Chapter 2

MODIFICATION OF NATURAL RUBBER USING EXPOXY RESIN

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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=114-118°C) 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.

![Structure of cardanol](image)

**Fig.2.1 Structure of cardanol**

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

- $n=0$, \((\text{CH}_2)_7(\text{CH}_2)_2\text{CH}_3\)
- $n=2$, \((\text{CH}_2)_7\text{CH} = \text{CH} (\text{CH}_2)_5\text{CH}_3\)
- $n=4$, \((\text{CH}_2)_7\text{CH} = \text{CH} - \text{CH}_2 - \text{CH} = \text{CH} (\text{CH}_2)_2\text{CH}_3\)
- $n=6$, \((\text{CH}_2)_7\text{CH} = \text{CH} - \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH} = \text{CH}_2\)

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.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mooney viscosity ML(1+4) at 100°C</td>
<td>82</td>
</tr>
<tr>
<td>Dirt content, % by mass, max</td>
<td>0.05</td>
</tr>
<tr>
<td>Volatile matter, % by mass, max</td>
<td>1</td>
</tr>
<tr>
<td>Nitrogen, % by mass, max</td>
<td>0.07</td>
</tr>
<tr>
<td>Ash, % by mass, max</td>
<td>0.60</td>
</tr>
<tr>
<td>Initial plasticity, min</td>
<td>30</td>
</tr>
<tr>
<td>Plasticity retention index</td>
<td>60</td>
</tr>
</tbody>
</table>
**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: 85-210
- 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 thiurum 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

**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 (2 moles) 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 (1 mole) was dissolved in a mixture of an excess of epichlorohydrin (2 moles) 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.

\[
\text{Fig. 2.2 Epoxidation of cardanol}
\]

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>NR (phr)</th>
<th>Resin (%)</th>
<th>ZnO (phr)</th>
<th>St.acid (phr)</th>
<th>MBTS (phr)</th>
<th>TMT (phr)</th>
<th>S (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>0</td>
<td>4</td>
<td>2</td>
<td>0.8</td>
<td>0.2</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>1</td>
<td>4</td>
<td>2</td>
<td>0.8</td>
<td>0.2</td>
<td>2.5</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>0.8</td>
<td>0.2</td>
<td>2.5</td>
</tr>
<tr>
<td>4</td>
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<td>3</td>
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<td>0.8</td>
<td>0.2</td>
<td>2.5</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>4</td>
<td>4</td>
<td>2</td>
<td>0.8</td>
<td>0.2</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 2.2 Formulation of HAF black filled NR samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>NR (phr)</th>
<th>Resin (phr)</th>
<th>ZnO (phr)</th>
<th>St.acid (phr)</th>
<th>HAF (phr)</th>
<th>Ar.oil (phr)</th>
<th>MBTS (phr)</th>
<th>TMT (phr)</th>
<th>S (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>0</td>
<td>4</td>
<td>2</td>
<td>30</td>
<td>3</td>
<td>0.8</td>
<td>0.2</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>1</td>
<td>4</td>
<td>2</td>
<td>30</td>
<td>3</td>
<td>0.8</td>
<td>0.2</td>
<td>2.5</td>
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<tr>
<td>3</td>
<td>100</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>30</td>
<td>3</td>
<td>0.8</td>
<td>0.2</td>
<td>2.5</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>3</td>
<td>4</td>
<td>2</td>
<td>30</td>
<td>3</td>
<td>0.8</td>
<td>0.2</td>
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<td>5</td>
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<td>3</td>
<td>0.8</td>
<td>0.2</td>
<td>2.5</td>
</tr>
</tbody>
</table>

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° 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,** $M_{II}$

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

$$0.9(M_{II}-M_1) + M_L ..................................................(2.1)$$

(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.

\[
\frac{M'_H - M'_L}{M'_H - M'_L} - 1 = \alpha \frac{m_{\text{filler}}}{m_{\text{rubber}}} \tag{2.3}
\]

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. \( m_{\text{filler}} \) and \( m_{\text{rubber}} \) 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

\[
\ln (a - x) = -kt + \ln a \tag{2.4}
\]

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.

\[
(a-x) = M'_H - M'_L \tag{2.5}
\]

\[
a = M'_H - M'_L \tag{2.6}
\]

\( M'_H \) and \( M'_L \) are the maximum and minimum torques, and \( M'_t \), the torque at time \( t \). So the equation becomes

\[
\ln (M'_H - M'_L) = -kt + \ln (M'_H - M'_L) \tag{2.7}
\]
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.

$$k = Ae^{-E_a RT} \quad \text{............................................................}(2.8)$$

$$\log k = \log A - \frac{E_a}{2.303RT} \quad \text{............................................................}(2.9)$$

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-l 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

\[
\text{Volume loss on abrasion} = \frac{\text{weight loss on abrasion}}{\text{specific gravity of the sample}}
\]

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.

\[
\text{Resilience} = \frac{R_h}{D_h} \times 100 \hspace{1cm} \text{(2.10)}
\]

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 vulcanize. 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,

\[
V_r = \frac{(D - FT) \rho_r^{-1}}{(D - FT) \rho_r^{-1} + A_i \rho_s^{-1}}, \hspace{1cm} \text{(2.11)}
\]

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.

\[
\rho_r = \text{density of rubber (g/cc)} \quad \rho_s = \text{density of the solvent}
\]

\( A_i \) = weight of the solvent absorbed (W-D)
Crosslink density is found out using Flory-Rehner equation

\[
CLD = \frac{-\ln(1 - V_r) + \chi V_r^2}{2 \rho_s V_s (V_r)^{\frac{1}{3}}} \tag{2.12}
\]

where \( V_s \) = molar volume of the solvent
\( \chi \) = 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.

(ii) 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: \( f(X) \):
\[ r = \frac{dX}{dt} = k(T)f(X) \]  (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 Arrhenius relationship:

\[ k(T) = A \exp\left(\frac{E_a}{RT}\right) \]  (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:

\[ f(X) = (1 - X)^n \]  (2.15)

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

\[ r = \frac{dW}{dt} = AW^n \exp\left(-\frac{E_a}{RT}\right) \]  (2.16)

\[ \ln r = \ln\left(-\frac{dW}{dt}\right) = \ln A + n\ln W - \frac{E_a}{RT} \]  (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 integral 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:

\[ \Delta \ln r = \Delta \ln \left(-\frac{dW}{dt}\right) = n \Delta \ln W - \frac{E_a}{R} \Delta (1/T) \]  (2.18)
Dividing 2.18 by $\Delta (1/T)$ gives

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

A plot of $[\Delta \ln r / \Delta (1/T)]$ against $[\Delta \ln W / \Delta (1/T)]$ 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 $\Delta \ln W$ gives

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

A plot of $[\Delta \ln r / \Delta \ln W]$ versus $[-\Delta (1/T) / R \Delta \ln W]$ should also be a 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 1 mg 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 1 mg. The percentage change in mass was calculated as follows:
Change in mass = \( \frac{M_2 - M_1}{M_1} \times 100 \) ...................................................... (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 gold 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 1231 cm\(^{-1}\) 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

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

Fig.2.5 Variation of cure time with resin content
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 vulcanize 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 up to 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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rate constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>0.2257</td>
</tr>
<tr>
<td>NR+ EPR 1%</td>
<td>1.1077</td>
</tr>
<tr>
<td>NR+ EPR 2%</td>
<td>1.5183</td>
</tr>
<tr>
<td>NR+ EPR 3%</td>
<td>1.0058</td>
</tr>
<tr>
<td>NR+ EPR 4%</td>
<td>0.1314</td>
</tr>
</tbody>
</table>

![Chart showing cure rate index and cure reaction constant of EPR modified samples.](image)

**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.

![Variation of tensile strength with resin content](image1)

**Fig.2.11** Variation of tensile strength with resin content

![Variation of 300% modulus with resin content](image2)

**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 up to 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.

![Graph of weight loss vs resin content](image)

**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 vulcanize 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
Chapter 2

Figure 2.24 Thermogram of synthesized EPR

Table 2.5. Characteristics of thermograms of NR vulcanizates

<table>
<thead>
<tr>
<th></th>
<th>NR</th>
<th>NR+com.EPR</th>
<th>NR+syn.EPR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Onset of degradation (°C)</td>
<td>312.72</td>
<td>313.98</td>
<td>315.49</td>
</tr>
<tr>
<td>Temperature at 50% degradation (°C)</td>
<td>388.99</td>
<td>385.76</td>
<td>393.37</td>
</tr>
<tr>
<td>Temperature at maximum degradation (°C)</td>
<td>384.23</td>
<td>380.76</td>
<td>387.63</td>
</tr>
<tr>
<td>Rate at maximum degradation (%/°C)</td>
<td>1.55</td>
<td>1.59</td>
<td>1.43</td>
</tr>
<tr>
<td>Residue (%)</td>
<td>4.29</td>
<td>4.49</td>
<td>4.99</td>
</tr>
</tbody>
</table>
Modification of natural rubber using epoxy resin

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation energy (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>206</td>
</tr>
<tr>
<td>NR+com.EPR</td>
<td>202</td>
</tr>
<tr>
<td>NR+syn.EPR</td>
<td>209</td>
</tr>
</tbody>
</table>

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), 1258.71 cm⁻¹ (symmetrical C-O str.) and 909.92 cm⁻¹ are characteristic of the epoxy group.
The WPE value of epoxy cardanol (EC) obtained by epoxidation of cardanol for nine hours was found to be 473.15. This corresponds to 2.12 eq/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

<table>
<thead>
<tr>
<th>Resin content (%)</th>
<th>Scorch time(min)</th>
<th>Cure time (min)</th>
<th>Maximum Torque(dNm)</th>
<th>Cure rate index (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.62</td>
<td>5.62</td>
<td>2.69</td>
<td>33.33</td>
</tr>
<tr>
<td>EC 2</td>
<td>1.54</td>
<td>2.88</td>
<td>3.04</td>
<td>74.62</td>
</tr>
<tr>
<td>4</td>
<td>0.78</td>
<td>1.81</td>
<td>3.09</td>
<td>97.08</td>
</tr>
<tr>
<td>6</td>
<td>0.61</td>
<td>1.89</td>
<td>2.86</td>
<td>84.74</td>
</tr>
<tr>
<td>8</td>
<td>0.48</td>
<td>2.07</td>
<td>2.50</td>
<td>62.89</td>
</tr>
</tbody>
</table>

Fig.2.30 Variation of cure time with resin content

Cure rate constants are determined from the slope of the plot of \( \ln(M_t-M_i) \) 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 $\ln (M_f - M_i)$ vs time of NR compound with 4% EC

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rate constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>0.2257</td>
</tr>
<tr>
<td>NR + EC 2%</td>
<td>1.4488</td>
</tr>
<tr>
<td>NR + EC 4%</td>
<td>1.8101</td>
</tr>
<tr>
<td>NR + EC 6%</td>
<td>1.2785</td>
</tr>
<tr>
<td>NR + EC 8%</td>
<td>1.086</td>
</tr>
</tbody>
</table>

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.

![Graph showing variation of weight loss on Soxhlet extraction](image)

**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.

![Graph showing the variation of retention of tensile strength on ageing at 70°C for 72 hrs.](image1)

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

![Graph showing the variation of retention of tear strength on ageing at 70°C for 72 hrs.](image2)

**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

<table>
<thead>
<tr>
<th></th>
<th>NR</th>
<th>NR+EC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Onset of degradation (°C)</td>
<td>312.72</td>
<td>308</td>
</tr>
<tr>
<td>Temperature at 50% degradation (°C)</td>
<td>388.99</td>
<td>393</td>
</tr>
<tr>
<td>Temperature at maximum degradation (°C)</td>
<td>384.23</td>
<td>387</td>
</tr>
<tr>
<td>Rate of degradation at maximum (%/°C)</td>
<td>1.55</td>
<td>1.43</td>
</tr>
<tr>
<td>Residue (%)</td>
<td>4.29</td>
<td>4.84</td>
</tr>
</tbody>
</table>

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 up to 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

<table>
<thead>
<tr>
<th>Resin content (%)</th>
<th>T₁₀ (min)</th>
<th>T₉₀ (min)</th>
<th>M₄ (dNm)</th>
<th>M₆ (dNm)</th>
<th>CRI (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR+HAF 0</td>
<td>1.67</td>
<td>3.77</td>
<td>0.066</td>
<td>4.26</td>
<td>47.60</td>
</tr>
<tr>
<td>2</td>
<td>0.92</td>
<td>2.54</td>
<td>0.071</td>
<td>4.67</td>
<td>61.70</td>
</tr>
<tr>
<td>4</td>
<td>0.69</td>
<td>2.42</td>
<td>0.100</td>
<td>4.81</td>
<td>57.8</td>
</tr>
<tr>
<td>6</td>
<td>0.62</td>
<td>2.50</td>
<td>0.113</td>
<td>4.70</td>
<td>53.91</td>
</tr>
<tr>
<td>8</td>
<td>0.59</td>
<td>3.72</td>
<td>0.120</td>
<td>4.43</td>
<td>31.95</td>
</tr>
</tbody>
</table>

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 up to 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.

![Graph showing variation of tensile strength of HAF filled NR vulcanizate with resin content](image)

**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.

References


