# Study on Preparation and Tribological Properties of Epoxy Resin/SiO₂ Hybrid Thin Film

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**ABSTRACT:** A series of organic–inorganic hybrid thin films are prepared by means of the sol–gel process in curing epoxy and hydrolyzing tetraethoxysilane. The epoxy group of γ-glycidyloxipropyltrimethoxysilane can be incorporated into the sol–gel network to form the interaction between the inorganic and organic phases. Inorganic and organic components can be mixed on the nanometer scales, thereby leading to the formation of so-called hybrid materials. Transmission electron microscopy examinations and atomic force microscopy are employed to study the morphology and roughness of the samples, respectively. In addition, the tribological behavior of dip-coating thin films is evaluated by the use of a dynamic/static friction precision measurement apparatus (unidirectional sliding tester). The influences of the contents of both the filler and the coupling agent on the tribological properties of the nanocomposite thin films are systematically studied. These results indicate that the films sliding against a GCr15 steel ball display excellent antiwear and friction reduction performance. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 38–43, 2005

**Key words:** thin films; gels; tribological behavior

## INTRODUCTION

Because of their excellent properties, extensive attention has been paid to hybrid materials in recent years. The behaviors of the organic and inorganic components in the materials usually play an important role in their properties. The sol–gel process is one of the important methods of preparing hybrid materials, and it has been widely used and investigated in industrial plants and labs developed for various applications for optical, electrical, and biochemical purposes.[1–3] The low temperature sol–gel process starting from organometallic precursors, such as silicates, titanates, and aluminates, is a convenient technique for the synthesis of the inorganic part of these hybrids.

The key to prepare homogeneous hybrids is to prevent phase separation and control phase domains that are <100 nm. In previous experiments, some workers directly mixed a polymer solution or monomer with a sol.[4,5] The method is mainly used for these hybrids for strong physical or chemical interfacial interactions between nanoparticles and the surrounding polymer matrix. Another method is to make use of coupling agents to produce chemical bonding between the two phases.[6,7] Various functional groups in the agents, such as amino, epoxy, vinyl, and allyl groups, can be incorporated into the sol–gel network to produce the interaction with the organic polymer. Moreover, the agents also contain alkoxysilane terminal groups that are capable of reacting with the metal alkoxide.

Research results on the preparation of the epoxy resin/inorganic particles hybrids have been reported. Matejka et al.[8,9] have attained epoxy–silica hybrids by different synthesis procedures. In the one-step procedure, all reaction components are mixed and reacted to form hybrids. In the two-step procedures, tetraethoxysilane (TEOS) is first prehydrolyzed in the presence of the catalyst toluenesulfonic acid, and then the hydrolyzed TEOS is mixed with the organic phase components diglycidyl ether of bisphenol A and D-2000 hardener to form hybrids. No coupling agents are employed in the two synthesis methods. Other experiments based on a functional group, such as the amine group, coupling agent have been developed to study the morphology of hybrid materials. For example, Mascia and Tang[10,11] have prepared hybrid materials from different molecular weight bisphenol A ep-

**TABLE I**
**Epoxy–Silica Hybrid Thin Films of Different A-187 and SiO$_2$ Contents**

| Sample number | A-187 (wt %) | SiO$_2$ (wt %) |
| --- | --- | --- |
| EP | 0 | 0 |
| BS2 | 0.5 | 5 |
| BS3 | 1 | 5 |
| BS4 | 2 | 5 |
| BS5 | 3 | 5 |
| BS6 | 4 | 5 |
| BS7 | 5 | 5 |
| SB2 | 4 | 5 |
| SB3 | 4 | 10 |
| SB4 | 4 | 15 |
| SB5 | 4 | 20 |
| SB6 | 4 | 25 |
| SB7 | 4 | 30 |

oxy resins, functionalized with phenylaminopropyl-trimethoxysilane (Y-9669) or bis($\gamma$-trimethoxysilyl propyl)-amine (A-1170), and silica. Nishijima et al.[12] have reported the preparation of a hybrid material based on an epoxy resin/silica system, using $N$-$\beta$-amino-ethyl-$\gamma$-aminopropylmethyldimethoxysilane as a coupling agent. However, little research work has been reported in early articles about the $\gamma$-glycidyloxipropyltrimethoxysilane (A-187) coupling agent containing an epoxy group to produce hybrid materials.

Epoxy resin is most commonly used for top coats in aerospace coating systems because of its high abrasion resistance.[13] In this work, we used A-187 containing epoxy groups as a coupling agent to prepare epoxy resin/silica hybrids. Research results such as the properties of the hybrid materials and the relationship of the content of both silica and the coupling agent on the tribological properties of the epoxy resin/silica hybrid thin film are reported in this article.

## EXPERIMENTAL

### Materials

The bisphenol A type resin (E-51) used for this experiment was purchased from Wuxi Resin Factory. Its average molecular weight is 370. The coupling agent A-187 was obtained from Shanghai Yaohua Chemical Factory.

4,4'-Diaminodiphenyl sulfone (DDS) and TEOS (purity > 95%) are used as the hardener and precursor, respectively. HCl (35 wt %) is used as a catalyst for the hydrolysis of the TEOS component. Tetrahydrofuran (THF) is used as a solvent. These reagent grade agents were purchased from Shanghai Chemical Agent Factory.

## Preparation of hybrid thin film of epoxy resin/silica

### Sol–gel process

The solution of water and TEOS (molar ratio = 3–4:1) is added into anhydrous ethanol (concentration of TEOS in the solvent is controlled at 15 wt %), and then the pH of the solution is adjusted in the range of pH 2–3 by using HCl solution. The system is stirred until the mixture becomes clear and deposits at about 12 h.

### Hybrid process

The epoxy resin dissolved in the THF and different ratios of silica sol solution or A-187 are both added into the previous prepared solution and then stirred until it becomes clear and transparent. Finally, the DDS hardener is added into the system.

The substrate glasses are cleaned and oxidized by a solution of 3:7 H$_2$SO$_4$/H$_2$O$_2$ to remove impurities and then purged by nonionic water and isopropyl alcohol, respectively. The thin film is attained by means of the dip-coating method. The vertical velocity is 42.5 cm/min. The solvent in the system is allowed to evaporate at room temperature, and then it is cured and dried in the following steps: 80°C for 2 h, 120°C for 3 h, 150°C for 2 h, and 180°C for 3 h. Achromic and transparent hybrid thin films are attained. The components and contents of all samples are described in Table I.

Table I shows the percentages of each component in the epoxy resin. The hardener in these hybrids is 33 wt % epoxy resin. We mix the epoxy solution with silica sol and keep the volume of the final solutions invariable so that we can procure hybrid thin films of about the same thickness.

## Characterization and analysis of the hybrids

The morphologic structures of the samples are observed by means of transmission electron microscopy (TEM; JEM-1200EX), and the surfaces of the fresh hy-
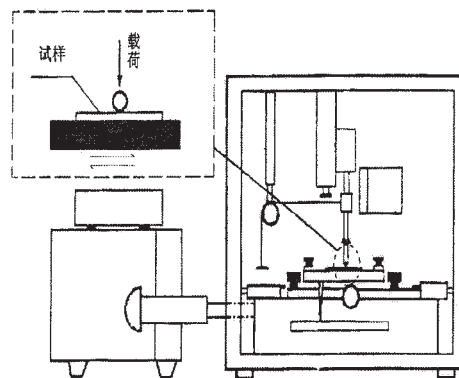


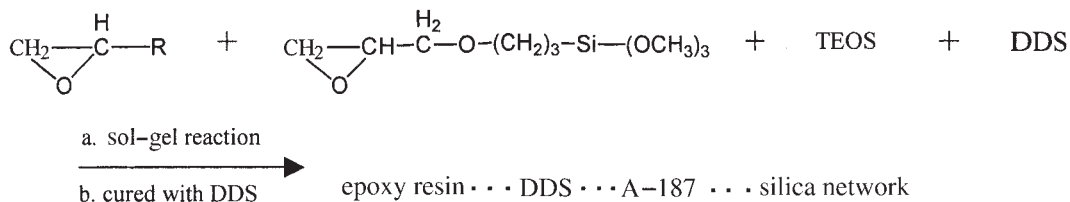**Figure 1** A sketch map of the tribological apparatus.

**Figure 2** A transmission electron micrograph of the epoxy–silica hybrid. Scale bar = 50 nm.

## RESULTS AND DISCUSSION

### Explanation of hybrid processing

The coupling agent in our experiment, A-187, contains an epoxy group in its molecular structure. Its behavior in the hybrids is obviously different from that of other coupling agents in early work such as $\gamma$-aminopropyl triethoxysilane (A-1100), which contains an amine group. The epoxy groups in both the epoxy resin and A-187 can be cured at the same time by the hardener (DDS in our experiment) in our system, thereby forming better net structures in the hybrids. In this way the organic and inorganic phases can produce the organic–inorganic hybrid interpenetrating network (IPN) or half-IPN structure. The bisphenol A epoxy resin structure is



and the formula of the A-187 coupling agent is



brid thin film are measured using atomic force microscopy (AFM; SPM-9500).

Abrasion tests are performed on a tribological apparatus. The sketch map is shown in Figure 1. In addition, a GCr15 steel ball is employed in this experiment. We regulate the cycles of abrasion at 30 and then collect the data of the friction coefficients and the abrasion width. Finally, the abrasion surfaces are observed with scanning electron microscopy (SEM; JSM-5600LV) micrographs.
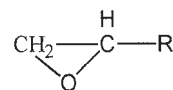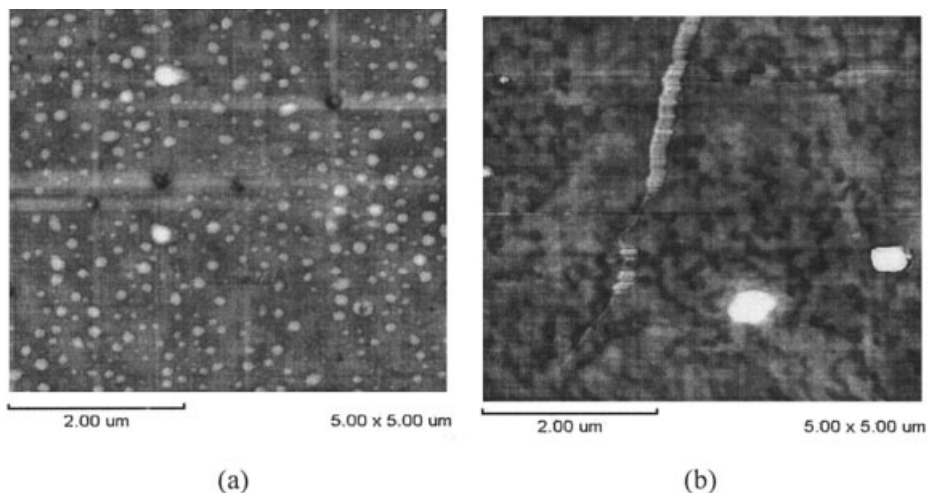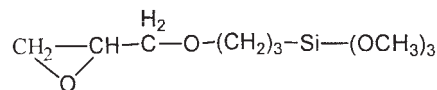
The chemical reaction is the following:





**Figure 3** AFM top views ($5 \times 5$ $\mu$m) of the surfaces of (a) SB7 and (b) BS7.
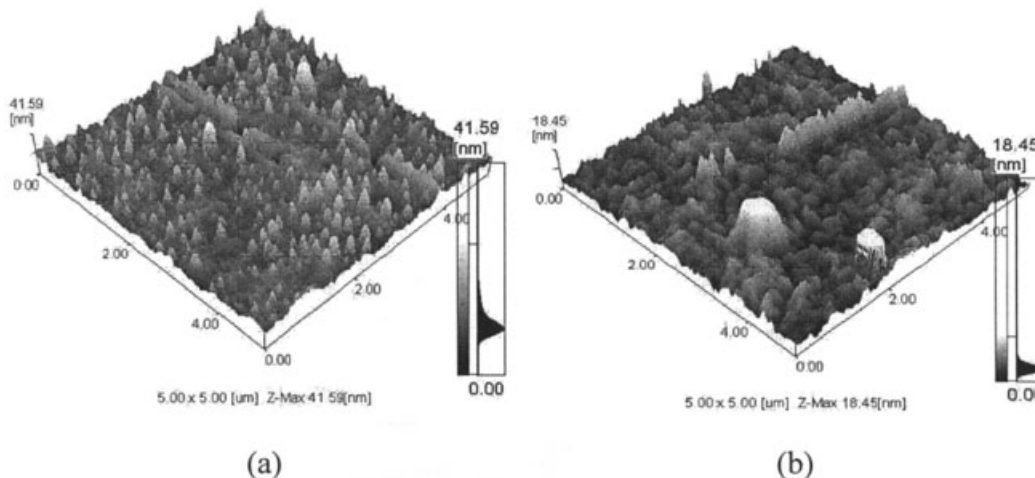
**Figure 4**  AFM topographic views (5 × 5 $\mu$m) of the surfaces of (a) SB7 and (b) BS7.

It can be seen from the structures that A-187 plays a bridge role between the silica and hardener. A large network is formed of organic and inorganic phases that interpenetrate each other.

## Morphology of hybrids

The observed morphology by the TEM micrograph in Figure 2 shows that the prepared epoxy–silica hybrid expresses a typical compatible epoxy creamer. The results suggest that the size of the nanoparticles is about 10 nm and transparent epoxy–silica hybrids have little or no organic–inorganic phase separation. The formation of the condensing structure is attributed to the use of the coupling agent.

Figure 3 shows two representative top views of the hybrids. We found that SB7 shows clearly discernible grain domains of much greater dimensions than BS7, and the average roughness of the high silica content SB7 sample is about double that of BS7. In SB7 [Fig. 3(a)] the average domain size is ~150 nm, but in BS7

[Fig. 3(b)] the domains almost disappeared. According to the results, the formation of the domain structure can be attributed to the development of microcolloidal particulation during the sol–gel reactions.[14] It is considered that the polymer and silica components can exist in each domain, in which the chains of one component are intimately entwined with those of another through the covalent bonding in the coupling agent, just as in the report of a poly(methylmethacrylate)–silica experiment.[15] In the BS7 sample, the contents of A-187 and SiO₂ are both 5%. The chain of the epoxy enwraps the silica and forms a continuous phase. In the curing process, silica components are rooted in the network of the resin by A-187. The observed phenomena show that there is a little phase separation in SB7, but not in BS7. This is probably a result of the high content of SiO₂ in SB7. In addition, the AFM image also shows that the domain size reaches about 150 nm in SB7, but the sizes of the grains basically are consistent. This obviously indicates the formation of silica particulation.
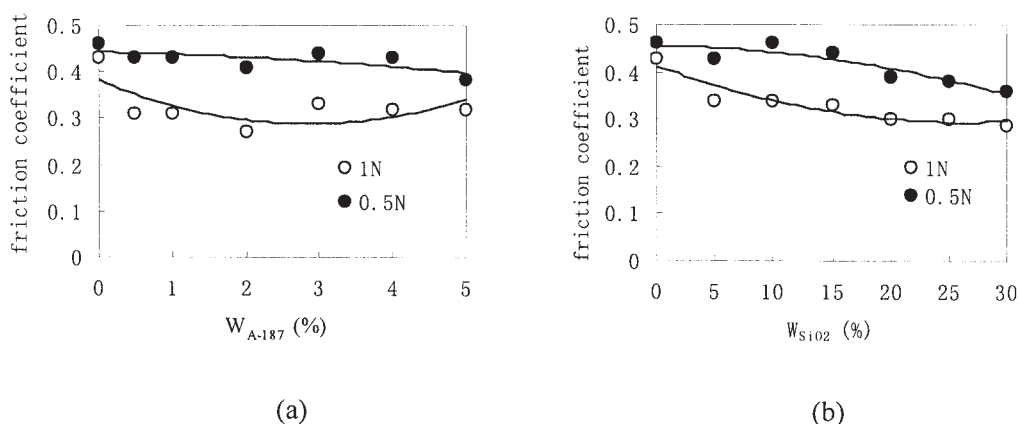


**Figure 5**  Variations in the friction coefficient with the weight fraction of (a) A-187 and (b) silica.
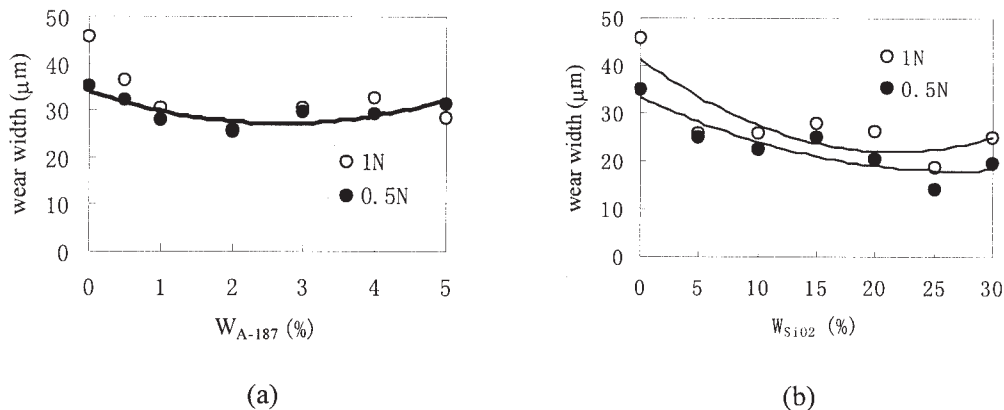
**Figure 6** Variations in the wear width with the weight fraction of (a) A-187 and (b) silica.

From the topographic views shown in Figure 4, we found that SB7 shows clearly discernible grain domains of much greater dimensions than BS7, and the average roughness of the high silica content SB7 sample is about twice that of BS7.

### Effects of contents of filler and coupling agent on tribological properties

Figure 5 shows the influences of the content of A-187 and silica on the friction coefficient. It is obvious that the pure epoxy resin thin film or hybrid thin films have a lower friction coefficient ($\mu$) than the substrate glass ($\mu = 0.78$), but the $\mu$ of each hybrid is smaller than that of pure epoxy. As the content (including A-187 and silica) is increasing, $\mu$ appears to have a decreasing trend. We presume that in the processes of hydrolyzing and condensation the Si—O groups connected with organic chains and made the whole chain become more flexible, so that hybrids have lower shear force in the rubbing process. In addition, we also

considered that A-187 not only ameliorated the interface between the two phases but also participated in the rubbing process. This discussion is in agreement with the results of two kinds of hybrids having lower $\mu$ at high load (1 N) than at low load (0.5 N).

The curves of the wear width versus the weight fractions of A-187 and silica are shown In Figure 6. Figure 6(a) demonstrates that the variations of the load and A-187 content in the hybrids will not produce a distinct change in the abrasion resistance, but as the content of silica increases the abrasion obviously decreases. The participation of silica intensifies the hybrids and endures a majority of load in the process of rubbing, but the coupling agent has none of these functions. Hybrids are easily destroyed at high load. The abrasion resistance is inferior to that at low load.

The mechanism of the rubbing process is analyzed according to the SEM pictures of the worn surfaces shown in Figure 7. The results show that
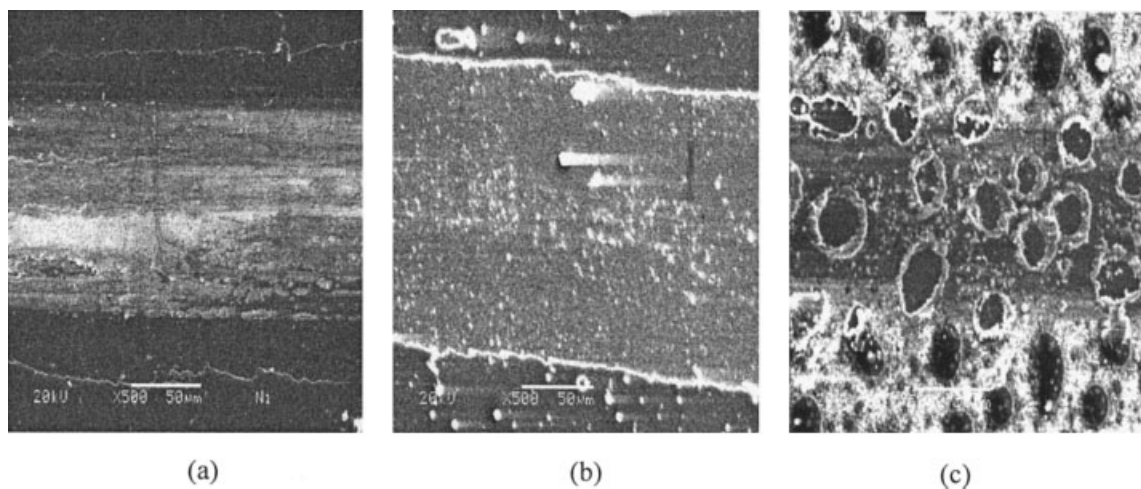


**Figure 7** An SEM picture of the worn surfaces of (a) pure epoxy, (b) BS7, and (c) SB7.

the worn surface of the pure epoxy thin film has severe plastic distortion and the materials are pushed to both sides of the rubbing steel. For this reason, the mechanism of adhesive abrasion is suggested. In Figure 7(b) there are some particles explored on the surfaces of the hybrids, but not the phenomenon of adhesive abrasion. The pure epoxy and the BS7 sample both show a large wear width. It is interesting to find that the surfaces of SB7 appeared to have an alveolate structure, which we still did not make clear, but the silica certainly improves the abrasion resistance of hybrids.

## CONCLUSIONS

In summary, epoxy resin has fine compatibility with silica when used with a coupling agent (A-187). Adding A-187 and silica can decrease the friction coefficient of hybrids, but only silica will improve the abrasion resistance of the whole materials.

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