

## Tribological Mechanism Improving the Wear Resistance of Polyurethane/Epoxy Interpenetrating Polymer Network via Nanodiamond Hybridization

Shaoling Xia,<sup>1,2</sup> Yingliang Liu,<sup>1</sup> Linqi Zhang,<sup>2</sup> Dongmei Wang,<sup>2</sup> Wenjun Zou,<sup>2</sup> Jin Peng,<sup>2</sup> Shaokui Cao<sup>1</sup>

<sup>1</sup>School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450052, People's Republic of China

<sup>2</sup>School of Materials Science and Engineering, Henan University of Technology, Zhengzhou 450001, People's Republic of China

Correspondence to: S. Cao (E-mail: caoshaokui@zzu.edu.cn) or Y. L. Liu (E-mail: liuylxn@sohu.com)

**ABSTRACT:** The excellent synergistic effect of physical/mechanical properties of polyurethane/epoxy (PU/EP) interpenetrating polymer network (IPN) and the validity of nanofilling have one potential to improve the wear resistance of polymeric materials. With the aim of practical application, PU/EP IPN nanocomposites are prepared with nanodiamond (ND) as a reinforcing additive. Results showed the uniform thermal stability and the excellent compatibility between PU and EP in ND-hybridized PU/EP IPN. Simultaneously, ND particles work as crosslinked points improving the physical/mechanical properties of ND-hybridized PU/EP IPN, especially the wear resistance. The measurement of tribological property and the scanning electron microscope indicated that the wear resistance is able to be improved a lot by the formation of IPN and by the addition of ND. Consequently, the tribological mechanism of PU/EP IPN nanocomposites comes into being. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40244.

**KEYWORDS:** nanoparticles; nanowires and nanocrystals; composites; synthesis and processing; surfaces and interfaces

Received 12 September 2013; accepted 30 November 2013

DOI: 10.1002/app.40244

### INTRODUCTION

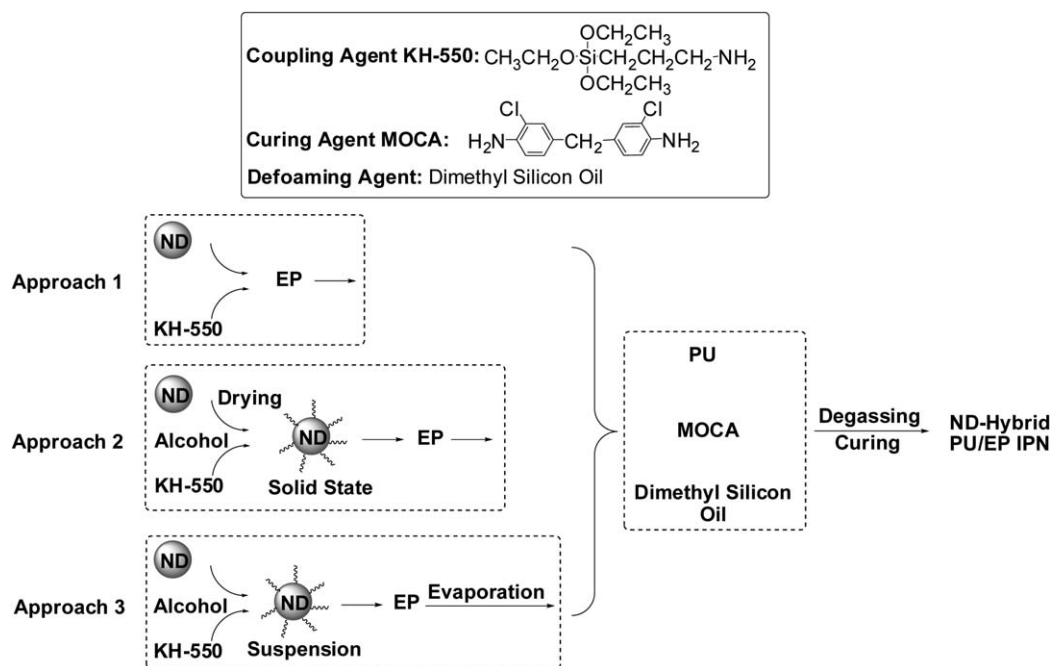
Polyurethane (PU) is widely applied at present as wear-resisting material, conveyor belt, cable sheath, and filter equipment due to its excellent physical properties, such as wear resistance, flexibility, and impact strength. However, the application of PU is somewhat limited by its relatively poor thermal stability and inferior mechanical properties. Therefore, a great amount of studies have been focused on the improvement of PU thermal and mechanical properties. One of them, the interpenetrating polymer networks (IPN) has been identified to be an effective way due to its excellent synergistic effect of thermal stability and mechanical properties induced by the forced compatibility of individual components.<sup>1–3</sup> IPN is usually considered to consist of two polymer networks holding together by permanent entanglement of covalent bonds on different polymer chains. Its preparation strategies include the simultaneous and sequential methods. For simultaneous method, the prepolymers and the cross-linking agents are mixed together. Then, the cross-linking reactions are carried out, simultaneously affording two continuous phases. For sequential method, one polymer network is formed in advance by swelling in the other polymeric monomer containing cross-linking agents. Sequentially, the other polymer

network is achieved through the *in-situ* polymerization reaction. However, epoxy (EP) resin is well known owing to its outstanding mechanical property and thermal stability. On account of good compatibility between PU and EP, the PU/EP composites will take on excellent physical/mechanical properties by synergistic effect. Furthermore, PU/EP IPN has been well researched to improve the mechanical property by the formation of PU/EP IPN<sup>4–7</sup> and by the reinforcement of aromatic fibers,<sup>8</sup> glass beads,<sup>9</sup> ZnO whisker,<sup>10</sup> etc. At the same time, the electroconductive property<sup>11</sup> and the damping property<sup>12–14</sup> are paid much attention, too. However, the wear resistance of PU/EP IPN is few studied up to now.<sup>15,16</sup>

The blending of nanofillers was considered an effective approach to improve the wear resistance of polymeric materials. It was found that the low content addition of nano-TiO<sub>2</sub> in short-fiber-reinforced EP could significantly reduce the friction coefficient and the wear rate.<sup>17</sup> The addition of silica nanoparticles is effective in reducing the wear rate of PMMA although the friction coefficient is increased from 0.27 to 0.4.<sup>18</sup> In addition, nano-Al<sub>2</sub>O<sub>3</sub> was also reported to have the synergistic effect in increasing the mechanical property and the wear resistance.<sup>19</sup> In recent years, nanodiamond (ND) is deemed as potential

Additional Supporting Information may be found in the online version of this article.

© 2013 Wiley Periodicals, Inc.



**Scheme 1.** Preparation procedures of ND-hybridized PU/EP IPN through three different approaches.

nanoadditive in polymeric materials due to its commercial availability and relative low cost. ND combines the excellent properties of both diamond and nanoparticles, such as high hardness, excellent wear resistance, good thermal conductivity, high specific surface area, and facile surface modification.<sup>20–22</sup> The effect of ND on the tribological behavior of polytetrafluoroethylene (PTFE) film was investigated in detail, indicating that the friction coefficient is reduced from 0.21 to 0.16 when 2 wt % ND is added into PTFE. Both the wear resistance and the thermal stability are improved very well.<sup>23</sup> Besides, the addition of ND also takes on an obvious antiwear and antifriction properties in lubricant<sup>24</sup> and a significant enhancement of hardness and elastic modulus.<sup>25,26</sup>

With the aim to apply PU as wear resistance materials, PU/EP IPN nanocomposites had been prepared with ND as a reinforcing additive. Simultaneously, the tribology property of PU/EP IPN nanocomposites was investigated primarily.<sup>27</sup> The results indicated that the tribology property is able to be improved a lot by the formation of IPN and by the addition of ND. Further to understand the improvement of tribological property in PU/EP IPN nanocomposites, the tribology mechanism of PU/EP IPN nanocomposites will be investigated in detail in this article by the measurement of dynamic thermomechanical analysis (DMA), scanning electron microscope (SEM), differential scanning calorimetry (DSC), and tribological property.

## EXPERIMENTAL

### Materials

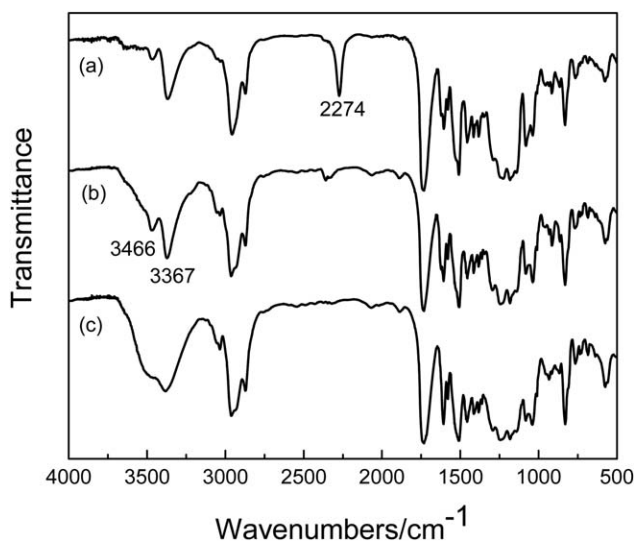
ND (UD200) with average diameter of 4–5 nm was obtained from Union Abrasive Materials and Abrasive Tools. EP resin with diglycidyl ether of bisphenol A (E-44) was supplied by Hunan Yueyang Baling Petrochemical Corporation. PU with NCO content of 6% was supplied by Institute of Chemistry,

Henan Academy of Sciences. 3,3'-Dichloro-4, 4'-diaminodiphenyl methane (MOCA) was purchased as curing agent from Suzhou Xiangyuan Special Fine Chemical. 3-Aminopropyl triethoxysilane (KH-550) was obtained as coupling agent from Hubei Wuda Organic New Materials. Dimethyl silicon oil was purchased as defoaming agent from Shandong Dayi Chemical. All the materials are technical grade and used without purification.

### Preparation of ND-Hybridized PU/EP IPN

Three different approaches were applied in the preparation of ND-hybridized PU/EP IPN with an attempt to get even distribution of ND in the matrix and better interfacial adhesion. The specific procedures were illustrated in Scheme 1 and described detailedly below:

- Approach 1: KH-550 and ND were directly added into the precursor EP. The mixture was stirred for 12 h at 70°C, followed by the ultrasonication of 2 h. Then, the precursor PU, the melt MOCA, and the defoaming agent were added in turn and homogenized, degassed, cured by two stages under the same conditions as the previous preparation of PU/EP IPN.<sup>18</sup> The first stage was carried out at 70°C for 3 h for pre-polymerization and the second stage at 120°C for 4 h for complete curing.
- Approach 2: With the aim of the better surface modification of ND by KH-550, alcohol was applied as a mediate. ND was added into the alcohol solution of KH-550 and stirred for 4 h. Then, the KH-550-modified ND was obtained as a caking solid by centrifugation and drying. The modified ND powder was presented by grinding and blended with the precursor EP. Then, the mixture was homogenized with the precursor PU, the melt MOCA and the defoaming agent and degassed, cured by the same procedure as Approach 1.



**Figure 1.** FT-IR spectra of PU/EP mixture with MOCA as curing agent (a: before curing, b: cured for 30 min, c: cured for 5 h).

- Approach 3: The surface of ND was also modified in alcohol by KH-550 as Approach 2. ND was added into the alcohol solution of KH-550 and stirred at 70°C for 4 h. The difference with Approach 2 was that the alcohol solution of KH-550-modified ND was kept and directly applied without the further centrifugation and drying in the flowing procedure. The reason is that the KH-550-modified ND could be well dispersed into the precursor EP. After the alcohol solution of KH-550-modified ND was directly added to the precursor EP, the mixture was stirred for 12 h followed by ultrasonication for 2 h. Finally, the remaining alcohol was evaporated in a vacuum oven for 2 h. Succeedingly, the precursor PU and other reagents were added to the alcohol-free dispersoid as Approaches 1 and 2. The mixture was homogenized, degassed, cured also by the same procedure as Approach 1.

The neat PU/EP IPNs were also presented by our previous procedure for comparison.<sup>27</sup> A series of PU/EP IPN samples were prepared with the different EP contents of 10, 20, 30, 40, and 50 wt %.

### Testing Methods

Fourier transform infrared spectroscopy (FT-IR, Shimadzu Prestige-21) was employed to monitor the curing reaction of PU/EP IPN. Its sample was prepared as the same as previous procedure.<sup>27</sup> The mixture of PU, EP and MOCA was diluted with acetone and then evenly spread on the surface of KBr sheet. Thermal stability was tested by thermal gravimetric analysis (TGA, Peking Optical Instrument Factory, WCT-2) with a heating rate of 10°C/min in air condition. DMA (NETZSCH, DMA242C) was detected to investigate the dynamic mechanical properties by using the compassing mode at a frequency of 1 Hz and at a heating rate of 3°C/min. Tensile strength and elongation were tested by tensile instrument (Jinan Faen Instrument Factory, WDW-S) according to GB/T 528–1998. Wear resistance was studied by a pin-on-disc friction wear testing machine (Lanzhou Zhongke, QG-700) at room temperature under dry condition. The counterpart pin is fabricated by steel with a

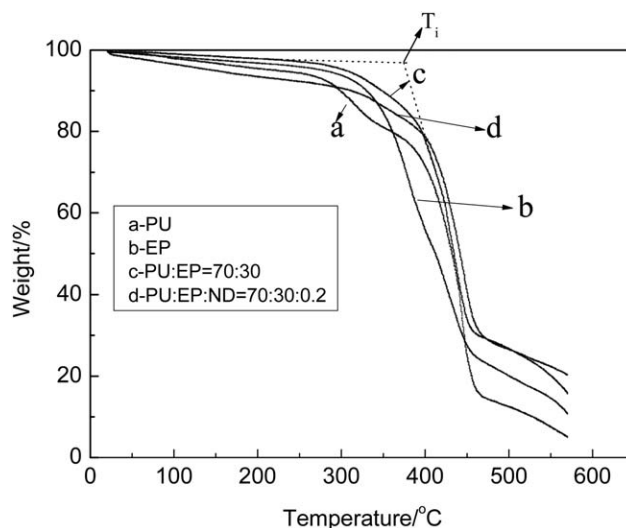
diameter of 5 mm. The normal load and sliding speed were 0.4 MPa and 0.5 m/s, respectively. Experimental data were collected during 10 min of wearing for disc-like samples with a diameter of 60 mm and a thickness of 5 mm.

### RESULTS AND DISCUSSION

Due to the excellent synergistic effect of physical/mechanical properties of PU/EP composites and the validity of nanofilling to improve the wear resistance of polymeric materials, PU/EP IPN nanocomposites have been previously prepared in our laboratory with ND as a reinforcing additive.<sup>27</sup> As a result, the tribology property is able to be improved a lot by the formation of IPN and by the addition of ND. Further, to understand the improvement of tribological property, the PU/EP IPN nanocomposites were investigated more detailedly. Consequently, the tribology mechanism of PU/EP IPN nanocomposites comes into being in this article by the measurement of DMA, SEM, DSC, and tribological property.

The FT-IR spectra of PU/EP mixture at different curing times in Figure 1 indicated that the curing reaction could be carried out very well. As shown in Figure 1, the stretching band of isocyanate-group (NCO) at 2274 cm<sup>-1</sup> becomes weaker with the curing reaction developed until the disappearance at the curing time of 5 h in Figure 1(c), illustrating the complete consumption of NCO groups in PU. At the same time, two N–H stretching bands at 3466 and 3367 cm<sup>-1</sup> could be observed in Figure 1(a,b), which corresponds to amine (NH<sub>2</sub>) groups in MOCA. Evidently, the signal at 3466 cm<sup>-1</sup> in Figure 1(c) becomes one shoulder peak, revealing that the NH<sub>2</sub> group in MOCA has been converted to urea group by reacting with NCO groups in PU.

The thermal stability of resulting nanocomposites was investigated by TG. The TG curves of PU, EP, PU/EP IPN, and ND-hybridized PU/EP IPN were shown in Figure 2. The DTG curves derived by the differential from the TG curves were also given in Supporting Information Figures s1–s4 of electric supporting information. One of them, the sample of ND-



**Figure 2.** TG curves of PU, EP, PU/EP IPN, and ND-hybridized PU/EP IPN.

**Table I.** TG and DTG Data of PU, EP, PU/EP IPN, and ND-Hybridized PU/EP IPN

Samples	$T_{\text{onset}}$ (°C)	$T_p$ (°C)
PU	254	296, 427, 532
EP	278	378, 408, 428, 581
PU : EP = 70 : 30	287	390 (sh), 412, 580
PU : EP : ND = 70 : 30 : 0.2	293	418, 590

Note: Summarized from Figure 2 and Supporting Information Figures s1–s4.  $T_{\text{onset}}$  is the onset degradation temperature;  $T_p$  is the peak temperature on DTG curves.

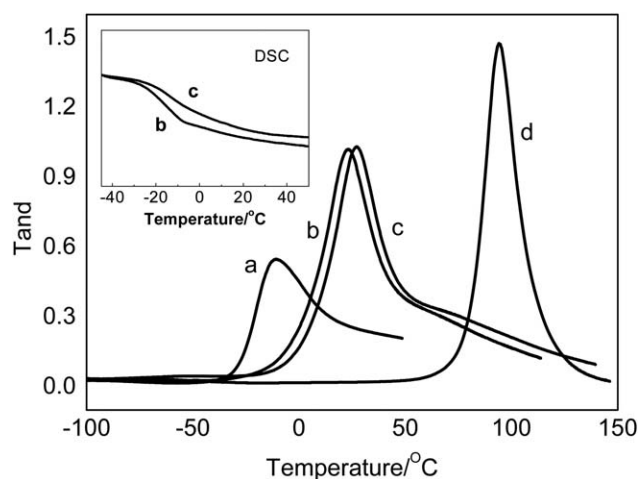
hybridized PU/EP IPN was prepared through Approach 3 so as that for DMA, DSC, and SEM. All the samples for TG measurements were cured with MOCA as a curing agent at two stages, which was respectively carried out at 70°C for 3 h and then at 120°C for 4 h. All the TG and DTG data were summarized in Table I. The onset decomposition temperature ( $T_{\text{onset}}$ ) of PU, EP, PU/EP IPN, and ND-PU/EP IPN hybrid are 254, 278, 287, and 293°C, respectively. In general, the thermal stability of binary blending polymers falls in between both polymer components. However,  $T_{\text{onset}}$  of PU/EP IPN is higher than that of PU and EP, indicating that PU and EP are held tightly together inside the PU/EP IPN network by strong intermolecular interactions, such as hydrogen bond or Van der Waals force between PU and EP. Additionally,  $T_{\text{onset}}$  of ND-hybridized PU/EP IPN is even higher than that of PU/EP IPN. This suggested that the ND particles dispersed inside PU/EP IPN work as crosslinked points, which could limit the movement of chain segments and consequently enhance the thermal stability. As shown in Supporting Information Figure s1, the decomposition peak at 296°C in the DTG curve of PU, which is ascribed to the degradation of isocyanate terminal group in PU, disappears in the DTG curve of PU/EP IPN in Supporting Information Figure s3. This indicated that the isocyanate terminal groups in PU are completely converted. This result is in accord with that of IR

**Table II.** DMA Data of PU, EP, PU/EP IPN, and ND-Hybridized PU/EP IPN

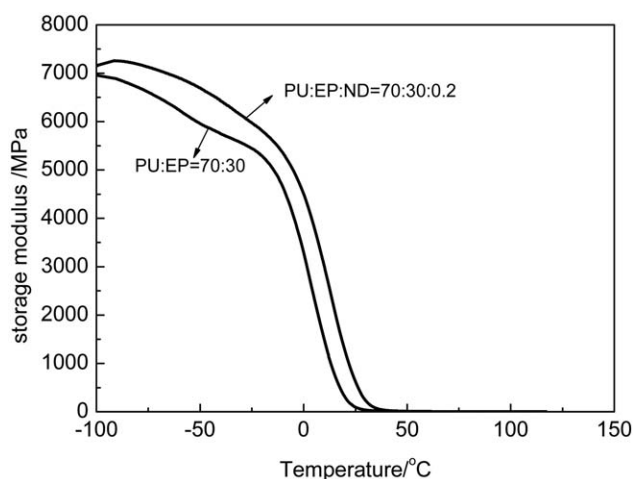
Samples	$T_g$ (°C)	$\tan\delta$	$\delta$
PU	-11.7	0.55	28.8°
EP	94.1	1.48	56.0°
PU : EP = 70 : 30	22.9	1.02	45.6°
PU : EP : ND = 70 : 30 : 0.2	27.0	1.03	45.8°

Note: Summarized from Figure 3.  $T_g$  is the glass transition temperature from DMA;  $\tan\delta$  is the dissipation factor;  $\delta$  is the phase angle.

measurement. Furthermore, the peak at 427°C in the DTG curve of PU in Supporting Information Figure s1 and the peaks at 378, 408, and 428°C in the DTG curve of EP in Supporting Information Figure s2 are turned into one peak at 412°C with a shoulder peak at 390°C in the DTG curve of PU/EP IPN in Supporting Information Figure s3, which is further changed to one single decomposition peak at 418°C in the DTG of ND-hybridized PU/EP IPN in Supporting Information Figure s4. These results told us that the thermal stability is increased gradually from PU or EP to PU/EP IPN and then to ND-hybridized PU/EP IPN. Especially, the single decomposition peak of ND-hybridized PU/EP IPN suggested the uniform thermal stability and the excellent compatibility between PU and EP, which is further proved by the following DMA measurement. The compatibility investigation of PU and EP inside IPN by DMA measurement was showed by the dissipation factor ( $\tan\delta$ )-temperature curves of PU, EP, PU/EP IPN (PU : EP = 70 : 30), and ND-hybridized PU/EP IPN (PU : EP : ND = 70 : 30 : 0.2) in Figure 3. All the DMA data were summarized in Table II. Generally, the peak temperature in  $\tan\delta$ -temperature curve is regarded as the glass transition temperature ( $T_g$ ) of the samples and the corresponding  $\delta$  is referred as phase angle, which is equal to 0° in ideal elastic response and to 90° in ideal viscous response. Evidently, both PU/EP IPN and ND-hybridized PU/EP IPN have only one glass transition of 22.9 and 27.0°C as shown in Figure 3, which was also confirmed by each single

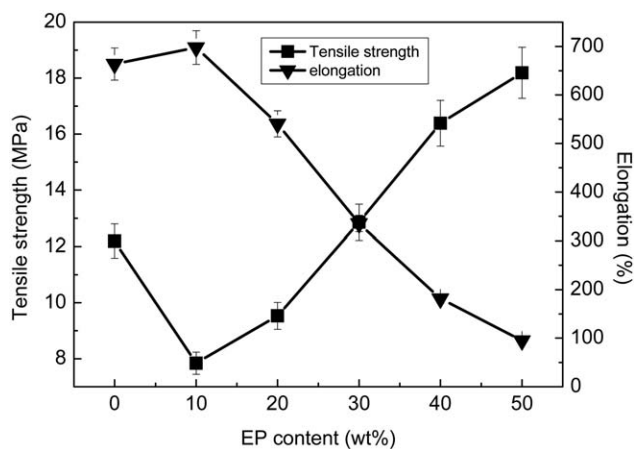


**Figure 3.**  $\tan\delta$ -temperature curves of PU (a), PU/EP IPN (b), ND-hybridized PU/EP IPN (c), and EP (d); The DSC curves of PU/EP IPN and ND-hybridized PU/EP IPN are shown in the inset.



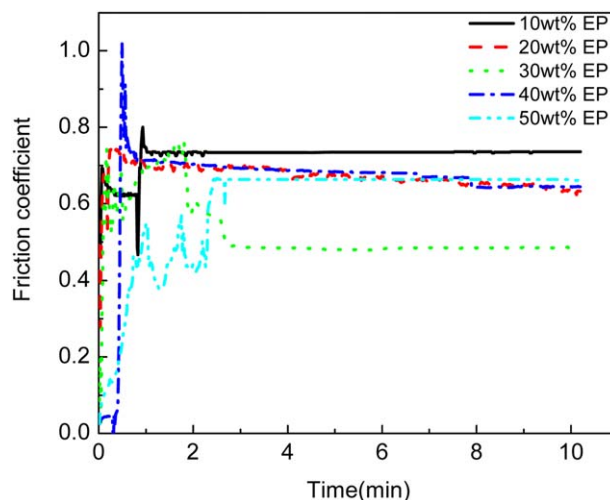
**Figure 4.** Storage modulus-temperature curve of PU/EP IPN and ND-hybridized PU/EP IPN.





**Figure 5.** Tensile strength and elongation of PU/EP IPN with different PU/EP ratio.

glass transition at  $-16.9$  and  $-6.9^{\circ}\text{C}$  of DSC diagram in the inset of Figure 3. Although there is an obvious difference in  $T_g$  existed between DMA and DSC due to the difference in measurement mechanism, it was out of question that these two results reveal the good compatibility between PU and EP inside IPN, indicating that intermolecular hydrogen bond or Van der Waals force could be more easily formed between two networks. This will be propitious to enhancing the physical/mechanical properties by synergistic effect of PU and EP inside PU/EP IPN. Besides, the values of dissipation factor  $\tan\delta$  of PU/EP IPN (1.02) and ND-hybridized PU/EP IPN (1.03), which are located between that of PU (0.55) and EP (1.48). Correspondingly, the phase angles of PU/EP IPN ( $45.6^{\circ}$ ) and ND-hybridized PU/EP IPN ( $45.8^{\circ}$ ) are between that of PU ( $28.8^{\circ}$ ) and EP ( $56.0^{\circ}$ ). This indicated that PU/EP IPN and ND-hybridized PU/EP IPN take on a comprehensive viscoelasticity of PU and EP, which is one main basic of polymeric physical/mechanical properties. It might be resulted from synergistic effect of PU and EP inside PU/EP IPN, which will be further proved by the following SEM measurement. In addition, the storage modulus-temperature curve in Figure 4 suggested that the storage modulus of ND-hybridized PU/EP IPN is higher than that of PU/EP IPN. The reason is that KH550-modified ND has huge surface energy and a great deal of amine groups on the surface. When ND particles were uniformly dispersed inside the PU/EP IPN, the amine groups on its surface could react with the isocyanate groups and EP groups inside PU/EP IPN. In this case, ND particles work as crosslinked points to restrain the movement of polymeric segments, leading to the increase of storage modulus.



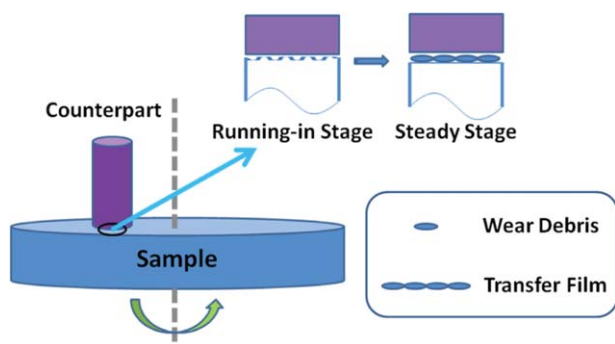
**Figure 6.** Sliding performance of PU/EP IPNs with different EP contents. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The optimal EP content of 30% used in the above measurements was confirmed by the measurement of tensile strength and elongation of PU/EP IPN with different EP content via tensile testing. The result in Figure 5 showed that the tensile strength of PU/EP IPN declines before the EP content of 10% and then gradually increased with the increase of EP content. It was reported that the EP phase could not form the continuous network but some separate particles when its content is  $<30\%$ .<sup>28,29</sup> These separate EP particles are filled into the PU network and act as defective points for tensile break, resulting in a smaller tensile strength. As the EP content increased up to 30 wt %, the continuous EP network could be formed and entwined with the PU network. In this case, the tensile strength was enhanced due to the synergistic effect of continuous PU and EP network inside PU/EP IPN. Nevertheless, the elongation of PU/EP IPN shows an opposite trend. In order to obtain the appropriate tensile strength and elongation, the EP content of 30% at the cross point of two curves in Figure 5 was selected to prepare the ND-hybridized PU/EP IPN in our experiments. The measurement of tribological behavior of PU/EP IPN with different EP contents in Figure 6, which was carried out by pin-on-disc friction wear testing machine, showed that the PU/EP IPN with 30 wt % EP content has a minimum friction coefficient of 0.49, which is defined as the average value in the steady stage. This result also suggested the formation of excellent binary interpenetrating network between PU and EP inside PU/EP IPN at the EP content of 30%. The specific wear rate shows the same trend as the friction coefficient and has the minimum

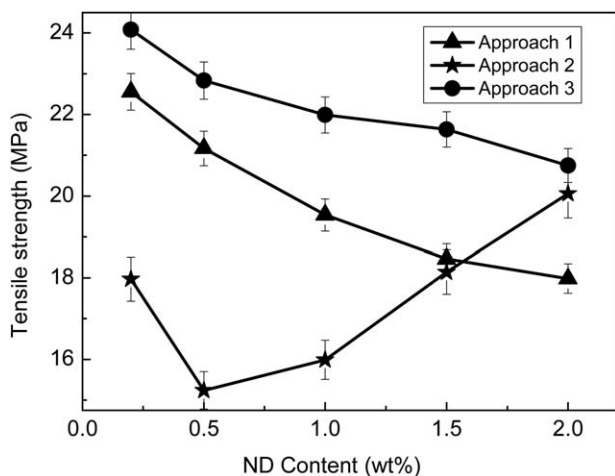
**Table III.** Specific Wear Rate and Friction Coefficient of PU/EP IPN with Different EP Content

EP Content (wt %)	10%	20%	30%	40%	50%
Specific Wear Rate ( $\times 10^{-5} \text{ mm}^3/\text{Nm}$ )	11.1	5.9	1.8	2.7	2.9
Friction Coefficient	0.736	0.671	0.485	0.674	0.663

Note: Summarized from Figure 6.

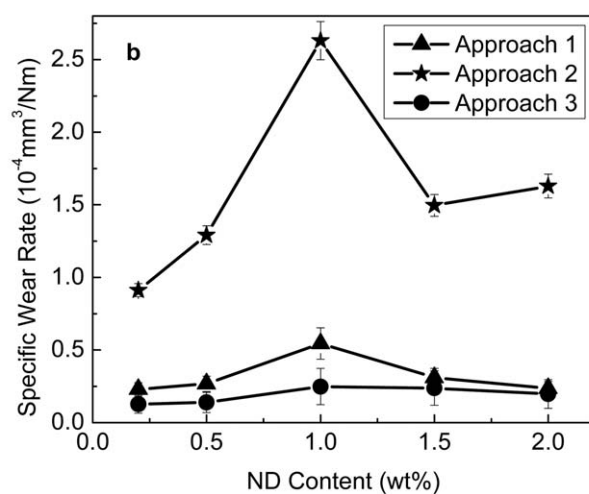
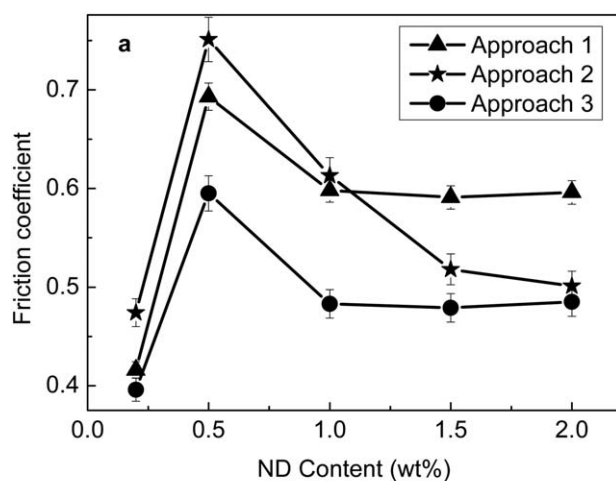


**Figure 7.** Illustration of sliding behavior during wearing process. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



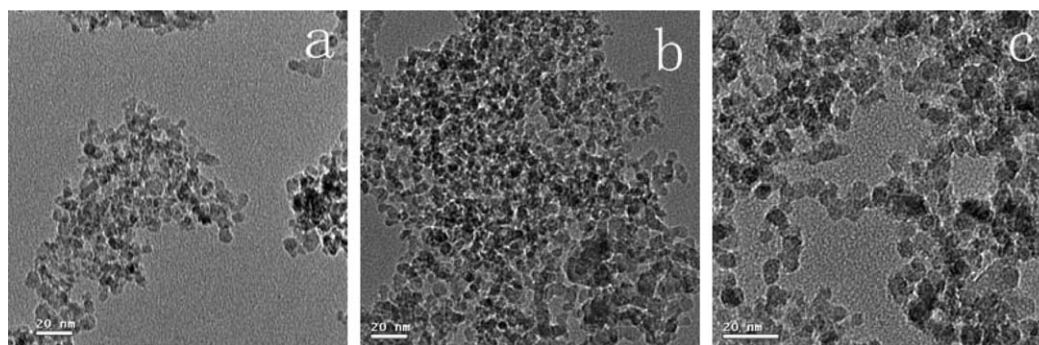
**Figure 8.** Tensile strength of ND-hybridized PU/EP IPN prepared through different approaches.

value of  $1.8 \times 10^{-5} \text{ mm}^3/\text{Nm}$  at 30% EP content, which is smaller than those of common polymer materials, such as  $2.10 \times 10^{-3} \text{ mm}^3/\text{Nm}$  of ultrahigh molecular weight polyethylene and  $2.17 \times 10^{-5} \text{ mm}^3/\text{Nm}$  of polyoxymethylene.<sup>30</sup> Obviously, the PU/EP IPN system is advantageous in wear resistance ability. The friction coefficient and specific wear rate of PU/EP IPN with different EP contents were listed in Table III. Notably, all the curves in Figure 6 showed the typical sliding behavior against metallic counterpart, belonging to polymeric composites.

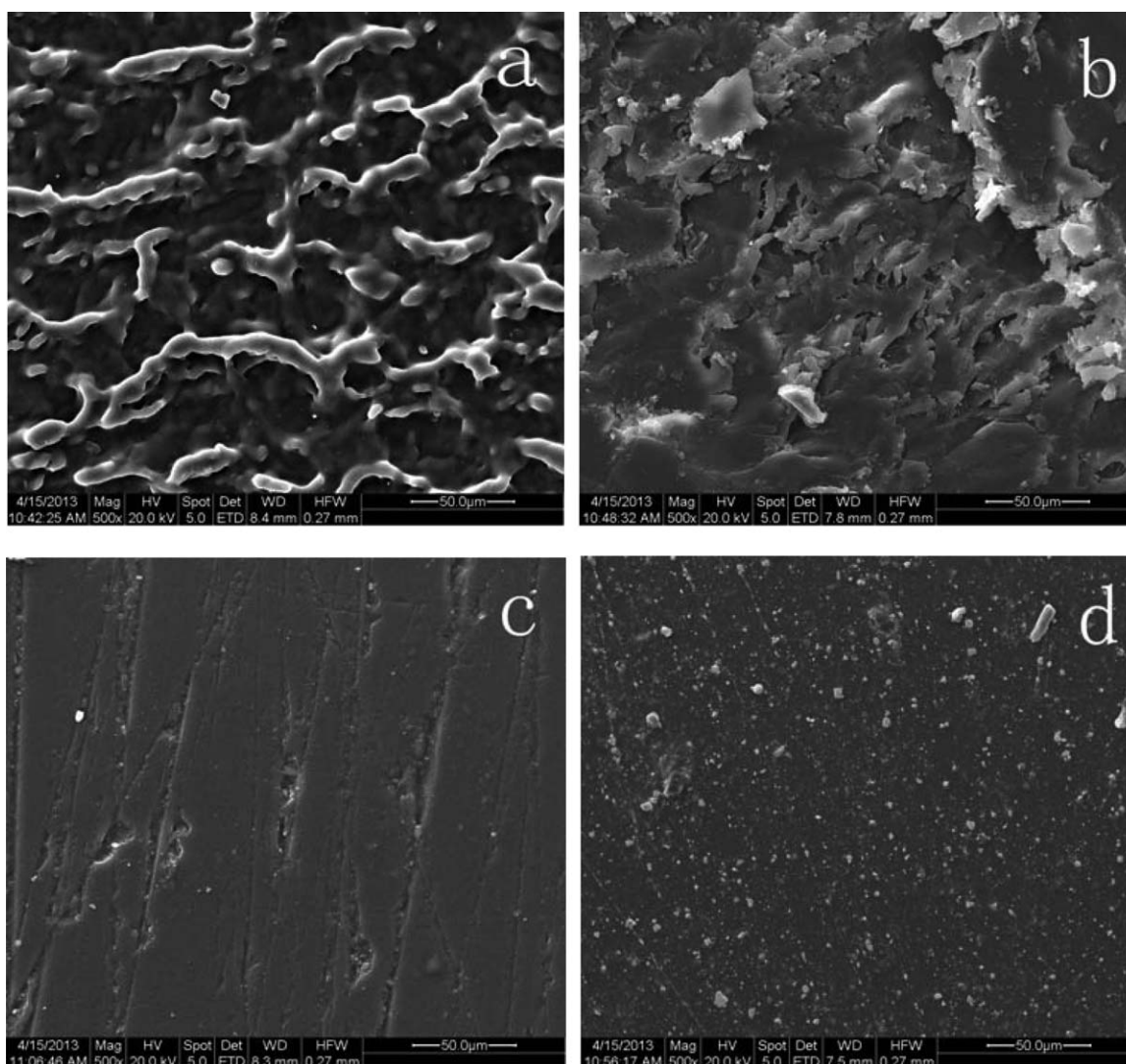


**Figure 10.** Friction coefficients (a) and specific wear rate (b) of ND-hybridized PU/EP IPN by different approaches.

There are two wearing stages on the sliding performance in Figure 6, that is, the running-in stage and the steady stage. It was concerned that the transfer film is gradually formed out of wear debris at the beginning of wearing so the friction coefficient is not stable and keep a rising trend. With the real contact area increased, a higher adhesive force is obtained. This process is described as the running-in stage. When the transfer film was formed, the friction coefficient turns into a relative stable value



**Figure 9.** TEM images of ND-hybridized PU/EP IPN with 0.2 wt % ND by Approach 1 (a), Approach 2 (b), and Approach 3 (c).



**Figure 11.** SEM morphology of friction surface of PU (a), EP (b), PU/EP IPN (c), and ND-hybridized PU/EP IPN (d).

during the steady stage.<sup>31–33</sup> The specific sliding behavior during wearing process was illustrated in Figure 7.

On the basis of the above experimental results, the EP content of 30% is fixed in investigating the effect of ND content on tensile strength, friction coefficient and specific wear rate of PU/EP IPN prepared through different approaches. The tensile strength of ND-hybridized PU/EP IPN with various ND contents was illustrated in Figure 8. All the ND-hybridized PU/EP IPN show a higher tensile strength than 12.9 MPa of neat PU/EP IPN. The highest tensile strength of 24.1 MPa was found in ND-hybridized PU/EP IPN with the ND content of 0.2% prepared by Approach 3. The samples prepared by Approach 2 exhibited the lowest tensile strength. The reason why three different approaches result in such a big difference in tensile strength is considered to be derived from different dispersion degree of ND particles in PU/EP IPN. The TEM images of ND-hybridized PU/EP IPN with 0.2 wt % ND by Approaches 1–3 were shown in Figure 9. As shown in Figure 9(b), a serious agglomeration

of ND is exactly observed in ND-hybridized PU/EP IPN via Approach 2, where ND particles treated with KH-550 in alcohol solution were dried at 120°C to obtain the caking solid. An excellent dispersion of ND is observed in ND-hybridized PU/EP IPN via Approach 3 as shown in Figure 9(c), where the ND particles treated with KH-550 alcohol solution was directly blended with EP precursor under vigorous stirring followed by ultrasonic dispersing. For ND-hybridized PU/EP IPN via Approach 1, ND and KH-550 was directly mixed into EP precursor, which cannot afford a good surface modification of ND via KH-550 hydrolysis in the absence of alcohol. The low tensile strength of ND-hybridized PU/EP IPN via Approaches 1 and 2 is due to the agglomeration of ND particles at different extent as shown in Figure 9(a,b).

The effect of ND on the wear resistance of PU/EP IPN was also investigated and the friction coefficient and specific wear rate of ND-hybridized PU/EP IPN by three different approaches were illustrated Figure 10. The ND-hybridized PU/EP IPN via



Approach 3 exhibited the minimum friction coefficient and specific wear rate due to a more homogeneous dispersion of ND particles in the IPN matrix. In this occasion, ND particles could exist independently in the transfer film and roll as a lubricant in the process of wear test as shown in Figure 7. The contact mechanism is changed to three-body mild abrasive wear due to the presence of ND particles in the contact region.<sup>31</sup> With the aim further to understand the tribology mechanism, the worn surfaces of PU, EP, PU/EP IPN (PU : EP = 70 : 30) and ND-hybridized PU/EP IPN (PU : EP : ND = 70 : 30 : 0.2) were detected by SEM as shown in Figure 11. The reciprocating friction was carried out on all the samples. Figure 11(a) shows the morphology of worn surface of pure PU. It could be seen that PU surface was damaged homogeneously. Only some slim ridges are left when the counterpart is moved away. At this time, a sign of melting could be seen on the edge of ridges. Evidently, the most of material on the surface has been worn off and melt under frictional heat. The friction mechanism of PU is attributed to adhesion wear since the surface was mainly damaged by viscosity flow. There are many cracks, fractures, and debris on the worn surface of pure EP in Figure 11(b). These characters indicated the typical abrasive and fatigue wear mechanism. Since EP is hard and brittle, the cracks on the surface are easily generated by repeated stressing, then gradually grow, and join each other until wear debris are detached. The resultant debris then acts as the abrasives aggravating the wear of countersurface. On the whole worn surface of PU/EP IPN in Figure 11(c), only some grooves could be seen. This phenomenon is caused by the soft-hard phase combination structure of PU/EP IPN on the surface, which are the EP phase in the hard region and the PU phase in the soft region. When the surface was exposed to the counterpart pressure, the PU soft region is depressed via elastic deformation while the EP hard region could not deform. Therefore, the hard region is ploughed into the soft region by counterpart pin. The situation will be changed by the addition of ND particles. The ND particles embedded in ND-hybridized PU/EP IPN result in some protuberances on the surface to suffer from the loading pressure during friction. As displayed in Figure 11(d), the microdots reveal that the ND particles are worn off and act as the rolling ball in the transfer film, decreasing the friction coefficient. This point is in accord with the friction model in Figure 7. Simultaneously, the worn groove of polymer IPN matrix in Figure 11(c) is inhibited to a large extent owing to the reinforcement of ND to PU soft phase. As we expected, the wear resistance of PU/EP IPN is improved outstandingly by the addition of ND.

## CONCLUSIONS

Due to the excellent synergistic effect of physical/mechanical properties of PU/EP composites and the validity of nanofilling to improve the wear resistance of polymeric materials, PU/EP IPN nanocomposites were prepared in our laboratory with ND as a reinforcing additive. The TG result showed the single decomposition peak of ND-hybridized PU/EP IPN, indicating the uniform thermal stability and the excellent compatibility between PU and EP. This point was also proved by DMA measurement. Simultaneously, it was suggested that ND particles

work as crosslinked points to improve the physical/mechanical properties of ND-hybridized PU/EP IPN, especially the wear resistance. One of them, Approach 3 is regarded as the best way to prepare ND-hybridized PU/EP IPN, which is the ND particles treated with KH-550 alcohol solution and directly blended with EP precursor, followed by the mixing with PU. With the aim to understand the tribology mechanism of PU/EP IPN nanocomposites, PU/EP IPN nanocomposites were characterized by the measurement of tribological property and SEM. The results told us that the tribology property is able to be improved a lot by the formation of IPN and by the addition of ND. Consequently, the tribological mechanism of PU/EP IPN nanocomposites comes into being.

## ACKNOWLEDGMENTS

The authors greatly acknowledge the financial supports from Zhengzhou Municipal Bureau for Science and Technology (No. 0910SGYG23258-1) and from the National Natural Science Foundation of China (NSFC, 20774088, 20874091, 21274133, and U1304212).

## REFERENCES

1. Anzlovar A.; Zigon M. *J. Polym. Sci. Part B: Polym. Phys.* **2002**, *40*, 115.
2. Desai S.; Thakore I. M.; Brennan A.; Devi S. *J. Appl. Polym. Sci.* **2002**, *83*, 1576.
3. Athawale V.; Kolekar S. *J. Macromol. Sci. A.* **2000**, *37*, 65.
4. Mahesh K. P. O.; Alagar M.; Jothibasu S. A. *J. Appl. Polym. Sci.* **2006**, *99*, 3592.
5. Chen C. H.; Chen M. H. *J. Appl. Polym. Sci.* **2006**, *100*, 323.
6. Park S. J.; Jin J. S. *J. Appl. Polym. Sci.* **2001**, *82*, 775.
7. Baek J. O.; Park S. J.; Gong H. J. *Macromol. Symp.* **2007**, *249–250*, 654.
8. Chen S. B.; Wang Q. H.; Wang T. M. *J. Reinf. Plast. Comp.* **2013**, *32*, 1136.
9. Bakar M.; Kostrzewa M. J. *Thermoplast. Compos.* **2010**, *23*, 749.
10. Ma C.; Chen E. F.; Sun T.; Shi S.; Fang Q. H. *J. Reinf. Plast. Comp.* **2012**, *31*, 1564.
11. Xi X. R.; He Z. M.; Yu C. S.; Lin W.; Qi X.; Wang L.; Xiong Q. *J. Adhes.* **2010**, *86*, 791.
12. Chen S. B.; Wang Q. H.; Wang T. M. *Mater. Des.* **2012**, *38*, 47.
13. Yu W. W.; Zhang D. Z.; Du M.; Zheng Q. *Eur. Polym. J.* **2013**, *49*, 1737.
14. Chen S. B.; Wang Q. H.; Wang T. M. *Mater. Chem. Phys.* **2011**, *130*, 680.
15. Jia Q. M.; Shan S. Y.; Wang Y. M.; Gu L. L.; Li J. B. *Polym. Adv. Technol.* **2008**, *19*, 859.
16. Jia Q. M.; Zheng M. S.; Shen R. J.; Chen H. X. *Polym. Int.* **2006**, *55*, 257.
17. Chang L.; Zhang Z.; Breidt C.; Friedrich K. *Wear* **2005**, *258*, 141.



18. Lin L. Y.; Kim D. E. *Tribol. Int.* **2011**, *44*, 1926.
19. Wetzel B.; Hauptert F.; Zhang M. Q. *Compos. Sci. Technol.* **2003**, *63*, 2055.
20. Krueger A. *Mater J. Chem.* **2008**, *18*, 1485.
21. Jee Y. A.; Lee M. Y. *Curr. Appl. Phys.* **2009**, *9*, 144.
22. Zhang X. Q.; Chen M.; Lam R. *ACS. Nano.* **2009**, *3*, 2609.
23. Lee J. Y.; Lim D. S. *Surf. Coat. Technol.* **2004**, 188–189, 534.
24. Chou C. C.; Lee S. H. *J. Mater. Process. Tech.* **2008**, *201*, 542.
25. Cunningham G.; Shenderova O.; Tyler T.; Ray M.; Walsh J.; Casulli M.; Hens S.; McGuire G.; Kuznetsov V.; Lipa S. *Diam. Relat. Mater.* **2007**, *16*, 1213.
26. Urmimala M.; Eswar P. K.; Ramamurty U.; Rao C. N. R. *Solid. State Commun.* **2009**, *149*, 1693.
27. Xia S. L.; Zhang L. Q.; Wang D. M.; Zou W. J.; Peng J.; Cao S. K. *Adv. Mater. Res.* **2012**, *558*, 1533.
28. Chiu H. T.; Chiu S. H.; Wu J. H. *J. Appl. Polym. Sci.* **2003**, *89*, 959.
29. Li Y.; Mao S. J. *J. Appl. Polym. Sci.* **1996**, *61*, 2059.
30. Unal H.; Sen U.; Mimaroglu A. *Trib. Int.* **2004**, *37*, 727.
31. Li C.; Klaus F. *Trib. Int.* **2010**, *43*, 2355.
32. Myshkin N. K.; Petrokovets M. I.; Kovalev A. V. *Trib. Int.* **2005**, *38*, 910.
33. Li Y. L.; Dae E. K. *Trib. Int.* **2011**, *44*, 1926.