

Fabrication of High Mechanical Properties and Wear: Resistance UHMWPE/PP Composites by Incorporating SiC Nanoparticles under a Consecutive Elongational Flow

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Article

Fabrication of high mechanical properties and wear—resistance UHMWPE/PP composites by incorporating SiC nanoparticles under a consecutive elongational flow

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Abstract: conclusions. The blends of ultrahigh molecular weight polyethylene/polypropylene (UHMWPE/PP) possess excellent processability, but limited by its reduced mechanical properties. Herein, the high mechanical properties and wear—resistance UHMWPE/PP composites were fabricated by the addition of silicon carbide (SiC) nanoparticles under a consecutive elongational flow without any other additives or solvents. The morphology and thermal properties, mechanical properties, wear resistance as well as scratch resistance of UHMWPE/PP/SiC composites were investigated. The mechanical properties and friction resistance of composites increase initially then decrease with the increase content of SiC. The optimum mechanical properties of UHMWPE/PP/SiC composites are achieved when the content of SiC is 3 phr. In addition, both the hardness and scratch resistance of composites improved upon increasing the content of SiC. These improved mechanical properties and wear resistance originate from the well disperison of SiC nanoparticles along with favourable interfacial adhesive under a consecutive elongational flow.

Keywords: UHMWPE; blends; silicon carbide (SiC); composites; mechanical property; friction resistance

1. Introduction

Polyethylene (PE) is regarded as one of most simples molecular chains in polymer materials, but its molecular weight larger than 1 million g/mol (ultrahigh molecular weight polyethylene, UHMWPE) shows great potential application in many important engineering applications, i. e. wear-resistant materials in industrial bearings and protective layer, due to its good self-lubricating ability, low friction coefficient, high impact strength, fatigue resistance and biological inertness [1–3]. However, owing to the relatively high average molecular weight of UHMWPE and irregular inter-chain entanglement results in high regional chain density and low mass flow rate, leading to a great obstacle in the processing of UHMWPE via. traditional processes, i.e. blow molding or extrusion processes [4,5]. In addition, the low surface hardness, low modulus of elasticity and bending strength as well as poor abrasion resistance of UHMWPE also greatly hind its application. It is therefore of great significance to develop industrially viable UHMWPE-based wear resistant materials through the regulation of polymer composition and optimization of processing technology.

Developing UHMWPE-based blends i. e. introducing low density polyethylene (LDPE), polyamide and poly (ethylene oxide) (PEO) etc. into the UHMWPE matrix, is a viable option to improve the processability [6,7]. But its mechanical properties may be adversely affected when excessive amounts of additives compounds with UHMWPE. Due to the superiority of polypropylene (PP) with high MFR value, mixture of a certain amount of PP with UHMWPE also can effectively improve the processing properties of UHMWPE-based blend [8]. Unlike high density polyethylene (HDPE), which penetrates the UHMWPE particles, PP acts as a lubricant which is distributed between the primary and secondary particles of UHMWPE, enhancing the processing properties, but with limited improvements in wear resistance and mechanical properties. In our previous work, we fabricated a series of ultrahigh molecular weight polyethylene/polypropylene (UHMWPE/PP) blends by an elongational-flow-field dominated eccentric rotor extruder (ERE), which generated strong interaction to enable excellent compatibility of UHMWPE and PP with enhanced wear resistance as compared to the shear flow field [9,10]. However, these blends still suffer from poor wear resistance under sever loading conditions, originating from the thermodynamic incompatibility between UHMWPE and PP, thus resulting in a relatively low interfacial adhesive [11].

Many strategies have been developed to improve the compatibility of blends, such as adding reactive polymers, block copolymers and functional nano-particles [12–14]. Among them, the unique properties of nano-particles have promoted a great deal of interest to improve the compatibility of blends and explore advanced multifunctional materials [15,16]. The silicon carbide nanoparticles (nano-SiC), possessing high hardness, resistance to abrasion, high thermal conductivity along with unique nanometer effect have been used as wear resistance modifier or thermal conductivity filler for the enhanced function of polymer composites [17,18]. Huang et al. found that the nano-SiC particles could improve mechanical properties and the heat resistance of the composites [19]. Sharma and his coworkers reported that nano-SiC particles led to reduced plastic deformation and wear loss of UHMWPE [20]. More recently, Gurgun investigated the wear behavior of UHMWPE/carbide composites at high temperatures [21]. However, the obtained samples were prepared by compression molding that it is difficult for a good dispersion of nano-SiC in UHMWPE matrix.

In this context, the SiC nanoparticles were used as a reinforcing modifier for UHMWPE/PP blends, and the UHMWPE/PP/SiC nanocomposites were fabricated by ERE. We also systematically investigated the morphology and thermal properties, mechanical properties, wear resistance as well as scratch resistance of UHMWPE/PP/SiC composites by using scanning electron microscopy (SEM), Raman mapping, differential scanning calorimetry (DSC), dynamic thermomechanical analysis (DMA), electronic universal testing machine, sliding friction and wear tester and scratch resistance tester respectively. our results show that a small amount of nano-SiC particles are dispersed evenly along with an improved interfacial thickness of UHMWPE/PP matrix due to the periodically changed elongational deformation generated by the converging/divergence flow of ERE, but the aggregation of nano particles occurs with 4 phr nano- SiC. The mechanical properties and friction resistance of composites increase initially then decrease with the increase content of SiC as a well dispersion of SiC nanoparticles along with a favourable stress transformation under a consecutive elongational flow, providing a new method for the design and fabrication of high performance UHMWPE composites with a broader application.

2. Materials and Methods

The Materials and Methods should be described with sufficient details to allow others to replicate and build on the published results. Please note that the publication of your manuscript implicates that you must make all materials, data, computer code, and protocols associated with the publication available to readers. Please disclose at the submission stage any restrictions on the availability of materials or information. New methods and protocols should be described in detail while well-established methods can be briefly described and appropriately cited.

Research manuscripts reporting large datasets that are deposited in a publicly available database should specify where the data have been deposited and provide the relevant accession numbers. If

the accession numbers have not yet been obtained at the time of submission, please state that they will be provided during review. They must be provided prior to publication.

Interventionary studies involving animals or humans, and other studies that require ethical approval, must list the authority that provided approval and the corresponding ethical approval code.

2.1 Materials

The average molecular weight of UHMWPE nascent powders is about 4.70×10^6 g/mol, which was provided by Celanese Corporation. PP (Z30s) was obtained from Sinopec Maoming Petrochemical Company (Guangdong, China). The nano-SiC particles were supplied from Changzhou Wei Lai Information Technology Co., Ltd (Jiangsu, China).

2.2. Sample preparation

The UHMWPE powder, PP particles and SiC powder were dried in a vacuum oven at 90 °C for 6 h. The mass ratio of UHMWPE/PP is 85:15, and the addition of SiC ranges from 0 to 4 phr. The compositions were premixed using a high-speed mechanical mixing for 10 min. Then, the above compounds were processed by using ERE at a speed of 25 rpm and a melting processing temperatures of 200 °C respectively. The extruded samples were immediately pressed into sheets at 17 MPa.

2.3. Sample characterization

The morphology and structure was examined by scanning electron microscopy (SEM: HITACHI-Regulus 8100, Japan) and confocal Raman spectroscopy (DXR2xi, Thermo Scientific, USA) with a 532 nm argon ion laser.

The crystallinity of samples was acquired by differential scanning calorimetry (DSC: Q20, TA, USA). The heating and cooling rate of the whole test process was set at 10 °C /min. Dynamic thermomechanical analysis (DMA: Q800, TA, USA) was used to analyze the thermo-mechanical properties of samples with a temperature range of 30-180 °C, a temperature rise rate of 3 °C/min, an amplitude of 5 μm and a test frequency of 1 Hz. The samples were tested for mechanical properties according to GB/T 1040.2-2006 standard, with the elongational speed set at 50 mm/min and at temperature of 23 ± 0.5 °C.

The tensile strength and elongation at break were performed using an microcomputer-controlled electronic universal testing machine (CMT4104, Shenzhen New Sansi Materials Testing Co., China). The M-200 plastic sliding friction and wear tester was used to determine the sliding friction and wear properties of the material according to the standard GB/T 3960-2006. The sample size was 30 mm x 7 mm x 6 mm and the test was carried out under dry friction conditions on 45# steel with a speed of 200 r/min. A shore D durometer was utilized to measure the hardness of the samples according to GB/T 2411-200. The scratch resistance (430 P-I, Erichsen, Germany) was measured according to VW internal standard PV 3952.

3. Results and discussion

3.1. Morphology

Figure 1 shows the morphology of UHMWPE/PP blend and UHMWPE/PP/SiC composites. It turns out that the UHMWPE/PP blend have a smooth fracture surface. When adding 1 phr SiC into the blend, nano-SiC particles are dispersed evenly in the matrix, which is contributed to nano-SiC particles were suffered from periodically changed elongational deformation generated by the converging/diverging flow of ERE [22]. The large cluster of nano-SiC particles were more efficiently broken into small cluster or even single nano particles, possibly suppressing coalescence with a stable the blending system [23]. Furthermore, the cryofractured surfaces of UHMWPE/PP/SiC composites show a relatively rough surface, giving evidence that the composites need more energy to generate a

new fracture surface. But the aggregation of nano particles occurs with 4 phr nano SiC particles as the notably high surface energy, thus leading to the decreased properties of the composites.

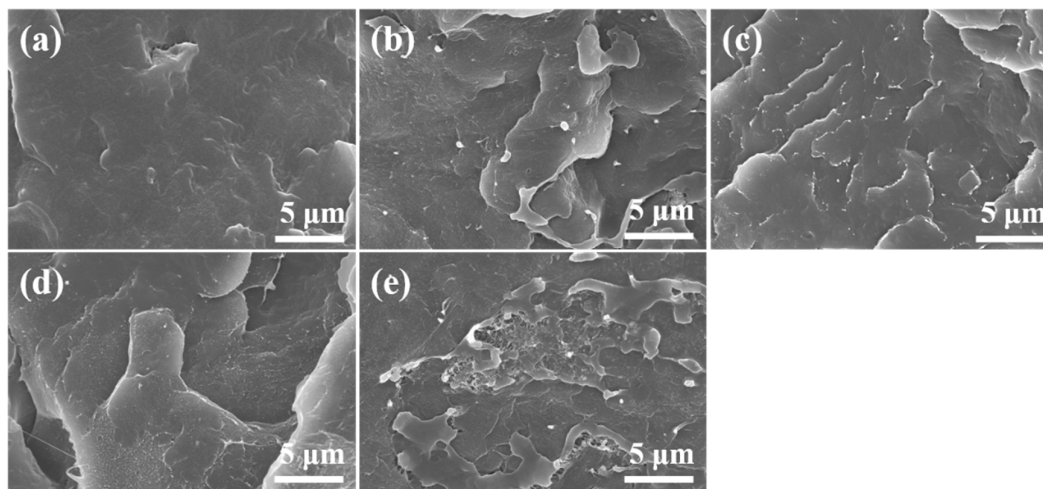


Figure 1. SEM images of cryofractured surfaces of UHMWPE and UHMWPE/PP/SiC composites: (a) 85/15/0; (b) 85/15/1; (c) 85/15/2; (d) 85/15/3 and (e) 85/15/4.

To understand the morphology development of UHMWPE/PP/SiC composites better, the Raman mapping were carried in our following part, as shown in Figure 2. As demenstrated by our prvious results, the blue part with is obviously dominated by the UHMWPE domain, and the red colour suggsets the main presence of of PP domain, while the green part means the coexistence of UHMWPE and PP domain. It is shown that no obviouse red part is found, which indicates no evidently PP agglomeration as a consecutive elongational flow generated by ERE. Interestingly, the green part is gradually increasing with the increasing SiC content, suggesting the increasing molecular difusion accompanied by an improved interfacial thickness, which might be more benefit for the stress transformation and the elongationa at break [24,25].

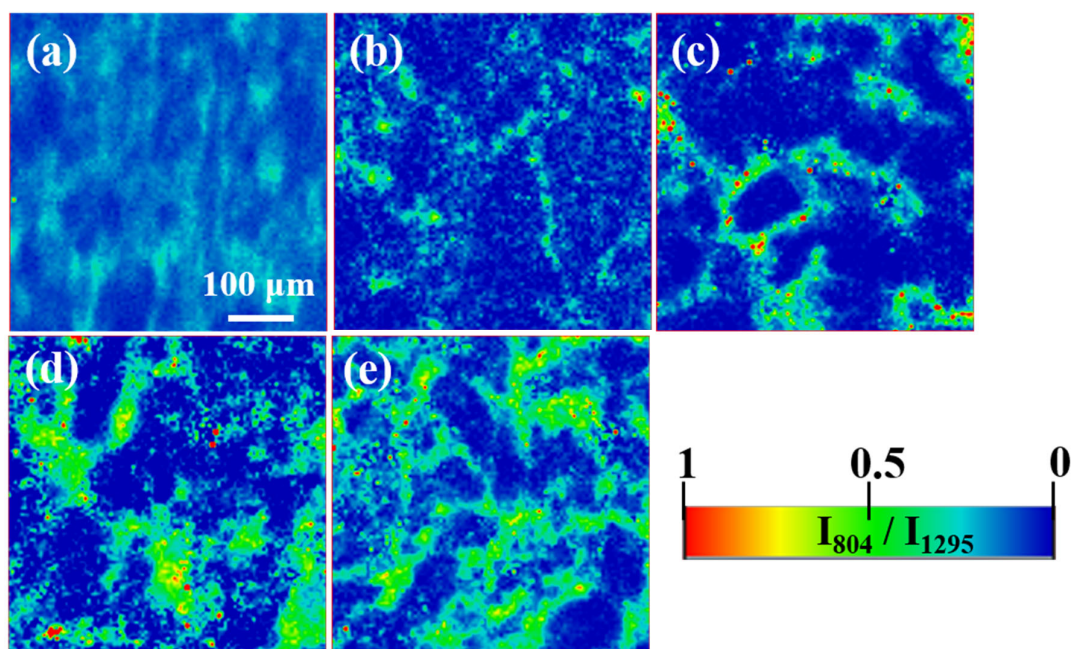


Figure 2. Raman mapping of ratio of the peak intensities for UHMWPE/PP/SiC composites: (a) 85/15/0; (b) 85/15/1; (c) 85/15/2; (d) 85/15/3 and (e) 85/15/4.

3.2. DSC analysis

Figure 3 shows the DSC curves of the UHMWPE/PP blend and UHMWPE/PP/SiC composites prepared under elongational flow, and the related results are summarized in Table 1. Clearly, the two melting (T_m) peaks that belong to UHMWPE and PP respectively was observed in the heating run, but their T_c and T_m values have no obviously change. Moreover, with the addition of 1 phr into the UHMWPE/PP blend, its crystallinity slightly increase from 49.8% to 51.9%, as appropriate amounts of nano-SiC particles could be worked as a heterogeneous nucleation agent to increase the crystallinity of UHMWPE [19]. However, with increasing nano-SiC content, the crystallinity of composites gradually decrease as the motion of polymer chain is impeded by the nano particles, thus hampering phase separation of the UHMWPE/PP blend and also decreasing their crystallization.

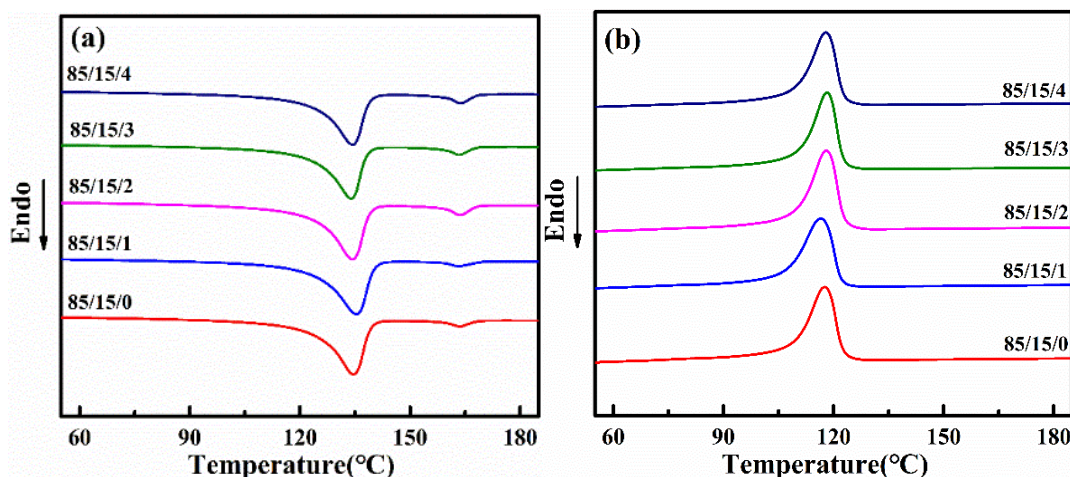


Figure 3. DSC curve of UHMWPE/PP/SiC composites: (a) secondary heating curve; (b) cooling curve.

Table 1. DSC related data of UHMWPE/PP/SiC composites.

Samples	T_c (°C)	T_m (°C)	ΔH_m (J/g)	X_c (%)
85/15/0	117.7	134.6	122.8	49.8
85/15/1	117.5	135.4	126.7	51.9
85/15/2	118.0	134.3	122.2	50.6
85/15/3	118.3	134.0	112.2	46.9
85/15/4	117.9	134.3	111.6	47.1

3.2. DMA

DMA is a useful tools to study thermo-mechanical behaviours of polymer composites. Figure 4 demonstrates the DMA curves of UHMWPE/PP and UHMWPE/PP/SiC composites. As shown in Figure 4a, the storage modulus for all the resulted samples exhibit an initial dramatic decrease, and then levels off at high temperature with increased temperature. Notably, the storage modulus of UHMWPE/PP/SiC is higher with respect to UHMWPE/PP, suggesting a better resistance to plastic deformation and yield stress that probably improve wear resistance. The related $\tan\delta$ - temperature curves in Figure 4b indicates that the UHMWPE/PP/SiC blend exhibits lower $\tan\delta$ than that of UHMWPE/PP blend. The decrease of loss factor help to decrease the coefficient of friction and hence the surface temperature, therefore improving the wear resistance [26]. The higher the storage

modulus, the stronger the rigidity of the material, which is beneficial to resist plastic deformation, thus improving the wear resistance. These above results can be contributed the limited motion of molecular chains by the addition of nano-SiC particles, resulting in the improved rigidity of UHMWPE/PP blends.

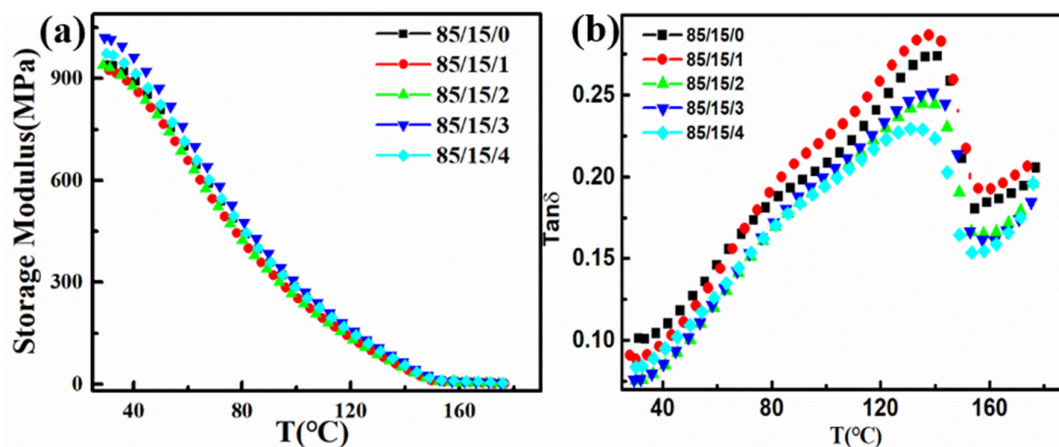


Figure 4. DMA curves of UHMWPE/PP and UHMWPE/PP/SiC composites: (a) storage modulus; (b) loss factor ($\tan\delta$).

3.3. Mechanical properties

Figure 2 shows the mechanical properties of UHMWPE/PP and UHMWPE/PP/SiC composites prepared under an elongational flow. The tensile strength and elongation at break of UHMWPE/PP are 25.3 MPa and 341.77%, respectively. When the addition of SiC into the blends from 1 phr to 3 phr, these values gradually increase. With 3 phr nano-SiC particles, the best tensile strength and elongation at break occurs, corresponding to increase by 30.16% and 36.11% respectively in comparison with UHMWPE/PP blend. These improved mechanical properties are attributed to the well dispersion of SiC nanoparticles along with a favourable interfacial adhesive under a consecutive elongational flow, thus reducing the stress transfer efficiency and crack propagation resistance [27]. But the mechanical properties slightly decrease when the addition SiC nanoparticles of 4 phr. This might be rationalized with the aggregation of nano particles that increase the stress concentration.

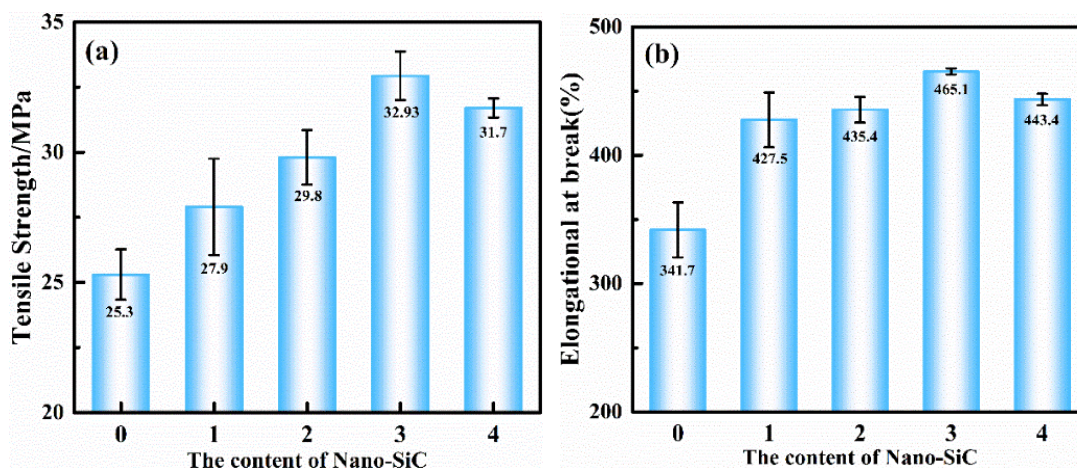


Figure 5. Tensile properties of UHMWPE/PP/SiC composites: (a) tensile strength; (b) elongation at break.

Moreover, the hardness value of UHMWPE, UHMWPE/PP and UHMWPE/PP/SiC composites is shown in Figure 6. The result shows that pure UHMWPE has the lowest hardness value as compared to UHMWPE/PP and UHMWPE/PP/SiC composites. The hardness value of UHMWPE/PP/SiC composites increases with increasing SiC content. Obviously, the addition of SiC of 4 phr into the polymer matrix, the UHMWPE/PP/SiC composites has the highest hardness value of 65.6 (Shore D). Because the nano SiC particles possessing relatively high hardness are served as excellent supporting point, effectively improving the ability of resistance to plastic deformation.

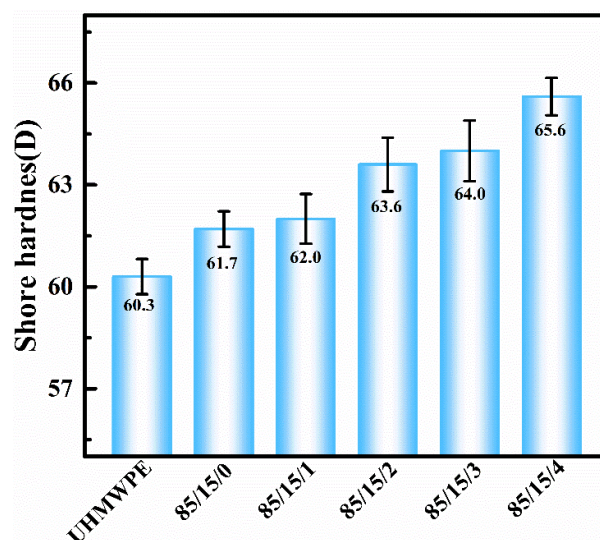


Figure 6. Shore hardness (D) of UHMWPE and UHMWPE/PP/SiC composites.

3.4. Friction properties

Figure 7 shows the Friction properties of UHMWPE/PP/SiC composites with different content of nano-SiC. As shown in Figure 7a, the friction coefficient curve of the all tested specimens reveals a similar change trend, which can be divided into two stages, which are the friction coefficient increases rapidly stage and the friction coefficient increases slowly stage. Noteworthy, with 1 phr nano-SiC, the friction coefficient of UHMWPE/PP/SiC composites decrease as compared with UHMWPE/PP blend, thus leading to a relatively lower weight loss of 0.4 mg, which can be explained by the increase in hardness of composite. However, the friction coefficient as well as the weight loss gradually increase when the content of nano-SiC increase over 1 phr. This is possibly due to the aggregation of nano particles that is prone to peel off under the force of friction, which is revealed by using SEM in the following part.

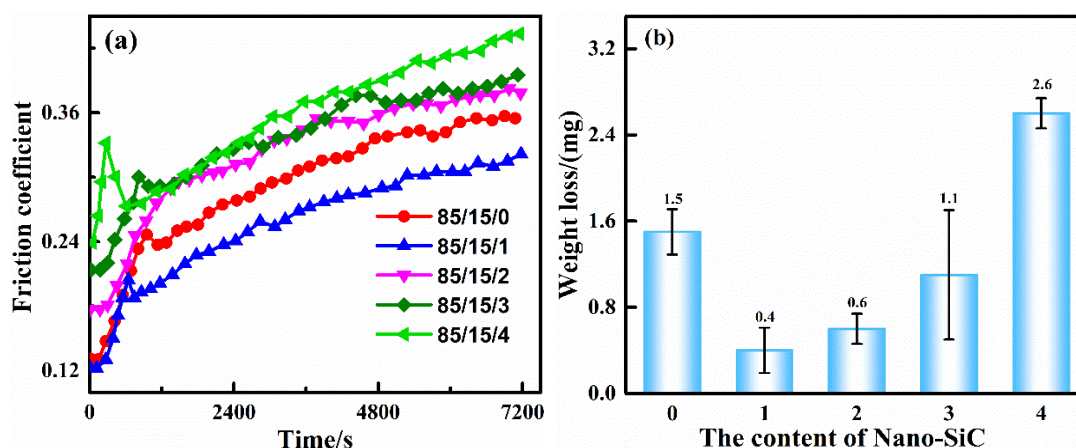


Figure 7. Friction properties of UHMWPE/PP/SiC composites with different content of Nano-SiC: (a) friction coefficient-time curve; (b) weight loss.

The worn surface morphology was investigated using SEM to reveal the wear mechanism of composites, as shown in Figure 8. Evidently, the friction morphology of UHMWPE/PP blend shows a serious wear damage as the relatively low surface hardness. With the addition of nano-SiC into the matrix, the surface damages are obviously reduced, suggesting that the relatively hard nano fillers has an effect on reducing the severity of micro-cutting mechanism [20]. More importantly, the nano-SiC particles display a ball-bearing effect on the surfaces of the friction pair, resulting a smooth and flat wear surface [28]. But the aggregation occurs with more nano-SiC particles, thus resulting in stress concentration accompanied by a more serious damage, as shown in Figure 4d,e.

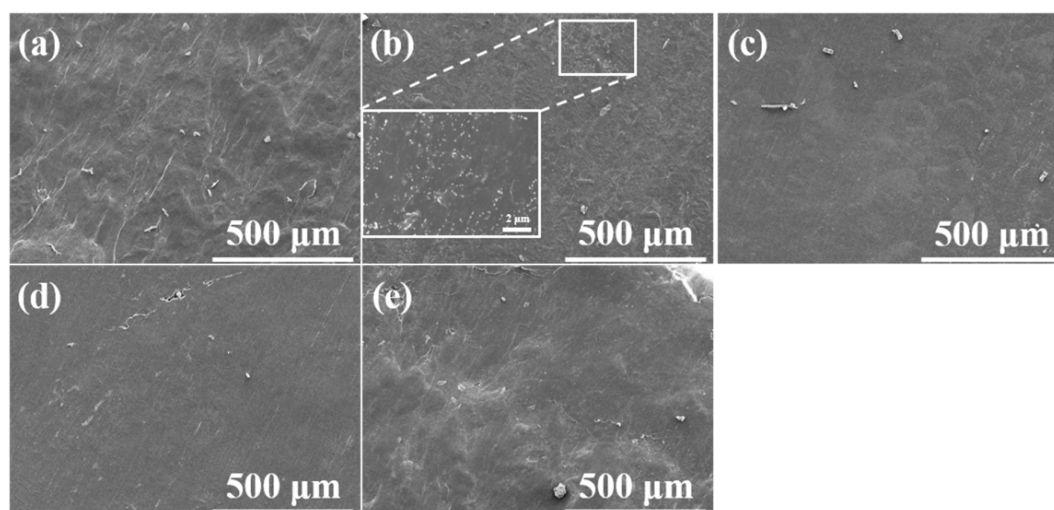


Figure 8. Friction morphology of UHMWPE/PP/SiC composites: (a) 85/15/0; (b) 85/15/1; (c) 85/15/2; (d) 85/15/3; (e) 85/15/4.

The test of cross scratch is valued by the width of scratch of samples, the narrower scratch, the better scratch resistance properties. Figure 9 shows the micrographs of the scratch of UHMWPE and UHMWPE/PP/SiC composites. As clearly shown in Figure 9a, pure UHMWPE have a comparatively wider scratch of 417.9 μm, due to its low hardness, thus easily leading to scratch by hard materials, which is one of the important factors that limit the wear properties of UHMWPE. The UHMWPE/PP blend show a narrower scratch of 396.1 μm as the hardness of PP is higher than that of UHMWPE. When the addition of SiC particles into UHMWPE/PP blend, the width of scratch gradually reduces as increasing the SiC content. The width of scratch reduces to 333.8 μm with 4 phr SiC content, a 20%

decrease as compared to pure UHMWPE. The reason can be rationalized with the relatively high modulus and hardness of SiC. With increase the SiC content, the hardness of UHMWPE/PP/SiC composites obviously increase, preventing the destruction of UHMWPE/PP blend structure by the needles, which is in good agreement with the obtained results from hardness value of UHMWPE/PP/SiC composites scratch width in Figure 6.

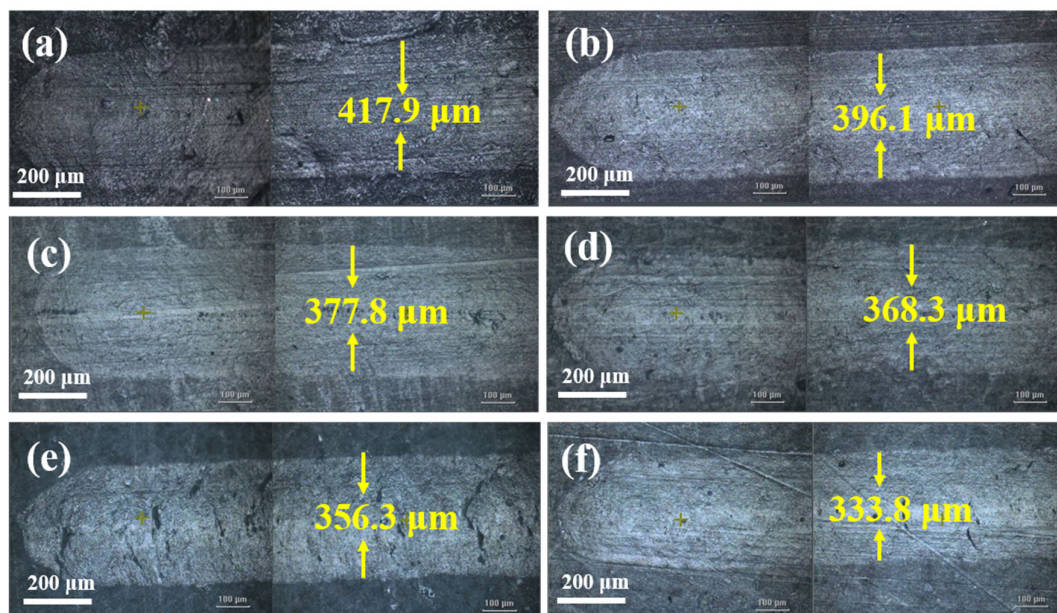


Figure 9. Micrographs of the scratch of UHMWPE and UHMWPE/PP/SiC composites: (a) UHMWPE; (b) 85/15/0; (c) 85/15/1; (d) 85/15/2; (e) 85/15/3; (f) 85/15/4.

4. Conclusions

In this work, the UHMWPE/PP/SiC composites with excellent mechanical properties and wear resistance were fabricated by the addition of SiC nanoparticles under a consecutive elongational flow without other additives or solvents. The morphology and thermal properties, mechanical properties, wear resistance as well as scratch resistance of UHMWPE/PP/SiC composites were fully revealed. The obtained results show that the mechanical properties and friction resistance of composites increase initially then decrease with the increase content of SiC. When the content of SiC is 3 phr, the mechanical properties of UHMWPE/PP/SiC composites reach to an optimum value, while the best wear resistance of composites is when the content of SiC was 1 phr. In addition, both the hardness and scratch resistance of composites improved upon increasing the content of SiC. The above results are due to the well dispersion of SiC nanoparticles along with favourable interfacial adhesive under a consecutive elongational flow. Our obtained results provide a new way to fabricate high performance UHMWPE products for a broader application.

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Conflicts of Interest: The authors declare no conflict of interest.

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