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Morphological studies of polyamide 1010/polypropylene blends

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Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to examine the morphology of blends of PA1010 and polypropylene (PP) compatibilized with polypropylene grafted with glycidyl methacrylate (PP-g-GMA). It is found that the morphologies are dependent on the content of glycidyl methacrylate in PP-g-GMA and the mixing time. The size of the dispersed PP particles decreases as the content of GMA in the PP-g-GMA increases for binary blends of PA1010 and PP-g-GMA. Similar results are obtained for changing the mixing time. Ternary blends of PA1010, PP, and PP-g-GMA indicate that morphologies depend on the content of glycidyl metyacrylate in the PP-g-GMA and the miscibility of PP and PP-g-GMA. By changing the content of GMA in PP-g-GMA, it was possible to introduce significant changes of morphology. A matrix removal TEM method is used to investigate the interfacial structure of PA1010/PP blends containing PP-g-GMA as a compatibilizer. This technique shows the reaction product between PA1010 and PP-g-GMA to be located at interface as a surrounding layer around domain particles. SEM observation on the interface shows that the adhesion between PA1010 and pure PP is very weak and their interface boundary is sharp. For the samples of PA1010 and PP-g-GMA, it was found that the interface was not so obvious, and the reaction between PA1010 and PP-g-GMA strengthens the interface significantly. © 1997 Elsevier Science Ltd.

(Keywords: polyamide 1010; PP-g-GMA; polypropylene)

INTRODUCTION

It is widely known that the final morphology of blend has a controlling influence on the properties of the blend. Block or graft copolymers have been used successfully as interfacial agents to control the morphology and strengthen the interfaces in blends of immiscible polymers. Blending polyamide 1010 with polypropylene (PP) leads to materials with improved chemical and moisture resistance, dimension stability, and reduced cost. However, to achieve these advantages, some form of compatibilization is generally required. Successful approaches involve addition of polypropylene grafted with maleic anhydride (PP-g-MAH) or polypropylene grafted with acrylic acid (PP-g-GMA) as a third component to the blend. It is well recognized that maleic anhydride can react with the end groups of PA to form either cyclic imide, amide acid or diamide structures, and acrylic acid can react with PA species to form esters. The resulting graft copolymers act as the compatibilizer for the blend. Previous papers[1–5] have reported such blends and the relationship between their morphology and mechanical properties. Generally, the compatibilizer reduces the phase dimensions, produces a more stable morphology by reducing the rate of domain coalescence during melt processing, and strengths the interface between the two phases in the solid state. However, there are very few studies[6–8] where morphology of the blends has been examined systematically. The improved assessment of morphology is useful for obtaining a better understanding of how the compatibilizer alters the development of phase morphology and how this in turn influences the final properties of the blend.

In this paper, we investigate the morphology of polyamide 1010/PP blends in some detail. The main focus is on the grafting degree of PP-g-GMA. The interface structure of the investigated polymer blends were carried out by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

EXPERIMENTAL

Polyamide 1010 used in this work in this work was supplied by Jilin Shijing Gou Union Co. (China); its trade name is P340. PP-g-GMAs were prepared by reaction extruding, their preparation reported in a previous report[9]. PP-g-GMAs with 0.26%, 0.33%, 0.57%, and 0.77% GMA were used in this works. The GMA content in PP-g-GMA was determined by chemical titration method[9]. Before blending, all samples were dried in a vacuum oven for a period of 12 h at 80°C. Blends were prepared using a Brabender single-screw extruder (L/D = 20) and a Brabender-like apparatus operating at about 210°C.

A scanning electron microscope, JXA-840, was used to observe the morphology of the binary and ternary blends. Before observation, the samples were etched with xylene for 40 min to increase the contrast.

The miscibility of PP and PP-g-GMA was determined by the method as follows. The first step consists of reaction of the PP-g-GMA with m-xylene diamine. This introduces aromatic groups into the PP-g-GMA phase which are

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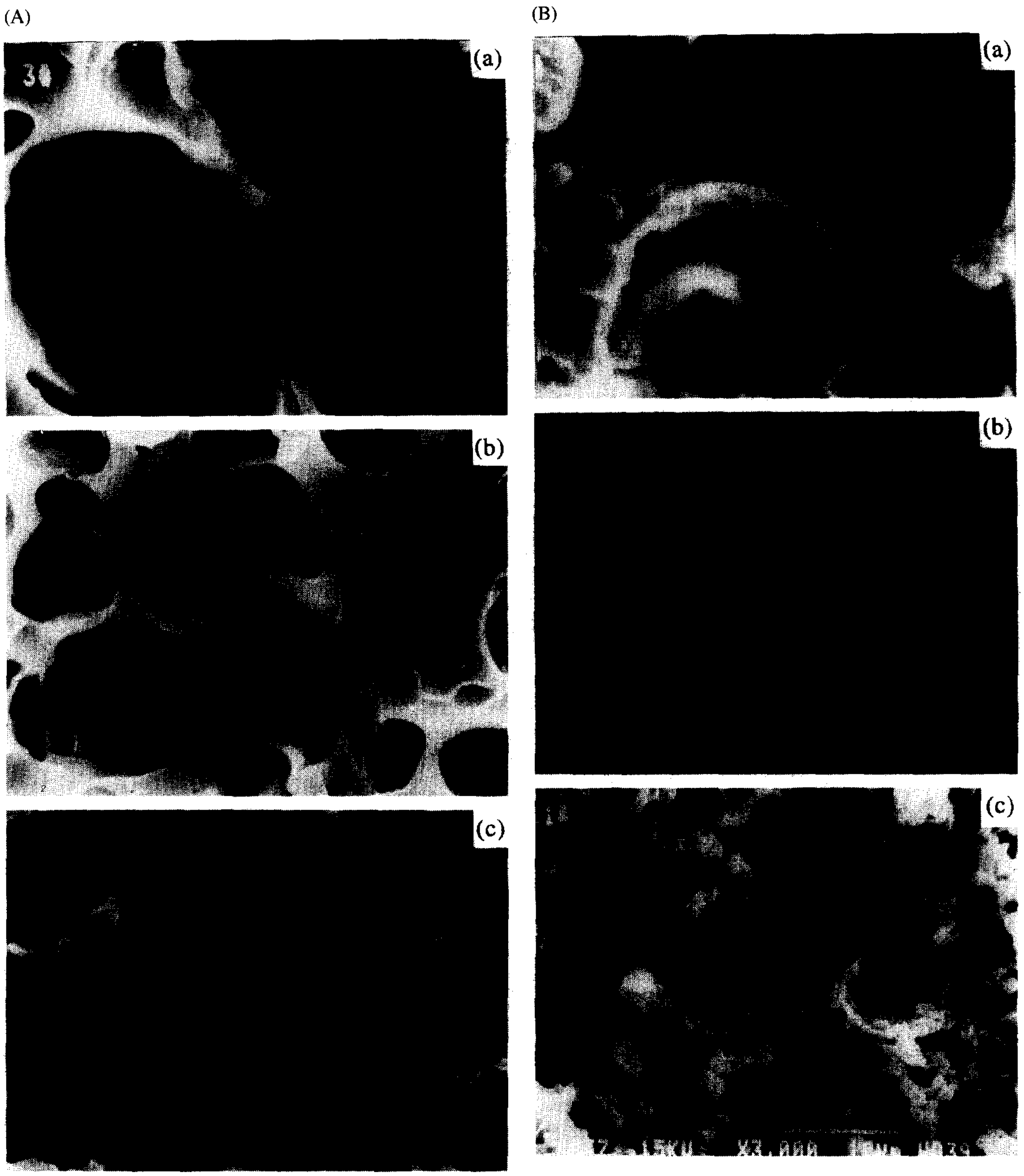

Figure 1 The SEM photomicrographs of (A) PA1010/PP (65/35) blends and (B) PA1010 and PP-g-GMA with 0.33% GMA (65/35) blends at mixing time: (a) 2.5 min, (b) 6.5 min, (c) 10.5 min

capable of reacting with RuO_4 staining agent. This selective staining of PP-g-GMA generates the necessary phase contrast to distinguish between PP and PP-g-GMA domains by the changes in electron density in TEM. The reaction was carried out by exposing samples of PP/PP-g-GMA blends to vapours of the diamine at 75°C for 2 h. After this the sample was washed with deionized water and dried in air. Microtoming of the sample was done according to the general procedure described as follows. Specimens for microscopy were prepared by trimming samples with a mill and a razor blade to form blocks and were further trimmed to the shape of a pyramid with the tip faced off to an area of approximately 0.2 × 0.2 mm. ALKB 8800 microtome was used to obtain thin section (20–40 nm thick). Sectioning was performed under cryogenic condition ($-$ 40°C) using a diamond knife. Morphology was carried out using JMA-2010 transmission electron microscope.

The SAXS measurements were performed on the Kratky compact small-angle system, which was equipped with a stationary-anode copper-target X-ray tube (wavelength 1.54 Å). All SAXS data were recorded with a one-dimensional position detector. The measured intensity was corrected for background scattering. A moving slit device was used to measure the absolute intensity.

In order to investigate the location of the reaction product, the matrix removal/TEM method was used. The unreacted PA1010 in the blends was completely extracted with formic acid (good solvent for PA1010). Then the insoluble part was embed in epoxy resin, and next the trimmed sample specimen was stained with phosphotungstic acid and used for TEM observation.

The characterization of the interface was performed as follows. The polymer couple consisted on one side of PA1010, and on the other side of PP(or PP-g-GMA). The specimen was prepared by pressing two sandwiches of pure PA1010 and PP (or PP-g-GMA) (thickness 5.50 mm) together at 200°C for 30 min. Then the joined samples were cut into small pieces under cryogenic condition at the

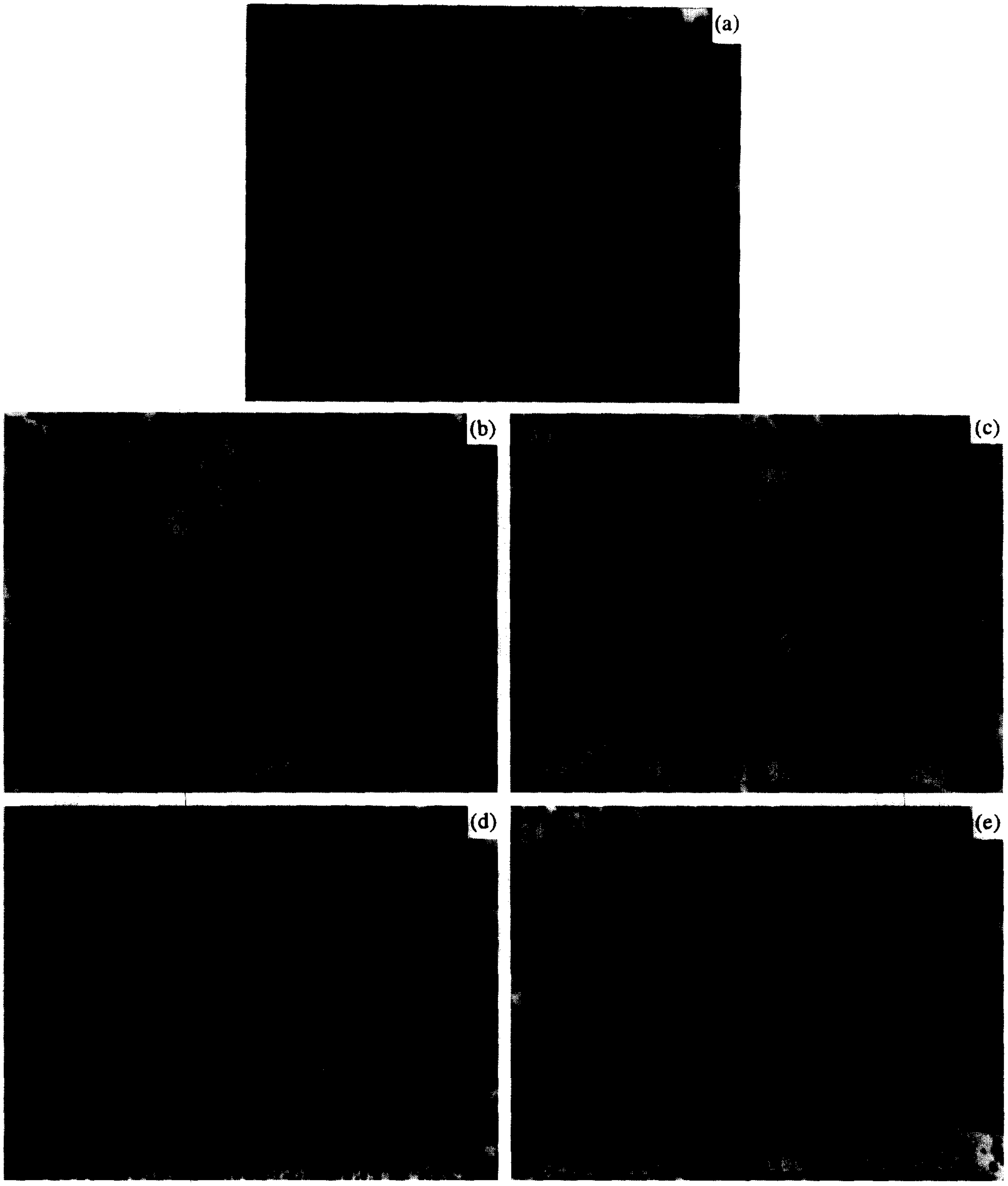

Figure 2 SEM photomicrographs of blends containing 65% PA1010 and (a) 35% PP, (b) 35% PP-g-GMA (0.26% GMA), (c) 35% PP-g-GMA (0.33% GMA), (d) 35% PP-g-GMA (0.57% GMA), (e) 35% PP-g-GMA (0.77% GMA)

interface of the two polymers. Phase contrast between the PA1010 and the polypropylene was achieved by staining the polyamide phase with an alcohol solution (1% by weight) of iodine for a period of 12 h. Electron micrographs were examined on a JXA-840 scanning electron microscope.

RESULTS AND DISCUSSION

The influence of mixing time on the morphology

The morphologies of the blends at several times of mixing are presented in *Figure 1A* for PA1010/PP and *Figure 1B* for PA1010/PP-g-GMA. Some general trends shared by the non-reactive and reactive blends are evident. At short mixing times the morphology is characterized by the large particles. The major influence of additional mixing time is the reduction in size of the larger particles in the distribution. The dispersed phase particles in the reactive blends are smaller than in the non-reactive blends. Also, the distribution of particle sizes is narrower. The smaller dispersed phase size in the reactive blends compared to non-reactive blends probably arises through several different effects: (1) reduction of the interfacial tension between

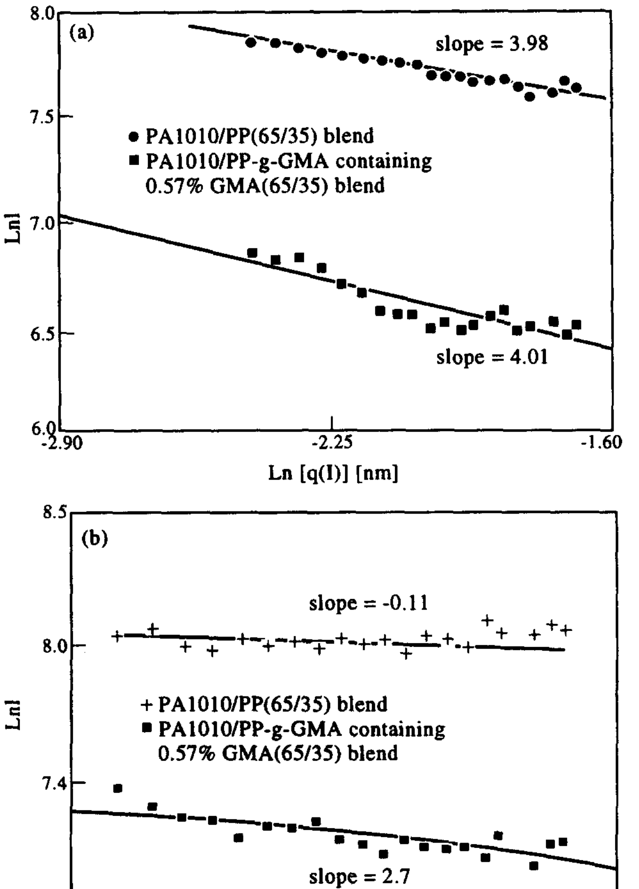

Figure 3 Ln[$I(Q)$] versus LnQ at different test temperature: (a) 25°C [correlation coefficients are 0.91 (●●) and 0.86 (■■), respectively], (b) 160°C [correlation coefficients are 0.81 (■■) and 0.79 (++), respectively]

the two phases, (2) inhibition of particle coalescence by the presence of the copolymer at the interface, (3) differences in the viscosity ratio between the two phases caused by temperature, and (4) differences in the effective shear stress applied to the blends during mixing.

Morphology of binary blends of PA1010 and PP-g-GMA

This work covers several content of glycidyl methacrylate contents for the functionalized polypropylenes. *Figure 2* shows a series of SEM pictures of blends of 65% PA1010 with 35% of different PP-g-GMA. Large PP particles which contain no reactive functionality are observed in the PA1010/PP blend, indicating very poor wettability of PP to PA1010. When the polypropylene contains only 0.26% grafted GMA, the dispersed particles formed have an average diameter of 10.11μm (*Figure 2b*); the particle size distribution is relatively narrow in this case. *Figure 2c–e* shows the cases that where the PP contains 0.33%, 0.57%, and 0.77% grafted GMA, respectively, the dispersed phase particles in these cases are much smaller in diameter than the blend with ungrafted PP. With the increasing of GMA content in PP-g-GMA, the dispersed size decreases.

Polypropylene is basically hydrophobic, whereas PA1010 is hydrophilic. Due to this fundamental difference, a good dispersion of the dispersed phase is difficult. In order to characterize the structure of the dispersed phase, the scattering spectra was analysed by using the Guinier[10] and the Porod[11] method. The porod region is first examined to evaluate approximately the shape of the particles. Porod has showed that Ln[$I(Q)$] as a function of LnQ should approach to a slope of -4 at the large Q value if the scatters have smooth surfaces and the particles are spherical in shape. For other smooth particles of different geometry, $I(Q)$ behaves differently. Cylinidrical particles should have a linear behaviour at the 'medium' Q range when the intensity is plotted as Ln[$QI(Q)$] versus Q^2. For a sheetlike particle, Ln[Q^2I(Q)] versus Q^2 would show linearity. We found that Ln$I(Q)$ gave good linearity than the other cases. Therefore, it is reasonable that we used the slope of Ln$I(Q)$ versus LnQ to characterize the shape of particle. *Figure 3* shows the Porod analysis of the investigated blends at several test temperatures. It is found that the slopes are all close to -4 in case of room temperature, which is a slope for a spherical particle. For the slope at 160°C, its values are in the range of -0.1 to -3.0, which is far higher than -4. Clearly, the testing temperature significantly alter the shape of the dispersed particles. Since the PP and PP-g-GMA particles are approximately spherical at room temperature, the size can be estimated by applying the Guinier analysis. The Guinier method is applicable at the small Q region, where the scattering intensity related to the radius of gyration according to:

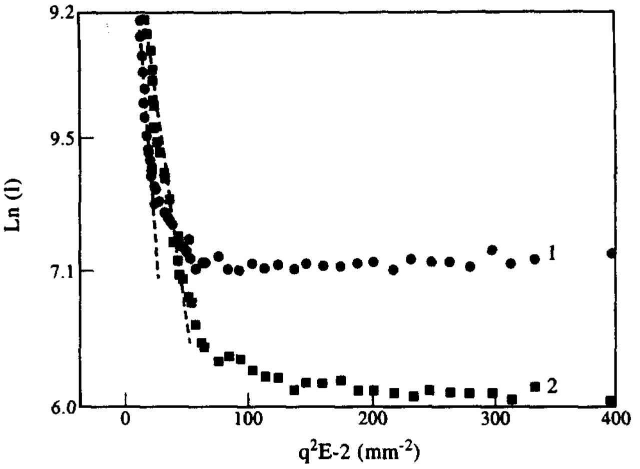

Figure 4 Cuinier analysis for (1) PA1010/PP(65/35) blend and (2) PA1010 and PP-g-GMA containing 0.57% GMA(65/35) blend

$$\mathrm{Ln}[I(Q)] = I_0 e^{1/3R_g^2Q^2} \quad QR_g \le 1$$

where R_g is the radii of gyration. In *Figure 4*, Ln[$I(Q)$] is plotted versus Q^2. From the initial slope, it can be concluded that the dispersed size decreased when PP-g-GMA replaces PP. These results are consistent with the above morphology.

Morphology of ternary PA1010/PP/PP-g-GMA blends

PA1010/PP blends can be compatibilized using PP-g-GMA, as reported in our earlier papers[12]. The morphologies of blends of PA1010/PP containing 10% PP-g-GMA with different GMA contents were showed in *Figure 5*. It is found that the morphology of investigated blends is clearly dependent on the GMA content in PP-g-GMA. The PA1010/PP shows a large size of dispersed phase and smooth surface. The ternary blend based on PP-g-GMA with a low content (0.26% and 0.33% GMA) show a narrow distribution of particle size (*Figure 5a,b*), and average particle diameter is 4.8 – 5.5 μm. For the blends containing PP-g-GMA with a higher amount of GMA (0.57%), the average particle diameter decreases to about 2.0 μm. In the

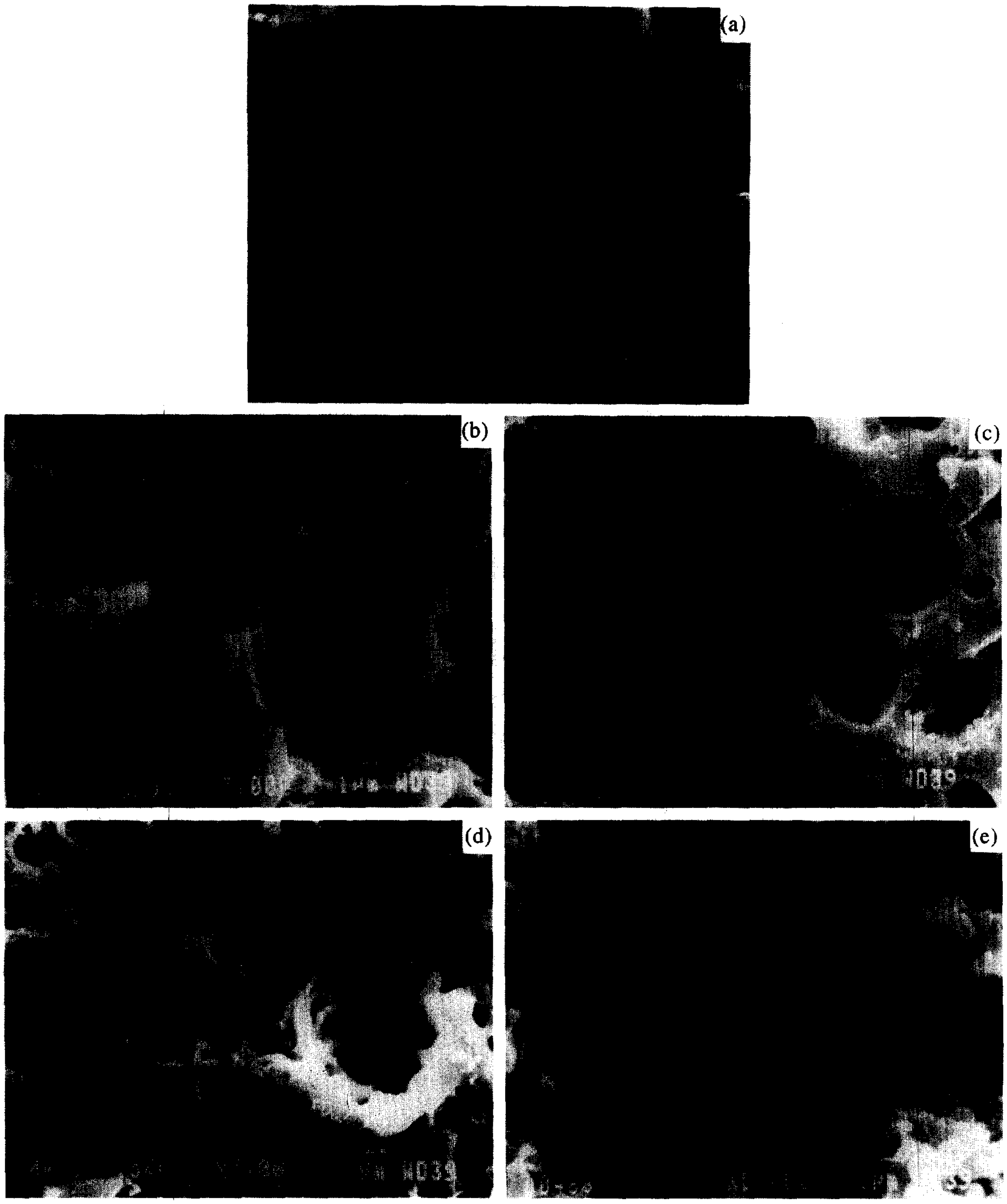

Figure 5 SEM photomicrographs of blends containing 65% PA1010, 25% PP and (a) 10% PP, (b) 10% PP-g-GMA (0.26% GMA), (c) 10% PP-g-GMA (0.33% GMA), (d) 10% PP-g-GMA (0.57% GMA), (e) 10% PP-g-GMA (1.07% GMA)

range 0–0.57% GMA content of PP-g-GMA, the more amount of GMA in PP-g-GMA, the smaller the dispersed phase diameter. However, when the PP-g-GMA with 0.77% of GMA was used, a larger size of dispersed phase was found (average particle size is 3.5 μm). In this case, there seem to exist two ranges of particle diameters: one with diameters in the range of 5 – 6 μm and the other particles in the size range of 0.1 – 1 μm.

The above morphology can be explained in terms of miscibility of PP and PP-g-GMA components in the melt blends. The phase behaviour of PP and PP-g-GMA mixtures is an important factor that determines morphology of the tenary PA1010/PP/PP-g-GMA blends. The notion of phase separation behaviour of PP/PP-g-MAH has been examined in a recent paper by Paul[13]. A series of photomicrographs of PP/PP-g-GMA blends by the diamine technique are given in *Figure 6*. The blends with the PP-g-GMA containing 0.26%, 0.33%, 0.57% GMA show relative uniform morphology. However, for PP blends with PP-g-GMA containing 1.07% GMA (*Figure 6d*), a phase separatedmorphology is clearly observed. Immiscibility in the blends of PP and PP-g-GMA could be explained by the fact that PP is non-polar molecule, whereas the PP-g-GMA is polar. The addition of higher content of GMA, the higher the tendency toward

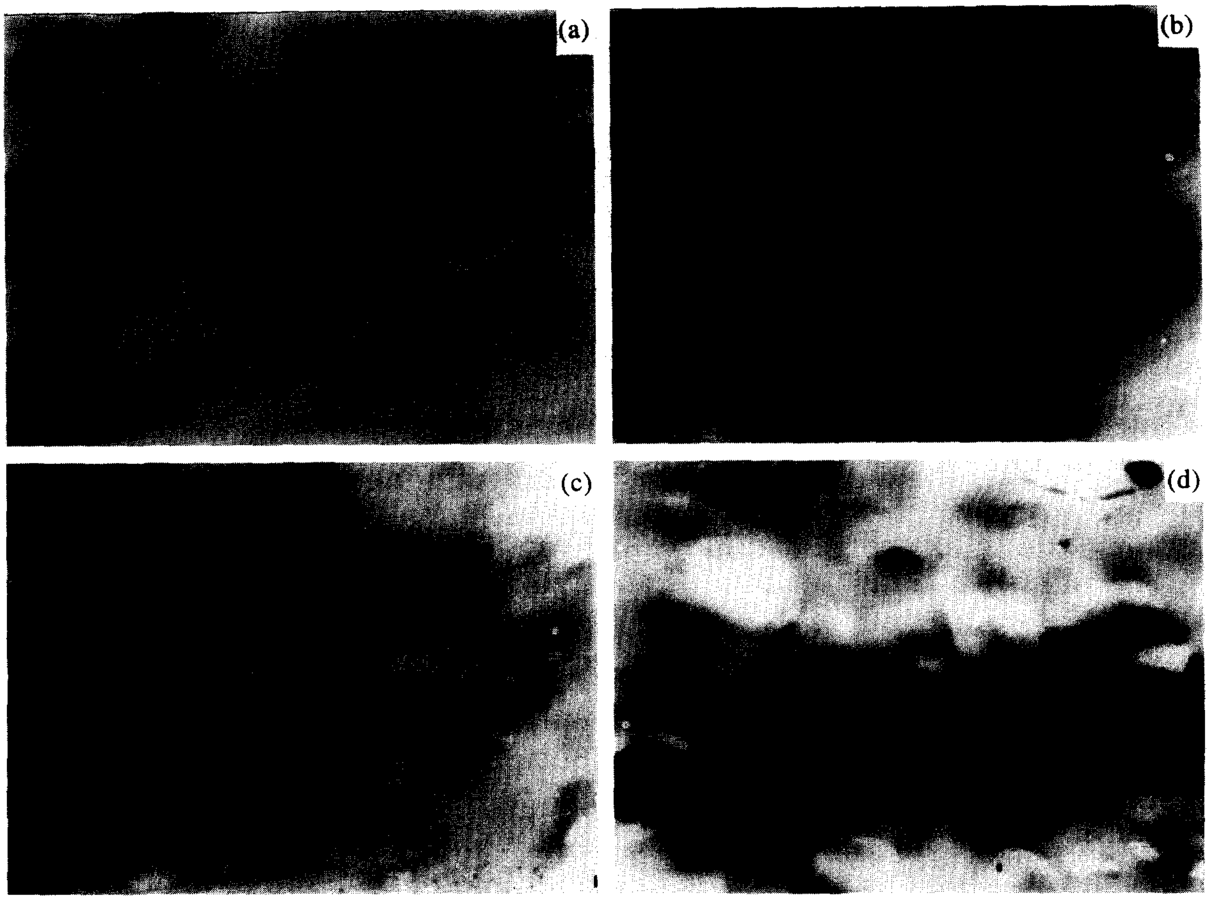

Figure 6 TEM photomicrographs of (a) 80/20 blend of PP and PP-g-GMA (0.26% GMA), (b) 80/20 blend of PP and PP-g-GMA (0.33% GMA), (c) 80/20 blend of PP and PP-g-GMA (0.57% GMA), (d) 80/20 blend of PP and PP-g-GMA (1.07% GMA); all samples were first reacted with m-xylene diamine and then stained with RuO_4

unfavourable interactions between the ungrafted PP and PP-g-GMA. For the blends containing lower content of GMA, PP and PP-g-GMA have good miscibility, PP and PP-g-GMA form the uniform morphology. If higher GMA content of PP-g-GMA (1.07%) were used, the mixture would form separate phases, the PP-g-GMA forms small particles in PA1010 matrix because of the graft reaction, while PP forms larger particles.

Interface morphological observation

Because properties of immiscible polymer blends are strongly dependent on the stabilization of interface between component polymers, it is meaningful to investigate the interface morphology aiming at understanding the role of compatibilizers. The location of the reaction product can be determined by TEM observation. By using the matrix removal TEM method, the free (unreacted) PA1010 has been extracted with formic acid, and the insoluble PA1010 have reacted with PP-g-GMA to form graft polymer. Using a selective stain of PA1010 with phosphotungstic acid or iodine, it is possible to observe interface structure. *Figure 7* shows the black stained layer of copolymer formed by PA1010 and PP-g-GMA around PP particles for the blends PA1010/PP-g-GMA (65/35) containing 0.57% GMA, and no stained layer was showed for the blend of PA1010/PP (65/35). These results indicate that the reaction product produced by the reaction during melt blending is located at the interface between PP and PA1010 as a compatibilizing layer which improves adhesion between PA1010 and PP.

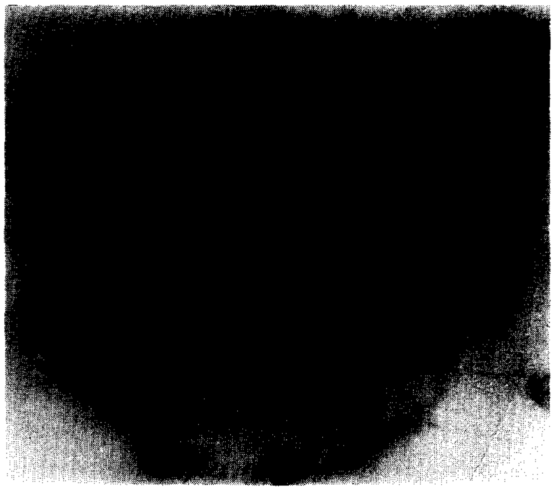

Figure 7 TEM observation of interface region with the matrix removal/TEM method for the blend of PA1010 (65%) and PP-g-GMA (35%) with 0.57% GMA content; phosphotungstic acid used as a staining agent

Figure 8 shows the SEM micrograph of the PA1010/PP, PA1010/PP-g-GMA interface. The lighter region on the left side of the micrograph is PP and the darker region on the right is PA1010 which has been stained with iodine. The interface of PA1010 and pure PP shows almost no mutual adhesion. Compared with the interface of PA1010 and PP, it is clearly seen that the interface containing PP-g-GMA have good adhesion at interface between the two polymers. As the increase of the GMA content in PP-g-GMA, the interface becomes smeared. When PP-g-GMA with 1.07% GMA content was used, it seemed to result in diffusion boundary because of the reaction formed in the interface.

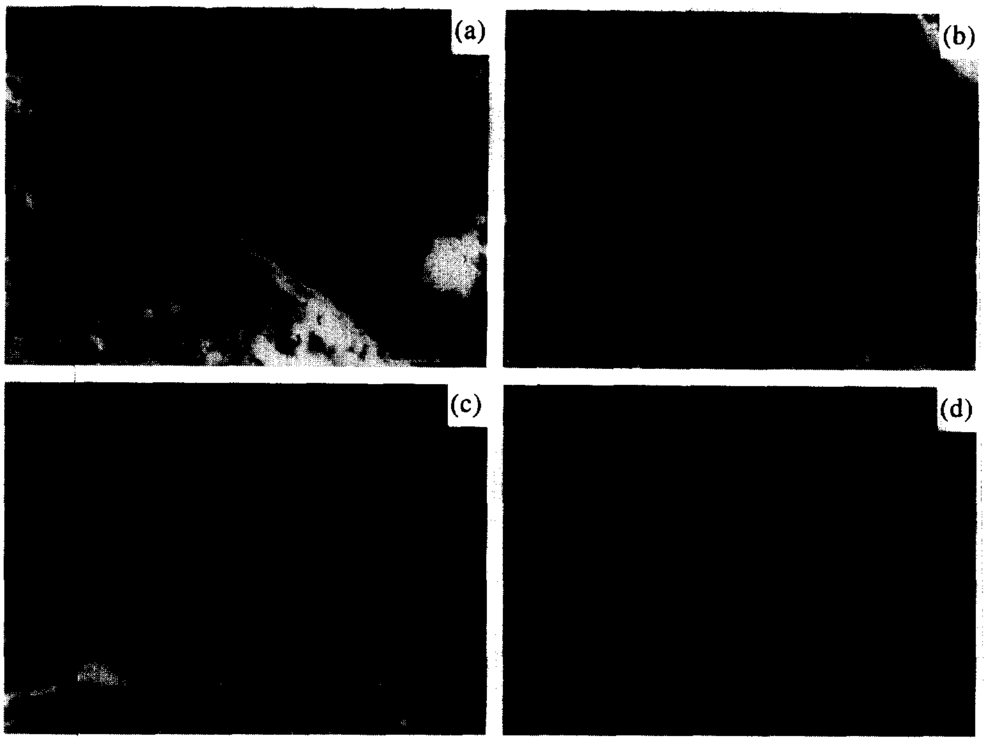

Figure 8 Scanning electron micrographs of the combined couple consisted on one side of PP, and other side of PP-g-GMA containing GMA content (a) 0, (b) 0.26%, (c) 0.33%, (d) 1.07%

CONCLUSIONS

The morphology of binary and ternary blends of P1010, PP, and PP-g-GMA were examined by SEM. With the increase of mixing time, the larger particle size decreased. Binary blends of PA1010 with PP-g-GMA showed that the PP-g-GMA particle sizes decreased as the GMA content of PP-g-GMA increased. The morphology of ternary blend of PA1010/PP/PP-GMA showed that the disperesed phase diameter decreased as The GMA content of PP-g-GMA increased from 0.26% to 0.57%. When the PP-g-GMA containing 1.07% GMA was used in the ternary blends, it was found that the dispersed phase diameter increased and two distribution ranges of particle sizes was observed. The resulting morphology was dependent on the GMA content in PP-g-GMA and on the miscibility of PP and PP-g-GMA. The PP-g-GMA used in this work with lower content GMA (0.26%–0.57%) had better miscibility with PP; and the mixture of PP-g-GMA containing higher content GMA (1.07%) with PP led to separate phase. Due to the different GMA content in PP-g-GMA, their corresponding morphology showed various patterns.

The results of the matrix removal/TEM indicated that the copolymer formed by PP-g-GMA and PA1010 located at the interface between PP and PA1010, and acted as a compatibilizing agent which strengthened the adhesion between two phases. By examining the interface morphology, it was found that the more GMA content in PP-g-GMA, the stronger the adhesion between PA1010 and PP-g-GMA.

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