

Thermomechanical Properties, Phase Structure, and Conductivity of Organic/Inorganic Hybrid Material Filled with a Conductive Filler

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ABSTRACT: Novel epoxy-based organic/inorganic hybrid materials filled with carbon black (CB) were synthesized from an epoxy resin and silane alkoxide via a sol-gel process. The phase structure and thermal and mechanical properties of the hybrid materials were studied in detail. It was revealed by transmission electron microscope observations that the filled CB particles formed a secondary aggregation structure and were uniformly dispersed in the aggregate. The storage modulus in the rubbery region increased and the peak area of the $\tan \delta$ curve in the glass-transition

region decreased with the hybridization of silica. Moreover, the conductive properties of the CB-filled hybrid systems were investigated. In the same volume fraction of CB, the conductivity of the hybrid systems was much higher than that of the unmodified system. This result was attributed to the excluded volume effect of the silica network. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1980–1984, 2003

Key words: epoxy resin; silane alkoxide; silica hybrid; carbon black; conductivity

INTRODUCTION

Conductive materials, which are constituted from organic polymers and conductive fillers, are used in such applications as electrification prevention, electromagnetic wave covers, heating elements, sensors, circuit formation material, and conductive adhesives.^{1,2} Much attention has been paid to improving the processability, flexibility, and thermal stability of such conductive materials. To attain these requirements, matrix polymers need to become higher-performance materials.

One technique for improving a matrix polymer's performance, such as its thermal and mechanical properties, is the preparation of organic/inorganic hybrid materials^{3,4} using a sol-gel process.^{5,6} With this process the characteristic properties of organic polymers (e.g., toughness, flexibility, and processability) and inorganic polymers (e.g., good thermal stability and good mechanical and optical properties) are able to be combined in matrix polymers.^{7,8}

Recently, much research on the phase structure and thermomechanical properties of hybrid materials has been reported.^{9,10} We previously reported^{11–13} on the preparation of epoxy-silica hybrid materials from an epoxy resin and a silane alkoxide via a sol-gel process, showing that these hybrid materials had good

thermal and dimensional stability and high strength in an elevated-temperature region. The phase structure of this system showed that nanometer-sized silica rich phases were uniformly dispersed in the epoxy matrix.

In the current study improvement of the thermal and mechanical properties of a carbon black-filled conductive epoxy system was undertaken by applying the epoxy-silica hybrid material as a matrix polymer. Moreover, the relationship of the morphology of the CB dispersion and the conductivity of the filled system was investigated as a function of the silica content.

EXPERIMENTAL

Materials

The epoxy resin used in this study was commercial-grade diglycidyl ether of bisphenol A (DGEBA; Epikote 828, epoxy equivalent: 190 ± 5 ; Japan Epoxy Resin Co., Ltd.). The curing agent was tetraethylenepentamine [TEPA (extragrade); Tokyo Kasei Co., Ltd], the silane alkoxide used as an inorganic source was silane alkoxide oligomer (SAO; MS-51, Mitsubishi chemical Co., Ltd.), and the conductive filler was carbon black (CB; Ketjenblack EC, Ketjenblack International Co., Ltd.).

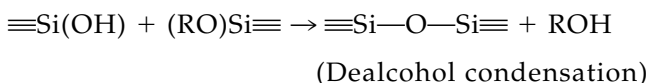
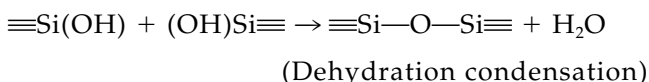
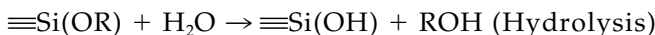
Preparation of epoxy-silica hybrid systems filled with CB

Prescribed amounts of DGEBA and CB were kneaded with a two-axis roll at 100°C to obtain a highly con-

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centrated master batch of CB. To enhance the affinity between DGEBA and CB, the master batch was aged for 3 days at room temperature. The aged master batch was diluted with DGEBA utilizing a two-axis roll at 60°C to obtain the prescribed compositions. Subsequently, SAO and TEPA were added into the DGEBA-CB slurry and kneaded once again. The resulting DGEBA/SAO/TEPA/CB mixtures were molded into sheets of 500 μm thick with a hot press at 60°C. The compounds were cured at 60°C, 100°C, and 150°C, then finally cured at 190°C for 4 h during each curing step.

In this preparatory process the following scheme was proposed to be used for the sol-gel reactions of silane alkoxide to yield epoxy-silica hybrid structures.



Hydrolysis of silane alkoxide occurred first by the reaction with water contained in the epoxy resin. The dehydration and dealcohol condensation reactions then occurred to form the network structure. Matejka et al.^{8,9} explained that the addition of an acid catalyst to an epoxy-silane alkoxide mixture should mainly accelerate the hydrolysis of the silane alkoxide and that the condensation reaction of the alkoxide is significantly promoted by the presence of a basic catalyst. TEPA, which was added as a curing agent in this study, has a relatively high basicity and thus acted as a basic catalyst for the condensation reaction of the silane alkoxide.

Measurement

Dynamic mechanical properties of the cured hybrid materials were determined using a nonresonance forced-vibration viscoelastometer (DVE-V4, Rheology Co., Ltd.) in air. The frequency and amplitude of the vibration were adjusted to 10 Hz and 5 μm , respectively. The measured temperature range was 50°C–250°C, and the heating rate was 2°C/min.

Coefficients of thermal expansion (CTE, α) of the cured hybrid materials were measured using a thermomechanical analyzer (TMA-100, Seiko Instruments Co., Ltd.). The temperature range measured was from 0°C to 250°C, and the heating rate was 5°C/min. The CTE values were calculated according to the following equation from the changes in the sample length with increasing ambient temperature.

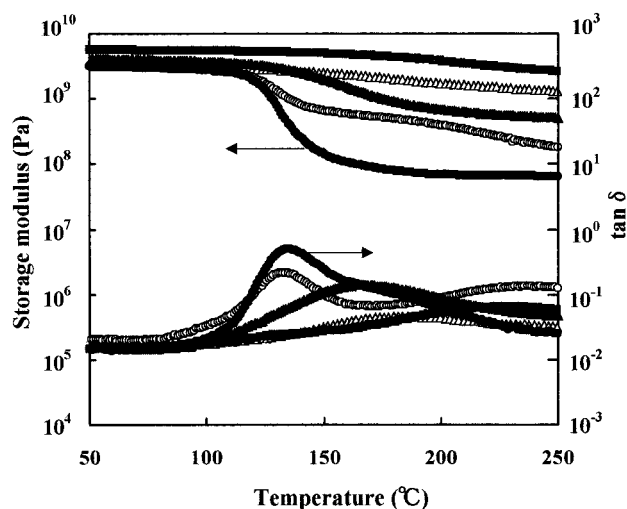


Figure 1 Dynamic mechanical properties of epoxy-silica hybrid systems filled with CB (15 wt %) and with an SiO_2 content (wt %) of: (●) 0 (unmodified), (○) 10, (▲) 20, (△) 30, (■) 40.

$$\alpha = (dL/dT) \times (1/L_T)$$

where dL/dT is the slope of tangential lines on the sample length-temperature curve, and L_T is the sample length at $T^\circ\text{C}$.

The hardness of the hybrids was measured using a micro-Vickers indenter (Shimadzu, HSV-30) with a maximum load of 1.96 N and loading time of 30 s.

Ultrathin sections of the DGEBA/SAO/TEPA/CB hybrids were observed using a transmission electron microscope (TEM; JEM 1210, JEOL Co., Ltd.) to study the morphology of the CB dispersion and the silica-rich phase. The specimens for the TEM observations were prepared using an ultramicrotome (Reichert Ultracut E, Leica Co., Ltd.) with a diamond knife. The specimens were not stained prior to the TEM observations.

The conductivity of the hybrids was measured using a direct current (dc) voltage source/monitor (TR6243, Advantest Co., Ltd.). The measurement was done according to a dc two-probe method. Specimens were coated with Ag paste as electrodes prior to examination.

RESULTS AND DISCUSSION

Thermomechanical properties

The temperature dependence of the dynamic mechanical properties of the cured hybrid systems filled with CB are shown in Figure 1. These samples contained different amounts (0–40 wt%) of the silica network and a constant value (15 wt %) of CB. The samples are designated by number codes that refer to their SiO_2 and CB weight percents. The codes are: 0–15 for 0 wt % SiO_2 /15 wt % CB; 10–15 is 10 wt % SiO_2 /15 wt %

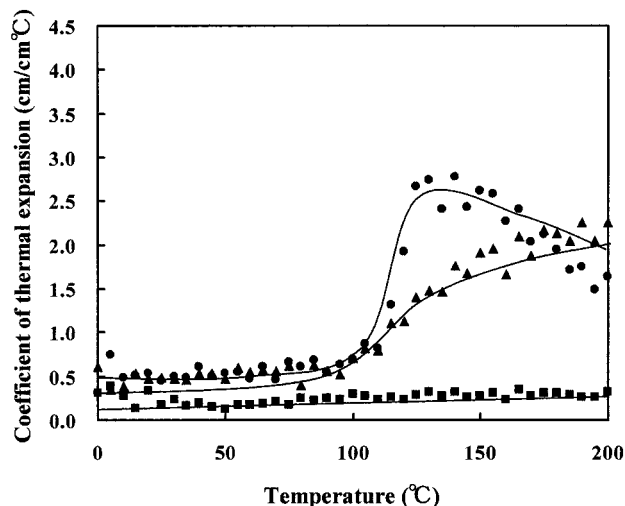


Figure 2 CTE of epoxy-silica hybrid systems filled with CB (15 wt %) and with an SiO₂ content (wt %) of: (●) 0 (unmodified), (▲) 20, (■) 40.

CB; 20-15 is 20 wt % SiO₂/15 wt % CB; 30-15 is 30 wt % SiO₂/15 wt % CB; and 40-15 is 40 wt % SiO₂/15 wt % CB. In the unmodified system (0-15), the storage modulus clearly decreased in the glass-transition temperature (T_g) region and had a very low value in the rubbery region. It is well known that a decrease in the modulus in the T_g region is a result of the micro-Brownian motion of the network chains. However, in the hybrid matrix systems (10-15, 20-15, 30-15, 40-15), the modulus in the rubbery region increased, and thus the glass-transition behavior became indistinct with an increase in the silica network content. This shows that the micro-Brownian motion of the epoxy network was strongly restricted by hybridization with the silica network. The storage modulus of the hybrid systems with more than 30 wt% of added silica showed no decrease in the glass-transition region and maintained a high modulus value even where the temperature was more than 200°C, the elevated temperature region. This means that the heat resistance of the cured epoxy resin was significantly improved by the hybridization with a silica network.

Coefficients of thermal expansion (CTEs) of the cured hybrid systems filled with CB (CB content: 15 wt %) are shown in Figure 2. The unmodified matrix system (0-15) clearly showed a glass-rubber transition. Compared with the unmodified system, the hybrid systems (20-15 and 40-15) had lower CTEs in the wide temperature region, especially the hybrid system (40-15) with a high silica content, which had a very low CTE, approximately 20 ppm/°C, throughout the entire measured temperature region. These results indicate that the mobility of the epoxy network was decreased, and thus an increase in the free volume of the epoxy matrix was prevented by the addition of the silica network. As shown in Figure 1, the micro-

Brownian motion of the network chains was suppressed in the epoxy-silica hybrids, even at a low silica content (20 wt %).¹¹ However, to decrease the CTE in the glassy region of the epoxy-silica hybrids, a high silica content (>40 wt %) was needed. From these results we believe that a more complete suppression of the network motion should produce a lower CTE of the hybrid materials.

The Vickers hardness values of the cured hybrid systems filled with CB (CB content; 15 wt %) are shown in Figure 3. Vickers hardness increased significantly with an increase in the silica content of the hybrid matrix. This result suggests that the uniform dispersion of the silica network into the epoxy network effectively improved the rigidity of the matrix resin. That is to say, the epoxy matrix would be reinforced with the rigid silica network dispersed uniformly.

Conductive properties

The conductive properties of the cured hybrid systems filled with various amounts of CB are shown in Figure 4. Compared with the unmodified system (silica content: 0 wt %), the conductivity of the hybrid systems containing CB increased with the addition of the silica network and reached a maximum value at 40 wt % of silica content. Then the conductivity decreased with an increase in the silica network content. In addition, the conductivity of the various CB-filled hybrid systems increased with an increase in CB content. It is well known that the conductivity of a CB-filled system is generated by the formation of a conductive path composed of CB particles. Thus, the improvement in conductivity with the addition of the silica network means that a good CB conductive path was formed in the hybrid matrix. However, the decrease in conduc-

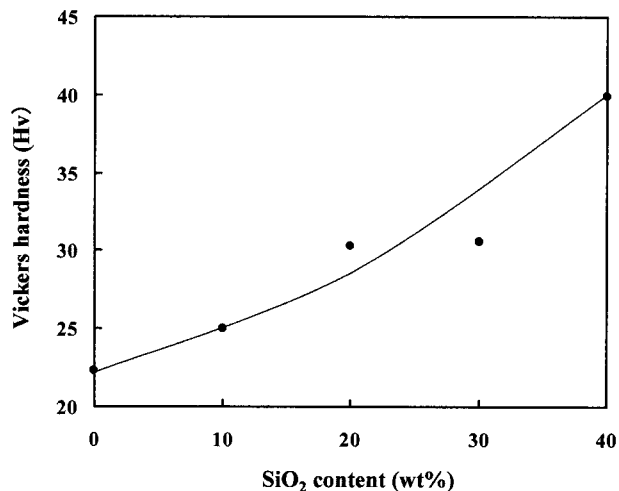


Figure 3 Vickers hardness of epoxy-silica hybrid systems filled with 15 wt % CB.

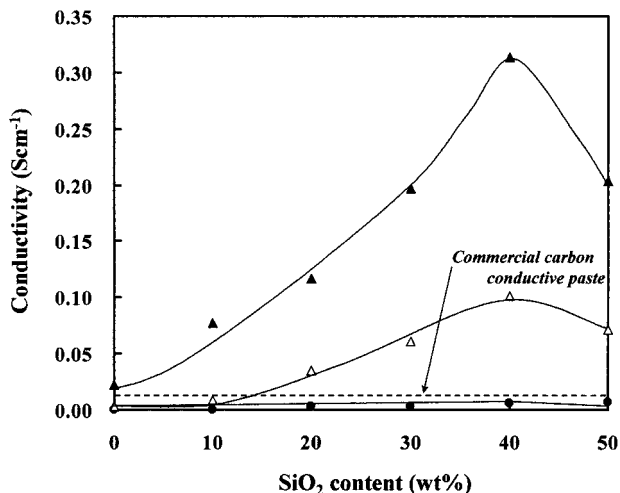


Figure 4 Conductive properties of epoxy-silica hybrid systems filled with CB content (wt %) of: (●) 5, (△) 10, (▲) 15.

tivity in the systems with a high silica content (>40 wt %) should mean that the formation of the conductive path in the matrix was prevented by the highly concentrated silica networks.

Furthermore, the hybrid systems that had a high CB content (the series with 10 or 15 wt % CB) showed greater conductivity than a commercial carbon-polymer conductive paste. The polymer matrix of a commercial paste usually contains about 10 wt % carbon. The CB-containing hybrid system was highly conductive at the same CB content, compared with the commercial carbon paste. From these results we expect that the application of hybrid materials as a matrix for a conductive paste would be useful in improving the heat resistance, heat shrinkage, and electric resistance of epoxy-carbon conductive adhesives.

To more clearly show the effect of hybridization of the silica network on the conductive property, the

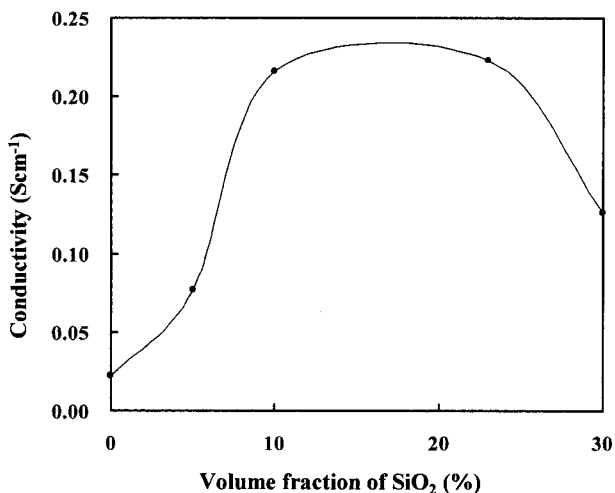


Figure 5 Conductivity of epoxy-silica hybrid systems filled with 10 vol % CB.

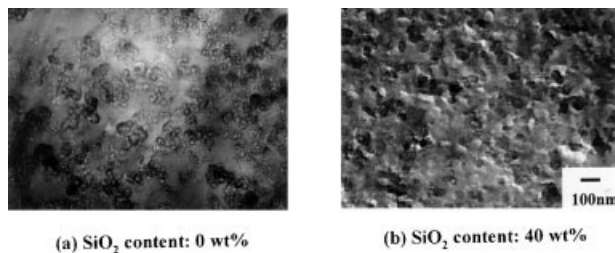


Figure 6 Transmission electron micrographs of epoxy-silica hybrid systems filled with 15 wt % CB.

changes in conductivity with the addition of the silica network were measured for the samples in which the volume fraction of CB was kept at a constant value (10 vol %). The relationship between the conductivity of the hybrids and the volume fraction of the silica network is shown in Figure 5. The conductivity of these samples increased with an increase in the volume fraction of the silica network and showed a maximum peak with a silica content of 10–20 vol %. Conductivity then decreased with the addition of any excess amount of the silica network. In these systems the content of CB was kept at a constant volume percent. Thus, this result shows that the dispersion morphology of CB in the epoxy matrix was changed with the addition of the silica network. We also concluded that the formation of an effective conductive path was accelerated by the hybridization of the silica network and thus that the conductivity of the CB-filled epoxy-silica hybrids had a maximum peak in the region containing the appropriate amount of CB.

Phase structure

The phase structures of the cured unmodified materials and of the hybrid materials filled with CB (0–15, 40–15) were investigated by using transmission electron microscopy (TEM). The TEM photographs are shown in Figure 6. In both systems it was observed that CB particles formed a secondary aggregation structure on scale of several hundred nanometers and that the units of the aggregation structure were uniformly dispersed in the unmodified and hybrid matrices. However, in the hybrid system (40–15), the silica network could not be observed in this magnified scale. This should mean that the silica-rich phase in

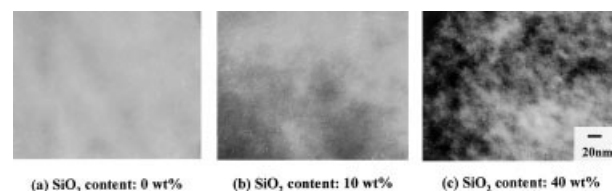


Figure 7 Transmission electron micrographs of epoxy-silica hybrid systems.

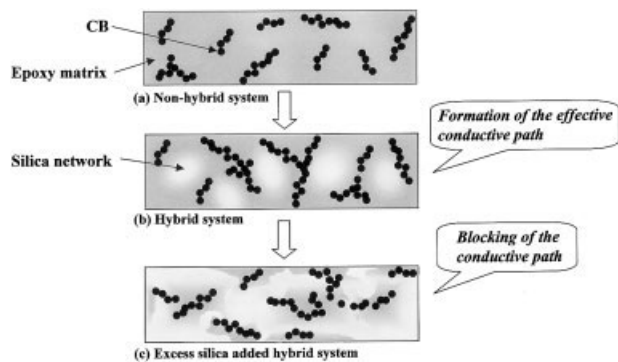


Figure 8 Schematic illustration of the excluded-volume effect of the silica network.

which the silica network was dissolved into the epoxy matrix should be dispersed on a nanometer scale.

To confirm the morphology of the silica-rich phase, the phase structures of the hybrid materials that were not filled with CB were observed under higher magnification. The TEM photographs are shown in Figure 7. The unmodified system, that is, a cured epoxy resin, showed a uniform structure over the entire area observed, whereas in the hybrid system of 10 wt % silica, dark shadowy areas about 30 nm in diameter were observed over the entire area of the specimen. The dark areas observed must be the silica-rich phase in which the silica network is highly concentrated in the epoxy matrix. In the hybrid system that contained 40 wt % of the silica network, many dark spots corresponding to the silica domains were observed, and these spots formed a cocontinuous phase in the epoxy matrix. These results show that the phase structure of epoxy-silica hybrids shifted from an epoxy-continuous to a silica-continuous phase structure as a function of silica content. In the system containing 40 wt % of the silica network, the TEM photographs revealed that the phase transition was just occurring.

It is natural to consider that in the CB-filled systems, the CB particles were more easily dispersed into the epoxy-rich phase than into the silica-rich phase. Therefore, it seems that the CB and silica networks are independently dispersed in the epoxy matrix, that is, with an increase in the volume fraction of the silica network, the added CB particles dispersed into the smaller region, which was the epoxy-rich phase. The scheme for the dispersion of CB particles into the epoxy matrix is shown in Figure 8. In the nonhybrid system [Fig. 8(a)], the CB particles formed a secondary aggregation structure uniformly dispersed in the epoxy matrix. In the hybrid system of low silica content (<40 wt %) [Fig. 8(b)], the silica-rich phase was dispersed as separate domains and thus limited the area in which the CB aggregates could be dispersed. By this excluded-volume effect, the secondary aggregation structure of the CB particles was more easily formed,

and thus the conductivity of the CB-filled epoxy-silica hybrids should increase with an increase in the silica content, as shown in Figures 4 and 5. In the hybrid system of high silica content (>50 wt %) [Fig. 8(c)], the silica-rich phase was formed in a continuous phase structure. In this system, the conductive path composed of the CB aggregates should be blocked by the continuous silica-rich phase. The decrease in the conductivity of the system hybridized with an excess amount of silica (Figs. 4 and 5) must be a result of the blocking effect of the continuous silica-rich phase on the conductive path.

CONCLUSIONS

Organic/inorganic hybrid materials filled with a conductive filler were synthesized from a silane alkoxide oligomer and a master batch of bisphenol A-type epoxy resin and carbon black via a sol-gel process. In the hybrid systems filled with CB, the storage modulus in the rubbery region increased, and the peak area of the $\tan \delta$ curves in the glass-transition region decreased with hybridization of the silica network. The coefficient of thermal expansion of the hybrid systems was considerably lower than that of the unmodified system. This may result from the suppression of the mobility of the epoxy network with the hybridization of the silica network.

Conductivity of the hybrid systems filled with CB was higher than that of the unmodified system. This may result from the excluded-volume effect of the silica network. However, the addition of an excess amount of the silica network decreased the conductivity of the hybrids. This is because of the blocking effect of the continuous silica-rich phase on the conductive path composed of the CB aggregates.

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