Molecular state of graft copolymers in the interfacial area of polyolefin and polar polymer

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In order to characterize the interface in polymer blends, a new method is suggested, in which the interface is exposed by selectively dissolving in solvent. By means of X-ray photoelectron spectrometry, we studied the molecular state in the interfacial area of graft copolymers of polyolefin and polar polymer. When the graft copolymers were used as compatibilizers, the backbone polymer and branch polymer diffused into the corresponding miscible polymer bulks. The specific interactions between some macromolecules were very strong; the small solvent molecule could not separate these macromolecules.

(Keywords: interface; graft copolymer; polymer blend)

Introduction

The interface is an important problem in polymer science. While studying adhesion between different polymers, scientists found that a polymer molecular chain could diffuse into another miscible polymer bulk through the interface, and entanglement occurred[1-4]. However, knowledge about interfacial structure of immiscible polymer pairs is limited. According to diffusion theory[1,2], mutual diffusion between immiscible polymers cannot occur. Therefore the interfacial adhesion between immiscible polymers is very weak.

By measuring peeling strength, Imachi[5] studied the relation between the adhesion strength of different polymer pairs and adhesion temperature. These polymer pairs were polyethylene (PE)/ethylene–vinyl acetate and nylon/polypropylene (PP). The results showed that the interfacial strength was a maximum when the adhesion temperature was close to the melting temperature of high-melting-point components.

One method for improving the interfacial adhesion of immiscible polymer pairs is the addition of a compatibilizer. Cho *et al.*[6] studied the effect of diblock polymer polystyrene (PS)-*b*-poly(methyl methacrylate) (PMMA) on the adhesion properties between PS and PMMA. Their results showed that the diffusion of components of block polymer into the corresponding homopolymer was a key factor to obtain high adhesion strength. Only if the molecular weight of homopolymer (PS) is lower than that of the corresponding component of block polymer (PS-*b*-polyisoprene (PI)), is PS miscible with PS-*b*-PI[7]. Felix and Gatenholm[8] noticed that the molecular weight of the compatibilizer is a key factor in improving the mechanical properties of cellulose/PP composite. We have studied compatibilization of polyolefin/polar polymer blends[9]. In this paper, a new method is established to study interfacial states of polyolefin/polar polymer blends.

Experimental

Materials. Linear low density polyethylene (LLDPE) and PP ($\bar{M}_n = 2.6 \times 10^4$) were obtained from Daqing Petroleum Corporation. Poly(vinyl chloride) (PVC) was obtained from Jilin Chemical Corporation. Poly(vinylidene fluoride) (PVF_2, $\bar{M}_n = 6 \times 10^4$) was obtained from Polysciences Inc. The graft copolymers of PP and poly(ethylene oxide) ((PP-MA)-*g*-PEO) and of methyl methacrylate on LLDPE (LLDPE-*g*-PMMA) were synthesized in this Laboratory. LLDPE-*g*-PMMA contains 8.5 wt% PMMA which is the dispersed phase in LLDPE matrix[10]. (PP-MA)-*g*-PEO contains 16 wt% PEO ($\bar{M}_n = 6500$) and PEO branched chains are the dispersed phase in PP matrix according to the fractionated crystallization of the PEO branched chains[11]. Xylene, cyclohexanone, tetrahydrofuran and acetone were all of A.R. grade.

Preparation of polymer interface. Samples for studying the interface of different blend combinations were prepared in the following manner. A polymer sample of about 40 mm × 10 mm × 1.5 mm was moulded between aluminium foils (or Teflon film) on a hot press machine. The hot pressed samples were cooled in air. In order to obtain a smooth and clean sample surface, the mould plates were polished and the sample surface was washed with alcohol or acetone. The samples were dried at 40°C in vacuum and stored in Petri dishes. In this manner, the films of LLDPE-*g*-PMMA and (PP-MA)-*g*-PEO were prepared. The thickness of the graft copolymer films was 5 μm.

The composite specimens were prepared in the following manner. The clean surface of the PVF_2 sample was brought into contact with that of the LLDPE sample; they were placed between the top and bottom mould plates, which were put on the press machine at the required temperature. After heating for 5 min, a small pressure was exerted on the mould plates to enable the surfaces of the two samples to contact completely. In order to prepare an ideal sample, a sheet of rubber was

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added between the mould plates and the samples, which improved the contact of the two sample surfaces. The pressed samples were cooled in air. During preparation of the LLDPE/LLDPE-*g*-PMMA/PVF_2 sample, the thin film of LLDPE-*g*-PMMA was sandwiched between LLDPE and PVF_2; other processes were the same as in the preparation of the LLDPE/PVF_2 sample.

The above composite samples were subjected to heat treatment. In order to prevent degradation, the composite specimens were put in test tubes. The atmosphere in the test tubes was replaced by argon gas, then the test tubes were put in a thermostated oil bath (170 or 180°C) for a certain time. After heat treatment, the LLDPE/PVF_2 composite specimens were immersed in cyclohexanone at 110°C, making PVF_2 dissolve slowly. The interfacial area was washed with alcohol and dried in a vacuum oven.

Observation of molecular states in interfacial area. X.p.s. spectra were recorded on an ESCALAB-MKII model spectrometer with a monochromatized MgKα X-ray source. The working conditions of the instrument were: voltage 13 kV, current 20 mA, operating pressure 5×10^{-8} mbar. All peak binding energies were referenced to the C–C peaks of polymers at 284.6 eV. The analyser pass energy was 50 eV.

Results and discussion

In contrast to functionalized polymers with small polar groups, the backbone and branch components of a graft copolymer have some length. When used as a compatibilizer, both its backbone and its branch components will diffuse into the corresponding polymer bulk. The mixing free energy (ΔG_m) of the blend system is at a minimum in this case. In general, on addition of a compatibilizer, the interfacial region of the blend is enlarged[12] and the interfacial tension is decreased[12,13]. Owing to the lack of a method for direct observation, the true picture of the interface of a blend is understood very little. It has not been directly demonstrated that a graft copolymer diffuses into the bulk components during the process of compatibilization.

Since the interface plays a very important role in heterogeneous blends, we advanced the method described in the Experimental section to study the molecular state at the interfacial region. From the experimental results of SEM, d.s.c. and *FT*i.r., we learned that LLDPE-*g*-PMMA was a good compatibilizer for LLDPE/PVF_2 blends[9]. The mechanism of compatibilization is that the LLDPE part is miscible with the bulk LLDPE through cocrystallization and the PMMA part is miscible with PVF_2 through specific interaction[14,15]. Thus the LLDPE backbone of the compatibilizer diffuses into the LLDPE bulk, and PMMA branches of the compatibilizer diffuse into the PVF_2 bulk at the interfacial region. The following model experimental results further illustrate the interfacial behaviour of this kind of compatibilization.

Table 1 Composition of the interface of LLDPE/PVF_2 and LLDPE/LLDPE-*g*-PMMA/PVF_2 composite films[a] (X.p.s. measurements)

Sample	LLDPE/PVF_2	LLDPE/LLDPE-*g*-PMMA/PVF_2	
Time for heat treatment (h)	0	0	4
Time for separation[b] (min)	1	8	not observed
Composition of interface (mol%)			
LLDPE	100	69.4	20.2
PMMA	0	28.3	6.2
PVF_2	0	2.3	73.6

[a] The interface was exposed by dipping the composite films in cyclohexanone at 110°C
[b] Time needed for LLDPE and PVF_2 films to separate

When an LLDPE/PVF_2 composite film was put into cyclohexanone at 110°C, it separated into LLDPE film and PVF_2 film in about 1 min. After the PVF_2 film had dissolved completely, the LLDPE film was put into pure cyclohexanone for 30 min at 110°C to remove residual PVF_2, and then washed with alcohol and dried. The exposed interface, as observed by X.p.s., did not show the existence of fluorine (F) atoms (*Table 1*). This is understandable in view of the incompatibility of a polar polymer with a polyolefin. Interdiffusion did not occur in this situation.

A sandwiched LLDPE/LLDPE-*g*-PMMA (LL-5)/PVF_2 composite film was treated in a similar manner. When dipped in cyclohexanone at 110°C, the LLDPE/LL-5/PVF_2 composite film separated into LLDPE film and PVF_2 film after about 8 min. After the PVF_2 film had dissolved completely, the original interface contained F atoms as observed by X.p.s. (*Table 1*). This implied that the interdiffusion of PMMA branched chains and PVF_2 occurred. The PMMA branched chains of LLDPE-*g*-PMMA had interacted with PVF_2 in the interfacial region, which prevented some of the PVF_2 from being dissolved away from the interfacial region by the cyclohexanone. This shows that some specific interactions between macromolecules are too strong to be separated by the use of solvents. It was observed that while there was only 8.5 wt% PMMA in LL-5 bulk, the interface had about 28 wt% PMMA. This shows that PMMA branched chains of LL-5 were enriched on the PVF_2 side in the interfacial region.

In another experiment, an LLDPE/LL-5/PVF_2 composite film was heated above the melting point of PVF_2 before treatment with cyclohexanone in order for interdiffusion of PMMA and PVF_2 to occur. For composite films that had been heat treated, there was no immediate separation of LLDPE and PVF_2 in cyclohexanone. Heat treatment apparently promoted the interdiffusion of PMMA branched chains and PVF_2 in the interfacial region. The entanglement strength of PMMA branched chains and PVF_2 is so high that cyclohexanone cannot destroy it. The PVF_2 side of the composite film dissolved slowly in the solvent. The exposed interface was washed and dried. X.p.s. showed that the content of F atoms in the interfacial region was very high, the content of PVF_2 being as high as 73.6 wt% in the interfacial region (*Table 1*).

In order to confirm the above results, we extended our studies to composite films of PP/PVC and PP/(PP-MA)-*g*-PEO/PVC. Two composite films were prepared in a similar way to the LLDPE/PVF_2 system. Thus the two composite films were dipped in tetrahydrofuran (THF). In the PP/PVC composite film, the PVC film separated from PP and dissolved further. But there was no separation between PP and PVC in the PP/(PP-MA)-*g*-PEO/PVC composite film. The PVC side of the composite film dissolved very slowly. The following X.p.s. results were obtained (*Table 2*).

Table 2 Relative composition of the interface of PP/PVC and PP/(PP-MA)-*g*-PEO/PVC composite films[a]

Sample	PP/PVC	PP/(PP-MA)-*g*-PEO/PVC
Time of separation[b] (min)	2	not observed
Composition of interface (mol%)		
C	88.9	80.6
O	8.5	5.3
Cl	2.6	14.1

[a] The interface was exposed by dipping the composite films in tetrahydrofuran
[b] Time needed for PP and PVC films to separate

1. The interface on PP of PP/PVC contained oxygen and chlorine atoms; the oxygen atoms could only come from oxidation of the PP surface during sample preparation; apparently a small amount of PVC molecules was adsorbed by these polar groups through physical interaction.
2. For PP/(PP-MA)-*g*-PEO/PVC composite film, the exposed interface on PP contained far more chlorine atoms (14 wt%). Katime *et al.*[16] showed that PEO is miscible with PVC. In PP/(PP-MA)-*g*-PEO/PVC composite film, there was specific interaction between PEO branched chains of (PP-MA)-*g*-PEO and PVC molecules, which prevented PVC molecules from being removed by THF.

In an ideal situation, an interfacial agent exists as a monomolecular layer at the interface. In this experiment, the thickness of the copolymer layer is 5 μm; the copolymer may exist as a layer several molecules thick between A and B. However, the effect of the copolymer in the latter is the same as that in the former. In the former, A chains are miscible with polymer A, and C chains of the copolymer are miscible with polymer B. In the latter, when the sandwich sample A/A-*g*-C/B is pressed on the hot press machine (the temperature is higher than the melting temperature and glass transition temperature of the components), the rearrangement of A-*g*-C molecular chains occurs at the interface of A/A-*g*-C and B/A-*g*-C. As in the case of maleated PP(PP-MA) sample prepared with different lining[17], A chains of A-*g*-C are enriched on the interface of A/A-*g*-C, and C chains of A-*g*-C are enriched on the interface of B/A-*g*-C. X.p.s. results have shown that PMMA chains of LLDPE-*g*-PMMA are enriched on the interface of PVF_2/LLDPE-*g*-PMMA (*Table 1*). The A chains of A-*g*-C are miscible with polymer A and interdiffusion occurs; similarly the C chains of A-*g*-C are miscible with polymer B and interdiffusion of B and C occurs. Therefore the A-*g*-C layer can cause polymer A to adhere to polymer B. When the thickness of the A-*g*-C layer is reduced and is close to zero under limiting conditions, A-*g*-C exists as a monomolecular layer at the interface of A and B. The situation is the same as an ideal situation. While the thickness of the copolymer layer changes, the segregation behaviour of A-*g*-C at the interface does not change.

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