

Effects of silanes on tribological properties of rubber composites

Xin Ge, Yinhang Zhang, Fei Deng, and Ur Ryong Cho

The friction coefficient and wear loss of clay/rubber composites containing three different silanes were experimentally determined.

Inorganic polymeric composites—made from polymer matrices and inorganic fillers (e.g., metal oxides or glass fibers)—are widely used in several industrial applications, e.g., for the manufacture of tires, cables, seals, and structural components of automobiles. The applications of these composites are enabled because of their outstanding properties, such as their high mechanical strength, thermal stability, flame retardancy, and gas barrier characteristics. Clay—economical and abundant in nature—is one of the most important inorganic fillers used in the fabrication of such polymer composites. Indeed, among clay/polymer composites, clay/rubber composites have been investigated for many years in both academic settings and for industrial use.^{1–3} Understanding the tribological properties (i.e., related to friction, lubrication, and wear) of clay/polymer composites is therefore an important part of determining their suitable applications.

Until now, theories related to the mechanisms of friction or wear have focused on two forces—adhesion and hysteresis—that compose the friction force (F_f).^{4,5} It was found that at low sliding velocities the friction of rubber is almost independent of velocity and temperature.⁶ At high sliding velocities, however, the coefficient of friction becomes a function of velocity.⁶ Additional research has been focused on other important aspects of F_f . For instance, a theory of the hysteretic contribution to rubber friction has been developed.⁷ In addition, the relationship between geometric factors and F_f has been explored.⁸ It was found that an entirely geometric contribution—including changes in contact angle—considerably increased the friction coefficient. The mechanism of friction, however, is complex and still debated. Although there have been some previous reports^{9,10} on the tribology of composite materials that include silanes as compatibilizers or modifiers, there is very limited literature dedicated to the effects of silanes on the tribology of clay/polymer composites.

In this work we have prepared a series of rubber composites and have compared their properties.^{11,12} We selected three silanes with different functional groups—(3-mercaptopropyl)trimethoxysilane (MPTMS), [3-(2-aminoethylamino)propyl]trimethoxysilane (AEAPTMS), and

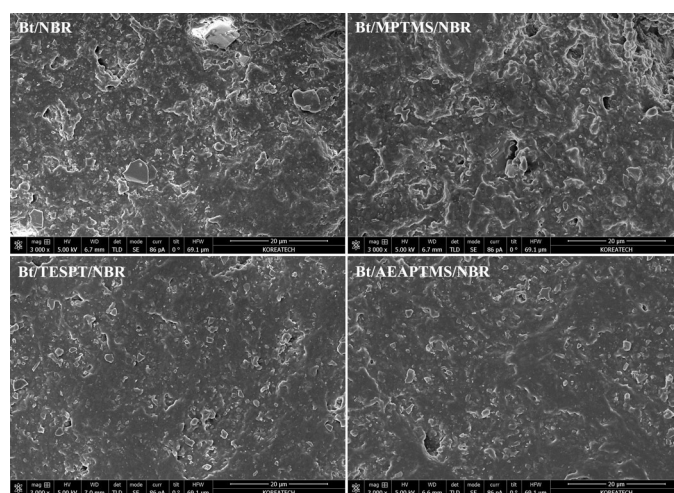


Figure 1. Scanning electron microscopy images of the worn surfaces of four clay/rubber composites. Top left: Composite of bentonite (Bt) and acrylonitrile butadiene rubber (NBR). Top right: Composite of Bt, NBR, and the silane (3-mercaptopropyl)trimethoxysilane (MPTMS). Bottom left: Composite of Bt, NBR, and the silane bis[3-(triethoxysilyl)propyl]tetrasulfide (TESPT). Bottom right: Composite of Bt, NBR, and the silane [3-(2-aminoethylamino)propyl]trimethoxysilane (AEAPTMS).

bis[3-(triethoxysilyl)propyl]tetrasulfide (TESPT)—to include in the composites. During the synthesis of the composites we added the silanes (as compatibilizers) into a mixture of acrylonitrile butadiene rubber (NBR) latex and an aqueous dispersion of bentonite (i.e., a clay mineral). In this process, the hydrolyzation and condensation of the silanes were catalyzed by ammonia. We then compounded the composites with other additives on a two-roll mill and cured them in a heating press at 160°C.

We used x-ray diffraction to characterize the influence of the different silanes on the interlayer spacing of the bentonite (Bt) within the composites. We found that with TESPT incorporated in the composites, the reflection at 6.2 (1.43nm) was weakened compared with the

Continued on next page

Bt/NBR composites, while with MPTMS the reflection almost disappeared. This indicates that MPTMS is more effective in exfoliating the Bt layers than TESPT. With AEAPTMS, the composites had larger interlayer distances, which reached up to 1.84nm.

In our experiments, we have also determined that F_f is composed of two factors during sliding on a dry elastomer/rigid contact interface, i.e., the adhesion force (F_a) and the hysteresis force (F_h). To measure the friction coefficient we applied a smooth surface to the composites. As we applied the silanes, the tribological properties of the composites were affected in different ways (see Table 1). Our results show that the F_a was enhanced in all the samples, i.e., by the addition of MPTMS, TESPT, and AEAPTMS. The composite containing MPTMS, however, was substantially harder than the other samples. This is the main cause of the small contact area and low friction coefficient of the Bt/MPTMS/NBR sample. In the wear loss test that we conducted, we used rough-surface abrading wheels. It has previously been suggested that F_a is negligible for rough contact interfaces.⁴ In that condition, F_h is the only factor that influences F_f . The Bt/MPTMS/NBR composite displayed the highest hysteresis value (0.35) among all the specimens, and its wear volume loss reached 0.11cm³. For the Bt/TESPT/NBR and Bt/AEPTMS/NBR samples, the wear loss was almost double that of neat NBR. This indicates that our hybrid composites performed poorly—with respect to wear resistance—compared with neat rubber materials.

When no silanes were incorporated into our materials, we were able to easily flake off large aggregations of Bt from the surfaces of the matrices (see Figure 1). This flaking caused the high wear loss of the samples. For our Bt/silane/NBR composites, however, the dispersion of Bt within the matrices was significantly improved. During abrasion we were able to pull out thin flakes of Bt, but this left only deep and small grooves. The geometry of the wear asperities also contributed to the wear loss of the samples. We believe that this could explain the highly corrugated wear asperity and high wear loss of the Bt/MPTMS/NBR composite.

Table 1. Experimentally measured tribological properties of the rubber composites.

Samples	Hysteresis ratio	Static friction coefficient at 4.5N load	Wear loss in volume (cm ³)
Neat NBR	0.15	1.3	0.03
Bt/NBR	0.27	2.0	0.12
Bt/MPTMS/NBR	0.35	0.5	0.11
Bt/TESPT/NBR	0.16	3.1	0.05
Bt/AEAPTMS/NBR	0.19	4.2	0.05

In this work we have prepared a series of composites made from rubber, bentonite, and three different silanes. We have also conducted a set of experiments on these samples to evaluate the various effects of silanes on the tribological properties of such clay/rubber composites. Although the adhesion force of the materials is improved by the inclusion of silanes, we find that our composite materials have higher wear losses than neat rubber. In our current work we are continuing to investigate and explore the mechanisms involved with friction and wear of our composite materials.

Author Information

Xin Ge, Yinhang Zhang, Fei Deng, and Ur Ryong Cho

Korea University of Technology and Education
Cheonan, South Korea

Xin Ge has been a PhD candidate since 2011. He majors in applied chemical engineering, and his work focuses on the development of high-performance polymer composite materials.

References

1. Q.-X. Jia, Y.-P. Wu, Y.-Q. Wang, M. Lu, J. Yang, and L.-Q. Zhang, *Organic interfacial tailoring of styrene butadiene rubber–clay nanocomposites prepared by latex compounding method*, **J. Appl. Polym. Sci.** **103**, pp. 1826–1833, 2007.
2. U. Sookyoung, C. Nakason, W. Thajaroen, and N. Vennemann, *Influence of modifying agents of organoclay on properties of nanocomposites based on natural rubber*, **Polym. Test.** **33**, pp. 48–56, 2014.
3. H. J. Maria, N. Lyczko, A. Nzihou, K. Joseph, C. Mathew, and S. Thomas, *Stress relaxation behavior of organically modified montmorillonite filled natural rubber/nitrile rubber nanocomposites*, **Appl. Clay Sci.** **87**, pp. 120–128, 2014.
4. P. Gabriel, A. G. Thomas, and J. J. C. Busfield, *Influence of interface geometry on rubber friction*, **Wear** **268**, pp. 747–750, 2010.
5. D. Tabor, *Hysteresis losses in the friction of lubricated rubber*, **Rubber Chem. Technol.** **33**, pp. 142–150, 1960.
6. K. A. Grosch, *The relation between the friction and visco-elastic properties of rubber*, **Proc. R. Soc. London A.** **274**, pp. 21–39, 1963.
7. B. N. J. Persson, *Theory of rubber friction and contact mechanics*, **J. Chem. Phys.** **115**, pp. 3840–3861, 2001.
8. M. Eriksson and S. Jacobson, *Tribological surfaces of organic brake pads*, **Tribol. Int'** **33**, pp. 817–827, 2000.
9. N. Tabsan, S. Wirasate, and K. Suchiva, *Abrasion behavior of layered silicate reinforced natural rubber*, **Wear** **269**, pp. 394–404, 2010.
10. N. Chand, P. Sharma, and M. Fahim, *Abrasive wear behavior of LDPE filled with silane treated flyash cenospheres*, **Compos. Interfaces** **18**, pp. 575–586, 2011.
11. X. Ge, M. C. Li, and U. R. Cho, *Novel one-step synthesis of acrylonitrile butadiene rubber/bentonite nanocomposites with (3-mercaptopropyl)trimethoxysilane as a compatilizer*, **Polym. Compos.** **36**, pp. 1693–1702, 2014.
12. X. Ge, Y. Zhang, F. Deng, and U. R. Cho, *Effects of silane coupling agents on tribological properties of bentonite/nitrile butadiene rubber composites*, **Polym. Compos.**, 2015. doi:10.1002/pc.23817