Chapter 4

Morphology and Mechanical Properties of Compatibilised Nylon Copolymer/EPDM Blends

Abstract

Nylon copolymer/EPDM blends are highly incompatible because of the large difference in the polarity and viscosity values, which lead to unfavorable interfacial interactions. In this chapter we have attempted to compatibilise nylon copolymer/EPDM blends by using EPM-g-MA as compatibiliser, which can improve the compatibility of the blends through interfacial chemical reactions. The final property of the reactively compatibilised blends depends upon the structure and distribution of the in-situ formed copolymer. The conformation of the compatibiliser at the interface was deduced. The phase morphology and mechanical properties of the blends have been analysed. Finally the experimental results have been compared with the theoretical predictions of Noolandi & Hong and Liebler.

The results discussed in this chapter have been submitted for publication in Polymers for Advanced Technologies
4.1 Introduction

Most of the blends are incompatible and have poor mechanical properties and unstable morphologies. Compatibilisation is necessary for such blends. Preformed graft or block copolymers have been traditionally added to act as compatibilisers. The compatibiliser added to the blend system reduces the interfacial tension and suppresses coalescence and thus leads to a finer phase dispersion and better stability against coalescence. Recently researchers have been paying much interest in combining the attractive features of incompatible polymers by interfacial reaction by adding functionalized additives to form block or graft copolymers in-situ during the blend processing.

Reactive compatibilisation has drawn much more importance in recent years and several reports are available on the reactive compatibilisation of various polymer blend systems [1-15]. The reactive compatibilisation based on the addition of a functionlised polymer, that reacts with the one or both blend components promotes an effective anchorage between the phases through chemical linkage. Moon and Choi have studied the miscibility of poly(vinyl chloride)/styrene-acrylonitrile blends prepared by melt extrusion [16]. Ma et al. [17] studied the effect of compatibilising agent and in situ fibril on the morphology, interface and mechanical properties of EPDM/nylon copolymer blends by using chlorinated polyethylene (CPE) as the compatibiliser. Mechanical properties of HDPE and reactive ethylene terpolymer blends were studied by Love et al.[18] recently. Wagenknecht et al. [19] have studied the effects of interface reactions in compatibilised ground tyre rubber polypropylene elastomeric alloys.
In this chapter we have attempted to compatibilise nylon copolymer/EPDM blends by using EPM-g-MA as compatibiliser. EPM-g-MA has been demonstrated as a low cost, and efficient compatibiliser for the immiscible and incompatible blends of nylon/EPDM. The use of maleated polymer in the blends of nylon/EPDM changes the phase formation drastically.

4.2 Results and Discussion

4.2.1 Processing characteristics

Haake torque rheometry was used to characterise the melt behaviour of nylon/EPDM blends. Fig. 4.1 shows the characteristic torque values of nylon, EPDM, uncompatibilised and compatibilised blends of 70/30 nylon copolymer and EPDM obtained after 8 minutes of mixing.

*Figure 4.1: Haake Torque of neat Nylon, neat EPDM and their blends with different levels of EPM-g-MA (a) 1% (b) 2.5% (c) 5% mixtures versus time (Mixing temperature was 180°C)*

At first torque shoots upon the introduction of nylon granules into the mixer. This is due to the increase in the viscosity by the introduction of cold nylon granules into the mixer. The viscosity then decreases, showing
the complete melting of the nylon. After two minutes of mixing, the EPM-g-MA coated EPDM is added to the molten nylon. The torque increases again due to the high viscosity of the rubber phase and finally the torque values level off. The levelling off of the torque is related to the good level of mixing. It is clear from the figure that compatibilised blends have much higher melt viscosity than uncompatibilised blends. The higher torque value of the compatibilised system indicates the occurrence of interfacial chemical reaction. It is also important to note that there exist a big difference between the viscosities of EPDM and nylon. The viscosity ratio of EPDM to nylon at the end of the mixing is found to be 11.3.

From the figure it is to be noted that there is no reaction with EPDM because the final torque of the compatibilised blends are more close to the torque values of neat nylon. From this result it is evident that only a mixing process is taking place with EPDM and that the anhydride can react only with the amine ends of the nylon chains. This type of the copolymer is ideal for reactive compatibilisation because it can react only with one phase and be miscible with the other phase that is located at the interface between the two phases.

4.2.2 Compatibilisation strategy

For reactive compatibilisation, a two step procedure involving premixing of EPDM and EPM-g-MA prior to its blending with nylon copolymer has been adopted. This is an efficient method for the compatibiliser to reach at the interface very fast to enable better adhesion between the two components.

The present compatibilisation strategy involves the compatibilisation of nylon copolymer with immiscible EPDM rubber by the introduction of a compatibiliser EPM-g-MA which is physically miscible with the EPDM
but has a chemical functionality (maleic anhydride group) which can react with the amine (–NH₂) or carboxyl group or even with the amide (peptide) linkages (–CO NH) of the nylon to form a graft copolymer at the interface as shown in the reaction scheme (Fig. 4.2) [20,21]. The mechanism of the interfacial chemical reaction is based on (a) the amine-anhydride reaction (high temperature) that involves an acid/amide intermediate which cycles to form an imide group and a water molecule [Fig. 4.2 (a)], or (b) an amide-anhydride mechanism (low temperature) that involves an acid/imide intermediate which cycles to a cyclic imide and an acid chain end [Fig. 4.2 (b)]. Since high temperature is used during melt mixing, amine-anhydride mechanism is valid in this case. The graft copolymers formed as a result of the reactions localise at the interface. As a result of the localization of the graft copolymer, (EPM-g-nylon) in between the nylon and rubber phase, the interfacial tension between the phases is lowered and coalescence of the droplets is suppressed by steric hindrance [22-24]. This will increase the interfacial adhesion and improve the properties.

(a) Amine-anhydride mechanism (At high temperature)
There is another possibility. The EPM-g-MA could have more than one anhydride group on each graft. This means multiple reactive sites and hence multiple graft reactions is possible that could lead to some chain extension of nylon. The product can act as a polymeric surfactant, thereby reducing the interfacial tension, inducing a finer and more uniform distribution of the dispersed phase. Depending on the amount of the elastomer, they can form either their own separate phases or an inter phase between EPDM and the nylon polymer (Fig. 4.3). Similar reactions of -NH₂ group with anhydride have been reported in the literature [25].
Figure 4.3: A) Ideal configuration of a graft block copolymer at the interface between the nylon and the EPDM phases

B) Formation of the separate elastomer phase. Stars mean the amide group formed by the chemical reaction in Fig. 4.2.

4.2.3 Molaü test

The Molaü test was conducted in this work in order to confirm the formation of graft copolymer between the nylon and EPDM. Nylon/EPDM blends with and without EPM-g-MA were immersed in formic acid and both formed white suspension just after vigorous mixing. The nylon phase is soluble in formic acid whereas the rubber phase is insoluble. As seen in the Fig. 4.4, nylon/EPDM blends show phase separation (Fig. 4.4 (a)) after 30 days of mixing, while turbidity persisted in the solution of the nylon/EPDM blend which was reactivity compatibilised by the addition of EPM-g-MA (Fig. 4.4(b)).
**Figure 4.4**: Molau test solutions in formic acid of blends of 70/30 (a) PA/EPDM and (b) PA/EPM-g-MA/EPDM after 30 days

The higher stability of the solutions of compatibiliser containing blends is due to the emulsifying effect of the graft copolymer formed between nylon and EPDM during the melt blending. Molau [26] and Illing [27] clearly demonstrated the ability of copolymers to emulsify polymer dispersions in solutions and, thus, to inhibit phase separation. They proposed that in the case of immiscible polymer solutions and a graft copolymer, formation of a white, colloidal suspension indicates the emulsifying action of the graft polymer. Carone et al. [28] observed similar behaviour for blends of polyamide 6/natural rubber with 3wt % of NR-g-MA.

### 4.2.4 Morphology of the blends

The morphologies of the uncompatibilised (nylon/EPDM) and compatibilised blends (nylon/EPM-g-MA/EPDM) were investigated. The effects of EPM-g-MA as a compatibiliser on the morphology of the 70/30 nylon EPDM blends shown by the scanning electron microscope are displayed in the Fig. 4.5.
In the uncompatibilised blend of nylon (Fig. 4.5a), the EPDM domains are relatively large and non-uniform because of the high viscosity difference between the dispersed phase and matrix phase. In fact the viscosity ratio between EPDM and nylon is 11.3. The compatibilised blends (Fig. 4.5(b-e)) show a different morphology. As seen in the Fig. 4.5, the rubber particle shapes are very complex which makes the determination of an average size difficult; nevertheless a quantitative measure of the micrographs of the 70/30 blend was done.

Figure 4.5: Scanning electron Micrographs of 70/30 blend containing different levels of EPM-g-MA (a) 0% (b) 1% (c) 2.5% (d) 5% (e) 10%
The diameter calculated from each particle is an average of a number of different dimensions measured at different possible axes of the particle. Fig. 4.6 (a & b) shows the histogram of the particles with different diameters. It is clear that compatibiliser containing blend showed smaller particle size compared to the corresponding composition without compatibiliser. The 70/30 nylon/EPDM blend showed a large number of big particles.

**Figure 4.6:** Rubber particle size distribution obtained from SEM micrograph of 70/30 (a) nylon/EPDM b) nylon/EPDM/2.5% EPM-g-MA blends
The domain distribution curves for the uncompatibilised and compatibilised systems shown in the Fig. 4.7 indicate the high degree of polydispersity in uncompatibilised systems, due to the large width of the distribution curve. A narrow distribution curve is obtained in the case of 2.5% concentration of the compatibiliser. As the compatibiliser concentration increases, the polydispersity decreases as evident from the decrease in the width of the distribution curve. This reduction in particle size and the uniformity in size distribution as a consequence of EPM-g-MA is due to its ability to encroach into the interface to prevent the coalescence.

**Figure 4.7:** Particle size distribution of 70/30 nylon/EPDM blends containing different amounts of EPM-g-MA compatibiliser

The reduction in particle size as a function of compatibiliser concentration is shown in the Fig. 4.8. From these figures, it can be understood that a drastic reduction in the domain size could be observed by the addition of 2.5wt% of EPM-g-MA into the uncompatibilised blend.
After the addition of 2.5wt% of compatibiliser, there is an increase in the domain size. This increase at higher compatibiliser concentration is due to the formation of micelles of the graft copolymer in the continuous nylon matrix and finally a levelling off is observed at higher compatibiliser concentrations. The equilibrium concentration of EPM-g-MA at which the domain size reached a critical value is called the critical micelle concentration (CMC), i.e. the critical concentration of the compatibiliser required to saturate the interface. It is clear that about 2.5% of EPM-g-MA is sufficient to produce a maximum reduction of the dispersed phase. Above the critical concentration, the compatibiliser may not modify the interface anymore, but forms micelles in the bulk phase. As the interfacial tension is directly proportional to domain size, CMC can be estimated from the plot of domain size versus copolymer concentration [29]. Many researchers [30-36] have extensively reported this type of equilibration in the dispersed phase domain size upon the increasing addition of compatibiliser. It is interesting to note that in most of the cases a 2.5 to 5% of the graft polymer is found to be
sufficient for interfacial saturation [29,33,34]. Several studies have been reported on the interfacial saturation by the addition of compatibilisers [35,36].

Morphological parameters of the 70/30 nylon/EPDM compatibilised blends are given in the Table 4.1. From the table it can be seen that the size of the dispersed EPDM phase decreases with the addition of a few percentage of EPM-g-MA followed by a levelling off at higher concentrations.

**Table 4.1**: Morphological parameters of the 70/30 nylon/EPDM compatibilised blends

<table>
<thead>
<tr>
<th>Blend</th>
<th>Composition</th>
<th>$\bar{D}_n$ (µm)</th>
<th>$\bar{D}_w$ (µm)</th>
<th>$\bar{D}_w / \bar{D}_n$</th>
<th>$A_t$ (µm²/µm³)</th>
<th>IPDC (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_{70}$</td>
<td>70/30</td>
<td>14.5</td>
<td>19.1</td>
<td>1.32</td>
<td>0.28</td>
<td>1.34</td>
</tr>
<tr>
<td>N$_{70,1}$</td>
<td>70/30/1</td>
<td>3.3</td>
<td>4.3</td>
<td>1.30</td>
<td>1.27</td>
<td>0.31</td>
</tr>
<tr>
<td>N$_{70,2.5}$</td>
<td>70/30/2.5</td>
<td>2.2</td>
<td>2.4</td>
<td>1.09</td>
<td>1.90</td>
<td>0.20</td>
</tr>
<tr>
<td>N$_{70,5}$</td>
<td>70/30/5</td>
<td>4.0</td>
<td>4.7</td>
<td>1.17</td>
<td>1.05</td>
<td>0.37</td>
</tr>
<tr>
<td>N$_{70,10}$</td>
<td>70/30/10</td>
<td>4.1</td>
<td>5.6</td>
<td>1.36</td>
<td>1.02</td>
<td>0.38</td>
</tr>
<tr>
<td>N$_{70,15}$</td>
<td>70/30/15</td>
<td>4.3</td>
<td>6.0</td>
<td>1.39</td>
<td>0.98</td>
<td>0.40</td>
</tr>
</tbody>
</table>

A larger amount of EPM-g-MA is added, the amount of compatibiliser that can immediately react with the nylon phase at the interface will be higher. The reaction of this compatibiliser causes a significant particle size reduction. In these smaller particles, the diffusion distance of the remaining EPM-g-MA towards the interface is decreased and the amount of the interfacial area is increased. It is also clear that the particle size in the uncompatibilised blends will determine the initial diffusion distance of EPM-g-MA towards the interface and the initial amount of reaction area. In
this way, parameters such as the viscosity ratio, interfacial tension and amount of dispersed phase which influence the particle size in the uncompatibilised blends will also affect indirectly the interfacial reaction rate. The reduction in the particle size with the addition of the EPM-g-MA is due to the stabilization of the blend morphology by the graft copolymer (EPM-g-Nylon) formed during the melt mixing. The graft copolymer formed at rubber–matrix interface reduces the interfacial tension and suppresses particle coalescence during mixing leading to smaller particles. Sundararaj and Macosko [24] suggested that the suppression of coalescence in compatibilised blends might also play a crucial role with respect to the particle size reduction. The reduced rate of coalescence in compatibilised blends is interpreted as being due to the increased steric hindrance at the interface as the dispersed particles become covalently bonded to the matrix. The mobility of the interface is a critical parameter for the coalescence of two dispersed particles [37]. In addition the presence of the graft copolymer at the blend interface broadens the interfacial region through the penetration of the copolymer chain segments into the corresponding adjacent phases [38]. From the various morphological parameters given in the Table 4.1, it is also seen that the polydispersity index decreases with increasing concentration of EPM-g-MA and found to be least with 2.5% compatibiliser followed by a dramatic increase. The decrease in the polydispersity index actually suggests the uniformity of the morphology.

Tang and Huang [39] proposed an equation for the average radius (R) of the dispersed particle as

\[
R - R_S = (R_0 - R_S) e^{-kC}
\]

where \(R_0\) and \(R_S\) are the average radii of dispersed particles at compatibiliser concentration zero and at saturation respectively (CMC), and
\( C \) is the concentration of compatibiliser. A plot of \( \ln (R-R_s) \) versus \( C \) can be used to obtain \( k \) from the slope. The above equation is based on the assumption that the change in the interfacial tension with the concentration of the compatibiliser is given by

\[
-d\sigma/dc = k(\sigma - \sigma_s)
\]

where \( \sigma \) is the interfacial tension at a compatibiliser concentration \( C \), \( \sigma_s \) is the interfacial tension at the saturation concentration and \( k \) is the rate constant for the change in interfacial tension with concentration of the compatibiliser. The \( k \) value is expected to increase with the level of compatibilisation and decrease with the degree of self-association in the blend [40]. The \( k \) values as a function of compatibiliser concentration for the 70/30 blends of nylon /EPDM are given in the Table 4.2. It is obvious from the table that \( k \) values increases up to 2.5 wt % of compatibiliser indicating interfacial saturation and then decreases with further increase in the compatibiliser concentration depicting the micelle formation due to the self association of the compatibiliser at higher loading.

**Table 4.2:** Effect of compatibiliser concentration on the rate constant in \( N_{70} \) blends

<table>
<thead>
<tr>
<th>Weight % of EPM-g-MA</th>
<th>K-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.745</td>
</tr>
<tr>
<td>2.5</td>
<td>1.104</td>
</tr>
<tr>
<td>5</td>
<td>0.94</td>
</tr>
<tr>
<td>10</td>
<td>0.29</td>
</tr>
<tr>
<td>15</td>
<td>0.27</td>
</tr>
</tbody>
</table>
Influence of EPM-g-MA concentration on the interfacial area per unit volume of 70/30 nylon/EPDM blend is given in the Fig. 4.9. It was found that interfacial area per unit volume increases gradually by the addition of the compatibiliser up to 2.5 wt % of compatibiliser and then decreases followed by leveling off, which is an indication of interfacial saturation.

![Graph showing influence of EPM-g-MA concentration on interfacial area.]

**Figure 4.9:** Influence of EPM-g-MA concentration on the interfacial area per unit volume of nylon/EPDM 70/30 blends

The critical interparticle distance (IPD) has been calculated from Wu's equation [41]. The IPD (Table 4.1) of binary blends are greater than corresponding compatibilised blends. So uncompatibilised blends are more brittle than compatibilised blends. The IPDC decreases up to 2.5 wt % of compatibiliser followed by an increase at higher compatibiliser concentration. This implies that the blends with higher compatibiliser concentration are prone to brittle failure. This may be due to the micellar aggregation of the compatibiliser beyond CMC (Table 4.1).

In short, the morphological parameters derived from micrographs of cryogenically fractured surfaces of compatibilised blends exhibit a finer,
more uniform and stable morphology than the uncompatibilised blends. This is due to the interfacial chemical reaction.

4.2.5 Conformation of the EPM-g-MA at the interface

We have estimated the area (Σ) occupied by a compatibiliser molecule of at the blend interface using the following expressions suggested by Paul and Newmann [42].

$$\Sigma = 3\phi AM / WRN$$  \hspace{1cm} (4.3)

Where $\phi_A$ is the volume fraction of the dispersed phase in the blend, $M$ is the number average molecular weight of the compatibiliser, $W$ is the weight of the compatibiliser required per unit volume of the blend, $R$ is the number average radius of the dispersed domains and $N$ is the Avogadro number.

The conformation of the compatibiliser at the interface can be predicted based on the interfacial area occupied by the copolymer at the blend interface. There are reports regarding the different physical models [43,44] illustrating the conformation of the copolymer at the interface. The two physical models reported in the literature regarding the conformations of the compatibiliser molecule at the interface are given in the Fig. 4.10.

In the fully extended model, the arms of the copolymer are extended into the corresponding homopolymer phase as shown in the Fig. 4.10 (a). In such case the area occupied by the copolymer at the interface is the cross sectional area of the extended copolymer molecule and this value is found to be $\sim 0.5nm^2$. In the completely flat model, the copolymer is believed to lie almost completely flat at the interface [Fig. 4.10 (b)]. In this case, the occupied area will be the lateral surface area of the entire copolymer molecule. This has been estimated based on the root mean square radius of gyration of the copolymer, as reported in the literature [45].
Figure 4.10: Physical model illustrating the conformation of the copolymer at the interface (A) fully extended model (B) completely flat model (C) intermediate model
In the case of 70/30 nylon/EPDM blend, the experimental value of the interfacial area $\Sigma$, occupied by the copolymer at the blend interface at CMC based on equation (4.4) is 2.13 nm$^2$. This value is intermediate between the fully extended model (0.5 nm$^2$) and the flat model (112 nm$^2$). So it is believed that the actual conformation of the compatibiliser at the blend interface is an intermediate conformation as shown in the Fig. 4.10(c), i.e. the compatibiliser at the interface is such that part of the segments lie at the interface and the rest penetrate into homopolymer phases as seen in the Fig. 4.10(c). The experimental observations made by Anastasiadis et al. [46] also support the intermediate conformation model given in the Fig 4.10 (c).

Molecular weight of the compatibiliser is also an important factor that influences the penetration of the segments into the homopolymer phases. According to Gaylord [47], in the case of high molecular weight compatibilisers macromolecular interactions hinder the complete penetration of each segment into the corresponding homopolymer phases, and therefore it can be argued that part of the copolymer may be staying at the interface and the rest penetrates into the homopolymer phases.

4.2.6 Comparison of the experimental compatibilisation data with theory

4.2.6.1 Noolandi and Hong's theory:

The theories of Noolandi [48] and Hong [43,44] can be applied to highly incompatible systems such as nylon/EPDM blends for concentration less than CMC. They suggested that a critical concentration of the compatibiliser is required to saturate the interface of binary polymer blends. They predicted that micellar aggregation of the copolymer takes place at the interface of the blend beyond the critical concentration of the blend. According to them the interfacial tension is expected to decrease linearly
with the addition of compatibiliser below CMC, and above the CMC a levelling off is expected. Therefore, the theoretical treatment of Noolandi and Hong is valid only for concentrations below CMC. According to Noolandi and Hong, in the absence of a solvent, for a ternary system A/A-b-B/B, the interfacial tension reduction or increment ($\Delta \gamma$) upon the addition of the copolymer, is given by the following equation.

$$\Delta \gamma = d \phi_c [(1/2 \chi \phi_p + 1/Z_c) - 1/Z_c \exp (Z_c \chi \phi_p / 2)] \quad \ldots \quad (4.4)$$

where $d$ is the width at half-height of the copolymer profile, reduced by the Kuhn statistical segment length, $\phi_c$ is the bulk volume fraction of the copolymer in the system, $\phi_p$ the bulk volume fraction of the polymer A or B, $\chi$ is the Flory-Huggins interaction parameter between A and B segment of the copolymer, and $Z_c$ is the degree of polymerization of the copolymer. According to this equation, the plot of interfacial tension reduction versus $\phi_c$ should give a straight line. Although this theory was developed for the action of symmetrical diblock copolymer A-b-B in incompatible binary system (A/B), this theory can be successfully applied to other systems, in which the compatibilising action is not strictly by the addition of symmetrical block copolymers [48]. Since interfacial tension is directly proportional to the particle size reduction as suggested by Wu [41], we can replace the interfacial tension reduction term by the particle reduction ($\Delta d$) term in Noolandi and Hong's equation. Therefore

$$\Delta d = K d \phi_c [(1/2 \chi + 1/Z_c) \exp (Z_c \chi / 2)] \quad \ldots \quad (4.5)$$

Where $\Delta d$ is the particle size reduction or increment upon the addition of the compatibiliser and $K$ is the proportionality constant. Thus our present work also suggests that there is a critical concentration of the copolymer required to saturate the blend interface. The addition of the compatibiliser
beyond this concentration leads to undesirable micelle formation, which very often reduces the total performance of the blend system.

The plot of domain size reduction ($\Delta d$) as a function of the volume fraction ($\phi_c$) of the EPM-g-MA for the 70/30 Nylon/EPDM blend is shown in the Fig. 4.11. It can be seen that at low EPM-g-MA concentration (below CMC), $\Delta d$ decreases almost linearly with the increase in the volume fraction of the graft copolymer whereas at higher concentration (above CMC) a leveling off is observed in agreement with the predictions of Noolandi and Hong.

![Figure 4.11: Effect of volume fraction of compatibiliser on the particle size reduction of 70/30 nylon/EPDM blend](image)

4.2.6.2 Leibler's theory

Leibler [49] examined the emulsifying effect of an A-B block copolymer as a compatibiliser in an immiscible blend of polymers A and B and predicted that the interfacial tension reduction is caused by the equilibrium adsorption of the copolymer at the interface. He suggested that at equilibrium, the droplet size distribution is controlled by rigidity and spontaneous curvature of radius of the interphase, both dependent on the
copolymers's molecular constitution. According to the author, the relation gives the interfacial tension reduction:

\[
\Delta \Gamma = -\left( \frac{kT}{a^2} \right) \left( \frac{3}{4} \right)^{1/3} \left( \Sigma / a^2 \right)^{-5/3} \left( Z_{CA} Z_A^{-2/3} + Z_{CB} Z_B^{-2/3} \right) \ldots (4.6)
\]

\( Z_{CA} \) and \( Z_{CB} \) are the number of A and B units in the copolymer respectively, \( Z_A \) and \( Z_B \) the degree of polymerization of A and B respectively, \( a \) the monomer's unit length, \( \Sigma \) the interfacial area per copolymer. In Leibler's theory [49], two brush limits were used. Among the two brush limits, we use the predictions based on the dry brush limit, in which the homopolymer does not penetrate the brush formed by the copolymers, based on the assumption that the reaction between reactive compatibiliser and the polymer with a different functional group occurs near the interface and as a result of that a graft copolymer stays near the interface. The interfacial tension reduction (\( \Delta \Gamma \)) obtained by the dry brush limit is independent of the homopolymer molecular weights and is given by [50].

\[
\frac{\Delta \Gamma}{\Gamma_0} = \left( \frac{\sqrt{48}}{9} \right) \mu^{3/2} (\chi N)^{-1/2} \ldots \ldots \ldots \ldots (4.7)
\]

Where \( \Gamma_0 \) is the interfacial tension of polymer blend without a compatibilisers, \( N \) is the total number of chain segments in an in-situ formed copolymer and \( \mu \) is the chemical potential, which is given by the equation:

\[
\mu = \ln f \chi N \ldots \ldots \ldots \ldots (4.8)
\]

where \( f \) is the volume fraction of the component in copolymer which is miscible to homopolymer forming the dispersed phase and \( \phi^+ \) is the volume fraction of a copolymer in the matrix phase and is given by
\[ \phi^+ = \frac{\phi_0}{\phi_m + \phi_d \exp\{\chi(N_A - N_B)\}} \] ............ (4.9)

where \( \phi_0, \phi_M \) and \( \phi_D \) represents the volume fraction of the copolymer, matrix and dispersed phase, respectively. \( N_A \) and \( N_B \) are the number of segments of the component in the copolymer miscible to the homopolymer forming the dispersed phase and that miscible to homopolymer forming the matrix phase, respectively. Since the value of \( \exp\{\chi(N_A - N_B)\} \) negligible compared to \( \phi_m, \phi^+ \) is expressed by \( \phi_0/\phi_m \).

The surface coverage \( \frac{\Sigma}{b^2} \) of one copolymer, i.e., the surface area occupied by one compatibiliser molecule per unit volume at the interface, is related to \( \mu \) and \( \chi \) [49,50] as

\[ \left[ \frac{\Sigma}{b^2} \right] = \left( \frac{3}{\sqrt{2}} \right) \left( \frac{N/\mu}{\chi} \right)^{1/2} \] ............ (4.10)

where \( \Sigma \) is the surface area per copolymer and \( b \) is the kuhn length, which refers to the effective monomer size for the equivalent freely jointed chain.

Since the dispersed particle reduction is directly proportional to the interfacial tension reduction, the following equation can be used:

\[ \frac{\Delta\Gamma}{\Gamma_0} = \left( \Gamma_0 - \Gamma \right)/\Gamma_0 \approx \frac{\Delta D}{D_0} = \left( D_0 - D \right)/D_0 \] ............ (4.11)

The variation in values of \( \chi \) as a function of EPM-g-MA in \( N_{70} \) blend is given in Fig. 4.12.
Figure 4.12: Effect of EPM-g-MA on the $\chi$ values calculated by the dry brush limit of Leibler’s theory

As the amount of EPM-g-MA increases, $\chi$ value decreases indicating enhanced interaction between the phases at interface in the presence of compatibiliser. Theoretically calculated $\chi$ values from Leibler’s theory is in good agreement with the experimental observation, which shows a decrease in particle size followed by a quasiequilibrium state beyond CMC due to interfacial saturation.

Changes in the calculated values of surface converge with EPM-g-MA of N$_{70}$ blend system by the dry brush limit of Leibler’s theory is given in the Fig. 4.13. This shows that interfacial area occupied by one copolymer molecule per unit volume, $\Sigma$ (surface coverage) decreases with increase in EPM-g-MA up to a certain compatibiliser concentration (2.5 wt%) and beyond that limit a slight increase is noted. The decrease in surface coverage indicates that smaller surface area is needed for a copolymer molecule as the concentration of EPM-g-MA increases and exhibits a similar behaviour to that calculated from equation (9) given by
Figure 4.13: Effect of EPM-g-MA on the $\Sigma/b^2$ values calculated by the dry bush limit of Leibler's theory

Paul and Newman [42]. This is because of the fact that as the $\chi_s$ value decreases, less stretching of graft copolymer chain is needed near the interface and the molecular state of the compatibiliser changes.

4.2.7 Fracture structure morphology and extent of interface adhesion

It has already been reported that in the case of immiscible blends comprised of crystalline and amorphous components, depending on whether the crystalline material is the dispersed phase or matrix, high levels of voiding or good apparent contact respectively could be obtained [41]. In view of this, we have examined the morphology of fracture surface of specimens from the tensile test using scanning electron microscopy. Fig. 4.14(a-c) shows the tensile fracture surfaces of nylon/EPDM blends at a ratio of 70/30 with and without the graft copolymer. The fracture surface of an uncompatibilised blend shows no adhesion between the two phases (Fig. 4.14a). So the interface showed high extent of debonding and void formation. For the compatibilised blends, the dispersed domains are small.
in size and the area of contact is larger (Fig. 4.5 b and c). This showed high degree of interfacial bonding and there is no sign of voids. The microfibrils between the matrix and the dispersed phase show signs of interfacial adhesion between the two phases. In fact a two-step mixing process in which the EPM-g-MA is mixed with the EPM phase gives more opportunity for the EPM-g-MA to diffuse towards the blend interface. In this method of mixing, the EPM-g-MA is forced to be at the blend interface.

Figure 4.14: SEM photograph of fracture surfaces of specimens from the tensile strength of 70/30 Nylon/EPDM blends with compatibiliser (a) 0 phr (b) 2.5 phr (c) 5 phr at Magnification 250
This will lead to a situation where the EPM-g-MA can react with the amino end group of nylon at the interface and the resulting graft copolymer will be easily located at the blend interface. As a result of this a good dispersion of nylon in the rubber phase is achieved. Therefore, EPM-g-MA acted as a compatibiliser and a smooth fracture surface was observed.

4.2.8 Mechanical properties

Compatibility between the component polymers of a blend has a profound influence on the properties of immiscible blends. The effect of compatibiliser concentration on mechanical properties of the 70/30 nylon/EPDM blends are summered in the Table 4.3.

Table 4.3: Tensile properties of 70/30 blends with EPM-g-MA as compatibilisers

<table>
<thead>
<tr>
<th>Blend</th>
<th>Tensile Strength (MPa)</th>
<th>Tear strength (N/mm)</th>
<th>Elongation at break (%)</th>
<th>Young's Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N_{70}</td>
<td>15.8±0.2</td>
<td>63±1</td>
<td>81.3±1.2</td>
<td>113±1</td>
</tr>
<tr>
<td>N_{70.1}</td>
<td>16.4±0.1</td>
<td>72±1.5</td>
<td>91.8±1.1</td>
<td>117±1.5</td>
</tr>
<tr>
<td>N_{70.25}</td>
<td>18.9±0.1</td>
<td>77±1.6</td>
<td>93.7±1.1</td>
<td>128±3</td>
</tr>
<tr>
<td>N_{70.5}</td>
<td>17.1±0.8</td>
<td>77±2</td>
<td>92.9±1.3</td>
<td>127±3.6</td>
</tr>
<tr>
<td>N_{70.10}</td>
<td>16.9±1.0</td>
<td>68±2.5</td>
<td>89.7±1.1</td>
<td>90.5±1</td>
</tr>
</tbody>
</table>

Compatibility between the component polymers of a blend has a profound influence on the properties of immiscible blends. The effect of compatibiliser concentration on the tensile strength and tear strength of 70/30 nylon/EPDM blends with different amount of compatibiliser is given in the Fig. 4.15. With the addition of the compatibiliser, the interfacial condition of the blend is improved. As the compatibiliser concentration
increases, the tensile strength and tear strength are found to increase up to 2.5% of the compatibiliser followed by a decrease. Increase in tensile strength and tear strength is due to the increase in interfacial adhesion between nylon and EPDM phases, which is evident from the SEM analysis with a finer and uniform dispersion of the EPDM phase in the nylon matrix (Fig. 4.5 c). Micrographs show maximum particle size reduction of EPDM when the concentration of the compatibiliser is 2.5%. Similar results have been reported for nylon/PP blends [51]. Mathew and Thomas [52] reported on the compatibilisation of acrylonitrile butadiene rubber (ABS)/PS blends by the addition of styrene acrylonitrile (SAN) copolymer in which addition of copolymer beyond CMC was found to adversely affect the mechanical properties.

![Graph of tensile and tear strength vs. weight % of compatibiliser](image)

**Figure 4.15:** Variation of tensile and tear strength of 70/30 nylon /EPDM blend as function of compatibiliser concentration

The plot of Young’s modulus and elongation at break (Fig. 4.16) of 70/30 nylon/EPDM compatibilised blends shows an increase in the values as a result of compatibilisation.
4.3 Conclusions

From this study the following conclusions can be made:

In this work the possibility of compatibilising Nylon/EPDM blends with EPM-g-MA as compatibiliser was explored. The compatibilising action of EPM-g-MA was associated with the reaction between the anhydride groups of EPM-g-MA with amino groups of nylon leading to the increase in interfacial adhesion between nylon and EPDM. At higher concentration of the compatibiliser, a leveling off is observed due to the critical concentration of the compatibiliser. The highest modulus for the 2.5wt% compatibiliser is due to the lowest particle size of the dispersed EPDM phase. It was concluded that the finer dispersion of the dispersed phase is the main reason for the improvement in the mechanical properties of the blends. Similar reports on mechanical property enhancement by the incorporation of maleic anhydride as compatibiliser into nylon61/ABS blends were reported by Jang and Kim [53]. The results of tensile strength, modulus and tear strength are in good agreement with the morphological findings.
formation of a graft copolymer at the blend interface. The phase morphology of the blend compatibilised with EPM-g-MA was investigated as a function of compatibiliser concentration. Presence of compatibiliser made the phase morphology more fine, uniform and stable by reducing the average particle size, inter particle distance and increasing the interfacial area per unit volume. There is a significant reduction in the domain size of the dispersed EPDM phase till CMC and there after a leveling-off in the domain dimensions at higher concentrations, which is an indication of interfacial saturation. The area occupied by the compatibiliser molecule at the blend interface revealed that conformation of the compatibiliser molecule at the interface is in between the fully extended and flat configurations. Compatibilisation resulted in an overall improvement in the mechanical properties such as tensile strength, Young’s modulus and tear strength of melt-mixed nylon/EPDM blends due to improved interfacial adhesion. The properties attain an optimum value when the reduction in domain size is maximum. From the mechanical properties and morphological data it is clear that the properties of the blends are substantially improved by the addition of compatibilisers. The experimental compatibilisation data have been compared with the theoretical predictions given by, Noolandi and Hong, Paul and Newman and Leibler and observed a reasonably good agreement between experiment and theory. Noolandi and Hong suggested that a critical concentration of the compatibiliser is required to saturate the interface of binary polymer blends.
4.4 References


41. S. Wu, Polymer, 26, 1855, 1985.
51. A. Leclair, B.D. Favis, Polymer, 37, 4723, 1996.