Chapter VI

Results and Discussion-
EPDM Rubber Nanocomposites
Introduction

EPDM (ethylene propylene diene monomer), a terpolymer was developed and commercialized in the late 1950s. With an annual production capacity of more than 1,000 KG in 1998, EPDM is currently the fourth elastomer by volume and has become more or less a commodity rubber. Actually, EPDM is the largest non-tire rubber and the annual growth rate is found to be around 4%. ExxonMobil, Dow and DSM and are market leaders. Elastomers, colloquially called rubbers, are an important class of materials with a large number of applications. Elastomers possess several significant defining characteristics:

1. They have a low glass transition temperature, $T_g$
2. They possess the property of elasticity.
3. The polymer is preferably free of crystallinity
4. The polymer is lightly crosslinked.

Invoking the theory of rubber elasticity, one considers a polymer chain in a crosslinked network as an entropic spring. When the chain is stretched, the entropy is reduced by a large margin because there are fewer conformations available. Therefore, there is a restoring force, which causes the polymeric chain to return to its equilibrium or un-stretched state, such as a high entropy random coil configuration, once the external force is removed. This is what the reason why rubber bands return to their original state. Some type of permanent structure is necessary to form a coherent solid and prevent liquid like flow of elastomer molecules. This is achieved by introducing a number of intermolecular chemical bonds known as crosslinks to make a loose three-dimensional molecular networking system.

The copolymer and terpolymer are used in the automotive industry for windows, hoses, gaskets, wipers, bumpers, belts, door seals, etc. Furthermore, they are used for cable insulation and for roofing. Additional uses are in white sidewall compounds of tires. A large number of commercial EPDM grades are produced. The main structural characteristics are the following.$^{(2-6)}$
- Concentration ratio of ethylene and propylene chain units (amorphous or crystalline grades)
- Co- or ter polymerization of ethylene, propylene and diene monomers (EPM or EPDM)
- The type and amount of ter monomer, chain branching, the type of cross-linking, mechanical properties.
- Molecular weight and molecular weight distribution
- Chain branching leading to difference in viscosity and processability
- Processability and price.

Copolymers which contain ethylene below 55 wt. % are completely amorphous and are not self reinforcing. At higher ethylene content of the order of 60 to 70 wt. %, the polymers contain long ethylene sequences, which form crystalline domains. These polymers are referred to as “sequential” grades and their processing behavior differs considerably from that of the normal amorphous grades. The partially crystalline domains form thermally reversible physical cross-links, which, as in thermoplastic elastomers, provide the elastomers with a higher mechanical strength without chemical crosslinks, but can worsen tensile properties in vulcanizates. Traditionally, sulfur vulcanization requires unsaturation and therefore fully saturated EPM can not be cross-linked with sulfur. Non-conjugated diene monomers have been introduced in EPM, yielding EPDM for sulfur vulcanization. For peroxide cross-linking the presence of the diene increases the cross-linking efficiency.

Fig. 6.1 Chemical structure of diene third monomers: (a) VNB, (b) DCPD and (c) ENB, as built into the polymer chain.
From a practical point of view, ENB and DCPD are the most important diene termonomers because of high amounts of diene that can be easily incorporated in commercial EPDMs\(^8\text{-}^{10}\). Increasing the amount of diene results in increase in crosslinking densities and, thus, in corresponding changes in mechanical and elastic properties.

6.2 Vulcanization of EPDM Rubber:

The term *vulcanization or cross-linking* is generally applied to rubbery or elastomeric materials. The cross-linked materials forcibly retract to their approximate original shape after a rather large mechanically imposed deformation. Viscoelastic properties of vulcanizates are largely influenced by the density of cross-links. According to the theory of rubber elasticity, the retractive force resisting to a deformation is proportional to the number of force bearing network chains per unit volume of elastomer\(^1\). An increase in the number of junctions or cross-links give an increase in the number of network chains. In a non-crosslinked linear high molar mass polymer (above its melting point) only chain entanglements cause viscoelasticity. Cross linking is a process of chemically producing network junctions by the insertion of crosslinks between the polymer chains. The crosslink may be a group of sulfur atoms in a short chain, a single sulfur atom, carbon-to-carbon bond, a polyvalent organic radical, an ionic cluster, or a polyvalent metal ion. The process is usually carried out by heating the rubber (mixed with the cross-linker) in a mold under pressure. Major effects of crosslinking on use-related properties are schematically\(^1\) shown in Fig. 6.2. It should be noted that the static modulus increases with crosslinking to a greater extent than does the dynamic modulus. The dynamic modulus is a composite of viscous and elastic behavior, whereas the static modulus is a measure of only the elastic component of rheological behavior.
Fig. 6.2 Effect of cross-linking on various physical properties of vulcanizates

Hysteresis is the ratio of the rate-dependent or viscous component to the elastic component of the complex modulus. It is a measure of the deformation energy which is not stored but which is converted to heat. Hysteresis is reduced with increase in crosslink formation. Tear strength, fatigue life, and toughness are related to the breaking energy. Values of these properties increase with small amount of cross-linking but they are reduced by further crosslink formation. Properties related to the energy-to-break increases with increasing both the number of network chains and hysteresis. Since hysteresis decreases as more network chains are formed, the energy to-break related properties reach a maximum at some intermediate crosslink density. It should be noted that the properties given in Fig. 6.2 are not only functions of crosslink density. They are also affected by the type of cross-links, the type of polymer, and the type and amount of filler.

The first and by far the most important cross-linking agent is sulfur, which is relatively inexpensive and yet vital to the rubber industry. For a number of elastomers, there are unsaturated double bonds on the polymer chain. Elastomers such as NR and SBR need only a small percentage of these double bonds to be utilized in order to produce a useful product; however this leaves a larger percentage of unreacted double bonds that are vulnerable to attack by oxygen, ozone and heat, deteriorating properties. At one extreme, a single sulfur atom connects the carbon atom of one chain to that of another. In practice the di- or tri-sulfidic links are predominant, as shown in the Fig. 6.3.
Efficient vulcanization can be achieved by adding to the rubber formulation a particular type of accelerator, which has available sulfur atoms in its molecule, and avoids using elemental sulfur altogether. In this case the accelerator, now more appropriately called a cross-linking agent becomes a sulfur donor. Efficient vulcanization can also be achieved by using a small amount of elemental sulfur, about 0.3 to 0.8 phr (parts per hundred rubber), together with larger amounts of accelerator (2-5 phr).

At the other extreme, the conventional cross-linking system comprises 2-3 phr elemental sulfur and smaller quantities of accelerator (0.5-1 phr). This produces predominantly multiple sulfur atoms in the crosslink, known as polysulfidic crosslinks, see Fig. 6.3. In between these two extremes lies the semi efficient vulcanization system using about 1.5 phr elemental sulfur and a correspondingly adjusted accelerator level. The symbol $S_x$ in Fig. 6.3 represents the multiple sulfur link.

Accelerated sulphur vulcanization results in the substitution of the labile allylic H-atoms by sulphur bridges, yielding alkenyl sulphides. The unsaturation of the third monomer is not consumed, but activates the allylic positions. Initially, accelerator residues are attached to the allylic positions via a sulphur bridge, yielding crosslink precursors (Fig. 6.4).
A crosslink consisting of many sulfur atoms would be more flexible than a crosslink consisting of a single sulfur atom. In terms of properties, this means that vulcanizates with a conventional cure system are generally better at relieving stress when flexed. Thus they have a better fatigue life in a repetitious (cyclic) deformation environment. A disadvantage is that sulfur to sulfur bonds are weaker (less thermally stable) than sulfur to carbon links and the conventionally cured system is therefore less heat resistant than a system from a semi-efficient or efficient vulcanization. Although sulfur is the best known and most used vulcanizing agent, there is another class of crosslinking agents known as peroxides. They don’t necessarily need the reactivity of a double bond to cure, nor do they need accelerators, although chemicals known as co-agents are often used to improve overall vulcanization.
Crosslinking with peroxides has been known for a long time, but gained importance with the development of the saturated synthetic rubbers. Based on the heat stability that can be obtained by peroxide vulcanization of diene rubbers, especially of EPDM, this type of vulcanization has achieved a great importance.

The temperature of decomposition (half-life) of the peroxide is the main determinant for the so called scorch temperature (which gives an indication when crosslinking starts to take place) and cure rate. The chemical structure of the peroxide determines its usefulness as a vulcanizing agent.

The chemical structure of all peroxides can be derived from hydrogen peroxide; the single substituted products are the hydroperoxides; the double substituted products are the peroxides:

- H-O-O-H hydrogen peroxides
- R-O-O-H hydroperoxides
- R-O-O-R peroxides

Hydroperoxides do not lead to the formation of crosslinks, but can interfere with the crosslinking capacity of other peroxides, respectively can degrade polymer molecules. They are therefore not important in the crosslinking of rubber. They are important in the radical initiation during polymerization and frequently initiate aging reactions.

For the crosslinking of rubber, only peroxides [Fig. 6.5] can practically be used, which are stable and not dangerous during the usual handling, and which, on the other hand, decompose sufficiently fast at customary curing temperatures. Peroxides with tertiary carbon atoms are less stable. One can distinguish two groups of organic peroxides that are stable enough for rubber processing. Almost all peroxides that are of interest in curing of rubbers can be derived from these basic types.
CHAPTER VI: Ethylene Propylene Diene Monomer [Epdm] Rubber Nanocomposites

Fig. 6.5 (a) peroxides with carboxy groups, (b) peroxides without carboxy groups

Peroxides typically react with the elastomer chains by removing hydrogen atoms from the carbon backbone of the polymer, thus creating highly active radicals on the chain, which attach to a similar site on another chain. This creates a carbon to carbon crosslink, which is stronger than a sulfur to carbon link and more thermally stable, as depicted in Fig. 6.6.

Fig. 6.6 Two polymer chains directly through a carbon atom from each elastomer chain

The mechanism of peroxide crosslinking is much less intricate than that of sulfur vulcanization. Crosslinking is initiated by the thermal decomposition of the peroxide. Next, the active radicals thus formed abstract hydrogen from elastomer chains to form macro-radicals. Finally, cross-linking results either from the combination of two macro-radicals or from the addition of a macro-radical to an unsaturated moiety of another
primary elastomer chains. Fig. 6.7 depicts the Peroxide cross-linking confers a higher heat aging resistance due to higher stability of C–C bonds as compared to C–S and S–S bonds. Peroxide cross-linking gives better compression set than sulfur cured cross-linking, at the expense of fatigue life and some tensile strength at high temperature. Peroxide curing can vulcanize some elastomers which cannot be cured with sulfur, because of a total lack of double bonds, for example the copolymer of ethylene and propylene rubber (EPM).

**Fig. 6.7** Simplified scheme of the peroxide curing of EPDM with dicyclopentadiene as third monomer.

An elastomeric non-crosslinked network can be pictured as an ensemble of long-chain molecules. Entanglements develop from the interpenetration of random-coil chains and are important in determining rheological, dynamic and fracture properties. By the introduction of a certain number of crosslinks or junctions between the chains at a very few points along their length it is possible to produce a network in which all the molecules are linked together and hence can no longer move independently. The structure
of the network depends on the kind and extent of the chemical crosslinking reaction. Mechanical properties of crosslinked elastomers are influenced not only by the volume average crosslink density but also by network heterogeneity. The influence of structural defects (such as residual sol, dangling chains, chain loops and the heterogeneity of the junction distribution) on the visco-elastic properties and the equilibrium swelling data is still under discussion. Local methods which probe molecular properties are very suitable for the determination of the degree of network heterogeneity.\textsuperscript{16}

**Several types of heterogeneity may occur in rubbery materials:**

1) molecular-scale heterogeneity, which is caused by the chemical heterogeneity of uncured elastomers, network defects and heterogeneous distribution of network junctions on a molecular level (Fig. 6.8).

![Schematic drawing of an ensemble of linear polymer chains being crosslinked into an infinite network](image)

**Fig. 6.8** Schematic drawing of an ensemble of linear polymer chains being crosslinked into an infinite network

2) Morphological heterogeneity of rubber compounds and other components due to spatially heterogeneous distribution in the rubber of coagents and fillers;

3) Spatial heterogeneity due to differences in curing conditions such as temperature and concentration of crosslinking agents throughout the sample volume.\textsuperscript{17}

Besides chemical crosslinks the following types of physical network junctions may occur in elastomeric materials:

(1) Temporary and trapped chain entanglements

(2) Junctions that are formed due to chain adsorption at the surface of active fillers
(3) Junctions that are formed by crystallites

(4) Junctions deriving from strong hydrogen and ionic bonds

(5) Junctions that are formed at the interface in polymer blends and in materials that reveal nano-scale phase separation.¹⁷

Knowledge about all the above mentioned types of junctions in the rubbery materials is important because the mechanical properties are influenced not only by the chemical crosslink density but also by the physical network junctions and network heterogeneity. In the case of peroxide-cured EPDM, the network has a complex structure with various types of chemical crosslinks, as well as both temporary and trapped entanglements. Usually, additional components such as residual sol, dangling chains, chain loops and differences in the distribution of the crosslinks may be present. Different types of network junctions are shown in Fig. 6.9.

The first picture in Fig. 6.9 shows an example of a perfect network, without entanglements and defects. The second and third pictures consist of the physical entanglements (temporary or trapped) between chains, by restricting the number of available configurations. The effect is comparable to that of a chemical crosslink and will tend to increase the modulus.

![Fig. 6.9 Types of functions compared to an ideal network](image)

The fourth type of junction occurs as a result of the linkage of two points on a single chain, giving rise to a closed loop which makes no contribution to the network elasticity. The fifth type consists of chains which are connected to the network at one end only; such terminal chains or loose ends make no contribution to the network elasticity.
In the case of filled rubbers or in the presence of coagents, the network structure is additionally complicated by physical and chemical interactions of the chains. The use of co-agents together with the peroxides can result in improved crosslink density. By use of the appropriate co-agent with the peroxide, properties such as dynamic flexibility, tear resistance and tensile strength can be improved to a level comparable or superior to the sulfur-cured systems, but with much better heat stability. There are various possible mechanisms for coagents to react. Since all common coagents contain terminal unsaturation, addition polymerization may be expected as the principal mechanism by which the co agents react in a rubber compound. It is well known that co agents can homo polymerize in domains, leading to co-vulcanization of these domains with the polymer.\(^{18,19}\)

These are the variables in the network structure that can be utilized to modify the properties of cured materials. However, they also cause difficulties in the analysis of network structures and complicate efforts to determine structure-property relationship.

In this thesis, effect of nanofillers [nano silica and nanoclay] on EPDM based peroxide cured vulcanizates have been studied and reported.

### 6.3 Results and discussion

#### 6.3.1. Rheological Studies of EPDM Nanoclay based PNCs

EPDM rubber compounding formulation was explained in chapter 2, in which the nanoclay and nanosilica were used as fillers at different loadings. Rheological data of EPDM based nanocomposites were reported in Table 6.1.

<table>
<thead>
<tr>
<th>Table – 6.1 Rheological properties of EPDM based nanocomposites</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rheological Properties</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Maximum torque, lbs</td>
</tr>
<tr>
<td>Minimum Torque, lbs</td>
</tr>
<tr>
<td>Ts1, min</td>
</tr>
</tbody>
</table>

Rajkumar.K 147
The effect of nanosilica in EPDM rubber composite is found strong in increasing the maximum torque as compared to that of nanoclay based EPDM rubber composites.

With increase in loading of nanosilica, maximum torque is found increasing which is due to the stronger interaction between the polymeric chains and nanosilica particles. It is evident from the data [Table 6.1] that nanosilica provides better interactive EPDM nanocomposites than that with nanoclay. The nano-clay found to have less interaction of polymer chains with nanoclay. Similar trend was found even with the minimum torque.

The Fig. 6.10 depicts scorch time and optimum cure time of nanocomposites containing nanofiller. These properties slightly increases with increase in dosage of nanofiller concentration, which could be due to intercalation of nano filler between the polymer matrix restricts the free radicals to come closures to cross linking and leading to hinder the curative and matrix interaction. The effect of nanosilica on OCT [t90] found to have reverse trend i.e., decreases which may be due to the fact that reactive groups present on the surface of silica nanoparticles might react with polymer and increase the rate of curing reaction.
6.3.2. Mechanical properties

Stress – Strain properties of nanocomposites were studied at room temperature using Zwick Tensile Tester. The results obtained from these stress – strain studies are depicted in Fig. 6.11.

![Graph showing stress-strain properties of nanocomposites](image)

(a) Tensile and Elongation. At break  
(b) Modulus properties

**Fig 6.11** Physical properties of EPDM - Nanoclay composites

The stress strain properties indicates that the nano filler improves the physical properties from 11 % to 20 % at an optimum level of 5 phr of nanosilica filler loading and then decreases with further loading (7 phr).

![Graph showing physical properties of EPDM Nanosilica composites](image)

(a)  
(b)  

**Fig 6.12** Physical properties of EPDM - Nanosilica composites

Fig. 6.12 illustrate physical properties [Tensile strength, Elongation at break, Modulus properties] of Nano silica based EPDM nanocomposites. As the Fig 6.12
indicates, after optimum loading of 5 phr of nanosilica fillers it acts as blocking agent between matrix and curing agent which reduces chemical interaction between two and consequently leads to weaken the strength and modulus of the cure compounds. The hardness was increasing from 67 to 70 as reported in Fig. 6.13 with the increase in nano filler loading from 0 to 7 phr.

![Graph](image1.png)

**Fig. 6.13** Hardness of EPDM (a) Nanoclay, (b) Nanosilica based Nanocomposites.

As Fig 6.13 indicates, hardness marginally increases with increase in loading of nanofillers. The fillers occupies the polymer matrixes and increases the stiffness and hence the resistance to deflection against the indentation of hardness.

### 6.3.3. Ageing studies

**Table 6.2** Retention of Physical Properties of EPDM based clay nanocomposites after ageing at 200 °C for 24 hrs

<table>
<thead>
<tr>
<th>Properties</th>
<th>Unit</th>
<th>ENC 0</th>
<th>ENC 3</th>
<th>ENC 5</th>
<th>ENC 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength</td>
<td>%</td>
<td>48</td>
<td>54</td>
<td>56</td>
<td>73</td>
</tr>
<tr>
<td>% Elongation at break</td>
<td>%</td>
<td>17</td>
<td>18</td>
<td>19</td>
<td>18</td>
</tr>
</tbody>
</table>

The after ageing properties (Table 6.2) indicates their retention of tensile strength and elongation at break are improved with introduction of clay doses.
Table 6.3 Retention of Physical Properties of EPDM based clay nanocomposites after ageing at 200 °C for 24 hrs

<table>
<thead>
<tr>
<th>Properties</th>
<th>Unit</th>
<th>ENS 0</th>
<th>ENS 1</th>
<th>ENS 3</th>
<th>ENS 5</th>
<th>ENS 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength</td>
<td>%</td>
<td>48</td>
<td>54</td>
<td>56</td>
<td>70</td>
<td>77</td>
</tr>
<tr>
<td>% Elongation at break</td>
<td>%</td>
<td>17</td>
<td>18</td>
<td>19</td>
<td>19</td>
<td>20</td>
</tr>
</tbody>
</table>

The after ageing properties (Table 6.3) indicates their retention of tensile strength and elongation at break are improved with introduction of silica doses.

6.3.4. Thermo-gravimetric analysis

Because ethylene–propylene–diene rubber (EPDM) is a widely used rubber in automotive and industrial rubber application including nuclear sectors, EPDM based nano composites shall have great commercial potential. Thermal stability of EPDM rubber based nanocomposites were investigated by Thermo gravimetric Analyzer [TGA] and the degradation behavior of the clay and silica based nanocomposites were shown in Fig. 6.14 & 6.15 respectively.

![Thermogram of EPDM based clay nanocomposites](image)

**Fig. 6.14** Thermogram of EPDM based clay nanocomposites
CHAPTER VI : Ethylene Propylene Diene Monomer [Epdm] Rubber Nanocomposites

The quantitative value of onset of degradation temperature and the temperature at which the maximum degradation has taken place also reported. For the nanocomposites, DTG curves show almost single-step degradation with well defined initial and final degradation temperature.

Table 6.4 Thermal Stability of EPDM nanoclay composite

<table>
<thead>
<tr>
<th>Nanocomposite code</th>
<th>Initial degradation Temp °C</th>
<th>Maximum degradation temp. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>ENC-0</td>
<td>422</td>
<td>448</td>
</tr>
<tr>
<td>ENC-3</td>
<td>424</td>
<td>451</td>
</tr>
<tr>
<td>ENC-5</td>
<td>426</td>
<td>453</td>
</tr>
<tr>
<td>ENC-7</td>
<td>427</td>
<td>454</td>
</tr>
</tbody>
</table>

The thermal stability of nanocomposites containing higher does of nano filler found to be more that that of less quantity fillers based nanocomposites.

Fig. 6.15 Thermogram of EPDM based silica nanocomposites

TGA study revealed that the initial degradation and maximum degradation due to thermal energy increases with increase in dose of nanosilica.
As the dose increases, the thermal stability of nanocomposites also increases. This result also corroborates with the resistance to thermal ageing at higher temperature. This is due to the reason of strong network with nanosilica – polymer interaction and hence, the strong bond between the polymer and filler leading to consumption of thermal energy for breaking the bond of Si-O-C in nanocomposites.

It is also seen that the nanocomposite containing nanosilica has more thermal stability than that containing nanoclay.

6.3.5. Electrical properties – Volume Resistivity of nanocomposites

Fig. 6.16 revealed that volume resistivity of EPDM Nanocomposites decreases with an increase of both the types of nanofillers. This could be due to the increase in network of conductivity within the EPDM matrix due to addition of conductive nanofillers.

![Fig. 6.16 Volume resistivity of EPDM based nanocomposites](image)
It is also seen that volume resistivity of EPDM vulcanizates with nanosilica show more significant decreases than that of the vulcanizates containing nanoclay. This shows that the nano silica contains more polarity due to Oxygen molecule than that of nanoclay resulting in the increase of conductivity of matrix.

### 6.3.6. Scanning electron microscopy & Energy Dispersive X-Ray Analysis

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>SEM IMAGES</th>
<th>EDS PLOT</th>
</tr>
</thead>
<tbody>
<tr>
<td>ENC-3</td>
<td><img src="image1.png" alt="SEM Image" /></td>
<td><img src="image2.png" alt="EDS Plot" /></td>
</tr>
<tr>
<td>ENC-5</td>
<td><img src="image3.png" alt="SEM Image" /></td>
<td><img src="image4.png" alt="EDS Plot" /></td>
</tr>
<tr>
<td>ENC-7</td>
<td><img src="image5.png" alt="SEM Image" /></td>
<td><img src="image6.png" alt="EDS Plot" /></td>
</tr>
</tbody>
</table>

*Fig. 6.17 SEM and EDS spectra of EPDM Clay Nanocomposites series*
Further to corroborate the above dispersion study, EDS spectroscopic studies were also taken on the scanned area of SEM micrographs to locate the dispersed silica Nano particles. The EDS spectra and these figures shows that as the loading of silica nano filler increases in the EPDM nanocomposites, the intensity of Nano Silica also found denser than that of the nano composite with the lower concentration of silica nano filler.
Fig. 6.19 (a) SEM image of ENS with 3 phr loading

Fig. 6.19 (b) EDS spectra of ENS with 3 phr loading

Fig. 6.19 (c) SEM image of ENS with 5 phr loading

Fig. 6.19 (d) EDS spectra of ENS with 5 phr loading

Fig. 6.19 (e) SEM image of ENS with 7 phr loading

Fig. 6.19 (f) EDS spectra of ENS with 7 phr loading

Fig. 6.19 SEM-EDS Analysis of Nano Silica Mapping in EPDM Rubber
6.3.7. X-Ray diffraction analysis:

Fig. 6.20 Overlay Plot of EPDM Clay Nanocomposites Series

Fig. 6.21 Overlay Plot of EPDM Silica Nanocomposites Series
CHAPTER VI : Ethylene Propylene Diene Monomer [Epdm] Rubber Nanocomposites

The XRD studies revealed that incorporation Nano Silica particles in EPDM polymer matrix leading to reduction in d spacing. This could be due to the intercalation of EPDM polymer chains between silica and clay nano particles. By the way it is seen the EPDM nano clay (Fig. 6.21) shows better peak value compared to EPDM nanosilica near 9 to 10, theta 2 theta values. Therefore it can be concluded that nanoclay (Fig. 6.22) shows better intercalation than nanosilica with EPDM rubber nanocomposite.

6.4 Fourier Transform Infra Red Analysis of nanocomposites

FT-IR spectra in the middle IR region (2000–400 cm\(^{-1}\)) were obtained on a Nicolet 6700 FT-IR spectrometer. The spectra were normalized to Si-O stretching band near 1041 cm\(^{-1}\) to enable direct comparison of the intensities of the absorption bands corresponding to vibrations of organic cations.

![FT-IR spectra of EPDM Nanoclay composites](image)

**Fig. 6.22** FT-IR spectra of EPDM Nanoclay composites

In the FT-IR–ATR spectra of EPDM (Fig. 6.23), there are bands at 1461 and 1376 cm\(^{-1}\), which originated from the deformation vibrations of the -CH\(_2\) group and the valention vibrations of the -CH\(_3\) in the propylene unit, respectively. The bands at 762 and
722 cm\(^{-1}\) present the deformation vibrations of \((-\text{CH}_2)\)_n-groups, where \(n \geq 5\), in the ethylene sequences of the EPDM backbone. \(^{(20,21)}\) At 861 cm\(^{-1}\), there is an absorption band, which originated from the deformation vibration of the C = C groups in ethylidene norbornene-ENB (EPDM rubber).

6.5 TEM study:

The nanostructure of the clay was observed in a transmission electron microscope (JEM-2100F, JEOL) with an accelerator voltage of 200 kV. The surface of the samples was first coated with gold and then a thin section of each specimen was prepared by using a focused ion beam (FB-2000A, Hitachi) and also a cryogenic ultra-microtome at 100 °C.

![TEM images](image)

(a) 3 Phr nanoclay  
(b) 5 Phr nanoclay  
(c) 7 phr nanoclay

**Fig. 6.23** TEM study of EPDM – Nanoclay composites

Fig. 6.24 depicts the picture of TEM study of EPDM – nanoclay polymer nano-composites and the picture revealed that the nanoclay was well dispersed within the EPDM polymer matrix.
6.6 Conclusion

1. Incorporation of nanofillers like Nanoclay and Nanosilica improves the physico-mechanical properties of nanocomposites. The increase in dosage of nanofillers showed the increasing trend for tensile strength and modulus properties till an optimum level and then decreases.

2. Thermal Characterization of EPDM nanocomposites were done using TGA and results revealed that the incorporation of nano fillers increases the minimum degradation temperature and maximum degradation of polymer nanocomposites [PNCs]. This was also corroborate with increase in thermal ageing studies of PNCs.

3. The enhancement of thermal stability of EPDM polymer nanocomposites was found to be more with nanosilica filler than that of nanoclay.

4. EPDM polymer nanocomposites containing nanofiller reduces the electrical resistance properties. The more reduction of volume resistivity was found for the nanocomposite containing nanosilica than that of polymer nanocomposites containing nanoclay.

5. FTIR-ATR studies indicated the presence of characteristics of functional groups of EPDM and nano fillers. This also revealed the presence of nanofillers dispersed within the polymer matrix.

6. The SEM / EDS spectra showed that the nanoparticles were well dispersed within polymer matrix and XRD studies confirmed the presence of nano fillers.

7. Picture of TEM study of EPDM – nanoclay polymer nanocomposites revealed that the nanoclay was well dispersed within the EPDM polymer matrix.

8. The incorporation of nanofillers in EPDM rubber compound decreases the volume resistively
6.7 References:

