Abrasion Resistance of Thermoplastic Polyurethane Materials Blended with Ethylene–Propylene–Diene Monomer Rubber

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ABSTRACT: The effect of ethylene–propylene–diene monomer rubber (EPDM) as an additive on the abrasion resistance of a thermoplastic polyurethane (TPU) resin was investigated. The mechanical properties and microstructure of the resultant TPU/EPDM composites were evaluated, and the surface morphology of the composites after abrasion testing was examined. The results showed that the addition of EPDM greatly improved both the mechanical properties and abrasion resistance of the TPU resin. A TPU/EPDM composite with 8 wt % EPDM demonstrated the highest tensile strength, the largest elongation at break, and the best overall performance. The abrasion of this composite was 27 mg, whereas that of the pure resin was 73 mg. With the further addition of EPDM, the abrasion resistance of the resultant composites decreased, whereas the viscosity increased. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 1851–1857, 2008

Key words: blends; elastomers; electron microscopy; extrusion; polyurethanes

INTRODUCTION

Thermoplastic polyurethanes (TPUs) are a recently developed class of polymer materials with excellent abrasion resistance and high resilience. As a result of these properties, they have been widely used in the manufacturing of oil and water pipes.[1] However, under extreme conditions, TPU materials are prone to cracking and damage, which can potentially result in liquid leakage. To overcome this problem, ultrahigh abrasion resistance and the right hardness are needed. However, the abrasion resistance of existing polyurethanes available on the market cannot meet our requirements. Therefore, modification by blending is required.

Polymers that have been blended with TPUs include polycarbonate,[2] polyoxymethylene,[3,4] polystyrene,[5] butadiene rubber (BR),[6] fluorinated poly(ether urethane)s,[7] poly(vinyl chloride),[8,9] styrene-acrytonitrile plastic (SAN),[10] polyamide,[11,12] and nanocomposite materials.[13–17] However, reports on the enhancement of the abrasion resistance of TPUs are rare. Liu et al.[18] studied the effect of calcium sulfate whiskers on the reinforcement and toughening of polyurethane. When the content of calcium sulfate whiskers was 5–10%, the mechanical properties of the composite material were optimized. Li et al.[19] studied the impact of white carbon black and alumina fillers on the abrasion resistance of polyurethane elastomers. They found that white carbon black fillers could reduce the abrasion resistance. The abrasion resistance of the composite increased first and then decreased as the amount of the filler increased. The abrasion resistance of the composite reached a maximum when 34 wt % white carbon black was added. Li and others[20–23] have studied the wear and abrasion resistance of TPUs and other materials as well.

On the basis of the aforementioned research on the modification of TPUs by blending, the abrasion resistance of polyurethane needs to be increased, and its hardness should be kept in the right range. Additionally, the modified materials must be compatible with the original pipe extrusion process. According to early studies,[24] ethylene–propylene–diene monomer rubber (EPDM), a material with a lower density and highly capable as a filling material, has excellent heat resistance, oxidation resistance, ozone resistance, weather-proofing properties, and age resistance and good compatibility with many polymers. Moreover, the temperature and processing method of EPDM are suited to the temperature range and extrusion processing of TPUs. In this study, by blending EPDM with TPUs first

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according to the theory of craze shear banding, we found a new method of blending EPDM with TPUs to increase the abrasion resistance. A composite with ultrahigh abrasion resistance was created. This could solve the cracking problem of oil and water pipes, extend the service life, save energy, and ultimately lower the cost of polyurethane pipe installation.

EXPERIMENTAL

Materials

The polyether-based TPU, with a density of 1.11 × 10^3 kg/m^3, a melt volume rate (MVR) of 24 cm^3/10 min (200°C, 10 kg), and a melting temperature of 185–215°C, was manufactured by Bayer Corp. (Leverkusen, Germany).

EPDM (ethylene content = 70 wt %, propylene content = 29.5 wt %, ethylidene norbornene content = 0.5 wt %), with a density of 0.88 × 10^3 kg/m^3 and a Mooney viscosity of 45 (ML 1 + 4 at 125°C), was manufactured by Dow Chemical Co. (United States).

Preparation of the blends

The TPU was dried at 100°C in an electric blast oven for 2 h. After cooling, it was mixed with EPDM in different weight ratios. After uniform mixing, the TPU/EPDM mixture was fed into a preheated twin-screw extruder (diameter = 25 mm, length/diameter = 48; Z8K-25, Coperion Machinery Equipment System Co., Ltd., Shanghai, China) for melt extrusion. During the extrusion process, after many experiments and adjustments of the processing values, the processing parameters of the TPU/EPDM blend were determined. The melting temperature was 190°C, the screw rotation speed was 243 rpm, and the feeding speed was 245 rpm. After extrusion, the TPU/EPDM samples were passed through a cooling water bath and then pelletized. Variations in the extrusion temperature from one composition to another were minimal.

Performance testing

Test of the mechanical performance

The blends were further dried at 100°C in an oven for 2 h. According to Chinese standard GB/T528-1998, standard III type samples were made with a precision injection-molding machine (270S, Arburg Co., Lossburg, Germany). The melting temperature was 210°C, with the mold kept at room temperature. The tensile properties were determined with a universal mechanical testing machine (5567Q5185, Instron Co., United States) in accordance with the standard. The test was carried out at 23°C at a stretching rate of 500 mm/min. Five measurements were carried out for each data point.

Hardness measurement method

The hardness was measured in accordance with Chinese standard GB/T531-1999.

Abrasion resistance testing method

Abrasion resistance was measured with a rotating cylindrical drum (GM-1, Xin Zhen Wei Test Machinery Co., Ltd., Jiangdu City, China) in accordance with Chinese standard GB/T 9867-1998. Under a load of 10 N, samples were rubbed with the roller abrasion cloth. The abrasion distance was 40 m. The sample weight was measured before and after the test. The weight loss was the abrasion loss (with an accuracy of 0.1 mg) and was used to measure the abrasion resistance. The smaller the loss was, the better the abrasion resistance of the material was. Each data point was obtained from the average value of five measurements.

Blend morphology

Samples of the TPU/EPDM blends were cooled in liquid nitrogen for 5 min and then broken. The fracture surface was cut into small flakes and then gold-coated The morphology of the fractured surfaces was observed with scanning electron microscopy (SEM; S-4700, Hitachi, Tokyo, Japan).

The morphology of the abrasion surface of the TPU/EPDM blends was observed with an entity microscope (KL1500, Leica, Wetzlar, Germany).

RESULTS AND DISCUSSION

Morphology

The micromorphology of blends provides a powerful proof for the dispersion of two phases in a blend, and this is helpful for understanding and explaining the changes in the macromechanical properties. The morphology of the fracture surfaces of TPU/EPDM blends can be observed clearly in SEM micrographs. Figure 1 shows the fracture surfaces of TPU/EPDM blends with different proportions. In the micrographs, the continuous phase is the TPU, whereas the spherical granules are EPDM.

As shown in Figure 1, the morphology of the blends forms a sea–island structure. EPDM is dispersed in the TPU matrix.

On the surface (or in the interior) of the elastomer, there are inevitably many cracks and defects, such as surface scratches, microporosity, microcrystalline impurities, grain boundaries, and interfaces. An elastomer under stress is prone to fracture from these

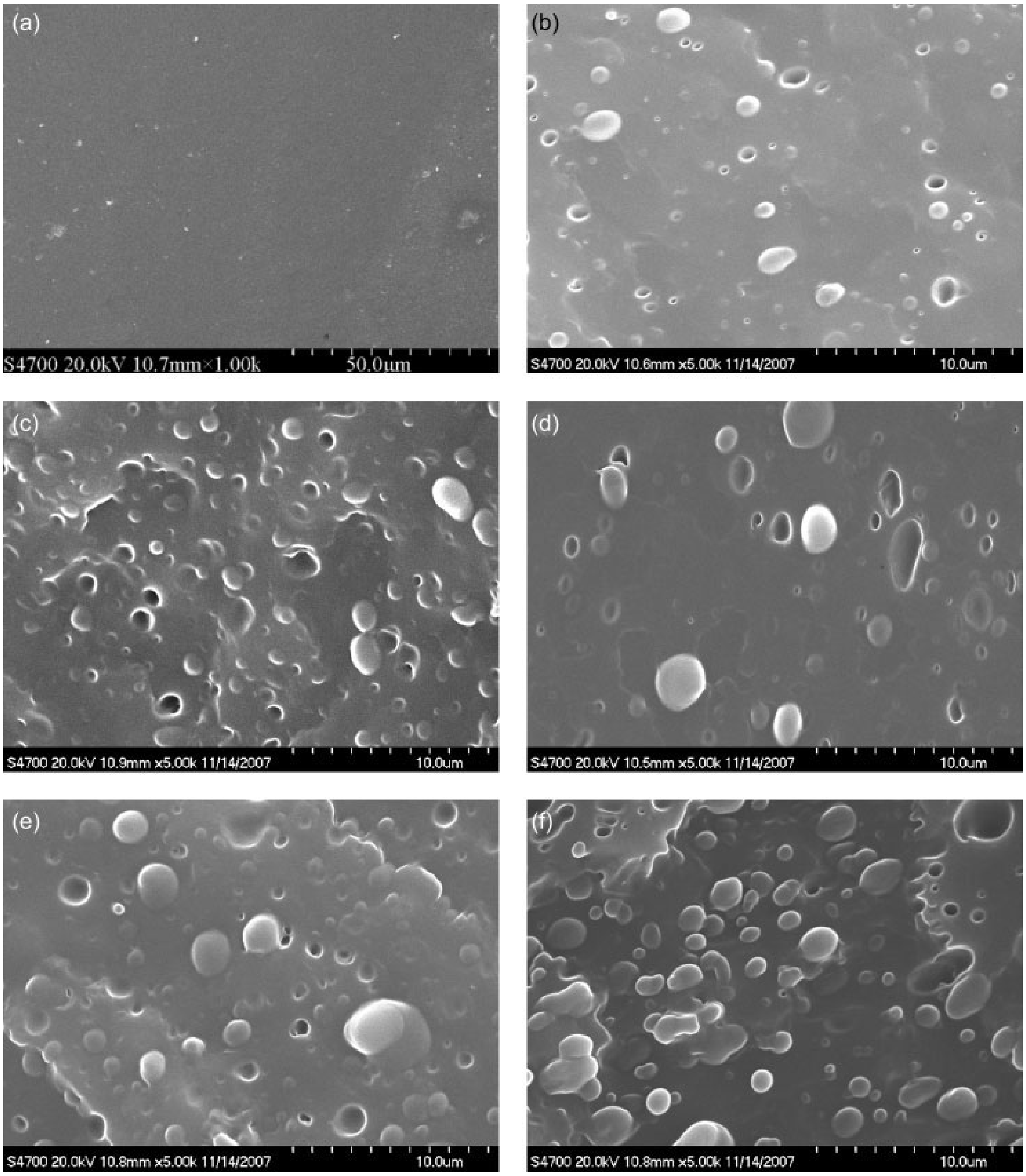

Figure 1 SEM micrographs of fractured surfaces of TPU/EPDM blends with weight ratios of (a) 100/0, (b) 95/5, (c) 92/8, (d) 90/10, (e) 85/15, and (f) 80/20.

weak points. The SEM images of the micromorphology of the TPU/EPDM blends show that the EPDM "small balls" in the blend are stress focus points, which can evoke a lot of shear zones in the matrix. Therefore, the outside energy applied to the blends can be dissipated through the formation of a shear zone. Here, EPDM plays the role of a buffer. It can to some degree improve the toughness of the TPU.

In general, the toughness of a composite system that uses rubbers as additives (e.g., EPDM rubber) is dependent on a number of characteristics of the dispersed rubber particles, including their size and dispersion uniformity and the formation of the interface. To induce a large number of shear zones, a sufficient amount of rubber is needed. With an increase in the rubber content, the toughness of the composite increases, the surface hardness decreases, and both the mechanical properties and the processing properties deteriorate. Rubber particles that are too small are not able to enhance the toughness of the

TABLE I
Mechanical Properties of TPU/EPDM Blends

TPU/EPDM	Hardness (Shore A)	Tensile strength (MPa)	Elongation at break (%)	Abrasion loss (mg)
100/0	82	30	540	73
95/5	82	32	570	31
92/8	81	34	590	27
90/10	81	31	580	33
85/15	80	28	540	40
80/20	79	26	520	42

composite system, and extremely large particles have an adverse impact on its mechanical properties. It has been found that the suitable size of rubber particles is generally about 1 μm.[25] The results show that dispersions of EPDM rubber particles within the composites have different degrees of uniformity. With the EPDM content at 8%, most EPDM rubber particles are 1 μm in size, and their dispersion within the composites is the best. A further increase in the amount of EPDM leads to a different shape of the formed particles. EPDM particles formed with an EPDM content of 20% appear as ellipsoids in comparison with the spherical ones formed with an EPDM content of 8%. The interface between the EPDM rubber phase and TPU matrix phase is thick and blurred (shown in Fig. 1), suggesting good interfacial adhesion between them. This may account for the enhanced toughness of the composite with the addition of EPDM. Previously, it has also been reported that high interfacial adhesion is critical for rubber additives to enhance the toughness of a composite system.[26]

Mechanical properties

The main mechanical properties of the TPU/EPDM blends are shown in Table I. Changes in the tensile strength, elongation at break, and hardness with various EPDM contents can be seen in Figures 2–4, respectively.

Table I and Figures 2 and 3 show that with increasing EPDM content, the tensile strength of the TPU/EPDM blends initially increases and then decreases. When the content of EPDM is not greater than 10%, the tensile strength of the blends is higher than that of the pure TPU, and this indicates better synergy. When the content of EPDM is 8%, the tensile strength of the blends reaches the maximum. When the content of EPDM is greater than 10%, the tensile strength of the blends decreases drastically. The changes in the elongation at break of the TPU/EPDM blends with the content of EPDM exhibit the same tendency as the changes in the tensile strength. Figure 4 shows that the hardness of TPU/EPDM blends decreases with increasing EPDM content. The experiments show that the processing performance also deteriorates with increases in EPDM. When the EPDM content is 20%, injection molding becomes difficult. These phenomena can be explained by the structural changes of the polyurethane elastomer. Polyurethane molecular chains are mainly composed of flexible chains or soft segments (rubber phase) and rigid chains of hard segments (plastic phase). The plastic phase is not soluble in the rubber phase,

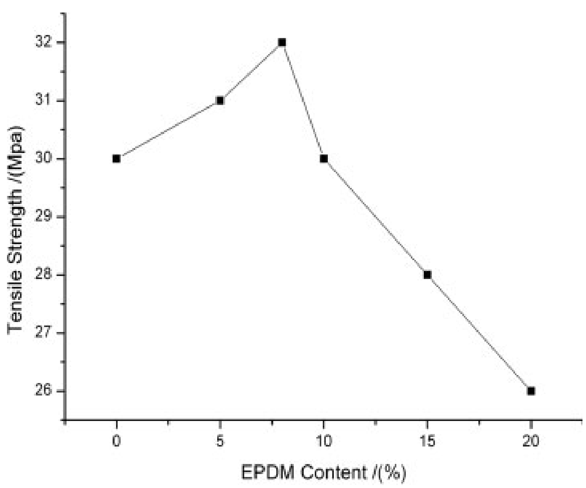

Figure 2 Tensile strength of TPU/EPDM blends versus the EPDM content.

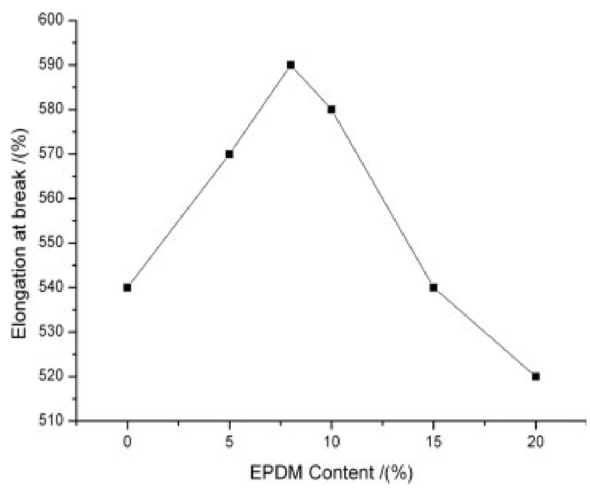

Figure 3 Elongation at break of TPU/EPDM blends versus the EPDM content.

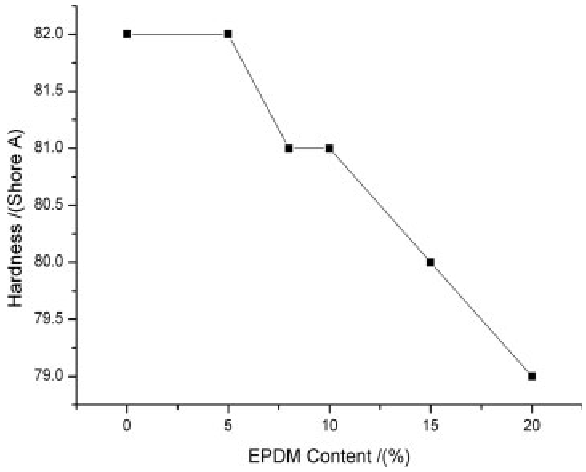

Figure 4 Hardness of TPU/EPDM blends versus the EPDM content.

but it can be uniformly distributed. At room temperature, the plastic phase acts as the elastic crosslinking point. The physical and mechanical properties of a polyurethane elastomer depend primarily on whether or not there is microphase separation and its extent. Generally, the higher the rigidity of chains in polyurethane is and the softer the flexible chains are, the more easily microphase separation will take place, and the better the physical and mechanical properties will be.[1] Adding a certain amount of low-hardness, high-resilience EPDM means increasing the softness of the flexible chain. This is beneficial to microphase separation. Therefore, the tensile strength and elongation at break of polyurethane will be increased. However, excessive EPDM will undermine the continuity of the matrices, affecting the microphase separation, decreasing the mechanical properties, and increasing the viscosity of the blends. With an increase in the EPDM content, the hardness is also reduced. This is mainly because EPDM is a soft rubber phase, and its hardness is lower than that of the TPU. Thus, the addition of EPDM can reduce the hardness of the matrix.

Abrasion resistance

Abrasion properties of the blends

Figure 5 shows that the pure TPU has a relatively high abrasion rate, reaching 73 mg. The addition of EPDM has a significant impact on the abrasion performance of the blends. With an increase in the EPDM content, the abrasion resistance of the blends is greatly enhanced compared with that of the pure TPU. When the EPDM content is 8 wt %, the abrasion resistance of the blends reaches the maximum. However, when the content is greater than 8 wt %, the abrasion resistance is reduced.

Analysis of the morphology and abrasion mechanism from the abrasion surfaces of the samples

The friction and abrasion of polymer materials is a complex and dynamic process, closely related to hardness, toughness, fatigue, and so on. To study the influence of EPDM on TPUs with respect to abrasion, the abrasion surfaces of the blends were analyzed with an entity microscope. The results are shown in Figure 6. The abrasion surface of the pure TPU has poor density, is uneven, and has a lot of debris rubbed off. During the course of the abrasion experiment, some thin white debris was extracted from the pure TPU samples. This showed that the abrasion mechanism of the pure TPU can be mainly attributed to severe adhesive abrasion, which occurs between the soft polymer surface and the hard and rough surface of the counterpart. According to adhesive abrasion theory, the friction between a TPU sample and sandpaper on a grinding wheel produces a "planing" effect on the TPU by the rough peaks of the sandpaper surface. It is very difficult to form a stable transfer film on the surface. Therefore, in the process of abrasion, adhesion easily happens.[27] At the same time, in the course of repeated friction, heat is generated. As a result, the temperature will be elevated, and the TPU surface will undergo thermoplastic deformation under the friction stress.[28] Consequently, the abrasion loss of the TPU is relatively large. It is apparent that the surfaces of composites with added EPDM are smoother than the surfaces of those with no EPDM. Figure 6(b–f) shows that "ditches" appear on the abrasion surface. The direction of the ditches has the same orientation as the sliding. This enhances the composite's ability to resist adhesive abrasion. Therefore, the abrasion mechanism has changed from adhesive abrasion to grain abrasion.[29] Gahr's study[30] noted

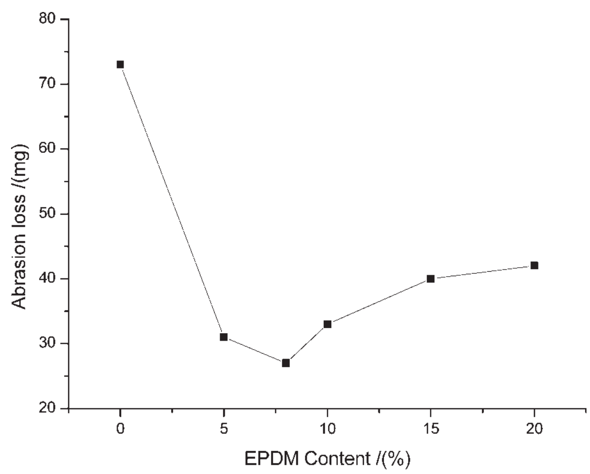

Figure 5 Abrasion loss of TPU/EPDM blends versus the EPDM content.

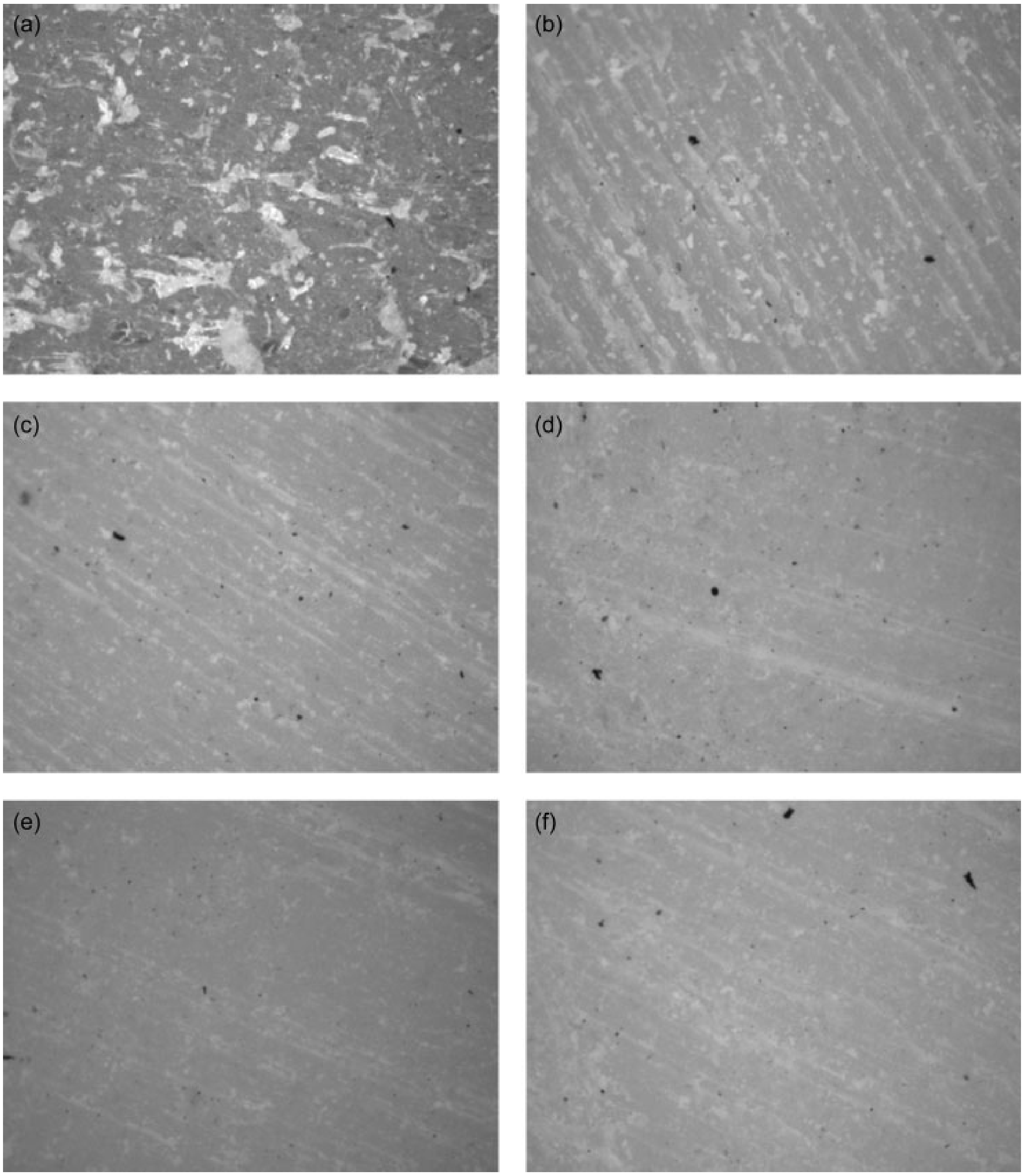

Figure 6 Entity microscope photographs of abrasion surfaces of TPU/EPDM blends with weight ratios of (a) 100/0, (b) 95/5, (c) 92/8, (d) 90/10, (e) 85/15, and (f) 80/20.

that in the course of abrasion, the formation of abrasion debris is related to the toughness of the material. The abrasion rate ($\dot{W}$) can be expressed as follows:

$$\dot{W} = \frac{P}{2Htg\alpha} + 12.13k\ \frac{P^{3/2} \cdot D \cdot \mu^2 \cdot H^{1/2}}{K_{IC}} \qquad (1)$$

where P is the surface pressure, H is the material hardness, 2α is the profile angle of the plow ditch (i.e., the vertex of abrasion with size D), μ is the friction coefficient, K_{IC} is the material toughness, and k is the relative frequency of abrasion debris caused by cracks and crack expansion.

The first item of the formula describes the abrasion caused by the microcutting operation of the abrasion grains. The second part item describes the abrasion as a result of local fracture expansion. This shows that the hardness and fracture toughness of the material have a great impact on the abrasion resistance. In a certain range of hardness, an increase in toughness is beneficial to the abrasion resistance. In a high-stress abrasion process, material toughness is an important factor affecting the abrasion rate. However, there is a maximum abrasion resistance at a certain value of toughness; beyond that, the abrasion resistance is reduced.

From the SEM photographs and the test data, it can be seen that adding EPDM to the TPU improves the abrasion resistance of the blends significantly. This can be attributed to an increase in the matrix toughness when the matrix hardness is slightly reduced. In this way, the abrasion resistance of the matrix is increased. The experimental results show that, when the EPDM content is less than 8%, the abrasion resistance is markedly improved compared with that of pure TPU. When the EPDM content is increased to 8%, the abrasion resistance is increased, with the improvement of the fracture toughness reaching its maximum. When the EPDM content is greater than 8%, the abrasion resistance decreases.

Equation (1) shows the relation between the abrasion rate, toughness, and hardness. The main reason is that the change in hardness is slight when the EPDM content is less than 8%. The SEM photographs show that the EPDM particles are turned into carriers of stress concentration and that the toughness of the matrix is increased as the EPDM content increases; therefore, the abrasion rate is decreased, and the abrasion resistance is increased. When the EPDM content is greater than 8%, the hardness of the matrix is reduced, and the ability of grain abrasion is reduced. Furthermore, when the EPDM content is relatively high, the TPU is unable to fill the gaps between the EPDM particles, and so the continuity of the matrix is undermined. This leads to a decrease in the abrasion resistance of the material. Therefore, in this study, the abrasion resistance was best when the EPDM content was 8%.

CONCLUSIONS

The addition of EPDM has a great impact on the performance of TPUs. With increasing EPDM content, the tensile strength and elongation at break of TPU/EPDM blends initially increase and then decrease. When the EPDM content reaches 8 wt %, the tensile strength and elongation at break are optimized. Furthermore, the addition of EPDM can reduce the hardness of TPUs.

The addition of EPDM changes the abrasion pattern of a TPU from adhesive abrasion to grain abrasion, and so the abrasion resistance of the TPU is improved remarkably. When the EPDM content is at 8 wt %, the abrasion mass is reduced from 73 to 27 mg, and the abrasion resistance almost doubles. Further increases in the EPDM content (>8%) cause the abrasion mass to increase.

With increasing amounts of EPDM, the processing performance of TPU/EPDM blends is reduced (the viscosity of TPU/EPDM blends is increased). When the EPDM content reaches 20 wt %, demolding becomes rather difficult in the process of injection.

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