Chapter 2

Experimental techniques and materials used

The specifications of the materials and details of the experimental techniques used in this study are given in this chapter.

2.1 Materials

2.1.1 Natural rubber (NR)

The natural rubber used in this study was ISNR-5 of Mooney viscosity (ML 1+4, 100°C) 85, obtained from the Rubber Research Institute of India, Kottayam. The Bureau of Indian standards specifications for the grade of rubber are given in Table 2.1 [1].

Table 2.1. BIS specifications of ISNR-5

<table>
<thead>
<tr>
<th>SI.No</th>
<th>Parameters</th>
<th>Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dirt content, % by mass, max</td>
<td>0.05</td>
</tr>
<tr>
<td>2</td>
<td>Volatile matter, % by mass, max</td>
<td>0.8</td>
</tr>
<tr>
<td>3</td>
<td>Nitrogen, % by mass, max</td>
<td>0.6</td>
</tr>
<tr>
<td>4</td>
<td>Ash, % by mass, max</td>
<td>0.6</td>
</tr>
<tr>
<td>5</td>
<td>Initial plasticity, Po, Min</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>Plasticity retention index (PRI), min</td>
<td>60</td>
</tr>
</tbody>
</table>
Rubber from the same lot has been used for the experimental since it is known that the molecular weight, molecular weight distribution and non-rubber constituents of natural rubber are affected by clonal variation, season, and use of yield stimulants and method of preparation [2].

2.1.2 Compounding ingredients

2.1.2.1 Vulcanizing agent
Sulphur was the vulcanizing agent used throughout the investigation. It was obtained from M/s Bayer India Ltd., Mumbai, India

2.1.2.2 Accelerators
(a) N-Cyclohexyl benzthiazyl sulphenamide (CBS)
It is a fast accelerator and was supplied by M/s Bayer India Ltd., Mumbai, India.

(b) Tetra methyl thiuram disulphide (TMTD)
TMTD is used as a secondary accelerator and was supplied by M/s Bayer India Ltd., Mumbai, India.

(c) Zinc oxide and stearic acid
Zinc oxide and stearic acid are used as an activator and co-activator respectively. It was collected from M/s CDH chemicals, Mumbai, India.

(d) Diethylene glycol (DEG)
DEG is used as an activator and was obtained from M/s CDH chemicals, Mumbai, India.

2.1.2.3 Filler
Organoclay (Cloisite 30B)
Organoclay is montmorillonite which is organically treated with methyl, tallow, bis-2-hydroxyethyl, quarternary ammonium chloride collected from Southern Clay Products Inc., USA.
Quaternary ammonium salt with the following structure is used as the modifier for cloisite 30B clay

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{OH} \\
\text{CH}_2\text{N}^+\text{T} \\
\text{CH}_2\text{CH}_2\text{OH}
\end{align*}
\]

T: Tallow (~65% C18, ~30% C16, ~5% C14)  
Anion: Chloride  
MT2EtOH: methyl, tallow, bis 2 hydroxyethyl, quaternary ammonium

Table 2.2 Characteristics of Organoclay

<table>
<thead>
<tr>
<th>Treatment/Properties:</th>
<th>Organic modifier</th>
<th>Modifier concentration</th>
<th>% moisture</th>
<th>% Weight Loss on ignition</th>
<th>Layer distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cloisite®30B MT2EtOT</td>
<td>90meq/100g clay</td>
<td>&lt;2%</td>
<td>30%</td>
<td>18.5 Å</td>
<td></td>
</tr>
</tbody>
</table>

2.1.3 Other chemicals

Toluene LR grade (E.Merck), maleic anhydride (MA) (Aldrich, 99% purity) and bromothymol blue (Sigma) were used.

2.2 Experimental methods

2.2.1 Preparation of maleic anhydride graft natural rubber (MA-g-NR)

MA-g-NR was prepared by the following procedure. NR was initially mixed with MA in a Brabender mixer at an rpm of 50 for 10 minutes at 70°C. This mix was then subjected to ⁶⁰Co gamma irradiation for a period of 1½ hours for giving 2.5kGy in a gamma chamber. Trials were conducted by varying the radiation doses (0.5kGy, 2.5kGy, 5kGy, 7.5kGy and 10kGy). The maleic anhydride was
also added in various concentrations (1, 3, 5 and 10). Grafted rubber was dissolved in 100ml of toluene at reflux temperature in order to separate unreacted MA. The polymer was then precipitated in acetone. Finally the recovered product was dried in a vacuum oven for 24hrs at 110°C.

2.2.2 Radiation grafting
Maleic anhydride mixed natural rubber was irradiated with gamma (γ) rays in a Gamma Chamber 5000 (figure 2.1). It is a compact self shielded cobalt-60 gamma irradiator providing an irradiation volume of approximately 5000cc. The material for irradiation is placed in an irradiation chamber located in the vertical drawer inside the flask. This drawer can be moved up and down with the help of a system of motorized drive, which enables precise positioning of the irradiation chamber at the center of the radiation field. Radiation field is provided by a set of stationary cobalt-60 sources placed in a cylindrical cage. The sources are doubly encapsulated in corrosion resistant stainless steel pencils and are tested in accordance with international standards. The samples were irradiated for different radiation doses at a dose rate of 2kGy per hour in air at room temperature.
2.2.3 Characterization of MA-g-NR

2.2.3.1 Determination of grafting efficiency

The grafting efficiency (MA content in MA-g-NR) was determined by refluxing weighed amount of the grafted rubber in xylene saturated with water for 1hr to hydrolyze the anhydride and then titrating against a solution of 0.05N ethanolic KOH using 1% thymol blue as indicator [3]. The grafted MA content was calculated using the following equation: [4]

\[
\text{MA (wt %)} = \left[ \frac{(N \times V \times 98)}{(2 \times W)} \right] \times 100 \% \quad (2.1)
\]
where $N$ and $V$ are respectively the concentration (mol/l) and volume (l) of potassium hydroxide-methanol standard solution and $W$ is the weight (g) of the MA-g- NR sample.

2.2.3.2 FTIR spectroscopy

The FTIR spectra were recorded on a Bruker Tensor 27 IR spectrometer from 4000 cm\(^{-1}\) to 400 cm\(^{-1}\) with a 0.5 cm\(^{-1}\) resolution and 14 scans were performed for each sample. Different functional groups and structural features in the molecules absorb energy at characteristic frequencies. The frequency and intensity of absorption are the indication of the bond strength and structural geometry in the molecule. A sample of maleated elastomer was extracted with diethyl ether for 24hrs to remove unreacted maleic anhydride. IR spectra of the sample after soxhlet extraction were recorded.

2.2.4 Mixing and homogenization of rubber clay nanocomposites

Incorporation of clay into maleated rubber was carried out by choosing an appropriate recipe and the mixing was carried out in a Brabender Plasticorder. It is a torque rheometer which is widely used for mixing, blending and to study processability of polymers such as mixing and extrusion and evaluation of the rheological properties of polymer melts [5]. It is used to measure the torque generated due to resistance offered by the material to mastication or flow under preselected conditions of shear and temperature. The heart of the torque rheometer is a jacked mixing chamber with horizontal rotors connected to a shaft. The volume of the chamber is approximately 40 cm\(^3\) for the model used (PL 3S). The resistance due to the mixing of the test material within the mixing chamber is measured with the help of dynometer balance. A dc thyrister controlled drive is used to control the speed of rotation of the rotors. The temperature of the mixing chamber can be varied up to 30°C which can be controlled and measured with the aid of a temperature controller and a recorder. Different types of rotors can be employed depending upon the nature of the polymer used. After selecting the
Temperature and the rotor speed, the rubber was charged into mixing chamber. When the nerve of the rubber had disappeared, compounding ingredients were added as per the sequence given in ASTM D 3182 (1982). Mixing was carried out at 60°C and at rpm speed. Homogenization of the compound was carried out using a laboratory (15x 33cm) two roll mill at a friction ratio 1:1.25. The temperature of the roll was maintained at 60°C and the compound was homogenized by passing the compound several times through the tight nip and finally made into a sheet at a nip gap of 3mm.

2.2.5 Determination of cure characteristics of the compounds

Cure characteristics of the mixes were determined as per ASTM D 2084-1995 using Rubber Process Analyser (RPA 2000-Alpha Technologies). It uses two directly heated, opposed biconical dies that are designed to achieve a constant shear gradient over the entire sample chamber. The sample of approximately 5g was placed in the lower die that oscillated through a small deformation angle (0.2°) at a frequency of 50cpm. The torque transducer on the upper die senses the force being transmitted through the rubber. The torque was plotted as a function of time and the curve was called a cure graph. The important data that could be taken from the torque-time curve were minimum torque (M_L), maximum torque (M_H), and scorch time (T_{10}), optimum cure time (T_{90}) and cure rate. Optimum cure rate corresponds to achieve 90 percent of the cure calculated using the equation 2.2 [6].

\[
\text{Optimum cure time} = \text{time to achieve a torque of } 0.9 \left( M_H - M_L \right) + M_L \quad (2.2)
\]

Cure rate index was calculated from the cure graph using equation 2.3

\[
\text{Cure rate index} = 100/ t_{90} - t_2 \quad (2.3)
\]

where \( t_{90} \) and \( t_2 \) are the times corresponding to the optimum cure and two units above minimum torque respectively.
2.2.6 Moulding of test specimens

Vulcanization of various test samples was carried out in an electrically heated hydraulic press having 45cm x 45cm platen at 150°C at a pressure of 200kg/cm² on the mould up to optimum cure times. Moulded samples were conditioned for 24hrs before testing. For samples having thickness more than 6mm (compression set, abrasion resistance etc) additional curing time based on the sample thickness was given to obtain satisfactory moulding.

2.3 Tests on vulcanizates

For the tests described below at least three specimens per sample were tested for each property and mean values are reported.

2.3.1 Modulus, tensile strength and elongation at break

Tensile properties of the nanocomposites were determined according to ASTM D 412 (1980) using dumbbell specimens on a Shimadzu Universal Testing Machine (model-AG1) with a load cell of 10kN capacity. All the tests were carried out at ambient temperature. Samples were punched out from compression moulded sheets along the mill direction using a dumbbell die. A bench thickness gauge was used to measure the thickness of the narrow portion. The sample was held tight by the two grips, the upper grip of which was fixed. The gauge length between the jaws at the start of each test was adjusted to 30mm and the rate of separation of the power actuated upper grip was fixed at 500mm/min for elastomeric specimens. The tensile strength, elongation at break and modulus were evaluated and printed out after each measurement by the microprocessor. The modulus and tensile strength are reported in mega Pascal (Mpa) unit and elongation at break in percentage (%).
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2.3.2 Tear resistance

Tear resistance of the samples was tested as per as ASTM D 624-1998, using unnicked 90° angle test specimens that were punched out from the moulded sheets, along the mill grain direction. The measurements were carried out at a crosshead speed of 500mm/m on a Shimadzu Model AG1 Universal Testing Machine according to ASTM standards, D 412-68 and D 624-54 respectively. The tear strength was reported in N/mm.

2.3.3 Hardness

The hardness of the moulded samples were tested using Zwick 3114 hardness tester in accordance with ASTM D 2240 (1981). The tests were performed on mechanically unstressed sample of 12mm diameter and 6 mm thickness. A load of 12.5Newton was applied and the readings were taken 10seconds after the intender made firm contact with the specimen. The mean value of three measurements is reported. The hardness values are reported in Shore A unit.

2.3.4 Compression set

The samples (6.5mm thick and 18mm diameter) in duplicate, compressed to constant deflection (25%) were kept 22hrs in an air oven at 70°C. After the heating period, the samples were taken out, cooled to room temperature for half an hour and the final thickness was measured. The compression set was calculated using equation 2.4.

\[
\text{Compression set (\%)} = \left(\frac{t_i - t_f}{t_i - t_s}\right) \times 100
\]  

(2.4)

where \(t_i\) and \(t_f\) are the initial and final thickness of the specimen respectively and \(t_s\) thickness of the spacer bar used. The procedure used was ASTM D 395 (1982)
2.3.5 Abrasion resistance

The abrasion resistance of the samples was measured using a DIN abrader. Sample having a diameter of 15mm and a length 20mm was kept on a rotating sample holder and 10Newton load was applied. Initially a pre-run was given for the sample and its weight was taken. The sample was then given a complete run and weight after final run was also noted. The difference in weight is the abrasion loss. It is expressed as the weight of the test piece getting abraded away by its travel through 42cm on a standard abrasive surface and expressed as the weight loss in gram (g). The abrasion loss was calculated using the equation 2.5,

\[ V = \Delta m / \rho \]  \hspace{1cm} (2.5)

Where \( \Delta m \) is the mass loss, \( \rho \) is the density of the sample and \( V \) is the abrasion loss in mm'.

2.3.6 Rebound resilience

The rebound resilience of the samples was determined as per ASTM D 1054 (1974) using Scott Rebound Pendulum. This test is used for the determination of impact resilience of solid rubber from measurement of vertical rebound of a dropped mass. Resilience is determined as the ratio of rebound height to drop height of a metal plunger of prescribed weight and shape, which is allowed to fall on the rubber specimen. Resilience is a function of both dynamic modulus and internal friction of rubber. The test specimen should have a thickness of 12.5mm and the standard temperature is 23 ± 2°C. Resilience is tested as follows. The instrument is leveled and the plunger is raised to the top of the guide rod. The resilience scale is positioned so that its full weight rests upon the specimen. It is locked in that position. The plunger is then released making sure it slides freely on its guide. The first three values are avoided. Record the next three values. Since the resilience scale is divided into 100 parts, the rebound height is equal to
The resilience in percentage. The rebound resilience was calculated as using the equation 2.6

\[
\text{Rebound resilience} \% = \frac{1 - \cos \theta_2}{1 - \cos \theta_1} \times 100
\]

(2.6)

where \(\theta_1\) and \(\theta_2\) are initial and rebound angles respectively, \(\theta_1\) was 45° in all cases.

2.3.7 Strain sweep studies

The strain sweep measurements on unvulcanized samples were conducted to study the rubber-filler interaction. Rubber Process Analyser (RPA 2000- Alpha Technologies) is a purposely modified commercial dynamic rheometer [7]. Such instrument was modified for capturing strain and torque signals, through appropriate software. Filled rubber compounds exhibit strong non-linear viscoelastic behaviour, the well-known Payne effect, i.e. the reduction of elastic modulus with increasing strain amplitude [8]. RPA can do strain sweep tests in which the variation of storage modulus (\(G'\)), loss modulus (\(G''\)) and complex modulus (\(G^*\)) with change in strain amplitude are measured. With respect to its measuring principle, the RPA cavity must be loaded with a volume excess of test material. In agreement with ASTM 5289, the manufacturers recommends to load samples of about 5.0g i.e.4.4cm\(^3\) for a standard filled rubber compound with a specific gravity of 1.14g/cc. Samples for RPA testing were consequently prepared by die cutting 46mm diameter disks out of around 2mm thick sheets of materials. The testing temperature was selected as 100°C; a temperature below the curing temperature and the shear strain was varied from 0.5% to 100% keeping the frequency measurements at 0.5Hz.
2.3.8 Dynamic mechanical analysis (DMA)

DMA works by applying an oscillating force to the material and the resultant displacement of the sample is measured. From this, the stiffness can be determined and tan δ can be calculated. Tan δ is the ratio of the loss component to the storage component. By measuring the phase lag in the displacement compared to the applied force it is possible to determine the damping properties of the material. Tan δ, storage modulus and loss modulus are plotted against frequency and clay loading. The dynamic mechanical thermal analysis was conducted using rectangular test specimens having a dimension of 30mm x 5mm x 2mm were tested under tension mode using a TA Instruments DMA Q-800 at a constant temperature of 60°C. The frequency was varied from 1 to 50Hz under frequency sweep mode at a rate of 2Hz/min. The samples were subjected to dynamic tension strain amplitude of 0.1146 %.

2.3.9 Air permeability

The instrument consists of a gas cell divided into two chambers by the membrane to be tested. The gas under test is admitted at known pressure from one side. The permeability can be studied either by measuring the pressure decrease at the high pressure side or the pressure increase at the low pressure side. A highly sensitive heat conductivity cell with temperature compensation of the signal to standard conditions, a chart recorder, a water cooling/heating thermostat for maintaining constant temperature in the measuring chamber and a rotatory two stage vacuum pump are the remaining portions of the measuring instrument. Permeability measurements were carried out according to ASTM D 1434 (1982). Test specimens of thickness 0.25mm were moulded and used for measurements. The equipment used was Lyssy Manometric Gas Permeability Tester L 100-2402.
The prepared film was used to divide the cell of the apparatus into chambers and air at a flow rate of 500 ml/min was admitted from the upper compartment. The lower compartment was connected to a suction pump through a capillary U tube. The conditioning of the test specimen for a definite period is calculated from the equation 2.7.

\[ T = \frac{b^2}{2D} \]  

(2.7)

where \( b \) is the thickness of the test piece in meter and \( D \), the diffusion coefficient in meter square per second. The preconditioning times will vary from few minutes to several hours and even days depending on the type of the samples. In practice the preconditioning time is the time taken for attaining \( 10^4 \) torr pressure in the lowest compartment. Then mercury is poured into the capillary to a fixed mark. The level of mercury in the capillary steadily decreases as the air permeates through the membrane. This change is recorded in a chart moving at a
speed of 180cm/hour. From the distance traveled by the pointer in the chart, the
time taken for the permeance of the sample \((t_s)\) is determined. Permeability of
the sample is then calculated by substituting the time taken by the standard PET
sample \((t_r)\) in the above chamber and under similar conditions using the equation
2.8.

\[
\text{Permeability of the sample} \quad P_m = \frac{T_r \times P_r}{t_m}
\]  

(2.8)

where \(P_r\) is the permeability of the standard PET sample. If air is used the value
of \(P_r\) is 30ml/m\(^2\) day.

2.3.10 Heat build up

The Ektron flexometer conforming to ASTM D 623-1999 was used for
measuring the heat build-up. A cylindrical sample of 25mm in height and 19mm
in diameter was used for test. The oven temperature was maintained at 100\(^0\)C.
The samples were placed in the preconditioning oven for 20minutes at 100\(^0\)C.
Preconditioning the test samples were subjected to a flexing stroke of 4.45mm
under a load of 10.9kg and the temperature rise at the end of 20minutes was
taken as the heat build up.

2.3.11 Crosslink density and swelling studies

The crosslink density of vulcanized samples was determined by the equilibrium
swelling method and using Florey-Rehner equation [9]. Approximately 0.3g
samples were accurately weighed and kept in toluene solvent taken in an airtight
container for 24hrs. The surface of the swollen samples was then gently wiped
using filter paper and weighed. The samples were placed again in the solvent and
weights were recorded at regular intervals, usually one hour, till equilibrium
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weight was obtained. The swollen samples were heated at 60°C for 24 hrs in an oven to remove the solvent. The deswollen weight was then determined. The volume fraction of rubber in the deswollen network was then calculated using the equation 2.9.

\[
V_r = \frac{(D - FT) \rho_r^{-1}}{(D - FT) \rho_r^{-1} + A_0 \rho_s^{-1}} \tag{2.9}
\]

where \(T\) = weight of test specimen, \(D\) = deswollen weight, \(F\) = weight fraction of insoluble component, \(A_0\) = weight of the absorbed solvent corrected for the swelling increment, \(\rho_r\) = density of the test specimen, \(\rho_s\) = density of the solvent.

A Swelling in toluene

In order to analyze the interaction between the components of the system, equilibrium swelling studies were carried out in toluene. Circular specimens of diameter 20mm were punched from the vulcanized elastomer sheet and were allowed to swell in toluene at room temperature. At different intervals, the amount of solvent entering the sample was assessed gravimetrically until equilibrium was reached, as evidenced by the constant weight of the sample. The mole% uptake of the solvent was calculated using the equation 2.10 [10].

\[
Q_t = \frac{\left[ \frac{M_{c(m)}}{M_{i(s)}} \right]}{\frac{M_{r(m)}}{M_{i(s)}}} \times 100 \tag{2.10}
\]

where \(M_{c(m)}\) is the mass of solvent at a given time, \(M_{i(m)}\) is the molecular weight of the solvent and \(M_{i(s)}\) is the initial weight of the specimen. At equilibrium swelling, \(Q_t\) was taken as \(Q_{\infty}\), the mole% uptake at infinite time. Sorption curves were obtained by plotting mole% uptake against square root of time. The effective diffusivity, \(D\) of the elastomer-solvent system was calculated from the initial portion of the sorption curves using the equation 2.11.
where $\theta$ is the slope of the initial portion of the sorption curve. Another parameter called sorption coefficient was calculated from the equilibrium swelling using the equation 2.12.

$$S = \frac{M_\infty}{M_0}$$  \hspace{1cm} (2.12)

where $M_\infty$ is the mass of the penetrant sorbed at infinite time and $M_0$ is the initial weight of the polymer sample. Sorption coefficient describes both initial penetration and dispersal of the penetrant molecules into the elastomeric network.

The permeation coefficient which is a characteristic parameter reflecting the collective processes of diffusion and sorption was calculated using the equation 2.13 [11].

$$P = DS$$  \hspace{1cm} (2.13)

**B Swelling in oils**

The percentage weight change of the nanoclay filled composites in different oils was studied by swelling a cut sample in oil for constant weight. The swelling characteristics was determined as a change in weight calculated using equation (2.14)

$$\text{Change in weight (\%) } = \frac{W_t - W_0}{W_0} \times 100$$  \hspace{1cm} (2.14)

where $W_t$ is the weight after immersion and $W_0$ is the original weight.
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2.3.12 Thermal analysis

Thermogravimetric analysis

The thermogravimetric analyzer used for the studies was TGA Q-50 (TA Instruments). It is a computer-controlled instrument that permits the measurement of weight changes in the sample as a function of temperature or time. It is programmed in the required temperature range to measure the weight change resulting from chemical reaction, decomposition, solvent and water evolution, Curie point transitions and oxidation of the sample materials. The temperature is scanned at a linear rate. The instrument has two components, an ultra sensitive microbalance and a furnace element. The balance is sensitive to 0.1 microgram and the furnace could be heated from ambient to 800°C at rates of 0.1 to 200°C per minute. For purging platinum the sample holder, nitrogen gas is used so as to study the oxidation, burning and thermal stability of the materials. The purge gas flows directly over the sample. The recommended flow rate of the sample purge was kept less than the flow rate of the balance purge at all times.

Evaluation of kinetic parameters

The TGA data can also be used for studying the kinetics of decomposition, which provide 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.

Formulation of the rate equation

For many kinetic processes, rate of reaction may be expressed as a product of a temperature dependent function; $k(T)$, and a composition- or conversion-dependent term; $f(X)$:
\[ r = \frac{dX}{dt} = k(T)f(X) \]  \hspace{1cm} (2.15)

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 equation (2.15) is the reaction rate constant, which is assumed to obey the usual Arrhenius relationship:

\[ k(T) = A \exp\left(-\frac{E_a}{RT}\right) \]  \hspace{1cm} (2.16)

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; \( f(X) \), is generally very complicated. A particular term 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:

\[ f(X) = (1-x)^n \]  \hspace{1cm} (2.17)

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

\[ r = \frac{dW}{dt} = AW^n \exp\left(-\frac{E_a}{RT}\right) \]  \hspace{1cm} (2.18)

\[ \ln r = \ln\left(-\frac{dW}{dt}\right) = \ln A + n \ln W - \frac{E_a}{RT} \]  \hspace{1cm} (2.19)

Published methods of deriving the kinetic parameters from TGA data center about equation (2.19). They may be either differential i.e. involving the derivative term; \(-dW/dt\) or integral i.e. based upon an integration of equation (2.19). The emphasis in these methods is on finding a way of plotting the data to
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provide a rapid visual assessment of the order of the reaction and its activation energy.

Differential method for determining rate equation parameters

The difference form of equation (2.19) at different temperatures is:

\[ \Delta \ln r = \Delta \ln (-dW/dt) = n\Delta \ln W - (E_a / R)\Delta(1/T) \]  

(2.20)

Dividing (2.20) by \( \Delta(1/T) \) gives

\[ \left[ \Delta \ln r / \Delta(1/T) \right] = n\left[ \Delta \ln W / \Delta(1/T) \right] - (E_a / R) \]  

(2.21)

A plot of \( \lfloor \Delta \ln r / \Delta(1/T) \rfloor \) against \( \lfloor \Delta \ln W / \Delta(1/T) \rfloor \) should be a straight line with slope equal to the order of reaction; \( n \), and an intercept of \(-E_a/R\).

Dividing (2.20) by \( \Delta \ln W \) gives

\[ \Delta \ln r / \Delta \ln W = n + E_a \left[ -\Delta(1/T) / R\Delta \ln W \right] \]  

(2.22)

A plot of \( \lfloor \Delta \ln r / \Delta \ln W \rfloor \) 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 [12]. 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.

Integral method

The integral methods involve the integration of equation (2.15) by separation of variables. By substituting equation (2.16) into this expression and defining \( \beta = (dT/dt) \) as the heating rate, the following is obtained:
\[ F(X) = \int_{0}^{X} f(X) \, dX = \int_{0}^{T} (A / \beta) \exp(-E_a / RT) \, dT \]  
\[ (2.23) \]

where \( T_0 \) is the initial temperature in the TGA analysis and \( T \) is the final temperature. For a constant heating rate \( \beta \) and if \( T_0 \approx 0 \), equation (2.23) becomes:

\[ F(X) = \int_{0}^{T} (A / \beta) \exp(-E_a / RT) \, dT \]  
\[ (2.24) \]

The different integral methods involve an approximation to the right-hand integral term in equation (2.24).

Among the integral methods, the Coats and Redfern approach [13] seems to be the most suitable from a practical point of view and is preferred over others and is applied here. The activation energy and the order of reaction were evaluated utilizing this equation for reaction order \( n \neq 1 \), which when linearized for a correctly chosen \( n \) yields the activation energy from the slope.

\[ \log \left[ 1 - (1 - a)^{1-n} / T^2 (1 - n) \right] = \log \left[ AR / \beta E \right] - E / 2.303 RT \]  
\[ (2.25) \]

where \( \alpha \) is the fraction decomposed, \( T \) is the temperature (K), \( n \) is the order of reaction, \( A \) is the Arrhenius constant, \( R \) is the universal gas constant, \( E_a \) is the activation energy and \( \beta \) is the heating rate. The plot of the left hand side of the equation (Y) against \( 1/T \) should be a straight line with slope \( = -E_a / (2.303R) \) for the correct value of \( n \).

**Differential scanning calorimetry**

The differential scanning calorimetry of maleated natural rubber gum and nanoclay loaded samples were recorded with 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
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Encapsulated in standard aluminium pans placed in the sample holder were subjected to the analysis.

2.3.13 Thermal ageing studies

Tests were carried out as per ASTM D 573-1999 [6]. Specimens of vulcanized rubber were exposed to the deteriorating influence of air at specified elevated temperature in an air oven, for known periods of time, after which their physical properties determined. These were compared with the properties determined on the original specimens and the changes noted.

2.3.14 Ozone resistance

The ozone test chamber manufactured by MAST Development Company, USA was used to study ozone cracking as shown in figure 2.3. The chamber provided an atmosphere with a controlled concentration of ozone and temperature. Ozone concentration selected was 50pphm, which is generated by an UV quartz lamp.

The test was carried out as per ASTM D 1149-99 specifications at 38.5°C. B type specimens were tested in duplicate and in the form of a bent loops. Rectangular strip of length 95mm, breadth 25mm and thickness 2 ± 0.2mm 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 24hrs. 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. Samples were exposed for longer time. Surfaces of the irradiated samples were scanned on a macro viewer of LEICA Q 500 IW image analyzer, images were acquired and the photo prints were taken.
2.3.15 Exposure to gamma radiation
Dumbbell shaped tensile test samples of $2 \pm 0.2\text{mm}$ thickness were irradiated with gamma ($\gamma$) rays in a Gamma Chamber 5000 (figure 2.1). The samples were irradiated for different radiation doses at a dose rate of 2kGy per hour in air at room temperature. The tensile strength was measured before and after irradiation and the percentage retention was calculated.

2.3.16 Dielectric measurements
Circular specimens of maleated rubber nanocomposite were used. The test samples were placed in between copper wires and are fixed on both sides of the
samples as electrodes. The capacitance, resistance and dielectric loss factor were measured in alternating current at room temperature using HP 4285 A LCR Hitester by varying the frequencies (0.1-8 MHz).

2.3.17 Test for Flammability

Flame resistance of vulcanisates of maleated natural rubber clay nanocomposites were evaluated as per UL 94 overview-test for flammability [14] of plastic materials for parts in devices and appliances. Method 94V, used for vertical burn test was applied. The test specimens were (strips of 12mm x 100mm and thickness 2.0mm cut from molded vulcanizates) held at one end in the vertical position. A burner flame was applied to the free end of the specimen for two ten seconds intervals, separated by the time it take for flaming combustion to cease after the first application. Two sets of three specimens were tested. The following were noted for each specimen.

Duration of flaming combustion after the first burner flame application.
Duration of flaming combustion after the second burner flame application.
Duration of glowing combustion after the second burner flame application.
Whether or not flaming drips ignite cotton placed below specimen.
Whether or not specimen burns up to holding clamp.

2.3.18 TEM analysis

The transmission electron microscopy was performed using a JEOL, JEM -2010 (Japan), TEM operating at an accelerating voltage of 200kV. The composite samples were cut by ultra-cryomicrotomy using a Leica Ultracut UCT. Freshly sharpned glass knives with cutting edge of 45° were used to get the cryosections of 50-70nm thickness. Since these samples were elastomeric in nature, the temperature during ultra cryomicrotomy was kept at -50°C (which was will below the glass transition temperature of EVA) [15]. The cryosections were collected individually on sucrose solution and directly supported on copper grid of 300-mesh size.
2.3.19 X-ray diffraction technique (XRD)

X-ray diffraction (XRD) was used to study the nature and extent of dispersion of the clay in the nanocomposite. XRD patterns were obtained using Bruker, D8 advance diffractometer at the wavelength CuK\(_\alpha\) = 1.54\(^0\), a tube voltage of 40kV and tube current of 25mA. Bragg’s law defined as \( n\lambda = 2d\sin\theta \), was used to compute the crystallographic spacing (d) for nanoclay. The samples were scanned in step mode by 1.0°/min, scan rate in the range of 2 to 12°.

The principle of X-ray diffraction technique is given in figure 2.4

![Figure 2.4 Principle of X-ray diffraction techniques](image)

The diffraction from two consecutive silicate layers that are separated by a distance d and the intercept X-rays of wavelength \( \lambda \) at an incident angle \( \theta \). The experimental 2θ values are the angle between the diffracted and incoming X-ray waves. The change in d spacing of the rubber nanocomposites is observed from the peak position in the XRD graphs in accordance with the Bragg equation 2.26

\[ n\lambda = 2d\sin\theta \]  

(2.26)

where \( n \) is the integer, \( \lambda \) is the wavelength and \( \theta \) is the incident angle.
**References**


