Chapter 9

Confined Crystallization Behavior of Isotactic Polypropylene in Isotactic Polypropylene/Acrylonitrile Butadiene Rubber Blends

Abstract

The confined crystallization behavior of isotactic polypropylene (iPP) in isotactic polypropylene/acrylonitrile butadiene rubber (NBR) blends has been studied by differential scanning calorimetry (DSC), wide angle X-ray scattering (WAXS) and scanning electron microscopy (SEM). The crystallization of the micro and nano scale droplets of iPP domains in the acrylonitrile butadiene rubber was observed under different undercoolings. It is found that the phenomenon of confined crystallization process will develop if the number of dispersed droplets is greater than the number of active heterogeneities originally present in the bulk polymer. The effects of blend ratio, different compatibilizer, compatibilizer concentration and cooling rate on the fractionated crystallization were analyzed using DSC. The existence of fractionated crystallization is shown to be related to the lack of active nuclei in the dispersed droplets and has been proved by means of self-seeding experiments. Nucleating action of compatibilizer has been studied in detail for first time.

The results of this chapter has been submitted for publication in chemistry of materials
9.1. Introduction

In polymer blends, the crystallization behavior of the crystallizable component will be strongly disturbed by the presence of the second component in the blend [1]. The morphology of the blend is a very critical factor for polymer crystallization [2]. The binary mixtures of immiscible polymers, where one of the components is in excess, usually display typical droplet-in-matrix phase morphology. The size of the dispersed particles depends on the blend composition, melt-viscosity, elasticity of the each phase, interfacial tension and mixing conditions [3,4]. When the dispersed phase component can crystallize, the particle size has a crucial impact on its crystallization behavior due to fractionated crystallization [5]. Crystallization is a phase transition that is controlled by nucleation and growth process [6]. The crystallization behavior of a polymer in a blend is affected by many factors, such as composition, thermal history, interfacial interactions, size of the dispersed particles and size distributions [7]. It was found that if the number of dispersed particles is greater than the heterogeneities present in the bulk samples, a new crystallization process develops at much lower temperature than those typically encountered in heterogeneously nucleated homopolymers. This process has been reported in the literature and the term fractionated crystallization has been introduced to describe this phenomenon [8]. Reversible crystallization and melting behavior of iPP was studied by Androsch and Wunderlich [9] with temperature modulated DSC. Fractionated crystallization behavior of the PP/PC blend was studied by Andrew et. al. [10]. Fractionated crystallization behavior and crystal phase of the PA6/functionalised polypropylene blend were analyzed by Psarski et al. [11]. The physical and mechanical properties of incompatible heterogeneous polymer blends may be enhanced by compatibilization through the
introduction of physical or chemical interactions between the components. The presence of functional groups along the polymer chains, or a third polymer leads to specific interactions with the other blend constituents and thereby enhances the interfacial adhesion and the overall characteristics of the blend systems [12-15]. Muller and coworkers showed that the addition of SEP as a compatibilizing agent in PS/iPP blends causes a reduction in particle size and that increases with the amount of SEP in the blend. This could lead to a higher super cooling for the crystallization of iPP (16).

In this chapter, the fractionated crystallization phenomenon shown by polypropylene in NBR/PP blend has been investigated in detail with respect to morphology [17,18]. The crystallization process has been followed by DSC. The existence of fractionated/homogeneous crystallization has been explained due to the lack of active nuclei in the dispersed droplets by means of self-seeding experiments[19-21]. The influence of physical, reactive compatibilization and successive self-annealing tests on the fractioned crystallization phenomenon has been analyzed. Effect of droplet size distribution and number of heterogeneities on the confined crystallization phenomenon of PP/NBR blend has been investigated in detail. This study also aims to understand the influence of compatibilizers on the crystallization behavior and to generate fundamental understanding of the nucleation effect of the compatibilizers on the confined crystallization behavior of the blends. No such attempts have been made in this direction to the best of my knowledge till date.
9.2. Results and discussion

9.2.1. Uncompatibilized blend: Effect of blend ratio

9.2.1.1. Morphology

Blend ratio has a profound influence on the particle size and size distribution of iPP/NBR blends. The cryo-fractured surfaces of the blends were analyzed using SEM and are given in figure 9.1a-f, where a and b show the fractured surfaces of PP/NBR 02/98 and PP/NBR 05/95 respectively. From this figure it can be seen that domain size and its distribution change with increasing concentration of PP. In figure 9.1a, the domain size is very small (less than 1µm) and distribution (monodispersed) is almost uniform. Further addition of PP into NBR shows a polydispersed morphology, where we can observe a non-uniform distribution of domains. Polydispersity of PP domains can be clearly understood from figure 9.1c, which is a magnified view of the figure 9.1b. SEM picture 9.1d belongs to PP/NBR 10/90, blend. Interestingly, this blend composition shows maximum number of crystallization peaks (fig.9.2a). Micrograph1e. shows the cryo-fractured surfaces of PP/NBR 15/85 blend. Phase morphology of the PP/NBR blends having 15/85 and 20/80 composition are given in figures 9.1e and f.
The quantified domain diameters calculated from the morphology analysis are shown in table 9.1. The blend having a composition 02/98 (PP/NBR) shows PP domains in the range of 250nm to 1µm and the number average domain diameter is 0.465 µm. When the PP content in the blend

<table>
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<th>Blend ratio NBR/PP/PP-MA/PP-COOH/PP-NBR block</th>
<th>$d_n$ (µm)</th>
<th>$d_w$ (µm)</th>
<th>$d_v$ (µm)</th>
<th>$d_n/d_v$</th>
<th>$N_v$ (cm³)</th>
<th>$N_n$ (cm⁻³)</th>
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<td>98/02/0/0/0</td>
<td>0.46</td>
<td>0.77</td>
<td>1.90</td>
<td>1.67</td>
<td>0.55 x 10¹⁰</td>
<td>0.38 x 10¹⁰</td>
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<tr>
<td>95/05/0/0/0</td>
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<td>2.70</td>
<td>4.88</td>
<td>2.16</td>
<td>0.82 x 10⁹</td>
<td>0.49 x 10⁹</td>
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<td>0.30</td>
<td>0.28 x 10¹¹</td>
<td>0.31 x 10¹⁰</td>
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</table>
increases, size distribution of the PP domains varies over a wide range. PP/NBR blend with 15wt% of PP shows a number average diameter of 2.56µm. Morphology of the blends has a crucial role in the crystallization behavior of these blends and this is discussed in the coming sections.

![Fig. 9.1](image)

**Fig. 9.1** a-e) Scanning electron micrographs of the uncompatibilized blends  
a) NBR/PP 02/98 b) NBR/PP 05/95 c) NBR/PP 10/90 d) NBR/PP 15/85 e) NBR/PP 20/80.

### 9.2.1.2. Fractionated crystallization of uncompatibilized blends

The crystallization behavior of the pure iPP and the blends is presented in figures 9.2 a-d. The pure iPP exhibits its usual behavior when cooled from the melt at a heating rate of 10°C/min by displaying an exothermic peak at 110°C, (fig 9.2a). It could be seen from the figure 9.2a that the crystallization behavior of the PP/NBR blend having compositions 02/98, 05/95, 10/90, 15/85 and 20/80 are very much different from neat PP. The crystallization
behavior of these blends are very peculiar, where the iPP was dispersed as fine droplets of diameter in between 250nm to 5µm in the crosslinked NBR matrix (figs 9.1a to f). In these blends iPP is in the dispersed state showing stepwise crystallization. Crystallization of iPP in the blend having a composition 02/98 and 05/95 PP/NBR was found to be suppressed and showed marked decrease in the T_c onset and T_c from the temperature region where the iPP usually crystallizes in the bulk i. e., at 110°C. This effect is due to the confinement of iPP into very fine droplets in the NBR matrix during the melt mixing. These droplets do not have sufficient nuclei for crystallization. In these two blend compositions, the heterogeneous nucleation of the semicrystalline phase was nearly suppressed. The T_c of 02/98 and 05/95 PP/NBR blends are 68.1 and 70.2°C respectively.
Fig. 9.2a-d). Effects of blend ratio and cooling rate on the fractionated crystallization behavior of neat PP and its blends a) Influence of blend ratio b) Neat PP at various cooling rate c) Effect of different cooling rate on the crystallization activities of NBR/PP 98/02, inset shows the change in $T_c$ as a function of cooling rate d) Result of different cooling rate on the crystallization activities of NBR/PP 90/10, inset shows the change in $T_c$ as a function of cooling rate.

In the case of iPP/NBR blends having composition 10/90, a different type crystallization exotherm was observed (fig 9.2a). Crystallization of the iPP component occurs in at least in three distinct steps, which are distinguished by the letters A, B and C in the order of decreasing $T_c$'s in the DSC analysis. The crystallization peaks for the above exotherms are 118.6,
101.3 and 69.6°C respectively. It can also be seen that exotherms A and B in the figures are so close to one another and one appears as a shoulder for the other.

Explanation for the appearance of three different exotherm in the blend is due to the fact that, during processing, iPP is dispersed into fine droplets. The content of the heterogeneities of each droplets could be different and also the polymer may contain different type of heterogeneities which become active at different super coolings depending on their specific interfacial energy differences with the molten polymer (9). Goossens and Groeninckx [22] and Huang et. al. [23] recently reported that these heterogeneities could be residues of catalyst, impurities, unmolten crystallites or solvent.

On the other hand, when the iPP becomes the continuous phase, the heterogeneity with the lowest specific interfacial energy difference with the polymer and the impurity, will be activated at lower super cooling and will dominate the crystallization of the polymer by secondary nucleation at the created crystals. This is very similar to the case of neat iPP where the crystallization occurs in one step as in figure 9.2b.

The heterogeneous nucleation is the commonly observed mechanism of initiation of polymer crystallization from the melt [24-26]. This type of nucleation is often promoted on surface of foreign bodies. Turnbull and Vonnegut [27] postulated that nucleating efficiency should increase with increasing closeness of match between lattice parameters of the substrate and the forming crystal. In this case there were no other heterogeneities that were highly active at lower super cooling to cause any nucleation, since the polymer crystallizes at normal temperature of 110°C. Inhibition of this mechanism will
work only when the original volume of the material was divided into tiny droplets or the forming crystals were poor or the numbers of active heterogeneities were low. In these cases one could see the exothermic peaks at greater super-cooling. This was the case for iPP/NBR blends having compositions 02/98 and 05/95 where the crystallization took place in single exotherm located at 68 and 70°C respectively (Fig.9.2a). Sylvie has already shown that crystallization of PP could take place at higher supercooling [28]. Both the blends 02/98 and 05/95 showed extremely fine particles of PP dispersed in the continuous NBR matrix.

Looking at the cooling curves of 15/85 iPP/NBR blend we could consider that only a certain number of droplets contain heterogeneities of type ‘B’ and ‘C’. The number of exotherm generated will greatly depend on the relative super cooling needed to activate each dominating nuclei within a certain number of droplets. It is also possible that some domains contain no effective heterogeneities at all, and in that case homogeneous nucleation will play. Such a situation occurred in the case of 80/20 blends where a small peak was observed at 45°C (Tc) (fig 9.2a). Homogeneous nucleation should occur at the highest attainable super-cooling (D). Therefore in the case of 90/10 composition it could be well understood that exotherms A, B and C were due to the presence of three different kinds of heterogeneities in the different crystallizing group of droplets, while exotherm ‘D’ (38°C) is due to the crystallization after homogeneous nucleation of the droplets without any impurities. Muller and co-workers [16] reported that iPP undergoes homogeneous nucleation at lower temperature (45°C). According to Cormia et al. [29] the homogeneous nucleation temperature is derived from droplet experiments (dispersed in liquid media) is around 85–87°C.
9.2.1.3. influence of cooling rate on the fractionated crystallization

Effects of the various cooling rates on the fractionated crystallization behavior were investigated using five different cooling rates. Two blend compositions were selected for this study. DSC thermograms of non-isothermal crystallization of the pure isotactic polypropylene at different cooling rates are shown in figure 9.2b. Due to the sufficient time available to activate nuclei at low cooling rates, the onset of crystallization exotherm appears at smaller super coolings, i.e., at higher temperature. $T_c$ onset was highest for the lowest cooling rate i.e., for $-1^\circ$C/min. $T_c$ (crystallization temperature) decreased with increasing cooling rate. Figure 9.2c shows the DSC cooling scan of the blend with a composition of NBR/PP 95/05. This blend shows the delayed crystallization phenomenon. Crystallization temperature is shifted towards the low temperature as the cooling rate increases; this is shown in the graph inset in this figure. At lower cooling rate, there was enough time to activate the nuclei for crystallization. But for high cooling rate, time available for activation was small, therefore crystallization temperature is shifted towards lower temperatures. As the cooling rate increases the range of crystallization ($T_{onset}$-$T_{endset}$) increases and highest is for the cooling rate $-20^\circ$C/min.

Figure 9.2d shows the change of fractionated crystallization exotherm on applying various cooling rates for NBR/iPP 90/10 blend. Different types of heterogeneities were activated at different under-cooling. When the cooling rate changes, the activation temperature for the crystallization ($T_c$) also changes. The heterogeneities are activated at higher temperature if the cooling rate is low. At lower cooling rates, nuclei will get enough time to activate. Reverse phenomena happens at higher cooling rates. The inset of figures 9.2c
and 9.2d show how different peaks (A, B, C and D) are affected by distinct cooling rates.

**9.2.2.1. Influence of compatibilizer on the blend morphology**

iPP/NBR blend having the highest number of exothermic peaks (10/90 PP/NBR) was selected for finding out the effect of compatibilization on the fractionated crystallization phenomenon. In this case we used various compatibilizing agents such as MA-PP, COOH-PP, graft copolymer prepared from the MA-PP and amine terminated NBR. Figures 9.3a-c show the morphology of 10/90 PP/NBR blend having different amount of MA-PP (1, 3, and 5wt%, respectively). The compatibilization is due to the polar-polar interaction between the nitrile group of NBR and the anhydride group of MA-PP which enhances the interaction between the pairs as reported by George et al. (30). It has been found that the addition of 5 wt% of MA-PP lowers the number average domain diameter (dn) from 1.5 to 0.5µm.
Fig. 9.3 a-i) Showing the scanning electron micrograph of the cryogenically fractured surfaces of compatibilized NBR/PP 90/10 blends with, a) MA-PP 1phr, b) MA-PP 3phr c) MA-PP 5phr. d) 1phr COOH-PP e) 3phr COOH-PP f) 5phr COOH-PP g) 1phr NBR-PP block h) 3phr NBR-PP block i) Schematic representation of the compatibilizer concentration on the dispersed PP domains.

SEM pictures taken from the cryogenically fractured surfaces of the COOH-PP modified NBR/iPP blends are shown in the figures 9.3 d-f, which
contains 1, 3 and 5 wt. percentage of the compatibilizer respectively. Addition of 5 wt percentage of the COOH-PP reduces the dn value from 1.5 to 0.52µm. This clearly proves the compatibilizing action of the COOH-PP in the NR/PP blend. The NBR/iPP blend compatibilized with carboxylated modified polypropylene shows similar results as those of maleic modified polypropylene systems. The polar-polar interaction between the carboxyl group and nitrile group favours compatibilization process.

The compatibilizing action of NBR-PP block copolymer in NBR/iPP blend having 90/10 blend ratio is shown in the figures 9.3g-h. The physical compatibilization of the blend system using NBR-PP block co-polymer, (block copolymer was prepared separately and then added into the NBR/PP blend interface) leads to very similar results as that of the previous compatibilizers.

![Graph showing domain size reduction (%) vs. compatibilizer concentration (wt%)](image)

**Fig.9.4.** Emulsifying action of compatibilizers as a function of compatibilizer concentration.

The main feature of compatibilization is the significant drop in dispersed domain size with the addition of compatibilizers. This is shown in figure 9.4. The
reduction in particle size may be taken as a direct evidence of emulsifying action of compatibilizer. It can also be noted that the efficiency of compatibilizers to act as emulsifying agent is different for different compatibilizers. For example initially more sharp reduction is observed in the case of PP-g-NBR compatibilizer followed by leveling off. At the critical micelle concentration of the compatibilizer, domain size becomes uniform and finer. The behaviors of the other two compatibilizers are identical. All the compatibilizers increases the number of the PP domains ($N_v$) in unit volume (table 9.1).

9.2.2.2. Confined crystallization

Let us now examine the confined crystallization behavior of the blends in the presence of three compatibilizers. The influence of different reactive and physical compatibilizers on the confined crystallization iPP in 90/10 NBR/iPP blend is shown in figures 9.5a-c. It is interesting to note that even by the incorporation of 0.5 phr maleic functionalized iPP, only one exothermic peak could be observed in the cooling scan which is very similar to the neat bulk iPP (fig. 9.2b). Higher concentration of MA-PP also shows a similar behavior. Thus reactive compatibilization significantly affects the fractionated crystallization phenomenon and leads to a single smooth exotherm. The situation was the same for other blend systems too in the presence of PP-MA. As discussed earlier, the addition of MA-functionalized iPP results in the reduction of particle size. The SEM micrograph 9.3 a-c. shows the reduction in domain diameter. The decrease in the interfacial tension and suppression of coalescence lead to better interaction between PP and NBR phases. Such reduction in particles size by the addition of compatibilizer results in the grater no of particles ($N_v = 0.17 \times 10^{10}$, number of particles calculated based on volume average diameter as per equation 2.5 (in chapter 2) by the addition of 1 wt percent of PP-MA). But this does not show any
further fractionated phenomenon, which means that there were enough active nuclei for the crystallization to occur at normal $T_c$.

**Fig. 9.5a-c)** Effect of compatibilizer concentration the confined crystallization behavior of NBR/PP blends a) Influence of maleic modified polypropylene on the fractionated crystallization behavior of NBR/PP 90/10 b) Influence of carboxylated modified polypropylene on the fractionated crystallization behavior of NBR/PP 90/10 c) Influence of NBR-PP block copolymer on the fractionated crystallization behavior of NBR/PP 90/10 blend.

From figure 9.5b it can be seen that 1 wt% addition of the COOH-g-PP makes substantial difference in the fractionated crystallization behavior. The
addition of just 1 wt% of carboxylated PP, shifts the crystallization exotherms to higher temperature, given in table 9.2. As the effect of compatibilization, the number of exotherms have been reduced to two; occurring at 100 and 118°C. But when the concentration of COOH-g-PP is increased to 3wt%, only one exotherm appears (at 118°C with a heat liberation of 81.3mJ/g.) and this totally changes the fractionated crystallization process.

Table 9.2. Enthalpy values of crystallization and T_c of NBR/PP blends for each step in fractionated crystallization.

<table>
<thead>
<tr>
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<th>D</th>
<th>C</th>
<th>B</th>
<th>A</th>
</tr>
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<tbody>
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<td>NBR/PP/PPMA/PP-COOH/PP-NBR block</td>
<td>ΔH_c (mJ/g)</td>
<td>T_c (°C)</td>
<td>ΔH_c (mJ/g)</td>
<td>T_c (°C)</td>
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<td>-</td>
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Influence of NBR-PP block physical compatibilizer on the stepwise crystallization of NBR/iPP blend is shown in figure 9.5 c. The addition of 1
wt\% of NBR-PP block copolymer shifts the peak to 112°C. This compatibilizer shows an increase of \( N_v \) from \( 0.70 \times 10^9 \) (uncompatibilized) to \( 0.52 \times 10^{10} \) (compatibilized), and the domain size distribution reaches the nanoscale, (a large number of domains in the nano size are seen). But the presence of compatibilizer offset the fractionated crystallization process. All the exotherms merge together and fractionated crystallization does not take place in this blend system. Addition of 3 wt\% PP-g-NBR decreases the width of the dynamic crystallization peak and the peak is shifted to 112.4°C which is close to the bulk crystallization of neat PP.

The disappearance of the fractionated crystallization in the presence of compatibilizer could be explained as follows. Due to the decrease in particle size (to the nano regime as a result of the confinement of the PP chains) and size distribution on account of compatibilization, interfacial area of the dispersed phase increases enormously. This leads to increased interaction between polar NBR phase and non-polar PP phase which in turn results in the migration of heterogeneities from the rubber phase to the iPP phase. Schematic representation of the strengthen of the interphased as a result of compatibilization and the nuclei migration during the melt blending in presence of compatibilizers is shown in the figure 9.6.a and b.
Fig. 9.6 a-b) Schematic representation of compatibilizer at the interphase and nuclei migration during melt mixing. a) Strengthening of interphase using graft copolymer formed by the reaction between MA-PP and liquid NBR. b) Schematic representation of the impurity migration during melt mixing.

The theory of nuclei migration phenomena in polymer blends has been proposed by Galeski and co-workers. [31]. According to this theory, in a polymer blend, the difference in interfacial free energies of the impurities with respect to both molten components is the driving force for the migration across the interface of the nuclei from one component to another. The tendency to minimize the interfacial energies favors, therefore, the migration of the heterogeneities toward that blend component in which their interfacial energies are lower. It can be argued that during the preparation of the blend, some unreacted catalyst or heterogeneous nuclei migrate towards the PP phase. This migration is accelerated in the presence of compatibilizers which increases the interfacial interaction between the dissimilar polymer pairs. So in the compatibilized melt iPP/NBR phase, two kinds of heterogeneous nuclei are present: the original iPP nuclei and the foreign nuclei migrated from NBR to iPP. We cannot discard another possibility where the compatibilizer itself can act as nuclei for crystallization. Therefore, the use of compatibilizers provide nucleation centers for the crystal growth. Surface growth of crystals and melt-interphase in chain folded lamellae in polymer crystals is well reviewed by Yamamoto [32]. Compatibilizers can act as substrate for the crystal growth. It is very important to add that present findings are very novel in the sense that all the previous studies suggested enhanced fractionated crystallization in presence of compatibilizers [31,33,34].

9.2.3. Supporting evidence for fractionated crystallization

9.2.3.1. Effect of self-seeding technique
In order to obtain evidence for fractionated crystallization, self seeding experiments were performed as reported elsewhere [19,35]. In figure 9.7a-b, the exotherms obtained after the annealing neat iPP at several temperatures are shown. The annealing temperatures were selected in such a way that one of them is much higher than the melting temperature of PP (the selected temperature was 220°C). This has been done in order to remove all crystals present in the system. The second temperature selected was 170°C and this is very close to the melting point of polypropylene. This will leave few crystals in the unmolten state. Third temperature selected was 165°C and this is the melting peak of polypropylene. This will leave much more crystals in the system than in the previous cases and will accelerate the crystallization process. It can be seen from figure 9.7a that \( T_c \) is shifted to higher temperature with decreasing annealing temperature. This self nucleation experiment provides an easy way to increase the nucleation density of the polypropylene, by leaving small crystal fragments in the molten state prior to the crystallization process (36). Polypropylene sample annealed at 220°C gives a peak at 110°C. When the pre-melting temperature is decreased to 170°C in the self-nucleation regime, \( T_c \) is shifted to 138°C. Further decrease in annealing temperature to 165°C, (this temperature is within the melting peak and leaves
(this temperature is within the melting peak and leaves enough crystal fragments) increases the $T_c$ to 140$^\circ$C.

![Graphs showing effects of self seeding techniques on the confined crystallization behavior of NBR/PP blends](image)

**Fig. 9.7.a-b)** Effects of self seeding techniques on the confined crystallization behavior of NBR/PP blends a) Outcome of self seeding technique on the crystallization behavior of polypropylene b) End result of self seeding technique on the fractionated crystallization behavior of NBR/PP 90/10.

Similar self seeding experiments were performed on PP/NBR blend having a composition of iPP/NBR 10/90 which shows three exotherms (Fig. 9.7b). Annealing at 220$^\circ$C gave three exotherms. Decreasing the annealing temperature to 170$^\circ$C led to the shifting of exotherms slightly towards higher temperatures. This confirms that unmolten crystals remaining at this temperature were not so high in the blend system. Further decrease in annealing temperature to 165$^\circ$C stops the confined crystallization phenomenon completely and increases the $T_c$ to 138$^\circ$C. Moreover it gives only a single
sharp exotherm. This clearly shows that crystals remaining at this temperature are sufficient to suppress the fractionated crystallization phenomenon. Therefore, it can be concluded that the reason for the fractionated crystallization is the absence of active nuclei in the system.

9.2.3.2. Wide angle X-ray scattering

The wide-angle x-ray scatterings were used to analyze the crystalline morphology developed during fractionated crystallization and is shown in figure 9.8. The intensities of the signals were very weak in the case of the blends having only 0 to 20wt% semicrystalline components. Isotactic polypropylene generally crystallized in three different crystalline structures α, β and γ forms, depending on the crystallization conditions.

![Fig. 9.8. WAXS diffraction pattern of pure iPP and fractionated crystallized samples showing the presence of α-spherulites.](image)

The WAXS pattern of pure iPP shows four maximas corresponding to 110, 040, 130 and overlapping 131, 041 and 111 planes, which were characteristics of α-monoclinic structure at 20 values of 21.6, 18.42, 16.71 and
13.99 respectively in X-ray diffractograms. It is clear that the major amount of iPP is crystallized in $\alpha$-monoclinic form. In the case of PP/NBR blend 02/98 the crystalline fraction was not sufficient to give a detectable diffraction pattern in the X-ray analysis. In this case, the amount of iPP was so small that we could not detect the signal corresponding to the homogeneous crystallization from the X-ray diffraction. The diffraction patterns of NBR/PP blends having a composition of 95/05, 90/10, 85/15 and 80/20 did not show $\beta$ form, because it was too small to be detected by WAXS. Majority of the crystals formed were in the $\alpha$-monoclinic form, which shows peaks at 20 values of 21.6, 18.42, 16.71 and 13.99. Peaks at 20 values 25.36 and 28.53 were contributed from $\beta$-crystalline structures.

9.3. Conclusion

The fractionated crystallization behavior of NBR/iPP blend has been analyzed as a function of blend ratio, nature (physical and reactive) and concentration of compatibilizers and cooling rate. It was observed that blend ratio and matrix/droplet morphology play a significant role in the development of fractionated crystallization. Among the various blend ratios studied, PP/NBR 10/90 exhibited three different crystallization exotherms. This clearly indicates the importance of blend ratio. In this case, iPP has dispersed into fine droplets having different heterogeneities. Hence, each of these droplets becomes active at different crystallization temperatures depending on their specific interfacial energy differences with the molten polymer.

Influence of the cooling rate on the normal and fractionated crystallization was investigated. It was observed that due to the difference in activation energy of the nuclei for crystallization, fractionated crystallization was affected by the cooling rate. Lowering of $T_c$ and broadening of crystallization
behavior of the pure iPP and various blend composition could be correlated with the kind of nuclei present in the system.

The influence of varies compatibilizer concentration and its nature (reactive and physical) on the confined crystallization behavior of NBR/iPP blends has been evaluated. Maleic modified polypropylene and carboxylated functionalized polypropylene were used for reactive compatibilization. NBR-g-PP block-copolymer was used as physical compatibilizer. It has been found that all these compatibilizers suppressed the fractionated crystallization phenomenon. The suppression of fractionated crystallization in the presence of compatibilizer could be due to the migration of impurities from the rubber phase to the PP phase which is associated with the improved interaction between the blend components. It can also be due to the nucleating activity of the compatibilizer itself. Further experiments are needed to verify this.

Self- nucleation experiments were carefully performed to understand the role of active nuclei to suppress fractionated crystallization process. Incorporating more active nuclei into the system will result in a bulk crystallization instead of fractionated crystallization. WAXS measurement showed that dispersed micro and nano domains can crystallize and the crystals were in $\alpha$-monoclinic form. Finally it is important to add that unlike the earlier studies, the observations of the present investigation on the fractionated crystallization process indicate that compatibilization can completely suppress the confined crystallization process.
9.3. References

1. Rostami S, Polymer 1990: 31; 899.


10. Andrew HL, Khait K, Torkelson JM, Polymer 2003: 44; 199-203.


