

# Morphology, Thermal Behavior, and Mechanical Properties of PA6/UHMWPE Blends with HDPE-*g*-MAH as a Compatibilizing Agent

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**ABSTRACT:** A functionalized high-density polyethylene (HDPE) with maleic anhydride (MAH) was prepared using a reactive extruding method. This copolymer was used as a compatibilizer of blends of polyamide 6 (PA6) and ultrahigh molecular weight polyethylene (UHMWPE). Morphologies were examined by a scanning electron microscope. It was found that the dimension of UHMWPE and HDPE domains in the PA6 matrix decreased dramatically, compared with that of the uncompatibilized blending system. The size of the UHMWPE domains was reduced from 35  $\mu\text{m}$  (PA6/UHMWPE, 80/20) to less than 4  $\mu\text{m}$  (PA6/UHMWPE/HDPE-*g*-MAH, 80/20/20). The tensile strength and Izod impact strength of PA6/UHMWPE/HDPE-*g*-MAH (80/20/20) were 1.5 and 1.6 times as high as those of PA6/UHMWPE (80/20), respectively. This behavior could be attributed to chemical reactions between the anhydride groups of HDPE-*g*-MAH and the terminal amino groups of PA6 in PA6/UHMWPE/HDPE-*g*-MAH blends. Thermal analysis was performed to confirm that the above chemical reactions took place during the blending process. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 232–238, 2000

**Key words:** PA6; UHMWPE; compatibilizer; blend

## INTRODUCTION

Multicomponent polymeric materials are frequently made by blending two or more miscible or immiscible polymers. It is very difficult to obtain good dispersion in polymer blends in which components are immiscible, particularly for combinations of polar polymers with nonpolar polymers. Due to their difference of polarities, the blends

usually separate into two distinct phases. The major component forms a matrix and the minor component forms domains. The size and shape of the domains greatly depend upon several factors, such as the ratio of the melt viscosities of components, interfacial tension and adhesion, and processing parameters. The final properties of these blends are strongly affected by the volume fraction of the components, the size and shape of domains, and the interfacial tension and adhesion between the two phases. Many publications<sup>1–7</sup> reported that the presence of a block or graft copolymer, which has similar structure or can react chemically with the blending components, could provide lowering of the interfacial energy, improvement of the interfacial adhesion between

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the two phases, and reduction of the size of dispersed particles in the blends.

Polyamide 6 (PA6) and ultrahigh molecular weight polyethylene (UHMWPE) are two important commercial polymers. PA6 is polycaprolactam, an engineering plastic used to make electrical, mechanical, and automotive parts due to its very high strength, wear and heat resistance, and ease of fabrication and processing. However, its impact strength, dimensional stability, and barrier properties to moisture are very poor, which limits its application in many fields. The above shortcomings of PA6 can be compensated by blending it with UHMWPE. As is well known, UHMWPE has high strength and modulus, high barrier properties to moisture, good wear resistance, and excellent impact strength at low temperature. Unfortunately, UHMWPE is immiscible with PA6. By simple blending of these polymers, we obtained a coarse-phase structure with low interfacial adhesion, leading to poor mechanical properties of the blend. Therefore, it is necessary to incorporate into the blended system a compatibilizer which forms bonds at the interface and imparts to the blend good mechanical properties. The wear resistance of PA6/UHMWPE blends, without addition of any compatibilizer, was examined by Tadao et al.<sup>8</sup> and Nidenori.<sup>9</sup>

In this work, we report the preparation of PA6/UHMWPE blends compatibilized with a high-density polyethylene (HDPE)-*g*-maleic anhydride (MAH) copolymer and the morphology, thermal behavior, and mechanical properties of PA6/UHMWPE/HDPE-*g*-MAH blends. The main purpose was aimed at understanding the effect of the content of the compatibilizer on the morphology, thermal behavior, and mechanical properties of this blending system.

## EXPERIMENTAL

### Materials

The PA6 ( $M_w = 3.5 \times 10^4$ ) used in this work was purchased from the Hei Longjiang Nylon Plant (Harbin, China). UHMWPE ( $M_w = 1.5 \times 10^6$ ) was kindly supplied by the Shanghai Gaoqiao Co (Shanghai, China). The HDPE used in this experiment was supplied by the Liaoning Panjin Petrochemical Co. (Panjin, China): Its trade name is HDPE5070 and its melt flow index is about 18 g/10 min. MAH and dicumyl peroxide (DCP) were commercial reagents, analytically pure. HDPE-*g*-

MAH was prepared in our laboratory by reactive grafting technology in an SHJ-30 reactive mode corotating twin-screw extruder with  $L/D = 44$  and  $D = 30$  mm; the processing conditions were the following: temperature (°C): 135, 140, 160, 180, 180, 180, 180, 180, 180, 180, and 175 from hopper to die, respectively; and screw rotation (rpm): 75. The HDPE-*g*-MAH contains 0.62% MAH by weight, as determined by acid–base titration.

### 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 of the components in a home-made 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 ratios 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, and 70/30/30.

### Measurements of Mechanical Properties

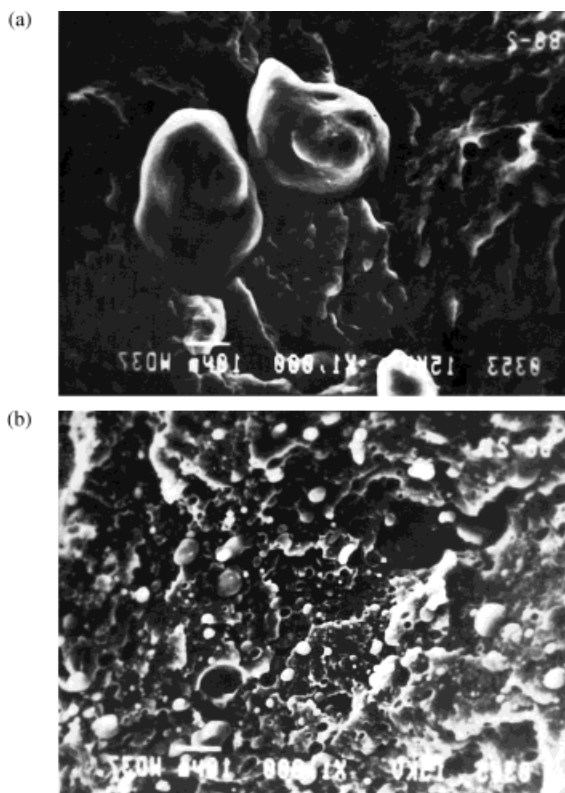
Melt-blended pellets were used to prepare mechanical test specimens using a JSWF17SA injection mold (made in Japan). Dumbbell-shaped specimens were used to measure the tensile strength and elongation at break of a sample. Tests were carried out on an Instron 1121 tester at room temperature with a crosshead speed of 50 mm/min. Measurements of the flexural modulus and strength of a sample were also performed with the same tester on the basis of ISO178-1975E. Determinations of the Izod impact strength 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 them in a vacuum oven kept at 80°C for 12 h.

### Morphological Observation

A scanning electron microscope, JXA-840 (made in Japan), was used to observe the morphologies of the blends. Before observation, the examined sections were coated with gold in a vacuum.

### Thermal Analysis

Thermal analysis was performed on a Perkin-Elmer DSC II apparatus. Thermograms were obtained by heating a sample from 50 to 250°C at a



**Figure 1** SEM micrographs of (a) PA6/UHMWPE (80/20 wt/wt) and (b) PA6/UHMWPE/HDPE-g-MAH (80/20/20 wt/wt).

heating rate of 10°C/min. The weight of a sample is about 10 g. All measurements were performed under a nitrogen atmosphere.

## RESULTS AND DISCUSSION

### Morphology

Figure 1 shows SEM micrographs of the PA6/

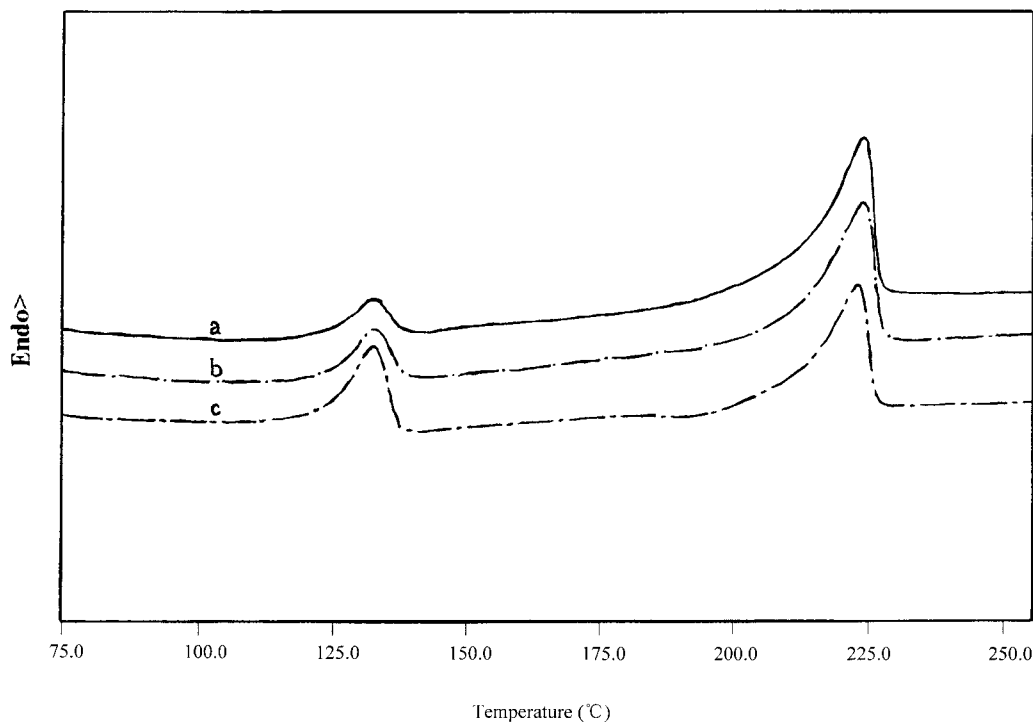
UHMWPE and PA6/UHMWPE/HDPE-g-MAH blends. The matrix is PA6 and the dispersed phase is UHMWPE or HDPE-g-MAH. The average size of the PE domains in the PA6/UHMWPE/HDPE-g-MAH blends is much smaller than that in the PA6/UHMWPE blends. In the compatibilized ternary blend, the diameter of the PE particles is about 2–4  $\mu\text{m}$  [Fig. 1(b)], but is as big as 30–35  $\mu\text{m}$  in the binary blend [Fig. 1(a)]. Homogeneous dispersion of the PE domains can also be observed in the PA6/UHMWPE/HDPE-g-MAH blend. For the PA6/UHMWPE binary blend, interfaces between the PA6 matrix and the UHMWPE domains are much clearer and smoother. However, interfaces of the PA6/UHMWPE/HDPE-g-MAH blend are rough and indistinct. The above features strongly suggest that the miscibility of PA6 and UHMWPE in the PA6/UHMWPE/HDPE-g-MAH blends is improved by compatibilization with HDPE-g-MAH, which probably originates from the chemical reaction between the anhydride groups of HDPE-g-MAH and terminal amino groups of PA6 in the PA6/UHMWPE/HDPE-g-MAH blends.

### Mechanical Properties

The main mechanical properties of the dried samples of the PA6/UHMWPE and PA6/UHMWPE/HDPE-g-MAH blends, such as tensile strength ( $\sigma_b$ ), Young's modulus ( $E_y$ ), elongation at break ( $\varepsilon_b$ ), flexural strength ( $\sigma_f$ ), flexural modulus ( $E_f$ ), and Izod impact strength, are listed in Table I. It can be noted that, when the weight ratio of PA6 and UHMWPE is 1 : 1, the modulus and strength of the blending system increased with the addition of HDPE-g-MAH. For example, the tensile strength of PA6/UHMWPE/HDPE-g-MAH (80/20/20) is 52.3 MPa, which is nearly 1.5 times the

**Table I** Mechanical Properties of the PA6/UHMWPE and PA6/UHMWPE/HDPE-g-MAH Blends

PA6/UHMWPE/HDPE-g-MAH (wt/wt)	$\sigma_b$ (MPa)	$E_y$ (MPa)	$\varepsilon_b$ (%)	$\sigma_f$ (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 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).

value of the blend of PA6/UHMWPE (80/20). This feature can be tentatively explained as improvement of interfacial adhesion and homogeneous dispersion of the domains of UHMWPE and HDPE-*g*-MAH in PA6/UHMWPE/HDPE-*g*-MAH. As shown in Table I, HDPE-*g*-MAH is also a good toughening agent for PA6/UHMWPE blends. With addition of HDPE-*g*-MAH, the Izod impact strength of a PA6/UHMWPE blending system increases gradually. For instance, the impact strength of the PA6/UHMWPE/HDPE-*g*-MAH (80/20/20) blend is about 15 J/m higher than that of the PA6/UHMWPE (80/20) blend. This improvement can be also explained as due to the homogeneous morphological dispersion and improved interfacial adhesion of the PA6/UHMWPE/HDPE-*g*-MAH blending system.

### Thermal Properties

DSC thermograms of the PA6/UHMWPE binary blends are shown in Figure 2. The melting temperature of UHMWPE and PA6 remains constant in different compositions. This feature suggests that PA6 and UHMWPE are completely immiscible. The melting temperature ( $T_m$ ), crystallization temperature ( $T_c$ ), and melting enthalpy

( $\Delta H$ ) of UHMWPE, HDPE-*g*-MAH, and PA6 are summarized in Table II. The  $T_m$  values of the pure UHMWPE and HDPE-*g*-MAH are 139.0 and 135.2°C, respectively. After blending them with PA6, only one PE melting peak appeared in their DSC heating thermograms. There is also no widening feature found in these peaks, compared with peaks of the pure UHMWPE and HDPE-*g*-MAH shown in Figure 3.  $T_m$  values of PE of the ternary blends are smaller than those of the pure UHMWPE or HDPE-*g*-MAH. In the cooling thermograms of the ternary blending system, two crystallization peaks, corresponding to UHMWPE and HDPE-*g*-MAH, appeared. Their  $T_c$  values are also smaller than is the related value of the pure UHMWPE or HDPE-*g*-MAH. The melting enthalpies per gram PE of the ternary blends are always less than the value of the pure UHMWPE or HDPE-*g*-MAH.

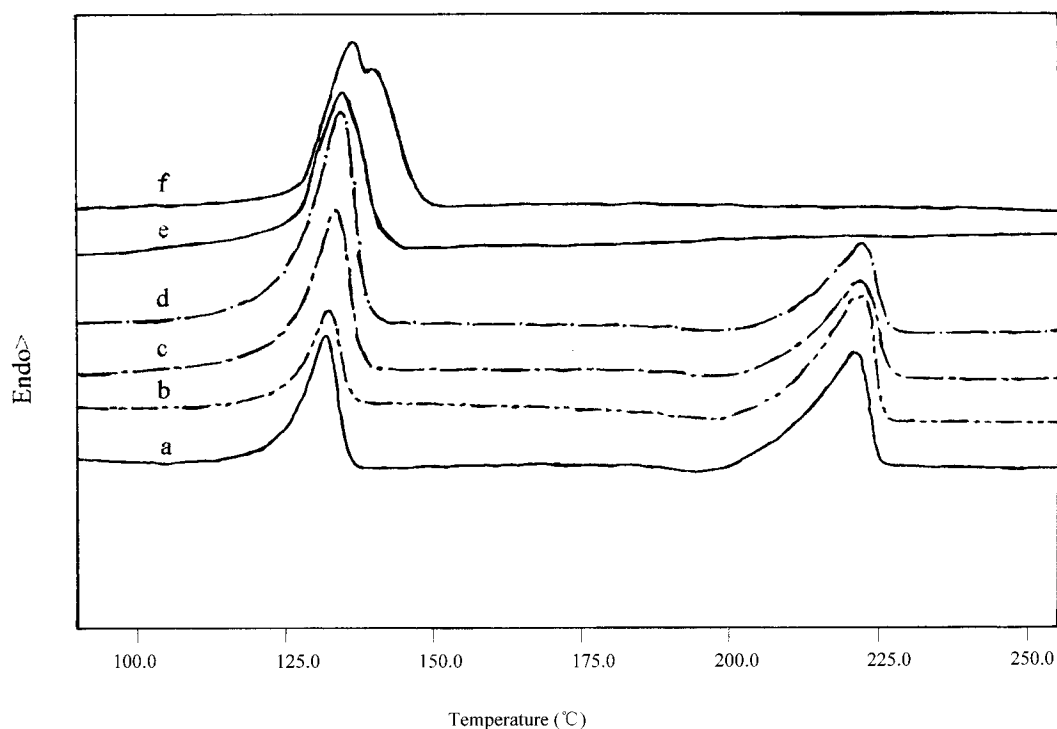
All these features can be explained as follows: UHMWPE and HDPE-*g*-MAH of PA6/UHMWPE/HDPE-*g*-MAH ternary blends could combine together as a dispersed phase, but they could not cocrystallize. Due to the chemical interaction of the terminal amino groups of PA6 and the anhydride groups of HDPE-*g*-MAH, some extent of the

**Table II** Thermal Parameters of PA6, UHMWPE, HDPE-*g*-MAH, PA6/UHMWPE, and PA6/UHMWPE/HDPE-*g*-MAH Blends

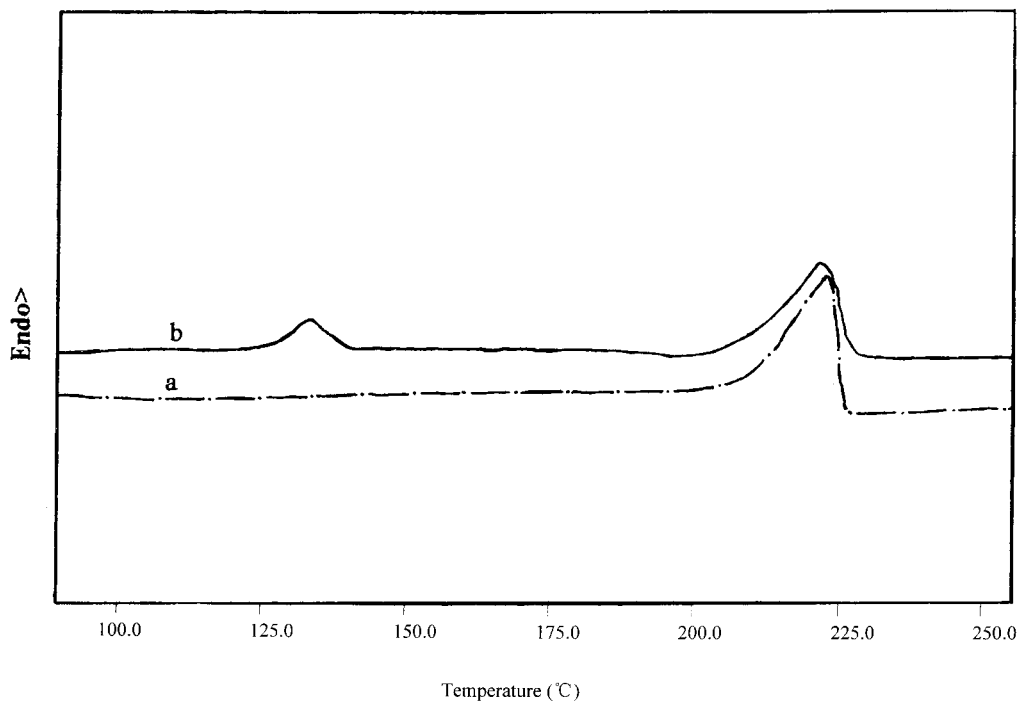
PA6/UHMWPE/ HDPE- <i>g</i> -MAH (wt/wt)	PA6			UHMWPE		HDPE- <i>g</i> -MAH		UHMWPE + HDPE- <i>g</i> -MAH
	$T_m$ (°C)	$T_c$ (°C)	$\Delta H$ (J/g)	$T_m$ (°C)	$T_c$ (°C)	$T_m$ (°C)	$T_c$ (°C)	$\Delta H$ (J/g)
100/0/0	224.4	175.1	87.1					
0/100/0				139.0	118.5			182.8
0/0/100						135.2	116.3	181.3
80/20/5	223.1	185.4	71.9	132.6	117.9	132.6	114.6	121.0
80/20/10	222.7	186.1	67.7	132.9	117.5	132.9	113.8	136.4
80/20/15	222.5	186.4	64.0	133.5	117.4	133.5	112.6	150.2
80/20/20	221.9	186.5	61.7	134.3	117.0	134.3	111.7	165.3

coupling structure would be produced between the PA6 matrix and PE domains, which would hinder the movement and fold of the PE molecular chains and its crystallization would become much more difficult. Therefore, the perfection and the crystallinity degree of the PE crystals would be decreased, which was reflected in lowering of its  $T_m$ ,  $T_c$ , and  $\Delta H$ . The  $T_m$ ,  $T_c$ , and  $\Delta H$  of the

PA6 of the PA6/UHMWPE/HDPE-*g*-MAH ternary blends, as a function of composition, are also shown in Table II. With addition of HDPE-*g*-MAH, the  $T_m$  values of PA6 decrease somewhat, which suggests that perfection of the PA6 crystals is reduced. However, the changing trends of the  $T_c$  and  $\Delta H$  of PA6 are completely different from PE. The  $T_c$  of PA6 in the ternary blends is about



**Figure 3** Thermograms of UHMWPE, HDPE-*g*-MAH, and PA6/UHMWPE/HDPE-*g*-MAH blends: (a) PA6/UHMWPE/HDPE-*g*-MAH (80/20/5 wt/wt); (b) PA6/UHMWPE/HDPE-*g*-MAH (80/20/10 wt/wt); (c) PA6/UHMWPE/HDPE-*g*-MAH (80/20/15 wt/wt); (d) PA6/UHMWPE/HDPE-*g*-MAH (80/20/20 wt/wt); (e) HDPE-*g*-MAH; (f) UHMWPE.



**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 h.

286°C, which is 10°C higher than the  $T_c$  value of the pure PA6. Also, the  $\Delta H$  of the PA6 of the ternary blends decreases with the addition of HDPE-*g*-MAH. The higher the content of HDPE-*g*-MAH the smaller is the  $\Delta H$  value of PA6. This feature can be tentatively explained as being due to the chemical reaction of terminal amino groups of PA6 with anhydride groups of HDPE-*g*-MAH and the hydrogen bonds present among the molecular chains of PA6 would weaken. As is well known, the crystallization of PA6 comes mainly from hydrogen-bond interaction of intra- or intermolecular chains. Weakening of the hydrogen-bond interaction of PA6 in the ternary blends should inhibit its crystallization.

Thermograms of the 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 225°C ( $T_m$  of PA6) appeared. This is due to 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 [Fig. 4(b)]. The peak at 225°C is attributed to the  $T_m$  of PA6, and the other one at 124°C is the melting peak of HDPE. This feature verifies that

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

## CONCLUSIONS

1. HDPE-*g*-MAH is a good compatibilizer for the PA6/UHMWPE blending system. After addition of HDPE-*g*-MAH, the morphology of the PA6/UHMWPE blends is significantly changed. The average size of the PE particles was reduced from 30–35 to 2–4  $\mu\text{m}$  and a more homogeneous dispersion of the PE domains was obtained.
2. Mechanical properties, such as tensile strength, Young's modulus, elongation at break, flexural strength, flexural modulus, and Izod impact strength, of the compatibilized PA6/UHMWPE blends are superior to those of the PA6/UHMWPE binary blends. The extent of improvement of the mechanical properties is dependent upon

the quantity of the HDPE-*g*-MAH materials.

3. The miscibility of PA6 and UHMWPE was improved by addition of HDPE-*g*-MAH. Decrease in the heat of fusion of PA6 in the ternary blend is due to that the terminal amino groups of PA6 react with the anhydride groups of HDPE-*g*-MAH: The interference of HDPE chains causes decrease in the heat of fusion of PA6. The chemical reactions taking place between the anhydride groups of HDPE-*g*-MAH and the terminal amino groups of PA6 could be verified by the appearance of the melting peak of HDPE in the PA6/UHMWPE/HDPE-*g*-MAH blends extracted with decalin.
4. Changes of the morphology, mechanical properties, and thermal behavior of the compatibilized PA6/UHMWPE system originated from improvement of the interfacial adhesion, which was induced by the fact that coupling reactions between the anhydride groups of HDPE-*g*-MAH and the terminal amino groups of PA6 happened during the melt-blending process. The possible chemical reactions were verified by

DSC characterization with the ternary blending sample extracted with the solvent, decalin.

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