

Properties of Poly(ethylene terephthalate) and Maleic Anhydride-Grafted Polypropylene Blends by Reactive Processing

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Received 13 January 1998; accepted 25 March 1998

ABSTRACT: The properties of poly(ethylene terephthalate) (PET) and polypropylene (PP) blends and PET/maleic anhydride-grafted PP (MAGPP) reactive blends were investigated. Two blend systems were immiscible based on $\tan \delta$ measured by dynamic mechanical analyzer (DMA). In case of PET/MAGPP blends, the reaction of ester groups of PET and MA sites on MAGPP occurred during melt mixing at 280°C for 30 min. The reaction was confirmed by a new peak between the glass transition temperatures of PET-rich and MAGPP-rich phase on $\tan \delta$ curves, as well as from the rheological properties. From the morphology, the improvement of the dispersibility in PET/MAGPP reactive blends was observed. The modulus of PET/MAGPP blends was higher than that of PET/PP blends, and the strength of PET/MAGPP blends showed the good adhesion compared with the PET/PP blends. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 389–395, 1998

Key words: poly(ethylene terephthalate); polypropylene; maleic anhydride; reactive blend; maleic anhydride-grafted polypropylene

INTRODUCTION

There are many studies about reactive processing of immiscible polymer blends. Reactive processing involves *in situ* reaction of functionalized components to form a block or graft copolymers at the interface between the phases.^{1–10} It is well known that maleic anhydride (MAH) reacts with polypropylene (PP)^{11,12} in the presence of radical reagents when mixed at the molten state. So, MAH has been used as a compatibilizer in immiscible polymer blends, especially the PP/polyamide (PA) system. The reactive processing of the PP/

Nylon 6 system was undertaken by Ide and Hasegawa.¹ They used maleic anhydride-grafted PP (MAGPP) and reported that the market dispersibility of the blend was obtained, resulting in improved mechanical properties. Chen and colleagues¹³ studied the phase morphology of nylon with polyethylene and polystyrene using MAH. Borggreve and Gaymans¹⁴ reported the impact behavior of the nylon and rubber system, considering the effect of the coupling agent, MAH. Recently, Li and associates¹⁵ analyzed the interface through the size reduction of dispersed particles and the stability of particle dispersion during reactive processing of the PP and PA system. Mainly, PA has been used in reactive processing with the modified PP due to the reaction of the amino-chain end of PA and MAH sites on MAGPP.

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Journal of Applied Polymer Science, Vol. 70, 389–395 (1998)

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CCC 0021-8995/98/020389-07

Table I Properties of Polymers Used in This Work

Materials	M_w	M_n	T_m^a (°C)	T_g^b (°C)
PP	232,000 (88,200) ^c	39,900 (21,400)	166.8	18.8
MAGPP ^d	131,600 (64,500)	27,200 (15,800)	166.3	20.2
PET	38,800 (32,000)	19,400 (16,000)	250.3	109.8

^a Values measured by differential scanning calorimetry.

^b Values measured by DMA.

^c Values measured by gel permeation chromatography after heat treatment at 280°C for 30 min.

^d MAH content was 1 wt %.

In this work, we tried to compare the properties of poly(ethylene terephthalate) (PET)/PP physical blends (without MAH) with PET/MAGPP reactive ones (with MAH). The glass transition temperatures, morphology, mechanical, and rheological properties of physical and reactive blends were measured.

EXPERIMENTAL

Materials

PP and MAGPP were supplied by Honam Petroleum Chemical Co. Ltd., and the weight average molecular weights (M_w) were 232,000 and 131,600, respectively. The lower M_w of MAGPP resulted from preparing it by the reaction of PP and MAH. MAH content in MAGPP was 1 wt %. PET was supplied by Tongkook Synthetic Fibers Co. Ltd., and its M_w was 38,800. The average molecular weight, the melting, and glass transition temperatures of the polymers used are listed in Table I.

Blend Preparation

Physical and reactive blends were prepared in the polymerization reactor¹⁶ (small batch scale) at 280°C for 30 min. Pure PP, MAGPP, and PET were treated to have the same thermal history for comparison.

Measurements

Thermal analysis was performed using a DuPont dynamic mechanical analyzer (DMA; DMA 983).

Samples were heated from -80°C to 150°C at a heating rate of 2°C/min with frequency of 1.0 Hz. The tensile properties, such as the initial modulus measured at 0.2% elongation and the tensile strength at yield, were measured using an Instron model 4467 universal instrument. Measurements were made at room temperature at a constant crosshead speed of 2 mm min⁻¹ on specimens that were made by Mini Max Molder (CS-183MMV-203). Data were taken as averages of at least five measurements. Morphology of the blends was measured by scanning electron microscopy (SEM) (Hitachi, S-2400SEM). Rheological properties (such as storage modulus, G' , and loss modulus, G'') were measured with frequency at 280°C by Physica, Rheo Lab. MC 120.

RESULTS AND DISCUSSION

Thermal Analysis

Because there is the large difference between blending temperature (280°C) and melting temperature (166°C) of PP and MAGPP, it needs to check the degradation of PP and MAGPP. The M_w of PP and MAGPP before and after heat treatment at 280°C for 30 min was measured by gel permeation chromatography (Waters 150C) at 140°C with the solvent trichlorobenzene and listed in Table I. Figure 1 shows the thermograms of pure PET, PP, and MAGPP at 280°C in nitrogen. The

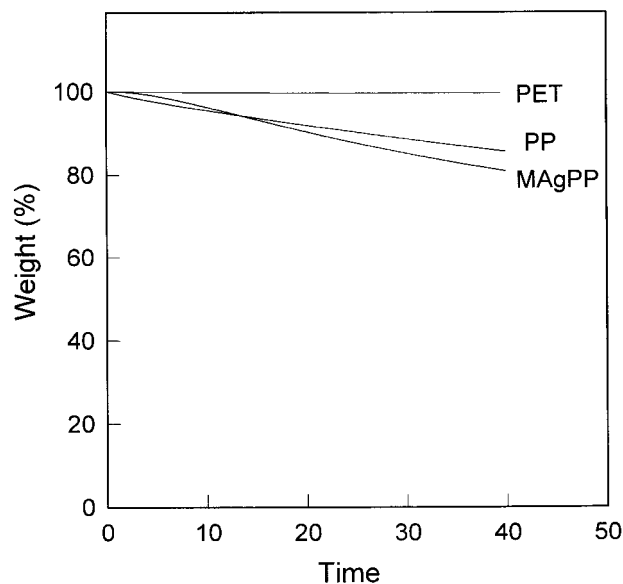


Figure 1 Thermal gravimetric analysis thermograms of PET, PP, and MAGPP at 280°C in nitrogen.

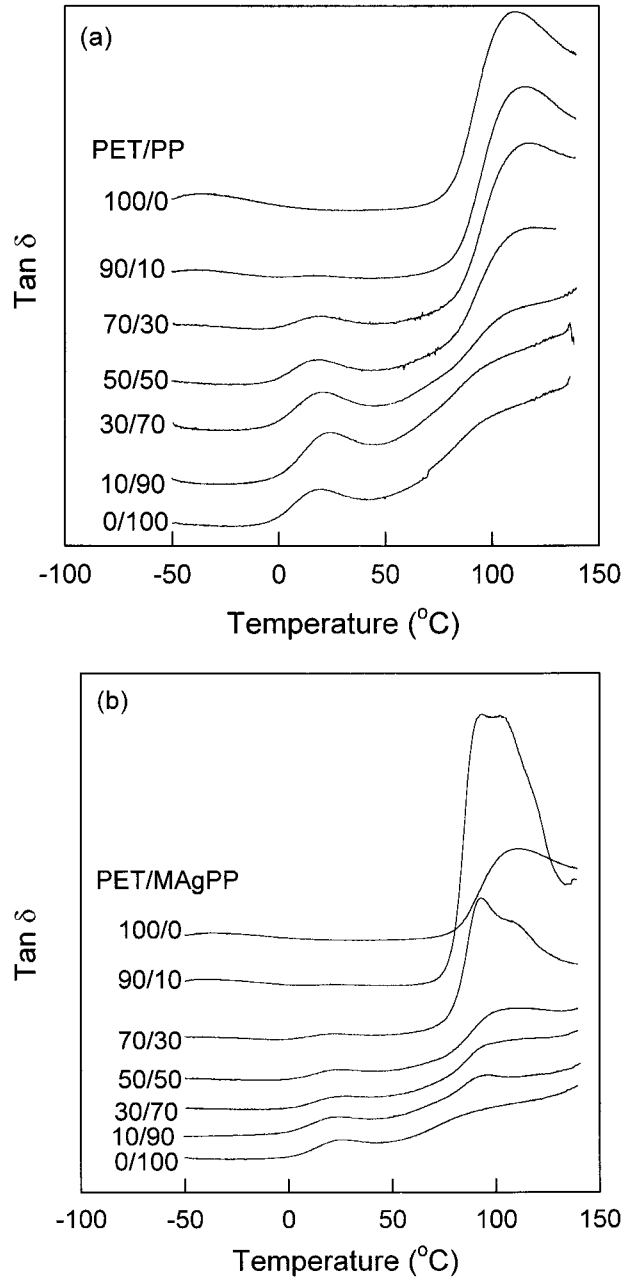


Figure 2 Temperature dependence of dissipation factor $\tan \delta$ for (a) PET/PP blends and (b) PET/MAGPP reactive blends.

weight of PET was not changed during melt mixing for 30 min, whereas those of PP and MAGPP were decreased ~ 10 and 15% , respectively. Degradation of PP and MAGPP during melt mixing was not serious, based on the mechanical properties of the blends that will be explained later.

Figure 2(a) shows $\tan \delta$ for PET/PP physical blends. It is an immiscible blend system that the

two glass transition temperatures are observed and do not change with the blend compositions. Figure 2(b) shows $\tan \delta$ for PET/MAGPP reactive blends, which is also an immiscible blend system. Above the blend compositions of PET70, the difference of $\tan \delta$ of two blend systems is observed. PET/PP (70/30) of Figure 2(a) shows the two glass transitions. On the other hand, PET/MAGPP (70/30) of Figure 2(b) shows triple glass transitions. It is thought that the center peak between the glass transition temperatures of PET and MAGPP is due to the reaction of ester groups of MAH sites on MAGPP and PET during melt mixing. The extent of reaction increases with PET composition on comparing PET/MAGPP (70/30) with (90/10). The reaction peaks in MAGPP-rich compositions (above 50) are not observed.

To know the behavior of a new peak in the PET/MAGPP (70/30) blend, the $\tan \delta$ of the blend was measured with reaction time at 280°C . Its result is shown in Figure 3. After 45 min, a new peak disappears, but the glass transition temperatures of the MAGPP-rich and PET-rich phases still remained. In reactive blends, the triple glass transition temperatures are not observed well. Just Porter and colleagues¹⁷ reported the triple glass transition in the polycarbonate and polyarylate system. The polycarbonate/polyarylate blend system goes to one phase with reaction time, resulting in a single glass transition temperature.

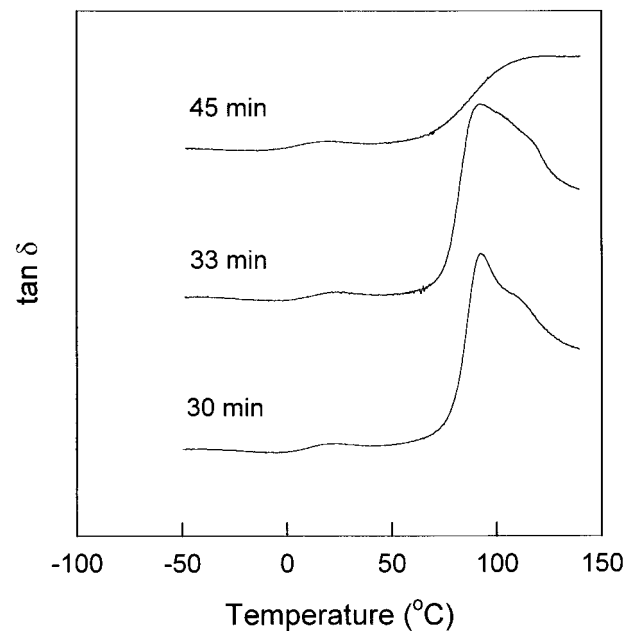


Figure 3 $\tan \delta$ with reaction time for the PET/MAGPP (70/30) blend at 280°C .

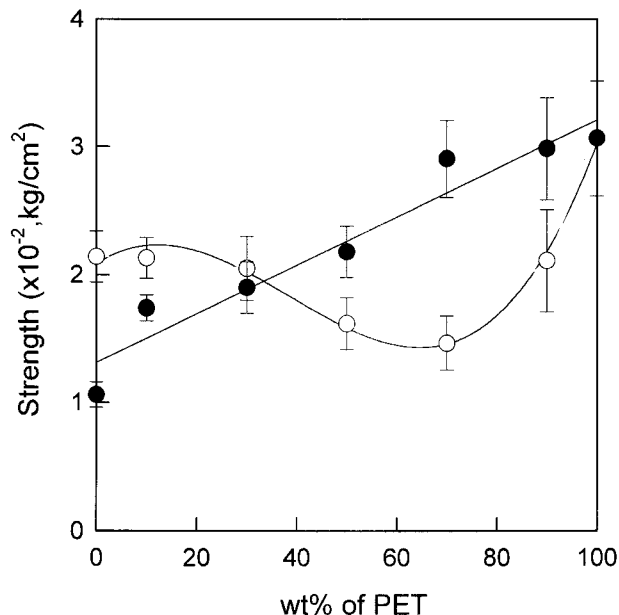


Figure 4 Tensile strength of PET/PP physical blends (○) and PET/MAgPP reactive blends (●) with the content of PET at yield.

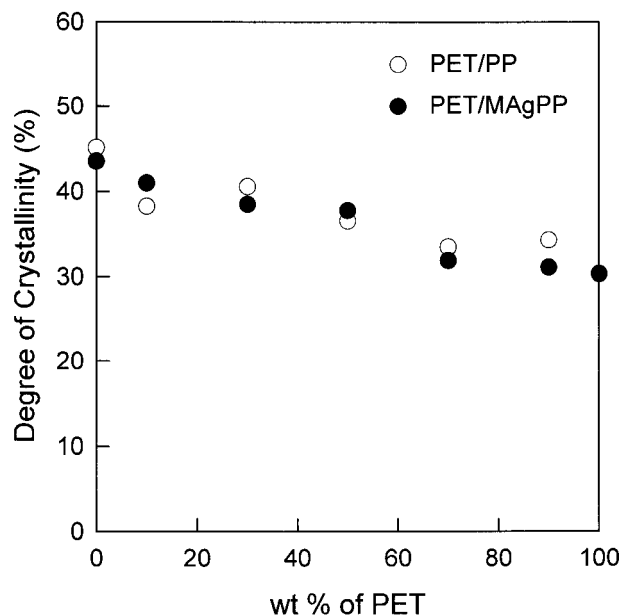


Figure 6 Degree of crystallinity of PET/PP physical blends (○) and PET/MAgPP reactive blends (●) with the content of PET.

In the PET/MAgPP (70/30) blend, however, it still showed two glass transitions after 45 min.

Mechanical Properties

Figure 4 shows the tensile strength at yield of

physical blends and reactive ones. In case of physical blends, the tensile strength with the content of PET exhibits the poor adhesion between PP and PET, whereas the reactive blends shows the good adhesion between them. It re-

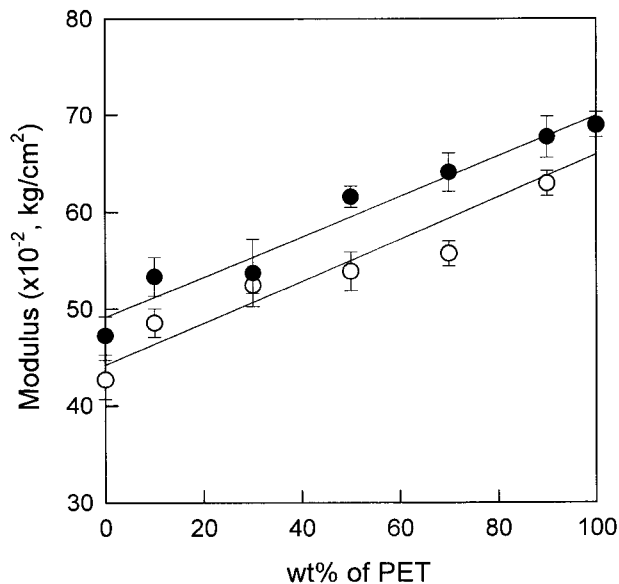


Figure 5 Initial modulus of PET/PP physical blends (○) and PET/MAgPP reactive blends (●) measured at 0.2% elongation with the content of PET.

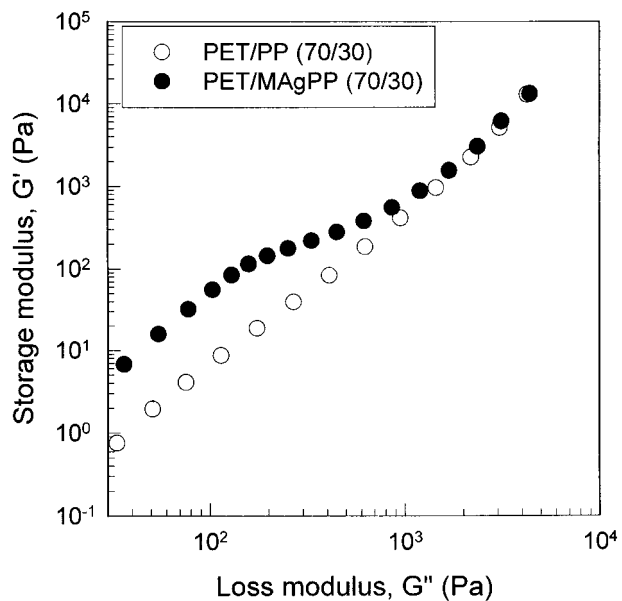


Figure 7 Plots of log storage modulus, G' vs. log loss modulus, G'' of the PET/PP (70/30) blend (○) and the PET/MAgPP (70/30) blend (●) at 280°C.

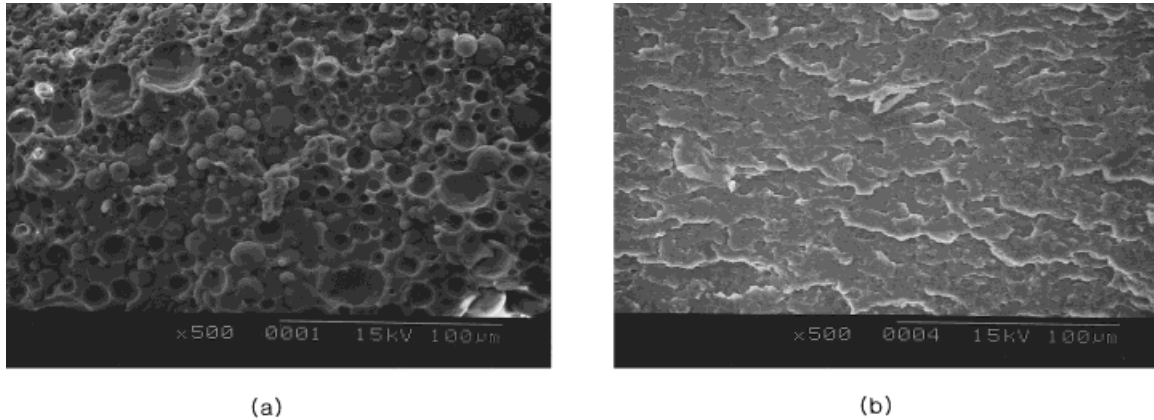


Figure 8 SEM photographs of (a) PET/PP (70/30) and (b) PET/MAGPP (70/30) blends.

sults from the reaction of ester groups in MAH and PET. It can be seen that there is a large difference in values of the tensile strength between pure PP and MAGPP. It resulted from the difference of the molecular weight shown in Table I. The important thing is that the strength value of pure MAGPP can be controlled when it is reacted with PET.

Figure 5 shows the tensile modulus at 0.2% elongation of physical blends and reactive ones. The reactive blends have the higher modulus than that of physical ones with the content of PET. The behaviors of the modulus of two blend systems are similar, which satisfies the mixture rule in the modulus for a multiple system that Nielson¹⁸ proposed.

The mechanical properties strongly depends on the degree of crystallinity. The degree of crystallinity was calculated by the heat of fusion of the PP peak, MAGPP peak, and PET peak of the

blends on the assumption that ΔH of PP¹⁹ and MAGPP was 189 J g^{-1} and ΔH of PET²⁰ was 140 J g^{-1} when they were all in the crystalline state. The result is shown in Figure 6. The difference between the degree of crystallinity of the physical blends and reactive ones was not observed with the blend compositions. It is thought that the difference between the mechanical properties of the blends is due to the reaction of the ester groups of MAH and PET during melt mixing.

Rheological Properties

To confirm the reaction, we measured the complex viscosity. From this data, $\log-G'$ and $\log-G''$ were calculated; results are shown in Figure 7. The open symbol is the PET/PP (70/30) physical blend, and the closed symbol is the PET/MAGPP (70/30) reactive blend. In case of physical blend, there is no interaction between phases at the

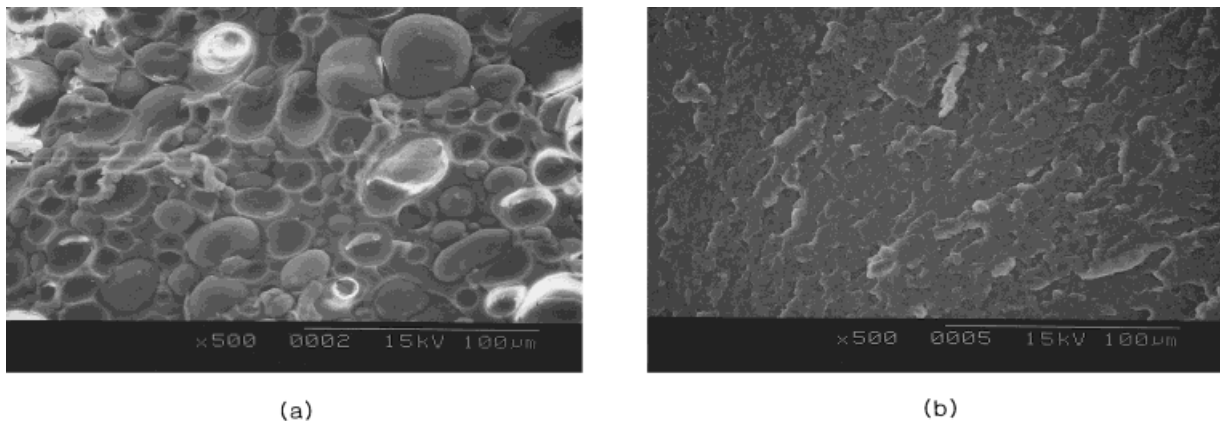


Figure 9 SEM photographs of (a) PET/PP (50/50) and (b) PET/MAGPP (50/50) blends.

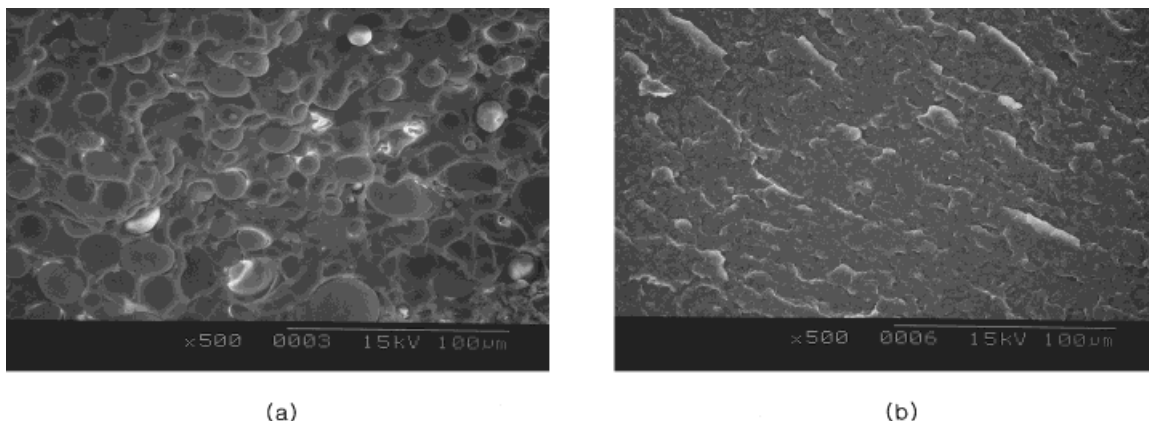


Figure 10 SEM photographs of (a) PET/PP (30/70) and (b) PET/MAGPP (30/70) blends.

interface, indicating the slope of 2. Whereas the plateau region was observed in the reactive blend. It shows the increase of the elastic property due to the interaction at the interface.

Morphology Study

Morphology of the blends as measured under SEM is shown in Figures 8–10. The great differences were observed between PET/PP physical blends and PET/MAGPP reactive blends. Figure 8 shows the dispersibility of the blends, where blend ratios of PET/PP and PET/MAGPP were 70/30; therefore, PP and MAGPP were the dispersed phase and PET was the dispersing medium. The PP phase in physical blend was easily observed. On the other hand, that of reactive blend was hardly distinguishable as the result of the improvement in dispersibility. This clear difference of dispersibility was attributed to the reaction of ester groups of MAH in MAGPP and PET. This behavior was also observed in other blend compositions in Figures 9 and 10. The interesting one is the dispersibility of 70% MAGPP, as well as 50% MAGPP. From the DMA data in Figure 2(b), a new peak was observed in PET-rich compositions, not in MAGPP-rich compositions. However, the improved dispersibility was observed in whole blend compositions of MAGPP and PET from the SEM photograph. As a result, there must be the reaction in whole blend compositions in reactive blends, even though it was not detected in $\tan \delta$ peaks.

CONCLUSIONS

The reactive blend of PET and MAGPP was prepared and compared with the properties of

PET/PP physical blend. From the thermal, morphological, mechanical, and rheological properties, the following observations were made.

1. PET/MAGPP reactive blends, as well as PET/PP physical blends, were immiscible.
2. From the DMA analysis, a new glass transition due to the reaction of the ester groups of PET and MAH sites on MAGPP during melt mixing was observed in PET-rich compositions above 70%.
3. Interaction at the interface of the PET/MAGPP 70/30 blend was confirmed through the rheological properties.
4. New peaks were not observed in MAGPP-rich compositions from DMA, whereas morphology indicated the improvement of the dispersibility in whole blend compositions.
5. The modulus of PET/MAGPP reactive blends was higher than that of PET/PP physical blends with blend compositions. The strength of PET/MAGPP blends showed the good adhesion, compared with PET/PP physical blends.

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