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Crystallization and melting behavior of polypropylene and maleated polypropylene blends

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Abstract

The melting behavior of blends of polypropylene (PP) and maleic anhydride grafted PP (mPP), crystallized both non-isothermally and isothermally, have been investigated by differential scanning calorimetry (DSC). Also the relationship between co-crystallization, phase separation and the corresponding crystallization conditions in the blends is presented. It has been found that either co-crystallization or phase separation in the blends can be obtained, depending on the crystallization conditions. If the cooling rate is very slow in the non-isothermal case, or the crystallization temperature is relatively high in the isothermal case, phase separation between PP and mPP molecules will be observed in the blends. Otherwise, co-crystallization between different molecules will dominate in the blend system. An effort was made to elucidate these phase phenomena with the aid of kinetic parameters by isothermal crystallization. Fractional values of the Avrami exponent are obtained, which range from 1.93 to 3.21, indicating an average contribution of simultaneous occurrence of various types of nucleation and growth of crystallization. The half-life $t_{1/2}$ of crystallization shows that incorporation of mPP in PP can either have little effect or greatly increase the crystallization rate of PP, depending on the crystallization temperatures. At higher crystallization temperatures, the crystallization rate of the blends is higher than both the pure homopolymers, resulting in phase separation morphology. The results by small angle X-ray scattering (SAXS) are consistent with those of the DSC measurements. It has been concluded that the crystallization kinetics, not the thermodynamics, mainly determine the final phase morphologies in this particular system.

Keywords: Polypropylene; Maleated polypropylene; Blend

1. Introduction

Miscibility of polymer blends has received extensive investigation, both theoretically and experimentally in the past few decades. The nature and characteristics of the amorphous/amorphous or amorphous/crystalline polymer blends are well accepted [1], [2], [3]. However, in crystalline/crystalline polymer blends, which contain crystal–crystal interactions as well as amorphous–amorphous interactions, the morphology is expected to be more complicated and their miscibility is not clearly understood.

Studies on the crystalline/crystalline polymer blends have been appearing in recent years. These systems include high-density polyethylene (HDPE)/linear low-density polyethylene (LLDPE) blends [4], [5], model linear and short-chain branched polyethylenes [6], and vinylidene fluoride- hexafluoroacetone copolymer/vinylidene fluoride-tetrafluoroethylene copolymer blends [7], and LLDPE and modified polypropylene blends [8], etc. A series of investigations on the deliberately designed system, i.e. stereoblock polypropylene/isotactic polypropylene blends were also reported [9]. [10], [11], [12]. In general, co-crystallization and phase separation phenomena were obtained for the above different systems.

Maleic anhydride (MAH) grafted PP (mPP) was proved to be an effective functional molecule for the reactive compatibilization between polypropylene (PP) and polyamide [13], [14], [15], [16]. However, the miscibility between PP and mPP has not received much attention. Recently, Baer and coworkers [17], [18] have shown that PP and mPP can either co-crystallize or phase separate, depending on the molecular weight and MAH content in mPP. In the case of high molecular weight and low MAH content, the pairs tend to co-crystallize, otherwise, phase separation will occur, which would greatly influence the mechanical properties of PP/mPP-based materials.

However, in crystalline/crystalline polymer blends, the resultant morphologies are not only attributed to thermodynamic factors but also to kinetic ones during subsequent

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crystallization. Little has been done to further understand this proposition. Thus, in this study, we prepared PP blends of different compositions with the mPP of low molecular weight and high MAH content. The dependence of phase morphologies on thermal treatments was systematically evaluated. The nature of co-crystallization and phase separation in PP and mPP blends was expected to be understood in depth.

2. Experimental

2.1. Materials and sample preparations

Polypropylene (PP) used in this study is commercial molding grade Daelim Poly PP, supplied by Daelim Industrial Co. (Daeduk, Korea). Its melt index is 12 g/10 min at 230°C (ASTM: D1238). The powder-like maleic anhydride grafted PP (mPP) was obtained from the Honam Petrochemical Co. (Daeduk, Korea). Its melt index (MI) is 2000 g/10 min at 230°C. MAH content was determined as 2.91×10^{-4} mol g^{-1} by titration.

Mixtures of PP and mPP powder were melt blended in a Brabender internal mixer at 190°C for 10 min. The mixed PPs were then quickly cooled down to room temperature. The PP granule and mPP powder were dried in vacuum at 50°C for 24 h prior to use.

2.2. DSC measurements

DSC measurements were made on a Perkin–Elmer DSC-7 thermal system purged with nitrogen. Its temperature scale was calibrated from the melting characteristics of indium. The experiments were conducted both non-isothermally and isothermally.

2.2.1. Non-isothermal crystallization

The sample was first rapidly heated up to 180°C, approx. 20°C higher than the melting point of PP, and maintained at this temperature for 10 min in order to erase any previous morphological history which the sample might be carrying. The sample then non-isothermally crystallized when it was cooled down to room temperature at different cooling rates. It was subsequently heated at a heating rate of 10°C min^{-1}. The samples were approx. 10 mg. All curves were normalized to the unit weight of the sample.

2.2.2. Isothermal crystallization

The sample weighing approx. 10 mg was heated to 180°C and kept for 10 min. It was then rapidly cooled down to a certain crystallization temperature and held isothermally at this temperature to obtain a crystallization exotherm. The results were treated with the help of Avrami theory.

2.3. Small angle X-ray scattering measurements

A small angle X-ray scattering experiment was conducted by using a synchrotron X-ray radiation source (3C2 beamline, wavelength 1.598 Å) at the Pohang Accelerator Laboratory. The system is equipped with a Si(111) double crystal monochromator, and a cylindrical mirror. The scattering intensity was corrected by background scattering.

3. Results and discussion

3.1. Crystallization and melting behavior of non-isothermally crystallized PP, mPP and their blends

3.1.1. Pure PP and mPP

The melting behavior of isotactic PP crystallized in a number of different ways, for example isothermal crystallization, quenched and annealing treatments, has been studied [19], [20], [21], [22], [23]. A common feature of all these investigations has been the observation of clear multiple fusion endotherms. This has been attributed to several factors such as two different crystal forms [19], [20], discrete bunching of crystallites of varying degrees of perfection [19], difference in crystallite size [21], etc. However, none of these factors can fully explain the observed results. In 1986, a systematic study was reported, which provided a better understanding of the multi-fusion process [23]. The main reason for such multiple endotherms was verified to be the recrystallization or reorganization of some crystallized fractions.

In this study, non-isothermal crystallization was conducted according to the method described in the experimental section. Fig. 1a shows the corresponding DSC thermograms for pure iPP obtained in the subsequent heating processes. Unlike isothermally crystallized specimens reported in the literature [23], the general feature of these curves is the dominance of the single fusion endotherm. As the cooling rate increases, the peak position remains constant but a shoulder appears in front of the melting and the curves therefore become less symmetric. For the specimens prepared at a lower cooling rate, the molecules have enough time to form perfect crystals. However, as the cooling rate increases, the crystallized fraction may consist of defective crystals as a result of higher supercooling. These defective crystals would undergo perfection during heating. Thus, this shoulder is due to the recrystallization or reorganization of crystals initially formed during non-isothermal crystallization. However, it follows that at rapid cooling rates as high as 40°C min^{-1} only a small amount of originally formed crystals will undergo recrystallization in the heating process, which can be qualitatively evaluated in terms of the relative areas under the resolvable melting peaks. The main melting peaks are, therefore, not influenced by the recrystallization effect in the case of non-isothermal crystallization.

Fig. 1b shows the fusion endotherms for mPP specimens crystallized under the same conditions as in Fig. 1a. Unlike pure iPP, the DSC curve for mPP shows either two

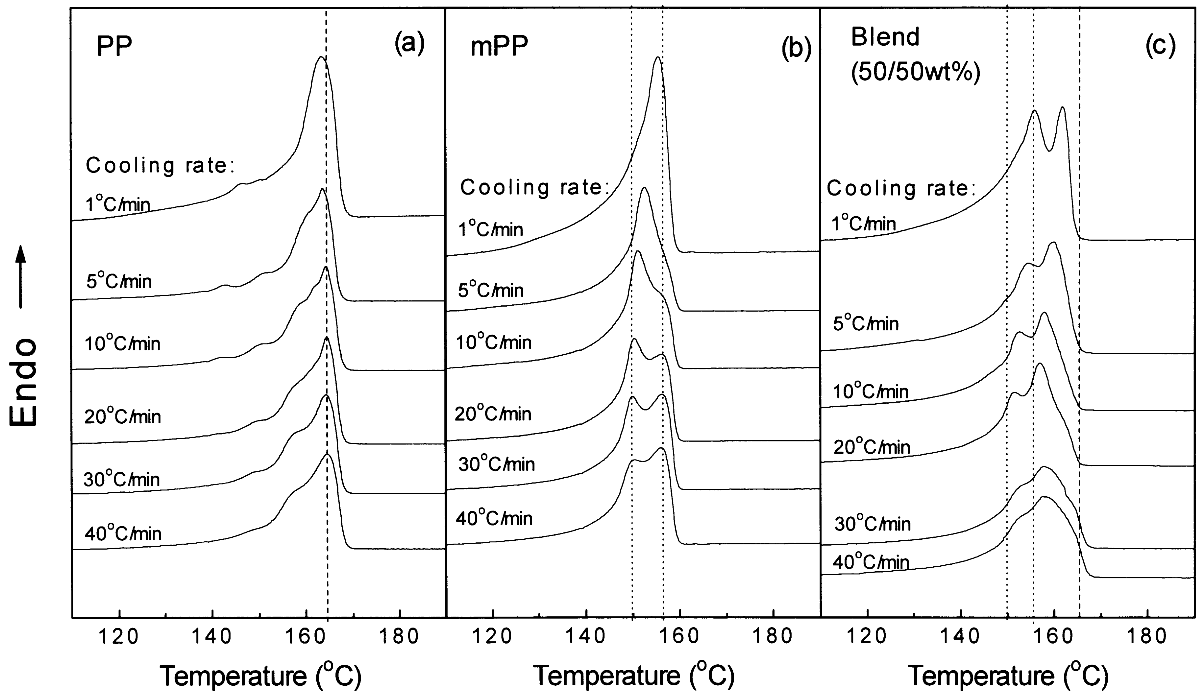

Fig. 1. DSC fusion endotherms for specimens of (a) pure PP; (b) mPP; and (c) the 50/50 blend prepared by non-isothermal crystallization at various cooling rates. The heating rate is 10°C min^{-1}.

endotherms or is resolvable into two. Henceforth, the peak at the lower temperature is called peak-I, whilst that at the higher temperature is called peak-II. Peak-I shifts to a lower temperature with an increasing cooling rate and becomes constant at 20°C min^{-1}, at which peak-II appears clearly and remains constant with the cooling rate. The effect of cooling rates on the relative area under peak-I and peak-II is also obvious. From the curves, it is observed that with the increase in cooling rate, the area under peak-I decreases, while the area under peak-II steadily increases. Owing to the presence of functional groups in the side of the mPP backbone molecules, imperfect crystals can easily form under conventional conditions. Thus, peak-I represents the melting of the crystals formed during the non-isothermal crystallization process, while peak-II is attributed to the melting of crystals of higher stability formed due to the recrystallization or reorganization of crystals initially formed during the non-isothermal crystallization. Non-isothermal crystallization is more complicated than isothermal crystallization. However, they are comparable in the sense of supercooling. When the cooling rate is low, it is similar to isothermal crystallization at higher temperature. Crystallization proceeds at a slower rate, resulting in more perfect and stable crystals. As the cooling rate increases, supercooling becomes greater and more defective crystals are obtained, which would undergo perfection during heating. Thus, peak-II appears and the area under this peak increases with the cooling rate. This trend is very similar to the case of isothermal crystallization of iPP in Ref. [23]. It follows that in non-isothermal crystallization, recrystallization would be quite obvious in mPP but not in iPP.

3.1.2. PP/mPP blends

Fig. 1c gives the heating DSC thermographs for the PP/mPP (50/50 wt) blends prepared at various cooling rates. The results show that the melting characteristics for the blends are closely related with the cooling rate. For the blend specimen prepared at a cooling rate as low as 1°C min^{-1}, two distinct melting peaks T_1 and T_2 appear in the subsequent heating process. As the cooling rate increases, the two peaks shift towards the lower temperature and the intensity of the peak T_1 becomes weaker and weaker. When the cooling rate is as high as 30°C min^{-1}, a single broad melting peak for the blends is obtained.

Combining the discussions of pure PP and mPP in Fig. 1a and Fig. 1b, the results can be summarized in Fig. 2. At the lower cooling rate, T_1 of the blend is observed to be almost the same as peak-I of pure mPP. As the cooling rate increases, the T_1 position shifts slightly to the lower temperature but it is still close to the peak-I of pure mPP. When the cooling rate increases further, T_1 disappears and one single melting peak is observed. On the other hand, only at very slow cooling rate T_2 of the blends becomes close to the melting temperature of pure PP. Then it shifts to the lower temperature with the cooling rate and becomes constant after one melting peak is obtained. It seems that, for the blend sample prepared at a lower cooling rate such as 1°C min^{-1}, PP and mPP crystallites melt separately, indicating the existence of phase separation between PP and mPP in the blend. For those specimens prepared at relatively high cooling rates, co-crystallization may dominate as characteristic of the single melting peak by DSC. If Fig. 1a and Fig. 1b are simply graphically overlapped by calculation of the

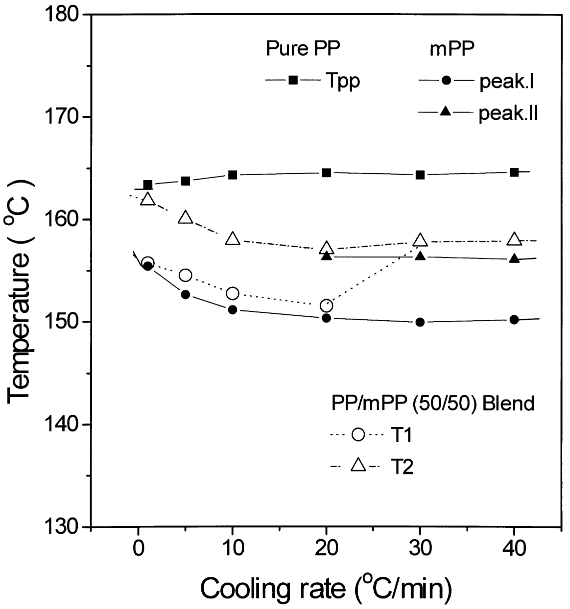

Fig. 2. Summary of the melting points of the specimens in Fig. 1.

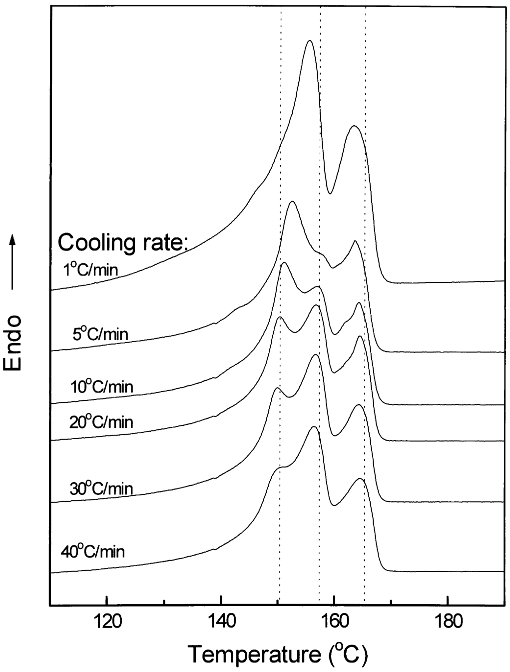

Fig. 3. Graphical overlap of DSC curves in Fig. 1a and Fig. 1b.

arithmetic mean, Fig. 3 showing multiple melting peaks will be obtained. Fig. 3 means that if the two components are phase separated, the melting curves of the blends prepared at different cooling rates should be multiple peaks. Comparing the results of Fig. 1c and Fig. 3, it follows that in Fig. 1c a different cooling rate does result in various morphologies, i.e. at a lower cooling rate phase separation may occur, while at higher cooling rates co-crystallization will dominate.

In the literature, multiple fusion endotherms of iPP were believed to be due to the recrystallization of originally formed imperfect crystals [23]. This effect has been proved to be obvious in mPP materials used in this non-isothermal crystallization. Thus, the question may be asked whether the double melting peaks in PP/mPP blends prepared at the lower cooling rate such as 1°C min^{-1} are due to the separate melting of PP and mPP crystallites, i.e. phase separation, or the recrystallization effect of imperfect crystals, or a combination of the two? Fig. 4a; Fig. 4b; Fig. 4c show the melting thermographs of different heating rates for pure PP, mPP and their 50/50 blend prepared at the cooling rate of 1°C min^{-1}. In pure PP, multiple fusion endotherms appear especially at the low heating rate. From the relative areas under the curves, the amounts of these crystallites undergoing recrystallization in the heating processes are expected to be very small. As the heating rate increases, the very small melting peaks due to recrystallization are depressed since less and less time is available for recrystallization to take place. A single melting peak is observed for all mPP material in Fig. 4b. It shows that the recrystallization effect is not obvious for the PP and mPP prepared at the cooling rate of 1°C min^{-1}, since slow cooling makes it possible to form more perfect and stable crystallites. However, for the PP/mPP blend, two distinct melting endotherms are obtained, as shown in Fig. 4c. In this case, recrystallization makes a very small contribution to the melting behavior of the blends and is mainly due to the separate melting of PP and mPP crystallites in the heating processes. The melting temperatures for the three materials are plotted in the same figure (Fig. 5). It is much clearer that T_1 and T_2 are near those of pure PP and mPP, respectively, in other words, T_1 and T_2 in the blend correspond to the melting of two individual components. The fact that T_1 and T_2 are between those of pure components means that phase separation of PP and mPP is not complete. In PP lamellar crystals, a small amount of mPP molecules may be incorporated, and vice versa.

The phase separation and co-crystallization phenomena can also be well depicted by the melting behavior of the blends with different compositions, as shown in Fig. 6. Fig. 6a gives the fusion endotherms of the blend samples crystallized at a cooling rate of 1°C min^{-1}. Two melting peaks appear for the blends of different compositions, which correspond well to the melting points of pure PP and mPP prepared under the same condition. If the relative areas under separate peaks are calculated, the corresponding ratios are consistent with the weight compositions in the blends. The melting temperatures T_1 and T_2 in the blends are mainly attributed to the separate melting of PP and mPP crystallites. Fig. 6b also shows the DSC fusion results of the blends crystallized at a fast cooling rate. Even though the melting profiles are irregular from sample to sample, a single fusion peak is obtained for all the blends, whose position is just between the melting temperatures of pure PP and mPP, indicating co-crystallization is characteristic of the blends at this cooling condition.

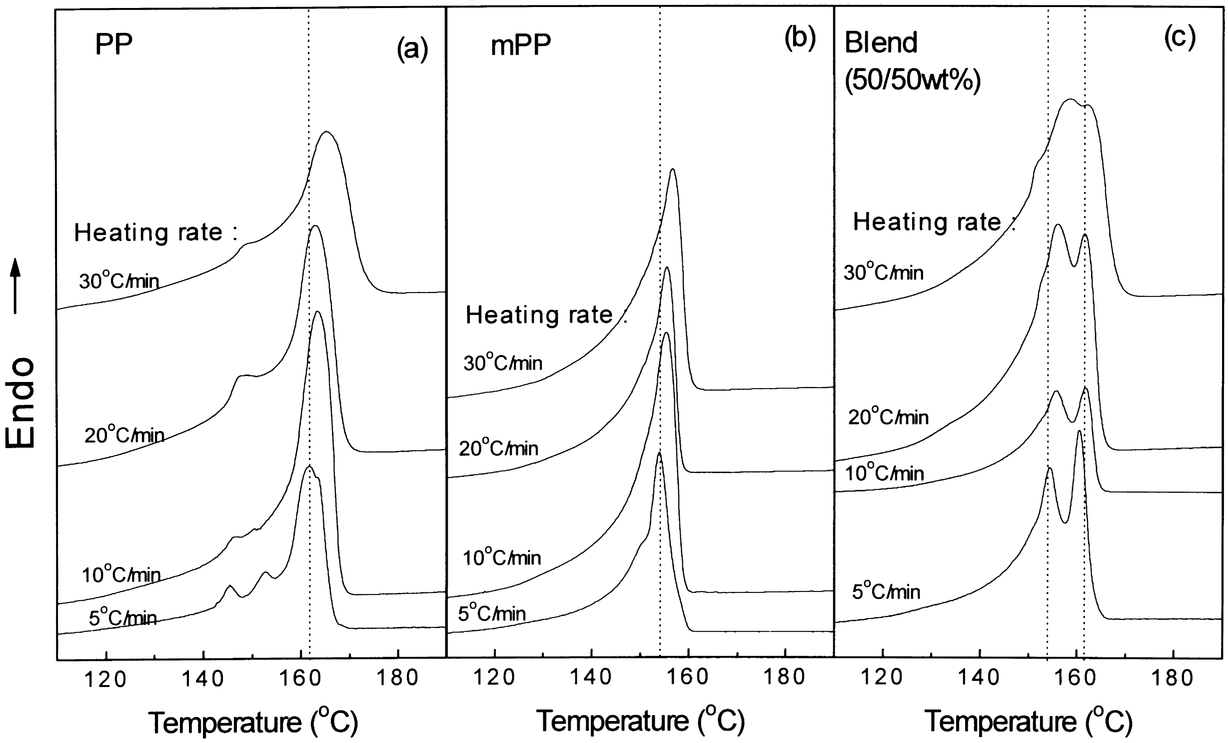

Fig. 4. DSC fusion endotherms for the specimens of pure PP, mPP and the 50/50 blend prepared by non-isothermal crystallization at a cooling rate of 1°C $\min^{-1}$. The subsequent heating rates are shown in the figure.

Further experiments were carried out to show the effect of thermodynamics on the morphological results. Fig. 7 gives the effect of melting time on DSC fusion endotherms for the 50/50 blends prepared after non-isothermal crystallization at cooling rates of 1 and 40°C $\min^{-1}$, respectively. It shows that the final morphological results are independent of the previous melting time, even as long as 2 h. These results imply that subsequent crystallization processes are the main factors determining the phase morphologies in this system.

From the above discussion, it is clear that, in the PP/mPP blends, either phase separation or co-crystallization is able to be obtained, depending on the non-isothermal crystallization kinetics. When the cooling rate is very slow, phase separation between PP and mPP crystallites occurs, which may result in PP and mPP crystallites. As the cooling rate increases, co-crystallization between different molecules will dominate in the blend systems.

3.2. Isothermal crystallization kinetics and the melting behavior

3.2.1. DSC measurements

For the samples isothermally prepared at various temperatures, similar results have been obtained. Melting behaviors of the specimens isothermally crystallized at 125 and 100°C are given in Fig. 8. This shows that at a low degree of supercooling PP and mPP crystallize separately, i.e. two distinct endotherms have been observed for the blends, which correspond to the melting points of pure PP and mPP, respectively. As the degree of supercooling increases, co-crystallization may dominate. From the viewpoint of supercooling, the significance of isothermal crystallization is similar to the non-isothermal case as discussed above, i.e. a high degree of supercooling results in fast cooling.

It is interesting to know how different morphologies have been formed under different crystallization conditions? To explain this problem, isothermal crystallization kinetics seems necessary.

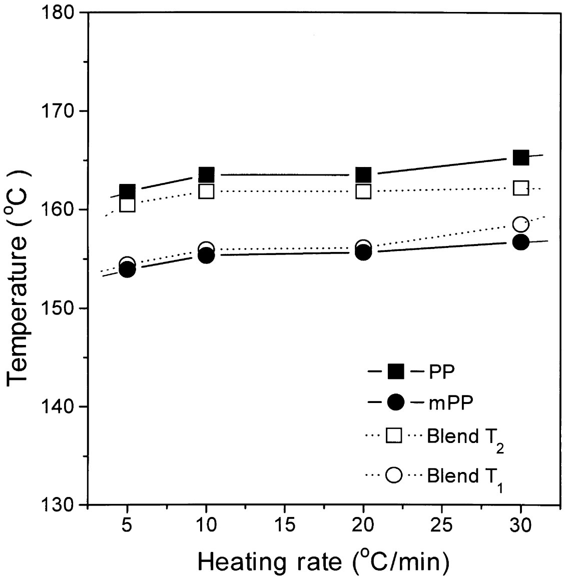

Fig. 5. Summary of the melting points for the specimens in Fig. 4.

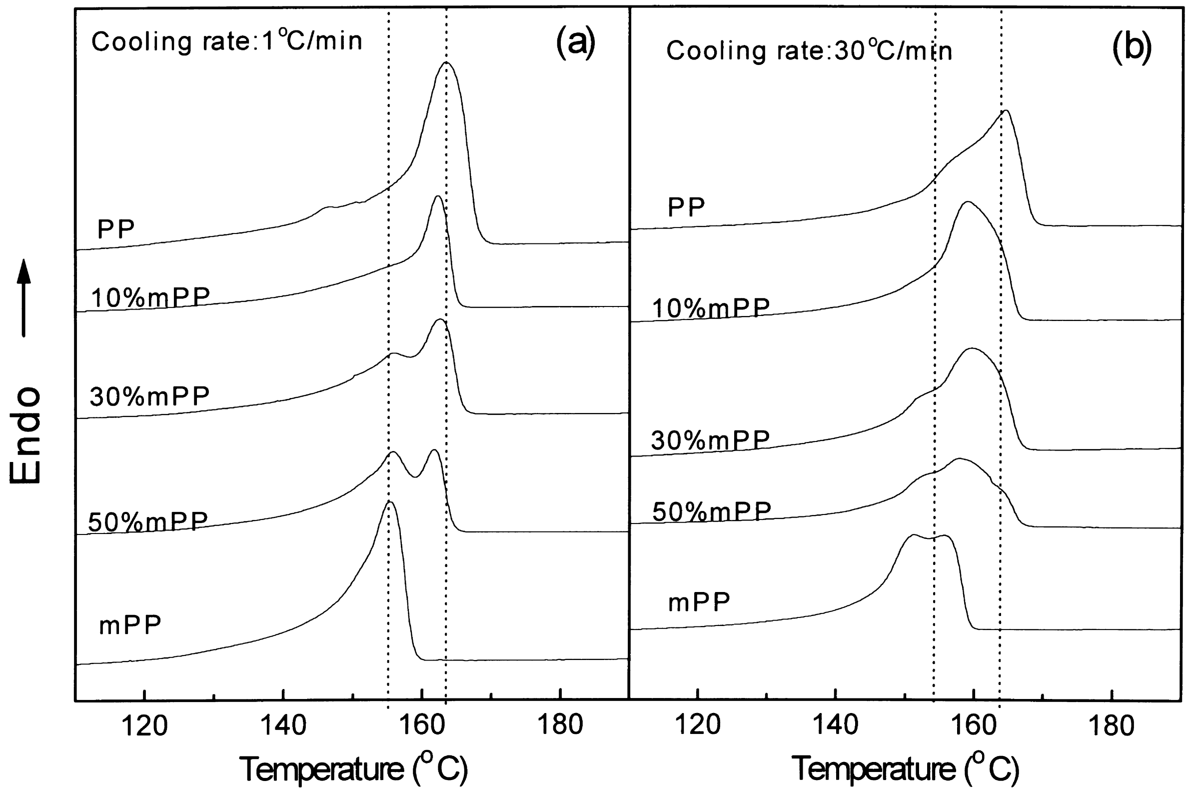

Fig. 6. DSC fusion endotherms for the specimens of pure PP, mPP and their blends prepared by non-isothermal crystallization at a cooling rate of: (a) 1°C min^{-1}; and (b) 30°C min^{-1}. The subsequent heating rate is 10°C min^{-1}.

Isothermal crystallization kinetics were conducted for pure PP, mPP and their blends of various compositions at different conditions. Values of the Avrami exponent n and the half-time of crystallization $t_{1/2}$ are shown in Fig. 9 and Fig. 10. The observed values of the Avrami exponent for the specimens vary from 1.93 to 3.21. Their fractional values would be considered representative of the nearest integral values or an average contribution of simultaneous occurrence of various types of nucleation and growth of crystallization, each conforming to different integral values of the exponent n.

The Avrami exponent n for the pure PP and mPP used in this study differs considerably with the variation of crystallization conditions. Fig. 9a shows a linear relation between the n values and the crystallization temperatures for mPP, but not for the pure PP. There is a noticeable difference in the n value with crystallization temperature. At lower crystallization temperatures, their exponents are similar, between the integers 2 and 3. However, at higher crystallization temperatures, the exponent of PP decreases to 1.97, which may be rounded off to the nearest integer 2, while that of mPP reaches 2.7, near the integer 3. A similar result is also obtained for the half-time $t_{1/2}$ of crystallization (Fig. 9b). At lower temperatures, both PP and mPP, whose $t_{1/2}$ values are almost the same crystallize fast. However, as the crystallization temperature increases, the difference in crystallization rate between pure PP and mPP becomes large. The above results imply that both pure PP and mPP have the same nucleation and growth mechanism only at lower temperatures.

The integral values of the Avrami exponent may imply the following possibilities [4]; [24]: (i) formation of three-dimensional crystallites with instantaneous nucleation ($n = 3$); (ii) formation of two-dimensional growth with instantaneous nucleation ($n = 2$); (iii) formation of two-dimensionally growing crystallites from sporadic nucleation ($n = 3$). From the relationship between the crystallization rate $t_{1/2}$ and temperature, it is clear that crystallization goes on quickly at low temperatures. As the temperature reaches 120°C and above, the crystallization rate exponentially decreases. Thus, at low temperatures, it is expected that both PP and mPP mainly form three-dimensional crystallites with instantaneous nucleation. The slightly lower values of n are attributed to the simultaneous occurrence of three-dimensional growth of crystallites from instantaneous nuclei ($n = 3$) and two-dimensional growth of crystallites from instantaneous nucleation ($n = 2$). At high temperatures, the nucleation and growth mechanism does not change for pure mPP. The decrease of the crystallization rate is due to the decrease of the nucleation rate and the growth rate with the increase of crystallization temperature. In the case of pure PP, the crystallization rate also becomes exponentially depressed. Its n value may be rounded off to the integer 2, representing the two-dimensional growth of crystallization with instantaneous nucleation.

As for the blends, irregular results are obtained. The

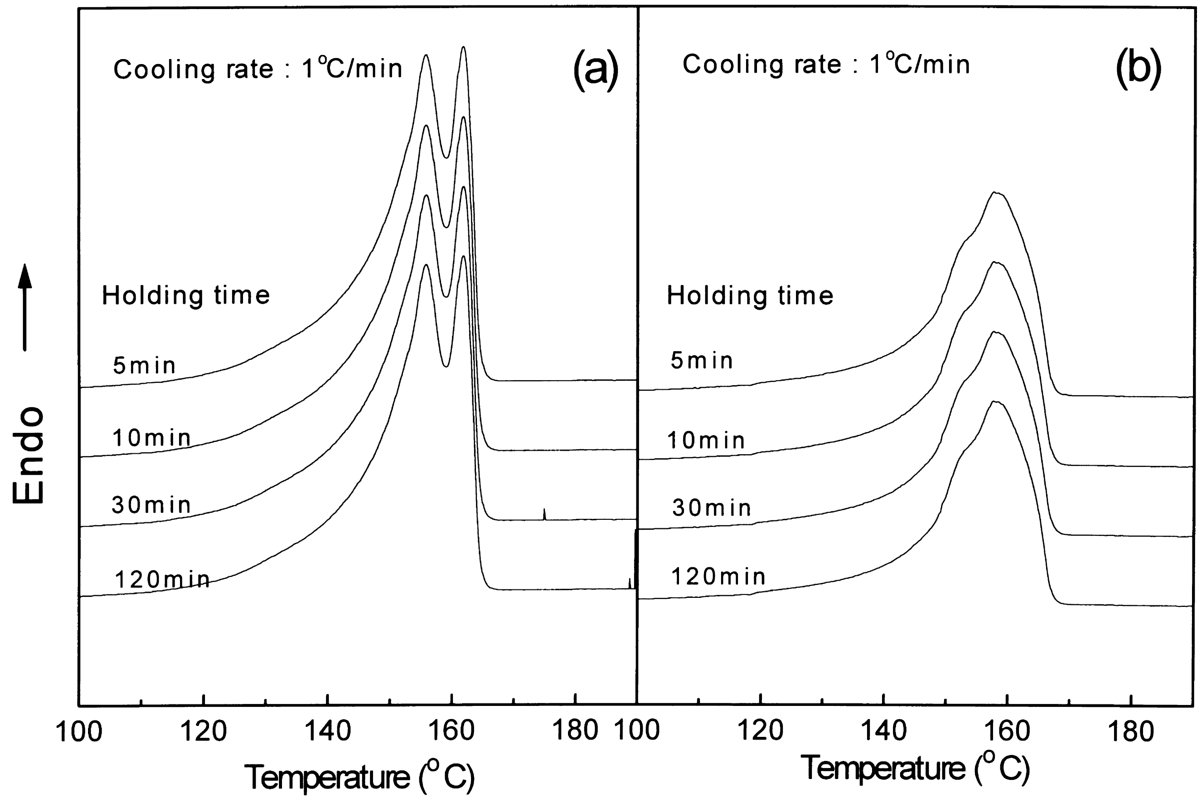

Fig. 7. Effect of holding time at 180°C on DSC fusion endotherms for the 50/50 blend prepared by non-isothermal crystallization at a cooling rate of (a) 1°C min^{-1}; and (b) 40°C min^{-1}. The subsequent heating rate is 10°C min^{-1}.

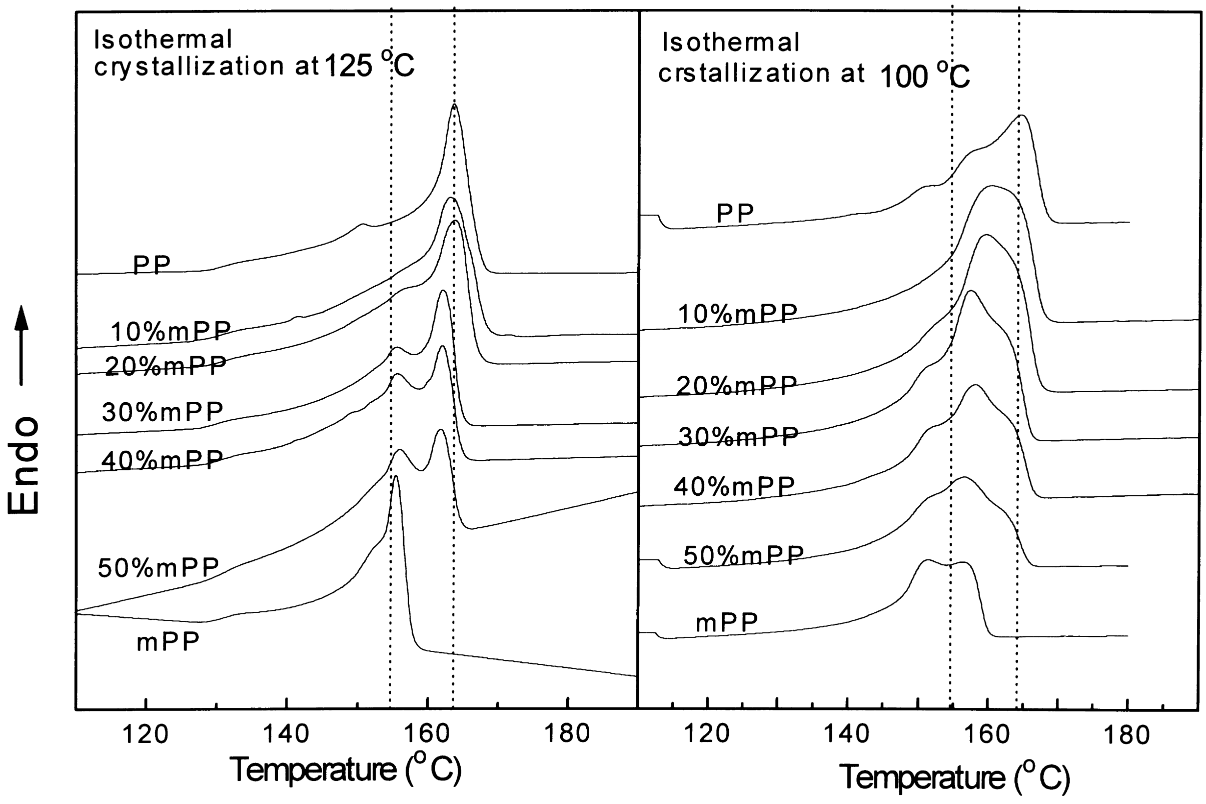

Fig. 8. DSC fusion endotherms for the specimens of pure PP, mPP and their blends prepared after isothermal crystallization at the temperatures 100 and 125°C, respectively. The subsequent heating rate is 10°C min^{-1}.

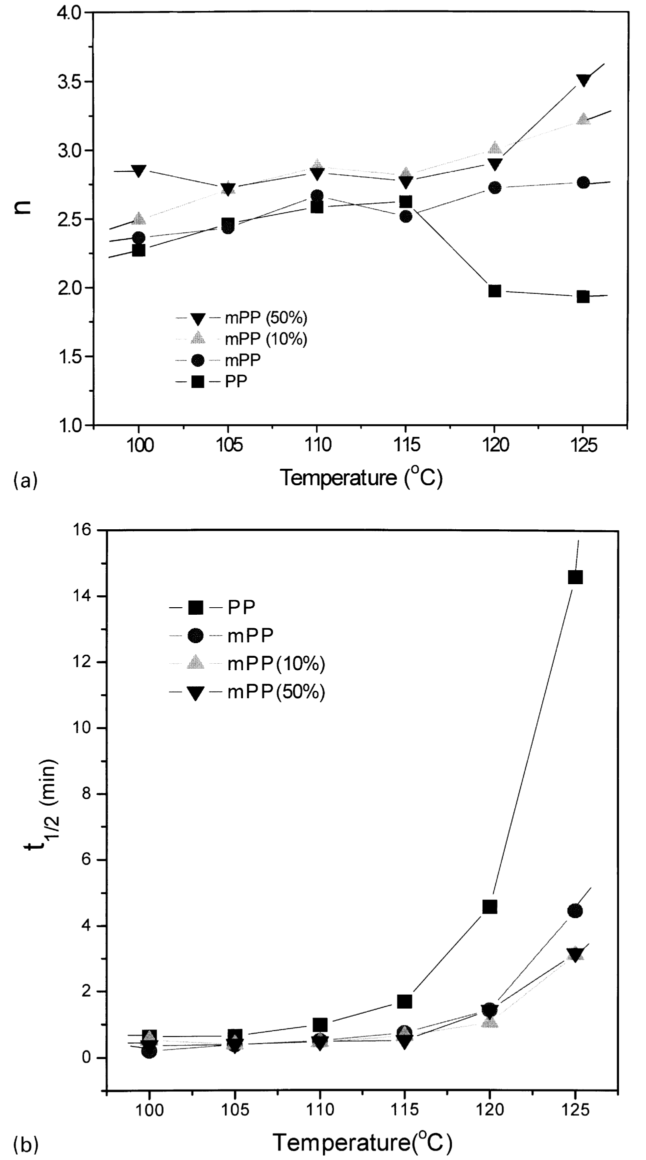

Fig. 9. (a) Avrami exponents, *n*; and (b) half-time of crystallization, $t_{1/2}$ in the isothermal crystallization processes at different temperatures for the specimens of PP, mPP and their blends.

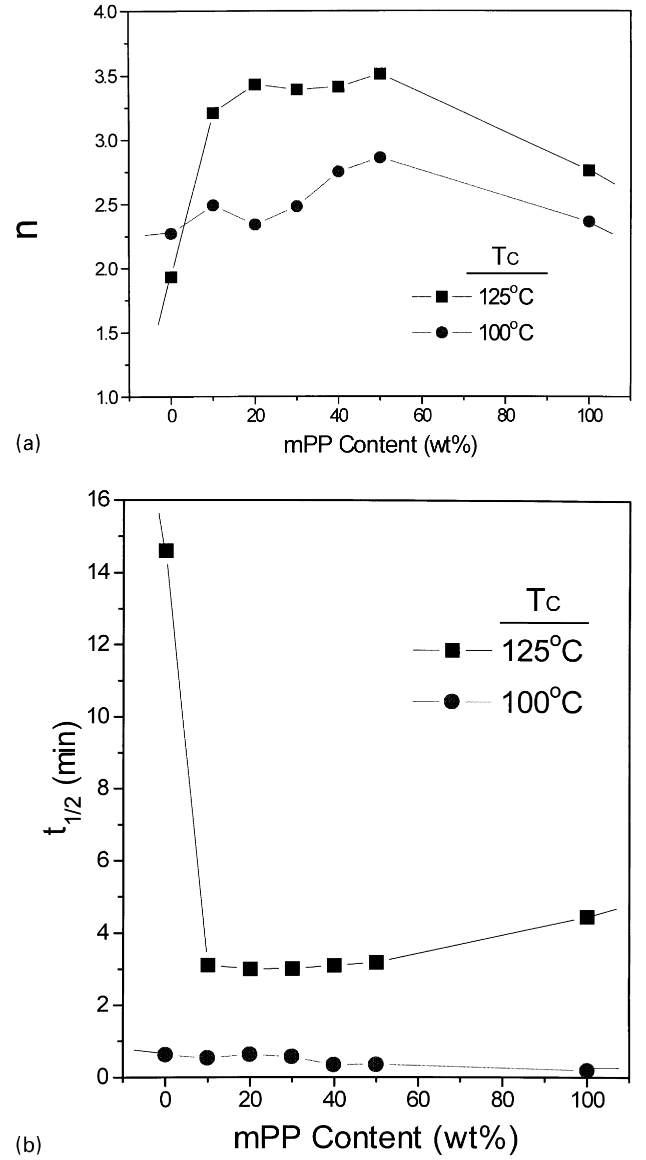

Fig. 10. (a) Avrami exponents, *n*; and (b) half-time of crystallization, $t_{1/2}$ in the isothermal crystallization processes at the temperatures 100 and 125°C, respectively, for the specimens of PP, mPP and their blends.

Avrami exponent *n* is slightly higher than that of pure PP and mPP, but mostly still less than the integral value 3 (Fig. 9a). The corresponding crystallization rates are unexpected. At lower temperatures, the crystallization rate of the blends is between or in the same order as those for pure PP and mPP polymers. However, as the temperature increases, even though the crystallization rate of the blends decreases, it becomes clearly faster than those for the corresponding pure polymers (Fig. 9b). Fig. 10 shows this trend more clearly. For the blends at lower temperatures, i.e. 100°C, the crystallization rate is between those of the two pure homopolymers, and the Avrami exponent is between the two integral values 2 and 3. At a higher temperature such as 125°C, the crystallization rates for all the blends are higher than both of the pure homopolymers.

As discussed above, different morphologies can be obtained at various crystallization conditions. At lower temperatures, the molecules of PP and mPP tend to co-crystallize, while at higher temperatures, the two different molecules will crystallize separately and form individual lamellar crystals. The crystallization kinetics in this case can be consistent with the following specific morphology results. At lower temperatures, both PP and mPP molecules crystallize fast, and the nucleation and growth rate are, in fact, comparable. So, once a nucleus is formed in the molten blends, the PP and mPP molecules have the same mobility to enter the crystals and form the co-crystal morphology. At higher temperatures, however, the crystallizability of PP and mPP molecules is quite different. At higher temperatures such as 125°C the crystallization rate of mPP

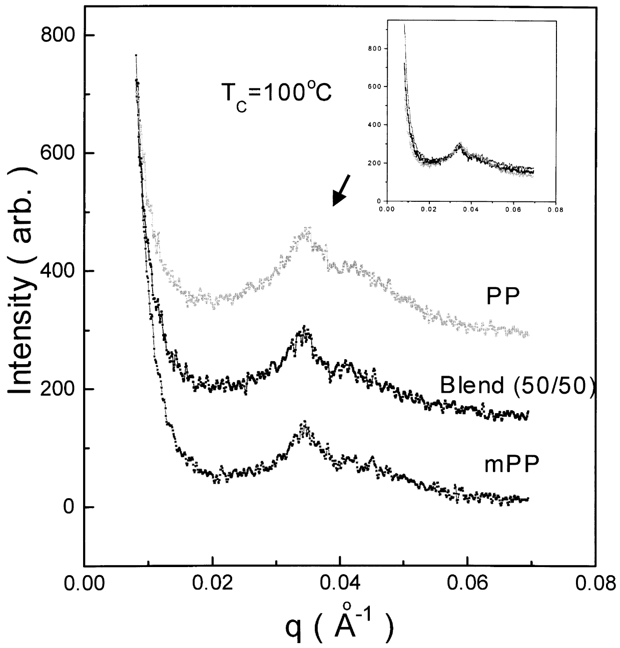

Fig. 11. SAXS profiles for the specimens of PP, mPP and their 50/50 blend isothermally crystallized at 100°C. Intensity was plotted against the scattering vector q, $(4\pi/\lambda)\sin(\theta/2)$ with λ and θ being the X-ray wavelength and the scattering angle, respectively.

molecules is almost 3-fold greater than that of PP molecules. Thus, as a nucleus appears, mPP molecules have a greater ability to form their individual lamellar crystals. That is the reason why phase-separated morphology has been observed. However, in this case, the crystallization rate for all the blends is even higher than that of pure mPP. This cannot be interpreted satisfactorily by the so-called ‘diluent effect’ [25], which generally reduces the crystallization rate. When mPP molecules crystallize first, if melted PP molecules serve as the solvent, the whole crystallization rate will be reduced. This seems contradictory to our experimental results. Here we term the reason for the enhanced crystallization as the ‘effect of nucleating activity’. At higher temperatures, mPP molecules nucleate and grow at a slow rate. So it can be regarded as a so-called quasi-equilibrium process. The nucleation of mPP molecules will make the thermal fluctuation favorable for the PP molecules nearby to form their own nuclei. Therefore, within the same time period, the nucleation rate of the blends should be higher than those of both pure polymers. A similar explanation can be found in other literature [25], which indicates that the crystallization rate of PP in the PP/PA blends is higher than the corresponding values of pure PP, related to the nucleating activity by the crystalline PA component. Furthermore, the existence of PP molecules is favorable for the mPP molecules to lower the effect of the polar groups, which may cause fewer crystal defects. Owing to the large difference in crystallization growth rate, individual lamellar crystals tend to form, even though the nuclei appear within the same temperature range.

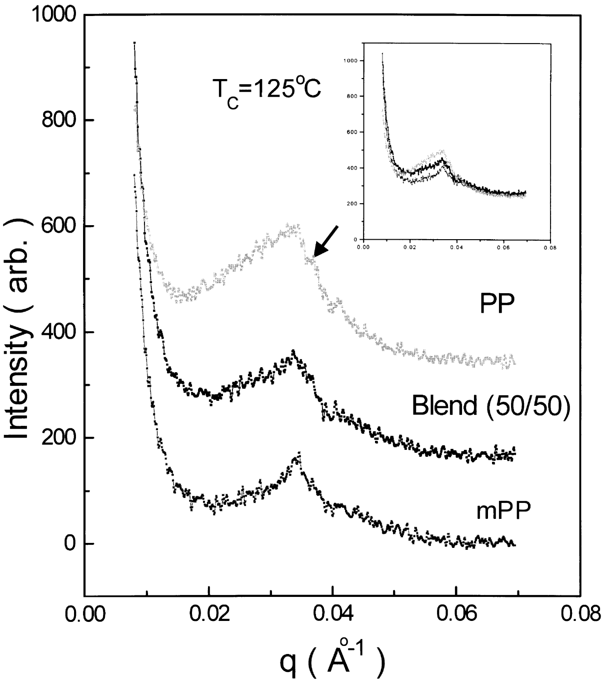

Fig. 12. SAXS profiles for the specimens of PP, mPP and their 50/50 blend isothermally crystallized at 125°C.

3.2.2. Small angle X-ray scattering measurements

Fig. 11 and Fig. 12 give the SAXS profiles for the specimens of PP, mPP and their blends isothermally crystallized at 100 and 125°C, respectively. A single scattering peak is observed for all samples. For the specimens isothermally crystallized at 100°C, the scattering profiles are similar in shape and peak position (i.e. the overlapped profiles shown in the small frame in the upper right hand of Fig. 11). At this condition PP, mPP and their blend crystallized fast. Thus, they have almost the same crystallization growth rate, resulting in similar results of crystalline dimension. However, for the specimens isothermally crystallized at 125°C as shown in Fig. 12, the scattering profiles are different in shape and slightly different in the peak position (i.e. the small frame in the upper right hand of Fig. 12). This means that crystals of different dimensions are obtained. This is attributed to the various crystallization growth rates of PP and mPP molecules under this crystallization condition. Furthermore, if the scattering profiles of PP and mPP are graphically averaged, the resulting profile is well overlapped with that of the 50/50 blend of the two polymers (Fig. 13). This is consistent with the previous DSC measurements that suggest that phase-separated morphology tends to form at high crystallization temperatures. The quantitative treatment of SAXS results will be reported in a forthcoming paper.

3.3. Additional explanations for the miscibility of PP and mPP mixtures

Owing to the complexity of the crystalline–crystalline polymer blend, especially the pairs with minor differences

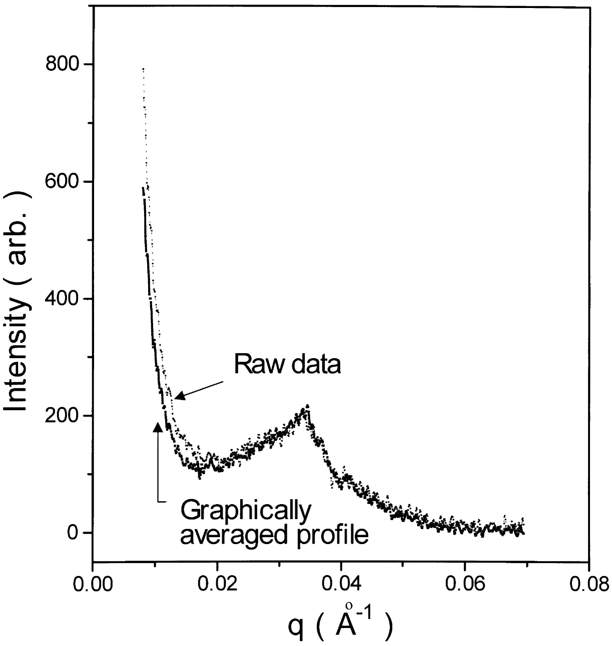

Fig. 13. Comparison of the profile for the PP/mPP (50/50) blend and the graphically overlapped profiles of pure PP and mPP isothermally crystallized at 125°C.

in chemical structure, phase morphologies are far more complicated than what we have discussed above. Thus, it is more scientific to interpret different morphologies as phase-separation dominance or co-crystal dominance.

It has been found that thermodynamics has little effect on the resulting phase morphologies in the PP and mPP blends. So, what is it like in the molten state, homogeneous or heterogeneous? In fact, when the blend melts, two types of interactions occur. One is interactions between the PP molecules and propylene segments of mPP, which is favorable for the miscibility of PP and mPP molecules. The other is the polar interactions among the maleic anhydride groups, which tend to cause the aggregation of mPP molecules. The competition of the two interactions determines the characteristics of the blend melt. From the viewpoint of thermodynamics, in the cases of mPPs with low molecular weight or high MAH content, miscibility between PP and mPP molecules would become poor. This can explain the results reported by Baer et al. [18]. However, in our case, the MAH content of mPP may be between the two extremes in Ref. [18]. The large difference in melt indexes of the constituent polymers shows that the molding grade PP has a much higher molecular weight than mPP. Thus, the miscibility between them is expected to be relatively poor. However, under any conditions, two distinctive phases, as Baer et al. [20] have shown, have not been observed. So, the blends should not be typically phase separated. It is assumed that the melt of the blend should not be ideally homogeneous, the density may fluctuate in different areas.

In the molten state, the two kind of interactions are expected to reach equilibrium within several minutes. So, thermodynamics seems to be an secondary important factor, while crystallization kinetics should play an key role in determining the resulting phase morphologies. Further studies such as time-resolved small angle X-ray scattering studies for the determination of crystal structure i.e. long spacing and lamellar thickness with time are required to characterize the resulting phase morphologies and crystallization behavior.

4. Conclusion

The blends of PP and mPP show either single or double fusion endotherms, depending on their previous crystallization condition. The double peaks correspond well to the melting points of pure PP and mPP, respectively, implying the separate melting of different lamellar crystals, while the single peak indicates the dominance of co-crystals in the blend system. A higher crystallization temperature in the isothermal case, and a slow cooling rate in the non-isothermal case are favorable for the occurrence of phase separation between PP and mPP lamellar crystals. Studies on the isothermal crystallization kinetics confirm that there is a correlation between the crystallization rate and the resulting morphologies.

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