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Studies on morphology and crystallization of polypropylene/polyamide 12 blends

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Scanning electron microscopy (SEM) and an image analyser are used to study morphologies of the fractured surface, etched by hot phenol, of polypropylene/maleated polypropylene/polyamide 12 (PP/PP-MA/PA12) = 65/10/25 blend and PP-MA/PA12 = 75/25 blend. The particle dimension and its distribution of PA12 dispersed phase in these blends are much lower and narrower than that of the PP/PA12 blends. Especially, most of the particles in the PP-MA/PA12 = 75/25 blend are smaller than 0.1 μm. The effect of the morphology of PP/PA12 blends on their crystallization behaviour is studied using differential scanning calorimetry and SEM. PA12 dispersed phase coarsens during annealing in the PP/PP-MA/PA12 = 65/10/25 blend. The mechanism of coarsening of the PA12 dispersed phase is a coalescence process. The intense mixing between the PP component and the PA12 component through reaction of PP-MA and PA12 leads to a change of dynamic mechanical behaviour of the components. A separation method is used to separate the polyolefin parts (precipitated from hot phenol), from PA12 parts (hot phenol filtrate). Of PP/PP-MA/PA12 = 65/10/25 blend, infra-red measurements and elementary analysis show that the precipitate has a lower PA12 content than the feed, whereas the filtrate has a higher PA12 content. From PP-MA/PA12 = 75/25 blend, PA12 contents in the precipitate and the filtrate are the same as in the feed. This implies that all PA12 has reacted with all PP-MA in the latter case while not in the former case. Using the method of interface exposure, interfacial reaction of PP-MA with PA12 is studied by X-ray photoelectron spectrometry (X.p.s.). Copyright © 1996 Elsevier Science Ltd.

(Keywords: morphology; crystallization; compatibilization)

INTRODUCTION

Since Ide and Hasegawa[1] found that maleated polypropylene (PP-MA) could improve the compatibility of a polypropylene/polyamide (PP/PA6) blend, much research has been reported[2-5] on polyolefin/polyamide blends. There are two characteristics in these blends: (1) reactive compatibilization and formation of polyolefin-*g*-polyamide *in situ*; (2) the blends are made of two crystalline components. Serpe *et al.*[2] studied the relationship of morphology and processing in polyethylene/polyamide 11 (PE/PA11) blends. In their research, they extracted PE/PA11 blends compatibilized by ethylene–maleic anhydride statistic copolymer (EMA) using toluene. Infra-red (i.r.) measurements showed that the insoluble fraction (mainly consisting of PA11) contained a carbonyl i.r. absorption at about 1790 cm^{-1} characteristic of EMA; on the other hand, the soluble fraction (mainly consisting of PE and EMA) contained an N-H i.r. absorption at about 1550 cm^{-1} that indicated the presence of PA11. It therefore seems that a graft copolymer is formed during mixing through reaction of anhydride with the terminal-NH_2 groups of PA11. Scott and Macosko[5] studied the interfacial reaction between styrene-maleic anhydride and PA11 using *FT*i.r. in a model experiment. Their results showed that the kinetics of reaction was strongly affected by molecular weight as well as temperature.

Lotz and Wittmann[6] found a specific epitaxial relationship of PP with PA. The fractionated crystallization of PP/PA6 blends have also been studied[7,8]. In addition, Liang and Williams[9] studied the effect of compatibilization on dynamic mechanical properties of PP/PA11 blends. Rosch and Mulhaupt[10] observed a characteristic morphological feature of PA/PA6 = 70/30 blend compatibilized by maleated polymers, that is, a continuous PP matrix containing dispersed core/shell microparticles with a PA6 core and compatibilizer shell, just as our results in LLDPE/EMA/poly(MMA-*co*-4-VP) blend[11]. In our previous papers, we studied compatibilization and crystalline structure of PP/PA12 blends[12] and simultaneous crystallization of compatibilized PP/PA12 blends[13]. The results showed that interfacial behaviour of compatibilizers had important effects on the crystallization behaviour of PP/PA12 blends. In this paper, we will further study morphology, its influence on crystallization properties of PP/PA12 blends, and formation of PP-*g*-PA12 graft copolymer in PP/PA blends.

EXPERIMENTAL

Isotactic polypropylene (PP), M_w 26 000, was from Daqing Petroleum Chemical Co. Polyamide 12 (PA12), M_W 8500, was purchased from Polysciences Co. (courtesy of Prof. Zhiliu Feng). Maleated PP (PP-MA), M_W 19 000, degree of grafting of MA 2.46 wt%, was synthesized in our laboratory.

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Blends of PP/PA12 were prepared according to the previous paper[13]. The fractured surface of the blends was etched in hot phenol[13]. The morphology of the etched fractured surfaces of PP/PP-MA/PA12 blends was observed with a HITACHI-S-570 scanning electron microscope (SEM) after coating with gold. The SEM photographs were analysed using an image analyser. The differential scanning calorimetry (d.s.c.) measurements were the same as in the previous paper[12]. Dynamic mechanical properties of the blends were measured from −150° to 150°C on a Rheovibron DDV-II-EA at a frequency of 3.5 Hz and a scanning rate of $1^{\circ}\mathrm{C\,min}^{-1}$. Preparation of the interface of polymers and observation of molecular states in the interfacial region were the same as in the previous paper[14].

The blends were separated according to the method below. A quantity of the blend was dissolved in a hot xylene/phenol = 3/1 (v/v) mixture. When a hot solution of PP/PP-MA/PA12 blend was added to a phenol, all PP molecules and most of the PP-MA molecules, and (PP-MA)-*g*-PA12 molecules with many PA12 branches precipitate, while unreacted PA12, a little PP-MA and most of the (PP-MA)-*g*-PA12 remained in the filtrate.

RESULTS AND DISCUSSION

SEM observation of morphology of compatibilized blends

The addition of maleated polypropylene (PP-MA) can improve the compatibility of components at the interface of polypropylene/polyamide 12 (PP/PA12) blend. At the same time, the average dimension of the dispersed phase decreases, and the interfacial adhesion between PP and PA12 is also improved[12]. However, the fractured surface is smooth. It is difficult to directly observe the morphology of the dispersed phase on a fractured surface of compatibilized PP/PA12 blends using SEM (*Figure 1*). Thus we used an etching method to dissolve the PA12 dispersed phase.

The fractured surface for SEM observation was prepared by keeping the fractured surface of the blends in phenol at 100°C for some time, then washing with hot phenol and acetone, and then completely drying. For a sample etched for 3 h, a clear morphology of the blends can be observed. The etching time was increased to 6, 8, 10 and 18 h, respectively. No finer morphology was observed after 6 h etching as compared to that etched for 3 h (*Figure 1*). No more morphological information was obtained when etched for 10 h and even 18 h. In this work, etching time used was 10 h unless specified otherwise.

The image analyser was used to analyse the SEM micrograph of the fractured surface. The PA12 dispersed phase shows a narrow distribution in PP/PP-MA/PA12 = 65/10/25 blend (*Figure 2*). The particle dimension is in the range of 0.1–0.5 μm and some even smaller than 0.1 μm. The particles < 0.1 μm are nano-scale particles. The properties of nano-scale particles are obviously different from that of common particles.

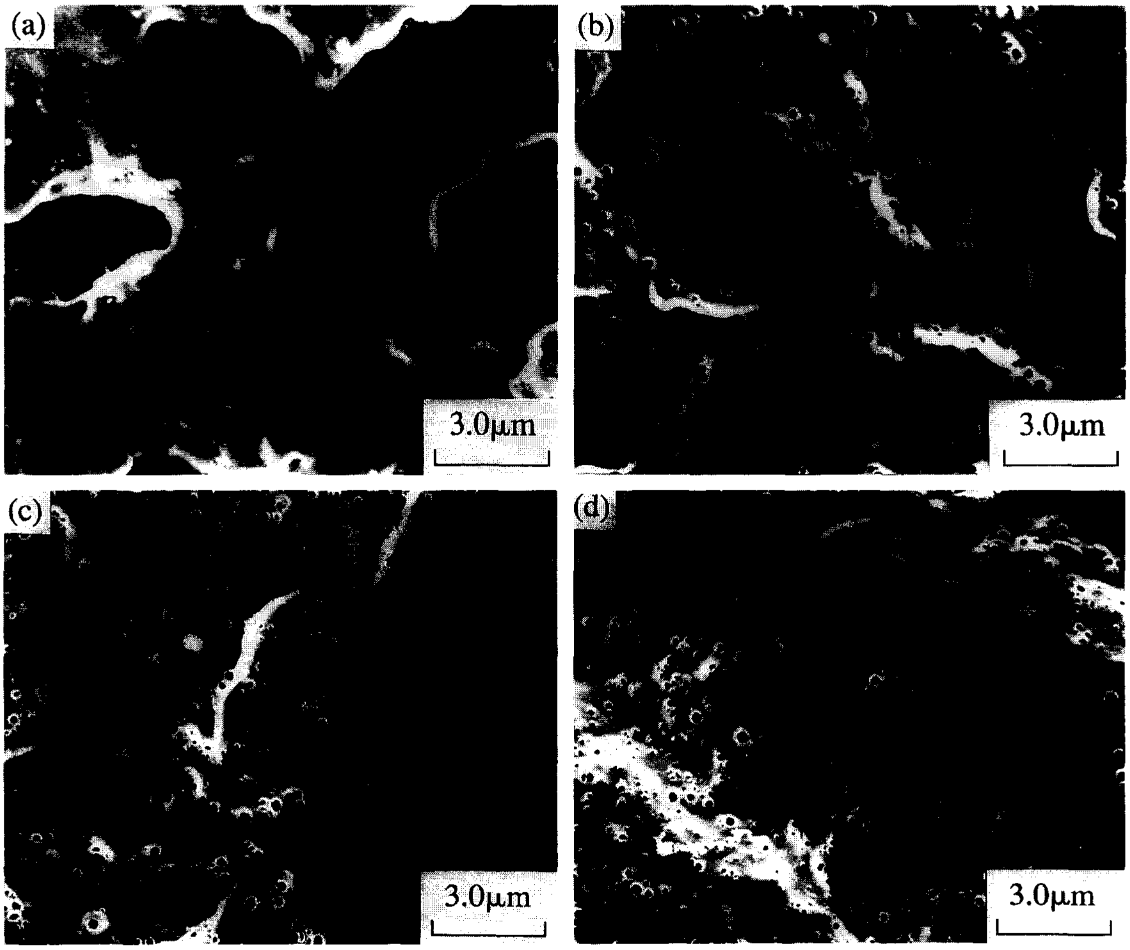

Figure 1 Effect of etching time on morphology of the PP/PP-MA/PA12 = 65/10/25 blend at 100°C. Etching time: (a) 0 h; (b) 3 h; (c) 6 h; (d) 10 h

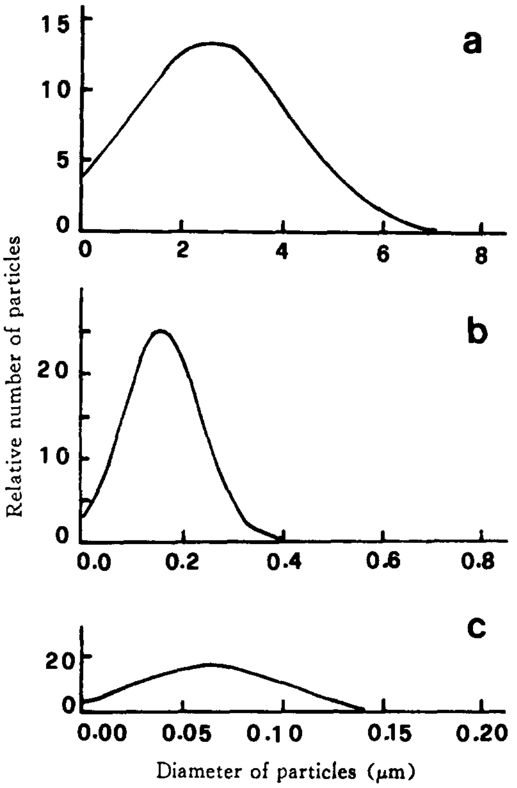

Figure 2 Effect of the compatibilizer on the size distribution of the dispersed phase particles in the blends. (a) PP/PA12 = 75/25; (b) PP/PP-MA/PA12 = 65/10/25; (c) PP-MA/PA12 = 75/25

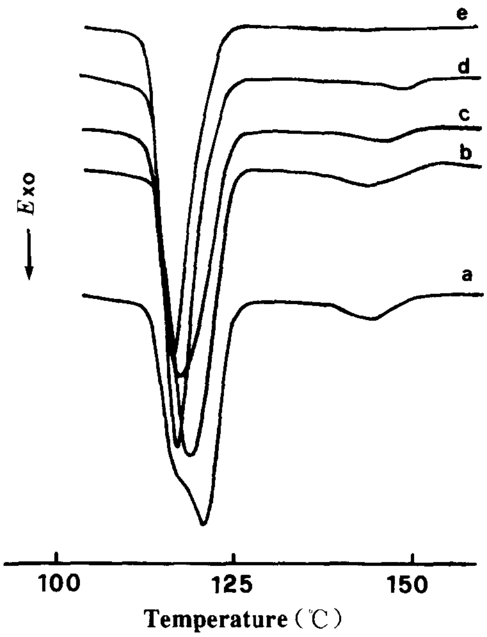

Figure 3 Effect of mixing time on crystallization behaviour of the PP/PP-MA/PA12 = 65/10/25 blend (PP-MA:MA 0.5wt%). (a) 10min; (b) 30min; (c) 60min; (d) 120min; (e) 240min

Table 1 Change of location of crystallization peaks with mixing time

Mixing time (min)	T_c of PP (°C)	T_c of PA12 (°C)
10	120.7	144.4
30	118.3	145.1
60	117.0	145.5
120	116.7	145.8
240	115.8	145.5

Table 2 The melt temperature of PA12 in PP/PA12 blends with various dimensions of PA12 dispersed phase

Dimension range (μm)	Average value (μm)	T_m (°C)
0.56–8.80	2.56	171.4, 179.0
0.08–0.83	0.271	177.6
0.08–0.42	0.159	177.1
0.04–0.24	0.065	178.4
0.02–0.14	0.032	178.0

Among the properties, the crystallization supercooling of nano-scale PA12 particles is much higher than that of PA12 common particles. This leads to the occurrence of PA12 fractionated crystallization[13]. For PP-MA/PA12 = 75/25 blend, most of particles are smaller than 100nm. In this case, the crystallization supercooling of PA12 particles is so large that PA12 does not crystallize normally. The coincidence of crystallization of PP and PA12 occurs. PP crystals induce the crystallization of nano-scale PA12 particles[13]. Nano-scale particles usually tend to enlarge owing to mutual collision and adhesion of particles. However, it is not possible that nano-scale PA12 particles enlarge in the PP/PA12 blends, as PA12 particles are embedded in PP matrix.

Effect of morphology on crystallization properties of PP/PA12 blends

There is a close relationship between morphology and properties of polymer blends. At a fixed stirring rate, the morphology of the PP/PP-MA/PA12 = 65/10/25 (PP-MA: 0.5MA/100P) blend changes with mixing time. With increase of mixing time, the average dimension of the PA12 dispersed phase gradually decreases. During the change of the blends, the crystallization behaviour of the blend also changes (*Figure 3*). When mixed for 10min, there is an obvious crystallization peak of PA12, and two PP peaks in the PP/PP-MA/PA12 blend, the 120°C peak being stronger than the 118°C one. On mixing for 30min, PA12 crystallization peak reduces; PP crystallization is shown as a single peak at 118.3°C. When the mixing time is 1h, PA12 crystallization peak decreases further; at the same time, the PP crystallization peak shifts to a lower temperature (117°C). There is a shoulder peak on the right side of this peak (*Figure 3*). When the blend is mixed for 4h, the PA12 crystallization peak in the blend almost disappears. At this time, the PP crystallization peak in the blend is the same as that of pure PP (*Table 1*).

From the above result, the dispersed state of PA12 affects the crystallization behaviour. During the change of the dispersed state, from PA12 bulk to 1μm particles and 0.1μm particles (nano-scale), the melt temperature of PA12 component does not change. This shows that the change of the dispersed state of PA12 in the above range has no effect on the crystalline state of PA12 (*Table 2*).

Effect of annealing on morphology and melting behaviour of the blend

It is known that addition of a compatibilizer improves dispersion in a blend, and the stability of its morphology. However, there is a limit to this, for example, when annealed. When a PP/PP-MA/PA12 = 65/10/25 tertiary

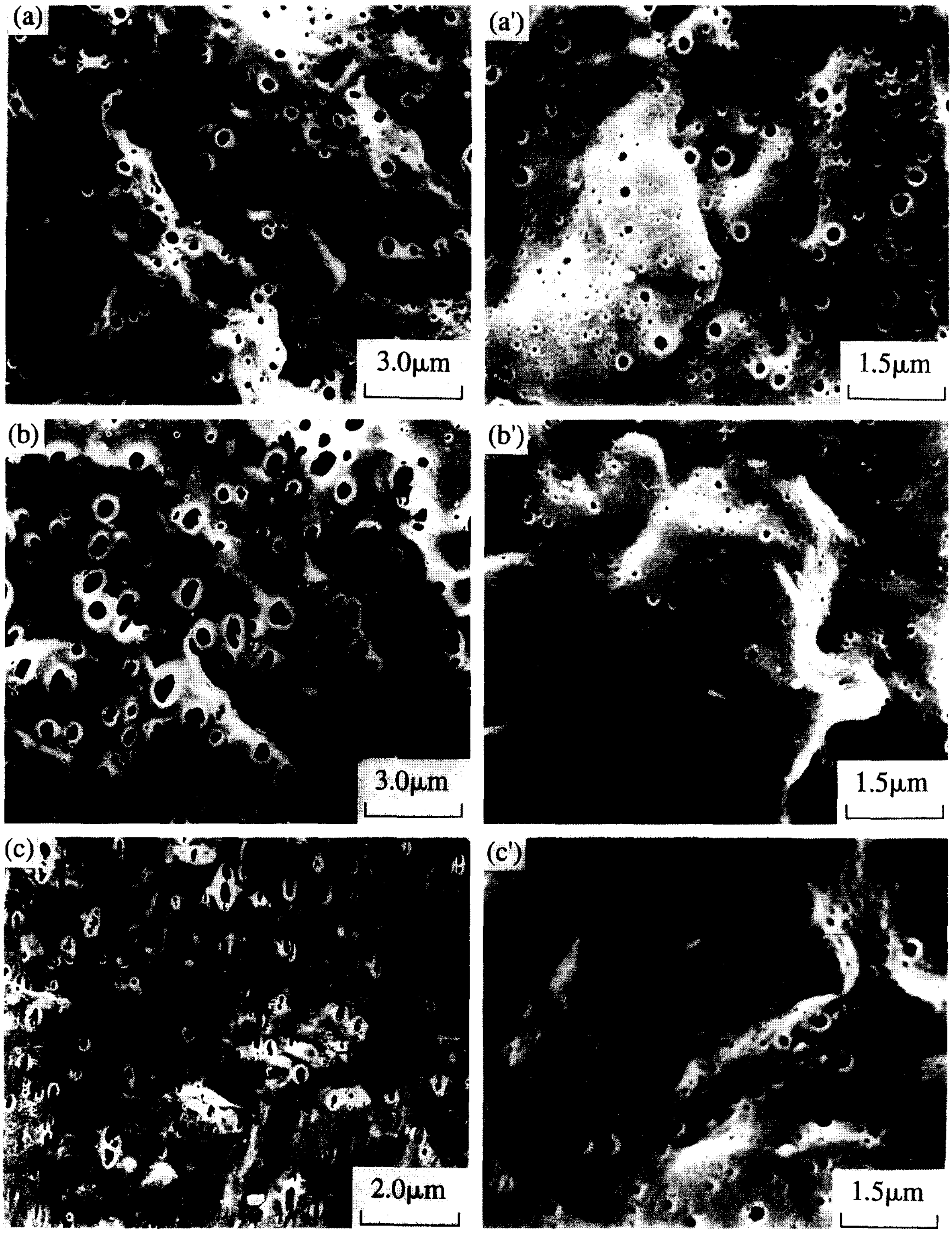

Figure 4 Effect of annealing time on morphologies of the PP/PP-MA/PA12 = 65/10/25 and PP-MA/PA12 = 75/25 blends. PP/PP-MA/PA12 = 65/10/25: (a) 0 h; (b) 2 h; (c) 5 h. PP-MA/PA12 = 75/25: (a') 0 h; (b') 2 h; (c') 5 h

blend is annealed at 180°C for 2 h, the size of the PA12 dispersed phase increases and part of the PA12 particles is non-spherical (*Figure 4*). Coarsening of the dispersed particles under 180°C continues up to 5 h of annealing.

Annealing also has an effect on the melting behaviour of the blends. Annealing leads to perfect crystallization of PA12, the melting peak of which becomes narrow, and the melting point increases (183°C) after the blend has been annealed for 2 h (*Figure 5*). A small peak at 177°C also appears. After annealing for 5 h, two PA12 melting peaks appear, one at 177°C and other at 187°C, the intensity of the former increasing and that of the latter decreasing.

Contrary to the PP-containing blend, the compatibility of components in the binary PP-MA/PA12 = 75/25 blend, a blend richer in MA moieties, the situation is different. Under the same annealing conditions, the dimension of the dispersed phase decreases with an increase in annealing time (*Figure 4*), just contrary to the case of the PP/PP-MA/PA12 = 65/10/25 blend. The higher concentration of MA yields a high degree of graft formation. Only unreacted PA12 and (PP-MA)-*g*-PA12 with many PA12 branches on the fractured surface of the

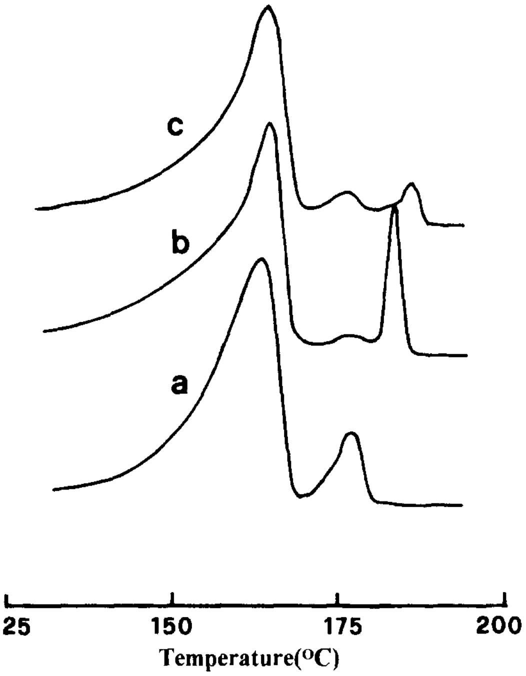

Figure 5 Effect of annealing at 180°C on melting behaviour of the PP/PP-MA/PA12 = 65/10/25 blend. Annealing time: (a) 0 h; (b) 2 h; (c) 5 h

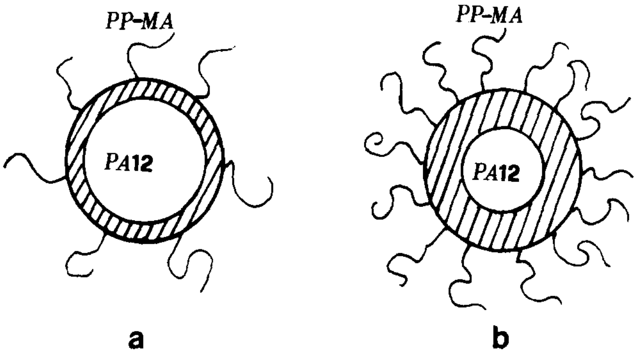

Figure 6 Change of interfacial layer during annealing. (a) Before annealing; (b) after annealing. Shadow area: PA12 molecules in (PP-MA)-*g*-PA12

blend are etched by phenol. Through interdiffusion more PA12 molecules graft onto the PP-MA backbone and the interfacial layer thus thickens (*Figure 6*). The following experimental results prove that PA12 in the interfacial layer cannot be etched.

Interfacial tension is a driving force in coarsening of the dispersed phase in heterogeneous polymer blends. In general, there could be two kinds of coarsening mechanisms: coalescence and Ostwald ripening[15]. In the coalescence process, dispersed particles move through the matrix and collide with one another to form fewer and larger droplets. In Ostwald ripening, smaller droplets dissolve and larger droplets grow, with the centres of mass of the particles stationary, though 'evaporation' will cause the smallest to disappear. In a compatibilized PP/PP-MA/PA12 = 65/10/15 blend, the dispersed phase PA12 is incompatible with the PP matrix. Therefore Ostwald ripening does not occur and the coarsening of PA12 dispersed phase is controlled only by coalescence. The fact that the shape of the particles of the dispersed phase changes from spherical to non-spherical on annealing can only come from coalescence.

Effect of compatibilization on dynamic mechanical properties of the blends

For binary heterogeneous polymer blends, whether or not compatibilizing ability of a compatibilizer is strong, the compatibilized blends are still heterogeneous. The glass transition temperature (T_g) of two components will depend on the mixing degree of each component with a responding segment of the compatibilizer. For A/C-*b*-D/B blends, in which component B is a dispersed phase, Auschra *et al.*[6] show three possible situations if the size of the dispersed phase is constant. When block copolymers are short, particles consist of an inner core region of pure B and an outer shell of intermixed D blocks and B. In this case, T_g of B will not change. When block copolymers are very long. D blocks penetrate the whole B phase and create a rather uniform segment density distribution and therefore a reduction in T_g predictable from the ratio D/B. Owing to the rather uniform segmental distribution, only moderate broadening of the glass transition is observed. However, medium long block copolymers lead to large segment density gradients across the whole B phase, and an extremely broadened glass transition. For A/A-*b*-B (or A-*g*-B)/B blends, if the T_g difference of each component with a responding segment of the compatibilizer is small; T_gs of components will not change in spite of intense mixing between the components and the compatibilizer. Otherwise, T_gs of components will change with mixing degree between the components and the compatibilizer.

However, it is not clear how T_gs of components change in a reactive compatibilized blend, in which compatibilizers are formed *in situ* and the segment lengths of compatibilizers are constant, just as in PP/PP-MA/PA12. The influence of compatibilization on the dynamic mechanical properties of PP binary blends with PA12 has been investigated (*Figure 7*). In general, the β-relaxation of PP (~ 10°C) and PA12 (~ 50°C) are thought to be the T_gs of the two components. Because of poor compatibility of PP with PA12, it is thus clear that the two main mechanical relaxation behaviours of the non-compatibilized blends represent only a simple addition of the β-transition of PP and the β-transition of PA12, indicating weak mechanical interactions between two components in the blends.

When a part of the PP is replaced by PP-MA, the interfacial compatibility of PP with PA12 is remarkably improved, and the size of PA12 particles reduces (*Figure 2*). However, the loss modulus E″ data from *Figure 7* indicate no difference in the β-relaxation process between the compatibilized blend and the non-compatibilized blends. When all PP are replaced by PP-MA, i.e. the blend of PP-MA/PA12 = 75/25, β-relaxation behaviour of the blend is obviously different from that of the two former blends. There is no obvious β-relaxation peak of PP-MA on the dynamic mechanical curves. Instead, a shoulder peak appears on the location of the β-relaxation peak of PP-MA. At the same time, the β-relaxation peak of PA12 shifts to higher temperature and becomes wider. As shown above, PA12 is dispersed as fine particles smaller than 0.1 μm in the PP matrix. The experimental results show that the β-relaxation behaviour of PP-MA is the same as

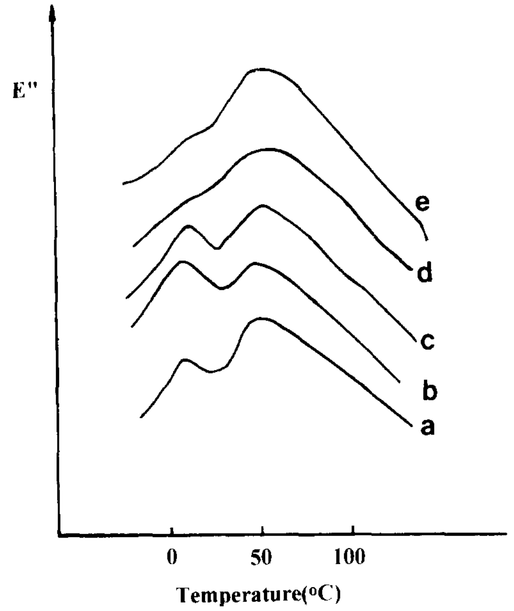

Figure 7 β-relaxation transition peaks of the blends. (a) PP/PA12 = 75/25; (b) PP/PP-MA/PA12 = 65/10/25; (c) PP/PP-MA/PA12 = 65/10/25 after annealing for 5h; (d) PP-MA/PA12 = 75/25; (e) PP-MA/PA12 = 75/25 after annealing for 5h

PP/PA12 or PP/PP-MA/PA12 or PP-MA/PA12
solution in xylene/phenol=3/1(v/v) mixture solvent

hot phenol

mixture

1) heat to evaporate xylene

2) cyclohexanone added

precipitate | **filtrate**

PP + most of PP-MA and some (PP-MA)-*g*-PA12 | **PA12 + little PP-MA and most of (PP-MA)-*g*-PA12**

Figure 8 Separation route of PP/PP-MA/PA12 and PP-MA/PA12 blends

Table 3 Compositions of the precipitate and the filtrate of the blends (the feed: PP/PA12 = 75/25)

Sample	PP (%)	PA12 (%)
PP/PP-MA/PA12		
Precipitate	88.7	11.3
Filtrate	65.6	34.4
PP-MA/PA12		
Precipitate	75.3 (76.3)[a]	24.7 (23.7)
Filtrate	74.9 (77.1)	25.1 (22.9)

[a] The data in parentheses come from element analysis measurements

that of PP. D.s.c. measurements showed that crystalline states of the blends did not change. Hence it is obvious that intense mixing of the two components results in change on β-relaxation behaviour of the blends. However, the intense mixing of PP-MA and PA12 results from chemical reaction of MA groups and amino groups. The above reaction leads to the formation of the graft copolymer (PP-MA)-*g*-PA12. The previous results showed that MA groups were mainly grafted onto the non-crystalline region of PP. The temperature of β-relaxation of PA12 is higher than that of PP. After PP-MA reacts with PA12, PA12 branches obstruct segmental motion in the PP amorphous region. Therefore β-relaxation peak of PP is dramatically suppressed. At the same time, PP backbone also blocks β-relaxation of PA12. This enables the β-relaxation peak of PA12 to shift to a higher temperature, and become wider. After the blends are annealed for 5h at 180°C, the dispersed phase size of PP/PP-MA/PA12 = 65/10/25 blend increases and that of PP-MA/PA12 = 75/25 blend reduces. During the above change, β-relaxation behaviour of the former does not change, but the β-relaxation peak of PA12 in the latter becomes narrow.

The above results show that the β-relaxation behaviour of the reactive compatibilized blends can reflect compatibilization only when the reactive compatibilization is strong enough.

Formation of graft copolymer of PP-MA with PA12 during blending

As mentioned above, PP-MA added to a PP/PA12 blend reacts with PA12 to form *in situ* a graft copolymer (PP-MA)-*g*-PA12. However, there is no method to show how much added PP-MA molecules had reacted with PA12. We carefully developed a route to separate PP/PA12, PP-MA/PA12 and PP/PP-MA/PA12 blends in order to study the *in situ* formation of the graft copolymer (*Figure 8*). When a well-mixed hot solution of PP/PP-MA/PA12 = 65/10/25 blend in a xylene/phenol = 3/1 (v/v) mixture is added to hot phenol (60°C), all PP, most of the PP-MA, and some of the grafted (PP-MA)-*g*-PA12 precipitate, while PA12, a little PP-MA and most of the (PP-MA)-*g*-PA12 remain in the filtrate. After evaporation of xylene and addition of a little cyclohexanone, the completely precipitated mixture is a uniform suspension. On the other hand, when a solution of a binary PP/PA12 blend is added to phenol, the precipitate appears as a mass. Both the precipitates are collected after centrifugation and washed with acetone.

As shown in *Figure 8*, the dissolution behaviour of the two components in a PP-MA/PA12 = 75/25 blend is different. Pure PP-MA stays in hot phenol, mainly as a bulky precipitate. It is now proven that at least part of the PP-MA participates in the form of (PP-MA)-*g*-PA12, according to change in the state of the precipitate. The solid from acetone precipitation of the filtrate has the same composition as the original blend (i.r. and elementary analysis, *Table 3*). Had not all of the PA12 reacted with PP-MA to form the graft copolymer, the remaining PA12 would have been still in the hot phenol. PA12 in the precipitate would be then lower and that in the filtrate higher than that in the feed. The fact that the compositions of the precipitate and the filtrate are the same as that of the feed proves that all PA12 molecules had reacted uniformly with PP-MA in formation of the graft copolymer, with excess MA groups unreacted (i.r., *Figure 9*).

In the blend PP/PP-MA/PA12 = 65/10/25, the content of PP in the precipitate is 86wt% and all anhydride of MA had completely transformed into amide due to its

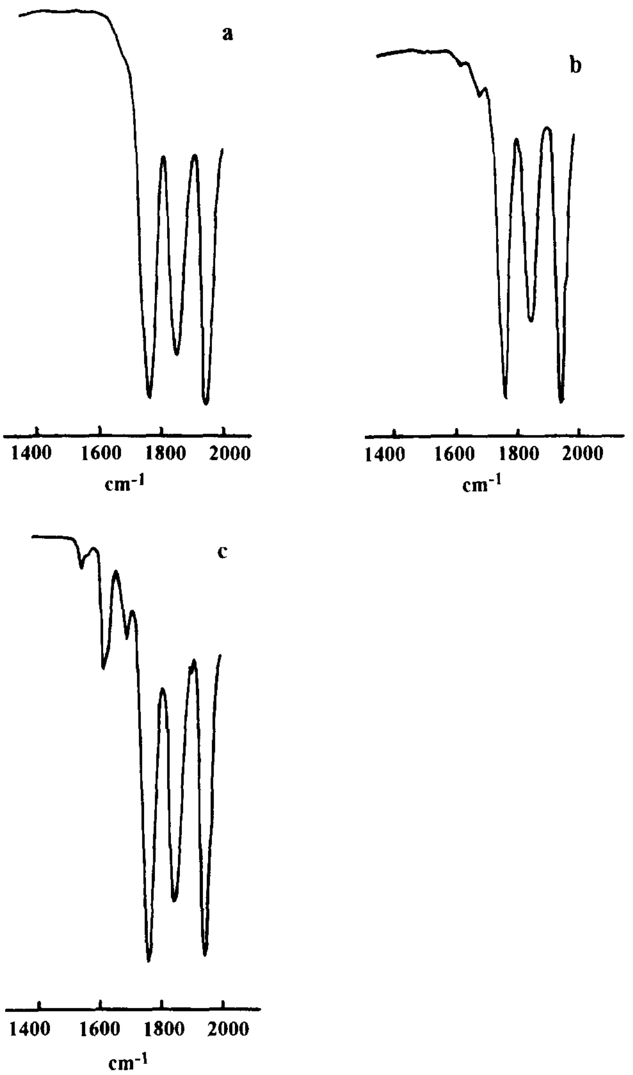

Figure 9 Infra-red spectra of the blends. (a) PP/PA12 = 75/25; (b) PP/PP-MA/PA12 = 65/10/25; (c) PP-MA/Pa12 = 75/25

Table 4 Effect of annealing on composition of the exposed interface[a]

Annealing time (min)	Content of N (%)	Content of PA12 (%)
0	2.2	32.4
45	2.6	38.1
120	3.7	55.7

[a] Annealing temperature is 172°C

reaction with amino groups of PA12. The solid form of the filtrate contains only 65 wt% of PP, lower than that of the feed, due to the fact that that part of the PA12 did not react with PP-MA (*Table 3*).

The following experimental results further prove that PP-MA can modify the interface of PP and PA12. PP layer of a composite film of PP/PA12, after heating for some time at 172°C under argon and dipped in xylene at 120°C or phenol at 100°C, separates from PA12 after 2 min. Elementary analyses show that composition on the exposed surfaces is the same as that of pure PA12 and PP, respectively. For PP-MA/PA12 composite films, no separation of PP layer from PA12 occurs. After immersed long enough in hot xylene, no nitrogen on the exposed surface is found; a part of PP-MA molecules has been absorbed on the exposed PA12 surface. After immersing at 172°C for 10 h in phenol, there is nitrogen on the exposed surface, increasing with increase in time at 172°C (*Table 4*). Thus, the content of PA12 on the exposed surface increases continuously. At 172°C PA12 molecules in the crystalline state does not change in conformation, but PP-MA in the melt might have its MA groups contacting the NH_2 groups of PA12, leading to formation of the graft copolymer in the interfacial region.

CONCLUSION

SEM of etched samples is an efficient and powerful method to observe morphology of compatibilized PP/PA12 blends. The particle dimension of PP/PP-MA/PA12 = 65/10/25 blend is in the range of 0.1–0.5 μm and even smaller than 0.1 μm. The distribution of the particle dimension of the dispersed phase in the compatibilized blend is narrower than in uncompatibilized blend. For PP-MA/PA12 = 75/25 blend, most of particles are smaller than 100 nm. The crystallization behaviour of PP/PP-MA/PA12 = 65/10/25 blend changes with morphology. The mechanism of coarsening of the PA12 dispersed phase in this blend is the coalescence process during annealing. Increase of the PP-MA relative content in the compatibilized PP/PA12 blends results in a dramatic improvement of PA12 dispersion and a subsequent change in the dynamic mechanical properties of the blends. In the PP/PP-MA/PA12 = 65/10/25 blend, all MA groups on PP-MA have reacted with terminal NH_2-groups of PA12. In the PP-MA/PA12 = 75/25 blend, all PP-MA and PA12 molecules participate in formation of (PP-MA)-*g*-PA12, regardless of excess of MA groups. Using the method of exposing interface, it is proven that MA on the PP-MA reacts with terminal NH_2-groups of PA12 during blending.

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