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Preparation of the HIPS/MA graft copolymer and its compatibilization in PA6/HIPS blends

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The graft copolymer of high impact polystyrene (HIPS) grafted with malice anhydride (MA) (HIPS-g-MA) was prepared with melt mixing in the presence of a free-radical initiator. The grafting reaction was confirmed by IR analyses and the amount of MA grafted on HIPS was evaluated by a titration method. 1–5 wt% of MA can be grafted on HIPS. HIPS-g-MA is miscible with HIPS. Its anhydride group can react with the PA6 during melt mixing the two components. The compatibility of HIPS-g-MA in the HIPS/PA6 blends was evident. Evidence of reactions in the blends was confirmed in the morphology and mechanical properties of the blends. A significant reduction in domain size was observed because of the compatibilization of HIPS-g-MA in the blends of HIPS and PA6. The tensile mechanical properties of the prepared blends were investigated and the fracture surfaces of the blends were examined by means of the scanning electron microscope (SEM). The improved adhesion in a 16%HIPS/75%PA6 blend with 9%HIPS-g-MA copolymer was detected. The morphology of fibrillar ligaments formed by PA6 connecting HIPS particles was observed.

1. Introduction

Multiphase plastics offer a route to combinations of properties generally not available in any single polymeric material [1]. However, simple blends of immiscible polymers generally exhibit poor mechanical properties that stem from the unfavourable interactions between their molecular segments. This is manifested as a coarse, unstable phase morphology that develops during melt processing and weak interfaces between the phases in the solid state.

Polymer immiscibility arises from the very small entropy gained by mixing different kinds of long chains. In fact, it will be shown that in the limit of high molecular weight, only polymer pairs with zero or negative heats of mixing can form one phase. It should be pointed that the polymer blends with superior mechanical properties in a two-component polymer system can't be manufactured, if the components are completely immiscible. Usually sharp interfaces and poor adhesion between the components bring about easy materials failure. Most of the presently important systems are miscible to the extent that a slight degree of mixing takes place, or interfacial bonding is developed directly, as in grafts or blocks [2]. In order to make polymer alloys with high performance from an immiscible polymer mixture, a compatibilizer must be used to improve the interfacial adhesion.

Both polyamide 6 (PA6) and high impact polystyrere (HIPS) are commodity polymers that possess unique properties individually. PA6 has been classified as a major engineering thermoplastic with excellent properties such as solvent resistance, easy processability and good mechanical characteristics. HIPS is a low price but tough thermoplastic with relatively poorer solvent resistance. Combination of PA6 and HIPS would be an ideal pair to produce a property balanced blend product. In practice, however, it is difficult to obtain good performance because PA6 and HIPS are immiscible. Although many studies on the compatibility of immiscible blends have been reported, such as the system of PA6/PS [3], PBT/HIPS [4], PA1010/HIPS [5], PA6/ABS [6], PA6/PP [7], studies on the preparation of functionalized HIPS via melt grafting of MA on HIPS and its effects on the compatibility of PA6 and HIPS blends have not been reported up to present.

In this paper, we attempt to graft MA on HIPS through reactive processing and the effect of *in situ* compatibilizer of HIPS-g-MA on the final morphology and mechanical property of the immiscible polymer blends of PA6 and HIPS were examined. Note that the anhydride group in HIPS-g-MA reacts easily with the amine group at the chain in PA6, and that HIPS-g-MA has good compatibility with HIPS due to the presence of structurally similar HIPS units in the polymer backbone, thus the physical and chemical interaction across the phase boundaries will control the overall performance of the polymer blends. A series of blends of HIPS/PA6 with good performance can be made by using the compatibilizer.

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2. Experimental

2.1. Materials

HIPS used in this study was a commercial product (492-J) manufactured by Yanshan Petrochemical Co, Beijing, China and its melt flow index is 3.1 g/10 min. The content of polybutadiene is 7% in HIPS. PA6 with $M_n = 19600$ was supplied by eighteenth plastic plant, shanghai, China.

Dicumyl peroxide (DCP), obtained from Xizhong chemical plant, Beijing, China, was used as an organic peroxide initiator. Its half-life is about 15 s at 190°C.

2.2. Maleation of HIPS

The graft reaction of HIPS with MA was carried out in the molten state by using a Brabender mixer processed at 50 rpm for 5 min at 180°C. HIPS was introduced into the mixing chamber first, then MA and DCP were added simultaneously. The product obtained in this way was dissolved in toluene, then the solution was precipitated in methanol in order to extract the unreacted MA and DCP from the product. The precipitate was collected and dried in vacuum for 24 h at 60°C. The polymer was dissolved in toluene again and the quantitative ethanolic KOH solution was added. The solution was violently stirred in order to make anhydride group hydrolyze completely. The MA content was determined by back titration with an isopropyl alcoholic HCl solution using phenolphthalein as an indicator. The grafting degree (GD) of MA was calculated from the following equation:

$$GD = \frac{[V_{\mathrm{KOH}}C_{\mathrm{KOH}} - V_{\mathrm{HCL}}C_{\mathrm{HCL}}] \times M_{\mathrm{MA}}}{2 \times W_{\mathrm{S}}} \times 100\%$$

where V, C, M and W_{S} are the volume, concentration, molecular weight and the weight of the sample, respectively.

2.3. Spectroscopic analysis

The presence of MA grafted onto HIPS were assessed using a FTS-7 Fourier transform infra-red (FTi.r, Bio Rad co.) spectrometer and an ESCA CAB MK-II (VG co.) electron spectrometer. Thin films, made from solution casting, were used for i.r. measurements.

2.4. Blend preparation

PA6 was dried for 12 h at 90°C before melt blending. The polymers were melt-mixed using a Brabender twin-screw extruder operated at a rotation speed of 20 rpm and a temperature range of 225–235°C.

The weight ratio of PA6 to HIPS in the blends was fixed at 75/25. The amount of HIPS-g-MA in the blends, GD of which is 4.7%, was chosen as 0, 3 and 9 wt% of the total weight of blends, respectively.

2.5. Morphology observation

Morphology of the blends was observed with a scanning electron microscope (SEM, JXA-840) at an accelerating voltage of 25 kv. The blend samples were fractured at liquid nitrogen temperature, and the fractured surface was coated with gold.

Specimens for transmission electron microscopy (TEM) observation were obtained by using cryoultramicrotomy at liquid nitrogen temperature. Ultrathin sections were stained with osmium tetroxide to enhance the contrast for the microscopy observations. A Jeol 1200EX TEM operated at 200 kv, was used to examine the morphology of these blends.

2.6. Tensile property measurement

Test specimens for mechanical properties were prepared by using a JSWF17SA injector with a barrel temperature of 225–235°C. Measurements of tensile properties of specimens were carried out on an Instron 1121 machine at room temperature with cross-head speed of 5 mm/min. Five specimens of each blend were tested and average values were taken as experimental data.

3. Results and discussion

3.1. Characterization of HIPS-g-MA

FTi.r. spectra of the HIPS and HIPS-g-MA are shown in Fig. 1. In the spectrum of HIPS-g-MA (Fig. 1b), the new absorption bands appeared at 1218, 1780 and 1857 cm^{-1}. However, these bands were not observed in the spectrum of HIPS. These characteristic bands are assigned to a C–O single bond (1218 cm^{-1}) and a C=O double bond (1789 and 1857 cm^{-1}) stretching in MA units that are introduced on the molecular chains of HIPS via the reactive extrusion process, because the unreacted MA has been removed from the sample. The most reliable evidence of the grafting reaction between HIPS and MA was conducted by the titration measurement. The grafting degree of MA on the HIPS is 4.7 wt%. It means that the oxygen content in the graft copolymer of HIPS and MA is 2.3%.

The grafting was also confirmed by using XPS spectra. Fig. 2 shows the XPS spectra of the HIPS and

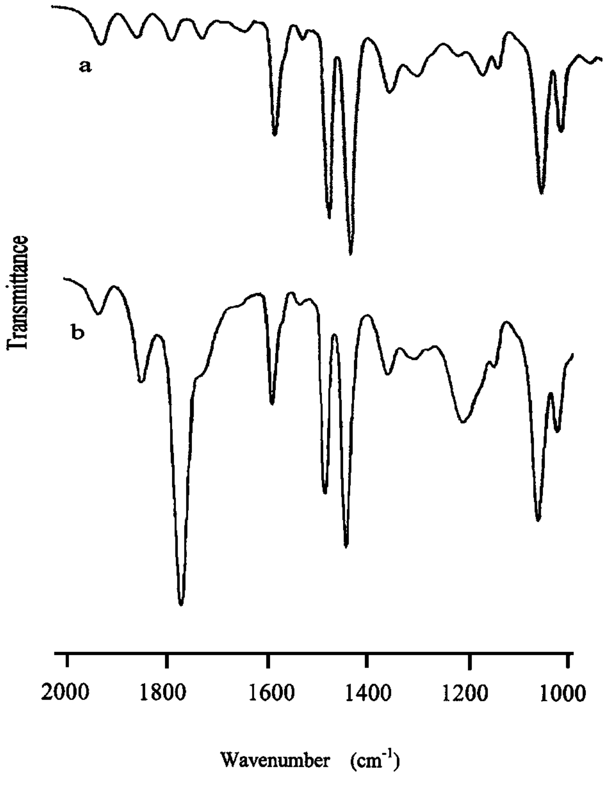

Figure 1 FTi.r. spectra of (a) HIPS and (b) HIPS-g-MA.

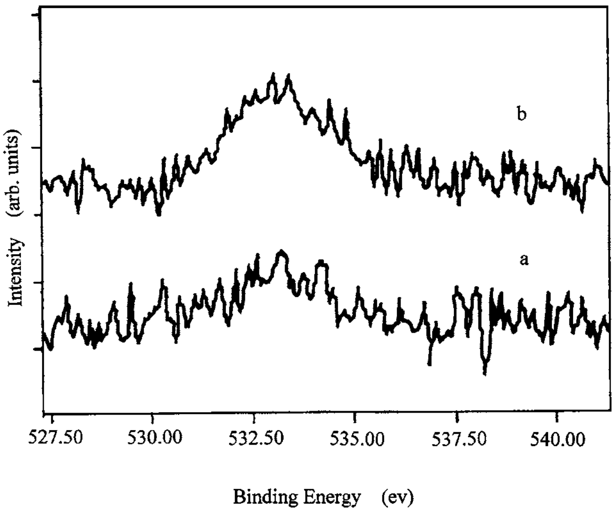

Figure 2 XPS spectra of (a) HIPS and (b) HIPS-g-MA.

HIPS-g-MA. The Binding Energy of O_{1s} is about 532.8 ev. The intensity of the oxygen peak of HIPS-g-MA is significantly larger than that of the HIPS. The ratio of the intensity between HIPS-g-MA and HIPS is about 2.2:1. This can be tentatively explained as follows. The weak O_{1s} peak of the HIPS is very difficult to identify and it originates from the absorbed oxygen from the air on the surface of the HIPS sample. On the other hand, the larger peak of O_{1s} related to the bonded oxygen atom of the HIPS-g-MA graft copolymer was observed obviously on XPS spectrum.

3.2. Morphology

The electron photomicrographs of the fracture surface of blends are shown in Fig. 3. SEM photomicrograph is the most convenient approach to differentiate the morphologies between a compatibilized blend and an uncompatibilized counterpart. An immiscible and incompatible blend usually results in coarser morphology than the compatibilized one and the finer phase domains are the indication of better compatibilization of the blend. The presence of a compatibilizer, usually distributed at interface, is able to reduce the interfacial tension and breakup the phase structure easier in a typical melt blending process, and the resultant separated phases are therefore more stable and have less tendency to recombine. In the SEM photomicrographs of the 75PA6/25HIPS blends, the dark holes are the HIPS phase that was separated from PA6 matrix. HIPS domains, for which the diameter ranged between 0.8 and 10 μm, have a well-defined spherical shape and a very broad size distribution. The large particle size with no evidence of adhesion between the matrix and dispersed phase confirmed the immiscibility of the two components. Also, the surfaces of the domains appear to be very smooth. This is a typical morphology of an immiscible blend. Some different features are observed for the ternary blends of PA6/HIPS/HIPS-g-MA. The presence of HIPS-g-MA reduced the domain size of the dispersed phase and narrowed its distribution significantly. Interfacial adhesion seemed to be improved with forming *in situ* the compatibilizer during the melt mixing. The rough fracture surfaces in the compatibilized blends were observed because the HIPS particles had adhered to the matrix material.

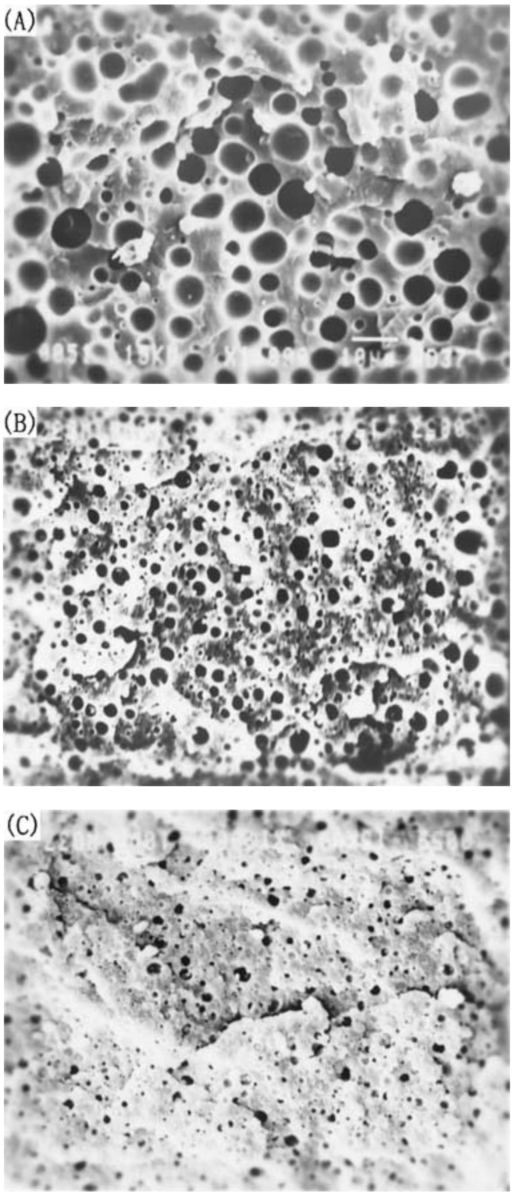

Figure 3 SEM photomicrographs of the PA6/HIPS/HIPS-g-MA blends. (A) 75/25/0, (B) 75/22/3, and (C) 75/16/9.

Interfacial tension, the shear rate of mixing and the viscosity ratio of the blending components are key parameters governing the degree of dispersion [8]. When the shear rate of mixing and the viscosity ratio of the blended polymers are constant, the interfacial tension of the blend plays an important role in reducing the domain size. Therefore, better dispersion and the improved interfacial adhesion should be attributed to formation of the grafting copolymer at the interface between PA6 and HIPS via reaction of MA in HIPS-g-MA with the terminal amine groups of PA6 during the melt extrusion.

However, the SEM technique does not make it possible to distinguish the finer morphological features, in particular, the character of HIPS dispersion in blends with 3 and 9 wt% of the graft copolymer, HIPS-g-MA. Majumdar *et al.* examined the morphologies of Nylon6/ABS blend compatibilized with SMA25 by TEM utilizing several different staining techniques [6]. In

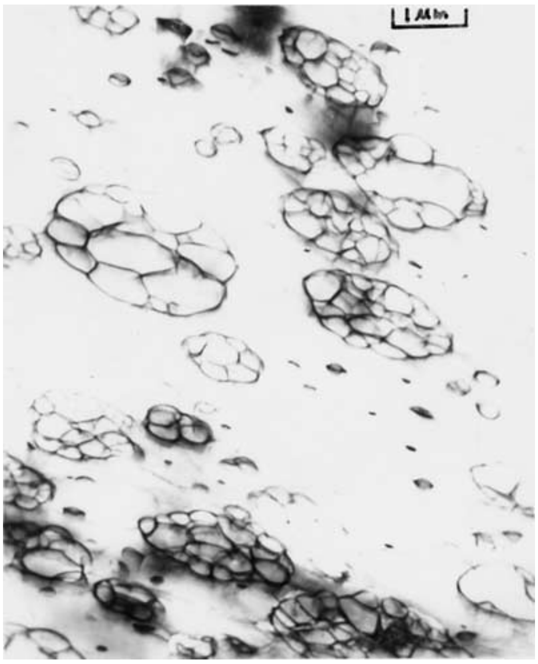

Figure 4 TEM photomicrographs of the HIPS material. The sample was stained with O_sO_4.

order to examine the morphology features of compatibilized blends of HIPS/PA6, ultrathin sections of the blends were studied by using TEM. Fig. 4 shows the TEM photomicrograph for the HIPS sample, 492-J, used in this work. The complex cellular structure was observed. The domain size has a broad distribution. Now, the morphologies of PA6/HIPS blends compatibilized with HIPS-g-MA are examined by TEM. Fig. 5 shows photomicrographs of the series of blends containing 75% PA6 with varying amounts of HIPS-g-MA. For the blends without any HIPS-g-MA compatibilizer, rubber particles in the cellular structure of the HIPS exist in certain regions in which the biggest diameter is about 10 μm. Comparing with the SEM photomicrograph, we can confirm that the regions are HIPS phases. The rubber particles in the cellular structure of the HIPS are entirely absent in the other regions which must consist primarily of PA6 (Fig. 5a). For the uncompatibilized blends, sharp boundaries and clear gaps between HIPS dispersed phase and PA6 matrix were observed. The biggest domain size is about 10 μm in diameter. In these domains, the continuous phase consists of polystyrene while the cellular structure shown in HIPS was observed in 75PA6/25HIPS blend as the secondary dispersed phase. The domain size and its distribution are similar to that in HIPS. These results show that the cellular structure features and the morphological characteristic in HIPS are not broken and they are kept in the PA6/HIPS blends totally. The worse miscibility between PA6 and HIPS can be conducted from these observations. O_SO_4 staining techniques reveal the features and the distribution of polybutadiene chains in the domains. As well known, polybutadiene forms the matrix in the cellar structure. It should be assigned as the third phase morphology in PA6/HIPS blends. For the compatibilized blends, the morphologies shown in Fig. 5b and c reveal that the sharp boundaries and clear gaps between the dispersed phase and the matrix have disappeared. Due to the interfacial reaction between PA6 and HIPS-g-MA, the interfacial situation between PA6 and HIPS is absolutely changed. Namely, the interface between PA6 and HIPS is diffused and no clear layer of PS, as could be seen in the blend of PA6/HIPS, can be identified. The site of the reaction on HIPS is the polybutadiene segment; hence, the PB chains should face toward the PA6 matrix through the reaction. It means that the molecular architecture will affect the morphology of the blends and that the compatibilizer located at the interface broadens the interfacial region and that the molecular chains of HIPS-MA-PA6 copolymer have penetrated into the adjacent phases of PA6 and HIPS. In fact, the secondary dispersed phase identified clear in the uncompatibilized PA6/HIPS blend can hardly be observed in the compatibilized blends. However, the third phase features are still maintained. After we examine the morphological features of the third dispersed phase carefully, the different characteristics among the compatibilized and uncompatibilized samples were confirmed. First, the regular spherical cellular structure shown in the uncompatibilized blends was not developed in the compatibilized blends. Secondary, the domains with cellular structure were distributed in the whole TEM images for compatibilized blends, on the contrary, they are concentrated in the PS domains in the uncompatibilized blend, i. e. a larger number of the third order of domains are visible in some regions while almost no domains are seen in other regions.

As well known, the graft copolymer of styrene and butadiene formed during the polymerization of HIPS located preferably on the interfaces between PS matrix and the domains with cellular structures and it is an effective compatibilizer for PS and polybutadiene in HIPS. However, the double bonds on molecular chains of PS-g-PB will react preferably with maleic anhydride to form the HIPS-g-MA copolymers since the soluble bonds have higher reactive during the grafting copolymerization initiated by free radicals, then they are transformed into new grafting copolymers, maleated HIPS-g-PA6 which will migrate into the interfaces between HIPS and PA6 from the interfaces between PS and cellular domains to accompany the grafting reaction between HIPS-g-MA and PA6. Therefor, the regular spherical domains were shown in the uncompatibilized blend of HIPS and PA6 while the irregular ones were created in the compatibilized blends of PA6/HIPS-g-MA. On the other hand, the reactive of double bonds of PB in HIPS inside the domains with the cellular structure was reduced because the slight cross links of their molecular chains will restrain the grafting reaction between PB and MA.

3.3. Tensile properties

Interfacial adhesion is an important parameter for controlling the mechanical properties of multiphase systems. Good adhesion between the matrix and dispersed phase may be essential for proper stress transfer without interfacial debonding. From the morphological observation we realized that the PA6-g-HIPS copolymer, which is formed during melt mixing, acts as a compatibilizer of the PA6/HIPS blends. The mechanical

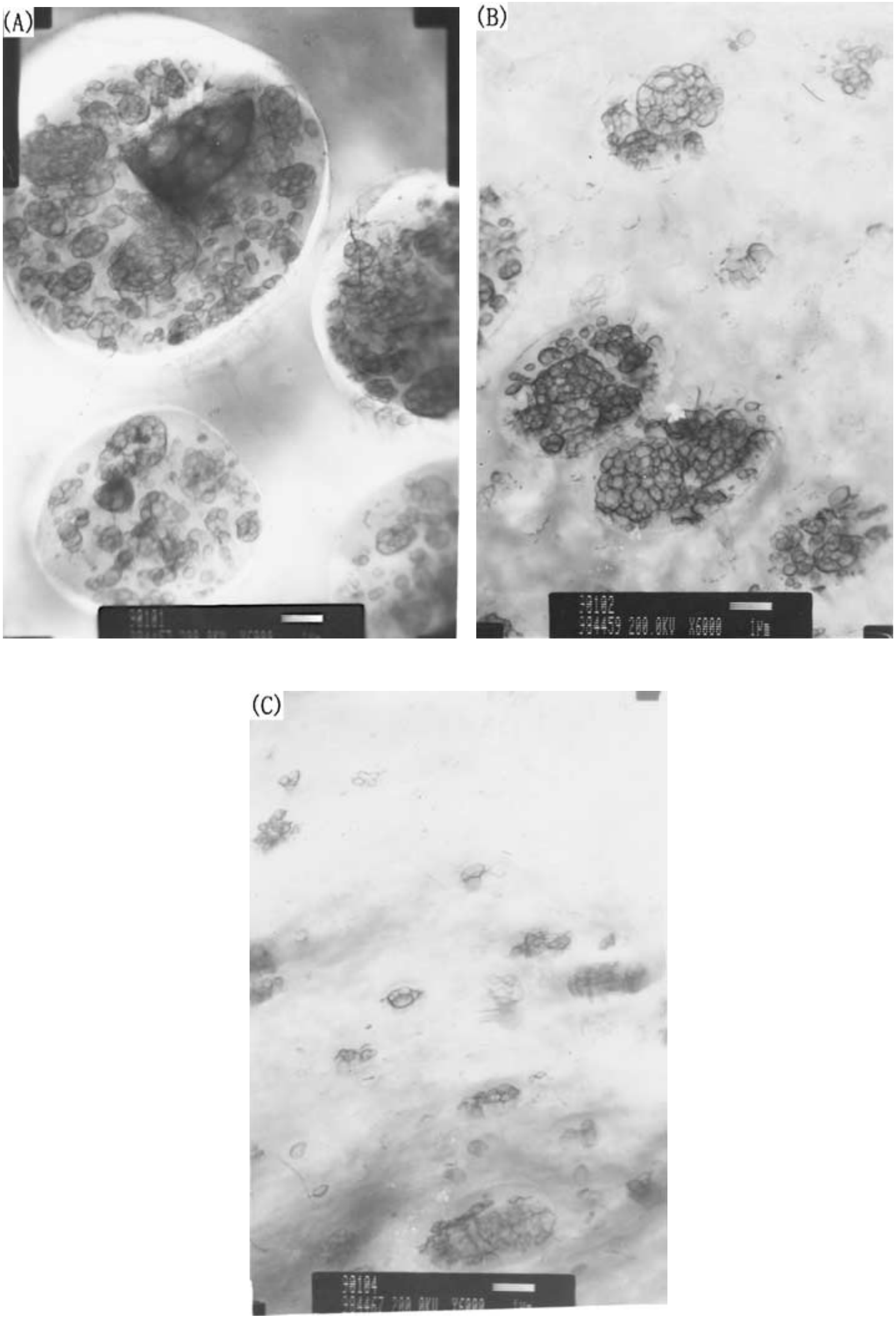

Figure 5 TEM photomicrographs for 75% PA6 blends containing (A) 0% (B) 3% (C) 9% HIPS-g-MA. The samples were stained with O_sO_4.

properties of binary and ternary blends are summarized in Table I, an increase in the tensile properties is observed when HIPS-g-MAs are introduce into blends of PA6/HIPS. The low tensile properties of PA6/HIPS blend can be related essentially to the larger size of the HIPS domains with a poor adhesion to the matrix. These domains act as gross material defects, causing premature rupture of the specimen soon after the beginning of yield. On the other hand, in PA6/HIPS/HIPS-g-MA blends, all particle size reduction and an improvement of interfacial adhesion, caused by the formation of PA6-g-HIPS copolymer at the interface between PA6 and HIPS, seem to lead to the improvement of mechanical properties.

TABLE I Tensile properties of ternary blends

PA6/HIPS/ HIPS-g-MA	Strength (MPa)	Energy (J)	Elongation (%)	Modulus (MPa)
75/25/0	41	1.3	30	1229
75/22/3	44	2.4	52	1246
75/16/9	62	20	207	1260

Because the tensile yield strength of the HIPS material is lower than that of the PA6 matrix, an indication of the interfacial strength is derived from the extent to which the HIPS particles are deformed when the blend fractures. SEM images of the fracture surface are given in Fig. 6 for compatibilized and uncompatibilized blends of PA6/HIPS. The distinct phase-separated domains having a size of 1–10 μm are clearly seen for the

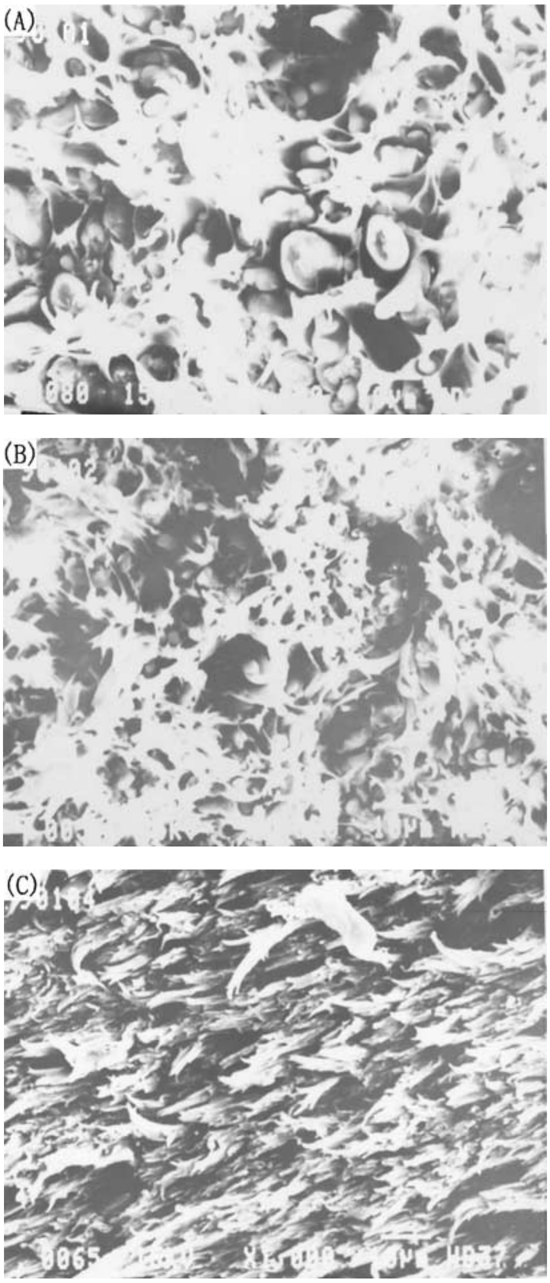

Figure 6 SEM photomicrographs of the tensile fracture surfaces containing (A) 0% (B) 3% (C) 9% HIPS-g-MA.

uncompatibilized blends, while there are hardly evidence of a phase-separated morphology in the compatibilized blends of PA6/HIPS/HIPS-g-PA6 after a tensile test. Some other changes in the fracture surfaces were observed on the SEM photomicrographs as the amounts of compatibilizer increases. On the fracture of the PA6/HIPS blends, undeformed HIPS particles with smooth surfaces debonded from the surrounding PA, which was pulled out and fabricated. This indicates that the interfacial adhesion is very poor between PA6 and HIPS. However, in PA6/HIPS/HIPS-g-MA blends, numerous thin ligaments connected HIPS particles to the deformed matrix and incorporated the particles into the fibrous PA6 area. This evidences that adhesion between HIPS and PA6 was good enough to prevent debonding during matrix drawing indicated and that the interfacial strength was higher than the fracture strength of the matrix. The ribbonlike features on the drawn ligaments were the result of recoil after they fractured. The better adhesion provided by 9 wt% HIPS-g-MA was manifest primarily in the ultimate elongation. The tensile energy and elongation at break of the PA6/HIPS/HIPS-g-MA blends were improved more than 10 times with adding HIPS-g-MA from 0 to 9 wt%. It was presumed that interfacial strength in the blends was determined primarily by interaction of the compatibilizer with PA, since adhesion to HIPS was provided by chemical linkages. The interaction of HIPS-g-MA with PA6 was strong enough to sustain particle-matrix adhesion as the compatibilizer was drawn along with the PA. Interfacial agents generated *in situ* during the process of melt mixing through reaction between chemical functionalities available in the polymer chains have been reported in literature. Both experimental observations and theoretical prediction indicate a reduction in the dispersed phase domain size. In addition, the presence of the compatibilizer at the interface broadens the interfacial region through penetration of the copolymer chains into the adjacent phase [9]. These factors mentioned above translated on the macroscale into higher fracture elongation for the blends.

4. Conclusion

High impact polystyrene was grafted with maleic anhydride in a mixer. The results of FTi.r. and XPS confirmed that the maleic anhydride units are incorporated in the HIPS. The introduction of MA units in HIPS was very effective for controlling the morphology of blends of PA6/HIPS/HIPS-g-MA. The domain size of the dispersed phase of ternary blends decreased with increasing HIPS-g-MA content in blends, while PA6/HIPS binary blends showed typical morphology of an incompatible blend.

The effects of the HIPS-g-MA concentration on the tensile properties of blends have been examined. The improved mechanical properties should be attributed to the interaction between HIPS-g-MA and PA6. For the tensile fracture of the compatibilized blends, no HIPS particles are visible on the fracture surface. This behavior indicates that the HIPS particles are firmly attached to the PA6 matrix, otherwise, the HIPS particles would have been dislodged from the matrix during the tensile fracture. With increasing HIPS-g-MA content from 0–9 wt%, the microscale deformation mode progressed from debonding to particle drawing and fibril fracture. Interfacial adhesion was postulated to increasing with increasing the HIPS-g-MA content in the blend.

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References

1. D. R. PAUL and S. NEWMAN (eds), "Polymer Blends" (Academic Press, New York, 1978).
2. J. A. MANSON and L. H. SPERLING, "Polymer Blends and Composites" (Plenum Press, NewYork, 1976).
3. H. J. WON, D. P. CHAN and S. L. MOO, *Polymer* **37** (1996) 1709.

4. D. Y. CHANG, W. F. KUO and F. C. CHANG, *Polym. Networks Blends* **4** (1994) 157.
5. G. X. CHEN, JUN. YANG and J. J. LIU, *J. Appl. Polym. Sci.* **71** (1999) 2017.
6. B. MAJUMDAR, J. KESKKULA and D. R. PAUL, *Polymer* **35** (1994) 3164.
7. S. SATHE, G. S. S. RAO, K. V. RAO and S. DEVI, *Polym. Eng. Sci.* **36** (1996) 2443.
8. S. WU, *ibid.* **27** (1987) 335.
9. B. MAJUMDAR, D. R. PAUL and A. J. OSHINSKI, *Polymer* **38** (1997) 1787.

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