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Tribological Properties of Epoxy + Silica Hybrid Materials

Witold Brostow^{1,*}, Wunpen Chonkaew¹, Tea Datashvili¹, and Kevin P. Menard^{1,2}

¹Laboratory of Advanced Polymers and Optimized Materials (LAPOM), Department of Materials Science and Engineering,
University of North Texas, Denton, TX 76203-5310, USA

²PerkinElmer LAS, 710 Bridgeport Ave, Shelton CT 06484, USA

Various amounts of nano size silica particles prepared by a sol-gel process were added to epoxy + amine systems. We have investigated tribological properties including friction and sliding wear resistance of hybrids so obtained, and also relationships between different tribological properties and surface topography. The thermal degradation behavior and thermal stabilities were determined by thermogravimetric analysis (TGA). The introduction of silica into bisphenol-A type epoxy resins does not affect significantly char formation in the epoxy resins; relatively small improvements in thermal stabilities is seen. At the same time, results from a pin-on-disc tribometer show that silica addition causes lowering of friction already at 1 part per hundred (phr) and very significant lowering of wear at 2 or more phr. We have found finer waves of the worn surface in the hybrids than in the neat epoxy. SEM results demonstrate that the silica particles improve the wear resistance by hindering crack propagation.

Keywords: Epoxy Nanohybrids, Wear Reduction, Friction Reduction, Polymer Tribology, Silica Nanofiller, Epoxy Thermal Stability.

1. INTRODUCTION

Epoxy resins constitute a class of widely used thermosetting polymers.^{1–10} Because of their high modulus, good heat resistance and good electrical resistance, they are used extensively in protective coatings, in microelectronics and in structural applications such as laminates and composites. However, there are also disadvantages. Epoxy resins with high crosslink density show low impact and low fracture toughness. Moreover, they have low thermal stabilities and poor tribological properties, namely high friction and low wear resistance – a problem they share with many polymers.¹¹ There are several possible approaches to improve those properties, such as blending with polymer liquid crystals,¹² blending with fluoropolymers,^{7,8} or adding inorganic fillers into the epoxy formulation to form organic-inorganic hybrids.^{13–29}

Literature shows that introducing fillers into polymers can improve certain properties such as color,²¹ optical storage,^{15,16} thermal stabilities,^{30–32} abrasion resistance,^{33,34} or thermomechanical properties.^{35,36} Rabello³⁷ reviewed advantages of using fillers while recent results from our laboratory^{38,39} also demonstrate such advantages. In this study silica particles prepared by sol-gel process were added directly into epoxy systems without any surface

treatment. Effects of silica contents on the tribological properties and thermal stability of epoxy + silica systems have been evaluated.

2. EXPERIMENTAL DETAILS

2.1. Materials

Methanol and hydrochloric acid (HCl) were supplied by Aldrich Chemicals. Tetraethylorthosilicate (TEOS) was supplied by Aldrich Chemicals. Diglycidyl ether of bisphenol A (DGEBA) used as an epoxy resin was purchased from System Three; its epoxide equivalent weight is 210 g·eq⁻¹. The PACM-2M, used as an amine curing agent, was kindly supplied by Air Products. The amine hydrogen equivalent weight of the hardener is 52.5 g·eq⁻¹. Those chemicals were used as received.

2.2. Preparation of Silica Particles

The first step in the sol-gel synthesis process is mixing of the components of the solution. The amounts were measured using a graduated plastic pipette and placed in an Erlenmeyer flask. Magnet stirring mixing the solution in the flask assured a homogeneous mixture. At all times the flask was sealed with a silicone lubricant to prevent evaporation. Sol-gel silica solutions were prepared by acid

*Author to whom correspondence should be addressed.

catalysis of TEOS and deionized water, with methanol used as solvent. The ratio of H₂O/TEOS/methanol/HCl was 0.1/0.2/0.6/1 × 10⁻⁴ mol%.

HCl was added into a conical flask, followed by water, ethanol and finally TEOS. Immediately after the chemicals were mixed, the flask was sealed. The mixture was allowed to mix at a medium speed of magnetic stirrer at room temperature; by this way, the solution does not excessively splash up onto walls of the flask. The resulting sol was then aged at room temperature 24 hours to promote formation of the inorganic network.

The final mixture was then subjected to evaporation. The evaporation of any residual solvent was carried out at room temperature and residual pressure of 228 Torr. The powder was ground and demoiatured in a conventional oven at 80 °C for 1 day before use. The particle size measured by SEM is between 44 and 61 nm. At higher Si concentrations partial agglomeration of the particles was seen.

2.3. Preparation of Epoxy-Silica Hybrids

Various concentrations in parts per hundreds (phr) of silica powder were mixed with DGEBA. The mixtures were then ultrasonicated for 3 hours in order to well disperse the silica particles and also to eliminate bubbles in the epoxy. The amine curing agent was then added and the mixture was stirred gently. The mixtures so obtained were transferred onto silicone molds and cured at 80 °C for 2 hours and then at 150 °C for 2 hours as recommended by the manufacturer.

2.4. Pin-on-Disc Tribological Testing

(a) Friction: Friction tests were carried out using Nanovea pin-on-disk tribometer from Micro Photonics Inc. The pin was a silicon nitride ball with the diameter of 3.2 mm. The pin was fixed in a holder on a loading lever arm. A constant normal load of 5.0 N was applied to the lever arm during the tests. The rotation speed of the disc was 200 rpm and the radius of wear track was 2.0 mm. The tests were performed for 10,000 revolutions under ambient conditions (22 °C).

(b) Wear rate: The wear rate k of the hybrids was determined as

$$k = V_m / (Wvt) \quad (1)$$

or

$$k = V_m / (Wx) \quad (2)$$

where W is the normal load, V_m is the volume of wear, v is the sliding velocity, t is the test duration and x is the sliding distance. The volume V_m was calculated as

$$V_m = 2\pi R_m A_m \quad (3)$$

where R_m is the radius of the wear track, and A_m the average cross section area of wear track.

A Micro Scratch Tester (MST) from CSEM Instruments was used to determine the average cross section areas of wear tracks. An indenter with diamond tip with the radius of 120 μm and conical angle of 90 °C was scanned across the wear tracks; the load applied was 0.03 N. The scan speed was 2.0 mm/min. The data, namely depth as a function of sliding distance of the indenter, from at least 8 points of wear tracks were analyzed with a Microcal Origin 6.0 program to determine the cross section area of wear track. The specimens were cleaned by a high pressure air prior to the measurements.

2.5. Scanning Electron Microscopy (SEM)

Micrographs of all blends were taken using a FEI Quanta Environmental Scanning Electronic Microscope (ESEM). The samples were mounted on a copper stub and coated with a thin layer of gold to avoid electrostatic charging during examination.

2.6. Thermal Gravimetric Analysis (TGA)

Thermal stabilities of the epoxy-silica hybrids were determined using a thermogravimetric analyzer Pyris 1 TGA from Perkin Elmer. The testing conditions used were: scanning the temperature under the N₂ atmosphere from 50 °C to 900 °C. The technique has been well explained by one of us⁴⁰ and also by Lucas and her colleagues.⁴¹

3. FRICTION AND SEM OF TRACKS

Friction results obtained from pin-on-disc tribometry for the hybrids at several silica contents as a function of sliding distance are shown in Figure 1. The curves obtained for both neat epoxy and the hybrid systems show a similar shape—except for the silica content of 4 phr.

As seen in Figures 1(a–h), the friction values for the neat epoxy and for most of our hybrid systems increase abruptly to a higher value within a short sliding distance. This region has been named a transition region. The failure of the surface during the sliding, resulting in the formation of a choppy transferred film from epoxy to a Si₃N₄ ball, has been believed to be one of the reasons⁴⁰ for such an abrupt change. As the sliding progresses, the friction drops to a lower value and then levels off; the transfer film becomes thinner and reaches a steady more uniform thickness. This region has been named a steady state region.

On the other hand, epoxy with silica content of 4 phr behaved differently from others. As seen in Figure 1(e), unlike neat epoxy or hybrids with other silica contents, a long steady state region, namely a plateau of friction, has been found before the transition region. After sliding for a period of time, friction increases again and reaches another

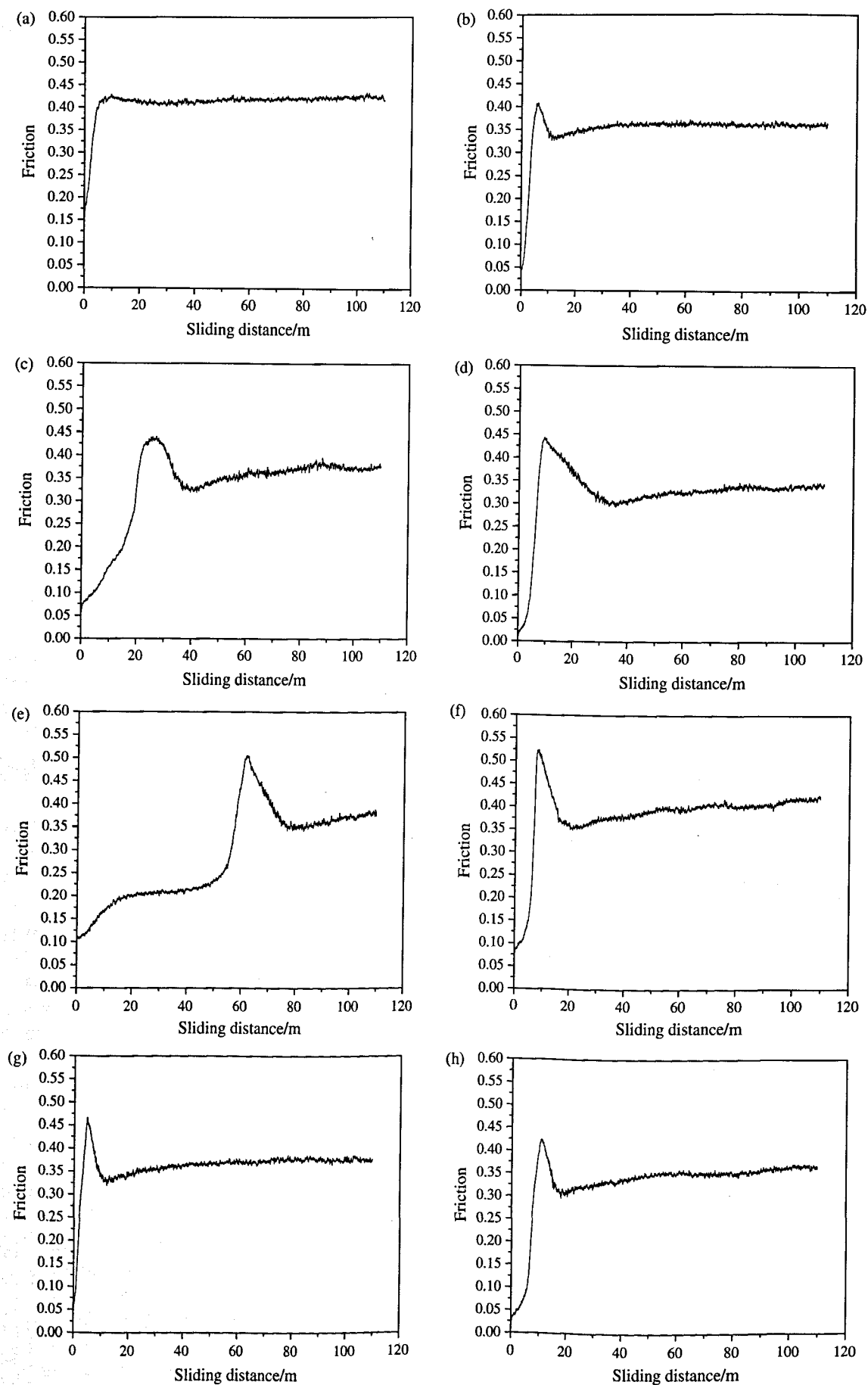


Fig. 1. Friction as a function of sliding distance for epoxy + silica hybrid systems at various silica contents; sliding against Si_3N_4 ball.

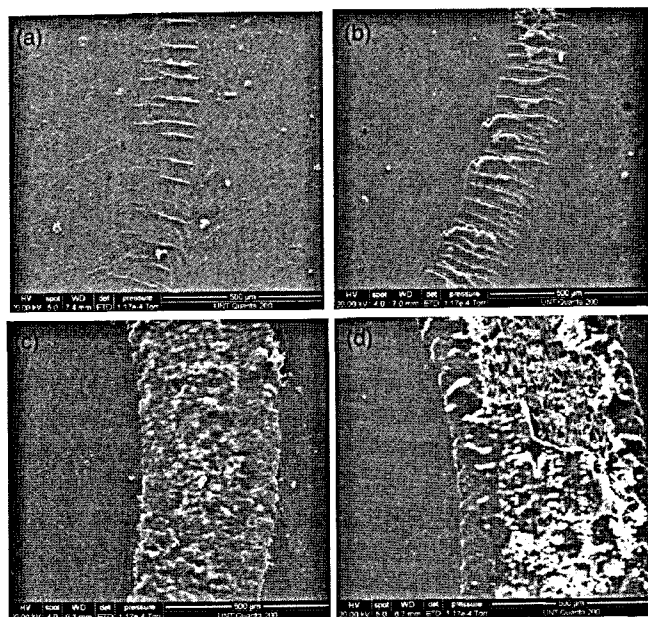


Fig. 2. Morphology of the wear tracks of epoxy + silica hybrids with silica content of 4 phr: (a) 1000 revolutions; (b) 4000 revolutions; (c) 10000 revolutions; also (d) wear track of neat epoxy at 10000 revolutions.

plateau. We have known that wear tracks provide pertinent information on scratching mechanisms.^{42–45} Thus, in order to elucidate this phenomenon, SEM was used to investigate wear tracks. Figure 2 shows SEM photographs for the epoxy hybrid with silica content of 4 phr at several sliding distances.

At 1000 revolutions or 12.57 m of sliding distance, wear of the hybrids with 4 phr silica content is very low; only small failures rather than serious damages on the surface are observed (Fig. 2(a)). At 4000 revolutions or 50.27 m of sliding distance (Fig. 2(b)), a distance slightly before the transition region, like other silica contents, the wear track for the hybrids with 4 phr silica is more pronounced; surface cleavages—a failure type of brittle materials—are obviously observed. A change in friction, consequently, has been observed. Bhushan⁴⁰ explained this type of behavior as follows: there was an increase in friction after the first steady state period; changes in the interface occurred further, such as roughening and appearance of trapped particles—what lead to an increase in friction to another plateau, a steady state region. Clearly the interface failed, and the friction became very high. Our results lead to a similar conclusion: a failure of surface produces significantly changes in friction in our epoxy + silica hybrid system.

We have summarized the average values of dynamic friction at the steady state region (after the transition period) and plotted as a function of silica contents. Those results are shown in Figure 3. Overall, introduction of silica powder into epoxy reduces the friction as compared to the neat epoxy + amine system. The lowest value is seen for the hybrids with 3 phr silica. We presume that silica

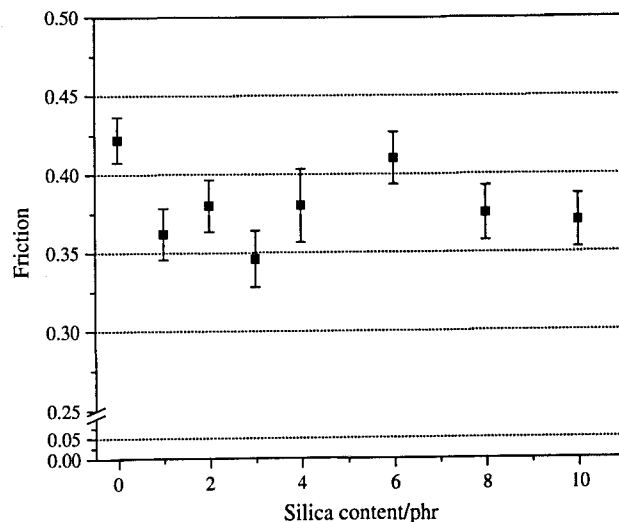


Fig. 3. Friction as a function of silica content for epoxy + hybrid systems against Si_3N_4 in the steady state region.

particles increase the asperities of the epoxy surface; this causes the reduction in an actual contact area between the Si_3N_4 ball and the epoxy surface. When more silica is added, we see a maximum on the curve at 6 phr silica; more silica particles have increased the contact area. At still higher silica concentrations we presume that a formation of the transfer film takes place.

4. WEAR RATE

Wear rate as defined by Eq. (2) for the epoxy-silica hybrids has been plotted as a function of silica content in Figure 4. The presence of silica particles decreases the wear rate significantly as compared to that of the neat epoxy up to 4 phr. Afterwards the wear rate of the hybrids starts to increase somewhat and then tends to level off. However,

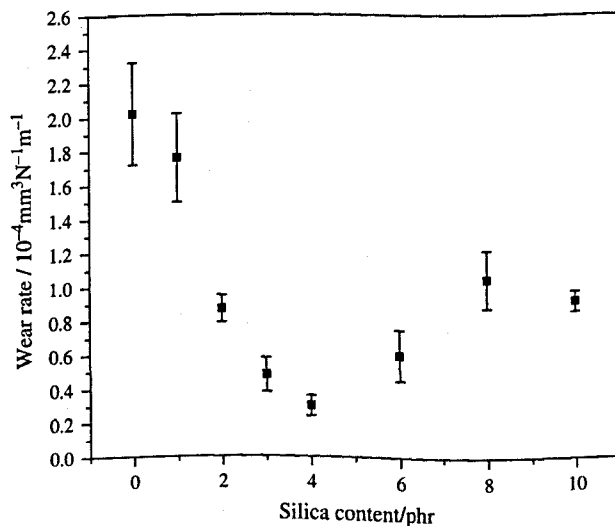


Fig. 4. Wear rate of epoxy + silica hybrids.

the wear rates at silica contents >4 phr are still quite low, 2–3 times lower than for the neat epoxy.

The SEM photographs under 150× magnification in Figures 2(c) and (d) show the wear track of the hybrids with 4 phr silica and the neat epoxy, respectively. Well defined wear tracks are observed in both systems. However, the wear track width of the hybrids is *much narrower* than that for the neat thermoset.

We have also investigated the surface topography along the wear track of the neat epoxy and the hybrid with 4 phr silica under 2000× magnification (Fig. 5). The worn surfaces for both systems show material waves along the sliding direction; the size of the waves for neat epoxy is clearly larger. Moreover, we have found that the fracture surface of neat epoxy seems more brittle and the cracks are formed perpendicularly to the sliding direction. In either case, an orientation is seen, expectedly

different from nanoindentation tracks.⁴⁶ We know that surface and interfacial tensions are important for properties of blends⁴⁷ as well as composites.⁴⁸ We infer there is a strong interaction between the epoxy matrix and the silica particles.

From SEM results we conclude that the silica particles improve the wear resistance by hindering the crack propagation in the epoxy matrix. We find finer waves of the worn surface for the epoxy + silica hybrid (Fig. 5(b)).

5. THERMAL STABILITY

Figure 6 shows a TGA thermogram of the epoxy + silica hybrids and the neat epoxy. The pattern of thermograms for the neat epoxy and the hybrids is similar. This shows that the thermal degradation mechanisms of the neat epoxy and hybrids are similar also.

Table I shows the thermal stability data for epoxy + silica hybrid materials corresponding to Figure 6. We have found that the initial decomposition temperature (IDT) and the temperature at the maximum rate of weight loss T_{max} of the hybrids increase slightly as the amount of silica increases. The char residuals of the hybrids (at 800 °C) are almost equal to their respective silica loading. Apparently the introduction of silica into bisphenol-A type epoxy

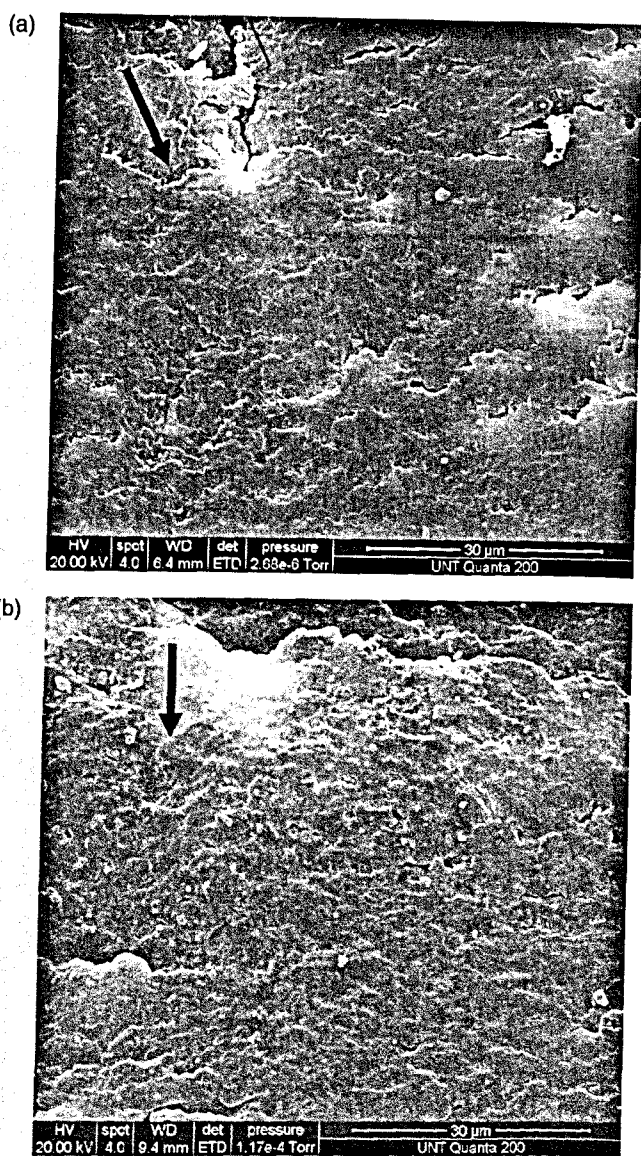


Fig. 5. Morphology of the worn surface of (a) neat epoxy and (b) the hybrid with 4 phr silica. An arrow represents the sliding direction.

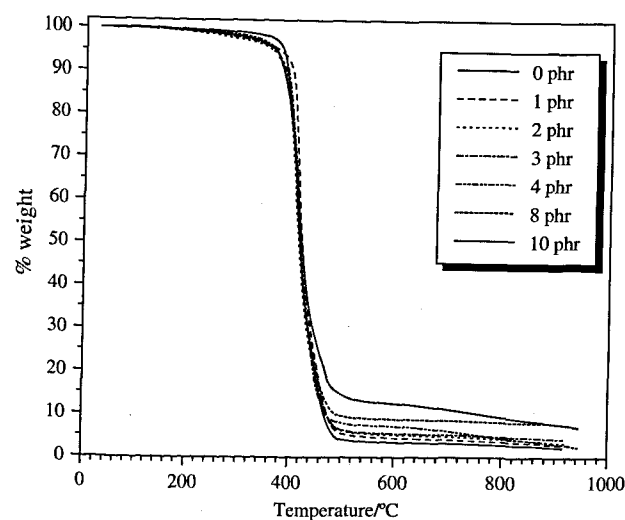


Fig. 6. TGA thermogram of epoxy + silica hybrids.

Table I. Thermal stability data for epoxy + silica hybrid material from TGA.

Silica content/phr	IDT/°C	T_{max} /°C	% weight residual at 800 °C
0	391.7	411.0	2.39
1	401.0	421.2	3.30
2	392.5	413.1	4.20
3	393.9	411.4	4.66
4	394.5	423.8	4.66
8	393.1	413.6	8.17
10	403.3	411.7	9.15

resins does not affect significantly char formation in the epoxy resins.

6. CONCLUDING REMARKS

Thermal stabilities of the epoxy have been improved only slightly when a certain small amount of silica was introduced into the epoxy. As far as thermal stability is concerned, a synergistic effect has not been found in our hybrids of silica and bisphenol-A type epoxy resins.

At the same time, we find that both friction and wear are lowered when certain amounts of silica particles are introduced into the epoxy system. However, above the silica powder concentration of 6 phr, the wear rate starts to increase again. Possibly, aggregation of the filler particles becomes significant at higher particle concentrations. In such a case the uniformity of dispersion of silica in the epoxy matrix is reduced—what causes an increase in wear rate. We recall how important it is to achieve a uniform distribution of the dispersed phase in the polymeric matrix.⁴⁹ In future work it seems worthwhile to modify the silica particles and to further investigate effects of particle dispersion on tribological properties.

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References and Notes

1. A. Y. Goldman, Prediction of the Deformation Properties of Polymeric and Composite Materials, American Chemical Society, Washington, DC (1994).
2. E. M. Pearce, C. E. Wright, and B. K. Bordoloi, *J. Mater. Ed.* 2, 931 (1980).
3. B. Bilyeu, W. Brostow, and K. P. Menard, *J. Mater. Ed.* 21, 297 (1999).
4. B. Bilyeu, W. Brostow, and K. P. Menard, *J. Mater. Ed.* 22, 107 (2000).
5. W. Brostow (ed.), Performance of Plastics, Hanser, Munich-Cincinnati (2000).
6. B. Bilyeu, W. Brostow, and K. P. Menard, *J. Mater. Ed.* 23, 189 (2001).
7. W. Brostow, P. E. Cassidy, H. E. Hagg, M. Jaklewicz, and P. E. Montemartini, *Polymer* 42, 7971 (2001).
8. W. Brostow, B. Bujard, P. E. Cassidy, H. E. Hagg, and P. E. Montemartini, *Mater. Res. Innovat.* 6, 7 (2001).
9. B. Bilyeu, W. Brostow, and K. P. Menard, *Polymer Compos.* 23, 1111 (2002).
10. M. Bratychak, W. Brostow, M. Gagin, O. Grynyshyn, and O. Shyshchak, *Mater. Res. Innovat.* 7, 47 (2003).
11. W. Brostow, J.-L. Deborde, M. Jaklewicz, and P. Olszynski, *J. Mater. Ed.* 25, 119 (2003).
12. W. Brostow (ed.), Mechanical, and Thermophysical Properties of Polymer Liquid Crystals, Chapman & Hall, London (1998).
13. B. M. Novak, *Adv. Mater.* 5, 422 (1993).
14. J. Varga and J. Karger-Kocsis, *Polymer* 36, 4877 (1995).
15. A. Dhanabalan, C. R. Mendonça, D. T. Balogh, L. Misoguti, C. J. L. Constantino, J. A. Giacometti, S. C. Zilio, and O. N. Oliveira, Jr., *Macromolecules* 32, 5277 (1999).
16. A. Dhanabalan, D. S. Dos Santos, Jr., C. R. Mendonça, L. Misoguti, D. T. Balogh, J. A. Jacometti, S. C. Zilio, and O. N. Oliveira, Jr., *Langmuir* 15, 4560 (1999).
17. M. Ochi, R. Takahashi, and A. Terauchi, *Polymer* 42, 5151 (2001).
18. Y. M. Xu and B. G. Mellor, *Wear* 251, 1522 (2001).
19. Z. Roslaniec, G. Broza, and K. Schulte, *Compos. Interfaces* 10, 95 (2003).
20. J. S. Sabo, J. Karger-Kocsis, O. Gryshchuk, and T. Czigany, *Compos. Sci. and Tech.* 64, 1717 (2004).
21. K. Alemaskin, I. Manas-Zloczower, and M. Kaufman, *Polymer Eng. and Sci.* 45, 1031 (2004).
22. R. Palkovits, H. Althues, A. Rumpelcker, B. Tesche, A. Dreier, U. Holle, G. Fink, C. H. Cheng, D. F. Shantz, and S. Kaskel, *Langmuir* 21, 6048 (2005).
23. O. Gryshchuk and J. Karger-Kocsis, *J. Nanosci. Nanotech.* 6, 345 (2006).
24. M. Bottini, F. Cerignoli, L. Tautz, N. Rosato, A. Bergamaschi, and T. Mustelin, *J. Nanosci. Nanotech.* 6, 3693 (2006).
25. J. Karger-Kocsis and D. Felhös, Tribology of Polymeric Nanocomposites, edited by K. Friedrich and A. K. Schlarb, Elsevier, Amsterdam (2007).
26. M. C. García-Gutiérrez, A. Nogales, D. R. Rueda, C. Domingo, J. V. García-Ramos, G. Broza, Z. Roslaniec, K. Schulte, and T. A. Ezquerro, *Compos. Sci. and Tech.* 67, 798 (2007).
27. J. Karger-Kocsis, *EXPRESS Polymer Letters* 1, 122 (2007).
28. L. B. Nohara, A. M. Kawamoto, E. L. Nohara, and M. C. Rezende, Presented at the 9o Congresso Brasileiro de Polimeros, Campina Grande, PB, October (2007).
29. J. M. Cavalcante, and L. H. de Carvalho, Presented at the 9o Congresso Brasileiro de Polimeros, Campina Grande, PB, October (2007).
30. G.-H. Hsiue, Y.-L. Lui, and H.-H. Liao, *J. Polym. Sci. Chem.* 39, 986 (2001).
31. Y. Liu, W. Wei, K. Hsu, and W. Ho, *Thermochim. Acta.* 412, 139 (2004).
32. Y.-L. Liu, C.-Y. Hsua, W.-L. Wei, and R.-J. Jeng, *Polymer* 44, 5159 (2003).
33. J. M. Durand, M. Vardavoulias, and M. Jeandin, *Wear* 181–183, 833 (1995).
34. X. S. Xing and R. K. Y. Li, *Wear* 256, 21 (2004).
35. F. Benard, I. Campitron, A. Laguerre, G. Vigier, and F. Laval, *Polym. Degrad. and Stab.* 91, 2119 (2006).
36. S. Kwon, T. Adachi, W. Araki, and A. Yamaji, *Acta Mater.* 54, 3369 (2006).
37. M. Rabello, Aditivacão de Polimeros, Artliber, São Paulo (2000), Chap. 10.
38. L. D. Perez, L. F. Giraldo, W. Brostow, and B. L. Lopez, *e-Polymers* no. 029 (2007).
39. L. F. Giraldo, W. Brostow, E. Deveaux, B. L. Lopez, and L. D. Perez, *J. Nanosci. Nanotech.* 8, 3176 (2008).
40. K. P. Menard, Performance of Plastics, edited by W. Brostow, Hanser, Munich-Cincinnati (2000), Chap. 8.
41. E. F. Lucas, B. G. Soares, and E. Monteiro, Caracterização de Polimeros, e-Papers, Rio de Janeiro (2001).
42. W. Brostow, W. Chonkaew, and K. P. Menard, *Mater. Res. Innovat.* 10, 389 (2006).
43. B. Bhushan, Introduction to Tribology, John Wiley & Sons, New York (2002), Chap. 5.

44. W. Brostow, H. E. H. Lobland, and M. Narkis, *J. Mater. Res.* 21, 2422 (2006).
45. W. Brostow, W. Chonkaew, L. Rapoport, Y. Soifer, and A. Verdyan, *J. Mater. Res.* 22, 2483 (2007).
46. B. D. Beake, G. A. Bell, W. Brostow, and W. Chonkaew, *Polymer Internat.* 56, 773 (2007).
47. W. Brostow, P. E. Cassidy, J. Macossay, D. Pietkiewicz, and S. Venumbaka, *Polymer Internat.* 52, 1498 (2003).
48. A. Kopczyńska and G. W. Ehrenstein, *J. Mater. Ed.* 29, 325 (2007).
49. W. Brostow, B. P. Gorman, and O. Olea-Mejia, *Mater. Letters* 61, 1333 (2007).

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