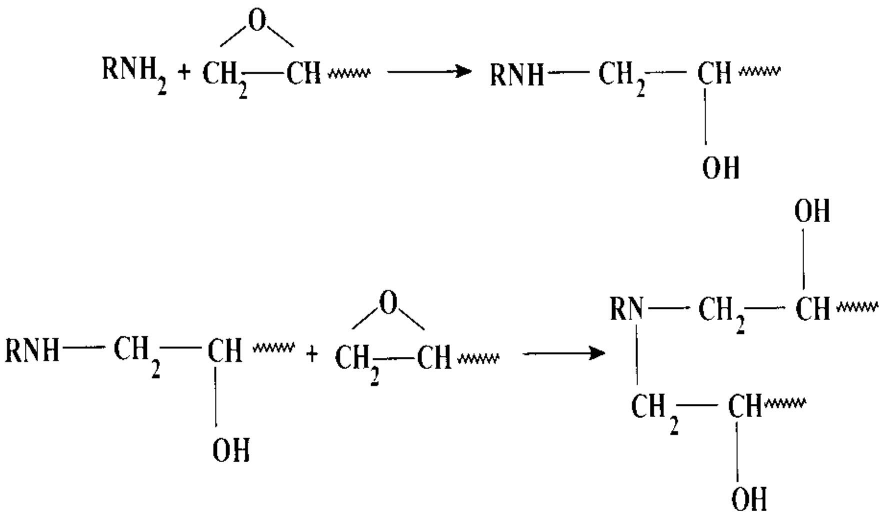
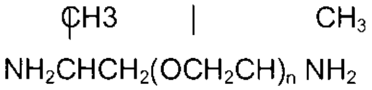
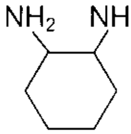
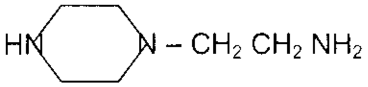
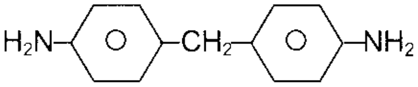
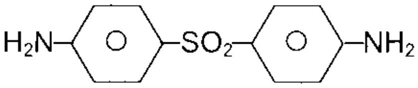
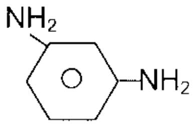


Table 1.7 Some commercial amine curing agents [173]

Formula	**Name**
$NH_2CH_2CH_2NHCH_2CH_2NH_2$ DETA,	Diethylenetriamine
$NH_2CH_2CH_2NHCH_2CH_2NH_2NHCH_2CH_2NH_2$ TETA,	Triethylenetetramine
 $NH_2\underset{}{\overset{CH_3}{\overset{\mid}{C}}}HCH_2(OCH_2\overset{CH_3}{\overset{\mid}{C}}H)_n\,NH_2$	Poly (oxypropylene) diamine
DAC, 	1,2–diamino cyclohexane
AEP, 	N-amino ethyl piperazine
MDA, 	Methylene di aniline
DDS, 	4,4'diaminodiphenylsulfone
MPDA, 	m – phenylene diamine

Epoxy resins are commercially used in coating, adhesive and structural applications. They have excellent adhesion to various substrates, outstanding chemical and corrosion resistance, very good electrical insulation, high tensile, flexural and compressive strengths, thermal stability, a wide range of curing temperatures and low shrinkage upon cure.

Several researchers have investigated the use of elastomers for toughening of epoxy resin [175-176]. But very few investigators have explored the modification of rubber using epoxy resins. Hani investigated the mechanical properties of composite material using natural rubber with epoxy resin [177]. Chuayjuljit S. et.al. investigated the behaviors of epoxy resin blended with epoxidized natural rubber [178]. They found that the impact strength of epoxy resin can be improved by blending with ENRs. Tensile strength and Young's modulus were found to decrease with an increasing amount of epoxide groups in ENR and also with an increasing amount of ENR in the blends. H. Ismail et.al studied the compatibilizing effect of epoxy resin on polypropylene/NBR blends. They found that the mechanical properties were improved [179]. Ismail Zainol et al. modified epoxy resin with liquid natural rubber and cure characteristics and mechanical properties were studied [180].

1.4.2 Polyester resins

A large number of thermoset polyester resins are commercially available and these can be conveniently classified into unsaturated polyesters, alkyds, vinyl esters etc.

a) Unsaturated polyester resin (UPR) [181]

Unsaturated polyesters are prepared by reacting a mixture of unsaturated and saturated dicarboxylic acids with diols. The condensate is then dissolved in an unsaturated co-reactant diluent like styrene, methyl methacrylate or diallyl phthalate to get a resin formulation. Styrene is the commonly used diluent. General purpose (GP) UP resin is prepared by the condensation of propylene glycol (PG) with a mixture of maleic anhydride (MA) and phthalic anhydride (PA). When crosslinking is initiated with the help of a catalyst and an accelerator styrene facilitates crosslinking at the sites of unsaturation in the polyester chains. More of the saturated acid reduces the number of crosslinking sites and consequently the crosslink density and brittleness of the cured resin. Since crosslinking occurs via free radical addition mechanism across the double bonds in the polyester chain and the reactive diluents no volatiles are given off during cure.

The initiators are activated by heat, multivalent metal accelerators or tertiary aromatic amine promoters which decompose the peroxides into free radicals. Two types of initiating systems are employed for cross-linking unsaturated linear polyesters with styrene- those effective at elevated temperature and those effective at room temperature. The most important initiators used at elevated temperature are peroxides which liberate free radicals as a result of thermal decomposition. The most widely used peroxide is benzoyl peroxide. Initiating systems effective at room temperature consist of mixtures of peroxide and an accelerator. The important peroxy materials used are methyl ethyl ketone peroxide (MEKP), cyclohexanone peroxide and benzoyl peroxide.

UPR has the following typical structure.

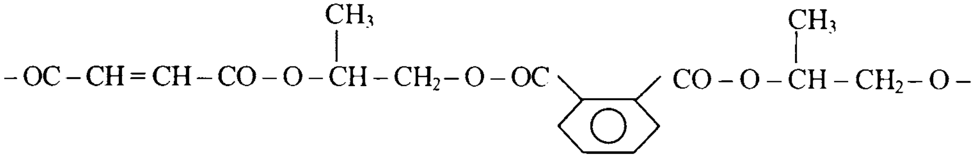


Table 1.8 Conventional catalyst system for unsaturated polyesters.

Catalyst	**Activator**	**Processing temperature (°C)**
Benzoyl peroxide	Dimethyl aniline	0-25
Methyl ethyl ketone hydroperoxide (MEKP)	Cobalt octoate	25-35
Cumene hydroperoxide	Manganese naphthenate	25-50
Lauryl peroxide	Heat	50-80
t-Butyl peroctoate	Heat	80-120
Benzoyl peroxide	Heat	80-140
2,5-Dimethyl-2,5-di (2-ethyl hexanoylperoxy) hexane	Heat	93-150
t-Butyl perbebzoate	Heat	105-150
di-t-Butyl peroxide	Heat	110-160
Dicumyl peroxide	Heat	130-175

A) Grades of polyester resins

A wide range of UP resins can be produced by appropriate choice of the following aspects: type and proportion of raw materials, degree of condensation, acid and hydroxyl numbers and the content and choice of cross-linking monomers and other additives. Important grades are the following.

a) General purpose (GP) orthophthalic resins (UPR)

UPR are blends of styrene with the condensation product of PG and a mixture of MA and PA. They are the cheapest and most widely used grade of polyester resin. These resins are used for making numerous products for indoor applications such as laminates, statues, pipes etc. and for low cost applications like telephone booths, tailors mannequins etc.

b) Isophthalic polyester resin (IUPR)

IUPRs are prepared by the condensation of a mixture of isophthalic acid (IA) and MA with PG in a two-stage process. The condensate obtained is mixed with styrene monomer to get an isophthalic resin formulation. These resins have better chemical and thermal resistance and are used as a matrix for high quality fibre-reinforced plastics used for outdoor applications. They are used in the manufacture of land transport vehicle bodies, sports car bodies, boat hulls, kiosks, aircraft radomes, swimming pools, water tanks, sports equipment, high pressure pipes of chemical plants, etc.

c) Bisphenol resin

These are polyesters prepared by condensing propoxylated or ethoxylated bisphenol A and a mixture of fumaric acid and phthalic acid or isophthalic acid. These resins are used for making tough FRP products for specialised applications. They have resistance to both acids and alkalies and have a higher heat deflection temperature.

d) Other grades

Transparent grade polyester resin is used for making roofing sheets and other transparent FRP panels. Special grade resins such as *elastic grades* have high flexibility and elongation at break due to the incorporation of long chain monomers and are used in a mixture with brittle types. *Flame resistant resins* contain chlorine or bromine in the polyester chain or in added compounds. *Chemical resistant resins* are synthesised from special raw materials like isophthalic acid, terephthalic acid, neopentyl glycol or ethoxylated or propoxylated bisphenol A.

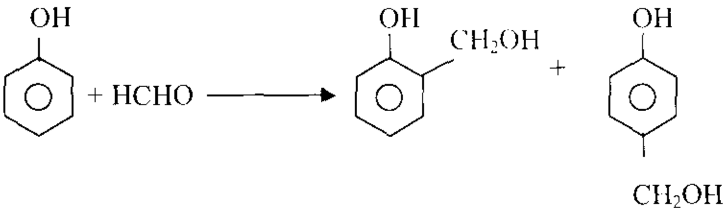
Table 1.9 Properties of commercial (GP) UP resins in the as-supplied state [182]

Property	Test method	Test value
Acid number	ASTM D 4662-87	10-30 mg KOH/g
Styrene content	DIN 16945	25-45%
Viscosity at 25°C	ASTM D 2393	0.2-4.5 Pa.s
Specific gravity at 25°C	ASTM D 4662-87	1.07-1.3
Flash point	DIN 51755	35°C
Refractive index at 25°C	DIN 53491	1.524-1.559

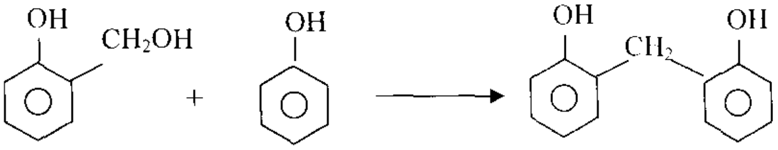
S. Chuayjuljit et.al. have prepared miscible blends of UPR and NR and studied the properties [183]. The samples prepared from ungrafted natural rubber exhibited the aggregation of the rubber component, whereas the samples prepared from grafted natural rubber showed good dispersion of the rubber component in a glassy matrix of UPE resin. They found that the amount of polystyrene grafted onto natural rubber and the graft copolymer content in polymer blend significantly affect the mechanical properties of the blend samples. Blends of natural rubber and UPR were prepared by P. Pachpinyo et.al [184]. They used different dispersion aids for preparing blends. It was found that, regardless of the type of dispersion aid, the impact strength of blended UPR samples was higher than that of the pure UPR samples. S.L. Abd-El-Messieh et.al.investigated the use of UPR as a compatibilizer in SBR/PVC blends [185]. S.H. El-Sabbagh et.al. have synthesized blends of natural rubber with aromatic polyester resin (186). They found that, better properties were obtained for the blends than that of rubber vulcanizates Most of these works are related to toughening of UPR with rubber particles [187].

1.4.3 Phenolic resin [188]

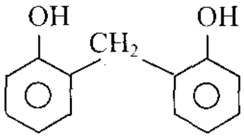
Phenolic resins were the first polymeric resins produced commercially from simple low molecular weight compounds. Phenol formaldehyde (PF) resins are prepared by the polycondensation between phenol and formaldehyde in the presence of either an acid or a base catalyst. The nature of the product is dependent on the type of catalyst and the mole ratio of reactants. The initial phenol-formaldehyde reaction products may be of two types, novolacs and resols. Novolacs are prepared by reacting formaldehyde and a molar excess of phenol under acidic conditions. Initially, the reactants slowly react to form o- and p- hydroxyl methyl phenols.



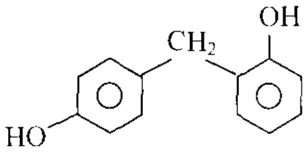
These rapidly condense to form bis(hydroxyphenyl) methane (HPM).



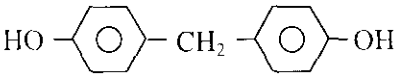
There are three possible isomers and their proportions depend on the pH of the reaction. 2,4'- and 4,4'- isomers are the main products under acidic conditions.



2,2' HPM

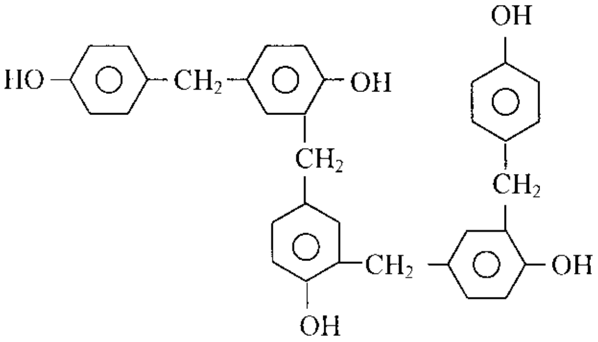


2,4' HPM



4,4' HPM

These isomers subsequently react with formaldehyde to form methylol derivatives which rapidly react with more phenol to form novolac resins. These resins are linear molecules containing 5-6 benzene rings. A typical example of the many possible structures is shown below.

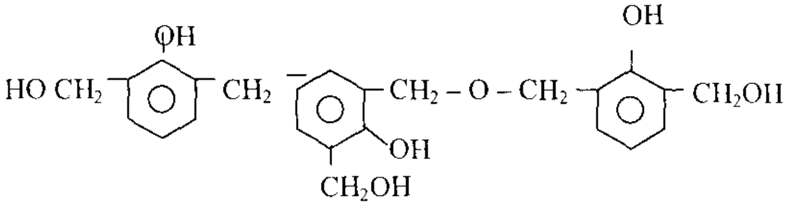


The resin can be stored for any length of time without crosslinking. Further crosslinking is affected by heating with compounds like hexamethylene tetramine which can form methylene bridges. The novolacs are also referred to as two-stage resins. The properties of an acid catalysed phenolic resin are shown in Table 1.10 . The typical acid catalysts used for novolac resins are oxalic acid, sulphuric acid, sulphonic acid and occasionally phosphoric acid.

Table 1.10 Novolac resin properties [189]

Property	
Formaldehyde-phenol molar ratio	0.75
NMR analysis	
2,2'(%)	6
2,4'(%)	73
4,4'(%)	21
GPC analysis	
M_n	900
M_w	7300
Phenol	4%
Water (%)	1.1
T_g(°C)	65
Gel time (s)	75

A resol is prepared by reacting phenol with an excess of formaldehyde under basic conditions. Although methylol formation is rapid subsequent condensation is slow. Hence low molecular weight liquid resols containing 2-3 benzene rings are formed. When the resol is heated crosslinking via the uncondensed methylol groups occurs. Resols are hence known as one-stage resins. A possible resol structure is as follows.



Phenolic resins are mainly used for moulding, bonding, surface coating, adhesive and laminating applications.

The properties of a resol resin are given in Table 1.11

Table 1.11 Properties of resol resins [189]

Property	
Formaldehyde-phenol ratio	2.0
GPC analysis	
M_n	280
M_w	500
Phenol(%)	6
T_g (°C)	35
Gel time (s)	65

British Resin Products Limited has developed a range of synthetic phenolic resins to reinforce both synthetic and natural rubbers [190]. Giller, Chow and Steiner reported that phenolic resin (novolac types) and hexamine, when incorporated in the rubber, cure in the normal way during vulcanization to increase hardness of the vulcanizates [191,192]. V. Nigam et al. studied the relative efficiency of different fillers eg., phenolic resin, carbon black and carbon black plus phenolic resin hybrid system in nitrile rubber vulcanizates for improvement of physico-mechanical properties [193]. Murke [194] studied the stabilization of NBR latex with cresol-formaldehyde condensate and observed that the coagulum compounded and vulcanized gave a product with good elasticity and thermal stability. Studies have also been carried out with NBR and phenolic resin based on cashew nut shell liquid [195,196]. Novolac type phenolic resins with hexamine have been commonly used as reinforcing filler as well as crosslinking agent in NBR for seals, valves and gasket applications. The chemistry of phenol-formaldehyde resin vulcanization of EPDM rubber, for the evidence of methylene crosslinks has been studied by Duin and Souphanthong [197]. Chaves et al. investigated the effects of phenolic resin on processing and mechanical properties of PP-EPDM-NBR blends [198]. Verghese et al studied the adhesive properties of neoprene-phenolic blends [199]. Nakason et al investigated the effect of phenolic resin as a compatibilizer in thermoplastic vulcanizates based on NR/HDPE blends [200].

1.4.4 Epoxidised phenolic novolacs [201]

Epoxidised phenolic novolac and cresol novolac resins are made by glycidylation of phenol/cresol – formaldehyde condensates (novolacs) obtained from acid catalysed condensation of phenol/cresol and formaldehyde. This gives random ortho and para methylene bridges (Fig.1.20). Epoxidation of novolacs with an excess of epichlorohydrin minimizes the reaction of phenolic hydroxyl groups with glycidylated phenol groups and prevents branching. A wide variety of novolac resins based on a range of phenols including cresols, ethyl phenols, t-butyl phenols, resorcinol, hydroquinone and catechol may be used to prepare epoxy novolac resins. An increase in the molecular weight of the novolac increases the functionality of the resin. The high functionality of novolacs increases the crosslink densities and improves thermal and chemical resistance. EPN resins range from a high viscosity liquid to a solid. The epoxy functionality is between 2.2 and 3.8. Commercial EPN 1138 (Ciba-Geigy) has a viscosity of 35000 mPa.s and a weight per epoxy value (wpe) of 178.

EPN 1139 has low viscosity (1400mPa.s) with wpe 175. The major applications of epoxy novolac resins have been in heat resistant structural laminates, electrical laminates, chemical resistant filament wound pipes and high temperature adhesives.

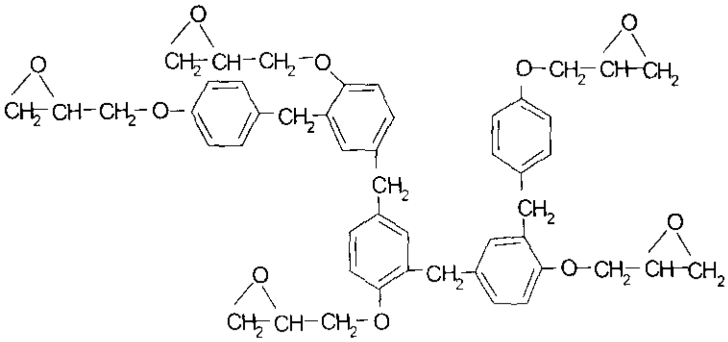


Fig.1.20 Typical structure of EPN

e) Miscellaneous resins

Other thermosetting resins are alkyd resins, vinyl esters, aminoplasts and polyurethanes. Alkyd resins are produced by reacting a polyhydric alcohol, usually glycerol, with a polybasic acid, usually phthalic acid and the fatty acids of various oils such as linseed oil, soyabean oil and tung oil. They are nowadays employed mostly in the surface coatings field. Vinyl esters are chemically the reaction products of epoxy resin and ethylenically unsaturated monocarboxylic acids like methacrylic acid with styrene added as a coreactant. Aminoplasts are a range of resinous polymers produced by the interaction of amines and amides with aldehydes. The important polymers belonging to this class are urea-formaldehyde and melamine- formaldehyde resins. Polyurethanes (PU) are polymers, which contain urethane groups (-NH-COO-) in the main chain formed by the reaction of a polyfunctional isocyanate and a polyol.

1.5 Scope and objectives of the thesis

The combination of high tensile strength and a high rebound elasticity, very good low temperature flexibility, excellent dynamic properties and very low heat build up make NR indispensable in several applications despite the availability of a great number of synthetic elastomers. However, due to the presence of extensive unsaturation and lack of polar groups, the age resistance and oil resistance of NR is very poor. The aim of this investigation is to improve the age resistance and oil resistance of NR by incorporating various thermoset resins.

The specific objectives of the study can be listed as follows.

1. To prepare epoxy resin (DGEBA) under controlled conditions and study its effect on the properties of NR. Epoxidised cardanol will also be synthesized and blended with NR for possible improvement in properties.
2. To prepare phenolic novolac resin of various formaldehyde/phenol ratios and use for modification of NR. Cardanol novolac resins will also be similarly prepared and employed for modification.
3. To prepare epoxidised novolac resins starting from phenol, p- cresol and cardanol and study the effects on the properties of NR. The effect of formaldehyde /phenol ratio of the novolacs will also be investigated.
4. To prepare unsaturated polyester resin of various maleic anhydride/phthalic anhydride ratios and study the effect on the properties of NR vulcanizate. It is also planned to study the effect of commercial UPR and IUPR on the properties of NR.

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Chapter

2

MODIFICATION OF NATURAL RUBBER USING EXPOXY RESIN

2.1 Introduction

In this chapter, effects of adding different epoxy resins on the properties of natural rubber are investigated. Both commercial and synthesized resins were used for modification. Cure characteristics and mechanical properties were studied. Properties were studied for both gum and filled samples. Epoxidised cardanol is another substance used for modification. Preparation of epoxy resins are also discussed.

2.2 Experimental

2.2.1 Materials

Bisphenol A (LR, M.W=228.29, 97% assay, MP=154-157°C) and epichlorohydrin (LR, M.W=92053, 98% assay, BP=114-118oC) were supplied by Research Laboratory, Mumbai, India. Benzene (M.W=78, 98% assay) and caustic soda (M.W=40, 97.05% assay) were obtained from E. Merck India Ltd, Mumbai. Commercial grade Epoxy Resin (103), and the room temperature amine hardener 301(Polyamine) were supplied by M/S Sharon Engineering Enterprises, Cochin. Cardanol was separated from cashew nut shell liquid (supplied by Vijayalakshmi Cashew Exports, Kollam, India) by distillation under reduced pressure. The pale yellow fraction collected at 206-208°C is cardanol.

Cardanol: Cashew nut shell liquid (CNSL) occurs as a viscous liquid in the soft honeycomb of the shell of the cashew nut. Cashew nut is the crop of the cashew tree, *Anacardium occidentale L* native to Brazil. The main constituents of CNSL are phenolic compounds with long side chain substitution at the meta position. Being cheap, CNSL can be a substitute for phenol in many applications. The use of CNSL in place of phenol is an excellent example of gainful utilization of a cheap agro by-product [1].

Naturally occurring CNSL contains mainly four components: cardanol, cardol, anacardic acid, and 2-methyl cardol. These components of CNSL are themselves mixtures of four constituents differing in side- chain unsaturation, namely saturated, monoene, diene, and triene. The structures of the side chains of varying degrees of unsaturation occurring in the four major components of CNSL are identical. The structure of cardanol is shown in Fig.2.1.

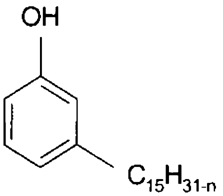


Fig.2.1 Structure of cardanol

For different values of n, the following structures result for the side chain.

n=0, $(CH_2)_7$-$(CH_2)_7CH_3$; n=2, $(CH_2)_7$ CH =CH $(CH_2)_5CH_3$

n=4, $(CH_2)_7$ CH=CH - CH_2 - CH=CH $(CH_2)_2CH_3$

n=6, $(CH_2)_7$ - CH =CH - CH_2 - CH =CH - CH_2 - CH =CH_2

The components of cardanol are identified as 3-pentadecyl anisole, 3- (8′- pentadecenyl) anisole, 1-methoxy-3-(8′, 11′- pentadecadienyl) benzene and 1-methoxy-3-(8′, 11′, 14′- pentadecatrienyl) benzene [2,3].

Natural rubber (*ISNR-5*) was obtained from Rubber Research Institute of India; Kottayam, Kerala. Specifications of ISNR-5 are given below.

Mooney viscosity ML(1+4) at 100°C - 82

Dirt content, % by mass, max - 0.05

Volatile matter, % by mass, max - 1

Nitrogen, % by mass, max - 0.07

Ash, % by mass, max - 0.60

Initial plasticity, min - 30

Plasticity retention index - 60

Zinc Oxide (activator) was supplied by M/s Meta Zinc Ltd, Mumbai and had the following specifications.

Specific gravity - 5.5
ZnO content - 98%
Acidity - 0.4%
Heat loss, max (2hrs. at 100°C) - 0.5%

Stearic acid (co-activator) was supplied by Goderej Soaps Pvt Ltd, Mumbai and had the following specifications.

Specific gravity - 0.85
Melting point - 50-69°C
Acid number - 185-210
Iodine number - 9.5
Ash content - 0.1%

Mercaptobenzothiazol disulphide (*MBTS*) (accelerator) was supplied by Bayer Chemicals, Mumbai and had the following specifications.

Specific gravity - 1.34
Melting point - 165°C

Tetramethyl thiuram monosulphide (*TMT*) (accelerator) was supplied by Flexys, Netherlands. It had the following specifications.

Melting point - 108°C
Moisture content - 0.12%
Ash content - 0.03%

Precipitated silica used was commercial grade supplied by Sameera Chemicals, Kottayam. The specifications are given below.

pH (5% aqueous solution) - 6.3
Specific gravity - 2.03
SiO2 in dried sample - 90%
Loss on heating (105°C) - 5.5%

High Abrasion Furnace Black (N330) used in the study was supplied by M/s Philips Carbon Black India Ltd., Kochi India. It had the following specifications.

Appearance - black granules
DBP absorption - 102 cc/ 100g
Pour density - 376kg/m^3
Iodine number - 82

Sulphur (crosslinking agent), was supplied by Standard Chemicals Co. Pvt.Ltd. Chennai and had the following specifications.

Specific gravity - 2.05
Acidity, max - 0.01%
Ash, max - 0.015
Solvents used

Toluene was supplied by Fine Chemicals Ltd.,Mumbai and had the following specifications.

Boiling point - 95°C
Acidity - 0.012
Alkalinity - 0.012
Non volatile matter - 0.002%

Acetone (AR) was supplied by Qualigens Fine Chemicals, India. It had the following specifications.

Minimum assay - 99.5
Wt / ml at 20°C - 0.789-0.791

2.2.2 Synthesis of epoxy resin

a) DGEBA [4]

Bisphenol A (1mole) was dissolved in a mixture of an excess of epichlorohydrin (6 moles) and 50cc water in a one litre three necked flask. The flask was equipped with a mechanical stirrer, thermometer and a Liebig's condenser. The mixture was heated gently (95-100°C) over a water bath till the epichlorohydrin began to boil. Heating was stopped and caustic soda (2moles) was added two pellets at a time down the condenser. The reaction was allowed to subside before more alkali was added. When all the caustic soda pellets had been added, the mixture was heated for 45 minutes. Heating was stopped as the mixture turned viscous. The excess epichlorohydrin was removed by vacuum distillation. The remaining mixture was extracted with benzene to precipitate sodium chloride which was removed by filtration under vacuum. The filtrate was distilled under vacuum to remove benzene and dried in vacuum for about 3 hours. The resin formed was a pale yellow viscous and glassy liquid. The properties of the resin thus synthesized were compared with those of commercial epoxy resin. The commercial and synthesized epoxy resins are designated as com.EPR and synth. EPR respectively.

b) Preparation of epoxidised cardanol [5]

Cardanol (1mole) was dissolved in a mixture of an excess of epichlorohydrin (2moles) and 20 cc water in a one litre three necked flask. The epoxidation was done as per the procedure described earlier for epoxy resin. The resultant dark brown epoxy cardanol resin was dried in vacuum for 3 hours. The epoxide equivalent of the resin was determined. The resin was characterized by IR spectroscopy.

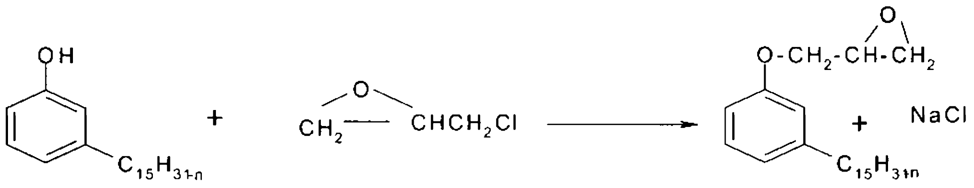


Fig. 2.2 Epoxidation of cardanol

2.2.3 Determination of epoxide equivalent (Weight per epoxide)

The epoxy content of liquid resins is expressed as weight per epoxide (wpe) or epoxide equivalent which is defined as the weight of the resin containing one gram equivalent of epoxide. The epoxy content can also be expressed as equivalents / Kg of the resin.

A common method of analysis of epoxide content of liquid resins involves the opening of the epoxy ring by a hydrogen halide (hydrohalogenation)[6]. Weight per epoxide values of the synthesized and commercial epoxy resins were determined by the pyridinium chloride method as per ASTM D 1652-73.

0.1 to 0.2 g of the epoxy resin was mixed with 2ml HCl in 25ml pyridine. The mixture was heated to reflux on a water bath for 45 minutes. The solution was cooled to room temperature and the unreacted acid present in it was estimated by back titration with standard NaOH solution (0.1N) using phenolphthalein indicator. A blank experiment was also carried out under the same conditions.

Epoxide equivalent = N x V/w, where N is the strength of the alkali, V the volume of the alkali used up and w the weight of the resin. Epoxide equivalent is obtained as eq/Kg from which wpe value of the resin can be calculated.

2.2.4 Compounding and curing

The mixes were prepared on a laboratory size two roll mill (16x33cm) at a friction ratio 1:1.25. The mixing was done according to ASTM D 3184-89(2001). The rubber was initially masticated well on the mill. The epoxy resin was incorporated into the gum rubber at various proportions (1, 2, 3& 4% weight of the rubber). Before addition the epoxy resin was mixed with 10% by weight of a room temperature amine hardener (301). Then the compounding ingredients were added in the following order: activators, accelerators, and sulphur. After mixing, the stock was passed six times through tight nip and finally sheeted out. Commercial epoxy resin, synthesized resin and epoxidised cardanol were all used in the same manner for compound preparation. Both gum and filled NR compounds were prepared. The formulations of the mixes are given in Table 2.1 and 2.2.

Table 2.1 NR formulation for varying resin content

Sample	NR (phr)	Resin (%)	ZnO (phr)	St.acid (phr)	MBTS (phr)	TMT (phr)	S (phr)
1	100	0	4	2	0.8	0.2	2.5
2	100	1	4	2	0.8	0.2	2.5
3	100	2	4	2	0.8	0.2	2.5
4	100	3	4	2	0.8	0.2	2.5
5	100	4	4	2	0.8	0.2	2.5

Table 2.2 Formulation of HAF black filled NR samples

Sample	NR (phr)	Resin (phr)	ZnO (phr)	St.acid (phr)	HAF (phr)	Ar.oil (phr)	MBTS (phr)	TMT (phr)	S (phr)
1	100	0	4	2	30	3	0.8	0.2	2.5
2	100	1	4	2	30	3	0.8	0.2	2.5
3	100	2	4	2	30	3	0.8	0.2	2.5
4	100	3	4	2	30	3	0.8	0.2	2.5
5	100	4	4	2	30	3	0.8	0.2	2.5

Cure characteristics of the mixes were determined at 150°C and vulcanization to optimum cure time was carried out in an electrically heated hydraulic press at 150°C. The moldings were cooled quickly in water at end of the curing cycle and stored in a cool dark place for 24 hours prior to physical testing.

2.2.6 Quality evaluation

The following evaluation methods were adopted for the compounds/ vulcanizates.

a) Cure characteristics

Cure characteristics of the mixes were determined at 150°C using Rubber Process Analyser, RPA 2000 supplied by Alpha Technologies, USA as per ASTM Standard, D 2084-01.

The instrument uses two directly heated opposing biconical dies with a die gap of 0.487 that are designed to achieve a constant shear gradient over the entire sample chamber. The lower die is oscillated at 50rpm and the torque transducer on the upper die senses the force being transmitted through the rubber. To determine the cure characteristics of the rubber compound, approximately 5g of the sample was placed in a sealed biconical cavity under pressurized conditions and submitted to harmonic torsional strain by the oscillation of the lower die through a small deformation angle of about 3^0 and the transmitted torque is measured. The following data can be taken from the torque-time curve.

(i) Minimum torque, M_L

Measure of the stiffness of the unvulcanized test specimen. It is the torque shown by the mix at the test temperature before the onset of cure.

(ii) Maximum torque, M_H

Measure of the stiffness or shear modulus of the fully vulcanized test specimen at the vulcanization temperature. It is the torque recorded after curing of the mix is completed.

(iii) Scorch time, T_{10}

It is the time taken for attaining 10% of the maximum torque.

(iv) Optimum cure time, T_{90}

Time taken for attaining 90% of the maximum torque.

Optimum cure time, (T_{90}) is the time corresponding to a torque equal to

$0.9(M_H-M_L) + M_L$ ....(2.1)

(v) Cure rate index (CRI)

which is a measure of the rate of cure was calculated using the formula,

$CRI = 100 / T_{90}-T_{10}$ ....(2.2)

(vi) Alpha value

Alpha (α) represents a filler specific constant independent of the cure system and closely related to the morphology of the filler [7]. This parameter has been used to characterize the filler structure existing in vulcanizates, in particular for carbon black. A low value of α indicates good filler dispersion.

$$\frac{M_H - M_L}{M_H^0 - M_L^0} - 1 = \alpha \frac{m_{filler}}{m_{rubber}} \quad \text{...(2.3)}$$

Where, M_H and M_L correspond to the maximum and minimum rheometric torques of compounds with filler and M_H^0 and M_L^0 that without filler. m_{filler} and m_{rubber} are mass of filler and rubber respectively.

(vii) Kinetics of vulcanization

The kinetics of vulcanization was studied from rheograph by the method [8] given below. The general equation for the kinetics of a first order chemical reaction is

$$\ln(a - x) = -kt + \ln a \quad \text{...(2.4)}$$

where, a = initial reactant concentration, x = reacted quantity of reactant at time t, and k = first order rate constant.

For the vulcanization of rubber, the rate of crosslink formation is monitored by measuring the torque developed during vulcanization. The torque obtained is proportional to the modulus of rubber. So the following substitutions can be made.

$$(a\text{-}x) = M_H - M_t \quad \text{..(2.5)}$$

$$a = M_H - M_L \quad \text{...(2.6)}$$

M_H and M_L are the maximum and minimum torques, and M_t, the torque at time t. So the equation becomes

$$\ln(M_H - M_t) = -kt + \ln(M_H - M_L) \quad \text{..(2.7)}$$

This equation is of the general form of a straight line which means that the cure reaction follows first order kinetics.

The energy of activation E_a of curing was determined using Arrhenius equation [9] given below.

$k = Ae^{-Ea\ RT}$ ....(2.8)

$\log k = \log A - E_a / 2.303RT$ ....(2.9)

where, A is the Arrhenius constant, E_a the activation energy, R the universal gas constant and T, the absolute temperature.

b) Tensile properties

The *tensile strength* is defined as the force per unit area of cross section, which is required to break the test specimen, the condition being such that the stress is substantially uniform over the whole of the cross section. The *elongation at break (EB)* is the maximum value of elongation expressed as a percentage of the original length. Within the elastic limit, the ratio of the tensile stress (force per unit area) to the actual strain is called *modulus* or more accurately it is the slope of the tensile stress-strain curve at a given strain.

The tensile properties were measured using Shimadzu Autograph AG-1 Series' Universal Testing Machine (UTM) with a grip separation of 40mm, using a crosshead speed of 500mm/min as per ASTM D 412-1998 (Method A). All the tests were carried out at 28±2°C. Dumb bell specimens were punched out of the moulded sheet along the mill grain direction using a dumb bell die (C-type). The thickness of the narrow portion was measured using a digital thickness gauge. The sample was held tight by the two grips or jaws of the UTM, the lower grip being fixed. The tensile strength, elongation at break and modulus were evaluated and printed out after each measurement by the microprocessor.

c) Tear strength

This test was carried out as per ASTM D 624-1998 using unnicked, 90° angle test pieces. The samples were cut from the compression moulded sheets parallel to the mill grain direction. The test was carried out on Shimadzu Autograph AG-1 Series' Universal Testing Machine (UTM) with a grip separation of 40mm, using a crosshead speed of 500mm/min. The test temperature was 28±2°C.

d) Hardness

The hardness (Shore A) of the moulded samples was determined using Zwick 3114 Hardness Tester in accordance with ASTM D 2240-1997. The tests were performed on unstressed samples of 30mm diameter and 6mm thickness. The readings were taken after 10 seconds of indentation since firm contact had been established with the specimen.

e) Abrasion loss

The abrasion resistance of the samples was determined using a DIN Abrader (DIN 53516). Samples having a diameter of 6±0.2mm and 12mm thickness were prepared as per ASTM D 3183 and the abrasion loss was measured as per ASTM D 5963-04. The samples were kept on a rotating sample holder and a 10N load was applied. Initially a pre-run was given for the sample and its weight taken. The weight after final run was also noted. The difference in weight is the weight loss on abrasion. The volume loss on abrasion was calculated using the equation

Volume loss on abrasion = weight loss on abrasion/ specific gravity of the sample

Abrasion resistance is the reciprocal of volume loss on abrasion. The density of the sample was measured using Archimedes principle.

f) Rebound resilience

Rebound resilience is the ratio of energy given up on recovery from deformation to the energy required to produce the deformation. It is expressed as percentage and is measured using a Vertical Rebound Resilience Tester as per

ASTM D 2632-01. A plunger weighing 28±0.5g is dropped from a height of 40cm to the sample of thickness 12.5mm and the rebound height is measured.

$$\text{Resilience} = \frac{R_h}{D_h} x100 \quad \text{.........} (2.10)$$

Where, R_h is the rebound height and D_h the drop height.

g) Soxhlet extraction

Soxhlet extraction is done to determine the amount of extractable matter in the rubber after crosslinking. Known weights of different samples of vulcanized rubber were packed in Wattman 1 filter paper and extracted in a Soxhlet apparatus using acetone as solvent and the loss of weight (%) was noted.

h) Crosslink density (10)

Swelling studies on the vulcanizates were done in toluene and crosslink densities calculated. A test sample of 10 mm diameter and 2 mm thickness was punched out from the central portion of the vulcanizate. It was accurately weighed and immersed in toluene in a closed vessel for 24 hours. The swollen sample was taken out and weighed. The sample was kept in vacuum or air for complete drying and the dry sample weighed. The volume fraction of the rubber V_r can be calculated from the relation,

$$V_r = \frac{(D-FT)\rho_r^{-1}}{(D-FT)\rho_r^{-1} + A_0\rho_s^{-1}} \quad \text{.........} (2.11)$$

where: F = weight fraction of the insoluble components. It is the ratio of the sum of the weights of components like ZnO, fillers etc. which are insoluble in the solvent and total weight of all components as per the compounding recipe.

ρ_r = density of rubber (g/cc) ρ_s = density of the solvent

A_0 = weight of the solvent absorbed (W-D)

Crosslink density is found out using Flory-Rehner equation

$$CLD = \frac{-\left[\ln(1-V_r)+\chi V_r^{\,2}\right]}{2\rho_r V_s (V_r)^{1/3}} \quad \text{...(2.12)}$$

where V_s = molar volume of the solvent

χ = interaction parameter of the rubber with the solvent

i) Thermogravimetric analysis

Thermogravimetric analysis was carried out on vulcanized samples using a Thermo Gravimetric Analyser Q-50, TA Instruments. It is a computer controlled instrument that permits the measurement of the weight changes in the sample material as a function of temperature. The sample was placed in a temperature programmed furnace. It was then subjected to a temperature change from room temperature to 800°C with a heating rate of 20°C/minute in nitrogen atmosphere. The corresponding weight changes were noted with the help of an ultra sensitive microbalance. Thermograms were recorded from room temperature to 800°C. The onset of degradation, the temperature at maximum degradation and residual weight in percentage were noted.

(i) Degradation kinetics

The TGA data can also be used to study the kinetics of decomposition which provides an insight into the thermal stability of polymeric materials. There are many proposed methods to calculate the kinetic parameters of decomposition and the reported values depend not only on the experimental conditions, but also on the mathematical treatment of data. One important method is the Freeman-Carrol approach.[11]

(ii) Formulation of the rate equation

For many kinetic processes, the rate of reaction may be expressed as a product of a temperature dependent function; k(T), and a composition- or conversion- dependent term; $f(X)$:

$$r = dX/dt = k(T)f(X) \quad \text{......(2.13)}$$

where T is absolute temperature in Kelvin; X is conversion i.e. weight of polymer volatilized / initial weight of polymer and r is the rate of change of conversion or composition per unit time; t. The temperature dependent term in Eqn. (2.13) is the reaction rate constant which is assumed to obey the usual Arrehenius relationship:

$$k(T) = A\exp(E_a / RT) \quad \text{......(2.14)}$$

where E_a is the activation energy of the kinetic process, A is the pre-exponential factor and R is the universal gas constant. The conversion-dependent function, $f(X)$, has generally a complicated form. A particular form is usually valid only for a limited range of experimental conditions. If it is assumed that a simple n^{th} order kinetic relationship holds for the conversion-dependent term such that:

$$f(X) = (1 - X)^n \quad \text{......(2.15)}$$

and that the quantity (1-x) can be replaced by W, the weight fraction remaining in a TGA run, then:

$$r = dW/dt = AW^n \exp(-E_a / RT) \quad \text{......(2.16)}$$

$$\ln r = \ln(-dw/dt) = \ln A + n\ln W - E_a / RT \quad \text{......(2.17)}$$

Published methods of deriving the kinetic parameters from TGA data center about Eqn. 2.17. They may be either differential i.e. involving the derivative term, -dW/dt or intergral i.e. based upon an integration of Eqn. 2.17. The emphasis in these methods is on finding a way of plotting the data to provide a rapid visual assessment the order of the reaction and its activation energy.

(iii) Differential methods for determining rate equation parameters

The difference form of Eqn. 2.17 at different temperatures is:

$$\Delta \ln r = \Delta \ln(-dW/dt) = n\Delta \ln W - (E_a / R)\Delta(1/T) \quad \text{......(2.18)}$$

Dividing 2.18 by $\Delta(1/T)$ gives

$$[\Delta \ln r / \Delta(1/T)] = n[\Delta \ln W / \Delta(1/T)] - (E_a / R) \quad \ldots\ldots\ldots\ldots\ldots\ldots (2.19)$$

A plot of *[Δ ln r/ Δ(1/T)]* against *[Δ ln W/Δ (1/T)]* should be a straight line with slope equal to the order of reaction, n, and an intercept of $-E_a/R$.

Dividing 2.18 by *Δ ln W* gives

$$\Delta \ln r / \Delta \ln W = n + E_a[-\Delta(1/T)/R\Delta \ln W] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.20)$$

A plot of *[Δ ln r /Δ lnW]* versus *[-Δ(1/T) / R Δ ln W]* should also be straight line of slope E_a and an intercept n. These two methods are generally attributed to Freeman and Carroll. In spite of its limited precision, it is quite convenient for processing the acquired TGA data. This method may be used to obtain a rapid but rough estimate of the kinetic parameters when a limited number of data points are available.

j) Ageing tests

(i) Oxidative ageing tests were carried out for 72 hours in accordance with ASTM 573-88 using an air oven at 70°C. Tensile properties and tear resistance of the samples were determined after ageing and 24 hours of conditioning at room temperature.

(ii) Oil ageing tests: Oil ageing was carried out as per ASTM D 471:98. Test specimens of circular shape (diameter 20 mm and thickness 2 ± 0.1 mm) were punched out from tensile sheets and initial weight in air was taken to the nearest 1mg accurately. The test specimens were immersed in hydraulic oil for 3 days at room temperature. After the immersion time, they were taken out and quickly dipped in acetone, blotted lightly with a filter paper and final weight of the specimen determined to the nearest 1mg. The percentage change in mass was calculated as follows:

$$\text{Change in mass} = \frac{M_2 - M_1}{M_1} x100 \quad \text{...} (2.21)$$

M_1 - initial mass of specimen in air and

M_2 - mass of specimen in air after immersion

Test results were calculated for six test specimens of the same sample and the average value taken.

k) Morphological studies- Scanning electron microscopy [12]

Scanning electron microscope (SEM) is a very useful tool in polymer research for studying morphology. Scanning electron microscope (JOEL JSM 840A Scanning Microscope) was used to investigate the morphology of the fractured surfaces. In this technique, an electron beam is scanned across the specimen resulting in back scattering of electrons of high energy, secondary electrons of low energy and X-rays. These signals are monitored by detectors (photo multiplier tube) and magnified. An image of the investigated microscopic region of the specimen is thus observed in a cathode ray tube and photographed using black and white film. The SEM observations reported in the present study were made on the fracture surface of the tensile specimens. Thin specimens were prepared and mounted on a metallic stub with the help of a silver tape and conducting paint in the upright position. The stub with the sample was placed in a JFC-1100E ion-sputtering unit for gold coating of the sample to make it conducting. The goald coated sample was subjected to SEM.

2.3 Results and discussion

2.3.1 Spectroscopic data

The FTIR spectrum of the synthesized epoxy resin is shown in Fig.2.2. The C-H stretching in epoxies is at 2960- 2990 cm^{-1}. Symmetrical stretching or breathing frequency is observed at 1231cm^{-1} and this is characteristic of the epoxy ring. The bands at 913 cm^{-1} (asymmetric ring stretching in which C-C stretches during contraction of C-O bond), 827 cm^{-1} and 757 cm^{-1} are typical of the epoxy group. The FTIR spectrum of commercial epoxy resin is given in Fig.2.3. Both samples show ample evidence of epoxide group.

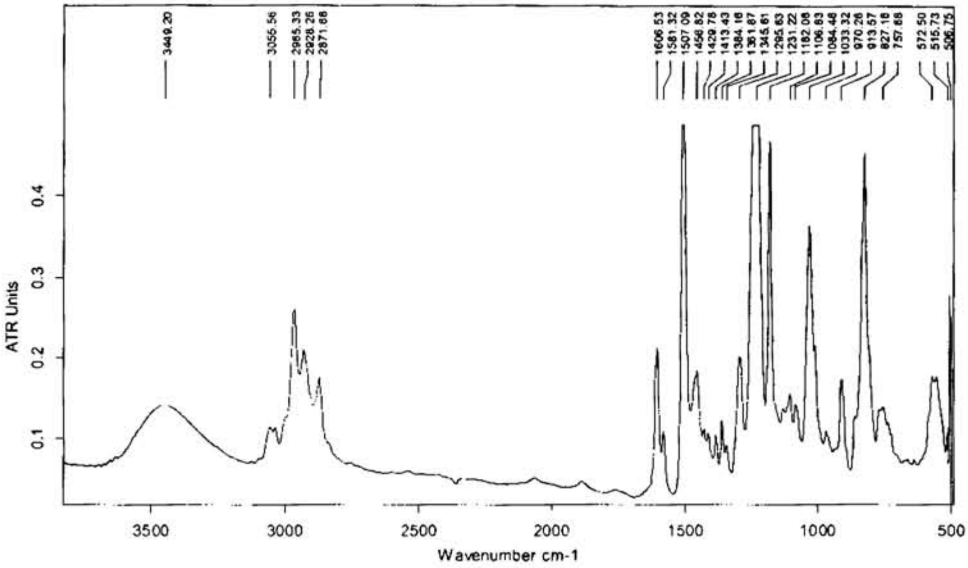


Fig.2.3 FTIR spectrum of synthesized EPR

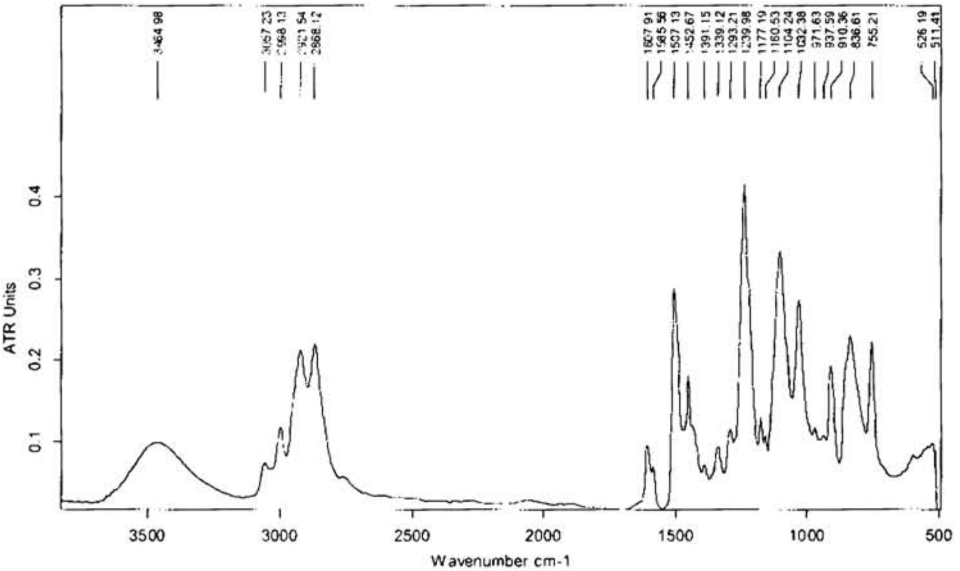


Fig.2.4 FTIR spectrum of commercial EPR

2.3.2 Epoxide equivalents

The weight per epoxide (wpe) values of the commercial and the synthesized epoxy resin samples are 187.7 and 180.36 respectively. These values correspond to epoxide equivalents 5.33 eq / kg and 5.52 eq. / kg respectively. The commercial resin usually contains diluents and flexibilizers and hence the lower epoxide content.

2.3.3 NR gum modified by EPR

Cure characteristics of the vulcanizates are shown in Table 2.3. The cure time falls dramatically on addition of resin. For each mix, cure time decreases with resin content upto 2% but increases beyond that value (Fig. 2.5). The effect of adding higher amounts of resin on the cure time is different for synthesized and commercial resins. Thus at 4% concentration the cure time shoots up to 12 minutes for the commercial resin compared to 2.78 minutes for the synthesized resin. This difference in behavior can be attributed to diluents added to the commercial epoxy resins. The initial decrease in cure time indicates that the incorporation of resin promotes the cure reaction of NR. This can be due to chemical reactions involving epoxy groups beneficial to sulphur crosslinking of rubber. Scorch time decreases with resin content. This is attributable to heat of mixing and accelerated curing rates which promote premature curing of the compound. The minimum torque increases with resin content and maximum torque increases upto 2% and subsequently decreases slightly. The influence of resin content on the torque values point to interaction between the rubber and resin.

Table 2.3 Cure characteristics of gum NR compound with EPR

Resin content (%)		Scorch time(min)	Cure time (min)	Maximum Torque(dNm)	Cure rate index (min^{-1})
0		2.62	5.62	2.69	33.33
Com.EPR	1	1.07	2.88	2.791	55.25
	2	0.83	3.29	2.467	40.65
	3	0.79	3.29	2.203	20.20
	4	0.84	12.1	2.105	8.88
Syn.EPR	1	1.58	3.39	2.857	55.24
	2	0.95	2.26	3.011	76.33
	3	0.80	2.26	2.756	68.49
	4	0.65	2.78	2.295	46.95

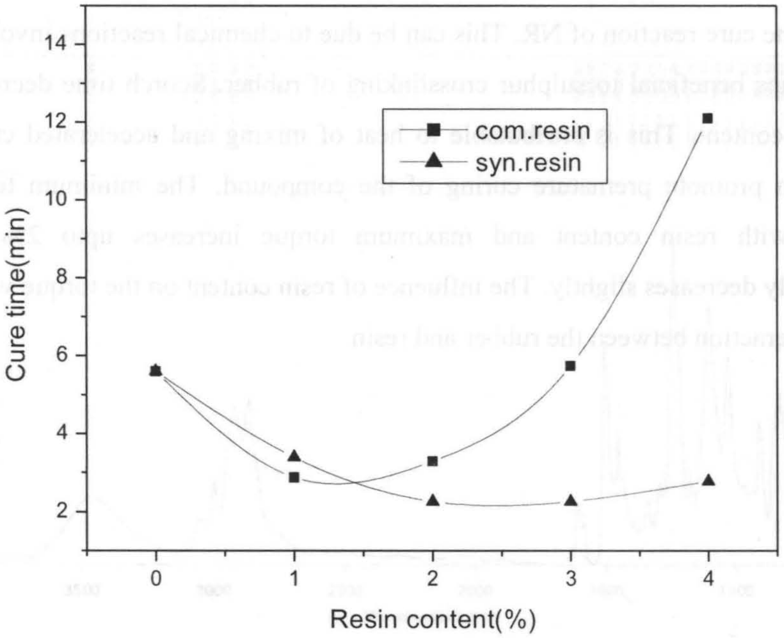


Fig.2.5 Variation of cure time with resin content

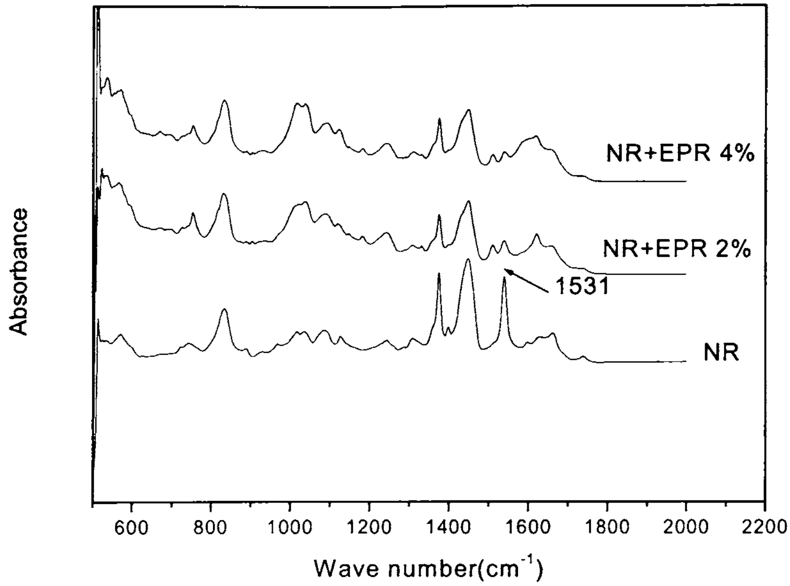


Fig.2.6 FTIR spectra of EPR modified NR vulcanizates

The decrease in cure time can be explained in the light of the FTIR spectra of NR vulcanizates with and without EPR (Fig.2.6). The peak at 1531 cm^{-1} in the NR vulcanizate is due to the N- H bending frequency. The N – H bond is formed in the accelerator MBTS by the abstraction of allylic hydrogen from NR and produces an active site for crosslinking process. The added modifier, epoxy, reacts with the N – H bond thus formed, facilitating the production of more active sites and hence a decrease in cure time. In addition, epoxies lead to a decrease in the intensity of N – H bending frequency. A scheme of the possible mechanism is shown in Fig.2.7.

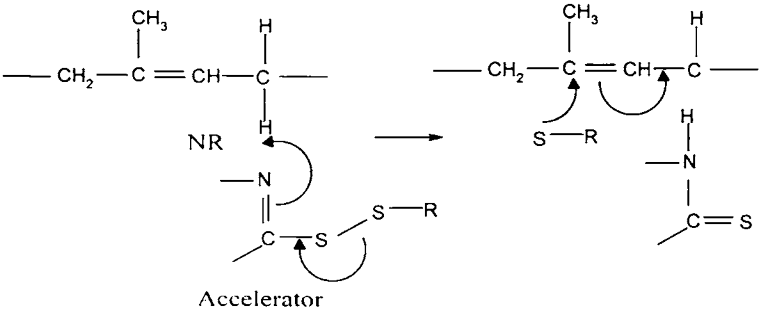


Fig.2.7 Mechanism of vulcanization

Cure kinetics: The plot of ln(M_h-M_t) versus time of the NR compounds are shown in Fig.2.8 and 2.9. They are found to be linear which proves that cure reactions proceed according to first order kinetics. From the slope of the straight lines, the corresponding rate constants were calculated. Cure rate constants of NR compounds with varying EPR content are shown in Table 2.4. The cure rate constant is found to increase with resin content upto 2% and then decreases. The cure rate constants and cure rate index are shown in Fig.2.10. Cure rate index is a parameter indicating the speed of the reaction. Both parameters indicate that lower percentages of epoxy resin accelerate the cure reaction.

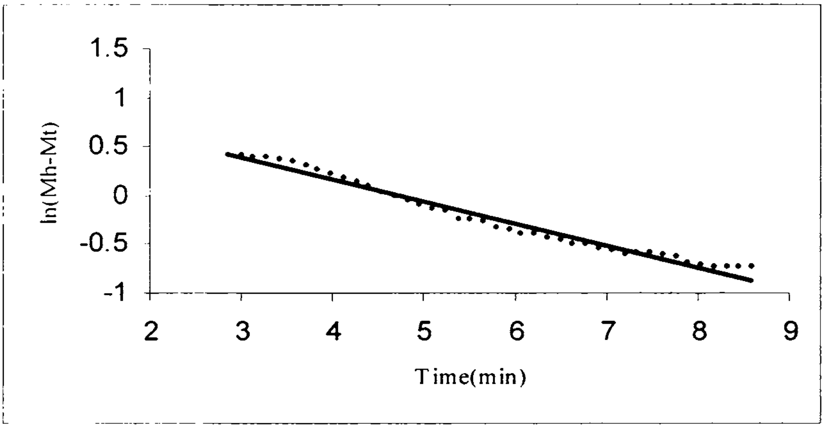


Fig.2.8 ln (M_h-M_t) vs time of NR compound

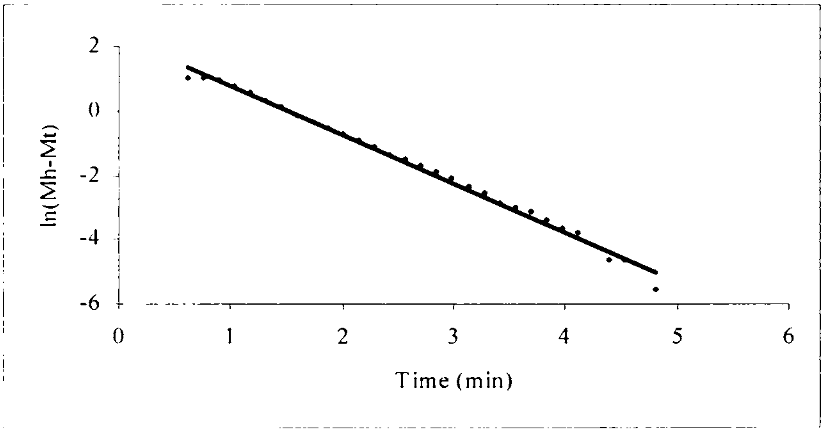


Fig.2.9 ln (M_h-M_t) vs time of NR compound with com.EPR

Table 2.4 Cure rate constants of EPR modified samples

Sample	Rate constant
NR	0.2257
NR+ EPR 1%	1.1077
NR+ EPR 2%	1.5183
NR+ EPR 3%	1.0058
NR+ EPR 4%	0.1314

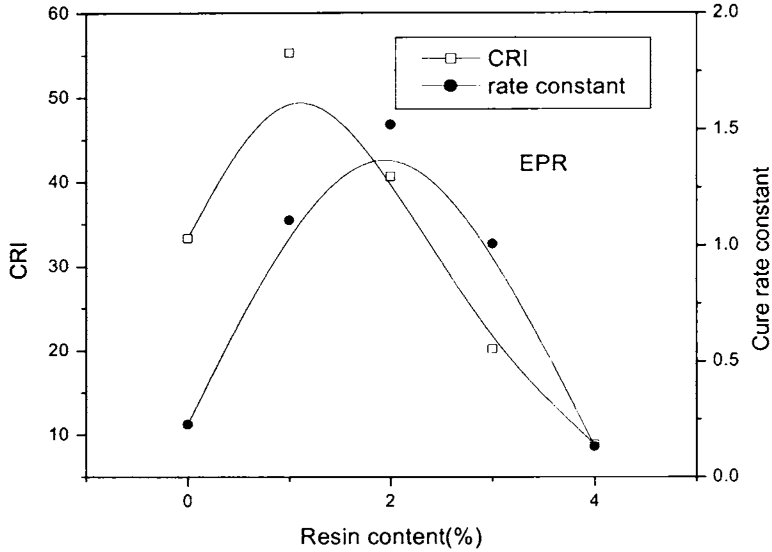


Fig.2.10 Cure rate index and cure reaction constant of EPR modified samples

Fig.2.11 shows the variation of tensile strength on addition of various percentages of resins, both commercial and synthesized. Both resins show a maximum tensile strength at 3%. It is possible that at higher percentages of resin, the accelerator gets depleted and the earlier mentioned interaction with epoxy resin does not take place. In that case a semi interpenetrated behavior replaces the initial fully interpenetrated state. It is also possible that the dispersion of the resin is not very effective at higher percentages resulting in a filler like behavior.

The marginal improvement in tensile modulus (Fig.2.12) on addition of resin is indicative of some extent of interpenetration. Although initially there is a stiffening of the rubber chains resulting in an improvement in modulus, the trend reverses on adding higher percentages.

Elongation at break (Fig.2.13) is governed by the extent of crosslinks present at the time of rupture after all interpenetration has been cleared. The presence of the resin and interpenetration negatively influence crosslinking between rubber chains to some extent. This effect is more pronounced in the case of commercial resin which possibly contains diluents.

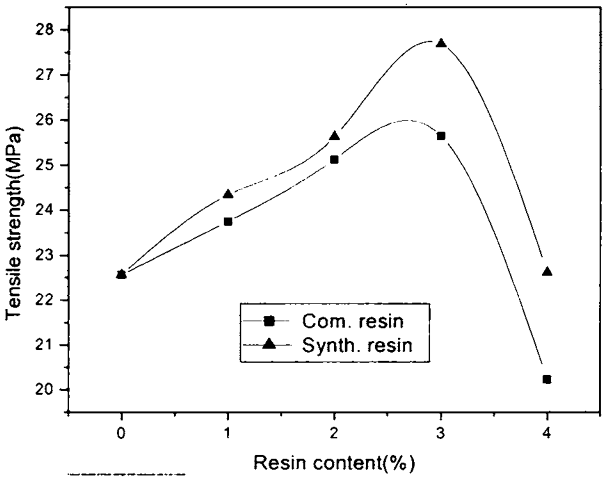


Fig.2.11 Variation of tensile strength with resin content

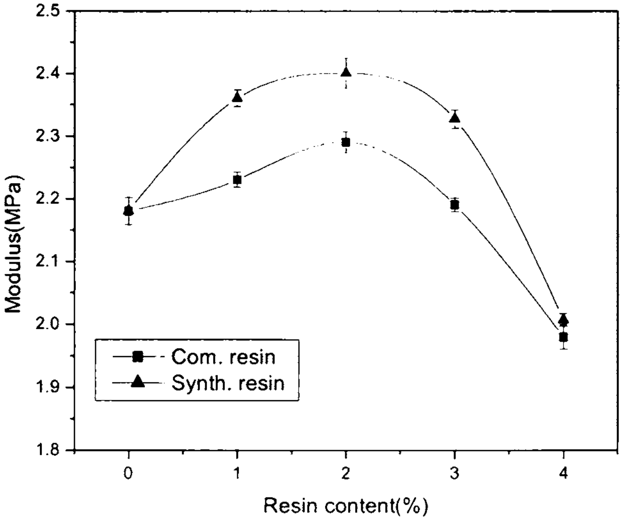


Fig.2.12 Variation of 300% modulus with resin content

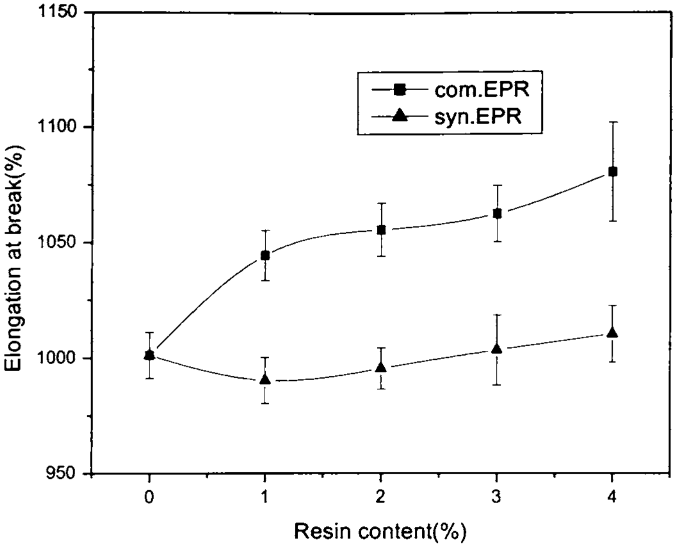


Fig.2.13 Variation of elongation at break with resin

Tear strength (Fig.2.14) also increases with resin content upto 3%. The improved tear strength also points to interpenetration. Hardness (Fig.2.15) also shows improvement upto 2% of the resin. The effect on abrasion loss (Fig.2.16) is only marginal.

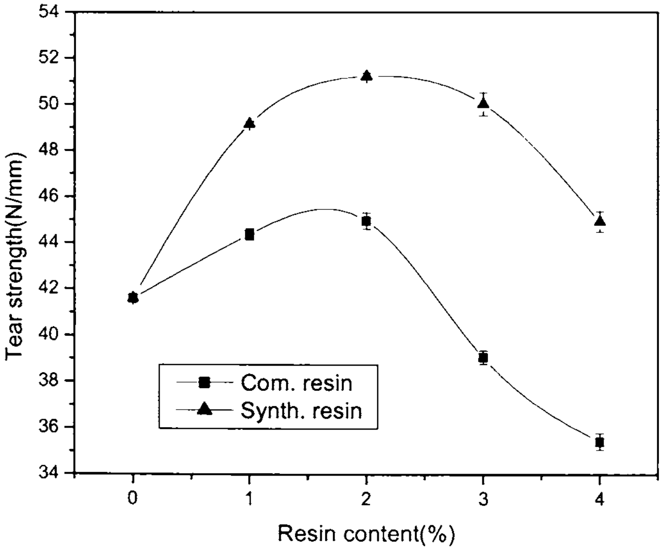


Fig.2.14 Variation of tear strength with resin content

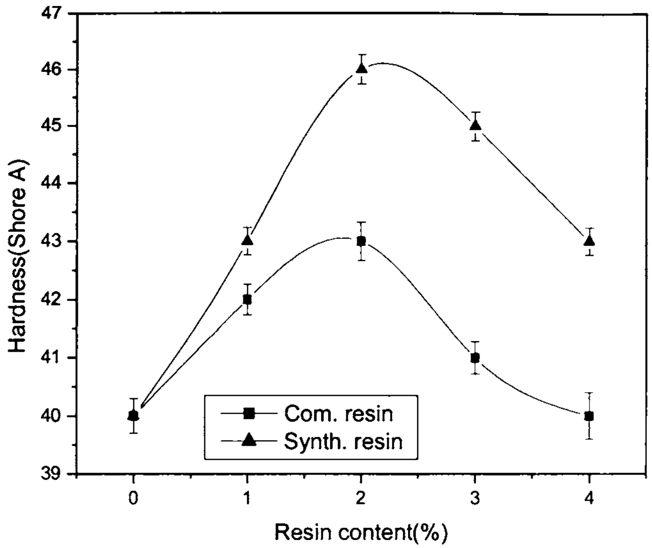


Fig.2.15 Variation of hardness with resin content

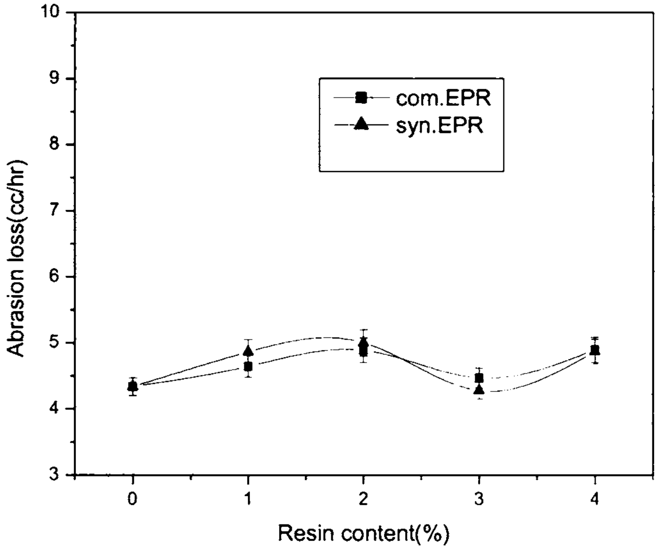


Fig.2.16 Variation of abrasion loss with resin content

Fig.2.17 shows the variation in weight loss on extraction with acetone. There is only a moderate increase in weight loss with resin content on extraction. The low extractability of the resin from the rubber proves that the resin has either undergone crosslinking between its own chains or taken part in interactions with the rubber chains.

On close examination of the curves of Fig.2.17 it is seen that upto 2% resin, the curves are rather flat. Beyond 3% the curves become steeper indicating higher weight losses on extraction. Hence it is possible to suppose that in this range the resin is more extractable being dispersed less effectively in the rubber matrix. Another possible explanation is the failure of epoxy groups to get crosslinked without help from accelerator molecules.

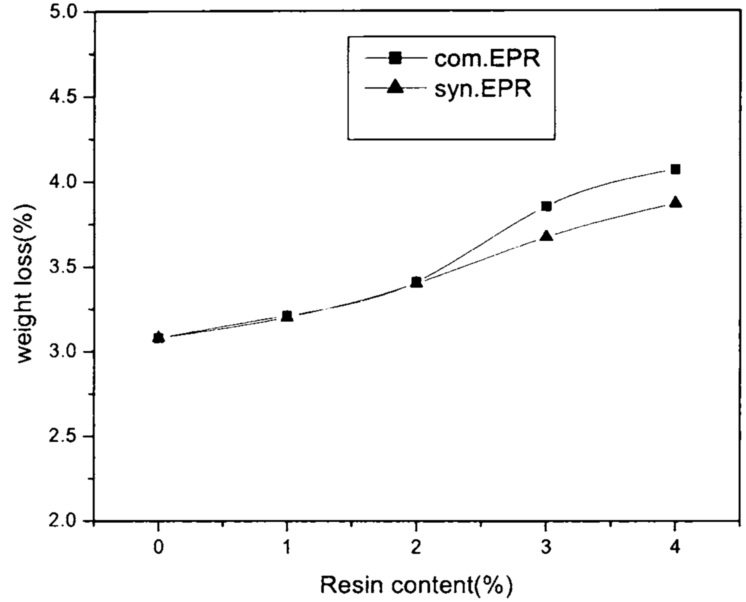


Fig.2.17. Variation of weight loss on soxhlet extraction

Figs. 2.18 and 2.19 depict the variation of retention of tensile and tear strengths of different samples after ageing at 70°C for 72 hours. In the absence of the resin the percentage retention of tensile strength after 72 hours of ageing is only about 55 % (Fig.2.18). On addition of resin this value increases steadily until at about 4% it is almost 100-115% of the original tensile strength. Similarly, in the case of tear strength there is a steady improvement in tear strength retention with resin content. The prolonged ageing process may help to make the crosslinking reaction of resin and/or chemical interaction between the rubber and the resin to go to completion. Hence the improvement in these two properties on ageing.

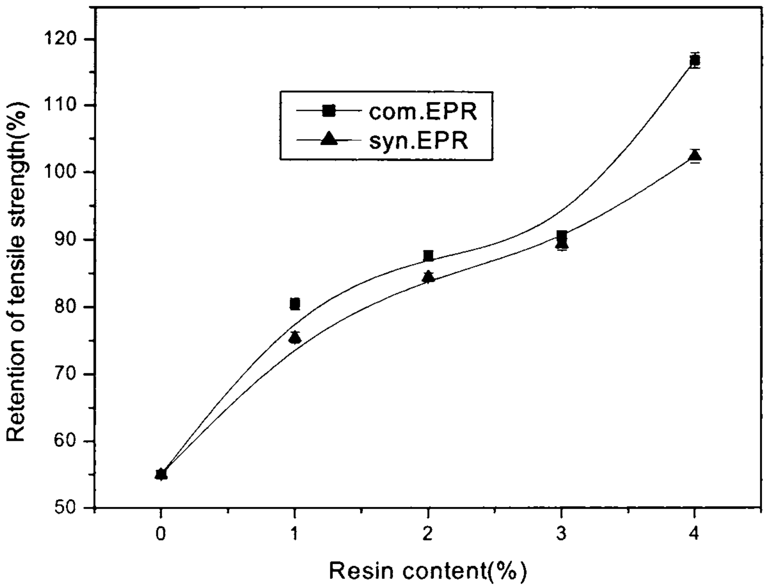


Fig.2.18 Variation of retention of tensile strength on ageing at 70°C for 72 hrs

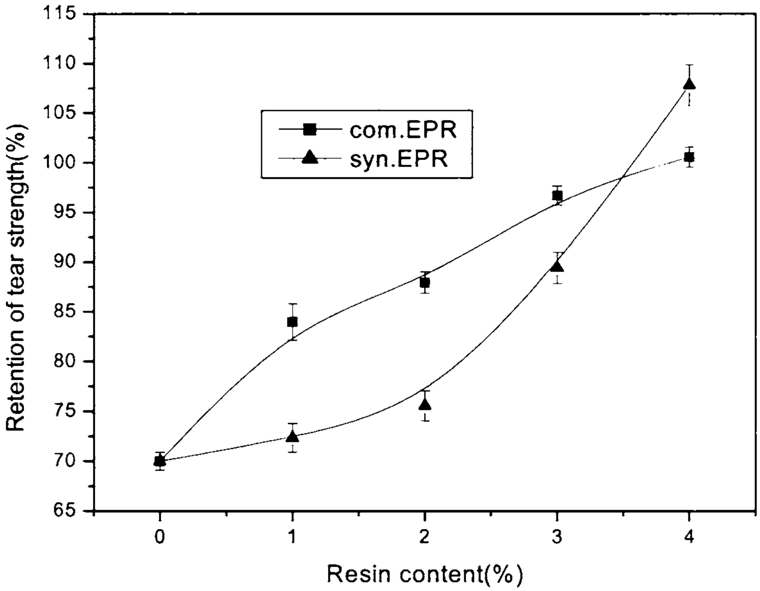


Fig.2.19 Variation of retention of tear strength on ageing at 70°C for 72 hrs

Fig. 2.20 shows that the addition of resin dramatically reduces the percentage mass of oil absorbed over a 72 hour period. Here again a 20-30% decrease is possible with only just 2% of resin. The presence of the resin in the crosslinked condition has made the rubber less penetrable for oil. Moreover, the polar nature of the resin reduces the interaction between the rubber chains and oil.

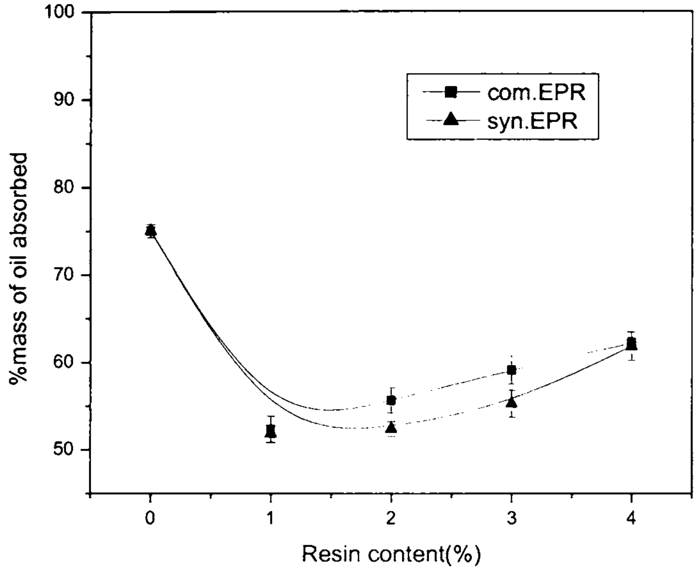


Fig.2.20. Variation of mass of oil absorbed in 72 hrs with resin content

Fig.2.21 shows the variation of crosslink density of NR vulcanizates with resin content. Crosslink density increases with resin content upto 1-3% and after that at higher percentages, it falls. The increase in crosslink density is attributable to possible chemical interactions between the rubber and resin as well as interpenetrating effects. Poor dispersion of the resin and the change from a fully interpenetrating to a semi interpenetrating network may be the reason for the lowered crosslink density at higher percentages.

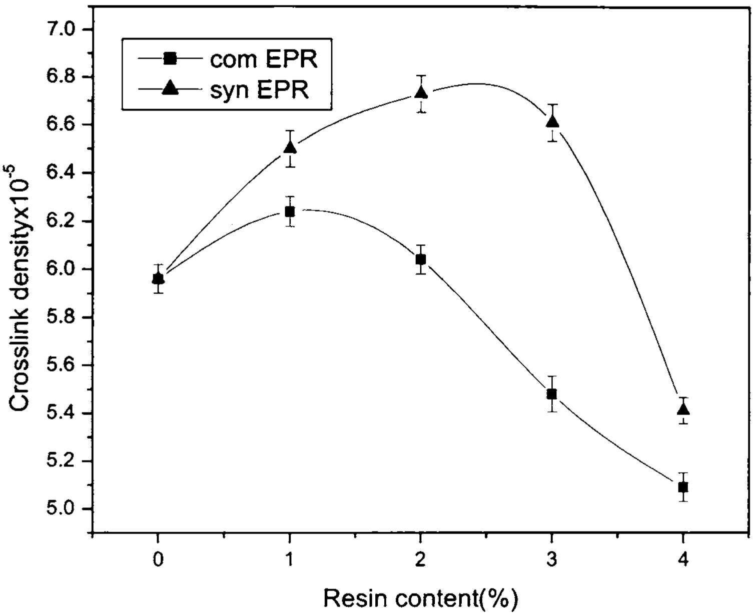


Fig.2.21. Variation of crosslink density with resin content

Figs. 2.22, 2.23 and 2.24 are the thermograms of NR vulcanizates with and without EPR. Thermogravimetric data of NR vulcanizates are given in Table 2.5. From the table it can be seen that the onset of degradation temperature, temperature at maximum degradation, temperature at 50% degradation and residue content are higher for vulcanizates containing synthesized EPR. This indicates that the EPR modified NR vulcanizate is thermally more stable than the unmodified samples. Freeman-Carrol plots are given in Figs. 2.25, 2.26, and 2.27. Activation energies are given in Table 2.6. Higher activation energy means more energy is needed to degrade the sample. This again proves the higher thermal stability of the EPR modified sample.

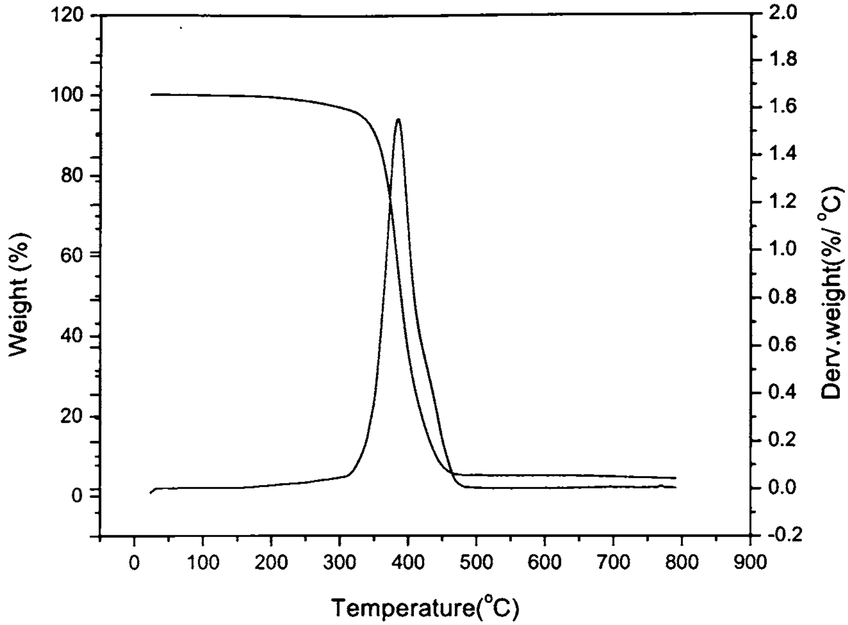


Fig. 2.22 Thermogram of NR vulcanizate

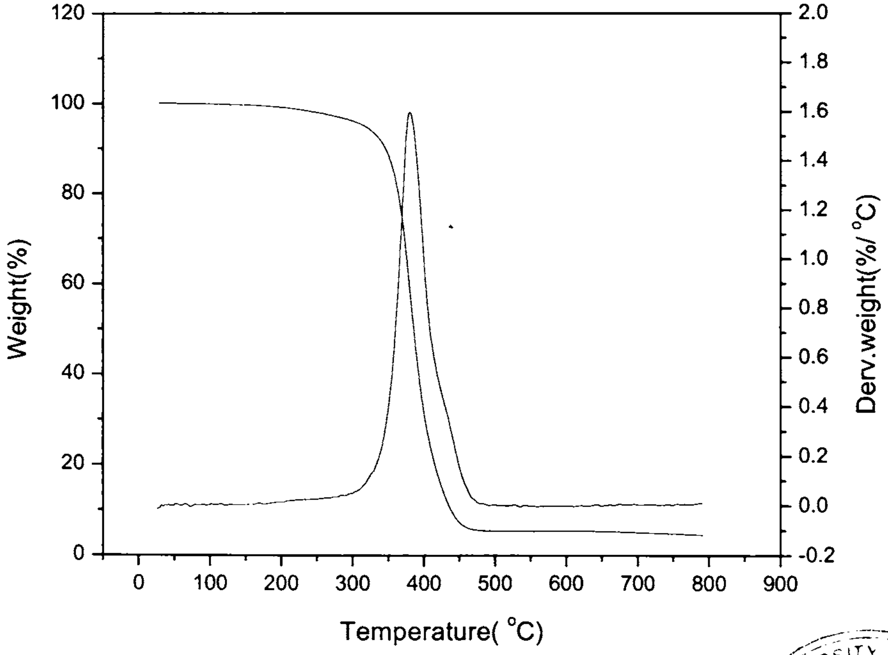


Fig.2.23 Thermogram of commercial EPR

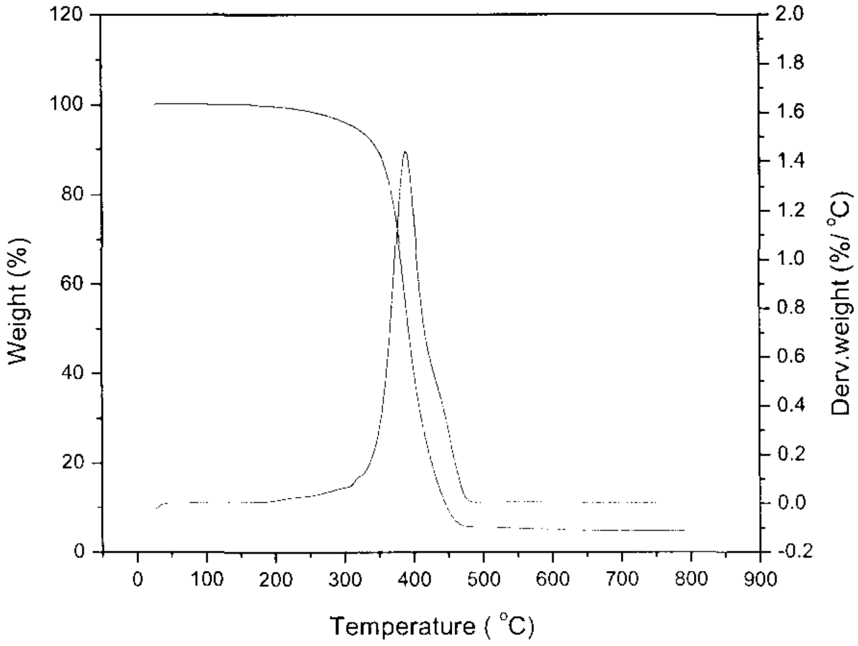


Fig.2.24 Thermogram of synthesized EPR

Table 2.5. Characteristics of thermograms of NR vulcanizates

	NR	**NR+com.EPR**	**NR+syn.EPR**
Onset of degradation (°C)	312.72	313.98	315.49
Temperature at 50% degradation (°C)	388.99	385.76	393.37
Temperature at maximum degradation (°C)	384.23	380.76	387.63
Rate at maximum degradation (%/°C)	1.55	1.59	1.43
Residue (%)	4.29	4.49	4.99

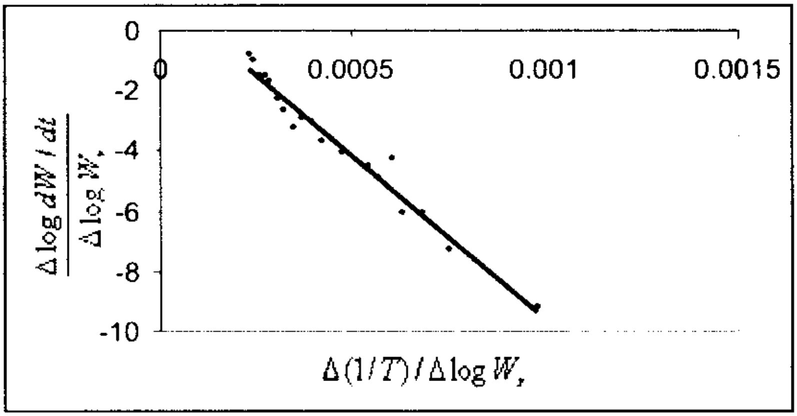


Fig.2.25 Freeman-Carrol plot of NR vulcanizate

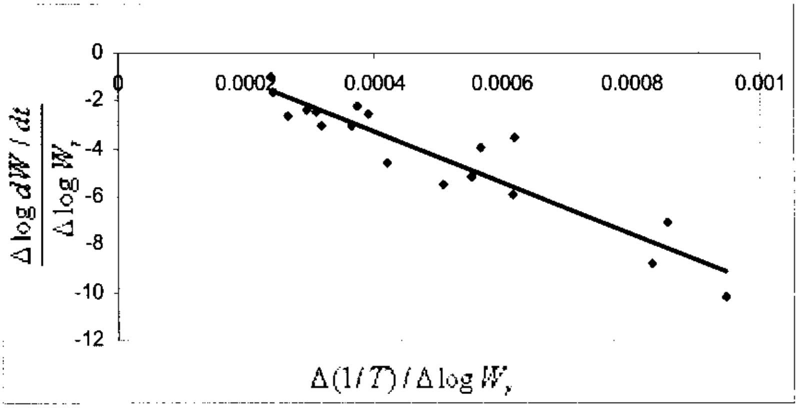


Fig.2.26 Freeman-Carrol plot of NR+ com.EPR

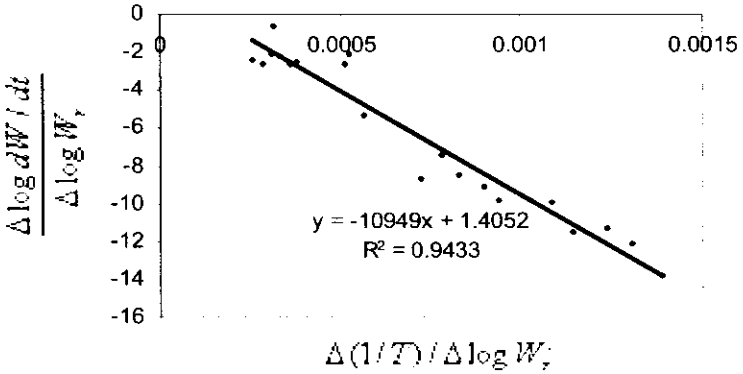
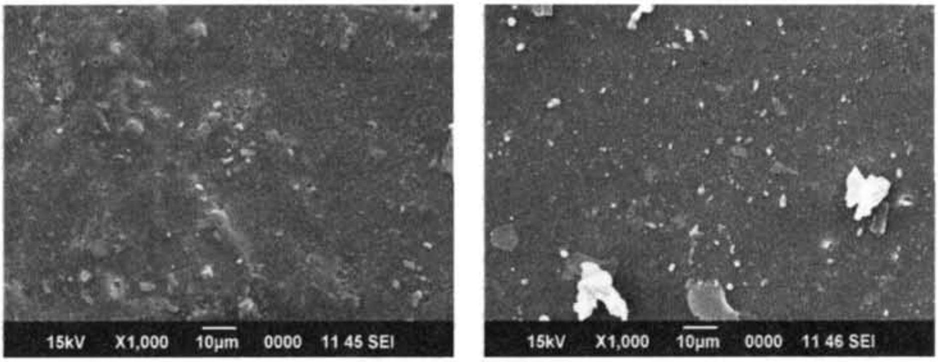


Fig.2.27 Freeman-Carrol plot NR+syn.EPR

Table 2.6 Activation energy of EPR modified samples

Sample	Activation energy(kJ)
NR	206
NR+com.EPR	202
NR+syn.EPR	209



(a) (b)

Fig.2.28 SEM micrographs of (a) NR (b) NR+2% EPR

Fig.2.28 shows the micrographs of gum NR with and without EPR. The distribution of EPR in the rubber is not very uniform although most particles are of similar size. The particles show clear boundaries indicating limited assimilation into the rubber. However in view of the improvement of properties it is to be supposed that a good part of the resin has blended with the rubber at the microscopic level.

2.3.4 Effect of epoxidised cardanol on the properties of NR vulcanizate

Section 2.2.2 explains the method of preparation of epoxy cardanol with the relevant chemical equation. This epoxidised compound has been utilized as a modifier for NR. The FTIR spectrum of EC is shown in Fig.2.29. The bands at 2923.98 cm^{-1} (C-H stretching of epoxide), 1258.71cm^{-1} (symmetrical C-O str.) and 909.92 cm-1 are characteristic of the epoxy group.

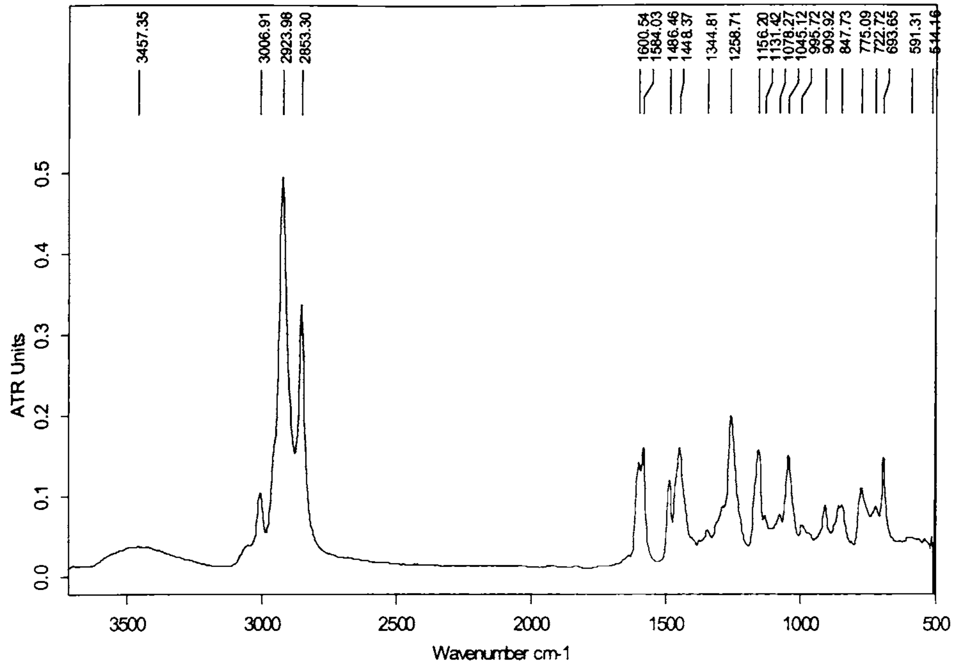


Fig.2.29 FTIR spectrum of epoxidised cardanol.

The wpe value of epoxy cardanol (EC) obtained by epoxidation of cardanol for nine hours was found to be 473.15. This corresponds to 2.12eq/Kg of epoxide. Cardanol being less reactive undergoes epoxidation to a smaller extent than phenol, only 61% of epoxidation in 9 hours [4]

Cure characteristics of the modified compounds are given in Table 2.7. Fig. 2.30 shows the variation of cure time with resin content, epoxidised cardanol in this case. The cure time falls drastically until 4% resin content. Beyond that there is only a very slight change in cure time. But from 0 to 4% of epoxidised cardanol the cure time falls by more than 60%. Hence the epoxy compound is chemically active and has a positive effect on the curing process. Interpenetrating effect can be one of the reasons for the faster cure time. Also it has been reported that cardanol undergoes chemical changes including vulcanization in a sulphur vulcanized NR compound.[13] Cure rate index is found to increase with EC upto 4%.

Table 2.7 Cure characteristics of NR modified with EC

Resin content (%)		Scorch time(min)	Cure time (min)	Maximum Torque(dNm)	Cure rate index (min^{-1})
0		2.62	5.62	2.69	33.33
EC	2	1.54	2.88	3.04	74.62
	4	0.78	1.81	3.09	97.08
	6	0.61	1.89	2.86	84.74
	8	0.48	2.07	2.50	62.89

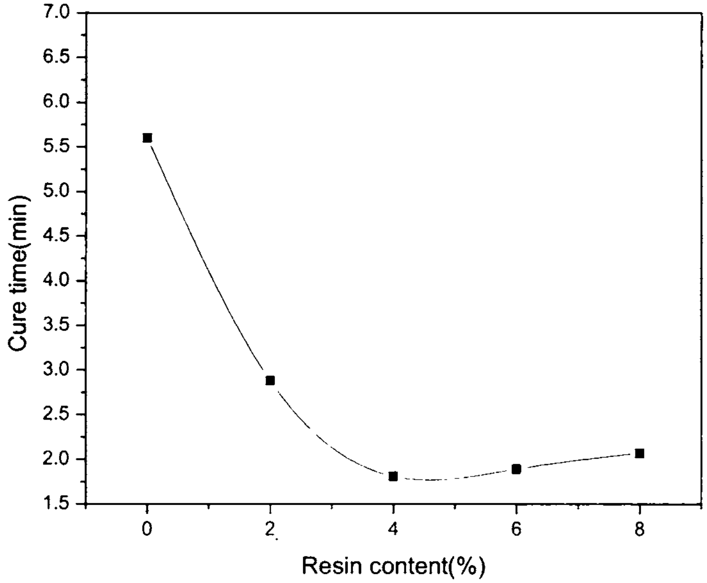


Fig.2.30 Variation of cure time with resin content

Cure rate constants are determined from the slope of the plot of $\ln(M_h-M_t)$ vs time. Values are tabulated in Table 2.8. EC accelerates the cure reaction of NR. Cure reaction constants are plotted along with CRI values in Fig.2.32.

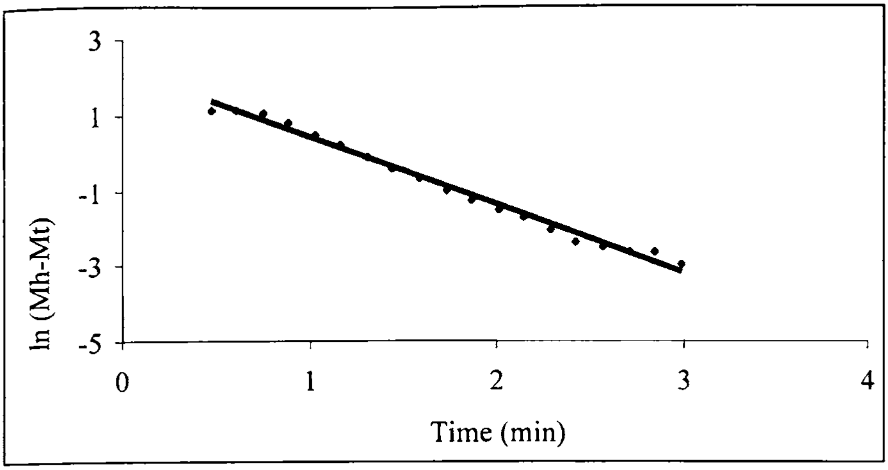


Fig. 2.31 ln $(M_h\text{-}M_t)$ vs time of NR compound with 4% EC

Table 2.8 Cure rate constants of NR compounds with varying EC content

Sample	Rate constant
NR	0.2257
NR+ EC 2%	1.4488
NR+ EC 4%	1.8101
NR+ EC 6%	1.2785
NR+ EC 8%	1.086

Tensile strength (Fig. 2.33) shows an increasing trend in the beginning followed by a flattening of the curve on addition of more resin. The lengthy side chain of the cardanol molecule can have an entangling effect leading to an increased tensile strength [13]. The possible sulphur vulcanization of the side chain indicated earlier may also be responsible for higher tensile strength. This effect diminishes as sulphur gets depleted.

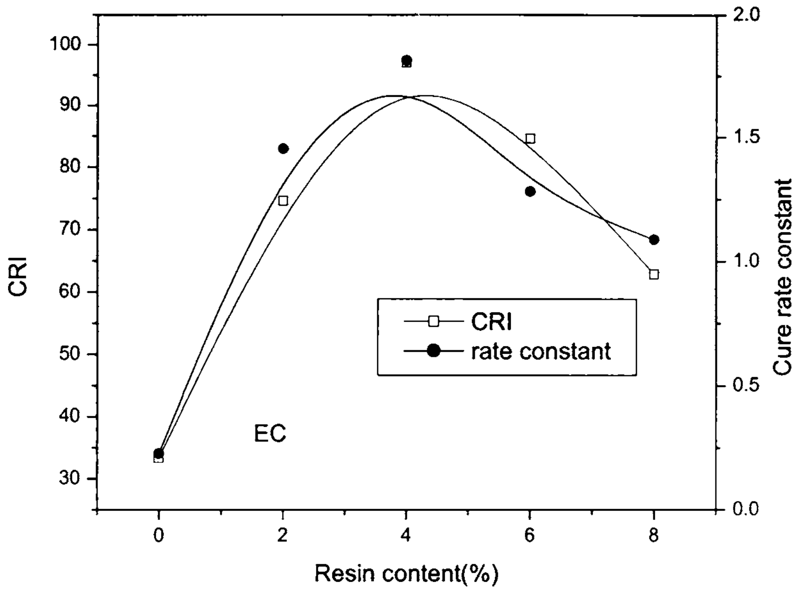


Fig.2.32 Cure rate index and cure reaction constant of EC modified samples

Fig.2.34 shows the change in 300% modulus with increase in resin content. There is a maximum at 4% resin content. On further addition of resin, the modulus value falls rapidly. Similarly, elongation at break (Fig.2.35) goes through a minimum at 4% resin content. Surface hardness (Fig.2.37) also behaves similarly. Referring to Fig.2.36 the fall in tear strength beyond 4% resin content can be due to fall in crystallinity as the amount of resin increases..

The effect of the epoxy ring reacting with the accelerator is limited to some extend as the epoxidised product is capable of forming only a dimer when the epoxy rings are opened by the NH group. Higher percentages of the substance can actually lead to fall in tensile properties by acting as a plasticizer.

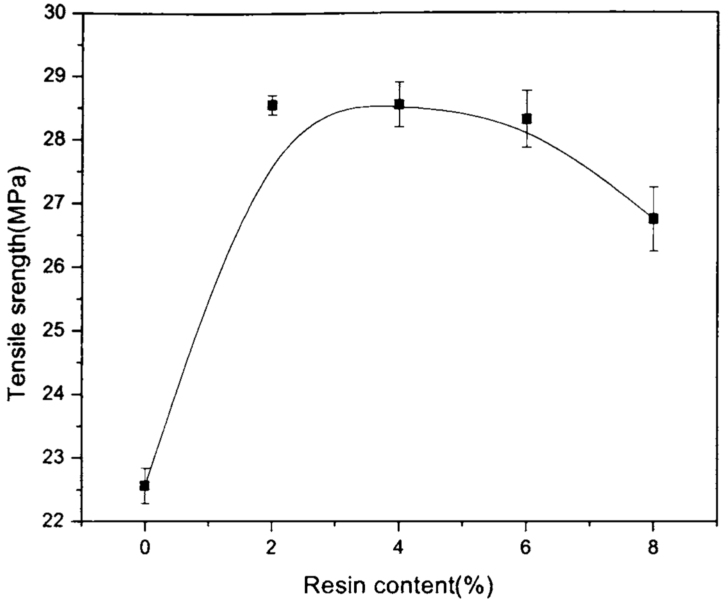


Fig.2.33 Variation of tensile strength with resin content

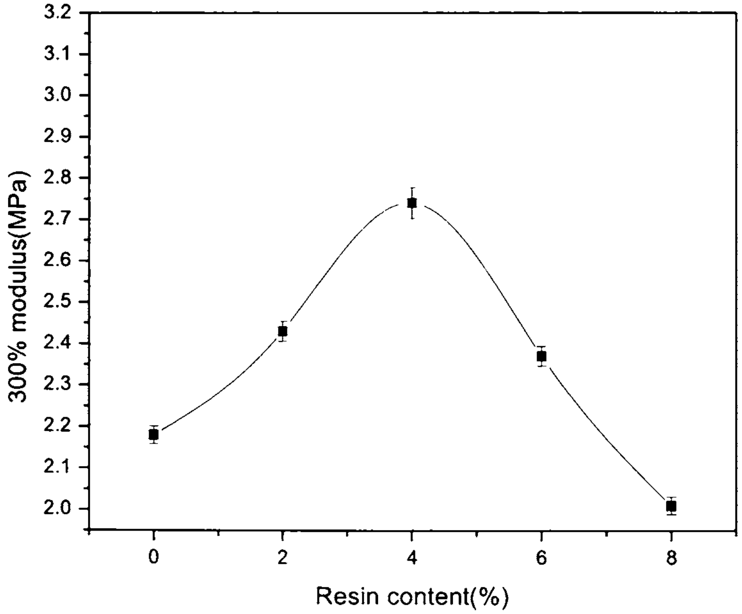


Fig.2.34. Variation of 300% modulus with resin content

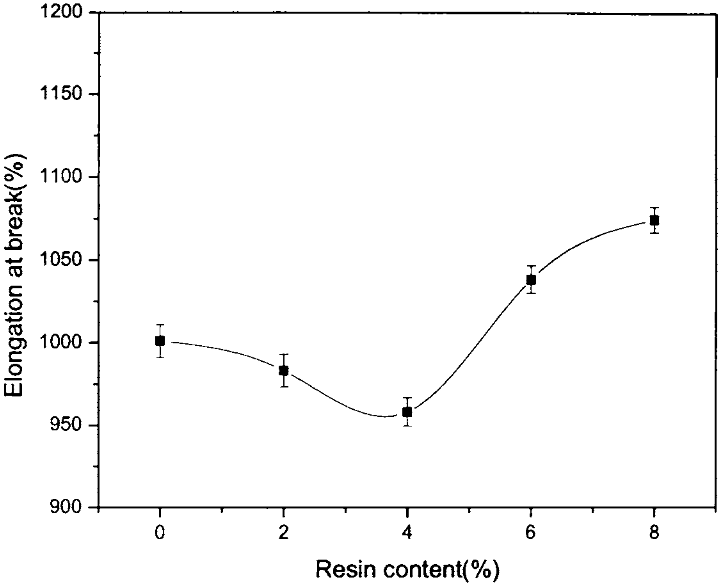


Fig.2.35 Variation of elongation at break with resin content

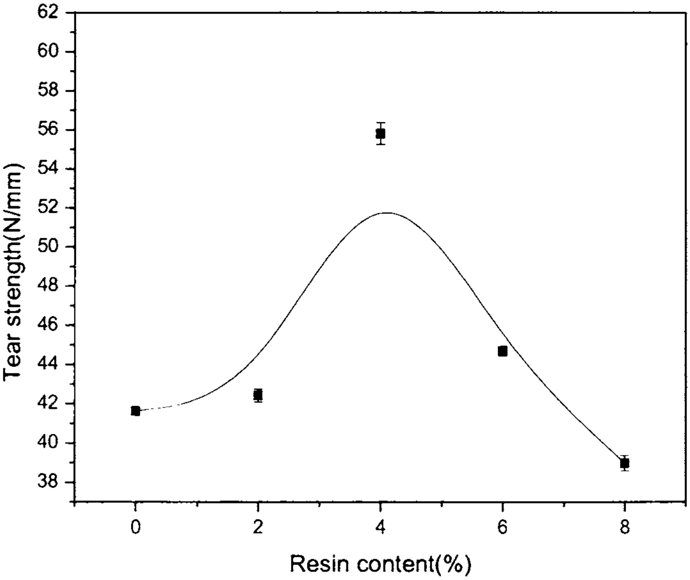


Fig.2.36 Variation of tear strength with resin content

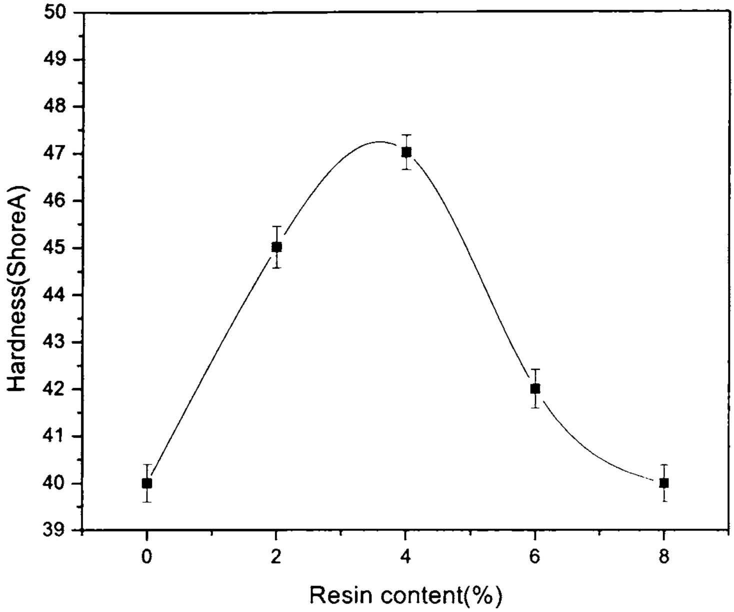


Fig.2.37. Variation of hardness with resin content

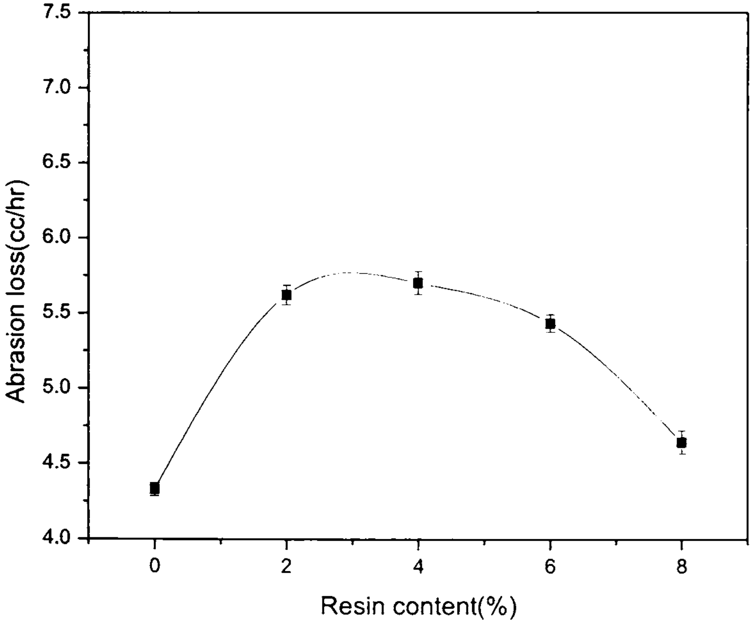


Fig.2.38 Variation of abrasion loss with resin content

Abrasion loss (Fig.2.38) also goes through a maximum with resin content. Fig.2.39 shows the weight loss on Soxhlet extraction with resin content. There is a gradual increase in weight loss percentage with increase in resin content. A part of the epoxidised cardanol appears to be extracted out of the vulcanizate. The major portions of the modifier remain in the rubber matrix due to either chemical interactions or the entangling effect of the side chain of the cardanol molecule.

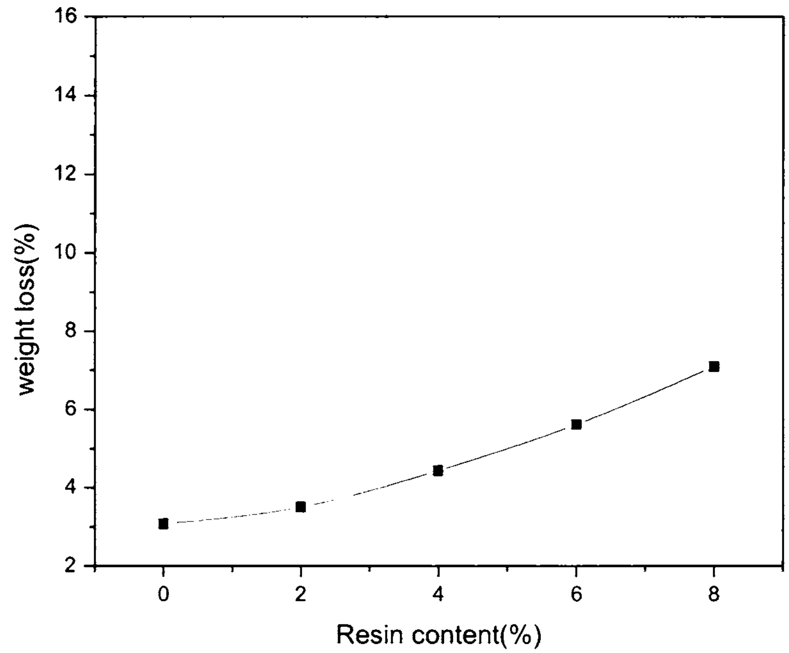


Fig.2.39. Variation of weight loss on soxhlet extraction

Figs.2.40 and 2.41 show the retention of tensile strength and tear strength after ageing for 72 hours at 70°C. Both these properties are retained to a much higher extent after ageing when more and more of the resin is added. It can be surmised that some chemical interactions between EC and NR continue through the ageing period. It is also possible that crosslinking or curing of the epoxy compound is completed during ageing. Judging by these two properties epoxidised cardanol improves the thermal ageing characteristics of the rubber.

Fig.2.42 shows that there is a sharp fall in the mass of oil absorbed when epoxidised cardanol is added to the rubber. There is a general improvement in oil resistance on addition of the resin. But this property is also an optimum at about 4% of the resin.

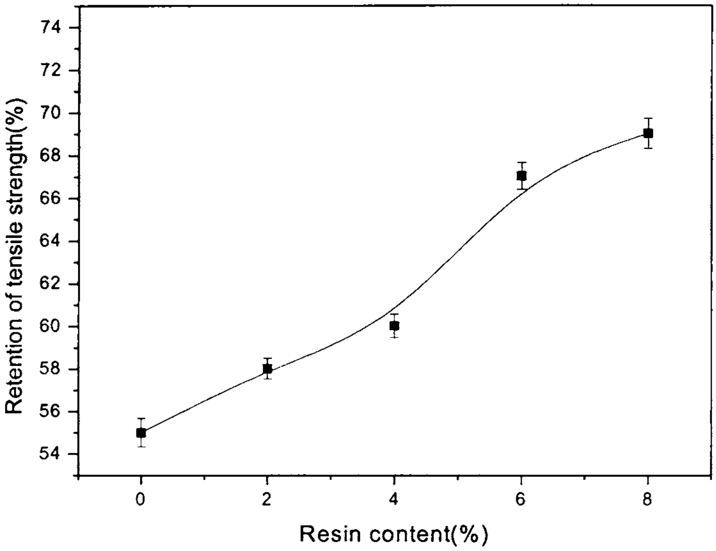


Fig.2.40. Variation of retention of tensile strength on ageing at 70°C for 72 hrs .

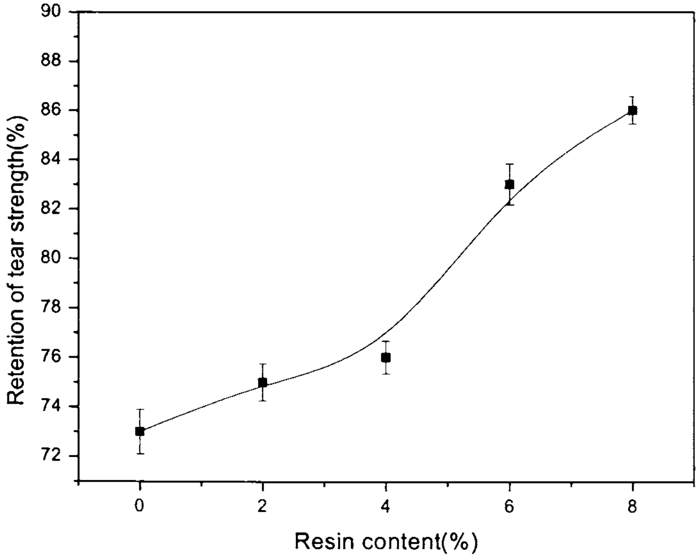


Fig.2.41 Variation of retention of tear strength on ageing at 70°C for 72 hrs.

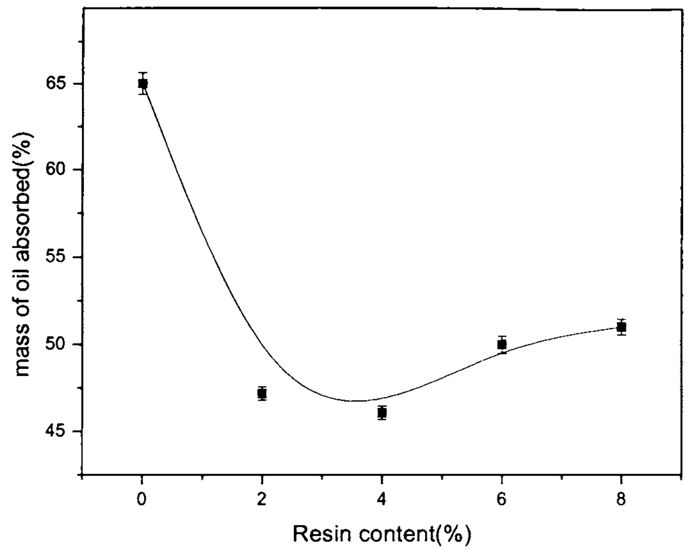


Fig.2.42 Variation of mass of oil absorbed in 72 hrs. with resin content

Thermogram of 4% EC modified NR vulcanizate is shown in Fig.2.43. Important observations are given in Table 2.9. Temperature of maximum degradation, 50% degradation temperature and residue content are higher for modified samples. Rate of degradation at maximum temperature is lower for modified samples.

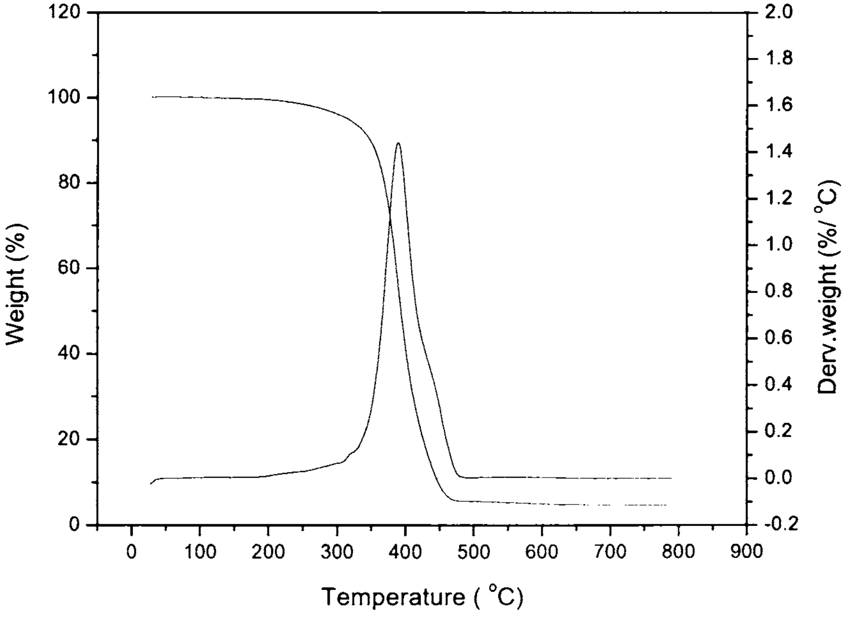


Fig.2.43 Thermogram of NR vulcanizate with 4% EC

Table 2.9. Characteristics of thermograms of NR vulcanizates

	NR	NR+EC
Onset of degradation (°C)	312.72	308
Temperature at 50% degradation(°C)	388.99	393
Temperature at maximum degradation (°C)	384.23	387
Rate of degradation at maximum (%/°C)	1.55	1.43
Residue (%)	4.29	4.84

2.3.5 Effect of commercial EPR on properties of HAF filled NR vulcanizate

Cure characteristics of the HAF black filled NR vulcanizates are shown in Table 2.10. The cure time falls on addition of resin upto 2% but increases beyond that value. The decrease in cure time indicates that the incorporation of resin promotes the cure reaction. Scorch time decreases with resin content. This is attributable to heat of mixing.

Table 2.10 Cure characteristics of HAF filled NR vulcanizate with EPR

Resin content (%)		**T_{10} (min)**	**T_{90} (min)**	**M_L (dNm)**	**M_H (dNm)**	**CRI (min^{-1})**
NR+HAF	0	1.67	3.77	0.066	4.26	47.60
	2	0.92	2.54	0.071	4.67	61.70
	4	0.69	2.42	0.100	4.81	57.8
	6	0.62	2.50	0.113	4.70	53.91
	8	0.59	3.72	0.120	4.43	31.95

Fig.2.44 shows the variation of tensile strength of the HAF filled NR vulcanizate with resin content. There is only a slight increase in tensile strength as the resin content goes upto 2%. This is attributable to the presence of the filler

which minimizes possible chemical interactions between the resin and the rubber at higher percentages of the resin. The filler may adsorb the modifier resin thus reducing the overall effect.

In the case of 300% modulus (Fig.2.45) it is seen that initially there is a slight increase in the modulus value on addition of resin. Moderate amounts of resin have a slight stiffening action on the rubber which soon disappears on addition of more resin. The fall in modulus at high percentages can be either due to the epoxy resin left unincorporated into the rubber or the resin interfering with the reinforcing action of the carbon black by getting adsorbed on the surface.

Fig.2.46 shows the variation of elongation at break with resin content. Elongation at break is minimum at around 2% resin. The reason given earlier in connection with the variation of modulus applies here also. The surface hardness (Fig.2.48) is also slightly affected by the resin content. Tear strength (Fig.2.47) increases upto 4% and then decreases. Interference of the resin with the crystallization process may be responsible for the fall at higher percentages.

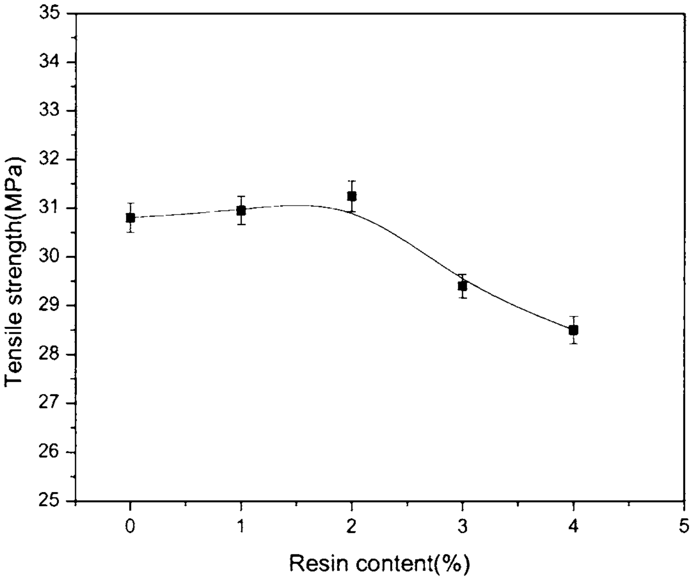


Fig.2.44 Variation of tensile strength of HAF filled NR vulcanizate with resin content

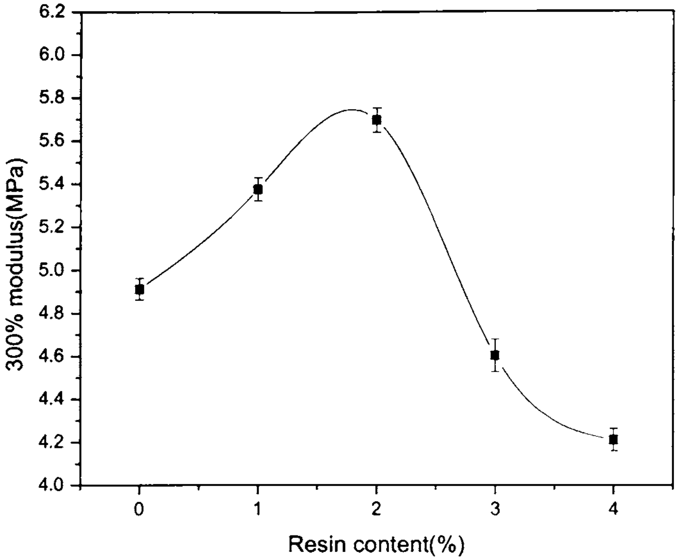


Fig.2.45 Variation of modulus of HAF filled NR vulcanizate with resin content

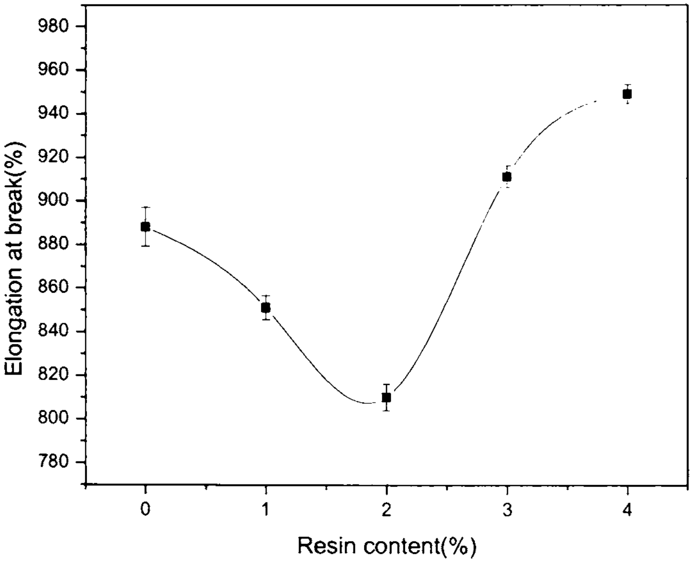


Fig.2.46 Variation of elongation at break of HAF filled NR vulcanizate with resin content

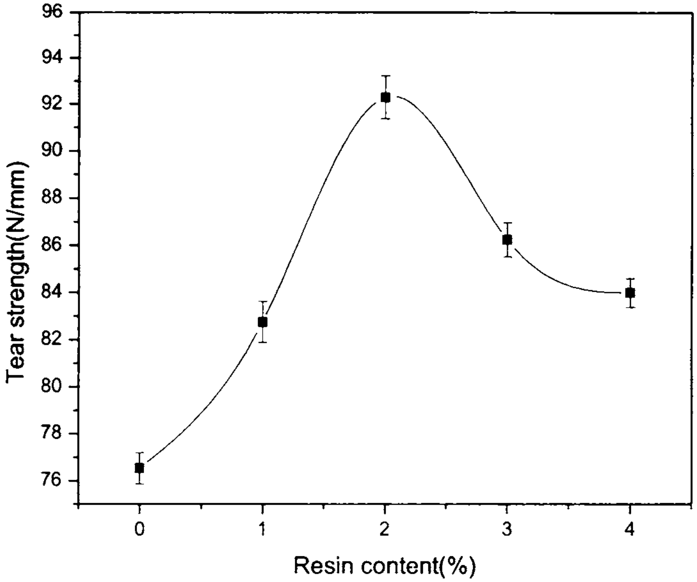


Fig.2.47 Variation of tear strength of HAF filled NR vulcanizate with resin content

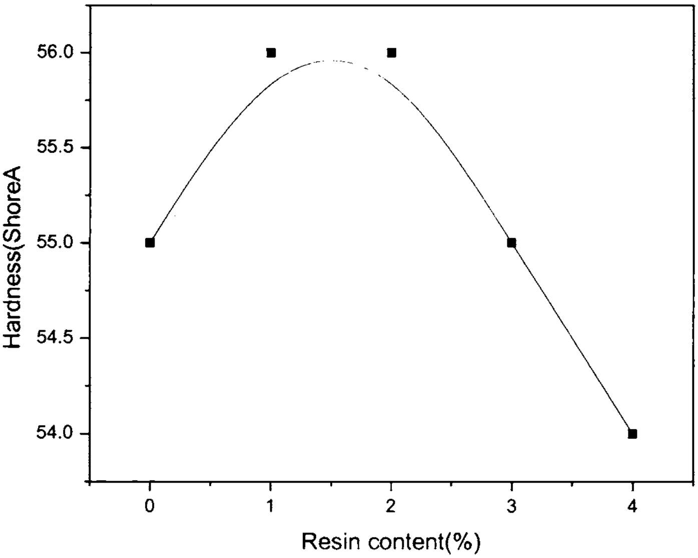


Fig.2.48 Variation of hardness of HAF filled NR vulcanizate with resin content

2.4 Conclusions

The absorption bands in FTIR spectrum of the synthesized resin are identical to that in standard spectra. Synthesized resin has greater epoxy content than the commercial sample. Incorporation of epoxy resin upto 4% into gum NR does not affect the processability. Cure time falls dramatically on addition of resin. Cure kinetic studies indicate the acceleration of cure reaction. Mechanical properties increase with resin content upto 2-3%. Enhancement of mechanical properties points to interaction of the resin with the rubber curatives. The low extractability of the resin proves that the resin has either undergone crosslinking between its own chains or taken part in interaction with the ingredients. The % retention of tensile strength and tear strength on thermal ageing increases steadily. Addition of resin dramatically reduces the percentage mass of oil absorbed over a 72 hr period. Crosslink density increases with resin content upto 2% resin. Thermogravimetric data show that NR modified by synthesized EPR is thermally more stable than the unmodified one.

In the case of EC modified samples, improvement in mechanical and cure properties is better than EPR modified ones. This may be due to the lengthy side chain of cardanol which can have an entangling effect on the rubber chains.

In the HAF filled compounds there is improvement in certain properties like modulus, tear strength and hardness upto about 2% of resin.

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Chapter

3

MODIFICATION USING PHENOLIC RESIN

3.1 Introduction

In this chapter, the effects of adding phenol formaldehyde resins, novolac type, on the properties of NR are investigated. Initial studies with a) resol type resins prepared in the laboratory using phenol and formaldehyde and b) commercial resol resins yielded vulcanizates with large bubbles which were not of acceptable quality. Hence the studies were limited to novolac resins. Both commercial and synthesized resins were used for modification. Cure characteristics, mechanical properties, ageing studies, thermal studies etc. were studied. Properties were studied for both gum and filled samples. Apart from conventional phenolic novolacs, cardanol novolac was also used for blending with natural rubber.

3.2 Experimental

3.2.1 Materials

Phenol, formaldehyde, sodium hydroxide and oxalic acid (LR grade) were supplied by Loba Chemie, Mumbai, India. Hexamethylene tetramine was supplied by Laboratory and Industrial Chemicals, Cochin and was industrial grade. Novolac powder containing 9% hexa was supplied from West Coast Polymers Private Limited, Kannur, Kerala, India.

Natural rubber (ISNR5) and compounding ingredients, their suppliers and other details are given in Section 2.2.1.

3.2.2 Synthesis of novolac resin [1]

a) Phenol formaldehyde novolac

The novolacs were prepared by reacting phenol with formaldehyde in the molar ratio 1:0.5 in the presence of oxalic acid catalyst in a 3-necked flask fitted with a mechanical stirrer, water condenser and thermometer. The reaction mixture was heated to 100°C and allowed to reflux for 2-3 hours. When the resin separated from the aqueous phase the reaction was stopped. The resin was neutralized with sodium hydroxide, filtered, washed with water and vacuum dried. Novolac resins containing phenol and formaldehyde in two other ratios viz 1:0.7 and 1:0.9 were also prepared. The resins with ratios 1:0.5, 1:0.7 and 1:0.9 are designated as Nov 0.5, Nov0.7 and Nov0.9 respectively.

A commercial sample of novolac resin (Hexa content 9%) supplied by M/S West Coast Polymers Private Limited was also used as a modifier for comparison purposes.

b) Cardanol formaldehyde novolac [1]

The same procedure was used to synthesize novolac resins from cardanol. Cardanol novolacs have been designated as CN 0.5, CN 0.7 and CN 0.9 based on cardanol / formaldehyde ratio (1:0.5, 1:0.7 and 1:0.9 respectively).

3.2.3 Compounding and curing

The novolac resin was incorporated into the gum rubber while compounding on a two roll mill. Before addition the resin was mixed with 10% by weight of hexamethylene tetramine as curing agent. Then the compounding ingredients were added in the following order: activators, filler (where applicable), accelerators, and sulphur. Mixes were prepared and cured as already described in Section 2.2.3. The formulations of the mixes are given in Tables 3.1, 3.2 and 3.3.

Table 3.1 Formulation for NR gum compound

Sample	NR (phr)	Resin (%)	ZnO (phr)	St.acid (phr)	MBTS (phr)	TMT (phr)	S (phr)
1	100	0	4	2	0.8	0.2	2.5
2	100	2	4	2	0.8	0.2	2.5
3	100	4	4	2	0.8	0.2	2.5
4	100	6	4	2	0.8	0.2	2.5
5	100	8	4	2	0.8	0.2	2.5

Table 3.2 Formulation of HAF black filled NR samples

Sample	NR (phr)	Resin (phr)	ZnO (phr)	St.acid (phr)	HAF (phr)	Ar.oil (phr)	MBTS (phr)	TMT (phr)	S (phr)
1	100	0	4	2	30	3	0.8	0.2	2.5
2	100	2	4	2	30	3	0.8	0.2	2.5
3	100	4	4	2	30	3	0.8	0.2	2.5
4	100	6	4	2	30	3	0.8	0.2	2.5
5	100	8	4	2	30	3	0.8	0.2	2.5

Table 3.2 Formulation for silica filled samples

Sample	NR (phr)	Resin (phr)	ZnO (phr)	St.acid (phr)	DEG (phr)	Silica (phr)	MBTS (phr)	TMT (phr)	S (phr)
1	100	0	4	2	1	15	0.8	0.2	2.5
2	100	2	4	2	1	15	0.8	0.2	2.5
3	100	4	4	2	1	15	0.8	0.2	2.5
4	100	6	4	2	1	15	0.8	0.2	2.5
5	100	8	4	2	1	15	0.8	0.2	2.5

3.2.4 Quality evaluation

The vulcanizates were tested according to relevant ASTM standards. The details of the test procedure as well as the ASTM standards applicable have already been furnished in Section 2.2.4.

a) Differential scanning calorimetry

The differential scanning calorimetry of NR vulcanizates was done on a Differential Scanning Calorimeter Q-100, TA instruments. The energy changes associated with transitions were recorded in a temperature range of -60 to 100°C. Samples of known weight encapsulated in standard aluminium pans placed in the sample holder were subjected to the analysis.

b) Ozone resistance

The ozone test chamber manufactured by MAST Development Company, USA was used to study ozone resistance. The chamber provided an atmosphere with a controlled concentration of ozone and temperature. Ozone concentration selected was 50 pphm, which is generated by a UV quartz lamp.

The test was carried out as per ASTM D 1149-99 specifications at 40°C. B type specimens were tested in duplicate and in the form of a bent loop. Rectangular strips of length 95 mm, breadth 25mm and thickness 2 ± 0.2 cut with the grain in the length direction from tensile sheets were folded and tied at 25mm length from the edges to get the required strain (>20%). These were then conditioned for 24 hours. The conditioned samples were exposed to the ozonized air in the chamber. Periodic observations of the surface of the samples were made for crack initiation. Photographs of the surface of the irradiated samples were taken.

3.3 Results and discussions

a) Gum NR modified by novolacs

Fig.3.1 shows the FTIR spectrum of phenol formaldehyde novolac resin 1:0.9. Characteristic absorptions were found around 3300 cm^{-1}(hydroxyl group, broad band), 3100cm^{-1}(aromatic C-H str. weak), 1594cm^{-1} and1500 cm^{-1} (phenyl ring) and 1475 cm^{-1}(CH$_2$ bending). The two strong bands around 1230 cm^{-1}and 1010 cm^{-1} are characteristic of C-O stretching in phenol and alcohol groups respectively [2].

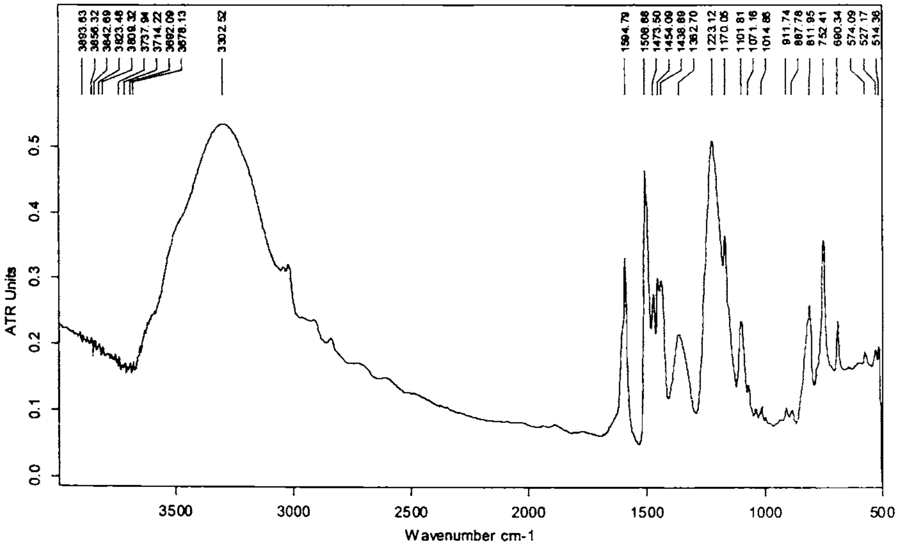

Fig.3.1 FTIR spectrum of phenol formaldehyde novolac resin

Figs. 3.2 and 3.3 show the FTIR spectra of modified NR and unmodified NR. The spectra show that no important chemical changes have taken place in the rubber by the incorporation of novolac resin.

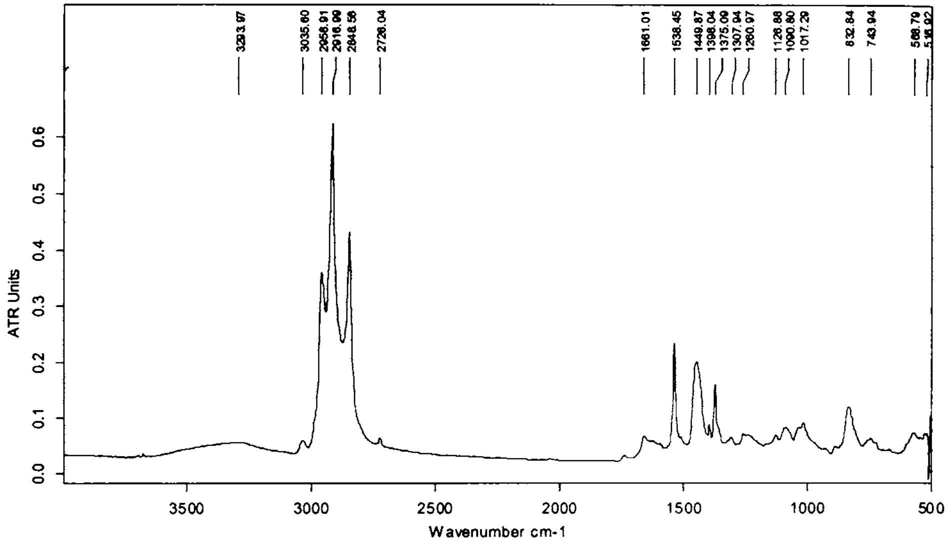

Fig.3.2 FTIR spectrum of novolac modified NR vulcanizate

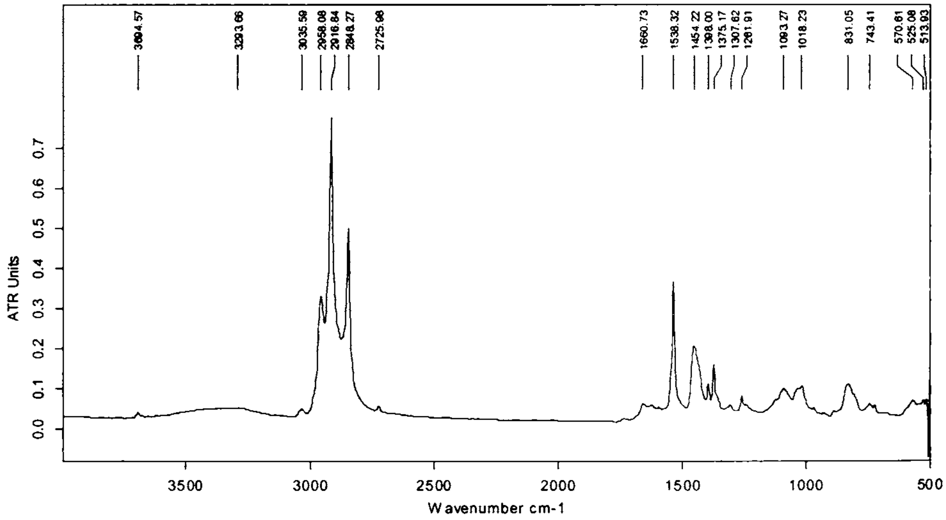

Fig.3.3 FTIR spectrum of NR vulcanizate

Curing studies indicate that initially there is a fall in cure time on addition of the resin. The presence of hexa methylene tetramine can have an accelerating effect on crosslinking with the rubber. [3] This can explain the shorter cure time at low percentages of resin. On addition of more resin the cure time tends to increase (Fig.3.4). The novolac molecules form large networks on crosslinking. This effect may lead to some hindrance to crosslinking of rubber chains at higher concentrations. Another possible explanation is imperfect dispersion of the resin at higher percentages which can lead to reduced interaction between rubber chains as well as between rubber chains and resin molecules. The acidic nature of the novolac molecules can also have a retarding effect on the crosslinking of the rubber. The lowest cure time are exhibited by blends containing commercial novolac resin.

The commercial resin shows better compatibility with the rubber. This leads to increasing torque levels during curing studies using higher percentages of the resin.(Table 3.1).

Table 3.1 Cure characteristics of gum NR vulcanizate with novolac resin

Resin content (%)		Scorch time(min)	Cure time (min)	Maximum Torque(dNm)	Cure rate index (min^{-1})
0		2.62	5.62	2.6	33.33
Commercial novolac	2	2.03	4.42	2.79	41.84
	4	1.82	4.20	2.86	42.01
	6	1.67	4.14	2.98	40.48
	8	1.64	4.49	3.10	35.08
Nov 0.5	2	2.33	4.73	2.59	41.66
	4	1.6	3.71	2.67	47.31
	6	1.38	4.13	2.58	36.36
	8	1.22	5.18	2.66	25.25
Nov 0.7	2	2.29	4.86	2.72	38.91
	4	1.77	4.34	2.77	38.91
	6	1.54	4.65	2.71	32.15
	8	1.33	5.10	2.88	26.52
Nov 0.9	2	2.31	5.46	2.79	31.74
	4	1.78	4.29	2.95	39.84
	6	1.68	4.35	2.84	37.45
	8	1.51	4.94	2.89	29.15

Cure rate index is found to be increase with resin content upto 4% of resin which indicates that novolac resin accelerates the curing reaction. This is confirmed by cure kinetics. The cure rate constant also follows the same trend as cure rate index (Table 3.2).

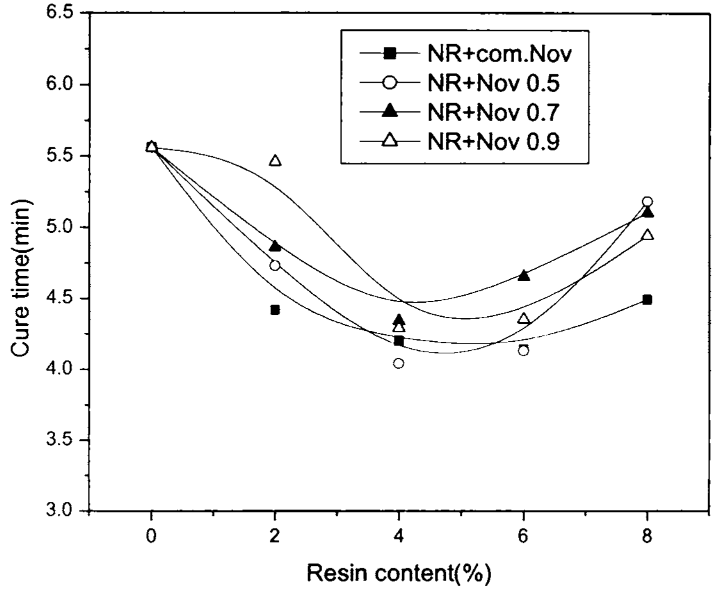

Fig.3.4 Variation of cure time with resin content

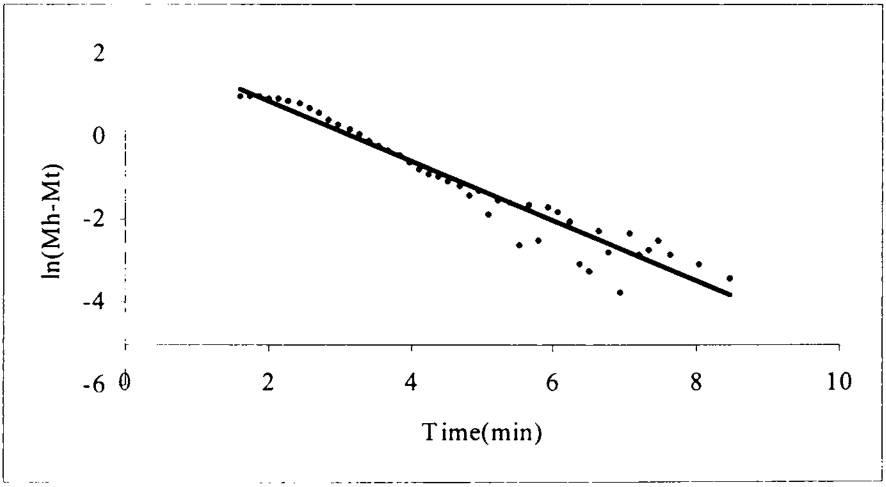

Fig.3.5 Plot of ln(Mh-Mt) vs t of NR+2% Nov 0.5

Figs. 3.5 to 3.8 are the plots of ln(Mh-Mt) vs time of NR compound with varying novolac-1. Cure rate constants are given in Table 3.2. When the resin content increases rate of the reaction increases upto 4% of resin followed by a slight decrease in cure reaction.

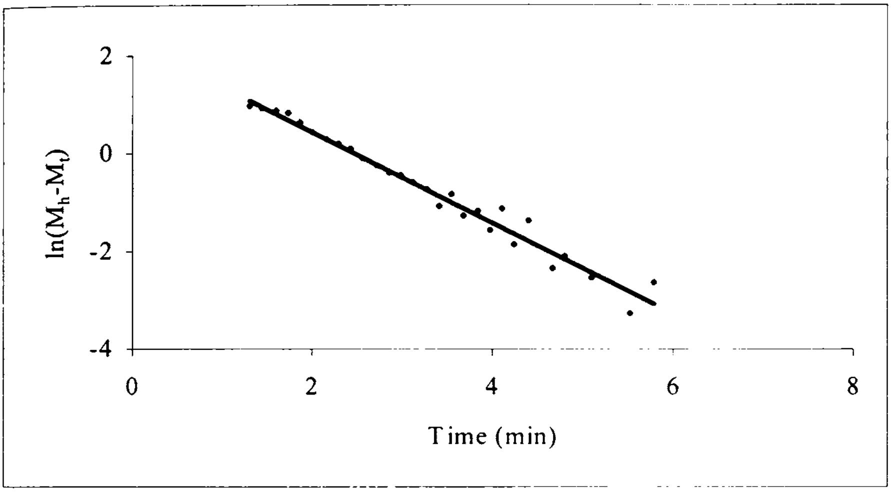

Fig.3.6 Plot of ln(Mh-Mt) vs t of NR+4% Nov 0.5

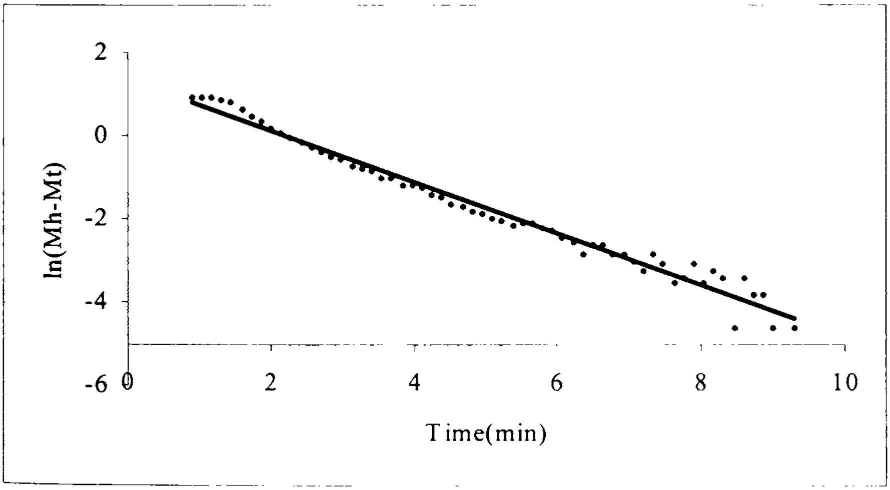

Fig.3.7 Plot of ln(Mh-Mt) vs t of NR+6% Novo 0.5

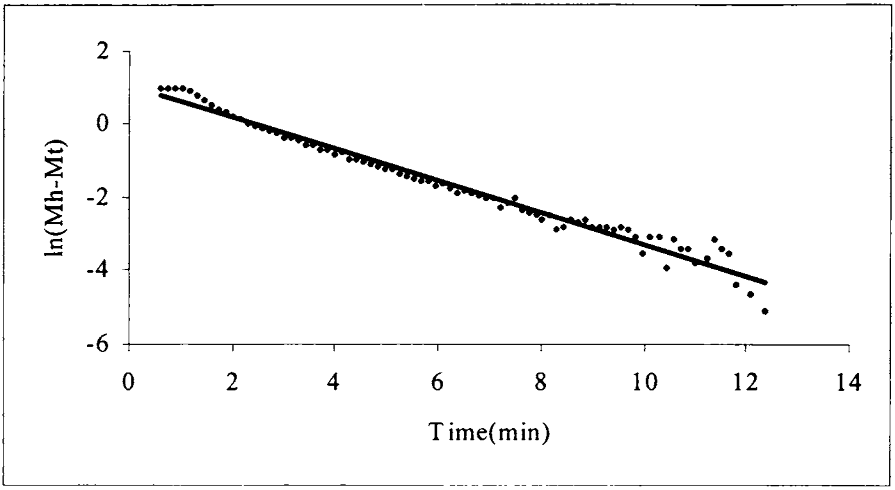

Fig.3.8 Plot of ln(Mh-Mt) vs t of NR+8% Nov 0.5

Table 3.2 Cure rate constants of NR compounds with varying novolac-1

Sample	**Cure rate constant(min^{-1})**
NR	0.2257
Novolac-1 2%	0.7306
Novolac-1 4%	0.9288
Novolac-1 6%	0.6229
Novolac-1 8%	0.4316

Fig.3.9 shows the variation of tensile strength on addition of various percentages of novolac resin (commercial as well as synthesized) to the rubber. The resin has been synthesized with phenol / formaldehyde (P/F) ratio varying from 1: 0.5 to 1: 0.9. Each resin shows a maximum tensile strength at some percentage ranging from 2 to 6%. The novolac resin with P/F ratio 1:0.5 shows the greatest improvement (~ 47% over virgin NR) in tensile strength at 4%. At this P/F ratio the number of benzene rings in the resin molecule will be

presumably the highest. Any interpenetrating effect between the rubber and the resin is likely to be maximum for this P/F ratio. Hence the better performance.

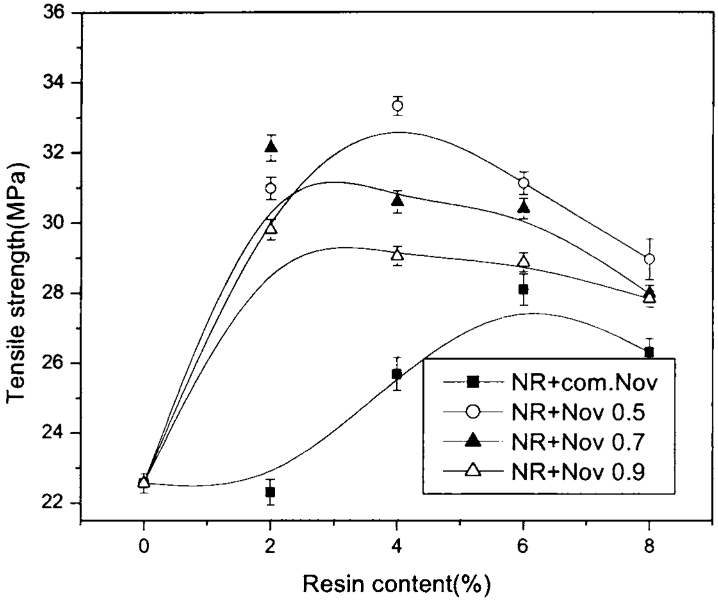

Fig. 3.9 Variation of tensile strength with resin content

The marginal improvement in tensile modulus and the increase of elongation at break (Figs.3.10&3.11) on addition of resin are pointers to some extent of interpenetration. Both these properties show maximum values at percentages of the resin varying from 2-6%. The improvement in modulus is not substantial. But the elongation at break shows enhanced values up to 2% resin but falls abruptly at higher percentages. Presumably the dispersion of the resin is not effective at higher percentages resulting in filler like behavior. Other reasons cited earlier in connection with tensile strength also apply here.

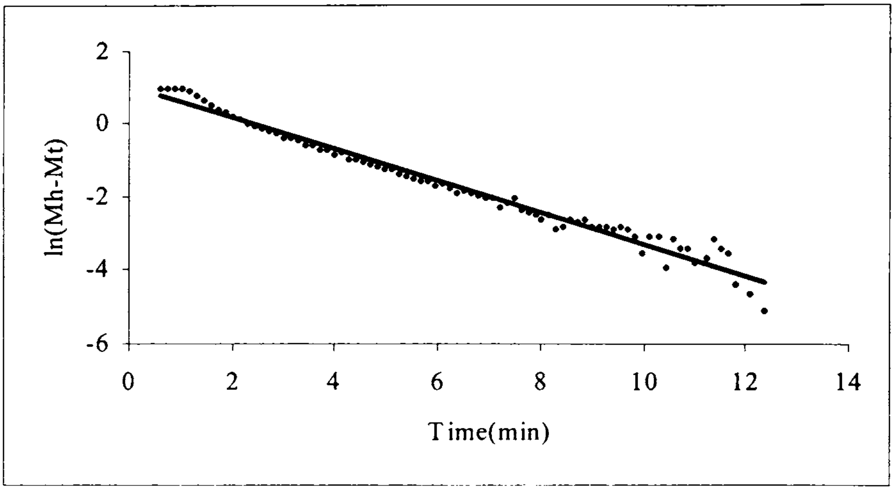

Fig.3.8 Plot of ln(Mh-Mt) vs t of NR+8% Nov 0.5

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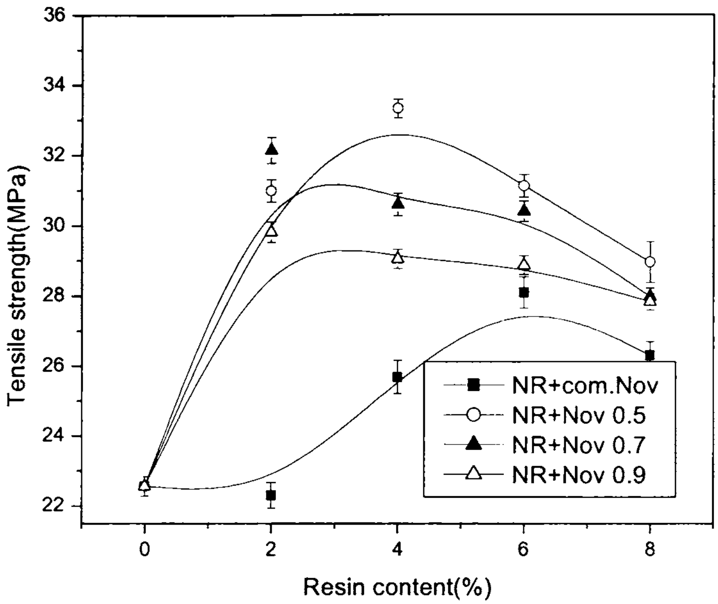

Fig. 3.9 Variation of tensile strength with resin content

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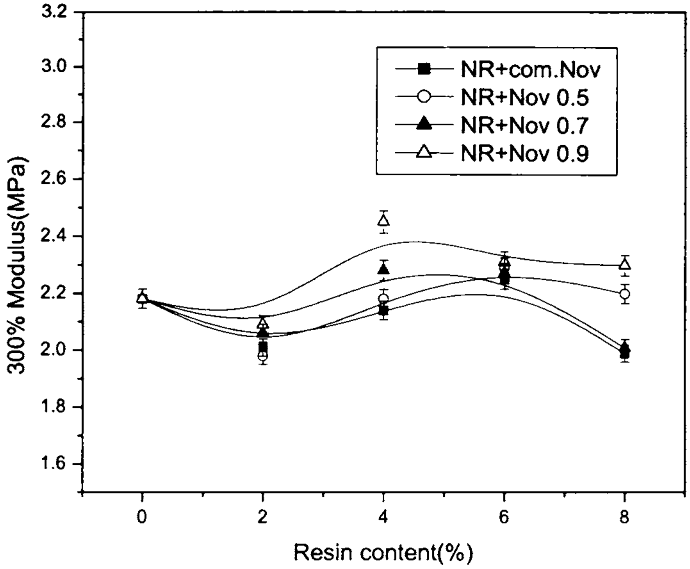


Fig. 3.10 Variation of modulus with resin content

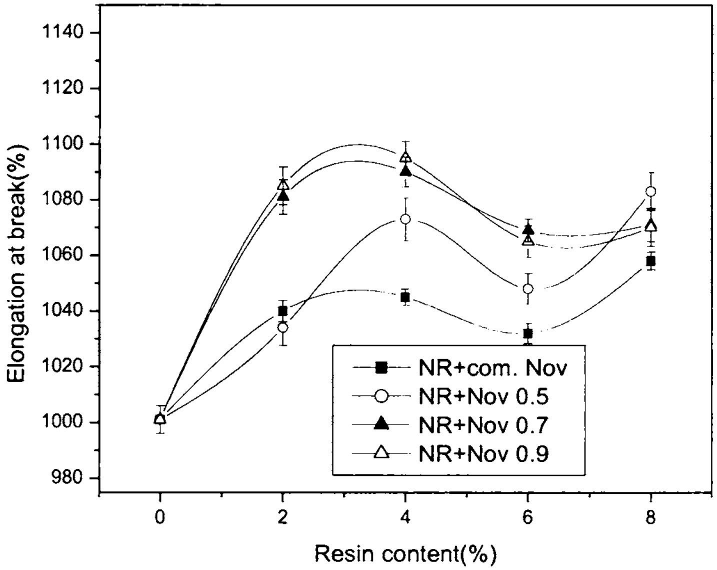


Fig.3.11 Variation of elongation at break with resin content

Coming to tear strength (Fig.3.12) there is a general improvement on addition of increasing amounts of resin. The sample of commercial resin shows the maximum improvement at 8% resin content (about 25% over that of the unmodified resin). This might be due to better compatibility between the rubber and resin. The improved tear strength also suggests interpenetration. Variation in surface hardness is shown in Fig.3.12. Hardness shows improvement upto 6% resin.

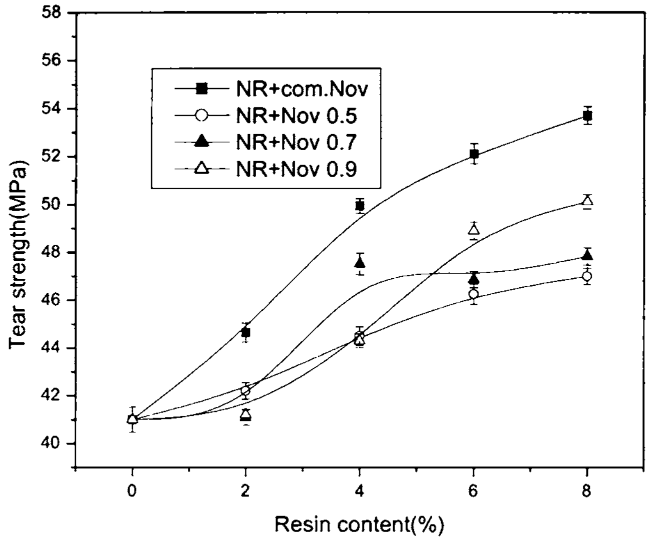


Fig.3.12 Variation of tear strength with resin content

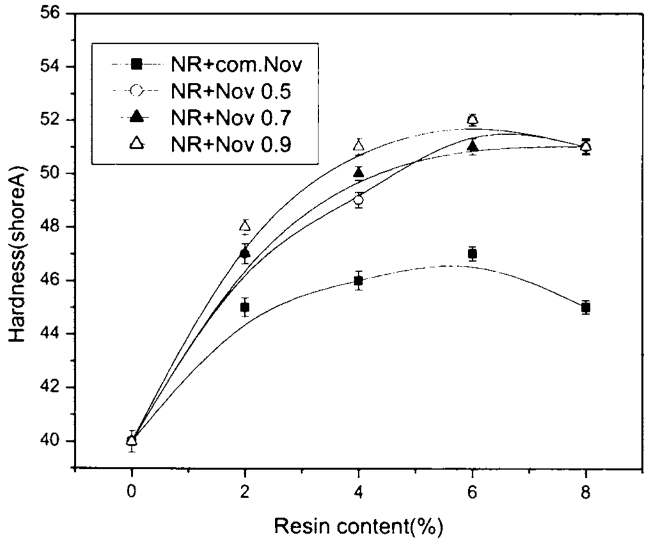


Fig.3.13 Variation of hardness with resin content

Fig. 3.14 shows the variation in weight loss on extraction with acetone. There is only a moderate increase in weight loss on extraction with resin content. The commercial resin seems to be more compatible judging from the weight loss. The low extractability of the resin from the rubber proves that the resin has either 1) undergone crosslinking between its own molecules or 2) taken part in interactions with the rubber chains. The occurrence of Chroman ring formation and/or quinone methide reaction [4,5] cannot be ruled out.

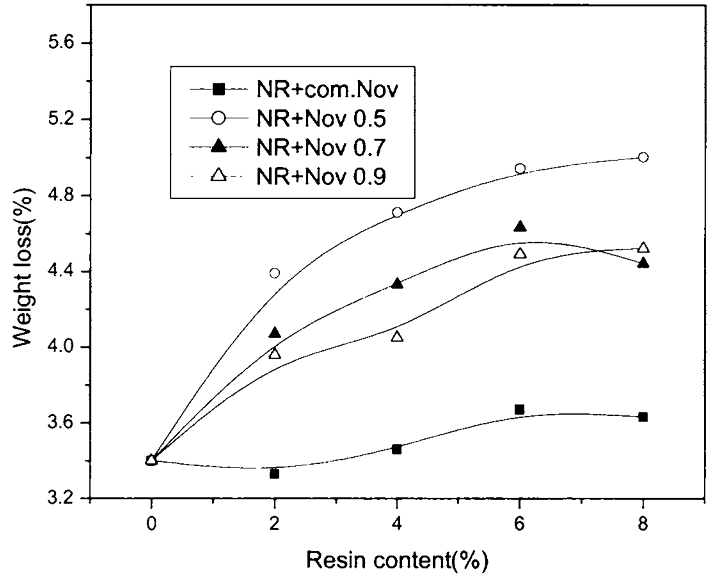


Fig.3.14 Variation of weight loss on soxhlet extraction with resin content

Figs. 3.15 and 3.16 depict the retention of tensile and tear strengths of different samples after ageing at 70°C for 72 hrs. In the absence of the resin the percentage retention of tensile strength after 72 hrs of ageing is only about 55%. On addition of resin this value increases steadily until at about 8% it is almost 100% of the original tensile strength. Similarly in the case of tear strength there is a dramatic improvement in tear strength retention at 2% resin. Although further increase is not substantial most samples show more than 100% retention of tear strength at 2%. The prolonged ageing process may help to make the crosslinking reaction of resin and/or chemical interaction between the rubber and the resin to go to completion. Hence the improvement on ageing.

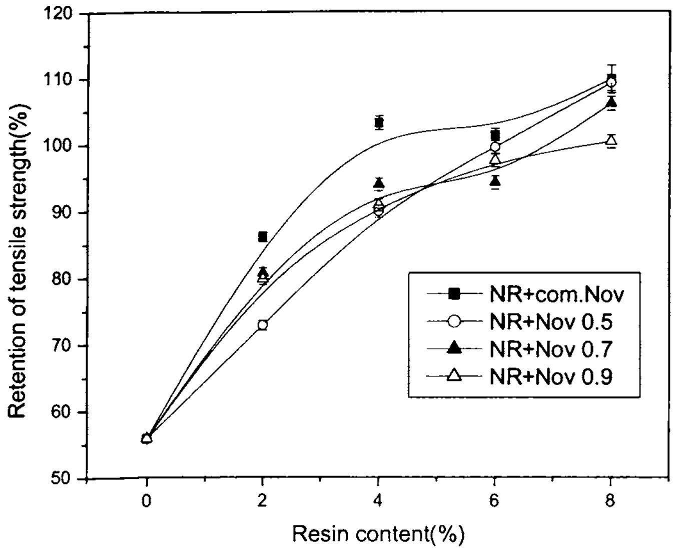


Fig.3.15 Variation of retention of tensile strength on ageing at 70°C for 72 hrs

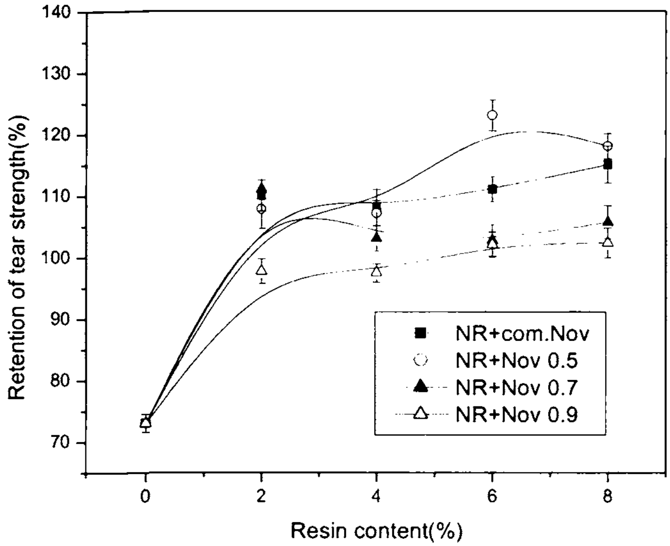


Fig. 3.16 Variation of retention of tear strength on ageing at 70°C for 72 hrs.

Fig. 3.17 shows that the addition of resin dramatically reduces the percentage mass of oil absorbed over a 72 hour period. The presence of the resin in the crosslinked condition has made the rubber less penetrable for oil. Moreover, the polar nature of the resin reduces the interaction between the rubber chains and oil.

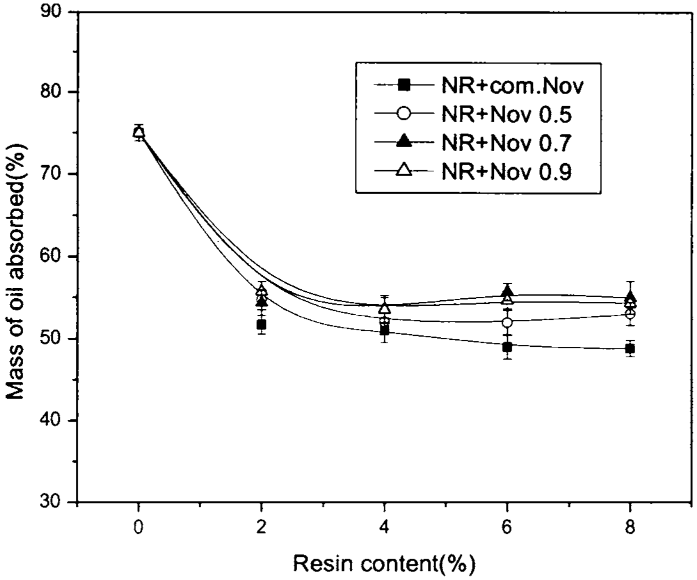


Fig.3.17. Variation of mass of oil absorbed with resin content

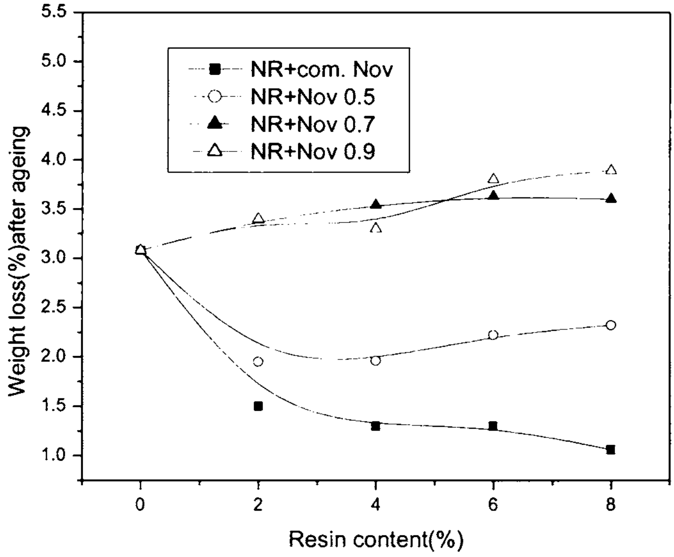


Fig.3.18 Variation of weight loss on soxhlet extraction after ageing

Fig. 3.18 shows the variation of the weight loss on Soxhlet extraction after ageing. For the commercial samples and the P/F ratio = 1:0.5 samples there is a sudden fall in weight loss after ageing. The effect of increasing resin content on this property is not substantial. Samples containing novolac of increasing formaldehyde content (1:0.7 and 1:0.9) exhibit no fall in weight loss on extraction after ageing. This is possibly related to increasing amounts of methylol groups which tend to get extracted by acetone.

Fig. 3.19 shows the variation of crosslink density with increasing resin content. Only the commercial samples show a slight increase in crosslink density by the addition of the resin. The synthesized samples on the other hand show a slight lowering of crosslink density on addition of resin. This could be related to formation of more and more bulky novolac molecules which can hinder rubber crosslinking.

Table 3.3 shows the important thermal data obtained from NR gum samples modified by different novolac resins. The improvement in thermal resistance is marginal. There is an increase in onset degradation temperature compared to the unmodified rubber. Similarly a slight increase in the residue percentage is obtained on addition of the novolac resins.

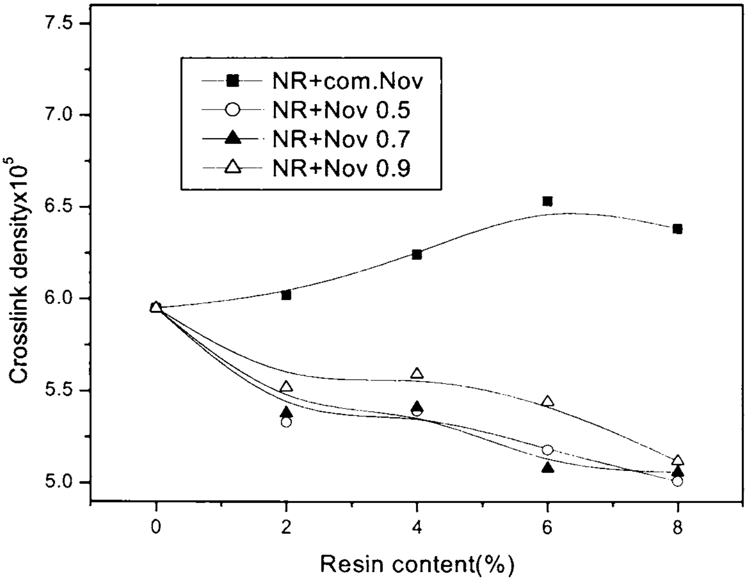


Fig.3.19 Variation of crosslink density with resin content

Table 3.3. Characteristics of thermograms of NR vulcanizates with novolac resin

	NR	**Nov 0.5**	**Nov 0.7**	**Nov 0.9**
Onset degradation temp.(°C)	312.72	318.66	318.46	316.94
Temp. at 50% degradation(°C)	388.99	390.79	390.01	389.02
Temp.at max. Degradation (°C)	384.23	386.08	385.30	384.36
Rate at max. Degradation (% / °C)	1.556	1.505	1.519	1.521
Residue (%)	4.297	5.023	5.738	5.554

Figs.3.20 to 3.22 are the Freeman-Carrol plots of novolac modified NR vulcanizates. These also show the better thermal stability of novolac modified samples. Calculated values of activation energies are slightly greater for modified samples than the unmodified sample (207.7kJ/mol).

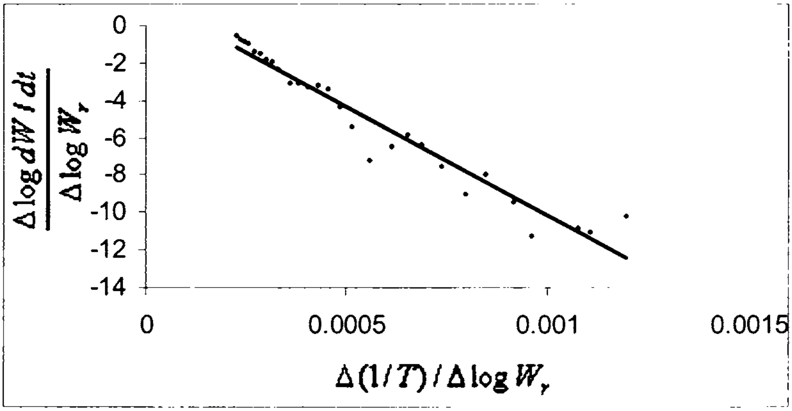


Fig.3.20 Freeman- Carrol plot of NR + novolac 0.5. Ea= 223.74 kJ/mol

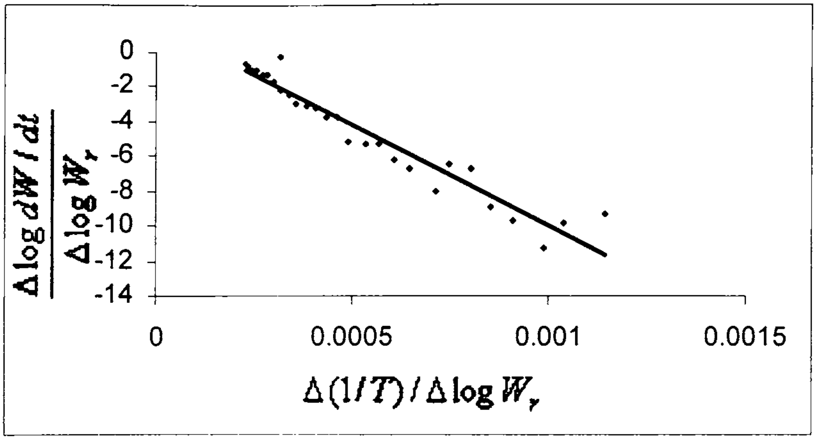


Fig. 3.21 Freeman- Carrol plot of NR + novolac 0.7. Ea=223.63kJ/mol

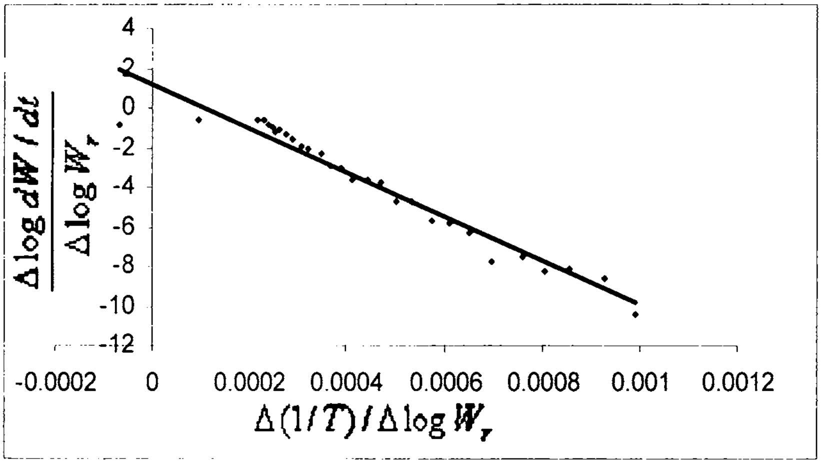


Fig.3.22 Freeman- Carrol plot of NR + novolac 0.9. Ea=213.01kJ/mol

The differential scans of NR samples and novolac modified samples are shown in Figs.3.23 and 3.24 . From the figures it can be seen that the glass transition temperature increases from -63.92 to -60.02 °C, a marginal increase.

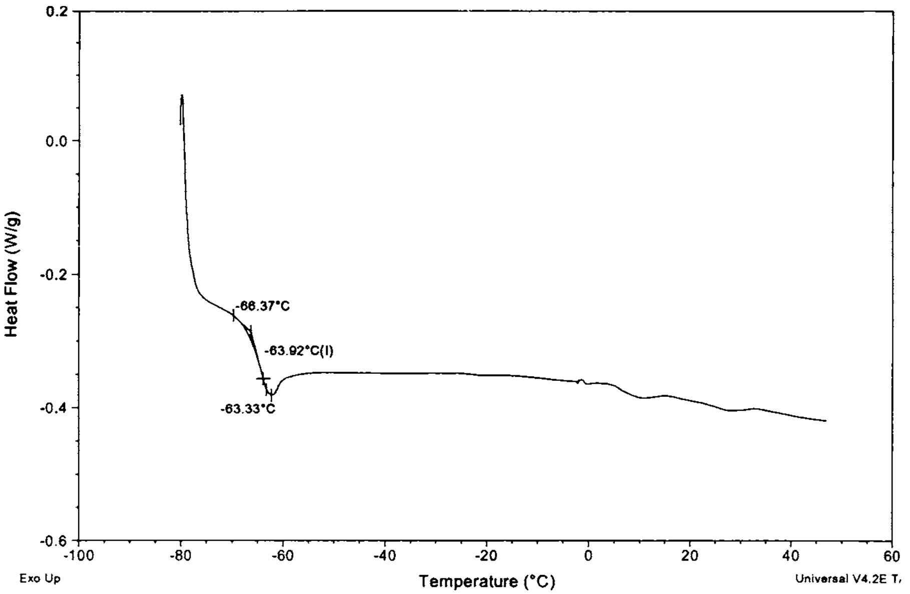


Fig.3.23 Differential scan of NR gum vulcanizate

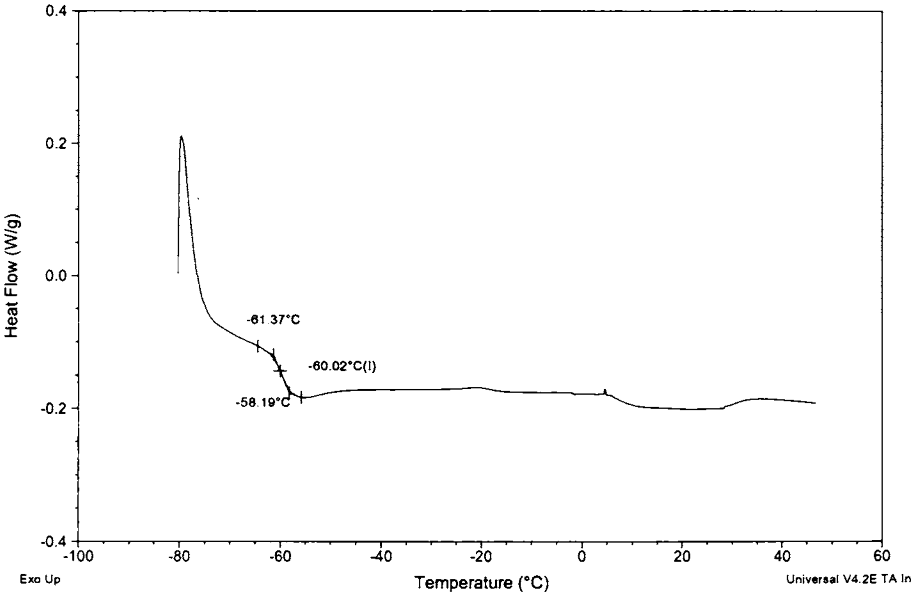


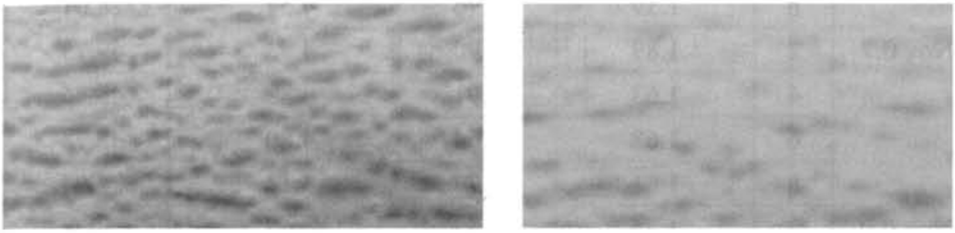
Fig. 3.24 Differential scan of NR vulcanizate with 4% of novolac 0.5

Photographs of ozone irradiated NR vulcanizate and novolac modified NR vulcanizates are shown in the Fig.3.25. The results are given in Table.3.4

.The results show that in the novolac modified samples crack initiated after 12 hours but in the unmodified samples crack initiated after 6 hours. Hence novolac bestow improved ozone resistance on NR.

Table 3.4 Results of ozone irradiation

Sample	Ozone resistance (50pphm, 40°C)
NR	Crack initiated after 6 hrs.
NR+novolac 0.5	Crack initiated after 12 hrs.



NR vulcanizate

NR+ novolac 0.5

Fig. 3.25 Ozone irradiated surfaces of NR vulcanizate and novolac modified vulcanizate.

b) HAF filled NR modified by novolacs

Fig.3.25 shows the variation of cure time of HAF filled NR vulcanizate on addition of various percentages of phenolic novolac resins. In general, there is an increasing tendency for cure time as more resin is added. One possible reason is the acidic nature of phenolic novolac molecule which can inhibit the rubber crosslinking reaction. Also, the slowing down of the curing reaction is exaggerated by the presence of the filler, HAF black. The addition of filler usually leads to a reduction of cure time. (Compare cure times in Figs. 3.4 and 3.26, for gum compound and filled compound, both without resin.) This is a wellknown phenomenon and is explained by the heat of mixing the filler. In this case, the resin can act as a plasticizer thus bringing down the heat of mixing. The increase in cure time can be an extreme case of this effect.

Table 3.5 Cure characteristics of HAF black filled NR vulcanizate with novolac resin

Resin content(%)		Scorch time(min)	Cure time (min)	Maximum Torque(dNm)	Cure rate index (min^{-1})
0		2.23	3.77	4.26	64.93
Nov 0.5	2	1.76	3.15	3.85	71.94
	4	1.57	3.31	4.19	57.47
	6	1.40	3.96	4.49	39.06
	8	1.39	4.96	4.54	28.01
Nov 0.7	2	1.89	3.90	4.53	49.75
	4	1.63	3.91	4.89	43.86
	6	1.68	4.64	4.80	33.78
	8	1.61	5.77	5.14	24.04
Nov 0.9	2	1.75	3.57	4.67	54.9
	4	1.49	3.91	5.06	41.32
	6	1.42	4.92	5.11	28.57
	8	1.44	6.72	5.24	18.94

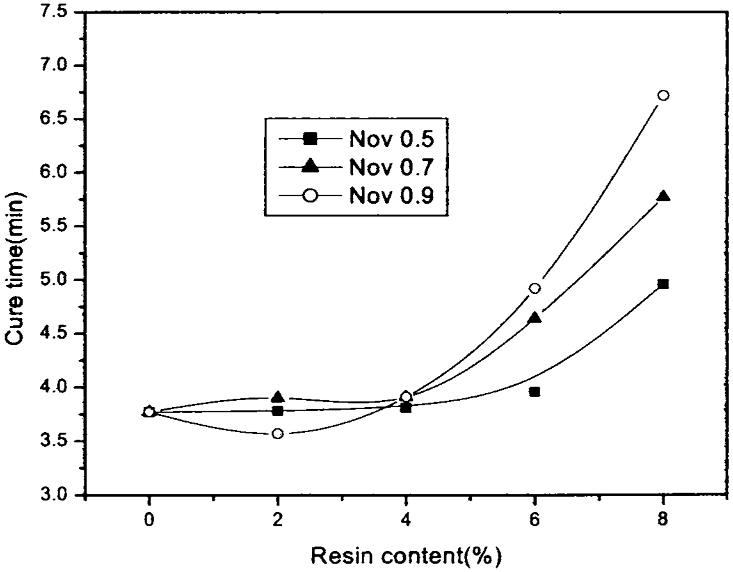


Fig.3.26. Variation of cure time with resin content

Fig.3.27 shows the variation of α value of 30 phr HAF filled samples with resin content. Lower α values indicate better dispersion. There is a general tendency for alpha to increase as the resin content increases. Hence filler dispersion is somewhat poorer at higher resin contents. However the change in alpha is only moderate.

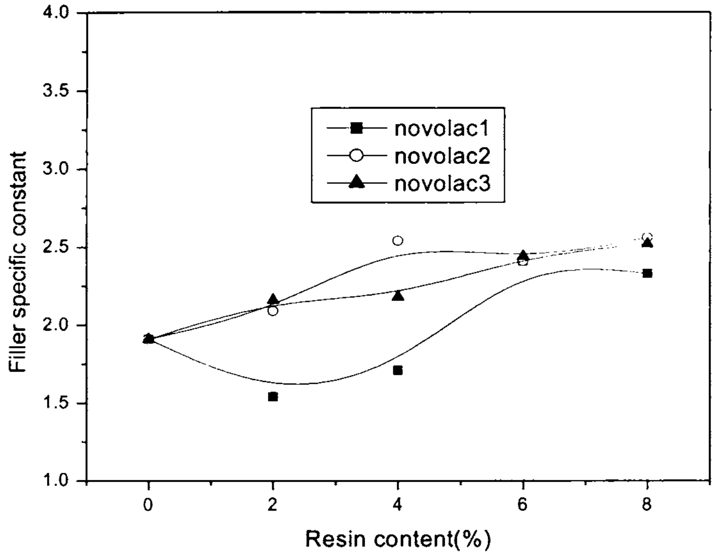


Fig.3.27 Variation of α value with resin content

Table 3.6 Cure rate constants of 30 phr HAF filled samples with novolac resin

Sample	Rate constant (min^{-1})
Nov 0.5 0%	1.5136
Nov 0.5 2%	1.2676
Nov 0.5 4%	0.881
Nov 0.5 6%	0.65
Nov 0.5 8%	0.5028

Table 3.6 gives comparative values of cure rate constants as the resin content goes up. There is a steady fall of the rate constant as the resin content goes up.

Fig. 3.28 shows the variation of tensile strength of HAF black filled NR with resin content. There is a slight fall in tensile strength beyond 4% resin. This can be attributed to some negative effect on the rubber crosslinking reaction by the presence of increasing amounts of resin. In the light of the arguments presented in the case of cure time, this behaviour is to be expected.

Modulus at 300% elongation is shown in Fig.3.29 as a function of the resin content. The resin has a slight stiffening effect on the rubber as indicated by a slight increase in modulus.

Elongation at break (Fig.3.30) is also found to fall on addition of the resin. The increase in modulus as well as the decrease in elongation at break suggest some amount of interpenetration in the components. Tear strength (Fig.3.31) varies within a narrow range as more resin is added.

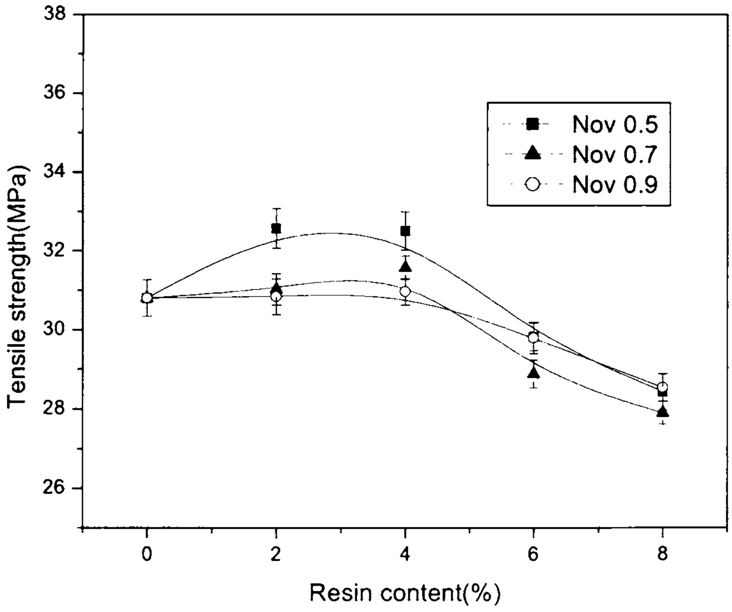


Fig.3.28 Variation of tensile strength with resin content

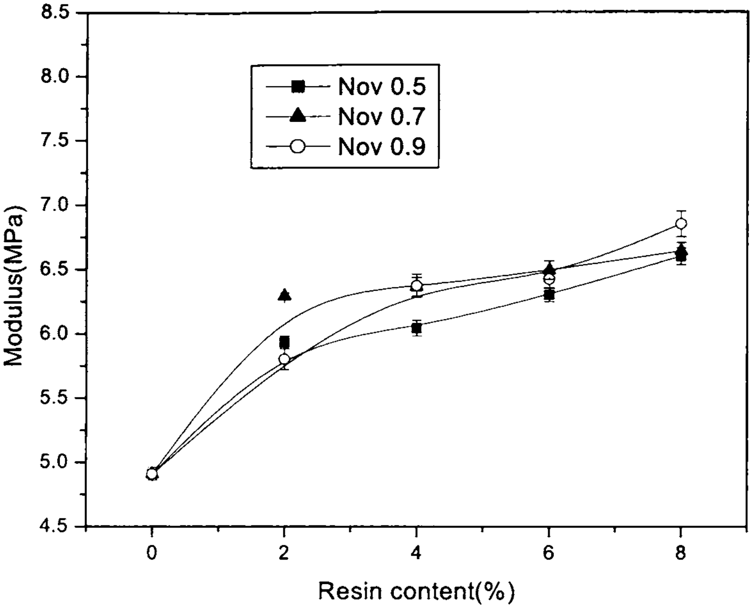


Fig.3.29 Variation of 300% modulus with resin content

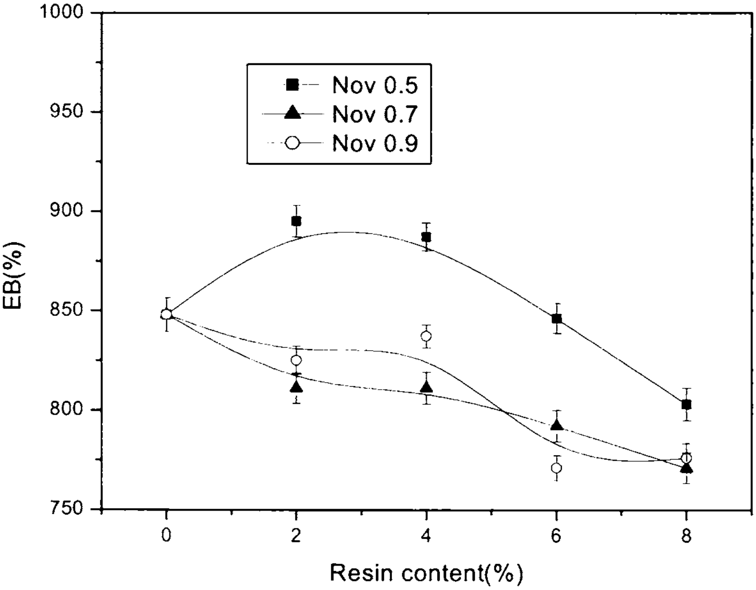


Fig.3.30 Variation of elongation at break with resin content

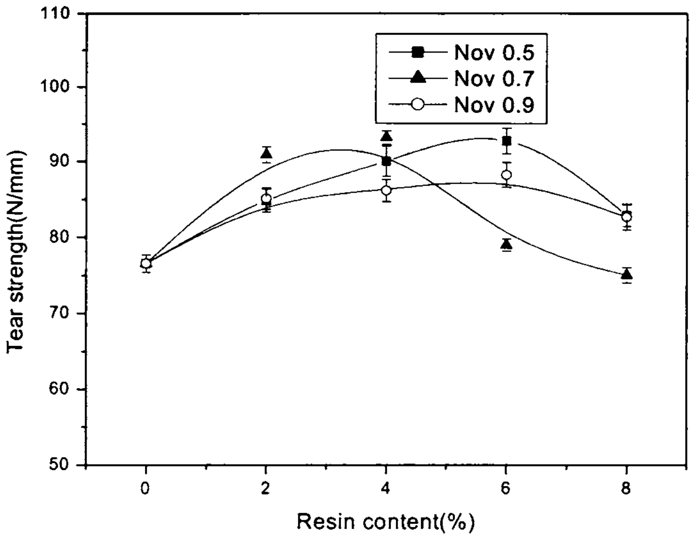


Fig.3.31. Variation of tear strength with resin content

Surface hardness of the rubber (Fig.3.32) has an increasing effect on addition of resin. This is to be expected from the thermoset nature of the resin. The hardness is already higher for filled samples but on addition of resin there is a steady increase in hardness and a plateau can be expected only at much higher percentages of the resin unlike results obtained for gum rubber.

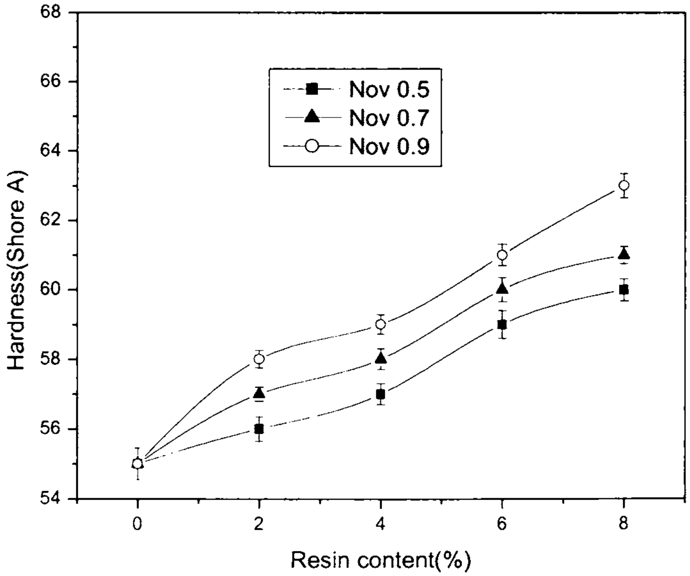


Fig.3.32 Variation of hardness with resin content

Fig.3.33 shows the variation of retention of tensile strength after ageing at 70°C for 72 hours. Here also there is a higher retention of tensile strength on ageing on addition of resin.

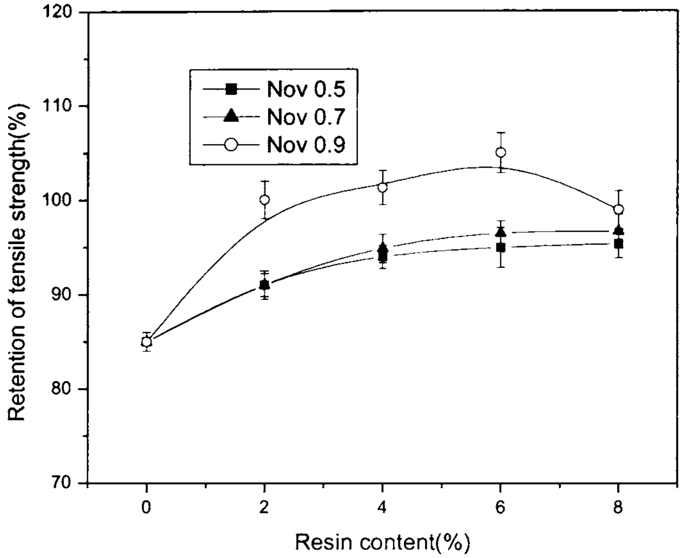


Fig.3.33 Variation of retention of tensile strength on ageing at 70°C for 72 hrs

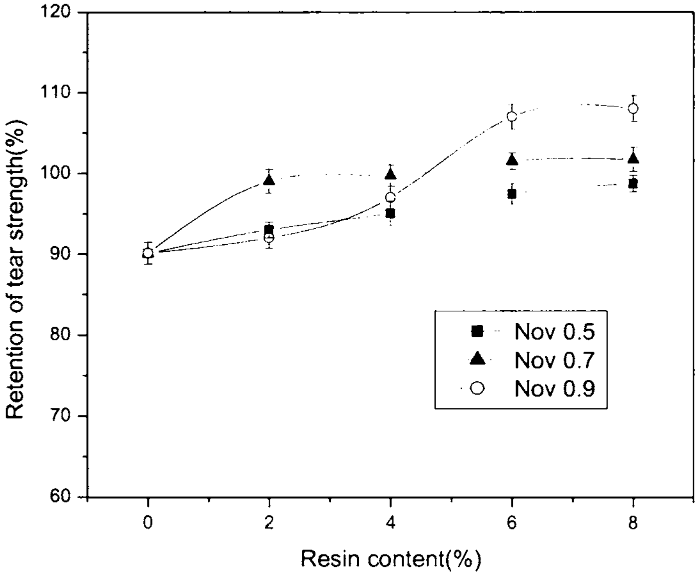


Fig.3.34. Variation of retention of tear strength on ageing at70°C for 72 hrs.

This behavior is more noticeable in the case of the resin containing relatively more formaldehyde. Similarly tear strength retention after ageing (Fig.3.34) also shows an increasing tendency on addition of more resin although the variation is less dramatic. It is possible that the crosslinking reaction of the resin as well as any likely interactions between resin and rubber go to completion on aging.

The presence of the resin leads to reduction in the mass of oil absorbed even in the presence of carbon black (Fig.3.35). Hence there is some improvement in oil resistance of the HAF black filled NR on addition of phenolic novolac resin.

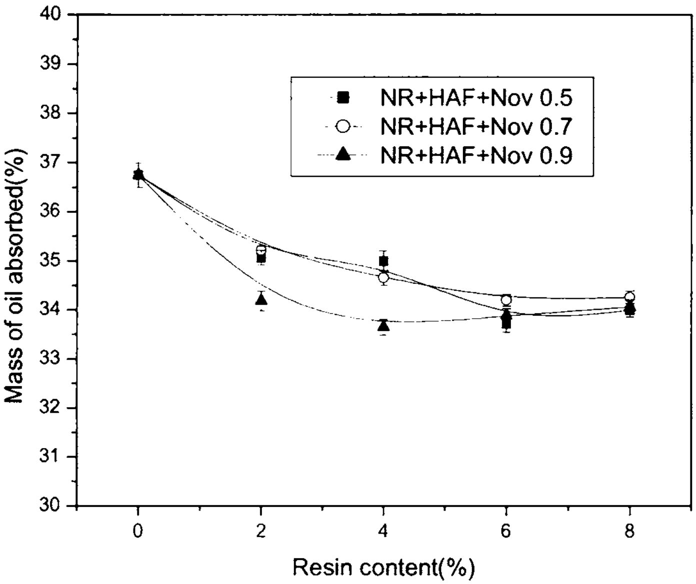


Fig.3.35 Variation of mass of oil absorbed with resin content

c) Silica filled NR modified by novolacs

Fig.3.36 shows the effect of novolac resin content on the cure time of silica filled NR vulcanizates. The increase in cure time is more noticeable than in the case of black filled NR. Silica has a tendency to adsorb curatives. In spite of adding glycols, this effect can persist to some extend.The heat of mixing is more severe in the case of silica [6]. But the presence of the resin can nullify this to some extend by acting like a plasticizer.

Table 3.7 Cure characteristics of silica filled NR vulcanizate with novolac resin

Resin content(%)		Scorch time(min)	Cure time (min)	Maximum Torque(dNm)	Cure rate index (min^{-1})
0		2.84	3.73	2.74	50.0
Nov 0.5	2	2.31	2.78	2.78	39
	4	2.64	2.78	2.78	27.6
	6	3.08	2.71	2.71	24.4
	8	3.72	2.70	2.70	21.13
Nov 0.7	2	2.53	2.63	2.63	40.6
	4	2.62	2.75	2.75	36.36
	6	2.76	2.82	2.82	25.0
	8	3.45	2.74	2.74	20.40
Nov 0.9	2	2.60	2.57	2.57	40.16
	4	2.69	2.71	2.71	30.2
	6	3.46	2.56	2.56	23.3
	8	4.11	2.61	2.61	17.7

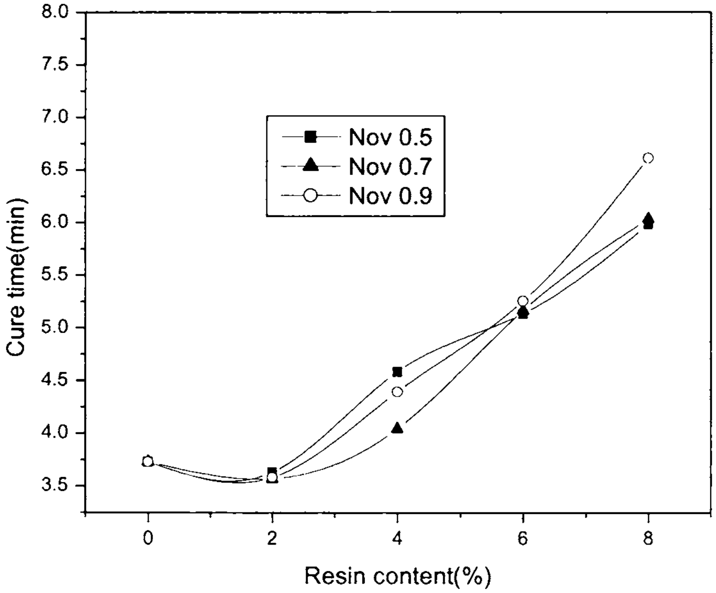


Fig.3.36 Variation of cure time with resin content

Tensile strength (Fig.3.37) is again negatively influenced by the presence of the resin similar to the case of black filled NR. This can be due to the inhibiting effect of the resin on the cure reaction.

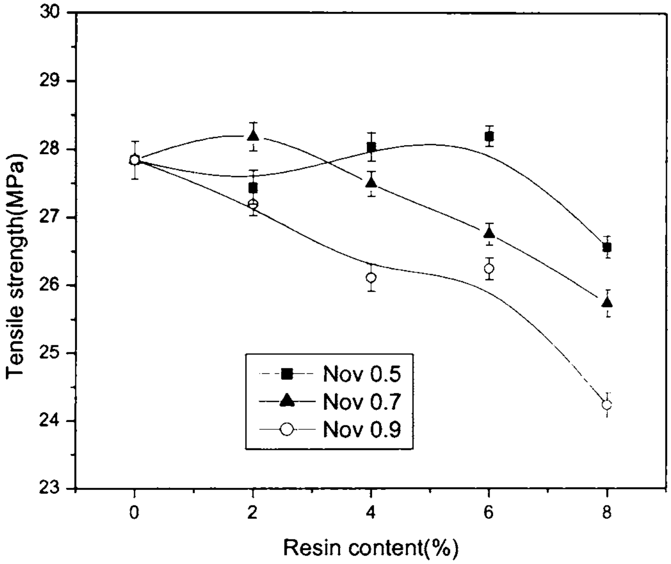


Fig.3.37 Variation of tensile strength with resin content

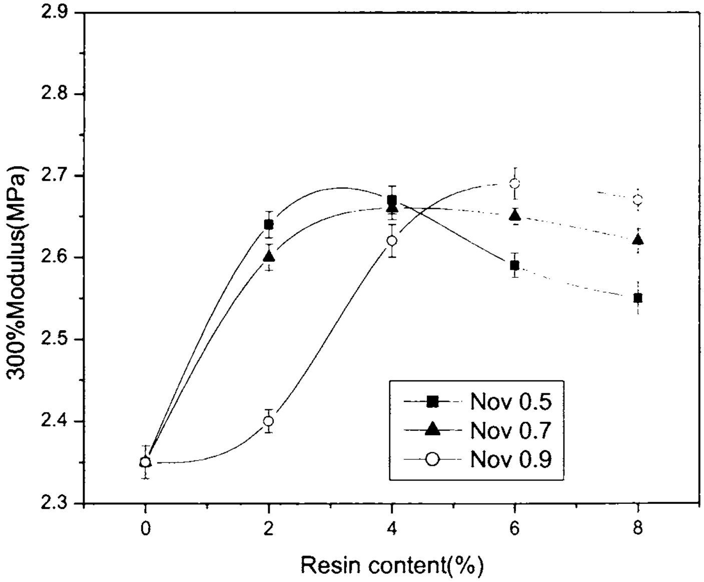


Fig.3.38 Variation of modulus with resin content

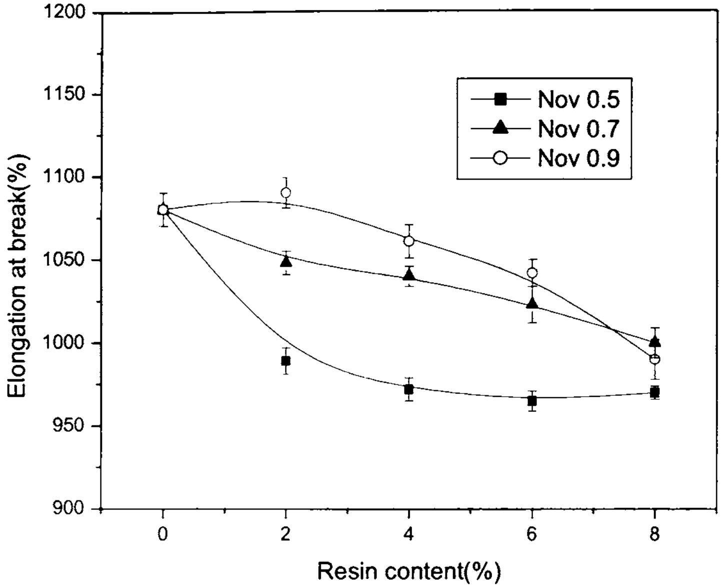


Fig.3.39 Variation of elongation at break with resin content

As in the case of black filled NR there is a increase in 300% modulus (3.38) and a fall in elongation at break (3.39) on addition of resin. Both can be attributed to moderate amounts of interpenetration between the components.

Moderate amounts of resin has a positive effect on the tear strength of the silica filled NR (Fig.3.40). The presence of the resin probably retards crack propagation due to interpenetration effects.

Surface hardness reaches a plateau at about 4% resin content (Fig.3.41). Beyond that percentage there is a slight reduction in surface hardness.

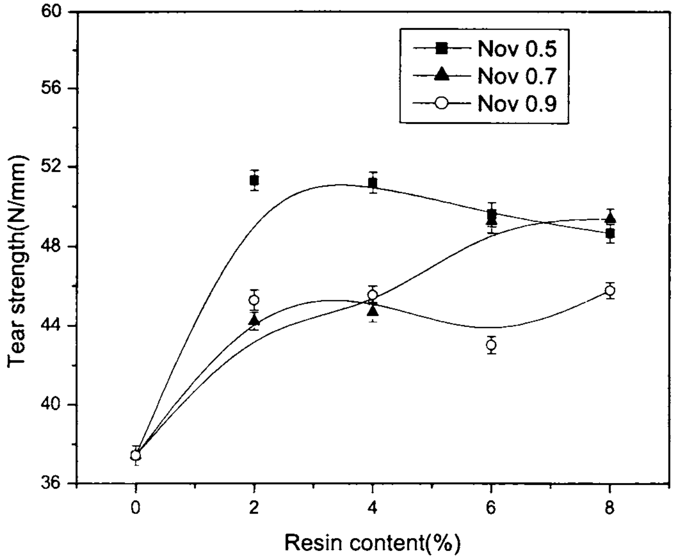


Fig.3.40 Variation of tear strength with resin content

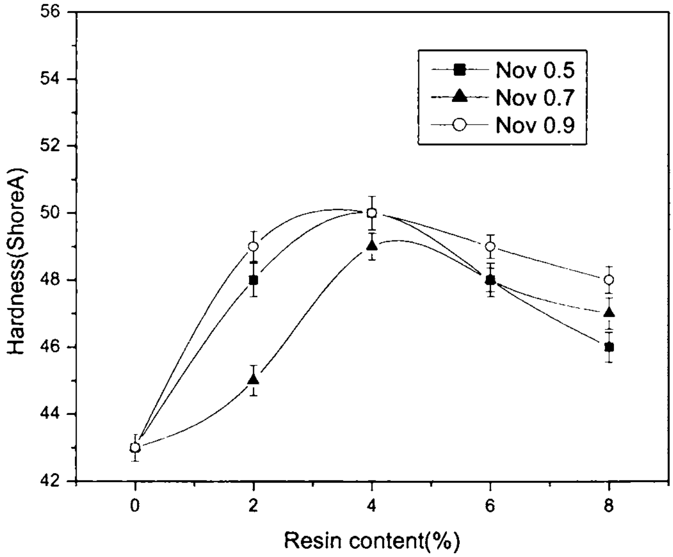


Fig.3.41 Variation of hardness with resin content

The retention of tensile strength on ageing at 70°C for 72 hours is depicted in Fig.3.42. For the most part there is higher retention in tensile strength when resin is added. Hence the addition of resin has led to better heat resistance for silica filled vulcanizate. A similar tendency is noticed in the case of retention of tear strength also (Fig.3.43). This again points to the usefulness of adding phenolic novolacs to silica filled NR vulcanizates.

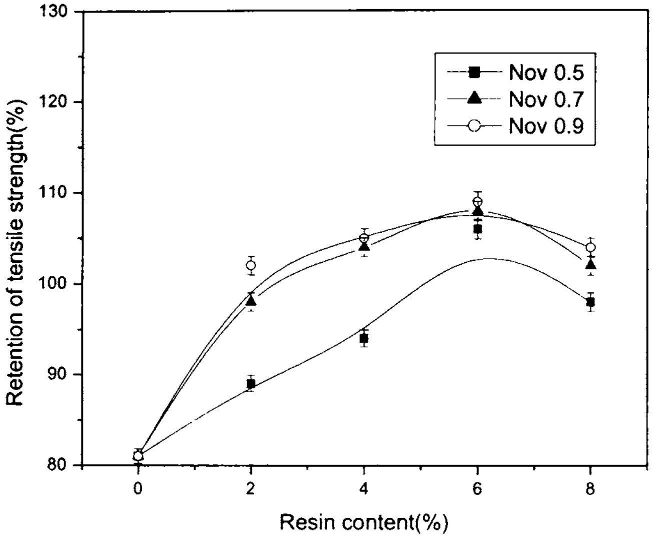


Fig.3.42 Variation of retention of tensile strength on ageing at 70°C for72hrs.

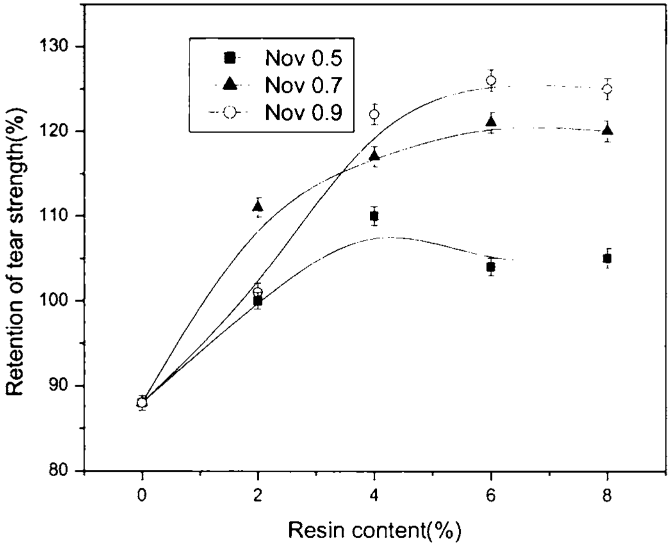


Fig. 3.43 Variation of retention of tear strength on ageing at 70°C for 72 hrs.

Fig.3.44 shows the variation of oil absorbed with resin content. There is a reduction in mass of oil absorbed upto 6% of the resin. Higher percentages (8%) are seen to somewhat reverse this tendency. In general the presence of the resin improves the oil resistance of silica filled NR.

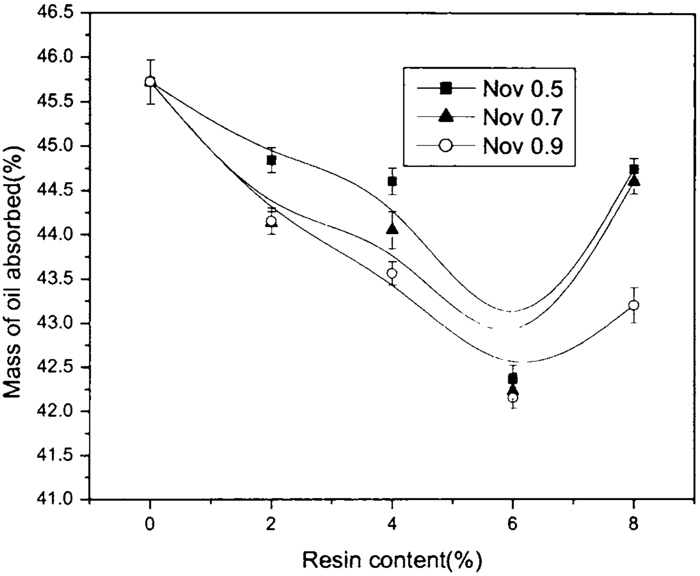


Fig.3.44. Variation of mass of oil absorbed with resin content

d) Gum NR modified by cardanol novolacs

Fig.3.45 shows the effect of cardanol novolac resin on the cure time of gum NR vulcanizate. The presence of the resin leads to a reduction in cure time unlike the earlier cases where increase in cure time was noticed on addition of the resin. This effect can be due to the structural features of cardanol. The long side chain of cardanol at the meta position can take part in crosslinking reactions involving sulphur. This can hasten the curing process. Moreover, entanglement of the side chain with the rubber chain can also speed up the cure.

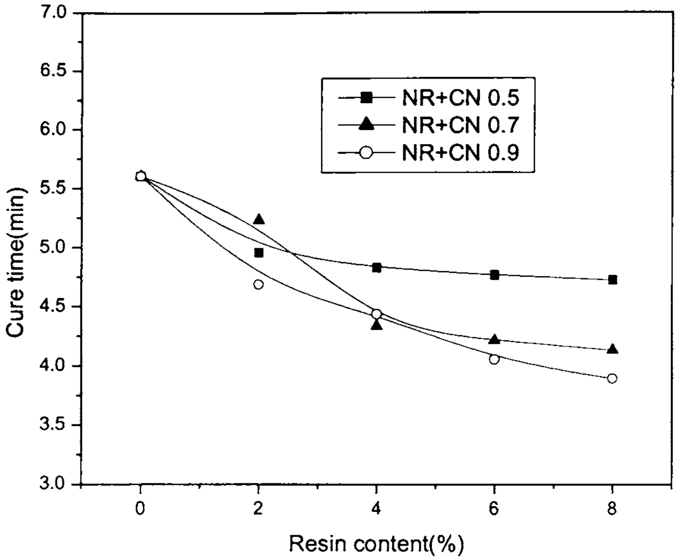


Fig. 3.45 Variation of cure time with resin content

The tensile strength of gum NR vulcanizates is seen to increase substantially on addition of cardanol novolac resin (3.46). Any inhibiting effect of the novolac resin on the cure reaction is more than offset by the long side chain of the cardanol molecule. As already suggested this sidechain can have chemical and physical interactions which are generally beneficial to the curing process. Hence the improved tensile strength.

There is an improvement in tensile modulus (Fig.3.47) on addition of the resin. Several reasons can be cited for this: possible interpenetration, vulcanization of the sidechain, physical entangling of the side chain etc.

There is also a slight increase in the elongation at break (Fig.3.48) on addition of the resin. This can be the result of disentangling of the sidechain during failure.

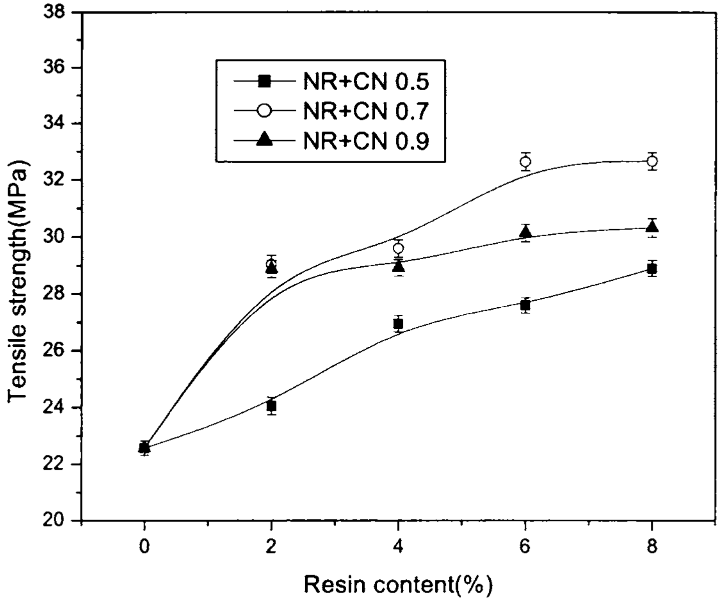


Fig.3.46 Variation of tensile strength with resin content

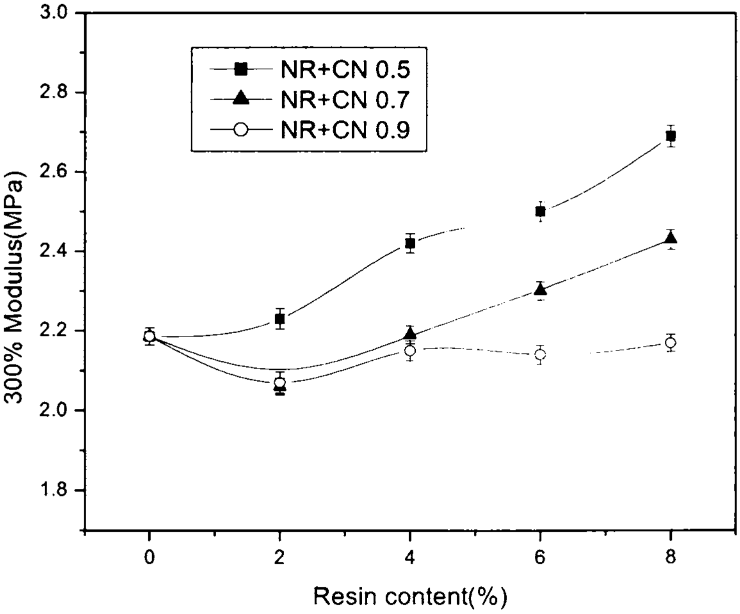


Fig.3.47 Variation of modulus with resin content

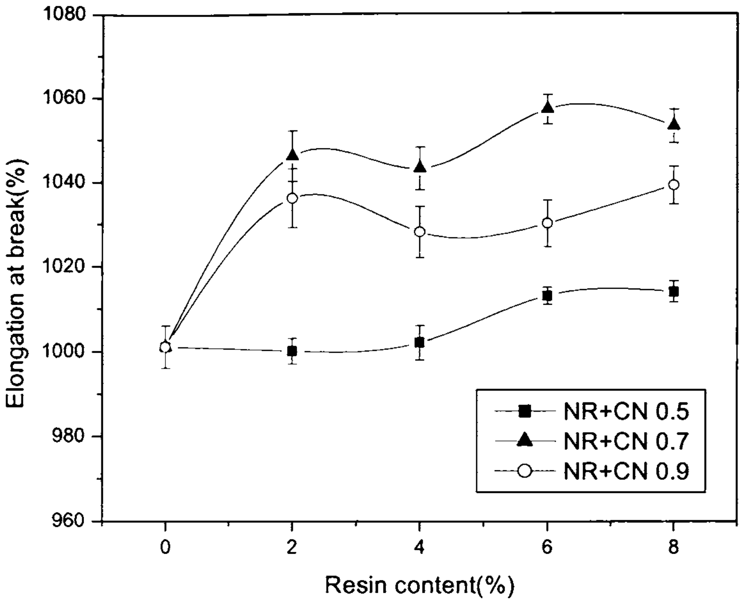


Fig.3.48 Variation of elongation at break with resin content

The increase in tear strength on addition of the resin (Fig.3.49) is in conformity with the effect on tensile strength. The entanglement of the sidechain and possible vulcanization of cardanol tend to retard crack propagation.

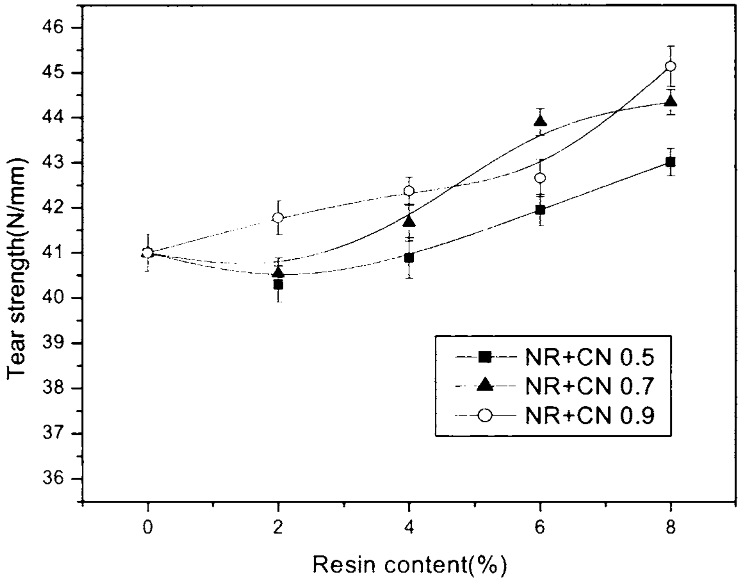


Fig.3.49 Variation of tear strength with resin content

Surface hardness (Fig.3.50) is another property showing improvement on addition of resin. The higher degree of crosslinking possible due to presence of the sidechain may be the underlying reason for this.

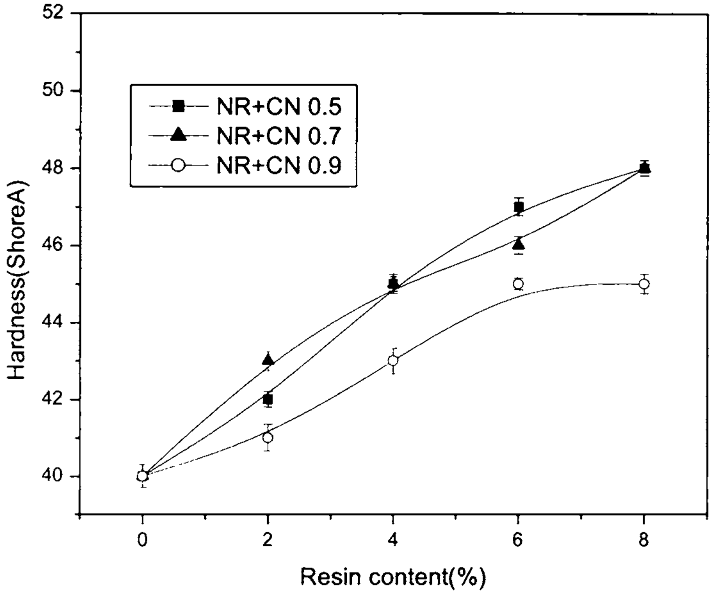


Fig.3.50 Variation of hardness with resin content

There is a moderate increase in weight loss on Soxhlet extraction with resin content (3.51). This behavior is similar to that of phenolic novolac. The amounts extracted are also similar.

The retention of tensile strength and tear strength (Figs.3.52 & 3.53) after ageing at 70°C for 72 hours is similar to ordinary phenolic novolacs. Both tensile and tear strength are retained after ageing to a higher degree by the presence of the resin.

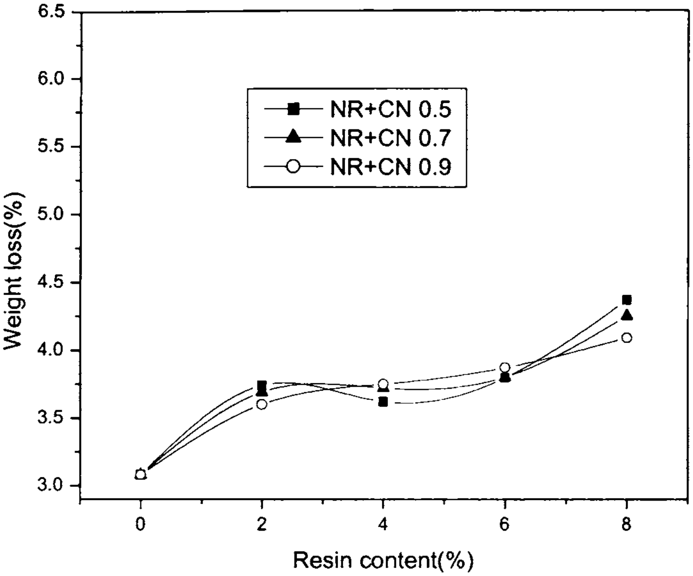


Fig.3.51 Variation of weight loss on soxhlet extraction with resin content

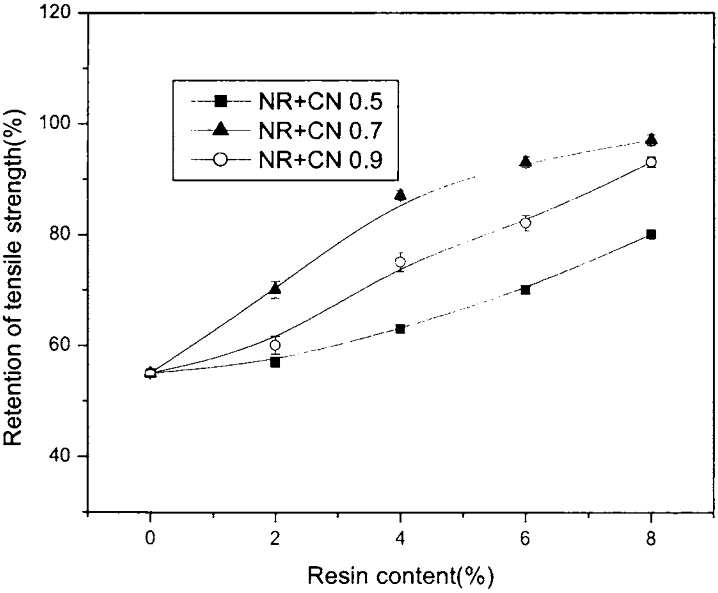


Fig.3.52 Variation of retention of tensile strength with resin content

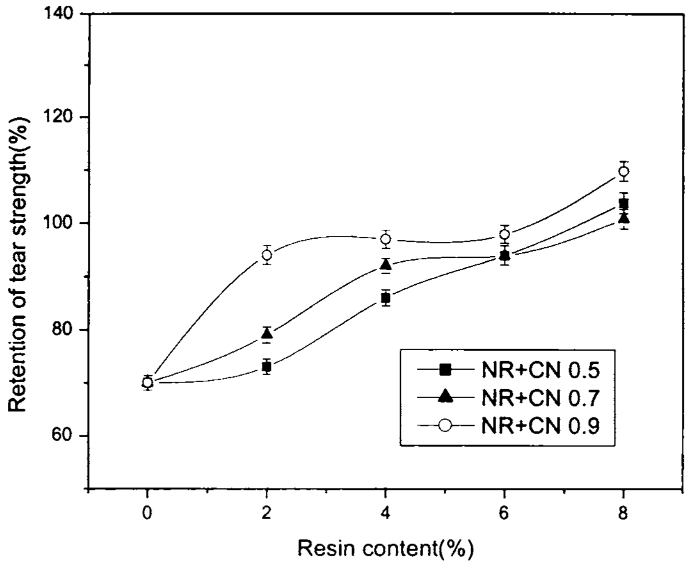


Fig.3.53 Variation of retention of tear strength with resin content.

Differential scan of NR vulcanizate with 4% CN 0.5 is shown in Fig.3.54. The glass transition temperature has increased to -59.63°C from the unmodified sample which has a value -63.92°C.

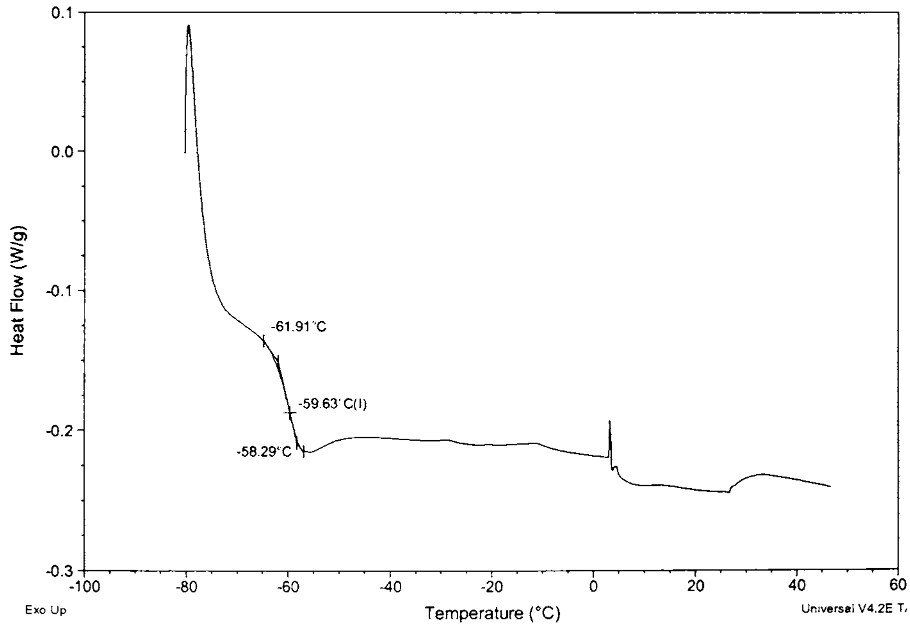
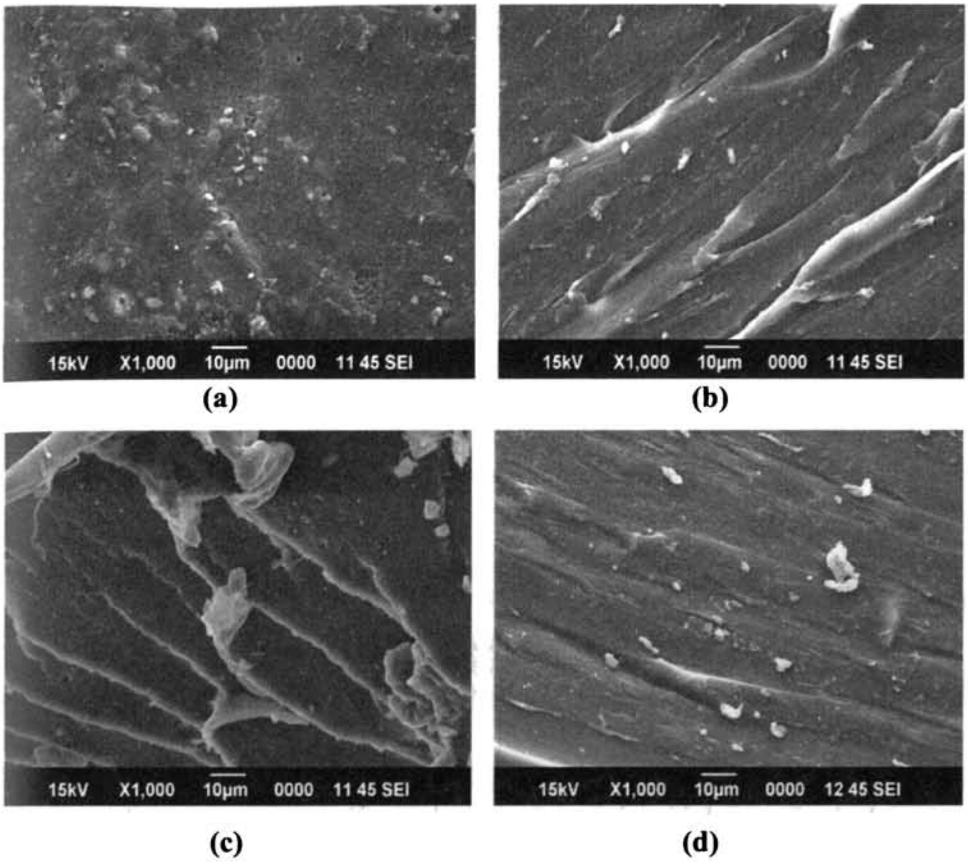


Fig.3.54 Differential scan of NR vulcanizate with 4% CN 0.5



(a) (b)

(c) (d)

Fig.5.55 SEM micrographs of **(a)** NR **(b)** NR+HAF **(c)** NR+novolac 4% **(d)** NR+HAF+novolac 4%

Fig.5.55 shows the micrographs of gum NR and filled NR and those modified with novolac 0.5. A large fracture surface area is noticed in the modified samples. This indicates greater energy absorption resulting from the presence of the resin.

3.4 Conclusions

There is a general improvement in tensile strength and tear strength of gum NR on addition of different novolac resins although a correlation with P/F ratio is not readily noticeable in most cases. The age resistance of NR shows a clear improvement on addition of various novolac resins from the view point of tensile strength and tear strength after ageing. As low a percentage as 2% gives substantial improvement. The blending with the resin has considerably reduced the oil absorption of NR. Here again a 20-30% decrease is possible with only just 2% of resin. There is only a moderate increase of weight loss on extraction with acetone after adding various percentages of resin which indicates that most of the resin has been chemically incorporated into the rubber matrix. The cardanol novolac resin has a somewhat more beneficial effect on the rubber. The effect of novolacs on the filled compounds is not as pronounced as in the case of gum compounds. The silica resin filled compounds show greater improvement in tear strengths on addition of the resin. However, for all filled compounds the improvement in thermal and oil absorption properties is still substantial.

Reference

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[2] R.M Silverstein and F.X Webster, Spectrometric Identification of Organic Compounds, 6th Edn. Ch.3, p-71-143, John Wiley & Sons Inc.New York (2002).

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Chapter

4

MODIFICATION USING EPOXIDISED NOVOLACS

4.1 Introduction

In this chapter the effects of adding epoxidised phenolic novolacs on the properties of NR vulcanizates are studied. Epoxidised phenol formaldehyde novolac (EPN), epoxidised p-cresol formaldehyde novolac (EPCN) and epoxidised cardanol formaldehyde novolac (ECN) were used for blending with NR. These resins were prepared in the laboratory. Properties were studied for both gum and filled samples.

4.2 Experimental

4.2.1 Preparation of epoxidised novolacs (EPNs) [1]

Various novolacs were prepared as per the method outlined in Section 3.2.2. The novolacs were subsequently epoxidated by the method described in Section 2.2.2.The epoxide equivalent was estimated by the method already outlined in Chapter 2 (Section 2.2.3). The resins with phenol formaldehyde ratios 1:0.5, 1:0.7 and 1:0.9 are designated as EPN 0.5, EPN 0.7 and EPN 0.9 respectively. EPCNs are designated as EPCN 0.5, EPCN 0.7 and EPCN 0.9 according to their p-cresol formaldehyde ratios 1:0.5, 1:0.7 and 1:0.9. ECNs are designated as ECN 0.5, ECN 0.7 and ECN 0.9 in accordance with cardanol formaldehyde ratios.

4.2.2 Compounding and curing

The resin was incorporated into NR by compounding on a two roll mill. Before addition, the resin was mixed with 10% by weight of amine hardener. NR compounds containing each of modifiers EPN, EPCN and ECN with three molar ratios were prepared and cured as already described in Section 2.2.4.

The formulations of the mixes are given in Tables 3.1, 3.2 and 3.3.

4.2.3 Quality evaluation

The vulcanizates were tested according to relevant ASTM standards. The details of the test procedure as well as the ASTM standards applicable have already been furnished in Section 2.2.4.

4.3 Results and discussion

4.3.1 Epoxide equivalents

The epoxy contents of various synthesized resins are given in Table 4.1.

Table 4.1 Epoxy equivalents of various resins

Type of epoxy	Weight per epoxide	Epoxide equivalents
EPN 0.5	210	4.7
EPN 0.7	186	5.37
EPN 0.9	171	5.85
EPCN 0.5	221	4.52
EPCN 0.7	193	5.18
EPCN 0.9	217	4.61

4.3.2 Modification using EPN

a) NR gum compound

The FTIR spectrum of the synthesized EPN 0.5 is given in Fig.4.1. The strong band at 1235.46 cm^{-1} denotes symmetrical C-O stretching (ring breathing frequency) in epoxides.

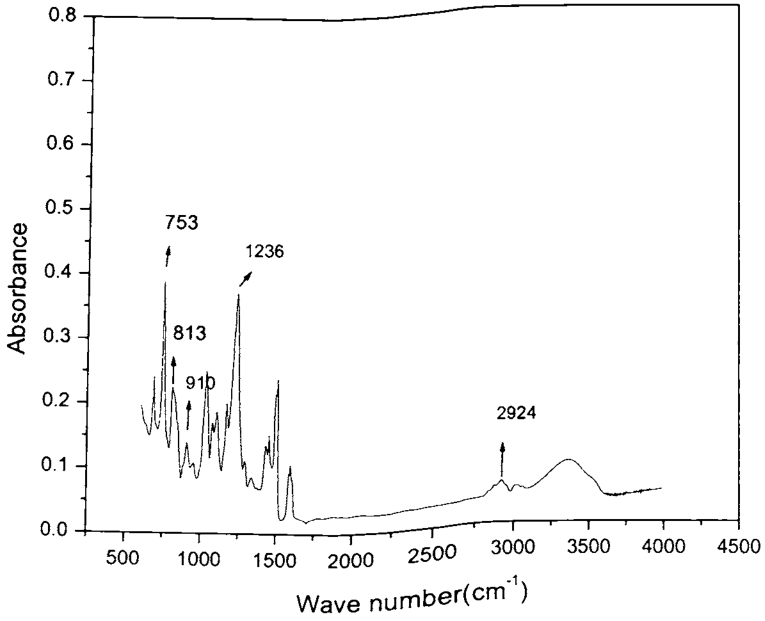


Fig. 4.1 FTIR spectrum of EPN 0.5

The C-H stretching in epoxides occurs at 2924.85cm^{-1}. Further, the bands at 910cm^{-1}, 813cm^{-1} and 753cm^{-1} are also typical of epoxides. The peak at 3300cm^{-1} (hydroxyl group, broad band), 1594 and 1500 (phenyl ring) and 1475 (CH_2 bending) are characteristic peaks of novolac [2].

Fig.4.2 shows the FTIR spectra of two cases of vulcanized NR namely (A) without EPN and (B) with EPN. The most notable difference in the absorbance pattern is the additional peak occurring at a wave number of 1168 cm^{-1}. This corresponds to the presence of a secondary alcohol group or a 1,3 disubstituted benzene structure in the EPN modified vulcanizate. The latter possibility can be eliminated as the meta position is not involved in phenol formaldehyde reactions. Hence this could be the result of the opening of the epoxy ring during the crosslinking process. This crosslinking can also contribute to the faster cure exhibited by the EPN modified rubber in addition to interpenetration effects.

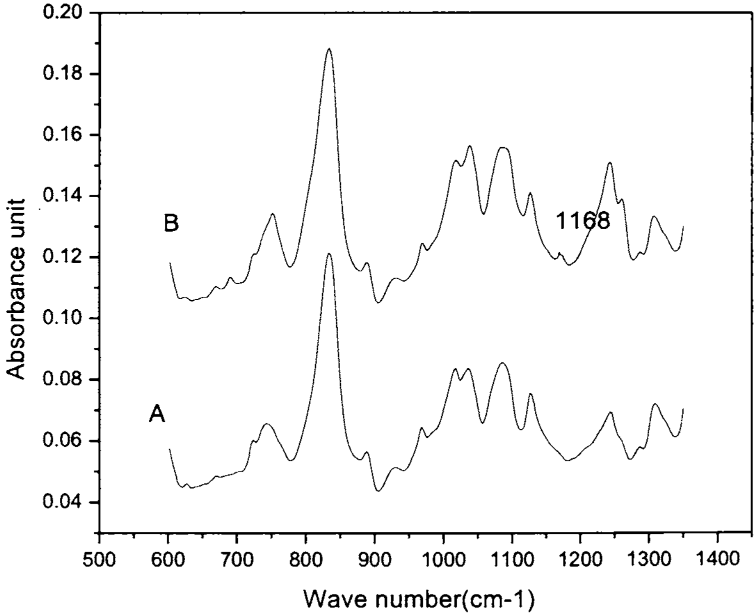


Fig. 4.2 FTIR spectra of A) NR vulcanizate without EPN, B) with EPN

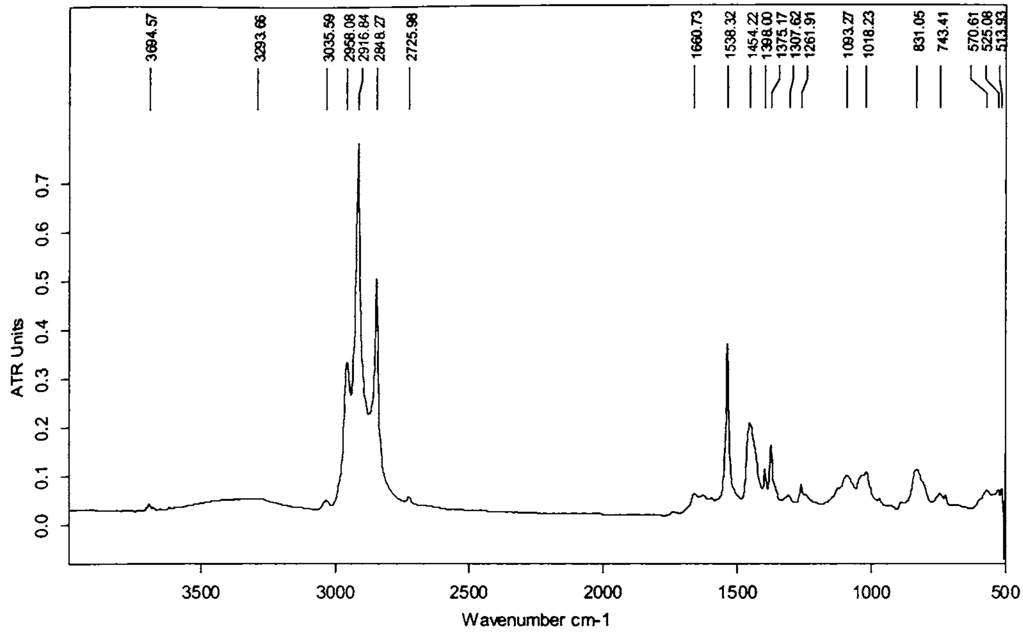


Fig.4.3 FTIR spectrum of NR vulcanizate

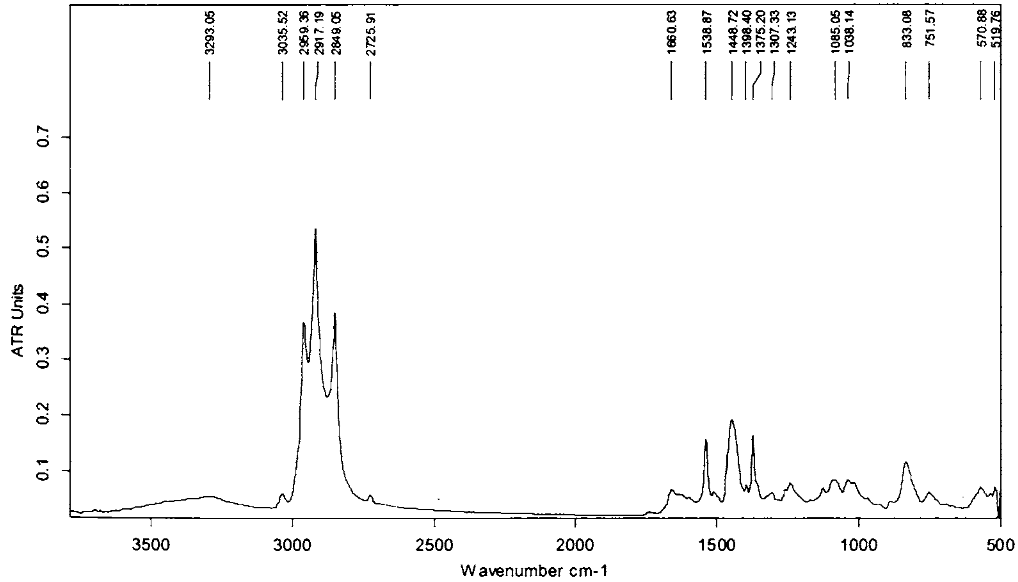


Fig.4.4 FTIR spectrum of 4% EPN 0.5 modified NR vulcanizate

Figs. 4.3 and 4.4 show the complete spectra of NR and NR modified by EPN 0.5. In addition to absorption at a frequency of 1168 cm^{-1} as already discussed; a notable difference is the lower height of the peak at 1538 cm^{-1} in the case of modified NR. Since this absorption is caused by NH group of MBTS the lowering of the peak can be explained in terms of the reaction proposed in Section 2.3 of Chapter 2. It can be surmised that the NH groups are utilized for the opening of epoxy group.

Cure characteristics of EPN modified NR are given in Table 4.2. On addition of EPN resin the cure time of the rubber compound decreases (Fig.4.5) considerably. This trend continues until beyond 4% resin when the cure time tends to increase. The reduced cure time is an indication of the chemical changes taking place on addition of the resin. The accelerated cure can be due to interpenetration between the resin and the rubber molecular chains apart from the possible epoxy-accelerator interaction suggested in Section 2.3. At higher percentages of the resin, say 8%, the cure time tends to increase. As the EPN percentage goes up it is possible that the crosslinking process of rubber is hampered. At lower percentages this effect may be negligible and the effective interpenetration helps to reduce the cure time. At higher percentages there is also a fall in crosslink density as will be reported later.

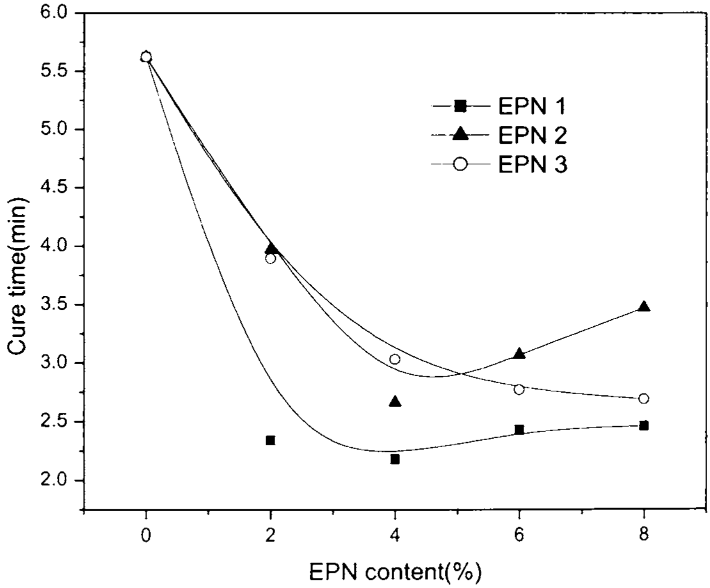


Fig.4.5 Variation of cure time of NR with resin content

Table 4.2 Cure characteristics of gum NR vulcanizate with EPN

Resin content (%)		**T_{10} (min)**	**T_{90} (min)**	**M_L (dNm)**	**M_H (dNm)**	**CRI (min^{-1})**
EPN 0.5	0	2.62	5.62	0.023	2.69	33.33
	2	1.04	2.34	0.01	2.98	76.9
	4	0.67	2.18	0.022	2.83	66.2
	6	0.56	2.43	0.03	2.71	53.4
	8	0.54	2.46	0.032	2.47	54.9
EPN 0.7	2	1.57	3.97	0.021	2.87	41.66
	4	1.16	2.66	0.032	2.76	66.66
	6	1.05	3.07	0.034	2.52	38.17
	8	0.52	3.47	0.056	2.48	51.2
EPN 0.9	2	1.75	3.89	0.042	2.79	46.7
	4	1.19	3.03	0.054	2.80	54.3
	6	0.95	2.77	0.055	2.76	54.95
	8	0.86	2.69	0.075	2.50	54.64

Cure rate constants of EPN modified NR samples are shown in Table 4.3.The cure rate constants and cure rate index follow the same trend. Plots of M_h-M_t vs time of NR and NR+EPN are shown in Figs.4.6 and 4.7.

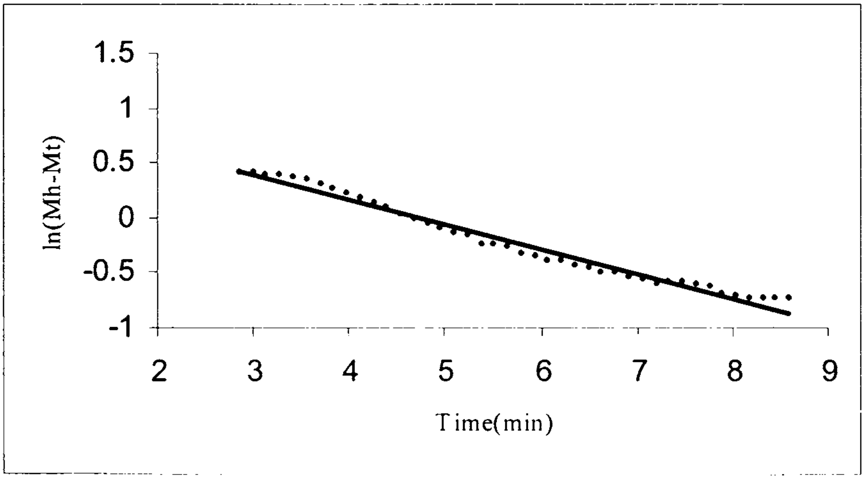


Fig.4.6 Plot of M_h-M_t vs time of NR, k = 0.2257

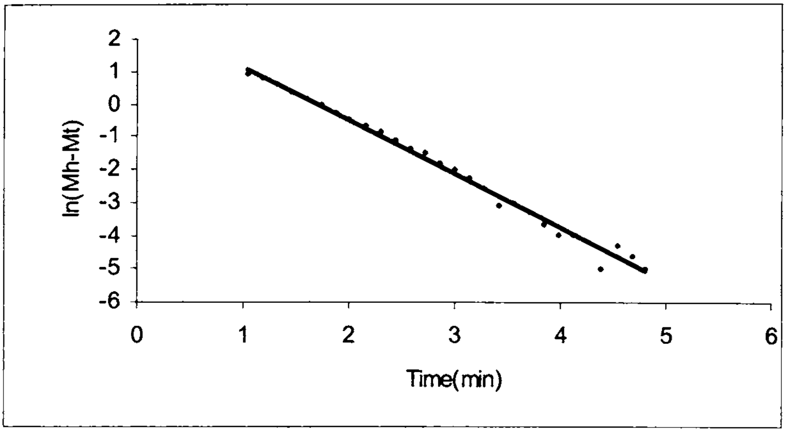


Fig. 4.7. Plot of ln(M_h-M_t) vs time of NR+4% EPN 0.5, k=1.6255

Table 4.3 Cure rate constants of EPN modified samples.

Sample	**Cure rate constant**
NR	0.2257
NR+EPN 0.5 -2%	0.8633
NR+EPN 0.5 -4%	1.6255
NR+EPN 0.5 -6%	1.0918
NR+EPN 0.5 -8%	1.1607

Fig.4.8 shows the variation of tensile strength on addition of various percentages of EPNs to the rubber. Each resin shows a maximum tensile strength at some percentage ranging from 2-6%. The resin with a phenol: formaldehyde (P/F) ratio 1:0.5 shows the greatest improvement (~ 32% over virgin NR) in tensile strength at 4%. At this P/F ratio, the number of benzene rings in the resin molecule as well as its molecular weight will be a maximum. Hence the excellent mechanical properties.

Tear strength (Fig.4.10) also increases with resin content upto 6%. The improved tear strength also points to interpenetration. The marginal improvement in tensile modulus (Fig.4.9) on addition of the resin further points to some extent of interpenetration. Although initially there is a stiffening of the vulcanizate resulting in an improvement in modulus, the trend reverses on adding higher percentages. Fig.4.11 shows the variation of surface hardness with resin content.

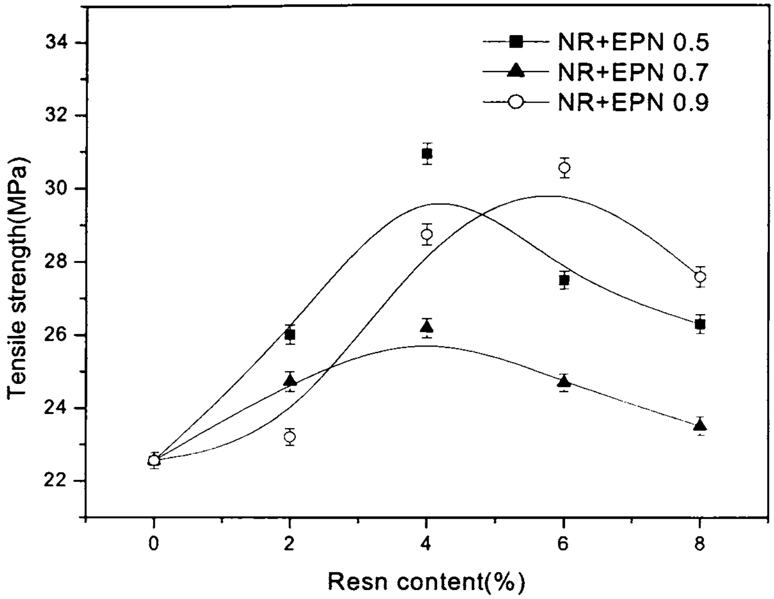


Fig.4.8 Variation of tensile strength of NR with resin content

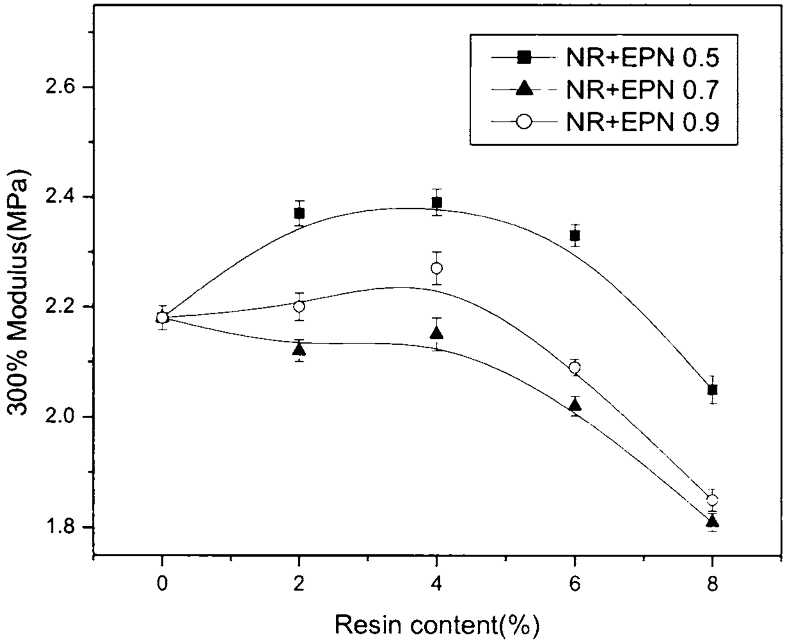


Fig.4.9 Variation of modulus (300%) with resin content

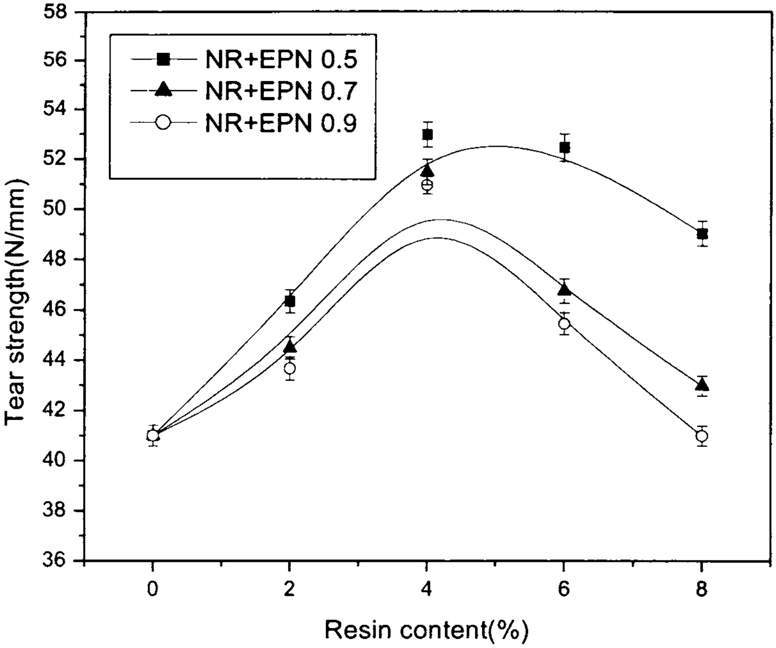


Fig.4.10 Variation of tear strength with resin content

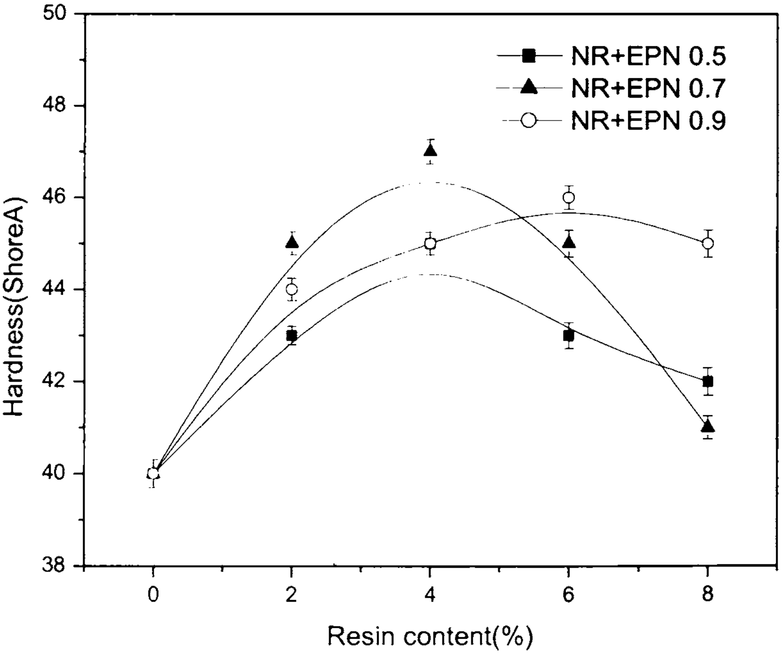


Fig.4.11 Variation of hardness with resin content

Figs. 4.12 and 4.13 depict the variation of retention of tensile and tear strengths of different samples after ageing at 70°C for 72 hrs. In the absence of the resin the percentage retention of tensile strength after 72 hrs of ageing is only about 55 % (Fig.4.8).

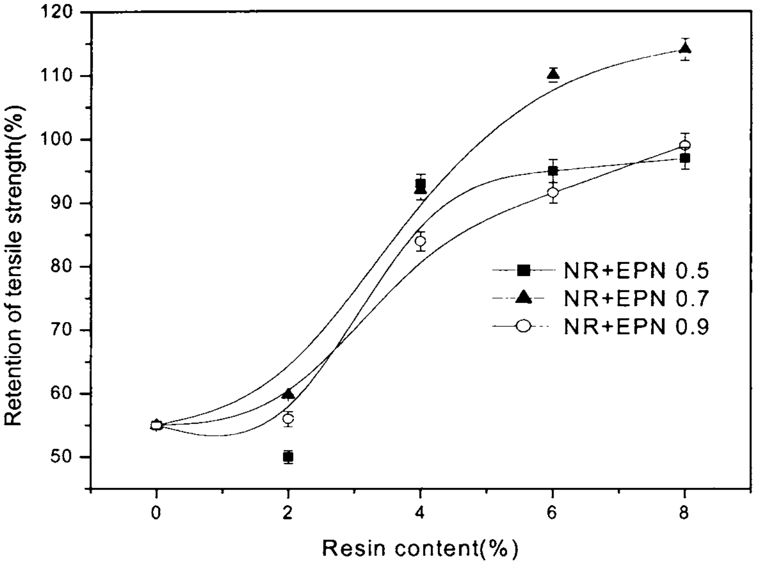


Fig.4.12 Retention of tensile strength with resin content on ageing at 70°C for 72 hrs

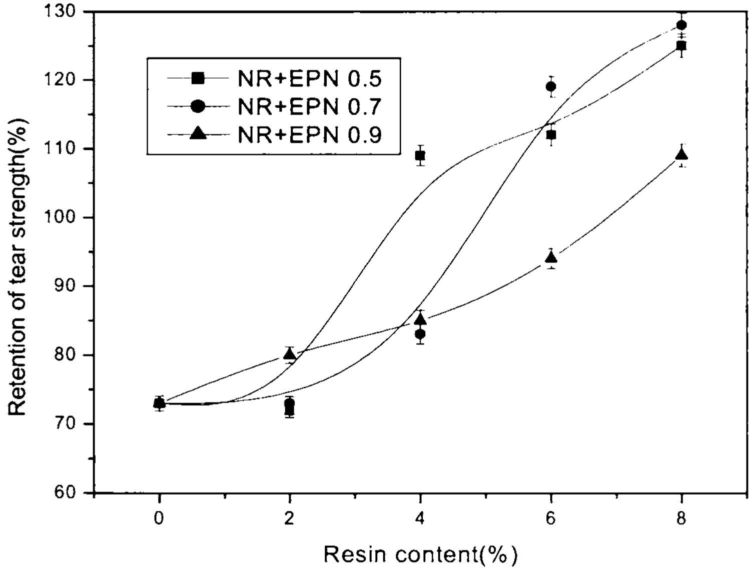


Fig.4.13 Retention of tear strength with resin content on ageing at 70°C for 72 hrs

On addition of the resin this value increases steadily until at about 8% it is almost equal to the original tensile strength. Similarly in the case of tear strength there is a dramatic improvement in tear strength retention at higher percentages of resin.The prolonged ageing process might have helped to make the crosslinking reaction of the resin and/or chemical interaction between the rubber and the resin to go to completion.

Fig. 4.14 shows that the addition of resin dramatically reduces the percentage mass of oil absorbed over a 72 hour period. Here again, a 20-30% decrease is possible with only just 2% of resin. The presence of the resin in the crosslinked/interpenetrated condition has made the rubber less penetrable for oil. Moreover, the polar nature of the resin reduces the interaction between the modified rubber matrix and oil.

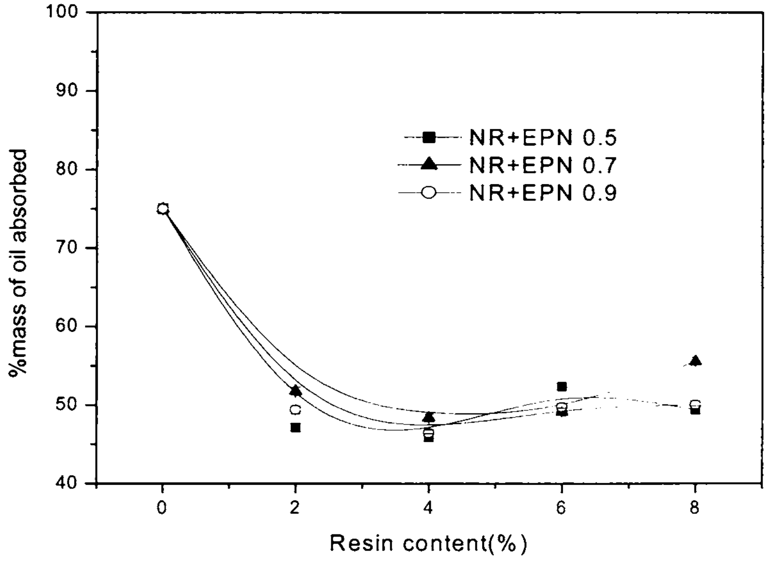


Fig.4.14 Variation of % mass of oil absorbed with resin content

Fig.4.15 shows the variation in weight loss on extraction with acetone. There is only a moderate increase in weight loss with resin content. The low extractability of the resin from the rubber proves that the resin has 1) undergone crosslinking between its own molecules 2) taken part in chemical interactions with the rubber or curatives or 3) given rise to interpenetrating networks. On close examination of Fig.4.15 it is seen that the curves are rather flat upto 4% resin. Beyond 4%, the curves become steeper indicating higher weight losses on extraction. Hence it is possible to assume that in this range the resin is more extractable being dispersed less effectively in the rubber matrix. Extractability is also higher when the formaldehyde content of the resin goes up.

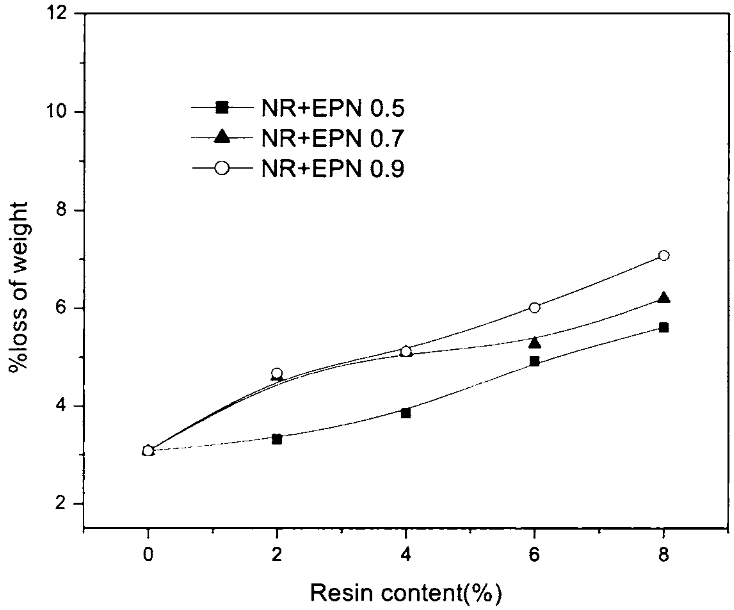


Fig.4.15 Variation of % loss of weight on Soxhlet extraction with resin content

Fig.4.16 shows the variation of crosslink density of NR vulcanizates with resin content. Crosslink density increases with resin content upto 4-6% and after that at higher percentages, it falls. The increase in crosslinking is attributable to interpenetrating effects as well as possible chemical interactions involving the epoxy group and the NH functionality generated by the accelerator as already suggested in Section 2.2.3. Poor dispersion of the resin or hindrance to rubber crosslinking may be the reasons for the lowered crosslink density at higher percentages.

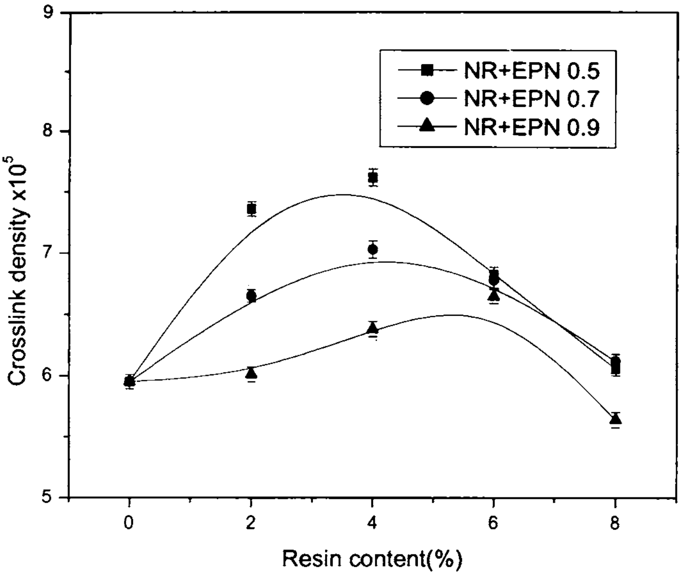


Fig. 4.16 Variation of crosslink density with resin content

Thermogravimetric data of EPN modified NR vulcanizates are given in Table 4.2 and 4.3. From the tables it can be seen that the onset of degradation temperature, temperature at maximum degradation, temperature at 50% degradation and residue content have increased marginally with resin content. Moreover, the maximum rate of degradation shows a marginal decrease with resin content. All these indicate the improved thermal stability of EPN blended NR vulcanizates.

Table 4.4 Characteristics of thermograms of NR vulcanizates with 4%EPN

	NR	**NR+EPN0.5**	**NR+EPN0.7**	**NR+EPN0.9**
Onset degradation temperature (°C)	312.72	318.98	318.85	320.67
Temperature at 50% degradation (°C)	388.99	392.16	388.45	391.23
Temperature at max.degradation (°C)	384.23	388.63	382.34	386.02
Maximum rate of degradation (%/°C)	1.55	1.509	1.514	1.486
Residue (%)	4.297	4.459	4.961	4.942

Table 4.5 Characteristics of thermograms of NR vulcanizates with varying amounts of EPN 0.5

EPN content (%)	0	2	4	6	8
Onset degradation temperature (°C)	312.72	320.71	318.98	323.58	325.98
Temperature at 50% degradation (°C)	388.99	389.86	392.16	390.83	388.95
Temperature at max.degradation (°C)	384.23	385.60	388.63	385.57	384.83
Maximum rate of degradation (%/°C)	1.55	1.542	1.509	1.492	1.534
Residue (%)	4.297	4.939	4.459	4.988	5.119

Figs. 4.17 to 4.20 represent the Freeman-Carrol plots of EPN modified NR vulcanizates with varying resin content. Activation energies of modified samples are slightly greater than the unmodified sample (E_a = 207 kJ/mol). This also indicates the thermal stability of EPN modified samples.

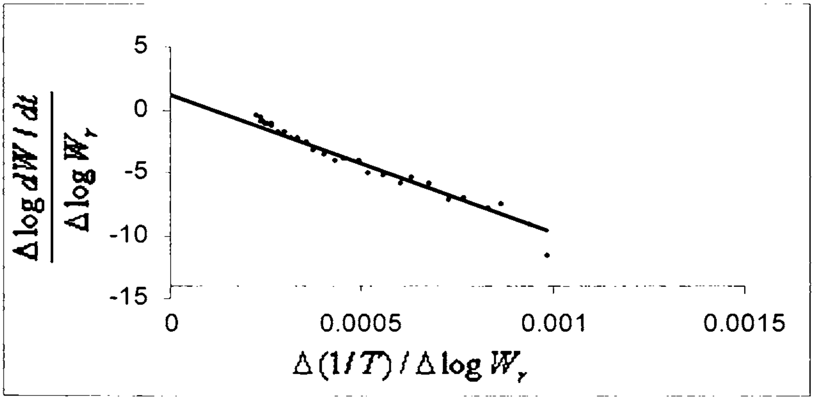


Fig.4.17 Freeman-Carrol plot of NR+EPN 0.5-2%, Ea=208.9kJ/mol

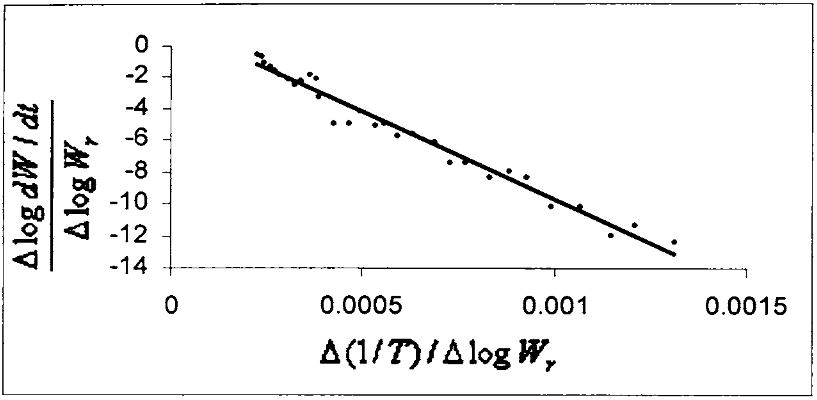


Fig.4.18 Freeman-Carrol plot of NR+EPN 0.5-4%, Ea=209.8 kJ/mol

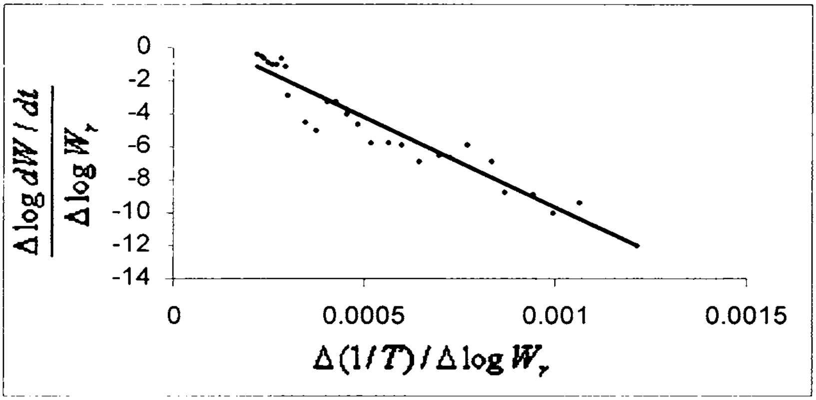


Fig. 4.19 Freeman-Carrol plot of NR+EPN 0.5-6%, Ea=208.78 kJ/mol

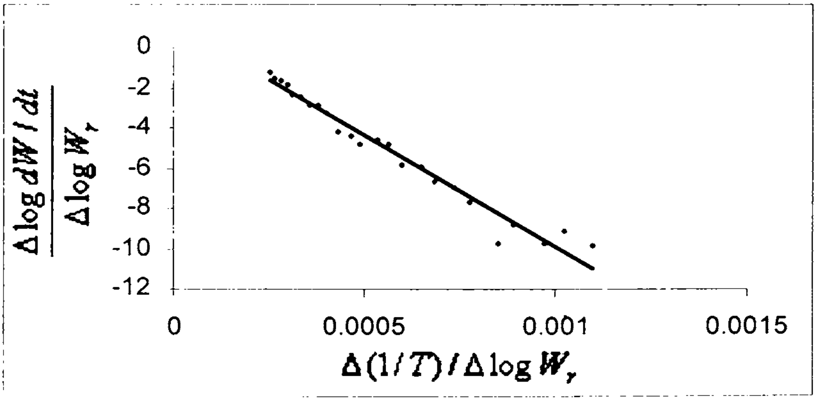


Fig. 4.20 Freeman-Carrol plot of NR+EPN 0.5-8%, Ea = 209.2kJ/mol

Differential scan of EPN modified NR vulcanizate is shown in Fig.4.21. DSC data (Table 4.6) show there is a slight increase in glass transition temperature. The presence of the resin has somewhat reduced the segmental mobility of the chains.

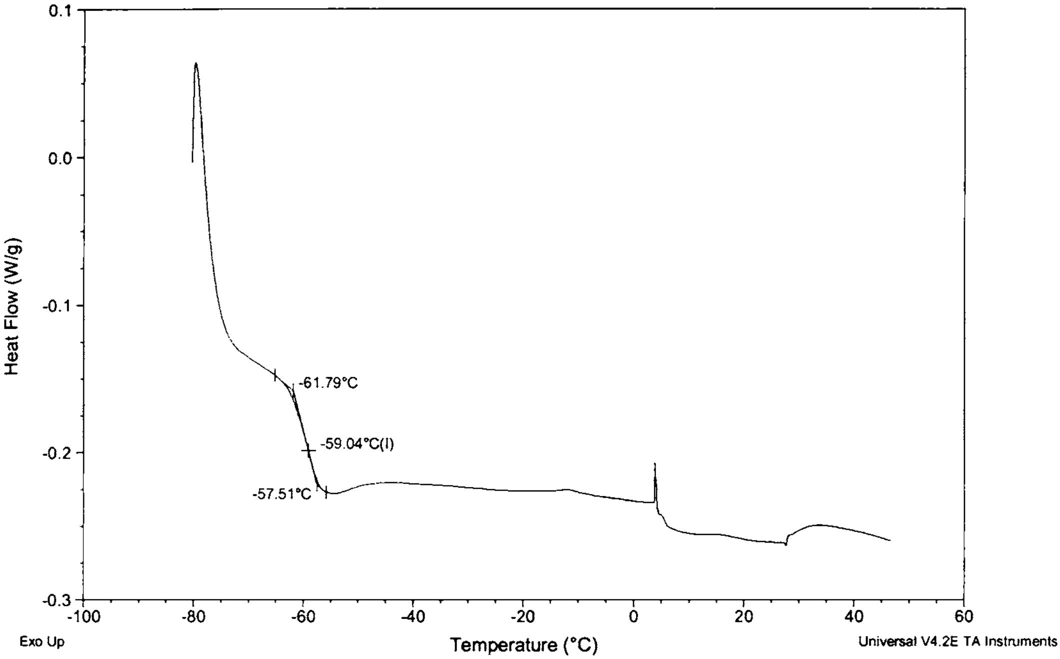


Fig.4.21 Differential scan of NR vulcanizate with 4% EPN 0.5

Table 4.6 DSC data of NR vulcanizates with 4% EPN 0.5

Property	NR	NR+EPN
Glass transition – onset (°C)	-66.32	-63.92
Glass transition – midpoint (°C)	-61.39	-59.04

b) Filled NR compounds

Results discussed in the following sections are based on NR compounds filled with silica and HAF black and modified by an EPN resin with P/F ratio of 1:0.5. The presence of fillers can have diverse effects on the properties of resin modified filled compounds. There is chance of adsorption of resin by the filler which can moderate the effect of the resin. Direct chemical interaction between the filler and resin cannot also be ruled out especially when thermal ageing is done at a later stage.

Cure characteristics are given in Table 4.7. Fig. 4.22 shows the effect of resin content on the cure time of silica filled as well as HAF black filled NR compounds. There is a reduction in cure time on addition of EPN in both cases. This can be attributed to interpenetration or chemical interaction between the rubber and resin. But the HAF black filled compound tends to take a longer cure time at higher resin percentages. This difference in behavior can be due to the dissimilar chemical structure as well as particle size of the two fillers. The difference in the heat of mixing in the case of silica can also account for this.

Increasing resin content gives a zig zag curve (Fig.4.23) in the case of tensile strength. The variations are modest and any direct correlation between the resin content and the tensile strength cannot be easily established. Both curves show a tendency to fall initially as well as at higher percentages of the resin.

Table 4.7 Cure characteristics of filled NR vulcanizate with EPN 0.5

Resin content (%)		**T_{10} (min)**	**T_{90} (min)**	**M_L (dNm)**	**M_H (dNm)**	**CRI (min^{-1})**
Silica filled	0	1.73	3.73	0.022	2.74	50.00
	2	1.19	2.93	0.032	2.89	51.8
	4	1.10	2.72	0.045	2.97	65.35
	6	0.76	2.59	0.064	2.93	54.60
	8	0.69	2.41	0.071	2.82	58.13
HAF black filled	0	1.67	3.77	0.066	4.26	47.60
	2	0.92	2.67	0.078	4.60	57.14
	4	0.67	2.34	0.111	4.86	59.88
	6	0.56	2.55	0.123	4.75	50.25
	8	0.52	2.80	0.133	4.40	43.80

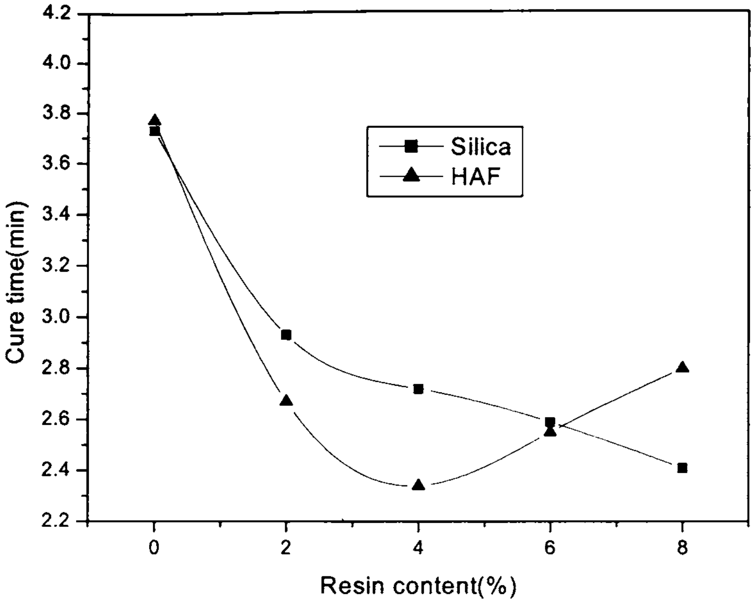


Fig. 4.22 Variation of cure time with resin content

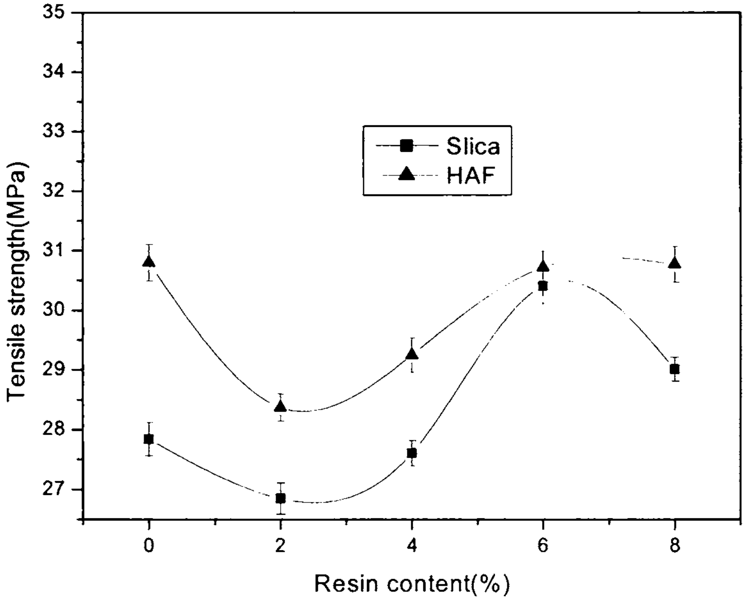


Fig.4.23 Variation of tensile strength with resin content

As can be seen from Fig.4.24, the 300% modulus is not seriously affected by the presence of the resin for both fillers. The same is true of elongation at break

(Fig.4.25). The tear strength (Fig.4.26) is also affected only to a small extend by the presence of the resin. Similar is the case of surface hardness shown in Fig.4.27, although a certain maximum is reached at about 6% resin. A similar behavior is seen in the case of tear strength also where the filled compounds show maxima at about 4% resin.

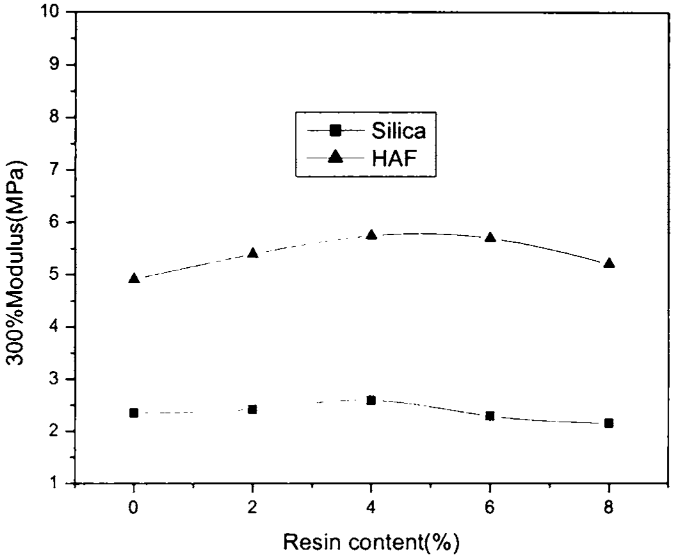


Fig.4.24 Variation of tensile modulus with resin content

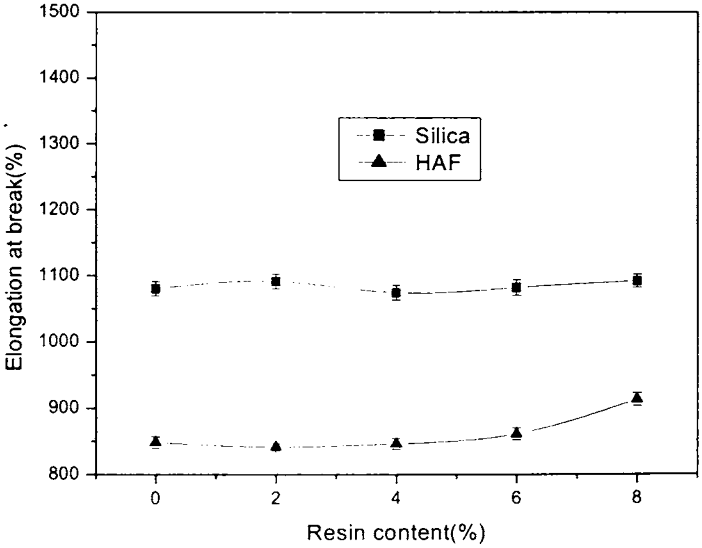


Fig.4.25 Variation of elongation at break with resin content

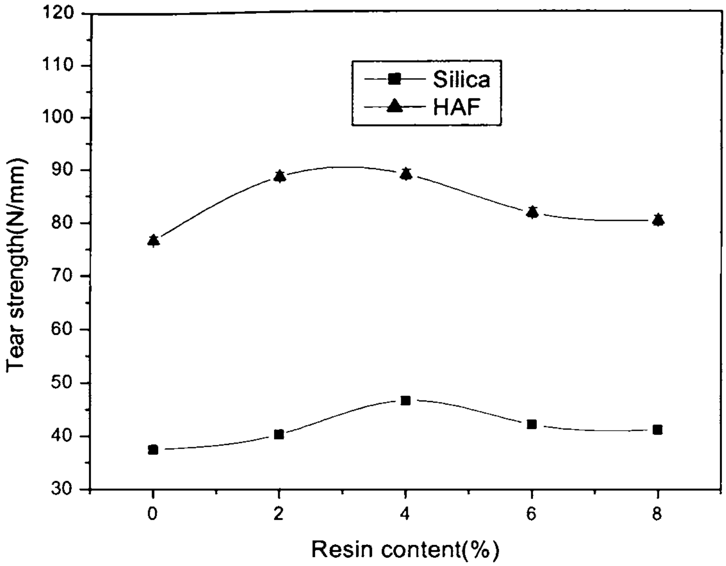


Fig.4.26 Variation of tear strength with resin content

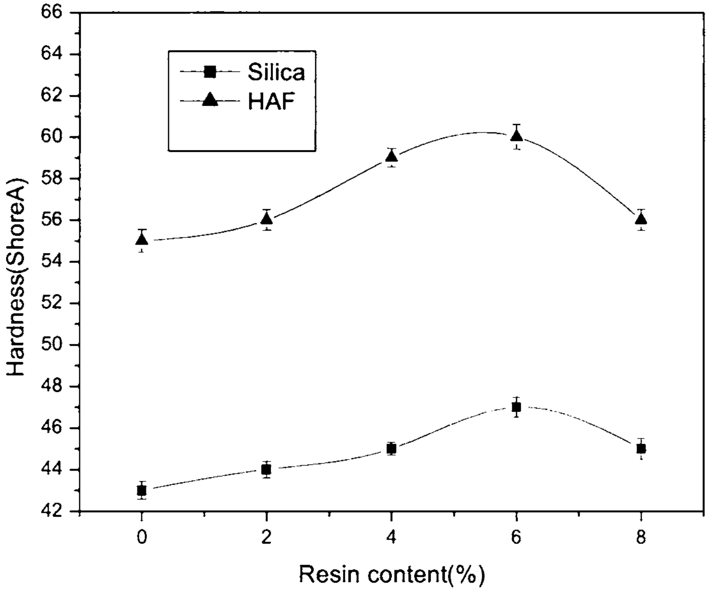


Fig.4.27 Variation of surface hardness with resin content

Retention of vulcanizate properties after ageing at 70°C for 72 hours is depicted in Figs.4.28 & 4.29. Fig.4.28 shows that there is a steady improvement in retention of tensile strength on ageing attributable to the presence of the resin. In the case of HAF black filled compound the retention of tensile strength after ageing crosses the 100% mark at 8% resin. This again proves the improved thermal stability of filled NR compound when modified by EPN. Retention of tear strength is also higher after ageing when EPN resin has been incorporated into the compounds.

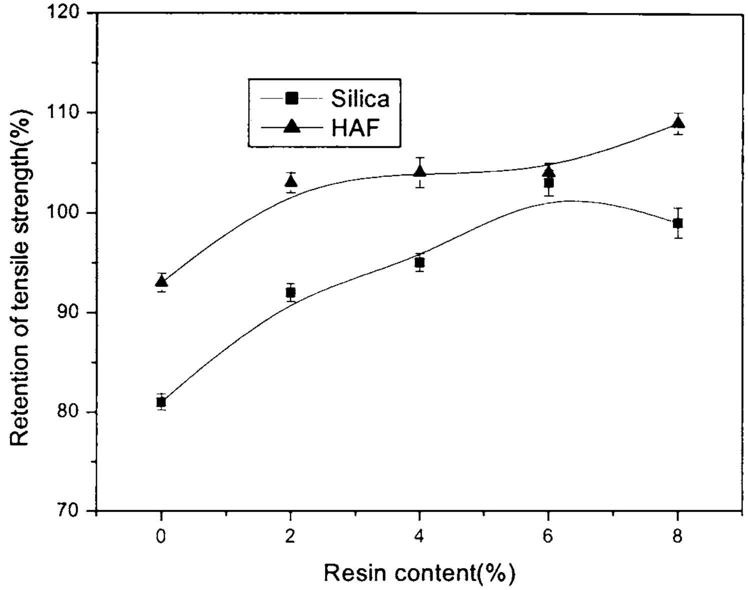


Fig.4.28 Variation of retention of tensile strength with resin content on ageing at 70°C for 72 hrs.

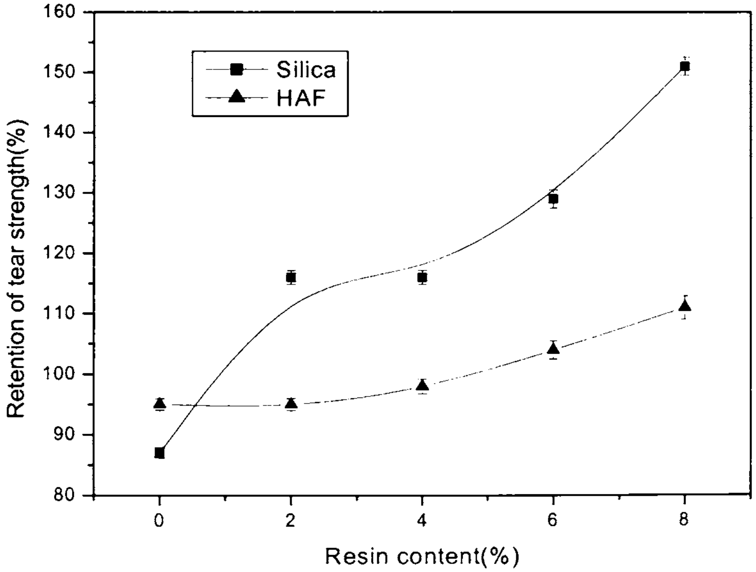


Fig.4.29 Variation of retention of tear strength with resin content on ageing at 70°C for 72 hrs.

Surprisingly in this case (Fig.4.29) the retention of tear strength after ageing is much higher in the case of silica filled compound than the HAF black filled compound. At 8% resin content the silica filled compound retains about 100% of the original tear strength. This suggests the possibility of filler resin interaction in the case of silica during ageing.

Fig.4.30 shows the effect of addition of resin on the mass of oil absorbed by the two filled compounds. Oil absorption initially falls substantially on addition of resin but remains steady on further addition of resin. So a small percentage of the resin can help to improve the oil resistance of both silica and HAF black filled NR compounds. The effect of addition of resin on the crosslink density of the vulcanizates is not substantial as shown in Fig.4.31.

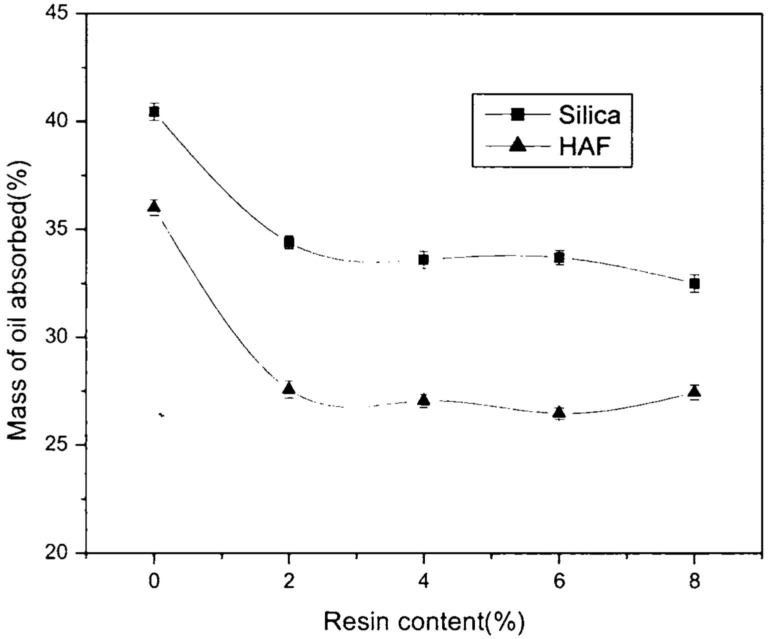


Fig.4.30 Variation of mass of oil absorbed with resin content

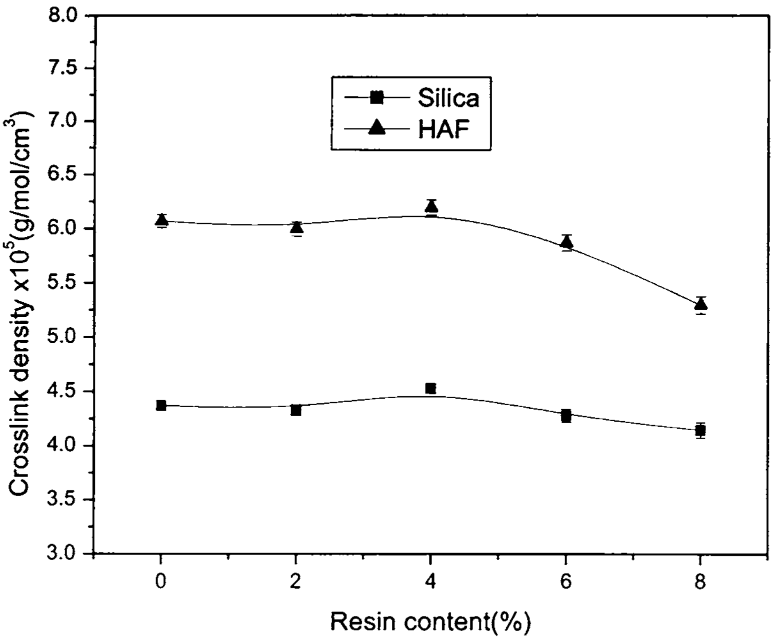


Fig.4.31 Variation of crosslink density with resin content

Thermal data of HAF filled NR vulcanizates with varying amounts of EPN 0.5 are given in the Table 4.8. This indicates that there is very little improvement in high temperature stability for the EPN modified HAF filled samples.

Table 4.8 Characteristics of thermograms of HAF black filled NR vulcanizates with varying amounts of EPN 0.5

EPN content (%)	0	2	4	6	8
Onset degradation temperature (°C)	299.6	295.09	298.25	295.15	283.95
Temperature at 50% degradation (°C)	401.5	398.78	398.80	398.36	397.92
Temperature at max.degradation (°C)	388.98	385.44	384.81	385.05	386.88
Maximum rate of degradation (%/°C)	1.109	1.174	1.180	1.186	1.206
Residue (%)	22.89	23.36	23.42	23.5	22.89

4.3.3 Gum NR modified by EPCN

Table 4.9 shows the cure characteristics of NR compounds containing varying amounts of EPCN. There is a general increase in minimum torque on addition of resin indicating that the compound viscosity tends to rise on addition of the resin. There is a drastic fall in the cure time as more and more resin is added to the compound (Fig.4.32). This effect levels off at about 5% EPCN. This is consistent with the behavior of EPNs (Section 4.3.2) as already reported. The shorter cure time can be due to one or several factors like intercomponent grafting, interpenetration etc. The cure rate index also shows an increasing tendency until about 5% EPCN.

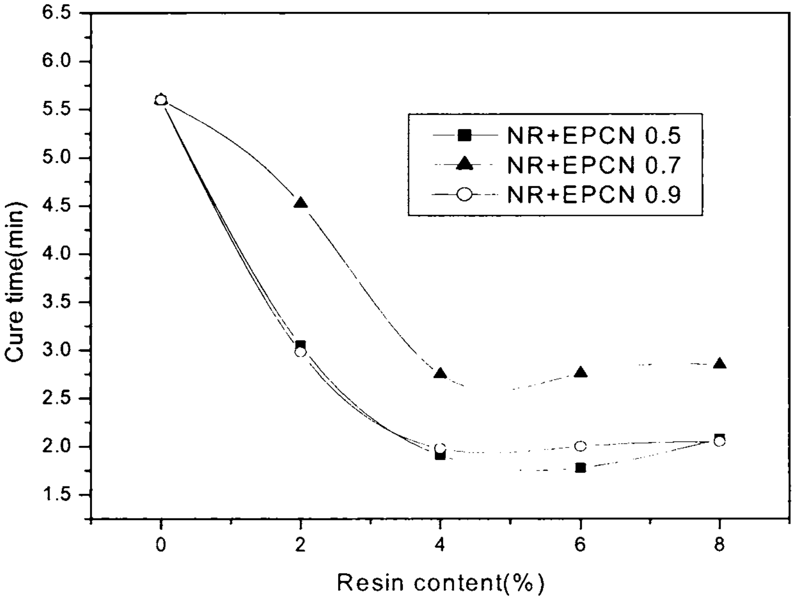


Fig.4.32 Variation of cure time with resin content.

Table 4.9 Cure characteristics of gum NR vulcanizate with EPCN

Resin content (%)		T_{10} (min)	T_{90} (min)	M_L (dNm)	M_H (dNm)	CRI (min^{-1})
EPCN 0.5	0	2.62	5.62	0.023	2.69	33.33
	2	1.61	3.05	0.035	2.97	69.4
	4	0.88	1.91	0.039	3.08	97.0
	6	0.67	1.78	0.059	3.05	90
	8	0.58	2.08	0.059	2.99	66.6
EPCN 0.7	2	2.14	4.52	0.022	2.74	42
	4	1.40	2.75	0.023	2.89	74
	6	1.31	2.76	0.029	2.78	68.9
	8	0.88	2.85	0.026	2.65	50.76
EPCN 0.9	2	1.67	2.98	0.020	2.98	76.3
	4	0.97	1.98	0.029	3.03	99
	6	0.74	2.00	0.032	3.02	79.3
	8	0.60	1.90	0.054	2.92	76.9

Fig. 4.33 shows the variation of tensile strength of vulcanizates with resin content. The tensile strength reaches a maximum at about 4-5% resin. This effect is more pronounced for EPCN 0.9 which contains comparatively more formaldehyde. It is likely that more methylol groups are present in EPCN 0.9. This makes participation of methylol groups in the epoxy crosslinking process more likely. Hence the greatest strength is observed when EPCN 0.9 is added.

There is a stiffening of the rubber which reaches a maximum at about 4-5% of EPCN. This is reflected in an increase in 300% modulus (Fig.4.34). This effect is seen to level off or even reverse at higher percentages of the resin. The increase in modulus is maximum for the EPCN with cresol/formaldehyde ratio equal to1/0.5. The molecular size is maximum for this ratio because of the presence of many benzene rings.

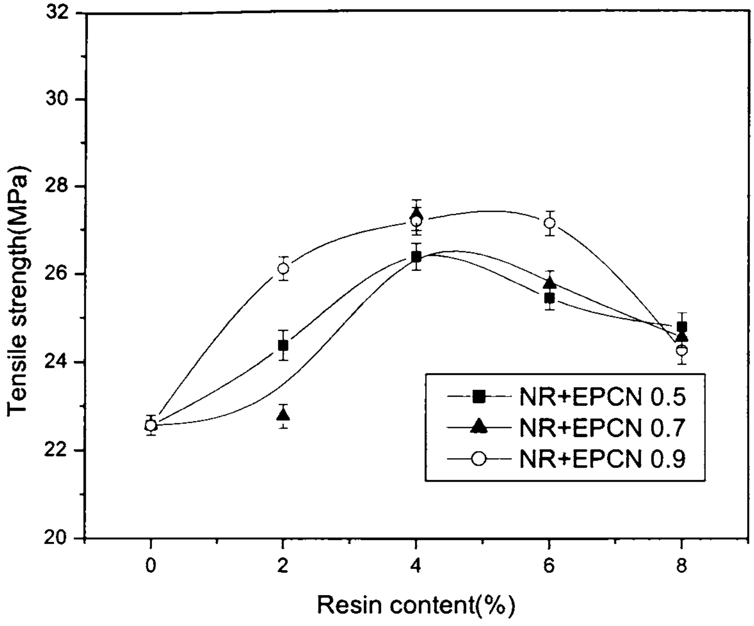


Fig.4.33 Variation of tensile strength with resin content.

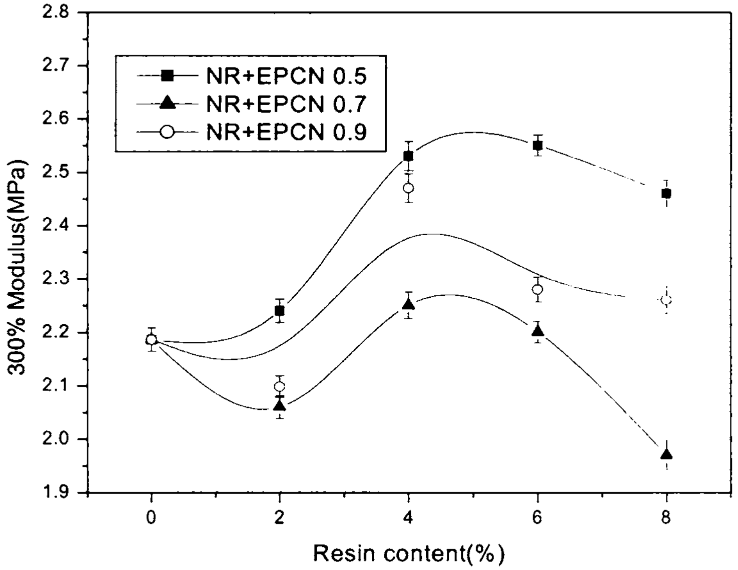


Fig.4.34 Variation of 300% modulus with resin content.

The elongation at break (Fig.4.35) also falls with increasing resin content. The presence of the resin is a hindrance to the stretching of the rubber molecules. This can be due to the physical presence of the EPCN molecule or chemical interaction between the rubber and resin or even some interpenetration. The cresol molecule by virtue of the methyl group can cause greater obstruction to the stretching of the rubber chain than the phenol molecule.

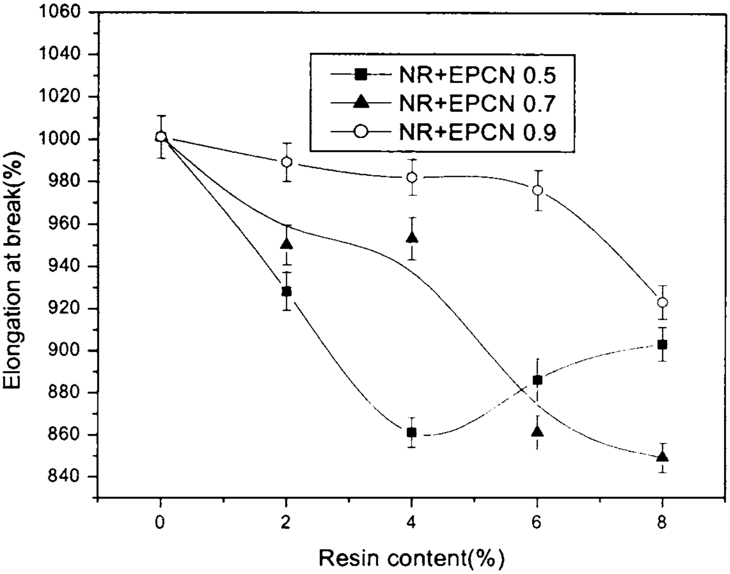


Fig.4.35 Variation of elongation at break with resin content.

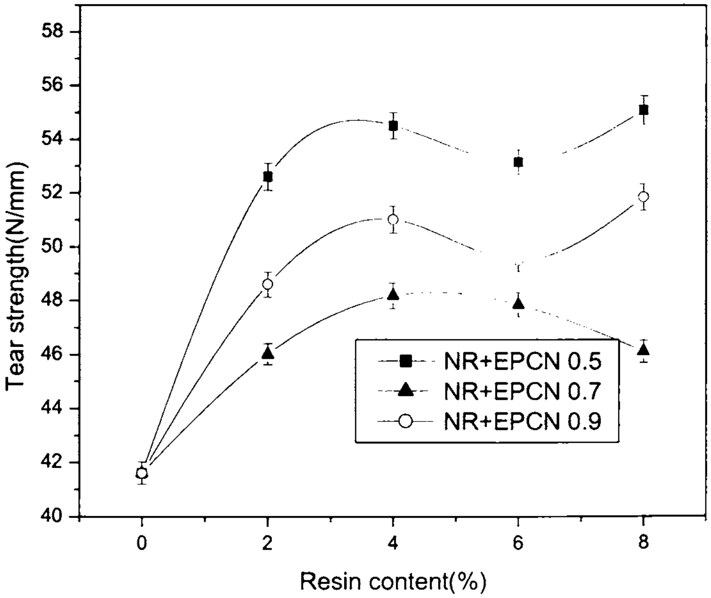


Fig.4.36 Variation of tear strength with resin content.

Tear strength variation is shown in Fig.4.31. It also shows an increasing tendency until about 4% resin. Beyond 4% this property tends to fall. There is no advantage to be gained by adding more than 4% of the resin. The same behavior is noted in the case of surface hardness (Fig.4.37).

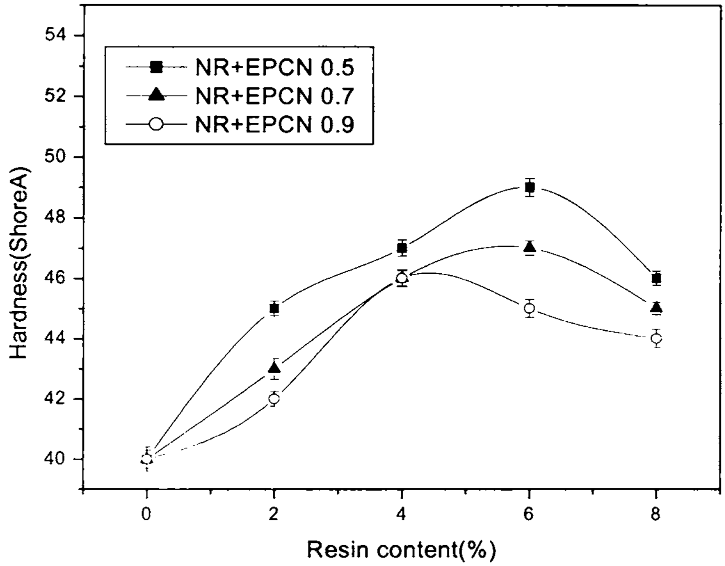


Fig.4.37 Variation of hardness with resin content.

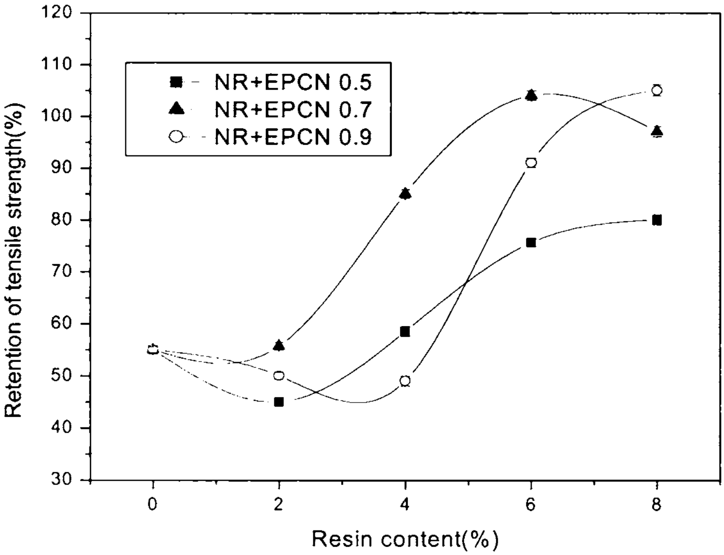


Fig.4.38 Variation of retention of tensile strength with resin content on ageing at 70°C for 72 hrs.

The retention of tensile and tear strengths on ageing vulcanized samples at 70°C for 72 hours is depicted in Figs.4.38 and 4.39. Both properties show an initial dip but as more and more resin is added higher values of tensile and tear strengths are attained. There is a definite improvement in thermal ageing characteristics on adding even moderate amounts of resin.

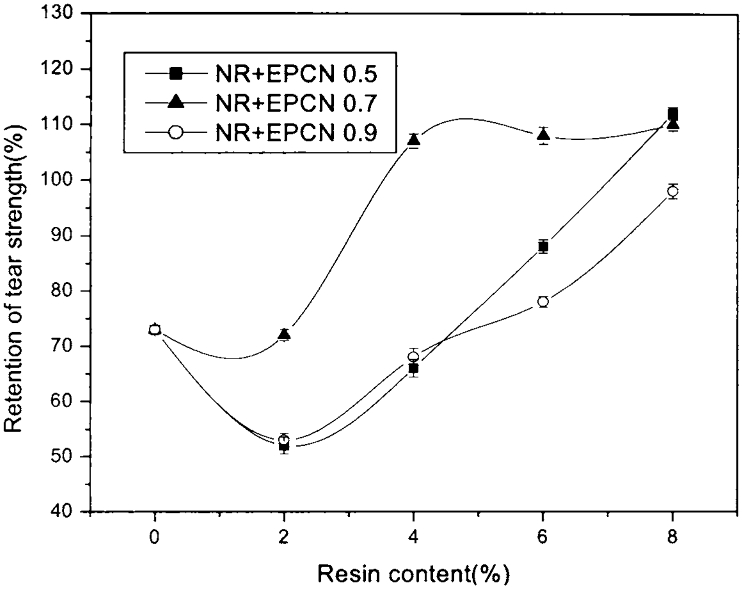


Fig. 4.39 Variation of retention of tear strength with resin content on ageing at 70°C for 72 hrs.

There is considerable reduction in the mass of oil absorbed by the vulcanizates when EPCN is added (Fig.4.40). But beyond 2% the mass of oil absorbed continuous to fall at a very flat rate. The addition of EPCN is generally beneficial in improving the oil resistance.

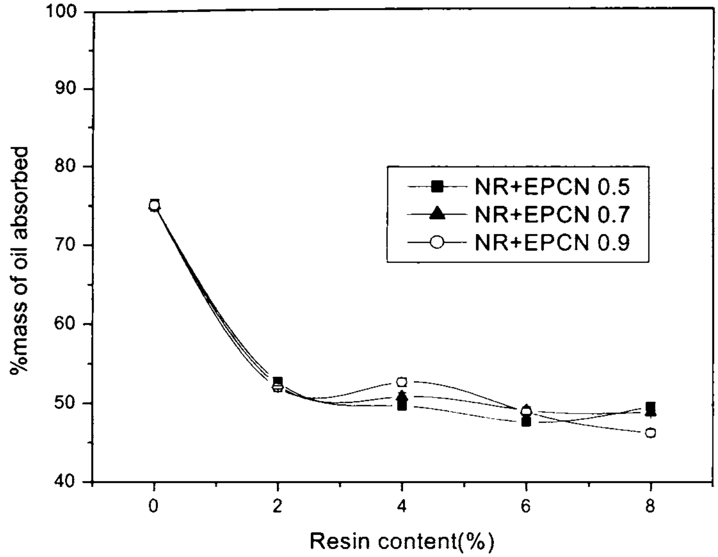


Fig. 4.40 Variation of mass of oil absorbed with resin content.

The crosslink density of NR compound (Fig.4.41) goes through a maximum at about 4% resin content. Beyond 4% there is a gradual decrease in crosslink density which can be due to increasing resistance to rubber crosslinking by the resin. In any case variation of crosslink density is only moderate for the range studied.

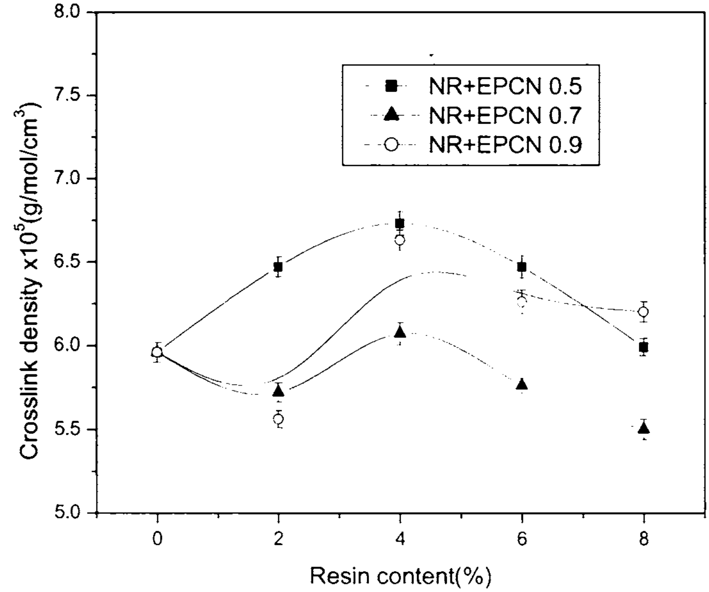


Fig.4.41 Variation of crosslink density with resin content

4.3.4 Modification using ECN

a) NR gum compound

This section deals with the results obtained when epoxidised cardanol novolac is added to the compound in moderate quantities.

Cure characteristics are given in Table 4.10. Fig.4.42 shows that the cure time has more than halved on addition of 4% resin. As in the other cases higher amounts of resin do not reduce the cure time further. The earlier arguments given in Section 2.3 apply here also.

Table 4.10 Cure characteristics of gum NR vulcanizate with ECN

Resin content (%)		T_{10} (min)	T_{90} (min)	M_L (dNm)	M_H (dNm)	CRI (min^{-1})
ECN 0.5	0	2.62	5.62	0.023	2.69	33.33
	2	1.61	3.41	0.003	2.79	55.55
	4	1.07	2.19	0.013	2.90	89.3
	6	0.70	1.78	0.029	2.91	92.6
	8	0.59	1.76	0.045	2.85	85.5
ECN 0.7	2	1.67	3.35	0.016	2.86	59.5
	4	0.99	2.14	0.021	2.98	86.9
	6	0.73	1.86	0.025	2.93	88.5
	8	0.59	1.87	0.031	2.89	78.1
ECN 0.9	2	1.32	2.66	0.016	2.95	74.6
	4	0.81	2.02	0.032	3.06	90.9
	6	0.63	1.91	0.026	3.14	71.9
	8	0.6	1.94	0.042	3.03	74.6

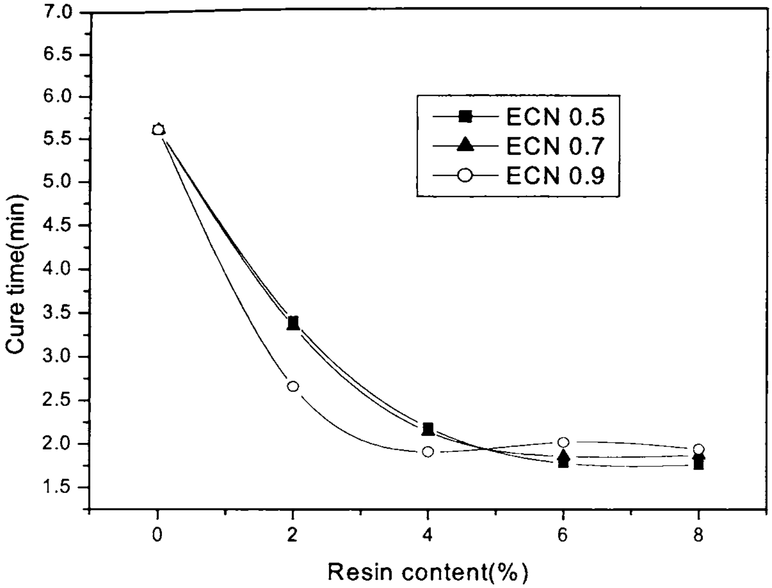


Fig.4.42 Variation of cure time with resin content.

Addition of ECN has a positive effect on the tensile strength of the vulcanizates (Fig.4.43). This effect is most noticeable in the case of ECN 0.9. As in the other cases ECN 0.9 is superior to other resins in this respect. The curves tend to flatten on adding more and more resin especially beyond 4%.

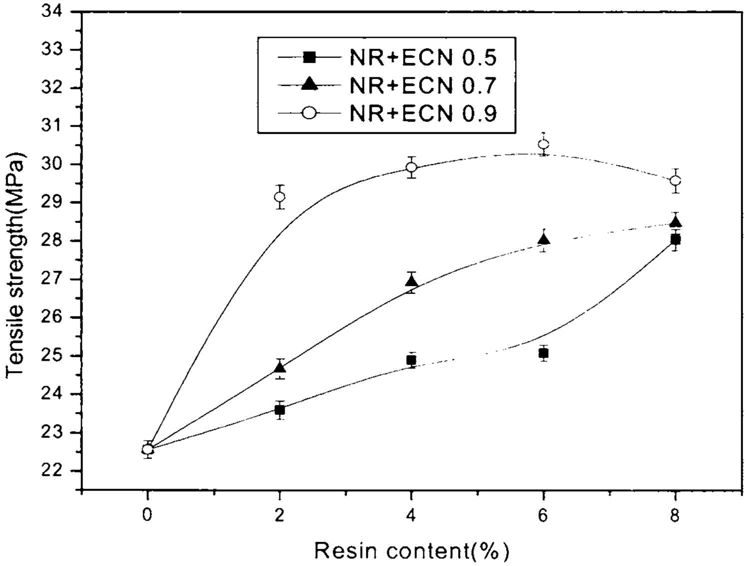


Fig.4.43 Variation of tensile strength with resin content.

Fig.4.44 shows that there is an increase in stiffness when ECN is added to NR. Although the increase is moderate this effect is noticed only upto about 4-6%. The elongation at break is not seriously affected by the presence of the resin as can be seen from Fig.4.45. The side chain of the cardanol molecule is flexible and does not cause any undue reduction in the elongation at break. Moreover, the presence of the side chain at the meta position leads to linear novolac chains

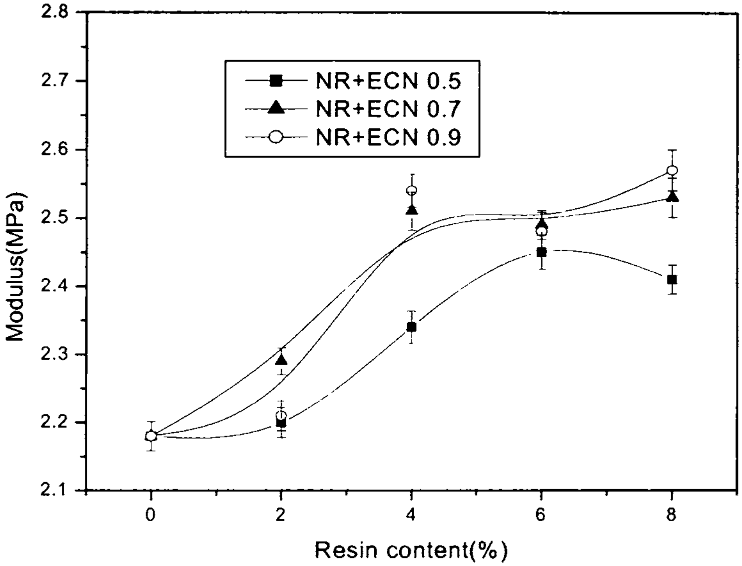


Fig.4.44 Variation of 300% modulus with resin content.

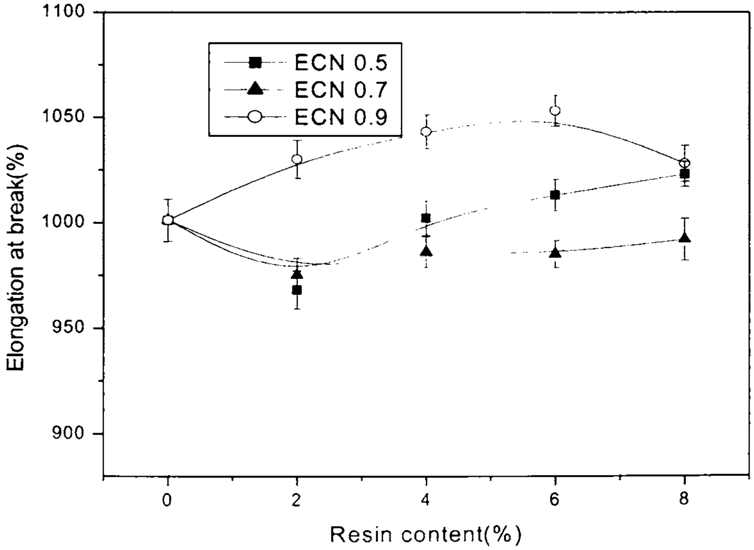


Fig.4.45 Variation of elongation at break with resin content.

Tear strength (Fig.4.46) tends to increase on addition of ECN. It is possible that the presence of the long side chain of the cardanol promotes intermolecular cohesion and greater tear strength. As often noticed this effect tends to taper off at higher percentages of the resin.

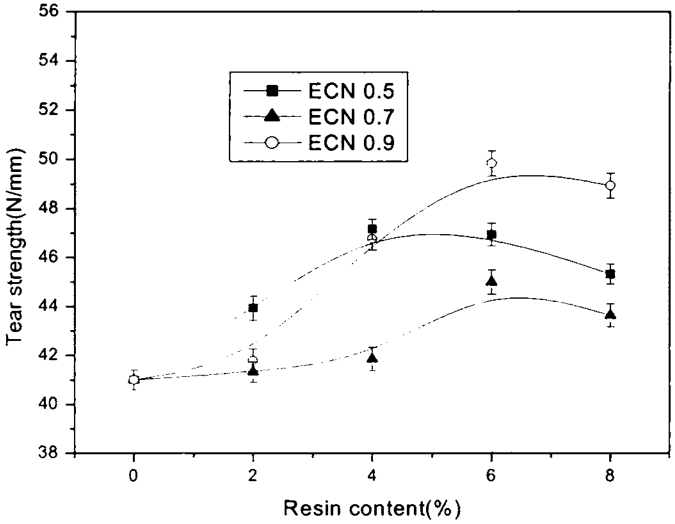


Fig.4.46 Variation of tear strength with resin content

As shown in Fig.4.47 there is a marginal increase in surface hardness on addition of the resin.

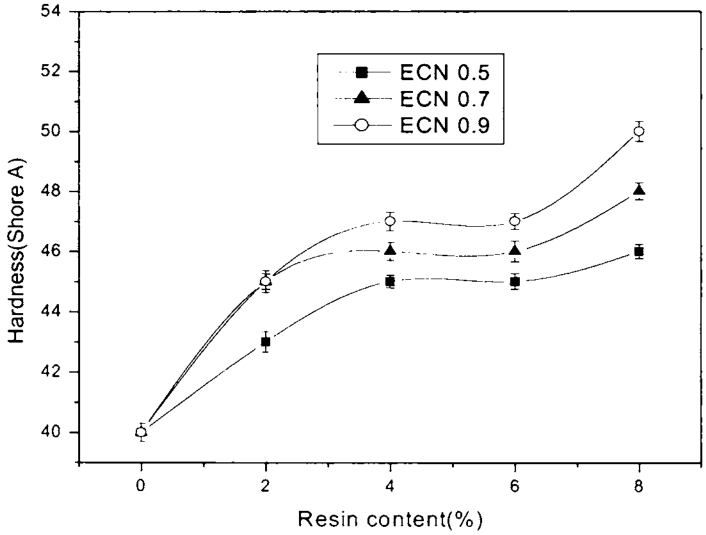


Fig.4.47 Variation of hardness with resin content

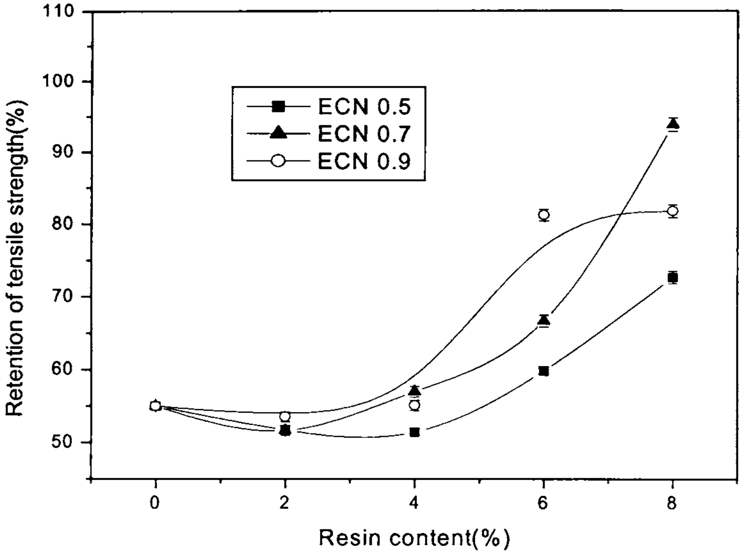


Fig.4.48 Variation of retention of tensile strength with resin content on ageing at 70°C for 72 hrs..

The results of ageing at 70°C for 72 hours are shown in Figs.4.48 and 4.49. Although initially the retention of tensile strength upto 4% resin is not much higher, beyond 4% the retention of tensile strength is substantially higher. This is true of the retention of tear strength also. The poor improvement in this property at lower resin content can be attributed to the lower reactivity of cardanol phenolics.

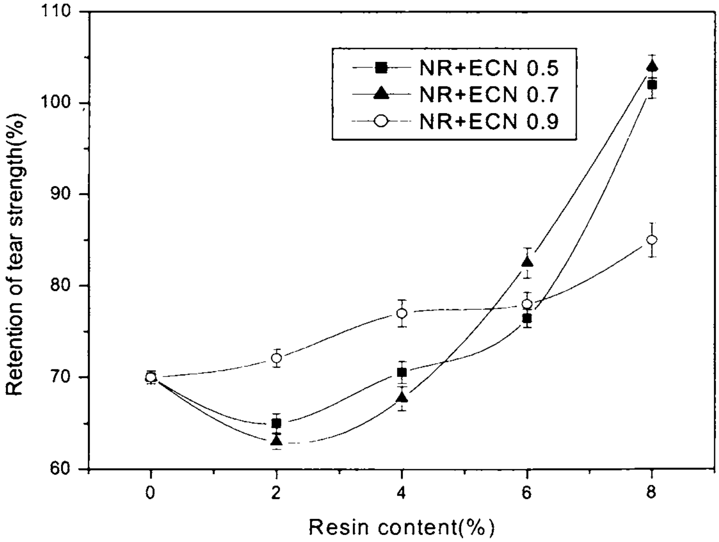


Fig.4.49 Variation of retention of tear strength with resin content on ageing at 70°C for72 hrs.

Fig.4.50 shows that there is reduction in the mass of oil absorbed when ECN is added. The effect tends to level off beyond 2% resin. Figs.4.51 and 4.52 show weight loss on Soxhlet extraction of ECN modified samples both before and after ageing. The extractability reduces on ageing. This is an indication of chemical incorporation of the resin into the matrix. Even at 8% resin the increase in weight loss is only 3% in Fig. 4.51 and 2% in Fig. 4.52.

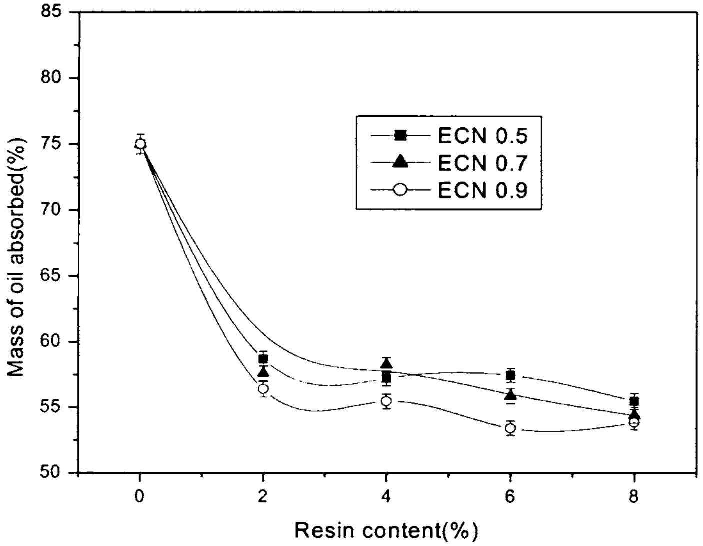


Fig.4.50 Variation of mass of oil absorbed with resin content.

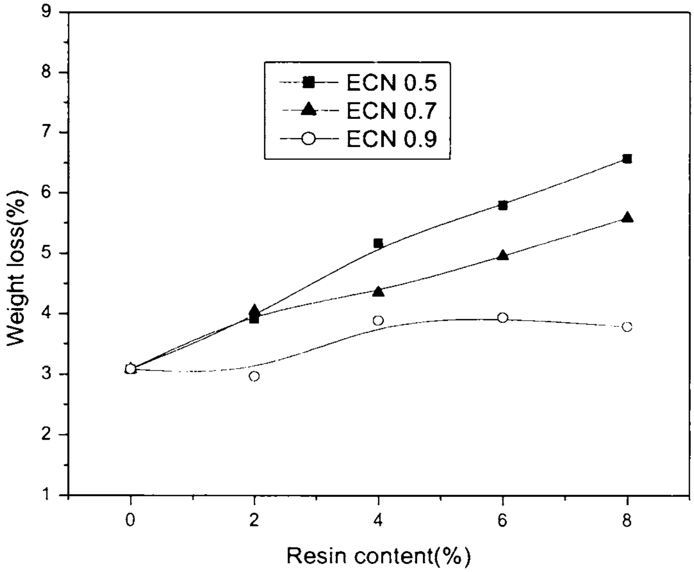


Fig.4.51 Variation of weight loss on Soxhlet extraction before ageing.

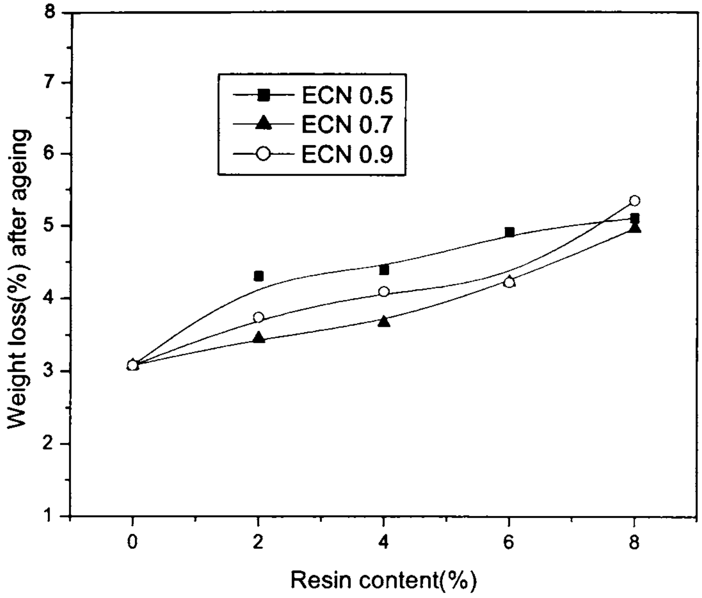


Fig.4.52 Variation of weight loss on Soxhlet extraction after ageing.

Fig.4.53 represents the differential scan of the ECN 0.5 modified NR vulcanizate. The glass transition temperature has increased from -63.3 to -59.9°C.

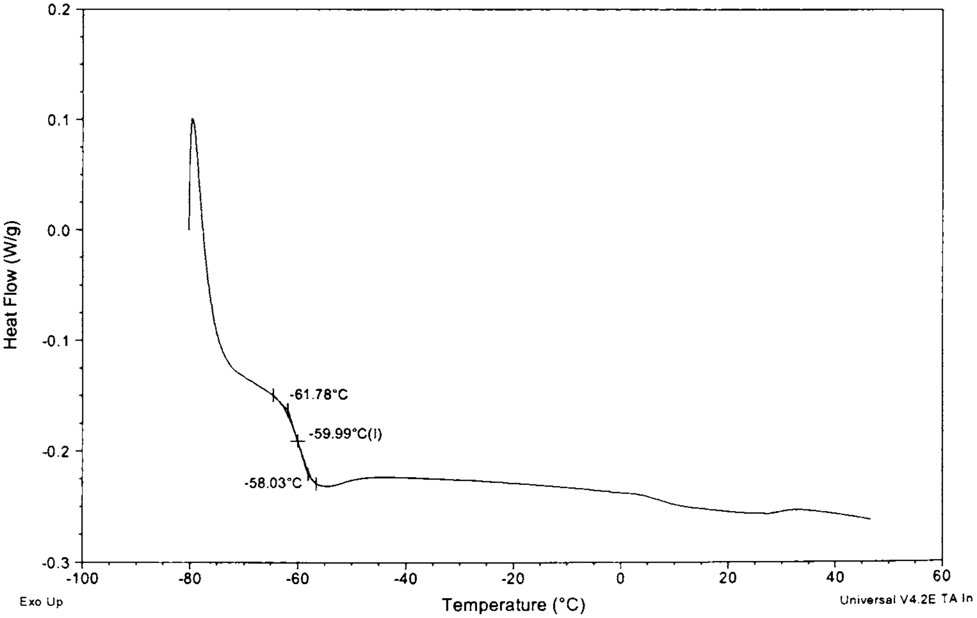


Fig.4.53 Differential scan of NR vulcanizate with 4% ECN 0.5

b) Filled compounds

Fig.4.54 shows the variation of cure time when NR is compounded with ECN and fillers, silica and HAF black. There is continuous reduction in cure time with resin content. This is consistent with the behavior of ECN when blended with unfilled NR.

Fig.4.55 shows the variation of tensile strength of the filled compounds when ECN is added. There is substantial increase in tensile strength of silica filled compounds compared to black filled compounds. Reasons for this behavior can be found in the chemical nature of silica or the difference in particle size and distribution between carbon black and silica. The reinforcement of silica in the presence of epoxy groups has already been reported (119).The larger amount of carbon black used and its very high surface area may blunt the effect of the resin on the rubber by surface adsorption of the resin.

Fig.4.56 shows the variation of 300% modulus of filled compounds in the presence of increasing amounts of resin. The curve shows a mild increasing trend. Black filled compounds have a higher modulus than the silica filled compounds. Similarly the effect of the resin on the elongation at break is also not substantial (Fig.4.57). Carbon black compounds show comparatively low elongation at break.

Tear strength (Fig.4.58) is also mildly affected by the presence of the resin. There is a slight increasing trend. Black filled compounds exhibit much higher tear strength than silica filled compounds. The presence of the resin also leads to slightly higher surface hardness in filled NR compounds (Fig.4.59).

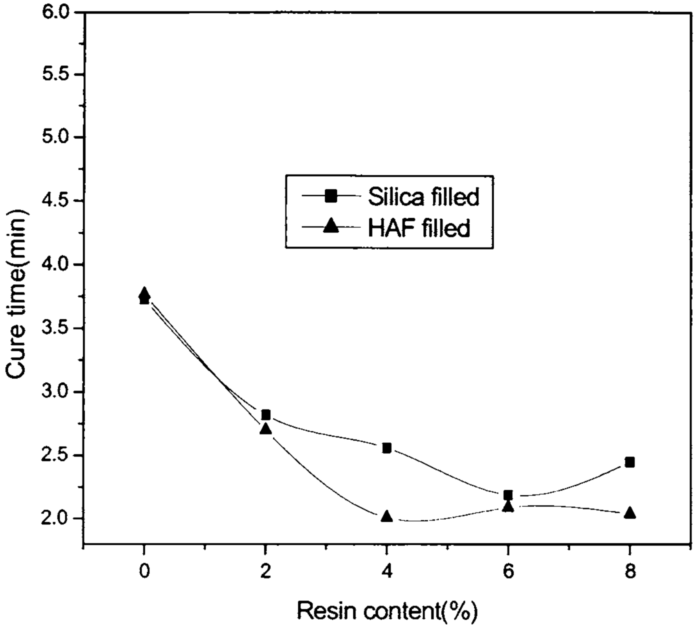


Fig. 4.54 Variation of cure time with resin content

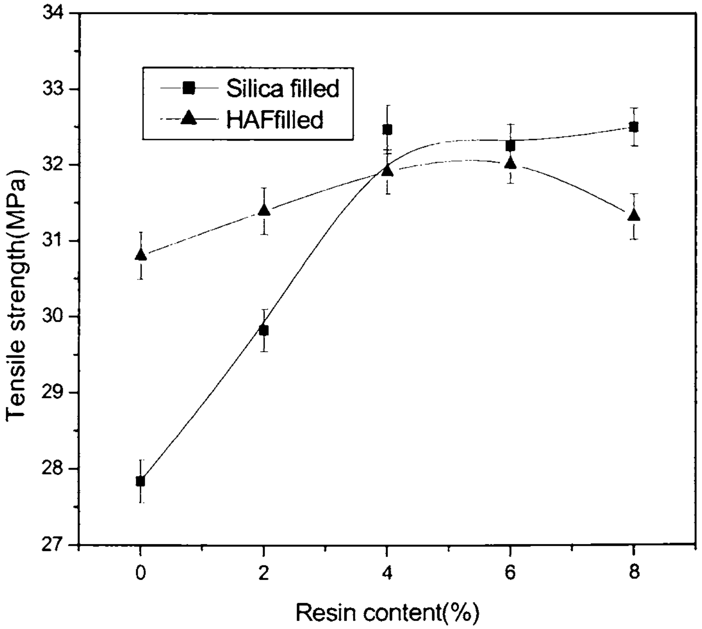


Fig.4.55 Variation of tensile strength with resin content

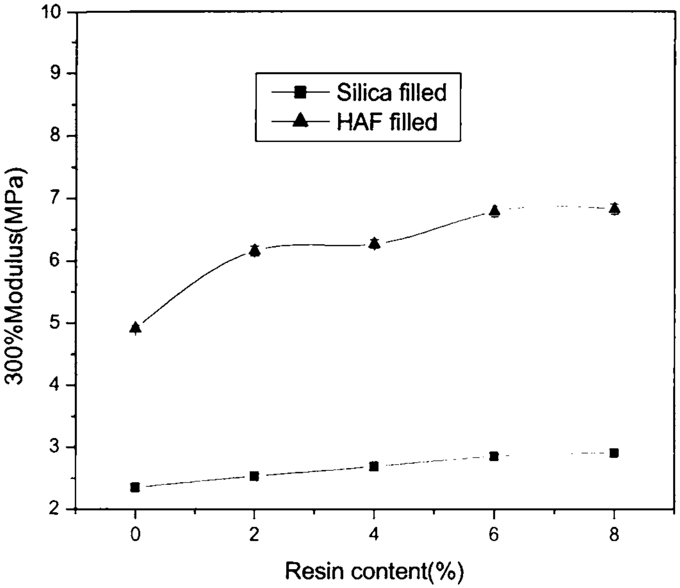


Fig.4.56 Variation of 300% modulus with resin content

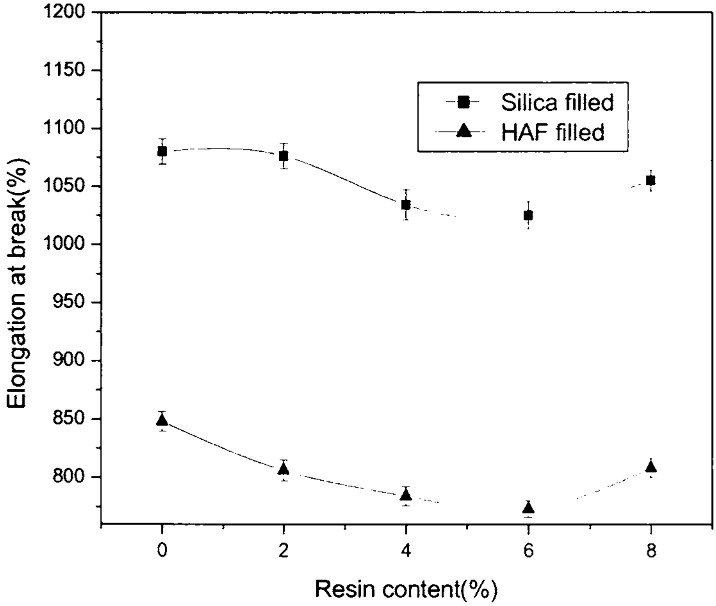


Fig. 4.57 Variation of elongation at break with resin content

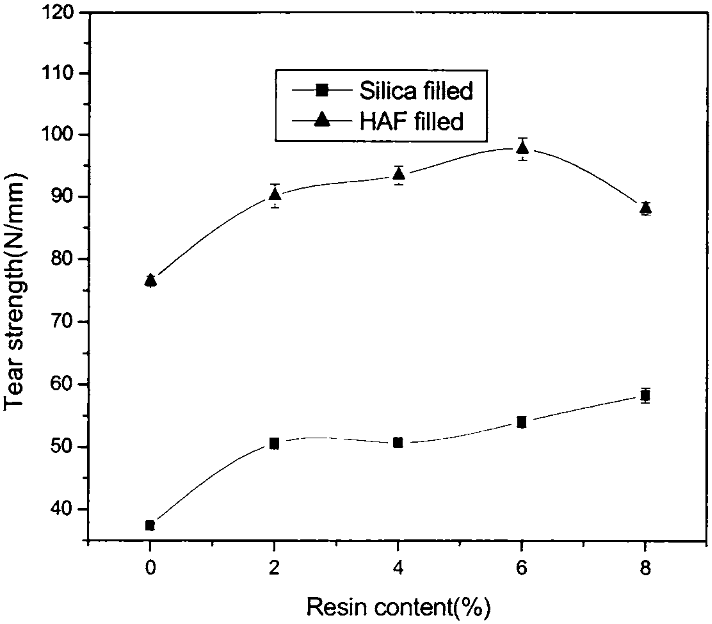


Fig. 4.58 Variation of tear strength with resin content

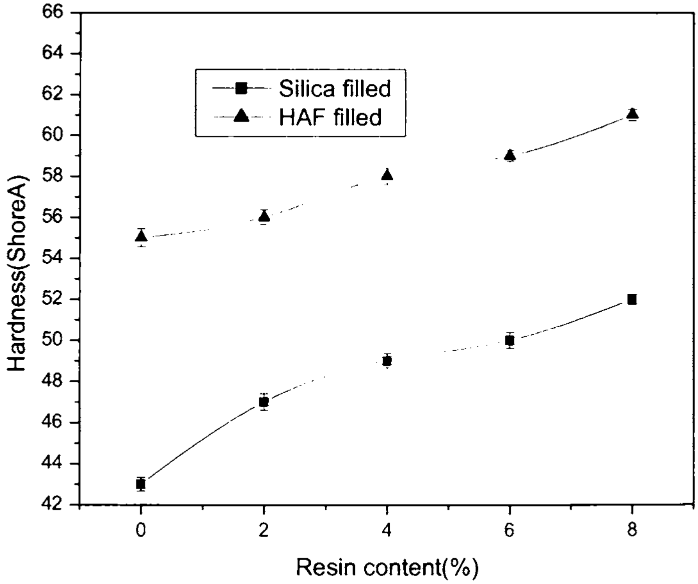


Fig. 4.59 Variation of hardness with resin content

Retention of tensile and tear strengths on ageing of filled compounds at 70°C for 72 hours is shown in Figs.4.60and 4.61. There is a gradual but steady rise in both these properties on addition of resin. Surprisingly, after ageing black filled compounds show lower levels of retention of tear strength. This behavior is similar to earlier observations in the case of filled NR compounds modified by EPN (Fig.4.29 Section 4.3.2).

Fig.4.62 shows that oil absorption by the filled vulcanized samples is not affected by the presence of the resin. The ECN resin is less polar by virtue of the chemical structure of cardanol. Hence in the presence of filler and processing oil the resin shows very little improvement in oil resistance.

Fig.4.63 is a plot of crosslink density vs resin content. There is a gradual but small increase in crosslink density on adding increasing amounts of the resin. Chemical interaction between the cardanol based resin and rubber chains may be responsible for this. Interpenetration can also contribute to this effect.

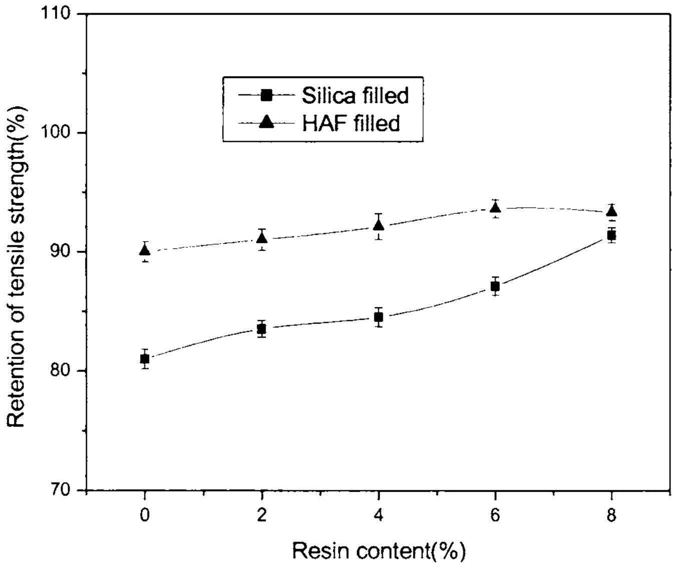


Fig. 4.60 Variation of retention of tensile strength with resin content on ageing at 70°C for 72 hrs.

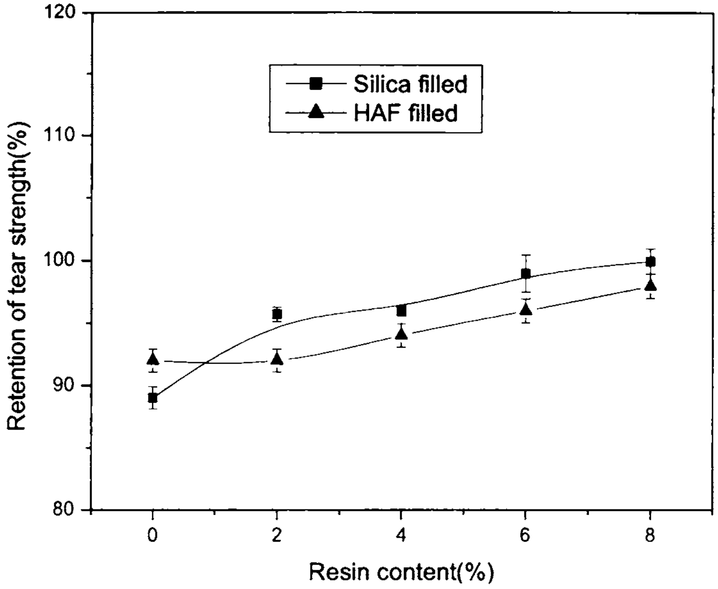


Fig. 4.61 Variation of retention of tear strength with resin content on ageing at 70°C for 72 hrs.

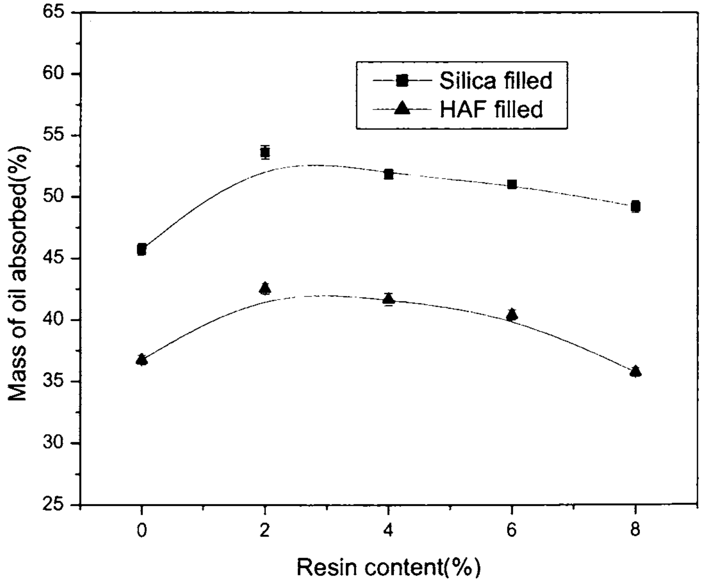


Fig. 4.62 Variation of mass of oil absorbed with resin content

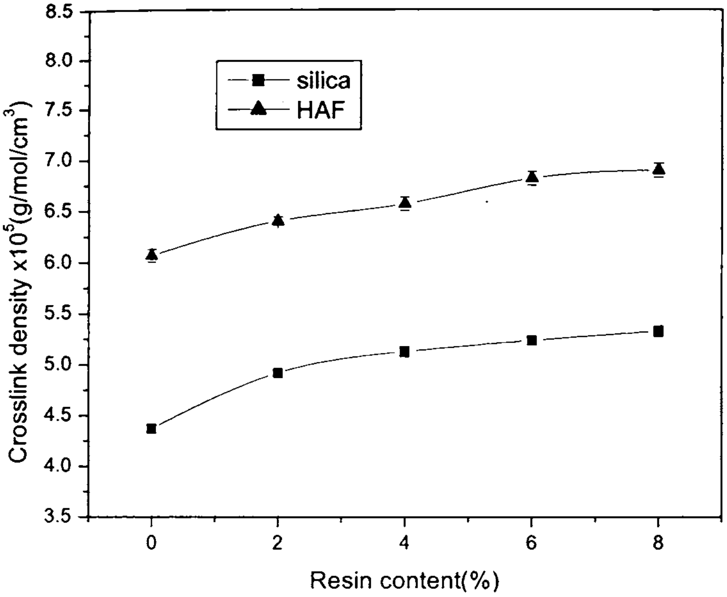


Fig.4.63 Variation of crosslink density with resin content

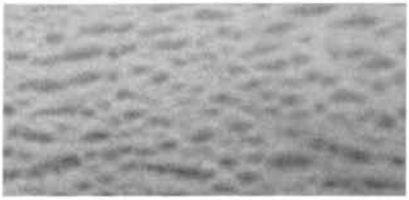
4.3.5 Ozone irradiation studies

Photographs of ozone irradiated NR vulcanizate and novolac modified NR vulcanizates are shown in Fig.4.22. The observations are given in Table.4.4 .The results show that in the EPN modified gum sample crack initiated after 12 hours but in the unmodified samples crack initiated after 6 hours. In the silica filled samples, crack initiated after 12hrs. in both modified and unmodified samples. But number of cracks is less in modified samples. HAF filled samples are relatively poor in ozone resistance. In these samples cracks are initiated after six hours modified or unmodified. The resin is able to improve the ozone resistance of NR in the absence of fillers. This effect may be attributed to one or both of two reasons.1) The resin may bloom to some extend on the surface of the rubber in the absence of fillers. In this respect, the behaviour of the resin may be similar to waxes added during compounding (3) 2) The resin may have acted as a shield against the attack of ozone on unsaturation present in the rubber which results in the formation of the ozonide moiety.

It is surprising that the resin is not able to improve the ozone resistance of black reinforced compounds. The presence of black may have caused this effect by obstructing the two mechanisms mentioned above.

Table 4.11 Results of ozone irradiation

	Ozone resistance (50pphm,40°C)
NR gum	Crack initiated after 6hrs
NR+EPN 0.5	Crack initiated after 12hrs
NR+silica	Crack initiated after 12hrs
NR+Silica+EPN 0.5	Crack initiated after 12hrs
NR+HAF	Crack initiated after 6hrs
NR+HAF+EPN 0.5	Crack initiated after 6hrs
NR+HAF+ECN 0.5	Crack initiated after 6hrs
NR+Silica+ECN 0.5	Crack initiated after 6hrs



NR

NR+EPN

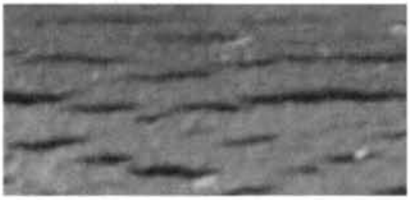
NR+Silica

NR+Silica+EPN

NR+Silica+ECN

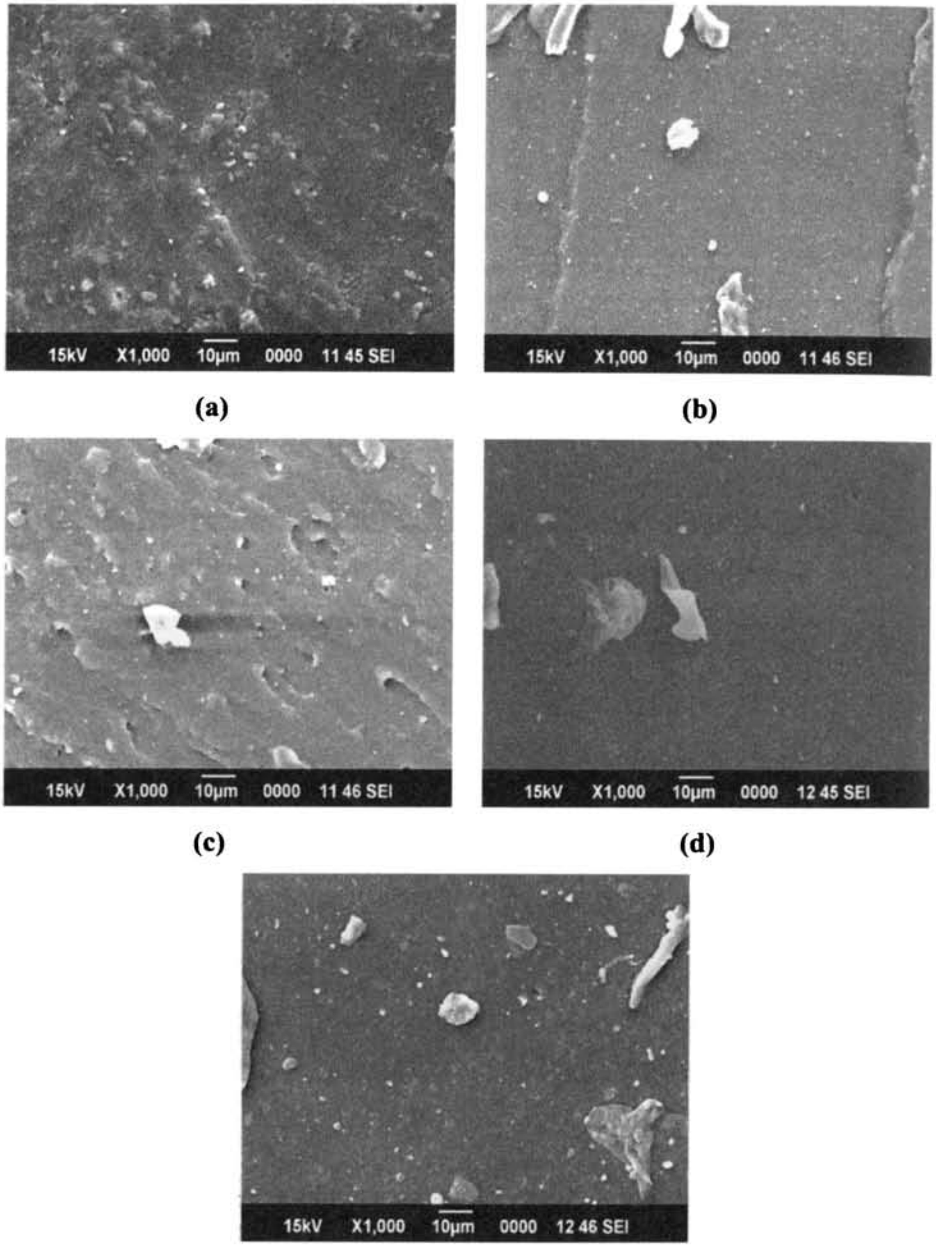
NR+HAF

NR+HAF+EPN



NR+HAF+ECN

Fig. 4.64 Photographs of ozone irradiated samples

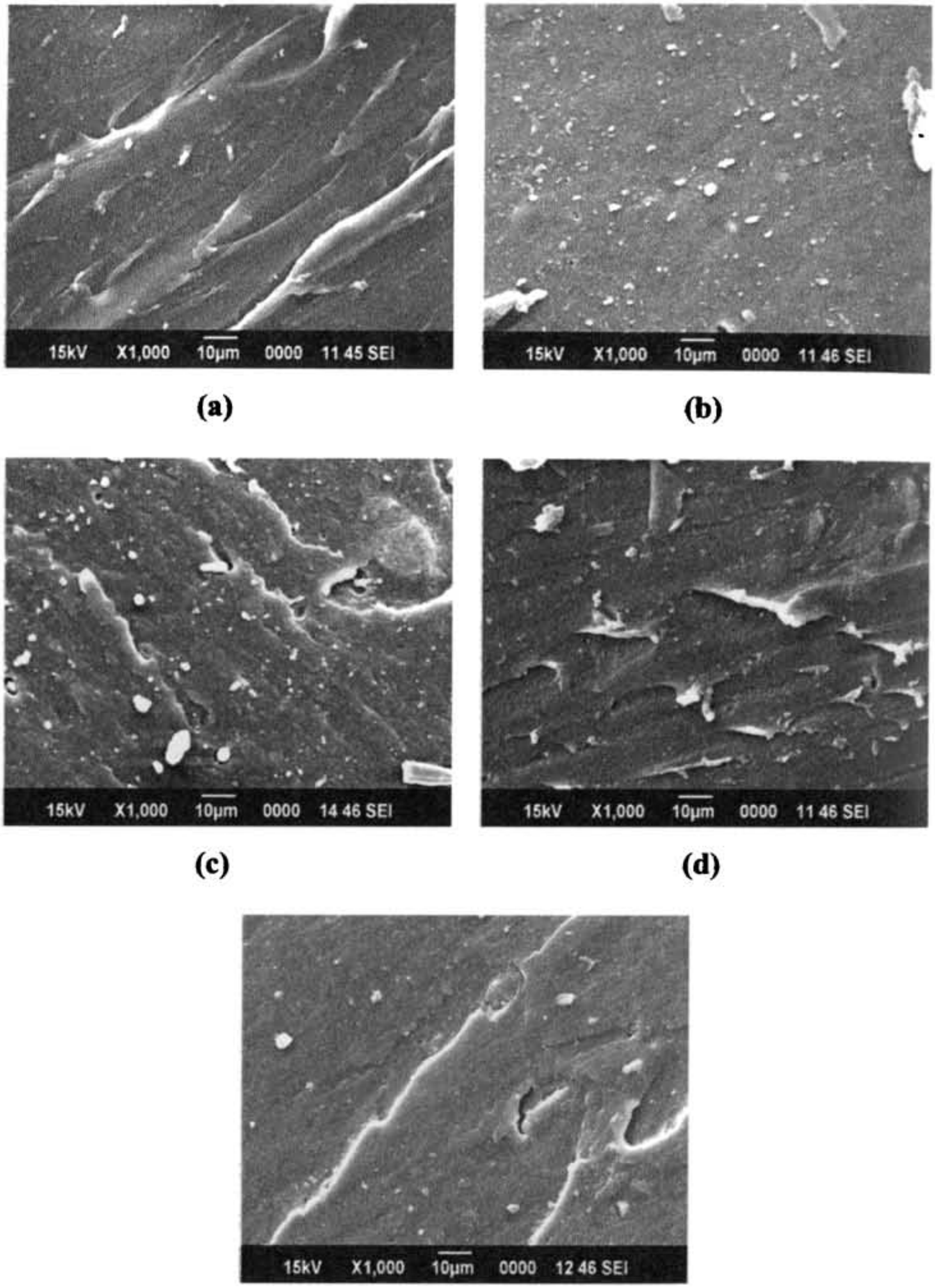


(a) **(b)** **(c)** **(d)** **(e)**

Fig.4.65 SEM micrographs of gum NR and modified NR with varying amounts of EPN 0.5. **(a)** 0% **(b)** 2% **(c)** 4% **(d)** 6% (e) 8%

Fig.4.65 shows the SE micrographs of gum NR and modified NR samples containing different amounts of EPN 0.5 resin. It is found that the distribution of the resin is more uniform at lower percentages. There is great heterogeneity in the size distribution of the resin particles. The clear boundaries of the larger particles indicate that the resin rubber blend retains a heterogeneous morphology. It is surprising that the milling operation has not resulted in a more uniform distribution of the resin. In spite of discrete resin particle visible in the micrographs it can be safely assumed that a large part of the resin has blended with the rubber to form homogeneous mixtures. Only then the property improvement observed in the modified rubber can be explained.

Fig.4.66 shows the micrographs of HAF black filled NR containing various amounts of EPN 0.5. The presence of the filler has facilitated a more uniform distribution of the resin. The failure pattern and the fracture surfaces indicate long ridges and valleys. Greater energy absorption is indicated by this.



(a) (b) (c) (d) (e)

Fig.4.66 SEM micrographs of HAF filled NR with varying amounts of EPN 0.5. (a) 0% (b) 2% (c) 4% (d) 6% (e) 8%

4.3 Conclusion

There is a general improvement in tensile strength and tear strength of gum NR on addition of different EPNs. The age resistance of NR shows a clear improvement on addition of various EPN resins from the view point of tensile strength and tear strength after ageing. The blending with the resin has considerably improved the oil resistance of NR. There is only a moderate increase of weight loss on extraction with acetone after adding various percentages of resin which indicates that most of the resin has been chemically incorporated into the rubber matrix. Thermogravimetric data confirm the improved thermal stability of EPN blended NR vulcanizates. Addition of only small amounts of EPN can be a useful method to improve the ageing and oil resistance of NR. Ozone resistance of the EPN modified samples (gum and silica reinforced) is found to be better than the unmodified samples.

There is a definite improvement in thermal ageing characteristics on adding even moderate amounts of EPCN. There is a considerable reduction in the mass of oil absorbed by the vulcanizates.

Addition of ECN increases the mechanical properties of the vulcanizates. Ageing resistance is also improved on addition of ECN.

In the case of filled compounds (HAF and silica) the cure time reduces on addition of the resins. There is considerable increase of tensile strength of silica filled NR on addition of ECN (and not other epoxidised novolacs) which is not visible with HAF black filled compounds. The retention of both tensile strength and tear strength of filled compounds are better after addition of resins. There is moderate improvement of ageing properties of filled compounds on addition of epoxidised novolacs. The oil resistance of filled compounds show definite improvement on compounding with various epoxidised novolacs with the exception of ECN.

Reference

[1] K.P Unnikrishnan, Ph.D Thesis, Studies on the toughening of epoxy resin, January (2006).

[2] R.M. Silverstein and F.X. Webster, Spectrometric Identification of Organic Compounds, 6th Edn. Ch.3, p-71-143, John Wiley & Sons Inc., New York (2002).

[3] L.G Wade, Organic Chemistry, 4th Edn.

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Chapter

5

MODIFICATION USING UNSATURATED POLYESTER RESIN

5.1 Introduction

In this chapter, the effects of unsaturated polyester resin (UPR) on the properties of natural rubber vulcanizates are investigated. UPR was prepared with varying MA/PA ratios and blended with natural rubber. The mechanical and ageing properties were studied. Commercial UPR and isophthalic resin (IUPR) were also used for modification. The effects of adding the resins were studied in gum as well as filled compounds.

5.2 Experimental

5.2.1 Materials

GP grade UP resin (HSR 8113M), isophthalic polyester resin (HSR 8131D), styrene, methyl ethyl ketone peroxide (MEKP), and cobalt naphthenate were of commercial grade, supplied by M/s Sharon Engineering Enterprises, Kochi. Dimethyl aniline, benzoyl peroxide, 1,2 propylene glycol (PG) (B.P=188°C, d^{20}=1.04), maleic anhydride (MA) (M.W = 98.06, 98.5% assay), phthalic anhydride (PA) (M.W = 148.12, 99%assay), xylene (B.P = 137-142°C, 95% assay), hydroquinone (M.P=169°C) and triphenyl phosphate were laboratory reagent (LR) grade supplied by E. Merck India Ltd, Bombay.

Specifications of commercial UP resin are given below.

Acid number - 10-30 mg KOH/g
Styrene content - 25-45%
Viscosity at 25°C - 0.2-4.5 Pa.s
Specific gravity at 25°C - 1.07-1.3
Refractive index at 25°C - 1.524-1.559

Details of natural rubber (ISNR5) and compounding ingredients, their suppliers and other particulars are given in Section 2.2.1.

5.2.2 UP resin preparation [1]

The principles of preparation of UP resin have already been discussed in Section 1.4. The resin preparation was done by polycondensation [2]. PG, MA and

PA were taken in the molar ratio 1.1:0.60:0.40 in a 1 litre three-necked RB flask equipped with a mechanical stirrer, N_2 inlet and a reflux condenser. A slight excess of PG (10%) was provided to allow for evaporation losses. The reaction was conducted with an inert blanket of N_2. 0.05% triphenyl phosphate was added to protect the light colour. The reaction mixture was heated at 210°C in a temperature-controlled heating mantle for several hours. The temperature was kept at 210°C, the optimum temperature at which MA in the cis configuration is isomerised to the less strained and more planar trans fumaric acid [3]. About 10ml of xylene was used to remove the water of hydration azeotropically. The acid value [4] was monitored every two hours. When the acid value became 40, vacuum was applied to bring it below 30 by removing residual reactants and the water of condensation. At this stage heating was discontinued. When the reaction mixture cooled down to 100°C, 0.02 wt % hydroquinone and subsequently, 40 wt % styrene were added and the mass mixed thoroughly. The resin was cooled to room temperature and stored in containers.

The unsaturation in the polyester chain arises from MA employed for the esterification. Hence the relative proportion of MA in the mixture of MA/PA influences the properties of the final blend. To ascertain this, different UP resins were additionally synthesized with varying MA/PA ratios viz. 30/70 & 90/10 and blended with NR.

5.2.3 Blend preparation

Since reports of blending of UPR with natural rubber are not available in literature, some preliminary experiments were conducted to determine the most suitable manner of addition as well as the best catalyst system. The most popular catalyst system for UPR consists of methyl ethyl ketone peroxide catalyst and cobalt naphthenate promoter. But this system was not selected for this study because of the deleterious effects of pro-oxidant cobalt on natural rubber [5]. Hence three other systems namely a) Dicumyl peroxide (DCP) b) Benzoyl peroxide (BPO) and c) Benzoyl peroxide and dimetyl aniline (BPO&DMA) were selected for the study.

Based on the mechanical properties of the rubber vulcanizate obtained (Table 5.2) on employing each of the above catalyst systems, BPO/DMA was selected for further studies.

Since UPR crosslinks to a gel after a few minutes of adding the catalyst and accelerator, it was necessary to find the optimum time interval (Fig.5.1) before adding it to the rubber on a two roll mill. The effect of varying the percentage of catalyst (Fig.5.2) was also investigated.

2.2.4 Rubber compounding and curing

The resin was incorporated into the gum rubber while compounding on a two roll mill. Before addition the resin was mixed with 1.5% by weight of benzoyl peroxide and dimethylaniline as curing agent. Then the compounding ingredients were added in the following order: activators, filler (where applicable), accelerators, and sulphur. Mixes were prepared and cured as already described in Section 2.2.4.The formulations of the mixes are given in Table 3.1,3.2 and 3.3.

2.2.5 Quality evaluation

The vulcanizates were tested according to relevant ASTM standards. The details of the test procedure as well as the ASTM standards applicable have already been furnished in Section 2.2.5.

2.3 Results and discussion

a) Preliminary studies

Table 5.4 lists the physical properties of natural rubber modified with 2% unsaturated polyester resin using different catalyst systems. These are compared with results obtained when 1) no catalyst is used for UPR and 2) no UPR is used. From an examination of tensile strength the combination of BPO and DMA gives the highest tensile strength to the blend. While in the absence of catalyst the addition of UPR leads to a comparable value of tensile strength, the combination of

MEKP and cobalt naphthenate gives much lower values. Oxidation and consequent chain scission of the rubber molecules due to the presence of cobalt ion may be responsible for this. The combination of BPO and DMA has been used in subsequent studies.

Table 5.1 Properties of natural rubber modified with com. UPR using different catalyst systems

Properties	NR+ UPR0%	NR+ UPR2%	NR+ UPR2% BPO	NR+ UPR2% DCP	NR+ UPR2% BPO+DMA	NR+ UPR2% MEKP+CoN
Tensile strength(MPa)	22.56	21.2	23.58	24.6	25.25	22.46
Modulus (MPa)	2.186	1.67	1.58	1.74	1.51	1.50
Elongation at break (%)	1001.8	1081	1297	1224	1281	1222
Tear strength (N/mm)	41.61	42.59	37	42.2	38.54	39.5
Hardness (Shore A)	35	36	35	37	35	35
Resilience(%)	63	68	68	74	70	64
Abrasion loss (cc/hr)	4.33	5.70	5.64	4.95	5.03	5.46

NR-natural rubber
BPO-benzoyl peroxide
DMA-dimethyl aniline
MEKP-methyl ethyl ketone peroxide
CoN-cobalt naphthenate

The effect of time elapsed after addition of BPO/DMA to the resin was studied by choosing different intervals namely 1, 2, or 3 minutes (Fig.5.1). Beyond 3 minutes the resin became too viscous for addition to rubber. The highest tensile strength is shown when 3 minutes are allowed to elapse.

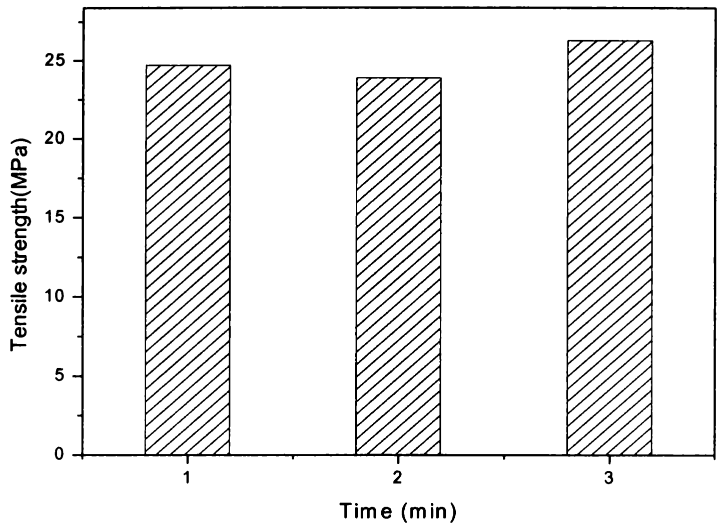


Fig. 5.1 Variation of tensile strength with time of addition of resin

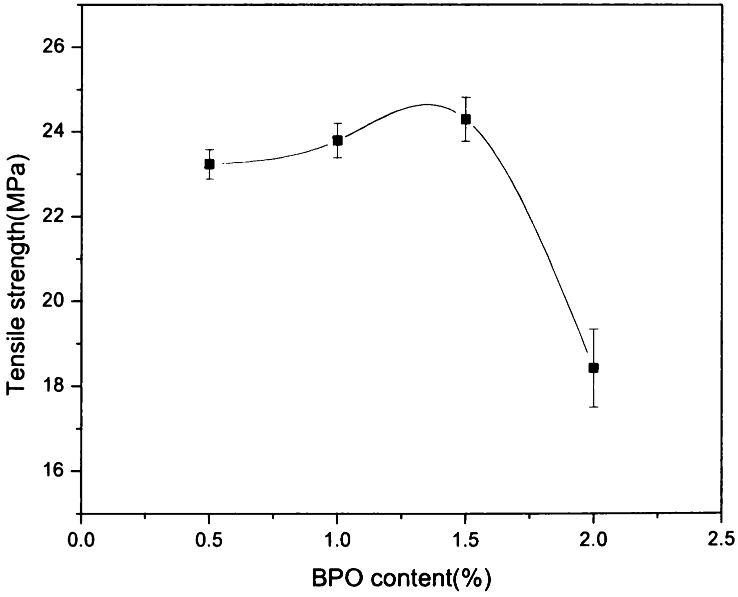


Fig. 5.2 Variation of tensile strength with benzoyl peroxide content

Hence this procedure was followed for later studies. Similarly the amount of BPO giving the best tensile strength to the vulcanizate for a constant DMA content of 0.5% of the resin was also estimated by following the tensile strength. The optimum value of BPO is found to be 1.5% (Fig. 5.2)

b) Effect of commercial and synthesized UPR on the properties of NR vulcanizate

Figs. 5.3 and 5.4 show the FTIR spectra of gum NR modified by UPR and unmodified NR respectively. The modified rubber shows evidence of C=O stretching frequency by the presence of the ester group (1731 cm^{-1}). The additional absorption peak at 1127 cm^{-1} can be due to a number of chemical moeties not directly attributable to known chemical changes.

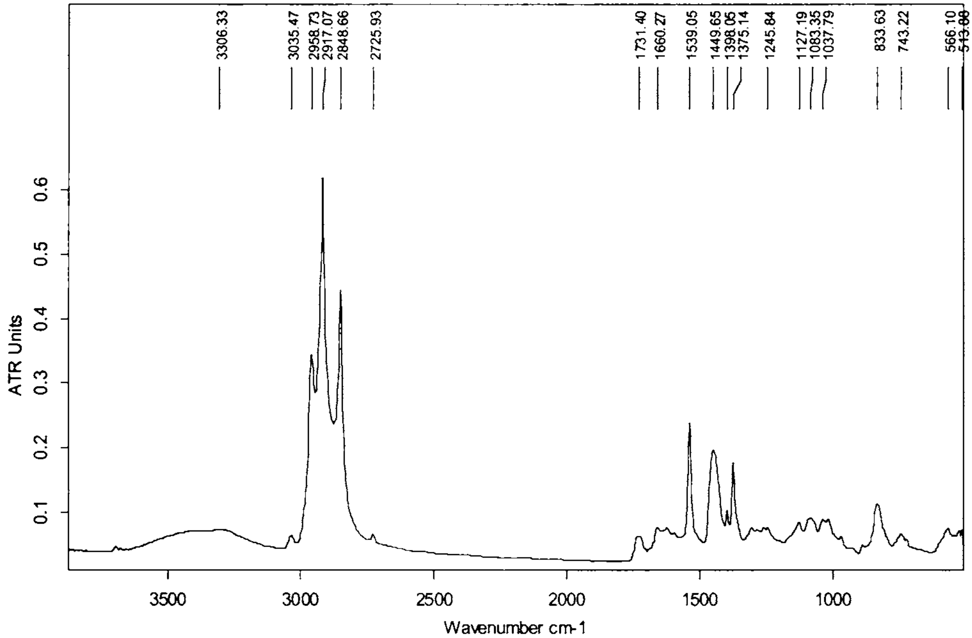


Fig.5.3 FTIR spectrum of vulcanized NR+4% UPR

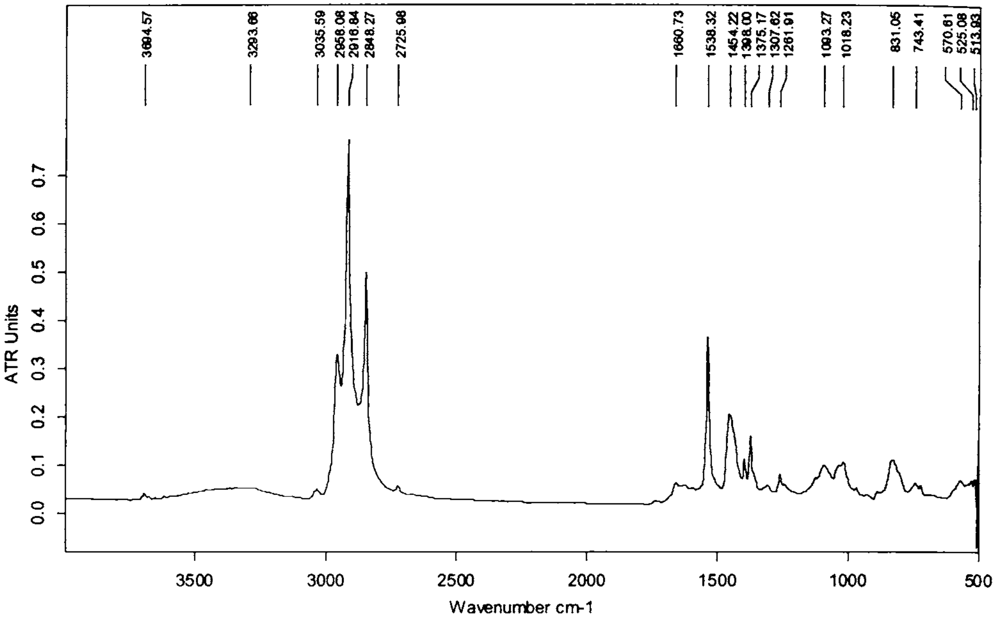


Fig.5.4 FTIR spectrum of NR vulcanizate.

Cure characteristics of NR with UPR are given in Table 5.2. Fig. 5.5 shows the variation of cure time with UPR content. Cure time increases with resin content. This indicates that unlike epoxy resins UPR does not activate the curing reaction. The increase in cure time may be due to the retarding effect of residual acidity in the resin on the crosslinking reaction.

Figs.5.6 to 5.10 represent the plots of ln (M_h-M_t) vs time of various UPR modified samples. Cure rate constants are given in Table 5.3 They indicate that cure rate decreases when the MA/PA ratio increases which means that the amount of unsaturation has a bearing on the retarding effect on the crosslinking reaction.

Table 5.2 Cure characteristics of gum NR vulcanizate with UPR

Resin content (%)		Scorch time(min)	Cure time (min)	Maximum Torque(dNm)	Cure rate index (min^{-1})
0		2.62	5.62	2.69	33.33
Commercial UPR	2	3.13	6.62	2.35	28.65
	4	3.56	6.94	2.26	29.58
	6	3.95	9.03	2.21	19.68
	8	4.27	11.63	2.18	13.58
UPR 1	2	3.52	8.01	2.31	22.27
	4	3.62	8.98	2.15	18.66
	6	4.09	12.96	2.29	11.27
	8	4.10	16.96	2.05	7.77
UPR 2	2	3.67	9.23	2.25	17.98
	4	3.89	10.99	2.04	14.08
	6	3.97	15.07	2.05	9.01
	8	4.05	17.71	1.82	7.32
UPR 3	2	3.95	8.71	2.27	21.01
	4	4.01	11.32	2.14	13.68
	6	4.49	18.01	1.76	7.39
	8	4.43	18.77	1.68	6.97

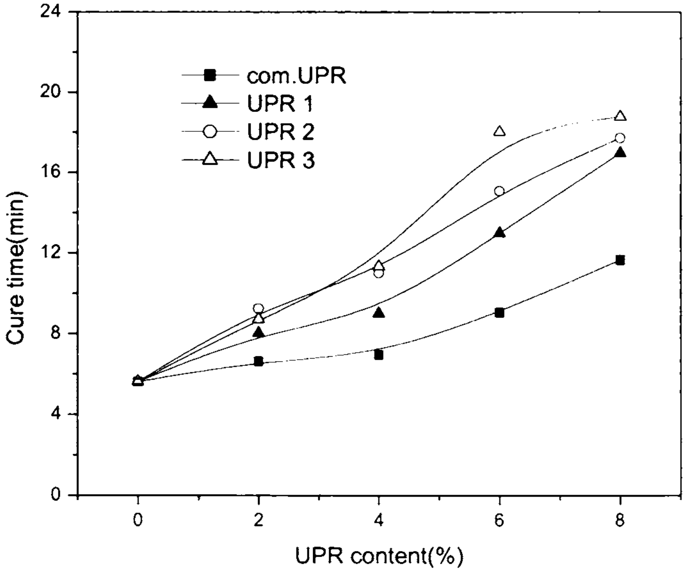


Fig. 5.5 Variation of cure time with resin content

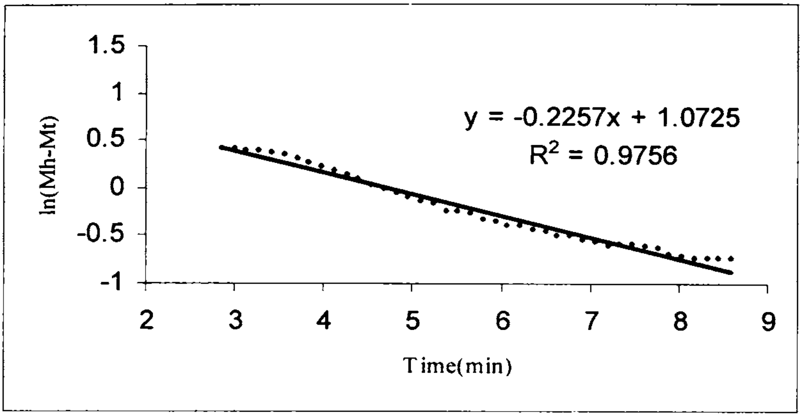


Fig.5.6 ln(M_h-M_t) vs t for NR compound

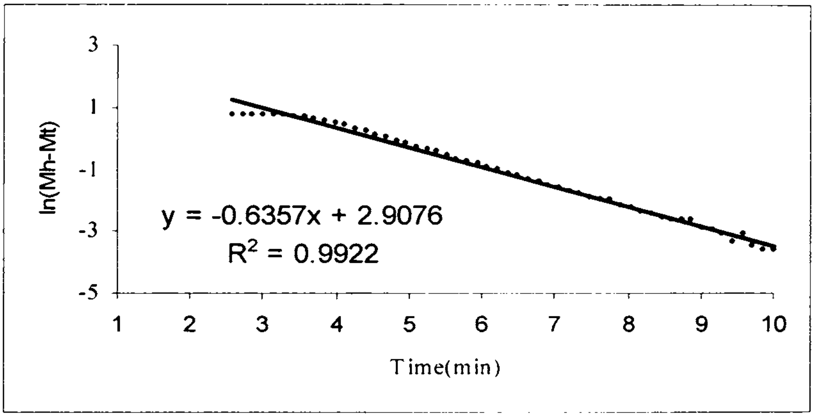


Fig.5.7 ln(M_h-M_t) vs t for NR compound with 4% UPR

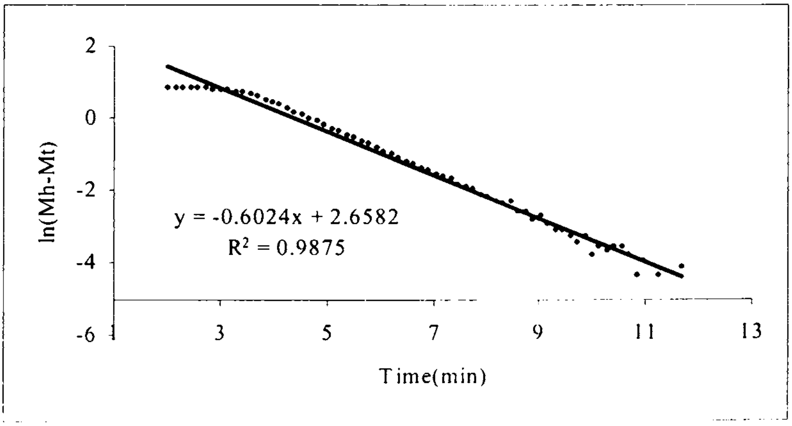


Fig.5.8 ln(M_h-M_t) vs t for NR compound with UPR-1

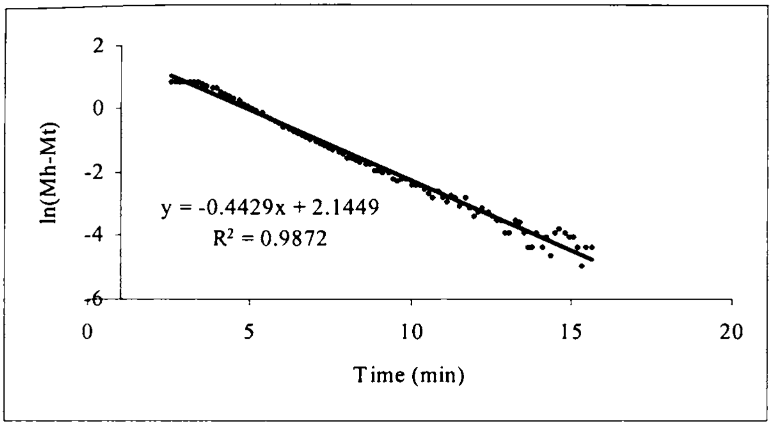


Fig.5.9 ln(M_h-M_t) vs t for NR compound with UPR-2

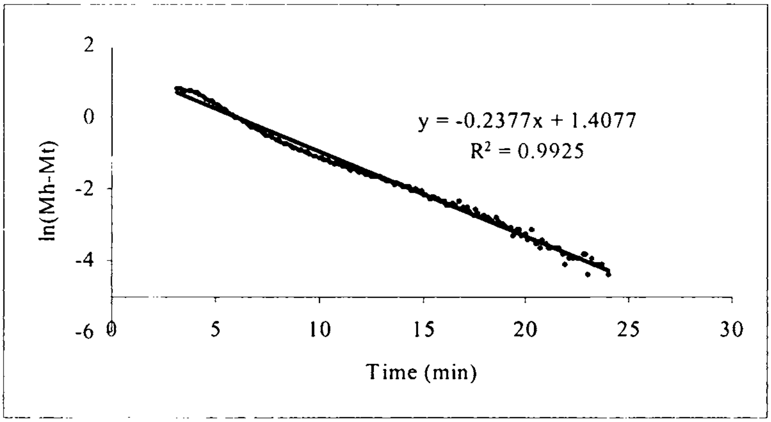


Fig.5.10 ln(M_h-M_t) vs t for NR compound with UPR-3

Table 5.3 Cure rate constants of UPR modified samples

Compound	**Rate constant (min^{-1})**
NR	0.2257
NR+com.UPR (4%)	0.6357
NR+UPR 1 (4%)	0.6024
NR+UPR 2 (4%)	0.4429
NR+UPR 3 (4%)	0.2377

Figures 5.11 to 5.20 show variation in different properties of vulcanizate on addition of UPR. Each of these figures also indicates the effect of using UPR of varying MA: PA ratios for NR modification. For comparison purposes the effect of using commercial UPR is also shown.

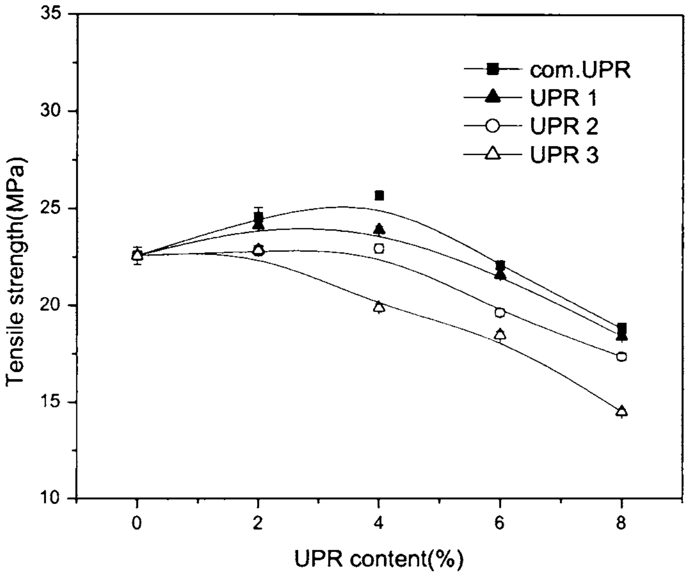


Fig.5.11 Variation of tensile strength with resin content

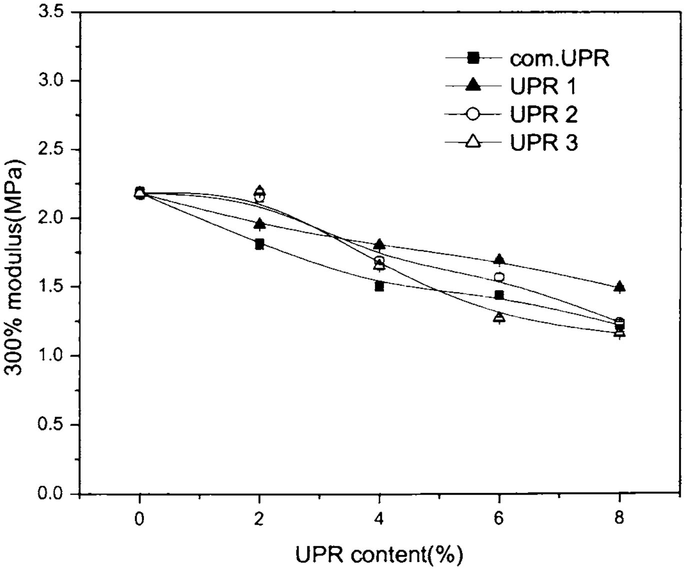


Fig. 5.12 Variation of 300% modulus with resin content

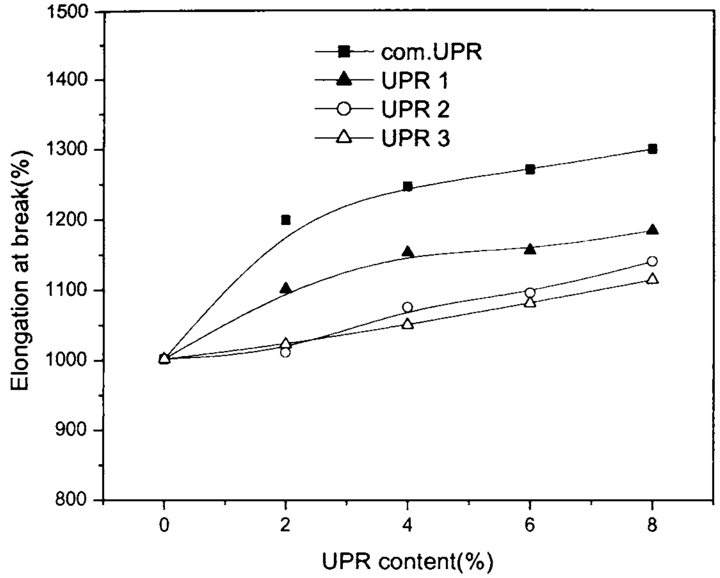


Fig.5.13 Variation of elongation at break with resin content

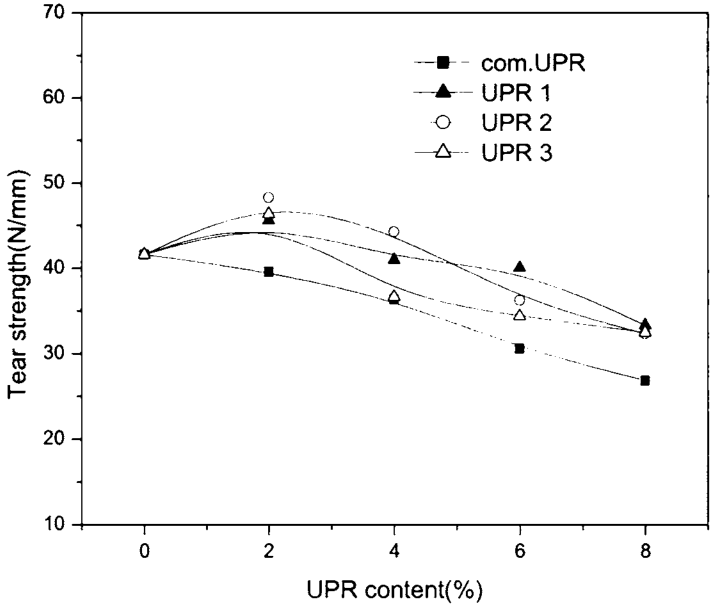


Fig.5.14 Variation of tear strength with resin content

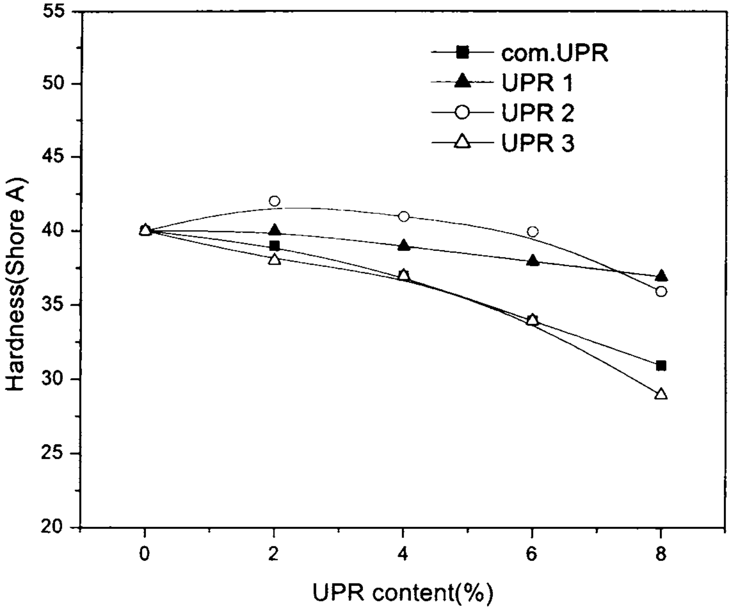


Fig.5.15 Variation of hardness with resin content

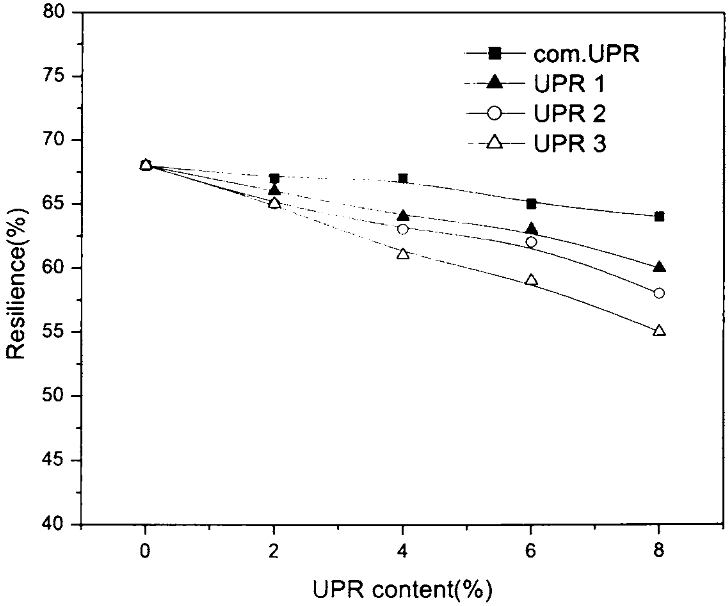


Fig. 5.16 Variation of resilience with resin content

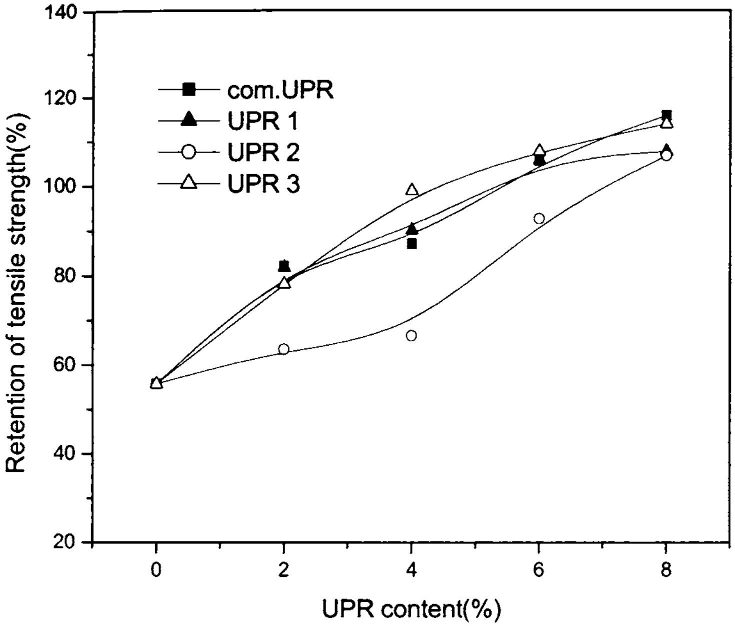


Fig.5.17 Variation of retention of tensile strength with resin content on ageing at 70°C for 72 hrs.

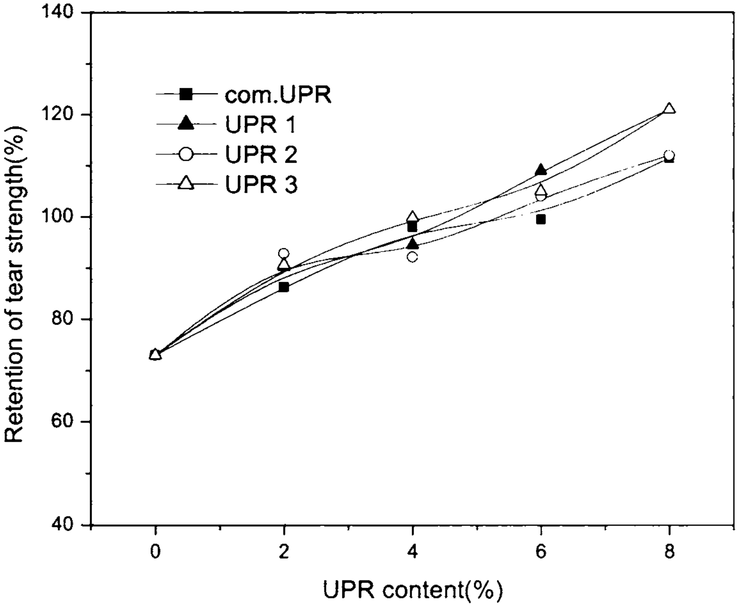


Fig.5.18 Variation of retention of tear strength with resin content on ageing at 70°C for 72 hrs

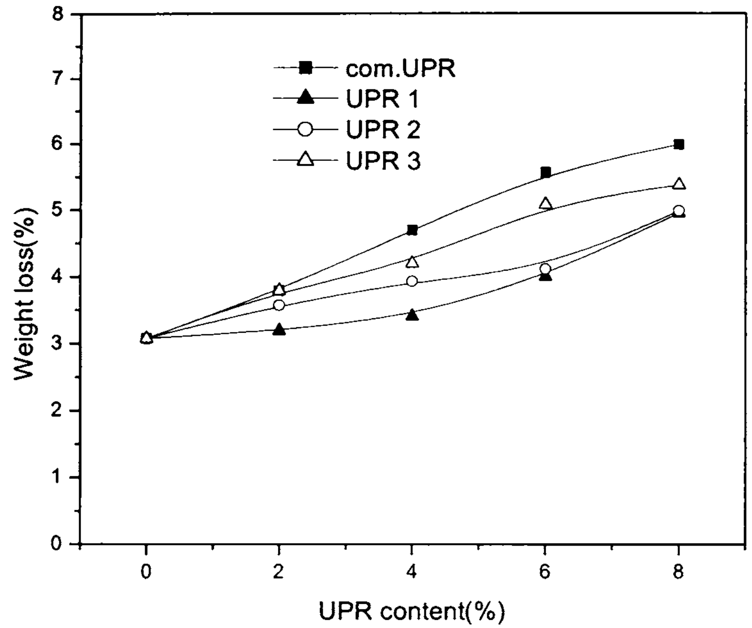


Fig.5.19 Variation of weight loss with resin content on Soxhlet extraction

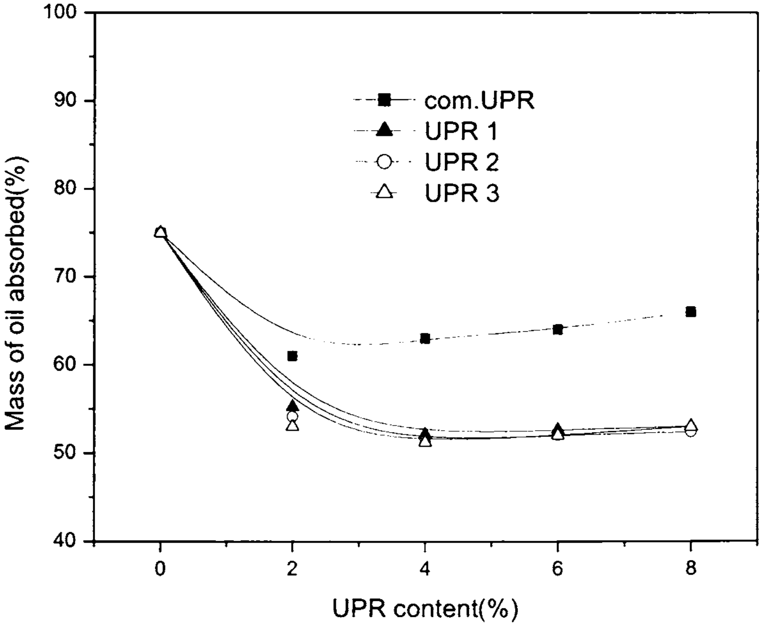


Fig.5.20 Variation of mass of oil absorbed with resin content

Fig.5.11 shows the variation of tensile strength with resin content. Until about 4% of the resin the tensile strength is more or less unchanged in most cases. Higher percentages of the resin show a negative effect on the tensile strength. Commercial UPR shows a slight superiority over the synthesized samples at 4%. A high MA:PA ratio is found to affect the tensile strength value negatively. This is evident from the position of the MA:PA = 90:10 curve. The presence of more and more unsaturation in the resin can lead to vulcanization and loss of curatives. This is a possible explanation. It is also possible that as more and more polystyrene crosslinks are established across polyester chains the crosslinking of rubber chains is inhibited, especially at higher resin concentrations and higher degree of unsaturation (higher MA content).

The effect on 300% modulus (Fig. 5.12) is more dramatic. The presence of the resin in increasing amounts causes a more rapid fall in modulus than tensile strength. This can also be explained in the light of the above arguments.

Elongation at break (Fig. 5.13) shows a gradual increase with increase in resin content. This can also be a consequence of the inhibiting effect of polystyrene crosslinks earlier discussed. A high MA content on the other hand does not permit high elongation because of extra crosslinks between polyester chains. Commercial UPR leads to higher elongation, a probable reason being a lower styrene content which leads to fewer numbers of crosslinks or shorter crosslinks between polyester chains.

Fig. 5.14 shows that tear strength falls on addition of polyester. Crystallinity is one factor that affects the tear strength directly [6]. The presence of polyester chains can prevent NR from attaining higher levels of crystallinity. The role of MA/PA ratio is not very clear in this case.

The effect of resin content on surface hardness is shown in Fig. 5.15. There is a gradual fall in surface hardness with increasing resin content. This can also be a consequence of reduced crosslinking between the rubber chains.

Resilience (Fig. 5.16) shows a gradual decrease on addition of the resin. The presence of the resin may be responsible for this. This can has a negative impact on heat build up in the rubber.

Fig. 5.17 shows an important positive effect of adding UPR to NR. The retention of tensile strength after ageing at 70°C for 72 hours shows an increasing trend as the resin content goes up. At 0% resin content the percentage retention of tensile strength is only 55% of the original value. The addition of UPR dramatically increases this value to the original tensile strength at 8% resin content. The thermal degradation of natural rubber on the continued action of heat has been arrested to some extent by this modification. There can be several possible explanations for this: (1) Free radical formation which is part of the degradation process has been reduced (2) Polyester network which has better thermal stability is supporting the rubber matrix under stress (3) More crosslinks have been established between the two components or even within the same component on ageing (4) The ageing process may take to completion any incomplete crosslinking reaction especially in the case of the resin.

Fig. 5.18 shows the effect of ageing at 70°C for 72 hours on tear strength. Here also there is a steady increase in the value on addition of resin. The increase in tear strength may be the result of additional crosslinks formed either as a part of the original crosslinking reaction or new crosslinks formed between the two components.

Fig 5.19 is a plot of the weight loss suffered by NR containing different amounts of resin on extraction with acetone. The weight loss on extraction shows an increasing tendency with increasing resin content. This can be attributed to the presence of uncrosslinked polyester chains likely to be present in the blend. A post curing operation (as happens during ageing) may complete the crosslinking of the resin.

Fig 5.20 gives the variation of the mass of oil absorbed by NR as the resin content goes up. The rubber was immersed in oil for three days and the change in weight was observed. There is substantial reduction in the mass of oil absorbed when 2% resin is added. Beyond this concentration there is not much change in the weight of oil absorbed. It is possible that as higher amounts of resin are added there is no proportional increase in crosslinking between the resin chains or between resin and rubber chains.

c) Effect of commercial UPR on the properties of filled NR

Cure characteristics are shown in Table 5.4. In silica filled and HAF black filled NR, cure time increases with UPR content (Fig. 5.21).

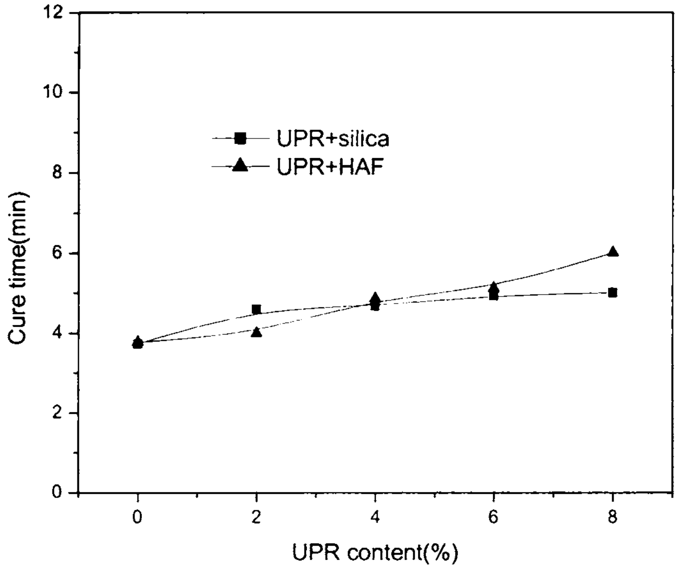


Fig.5.21 Variation of cure time with resin content

Table 5.4 Cure characteristics of filled NR vulcanizate with UPR

Resin content (%)		Scorch time(min)	Cure time (min)	Maximum Torque(dNm)	Cure rate index (min^{-1})
Silica filled	0	1.73	3.73	2.74	50
	2	2.09	4.60	2.84	39.84
	4	2.33	4.68	2.84	42.55
	6	2.51	4.94	2.59	41.15
	8	2.47	5.01	2.56	39.37
HAF filled	0	1.67	3.77	4.26	47.6
	2	1.78	3.99	4.35	45.25
	4	2.02	4.86	4.27	35.21
	6	2.45	5.12	4.21	37.45
	8	2.56	6.01	3.98	28.98

Figures 5.22 to 5.26 show the variation of tensile strength, 300% modulus, elongation at break, tear strength and surface hardness in the case of each of silica filled and HAF black filled rubber vulcanizates on addition of different amounts of UPR. In general HAF black filled compounds show better properties in conformity with the known fact that carbon black is a better reinforcement than silica for NR. The effect of increasing amounts of UPR is not very noticeable although 300% modulus and tear strength increase in value upto 4% of resin.

In the case of tear strength the percentage increase on addition of 4% resin is about 20% for black filled compound. Silica filled compounds show less sensitivity to resin content with the exception of tensile strength which shows a decreasing tendency on addition of more and more resin. Hence filled compounds are less influenced by the resin than gum compounds. The surface activity of the filler particle can possibly account for this. The surface absorption of the resin or its curatives by the filler material cannot be ruled out.

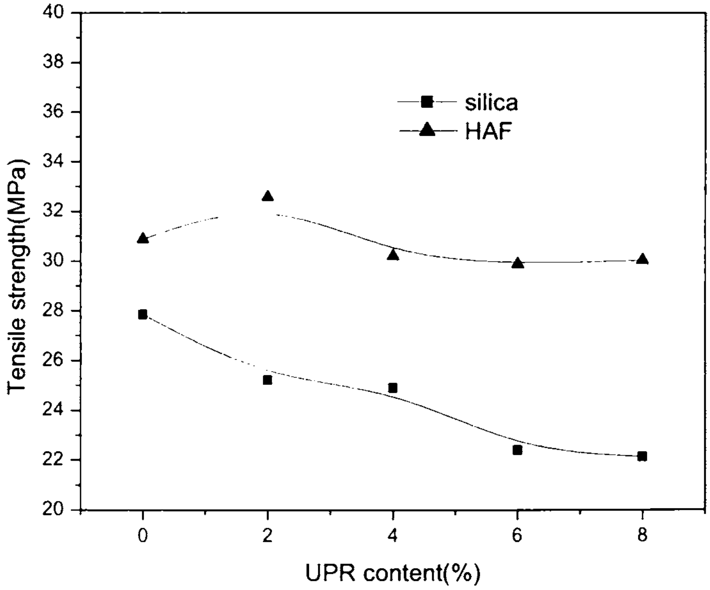


Fig.5.22 Variation of tensile strength with resin content

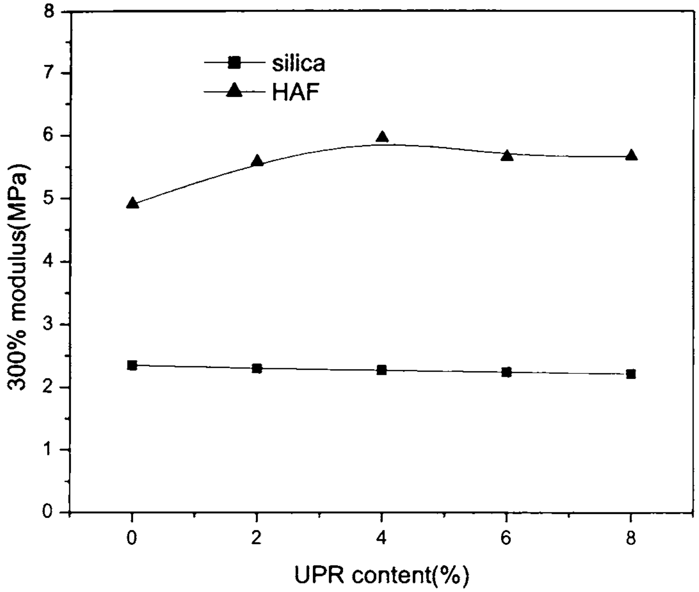


Fig.5.23 Variation of 300% modulus with resin content

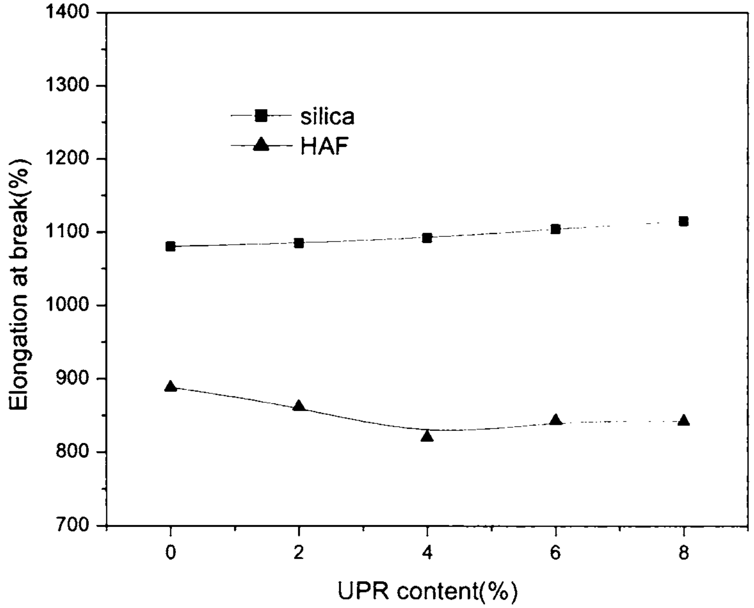


Fig.5.24 Variation of elongation at break with resin content

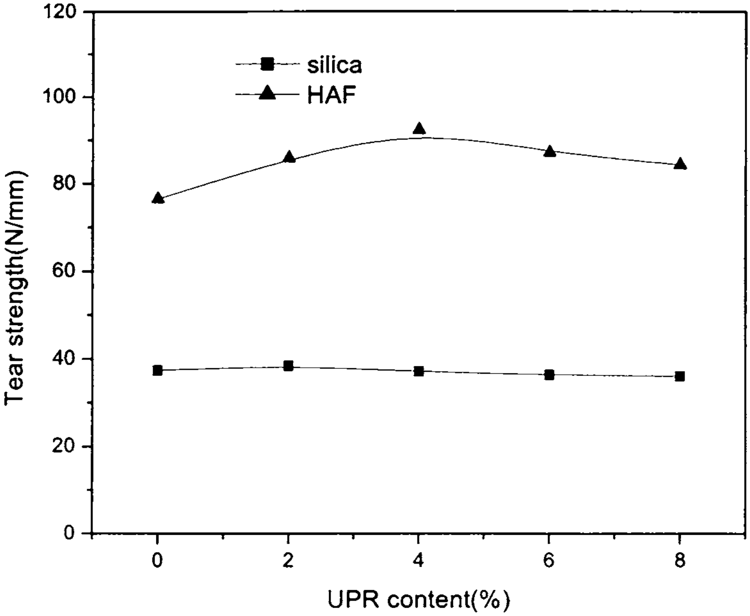


Fig. 5.25 Variation of tear strength with resin content

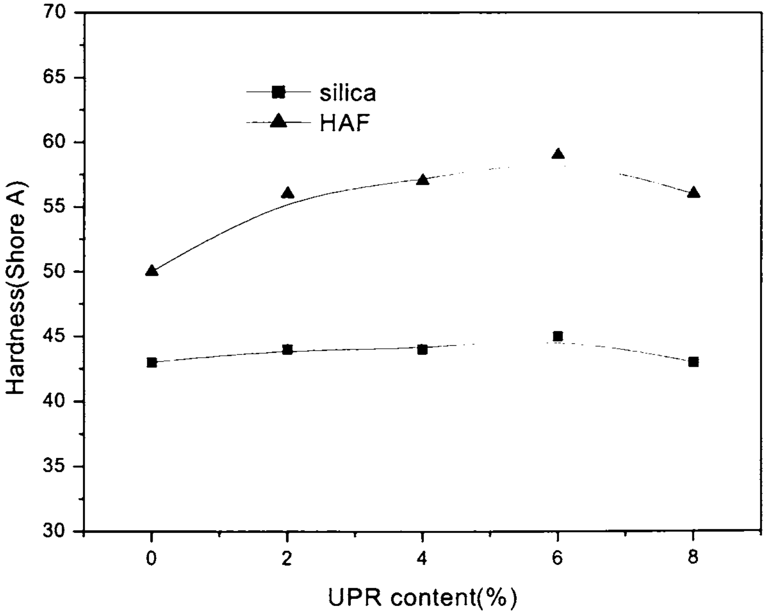


Fig.5.26 Variation of hardness with resin content

Fig.5.27 shows the effect of the resin on the mass of oil absorbed by filled NR. There is a slight reduction in oil absorption.

Fig.5.28 shows the retention of tensile strength with resin content after ageing at 70°C for 72 hours. The loss of tensile strength is moderate in filled compounds even in the absence of UPR. The retention of tensile strength shows a slight increase on addition of more of resin.

Fig.5.29 shows the effect of resin content on tear strength after ageing of filled NR. The increase in retention of tear strength with resin content is very much noticeable. Since the presence of resin is not conducive to increased crystallinity some other phenomenon is responsible for this. It is possible that the resin molecule (or crosslinked particles) might be acting as crack stoppers after initiation of the crack. The ageing process can lead to complete curing of the resin which cannot be taken for granted in the case of the unaged materials.

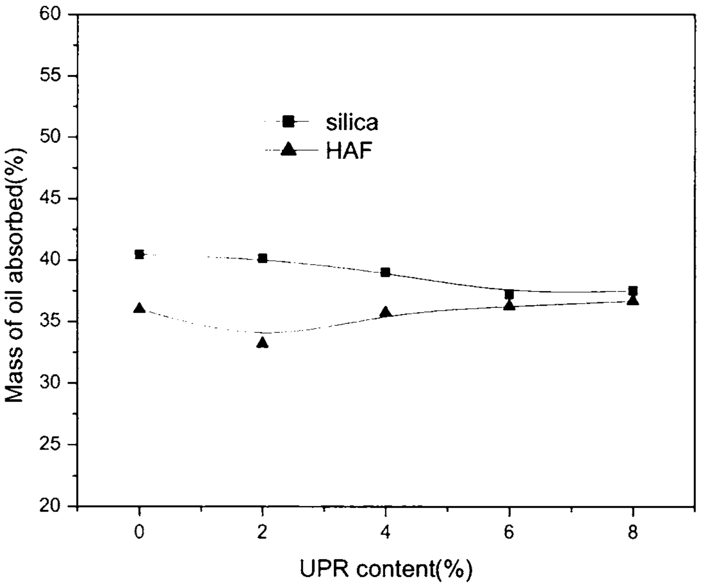


Fig.5.27 Variation of mass of oil absorbed with resin content

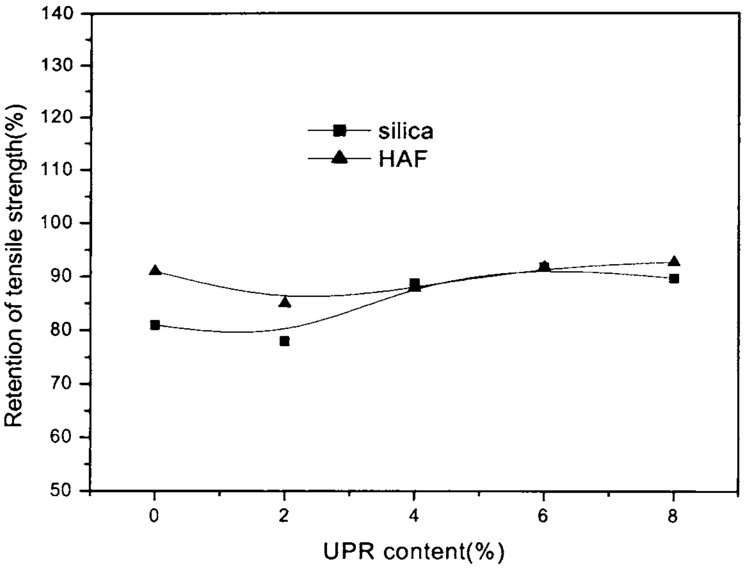


Fig.5.28 Retention of tensile strength on ageing at 70°C for 72 hrs

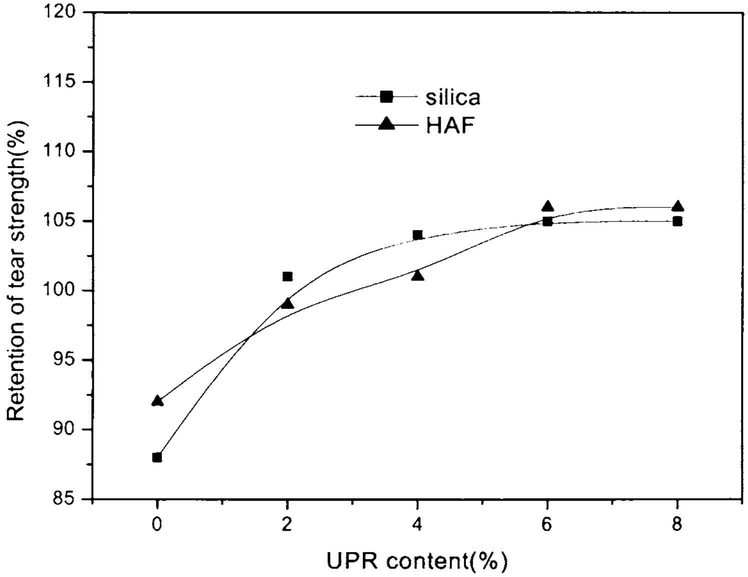


Fig.5.29 Retention of tear strength on ageing at 70°C for 72 hrs

d) Effect of IUPR on the properties of gum and filled NR vulcanizate

Cure characteristics are shown in Table 5.5. Fig.5.30 shows the variation of cure time with IUPR content. Cure time increases with resin content. This indicates that IUPR also does not activate the curing reaction.

Table 5.5 Cure characteristics of NR vulcanizate containing IUPR

Resin content (%)		Scorch time(min)	Cure time (min)	Maximum Torque(dNm)	Cure rate index (min^{-1})
Gum	0	2.62	5.62	2.69	33.33
	2	2.59	5.56	2.49	33.67
	4	2.87	5.51	2.37	37.88
	6	2.96	5.72	2.28	36.23
	8	3.13	6.39	2.12	30.67
Silica filled	0	1.73	3.73	2.74	50
	2	2.02	4.21	2.70	45.66
	4	2.16	4.69	2.54	39.53
	6	2.0	4.57	2.39	38.91
	8	2.05	5.22	2.31	31.54
HAF filled	0	1.67	3.77	4.62	47.6
	2	1.98	3.92	4.34	51.55
	4	2.32	4.56	4.19	44.64
	6	2.54	4.96	4.08	41.32
	8	2.64	6.36	3.98	26.88

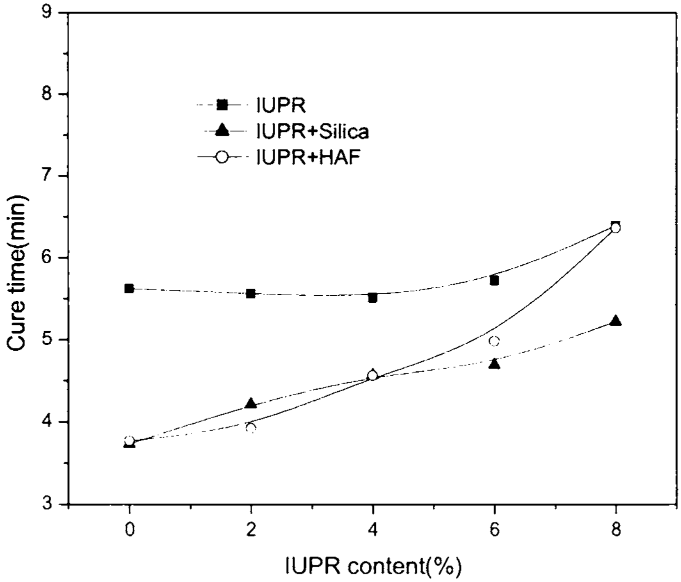


Fig.5.30 Variation of cure time with resin content

Fig.5.31 shows the variation of tensile strength of gum and filled NR when various amounts of IUPR are added. Only a small increase in tensile strength is noticed on addition of resin. A similar trend is noticed in the case of 300% modulus, elongation at break, tear strength and surface hardness (Figs.5.32 to 5.35). A total lack of chemical interaction between the resin and rubber and the adsorption effects of the filler on the resin are possible reasons for this.

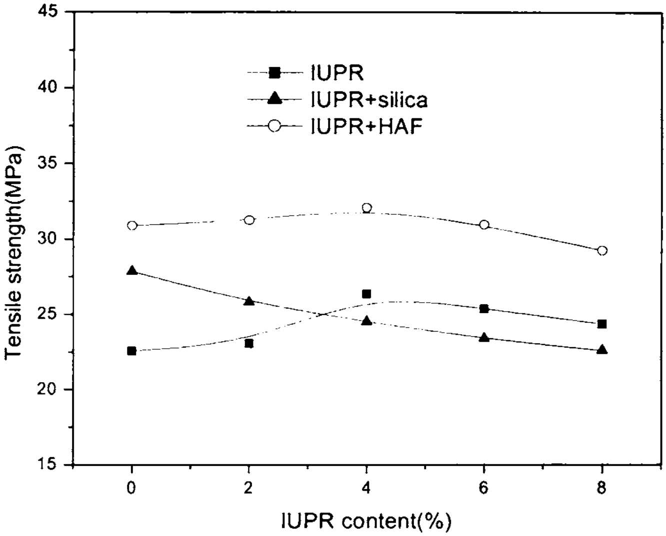


Fig.5.31 Variation of tensile strength with resin content

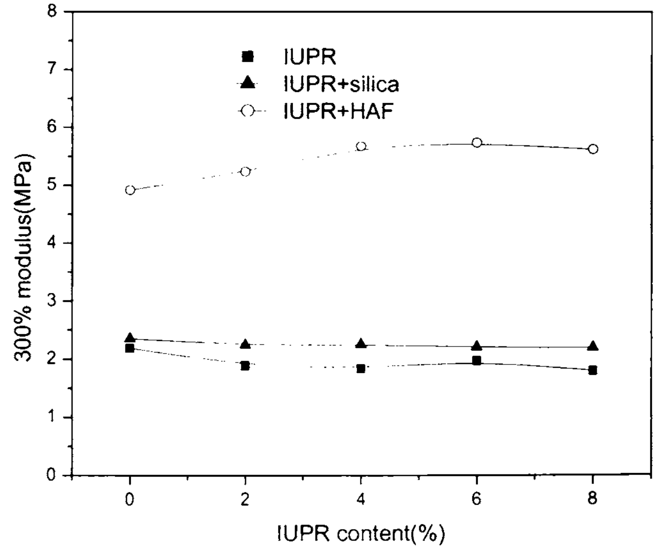


Fig.5.32 Variation of 300% modulus with resin content

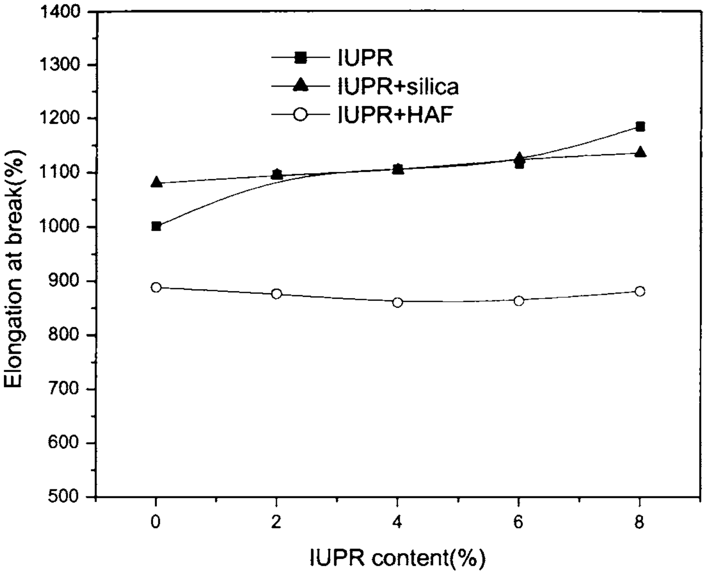


Fig.5.33 Variation of elongation at break with resin content

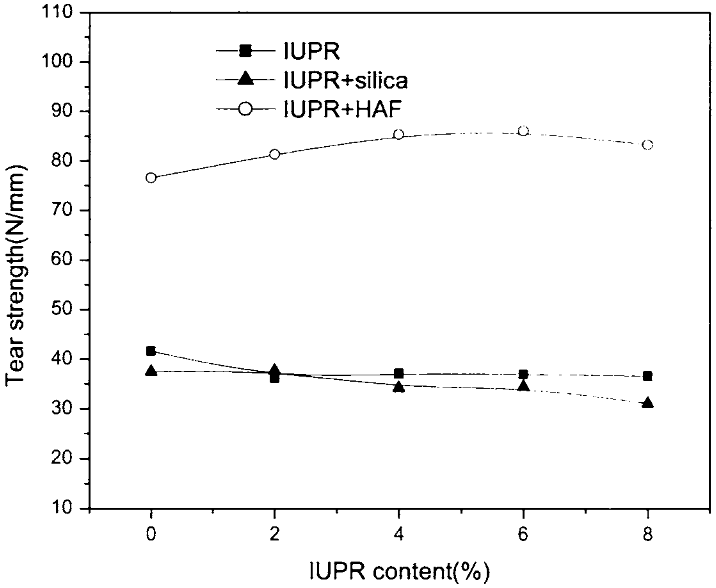


Fig.5.34 Variation of tear strength with resin content

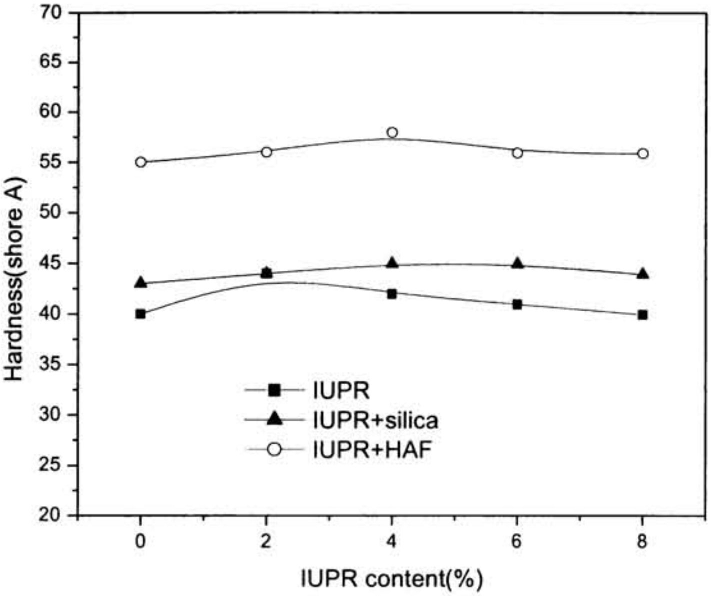


Fig.5.35 Variation of hardness with resin content

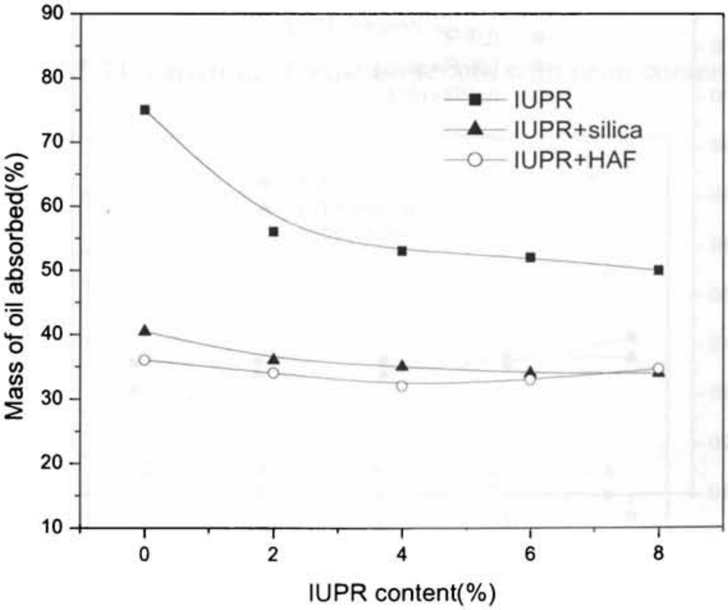
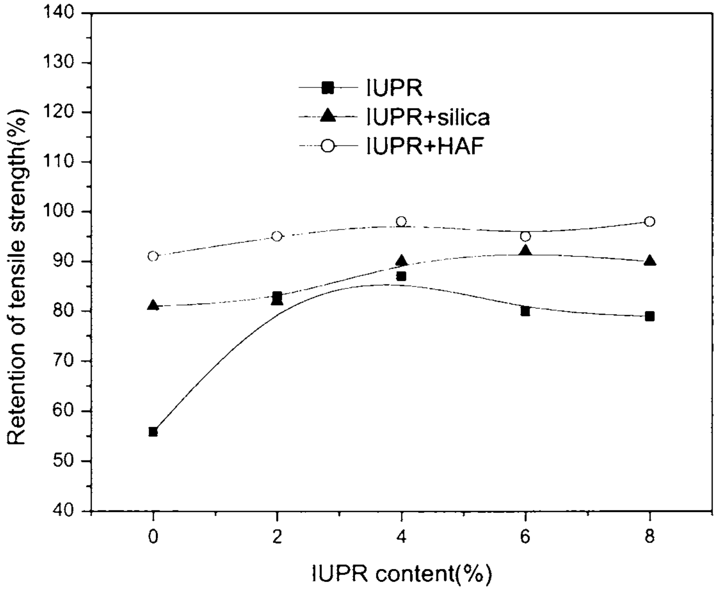


Fig. 5.34 Variation of mass of oil absorbed with resin content

The mass of oil absorbed falls steeply (Fig. 5.36) with resin content in the case of gum rubber mixed with IUPR. This is similar to the behavior of UPR. The presence of the resin probably acts as a polar barrier for absorption of the oil by the rubber. The presence of the filler particles on the other hand apparently interferes with this process. Hence the lack of sensitivity to resin content in the case of silica and HAF filled compounds.

Fig.5.37 shows the variation of retention of tensile strength with resin content on ageing at 70°C for 72 hours. As in the case of UPR only the gum compound benefits from the addition of IUPR. At 4% resin content the increase in retention of tensile strength is about 80% over samples containing no resin. Filled compounds on the other hand are not much affected by the resin content.

As in the case of UPR there is a general increase in retention of tear strength on ageing on addition of IUPR (Fig.5.38). This effect is more noticeable in gum compounds where at 6% resin the increase in retention of tear strength is about 40-45%.



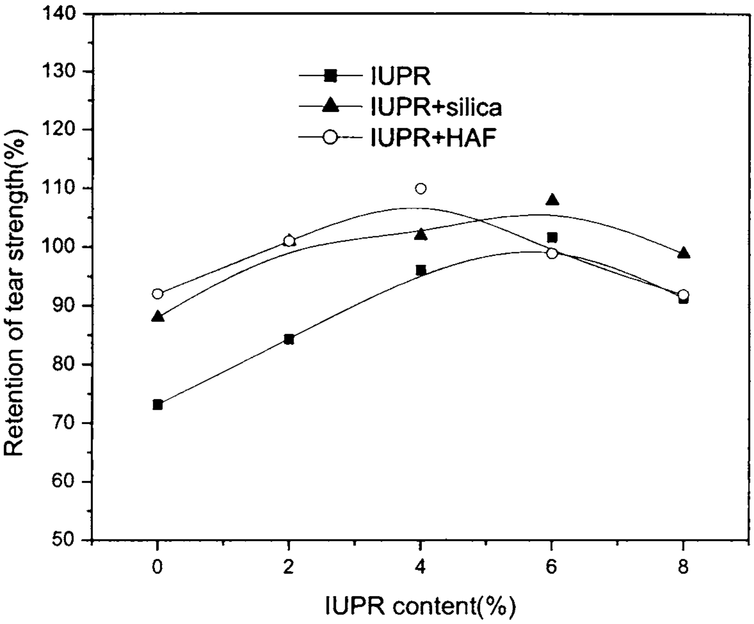


Fig.5.38 Retention of tear strength on ageing at 70°C for 72 hrs

Fig.5.39, 5.40 and 5.41 show the thermograms of samples of NR, NR+UPR, and NR+IUPR respectively. The onset point of degradation is slightly higher for NR modified with UPR and IUPR. The residue content is also slightly higher. The thermal data are given in Table 5.7 and 5.8. Thermal stability of the modified compounds is comparable to the unmodified sample. Thermal stability is not affected by changing the MA/PA ratio.

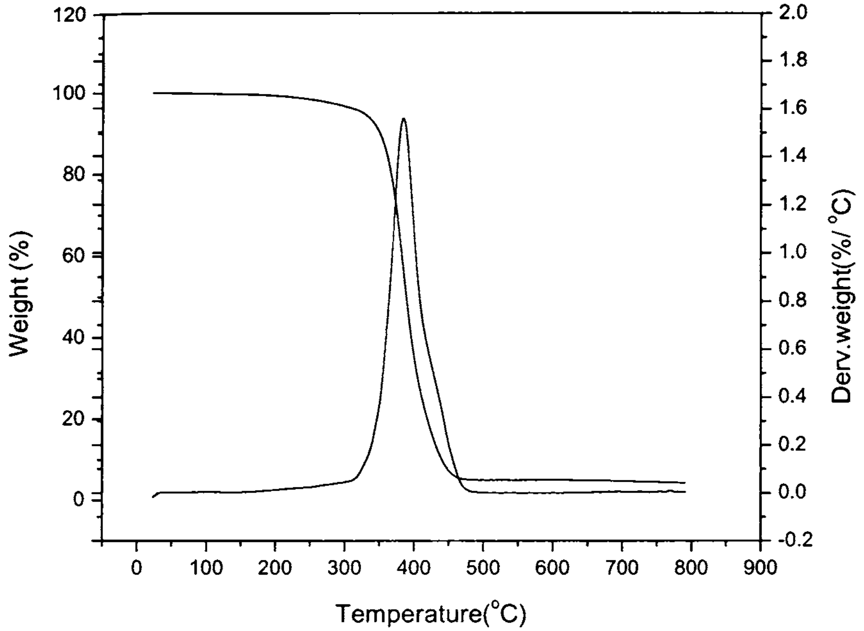


Fig.5.39 Thermogram of NR vulcanizate

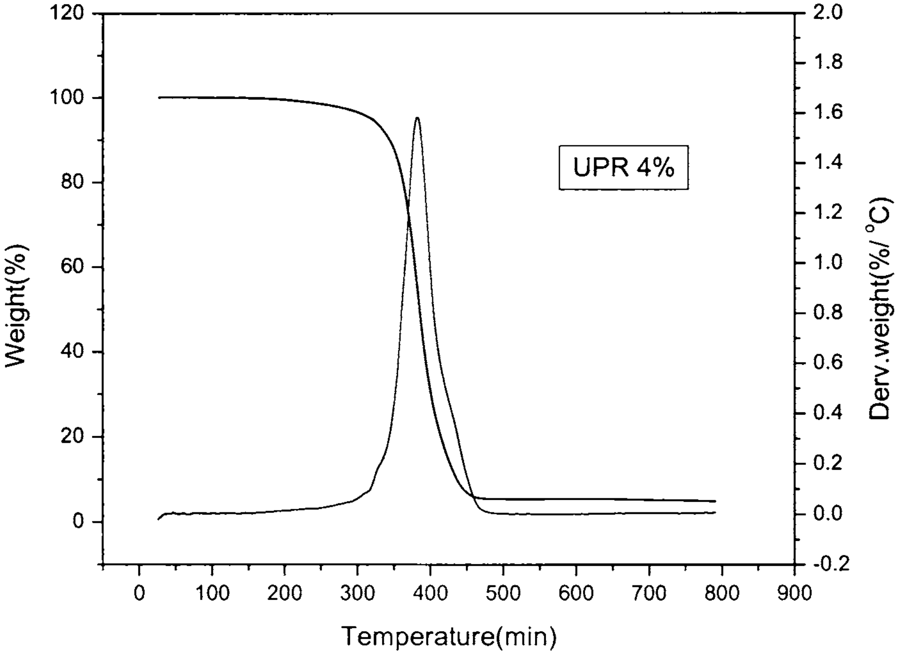


Fig.5.40 Thermogram of 4%UPR loaded NR vulcanizate

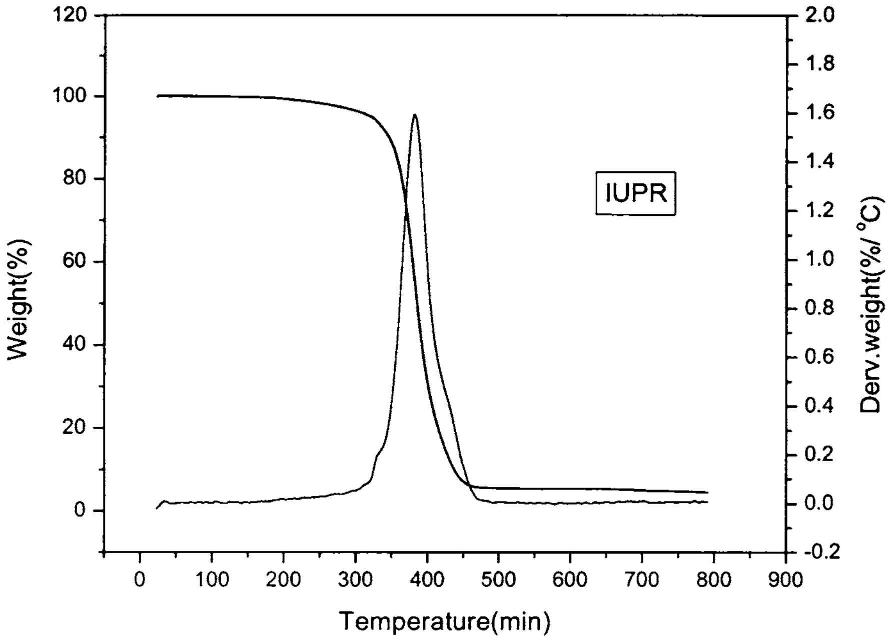


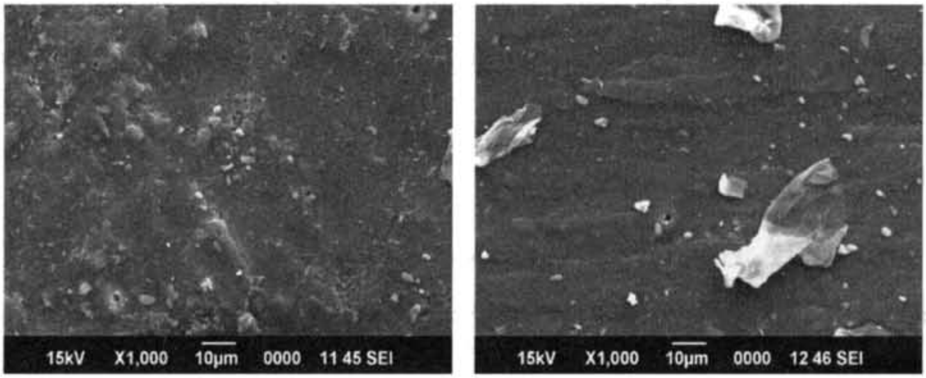
Fig.5.41 Thermogram of 4%IUPR loaded NR vulcanizate

Table 5.7 Thermal data of vulcanized NR with and without resin

Property	**NR**	**NR+4% UPR**	**NR+4%IUPR**
Onset of degradation (°C)	312.72	317.47	317.53
Temperature of 50% degradation (°C)	388.99	385	385.17
Maximum degradation temperature (°C)	384.23	382.37	381.68
Maximum rate of degradation (%/ °C)	1.556	1.583	1.586
Residue (%)	4.297	4.811	4.492

Table 5.8 Thermal data of vulcanized NR with 4% of synthesized UPR

Property	NR+UPR 1	NR+UPR 2	NR+UPR 3
Onset of degradation (°C)	293.94	300.47	301.62
Temperature of 50% degradation (°C)	391.32	391.54	391.15
Maximum degradation temperature (°C)	388.12	387.08	387.98
Maximum rate of degradation (%/ °C)	1.567	1.553	1.528
Residue (%)	5.09	5.21	5.497



(a) (b)

Fig. 5.42 SEM micrographs (a) NR (b) NR+UPR 4%

Fig.5.42 shows the micrographs of gum NR and NR modified by commercial UPR respectively. The dispersion of the resin is not very uniform. This can be judged from the size of the resin particles.The short gel time of the resin after addition of catalyst and accelerator is partly responsible for this. Because the improvement in mechanical properties of the rubber is very modest it is likely that most of the UPR remains distributed as discrete particle without much chemical interaction with the rubber chains.

5.4 Conclusion

The properties of the modified rubber are somewhat negatively influenced by the extent of unsaturation in the UPR. Only a moderate improvement in tensile

strength is obtained on addition of UPR to NR at the optimal concentration of 4%. The tensile strength is more or less unchanged in most cases. Commercial UPR shows a slight superiority over the synthesized samples at 4%. A high MA:PA ratio is found to affect the tensile strength value negatively. The retention of tensile and tear strength after ageing at 70°C for 72 hours shows an increasing trend as the resin content goes up. Not much improvement in tensile strength is noticed on addition of IUPR resin Some improvement in ageing resistance is noticeable. The presence of fillers blunts the effect of the resin for most properties.

The addition of the resin (both UPR and IUPR) leads to reduced oil absorption in all cases, filled and unfilled. Hence UPR modification has improved the oil resistance of NR.

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Chapter

6

SUMMARY AND CONCLUSION

Summary and conclusion

Properties of gum NR and filled NR modified by various thermoset resins are summarized in Table 6.1 and 6.2 respectively.

Table 6.1 Summary of properties gum NR modified by various thermoset resins

Maximum improvement achieved (%) / resin content (%)									
Property	**Epoxy resin**		**Phenolic novolacs**		**Epoxidised phenolics**			**Unsaturated Polyester resin**	
	EPR	**EC**	**Novolac**	**CN**	**EPN**	**EPCN**	**ECN**	**UPR**	**IUPR**
Cure time(min)	-60/2	-67/4	27/4 (0.5)	-30/8 (0.9)	-61/4 (0.5)	-66/4 (0.5)	-68/8 (0.5)	23/4	-2/4
Tensile strength(MPa)	23/3	26/4	47/4 (0.5)	44/6 (0.7)	37/4 (0.5)	21/4 (0.7)	35/6 (0.9)	13/4	16/4
Modulus (MPa)	25/2	25/4	12/4 (0.9)	10/8 (0.5)	9/4 (0.5)	16/6 (0.5)	17/8 (0.9)	-31/4	-2/4
EB(%)	11/4 (com)	-4/4	7/4 (0.5)	5/6 (0.7)	-	-14/4 (0.5)	5/6 (0.9)	24/4	10/4
Tear strength (N/mm^2)	23/2	34/4	29/8 (com.)	10/8 (0.9)	29/4 (0.5)	32/8 (0.5)	19/6 (0.9)	-12/4	-10/4
Hardness (ShoreA)	15/3	17/4	30/6 (0.5)	20/8 (0.5)	17/4 (0.7)	22/6 (0.5)	25/8 (0.9)	-7/4	5/4
Retention of tensile strength(%)	61/4 (com)	14/8	54/8 (0.5)	42/8 (0.7)	59/8 (0.7)	50/8 (0.9)	39/8 (0.7)	61/8	32/4
Retention of tear strength(%)	38/4	13/8	70/6 (0.5)	34/8 (0.5)	55/8 (0.7)	39/8 (0.5)	34/8 (0.7)	38/8	28/6
Oil absorption(%)	23/2	27/4	26/8 (com)	-	-29/4 (0.5)	-27/6 (0.5)	-21/6 (0.9)	-12/4	-25/8
Crosslink density	13/2		9/6 (com)	-	25/4 (0.5)	13/4 (0.5)	-	-	-

Table 6.2 Summary of properties filled NR modified by various thermoset resins

Maximum improvement achieved (%) / resin content (%)											
Property	EPR	Novolac		EPN 0.5		ECN 0.5		UPR com.		IUPR com.	
	HAF	Silica	HAF	Silica	HAF	Silica	HAF	Silica	HAF	Silica	HAF
Cure time (min)	-35/2	77/8 (0.9)	78/8 (0.9)	-35/8	-38/4	-41/6	-46/4	25/4	28/4	22/4	21/4
Tensile strength (MPa)	3/2	1/6 (0.5)	5/4 (0.5)	9/6	0/8	17/4 (0.5)	4/6 (0.5)	-10/4	5/2	-12/4	4/4
Modulus (MPa)	15/2	14/6 (0.9)	39/8 (0.9)	10/4	17/4	24/8	39/8	-3/4	21/4	-4/4	16/4
EB(%)	-8/2	-10/6 (0.5)	5/2 (0.5)	1/8	7/8	-5/6	-8/6	1/4	-5/4	2/4	-3/4
Tear strength (N/mm^2)	20/2	37/4 (0.5)	21/4 (0.7)	24/4	16/4	56/8	27/8	3/2	20/4	-8/4	11/4
Hardness (ShoreA)	10/2	16/4 (0.5)	14/8 (0.9)	9/6	9/6	21/8	11/8	4/6	8/6	4/4	1/4
Retention of tensile strength(%)		28/6 (0.9)	20/6 (0.9)	22/6	16/8	10/8	8/6	11/6	2/8	11/6	7/8
Retention of tear strength(%)		28/6 (0.9)	17/8 (0.9)	62/8	19/8	11/8	6/8	17/6	14/6	20/6	18/4
Oil absorption(%)		-3/6 (0.9)	-3/4 (0.9)	-8/8	-9/4	3/8	-1/8	-8/6	-3/2	-6/6	-4/6

Important conclusions resulting from this research work can be summarized as follows.

Epoxy resin

- There is a sharp reduction in cure time of gum NR on addition of epoxy resins at low concentrations (less than 6%). Epoxidised cardanol is outstanding in this respect.
- Tensile strength, Young's modulus and tear strength of epoxy modified NR show improvement upto 25 to 34% on addition of DGEBA or epoxidised cardanol.
- Retention of mechanical properties (≈ 61% of tensile strength) on thermal ageing is more impressive in the case of DGBA. In this respect epoxidised cardanol show only moderate improvement.
- Oil absorption is reduced by 23 to 27% on addition of epoxy resins.
- In the case of HAF black filled NR modified by DGEBA moderate improvement in modulus and tear strength is achieved (15 and 20%).
- The cure time of HAF black filled NR modified by DGEBA is only moderately affected by the presence of the resin.
- The extractability of DGEBA added to NR gum compounds is very low.

Phenolic novolacs

- The effect of addition of phenolic novolacs into NR gum is concentration dependent and limited to a narrow range. But in the case of cardanol novolac there is a steady reduction in cure time.
- In the case of gum NR modified by novolacs there is considerable improvement in tensile strength and surface hardness. The tensile strength improvement is maximum in the case of phenolic novolac (47%).

- The improvement in retention of tensile strength and tear strength is excellent in the case of gum NR modified by phenolic novolac. In the case of cardanol novolac also this effect is noticed.
- In the case of HAF and silica filled NR noticeable improvement is obtained for Youngs modulus and tear strength.

Epoxidised novolacs

- In the case of epoxidised novolacs there is a general reduction in cure time on addition of the resin. This effect is maximum in the case of ECN where the cure time falls from 5.56 to 1.86 minutes for gum NR. All epoxidised novolacs reduce the cure time for both filled and unfilled compounds.
- Tensile strength and tear strength are positively influenced by the presence of epoxidised novolacs in the case of gum NR. Epoxidised phenolic novolac shows maximum effect in this respect.
- Retention of tensile strength on ageing is also good, especially in the case of epoxidised phenolic novolac (53-58% improvement).
- In the case of filled compounds silica reinforcement shows better results in the presence of epoxidised phenolic novolacs when tear strength and retention of tear strength are considered. The tensile strength of ECN modified silica filled NR shows a dramatic increase on addition of ECN.
- Modest increase in oil resistance is noticed on addition of epoxidised novolacs.

Unsaturated polyester resin

- A cure system consisting of benzoyl peroxide and dimethylamine was found to be most suitable for incorporation of UPR in NR.
- The addition of UPR is found to increase the cure time of NR compounds.

- A modest increase in tensile strength is noticed on addition of UPR or IUPR although the presence of fillers reduces this effect.
- In the case of gum NR modified by UPR and IUPR, retention of tensile strength and tear strength on ageing is excellent.

In the case of epoxy compounds including epoxy novolacs there is the possibility of chemical interaction between epoxy ring and the accelerator leading to acceleration of cure.

Cardanol based resins in general tend to speed up the cure by virtue of the long side chain which has an entangling effect and also offers the possibility of sulphur vulcanization.

Addition of various thermoset resins improves the thermal properties as evidenced by retention of mechanical properties. This effect is more noticeable in gum compounds. In this respect epoxy resins show the best results.

The presence of thermoset resin has improved the oil resistance of NR. In this respect also epoxy resins show maximum improvement.

Future outlook

- The effect of thermoset resins on filled compounds is somewhat subdued. Underlying reasons for this can be investigated.
- The mechanism by which the tensile strength of silica filled compounds has become enhanced by epoxy resins can be studied.
- The reduction of cure time holds promise for reduction of the moulding cycles. Studies have to be made to commercially employ this result.

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ACM	Acrylic Rubber
ACR	Acrylic Rubber
ASTM	American Society of Testing and Materials
BR	Butadiene rubber
CBS	N-cyclohexyl-2-benzothiazylsulfenamide
cm	Centimeter
CN	Cardanol-formaldehyde novolac
CNSL	Cashew nut shell liquid
CR	Chloroprene rubber
CRI	Cure rate index
DEG	Diethylene glycol
DGEBA	Diglycidyl ether of bisphenol A
DSC	Differential scanning calorimetry
DTG	Differential thermogravimetric analysis
E_a	Activation energy
EB	Elongation-at-break
EC	Epoxy cardanol
ECN	Epoxidised cardanol novolac
EPDM	Ethylene propylene diene rubber
EPN	Epoxidised phenolic novolac
EPCN	Epoxy para cresol novolac
EPR	Epoxy resin
F:P	Formaldehyde: Phenol
FTIR	Fourier Transform infrared
g	Gram
GP	General purpose
GPC	Gel permeation chromatography
HAF	High Abrasion Furnace Black
hrs.	Hours
HMP	Hydroxymethylated phenol
HMTA	Hexamethylenetetramine
IIR	Isobutylene isoprene rubber
kg	Kilogram

L.R.	Laboratory reagent
m	meter
MA	Maleic anhydride
MF	Melamine- formaldehyde
min	Minutes
ml	Millilitre
$\overline{M}_n$	Number average molecular weight.
mol	Mole
$\overline{M}_w$	Weight average molecular weight
MEKP	Methyl ethyl ketone peroxide
mm	Millimeter
MP	Melting point
MPa	Mega Pascal
MW	Molecualr weight
N	Newton
NBR	Acrylonitrile-butadiene rubber (nitrile rubber)
nm	Nanometre
NMR	Nuclear magnetic resonance
NR	Natural rubber
PA	Phthalic anhydride
PF	Phenol formaldehyde
phr	Per hundred rubber
PMMA	Polymethyl methacrylate
PU	Polyurethane
RH	Rubber hydrocarbon
rpm	Revolutions per minute
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
T_g	Glass transition temperature
TMT	Tetramethyl thiuram monosulphide
TMTD	Tetra methyl thiuram disulphide
UPR	Unsaturated polyester resin
UTM	Universal Testing Machine
wpe	Weight per epoxy

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