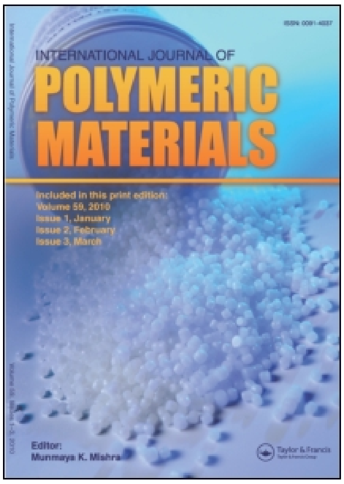

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The Effect of Compatibilizer on Morphology and Mechanical Properties of PA6/UHMWPE Blends

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This work deal with the effect of compatibilizer on the morphological and mechanic properties of polyamide 6 and ultrahigh molecular weight polyethylene (PA6/UHMWPE) blends. The blends were prepared by means of a twin-screw extruder. The compatibilizer was produced by grafting maleic anhydride (MAH) onto high density polyethylene (HDPE). The resulting HDPE-g-MAH was used to prepare ternary blends of PA6/HDPE-g-MAH/UHMWPE by melt mixing. The size of domain of UHMWPE in PA6/HDPE-g-MAH/UHMWPE blends is much smaller than that in PA6/UHMWPE blends. It was found that mechanical properties of PA6/HDPE-g-MAH/UHMWPE blends obviously surpassed that of PA6/UHMWPE blends. These behavior could be attributed to chemical reactions between MAH in HDPE-g-MAH and terminal amino groups of PA6. Thermal analysis were performed to confirm the possible chemical reactions taken place during the blending process.

Keywords: Polyamide 6; ultrahigh molecular weight polyethylene; compatibilizer; blends

INTRODUCTION

Polymer blends and alloys have been widely studied, especially the preparation method, statistical thermodynamic approach on compatibility, mechanical properties, and the formation of structures in various blend or alloy systems, and summarized in several books [1-4]. Nowadays it is one of the most important subjects from the viewpoint

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of material design for polymer, which is directly related to an actual application in the polymer industry. General, simple blends of polymer exhibit unstable phase morphologies and poor properties. In typical immiscible polyblending system, a satisfactory physicomechanical behavior critically depends on the proper interfacial tension to generate a small phase size and strong interfacial adhesion to transmit force effectively between two phase. Many articles [5–11] have reported that the presence of a block or graft copolymer having appropriate chemistry structure can provided lowing of interfacial energy, and improvement of the interfacial adhesion between two phase, and the final morphological effect is a reduction of dispersed particle in the blends.

PA6 and UHMWPE are often blended with other polymers to improve their performances for some special applications. Several authors [12–15] have reported rheological behavior and mechanical properties PA/HDPE, PA/UHMWPE and HDPE/UHMWPE blends. The wear resistance properties of PA6/UHMWPE/HDPE blends without addition of any compatibilizer have been examined by Tadao and Nidenori [16, 17].

In the present paper, morphology and mechanical properties of PA6/UHMWPE blends using HDPE-g-MAH a compatibilizer have been investigated. The purpose is aimed at understanding the effect of HDPE-g-MAH on the morphology and mechanical properties of PA6/UHMWPE/HDPE-g-MAH blends.

EXPERIMENTAL

Materials

PA6 used in this work was purchased from Hei Longjiang Nylon Plant (China). UHMWPE ($M_W = 1.5 \times 10^6$) was kindly supplied by Jilin University of Technology, China. The compatibilizer, HDPE-g-MAH was prepared in our lab by means of reactive extruding method. The content of MAH is 0.62 wt%.

Preparations of PA6/UHMWPE and PA6/UHMWPE/HDPE-g-MAH Blends

Binary PA6/UHMWPE and ternary PA6/UHMWPE/HDPE-g-MAH blends were prepared by reactive blending the components in a home-made SHJ-30 twin-screw extruder ($\Phi = 30$ mm and L/D = 44) at a constant speed of 175 rpm. The processing temperature was about 220 ~ 230°C. the weight ratio of PA6/UHMWPE/HDPE-g-MAH were 90/10/0, 90/10/5, 90/10/10, 80/20/0, 80/20/5, 80/20/10, 80/20/15, 80/20/20, 70/30/0, 70/30/30.

Measurements of Mechanical Properties

The melt-blended pellets were used to prepare test specimens by using a JSWF17SA injector (made in Japan) for the measurement of mechanical properties. Dumbbel-shaped specimens were prepared for tensile property measurements. Tests were carried out on Instron 1121 tester at room temperature with a cross-head speed of 50 mm/min. Measurements of flexural modulus and strength were also performed with the same Instron 1121 tester on the basis of ISO178-1975E. Izod impact strength measurements were carried out with an XJU-22 impact tester made in China on the basis of ISO/R180-1961. All dried specimens were obtained by putting specimens in a vacuum oven at 80°C for 12 h.

Morphological Observation

The mechanical properties of the heterogeneous polymer blends were found to be related to their microstructure, especially size and shape of the dispersed phases. In order to determine the particle size and size distribution of the dispersed phase in the blends, the overall morphology of specimens broken in liquid nitrogen was examined. Sections were vacuum coated with gold and examined in a scanning electron microscope (JXA-840). Before observation. The morphology of sections of specimens for tensile and impact tests were also examined by SEM.

Thermal Analysis

The thermal behaviors of blending samples was performed on a Perkin-Elmer DSC II apparatus. The thermograms were obtained by heating from 50 to 250°C at a heating rate of 10°C/min. All measurements were performed under nitrogen atmosphere.

RESULTS AND DISCUSSION

Overall Morphology

Figure 1 shows SEM micrographs of PA6/UHMWPE and PA6/UHMWPE/HDPE-g-MAH blends. The matrix is PA6 and the dispersed were UHMWPE and HDPE-g-MAH domains in PA6/UHMWPE/HDPE-g-MAH blends. We can see that average size of UHMWPE particle in PA6/UHMWPE/HDPE-g-MAH blends are much small than that of UHMWPE in PA6/UHMWPE blends. As shown in Figures 1(a) and (b), the diameters of particle of UHMWPE domains in PA6/UHMWPE blends are about 30–35 μm and those of UHMWPE and HDPE-g-MAH domains in PA6/UHMWPE/HDPE-g-MAH blends are about 2–4 μm. Homogeneous dispersion of UHMWPE and HDPE-g-MAH domains in PA6/UHMWPE/HDPE-g-MAH blends can be observed in Figure 1(b). Interfacial between PA6 matrix and UHMWPE domains are much clear and smooth for PA6/UHMWPE blends. This indicated that the interfacial adhesion between PA6 matrix and UHMWPE domains was very poor: they are completely immisicible. However, interfacial between PA6 matrix and domains of UHMWPE and HDPE-g-MAH in PA6/UHMWPE/HDPE-g-MAH are rough and instinct. The above results strongly suggest that miscibility of PA6 and UHMWPE in PA6/UHMWPE/HDPE-g-MAH blends was improved by possible coupling reactions between MAH in HDPE-g-MAH and terminal amino groups of PA6 in PA6/UHMWPE/HDPE-g-MAH blend.

Thermal Properties

DSC thermograms of PA6/UHMWPE binary blends are shown in Figure 2. In the binary blend system, the melting temperature of UHMWPE and PA6 remains constant in different compositions. This feature suggests that PA6 and UHMWPE are completely immiscible. Figure 3 is the DSC thermograms of PA6/UHMWPE/HDPE-g-MAH in heating run. We can see that the Tm of UHMWPE and HDPE-g-MAH are same, Tm of UHMWPE and HDPE-g-MAH increased and Tm of PA6 decreased as HDPE-g-MAH increased, respectively. Due to PA6 is matrix, its Tm change to low temperature are not obviously.

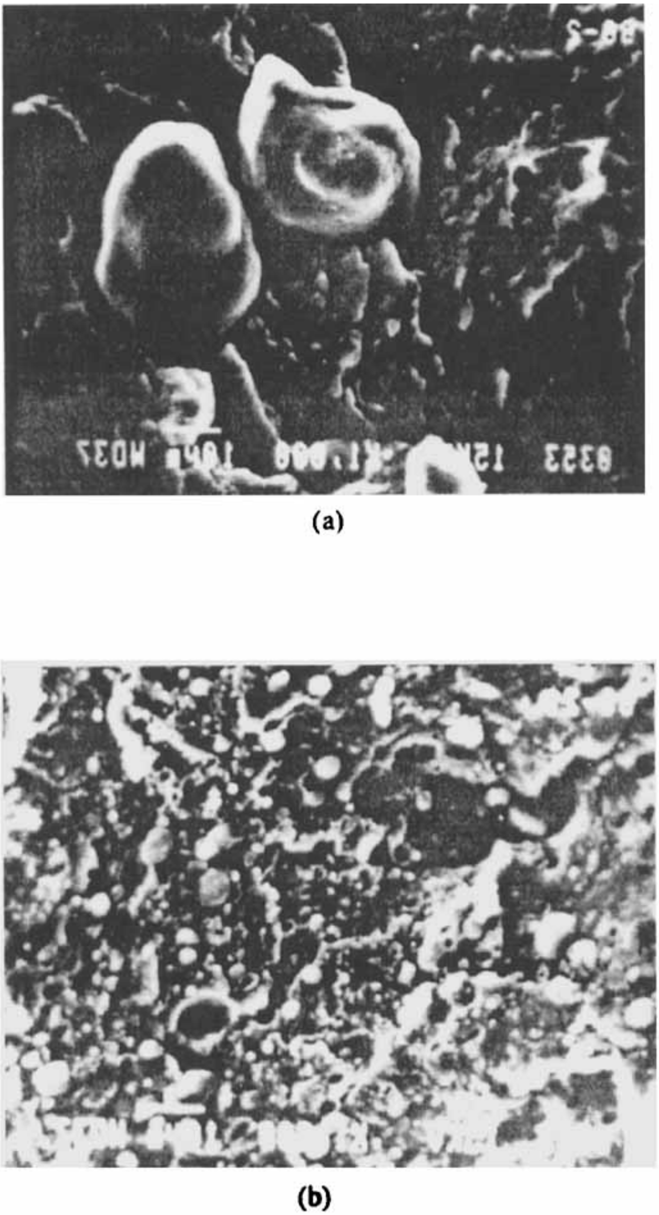

FIGURE 1 SEM micrographs of (a) PA6/UHMWPE (80/20 Wt/Wt) and (b) PA6/UHMWPE/HDPE-g-MAH (80/20/20 Wt/Wt).

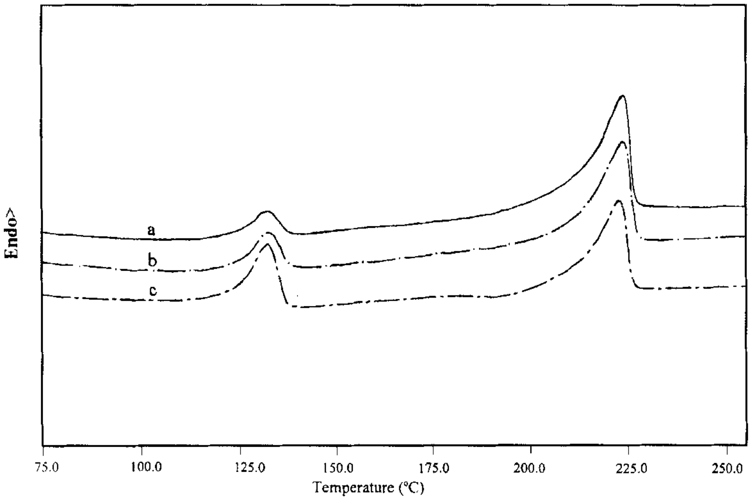

FIGURE 2 Thermograms of PA6/UHMWPE blends: (a) PA6/UHMWPE (90/10 Wt/Wt); (b) PA6/UHMWPE (80/20 Wt/Wt); (c) PA6/UHMWPE (70/30 Wt/Wt).

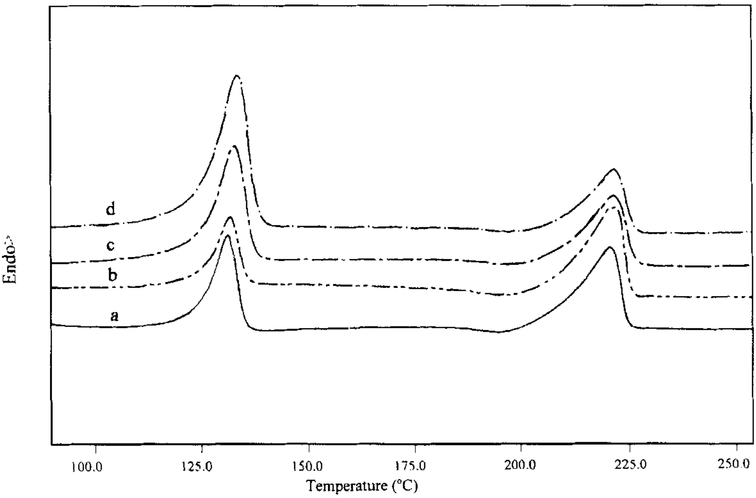

FIGURE 3 Thermograms of PA6/UHMWPE/HDPE-g-MAH blends: (a) PA6/UHMWPE/HDPE-g-MAH (80/20/5 Wt/Wt) $\Delta H = 71.9$ J/m; (b) PA6/UHMWPE/HDPE-g-MAH (80/20/10 Wt/Wt) $\Delta H = 67.6$ J/m; (c) PA6/UHMWPE/HDPE-g-MAH (80/20/15 Wt/Wt) $\Delta H = 64.0$ J/m; (d) PA6/UHMWPE/HDPE-g-MAH (80/20/20 Wt/Wt) $\Delta H = 61.7$ J/m.

This feature suggests that the miscibility of PA6 and UHMWPE was improved by addition of HDPE-g-MAH. And the ΔH of PA6 of the ternary blends decrease with the addition of HDPE-g-MAH. The higher the content of HDPE-g-MAH is, and the smaller the ΔH value of PA6. This feature can be tentativley explained as the fact that due to the chemical reaction of terminal amino groups of PA6 with anhydride groups of HDPE-g-MAH, hydrogen bonds present among the molecular chains of PA6 would weaken. As well known, the crystallization of PA6 mainly come from hydrogen bond interaction of intra-orinter-molecular chains. Weakening of hydrogen bond interaction of PA6 in the ternary blends should detract its crystallization.

Thermograms of PA6/UHMWPE and PA6/UHMWPE/HDPE-g-MAH blends extracted with decalin are shown in Figure 4. Figure 4(a) corresponds to the insoluble residue of PA6/UHMWPE. Only one peak of fusion at 224.4°C (Tm of PA6) appeared. This is due to fact that the blending component, UHMWPE was completely extracted by decalin from the PA6/UHMWPE blend. However, two peaks can be observed in the thermogram of the residue of PA6/UHMWPE/HDPE-g-MAH Figure 4(b). The peak at 222.1°C is attributed to the Tm of PA6, and the other one at 134.4°C is the melt peak of HDPE. This

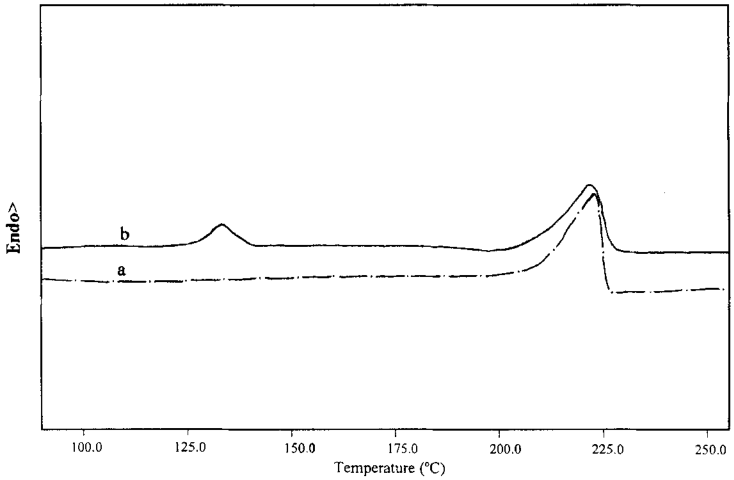

FIGURE 4 Thermograms of (a) PA6/UHMWPE (80/20 Wt/Wt) and (b) PA6/UHMWPE/HDPE-g-MAH (80/20/20 Wt/Wt) after extraction with decalin for 10 hours.

feature verifies that some chemical reactions occurred between MAH of HDPE-g-MAH and terminal amino groups of PA6 during the blending process of PA6 with UHMWPE and HDPE-g-MAH. The coupling reaction between two blending components made HDPE impossible to extract by decalin from the ternary blend.

Mechanical Properties and Related Morphology

The main mechanical properties of dried sample of PA6/UHMWPE and PA6/UHMWPE/HDPE-g-MAH blends, such as tensile strength (σ_b), Young's modulus (E_y), elongation at break (ε_b), flexural strength (σ_f), flexural modulus (E_f) are listed in Table I. It can be noted that when the weight ratio of PA6 and UHMWPE are same, the σ_b, E_y, ε_b, σ_f and E_f of PA6/UHMWPE/HDPE-g-MAH blends are higher than those of PA/UHMWPE blends. For example, the tensile strength of PA6/UHMWPE/HDPE-g-MAH (80/20/20) are 52.3 MPa, which is about 1.5 times that for the binary PA6/UHMWPE (80/20) (35.2 MPa). The improvement in tensile strength can be attributed to the change of their morphology and the improved interfacial adhesion. The interfacial adhesion can be further conformed by SEM photographs of fraction sections of specimens for tensile tests. As shown in Figure 5(a) the fracture surface of the PA6/UHMWPE specimen is smooth. The holes left by pulled out UHMWPE domains are round as these have suffered no deformation, and indicates that the interfacial strength is very low. In contrast to this feature, fracture surfaces of

TABLE I Mechanical properties of the PA6/UHMWPE and PA6/UHMWPE/HDPE-g-MAH blends

PA6/UHMWPE/ HDPE-g-MAH (Wt/Wt)	σ_b (*MPa*)	E_y (*MPa*)	ε_b (%)	σ_f (*MPa*)	E_f (*MPa*)
90/10/0	47.1	1190	19.4	67.7	1397
90/10/5	50.4	1202	39.2	69.1	1402
90/10/10	54.2	1217	132.1	72.4	1411
80/20/0	35.2	996	15.3	54.6	1181
80/20/5	42.3	1038	29.8	57.2	1208
80/20/10	48.5	1120	40.5	60.4	1219
80/20/15	50.8	1137	67.4	62.3	1228
80/20/20	52.3	1149	89.2	64.2	1235
70/30/0	28.7	809	18.8	40.2	1008
70/30/30	47.9	1056	127.8	54.7	1093

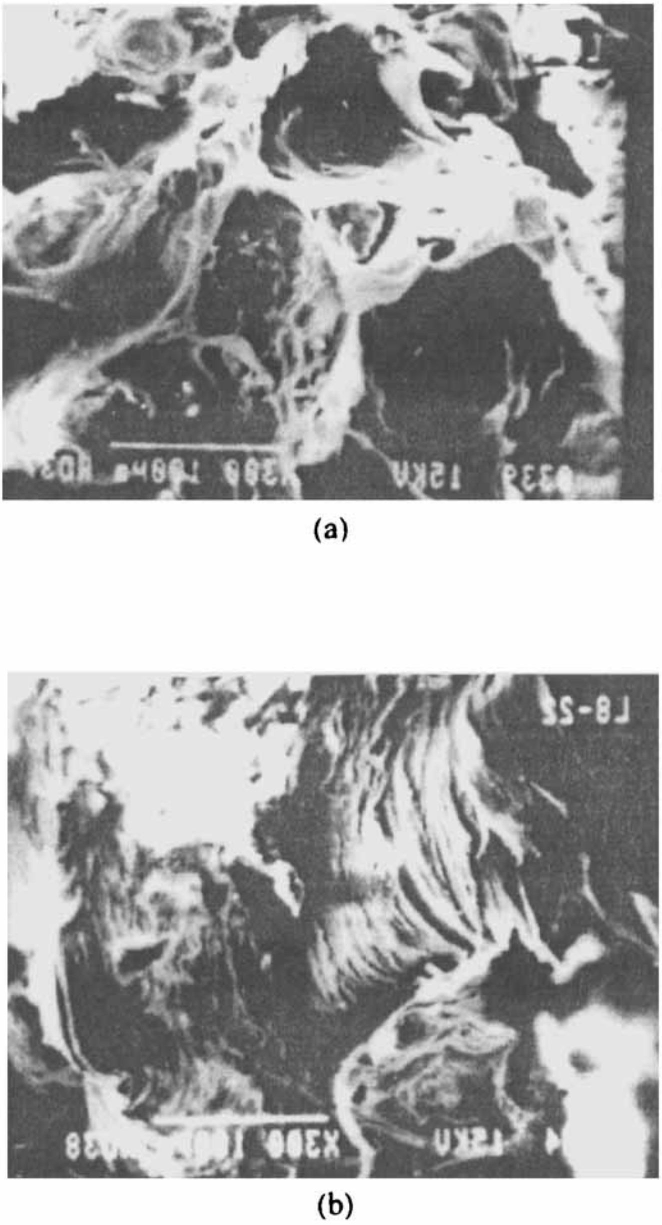

FIGURE 5 The morphologies of the tensile fracture surfaces: (a) PA6/UHMWPE (80/20 Wt/Wt); (b) PA6/UHMWPE/HDPE-g-MAH (80/20/20 Wt/Wt).

compatibilized specimens (Fig. 5b) are much rougher. Fibrous structure can be observed in the ternary blends. These results indicate that the interfacial strength is significantly improved, which is due to chemical reactions between MAH in HDPE-g-MAH and terminal amino groups of PA6 in PA6/UHMWPE/HDPE-g-MAH.

Izod impact strength of dried speciments of PA6/UHMWPE/HDPE-g-MAH blends with different amounts of HDPE-g-MAH are shown in Figure 6. We can see when the weight ratio of PA6 and UHMWPE are same, the more amount of HDPE-g-MAH, the higher the Izod impact strength of PA6/UHMWPE/HDPE-g-MAH is. For example, the impact strength of PA6/UHMWPE/HDPE-g-MAH (80/20/20) blends is about 15 J/m higher than that of PA6/UHMWPE (80/20) blends. This results can be also attributed to the homogeneous morphological dispersion and improved interfacial adhesion of PA6/UHMWPE/HDPE-g-MAH blends.

SEM micrographs of Izod fracture surfaces of PA6/UHMWPE binary and PA6/UHMWPE/HDPE-g-MAH ternary blends are reported in Figure 7. It is observed that the fracture surfaces of the noncompa-

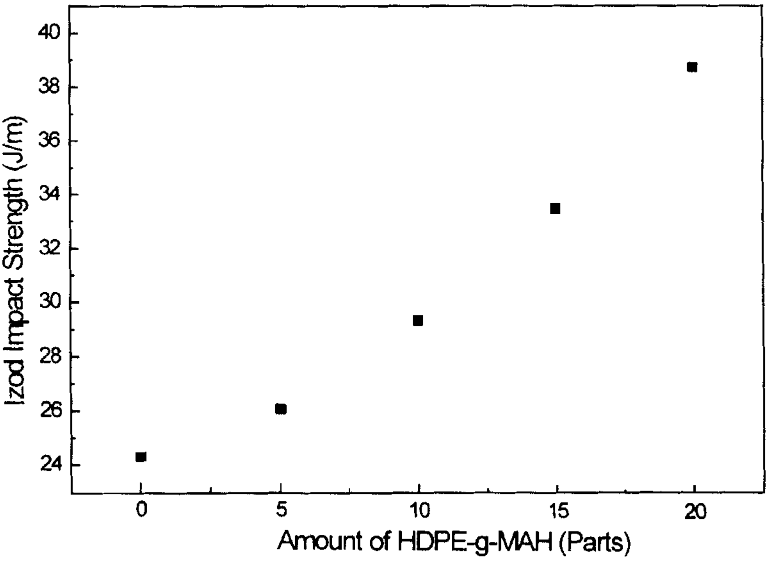

FIGURE 6 The relationship of Izod impact strength *versus* amounts of PA6 in PA6/UHMWPE/HDPE-g-MAH (PA6/UHMWPE 80/20 Wt/Wt) blends.

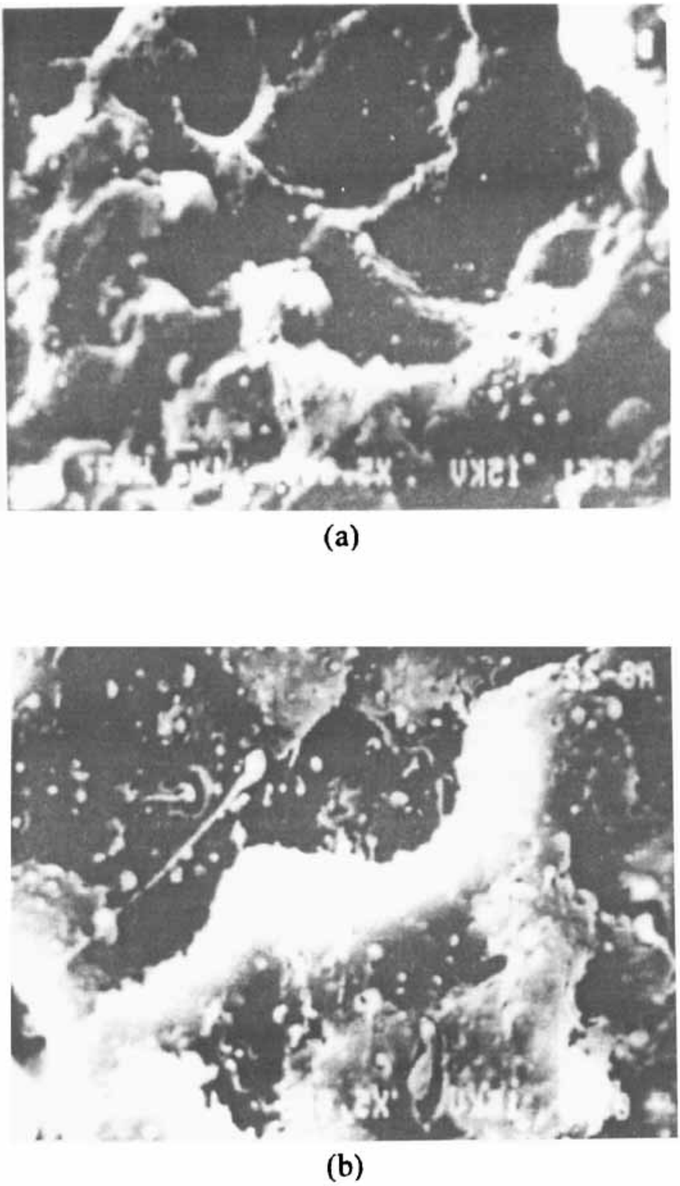

FIGURE 7 The SEM pictures of impact fracture surfaces: (a) PA6/UHMWPE (80/20 Wt/Wt); (b) PA6/UHMWPE/HDPE-g-MAH (80/20/20 Wt/Wt).

tibilized blend is relatively smooth, when HDPE-g-MAH is added to the blend, on the other hand, the fracture surfaces of the compatibilized blend is rather rough. SEM photomicrogrpahs of fracture surfaces for compatibilized blend shows extensive matrix yielding, and that for noncompatibilized shows very little matrix yielding. These features suggest that interfacial adhesion between PA6 matrix and UHMWPE domains is improved after addition of HDPE-g-MAH.

CONCLUSIONS

1. The morphology of PA6/UHMWPE blend is significantly changed after addition of HDPE-g-MAH. The average size of UHMWPE particles reduced from 30–35 μm to 2–4 μm and more homogeneous dispersion of UHMWPE domains was observed.
2. Mechanical properties of PA6/UHMWPE/HDPE-g-MAH blends are superior to PA6/UHMWPE blends. This can be attributed to the homogeneous morphological dispersion and the improved interfacial adhesion between PA6 and UHMWPE in PA6/UHMWPE/HDPE-g-MAH blends.
3. Thermal analysis shows misibility of PA6 and UHMWPE was improved by addition of HDPE-g-MAH, and the heat of fusion for PA6 decreased as compatibilizer contractions increased. The chemical reactions taken place between anhydride groups of HDPE-g-MAH and terminal amino groups of PA6, which could be verified by the appearance of melt peak of the HDPE in PA6/UHMWPE/HDPE-g-MAH blends extracted with decalin.

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