

Study of a Compatibilized Ultra-High-Molecular-Weight Polyethylene and Polyurethane Blend

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Received 31 July 2000; accepted 14 November 2000

ABSTRACT: Ultra-high-molecular-weight polyethylene (UHMWPE) and thermoplastic polyester-type polyurethane (PU) were blended with polyethylene-grafted maleic anhydride (PE-*g*-MAH) added as a compatibilizer. A dual roller was used as a mixer, and all specimens were produced by the compression molding method. It was found that without compatibilizer, UHMWPE and PU were immiscible polymers and mixing PE-*g*-MAH reduced the size of the dispersed PU domains by a factor of 10 to reach 0.5–5 μm and caused a more uniform distribution of the PU phase in the UHMWPE matrix. Also, PE-*g*-MAH influenced the crystallinity of UHMWPE, increased the amorphous region in the UHMWPE phase, and improved interfacial adhesion. The threshold concentration of compatibilizer was 10 wt %, and the compatibilized UHMWPE/PU composites had improved mechanical properties and lower wear rate than the uncompatibilized composite. At some ratio points, compatibilizer composites even had better wear-resistance properties than pure UHMWPE. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3290–3295, 2001

Key words: UHMWPE; thermoplastic polyurethane; composite; compatibilization; wear resistance

INTRODUCTION

Ultra-high-molecular-weight polyethylene (UHMWPE) is a thermoplastic polymer with outstanding features. It possesses excellent mechanical properties, very high impact strength, good sliding, chemical resistance, and distinguished wear-resistance properties. Polyurethane (PU) is a thermoplastic polymer with good toughness and a high elasticity of elastomer, and it can be processed after being heated. PU also has the best wear-resistance properties among elastomers, so it has been widely used in many different fields. Mixing UHMWPE and PU is plastic–rubber type blending and could widen the range of wear-resistance materials.

However, while blending UHMWPE and PU, some problems exist:

1. The difference in molecular weight: UHMWPE has very large molecular weight, at least above million grade, much higher than PU and other blend components. Because of its high molecular weight, UHMWPE has serious intertwinement, which leads to a high melt viscosity, which makes it difficult to blend UHMWPE and other polymers. While blending UHMWPE and other polymers, one solution to this problem is to use the melt casting method. This method can increase possible physical crosslinking, which is entanglement as a result of mixing in the solution blending.^{1,2} Besides, S.H. Teoh, using biaxially stretched UHMWPE membrane immersed into PU dimethylformamide (DMF) solvent, showed

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Journal of Applied Polymer Science, Vol. 81, 3290–3295 (2001)
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that the PU molecule penetrates micro-holes on UHMWPE membrane to form an interpenetrating network (IPN) network structure.³

2. The difference in polarity: UHMWPE is regarded as a nonpolar polymer, whereas PU is a polar one. It is well known that a difference in polarities will make polymer blends separate into distinct phases, and interfacial adhesion of the components will be very poor. One way usually used to improve miscibility is to add compatibilizer. Some copolymers or graft polymers that possess reactive groups and have similar chemical structures can reduce the size of dispersed domains and enhance interfacial adhesion.⁴⁻⁶ Another way is to use gas treatment or plasma graft technology. Through the treatment of polymer particles in special gasses, such as fluorine, oxygen, argon, and so on,^{7,8} some polar reactive groups can be introduced onto the surface of polymers. This also can lower the interfacial energy and improve the microscopic morphology when treated polymers blend with other components.

Because UHMWPE and PU are immiscible polymers, in this study, we used a dual roller as a mixer and added polyethylene-grafted maleic anhydride (PE-*g*-MAH) as a compatibilizer. By means of high shear force produced by the dual roller and the compatibilization of PE-*g*-MAH, our goal was to improve the miscibility of UHMWPE and PU and assess the mechanical, thermal, and wear-resistance properties of the composite.

EXPERIMENTAL

Materials

The UHMWPE used in this study was MII (viscosity-average molecular weight = 2×10^6) produced in Beijing No. 2 Auxiliary Agent Factory (China). Polyester-type PU was JZ85 obtained from Tianjin Polyurethane Factory (China). JZ85 is a thermoplastic PU elastomer of polyester of adipic acid. Its shore hardness is 85, and its relative density is 1.22. High-density polyethylene (HDPE) was from Yanshan Petroleum Factory (Beijing, China). Its melting index was 4.0. The investigated compatibilizer was HDPE grafted with 2 wt % maleic anhydride (PE-

g-MAH). The compatibilizer was produced in the laboratory with the reactive extrusion method.

Blending and Preparation

Prior to mixing, PU was dried at 80°C for 4 h. Blending was done with an open-to-air-type dual roller, which operated at a temperature of 180°C; the dual roller's rotation speed was 20 rounds/min. At first, UHMWPE was placed on the dual roller to melt for 2 min. Then, PU and PE-*g*-MAH were added. The total mixing procedure took 10 min. A thermal gauge was used to measure the temperature on the surface of the dual roller before and after the mixing procedure. When the surface temperature reached 180°C, by decreasing heating power to compensate heat loss to air, we kept the processing temperature constant. After the mixing procedure, the composite was preheated to 180°C for 15 min and was then molded to a plate at a pressure of 70 MPa for 10 min. After molding was finished, the composite was cooled to room temperature at a cooling speed of 10°C/min.

All specimens for morphology, thermal, mechanical, and wear tests were cut and machined from a final compression-molded material plate. In this study, the weight percent of compatibilizer was the weight of PE-*g*-MAH divided by the total weight of UHMWPE and the PU components. That is, UHMWPE/PU/PE-*g*-MAH with a weight ratio of 75/25/10 was the same as UHMWPE/PU (75/25) with 10 wt % PE-*g*-MAH.

Characterization

Morphology Observation

The morphology of materials was observed by a scanning electron microscope (JEOL JSM-6301F, Japan). The composite specimens were fractured in

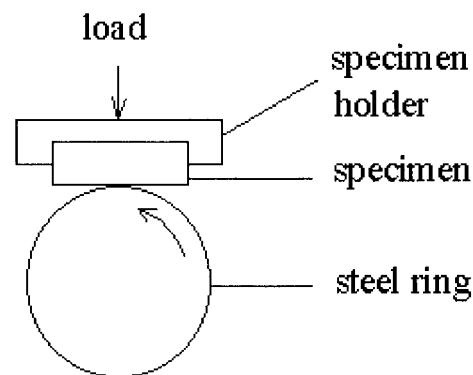


Figure 1 Schematic diagram of wear testing.

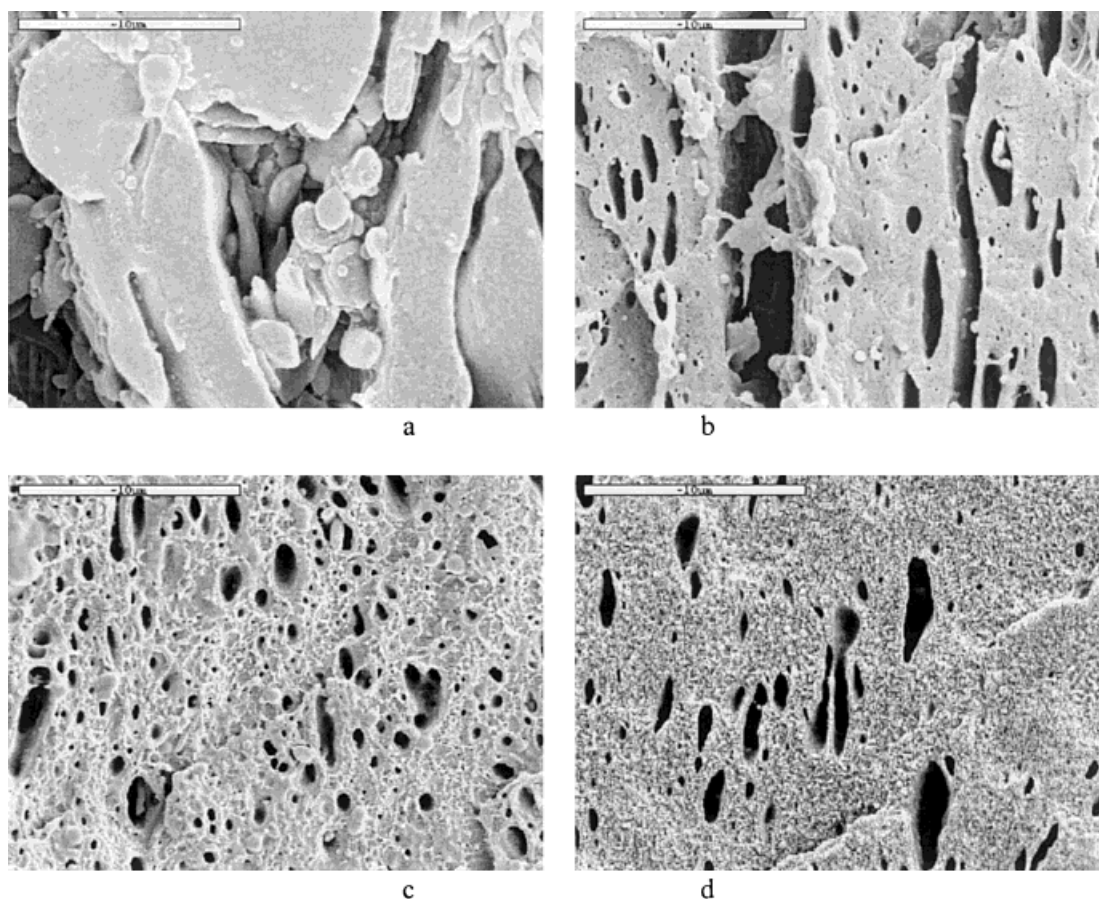


Figure 2 SEM photos of the UHMWPE/PU/PE-g-MAH composite (the white bar at the left top corner of each image represents 10 μm). UHMWPE/PU/PE-g-MAH: (a) 75/25/0, (b) 75/25/5, (c) 75/25/10, and (d) 75/25/20.

liquid nitrogen, and the fractured sides were immersed in N,N' -dimethylformamide (DMF) to etch away the PU phase. The specimens were thoroughly dried in a vacuum and were coated with gold prior to scanning electron microscopy (SEM) observation.

Thermal Analysis

The differential scanning calorimetry (DSC) experiment was carried out with a DSC 2910 (TA Instrument, USA). Samples of 5 mg were heated from 300 to 500 K at a scanning rate of 10 K/min under a nitrogen atmosphere.

Test of Mechanical Properties

All specimens were conditioned at 25°C for at least 48 h before testing. Dumbbell-shaped specimens were cut from a molded UHMWPE/PU composite

plate. Tensile tests were carried out on an LJ-1000 tensile tester (Guangzhou Testing Instrument Factory, China) at a crosshead speed of 50 mm/min, according to ISO 527/1-1993E.

Wear-Resistance Test

Sliding wear tests were done on an M200 wear tester (Chengde, China) at 25°C. The wear test method is shown in Figure 1. A steel ring was rotated at the speed of 200 rounds/min. The diameter of the steel ring was 40 mm, and the thickness was 10 mm. During the test, load exerted on the specimen was 20 kg, and the test lasted 2 h. The composite specimen blocks were weighed to the nearest 0.1 mg before and after the wear testing. Net wear losses were adopted to evaluate wear-resistance properties.

Table I DSC Data for the UHMWPE/PU Composite

| UHMWPE/PU/PE-g-MAH | UHMWPE T_m (°C) | UHMWPE PE-g-MAH ΔH_m (J/g) |
|--------------------|-------------------|------------------------------------|
| 100/0/0 | 139.84 | 183.2 |
| 75/25/0 | 132.98 | 141.4 |
| 75/25/5 | 132.94 | 125.2 |
| 75/25/10 | 130.16 | 128.0 |
| 75/25/20 | 129.31 | 127.5 |

RESULTS AND DISCUSSION

Morphology

Typical morphologies of UHMWPE/PU blends are shown in Figure 2. For UHMWPE/PU blends, the UHMWPE phase forms the matrix, and the PU phase is segregated into spherical domains. Because PU was already solved away by DMF, black holes represent the original PU phase. The SEM photo of UHMWPE/PU without compatibilizer shows that the PU phase was separated into large particles, ranging from 5 to 50 μm , in the UHMWPE matrix. For the compatibilized UHMWPE/PU blends, a significant difference was observed in the morphology. The mean size of the PU phase decreased by a factor of 10 to reach 0.5–5 μm . In comparison to the composite without compatibilizer, the dimension of the minor phase not only decreased but also attained a more uniform distribution in blends that contained compatibilizer. Also, although distribution of the PU phase was greatly improved, the surface of the holes left by the DMF solution appeared to be smooth. The dispersed minor phase basically remained oval in shape at cross-section, so it could be derived that the PU phase separated in blends was not made up of spherical particles. It is believed that this phenomenon was mainly caused by high shear force produced by the dual roller, which stretched the PU phase into long particles during mixing and made them oriented along the direction of shear force.

Thermal Analysis

The melting temperature (T_m) and the melting enthalpy (ΔH_m) of UHMWPE and PE-g-MAH are summarized in Table I. When UHMWPE and PU kept the same weight ratio of 75/25, the T_m of UHMWPE decreased steadily when the compatibilizer PE-g-MAH was gradually increased. As the content of PE-g-MAH in the composite

reached 10 wt %, T_m decreased sharply from 132.94 to 130.16°C. Whereas at other ratio points, T_m just decreased at a slower speed. As shown in the DSC thermogram in Figure 3, there was only one sharp melting peak, which suggests high compatibilization of UHMWPE and PE-g-MAH. The reason could be that UHMWPE and PE-g-MAH have the same main chain chemical structure, and only a few maleic anhydride groups were grafted onto the HDPE chain. Because there was no indication of the two melting peaks of UHMWPE and PE-g-MAH, it was difficult to distinguish the ΔH_m 's of UHMWPE and PE-g-MAH, so ΔH_m includes the melting enthalpy of both. The ΔH_m for 100% crystallinity of polyethylene (PE) was calculated as 293 J/g.⁹ Adding compatibilizer decreased the crystallinity of UHMWPE. When two polymers have an interaction in amorphous-region domains, T_m decreases in blends.¹⁰ The slightly decreased T_m of PE is caused by the amorphous interaction in the PE phase.¹¹ Clearly, the interaction could only happen between the anhydride groups of PE-g-MAH and the isocyanate groups of the PU component, which mainly emerge at the interface of the UH-

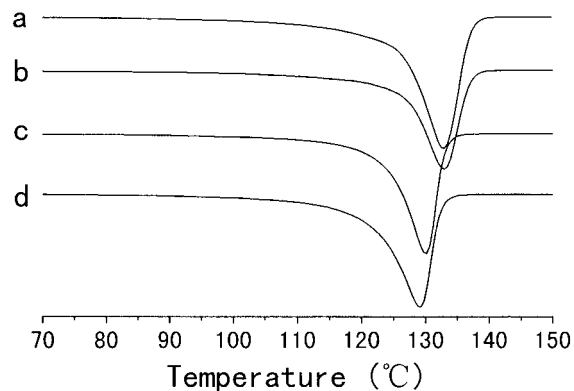


Figure 3 DSC thermogram of the UHMWPE/PU composite. UHMWPE/PU/PE-g-MAH: (a) 75/25/0, (b) 75/25/5, (c) 75/25/10, and (d) 75/25/20.

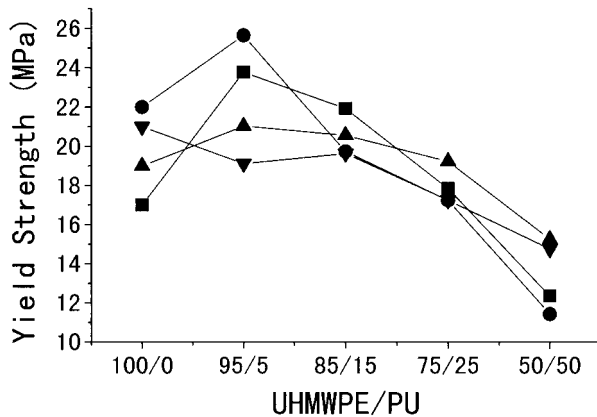


Figure 4 Tensile yield strength of the UHMWPE/PU composite. PE-g-MAH content: (■) 0, (●) 5, (▲) 10, and (▼) 20 wt %.

MWPE matrix and the PU domain. Because of this coupling interaction, the UHMWPE molecular movement was hindered, which resulted in the reduction of the crystallinity of UHMWPE and an increase in the amorphous region in the UHMWPE matrix near the interface.

Tensile Properties

Figure 4 shows the tensile yield strength of the UHMWPE/PU composite when different ratios of compatibilizer were added. All yield strength values almost had a tendency to decrease with the increase in the PU component in the blend. One exception was that although the ratio of the UHMWPE/PU composite was 95/5, the composite could reach the maximum value in the series through the addition of the same amount of compatibilizer. The yield strength of the pure UHMWPE was 17 MPa. The blend of UHMWPE/PU (95/5), with 5 wt % compatibilizer added, had a yield value of 25.6 MPa. Figure 4 shows that when the ratio of UHMWPE/PU was kept the same, mixing different amounts of compatibilizer could not make the yield strength value have significant difference.

The elongation values at break (ϵ_b 's) of the composite are shown in Figure 5. The figure reveals that the compatibilizer had a much more noticeable effect on ϵ_b than on the yield value. When compatibilizer was not added, at all ratio points UHMWPE/PU had very low ϵ_b . Compatibilizer at 5 wt % still had no effect on compatibilization until PE-g-MAH reached 10 wt %.

In the tensile test, the data on ϵ_b , which is a sensitive indication of component interface adhe-

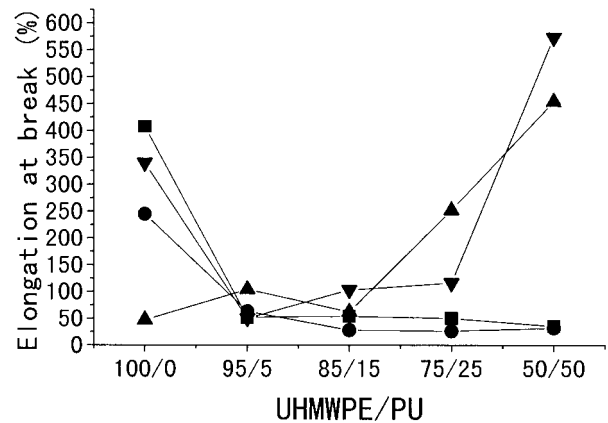


Figure 5 ϵ_b of the UHMWPE/PU composite. PE-g-MAH content: (■) 0, (●) 5, (▲) 10, and (▼) 20 wt %.

sion in the polymer alloys, supported the view that UHMWPE and PU were immiscible and PE-g-MAH could be a compatibilizer for the blend. It was interesting that 10 wt % compatibilizer became a critical content. From the SEM photos and DSC analysis, we also found that 10 wt % PE-g-MAH was key point in compatibilization. This may mean that to achieve perfect compatibilization, a certain content of polar anhydride groups must be introduced into the UHMWPE/PU composite.

Wear-Resistance Test

Wear results are presented in Figure 6. The wear rates of the composite significantly increased after a weight ratio of the UHMWPE/PU composite of 85/15 was reached. With low content of PU, at

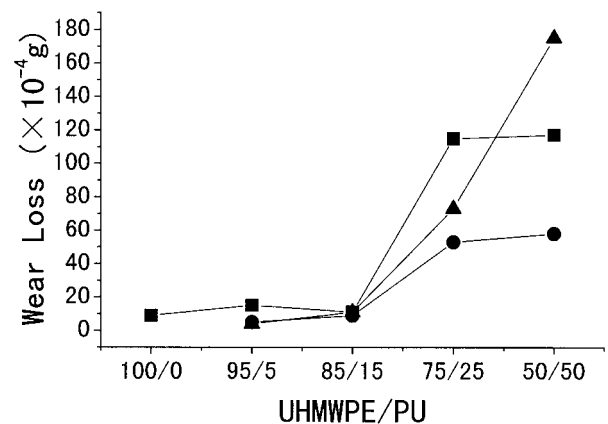


Figure 6 Wear test data of the UHMWPE/PU composite. PE-g-MAH content: (●) 0, (■) 10, and (▲) 20 wt %.

95/5 and 85/15, the wear rate of the composite kept the same grade as pure UHMWPE. Net wear losses of UHMWPE/PU/PE-*g*-MAH (95/5/10 and 95/5/20) were 0.0005 and 0.0004 g, respectively, both less than the wear loss of pure UHMWPE (0.0009 g). Also, the wear losses of compatibilized blend were lower than of the uncompatibilized blend. Especially for composite with 10 wt % PE-*g*-MAH, the wear loss was almost half of the loss of bend with 0 wt % compatibilizer. This was mainly attributed to the improved interfacial adhesion between the two phases after PE-*g*-MAH was, which made it difficult that the dispersed PU was worn away from the matrix.

CONCLUSIONS

From the results presented in this article, we can conclude that PE-*g*-MAH could become a compatibilizer in a UHMWPE/PU composite. From SEM photos and thermal analysis, PE-*g*-MAH at a certain content in composite, 10 wt % threshold content in this study, can reduce the size of the dispersed PU domains and enhance the interfacial adhesion of the PU and UHMWPE phases. The effect of compatibilization behaves so that mechanical and wear-resistance properties are

improved. In addition, the compatibilized composite at some weight ratios even has better wear-resistance properties than pure UHMWPE.

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