CHAPTER IV
CHARACTERISATION

Characterizing the prepared polymer blends and composites for the presence of respective additives is a key step in material science. Presence of various functional groups within the matrices is ascertained by FT-IR spectroscopy. Changes in the structural arrangement of atoms, chains and layers within the samples are verified through XRD studies.

4.1 Fourier Transform-Infra Red (FT-IR) Spectroscopy

Fourier Transform Infra Red spectroscopy is an efficient tool in detecting the functional group present in a given sample. In polymer composites, FT-IR spectroscopy facilitates the identification of the type of chemistry of the bonds present in the blends thereby giving a clear view of the components and fillers present in the blend or composites.

4.1.1 EPDM-Neoprene Blends

Various blends were prepared by mixing differing percentages of neoprene with EPDM. The IR spectroscopic analysis was done to locate the presence of neoprene with EPDM.

The FT-IR spectrum of EPDM rubber (Figure 4.1) shows \( \text{C-H} \) stretching (2925 and 2580 cm\(^{-1}\)), \( \text{C=C} \) stretching (1630 cm\(^{-1}\)), \( \text{CH}_2 \) bending (1460 and 720 cm\(^{-1}\)) and \( \text{CH}_3 \) bending (1375 cm\(^{-1}\)) [1-3]. The signal at 910cm\(^{-1}\) is also characteristic of the EPDM rubber (=CH-CH\(_2\)-).

The infra red spectra of neoprene (CR) (10, 20 and 25phr)-filled EPDM have the signals corresponding to EPDM, as well as those (745, 819, 1376, and 1641 cm\(^{-1}\)) characteristic of neoprene (CR) rubber [7]. This is indicative of the blending of EPDM with neoprene rubber.
Figure 4.1: FT-IR spectrum of virgin EPDM (E)

Figure 4.2: FT-IR spectrum of EPDM/10% neoprene (E 10N)
Figure 4.3: FT-IR spectrum of EPDM/20% neoprene (E 20N)

Figure 4.4: FT-IR spectrum of EPDM/25% neoprene (E 25N)
4.1.2 CA-MMT filled EPDM/Neoprene composites

The IR spectra of both MMT and CA-MMT exhibit absorption band at 1090 cm⁻¹ which is characteristic of Na-MMT. The organoclay, CA-MMT exhibited the characteristic signals of C–H stretching at 2921 and 2850 cm⁻¹ as well as the one at 1469 and 724 cm⁻¹ related to -CH₂, establishing that the alkyl ammonium has been exchanged with cations of the MMT interlayer [4-5].

The FT-IR spectra of CA-MMT clay-filled EPDM and EPDM/neoprene blends shown in Figures 4.6 and 4.7 have the expected peaks in the region 1090, 2921, 2850, 1469, and 724 cm⁻¹ which are characteristic of the CA-MMT. This shows the presence of CA-MMT within the polymer layer of EPDM rubber matrix. The spectrum of EPDM/neoprene blend filled with CA-MMT (Figure 4.7) have absorptions at 745, 819, 1376, and 1641 cm⁻¹ which are characteristic of neoprene (CR) rubber [6] along with that of CA-MMT in the EPDM/neoprene composites.
Figure 4.5: FT-IR spectra of (a) MMT and (b) CA filled MMT
Figure 4.6: FT-IR spectrum of EPDM/5% CA-MMT (E 5M)

Figure 4.7: FT-IR spectrum of EPDM/20% neoprene/5% CA-MMT (E 20N 5M)
4.1.3 Kaolinite filled EPDM/Neoprene composites

In the IR spectrum of kaolinite (Figure 4.8), the peak at 3620 cm\(^{-1}\) corresponds to the inner O-H stretching, while the 3710 cm\(^{-1}\) peak corresponds to the in-phase stretching of the three inner-surface O-H groups, and the signals at 3669 cm\(^{-1}\) and 3652 cm\(^{-1}\) correspond to the anti-phase stretching modes of the inner-surface O-H groups. The absorption at 1008 cm\(^{-1}\) and 1032 cm\(^{-1}\) could be attributed to the anti-symmetric stretch of equatorial Si-O bonds. The in-phase stretch of apical Si-O bonds appears at 1134 cm\(^{-1}\) and the peak at 1090 cm\(^{-1}\) corresponds to the symmetric stretch of equatorial Si-O bonds. The absorption at 1090 cm\(^{-1}\) is characteristic of kaolinite [5].

After processing, the kaolinite-filled EPDM (Figure 4.9) exhibits the characteristic signals at 1090 cm\(^{-1}\) and 3710 cm\(^{-1}\) which are absent in the virgin EPDM. This suggests the presence of kaolinite layers within EPDM matrix. Also the difference in frequency of absorption of virgin EPDM and kaolinite-filled EPDM at 2700-3000 cm\(^{-1}\) shows a definite morphological change. The other characteristic peaks in the regions 1008, 1032, 1134, 3620, 3669 and 3652 cm\(^{-1}\) unequivocally establish the presence of kaolinite clay particles within the EPDM matrix [5].

The presence of characteristic peaks in the regions 1008, 1090, 1032, 1134, 3620, 3669, 3710 and 3652 cm\(^{-1}\) in the FT-IR spectrum of kaolinite-filled EPDM/Neoprene composites (Figure 4.10) is indicative of kaolinite clay particles within the EPDM matrix. The absorption peaks at 745, 819, 1376, and 1641 cm\(^{-1}\) are characteristic of neoprene (CR) rubber [7].
Figure 4.8: FT-IR spectrum of kaolinite
Figure 4.9: FT-IR spectrum of EPDM filled with 5% kaolinite (E 5K)

Figure 4.10: FT-IR spectrum of EPDM/20% neoprene/5% kaolinite (E 20N 5K)
4.1.4 Graphite filled EPDM/Neoprene Composites

The FT-IR spectrum of the graphite powder has a small sharp peak at 1657 cm\(^{-1}\) (Figure 4.11) which is characteristic of the C=C bonds present in the graphite layers. The broad band in the region 1000-1250 cm\(^{-1}\) is characteristic of vibrations between the graphene layers in graphite [8] and the broad band at 3300-3675 cm\(^{-1}\) may be due to possible moisture content.

The FT-IR spectrum of EPDM filled with 5%wt graphite (Figure 4.12) having a signal at 1657 cm\(^{-1}\) denotes the presence of graphite in the rubber matrix.

The presence of peaks at 745, 819, 1376, and 1641 cm\(^{-1}\) characteristic of neoprene (CR) rubber and sharp signal at 1656 cm\(^{-1}\) characteristic of graphite in the graphite-filled EPDM/neoprene composite (Figure 4.13) confirm the presence of both neoprene and graphite within the composite.

The FT-IR spectra of various blends and composites have established the effective presence of the respective components within the matrices.
Figure 4.11: FT-IR spectrum of graphite
Figure 4.12: FT-IR spectrum of EPDM/5% graphite (E 5G)

Figure 4.13: FT-IR spectrum of EPDM/20% neoprene and 5% graphite (E 20N 5G)
4.2 X-RAY DIFFRACTION STUDIES

The x-rays are found deflected from their direction by interaction with the nuclei or electrons of polymer/solvent molecules in a sample known as X-ray diffraction. Experiments in the range $0:6 < Q < 15 \text{ Å}^\circ$ provide most of the informations relevant to the determination of unit-cell dimensions and are conventionally referred to as wide-angle scattering, which probe a distance scale $0:4 < D < 10\text{ Å}^\circ$. Wide-angle x-ray scattering (WAXS), with a wavelength 1Å°, has been the principal technique for the determination of polymer crystal structures [7]. Unit cell dimensions [9], along with details of the WAXS technique [10] are given in standard reference works [7, 9 and 10].

Although Bragg’s law does not apply to perfectly amorphous materials, the Fourier or inverse relationship between the structure in real-space ($r$) and the scattering in Q-space, means that $D = 2\pi/Q$ may be applied to all first order types of scattering. Thus, data at lower Q-values probe longer length scales, and x-ray methods have been widely used to determine chain dimensions in dilute solution, lamellar spacing in crystalline polymers, etc [11].

For most applications in polymer science, x-ray scattering is an example of predominantly elastic scattering, where the incident and scattered radiation have the same energy or wavelength. Such experiments give information on the time-averaged structure and conformation of polymer molecules.

Molecular structure in some resins could be attributed to the existence of solid crystals with a definite geometric form. Such structures are characterized by lattice formation and compactness with certain percentage of the polymer sample forming crystals. Crystallinity in polymers occurs in two stages: nucleation and growth of nuclei. In most materials, crystallinity occurs from growing nuclei to produce repeating units that form lattices throughout the material.
Polymers can be crystalline, semi-crystalline or amorphous. Crystallinity in a polymer exhibits a distinct endothermic energy transition or melting event taking place through destruction of lattice structure whereas a non-crystalline polymer shows a glass transition event or just softening. The crystallinity is calculated here based on the intensity of crystalline and amorphous states obtained from the XRD plots. The percentage crystallinity and crystal index are evaluated from,

\[
\text{Percentage (\%) Crystallinity} = \frac{I_c}{I_c + I_a} \times 100
\]

\[
\text{Crystallinity Index} = \frac{I_c - I_a}{I_c}
\]

where, \(I_c\) is the intensity of crystalline phase and \(I_a\) is the intensity of amorphous phase.

### 4.2.1 Functionalization of MMT to CA-MMT

The X-ray diffraction patterns of MMT and CA-MMT (Figure 4.14) indicate that the silicate layer (001) reflection of MMT has a peak position at \(2\theta = 7.35\) while for CA-MMT, the peak position is at \(2\theta = 4.7\). Calculations from peak positions using Bragg’s law, give the \(d_{001}\) spacing of MMT as 1.21nm and that of CA-MMT as 1.9nm. The increase of interlayer spaces lowers the interlayer attractive force. The cetyl ammonium group has entered in between the layers of the MMT clay thereby increasing the layer spacing. Thus introduction of alkyl group in the MMT clay has introduced intercalation of the clay layers.
Table 4.1: Crystallinity of the Blends and Composites

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>% Crystallinity</th>
<th>Crystal Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>71.41</td>
<td>0.5996</td>
</tr>
<tr>
<td>E 5N</td>
<td>71.08</td>
<td>0.5931</td>
</tr>
<tr>
<td>E 10N</td>
<td>71.33</td>
<td>0.5989</td>
</tr>
<tr>
<td>E 15N</td>
<td>71.45</td>
<td>0.6004</td>
</tr>
<tr>
<td>E 20N</td>
<td>71.47</td>
<td>0.6009</td>
</tr>
<tr>
<td>E 25N</td>
<td>72.70</td>
<td>0.6246</td>
</tr>
<tr>
<td>E 20N 5M</td>
<td>71.82</td>
<td>0.6077</td>
</tr>
<tr>
<td>E 5M</td>
<td>72.80</td>
<td>0.6265</td>
</tr>
<tr>
<td>E 20N 5M</td>
<td>71.82</td>
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</tr>
<tr>
<td>E 7K</td>
<td>74.71</td>
<td>0.6615</td>
</tr>
<tr>
<td>E 20N 7K</td>
<td>73.32</td>
<td>0.6361</td>
</tr>
<tr>
<td>E 5G</td>
<td>73.05</td>
<td>0.6311</td>
</tr>
<tr>
<td>E 20N 5G</td>
<td>70.63</td>
<td>0.5843</td>
</tr>
</tbody>
</table>

Figure 4.14: Small angle XRD spectra of MMT and CA-MMT
4.2.2 EPDM/Neoprene Blends

The XRD pattern of EPDM/neoprene blends (Figure 4.15 to 4.19) shows an initial decrease and steady increase of crystallinity on addition of neoprene to EPDM matrix. Initially when neoprene was added to EPDM, the 2θ value decreased to 19.29° from 20.76°. This is significant when crystallinity decreases from 71.41 to 71.08%. On further addition of neoprene, the angle steadily increased thereby showing a small increase in crystallinity to 72.70% for EPDM filled with 25 phr of neoprene.

The crystal index also initially decreases on introduction of neoprene into EPDM from 0.5996 to 0.5931 and then on further addition of neoprene it increases to 0.6246 (E 25N). This increase may be due to the crystalline nature of neoprene compared to EPDM. However smaller additions of neoprene has failed to increase the crystallinity of the blend, as it (neoprene) gets dissolved in the EPDM, increasing the disorder in the system.
Figure 4.15: XRD pattern of EPDM (E)

Figure 4.16: XRD pattern of 5% Neoprene filled EPDM (E 5N)
Figure 4.17: XRD pattern of 10% Neoprene filled EPDM (E 10N)

Figure 4.18: XRD pattern of 20% Neoprene filled EPDM (E 20N)
Figure 4.19: XRD pattern of 25% Neoprene filled EPDM (E 25N)
4.2.3 CA-MMT filled Composites

The alkyl functionalized MMT clay when applied to EPDM and EPDM/neoprene blend, composites with intercalated structures were obtained. The XRD peak for CA-MMT (Figure 4.20) at 17.84° is missing from the XRD pattern of the composites (Figure 4.21, 4.22), revealing the introduction of dislocation in the layers of the CA-MMT, which is already functionalized to a small increase in the inter-layer distance. This shows symptoms for formation of nanocomposites to be inferred from SEM analysis. Most of the other peaks of the CA-MMT clay remain unaltered in the XRD pattern of the CA-MMT filled composites.

The peak at 2θ° representing polymers, shows a small decrease of the angle 2θ value from 20.63 for CA-MMT filled EPDM to 20.0° for CA-MMT filled EPDM/neoprene blend. This decrease in angle (2θ) on introduction of neoprene has decreased the crystallinity of the composites (72.80 to 71.82%). Addition of neoprene has disturbed the higher order crystallinity shown by the clay filled EPDM composites. The neoprene added might have retarded the cross-linking density of the polymer (crystal index has also decreased from 0.6265 to 0.6077).
Figure 4.20: XRD pattern of Cetyl Ammonium Modified MMT (CA-MMT)

Figure 4.21: XRD pattern of EPDM/5% CA-MMT (E 5M)
Figure 4.22: XRD pattern of EPDM/20% Neoprene /5% CA-MMT (E 20N 5M)
4.2.4 Kaolinite filled Composites

From the X-ray profile of kaolinite (Figure 4.23), EPDM (Figure 4.15) and the kaolinite-filled EPDM (Figure 4.24), the basal spacing of (001) and (002) planes are $7.214 \times 10^{-1}$ nm and $3.587 \times 10^{-1}$ nm respectively, showing the characteristic peaks of kaolinite in Figure 4.23 and 4.24. The absence of other characteristic diffraction peaks of kaolinite in Figure 4.24 between $20^\circ$-25$^\circ$ and 35$^\circ$-40$^\circ$ goes to prove the special directional and parallel arrangements of kaolin platelets within the rubber matrix, consistent with the dispersed pattern observed from the SEM analysis (discussed later). Further, the EPDM polymer has also intercalated between the layers of the kaolinite as shown by the increase in d-spacing with the consequent shifting of 2θ value (24.97 to 24.73).

Further, when neoprene is included in EPDM/kaolinite composites (Figure 4.25), there is no shift in the 2θ value indicating the absence of further intercalation of the kaolinite layer on the introduction of neoprene within the matrix which is due to the non-expandable nature of kaolinite. Also, the other characteristic peaks of kaolinite are absent as in the case of EPDM/kaolinite composites (Figure 4.24).

Comparing the position of peak of the polymer at the region around $20^\circ$ in the EPDM/kaolinite composite (Figure 4.24) and EPDM/neoprene/kaolinite composite (Figure 4.25), there is a small decrease on the addition of neoprene (20.43 to 19.89$^\circ$). Moreover, a decrease in the crystallinity from 74.71 to 73.32%, shows a similar trend with that of the CA-MMT filled composites where inclusion of neoprene has reduced the crystallinity of the polymer clay-filled composites. The crystal index also decreases from 0.6615 for EPDM/kaolinite composites to 0.6361 for EPDM/neoprene/kaolinite composites. Thus the addition of neoprene
Figure 4.23: XRD pattern of Kaolinite

Figure 4.24: XRD pattern of EPDM/7% Kaolinite (E 7K)
Figure 4.25: XRD Pattern of EPDM/20% Neoprene/7% Kaolinite (E 20N 7K)
has introduced a decrease in the cross-linking density of the composites due to the difference in monomer type.

### 4.2.5 Graphite filled Composites

In the graphite-filled composites the XRD peak of the polymer is around $20^\circ$. The maximum intensity of the EPDM-graphite composites (Figure 4.27) is at $20.6^\circ$ whereas in EPDM/neoprene-filled graphite composites (Figure 4.28) it is at $20.1^\circ$. This small change due to the presence of neoprene has reduced the crystallinity from 73.05 to 70.63%. The crystal index of the graphite-filled EPDM composites (0.6311) decreases (0.5843) for EPDM/neoprene blend filled with graphite. This decrease in crystallinity may be attributed to the decrease in cross-linking density by the introduction of neoprene within the EPDM matrix. In the other filler added composites too, addition of neoprene has reduced the crystallinity.

Comparing the X-ray diffractograms of graphite (Figure 4.26) and the graphite filled composites (Figure 4.27-4.28), there is no significant change in position of the peaks of graphite. This shows that no exfoliation or intercalation of the graphite layers has taken place during the processing of the materials. The preparation conditions are not sufficient enough to impart any change in the graphite layers.
Figure 4.26: XRD pattern of Graphite
Figure 4.27: XRD Pattern of EPDM/5% Graphite (E 5G)
Figure 4.28: XRD pattern of filled EPDM/20% Neoprene/5% Graphite (E 20N 5G)
4.3 References


