Surface enrichment of polypropylene-graft-poly(methyl methacrylate) on polypropylene

Hanjia J. Chen · Yafei F. Zhu · Yi Zhang · Jiarui R. Xu

Abstract To overcome disadvantage of polypropylene induced by its low surface energy, poly(methyl methacrylate) was grafted onto polypropylene and entrapped into polypropylene as macromolecular surface modifier. The effects of copolymer structures, contact dies and content of modifiers on their surface enrichment were studied by attenuated total reflection infrared spectroscopy (ATR-FTIR), contact angle measurements (CDA) and scanning electron microscopy (SEM). Lower content and higher surface energy dies were in favor of the copolymer to enrich on the PP surface. PPw-g-PMMA with low PMMA graft density, long length of PMMA was distributed in PP with smaller phase domains and concentration gradient, especially at lower loadings in blends, which favored its selective enrichment on the surface of PP. The modified material exhibited excellent solvent-resistance. The results indicated that PPw-g-PMMA can transfer to the surface of blends and effectively increase the hydrophilicity of PP, which offer a convenient technique to functionalize the surface of polymers with lasting-effectiveness compared with modification by homopolymers.

H. J. Chen · Y. Zhang · J. R. Xu (✉)
School of chemistry and chemical Engineering,
Key Laboratory for Polymeric Composite and Functionality
Materials of Education, Materials Science Institute,
Sun Yat-sen University,
Guangzhou 510275, People's Republic of China
e-mail: xjr@mail.sysu.edu.cn

H. J. Chen
School of Science, Shantou University,
Shantou 515063, People's Republic of China

Y. F. Zhu
Instrument and Testing Center, Sun Yat-sen University,
Guangzhou 510275, People's Republic of China

Introduction

The surface properties of polymeric material are important in numerous applications, such as adhesives, coatings and lubricants. It is of longstanding interest to find low-cost and reliable methods to make polypropylene (PP) surface functionalization. Blending with surface modifier is widely recognized as a potential technique to overcome disadvantage of polypropylene's low surface energy and improved its properties of dyeing, adhering, coating, or compatibility with polar polymers [1–3]. Macromolecular surface modifiers can anchor to host polymers by strong intermolecular interaction and therefore avoid to be detracted from host polymers when the products were frictionized or washed with water and organic solvents and keep their lasting effectiveness [4]. Macromolecular surface modifiers are stable and don't decompose when thermal-molded with PP, which overcomes poor thermostability of small surfactants. However, the structure of macromolecular surface modifiers should be designed carefully so as not to hinder the surface modifier to preferred-diffuse onto the surface and lower the efficiency of surface modifiers [5–7].

Poly(methyl methacrylate) has been used to blend with PP so as to increase polyolefin's surface polarity long time ago. But the effective concentration was found as high as 30%, which lowered the mechanics and optic performance of PP due to their poor compatibility [13]. Little attention has been paid to PP surface modification by blending with macromolecular surface modifiers due to the difficulty of preparing the block or graft copolymer of PP. Bergbreiter

[8] has used boron-promoted radical polymerization and a vinyl-terminated polypropylene oligomer to synthesize block cooligomers of propylene and tert-butyl acrylate to functionalize the surface of polypropylene, but the procedure included the preparation of unsaturated-terminated polypropylene and its hydroboration or oxidation, which was not suitable for large-scaled production. In our previous investigations [9–12], several surface modifiers for PP and PE were synthesized and used to improve their hydrophilicity. We have demonstrated that the initial degradation temperatures of PPw-g-PMMA all exceed over 250 °C, higher than usual temperatures for processing PP, indicating that the copolymers would be suitable for the surface modification of PP in terms of the thermal stability [14]. We also have revealed that the copolymers show a melting peak similar to that reported for PP. It is important that the surface modifier could form similar crystalline structure with the host polymer so that the surface modifier can incorporate firmly with the host polymer.

In this study, a series of PP-g-PMMA with different structures were used as macromolecular surface modifiers and 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 and guide the further preparation of macromolecular surface modifiers. By controlling the microstructure of the oligomer, polypropylene compatibility and the experimental details of the entrapment process, we could achieve modest to good surface selectivity and left the bulk physical properties of the polymer intact due to the enrichment of major portion of the additive on the surface, which was of particular interest in surface modification of polymer.

Experimental

Materials

Polypropylene (H030SG, MI=3.5) was supplied by India Reliance Co. Polypropylene grafted poly(methyl methacrylate) was prepared by coupling polypropylene-maleic anhydride copolymer with hydroxyl-terminated poly(methyl methacrylate) in xylene according to the literature [14]. Other reagent-graded chemicals such as xylene and acetone were used as commercially supplied 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 cast in a stainless steel mold at 190 °C. The thickness of films were about 80~100 μm.

Determination of ATR-FTIR and IR

The surface composition of the blending film was investigated by attenuated total reflection infrared spectroscopy (ATR-FTIR) using a Nicolet 210 FTIR spectrometer with a variable-angle multiple-reflection ATR accessory, which allowed the external angles of incidence to be continuously varied from 30 to 70°. The ATR internal reflection element used was a Zn–Se crystal. Typical ATR spectra were obtained at a crystal with 45° over a range of 250 cm^{-1} to 4,000 cm^{-1}. IR spectra were 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 Inc.OCA-20 contact angle goniometer at ambient temperature. All measurements were preformed 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 (SEM) observations

A JSM-6330F SEM 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 experiments

The modified films were dipped in ethanol for an enactment time, then remove off the solvent and determine the composition of modifier on the surface of film by ATR-FTIR.

Results and discussion

Attenuated total reflectance infrared spectroscopy has long been used for qualitative analysis of polymer surface composition. The major problem faced in quantitative analysis using this spectroscopy is the necessity of achieving good contact between the polymer film and the internal reflection element. This is an essential factor in obtaining reproducible results [15]. In order to minimize the impact of this intrinsic problem in measurement of absolute absorbance, the technique of "band ratioing" was developed and it has been testified that the error of the peak area ratios of interest can be reduce 5% or below.

To evaluate the surface enrichment of the added modifiers, both ATR-FTIR and FTIR measurements were used to obtain the quantitative information of the composition on the surface and in bulk, respectively. One of the representative ATR spectra of PPw-g-PMMA/PP blend was shown in Fig. 1.

The bands at about 1,103 cm^{-1} of PP and 1,735 cm^{-1} of PPw-g-PMMA were assigned to C–C groups in PP and C=O group in PPw-g-PMMA, respectively. Although the band at 1,103 cm^{-1} also appeared in PPw-g-PMMA due to the containing of PP main chain, compared with that of 1,735 cm^{-1}, the peak area of 1,103 cm^{-1} can be neglected. Therefore infrared peak area ratio of 1,735 cm^{-1} of PPw-g-PMMA and 1,103 cm^{-1} of PP were defined and used to determine PP surface composition of the blends as followed:

$$R = \frac{A_{1,735}}{A_{1,103} + A_{1,735}} \qquad (1)$$

A higher value of R reveals higher concentration of PPw-g-PMMA in the surface measurements.

Effect of additive concentration on surface enrichment

As having been proved by many researchers, solvents used in cast films have effect on the surface properties of polymers or blends. In order to avoid this effect of solvent, the blend films containing oligomers with PMMA content of 17.5% (molecular weight of PPw and PMMA were 5,000 and 4,300 respectively) at different loadings were prepared by melt-casting. Plots of the surface and bulk contents of PPw-g-PMMA of cast films to loadings were shown in Fig. 2. The surface enrichments of PPw-g-PMMA were found in the blend films at lower 3% loadings, especially at lower loadings of copolymer. With increasing the contents of PPw-g-PMMA in blends, the phase domains of additives increased, which hindered the migration of PPw-g-PMMA
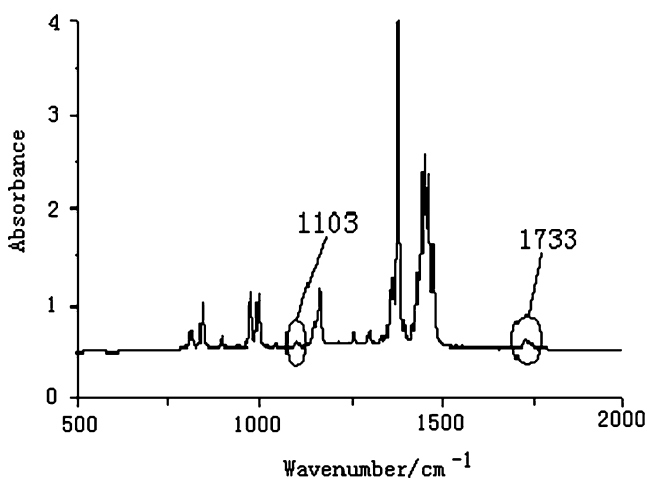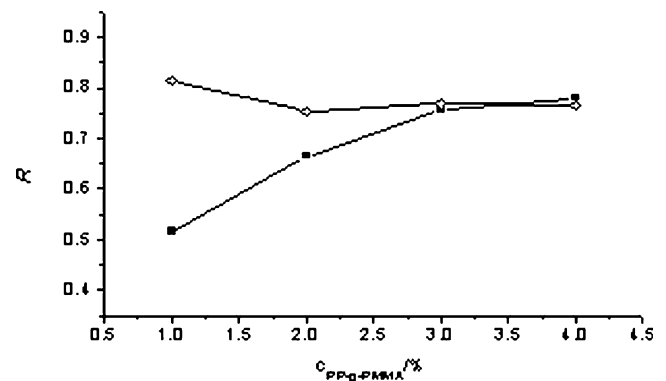

Fig. 2 The peak area ratio at different contents of PPw-g-PMMA in PP blends. *Open circle* Surface; *filled square* bulk

to segregate on the steel interface. Above a certain concentration(3.0%), PMMA chain would phase separate into the bulk because the surface volume was limited. A more normal distribution due to the phase segregation of PPw-g-PMMA throughout the bulk polymer was obtained. This normal distribution might take the form of PMMA aggregates throughout the film. Below this concentration, the surface volume can accommodate essentially all of the graft oligomer present. Therefore the surface selectivity of PPw-g-PMMA can be observed. Similar studies of films containing PPw-g-PMMA with different structures such as PMMA molecular weight of 1,000 and 7,000 also showed that the contents of PPw-g-PMMA at the ATR-FTIR surface was also increased relative to what would have been expected at lower loadings of PPw-g-PMMA in blends.

The surface enrichment of PPw-g-PMMA was also confirmed by its surface depth gradient. A depth distribution of PPw-g-PMMA on the surface of cast films containing oligomer with 58.6% PMMA content and PMMA molecular weight 7,000 was shown in Fig. 3. Where the depth of penetration of the excursion wave in ATR spectra is given by Eq. 2 [4].

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

Fig. 1 Representative ATR spectroscopy of PPw-g-PMMA/PP blend
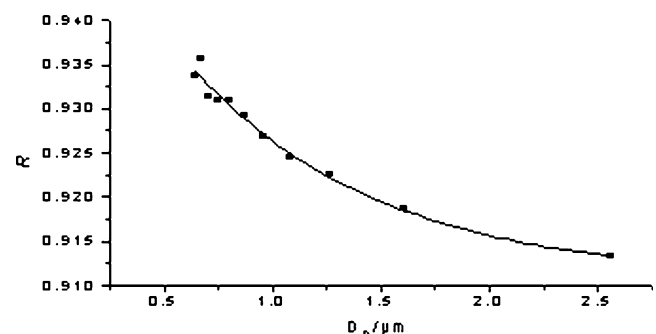

Fig. 3 Surface concentration gradient of PPw-g-PMMA in PP blend film containing 3% PPw-g-PMMA

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 the penetration for different angles of interest were calculated.

The contents of PPw-g-PMMA did decrease with increasing the detectability depth. This reflected a preferential migration of PMMA blocks to the interface when the film was melt-cast on the steel. Steel is a high-energy interface. Thus PMMA blocks were expected to be in contact with the interface of steel so that the system could be in lowest-energy state. This behavior was precedented both for a number of other pure polymers and polymer mixtures and blends [16, 17]. For example, poly(ethylene glycol) block was found to migrate to the glass interface when the blend film of polyethylene-poly(ethylene glycol)/PP was cast on the glass. In this case, there was a preferential segregation of high-energy component to the higher energy interface.

Effect of PMMA contents in PPw-g-PMMA on surface enrichment

The PMMA contents also influence the segregation phase and surface selective enrichment of PPw-g-PMMA on PP. the surface excess of PPw-g-PMMA with different PMMA contents were shown in Fig. 4, where the surface excess of PPw-g-PMMA was defined as following:

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

Where R_s and R_v were the peak area ratios on surface and in bulk, respectively.

A higher surface excess was found on PP blend containing PPw-g-PMMA with lower PMMA contents, especially at lower PPw-g-PMMA contents. For example,
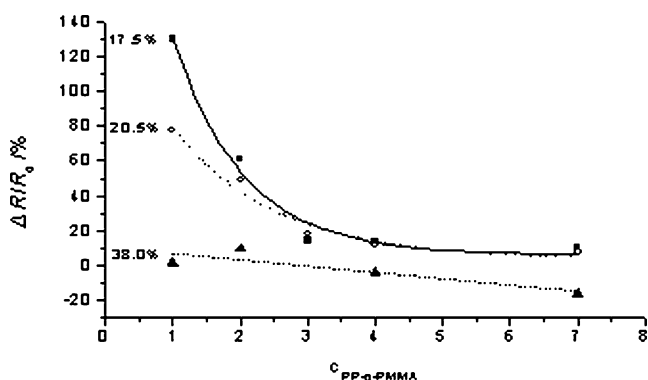

Fig. 4 The influence of PMMA content in PPw-g-PMMA on surface excessive degree in PPw-g-PMMA/PP blends film

130 and 10% surface excess were observed on the surface of PP blends containing PPw-g-PMMA with 17.5 and 38.0% PMMA contents at 1% loading, respectively. With increasing the loadings of PPw-g-PMMA, the difference of surface excess reduced. The results were due to the phase domains of PPw-g-PMMA formed in PP. Compared with PP, PMMA is a strong polar side chain, and therefore PPw-g-PMMA with higher density of PMMA side chains tends to segregate in PP with larger phase domains, which hinders the modifier to migrate to the molding interface.

Effect of molecular weight of PPw in PPw-g-PMMA on surface enrichment

PPw is used as the phile-host block in our additives. Molecular weight of PPw in PPw-g-PMMA effects the interaction between host polymer and modifier. In general, this interaction increases the compatibility of PPw-g-PMMA with PP, therefore PPw-g-PMMA with higher molecular weight of PPw should be distributed in PP with smaller phase domains as shown in Fig. 5, which was in favor of PPw-g-PMMA to migrate onto the surface of blends inducing by high-energy interface. On the other hand, long blocks of PPw also meant strong interaction between host polymer and the modifier, which hindered the modifier to diffuse onto the surface. In conclusion, the surface selective enrichment of PPw-g-PMMA lied on the balance of above-mentioned factors. The surface excess degrees of PPw-g-PMMA at different loadings were shown in Fig. 6. Although PPw-g-PMMA with higher molecular weight of PPw distributed in PP with smaller phase domains, their surface excess degree were obviously lower than that of graft copolymers with shorter PPw main chains, especially at lower loading. For example, PPw-g-PMMA with PPw molecular weight 5,000 had over 80% excess on the surface at 1%wt loading, but no surface enrichment was observed on blends of PPw-g-PMMA with PPw molecular weight higher 9,000. This indicated that the diffusion-resistance of modifier derived from the interaction between PP and PPw-g-PMMA was in dominant. The result also implied that strong interaction between host polymer and modifier was not in favor of the modifier to migrate to the surface. However, once the modifier was enriched on the surface of material, this strong interaction may increase the last-effectiveness of modification. To obtain a perfect surface modified material by blending, the modification effect and last-effectiveness should be kept balance.

Effect of PMMA molecular weight on PPw-g-PMMA surface enrichment

Length of PMMA is one of the important characteristics of the copolymer. It must influence the phase domains of

Fig. 5 SEM micrographs of PPw-g-PMMA in 3% PPw-g-PMMA/PP blends film. Molecular weight of PPw in PPw-g-PMMA **a** 5,000, **b** 9,000, **c** 15,000
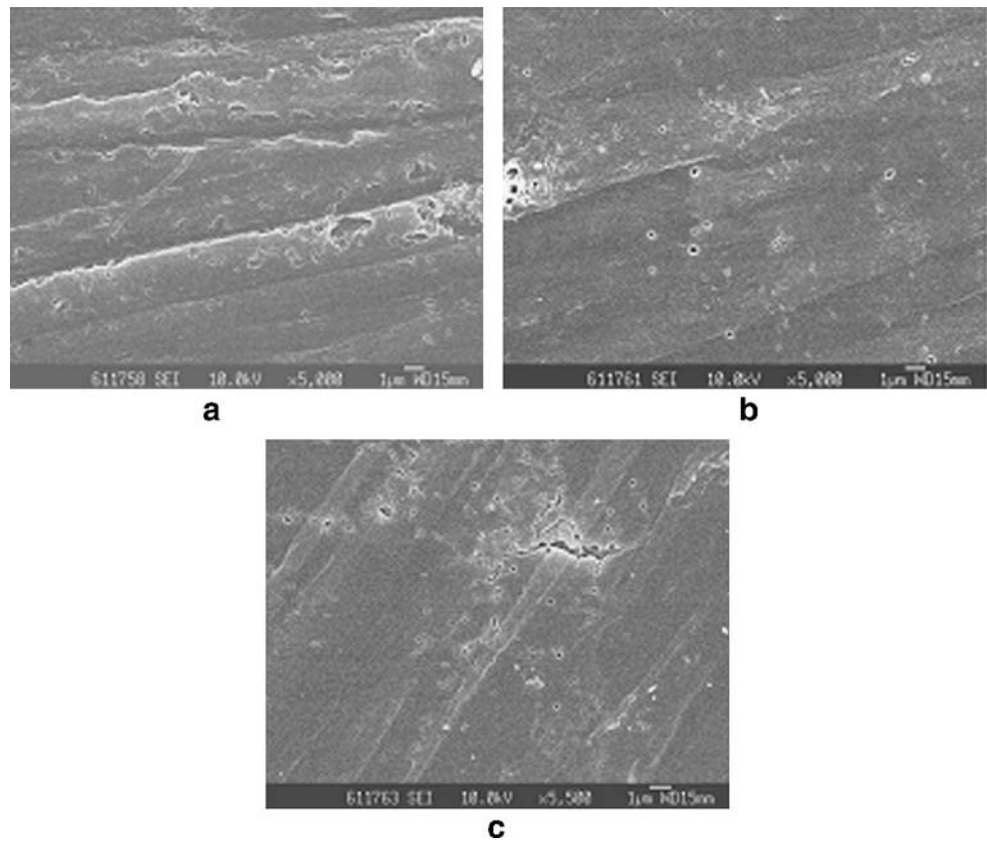
copolymer in PP. Therefore the difference of length of PMMA in PPw-g-PMMA must result in their different selective enrichment. The surface contents of PPw-g-PMMA with different lengths of PMMA were shown in Fig. 7. The contents of PPw-g-PMMA located on the surface increased with increasing the loadings of PPw-g-PMMA and the length of PMMA in PPw-g-PMMA. It seems that PPw-g-PMMA with higher PMMA molecular weight has better prefer-enrichment. Considering that higher PMMA contents on surface can be found at same loadings of PPw-g-PMMA with higher PMMA molecular weight in PP. The above result can not reflect the diffusion of the copolymer

effectively. Therefore the surface excess percentage of PPw-g-PMMA on PP was used to express the surface enrichment.

The surface excess percentages of PPw-g-PMMA on PP were shown in Fig. 8. Higher surface excess were found on the surface of blends containing PPw-g-PMMA with lower PMMA molecular weight, especially at lower loadings of PPw-g-PMMA. This implied that shorter PMMA side chain in PPw-g-PMMA was in favor of the diffusion of PPw-g-PMMA to the interface, and increased its surface enrichment, although the surface contents of PPw-g-PMMA with higher PMMA molecular weight determined by ATR-
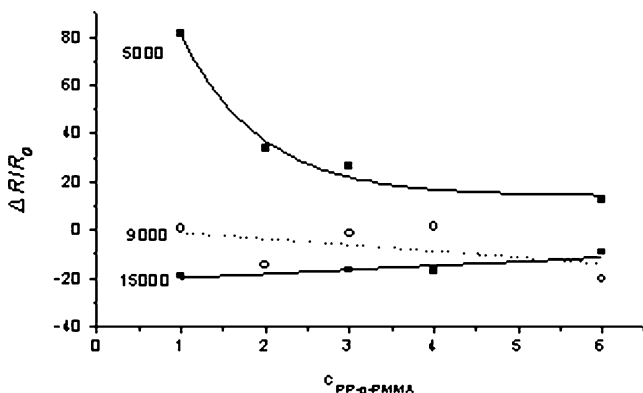

Fig. 6 The influence of molecular weight of PPw segment in PPw-g-PMMA on surface excessive degree of PPw-g-PMMA in PPw-g-PMMA/PP blends film
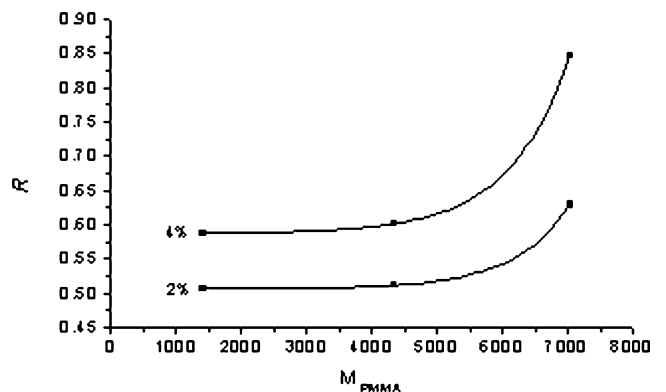

Fig. 7 The influence of molecular weight of PMMA segment in PPw-g-PMMA on surface peak area ratios of PPw-g-PMMA/PP blends film
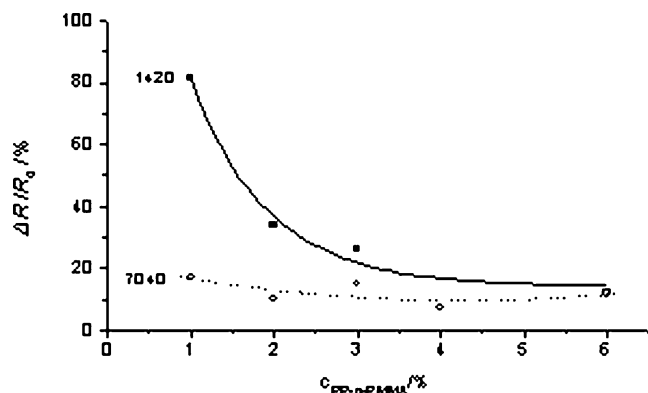
Fig. 8 The influence of molecular weight of PMMA segment in PPw-g-PMMA on surface excessive degree of PPw-g-PMMA in PPw-g-PMMA/PP blends film

FTIR were higher than that of lower PMMA molecular weight. The result was due to the larger phase domains of PPw-g-PMMA with higher PMMA molecular weight formed in PP as often found in polymer blends, which hindered the additives to diffuse to the interface.

Effect of contact interface on surface enrichment

The difference of interface energy is one of the most important driving forces for modifier to migrate to the blend interface. Steel, polyimide and poly(tetrafluoroethylene) are often used as the representative interface of strong, weak and nonpolarity, respectively. Therefore the blend films were melting-cast in contacting with the above mentioned interfaces to investigate the effect of contact dies on PPw-g-PMMA surface enrichment. The peak area ratios on the surface with different contact dies and loadings of PPw-g-PMMA were shown in Fig. 9. The contents of PPw-g-PMMA on the surface of blend films formed in contacting with steel and polyimide were higher than that in bulk, especially at lower loadings of PPw-g-PMMA, indicating that PPw-g-PMMA was enriched on the surface by inducing of high energy interface. The function-
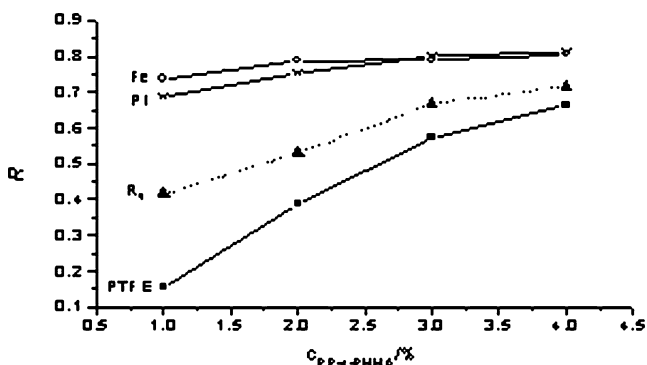
alized polypropylene in this work has essentially two types of component, namely the high polar portion contributed by the PPw-g-PMMA units and the nonpolar portion by the polypropylene units. When the films were melt-cast in contacting with steel or polyimide, the copolymer would preferentially migrate to the interface so that the system could be in lowest energy state. In contrast, PP was induced to migrate to the interface of poly(tetrafluoroethylene), whose interface energy was very low. With increasing the loadings of PPw-g-PMMA, the effect of interface on surface enrichment reduced. All these implied that the interface energy was the most important driving force for surface enrichment in the blends. The depth distribution of PPw-g-PMMA on the surface shown in Fig. 10 also confirmed this result. The contents of PPw-g-PMMA on the surface contacting with steel in preparation were higher than that of polyimide. More obvious depth distribution of PPw-g-PMMA can be observed in films melting-cast on steel than that on polyimide.

Effect of modifier on contact angle of modifier/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 [18]. In this study, PPw-g-PMMA was blended with PP and their water contact angles with different modifiers' contents were measured by contact angle goniometer. The results were listed in Table 1. The contact angle of blend film under contacting steel was decreased to 91.9° at 1% loadings of PPw-g-PMMA. Although due to the weak polarity of PPw-g-PMMA, the contact angles of PPw-g-PMMA/PP blends did not decrease so much as poly(ethylene glycol)/PP blends. The contact angles of blends films were uniformly much less than that found for pure PP, implied that there
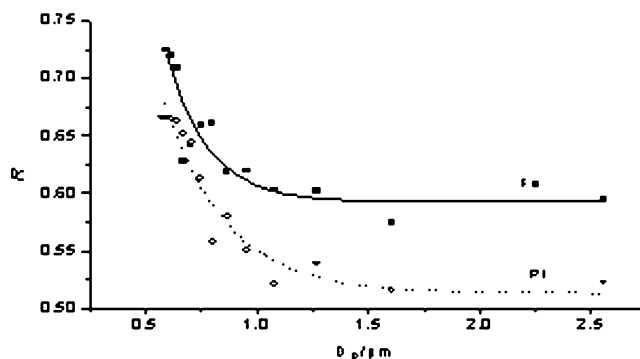

Fig. 9 The surface peak area ratio of PPw-g-PMMA/PP blends formed under different contact dies

Fig. 10 Surface concentration gradient of PPw-g-PMMA in PP blends contacting with different dies

Table 1 Contact angles of PPw-g-PMMA/PP film under different dies

Sample	Die	0%	1%	2%	3%	4%
PPw-g-PMMA/	Fe	119.8	91.9	92.0	97.6	97.6
PP	PI	119.8	109.1	110.6	106.3	108.9

Fig. 11 The change of modifiers in the surface vs the immersion time in ethanol *1, 2* PPw-g-PMMA with M_{PPw} 5,000, 9,000

was a preferential migration of PMMA blocks to the contact interface when the film was formed on the steel. With increasing the loadings of PPw-g-PMMA, the contact angles of blend films increased. This is 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 selectivity. Depending on the wavelength of the incident radiation and the reflection crystal, the layer of ATR-FTIR involved is about 1.2 μm, while the contact angle responds to functional groups in the outer 5 Å of the polymer [19].

When the contact interface was replaced by polyimide in preparing the films, which was often classified as weak polar interface, although the water contact angles of blend films were lower than that of pure PP, implied that some of PPw-g-PMMA enriched on the surface, the degree of enrichment of PPw-g-PMMA obviously lowered than that of correspond films formed on steel.

Evaluation of the solvent-resistance of modified PP film

The important difference between surface modification by blending and chemical graft modification is that the modifier on the former has no any chemical bond linking to the host polymer. Therefore the structure of modifier should be designed carefully so that the surface modifier can not be detracted easily when the modified material is contacted with water or chemical solvents. In most cases, modified materials may be often contacted with water, so the property of chemical solvents similar to water was chosen to detect the solvent-resistance of modified PP. Herein we observed the solvent-resistance of modified materials by dipping the functionalized PP into ethanol for an enactment time and determining the contents of modifier on the surface by ATR-FTIR after removal off alcohol. The results were shown in Fig. 11. The contents of PPw-g-PMMA with PPw molecular weight 5,000 on the surface increased with increasing the dipping time at the first 5 min, indicating that PPw-g-PMMA can diffuse onto the surface with faster velocity. Although PPw-g-PMMA located on surface was relatively easy to be extracted, more of PPw-g-PMMA located at sub-layer was induced to supply these losses by alcohol, which increased the contents of PPw-g-PMMA on the surface. With increasing the dipping time, this supply
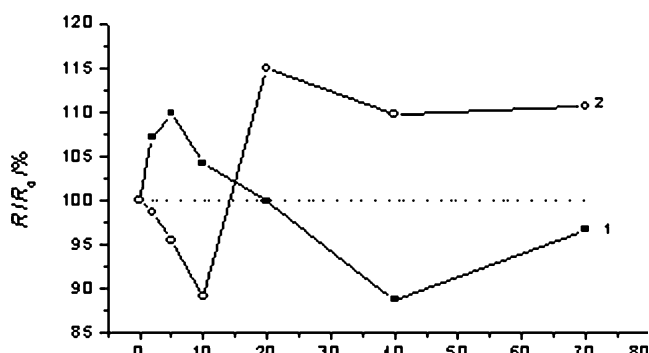
reduced due to the lower content of PPw-g-PMMA in sub-layer, the contents of PPw-g-PMMA on the surface decreased gradually. Compared with PPw-g-PMMA with PPw molecular weight of 5,000, the interaction between PP and PPw-g-PMMA with PPw molecular weight of 9,000 obviously increased, which heightened the solvent-resistance of PPw-g-PMMA, but also lowered the velocity of migration of PPw-g-PMMA in PP. Therefore at the first 10 min, PPw-g-PMMA located at the outmost layer reduced gradually. However, the losses decreased with increasing the dipping time, therefore the contents of PPw-g-PMMA at the ATR-FTIR layer increased beyond that of before dipping. In conclusion, the losses of PPw-g-PMMA on the ATR-FTIR surface was not exceeded 5% by dipping in alcohol for 70 min as showing in Fig. 11, indicating that the interaction between PP and PPw-g-PMMA was large enough to prevent PPw-g-PMMA from detracting when the modified material was in contact with water or organic solvents.

Conclusion

PPw-g-PMMA graft copolymers additive can preferred-diffuse to the surface of blends and effectively increase the hydrophilicity of PP. The surface enrichment of PPw-g-PMMA in PP blend film is obviously influenced by the structure of copolymer, content of additives and the contact interface. Lower content and higher surface energy dies are in favor of the copolymer to enrich on the PP surface. PPw-g-PMMA with low PMMA contents, long length of PMMA favors its selective enrichment on the surface of PP and had smaller phase domains in PP, especially at lower loadings in blends. The graft copolymers of PMMA have stronger solvent-resistance than PMMA.

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