Effects of Compatibilization on Fractionated Crystallization of PA6/PP Blends

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SYNOPSIS

In polymer blends, the crystallization of the dispersed semicrystalline component depends on the type and distribution of the nucleating heterogeneities and on the level of the dispersion. Either fractionated or coincident crystallization may result. In this study, the effect of compatibilizers on the crystallization of polyamide 6/isotactic polypropylene (PP) blends was investigated. The morphology was controlled with 10 wt % of four different commercial compatibilizers—PPgMAH, EBAgFA, SEBSgMAH, and E-EA-GMA—each leading to specific morphology and crystallization behavior. The compatibilized blends show more complex crystallization compared with the corresponding binary blends. In the compatibilized blends, the dispersed PA6 seems to crystallize coincidently with PP, probably due to its small particle size. The crystallization of PP takes place at temperatures above the bulk value at all compositions in blends compatibilized with PPgMAH and blends without the compatibilizer. By contrast, in blends compatibilized with EBAgFA, SEBSgMAH, and E-EA-GMA, the crystallization takes place either at PP bulk temperature or over the temperature range of 76–87°C at the cooling rate of 10°C/min. The amount of the shift cannot be explained solely by the size of the PP dispersion. © 1993 John Wiley & Sons, Inc.

1. INTRODUCTION

Retarded crystallization of a polymer component has been observed in polymer solutions where the semicrystalline polymer droplets are suspended in an inert liquid and also in immiscible polymer blends, where the continuous phase corresponds to the inert liquid of a suspension.[1]

The retarded crystallization has been explained in terms of the size distribution of the polymer droplets and the number and type of nucleating heterogeneities. Primary nucleation is usually the rate-determining step, i.e., the crystal growth spreads rapidly once the crystal seeds have been created.[2] If the dispersion of the minor semicrystalline polymer component is made finer, a limit may be approached in which the number of the usually active nucleating heterogeneities is smaller than the number of the

dispersed particles. In this case, heterogeneous nucleation due to another type of nucleator takes over or the nucleation is retarded until homogeneous nucleation begins.[1,3,4]

Crystallization of the minor component may thus take place in several steps with widely different undercoolings. This phenomenon is known as fractionated crystallization. The crystallization of the minor component can also take place coincidently with the major blend component.

The intimate connection between the morphology and the crystallization of the minor component has been investigated in binary blends by using DSC exotherms: Studies have been reported for PE/POM,[1,5] POM/EVA,[6] PE/PS,[7,8] PVDF/PA6,[1,4] PVDF/PA6.6,[3] and PVDF/PBTP.[1,4] The morphology of blends has been controlled by consecutive extrusions in some of the above works.

The practical blends, however, are, in general, not binary but contain compatibilizers that are used to control the morphology.[9] In this case, more complex crystallization behavior occurs. In this work, the

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crystallization in polyamide 6/polypropylene blends with four typical commercial compatibilizers is investigated: EBAgFA, PPgMAH, SEBSgMAH, and E-EA-GMA.[10] The polymers and compatibilizers are described in Table I.

The crystallization processes were characterized by DSC and the morphology was characterized by scanning electron microscopy (SEM). Additional studies with transmission electron microscopy are reported elsewhere.[11]

2. EXPERIMENTAL

Polyamide (PA) 6/polypropylene (PP) blends were mixed using the Berstorff ZE25 corotating twin-screw extruder at PA weight fractions of 0, 0.2, 0.4, 0.6, 0.8, and 1.0 relative the total weight of PA6 and PP. The polyamide was dried at 80°C for at least 16 h before extrusion.

Dynamic crystallization studies were carried out with the Mettler DSC 30S differential scanning calorimeter. The samples were first annealed at 260°C for 5 min. Then, the crystallization exotherms and subsequent melting endotherms were recorded between 30 and 260°C at a sweep rate 10°C/min. The thermal time constant of the calorimeter was approximately 7 s.

The morphologies were examined by SEM. An image-analyzing program was used to study the particle sizes.[12] The program identifies closed loops in the SEM pictures and interprets them as the dispersed particles. This method is particularly convenient because artifacts such as fracture lines and the variable darkness of the pictures do not complicate the analysis.

3. RESULTS

3.1. Crystallization of Polyamide 6/ Polypropylene Blends

Figure 1(a)–(d) illustrates the DSC cooling and melting thermograms of PA6 : PP blends of different compositions. (See Table I for the materials.) The weight fraction of the compatibilizer was 10% of the total blend weight. Thermograms of bulk PA6 and PP and blends without compatibilization are provided as reference.

The crystallization temperature of the minor polymeric component is in some cases shifted, depending on the PA6 : PP composition, the compatibilizer, and the resulting morphology. However, the separate PA6 and PP melting peaks were in the melting thermograms at their expected positions, typical of immiscible blends.

Figure 1(a) depicts the crystallization exotherms of PA6 80 : PP 20 at the sweep rate of 10°C/min. The dispersed PP crystallized at roughly the same temperature in the blend without the compatibilizer or in that with 10% PPgMAH. The temperature is roughly 5°C above the crystallization temperature of bulk PP. By contrast, the PP component of the other blends crystallized at unusually low temperatures ranging from 76 to 87°C. Therefore, blends with compatibilizers I, III, and IV behave qualita-

Table I   The Polymers and Compatibilizers Used

Blend Polymers		
Polypropylene	Neste VC 12 12H	
Polyamide 6	BASF Ultramid B3	

| Compatibilizers	Abbreviation	Weight Fraction of Total Blend Weight
I Ethylene butylene acrylate grafted with 0.4% of fumaric acid	EBAgFA	10%
II Polypropylene grafted with 0.2% of maleic anhydride	PPgMAH	10%
III Styrene ethylene butylene styrene elastomer grafted with 2% of maleic anhydride	SEBSgMAH	10%
IV Ethylene ethyl acrylate glycidyl methacrylate containing 8% of glycidyl methacrylate	E-EA-GMA	10%
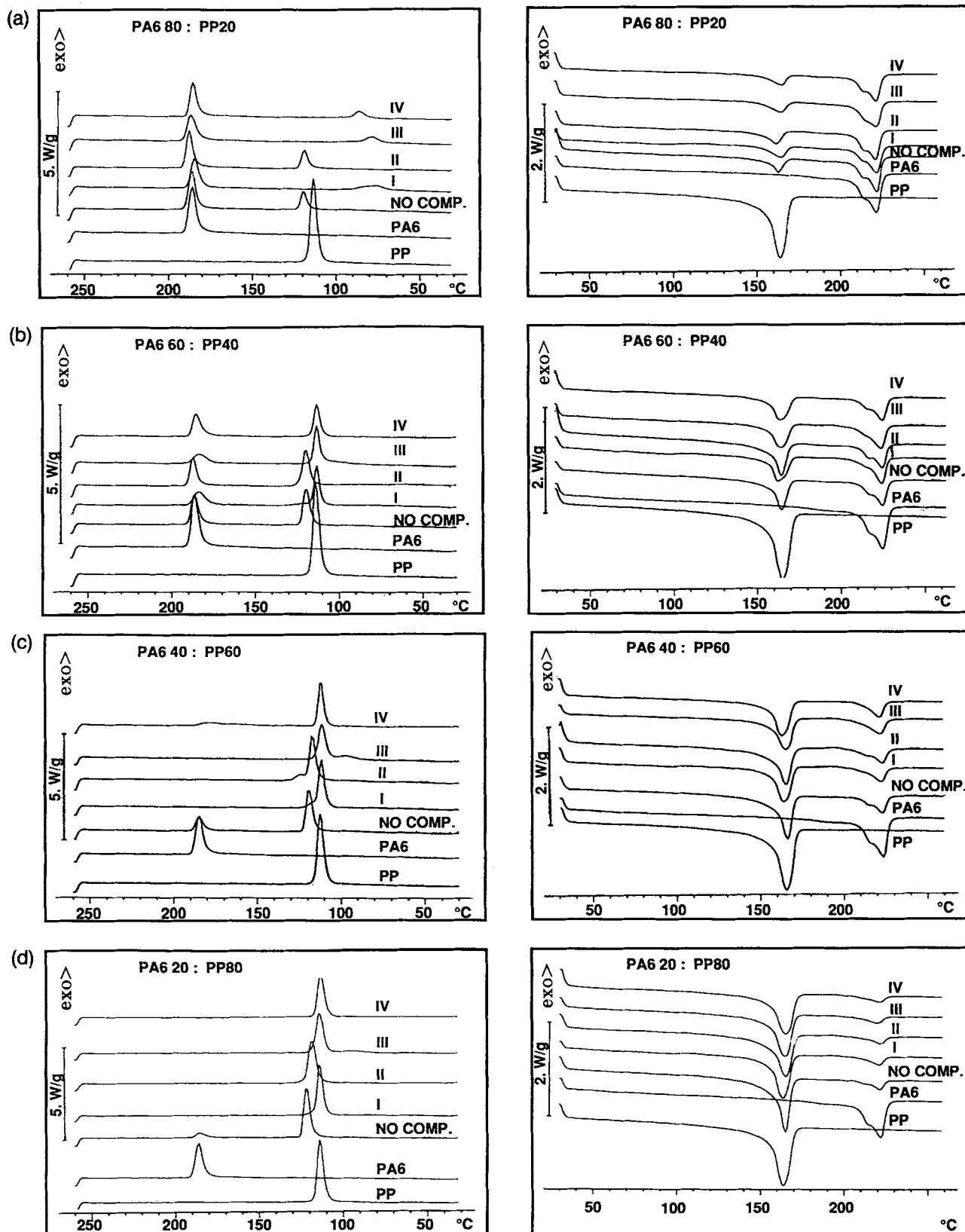
Figure 1 Crystallization and melting thermograms of PA6 80 : PP 20, PA6 60 : PP 40, PA6 40 : PP 60, and PA 20 : PP 80 blends at the sweep rate of 10°C/min. The numerals I–IV refer to blends compatibilized with 10 wt % of EBAgFA, PPgMAH, SEBSgMAH, and E-EA-GMA, respectively (see Table I).

tively similarly, and blends with compatibilizer II and no compatibilizer behave similarly.

To confirm that the shifted low-temperature peaks were really due to PP crystallization, the following test was performed with PA6 80 : PP 20 compatibilized with 10% SEBSgMAH. First, DSC thermograms were recorded between 260 and 30°C and the exothermic peak was observed at 87°C. The subsequent melting showed that both PP and PA6 had crystallized. When the sample was recooled down to 100°C, no peak due to PP was observed in the corresponding melting endotherm. Thus, the low-temperature exothermic peaks in Figure 1(a) must be due to crystallization of the dispersed PP phase, in which case the compatibilizer has affected the crystallization of the minor blend component. In all cases in Figure 1(a), the PA6 components crystallize at the bulk temperatures.

Figure 1(b) shows that in PA6 60 : PP 40 no shifts of the PP crystallization to low temperatures can be observed. However, the crystallization of PP suggests the same classification of the blends according to the compatibilization as in Figure 1(a): Blends without compatibilizer and that with compatibilizer II crystallize above the PP bulk temperature, whereas in the remaining blends, PP crystallizes at the bulk value. PA6 crystallizes at the bulk value.

A qualitatively different situation is encountered in blends PA6 40 : PP 60 where PP is the major component [see Fig. 1(c)]. Only in the blend without the compatibilizer does PA6 show a trace of crystallization at the bulk temperature. In the other cases, the crystallization of PA6 is shifted to low temperatures where the crystallization takes place together with PP, as will be shown later in Figure 5. The PP crystallization is as is shown in Figure 1(b).

Figure 1(d) depicts PA6 20 : PP 80. The behavior is qualitatively similar to that shown in Figure 1(c).

The thermal properties of blends compatibilized with 10% SEBSgMAH are shown in Figure 2. For PA6 100 : PP 0, the crystallization behavior of PA6 is the same as that in the bulk. For PA6 80 : PP 20, the PA6 crystallization remains at its bulk value, whereas the crystallization of PP is shifted to low temperature. In blends PA6 60 : PP 40, PA6 40 : PP 60, PA6 20 : PP 80, and PA6 0 : PP 100, the crystallization peak of PP was at the position where PP usually crystallizes in the bulk, and no separate PA6 crystallization peaks were observed. PA6 crystallizes coincidently with PP.

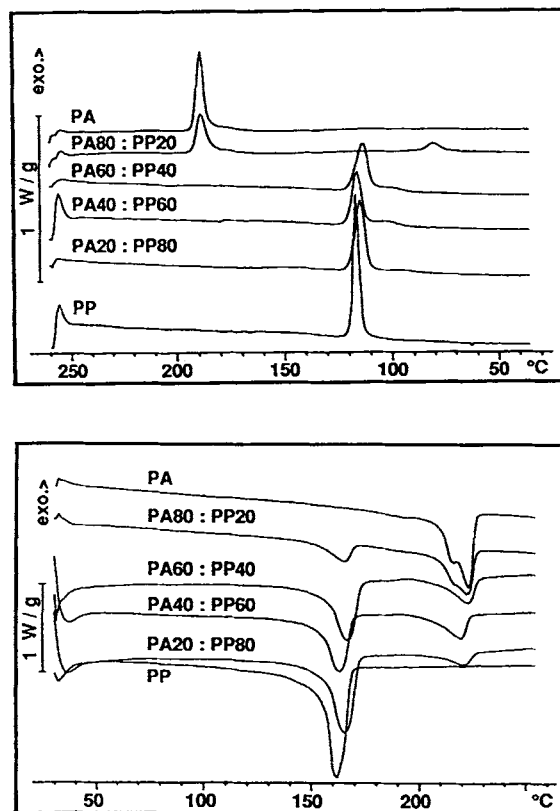In summary, the crystallization of the minor crystalline phase in an immiscible blend may shift

Figure 2 Crystallization and melting thermograms of PA6/PP blends compatibilized with 10% of SEBSgMAH at the sweep rate of 10°C/min.

to a lower temperature than in the crystallization of the bulk. This phenomenon is called fractionated crystallization. Crystallization may take place separately at lower temperatures or coincidently with the major phase. In this work, we have demonstrated that compatibilization has a marked effect on the fractionation behavior.

3.2. Crystallization of PA6/SEBSgMAH Blends

The above experiments showed that in PA6/PP blends large shifts in crystallization temperatures may be encountered depending on the compatibilizer. To shed more light on the fractionated crystallization in the special case when SEBSgMAH is used, binary blends of PA6/SEBSgMAH were made with the Berstorff ZE25 twin-screw extruder.

Figure 3 shows the crystallization exotherms and melting endotherms recorded at a sweep rate of 10°C/min. The crystallization peaks of PA6 are in the usual position of approximately 190°C when the PA6 weight fraction is greater than 0.6, i.e., when PA6 is the major phase. When the PA6 weight frac-
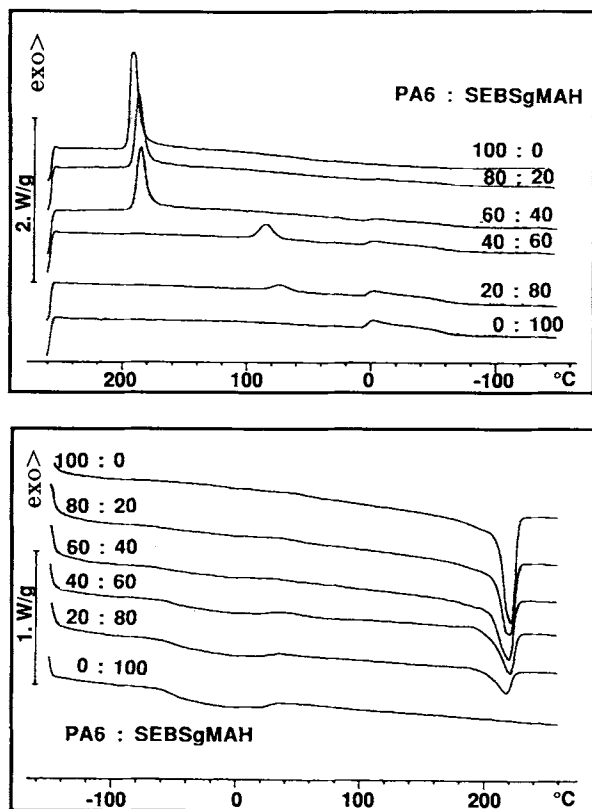
the PA6 weight fraction of 0.8, where a large shift is observed. In these blends, the crystallization of PP shows large fractionation. On the other hand, in blends without compatibilizer and in the blend with PPgMAH, the PP crystallization is above the bulk crystallization temperature. In these blends, no fractionation of PP crystallization was observed.

The previous observations apparently show that the most complex crystallization conditions in blends are encountered in the special case (i) when the blend component is the minor component and (ii) when the blend component is the one with the lower crystallization temperature in the bulk. Therefore, a closer look at PA6 80 : PP 20 blends is suggested.

Figure 6 depicts the morphologies of PA6 80 : PP 20 blends. The samples have been prepared by breaking an extruded rod at liquid nitrogen temperature. The morphology of at least five different positions have been investigated for each blend. The
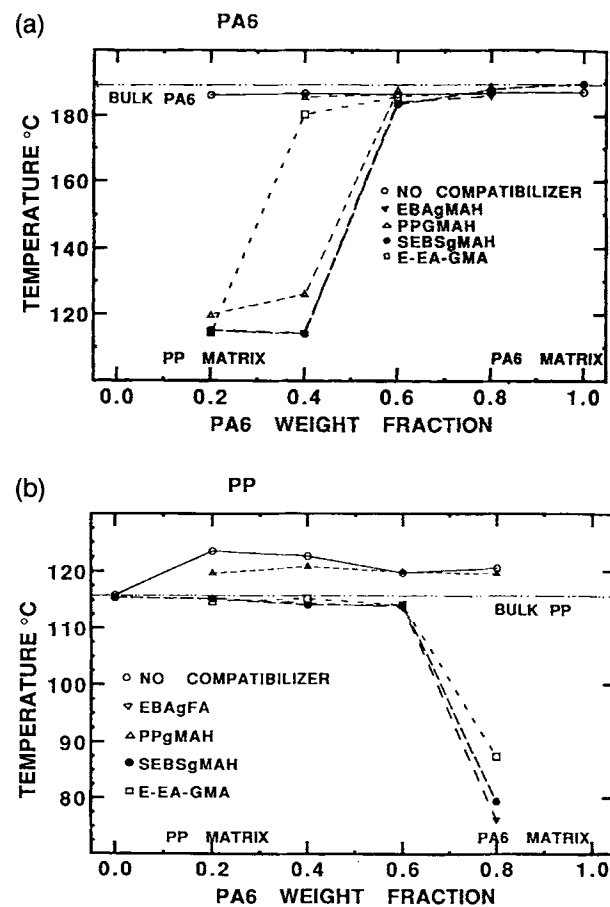

Figure 3 Crystallization and melting thermograms of binary blends PA6/SEBSgMAH.

tion is only 0.4 or 0.2, the main PA6 crystallization is shifted to lower temperatures of 84 and 74°C, respectively.

4. DISCUSSION

In the following, the crystallization peak positions (Fig. 4) and peak areas (Fig. 5) will be analyzed as a function of the PA6 weight fraction. Figure 4(a) illustrates the crystallization temperature of the PA6 component. The position of the bulk PA6 crystallization temperature is also indicated. Large deviations from the bulk values are observed when the PA6 weight fraction is 0.2. In the case 0.4, the actual crystallization depends on the compatibilizer. In the blends without compatibilizer, no shifts to low temperatures are observed. No other clear trends can be identified.

Figure 4(b) shows the corresponding PP crystallization. There the classification of the blends according to the compatibilizer described previously is clear: In blends compatibilized with EBAgFA, SEBSgMAH, and E-EA-GMA, PP crystallizes at the bulk PP temperature, except in the blend with

Figure 4 Crystallization temperatures of PA6 and PP as a function of the PA6 weight fraction at the sweep rate of 10°C/min.
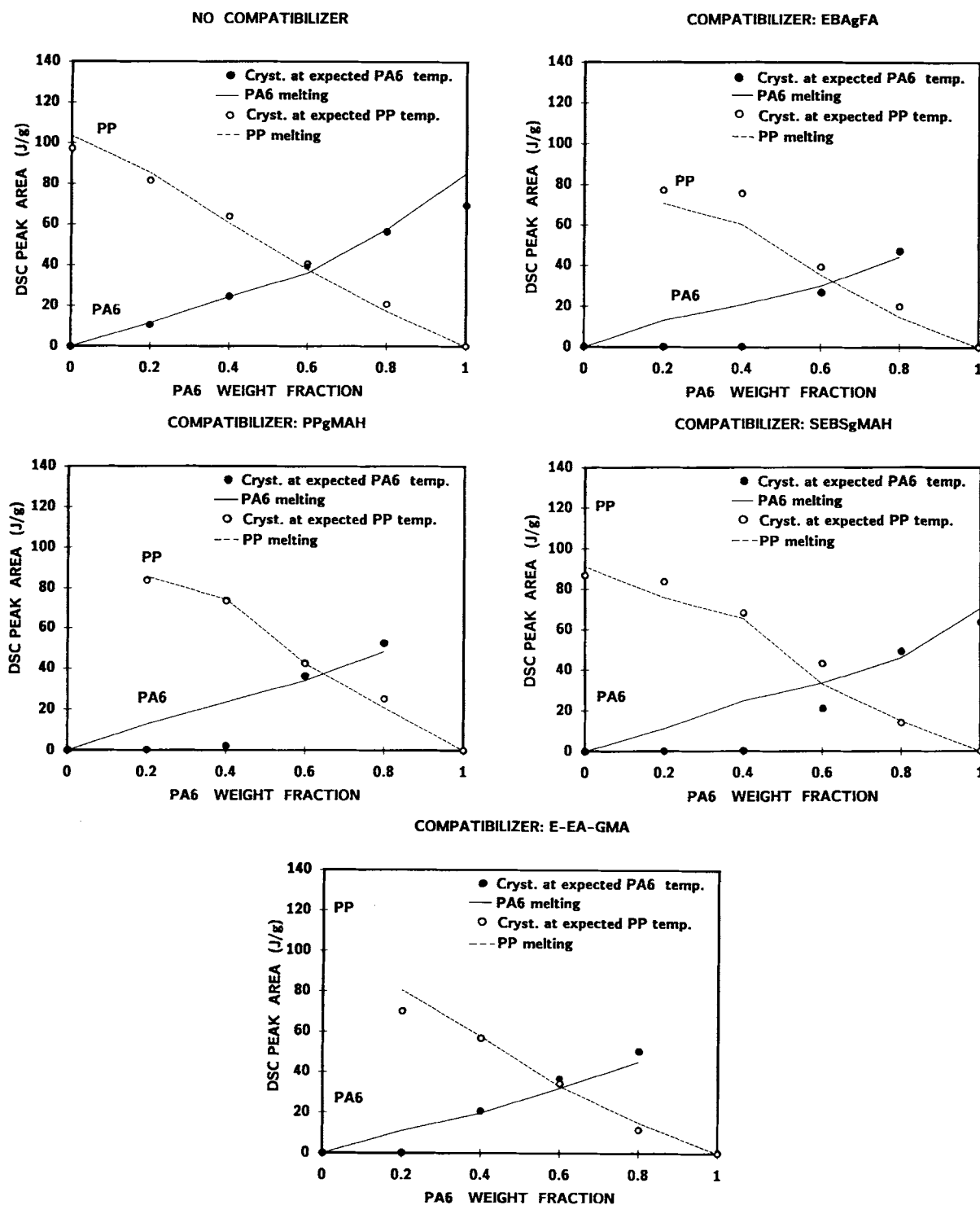
Figure 5   The DSC crystallization and melting peak areas at the expected temperature of PA6 and PP crystallization.

particle sizes were analyzed by using an image-analyzing algorithm.[12] The number of analyzed particles was approximately 400 for each blend.

Figure 7 shows the observed PP crystallization temperatures as a function of average PP particle

size for PA6 80 : PP 20 blends. The classification to blends compatibilized with EBAgFA, SEBSgMAH, and E-EA-GMA and, on the other hand, to blends compatibilized with PPgMAH and blends without compatibilizer is clear. The blends of the first group
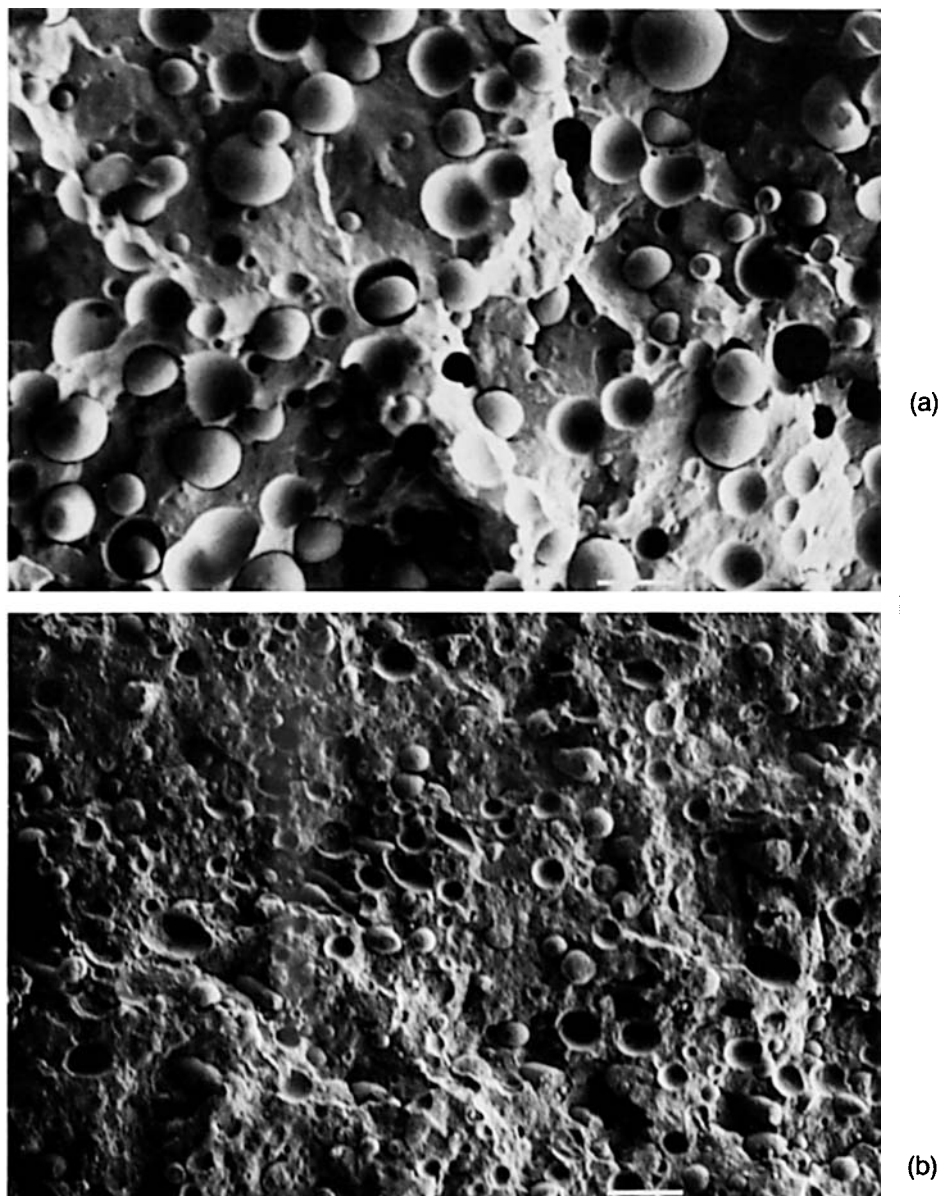
Figure 6 Scanning electron microscope pictures on the morphologies of PA6 80:PP 20 blends: (a) no compatibilizer; (b) 10 wt % EBAgFA; (c) 10 wt % PPgMAH; (d) 10 wt % SEBSgMAH; (e) 10 wt % E-EA-GMA. Scale bar 10 μm.

are subject to large shifts of crystallization to low temperature, whereas in the latter blends, the crystallization of PP is shifted upward. Thus, Figure 7 suggests that in the compatibilized blends the shifts are not simply related solely to the dispersed particle sizes. The crystallization of PP reflects complex interplay among the polymer components, compatibilizers, and the particle size.

The observed crystallization behavior of the compatibilized PA6/PP blends can be explained in terms of fractionated crystallization. Nucleation is expected to be the rate-determining step of the crys-

tallization process for the minor crystalline component.[2] In the limit of very fine dispersion, the number of droplets of the minor component may become larger than the number of main nucleating heterogeneities and the nucleation may then be controlled by another type of heterogeneity. In the limiting case of very fine dispersion, the minor component may even be nucleated homogeneously.[1]
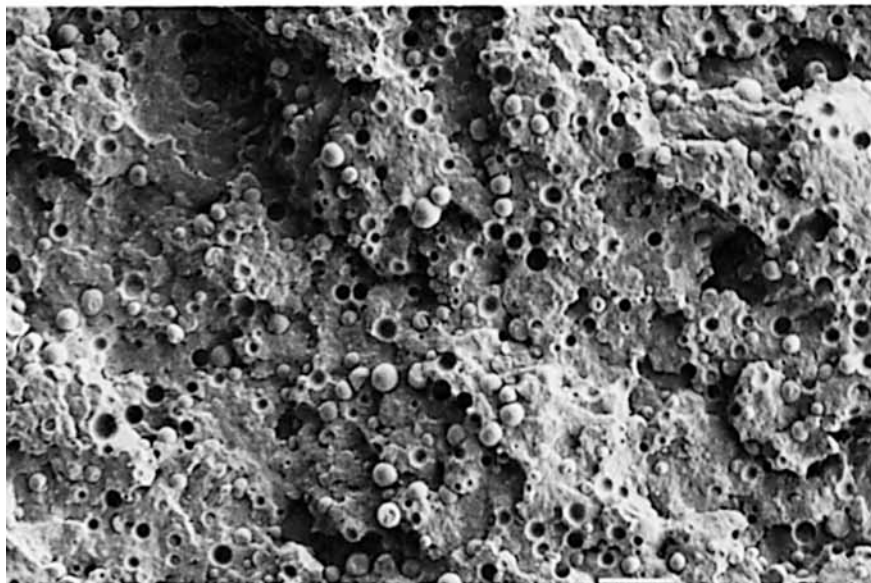
The "unfractionated" crystallization of PA6 80 : PP 20 blends without compatibilizers and blends compatibilized with PPgMAH might be explained in the following way: In the uncompatibilized blend,
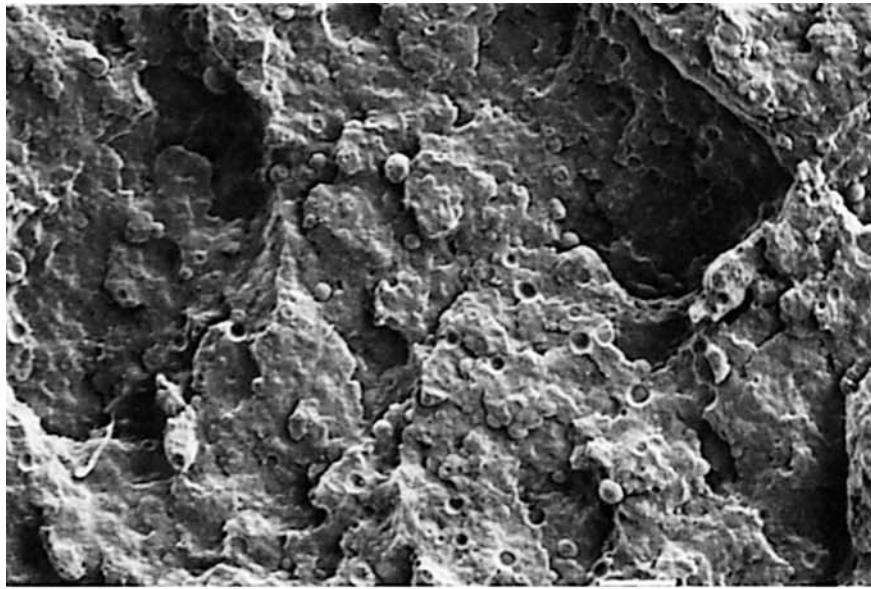
(c)
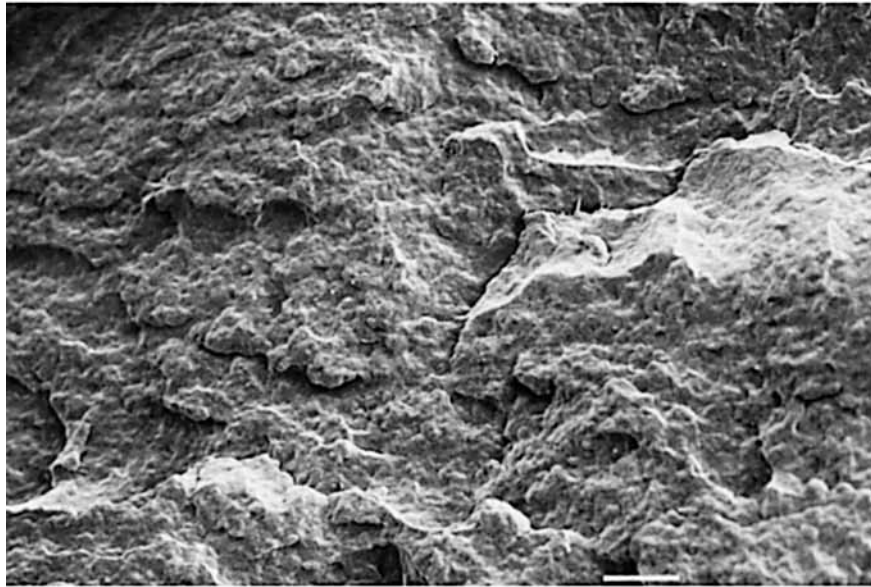
(d)

(e)

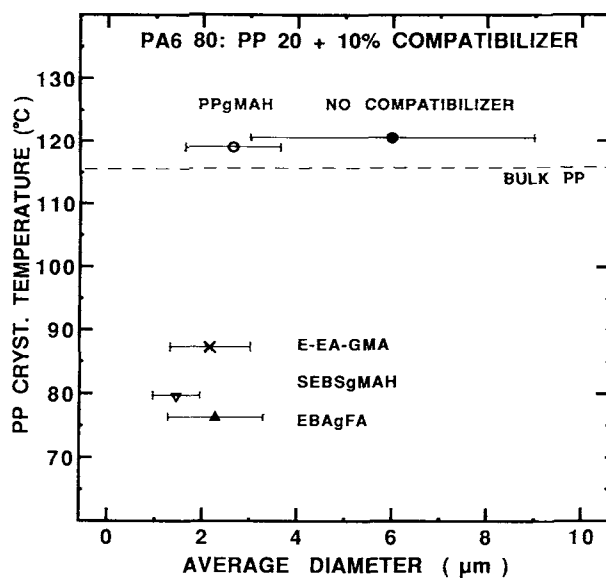**Figure 6** *(Continued from the previous page)*

Figure 7   Crystallization temperature of the PP component in PA6 80:PP 20 blends as a function of the average PP dispersion size.

the dispersion is so coarse that practically every PP droplet contains the heterogeneities that usually nucleate PP. In the case of compatibilization with PPgMAH, in spite of the fineness of the morphology, the nucleation apparently occurs as efficiently as in the "bulky" uncompatibilized blends. The three compatibilizers EBAgFA, SEBSgMAH, and E-EA-GMA are expected to be immiscible both with PP and PA6 and form, therefore, an interlayer between the components, whereas PPgMAH is partly soluted in the PP phase. The interlayer between the two phases may inhibit the nucleating activity of PA6 matrix toward the dispersed PP phase.

Our results may be compared with those of Ghijsels et al.[13] for PP/SBS blends, where the PP minor phase in the amorphous SBS matrix was found to crystallize at higher undercoolings corresponding to the temperatures of 74 and 44°C. It is not clear whether the crystallization at 74°C was due to homogeneous nucleation or due to another type of heterogeneity. The crystallization at 44°C was suggested to be due to the smectic phase of PP. Apart from minor differences as to the exact temperature, the PP crystallization temperature of 74°C is quite close to our fractionated crystallization temperatures of PP.

Only in the uncompatibilized blend of PA6 20 : PP 80 did the PA6 minor component crystallize at its usual temperature. In this case, the dispersion is quite coarse; the average particle size of PA6 is 2.5 μm. In the compatibilized PA6 20 : PP 80-blends,

the PA6 crystallized coincidently with PP. Such a coincidence of crystallization may be evidence of nucleating activity between the polymer components.[1,3] Coincident crystallization has also been observed in other blends such as PVDF/PA6.[1,3]

5. CONCLUSIONS

Compatibilized blends show more complex crystallization than do the corresponding binary blends. Crystallization of a blend component can shift to low temperatures if it is the minor component, i.e., its crystallization can be fractionated.

In binary PA6/PP blends, no fractionation of the minor component crystallization was observed, probably because of the large size of the dispersed particles. In the compatibilized PA6/PP blends, the presence or absence of fractionation depended on the compatibilizer.

The investigated blends could be divided into two groups according to the PP crystallization behavior:

The first group consisted of blends without compatibilizer and blends compatibilized with 10% PPgMAH. In all these blends, PP crystallized at temperatures 7–15°C higher than in bulk PP at the selected sweep rate of 10°C/min. Especially, when PP is the minor component, there was no fractionation of the PP crystallization.

In the second group of blends containing 10% EBAgFA, SEBSgMAH, and E-EA-GMA (with no PP blocks in the compatibilizers), PP crystallization took place at the bulk temperature or a large fractionation down to temperatures 76–87°C took place in the blends of PA6 80 : PP 20. This may have been due to the fineness of the dispersion, the inefficient nucleating activity of the compatibilizer, or the interfacial layer of a compatibilizer between the phases.

In contrast to binary blends without compatibilizer, it seems that in compatibilized blends the crystallization of the minor component cannot be explained solely by the size of the dispersion. Fractionation of crystallization may yield information on the characteristic interfacial energies between the polymeric components in the blend.

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