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The interfacial tension and morphology of reactive polymer blends

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Abstract

Interfacial tension and morphology of polyamide6 (PA6) and polypropylene (PP) blends containing polypropylene grafted with maleic anhydride (PPMAH) as reactive compatibilizer were studied by Neumann Triangle method, Scanning Electron Microscopy and Transmission Electron Microscopy. It was observed that there was a significant reduction of interfacial tension due to the in situ formed copolymer at the interface acting as an emulsifier, and there was a limiting value of the interfacial tension under a saturation concentration of compatibilizer ($C_{\text{saturation}}$) at which the interface was saturated by the in situ formed copolymer. For the morphology, there was also a critical concentration of the compatibilizer (C_{critical}). For decreasing the size of the dispersed phase, there was no further decrease in the dispersed particle size above C_{critical} . The areal density of the in situ formed copolymer (Σ_{critical}) was estimated, and it was concluded that to emulsify the PA6/PP blend, 100% coverage of the interface by the in situ formed copolymer was not required; up to 63.7% coverage of the interface is sufficient. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Most polymer pairs are immiscible due to the positive enthalpy change of mixing and a negligible entropic contribution to free energy of mixing, the resulting high interfacial tension and poor adhesion often leading to poor mechanical properties. Therefore, the compatibilization is necessary for the immiscible polymer blends. The compatibilizers are block or graft copolymers that may be premade or

formed in situ during the melt process through the use of appropriate reactive functionalities.

Recently, reactive compatibilization has received much attention for the development of polymer blends. The reaction kinetics, the in situ formed copolymer structure and content, are the key factors to govern the properties of the reactive blending systems. A judicious selection of a compatibilizer can reduce interfacial tension between blend components, suppress the dispersed phase coalescence, and improve the mechanical properties effectively. What are the critical amounts of the compatibilizers to emulsify blends? How large is the interfacial area occupied by the copolymer needed to obtain the

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lowest interfacial tension and to prevent the particle coalescence to the smallest degree? Is the copolymer concentration for the saturation of the interfacial tension equal to that for suppressing the coalescence? To obtain the best dispersion of the dispersed phase, is it necessary to saturate all interface by the in situ copolymer? These questions are very important to clarify the compatibilization mechanisms of reactive blending systems and understand the performance of a compatibilized blend. There are numerous studies [1–9] in the literature about the compatibilization of polymer blends, but very few [1,2,10] contained data about the interfacial tension and exact amounts of the in situ formed copolymer; thus, the above questions still remain unclear. The purpose of this work is to study the relationship of the compatibilizer concentration with the interfacial tension and morphology, and correlate them with the amounts of the in situ formed copolymer in the reactive blends.

2. Experimental

2.1. Material and blending

Polypropylene with a number average molecular weight $M_n = 50,000$ and polydispersity index 3.8 was purchased from Aldrich; its melt flow index based on ASTM D1283 is 35 g/10 min. Melting temperature and density are 165°C and 0.90, respectively. Polyamide-6 with $M_n = 17,000$ and polydispersity index 2 was from BASF; it has an average of one NH_2 end per chain. Polypropylene grafted with maleic anhydride (PPMAH) with $M_n = 23,000$ was prepared by melt grafting, using the preparation and characterization method reported in the previous publication [8]. A specially designed Brabender-like apparatus was used to prepare PPMAH; the composition of the reaction mixture was 97 wt.% PP, 2.95% MAH, and 0.05 wt.% dicumyl peroxide (DCP), reaction temperature is 170°C. MAH was grafted onto PP chains randomly, and the amount of MAH determined by chemical titration was 0.44 wt.%, about 1.02 MAH per PPMAH based on the M_n . The blends were prepared using a Brabender-like mixer at 240°C. Blends of PA6 and PP were mixed with different amounts of PPMAH, using the PA6 fraction 80 wt.% and a total weight fraction of PP + PPMAH

of 20 wt.%. The materials were dried at 80°C in a vacuum oven for 12 h before blending.

2.2. Measurements of interfacial tensions

The Neumann Triangle (NT) concept [11–13] has been successfully used for the interfacial tension determination of reactive blends in the previous publication of one of the authors of this paper [10]. Two polymer plates (PS, PA6) with 1 mm thickness were prepared by a compression molder. Small pieces of PP or a mixture of PP + PPMAH (0.4×0.4 mm) were sandwiched between two other polymer plates (PS and PA6). The sandwiched sample was first heated to 180°C, and kept at that temperature for 10 min. Then, the sample was increased to 240°C within 1 min and annealed at 240°C for 30 min under vacuum. After annealing, it was quenched by putting it in ice water. The cross-section of the sample was observed by an optical microscope under transmission mode.

To obtain the in situ formed copolymer amounts in process of the interfacial tension measurement, we imitate the process of NU measurements to prepare the PA6 plates (1 mm in thickness) and plates with 0.4 mm thickness of the mixtures of PP + PPMAH, and then put PA6/PP + PPMAH sheets together between two glass covers. After annealing the laminated PA6/PP + PPMAH for the same period (30 min) as the interfacial tension measurements in vacuum, the unreacted PA6 was dissolved by formic acid. XPS was used to evaluate the interface. Assuming the N_{1s} came exclusively from PA6, from the overall atomic concentration ratio of N to C, we can determine the amounts of PA6 coupled to PPMAH. The elemental measurements were carried out by ESCA CAB MK-II electron spectrometer.

2.3. The extraction experiments and estimation of the areal density of the in situ formed copolymer

The PA6/PP blends containing 25% PPMAH (based on dispersed phase) were pressed into thin films by a compression molder. 2.0 g of thin films was extracted in 140 ml xylene for 48 h to remove the unreacted PPMAH. The resulting residue was washed with water and dried in vacuum oven at 80°C for a week, and weighted. The weight of the

residue was found to be 1.6251 g. By assuming that the remaining PP and the PPMAH reacted with PA6, from the extraction experiment it is evident that 25% of the added PPMAH in the blending process reacted with PA to form the in situ copolymer.

Since there is approximately an average of 1.02 MAH per PPMAH chain, it is reasonable to assume that one PA6 reacted with one PPMAH, and the number of in situ formed copolymer should be identical to the number of reacted PPMAH. In the extracted experiments, it was shown that 25% of the added PPMAH reacted with PA6 in the melt blending process; thus the areal density of the copolymer chains/nm² can be calculated based on the assumption that all the formed copolymer is in the interface:

$$\Sigma = (\text{in situ formed copolymer chains/vol}) / (\text{interfacial area/vol}) = N_a W / S_{sp} M_n = R N_a W / 3 \phi_d M_n \quad (1)$$

where S_{sp} is the interfacial area per unit volume, R the average radius of the dispersed phase, N_a Avogadro's number, W the weight of the reacted PPMAH per unit volume of the blend, ϕ_d the volume fraction of the dispersed phase, and M_n the number average molecular weight of PPMAH.

2.4. Morphology analysis

The blending test specimens were cryofractured by liquid nitrogen and the fracture surface was examined by a JSM-T300 scanning electron microscope. The cross-sectional area of each particle on the micrograph was measured by an image analyzer, then converted to the diameter of a particle. The average size of dispersed phase was obtained by measuring 200–300 particles. The stability of morphology and particle coarsening in quiescent melt was determined by annealing the samples in a compression molder at 240°C. The specimens were quenched in ice water after annealing in order to freeze the morphology. Jeol 1200EX transmission electron microscope was also used to observe the morphology stability. The samples were cut from the welded sheet. The cubic sample was pretrimmed with a glass knife and then microtomed with 35 Diatome diamond knife using a Reichert Ultracut S

microtom. Sections were stained with phosphotungstic acid that can selectively stain PA6.

3. Results and discussion

3.1. Interfacial tension

The interfacial tensions for PA6/PP with different amounts of the compatibilizer are given in Fig. 1. It is clear that the addition of PPMAH led to a decrease in the interfacial tension between PA6 and PP due to the formation of PA6-graft-PP copolymer; the copolymer plays the role of a surfactant between PA6 and PP. It should be noted that there is a saturated concentration of the compatibilizer, beyond which no further decrease of interfacial tension is observable. In this study, the limiting value of the interfacial tension between PA6/PP upon addition of PPMAH is 4.16 dyn/cm. The critical concentration of the compatibilizer for obtaining the equilibrium of the interfacial tension is estimated to be 0.3 wt.% from Fig. 1. The interfacial tension is dependent on the compositions at the interface; the leveling off is an indication of interfacial saturation. It seems to mean that all the interface has been covered by the in situ formed copolymer at the saturation concentration of the compatibilizer (0.3 wt.%); further increase in PPMAH does not change the interface compositions. To confirm this, XPS obtained from the laminated PA6/PP sample with 0.3 wt.% PPMAH after removing unreacted PA6 is shown in Fig. 2. The C/N atomic ratio is 6.114/1, it is very close to the neat PA6, indicating that the interface has been saturated by the in situ formed copolymer.

Since only the NH₂ end group in PA6 reacted with the MAH in PPMAH, one PA6 chain contained exactly one NH₂ end group. The saturation surface concentration of the copolymer $\Sigma_{\text{saturation}}$ can be estimated by assuming a dense monolayer at the interface [14]:

$$\Sigma_{\text{saturation}} = N_a \rho d / M_n \quad (2)$$

where d is the thickness of the PA6 layer; it is obtained by [14]:

$$(N/C)/(N/C)_{\infty} = 1 - \exp(-d/\Lambda) \quad (3)$$

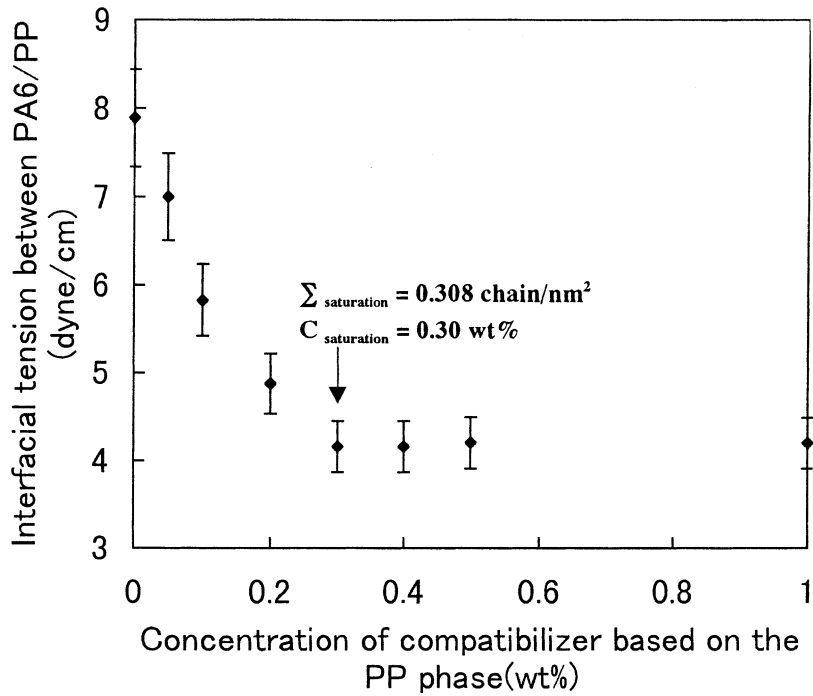


Fig. 1. The interfacial tension as a function of the compatibilizer (PPMAH) concentration. Each datum was the average value of five measurements, and the experimental error is within 15%.

(N/C) and $(N/C)_\infty$ are the normalized N_{1s} counts for studied samples and pure PA6, respectively. Δ is

the escape length of N_{1s} electrons including the takeoff angle of the instrument and was estimated to

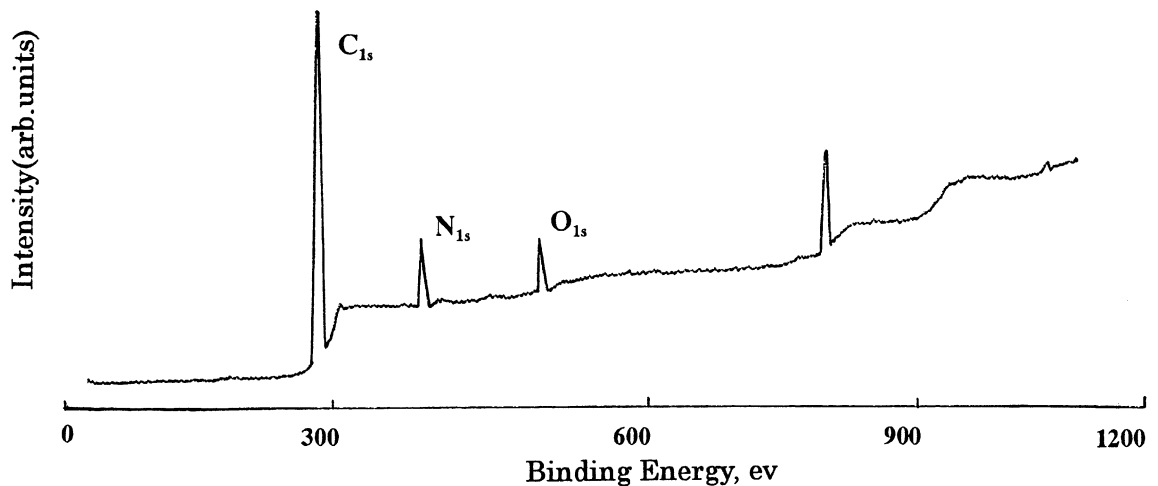


Fig. 2. The XPS spectra of the interface of laminated PA6/PP containing 0.3 wt.% PPMAH in PP phase; unreacted PA6 has been removed by extraction in formic acid.

be 19 Å in the literature [15]. N_a is the Avogadro's number, ρ is the mass density of PA6 and M_n is the number average molecular weight of PA6. The number of in situ formed copolymer per unit interfacial area ($\Sigma_{\text{saturation}}$) is calculated to be 0.308 chains/nm², i.e. 0.308 PP-graft-PA6 copolymer chains per unit interfacial area is the critical concentration for saturating the interface, and the area occupied per molecule of copolymer is 3.24 nm⁻².

3.2. Morphologies of PA6/PP blends

The influence of the reactive compatibilizer on the phase morphology of polymer blends is dependent on the ability of the in situ formed copolymer to reduce the interfacial tension between the dispersed phase and matrix and to suppress the particle coalescence. The efficiency of this process is related to the mixing condition, the amounts, structure and location of the in situ formed copolymer. Fig. 3 shows several SEM pictures with different amounts of compatibilizer,

and Fig. 4 shows the plot of the dimension of the dispersed phase as a function of the amounts of the compatibilizer. There is a sharp decrease in the dispersed phase with the addition of small amounts of compatibilizer, followed by a leveling off as the compatibilizer content is increased above the critical saturation concentration, $C_{\text{critical}} = 25$ wt.% (based on the dispersed phase). It should be stressed that the term 'saturation' used does not mean that all the interface are covered by the in situ formed copolymer, it only refers to the point where the dispersed particle size is no longer dependent on the amounts of the interfacial agent.

It is found that the critical concentration, $C_{\text{critical}} = 25$ wt.%, is much larger than the critical concentration (0.3 wt.%) for the interfacial saturation from the interfacial tension measurements. We should stress that the morphology was obtained in the dynamic blending, while the interfacial tension measurements were carried out in a static condition; the interfacial geometry is different for two cases. Therefore, in order to make a fair comparison, the molecular chains per unit interfacial area of the in situ

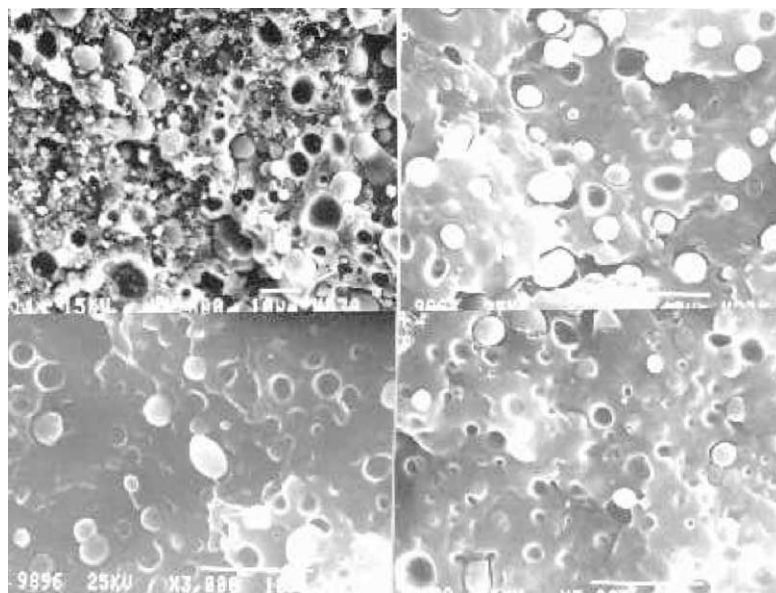


Fig. 3. The dependence of morphology on the compatibilizer concentration in mixing process: PA6/PP = 80/20 (upper left); PA6/PP/PPMAH = 80/18/2 (upper right); PA6/PP/PPMAH = 80/16/4 (bottom left); PA6/PP/PPMAH = 80/15/5 (bottom right).

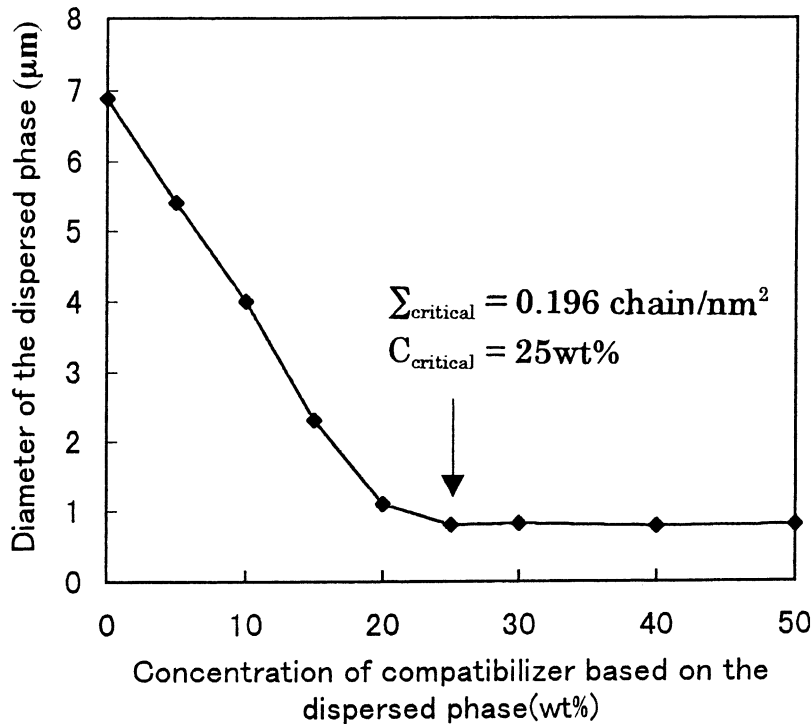


Fig. 4. The dependence of the particle size on the concentration of compatibilizer based on the concentration of the dispersed phase.

formed copolymer should be used instead of the concentration of the compatibilizer.

3.3. Areal density of the *in situ* formed copolymer

At $C_{\text{critical}} = 25$ wt.%, the content of *in situ* formed copolymer Σ_{critical} is 0.1963 chain/nm² using extraction experiments and Eq. (1), and the area occupied per molecule of copolymer is 5.09 nm⁻². The area occupied per molecule was calculated to be 5 nm² per molecule for the PA6/PP/Surllyn blends [16], 2.6 nm² for LDPE/PS/SEBS system [17], 8–10 nm² for the PP/PET/SEBS-g-MA blends [18]. It is seen that our estimated value is comparable with those in the literature.

It should be noticed that the estimated Σ_{critical} (0.1963) was based on the assumption that all of the non-extracted PPs are the reacted PPMAH, and all the *in situ* formed copolymer located at the interface, so Σ_{critical} (0.1963) is the maximum limiting value. It is important to observe that Σ_{critical} (0.1963) is smaller than the $\Sigma_{\text{saturation}}$ (0.308). It implied that the

interface of PA6/PP (80/20) blend with 25 wt.% compatibilizer is not saturated by the *in situ* formed copolymer in the blending process, and the interfacial tension should continue to decrease with increasing Σ . Assuming that all copolymer is located at the interface in the blending process, we can obtain the fractional coverage of the interface by the *in situ* formed copolymer $\Sigma_{\text{critical}}/\Sigma_{\text{saturation}}$. To obtain a limiting dispersed phase size, interfacial coverage is about 63.7%. It means that 63.7% coverage of the interface with the formed copolymer is enough to emulsify the blend. However, the limiting value of the interfacial tension is not reached at the coverage of 63.7%; thus, interfacial tension should continue to decrease with the increase of the interfacial coverage until all interface is saturated by the copolymer. The present result indicated that the particle sizes are not dependent on the amounts of the copolymer at the interface once the critical coverage is reached (63.7%); further increase of the interfacial coverage, in other words, further decrease in the interfacial tension, has little influence on the dispersed particle

size. The result seems to indicate that the reduction of the particle size mainly results from the contribution of suppressing the coalescence, and the contribution of interfacial tension reduction is small. This is somewhat same with Sundararaji's conclusion [1], which reported that the only advantage of the compatibilizer or the main contribution from the compatibilization by a copolymer is steric stabilization, not reduction of the interfacial tension, since they found the limiting particle size is identical to that of uncompatibilized blends at low concentration of dispersed phase, and very little reaction (even 1 wt.% reactive component) is sufficient to stabilize the morphology during mixing.

In the present study, a relatively high dispersed phase is employed; the emulsification of the blend is assumed to be mainly from suppressing the coalescence. Although there is a reduction in interfacial tension, this reduction is not nearly as important as the elimination of coalescence through the interfacial stabilization, as reported in our previous paper [19].

3.4. The morphology stability upon static annealing

From the above results, 25 wt.% compatibilizer based on the dispersed phase is sufficient to prevent the coalescence at dynamic mixing condition. We now check the case of static. Fig. 5 shows the TEM pictures measured under static after 2 min of melt mixing as a function of annealing time. The micrographs are typical pictures of polymer melt blends. The morphology for the blend without a compatibilizer is rather unstable, and it is clear that particle diameter increases with annealing. The particle coarsening results from Ostward ripening (evaporation–condensation) or particle coalescence [20–24]. It is difficult to determine which mechanism dominates, since some parameters in the present study are unknown for the calculation of K_C and K_{OR} (K_C and K_{OR} are the coarsening constant for coalescence and Ostwald ripening mechanism, respectively). It seems that from Fig. 5 some particles coalesce with each other because of their moving freely with re-

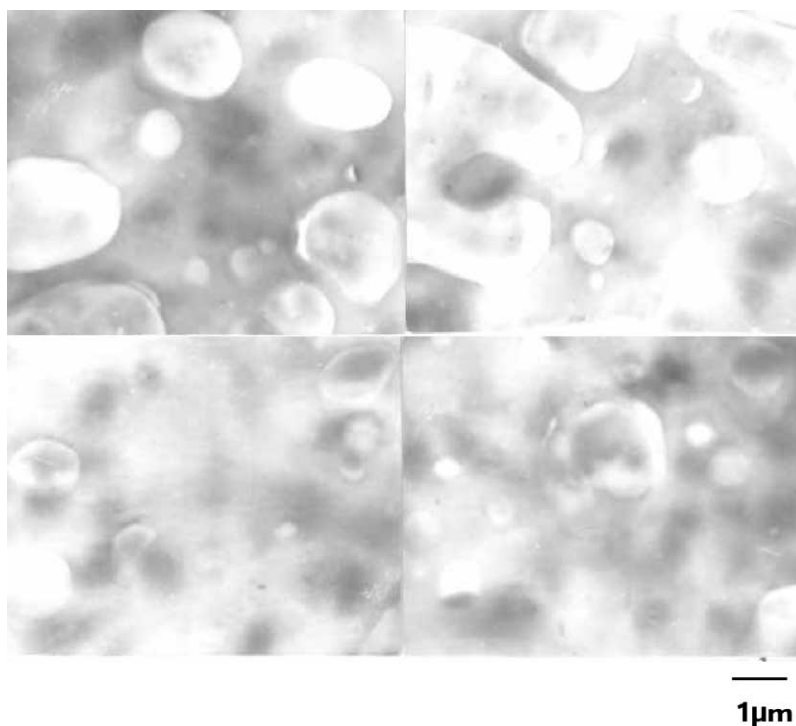


Fig. 5. TEM coarsening pictures of PA6/PP blends compatibilized with and without PPMAH: (1) upper left: without PPMAH, immediately after 2 min of mixing at 240°C; (2) upper right: without PPMAH, after 20 min annealing at 240°C; (3) lower left: with 25 wt.% PPMAH, immediately after 2 min of mixing at 240°C; (4) lower right: with 25 wt.% PPMAH, after 20 min annealing at 240°C.

spect to the matrix, i.e. the mobile interface [5]. With 25 wt.% compatibilizer, it was shown that a stable morphology, i.e. the average domain size, did not change with the annealing time.

The coarsening constant of Ostward ripening K_{OR} is expressed as follows [20]:

$$K_{OR} = (8D\nu_m\gamma C_e/9kT)(1 + 0.74V_{particle}^{1/2})^3 \quad (4)$$

where D is the diffusion coefficient, ν_m the molecular volume of diffusing species, γ the interfacial tension, C_e the equilibrium mole fraction of blend components in the matrix, thermal energy kT . If Ostward ripening operates at the annealing process, an increase in particle size with a reduced growth rate due to the reduction of the interfacial tension for the reactive blends should be observed. The constant particle size of the compatibilized blend implied that the coalescence dominated instead of Ostward ripening. From $K_C = 2kTV_{particle}/\pi\eta g$, where $V_{particle}$ is the volume fraction of dispersed phase and η the matrix viscosity [18], it is reasonable that the coalescence rate is large since the matrix viscosity (PA6) at the investigated temperature is low. The chemical reaction can lower the movement of the dispersed phase and decrease the particle collision chance significantly. Even though particles contact each other, the in situ formed copolymer at the interface acted as a wall to eliminate the combination of the dispersed phase, if there are enough copolymer at the interface.

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