

Material Properties

Mechanical and tribological behavior of compatibilized ultra-high-molecular-weight polyethylene/liquid crystalline polymer composites

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Abstract

Ultra-high-molecular-weight polyethylene/liquid crystalline polymer composites (coded as UHMWPE/LCP) compatibilized with polyethylene-grafted maleic anhydride (PE-g-MAH) were prepared by compression molding. The effect of the compatibilizer on the mechanical, thermal, and tribological properties of the UHMWPE/LCP composites was investigated, based on the evaluation of the composites' properties and examination of the fracture sections by means of scanning electron microscopy. It was found that the incorporation of the PE-g-MAH contributed to decrease the melting points of the composites and decrease their crystallinity to some extent. Moreover, the inclusion of the PE-g-MAH compatibilizer helped to greatly increase the tensile rupture strength and tensile modulus of the composites, which was beneficial to improving the wear resistance. Such improvements in the tensile and tribological behavior of the UHMWPE-matrix composites by the PE-g-MAH compatibilizer could be closely related to the enhanced cross-linking function of the composites in the presence of the compatibilizer.

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1. Introduction

The innovations in modern technology have been placing ever-increasing demands on advanced composite materials. Of the most commonly used composite materials in modern engineering, the polymer-matrix composites, have been finding increased applications owing to their much lower weight and better corrosion resistance and biocompatibility than the metal-matrix and ceramic-matrix ones [1]. For example, ultra-high-molecular-weight polyethylene (UHMWPE) has been widely used in bearing applications due to its good chemical stability, biocompatibility, and friction

reducing and antiwear ability [2]. It has also been used as some components or parts of machines in chemical engineering, textile engineering, transportation engineering, agricultural engineering, food processing, and the paper making industry, because of its excellent chemical corrosion resistance, water-repellent function, adhesion resistance, and self-lubricity [1]. Specifically, UHMWPE has been applied as a material of an acetabular prosthesis component in hip and knee total joint replacement for more than 30 years [3,4]. It is well known that the wear resistance of UHMWPE can be significantly increased by the addition of various fillers to form UHMWPE composites [5–10]. Therefore, many attempts have been made to improve the wear resistance and mechanical properties of UHMWPE. A widely practiced approach in this respect is the combination of UHMWPE with other polymers to form blends which

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may lead to the creation of attractive new composite materials. Hashmi and co-workers investigated the friction and wear behaviors of the blends of UHMWPE with polypropylene [8], and found that wear loss of 15 wt% UHMWPE filled PP blend was significantly lower compared to PP. Reduction in wear loss of UHMWPE filled PP blend has been attributed to the reduction in temperature of the contact surface. Hao Yuan and co-worker studied a compatibilized UHMWPE and polyurethane (PU) blend [20] and found that polyethylene-grafted maleic anhydride (PE-g-MAH) added as compatibilizer at a concentration of 10 wt% resulted in improved mechanical properties and lower wear rate than the uncompatibilized composite. The reinforcement of PP by several liquid crystalline polymers (LCPs) was focused on in the past decade [11–15], and it was found that this kind of reinforcement contributed to increased interfacial adhesion, less phase separation and more uniform LCP dispersed phase distribution. Liquid crystalline polymers are excellent engineering plastics that have been used in a wide spectrum of applications due to their high strength, high modulus, excellent toughness, and high resistance to chemicals and physical abrasion. UHMWPE is a thermoplastic polymer that also has good wear resistance. Therefore, we suppose that it could be feasible to prepare novel polymer blends using LCP and UHMWPE. However, the effectiveness of reinforcing UHMWPE by forming a blend with LCP is limited, since UHMWPE and LCP are immiscible polymers and have a large difference in polarity. In other words, the polar LCP as the reinforcing agent and the nonpolar UHMWPE in the blend have poor interfacial bonding and are easy to separate from each other. It is therefore imperative to use a compatibilizer that improves the dispersion and adhesive ability between different polymers [9]. Some copolymers or graft polymers that possess reactive groups and have similar chemical structure can reduce the size of the dispersed phase and enhance the interfacial bonding. For example, polar PE-g-MAH has good adhesion with metal and glass or ceramic, and it also has good compatibility with some polymers, due to its molecular chain with polar groups. PE-g-MAH as a compatibilizing agent in many polymer/polymer alloys has been extensively reported [16–19]. Unfortunately, little has been reported about the effect of the compatibilizer on the wear resistance of UHMWPE/LCP composites. Accordingly, UHMWPE was blended with LCP polymer in the presence of PE-g-MAH as a compatibilizer so as to prepare novel UHMWPE/LCP composites with much better interfacial bonding. This article deals with the effect of PE-g-MAH incorporation on the friction and wear behavior of the resulting UHMWPE/LCP composites.

2. Experimental

2.1. Materials

The LCP used for this study was Vectra B130, which was purchased from Polyplastics Co., Ltd. (Japan). It is a wholly aromatic liquid-crystal poly (ester-co-amide). This polymer was reportedly synthesized from 60% hydroxynaphthoic acid, 20% terephthalic acid, and 20% aminophenol as the monomers. The UHMWPE matrix was purchased from the Second Factory of Auxiliary Agents of Beijing (Beijing, China). The molecular weight of the UHMWPE was 3.5×10^6 g/mol. The maleic anhydride grafted high-density polyethylene (HDPE) compatibilizer, PE-g-MAH, of grafting degree 3.5 wt%, was kindly supplied by the Petrochemical Research Institute of Lanzhou Petrochemical Corporation.

2.2. Sample preparation

Before processing, the LCP pellets were dried for at least 24 h in a convection oven at 120 °C. UHMWPE powder was dried for at least 8 h in the same oven at 80 °C. The dried UHMWPE and LCP were mixed with PE-g-MAH in a torque rheometer mixer (HAAKE Rheocord90 system, Germany) at 240 °C and 60 rpm for 5 min. The UHMWPE matrix was pre-blended with PE-g-MAH at mass fractions of 10% and 20%, respectively, then the compatibilized UHMWPE was mixed with LCP at mass fractions from 5% to 80%. The mixtures were pre-heated at 240 °C for 30 min and then molded to plates of size $6 \times 7 \times 30$ mm under 20 MPa at 240 °C. The composite plates to be tested were obtained after cooling the molded specimens in ambient air.

2.3. Morphological and thermal analyses

The composite specimens were fractured in liquid nitrogen and the fractured sections and worn surfaces of the composite samples were coated with a thin layer of gold to allow the morphology observation on a scanning electron microscope (JEOL-5600LV SEM).

The differential scanning calorimetric (DSC) analysis of the composites was carried out on a Perkin–Elmer DSC instrument at a heating rate of 10 °C/min in a nitrogen atmosphere.

2.4. Evaluation of mechanical and tribological properties

The mechanical properties of the composites were determined on an INSTRON-1121 tester at room temperature and a crosshead speed of 100 mm/min,

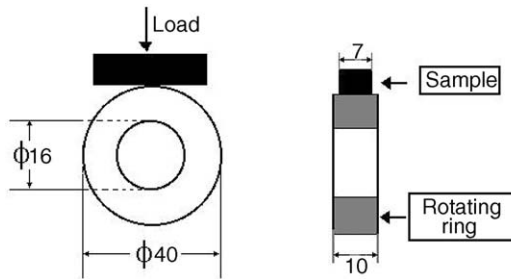


Fig. 1. Schematic diagram of the frictional pair contact configuration.

according to ISO 178-1993. The mechanical properties were calculated from the data of at least five identical samples.

An M-2000 friction and wear tester (Xuanhua Tester Factory, China) was used to examine the friction and wear behavior of the UHMWPE/LCP composites sliding against SAE52100 steel in a block-on-ring configuration. The schematic diagram of the friction and wear tester is shown in Fig. 1. The block specimens of size $6 \times 7 \times 30$ mm were made of the UHMWPE composites and the counterpart rings of diameter 40 mm and thickness 10 mm were made of SAE52100 steel. The friction and wear tests were performed at a normal load of 200 N, sliding velocities of 0.424 and 0.856 m/s, and ambient temperature about 25 °C.

3. Results and discussion

3.1. Morphology

Fig. 2 shows the SEM micrographs of the fractured sections of the UHMWPE/LCP composites with and without PE-g-MAH compatibilizer. The uncompatibilized composite shows obvious signs of phase separation and the interfacial gap between the LCP and the UHMWPE matrix on the fractured section is clear (see Fig. 2a). Those interfacial gaps are attributed to a poor interfacial combination between the LCP as the reinforcing agent and the UHMWPE matrix. Contrary to the above, the fractured section of the composite compatibilized with PE-g-MAH has a fuzzy morphology (see Fig. 2b), which is especially so when the mass fraction of the PE-g-MAH is 10%. This indicates that in this case the LCP is well bonded to the UHMWPE matrix, which contributes to retard the rupture through the LCP/UHMWPE interface and harmonize the plastic deformation of the LCP reinforcing agent. Moreover, with the increase in the content of PE-g-MAH, the interfacial gaps between the LCP and the UHMWPE matrix on the fractured surface becomes

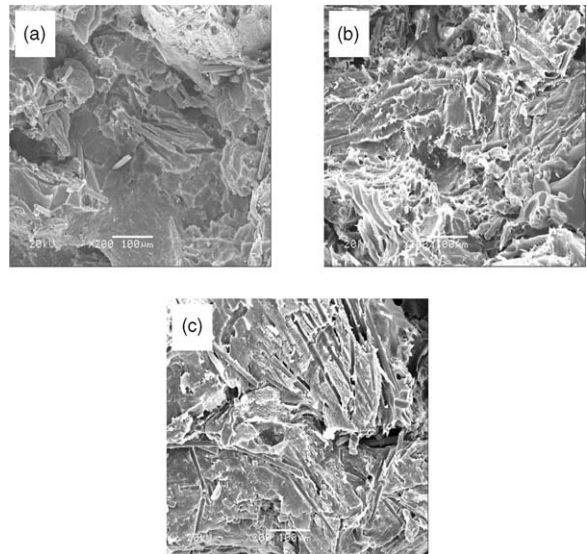


Fig. 2. SEM photographs of UHMWPE/LCP composites: (a) without PE-g-MAH; (b) with 10% PE-g-MAH; (c) with 20% PE-g-MAH.

clear (see Fig. 2c), which indicates that an excess of compatibilizer leads to damage to the interfacial bonding of the UHMWPE/LCP composite.

3.2. Thermal analysis

The DSC curves of pure UHMWPE, UHMWPE/LCP, and UHMWPE/PE-g-MAH/LCP composites are shown in Fig. 3, and the corresponding melting

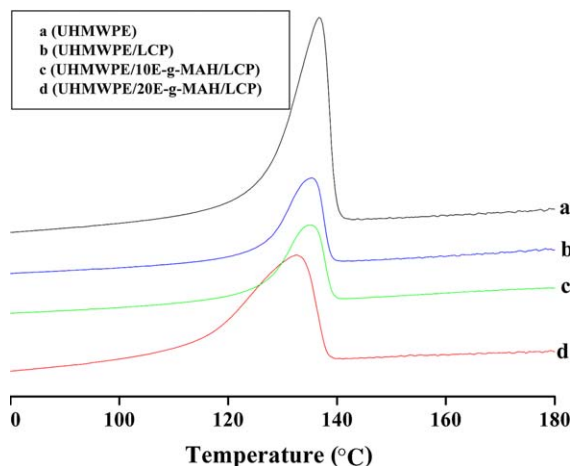


Fig. 3. DSC curves of UHMWPE and various UHMWPE/LCP composites. (a) UHMWPE, (b) UHMWPE/40 wt% LCP, (c) UHMWPE/10 wt% PE-g-MAH/LCP composite, (d) UHMWPE/20 wt% PE-g-MAH/LCP composite.

temperature (T_m) and melting enthalpy (ΔH_m) are presented in Table 1. As shown in Fig. 3, UHMWPE, UHMWPE/LCP composite, and UHMWPE/PE-g-MAH/LCP composite show only one melting peak on the DSC curves, which is attributed to the same backbone structure of the UHMWPE and PE-g-MAH. Thus, the ΔH_m listed in Table 1 includes the melting enthalpies of both the UHMWPE and PE-g-MAH. The crystallinity percentages of various PE-matrix composites can be calculated as the ratios of ΔH_m to ΔH_m^0 , where ΔH_m refers to the heat of fusion of the composites tested and ΔH_m^0 to that of total crystalline polyethylene. Therefore, the crystallinity percentages of the UHMWPE matrix, UHMWPE/40% LCP composite, UHMWPE/10% PE-g-MAH/40% LCP composite, and UHMWPE/20% PE-g-MAH/40% LCP composite are calculated to be 56.79%, 42.39%, 38.98%, and 36.72%, respectively, by taking into account the ΔH_m of 100% crystalline polyethylene (293 J/g), the ΔH_m of UHMWPE (166.4 J/g), the ΔH_m of PE of UHMWPE/40% LCP composite (124.21 J/g), the ΔH_m of the PE in the UHMWPE/10% PE-g-MAH/Cu composite (114.22 J/g), and the ΔH_m of the PE in the UHMWPE/20% PE-g-MAH/Cu composite (107.58 J/g). The UHMWPE/PE-g-MAH/LCP composite of a lower PE-g-MAH content has a relatively higher crystallinity percentage, which might imply that the inclusion of the compatibilizer contributed to decrease the crystallization of UHMWPE. Besides, as listed in Table 1, the inclusion of the LCP leads to a decrease in the melting point of the UHMWPE, while the doping of the PE-g-MAH further decreases the melting point to some extent. This is supposed to be attributed to the interaction in the amorphous region domains of the two polymers, which leads to a decrease in the T_m of the blends. The slightly decreased T_m of PE is also caused by the amorphous interaction in the PE phase. The interaction could only happen between the anhydride groups of PE-g-MAH and the amino groups of LCP, and the two kinds of active groups are mainly located at the UHMWPE/LCP interface. Subsequently, the UHMWPE molecular movement is hindered due to the coupling interaction, which results in

the reduction of the crystallinity of UHMWPE matrix near the interface.

3.3. Mechanical and tribological properties

Fig. 4 shows the variation of the mechanical properties of UHMWPE/LCP and UHMWPE/PE-g-MAH/LCP composites with the weight fraction of LCP. It is seen that the tensile strengths of the two kinds of composites increase with increasing LCP content, which is attributed to the reinforcing effect of the LCP. At the same time, the compatibilized ternary composites have larger tensile strengths than the binary composites with the same LCP content and the pure UHMWPE (see Fig. 4(a)). That is, the UHMWPE/LCP composites compatibilized with various weight fractions of PE-g-MAH (10–20%) have much larger tensile strengths

Table 1

Melting temperature (T_m) and melting enthalpy (ΔH_m) of UHMWPE-based composites

UHMWPE/PE-g-MAH/LCP (weight ratio)	UHMWPE T_m ($^{\circ}\text{C}$)	UHMWPE PE-g-MAH ΔH_m (J/g)
100/0/0	139.50	166.41
60/0/40	135.33	124.21
60/10/40	135.00	114.22
60/20/40	132.67	107.58

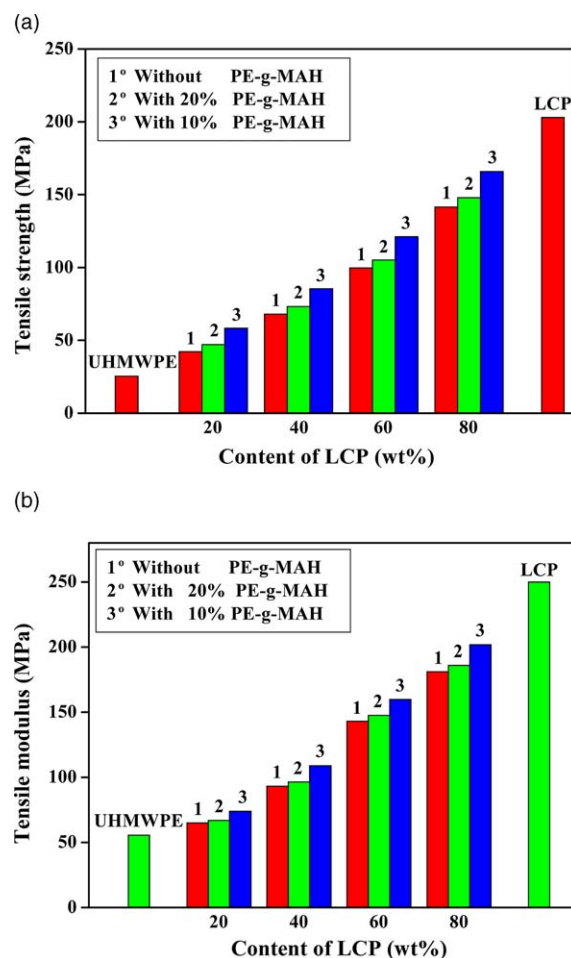


Fig. 4. Mechanical properties of the UHMWPE/PE-g-MAH/LCP composites. (a) Tensile strength vs. LCP content. (b) Tensile modulus vs. LCP content.

than the uncompatibilized ones. For example, the UHMWPE/20% LCP composite has a tensile strength of 42.3 MPa, while the ternary UHMWPE/10% PE-g-MAH/LCP composite has a tensile strength of 58.3 MPa. Similarly, the incorporation of the PE-g-MAH compatibilizer also leads to a significant increase in the tensile modulus of the UHMWPE composite (see Fig. 4(b)). As the LCP content in the composites increases from 20% to 80%, the tensile modulus of the compatibilized composites rises by a factor of 1.3–3.6 as compared to that of pure UHMWPE. This is because the PE-g-MAH containing polar functional groups contributes to greatly increase the interfacial bonding of the UHMWPE/LCP composites. To sum up, the incorporation of the PE-g-MAH compatibilizer contributes to increase the tensile strength and tensile modulus of the UHMWPE/LCP composites, which is especially so at a PE-g-MAH content of 10 wt%. Such a finding is similar to what has been observed for the UHMWPE/polyurethane composites [20] and to our previous finding as well. In addition, it is worth pointing out that improved mechanical properties of the ternary composites are obtained at a PE-g-MAH mass fraction of 10% rather than 20%. This could be intrinsically related to the effect of the compatibilizer on the interfacial bonding of the composites. That is, the optimized interfacial bonding is realized at a volume fraction of PE-g-MAH of 10%, whilst an excess amount of PE-g-MAH leads to weakened interfacial bonding and more severe structural inhomogeneity of the blend, and hence to lower tensile strength.

Fig. 5 shows the variation of the wear rates of UHMWPE/LCP composites sliding against SAE52100 steel with the LCP content under a normal load of 200 N and sliding velocity of 0.856 m/s. The inclusion

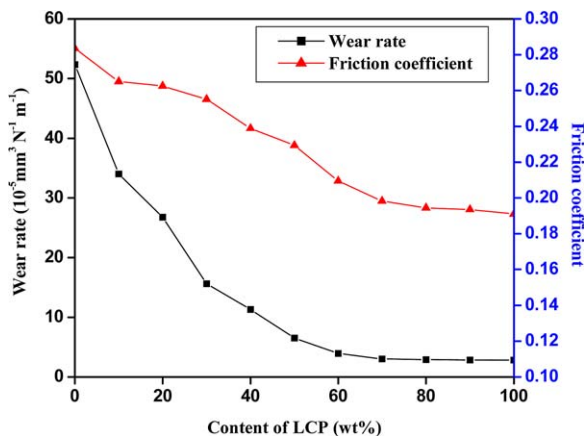


Fig. 5. Variations of the wear rates and friction coefficients of UHMWPE/LCP composites with LCP content (normal load 200 N, sliding velocity 0.856 m/s).

of the LCP leads to decreases in the wear rate of the UHMWPE/LCP composites, and the wear rate decreases with increasing LCP content until it assumes a stabilized value at a LCP weight fraction of 60%. Moreover, although LCP has much better wear resistance than the pure UHMWPE, its introduction at a smaller weight fraction (40%) leads to only a minor decrease in the wear rate of the UHMWPE/LCP. Fortunately, the wear rate of the UHMWPE/LCP composite is strikingly decreased when the weight fraction of the LCP reaches 60%. The smallest wear rate is recorded for the composites of a LCP weight fraction within 60–80%. This observation can be attributed to the filling- and reinforcing-modification effects of the LCP. In other words, the LCP with higher mechanical strength blended in the UHMWPE composites may function to increase the ability of the composite to resist shearing in the sliding process, which contributes to greatly improve the wear resistance.

Fig. 6 shows the variations of the wear rate of the compatibilized ternary composites UHMWPE/PE-g-MAH/LCP sliding against SAE52100 steel with the weight fraction of the LCP. It is seen that the ternary composites containing 10–20% PE-g-MAH have lower wear rates than the uncompatibilized UHMWPE/LCP binary composite under a normal load of 200 N. Specifically, the ternary composite containing 10 vol% PE-g-MAH registers the lowest wear rate.

Fig. 7 shows the variations of the wear rate and friction coefficients of UHMWPE/LCP and UHMWPE/PE-g-MAH/LCP composites with normal load at a sliding velocity of 0.856 m/s. It is seen that the wear rates of both the UHMWPE/PE-g-MAH/LCP and UHMWPE/LCP composites increase with increasing

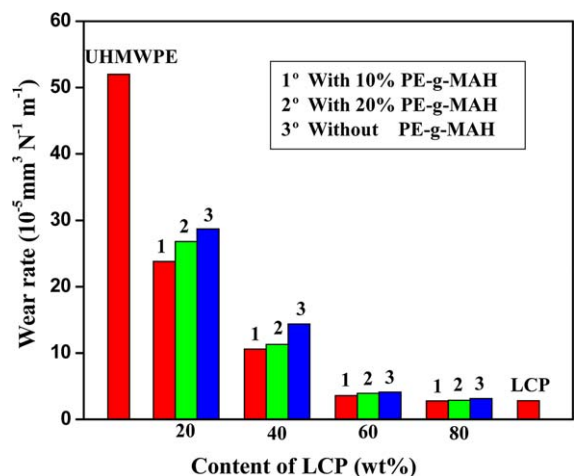


Fig. 6. Variations of the wear rates of UHMWPE/LCP and UHMWPE/PE-g-MAH/LCP composites with LCP content (normal load is 200 N, sliding velocity is 0.856 m/s).

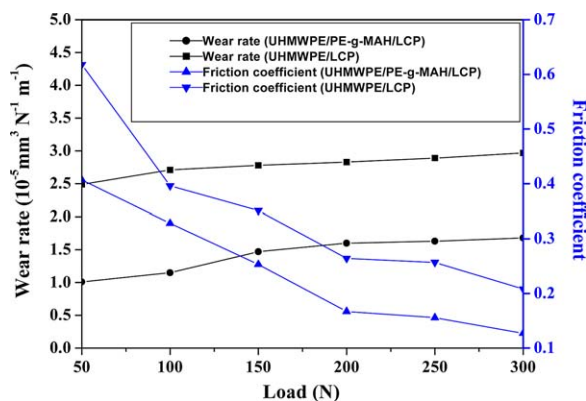


Fig. 7. Variations of the wear rates and friction coefficients of UHMWPE/LCP and UHMWPE/PE-g-MAH/LCP composites with normal load at a sliding velocity of 0.856 m/s.

applied load until they assume nearly constant values at a load above 200 N. The compatibilized ternary composite sliding against the steel at normal load records a small wear rate as much as about half of that of the uncompatibilized binary composite. Moreover, the friction coefficients for the two kinds of UHMWPE–matrix composite also decrease with increasing applied normal load and reach a minimum at a normal load of 300 N. From the results shown in Figs. 6 and 7, it is concluded that the compatibilized composites exhibit excellent friction reducing and anti-wear behavior in comparison to the uncompatibilized ones.

All the samples for the above-mentioned investigations were tested in the longitudinal direction. There-

fore, it is imperative to investigate the mechanical and tribological properties of the composites in transverse direction so as to provide information about the anisotropy of the composites. The tensile and tribological properties of the UHMWPE/LCP with and without PE-g-MAH in the longitudinal and transverse directions are shown in Table 2. It is seen that the composites register higher tensile strength and modulus and lower wear rates in the longitudinal direction than in the transverse direction. Besides, the UHMWPE/LCP composites of a higher LCP content (above 60%) have a stronger anisotropy than the ones of lower LCP content, which indicates that the mechanical and tribological behavior of the UHMWPE/LCP composites with a higher LCP content is dominated by the LCP and the content of PE-g-MAH.

4. Conclusions

The incorporation of PE-g-MAH as a compatibilizer contributes to significantly increase the tensile strength and wear resistance of UHMWPE–matrix composites blended with LCP, which is closely related to the cross-linking reinforcing action of the compatibilizer. UHMWPE/PE-g-MAH/LCP ternary composite with a compatibilizer weight fraction of 10% has the best wear resistance among the tested composite specimens. Thus, it is suggested to set the critical weight fraction of the PE-g-MAH in the UHMWPE/PE-g-MAH/LCP composite as 10%. The UHMWPE/LCP composites of a higher LCP content (above 60%) have stronger anisotropy than the ones of a lower LCP content, which indicates that the mechanical and tribological behavior of the UHMWPE/LCP composites with a higher LCP content is dominated by the LCP and the content of PE-g-MAH.

Table 2

Mechanical and tribological properties of the UHMWPE/10%/PE-g-MAH/LCP composites in longitudinal and transverse directions

LCP (%)	Tensile strength (MPa)	Tensile modulus (MPa)	Wear rate ($10^{-5} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$)
Longitudinal direction			
20	58.3	74.1	23.8
40	85.4	108.9	10.6
60	121.2	159.8	3.62
80	165.9	201.7	2.78
100	203.7	250.2	2.63
Transverse direction			
20	54.2	72.5	27.9
40	63.5	97.5	12.7
60	70.9	123.9	5.72
80	80.7	137.9	4.36
100	98.6	159.6	4.21

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