Enrichment of Poly(butyl methacrylate) and Its Graft Copolymer of Polybutadiene on the Surface of Polypropylene Blend

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ABSTRACT: The enrichment and diffusion of poly(butyl methacrylate) (PBMA) and its graft copolymer of polybutadiene on the surface of polypropylene (PP) blends were investigated using attenuated total reflection infrared spectroscopy (ATR-FTIR), contact angle measurements (CDA), and scanning electron microscopy (SEM). It has been found that the selective aggregation of the PBMA and its copolymers on the surface of blends is mainly affected by the content, molecular weight, and the segregated domains. Lower content and higher surface energy die are in favor of the enrichment of additives on the surface of PP. PBMA with higher molecular weight has lower diffusivity and bigger phase domains, which results in its lower enrichment on the surface of PP blend film. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 3049–3057, 2008

Key words: polypropylene; poly(butyl methacrylate); surface enrichment; selective aggregation; polybutadiene-*grafted*-poly(butyl methacrylate)

INTRODUCTION

The surface composition and structure of solid organic polymers influence many of their properties and applications. Examples of technologically important applications affected by a polymer's surface composition include wetting permeability, adhesion, friction, dyeing, and biocompatibility. There is a longstanding need for low-cost, reliable methods for functionalizing polypropylene (PP) surface due to its merit such as inexpensiveness and convenience in processing.[1–3] A process that is selective for the surface modification of a polymer is of particular interest in that it leaves the bulk physical properties of the polymer intact. Much of the focus of the current interest in surface functionalization of polymers aims toward these objectives. Since PP by itself does not have any functional groups other than C—C or C—H bonds, existing derivation techniques are often chemically harsh. In most cases, derivation of the surface involves reactions that produce chain scission. Procedures involving chromic acid etching,[4] sulfonation,[5] and plasma treatments[6] are common synthetic examples. However, migration of functionalized additives dispersed in a host polymer to the host polymer's surface has long been recognized as a potential solution to this problem,[7–9] whereas surface modification with lower surfactants has much limitation such as their poor thermal stability and their easy detraction from host polymers when the products are frictionized or washed with water or organic solvents.[10] Macromolecular surface modifiers can keep their lasting effectiveness, but they usually have relatively lower efficiency if they are used irrelevantly.[11] In the past years, many macromolecular surface modifiers had been used to increase the surface properties of polyethylene.[10,12,13] In our prior researches,[14–16] several surface modifiers for PE were synthesized and used to improve its hydrophilicity. However, little attention is paid to PP surface modification by blending with macromolecular surface modifiers due to the complicated synthesis methods of modifiers.[17–19]

Long time ago, poly(butyl methacrylate) (PBMA) has long been used to increase the surface properties of polyethylene by blending, but the effective concentration was found as high as 30%, which lowered the mechanical and optic performance of PE due to their poor compatibility.[20] To overcome these limitations, polybutadiene-*grafted*-poly(butyl methacrylate) (PB-*g*-PBMA) copolymer was synthesized so that the

surface hydrophilicity of PP can be obtained by blending small amount of copolymers with PP without influencing the bulk properties of the polymer. Another objective of the present study is to investigate the effect of surface modification of PBMA graft copolymers so as to guide the further preparation of PP modifiers. For this purpose, a series of PBMA and PB-g-PBMA with different structures were blended with PP to investigate the effect of structure and contact die on surface enrichment of additives by determining the composition on surface and in bulk by ATR-FTIR and CDA. As a comparison, the enrichment of PBMA is also investigated.

EXPERIMENTAL

Materials

Polypropylene is supplied by Bombay/India Reliance Co., H030SG, MI = 3.5. Hydroxyl-terminated poly(butyl methylacrylate) is synthesized by chain-transfer free radical polymerization in xylene at 60°C; its number-average molecular weights are 1000, 2200, 8400, and 15,500.[21] Polybutadiene is obtained from Beijing (China) Yanshan Petrochemical; its number-average molecular weight is 1000. Maleated polybutadiene was synthesized by grafting maleic anhydride into polybutadiene at 180°C; the content of maleic anhydride in the grafted polymer is 3.5%. Polybutadiene-graft-poly (butyl methacrylate) is synthesized by coupling of maleated polybutadiene with hydroxyl-terminated poly(butyl methacrylate) in xylene at 140°C.[22] Other reagent-grade chemicals such as xylene and ethanol were used as received without further purification.

General procedure for blend film casting

PP and macromolecular surface modifiers were blended in xylene by heating the mixture to 140°C for 30 min. After distilled off xylene in a vacuum oven, the films were obtained by melt-casting in a stainless steel mold at 190°C. The thickness of films were about 80–100 μm.

Determination of ATR-FTIR and IR

The composition of the blending film surface was investigated by ATR-FTIR using a Nicolet 210 FTIR spectrometer with a variable-angle multiple-reflection ATR accessory, which allows the external angles of incidence to be continuously varied from 30 to 70°. The ATR internal reflection elements used was a Zn-Se crystal. Typical ATR spectra were obtained at a crystal with 45° over a range of 250 to 4000 cm^{-1}. IR was also recorded using a Nicolet 210 FTIR spectrometer with a scan number of 32.

Contact angle measurements

Contact angles of the film surface were determined using a Dataphysics OCA20 contact angle goniometer at ambient temperature. All measurements were performed using the sessile drop method and made with drops of 1 μL distilled water after about 15 s. The reported values were the average of eight measurements at various places on the same film sample. The values of contact angle measurements varied by ±3°.

Scanning electron microscopy

JSM-6330F was used to study the appearance of modified PP after the modifiers of film were eroded by a mixture of potassium dichromate and concentrated sulfuric acid.

Solvent-resistance experiment

The modified films were dipped in ethanol for an enactment time at room temperature. The composition of modifier on the surface of films was determined by ATR-FTIR after removing off the solvent.

Determination of diffusion of additives in PP blends film

The blend films were annealed in enactment temperature in air for an enactment time and cooled rapidly with liquid nitrogen. Then the surface contents of modifier were determined rapidly by ATR-FTIR.

RESULTS AND DISCUSSION

To evaluate the surface enrichment of the modifiers added, both ATR-FTIR and FTIR measurements were used to obtain quantitative information about the composition on surface and in bulk of blends, respectively. To obtain reliable results and eliminate the effect of contact between the polymer film and the internal reflection element,[10] the technique of "band ratioing" was developed and it was testified that the error of the peak area ratios of interest is 5% or below. Infrared peak area ratios of 1735 cm^{-1} of PBMA to 1103 cm^{-1} of PP were therefore used to determine PP surface composition of the blends as follows:

$$R = \frac{A_{1735}}{A_{1103} + A_{1735}} \quad (1)$$

Effect of amount of PBMA and contact die on surface enrichment

Loading and contact interface are the most important factors in effecting the surface enrichment of macromolecular modifiers. The former deals with the
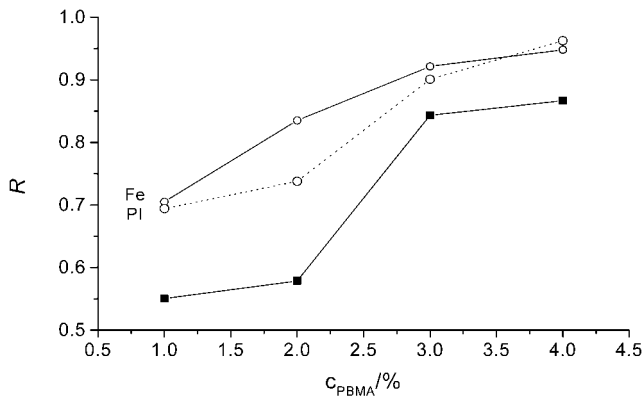
Figure 1 Peak area ratios at different contents of PBMA$_{2200}$ in PP blend. ◯: surface; ■: bulk.

phase domains of modifiers in blends, which influences the diffusion kinetics of modifiers. The later relates to surface enrichment thermodynamics, involving the driving force for the modifiers to migrate onto the surface. In this study, PBMA with molecular weights of 1000, 2200, 8400, and 15,500 were chosen to investigate the effect of loading in blend and contact interface on their surface enrichment. The typical results were shown in Figures 1 and 2. The depth of penetration of the excursion wave in ATR spectra in Figure 2 is given by eq. (2)[23]

$$d_p = \frac{\lambda}{2\pi n_1 \left[\sin^2 \theta - (n_2/n_1)^2\right]^{\frac{1}{2}}} \quad (2)$$

where λ is the wavelength of the radiation in microns; d_p is the depth of penetration of the IR radiation; n_1 and n_2 are the refractive of the ATR crystal and polymer film, respectively; and θ is the angle of incidence
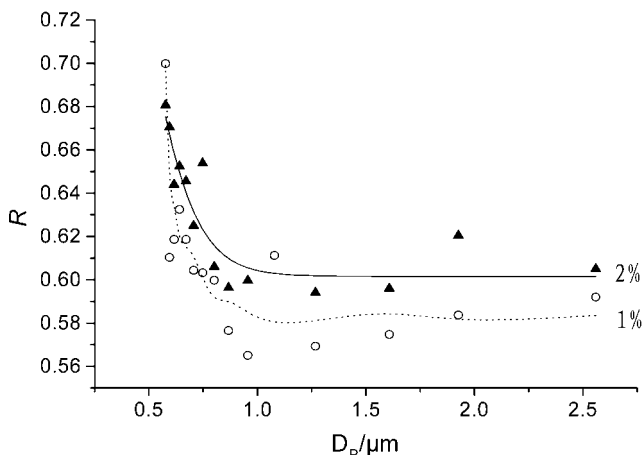
of the IR beam on the ATR crystal. On the basis of this equation, the depths of penetration for different angles and for the wavelengths of interest were calculated.

The obvious surface enrichments of PBMA with different molecular weights can be observed at lower loadings in blends, especially for PBMA$_{1000}$ and PBMA$_{2200}$, either the contact interface of films in thermal casting was steel or polyimide. This can be further confirmed by the depth gradient of PBMA$_{1000}$ shown in Figure 2. The peak area ratios of PBMA$_{1000}$/PP did increase as the depth of analysis decreased. Most of PBMA$_{1000}$ was distributed in the outer of 1.0 μm and that the degrees surface excess of films formed in steel were more than those casting in polyimide. At very low concentrations, i.e., below the saturation concentration, the additive migrates to the surface of the blend if that is accompanied by a decrease of the surface free energy. On higher surface loadings, the bulk concentration may exceed saturation and phase separation in the bulk follows. The surface loading then remains constant up to higher concentrations of the additive.[10]

Effect of molecular weight of PBMA on surface enrichment

Molecular weight is one of the most important parameters of polymers. To intuitively express the effect of molecular weight of PBMA on surface enrichment, a degree of surface excess of PBMA was defined as following expression:

$$\Delta R = \frac{R_S - R_V}{R_V} \times 100\% \quad (3)$$

where R_S and R_V were the peak area ratios on surface and in bulk, respectively.

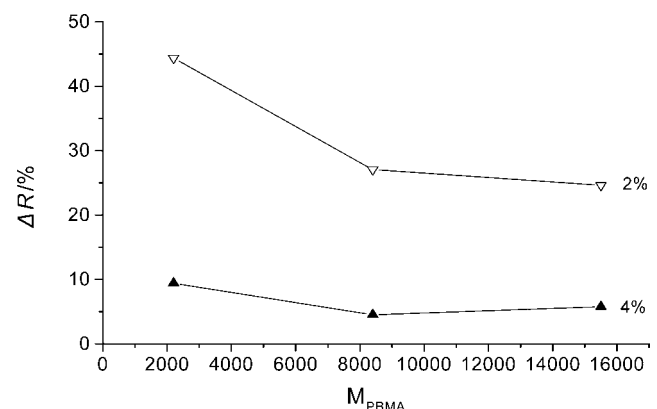The results were shown in Figure 3. The surface enrichment of PBMA was observed even though the

Figure 2 Surface concentration gradient of PBMA$_{1000}$ in PBMA$_{1000}$/PP blend formed under contacting with polyimide.

Figure 3 The influence of molecular weight of PBMA on surface excessive degree of PBMA in PBMA/PP blend film formed under contacting with steel.
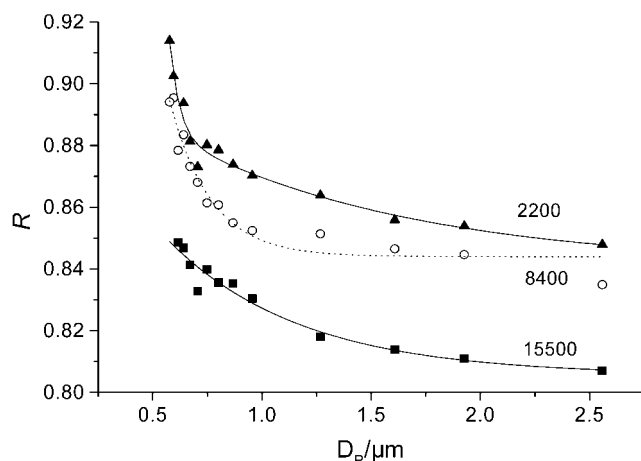
Figure 4 Surface concentration gradient of PBMA with different molecular weights in 3% PBMA/PP blend film formed under contacting with PI.

molecular weight of PBMA was 15,500 and the loading of PBMA in blend was 4%. Another result was that the effect of molecular weight of PBMA on surface enrichment was more obvious at lower loading of PBMA in blend. However, if polyimide (PI) was selected as the interface of thermal molding, the corresponding degrees of surface excess were less than those of film formed by contacting with steel. The surface excess of $PBMA_{2200}$ was observed in the loadings of 1–4% PBMA in blends, while the excess of $PBMA_{8400}$ appears only loadings below 2%. Since PBMA is not compatible with PP, the phase separation must occur together with the surface enrichment and diffusion of PBMA.[24] Smaller phase domains of PBMA can be observed in the blend film of PBMA with smaller molecular weight. Therefore, higher selectivity of PBMA with smaller molecular weight can be expected. Compared with smaller molecular weight, since there is stronger interaction among molecules of PBMA with higher molecular weight, it can be observed that the bulk phase separation occurs at lower concentrations at higher molecular weight of the additive; a concentration of 2–3% seems to be well above saturation for $PBMA_{8400}$ and $PBMA_{15,500}$ and very little change in the surface excess would thus be observed.

The depth gradient of PBMA in Figure 4 also confirmed the above results. The concentration gradient of $PBMA_{2200}$ was more obvious than that of $PBMA_{8400}$ and $PBMA_{15,500}$ in 3% PBMA/PP blend films formed under contact with polyimide. Higher contents of PBMA were observed on the surface containing PBMA with lower molecular weight. This implied that more $PBMA_{2200}$ is enriched on the surface and PBMA with lower molecular weight has higher surface selectivity. The results may owe to the bigger phase domains of PBMA with higher molecular weight, which results in higher resistance for

PBMA to migrate to the surface and lower their surface enrichment on PP.

Enrichment of PB-g-PBMA on the surface of PP

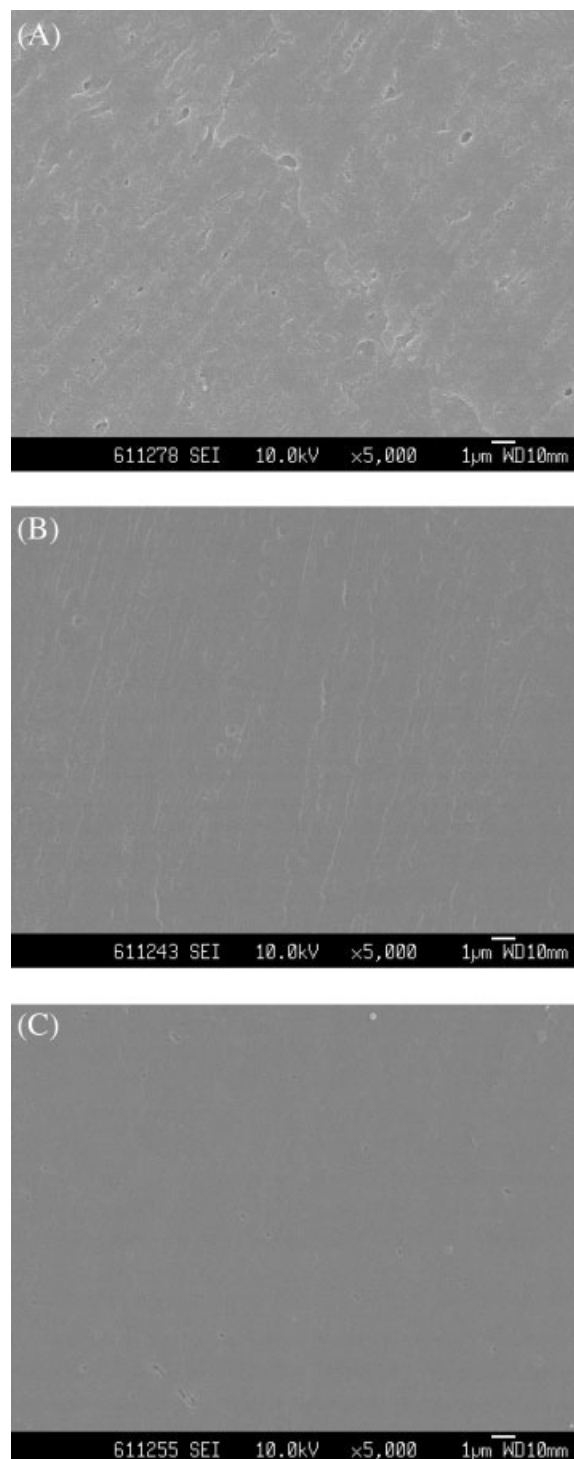In our previous research on synthesis and characterization of PB-g-PBMA, we have cursorily confirmed

Figure 5 SEM micrographs of PB-g-PBMA in 3% PB-g-PBMA/PP blend film. Contact die: (A) steel, (B) polyimide, (C) PTFE.
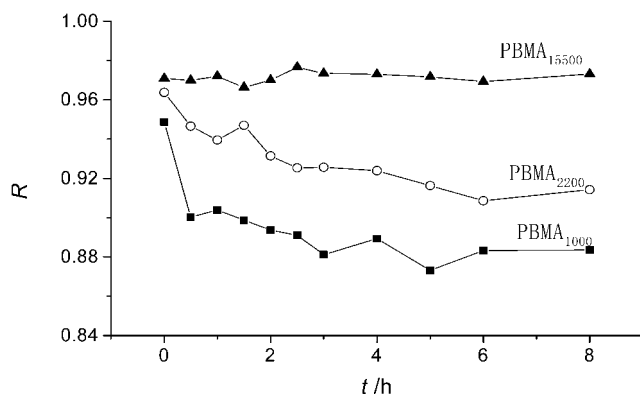
Figure 6 Diffusion of PBMA with different molecular weights in PP blends at 20°C.

that PB-*g*-PBMA can preferentially diffuse to the surface and be used as a macromolecular surface modifier of PP, especially at the lower loadings.[22] In this study, three different contact dies were selected to investigate the effect of contact interface on the surface enrichment of PB-*g*-PBMA. The SEM micrographs of 3% PB-*g*-PBMA/PP films formed under three different dies were shown in Figure 5. Large amount of PB-*g*-PBMA were distributed on the surface by melt-casting under contact with steel. In contrast, only a little of PB-*g*-PBMA is enriched on the interface of PP and poly(tetrafluoroethylene) (PTFE). This implied that high interface energy is in favor of the high energy component to migrate to the surface. Steel and PTFE are the representatives of high and low surface energy interface, respectively. PB-*g*-PBMA, the relative higher surface energy component, would be induced to diffuse to the high energy steel interface, or in contrast, PP will migrate to the interface of PP and PTFE so that the system can be in lowest energy. The surface energy of polyimide lies between steel and PTFE; so, the contents of PB-*g*-PBMA on the surface cast contacting with polyimide is higher than that formed under PTFE, but lower than that on steel interface.

Diffusion of PBMA and PB-*g*-PBMA in PP

Diffusion and phase separation often occur in multicomponent system and often greatly influence the surface properties of materials. Surface enrichment of modifier in host polymer is in nature of the phase-separated and diffusion of modifier onto the surface, therefore, diffusivity of modifier in host polymer is essential for understanding the surface enrichment of modifiers on the material.

To avoid the distortion of blend films, temperature of 20°C was chosen to investigate the diffusion of PBMA in PP. Although the temperature was lower than that in molding at temperature of over the

melting point of PP, which was the temperature that the modifier actually diffused to the surface, the diffusivity of PBMA and PB-*g*-PBMA at this temperature can be also used to effectively evaluate their surface selective enrichment.

The influences of diffusion time on peak area ratios of PBMA with different molecular weights at 20°C were shown in Figure 6. From the peak area ratios, the nonlinear regression curve of $PBMA_{1000}$ and $PBMA_{2200}$ can be obtained according to eq. (4). The results were shown in Figure 7. The diffusion coefficients of $PBMA_{1000}$ and $PBMA_{2200}$ at 20°C can be calculated by constants of nonlinear regression a according to the following expression[25]:

$$\left(\frac{1}{1-\frac{1}{R_t}}\right)\left(1-\frac{1}{R_\infty}\right) = \frac{1 - 1.273\exp(at)}{1 - 1.273\exp(bt)} + c \quad (4)$$

where R_t and R_∞ are the peak area ratios at time of t and diffusion equilibrium; b and c are the constants of regression equation; a is the constant relating to D_1, the diffusion coefficient of PBMA, $a = -\frac{D_1\pi^2}{4L^2}$, where L is the half thickness of film. The diffusion coefficients of PBMA at 20°C were listed in Table I.

Because of the bigger phase domains in PP, the peak area ratios of $PBMA_{15,500}$ were unchanged with the annealing time, suggesting that no diffusion of $PBMA_{15,500}$ occurred at 20°C in this situation. However, because of the inducing of low surface energy air, the peak area ratios of $PBMA_{1000}$ and $PBMA_{2200}$ on the surface decreased with the annealing time, especially in $PBMA_{1000}$/PP blend, implying that the migration of $PBMA_{1000}$ and $PBMA_{2200}$ to the inner of films happened. The results indicated that smaller molecular weight favored to form smaller phase domains of PBMA in PP, which reduced the diffusion resistance of PBMA in PP. This is also confirmed by their diffusion coefficients listed in Table
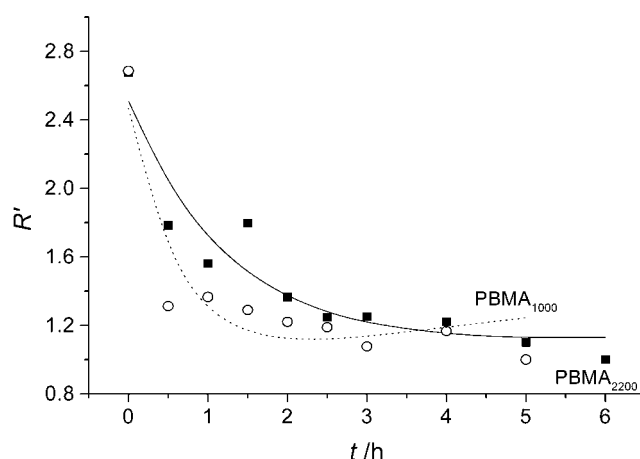

Figure 7 Fitting curves of PBMA with different molecular weights in PP blends at 20°C.

TABLE I
Regression Coefficients of the Diffusion Function in PBMA/PP Blends at 20°C

Sample	Constants of Regression			L (μm)	D_1 ($\times 10^{-11}$ cm^2 s^{-1})	D_2 ($\times 10^{-11}$ cm^2 s^{-1})
	a	B	c			
PBMA$_{1000}$	−0.37062	0.25634	1.46759	12.5	6.53	−4.51
PBMA$_{2200}$	−0.16238	0.1035	1.50901	10	1.83	−1.17

I. The modifiers used were oligomers with molecular weights of 1000 and 2200. High solubility and small phase domains in PP can be expected, which resulted in rather high diffusivity for the oligomer in PP. The diffusion coefficient of PBMA$_{1000}$ is about four times bigger than that of PBMA$_{2200}$, indicating that PBMA with lower molecular weight has a bigger diffusivity in PP.

In conclusion, the effect of molecular weight of PBMA on its surface modification has two opposite results due to its diffusion. Fast diffusion of additives with smaller molecular weight can drive more additives to enrichment on the surface in the process of thermal molding before congealed, which is one

of the important factors for high efficiency of small molecule additives, but it may also result in the fast migration back of the functional groups or chain blocks when the modified material is contacted with improper interface.

The further confirmation for the effect of molecular weight on phase domains and diffusion is the SEM micrograph. The SEM micrographs of PBMA$_{1000}$ and PBMA$_{2200}$ were shown in Figure 8. Because of the strong interactions among molecules of PBMA with higher molecular weight, bigger phase domains of PBMA$_{2200}$ are formed in PP, which results in bigger diffusion resistance and lower the surface enrichment of PBMA on PP as described before.

Temperature is the important factor for effecting the diffusion of additives. The diffusion fitting curves of PB-g-PBMA with annealing time at different temperatures were shown in Figure 9. The peak area ratios of PB-g-PBMA reduced with increasing annealing time, implying that PB-g-PBMA located on the surface migrated to the inner of films due to the induction of air. Another phenomenon we can observe was that the annealing temperature had a great effect on the diffusion of PB-g-PBMA in PP. The great changes of peak area ratios at higher temperature indicated that the diffusion velocity of PB-g-PBMA in PP increased with increasing annealing temperature. This can be further confirmed by the diffusion coefficients listed in Table II. The diffusion coefficient of PBMA at higher temperature is obviously bigger than that at lower annealing tempera-
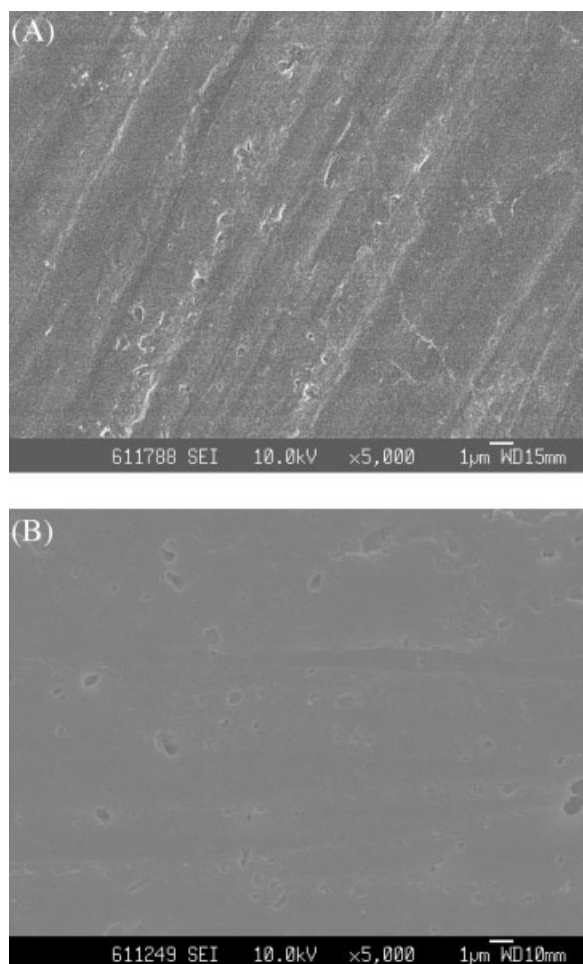

Figure 8 SEM micrographs of PBMA in 3% PBMA/PP blend film. Molecular weight of PBMA: (A) 1000, (B) 2200.
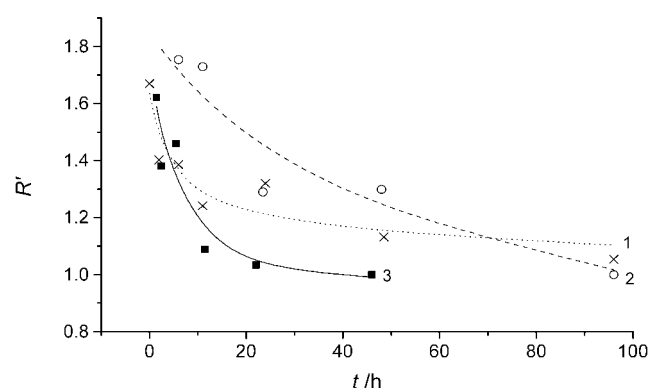

Figure 9 Diffusion fitting of PB-g-PBMA in PP blends at different temperatures. 1: 5°C, 2: 20°C, 3: 68°C.

TABLE II
Nonlinear Regression Coefficients of the Diffusion Function in PB-g-PBMA/PP Blends at Different Temperatures

T (°C)	Constants of Regression			L (μm)	D_1 ($\times 10^{-11}$ cm^2 s^{-1})	D_2 ($\times 10^{-11}$ cm^2 s^{-1})
	a	b	c			
5	0.0062	0.0099	0.5018	20.5	−0.292	−0.466
20	0.04594	0.01111	0.95545	18	−1.68	−0.406
68	0.16106	0.31289	0.9902	14.5	−3.82	−7.41

ture. Therefore, the modified materials with PB-g-PBMA should not be deposited in air for a long time; otherwise, the modified effect may reduce.

SEM micrographs shown in Figure 10 revealed another disadvantageous influence of annealing. After annealing at 68°C, the phase domains of PB-g-PBMA on the surface increased obviously as a result of phase amalgamation; their distributions on the surface also were not uniform, which may debase the adhesive intensity of coating if the modified material is doped.
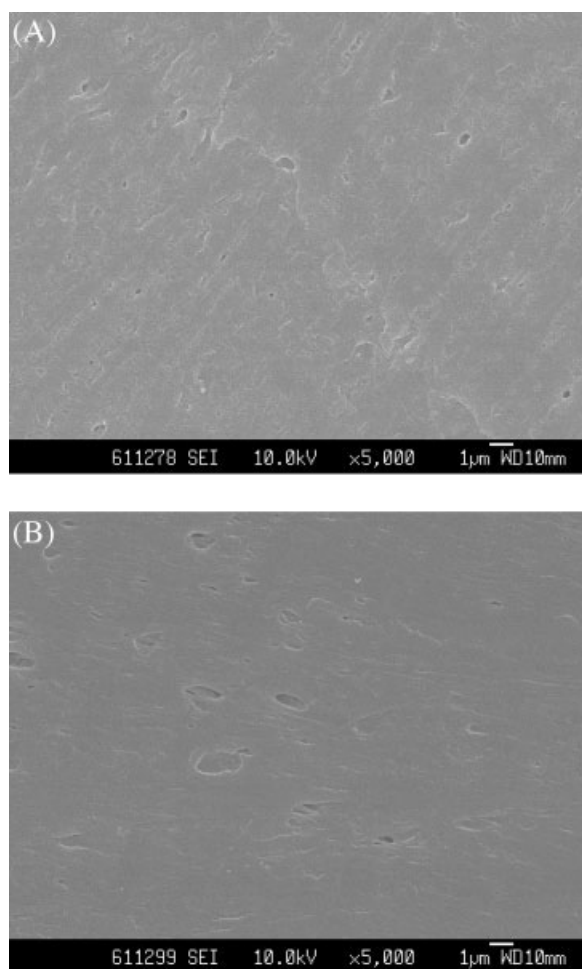

Figure 10 SEM micrographs of 3% PB-g-PBMA/PP before and after annealing at 68°C. (A) Before heat treatment; (B) after heat treatment at 68°C in air.

Effect of PB-g-PBMA on contact angle of PB-g-PBMA/PP blends films

Water contact angles have been shown to be very sensitive to the nature of the functional groups at a few angstroms of the upper layer on the surface for functionalized polymers. Measurement of water contact angles gives a good estimate of the polarity and the mobility of the polymer chains present in the outmost atomic layers of the surface.[26] In this study, PB-g-PBMA was blended with PP and their water contact angles were measured by contact angle goniometer. The results were shown in Table III. The contact angles for the surface of blends were uniformly much less than that found for the surface of pure polypropylene. This reflected a preferential migration of modifier blocks to the contact-angle interface when the blend film was formed on steel. Steel is a high-energy substrate; so PB-g-PBMA is expected to be contacted with steel and polypropylene migrates to the inside of film.

The data in Table III also showed the influence of modifiers' contents on the contact angles of film prepared under steel. The contact angles increased with increasing the content of PB-g-PBMA, suggesting that the content of PB-g-PBMA decreases with increasing amount of modifier in blend. This was in opposition to that determined by ATR-FTIR. The difference between ATR-FTIR and contact angle is due to the various-depth regimes attended for contact angle and ATR-FTIR analysis techniques. In general, ATR-FTIR is much less surface-selective. Depending on the wavelength of the incident radiation and the reflection crystal, the layer of ATR-FTIR involved is about 1.2 μm.[25] Contact angle responds to functional groups in the outer 5 Å of the polymer.

In conclusion, PB-g-PBMA can be enriched on the surface of PP and lower the contact angle of modi-

TABLE III
Influence of Content of Modifier on Contact Angle of Modifier/PP Blend Film

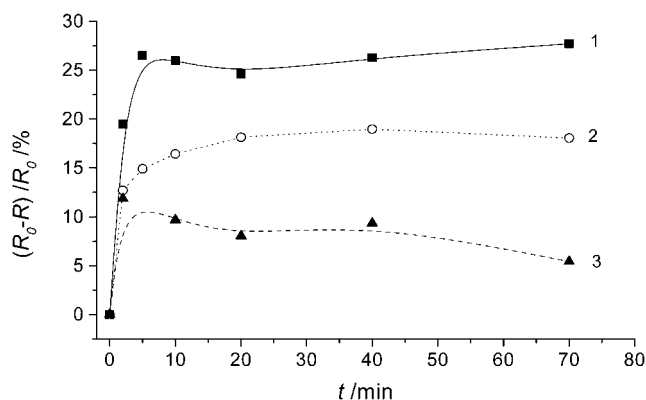| Modifiers	PB-g-PBMA
0	119.8
1%	92.3
2%	94.5
3%	98.7
4%	103.1

Figure 11 Losses of modifiers on surface with the immersion time in ethanol. 1: $PBMA_{2200}$, 2: $PBMA_{15,500}$, 3: PB-g-PBMA.

fied material in a certain extent. Although the degree is not so much as that of representative polar oligomers such as poly(ethylene glycol), the polar surface of modified PP can help us to extend its uses in some fields and increase the interface intensity of multilayer material.

Evaluation of solvent-resistance of modified PP

The difference between blend surface modification and chemical graft modification is that the modifier from the former has no any chemical bond linking to the host polymer, which means that the modifier is relatively easy to be detracted from the host polymer if the structure of modifier is designed irrelevantly. Considering that the modified PP may often be in contact with water or other organic solvents, herein we observed the solvent-resistance of modified materials by dipping the functionalization PP into ethanol for an enactment time and determining the composition by ATR-FTIR.

The losses of peak area ratio with immersion time were shown in Figure 11. Because of the weak interaction between PBMA and host PP, the $PBMA_{2200}$ content on surface was dropped obviously at the losses of 28% within the first 5 min in $PBMA_{2200}$-modified film by strong dissolving of ethanol. However, the losses of $PBMA_{15,500}$ were relatively slower than that of $PBMA_{2200}$. The maximum loss of $PBMA_{15,500}$ occurred at 20 min for the loss of 18%, suggesting that PBMA with higher molecular weight is of better solvent-resistance, which also means that there are stronger interactions between PP and PBMA with higher molecular weight. With further increasing the immersion time, the losses of PBMA in the surface were unchanged. The contents of PB-g-PBMA on the surface declined fleetly after immersing for 2 min in ethanol, implying that there are large numbers of PB-g-PBMA enriching on the surface of PP and their interaction with PP is relatively

infirm. After that, the surface contents of PB-g-PBMA increased slightly with increasing immersion time. However, the losses of PB-g-PBMA are kept below 10%, indicating that the modified material has stronger ethanol-resistance.

The result was rationalized to the balance between diffusion of modifiers and extraction of ethanol. Ethanol is a representative polar organic solvent. It can dissolve PBMA if the molecular weight of PBMA is rather small. When it contacts with modified material, two different effects can be observed. The first is the extraction, which can lower the surface content of modifier if the modifier cannot incorporate to the host polymer firmly. The second is induction, which can induce the modifiers to migrate from the inside of film to the surface and increase the surface enrichment of modifier. The modifier used was an oligomer with molecular weight of 1000 and 2200. High solubility and small phase domains in PP can be expected, which resulted in rather high diffusivity for this oligomer in PP. However, because of the weak interaction between PBMA and PP in the blend film, the extraction of ethanol is dominant; so the decreasing of PBMA on surface is mainly observed. Although the relatively strong interaction between PB-g-PBMA and PP can be expected compared with PBMA, which can avoid the dissolution of PB-g-PBMA by ethanol, this strong interaction also hinders the modifier located in sublayer to migrate to the surface and makes up the losses.

CONCLUSION

The results of ATR-FTIR and contact angle have confirmed that the PBMA and its graft copolymers can preferably diffuse to the surface of blends and effectively increase the hydrophilicity of PP. The surface enrichment of PBMA and its copolymers on PP blend film is obviously influenced by the molecular weight, content of additives, and the contact interface. Lower content and higher surface energy die are in favor of the PBMA and its graft copolymers to enrich on the PP surface. Diffusion experiments and SEM also indicate that PBMA with higher molecular weight has lower diffusion velocity and bigger phase domains, which results in its lower enrichment on the surface of PP blend film. The graft copolymers of PBMA have stronger solvent-resistance than PBMA.

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