PART II

Reactive Compatibilisation of Polypropylene/Polyamide 12 Blends
Chapter 7

Phase Morphology Studies

This chapter reports the effect of blend ratio and reactive compatibilisation on the phase morphology of PA12/PP blends. Polypropylene grafted with maleic anhydride is used as compatibiliser precursor. The compatibilisation mechanism is based on the generation of a graft copolymer by interfacial chemical reaction. The effect of reactive compatibilisation on the morphological parameters is studied in detail with special attention given to morphology refinement as a function of compatibiliser concentration, attainment of critical micelle concentration and phase coarsening under quiescent conditions. The experimental results are theoretically modelled using established compatibilisation theories proposed by Noolandi and Hong, Tang and Huang, Paul and Newman and Leibler. The interfacial situation of compatibiliser at lower and higher compatibiliser concentrations is discussed.
7.1. Introduction

It is widely recognised that morphology is the principal deciding factor of ultimate properties of a heterogeneous polymer blend system. The blend morphology is determined by factors which are related to material parameters and processing conditions [1]. A major complicating factor in the case of immiscible polymer blends is the intrinsic instability of the morphology in the melt, which depends on shear or elongational stress, viscosity ratio, blend composition, interfacial tension and processing temperature. Usually, immiscible polymer blends are characterised by a coarse and unstable morphology coupled with poor interfacial adhesion between the individual phases. Therefore the real challenging problem in the field of multiphase polymer blend systems is the manipulation of the phase structure via judicious control of the melt flow during processing and interfacial interactions.

The fundamental reasons responsible for the unstable morphology are the unfavourable interactions at the interface between the components which create a high interfacial energy and low interfacial thickness, which would, in turn lead to poor interfacial adhesion between the phases that may result in premature failure of the interface upon stress transfer [2]. Further, coalescence of the dispersed phase makes the dispersed particles larger and non-uniform, leading to an unstable morphology. Therefore the key to overcome problems related to the coarse morphology of multi component polymer blends is to reduce the interfacial tension in the melt and diminish the rate of coalescence under static and quiescent conditions. These can be achieved by the addition of compatibilisers.

Nowadays, attention has been focused on reactive compatibilisation technique as it is very fast, easy and cost effective [3-5]. The basic principle underlying reactive compatibilisation is that one can generate graft or block copolymers in situ by making use of the functionalities present in one or more polymers, during melt processing. In reactive compatibilisation, the in situ formed copolymers, as a result of interfacial chemical reaction, act as compatibilisers. This method has been employed in a number of blend systems [6-57] especially those containing polyamide (PA) as one of the components due to its inherent chemical
functionalities, i.e., amine or carboxyl groups and even amide linkage itself. The amine end group of PAs can react with other functional groups, for example, maleic anhydride group of other polymers to generate block or graft copolymers in situ which can act as potential compatibilisers. This reaction (involving maleic anhydride, MA) has been the most widely used one mainly due to the fact that it is relatively easy to graft MA on to many polymers at normal processing temperature without homo-polymerisation.

Effect of reactive compatibilisation on the morphology of polymer blends has been reported several times in literature [7-24]. It is important to note that the refining and stabilizing effects of a compatibiliser on blend morphology depend on its ability to lower the interfacial tension [25-31] and to decrease the possibility of coalescence of droplets [32-44] which, in turn, depend on several factors such as the type and amount of the functional group present in compatibiliser [45-51], reactive group content and end group configuration of the polymer [52,53], the miscibility of the compatibiliser with one of the phases [45] and its conformation, molecular architecture and stability at the interface [13,54-57].

This chapter aims at making fundamental investigations on the effect of reactive compatibilisation on the morphology of PA12/polypropylene (PP) blends. These blends are highly immiscible and incompatible owing to the unfavourable interfacial interactions. PP grafted with maleic anhydride (PP-g-MA) was used as the compatibiliser. The main focus of the study is to monitor the effect of compatibilisation on morphological parameters of dispersed droplets. Attempts have also been made to compare the experimental results with the established compatibilisation theories.

7.2. Results and discussion

7.2.1. Uncompatibilised blends

The morphology of cryogenically fractured and extracted surfaces of PA12/PP uncompatibilised blends can be evaluated from Fig. 7.1.
As mentioned earlier, owing to the strong unfavourable interfacial interactions (high interfacial tension) in the blends, all micrographs exhibit two-phase morphology. More specifically, all blends except $N_{50}$ and $N_{60}$ possess a typical matrix/droplet morphology in which the minor component exists as dispersed domains in a matrix of major component.

Figure 7.2 presents the influence of blend ratio on the average domain size ($\bar{D}_n$ and $\bar{D}_w$) of dispersed particles. It is seen from the figure that, as the wt% of the dispersed phase increases, particle size increases. It is important to note that for a given dispersed phase concentration (for example, $N_{90}$ and $N_{10}$) PP domains are smaller than corresponding PA dispersed domains. This is not unexpected and the obvious reason is that the relatively less viscous component (PP) forms smaller dispersed particles in more viscous matrix phase (PA) when all other factors (viz., processing conditions, composition, etc.) are kept constant, due to the relatively more restricted diffusion effects imposed by the matrix phase on the
coalescence of dispersed particles and the increased shear stress effects resulting from the more viscous matrix phase.

![Graph showing domain diameter vs. Weight % of PP](image)

**Figure 7.2:** Effect of blend ratio on the dispersed phase particle size in uncompatibilised PA12/PP blends

This can be evidenced from the complex viscosity values of PA12 and PP presented in Fig. 7.3.

![Graph showing variation of complex viscosity](image)

**Figure 7.3:** Variation of complex viscosity of PA12 and PP as a function of frequency

It is seen that PA12 possesses greater viscosity in the whole frequency range. Being more viscous, PA12 imposes greater restricted diffusion effects on the coalescence of PP dispersed particles, which in turn results in smaller PP
dispersed domains. On the other hand when PP forms the matrix phase, the coalescence of PA dispersed phase becomes relatively easy due to the lower viscosity of PP.

Figures 7.4 and 7.5 demonstrate the effect of blend ratio on the polydispersity index and domain distribution of the dispersed phase, respectively in PA12/PP uncompatibilised blends.

**Figure 7.4:** Effect of blend ratio on the polydispersity of dispersed particles in uncompatibilised PA12/PP blends

**Figures 7.5:** Effect of blend ratio on the domain distribution of dispersed particles in uncompatibilised PA12/PP blends
It is evident from the figures that PA12/PP uncompatibilised blends possess a broad, non-uniform and unstable morphology. It can also be seen that as the wt% of the minor component in the blends increases, the non-uniformity increases with simultaneous depletion in the stability. The interfacial area per unit volume (Ai) of dispersed particles presented in Fig. 7.6 implies that blend ratio has no appreciable effect on Ai (except in N40 which shows relatively lower value). However, one can see that PP dispersed particles possess relatively higher values. On the other hand, the interparticle distance of dispersed particles (IPD) given in Fig. 7.7 reveals that there is little change in IPD up to 20wt% of the dispersed phase and, beyond this limit, a decrease in IPD is seen in both PA and PP rich blends. However, interestingly, IPD of N40 is slightly greater than that of N30. In short, all morphological parameters display that PA12/PP blends are highly incompatible with a broad, non-uniform and unstable morphology.

Figure 7.6: Effect of blend ratio on the interfacial area per unit volume of dispersed particles in uncompatibilised PA12/PP blends
Two important facts can be obtained from the morphology of the uncompatibilised blends; (a) all blends exhibit a non-uniform and unstable morphology and (b) as the wt% of the dispersed phase increases, the morphology becomes less stable. This can be explained in terms of interfacial tension and coalescence effects. As mentioned earlier, it is unequivocally established that the final morphology is determined by the deformation-disintegration phenomena and coalescence. The relative importance of applied viscous force and counteracting interfacial force can be expressed by Taylor equations (equations 1 and 2) derived from the studies of deformation and disintegration of the dispersed phase for Newtonian systems in simple shear fields in the absence of coalescence effects [59]. Taylor defined a dimensionless parameter $E$ which is given as equation 1.

$$E^* = Ca \left[ \frac{(19p + 16)}{(16p + 16)} \right]$$

(7.1)

$Ca$, capillary number, represents the ratio of viscous to surface tensional forces.

$$Ca = \frac{\eta_m \dot{\gamma} R}{\sigma}$$

(7.2)

where $\eta_m$ is the viscosity of the matrix, $p$ the viscosity ratio of the droplet phase to the matrix, $R$ the radius of the droplet, $\dot{\gamma}$ the shear rate and $\sigma$ the interfacial
tension. If $Ca$ is small, the interfacial forces dominate and a steady drop shape develops. When $Ca$ exceeds a critical value, $Ca_{crit}$, the droplet will deform and subsequently breaks up under the influence of interfacial tension.

Taylor also derived an expression for $Ca_{crit}$ in the simple shear flow from a Newtonian flow as:

$$Ca_{crit} = \frac{1}{2} \left[ \frac{16p + 16}{19p + 16} \right]$$

Using $Ca = Ca_{crit}$, the droplet diameter $D$ can be calculated as:

$$D = \frac{2Ca_{crit} \sigma}{\gamma \eta_m}$$

Later, Wu [60] modified this equation as:

$$D = \frac{4\sigma p^{1.84}}{\gamma \eta_m}$$

The exponent is positive for $p>1$ and negative for $p<1$.

Serpe et al. [61] further modified this equation by using the blend viscosity rather than the matrix viscosity and by considering a term of composition (thus coalescence effects), as follows:

$$D = \frac{4\sigma \left( \frac{\eta_d}{\eta_b} \right)^{0.84}}{\gamma \eta_b \left[ 1 - (4\phi_d \phi_m)^{0.5} \right]}$$

where $\eta_d$ is the viscosity of the dispersed phase and $\phi_i$ is the volume fraction of component $i$.

From Taylor equations, it is seen that the size of dispersed particles is directly related to the interfacial tension between the two phases. At the same time, Favis [62] has shown that blend morphology is not sensitive to 2-3 fold changes in shear stress and shear rate in an internal mixer. Moreover, a direct experimental confirmation of interfacial tension/particle size relationship as predicted by Taylor theory has been demonstrated by Lepers et al. [28] who argued that in the absence of coalescence effects, there is a close 1:1 relationship between morphology and interfacial tension. Liang et al. [29] have investigated on the correlation between
the interfacial tension and dispersed phase morphology in interfacially modified blends. They demonstrated a direct experimental confirmation of the interfacial tension/phase size relationship as predicted by Taylor theory. According to the authors, there is a 1:1 relationship between droplet size and interfacial tension that is independent of the emulsification efficacy of the compatibiliser. So the high interfacial tension situation due to the unfavourable interactions at the interface between the components in uncompatibilised PA12/PP blends is one of the basic reasons for the existence of a non-uniform unstable morphology.

Further, Tokita [63] derived an expression for the particle size of the dispersed phase in polymer blends that incorporates composition as variable. According to this theory, at equilibrium, when coalescence and break down are balanced, the equilibrium particle size \( d_\varepsilon \) is given by:

\[
d_\varepsilon = 24 P_\tau \sigma / \pi \tau d \left\{ \phi_d + \left( 4 P_\tau E_{sk} / \pi \tau d \right) \phi_d^2 \right\}
\]

(7.7)

where \( \tau_{12} \) is the shear stress, \( \sigma \) the interfacial tension, \( E_{sk} \) the bulk breaking energy, \( \phi_d \) the volume fraction of the dispersed phase and \( P_\varepsilon \) the probability for a collision to result in coalescence. Tokita's theory predicted that particle size at equilibrium diminishes as the magnitude of the stress field increases while an increase in interfacial tension between the phases and volume fraction of the dispersed phase result in an enhancement of particle size. Thus, the increase in particle size with increase in concentration of the dispersed phase in PA12/PP blends is mainly due to the increase in coalescence which may arise due to any of the following interactions such as: (i) van der Waals' forces between neighbouring particles (ii) random mechanical forces exerted on dispersed particles by irregular motion (iii) capillary forces (iv) buoyancy resulting from different gravitation of the two components (can be neglected for systems with little difference in density) and (v) friction resulting from viscous flow. In short, the broad, non-uniform and unstable morphology of uncompatibilised blends is basically derived from the high interfacial tension and coalescence conditions, and the composition dependence of morphology is a direct result of coalescence.
7.2.2. Compatibilised blends

The mechanism of the interfacial chemical reactions is based on (a) the amine-anhydride reaction which involves an acid/amide intermediate that cyclises to produce an imide group and a water molecule (Scheme 7.1a), or (7.1b) an amide-anhydride mechanism which involves an acid/imide intermediate which cyclises, leading to a cyclic imide and an acid chain end (Scheme 7.1b) [58].

Scheme 7.1a: Amine-anhydride mechanism

Scheme 7.1b: Amide-anhydride mechanism

Scheme 7.1: Mechanism of interfacial chemical reaction between PA12 and PP-g-MA

The effect of compatibiliser concentration on the morphology of dispersed phase in N_{70} and N_{30} blends can be evaluated from the SEM micrographs of cryogenically fractured and extracted surfaces of the specimens demonstrated in Figs. 7.8 and 7.9, respectively.
Figure 7.8: SEM micrographs of $N_{70}$ blends with and without compatibiliser

Figure 7.9: SEM micrographs of $N_{30}$ blends with and without compatibiliser
Figure 7.10 presents the effect of compatibiliser concentration on the dispersed particle size in N_{70} and N_{30} blends. A drastic reduction in particle size with increase in compatibiliser concentration can be seen in both blends. A more significant drop in particle size is observed in N_{30} blends. In both blends, after the initial sharp decline in particle size, a quasi-equilibrium state is attained beyond CMC (5wt% of compatibiliser). It is also observed that a levelling off of particle size is achieved at the same compatibiliser concentration in both blends.

![Graph](image)

**Figure 7.10**: Effect of PP-g-MA on the dispersed particle size of PA12/PP blends

Effect of compatibiliser concentration on the domain distribution of N_{70} and N_{30} blends is given in Figs. 7.11-7.13. Distribution becomes narrow indicating a more fine, uniform and stable morphology in the presence of compatibiliser. However, it is interesting to note that for N_{70} blends, beyond CMC (5wt%), there is little change in distribution of particles while in N_{30} blends, 10wt% compatibiliser provides more uniform particle distribution.
Figure 7.11: Effect of PP-g-MA on the polydispersity index of PA12/PP blends

Figure 7.12: Effect of PP-g-MA on the domain size distribution of dispersed particles in N_{70} blends

Figure 7.13: Effect of PP-g-MA on the domain size distribution of dispersed particles in N_{30} blends
In Fig. 7.14, one can see an appreciable increase in Ai of dispersed particles with increase in compatibiliser concentration up to 5wt% of compatibiliser (CMC). Beyond that limit, an almost levelling off in Ai is observed. On the other hand, just reverse trend is seen in the case of interparticle distance (IPD) of the blends displayed in Fig. 7.15. It is seen that IPD of particles decreases with increase in compatibiliser concentration up to CMC and beyond that limit, a levelling off in IPD results.

**Figure 7.14:** Effect of PP-g-MA on the interfacial area per unit volume of dispersed particles in PA12/PP blends

**Figure 7.15:** Effect of PP-g-MA on the interparticle distance of dispersed particles in PA12/PP blends
The main features that can be seen in the morphological investigation of compatibilised blends comprise: (a) stabilisation of morphology in presence of compatibiliser as envisaged from morphological parameters and (b) accomplishment of a quasi equilibrium state in morphological parameters beyond CMC owing to interfacial saturation. The former can be explained by taking into account of both reduction in interfacial tension and coalescence rate as a result of emulsification while the latter is due to the micelle formation of the excess compatibiliser in one of the phases as well as the change in its molecular state at interface. Anastasiadis et al. [26] have observed a sharp decrease in interfacial tension with the addition of small amount of compatibiliser followed by a levelling off as the copolymer concentration is increased above the apparent CMC.

It has been reported that the dominant mechanism for particle size reduction is the coalescence suppression [32-35,64-68]. The compatibiliser has been proposed to act as a steric stabiliser, due to compression of part of the compatibiliser extending into the matrix [32,33]. Macosko and co workers [33] have reported that the principle role of copolymers in controlling morphology appears to be in preventing coalescence. Preventing dynamic coalescence leads to size reduction, while preventing static coalescence results in stability or compatibilisation. They have estimated that less than 5% of the interface needs to be covered to prevent dynamic coalescence while 20% is necessary to impart static stability. Lyu et al. [66,67] have examined the role of PS-PE diblock copolymer on coalescence suppression in PS/HDPE blends and found that coalescence was significantly suppressed with the addition of compatibiliser. The minimum copolymer required to completely suppress coalescence was measured to be about 0.20 chain/nm² for 20-20 kg/mol PS-PE. They also argued that steric repulsive interaction between the rigid block copolymer layers in particle surfaces contributed to the coalescence suppression. At the same time, a different mechanism has been emerged from a number of studies which suggest that the bulk flow convects the compatibiliser away from the film region and the stress arising from the resulting gradient in interfacial tension (Marangoni stress) retards the drainage of the film between the droplets [34,35,68]. (Both these mechanisms of compatibilisation are discussed in Chapter 3).
7.2.3. Phase coarsening under quiescent conditions

It has been suggested that the amount of compatibiliser surface coverage necessary for stabilizing blend morphologies during static coalescence may be significantly higher than the concentrations required during mixing [33], possibly caused by longer contact times which allow for a greater extent of molecular rearrangement at the interface. Therefore phase coarsening under quiescent conditions (static coalescence) is a topic of considerable interest. Several researchers have shown that reactive compatibilisers locate at the interface as steric stabiliser and offer stability against static coalescence [9,32,33].

In order to get an idea about the phase coarsening under quiescent conditions, we annealed the samples for 60 min at 190°C. The SEM micrographs of both uncompatibilised and compatibilised N30 and N50 blends before and after annealing are given in Figs. 7.16 and 7.17. From the figures, it is clear that compatibilisation could significantly suppress the static coalescence. It is seen that co-continuous phase structure of uncompatibilised N50 blend changes to an almost matrix/droplet morphology on annealing (Fig. 7.17a). This is due to the highly mobile interface of uncompatibilised blends derived from unstable phase morphology. It is important to note that compatibilisation stabilised the morphology of N50 blend (Fig. 7.17b) since it could retain its co-continuous morphology upon annealing. Another conformation about the role of reactive compatibiliser in preventing the static coalescence can be drawn from the Table 7.1. In the absence of compatibiliser, 125% increase in dispersed particle size is observed for N70 blends (For N90 blends, the particle size is so large that a comparison makes no sense). Note that for PP/HDPE system discussed in chapter 3 we observed 40% increase in dispersed particle size for uncompatibilised blends upon annealing.
Figure 7.16: SEM micrographs showing the effect of annealing on the dispersed particle size of (a) uncompatibilised $N_{70}$ blend (b) $N_{70}$ blend compatibilised with 5wt% PP-g-MA (c) uncompatibilised $N_{20}$ blend (d) $N_{20}$ blend compatibilised with 5wt% PP-g-MA.

Figure 7.17. SEM micrographs showing the effect of annealing on the co-continuous morphology of (a) uncompatibilised $N_{80}$ blend (b) $N_{80}$ blend compatibilised with 5wt% PP-g-MA.

The huge difference in percentage increase of dispersed particle size between the two systems is due to the more incompatible nature of PA12/PP system owing to the polarity difference between the polymers in this case. Note that addition of
5wt% compatibiliser (CMC) in N_{70} and N_{30} blends suppressed the static coalescence considerably. It is also important to note that compatibilised N_{30} blend has more tendency to undergo coalescence than compatibilised N_{70} blend. This is basically due to the less diffusional force in N_{30} compared to N_{70} in molten state owing to the relatively less viscous PP matrix. In short, reactive compatibilisation of PA12/PP blends stabilised the morphology significantly by suppressing phase coarsening under quiescent conditions.

<table>
<thead>
<tr>
<th>Blend</th>
<th>Domain diameter ($D_n$, µm)</th>
<th>% increase in size</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unannealed</td>
<td>Annealed</td>
</tr>
<tr>
<td>N_{70}</td>
<td>9.2</td>
<td>20.6</td>
</tr>
<tr>
<td>N_{70} + 5wt% PP-g-MA</td>
<td>4.8</td>
<td>5.25</td>
</tr>
<tr>
<td>N_{30}</td>
<td>12.2</td>
<td>Very large</td>
</tr>
<tr>
<td>N_{30} + 5wt% PP-g-MA</td>
<td>4.3</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Table 7.1: Effect of annealing on the average domain size of PA12/PP blends in the presence and absence of compatibiliser

7.2.4. Comparison of the experimental compatibilisation data with theory

Noolandi and co workers [69,70] developed mean field theories of polymer interfaces. Leibler's theory is valid for nearly miscible systems where as mean field theories are applicable to highly immiscible systems. According to Noolandi [70], the effect of copolymer on surface tension between the two phases is mainly influenced by the contributions from a series of factors such as lowering of interaction energy between the immiscible homopolymers, the broadening of the interface between the homopolymers, the entropy reduction in the system, decrease in energy of interaction of the two blocks with each other and a large decrease in the interaction energy of the oriented blocks with homopolymers. However, it should be noted that the localisation of copolymer at the interface and the separation of blocks into corresponding homopolymer phases and the simultaneous reduction in interfacial tension between the phases depend on various factors such as mixing conditions, interaction of the compatibiliser with the dispersed phase, molecular weight and composition of the compatibiliser, the rate of absorption and orientation of the compatibiliser at the interface. Based on these
facts and by neglecting the loss of conformational entropy, Noolandi derived an equation for the interfacial tension reduction as:

$$\Delta \Gamma = d \phi \left[ 1/2 \chi + 1/Z_c - 1/Z_c \exp(Z_c \chi / 2) \right]$$

(7.8)

where $d$ is the width at half height of the copolymer profile reduced by the Kuhn statistical segment length, $\phi$, the bulk copolymer volume fraction of the copolymer in the system, $Z_c$ the degree of polymerisation of the copolymer and $\chi$ the Flory-Huggins interaction parameter between A and B segments. Although the theory was developed for the action of a symmetrical di block copolymer, A-b-B, it can be applicable to other systems too where the compatibilising action is not strictly by the addition of block copolymers. As the interfacial tension reduction is directly proportional to the particle size reduction ($\Delta D$) [60], it can be argued that

$$\Delta D = K d \Phi_c \left[ 1/2 \chi + 1/Z_c \exp(Z_c \chi / 2) \right]$$

(7.9)

where $K$ is a proportionality constant. Fig. 7.18 represents the percentage reduction in particle size as a function of compatibiliser concentration in N70 blends. It can be seen that below CMC, the drop in $\Delta D$ is almost linear, whereas beyond CMC, a levelling off is observed. This is in agreement with the predictions of Noolandi and Hong [69].

Figure 7.18: Effect of PP-g-MA on the domain size reduction of N70 blends
The interfacial area per unit volume occupied by each compatibiliser molecule is given by the expression [71]:

$$\Sigma = \left( \frac{3\phi M}{RNW} \right)$$  \hspace{1cm} (7.10)

where N is Avogadro number, M the number average molecular weight of the compatibiliser, R the average radius of the dispersed phase, \(\phi\) the volume fraction of the dispersed phase and W the weight of the compatibiliser required per unit volume of the blend. When \(\phi\) and M are kept constant, \(\Sigma\) depends on the values of R and W. R decreases with increase in the weight fraction of the compatibiliser and \(\Sigma\) may either decrease or not change or increase. Hosoda et al. [72] have reported that the product of RW remained constant and did not change with W for PP-g-MA/PA 30/70 blend. On the other hand, Tang and Huang [73] found a decrease in \(\Sigma\) with an increase in compatibiliser concentration in four blends, viz. PA/PP = 90/10, 10/90 and PA/PE = 90/10, 10/90. The effect of compatibiliser concentration in PA12/PP blends on \(\Sigma\) can be evaluated from Fig. 7.19. We observed a decrease in \(\Sigma\) with increase in concentration of the compatibiliser. This does not mean that as the amount of compatibiliser in the blend increases, the tendency to form micelles increases. A plausible explanation is that when the concentration of compatibiliser is less, each molecule occupies more interfacial area than when the compatibiliser concentration is high, where the compatibiliser molecules are forced to arrange themselves at the interface so as to occupy smaller interfacial area per compatibiliser molecule. Thus, one can conclude from the above facts that the molecular state of compatibiliser changes with the concentration of the compatibiliser in the blend. (A similar information was obtained for the compatibilisation of PP/HDPE blends, see chapter 3).
Leibler [74] examined the emulsifying effect of an A-B copolymer in an immiscible blend of polymers A and B and predicted a reduction of interfacial tension caused by 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 copolymer's molecular constitution. According to the author, the interfacial tension reduction is given by the relation:

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

where \(Z_{CA}\) and \(Z_{CB}\) are the number of A and B units in the copolymer respectively, \(Z_A\) and \(Z_B\) the degree of polymerisation of A and B respectively, \(a\) the monomer's unit length and \(\Sigma\) the interfacial area per copolymer. In Leibler's theory, a block copolymer was used as a compatibiliser. Between the two brush limits in Leibler's theory [74], prediction based on dry brush limit in which the homopolymer does not penetrate the brush formed by the copolymer, has been used. Based on the assumption that the reaction between reactive compatibilizer and the polymer with a different functional group occurs near the interface, the following equation can be used for the interfacial tension reduction \(\Delta \Gamma\) obtained by the brush limit which is independent of the homopolymer molecular weights.
\[ \frac{\Delta \Gamma}{\Gamma_0} \approx \left( \sqrt{\frac{48}{\eta}} \right) \mu^{\frac{1}{2}} (\chi N)^{-\frac{1}{2}} \quad (7.12) \]

where \( \Gamma_0 \) is the interfacial tension of polymer blend without a compatibiliser and \( \mu \) is the chemical potential which is given by the equation:

\[ \mu = \ln \phi^* + f \chi N \quad (7.13) \]

where \( f \) is the volume fraction of the component in copolymer which is miscible to homopolymer forming the dispersed phase and

\[ \phi^* = \frac{\phi_i}{[\phi_m + \phi_d \exp\{\chi (N_A - N_B)\}]} \quad (7.14) \]

where \( \phi_0 \), \( \phi_m \), and \( \phi_d \) represent 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 \( \exp\{\chi (N_A - N_B)\} \) is negligible compared to \( \phi_m \), \( \phi^* \) is expressed by \( \phi_i / \phi_m \).

The surface coverage of one copolymer, i.e., the surface area occupied by one compatibiliser molecule per unit volume at the interface, is related to \( \mu \) and \( \chi \) as

\[ \left[ \frac{\Sigma}{b^2} \right] = \left( \frac{3}{2} \right) \left( \frac{N}{\mu} \right)^{\frac{1}{2}} \quad (7.15) \]

where \( b \) 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:

\[ \frac{\Delta \Gamma}{\Gamma_i} \approx \frac{(\Gamma_0 - \Gamma)}{\Gamma_0} \approx \frac{\Delta D}{D} = \frac{(D_0 - D)}{D_0} \quad (7.16) \]

The variation in values of \( \chi \) as a function of PP-g-MA in N70 and N30 blends is given in Fig. 7.20. It is seen from the figure that N30 blends exhibited lower \( \chi \) values in presence of compatibiliser. As the amount of PP-g-MA increases, \( \chi \) values
diminish indicating enhanced interaction between the phases at interface in presence of compatibiliser. However, the theoretically calculated $\chi$ values from Leibler's theory show apparent conflict with the experimental observation, which shows a decrease in particle size followed by a quasi-equilibrium state beyond CMC owing to interfacial saturation.

![Graph](image.png)

**Figure 7.20:** Effect of PP-g-MA on the $\chi$ values calculated by the dry brush limit of Leibler's theory

For $\chi$ values there exists no true levelling off beyond CMC, especially for $N_{30}$ blends. It is also interesting to note that the $\chi$ values, calculated using Leibler's theory in presence of compatibiliser are appreciably less than $\chi$ value (0.365) obtained for PA12/PP uncompatibilised blends theoretically calculated (from molar attraction constants from Hoy's scale) using Hildebrand-Scatchard-van Laar equation:

$$\chi_{12} = \frac{V_r}{RT} (\delta_1 - \delta_2)^2$$  \hspace{1cm} (7.17)

where $V_r$ is the reference volume, $\delta_1 = 9.69$ (cal/cm³)¹/² and $\delta_2 = 7.82$ (cal/cm³)¹/² the solubility parameters of PA12 and PP, respectively and T is the temperature in absolute scale. The big difference between the two may be due to the fact that: (i) Leibler's theory was originally proposed for nearly compatible blends and (ii) Leibler's theory was formulated basically for block copolymers (the reaction between PA12 and PP usually leads to graft copolymers).
The effect of PP-g-MA on the calculated values of surface coverage of one copolymer presented in Fig. 7.21 shows that the surface coverage (interfacial area occupied by one copolymer molecule per unit volume, $\Sigma$), in general, decreases with increase in PP-g-MA up to a certain compatibiliser concentration (5 and 10wt% for $N_{30}$ and $N_{70}$ blends, respectively) and beyond that limit a slight increase is noted.

**Figure 7.21:** Effect of PP-g-MA on the $\Sigma/b^2$ values calculated by the dry brush limit of Leibler's theory.

The decrease in surface coverage indicates that smaller surface area is needed for a copolymer molecule as the concentration of PP-g-MA increases and exhibits a similar behaviour to that calculated from equation (7.10) given by Paul and Newman [71]. This is fundamentally because of the fact that as the $\chi$ value decreases, as mentioned earlier, less stretching of graft copolymer chain is needed near the interface and the molecular state of the compatibiliser changes. However, the $\Sigma$ calculated using equation 7.10 offers an apparent conflict with the calculated values of $\Sigma$ using equation (7.15); i.e., (i) when equation (7.10) is used, a gradual decrease in $\Sigma$ is observed with increase in PP-g-MA concentration for the whole range of compatibiliser composition whereas an increase was noted beyond a certain level of compatibiliser concentration (5 wt% for $N_{30}$ and 10wt% for $N_{70}$ blends) when equation (7.15) is used, (ii) The values obtained from equation (7.10) are considerably smaller than those from equation (7.15) which can be explained if we consider the fact that $\Sigma$ calculated using
equation (7.10) is based on the assumption that all the compatibiliser molecules go to the interface.

Based on the fact that upon the addition of compatibiliser, interfacial tension $\sigma$ decreases and on assumption that the decrease is directly proportional to the interfacial tension difference at a particular compatibiliser concentration $C$ and CMC, then:

$$-\left(\frac{d\sigma}{dC}\right) = K (\sigma - \sigma_i)$$ (7.18)

where $K$ is the rate constant for the change in interfacial tension with concentration of the compatibiliser, $\sigma$ the interfacial tension at a given compatibiliser concentration, $C$ and $\sigma_i$ the interfacial tension at CMC. From the above expression, Tang and Huang [73] eventually derived the following equation:

$$R - R_i = (R_0 - R_i) e^{-KC}$$ (7.19)

where $R_0$, $R$ and $R_i$ are the average radius of dispersed particles without compatibiliser, at a given compatibiliser concentration and compatibiliser concentration at CMC respectively.

<table>
<thead>
<tr>
<th>Weight % of PP-g-MA</th>
<th>$K$ value</th>
<th>$N_{70}$</th>
<th>$N_{30}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.39</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.40</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.94</td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.29</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>0.19</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.13</td>
<td>0.12</td>
<td></td>
</tr>
</tbody>
</table>

**Table 7.2:** Effect of compatibiliser concentration on the rate constant for the change in interfacial tension ($K$) in $N_{70}$ and $N_{30}$ blends

A plot of $\ln \left( R - R_i \right)$ versus $C$ can be used to obtain $K$ from the slope. Aravind et al. [75] have shown that $K$ value reaches a maximum at CMC and beyond that limit a decrease in $K$ value is observed. The $K$ value obtained as a function of compatibiliser concentration for PA12/PP blends are depicted in Table 7.2. It is
obvious from the table that $K$ value increases with increase in compatibiliser concentration, reaches a maximum at CMC and decreases beyond that limit. From the table it is obvious that the rate constant for the reduction in interfacial tension upon compatibiliser incorporation is appreciable up to CMC. Note that both $N_{70}$ and $N_{30}$ blends possess almost same $K$ values beyond CMC.

7.3. Conclusion

The present chapter was devoted to evaluate the morphology of PA12/PP blends with and without reactive compatibiliser. The morphological parameters of uncompatibilised blends revealed that these blends are highly incompatible with a two-phase non-uniform unstable morphology. The high interfacial tension situation due to the unfavourable interactions at the interface between the components in uncompatibilised PA12/PP blends was one of the reasons for the existence of a non-uniform unstable morphology. As the concentration of the dispersed phase increased, the incompatibility increased. This was mainly due to the increased rate of coalescence with increase in concentration of the minor phase in the blends.

Compatibilisation of the blends refined the morphology of the blends by drastically reducing the average particle size as well as inter particle distance and increasing the interfacial area per unit volume. The optimum compatibiliser concentration was observed at critical micelle concentration up to which a linear drop in particle size was seen as predicted by the theories of Noolandi and Hong, and beyond which a levelling off in morphological parameters has been noted owing to interfacial saturation. The morphology refinement in the presence of compatibiliser was mainly due to its efficiency to decrease the interfacial tension and to suppress the rate of coalescence by acting as either steric stabiliser or by generating Marangoni stress at the interface. In addition, presence of compatibiliser at the interface could successfully stabilised the phase morphology by preventing static coalescence on annealing. The experimental compatibilisation data have been compared with the theoretical predictions given by, Noolandi and Hong, Paul and Newman, Leibler and Tang and Huang. We observed a reasonably good agreement between experiment and theory. From the interfacial coverage of compatibiliser molecules per unit volume as a function of compatibiliser concentration, it was concluded that
there is a change in the molecular state of compatibiliser with increase in compatibiliser concentration.

7.4. References


