

TRANSPARENT WEAR-RESISTANT ACRYLATE-BASED COATING WITH HIGHLY FILLED NANOSILICA PARTICLES

Hui Zhang, Hui Zhang, Zhong Zhang
National Center for Nanoscience and Technology, China
No.11 Beiyitiao Zhongguancun, Beijing 100190, China
zhong.zhang@nanoctr.cn

SUMMARY

In the present study, a urethane-acrylate oligomer was mixed with varied concentrations of nanosilica particle sol, spin-coated onto polycarbonate substrate and finally cured by UV light. Super scratch resistance was achieved by the almost perfect dispersed nanoparticles. Wear performances were characterized by various approaches and wear mechanisms were discussed based on worn-surface observations. This work has been partly published in Tribology International.

Keywords: silica nanoparticles, nanocomposites, hybrid coating, wear resistance

INTRODUCTION

Hybrid UV-curable nano-coatings are one of the most attractive topics in nanomaterials which have achieved the transition from fundamental researches to practical applications. In recent years, organic/inorganic hybrid nano-coatings have been successfully used in a wide range of applications [1-4], especially on polycarbonate (PC) which have several advantages over the use of conventional transparent materials (glasses, PMMA). UV-curing has become a well-accepted technology due to its unique advantages [5].

The nanoparticles are under consideration in hybrid coatings since they can give special hints to improve the hardness, elastic modulus and wear resistance of host polymeric coatings without losing their transparency once nanoparticles are homogeneously distributed in the polymer matrices [4, 6-9]. An effective method for obtaining these agglomerate-free hybrid coatings is the in situ sol-gel technique, which introduces different content of nanoparticles into monomers or oligomers by chemical reactions [4, 10-13].

In polymeric coatings, nanoparticles have been used to upgrade the level of resistance to wear and friction. Apart from the mostly used nanosilica particles, other nanoparticles were also chosen to improve the wear resistance of polymeric resins, such as nano-alumina, nano-titania and nano-zirconia et al [9]. Such improvements are usually ascribed to the strong interfacial interactions between organic and inorganic phases. For example, the interphase around nanoparticles was reported to become harder than the bulk polymer matrix [4, 11]. Moreover, chemical groups on the surface of nanoparticles

could result in more covalent linkage between particle and matrix [14]. An interesting finding is that nanoparticles, combining with a proper amount of micron-sized particles, can further improve the wear resistance of polymeric coating, which was superior to that of materials filled with nanoparticles or micron-sized particles only [7, 8, 15]. In addition, nanoparticles can increase the glass transition temperatures (T_g) of some polymer systems [12, 16]. From the point of view of long-term wear process, the increased T_g allows the nanocomposites to endure much friction heat during wear and to have better wear resistance, as compared to the host polymers without nanoparticles.

As mentioned above, nanoparticles play an essential role in improving the wear-resistance of polymer coatings. Although there are lots of investigations on hybrid nano-coatings in the literature [4, 15, 17, 18], the nanoparticle contents in those works are relatively low, this is mainly due to the difficulty in dispersing and preparing high-concentration nano/polymer coatings. In this work we successfully prepared acrylate-based coatings filled with high concentration of silica nanoparticles without any agglomerates, and their mechanical properties, wear resistance and optical properties were systematically studied.

EXPERIMENTAL

Materials and Characterization

A commercially available hexa-functional aliphatic urethane-acrylate (UA) oligomer and trimethylolpropane triacrylate (TMPTA) that was a commonly-used reactive diluent with three functional groups were supplied by Cytec Industries Inc.. A colloidal nanosilica sol with a trademark 'C150' was kindly supplied by nanoresins AG, Germany. It consisted of about 50 wt.% sol-gel-formed silica nanoparticles and 50 wt.% TMPTA serving as the solvent. A radical photoinitiator (1-hydroxycyclohexyl phenyl ketone, Irgacure 184) was obtained from Ciba Specialty Chemicals. All these chemicals were used without further purification..

The nano-coatings were cured at room temperature for 180 s using a hot embossing system HEX01 equipped with UV unit (JENOPTIK Mikrotechnik GmbH). The thickness of resultant solid coatings can be controlled in the range of 20-30 μm . The detailed formulation of the coatings prepared is summarized in Table 1. The solid coatings were sliced into ~ 100 nm-thick sections which were observed by a transmission electron microscope (Tecnaï 20, FEI, USA) at an acceleration voltage of 120 kV to evaluate the dispersion of silica nanoparticles in coatings visually. Transmittance of the prepared coatings in the range of ultraviolet-visible wavelength was evaluated by a UV-vis-NIR scanning spectrophotometer with a scanning speed of 266.75 nm/min (Lambda950, Perkin-Elmer Inc., USA) using air as reference. The scratch resistance of the coatings was characterized by a commercial pencil hardness tester (Tianjin Testing Equipment, China) according to the standard GB/T 6739-1996. The nano-indentation hardness (H) and elastic modulus (E) of the coatings were measured using a nano-indenter (Nano Indenter XP, MTS systems Co., USA) equipped with a three-sided pyramid tip (Berkovich tip). The fretting behaviour of the coating samples under reciprocating sliding was evaluated using a universal micro-tribotester (UMT-2, Center For Tribology Inc., USA), the configuration of which is schematically shown in Fig. 1. The worn surfaces of the nano-coatings and steel ball were examined by

a white light interferometer (MicroXAM, ADE Phase Shift Inc., USA), an optical microscope (Leica DM4000M, Leica, Germany) and a scanning electron microscope (S-4800, Hitachi Co., Japan), respectively.

Table 1. Compositions of coating samples with various nanosilica particle contents

Coating sample	Theoretical silica content [wt.%]	C-150* [wt.%]	UA [△] [wt.%]	TMPTA [△] [wt.%]	Irgacure 184 [wt.%]
Neat coating	0	0	33.3	66.7	4
10 wt.% nano-SiO ₂	10	20.0	30.0	50.0	4
25 wt.% nano-SiO ₂	25	50.0	25.0	25.0	4
40 wt.% nano-SiO ₂	40	80.0	20.0	0	4

*C-150 is a trademark of colloidal nanosilica sol containing about 50 wt.% sol-gel-formed silica nanoparticles and 50 wt.% TMPTA serving as the solvent.

[△]In final coating formulations, the weight ratio of UA to TMPTA maintained constant (UA/TMPTA=1/2).

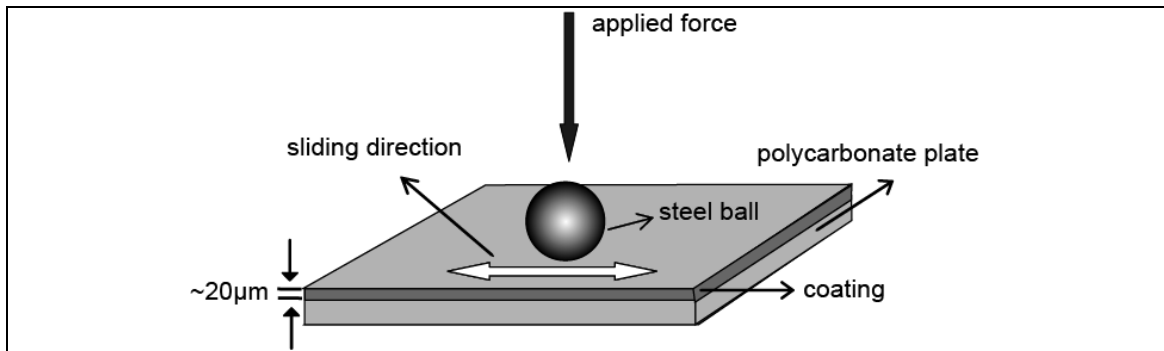


Fig. 1. Schematic illustration of the long-term fretting test, carried out under an applied force of 0.4 N and a sliding speed of 30 rev/min for sliding time of 60 min

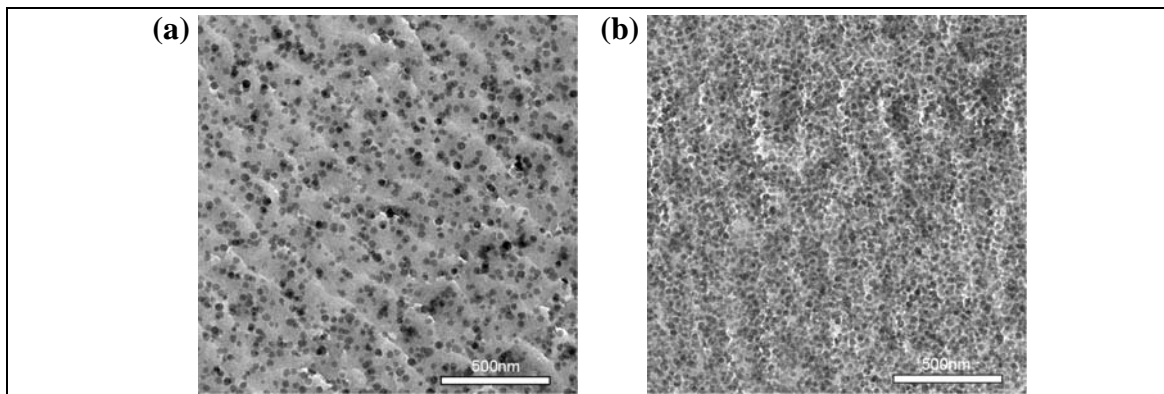


Fig. 2. TEM micrographs of ultra-thin sections taken from the coating samples filled with (a) 10 wt.% and (b) 40 wt.% nanosilica particles.

RESULTS AND DISCUSSION

TEM Observation and Transmittance

The TEM micrographs shown in Fig.2 (a) and (b) reveal the homogeneous dispersion of nanosilica particles in the polymeric coatings. No agglomerates can be found even at very high nanoparticle contents (40 wt.%). As shown in Fig.3 (a), the transmittance of the prepared coatings ($\sim 20 \mu\text{m}$ in thickness) in the range of visible wavelength was only slightly decreased with increasing the concentration of nanosilica particles. Even the nanosilica concentration reached up to 40 wt.%, the transmittance of the coating was still 99%. On the other hand, the nanosilica particles showed some ultraviolet screening effects. As seen in Fig.3 (b), significant absorption occurred in the ultraviolet region with increasing the nanosilica content. As an example, for the neat coating, the ultraviolet light transmittance at 300 nm was approximately 84%, and it decreased to be 54% for the 40 wt.% nanoparticle-filled coating.

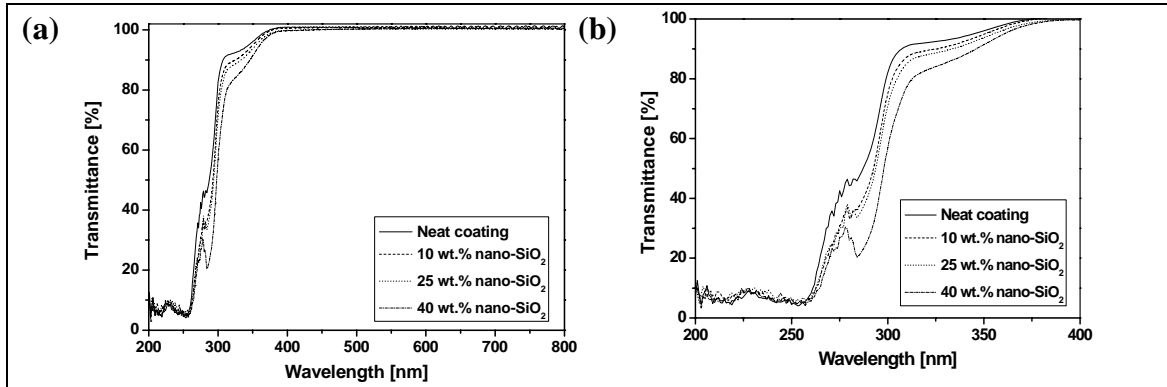


Fig. 3. Optical transmittance of the coating samples as a function of light wavelength (a) in visible light region, (b) in ultraviolet region.

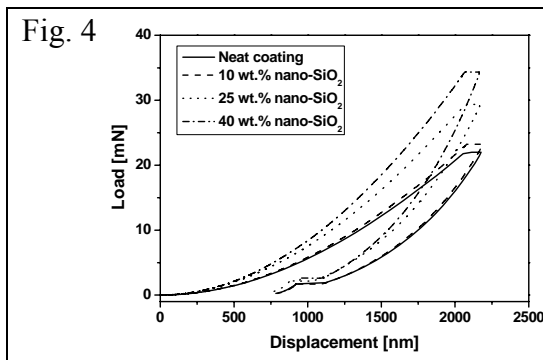


Fig. 4. Load-unload cycles of nano-indentation tests performed on the coating samples containing different nanosilica content.

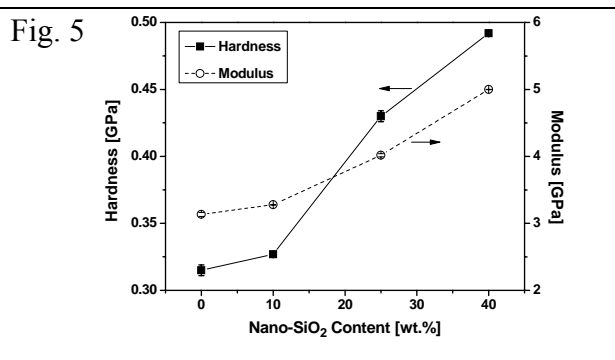


Fig. 5. Hardness and elastic modulus of coating samples as a function of the nanosilica content.

Nano-indentation Test

The typical load-unload cycles performed by nano-indentation in the coatings with different content of nanosilica particles are shown in Fig.4. It can be clearly seen that the maximal applied forces at the depth of 2 μm were 22 mN and 34 mN for the neat coating and 40wt.% nanoparticle-filled coating, which indicating the enhanced load-bearing ability of nano-coating. Fig.5 displays the results of the hardness and elastic modulus of coatings as a function of nanosilica content, which was calculated following the Oliver and Pharr methodology [19]. A pronounced rise in both hardness and modulus were achieved with the increase of nanosilica content. The hardness increased by about 53% from less than 0.32 GPa for the neat coating to 0.49 GPa for the 40 wt.% nanosilica filled coating. Similarly, the elastic modulus increased by about 56% from 3.2 GPa for the neat coating to 5.0 GPa for coatings containing 40 wt.% nanosilica particles.

Scratch and Fretting Resistance

Pencil hardness test is a standard industrial method which can roughly evaluate the short-term scratch resistance of the nano-coatings. As seen in Fig.6, the pencil hardness shows continuous improvement with increasing nanosilica content. The pencil hardness has the most improvement to three higher grades till 40 wt.% nanosilica content. The improvement of pencil hardness owing to addition of nanofillers has been reported by other researchers [4, 12, 20]. After pencil hardness tests with a 3H grade pencil, the scratched tracks of coatings were studied by an optical microscope, as shown in Fig.7. It can be found that the unfilled neat coating fractured and formed fishbone-like cracks along the scratched track, however, in the case of nano-coatings, no obvious cracks were found. The improved scratch resistance of coating after addition of nanosilica particles is mainly ascribed to the improved basic mechanical properties of nano-coatings (hardness and modulus).

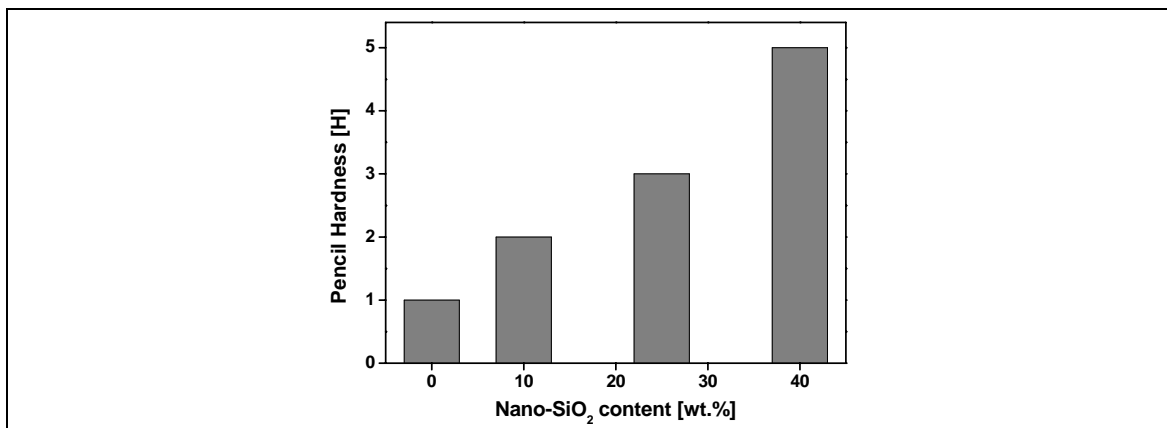


Fig. 6. Pencil hardness of the coating samples as a function of the nanosilica content.

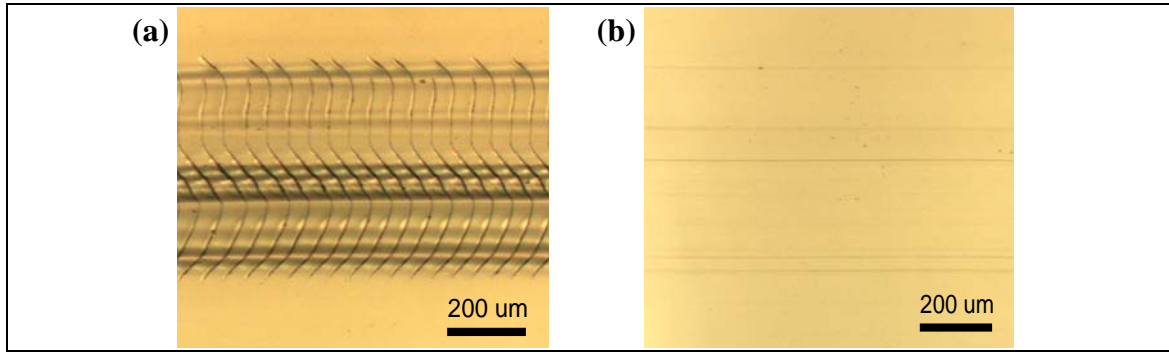


Fig. 7. Optical microscopy photos of scratched surfaces of the coating samples measured with a 3H grade pencil: (a) neat coating and (b) 40 wt.% nanosilica particles.

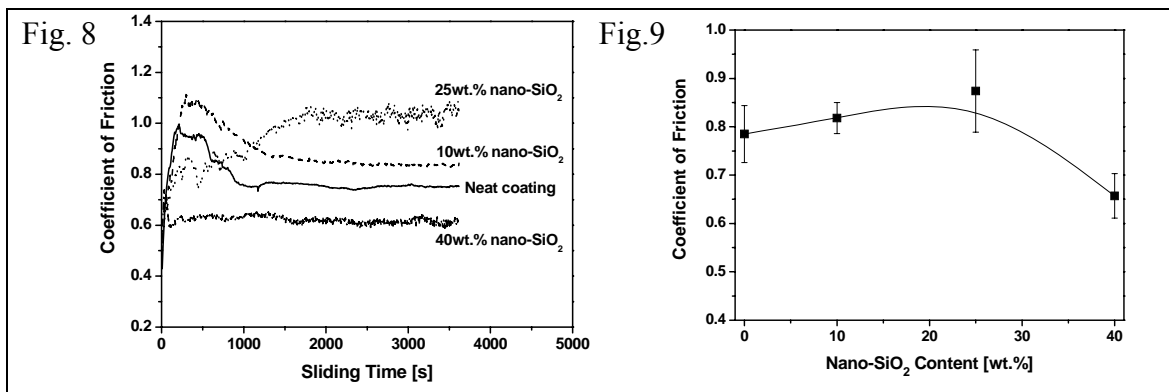


Fig. 8. Typical curves of COF vs. sliding time for the coating samples, measured under an applied force of 0.4 N and reciprocating speed 30 rev/min for sliding time of 60 min.

Fig. 9. COF values of coating samples as a function of the nanosilica particle content.

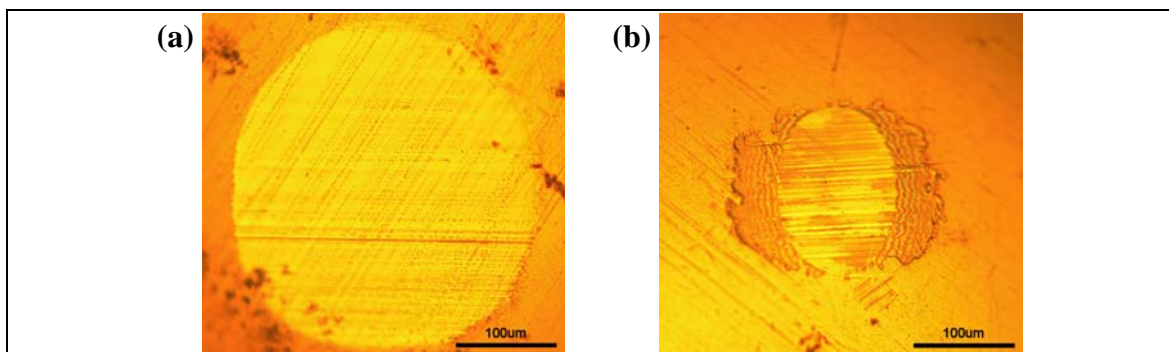


Fig. 10. Worn scars left on the steel balls after fretting tests: (a) neat coating (b) with 40 wt.% nanosilica particles.

As shown in Fig.1, the long-term fretting resistance of the prepared coatings was evaluated using a UMT tester. The typical tribological curves of coatings are given in

Fig.8. At the initial stage of fretting, an unstable process, the so-called ‘running-in period’, took place for all coating samples. The running-in period lasted for ~200 to ~1000 s, depending strongly on the composition of samples. Interestingly, it reduced with addition of nanosilica particles, and this was especially evident at 40 wt.% particle content. Fig.9 shows the variation of average COF values of coatings with changing of the nanosilica content. Here, the average COF values were estimated from the stable stages in the tribological curves shown in Fig.8 (see also Table 2). The COF value rose slightly at the nanosilica content below 25 wt.%, thereafter, it dropped significantly at higher nanosilica content. About 20% decrease in COF was achieved at 40 wt.% nanosilica content. Since no transfer film was formed on the counterpart (cf. Fig.10), the COF value of the hard coating is assumed to be mainly dominated by the real contact area between coating and counterpart, i.e. the smaller real contact area means the lower COF value between friction parts. In our work two possible factors, i.e. surface roughness and hardness of the coatings are responsible for the magnitude of real contact area. Firstly, it is found from Table 2 that the initial surface roughness of coating characteristic of R_a and R_q was increased with nanosilica content. This would result in more contact between the friction parts during the running-in period, the COF value increase slightly below 10 wt.%. After the running-in, the friction between the nanocomposite debris and the steel ball became intense with increasing the content of nanosilica. Thus, the stable COF value rose slightly at the nanosilica content below 25 wt.%. Secondly, it was well known that the gaps between nanoparticles reduced even smaller than the diameter of the nanoparticle in 40 wt% filled coatings shown in Fig.2b. Therefore, the real contact occurred between the steel ball and the stiffer nanofillers. Due to this hardening effect of nanoparticles as proved in Fig.5, the impression on coating, which was caused by the steel ball, was decreased with nanosilica content. As a proof of this point, Fig. 10 shows that under the same applied force the worn scar on the steel ball is much smaller for the nano-coating than for the neat coating. The COF value decreased to a lower value owing to the apparently decreased contact depth and area. As a result of the competitive factors in the testing process, the COF value exhibited the tendency that is illustrated in Fig.9.

Table 2. Initial roughness of the coating samples and their coefficient of friction

Coating sample	Surface roughness		Coefficient of friction
	R_a^* [nm]	R_q^* [nm]	
Neat coating	2.8	3.4	0.79
10 wt.% nano-SiO ₂	3.3	4.0	0.82
25 wt.% nano-SiO ₂	3.8	4.8	0.87
40 wt.% nano-SiO ₂	5.2	6.2	0.65

* R_a and R_q stand for the average roughness and root mean square roughness, respectively.

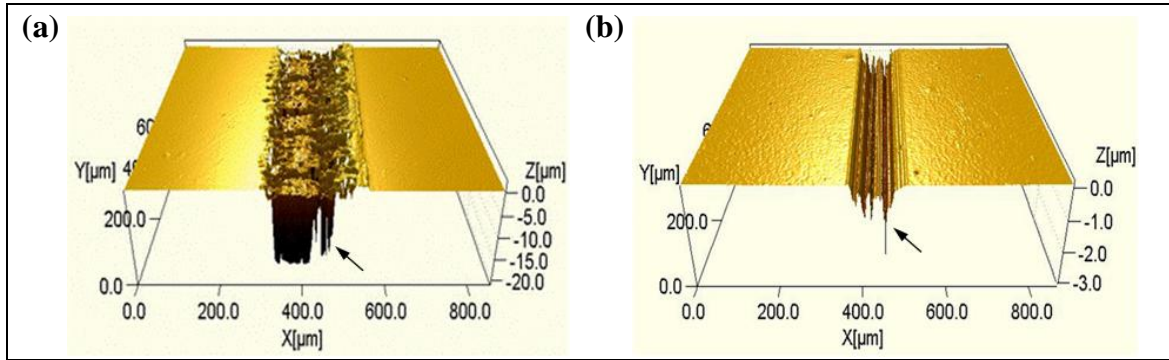


Fig. 11. 3D worn surfaces of the coating samples after fretting tests: (a) neat coating (b) with 40 wt.% nanosilica particles. The arrows indicate cracks formed on fretting wear.

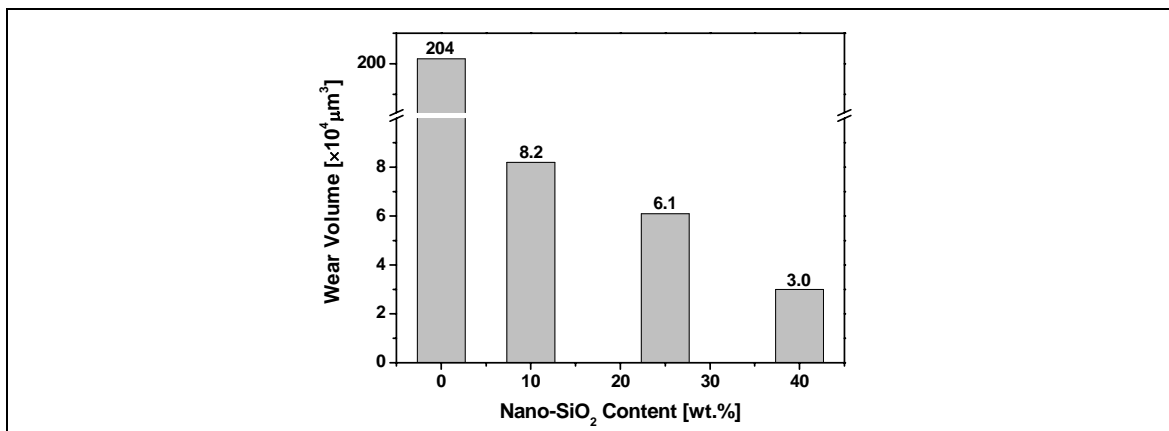


Fig. 12. Wear rate of the coating samples as function of nanosilica particle content.

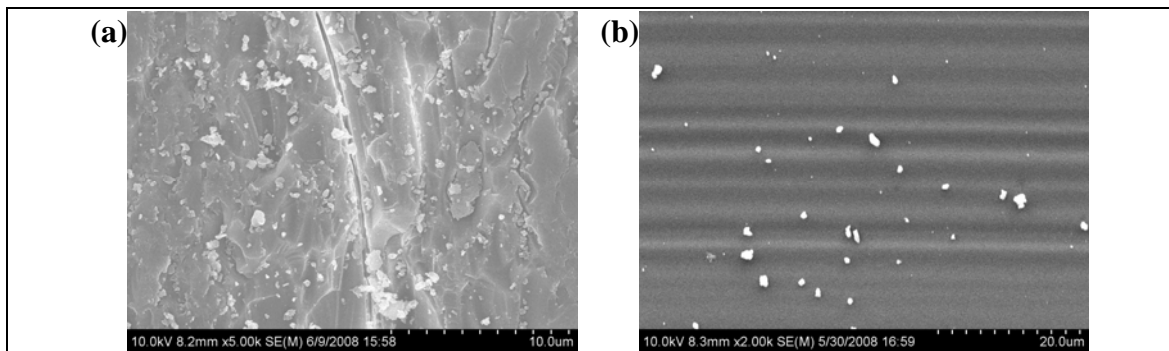


Fig. 13. SEM micrographs of worn surfaces of the coating samples after fretting tests: (a) neat coating (b) with 40 wt.% nanosilica particles.

Fig.11 gives the comparison of three dimensional worn surfaces between unfilled and filled coating samples after fretting test. As shown in Fig.12, the wear rate was dramatically decreased with increasing of nanosilica particles. About 68-fold decrease in wear volume was achieved after addition of 40 wt.% nanosilica particles. Addition of nanosilica particles can inhibit the crack formation and propagation on fretting process.

Actually, it has been reported previously that nanoparticles can effectively toughen brittle thermosetting materials under both static and dynamic loadings [21, 22]. This point can be further evidenced on the microscale by the SEM worn surfaces shown in Fig.13, where neat coating sample presents coarse worn surface with numerous debris and cracks (Fig.13a), which is typical surface fatigue of material. However, only some inconspicuous grooves are visible in the case of nano-coating with 40wt.% nanosilica particles (Fig.13b).

CONCLUSIONS

Based on the present work devoted to investigate the wear resistance of transparent coatings filled with varied nanosilica content, the following conclusions can be drawn:

1. Agglomerate-free acrylate-based nano-coatings were successfully prepared via a special sol-gel method. Even at 40 wt.% nanosilica particle content, all nano-coating samples showed high visible light transmittance and some ultraviolet screening effects.
2. The nanosilica particles were found to improve the basic mechanical performance of acrylate-based coating effectively. The addition of 40 wt.% nanoparticles enhanced the hardness and modulus by ~53% and ~56%, respectively, in comparison with the unfilled coating.
3. Both short-term (pencil scratch) and long-term (fretting) wear resistance of the nano-coatings was dramatically improved with increasing nanosilica content. The pencil hardness and the wear volume had the most improvement to three higher grades till 40 wt.% nanosilica content. The possible wear-reduction mechanisms of nano-coatings were likely due to the enhanced hardness, modulus as well as crack growth resistance induced by nanoparticles. Especially, the crack growth resistance should not be neglected on the fretting wear, because the material fatigue occurred easier under such test conditions.

ACKNOWLEDGEMENTS

This work was jointly sponsored by a Key Research Program of the Ministry of Science and Technology of China (Grant No. 2006CB932304), and a Key Item of the Knowledge Innovation Project of Chinese Academy of Sciences (Grant No. KJCX1.YW.07). The financial support of the Science and Technology Department of Anhui Province through Chery Automobile is also appreciated. The authors are grateful to nanoresins AG for the support of nanocomposite master batch, as well as to the funding support by the State Key Laboratory of Tribology, Tsinghua University for using their facilities.

References

- [1] Charitidis C, Laskarakis A, Kassavetis S, Gravalidis C, and Logothetidis S. Superlattices and Microstructures 2004;36(1-3):171-179.

- [2] Malzbender J and de With G. *Surface & Coatings Technology* 2001;135(2-3):202-207.
- [3] Soloukhin VA, Posthumus W, Brokken-Zijp JCM, Loos J, and de With G. *Polymer* 2002;43(23):6169-6181.
- [4] Wu LYL, Chwa E, Chen Z, and Zeng XT. *Thin Solid Films* 2008;516(6):1056-1062.
- [5] Decker C, Keller L, Zahouily K, and Benfarhi S. *Polymer* 2005;46(17):6640-6648.
- [6] Y. Wang SL, J.L. Luo, Z.H. Xu. *Wear* 2006;260:976–983.
- [7] Bauer F, Flyunt R, Czihal K, Ernst H, Naumov S, and Buchmeiser MR. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms* 2007;265(1):87-91.
- [8] Bauer F, Flyunt R, Czihal K, Langguth H, Mehmert R, Chubert RS, and Buchmeiser MR. *Progress in Organic Coatings* 2007;60(2):121-126.
- [9] Li C, Jordens K, and Wilkes GL. *Wear* 2000;242(1-2):152-159.
- [10] Zhang H, Zhang Z, Yang JL, and Friedrich K. *Polymer* 2006;47(2):679-689.
- [11] Wouters MEL, Wolfs DP, van der Linde MC, Hovens JHP, and Tinnemans AHA. *Progress in Organic Coatings* 2004;51(4):312-319.
- [12] Amerio E, Sangermano M, Malucelli G, Priola A, and Voit B. *Polymer* 2005;46(25):11241-11246.
- [13] Tanglumlert W, Prasassarakich P, Supaphol P, and Wongkasemjit S. *Surface and Coatings Technology* 2006;200(8):2784-2790.
- [14] Xu J, Pang W, and Shi W. *Thin Solid Films* 2006;514(1-2):69-75.
- [15] Bauer F, Flyunt R, Czihal K, Buchmeiser MR, Langguth H, and Mehnert R. *Macromolecular Materials and Engineering* 2006;291(5):493-498.
- [16] Amerio E, Sangermano M, Malucelli G, Priola A, and Rizza G. *Macromolecular Materials and Engineering* 2006;291(10):1287-1292.
- [17] Wu LYL, Soutar AM, and Zeng XT. *Surface and Coatings Technology* 2005;198(1-3):420-424.
- [18] Wu LYL, Tan GH, Zeng XT, Li TH, and Chen Z. *Journal of Sol-Gel Science and Technology* 2006;38(1):85-89.
- [19] Oliver WC and Pharr GM. *Journal of Materials Research* 1992;7(6):1564-1583.
- [20] Sangermano M, Malucelli G, Amerio E, Priola A, Billi E, and Rizza G. *Progress in Organic Coatings* 2005;54(2):134-138.
- [21] Zhang H, Zhang Z, Friedrich K, and Eger C. *Acta Materialia* 2006;54(7):1833-1842.
- [22] Wetzels B, Rosso P, Hauptert F, and Friedrich K. *Engineering Fracture Mechanics* 2006;73(16):2375-2398.