Chapter 6
Dynamic Mechanical Analysis

Abstract

Dynamic mechanical analysis is a valuable tool for structural analysis of polymers and can be used to predict the miscibility of polymeric blend systems. In this chapter, the dynamic mechanical properties such as storage modulus, loss modulus and tanδ were discussed with special reference to the effect of blend ratio, compatibilisation and dynamic vulcanization over a temperature range −100 to 150°C. The experiment was performed over a series of frequencies. Attempts have also been made to correlate the dynamic mechanical properties with the morphology of the system. The experimental storage modulus data were compared with theoretical predictions.

The results discussed in this chapter have been accepted for publication in EXPRESS Polymer Letter.
6.1 Introduction

Thermoplastic elastomers (TPEs) are being used in a variety of applications because of their desirable mechanical properties and recyclability [1,2]. Polymers and their blends are viscoelastic materials, which have the combined characteristics of a viscous liquid and elastic solid. Elastic materials have a capacity to store mechanical energy with no dissipation of energy; on the other hand, a viscous fluid has a capacity for dissipating energy. When polymeric materials are deformed, part of the energy is stored as potential energy and part is dissipated as heat. The energy dissipated as heat manifests itself as mechanical damping or internal friction. Therefore the interpretations of these properties at molecular level are of great scientific and practical importance in understanding the mechanical behaviour of the polymers.

Dynamic mechanical thermal analysis (DMTA) has proved to be an effective tool in the characterisation studies of viscoelastic materials. This test method is widely used for investigating the structure and viscoelastic behaviour of polymeric materials for determining their stiffness and mechanical damping characteristics of a cyclically deformed material as a function of temperature for various applications.

In dynamic mechanical thermal analysis (DMTA), the sample is subjected to an alternating sinusoidal strain and the stress is measured simultaneously. Since the stress and strain are generally not in phase, modulus and phase angle (damping term) can be determined. Dynamic mechanical results are generally given in terms of complex moduli, $E^*$ which can be represented as

$$E^* = E' + iE''$$  \hspace{1cm} \text{...........(6.1)}$$
Where \( E' \) is the real part of the modulus and \( E'' \) is the imaginary part of the modulus. \( E' \) is the storage modulus (in phase modulus) due to the stored elastic energy in the material and \( E'' \) is the loss modulus (90° out of phase modulus) due to viscous dissipation. \( E' \) represents the elastic response and \( E'' \) represents the viscous response of a material when it is subjected to a deformation. The angle that reflects the time lag between the applied stress and strain is \( \delta \) (the ratio of the moduli) and is defined by

\[
\tan \delta = \frac{E''}{E'}
\]

The dynamic properties are of direct relevance to a range of unique polymer applications concerned with isolation of vibrations or dissipation of vibrational energy in engineering components. This technique helps us to evaluate glass transition temperature (\( T_g \)) of the blends and the individual components from which we can assess the miscibility of the blends. A single \( T_g \) for the blends is an indication of miscibility, while two separate \( T_g \)'s indicate immiscibility of the system. The dynamic mechanical properties like storage modulus (\( E' \)), loss modulus (\( E'' \)), and loss tangent (\( \tan \delta \)) of polymer blends are sensitive not only to different molecular motions but also to various transitions, relaxation processes, structural heterogeneity, extent of crosslinking and the morphology of multiphase systems. The damping in the system or energy loss per cycle can be measured from the tangent of the phase angle.

Several researchers [3-10] have investigated effects of blend ratio, compatibilisation and dynamic vulcanisation on the dynamic mechanical properties. Bhowmick and Datta [11] used DMTA for studying the miscibility of ethylene propylene rubber (EPR) and chloro-sulphonated polyethylene (CSPE) rubber blends. They found that EPR exhibited \( T_g \) at -43°C and CSPE exhibited \( T_g \) at -14°C. The presence of two transitions
clearly indicated the immiscibility of the blend. Al-Malaika and Kong [12] studied the compatibilisation of functionalised EPR with GMA. Examination of the DMA of the reactive and physical compatibilised blends shows a smaller separation between the glass transition temperatures. Rajan et al. [13] have studied the dynamic mechanical properties of PP in the thermoplastic elastomeric state. The $\alpha$- relaxation peaks of PEEK and PES and their blends were studied by Nandan et al. [14]. Sirqueira and Soares [15] have studied the dynamic mechanical properties of the functionalized ethylene propylene diene rubber (EPDM) in natural rubber/EPDM blends. Karger-Kocsis and Kis [16] have investigated morphology and dynamic mechanical properties of EPDM/PP blends and PP block polymers. In these blends as the concentration of EPDM increases, $E'$ of the blends decreases. The dynamic mechanical spectrum showed two separate damping peaks and therefore has a two-phase morphology indicating that the blend is incompatible. Guo et al. [17] studied dynamic mechanical properties of PA6/PS blend by the addition of poly(styrene-b-ethylene oxide) (SbEO). It has been reported that compatibility and mechanical properties of the blends PA6/PS can be improved by addition of poly(styrene-b-ethylene oxide) (SbEO). Krishnaswamy et al. [18] and GopaKumar et al. [19] found that the compatibilisation does not affect the transition temperature of the respective components while several other researchers [20-22] have reported that the incorporation of the compatibiliser leads to obvious shifting of $T_g$s. These authors are of the opinion that the effect of compatibilisers on the position of $T_g$ is a reflection of the extent of compatibilisation. Moly et al. [23] have studied the effect of compatibilisation on the dynamic mechanical properties of LLDPE/EVA blends and found that compatibilisation increased the storage modulus of the system which is due to the fine
dispersion of EVA domains in the LLDPE matrix providing an increased interfacial interaction.

In this chapter, effects of blend ratio, compatibilisation and dynamic vulcanization on the dynamic mechanical properties of nylon copolymer/EPDM blends were investigated. Viscoelastic properties like storage modulus, loss modulus and tan δ were evaluated as a function of temperature. The area under the loss curve is evaluated to investigate the damping behaviour. The dynamic mechanical properties have been correlated with the morphology of the blends. Attempts have also been made to correlate the experimental viscoelastic data with various theoretical models.

6.2 Results and Discussion

6.2.1 Effect of blend ratio (Uncompatibilised blends)

The results of dynamic mechanical analysis add information about the behaviour of the blends and phase morphology. The effects of temperature and blend ratio on the storage modulus (E') of the samples at a frequency of 10Hz are given in the Fig. 6.1.
Figure 6.1: Storage modulus (E') curves as function of temperature for nylon, EPDM and their blends

The value of storage modulus, E' signifies the stiffness of the material. All the curves show three distinct regions: a glassy high modulus region where the segmental mobility is restricted, a transition zone where a substantial decrease in the E' values with increase of temperature and a rubbery region (the flow region) where a drastic decay in the modulus with temperature. The storage modulus curve of EPDM (N₀) shows a typical behaviour of an unvulcanised elastomer. EPDM shows a high modulus below its Tₑ followed by a drastic drop in its magnitude around -52°C which indicates distinct transition from glassy to rubbery state. At any fixed rate of deformation, the temperature at which E' starts to decrease rapidly corresponds to the Tₑ. But in the case of nylon, changes in the storage modulus are less severe around the glass transition zone because of its semi-crystalline nature. In the semi-crystalline materials like nylon, the crystalline chains are arranged in a regular order, and it will remain intact until the temperature reaches the melting point (Tₘ). Only the amorphous part undergoes segmental motion. So, in the case of nylon, the storage modulus decreases to a smaller extent than EPDM does in the transition.
It may be noted that nylon has the maximum and EPDM has the minimum $E'$ values. The $E'$ values of the blends are found to be intermediate between those of pure components depending on the proportion of EPDM. At very low temperature, modulus of the blends are high. The blends show transition and plateau region corresponding to EPDM and Nylon. The Storage modulus decreased with increase in temperature and finally levels off at high temperature. It is seen from the Fig. 6.1 that the value of storage modulus decreases with increase in the concentration of EPDM content, which is more pronounced at the high temperatures. On adding more EPDM, the crystallinity is reduced. Therefore the modulus of EPDM rich blends decreases much faster at high temperatures. EPDM is having very low modulus in the rubbery plateau. The two-step curves in the figure for the blends are due to two-phase morphology indicating immiscibility. The above results are very much in agreement with the studies of Karger-Kocsis and Papke [24]. The change from dispersed phase morphology in $N_{30}$ to co-continuous morphology in $N_{50}$ leads to an increase in modulus. In co-continuous structures the storage modulus-temperature dependence reflects a greater contribution of both components, whereas in dispersed structures, the blend modulus is dominated by the matrix component [25-27]. The relationship between $E'$ at a given temperature can also determine the region of phase inversion and the existence of co-continuous structures, as shown by Dedecker and Groeninckx [28] for reactivity compatibilised PA6/PMMA blends.

Variation of loss modulus ($E''$) with temperature of nylon, EPDM and nylon/EPDM blends is given in Fig. 6.2.
Figure 6.2: Loss modulus ($E''$) curves as function of temperature for nylon, EPDM and their blends

The loss modulus peak corresponds to the maximum heat dissipation per unit deformation. The $T_g$ was selected as the peak position of $E''$ when plotted as a function of temperature. From the figure, it is clear that $N_{100}$ shows a peak around 13°C corresponding to the $T_g$ of nylon whereas EPDM ($N_0$) shows a peak around -44°C. Another important observation that can be made from the figures is that nylon exhibits a strong $\beta$ relaxation around -57°C. However two distinct peaks each exactly corresponding to the $T_g$ of nylon and EPDM can be observed in all the blends indicating the incompatibility and immiscibility between the phases. The loss modulus increases with increase in EPDM content. The chain mobility of the polymer can be understood from the area under the loss modulus versus temperature curve [29].

Various researchers [28,24,30-32] used dynamical mechanical investigation to predict the miscibility of polymeric systems. Generally for incompatible system, the tan $\delta$ verses temperature curve shows two damping peaks corresponding to the $T_g$ of individual polymers [24]. When blend components are compatible, a single peak is found for the combined
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processes [31]. Broadening of the transition occurs in the case of partially compatible systems [32]. Shift in the \( T_g \) to higher or lower temperatures as a function of composition also indicates the partial miscibility or compatibility. Fig. 6.3 shows the variation of loss tangent (\( \tan \delta \)) with temperature for the neat polymers and nylon/EPDM blends. The main relaxation processes in the amorphous region for the nylon and EPDM phases in the blends can be detected from the damping curves presented in the Fig. 6.3.

![Figure 6.3: Tan \( \delta \) curves as function of temperature for nylon, EPDM and their blends](image)

As the temperature increases, damping goes through a maximum near \( T_g \) in the transition region, and then a minimum in the rubbery region. At \( T_g \), micro-Brownian motion of molecular segments begins where short range diffusion can take place. The damping is low below \( T_g \) because thermal energy is insufficient to cause rotational and transnational motions of the segments [33]. As a result of this, the chain segments are frozen in. So, below \( T_g \), the molecular slip resulting in viscous flow is low. Above \( T_g \) also the damping is low because molecular segments are very free to move
about and there is little resistance for their flow. Hence, when the segments are either frozen in or are free to move, damping is low. In the transition region a part of the segments are free to move about and the remainder are not so free. A frozen segment stores energy through deformation and it ultimately releases it as viscous energy when it becomes free to move. The tan δ curve of EPDM shows a peak at -32°C due to the α-transition arising from the segmental motion. This α-transition corresponds to the $T_g$ of EPDM. Nylon shows the glass $T_g$ at 26°C.

Another important observation that can be made from the Figs. (6.2 & 6.3) is that nylon exhibits a strong β relaxation [34] around -55°C. It is believed that the β damping peak is due to the rotational motion of water molecules [35] and/or the water/polymer complex [36]. It has also been observed that the position and height of the β peak depends on the concentration of the absorbed water [37]. The temperature of this peak is influenced by nylon moisture content. Some researchers related this secondary transition to movements involving carbonyl groups, which have formed hydrogen bonds with absorbed water [38,39]. The absence of the β relaxation peaks in the blends indicates that addition of EPDM into nylon decreased the water uptake property of nylon (Chapter 9). EPDM has higher damping than nylon because of its rubbery nature and the flexible rubber chains respond rapidly towards a cyclic loading. Since the rubber is uncrosslinked, the uncoiling and recoiling process on the application and removal of the stress makes more permanent deformation and thereby registering the highest loss tangent ($\tan \delta_{max}$) values. As can be seen from the figures, all the blend compositions show two distinct and clearly separate tan δ peaks corresponding to the $T_g$s of nylon and EPDM indicating that the blends are incompatible. The $T_g$ values obtained from the loss modulus curve and tan δ curves are given in Table 6.1.
As usual, the $T_g$ values obtained from $E''$ curves are lower than those from tan $\delta$ curves. The $T_g$ values taken from the tan $\delta$ peaks of virgin polymers and blends at different frequencies are given in Table 6.2. In all cases the $T_g$ values increase with the frequency. As the mechanical frequency is increased the position of the glass-rubber transition moves to a higher temperature because the polymer chains need more energy to respond to the shorter time scale stresses imposed at higher frequencies. The shift in the $T_g$ values upon the addition of the EPDM especially at higher concentrations of EPDM may be due to enhanced chain mobility of nylon due to the plasticising action of the flexible EPDM phase. The EPDM has got the highest damping peak height. It is accepted that higher the tan $\delta_{\text{max}}$ the greater the mechanical losses.
Table 6.2: $T_g$ ($^\circ$C) values of various nylon/EPDM blends at various frequencies obtained from $\tan \delta_{\text{max}}$

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>$N_0$</th>
<th>$N_{30}$ Due to EPDM</th>
<th>$N_{30}$ Due to nylon</th>
<th>$N_{50}$ Due to EPDM</th>
<th>$N_{50}$ Due to nylon</th>
<th>$N_{70}$ Due to EPDM</th>
<th>$N_{70}$ Due to nylon</th>
<th>$N_{100}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>-41</td>
<td>-45</td>
<td>17</td>
<td>-47</td>
<td>20</td>
<td>-51</td>
<td>17</td>
<td>13</td>
</tr>
<tr>
<td>1</td>
<td>-38</td>
<td>-39</td>
<td>20</td>
<td>-42</td>
<td>22</td>
<td>-47</td>
<td>21</td>
<td>19</td>
</tr>
<tr>
<td>10</td>
<td>-32</td>
<td>-31</td>
<td>31</td>
<td>-37</td>
<td>27</td>
<td>-44</td>
<td>26</td>
<td>26</td>
</tr>
</tbody>
</table>

These losses are related to high energy input required for the motion of the molecular chains of the polymer as the transition is being approached [40]. The results also suggested that increasing the rubber content caused an increase of elastic behaviour. A small hump in the $\tan \delta$ peak at lower temperature (-73°C) of $N_{30}$ may be due to motion of the side chain and imperfection.

The damping behaviour of the blends increases with an increase in the concentration of EPDM rubber. The variation of $\tan \delta_{\text{max}}$ of blend as a function of EPDM content measured at 10Hz is shown in the Fig. 6.4. EPDM shows maximum value of $\tan \delta$ indicating its excellent damping behaviour. In the blends with nylon, the crystalline plastic phase acting as physical crosslinks imposes some restriction towards cyclic loading and the $\tan \delta_{\text{max}}$ decreases with increases in nylon content. The increase in the damping and $\tan \delta_{\text{max}}$ with increase in EPDM content is due to the reduction in the crystalline volume of the system on increasing the concentration of EPDM whose damping is always higher than nylon.
Figure 6.4: Variation of $\tan \delta$ of nylon, EPDM and nylon/EPDM blends with EPDM content

The increase in $\tan \delta_{\text{max}}$ of N$_{30}$ (70% of EPDM) in the Fig. 6.4 can be explained on the basis of morphological changes. Examination of the morphology of the blends by scanning electron microscope (Chapter 3 Fig. 3.2) reveals that for blends containing 70% EPDM, the nylon phase is dispersed as spherical particles (observed as semi-spherical holes after etching by hot xylene to remove the EPDM phase) in the continuous EPDM matrix. In N$_{30}$, the rubber phase has become continuous and its response towards a cyclic loading is more effective and thereby exhibiting highest $\tan \delta_{\text{max}}$. In N$_{70}$, nylon is found to form the continuous phase in the blends due to its increased concentration. In this contribution of rubber towards $\tan \delta_{\text{max}}$ is restricted by the crystalline plastic phase. N$_{50}$ blend shows a co-continuous morphology and the rubber particles exist as large domains and their contribution towards $\tan \delta_{\text{max}}$ is increased. SEM micrographs of the blends show a clear two phase morphology with the rubber particles being coarsely dispersed in the continuous nylon phase and
having clear and sharp interfacial boundaries which may be attributed to high interfacial tension indicating poor adhesion at phase boundaries, and this is a manifestation of the incompatibility of the polymer components in these blends. It is well known that blends based on immiscible polymer pairs are characterized by high interfacial tension, which makes the dispersion during the blending operation difficult, and contributes to unstable morphology and poor adhesion [41-43].

The activation energy, $E$ for the glass transition of the blends can be calculated from the Arrhenius equation.

$$\log f = \log A - 2.030E/RT \quad \text{(6.3)}$$

Where $f$ is the experimental frequency of transition, $A$ is the frequency factor, $E$ is the activation energy, $R$ is the universal gas constant, $T$ is the temperature corresponding to the maximum of the tan $\delta$ curve in Kelvin scale (K). The plots of $\log f$ versus $1/T$ were constructed and the values of the activation energies were calculated from the slope of the plots. The slope corresponds to the activation energy of the viscous flow that accompanies the glass transition. The Arrhenius plot corresponding to EPDM transition in 70/30 nylon/EPDM blend is given in the Fig. 6.5.

**Figure 6.5:** Arrhenius plot corresponding to EPDM transition in 70/30 nylon / EPDM blends
Activation energy values are given in the Table 6.3. The blends show higher activation energy than the EPDM. Due to the amorphous nature of the EPDM, it is less sensitive to temperature and hence the activation energy decreases with increase in EPDM content. The chain flexibility increases with increase in the rubber content. As the flexibility increases, the crystallinity decreases and the activation processes becomes much easier. As a result of this the activation energy decreases.

**Table 6.3: Activation energy for the transition of EPDM phase in Nylon/EPDM blends**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation energy (E)(J/mol⁻¹) for EPDM phase transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₇₀</td>
<td>423</td>
</tr>
<tr>
<td>N₅₀</td>
<td>261</td>
</tr>
<tr>
<td>N₃₀</td>
<td>189</td>
</tr>
<tr>
<td>N₀</td>
<td>51</td>
</tr>
</tbody>
</table>

### 6.2.2 Theoretical analysis of storage modulus

Model studies were carried out to assess the behaviour of the two-phase blend from the component property data. The various composite models such as Parallel, Series, Coran's, and Thakayanagi have been used to predict the viscoelastic behaviour of the binary blends. All the models were once explained in chapter 3, under mechanical properties. Only the difference may be given.
Figure 6.6: Experimental and theoretical curves of storage modulus of Nylon/EPDM blends as a function of volume fraction of nylon at 25°C.

The curves resulting from the different theoretical models and that of the experimental data for the variation of storage modulus at 25°C with volume fraction of nylon are given in the Fig. 6.6. Coran’s model (n=2) fits well with the experimental curve and the Takayanagi model with 45% parallel coupling agrees to some extent with the experimental curve. The series is the lower bound over the entire composition range.

6.2.3 Effect of compatibilisation

As discussed in the above section, the nylon copolymer/EPDM blends are incompatible. The incorporation of a compatibiliser into an immiscible blend reduces the interfacial energy of the phases, stabilizes the morphology against coalescence and improves the interfacial adhesion. As a result, systems with improved and reproducible properties are obtained.
The variation of $E'$ as a function of temperature for 70/30 nylon/EPDM blends compatibilised with different concentrations of EPM-g-MA is shown in the Fig. 6.7.

![Diagram showing the variation of $E'$ as a function of temperature for different compatibilised blends.](image)

**Figure 6.7:** Effect of compatibilisation on the variation of storage modulus as a function of temperature in $N_{70}$ blends

The $E'$ values of compatibilised $N_{70}$ blends are higher than that of uncompatibilised blend at the same temperature. The addition of EPM-g-MA makes the blend technologically compatible to some extent even though molecular level miscibility cannot be achieved. Even by the addition of 1% compatibiliser, the $E'$ of the blends shifted towards the lower temperatures, i.e., below the $T_g$ of nylon. The increase in the modulus upon the addition of the compatibiliser is due to the increase in the interfacial adhesion caused by the emulsifying effect of the copolymer formed by the reaction between EPM-g-MA and nylon. The presence of compatibiliser improves the interfacial adhesion by enhancing the interfacial thickness and thereby facilitating the stress transfer between the components. The increased interfacial interaction is evident from the small and uniform dispersion of EPDM particles upon the addition of EPM-g-MA (Chapter 4 Figure 4.5). A decrease in $E'$ by the addition of 10wt% EPM-g-MA indicates the formation of micelles in the nylon matrix. At higher loading of
the compatibiliser, modulus value decreases due to the formation of agglomerates of the compatibiliser molecule. At a temperature above 60°C all the blends show nearly the same values of $E'$. 

Now let us consider the effect of compatibilisation on the $T_g$'s of the blends. Fig. 6.8 depicts the change of loss modulus ($E''$) as a function of temperature for nylon/EPDM blends compatibilised by EPM-g-MA.

![Figure 6.8: Effect of compatibilisation on the variation of loss modulus as a function of temperature in $N_{70}$ blends](image)

The $E''$ values of the compatibilised systems are higher than those of $N_{70}$ uncompatibilised blend. The shifts in the $T_g$ values of the nylon phase of the compatibilised blends compared to the uncompatibilised blends indicate the strong interaction between the nylon and EPDM as a result of reactive compatibilisation. Thus a shifting of $T_g$ values of the components is taken as an indication of miscibility enhancement and therefore can be considered as an evidence for compatibilisation [42]. Due to the interfacial chemical reaction, the mobility of the nylon phase decreases. In the compatibilised blends the linked segments do not have the degree of mobility as the unlinked segments have, so that the effective number of segments free to completely relaxed has decreased. So there is a shift towards lower $T_g$. The $T_g$ values obtained (Table
6.4) from $E''$ vs temperature is always less than that obtained from $\tan \delta$ maximum.

Table 6.4: Effect of compatibilisation on the $T_g$ values of EPDM and nylon in N70 blends at 10Hz

<table>
<thead>
<tr>
<th>Blends</th>
<th>Glass transition temperature ($^\circ$C)</th>
<th>Glass transition temperature ($^\circ$C)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>From $E''$ vs. T curve</td>
<td>From $\tan \delta$ vs. T curve</td>
</tr>
<tr>
<td></td>
<td>EPDM Phase</td>
<td>Nylon Phase</td>
</tr>
<tr>
<td>N70</td>
<td>-46</td>
<td>16.7</td>
</tr>
<tr>
<td>1% Compatibiliser</td>
<td>-44</td>
<td>-11</td>
</tr>
<tr>
<td>2.5% Compatibiliser</td>
<td>-44</td>
<td>-9.3</td>
</tr>
<tr>
<td>5% Compatibiliser</td>
<td>-44</td>
<td>-9.3</td>
</tr>
<tr>
<td>10% Compatibiliser</td>
<td>-38</td>
<td>-12</td>
</tr>
</tbody>
</table>

The DMA is a classical method for the determination of miscibility because the height and position of the mechanical damping peaks are affected remarkably by miscibility, intermolecular interaction, interface feature and morphology. The variation of $\tan \delta$ as a function of temperature of the compatibilised blends is given in the Fig. 6.9. The compatibilised blends also show the presence of two peaks corresponding to the $T_g$'s of Nylon and EPDM similar to those of the uncompatibilised blends. This indicated that compatibilisation does not alter the degree of miscibility. On a thermodynamic sense the broadening of the peaks is the indication of the compatibilisation. The general broadening of the $\tan \delta$ peaks is associated with increased molecular mixing [43], which is expected. As the
compatibility increases, the interpenetration of the components increases [44].

![Figure 6.9: Effect of compatibilisation on the variation of tan δ as a function of temperature in N70 blends](image)

The $T_g$ values shows that significant miscibility increase does not occur for the compatibilised blends. However, domain boundary mixing [45] or interface mixing [46] has been shown to cause an increased temperature dependence of storage modulus and increased level of loss modulus between $T_g$ for compatibilised relative to uncompatibilised blends. From the Fig. 6.9, it is clear that 2.5% compatibiliser loaded blend shows the higher tan δ than other blends in various temperatures. This may be due to the maximum interfacial interaction provided by the compatibiliser. This is evident from the SEM analysis also. Maximum particle size reduction is obtained for 2.5% of compatibiliser (Chapter 4 Figure 4.5).

We can conclude that both electron microscopy and dynamical mechanical analysis clearly show that the system is still phase separated even in the presence of the compatibiliser and tan δ curve also indicates that compatibiliser addition could not make the system completely miscible. This is in agreement with the conclusions made by Paul [47] that
if two polymers are far from being miscible, then no copolymer is likely to make a single phase system. In a completely immiscible system, the main role of the copolymer is to act as an interfacial agent.

6.2.4 Effect of dynamic vulcanisation

During dynamic vulcanization the crosslinked elastomer becomes uniformly and finely distributed in the plastic matrix and attains a stable morphology as shown schematically in the Fig. 6.10. Upon cross linking, the plastic phase maintains the rapid processability and lightly vulcanised rubber particles impart improved strength. In the present study, the crosslinking systems used are sulphur (S), peroxide (DCP), mixed system (sulphur (S)+peroxide (D)) and mixed system (SD) with compatibiliser EPM-g-MA. The sulphur vulcanised system produces mono and polysulfide linkages, a peroxide system gives rise to C-C linkages, a mixed system produces both polysulphide linkage and C-C linkages and mixed system with compatibiliser produces chemical bonds in addition to the polysulphide linkage and C-C linkages. Schematic representation of the network structure in these curing systems is shown in the Chapter 5 (Fig.5.6). The dynamic vulcanization is efficient only in the rubber-rich blends. So we cannot expect much enhancement of dynamic mechanical properties.
The variation of $E'$, $E''$ and $\tan \delta$ of the 70/30 nylon copolymer/EPDM blend with different crosslinked systems are given in the Figs. 6.11-6.13. The variation of $E'$ values of dynamically vulcanised blends with temperature is shown in the Fig. 6.11. In this figure one can see three distinct regions corresponding to glassy, transition and rubbery region as in the case of uncrosslinked blends. The storage modulus of the vulcanised blends shows higher values than the uncrosslinked system in the entire temperature range, while the mixed system with compatibiliser shows the highest values. This is because in the case of mixed system with compatibiliser in addition to the crosslinks, some sort of chemical reaction also takes place and as a result of this there is a profound increase in the stiffness of the material. As expected, the mixed system shows the intermediate behaviour. Dynamic crosslinking has been reported as a means of imparting interfacial bonds between the phases in EPDM/PP [48] blends.

The loss modulus of the vulcanised systems shown in the Fig. 6.12 indicates that loss modulus also increases upon vulcanization. It is evident from the Fig. 6.12 that in N$_{70}$ vulcanised with DCP, the peak corresponding
to the transition of nylon phase is shifted to lower temperature, and that of EPDM rubber is unaffected. The changes in the $T_g$ values of nylon in the vulcanised blends can be explained on the basis of crystallinity and crosslinking. Addition of DCP adversely affects the crystallinity of nylon. So in the vulcanised blends, the $T_g$ value of nylon is a compromise between the extent of crystallization and crosslinking. Here also, the sulphur and the mixed systems have got the lowest values.

**Figure 6.11:** Effect of dynamic vulcanisation on the storage modulus ($E'$) of $N_{70}$ blend with temperature

**Figure 6.12:** Effect of dynamic vulcanisation on the loss modulus ($E''$) of $N_{70}$ blend with temperature
Two separate peaks corresponding to the T$_g$s of EPDM and nylon can also be observed in the figure.

The variation of the tan $\delta$ with temperature (Fig. 6.13) also shows the same trend as that of the loss modulus but only a slight increase in the tan $\delta$ values by the introduction of crosslinks are observed. This may be due to the fact that after vulcanization the system becomes more crosslinked and the chain segments have restricted mobility.

![Figure 6.13: Effect of dynamic vulcanization on the Tan $\delta$ of N$_{70}$ blend with temperature](image)

As a result, the system becomes more elastic and the dissipation of energy as heat is minimized. T$_g$ values of vulcanised blends obtained from the $E''$ and tan $\delta$ curves are presented in Table 6.5. There will not be considerable shift in the T$_g$ values in the presence of crosslinking agents. This indicates that vulcanization does not enhance the molecular level miscibility. The peak width at half height of dynamically crosslinked blends is slightly higher than that of uncrosslinked blends. This indicates increased interaction between the components upon dynamic crosslinking.
Table 6.5: Effect of vulcanization on the $T_g$ values of EPDM and nylon in N$_{70}$ blends at 10Hz

<table>
<thead>
<tr>
<th>Blends</th>
<th>Glass transition temperature ($^\circ$C)</th>
<th>From $E''$ vs. $T$ curve</th>
<th>From tan $\delta$ vs. $T$ curve</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EPDM Phase</td>
<td>Nylon Phase</td>
<td>EPDM Phase</td>
</tr>
<tr>
<td>N$_{70}$</td>
<td>-46</td>
<td>16.7</td>
<td>-44</td>
</tr>
<tr>
<td>N$_{70}$S</td>
<td>-45</td>
<td>16</td>
<td>-42</td>
</tr>
<tr>
<td>N$_{70}$DCP</td>
<td>-45</td>
<td>14</td>
<td>-42</td>
</tr>
<tr>
<td>N$_{70}$SD</td>
<td>-44</td>
<td>17</td>
<td>-42</td>
</tr>
<tr>
<td>N$_{70}$SD+ Compatibiliser</td>
<td>-44</td>
<td>17</td>
<td>-42</td>
</tr>
</tbody>
</table>

The morphology of the nylon/EPDM blends vulcanised by different crosslinking systems is given in the Chapter 5 (Figure 5.2). From the figure it is seen that in the mixed system with 2.5wt% compatibiliser has got fine and uniform distribution of the particles and hence the crosslinking is more effective.

6.2.5 Degree of entanglement density

Degree of entanglement of the polymer blends can be obtained from dynamic mechanical analysis. We can use the $E'$ data for determining the entanglement density using the equation

$$N = \frac{E'}{6RT} \quad \ldots \ldots \ldots (6.4)$$

where $E'$ is the storage modulus obtained from the plateau region of $E'$ versus temperature curve, $R$ is the universal gas constant and $T$ is the absolute temperature. A higher degree of entanglement is exhibited by the vulcanised blends when compared to the unvulcanised blends. This is
because by the addition of crosslinking agents the entanglement between the homopolymers increases and a better adhesion is achieved as a result of decrease in the interfacial tension. The value for degree entanglement between nylon and EPDM are given in the Table 6.6.

**Table 6.6: Entanglement Density of N\textsubscript{70} Vulcanised blends at 10Hz**

<table>
<thead>
<tr>
<th>Blend system</th>
<th>Temperature (°K)</th>
<th>Entanglement Density (mol/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{70}</td>
<td></td>
<td>93</td>
</tr>
<tr>
<td>N\textsubscript{70}S</td>
<td></td>
<td>104</td>
</tr>
<tr>
<td>N\textsubscript{70}DCP</td>
<td>240</td>
<td>113</td>
</tr>
<tr>
<td>N\textsubscript{70}SD</td>
<td></td>
<td>108</td>
</tr>
<tr>
<td>N\textsubscript{70}SD+Compatibiliser</td>
<td></td>
<td>115</td>
</tr>
</tbody>
</table>

From the morphology studies, it is clear that, by the addition of the compatibiliser the particle size decreased leading to a better adhesion. It is interested to note that, in the case of mixed vulcanised system with compatibiliser shows the highest entanglement density and the mixed system has got the entangled density in between the sulphur vulcanised and DCP vulcanised systems.

### 6.3 Conclusions

In uncompatibilised blends, nylon showed the maximum and EPDM showed the minimum storage modulus. The storage modulus of blends was found to be intermediate between the pure components. For the uncompatibilised blends, loss modulus and tan δ values did not give any information about the favourable interactions between nylon and EPDM, as their transition peaks (T\textsubscript{g} of nylon ~ 26°C, T\textsubscript{g} of EPDM ~ -32°C and β-
relaxation of nylon ~ -55°C) experienced no shift as a function of blend ratio. As the concentration of the EPDM rubber increased the storage modulus decreased and the damping and loss modulus increased. The experimental data of uncompatibilised blends were theoretically modeled and observed that Coran’s model \((n=2)\) was best suited for the present system and the Takayanagi model with 45% parallel coupling agreed to some extent. The addition of EPM-g-MA as compatibiliser improved the viscoelastic properties indicating improved interaction between the two components in the compatibilised system. During dynamic vulcanization, the change in \(\tan \delta\) values of the blends indicated the improvement in the miscibility of the nylon and EPDM. A higher degree of entanglement is exhibited by the dynamically vulcanised blends as compared to the unvulcanised blends. Morphology has also a profound influence on the dynamic mechanical properties of the blends.

6.4 References


