PART I

Physical Compatibilisation of Polypropylene/High Density Polyethylene Blends
Chapter 3

Phase Morphology Studies

This chapter is devoted to investigate the phase morphology of PP/HDPE blends in the presence and absence of compatibilisers. Ethylene propylene random copolymers with three different monomer fractions are used as compatibilisers. The effect of these random copolymers on the various morphological parameters is studied in detail with special attention given to morphology refinement in the presence of compatibilisers, establishment of critical micelle concentration, efficiency of compatibilisers and phase coarsening under quiescent conditions. The highlight of this chapter is that based on the results, we put forth a new model to explain the interfacial situation and the compatibilising action of random copolymers at interface. The experimental results are theoretically modelled using established compatibilisation theories. The interfacial situation of compatibiliser at lower and higher compatibiliser concentrations is illustrated pictorially.

The results of this chapter have been submitted for publication in Macromolecules
3.1. Introduction

Blending of two polymers usually results in an immiscible system owing to high molecular weights of individual polymers and negligible combinatorial entropy of mixing contribution. These blends are characterised by a coarse, unstable morphology coupled with poor interfacial adhesion between the phases. As a result, their performance will be inferior to even neat polymers and irreproducible. Since it is unequivocally established that most of the ultimate properties (toughness, strength and crack resistance, optical, rheological and dielectrical properties) of polymer blends are strongly influenced by the type and fineness of phase structure, morphology control of polymer blends has been emerging as an area of continuous interest to polymer material scientists for the last few decades. The mechanism of development of morphology from pellet sized or powder sized particles in polymer blends is directly derived from the complex interplay of material parameters and processing conditions. Therefore the greatest challenge in the field of multiphase polymer blend research is the manipulation of polymer structure via judicious control of the melt flow during processing and the interfacial interactions. As indicated earlier, 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. Another aspect that deserves attention is the coalescence of the dispersed phase, which makes the dispersed particles larger and non-uniform, leading to an unstable morphology.

The main objective of the present chapter is to investigate the effect of compatibilisation on the phase morphology of PP/HDPE blends. The non-reactive compatibilisation route (physical compatibilisation) has been adopted. The compatibiliser was ethylene propylene terpolymer (EPDM) random copolymers. In the present work we have used random copolymers with three different monomer ratios in order to estimate the dependence of the compatibilising efficiency on copolymer composition. The details of the compatibilisers are given in Table 2.1 in
Chapter 2. Further, based on our experimental results we have proposed a new model for the compatibilising action of random copolymers at the interface.

3.2. Results and discussion

3.2.1. Uncompatibilised blends
The SEM micrographs given in Fig. 3.1 demonstrate the phase morphology of cryogenically fractured surfaces of uncompatibilised PP/HDPE blends. All the micrographs clearly disclose two-phase morphology of typical uncompatibilised blends. One can distinguish two types of morphology from the figure: (a) dispersed droplet type morphology in blends up to 40wt% HDPE (where HDPE forms the dispersed phase) and up to 30wt% PP (where PP forms the dispersed phase) and (b) co-continuous phase structure in blends with 50 and 60wt% HDPE. From the dispersed droplet type morphology, morphological parameters such as average domain size ($\bar{D}_x$ and $\bar{D}_w$), domain distribution, interfacial area per unit volume ($A_i$) and interparticle distance (IPD) have been calculated using equations given in Chapter 2.2.

The influence of blend ratio on the average domain diameters ($\bar{D}_x$ and $\bar{D}_w$) of PP/HDPE uncompatibilised blends is presented in Fig. 3.2. From the figure, it is seen that, as the wt % of HDPE in PP matrix increases, particle size increases and beyond a certain limit of composition (40 wt%) both HDPE and PP form bi-continuous phase structure at which a phase inversion occurs and after this point (60 wt%), HDPE forms the matrix in which PP phase is distributed as dispersed particles. This is a typical morphology of an incompatible heterogeneous binary blend.
Figure 3.1: SEM micrographs of uncompatibilised PP/HDPE blends
The difference in particle size of dispersed PP and HDPE phases for a given dispersed phase concentration (e.g., 10/90 and 90/10) can be explained by considering the relative difference in their viscosities in the blend (see Fig. 3.3). Usually the less viscous component (HDPE) forms smaller dispersed particles in more viscous matrix (PP) due to comparatively restricted diffusion effects on coalescence of particles and increased shear stress resulting from the more viscous matrix phase.

Figure 3.3: Complex viscosities of PP and HDPE as a function of frequency at 190°C
Figure 3.4 demonstrates the effect of blend ratio on the domain distribution of dispersed phase in PP/HDPE uncompatibilised blends. It is obvious from the figure that blends containing 10wt% of minor component (both H₁₀ and H₉₀) show the narrowest while H₄₀ and H₇₀ show the broadest distributions of particles. The distribution of domains in all the other blends remains in between these two limits. This is well expected and can be directly related to the relative stability of phase structure. As mentioned earlier, when the concentration of dispersed phase increases, due to the enhanced unfavourable cross-correlations of the component polymers at the interface between them (derived from the surface tensional forces), the morphology becomes more coarse and unstable. It is noteworthy that blends with dispersed HDPE phase possess more uniform morphology compared to those with dispersed PP phase (compare domain distribution curves of H₂₀ and H₃₀ with H₆₀ and H₇₀, respectively). The relatively more viscous PP matrix facilitates the generation of more uniform dispersed morphology. Similar information about the distribution of dispersed particles can be evaluated from Fig. 3.5, which presents the influence of blend ratio on the poly dispersity index, pdi, of dispersed particles in PP/HDPE uncompatibilised blends. The relatively lower pdi values of blends with HDPE dispersed phase compared to those of blends with PP dispersed phase are an indication of relatively ‘more stable’ morphology associated with the former blends. However H₄₀ exhibits an exceptionally high pdi, which is not unexpected since the composition is near to the onset of co-continuity.

Figure 3.4: Effect of blend ratio on the domain distribution of uncompatibilised PP/HDPE blends
Figure 3.5: Effect of blend ratio on the polydispersity index of uncompatibilised PP/HDPE blends

Figure 3.6 displays the effect of blend ratio on the interfacial area per unit volume (Ai) of PP/HDPE uncompatibilised blends. It is evident from the figure that Ai diminishes with increasing concentration of minor component in the blend. Blends with dispersed HDPE phase possess greater interfacial area compared to the corresponding blends with PP dispersed phase. This is because Ai depends on the average domain size of dispersed particles. On the other hand, on the basis of Ai values, one can claim that blends with lower Ai exhibit maximum unfavourable interactions (derived from maximum interfacial tension) at the interface and thus associated with more coarse, non-uniform and unstable morphology. However, this need not to be true since $H_{40}$ possesses the more coarse, non-uniform and unstable morphology according to the distribution of domains.
Effect of blend ratio on the interfacial area per unit volume of uncompatibilised PP/HDPE blends is shown in Fig. 3.7. The higher value of IPD indicates the tendency of a material to be failed brittley upon mechanical loading. It is obvious from the figure that with increasing concentration of dispersed phase in the blend, IPD increases in all blends except for H₄₀ suggesting that the blends are prone for brittle failure with increasing concentration of minor component. In short, the morphological parameters showed that all blends are associated with two-phase unstable morphology owing to the high interfacial tension and greater coalescence effects in the absence of favourable interactions at interface between the phases. As the concentration of one phase in the blends increases, the incompatibility intensifies.
Phase Morphology Studies

Figure 3.7: Effect of blend ratio on the interparticle distance of uncompatibilised PP/HDPE blends

3.2.2. Compatibilised blends

The effect of compatibilisers on the morphology of polymer blends relies in its ability to act as 'interfacial emulsifying agent', i.e. to reduce the interfacial tension between the components and to retard the rate of coalescence. SEM micrographs of cryogenically fractured surfaces of compatibilised H_20 blends are presented in Fig. 3.8. The morphological parameters derived from Fig. 3.8 are presented in Figs. 3.9-3.12.

Figure 3.8: SEM micrographs showing the morphology of H_20 blends compatibilised with three different random copolymers
Figure 3.9 gives the effect of compatibilisers on the number average domain diameters of these blends. The main feature is the significant drop in dispersed particle size with the addition of compatibilisers. One can also infer that after an initial sharp decline in particle size, a quasi-equilibrium size is attained beyond a certain compatibiliser concentration ($C_{\text{crit}}$) called critical micelle concentration (CMC). A levelling off in particle size can be noticed beyond CMC due to the interfacial saturation. The decrease in particle size may be taken as a direct evidence of emulsifying action of compatibiliser. It can also be noted that the efficiency of compatibilisers to act as emulsifying agent is different for different compatibilisers. 0.5E provides minimum particle size where as 0.6E and 0.7E performed almost equally efficient in decreasing particle size. It is important to note that 3wt% 0.5E is sufficient for interfacial saturation while 5wt%. 0.6E and 0.7E are required to attain CMC.

![Graph showing effect of compatibilisation on dispersed particle size](image)

**Figure 3.9:** Effect of compatibilisation on the dispersed particle size of H20 blends

Effect of compatibilisation on interfacial area per unit volume of H20 blends given in Fig. 3.10, which displays that there is significant improvement in interfacial area in presence of compatibilisers in such a way that the efficiency of compatibilisation is in the order $0.5E \geq 0.6E \sim 0.7E$. Attention should be paid to the fact that initial addition of compatibiliser results in rapid rise in Ai and beyond $C_{\text{crit}}$ an almost levelling off is seen in all cases.
**Figure 3.10:** Effect of compatibilisers on the interfacial area/unit volume of H<sub>2</sub>O blends

Fig. 3.11 presents the effect of compatibilisation on the interparticle distance of dispersed particles in H<sub>2</sub>O blends. IPD sharply decreases upon the initial incorporation of compatibiliser, reaches a minimum at 3wt% 0.5E and 5wt% 0.6E and 0.7E and beyond that, levels off. This means that compatibilisation appreciably decreased the tendency of the blend to undergo brittle failure. The efficiency of compatibilisers is in the order 0.5E>0.6E>0.7E. Beyond CMC, compatibilisers have no appreciable effect on IPD.

**Figure 3.11:** Effect of compatibilisation on the interparticle distance of dispersed phase in H<sub>2</sub>O blends
Figures 3.12a-c present the effect of compatibilisers on the distribution of dispersed particles in H_20 blends. Domain distribution becomes narrower in presence of compatibilisers, especially 0.5E. Emphasis should be given to the fact that there is no further narrowing of distribution curve beyond C_{crit} in all cases. This observation suggests that compatibilisers made the morphology more fine, uniform and stable and beyond CMC, there is little effect.
In summary, the morphological parameters of compatibilised blends clearly established the interfacial emulsifying action of compatibilisers. The major observations include:

(i) average particle size and IPD decreased considerably whereas interfacial area significantly improved and domain distribution became narrower in the presence of compatibilisers.

(ii) A critical concentration of compatibiliser has been observed in all cases beyond which there is no net improvement in interfacial properties.

(iii) 0.5E was found to be more efficient than 0.6E and 0.7E which were equally efficient.

3.2.2.1. Morphology refinement in the presence of compatibiliser

It has been well established that compatibilisers locate at the interface between the components and decrease the unfavourable cross-correlations between the component polymers. This decreases the interfacial tension between the individual polymers. Additionally, the compatibiliser molecules decrease the possibility of coalescence. Thus the elementary reasons for the morphological refinement in the presence of compatibilisers are the interfacial tension reduction and coalescence suppression.
The effect of compatibilisation on the interfacial tension has been studied by several researchers [1-8]. Hu et al. [1] applied a modified pendant drop method to measure the interfacial tension of immiscible homopolymer blends. They used the binary homopolymer blend polystyrene/polydimethylsiloxane (PS/PDMS) and a nearly symmetric diblock copolymer P(S-b-DMS). They found that the interfacial tension of the blend is initially decreasing with increasing the compatibiliser concentration, and then attains a constant value above a certain critical concentration. Anastasiadis and co-workers have shown that small amounts (e.g., 1% or less) of compatibiliser can considerably reduce the interfacial tension by 80–90% [2]. Lepers et al. [6] argued that in the absence of coalescence effects, there is a close 1:1 relationship between morphology and interfacial tension. Liang et al. [7] have investigated on the correlation between the interfacial tension and dispersed phase morphology in interfacially modified blends of linear low density PE (LLDPE) and polyvinyl chloride (PVC) and based on the results, they demonstrated a direct experimental confirmation of the interfacial tension/phase size relationship as predicted by Taylor theory.

Several experimental studies have shown that addition of compatibilisers causes a dramatic decrease in the rate of coalescence [9,10-21]. It has been hypothesised that a compatibiliser promotes morphological refinement more by coalescence suppression during processing than by promoting the break-up of droplets. Sundararaj et al. [9] proposed that the steric interaction between copolymers balanced the force that drives the droplets to approach each other and the coalescence of the droplets was prevented.

Ramic et al. [10] reported a severe reduction in coalescence efficiency when a very small amount of compatibiliser was absorbed at the interface. They reported that the coalescence rate decreased only slightly upon further increasing the block copolymer concentration. Hu et al. [11] presented quantitative data for the coalescence efficiency in a linear flow by the visual observation of two equally sized drops. For very small concentrations of compatibiliser, which caused negligible changes in interfacial tension, a drastic reduction of coalescence was observed. Macosko and co-workers [14] have reported that the principle role of
compatibiliser in controlling morphology appears to be in preventing coalescence. Lyu et al. [22,23] have shown that the minimum copolymer coverage ($\Sigma_{\text{min}}$) for suppressing coalescence was independent of, or very weakly correlated with, the shear rate ($\gamma$). Steric repulsive interaction between the rigid copolymer layers in particle surfaces was thought to contribute to this coalescence suppression.

It has also been assumed that the copolymers at droplet surfaces resisted the droplets to approach each other, and thus the coalescence between droplets was suppressed [24-26]. According to this concept, the bulk flow convects the compatibiliser away from the film region and the stress resulting from the gradient in interfacial tension (Marangoni stress) retards the drainage of the film between the droplets as shown in Fig. 3.13a. On the basis of a similar concept, Blawzdziewicz et al. [27] proposed another mechanism and suggested that copolymer layers at droplet surfaces were incompressible and the droplet surfaces were essentially immobile as given in Fig. 3.13b.

![Figure 3.13: Two mechanisms proposed for coalescence suppression: (a) surface tension gradient (Marangoni) force and (b) steric repulsion](image)

Lyu [28] assumed that the compatibilizers suppress coalescence by preventing the rupture process of the matrix film between the droplets. Van der Waals interaction between the droplets compresses the film. The compression force increases when there is a fluctuation in the facing surfaces of the droplets. Thus, the fluctuation tends to grow. However, as the surfaces fluctuate, the interfacial energy increases due to the increase in surface area, which damps the fluctuation. When the film is thick, the compression force is negligible; the surface fluctuation is always damped. However, when the film thickness is smaller than a critical value ($h_c$), the van der Waals compression force exceeds the damping force, the
fluctuation grows, and the film becomes unstable and ruptures (Fig. 3.14 a and b) \[29,30\] and the rupture will be suppressed if there are compatibilisers at the interface (Fig. 3.14 c) \[28\].

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure314.png}
\caption{Schematic of the rupture processes of the film of the matrix between the two droplets. Rupture was suppressed if there were copolymers at the interfaces of droplets (Ref. 30).}
\end{figure}

Thus the improved morphological parameters of dispersed phase in PP/HDPE blends can be taken as a direct evidence for the refining and stabilising effect of compatibiliser on the morphology by (i) lowering of interfacial tension and (ii) suppressing coalescence. Further, the presence of compatibiliser in smaller amount results in entropy loss, which is compensated by enthalpic effects which tend to reduce the number of unfavourable interactions between the segments of two immiscible polymers.

### 3.2.2.2. Attainment of CMC

The attainment of CMC at a critical copolymer concentration beyond which all morphological parameters virtually display a levelling off, indicates that 3wt\% of 0.5E and 5wt\% of 0.6E and 0.7E are sufficient for the interfacial saturation. It should be noted that the amount of added copolymer is a key factor in controlling the phase dispersion and phase dimensions in all type of compatibilisation processes. In general, the dispersed particle size drastically decreases up on addition of a few percentage copolymer, reaches a critical concentration beyond that limit the copolymer has no interfacial compatibilising efficiency since it (copolymer) usually dissolves in one of the phases and forms its own micelles.
This means that at high concentrations an increase of the compatibiliser content does not lead to a significant decrease of interfacial tension and/or of the coalescence rate. One can predict that beyond this limit, it is very difficult for the compatibiliser molecules to go to and/or stay at the interface. There are chances for the formation of micelle by the agglomeration of excess copolymer molecules and remain randomly entrapped in one of the phases. Thus it is believed that the CMC corresponds to the interfacial saturation of the dispersed phase by modifier molecules. In PP/HDPE compatibilised system 3 (in the case of compatibiliser 0.5E) or 5wt% (in the case of compatibilisers 0.6E and 0.7E) of compatibiliser can be taken as interfacial saturation point.

3.2.2.3. Efficiency of compatibilisers

It is quite important to consider the fact that there is notable difference in the performance of compatibilisers. Note that all these compatibilisers are random copolymers with no considerable difference in molecular weights. It is well known that the molecular weight of compatibiliser makes difference in their compatibilising efficiency. However, it can be ruled out in present case since there is no considerable difference in molecular weight of compatibilisers. So the difference may arise due to the difference in E/P ratio of copolymers.

There are several theoretical and experimental results that support the compatibilising action of a random copolymer in an immiscible polymer system [31-36] although the mechanism whereby a random copolymer strengthens the interface between two immiscible polymers is still controversial. It has been suggested that each copolymer molecule can form loops that penetrate into the homopolymers on both sides [31,37] of the interface, and so, each copolymer molecule forms a number of stitches. In the case of a random copolymer, a single polymer chain may make multiple crossings at the interface [31,38,39-41]. Hence, the number of times one chain crosses the interface can be large, as shown in Fig. 3.15, and, thus, the copolymer may effectively "stitch" the two immiscible homopolymers together. However, the effectiveness of each stitch is unknown since the loop may not be long enough to entangle well with the homopolymers. There were suggestions that the loops may be longer than expected from the
average Flory-Huggins parameter $\chi$ between the random copolymer and the homopolymer due to selection of particular random sequences, but it is now clear that such an effect is unlikely [42].

![Figure 3.15](image)

**Figure 3.15:** Schematic diagram of the organization of a random copolymers at the interface between homopolymers comprised of the same basic units

Dai et al. [31] have reported that long random copolymers with symmetric monomer fraction ($f \sim 0.5$) could act as efficient compatibilisers. They observed that compatibiliser with $f \sim 0.5$ is more effective than those with $f \sim 0.8$, in strengthening the interfaces between immiscible homopolymers, and also more effective than diblock copolymers. The exceptional effectiveness of the symmetric random copolymer was attributed to the fact that random copolymer crosses the homopolymer interface multiple times and thereby maximises the number of entanglements with each of the immiscible homopolymers. Note that a long random copolymer with $f \sim 0.5$ is likely to have the same (Gaussian) conformation in either homopolymer and therefore also at the interface, since on the average there is no thermodynamic driving force to break the spherical symmetry, unlike the case of an AB diblock copolymer which has the A block mostly in homopolymer A and the B block mostly in the homopolymer B at A-B interface. A Gaussian random copolymer at the interface with $f \sim 0.5$ maximises the entropy, but does nothing to lower the enthalpy, which is the major cause of compatibiliser localisation at a homopolymer/homopolymer interface for diblock copolymers [43]. This process will be particularly effective if the homopolymer molecular weights are much less than those the random copolymers, as in the experiments carried out by Dai et al. [31]. A beneficial side effect of this process is the formation of
numerous entanglements of both homopolymers with the random copolymer, with the maximum number occurring for f \sim 0.5. For f < 0.5 or f > 0.5, the homopolymer corresponding to the majority monomer fraction will form a larger number of entanglements with the random copolymer than for f \sim 0.5, but the other homopolymer will form a smaller number, and since the strength of the interface is determined by the weakest link, the strength decreases rapidly for asymmetric copolymers, as observed.

Noolandi and Shi [44] have reported that for asymmetric random copolymers, the orientational ordering at the interface becomes important. In addition, there is a smaller number of entanglements of one of the homopolymers with the copolymer than for f \sim 0.5. For the symmetric case (f \sim 0.5), the conformational entropy of the copolymer is maximised, as is the number of entanglements of both homopolymers with the copolymer. According to these authors, while for specially prepared homopolymer/copolymer/homopolymer sandwiches the interfaces are indeed reinforced by random copolymer, for melt blending symmetric random copolymers used at the same levels as diblock copolymers will have little effect as compatibilisers because of the lack of a driving force for thermodynamic localisation at the homopolymer/homopolymer interfaces.

Based on the aforementioned discussion, it can be concluded that compatibiliser 0.5E is the most efficient compatibiliser mainly because of the fact that it is 'compositionally' symmetric (f \sim 0.5) which enhance the conformational entropy of the copolymer at the interface. At the same time, the number of entanglements of PP or HDPE homopolymers with the EPDM compatibiliser is maximum when the copolymer is symmetric, consequently the copolymer exhibited a more 'balanced conformation' at the interface.
3.2.2.4. Phase coarsening under quiescent conditions

As mentioned earlier, phase coarsening or coalescence in multiphase polymer blend systems in molten state is a topic of considerable research interest and is discussed in detail under section 1.4.2. Coalescence, usually, occurs in polymer systems due to collisions that are driven by (i) applied shear force or bulk flow during processing and is termed as shear induced coalescence or dynamic coalescence (ii) van der Waals' force of attraction under quiescent condition and is called static coalescence. It is important to note that preventing dynamic coalescence leads to droplet size reduction while preventing static coalescence results in morphological stability. Very recently, Yuan and Favis [45] have investigated the influence of efficacy of interfacial modification on coarsening of co-continuous blends during quiescent annealing and shown that the co-continuous phase size grows linearly without modifier, whereas the addition of interfacial modifiers significantly suppresses the phase coarsening and results in nonlinear phase growth behaviour. They have also reported that the effect of the diblock copolymer on suppressing coarsening is much more effective than that for the triblock case clearly supporting the tendency toward micelle formation for that latter modifier. Macosko and co-workers [14] estimated that less than 5% of the interface needs to be covered to prevent dynamic coalescence while 20% is necessary to input static stability. Further, these authors reported that random copolymers are not efficient in preventing static coalescence as they noted a significant increase in the size of dispersed phase on annealing [46,47]. They claimed that encapsulating layer of copolymer didn't provide stability against static coalescence. A similar observation was made by Joseph et al. [48] in which they found that SBR random copolymers couldn't provide stability to PS/PB blends against static coalescence.

In this respect, it is very important to study the effect of annealing on the dispersed particle size since otherwise, it calls into question the effectiveness of random copolymers as practical compatibilisers. For this, we annealed the samples for 60min at 180°C. From Figs. 3.16 and 3.17, which present the SEM micrographs of cryogenically fractured, extracted and annealed H₂₀ and H₅₀ blends in the
presence and absence of compatibilisers, one can distinguish the morphologies before and after annealing.

Figure 3.16: SEM micrographs showing the effect of annealing on the dispersed particle size of (a) uncompatibilised H20 blend (b) H20 blend compatibilised with 3wt% 0.5E (c) H20 blend compatibilised with 5wt% 0.6E (d) H20 blend compatibilised with 5wt% 0.7E

Figure 3.17: SEM micrographs showing the effect of annealing on the co-continuous morphology of (a) uncompatibilised H50 blend (b) H50 blend compatibilised with 3wt% 0.5E
We estimated the average domain size of the dispersed phase from the SEM micrographs of annealed H_{20} blends. The effect of annealing on the $\bar{D}_n$ of H_{20} blends with and without compatibilisers is displayed in Table 3.1. It is believed that in the case of unmodified blends, the driving force for capillary pressure effects is so high that it is the capillary instability phenomena that dominate the coarsening and hence result in a linear growth of pore size with annealing time. When interfacial modifiers are added, the influence of reduced interfacial tension and lower pore size significantly diminish both capillary pressure effects and capillary instability phenomena. It is obvious from the table that the phase coarsening is considerable in uncompatibilised blends compared to that in H_{20} blends compatibilised with 3wt% (CMC) symmetric compatibiliser (0.5E). Particle size increased by 40% after 60min annealing in uncompatibilised blends while only 6% increase in particle size is observed in compatibilised blends. On the other hand, it is important to note that compatibilised blends with 5wt% (CMC) unsymmetric compatibiliser underwent significant phase coarsening, like uncompatibilised blends. However, note that the particle size of these blends is still less than that of unannealed uncompatibilised blends. This suggests that even though, unsymmetric compatibilisers are efficient in preventing the dynamic coalescence (not as efficient as symmetric copolymers) during processing, they are less efficient to prevent static coalescence. In addition, it is also important to note that symmetric random copolymer is efficient to stabilise the phase morphology against static coalescence that occurs in co-continuous phase structure. It is obvious from the figure that the co-continuous morphology of uncompatibilised H_{50} blend is unstable and is partially converted to matrix/droplet morphology on annealing. On the other hand, H_{50} with 3wt% 0.5E provide morphological stability as there is no change in the co-continuous phase structure of the blends on annealing. Thus it can be concluded that, unlike unsymmetric random copolymers which cannot provide stability against static coalescence, symmetric random copolymer is equally efficient in preventing both the dynamic as well as static coalescence and therefore could be used as efficient compatibilisers.
<table>
<thead>
<tr>
<th>Blend</th>
<th>Average domain diameter ( \bar{D}_n ), ( \mu m )</th>
<th>% increase in size</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>Unannealed</td>
<td>Annealed for 60min</td>
</tr>
<tr>
<td>H2O</td>
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<td>3.29</td>
</tr>
<tr>
<td>H20_0.5E3</td>
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<td>1.32</td>
</tr>
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<td>H20_0.6E5</td>
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<td>1.95</td>
</tr>
<tr>
<td>H20_0.7E5</td>
<td>1.50</td>
<td>2.13</td>
</tr>
</tbody>
</table>

**Table 3.1:** Effect of annealing on the average domain size of H20 blends in the presence and absence of compatibiliser

### 3.2.3. New model for the emulsifying action of random copolymers

As mentioned earlier, the location of the compatibiliser at the interface between the individual phases of blend is one of the most important requirements for efficient compatibilisation and morphology stabilisation during processing. However, there are chances for the rejection of copolymer from the interface because of the energetically unbalanced design of the copolymer at the interface. In view of this fact, we propose a new model to explain the efficiency of symmetric random copolymers as compatibilisers. When the copolymers have a symmetric conformation, the compatibiliser molecules attain a balanced and therefore a stable conformation at the interface. During processing and annealing thereafter, due to the combined effect of bulk flow and the diffusional forces exerted by other compatibiliser molecules at the interface, the compatibiliser molecules experience a stress and these molecules are forced to rearrange themselves at the interface to get a more stable conformation to avoid pullout from the interface. At this stage, the balanced conformation facilitates copolymer to remain at the interface due to the optimal interaction balance between its own sequence and respective individual phases of the blend and resists the rejection of compatibiliser from the interface during processing. Thus the compatibiliser molecules retain their position at the interface, but in a rearranged fashion as seen in Fig. 3.18.

However, when the compatibilisers have an unbalanced conformation, it will be very difficult for them to retain their position at the interface and some of these
molecules may be expelled out from the interface (so-called 'decompatibilisation' process) leading to micelle formation. (This may happen during the processing or annealing and thereby favours both dynamic and static coalescence processes). At the same time the compatibiliser molecules, which retain their position at the interface are in a rearranged state so that they occupy less interfacial area compared to symmetric compatibiliser molecules (Fig. 3.19). Thus based on our new model, a symmetric copolymer is more efficient compared to unsymmetric one at least due to two reasons: (i) they occupy more interfacial area compared to unsymmetric ones and (ii) they resist decompatibilisation and thereby the micelle formation more than that by unsymmetric compatibilisers. Additionally, it can be concluded that due to a balanced design, symmetric copolymers retard the coalescence process more than the unsymmetric copolymers by facilitating greater Marangoni stress or steric stabilisation.
bulk flow and diffusional force due to incoming copolymers

Symmetric copolymer/Balanced conformation

Copolymer molecules stay at the interface rather than forming micelle/interfacial area occupied by compatibiliser is greater

Figure 3.18: Schematic diagram of the conformation of symmetric compatibiliser at the interface
bulk flow and diffusional force
due to incoming copolymers

Unsymmetric copolymer/
unbalanced conformation

Interfacial area occupied by the
compatibiliser molecules is less

Figure 3.19: Schematic diagram of the conformation of unsymmetric compatibiliser at the interface
3.2.4. Comparison of the experimental compatibilisation data with theory

According to Noolandi [49], 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, a 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 localization 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:

\[ \Delta \gamma = d \Phi_c \left[ 1/2 \chi + 1/Z_c - 1/Z_c \exp(Z_c \chi/2) \right] \] (3.1)

where \( d \) is the width at half height of the copolymer profile reduced by the Kuhn statistical segment length, \( \Phi_c \) the bulk copolymer volume fraction of the copolymer in the system, \( Z_c \) is the degree of polymerisation of the copolymer and \( \chi \) is 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, Wu [50] argued that

\[ \Delta D = Kd \Phi_c \left[ 1/2 \chi + 1/Z_c \exp(Z_c \chi/2) \right] \] (3.2)

where \( K \) is proportionality constant. Fig. 3.20 represents the percentage reduction in particle size as a function of compatibiliser concentration with respect to the minor phase. It can be seen that, below a CMC, the drop in \( \Delta D \) is almost linear,
where as beyond CMC, a levelling off is observed. This is in agreement with the predictions of Noolandi and Hong [51]. A similar trend can be assessed from Fig. 3.21, which gives the variation in $\Delta D$ as a function of compatibiliser concentration with respect to the total blend concentration. From these figures, it is possible to evaluate both the efficiency of compatibilisers as well as the optimum amount of compatibiliser required to saturate the interface with respect to the minor phase as well as total blend concentration.

**Figure 3.20:** Effect of compatibilisers (with respect to minor phase) on percent domain size reduction of H20 blends

**Figure 3.21:** Effect of compatibilisers (with respect to blend) on percent domain size reduction of H20 blends
The interfacial area per unit volume occupied by each compatibiliser molecule is given by the expression [52]:

\[ \Sigma = \left( \frac{3\phi M}{RNW} \right) \]  

(3.3)

where \( N \) is Avogadro number, \( M \) is the number average molecular weight of the compatibiliser, \( R \) is the average radius of the dispersed phase, \( \phi \) is the volume fraction of the dispersed phase and \( W \) is the weight of the compatibiliser required per unit volume of the blend. When \( \phi \) and \( M \) are kept constant, \( \Sigma \) depends on the product \( RW \). \( R \) decreases with increase in the weight fraction of the compatibiliser and \( \Sigma \) may either decrease, or remains the same or increase. Hosoda et al. [53] have reported that the product \( RW \) remained constant and did not change with \( W \) for PP-g-MA/PA30/70 blend. On the other hand, Tang and Huang [54] found a decrease in \( \Sigma \) with an increase in compatibiliser concentration in four blends, viz. PA/PP= 90/10, 10/90, PA/PE= 90/10, 10/90. The effect of compatibiliser concentration in \( H_{2o} \) blends on \( \Sigma \) can be evaluated from Table 3.2.

<table>
<thead>
<tr>
<th>Weight % of compatibiliser</th>
<th>0.5E</th>
<th>0.6E</th>
<th>0.7E</th>
</tr>
</thead>
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<td>45.3</td>
<td>48.3</td>
</tr>
<tr>
<td>3</td>
<td>20.3</td>
<td>16.9</td>
<td>18.0</td>
</tr>
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<td>13.1</td>
<td>10.9</td>
<td>11.7</td>
</tr>
<tr>
<td>10</td>
<td>6.9</td>
<td>5.8</td>
<td>6.2</td>
</tr>
<tr>
<td>15</td>
<td>4.3</td>
<td>3.6</td>
<td>3.9</td>
</tr>
<tr>
<td>20</td>
<td>3.2</td>
<td>2.7</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Table 3.2: Effect of compatibiliser concentration on the interfacial area occupied per molecule of compatibiliser in PP/HDPE compatibilised blends

We observed a decrease in interfacial area 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 forced to arrange themselves in the interface so as to occupy smaller interfacial area per compatibiliser molecule. A schematic picture of both situations is given in Fig. 3.22. Thus, it can be concluded from the above facts that the molecular state of compatibilisers change with the concentration of the compatibiliser in the blend.

Leibler [55] 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:

$$\Delta \Gamma = -(kT/\alpha^2)(3/4)^{1/3}\left(\Sigma/\alpha^2\right)^{-5/3}\left(Z_{CA}Z_{A}^{-2/3} + Z_{CB}Z_{B}^{-2/3}\right)$$

(3.4)
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, $\Sigma$ 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 [55] 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 interfacial tension reduction ($\Delta \Gamma$) obtained by the brush limit is independent of the homopolymer molecular weights, the following equation can be used for calculating the interaction parameter, $\chi$:

$$\frac{\Delta \Gamma}{\Gamma_0} = \left( \frac{9}{48} \right)^{\frac{1}{2}} \mu^{\frac{1}{2}} (\chi N)^{-\frac{1}{2}}$$  \hspace{1cm} (3.5)

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:

$$\mu = \ln \phi^* + f \chi N$$  \hspace{1cm} (3.6)

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

$$\phi^* = \frac{\phi_0}{\phi_m + \phi_d \exp \{ \chi (N_A - N_B) \}}$$  \hspace{1cm} (3.7)

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 $\phi_0/\phi_m$. Since the dispersed particle reduction is directly proportional to the interfacial tension reduction, the following equation can be used:
The variation in values of $\chi$ as a function of compatibiliser concentration is given in Fig. 3.23. As the amount of compatibiliser increases, $\chi$ values diminish indicating enhanced interaction between the phases at interface in the presence of compatibiliser. It is seen that there is no true levelling off in $\chi$ values indicating an apparent conflict with the morphological parameters. However, one can also find that blends with symmetric copolymer registered the minimum $\chi$ values indicating maximum interaction as evidenced from the morphology. It is also interesting to note that the $\chi$ values calculated using Leibler's theory in presence of compatibiliser are considerably less than $\chi$ value (0.0428) obtained for uncompatibilised $H_{20}$ blends theoretically calculated (from molar attraction constants from Hoy's scale) using Hildebrand-Scatchard-van Laar equation:

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

where $V_r$ is the reference volume, $\delta_1$ and $\delta_2$ the solubility parameters of PP and HDPE respectively and $T$ is the temperature in absolute scale. Thus, it is observed that the experimental data are in reasonable agreement with the Leibler's theory.

**Figure 3.23:** Effect of compatibiliser on the $\chi$ values calculated by the dry brush limit of Leibler's theory
Based on the fact that on adding 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:

$$-\left(\frac{d\sigma}{dC}\right) = K (\sigma - \sigma_s)$$  \hspace{1cm} (3.10)

where $K$ is the rate constant for the change in interfacial tension with concentration of the compatibiliser, $\sigma$ is the interfacial tension at a given compatibiliser concentration $C$ and $\sigma_s$ is the interfacial tension at CMC. From the above expression, Tang and Huang [54] eventually derived the following equation:

$$R - R_s = (R_0 - R_s) e^{-Kc}$$  \hspace{1cm} (3.11)

where $R_0$, $R$ and $R_s$ are the average radius of dispersed particles without compatibiliser, at a given compatibiliser concentration and compatibiliser concentration at CMC respectively. A plot of $\ln (R - R_s)$ versus $C$ can be used to obtain $K$ from the slope.

Aravind et al. [56] 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 H20 blends are depicted in Table 3.3. It is obvious from the table that $K$ value increases with compatibiliser concentration for 0.5E, reaches a maximum at CMC and decreases beyond that limit. However, interestingly, for other compatibilisers, it is seen that, maximum value of $K$ is obtained on the initial addition of compatibiliser, a decrease in $K$ value is noted on further addition, after that an increase is observed corresponding to CMC and beyond that limit $K$ value decreases linearly.
<table>
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</thead>
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</table>

Table 3.3. Effect of compatibiliser concentration on the rate constant for the change in interfacial tension (K) in PP/HDPE 80/20 compatibilised blends

3.3. Conclusion

This chapter was devoted to evaluate the morphology of PP/HDPE blends in presence and absence of compatibilisers. It was found that these blends are highly incompatible and characterised by a two-phase non-uniform unstable morphology in the absence of compatibiliser due to high interfacial tension and coalescence effects. As the concentration of the dispersed phase increased, the incompatibility enhanced and relatively less unstable morphology was obtained when HDPE forms the dispersed phase.

Compatibilisation of the blends immensely improved the morphology of the blends by drastically reducing the average particle size as well as interparticle distance and increasing the interfacial area per unit volume. The optimum compatibiliser concentration was observed at critical micelle concentration (CMC) 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. Copolymer with a relatively balanced design in terms of ethylene/propylene (E/P) ratio was the best interfacial emulsifying agent. We have estimated the stability of phase morphology against static coalescence in the presence and absence of compatibilisers. The percentage increase in particle size in uncompatibilised as well as blends with 5wt% unsymmetric compatibiliser was
found to be almost same. This revealed that unsymmetric compatibilisers didn't provide stability against static coalescence as the particle size increased significantly on annealing. On the other hand, symmetric compatibiliser was found to be very efficient against static coalescence compared to the unsymmetric ones. The values of interfacial area occupied per compatibiliser molecule suggested that the molecular state of compatibiliser changes with concentration. Attempts have also been made to compare the experimental data with established theories predicted by Noolandi and Hong and Leibler. Finally, we have proposed a new model for explaining the interfacial situation and the compatibilising action of random copolymers at interface based on compatibilisation-decompatibilisation equilibria.

3.4. References


