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Phase structure and mechanical and adhesion properties of epoxy/silica hybrids

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Abstract

Organic/inorganic hybrids containing 4– to 19.8 wt% of silica were synthesized from an epoxy resin diglycidyl ether of bisphenol-A (DGEBA) and a γ-glycidoxypropyltrimethoxysilane (GPTMS) or a tetramethylorthosilicate (TMOS) by utilizing a sol/gel process. In the DGEBA/GPTMS hybrids, the storage modulus in the rubbery region increased and the peak area of the tan δ curves in the glass transition region decreased, respectively, with the hybrization of small amounts of silica. This may result from the suppression of the epoxy network moiety with the incorporation of the silica network. Observation using transmission electron microscopy (TEM) revealed that the silica networks are uniformity dispersed in the hybrids. Furthermore, the hybrids with GPTMS showed a very high adhesion strength for the silicone rubber. Results from the X-ray microanalysis show that the silica networks are concentrated in the interfacial area of the adhesive joints with silicone rubber. In the swelling test of silicone rubber with the epoxy resin containing GPTMS, the degree of swelling increased with increasing GPTMS content. The high adhesion strength observed in the DGEBA/GPTMS hybrids was caused by the immersion of the adhesives into the surface layer of the silicone rubber substrate, which was attributed to the good affinity between GPTMS and the silicone rubber. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Epoxy resin; Silica network; Organic/inorganic hybrid

1. Introduction

Organic polymers usually have some superior characteristics with respect to their toughness, flexibility and processability. On the other hand, inorganic polymers have high heat resistance and good mechanical and optical properties. Recently, organic/inorganic hybrid materials have been investigated as promising materials by combination of the superior properties of both the organic and inorganic polymers [1–4]. Sol/gel process [5] is a method for preparing inorganic polymers at a low temperature. By using the sol/gel process, we could combine the organic substances, which would be decomposed at a relatively low temperature, with inorganic substances, which have a high heat resistance.

Many organic/inorganic hybrids are formed by incorporating a functional organic polymer into the matrix of an inorganic network synthesized from the condensation polymerization of some metal alkoxides. Chujyou et al. [6,7]reported that the hybrids of an inorganic silica network with organic polymers, which could form hydrogen bonding between the inorganic and organic components, could produce homogeneous and transparent glassy materials. It has been clarified that the phase structure of hybrids strongly depends on the interaction between the inorganic and organic components. Huang et al. [8,9]studied hybrid materials, which were prepared by the incorporation of a silicone elastomer into a silica network. They reported that the structure and mechanical properties of the hybrids are significantly affected by the process conditions, such as the amount of catalyst, molecular ratio of inorganic/organic compounds and molecular weight of organic compound.

The organic/inorganic hybrids in which an inorganic material is incorporated into an organic polymer matrix have also been studied by many investigators. Yano et al. [10] studied the structure and mechanical properties of the poly(vinylalcohol)/silica hybrid systems. They reported that the micro-Brownian motion of the organic polymer is strongly restricted by the inorganic silica network combined with the matrix on a molecular scale and thus the mechanical strength of the hybrid increases with an increase in the silica content.

In the present study, the epoxy-based organic/inorganic hybrid materials were prepared using the bisphenol-A type epoxy resin and silanealkoxide as the organic and inorganic sources, respectively. The thermal mechanical properties and the phase structure of the epoxy/silica hybrids were

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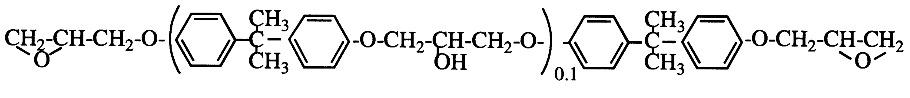
investigated in detail. In addition, these hybrids showed a very high adhesive bonding strength for silicone rubber whose surface is extremely hydrophobic and is not suitable for adhering with an epoxy resin. Thus, their bonding properties and adhesion mechanism for silicone rubber were also investigated.

2. Experimental

2.1. Materials

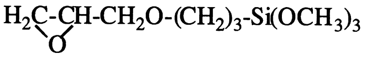
The epoxy resin used in this study was a commercial grade of diglycidyl ether of bisphenol-A (DGEBA:Epikote 828, epoxy equivalent: 190 ± 5Yuka-shell Epoxy Co.).



The curing agent used was tetraethylenepentamine (TEPA, extra-grade, Tokyo Kasei Co., Ltd.).

$H_2N–(CH_2–CH_2–NH)_3–CH_2CH_2–NH_2$

The silane alkoxides used as inorganic sources were 3-glycidoxy-propyltrimethoxysilane (GPTMS, extra-grade, Kanto Chemical Co., Ltd.)



$H_2C\text{-}CH\text{-}CH_2O\text{-}(CH_2)_3\text{-}Si(OCH_3)_3$

and tetramethoxysilane (TMOS, extra-grade, Tokyo Kasei Co., Ltd.). The former $Si(OCH_3)_4$ alkoxide has a functional (epoxy) group, which can react with the organic component. Thus it is natural to consider that the magnitude of the interaction between the organic and inorganic components in the hybrids synthesized from the former silane alkoxide is higher than that of the hybrids prepared from the later alkoxide.

The substrate was a silicone rubber sheet (K-125, Togawa Rubber Co.). All the reagents and silicone rubber sheet were used as received.

2.2. Preparation of DGEBA/GPTMS hybrid materials

Prescribed amounts of GPTMS were added to DGEBA with stirring at 80°C. In addition, a stoichiometric amount of curing agent for the epoxy group and 1 phr of H_2O were added and then the mixtures were vigorously stirred to obtain homogeneous solutions.

The resulting homogeneous compounds were poured into an aluminum container in order to prepare the epoxy/silica hybrid plates. The compounds were first cured at 60, 100 and 150°C, then finally cured at 190°C for 4 h during each curing step. Table 1 shows the starting composition and the percent silica (wt%) of the hybrid materials determined by TGA.

2.3. Adhesion of DGEBA/GPTMS/TMOS hybrid materials to silicone rubber

Several mixtures of DGEBA and silane alkoxides containing 6 wt% of silica were prepared by controlling the fraction of GPTMS and TMOS. In these systems, the molecular weight of silica was estimated to be 52.1 ($SiO_{3/2}$) and 60.1 (SiO_2)g mol^{-1} for GPTMS and TMOS, respectively. The silicone rubber sheets were coated with the mixture of DGEBA and silane alkoxide to prepare the specimens for the lap shear and 90° peel test (Fig. 1A and B). The mixture used as adhesives were cured at 60, 100, 150 and 190°C for 4 h during each curing step. The silicone rubber was not treated with any surface modifier and was backed by a metal plate to prevent any excessive deformation of the substrate itself. As the adherend failure was observed in several specimens and the bonding area could not be measured exactly, the bonding strength of the specimens were expressed by kgf.

2.4. Measurements

The conversions of the epoxy group of DGEBA and

Table 1
Composition before curing and silica content of hybrid materials

Sample code	Composition before curing (mol)			Silica content	
	DGEBA	TEPA	GPTMS	wt% (calc)[a]	w% (expt)[b]
Unmodified	1.00	0.286	–	0.0	0.0
GPTMS-4	1.00	0.342	0.392	4.0	3.8
GPTMS-6	1.00	0.378	0.644	6.0	5.8
GPTMS-10	1.00	0.475	1.33	10.0	9.6
GPTMS-14	1.00	0.634	2.44	14.0	13.6

[a] Calculated from reactant stoichiometry.

[b] Experimentally determined from TGA measurements at 800°C in air.

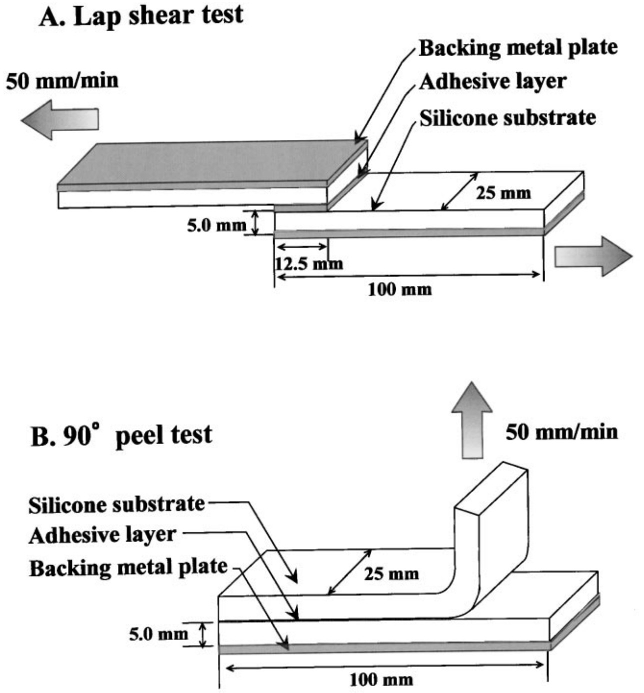


Fig. 1. Shape and dimensions of adhesive joints in lap shear and 90° peel tests.

methoxy group of GPTMS were followed by FT-IR (Spectra 2000, Perkin Elmer Co., Ltd.) measurements. The conversion of the epoxy and alkoxide groups were calculated from the changes in the magnitude of the adsorption peaks at 910 and 2836 cm^{-1} with curing time, respectively.

The weight percent of silica of the hybrid materials was determined by thermo-gravimetric analysis (TGA: THERMOFLEX TAS-200 TG8110D, RIGAKU Co., Ltd.) by heating in air over the temperature range of 20–1000°C, at the rate of 5°C min^{-1}. The residual weight of all specimens was kept a constant after heating over 800°C. Since the organic component seems to have almost completely decomposed in the temperature region over 800°C, the values of the residual weight were used as the silica content in the hybrid materials.

The ultra-thin sections of the DGEBA/GPTMS hybrids were observed using a transmission electron microscope (TEM: JEM-1210, JEOL Co., Ltd.) to study the microphase structure of the hybrids. The specimens for the TEM observations were prepared using an ultramicrotome (REICHERT ULTRACUT E, Leica Co., Ltd.) with a diamond knife. Prior to the TEM observations, the specimens were not treated with any staining techniques.

The dynamic mechanical properties of the cured hybrid materials were determined using a non-resonance forced vibration viscoelastometer (DVE-4, Rheology Co., Ltd.) in air. The frequency and amplitude of the vibration were adjusted to 10 Hz and ±5 μm, respectively. The temperature range was from −150 to 250°C and the heating rate was 2°C min^{-1}, respectively.

The lap shear and 90° peel strength of the joints (Fig. 1A and B) were measured using an Instron-type tensile machine (Shimazu Autograph, AGS-2000E) at a cross-head speed of 50 mm min^{-1}. For the lap shear strength of the joints with the DGEBA/GPTMS hybrid materials, the temperature range was from 25 to 180°C.

The Si distribution in the adhesive layer of the joints was investigated using an X-ray microanalyzer (XMA:JED-2001, JEOL Co., Ltd.). The specimen was coated with a thin layer of carbon to improve the conductivity and prevent charging.

A piece of silicone rubber ($20 \times 10 \times 5\ \mathrm{mm}^3$) was swollen in DGEBA or a mixture of DGEBA and GPTMS, which contained different silica contents from 6 to 19.8 wt% at 60°C for 3 days. In these swelling tests, the curing agent was not added to all the mixtures. The degree of swelling was defined as

$$\text{Degree of swelling (wt\%)} = (W_{\mathrm{wet}} - W_{\mathrm{dry}}) \times 100/W_{\mathrm{dry}}, \quad (1)$$

where W_{wet} and W_{dry} are the weights of the swollen and dried silicone rubbers, respectively.

3. Results and discussion

3.1. Preparation of DGEBA/GPTMS hybrid materials

The changes in the conversion of epoxy and silane alkoxide groups with curing time in the epoxy/silica hybrid is shown in Fig. 2. The conversion of these groups was estimated from the changes in the peak area at 2836 (alkoxide) and 910 cm^{-1} (epoxy), respectively. The conversion of the epoxy and silane alkoxide groups increased in almost the same manner during curing. This means that the epoxy and silica networks were almost simultaneously constructed to form the hybrid system. In addition, the final conversion of both groups is over 90%. Very little unreacted epoxy and

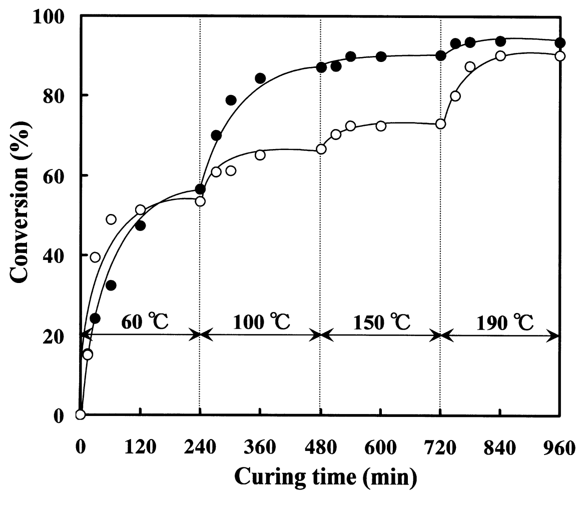


Fig. 2. Chemical conversion of epoxy and methoxy groups (GPTMS-6). (●) epoxy group, (○) methoxy group.

alkoxide groups remained in the hybrid system after the post-curing at 190°C. These results show that both the epoxy resin and the silane alkoxide should form tightly crosslinked networks.

The following reaction mechanisms are proposed for the sol/gel reaction of the silane alkoxide:

$$\equiv\mathrm{Si(OR)} + \mathrm{H_2O} \rightarrow \equiv\mathrm{Si(OH)} + \mathrm{ROH} \qquad \text{(Hydrolysis)}$$

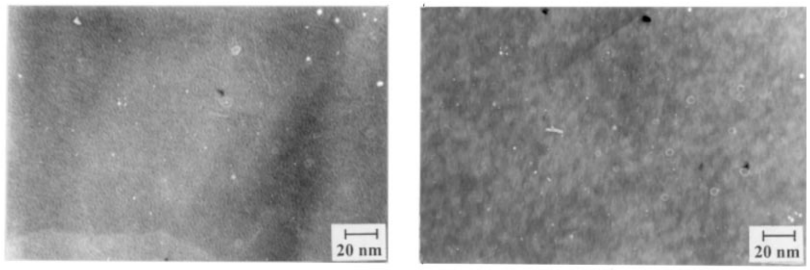
$$\equiv\mathrm{Si(OH)} + \mathrm{(OH)Si}\equiv \rightarrow \equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{H_2O} \qquad \text{(Dehydration condensation)}$$

$$\equiv\mathrm{Si(OH)} + \mathrm{(RO)Si}\equiv \rightarrow \equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{ROH} \qquad \text{(Dealcohol condensation)}$$

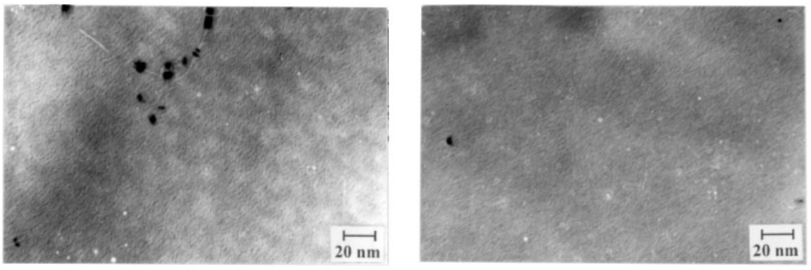
Hydrolysis of the silane alkoxide first occurs by the reaction with water contained in the epoxy resin. The dehydration and dealcohol condensation reactions then occur to form the network structure. Matejka et al. [11] described that the addition of an acid catalyst to the epoxy/silane mixture should mainly accelerate the hydrolysis of the silane alkoxide and the condensation reaction of the alkoxide is significantly promoted by the presence of a basic catalyst. The aliphatic polyamine, which is added as a curing agent in this study, has a relatively high basicity and thus acts as a basic catalyst for the condensation reaction of the silane alkoxide. As shown in Fig. 2, the conversion of the alkoxide group is over 90%. This result means that the silane alkoxide should form a densely crosslinked network through the condensation reaction of the alkoxide group.

3.2. Morphology of DGEBA/GPTMS hybrid materials

Unmodified epoxy resin and several DGEBA/GPTMS hybrid materials with different silica contents from 6 to 14 wt% were used as samples for the TEM observations. Fig. 3 shows the morphology of the hybrid materials identified by TEM. The unmodified system has a uniform structure over the entire area, while in the hybrid with 6 wt% silica, very small dark spots in which the silica network is highly concentrated, are observed over the entire area of the hybrid material. It can be seen that the silica incorporated in the hybrid is about 5–10 nm in size. It is well known that the silica network spreads out like a hyper-branched cluster under basic conditions [12]. In this report, TEPA, which has a relatively high basicity, was used as the curing agent. Therefore, the silica network probably formed a cluster structure rather than a chain network. However, GPTMS used as an inorganic source has an epoxy group and this group reacted with TEPA. These results mean that the fine silica particles observed by TEM (Fig. 3) are not the pure silica network. It is natural to consider that the fine silica particles are composed of silica and a part of epoxy network



(epoxy resin) **(GPTMS-6)**



(GPTMS-10) **(GPTMS-14)**

Fig. 3. Transmission electron micrographs of epoxy/silica hybrid systems.

which should form an interpenetrating network structure between the organic and inorganic components with a covalent bond. Moreover, in the hybrid material containing 10 wt% silica, the area of the dark portions should mean that the silica/epoxy interpenetrating network had increased. However, a uniform microstructure was again observed in the system containing 14 wt% silica. The number of silica clusters containing the epoxy resin (dark spots) with the size of about 10 nm increased with an increase in the amount of GPTMS used as the inorganic source and covered the entire area of the epoxy matrix with increasing silica content. Matejka et al. [13] described that the dispersibility of the silica network progressed with an increase in the interaction as a covalent bond between the organic and inorganic phases. Similarly, in this system, it is considered that the silica network cluster containing some quantities of epoxy resin was finely dispersed in the epoxy matrix along with the formation of covalent bonds between the organic and inorganic phases. The uniform microstructure observed in the system containing 14 wt% silica was caused by the uniform dispersion of the innumerable 10 nm dark spots over the entire area of the matrix.

3.3. Dynamic mechanical properties of DGEBA/GPTMS hybrid materials

The temperature dependence of dynamic mechanical properties of the DGEBA/GPTMS hybrids containing different amounts of silica network is shown in Fig. 4. In the unmodified system, the storage modulus was clearly decreased in the glass transition region (T_g) and had a very low value in the rubbery region. It is well known that the decrease in the modulus in the T_g region is due to the micro-Brownian motion of the network chains. However, in the hybrid systems, the modulus in the rubbery region increased with an increase in the silica contents and thus the glass transition behavior became indistinct. This result shows that the micro-Brownian motion of the epoxy network is strongly restricted by the hybrization with the silica network. The storage modulus of the hybrid systems with over 10 wt% silica showed no decrement in the glass transition region and kept at a high value even in the high temperature region over 200°C. This means that the heat resistance of the cured epoxy resin is significantly improved by the hybrization with a silica network and the DGEBA/GPTMS hybrids (silica content: > 10 wt%) could maintain the glassy state up to their decomposition temperature.

It is well known that a cured epoxy resin clearly shows a large tan δ peak in the glass transition region. Also, in this study, the unmodified epoxy system showed a large tan δ peak in the glass transition region. However, the area of the tan δ peak decreased with the hybrization of the silica network into the epoxy resin. In the hybrids of DGEBA/GPTMS (silica content: >10 wt%), the tan δ peak in the glass transition region completely disappeared and no other tan δ peaks appeared in the measured temperature range. These results show that the silica network is dispersed in the epoxy network in a molecular order and the motion of network chains is strongly restricted in the epoxy/silica hybrids. These phenomena were also observed in other hybrid materials [14,15]. However, the complete disappearance of the tan δ peak was hardly achieved and the hybrid material required the addition of large amounts of inorganic components for the large change in the tan δ peak. However, as shown in Fig. 4, the molecular motion of the network chains in the DGEBA/GPTMS hybrids was effectively restricted by the hybrization with small amounts of silica network. Thus, it is concluded that the epoxy and silica networks in the hybrid system should be combined in molecular order by covalent bonds.

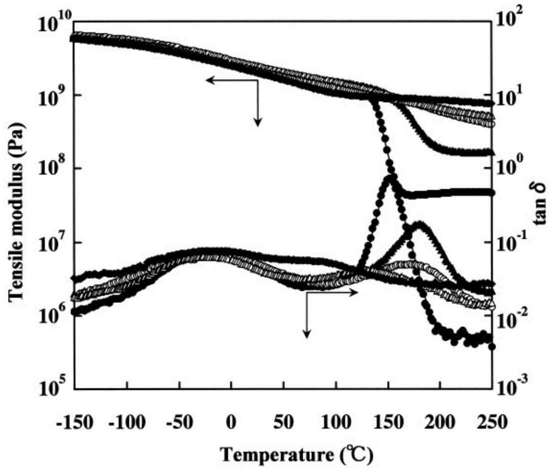


Fig. 4. Dynamic mechanical properties of epoxy/silica hybrid systems. (●) Unmodified; (▲) GPTMS-4; (○) GPTMS-6; (△) GPTMS-10; (◆) GPTMS-14.

3.4. Bonding properties and mechanism of DGEBA/GPTMS hybrid materials

The adhesive bonding properties of the DGEBA/GPTMS hybrids for silicone rubber were investigated. The lap shear and the 90° peel strength were measured using the substrates shown in Fig. 1A and B. Fig. 5 shows the lap shear strength during the curing process of the silicone rubber joints bonded with the DGEBA/GPTMS hybrids containing different amounts of the silica network. The bonding strength of all the cured systems increased with curing. However, the silicone rubber joint bonded with the unmodified epoxy resin showed a contact failure and thus a very low bonding strength even during the final stage of curing. This result means that the silicone rubber is not suitable for adhering to an epoxy resin. However, in the hybrid systems, the joints bonded with the hybrid containing 4 wt% silica showed an adherend failure of the silicone rubber substrate during the final stage of curing. Thus, it is clear that the hybrization of the silica network into epoxy matrix was effective for improving the adhesion between the epoxy resin and the

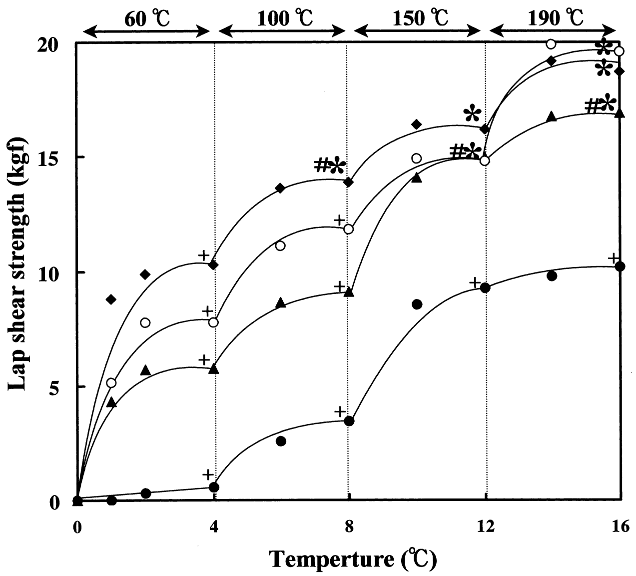


Fig. 5. Lap shear strength of epoxy/silica hybrids with the progress of curing (GPTMS). Symbols as in Fig.4; (+) contact failure; (#) cohesive failure; (*) adherend failure.

silicone rubber substrate. In general, the improvement in the bonding strength of the silicone rubber was achieved by the surface treatment or modification with gas plasma, etc. [16–21]. The addition of GPTMS to the epoxy resin may have made it possible to adhesively bond silicone rubber without any surface treatment.

The effect of the GPTMS contents on the bonding strength of the silicone rubber joints was investigated. The unmodified epoxy resin and DGEBA/GPTMS hybrids with different silica contents from 1 to 19.8 wt% were used for the 90° peel test as adhesives. The results of the peel tests are shown in Fig. 6. In this figure, the dotted line shows the peel strength of the samples bonded with unmodified epoxy resin. The peel strength increased with an increase in the silica contents. The maximum value of the peel strength was observed at 14 wt% of the silica content and then the peel strength suddenly decreased. This may result from the increase in the brittleness with the addition of an excess amount of GPTMS because the cohesive failure was observed in the adhesive joint with the hybrid containing more than 14 wt% silica. This result means that the bonding strength of the epoxy resin for silicone rubber was significantly improved with the hybrization of GPTMS. However, the addition of the excess amount (more than 14 wt%) of the silica networks made the adhesion layer brittle and led to a decrease in the bonding strength.

The temperature dependence of the lap shear strength with unmodified and modified epoxy resins were measured in the 25–180°C region as shown in Fig. 7. In all the specimens, a large decrease in the bonding strength was observed in the 100–120°C region. For the DMA results of the DGEBA/GPTMS hybrids (Fig. 4), the storage modulus of the hybrid systems with over 10 wt% added silica showed no decrease in the high temperature region over 200°C. Therefore, it is considered that the large decrease in the bonding strength observed in the 100–120°C region was not caused by the glass–rubber transition of the DGEBA/GPTMS hybrids used as adhesives. The bonding strength of the specimens with the hybrid containing 14 wt% silica measured at 120°C was lower than that of the specimens with a hybrid containing 4 wt% silica at 25°C, though adherend and cohesive failure were observed in the former and latter specimens, respectively. This result showed that though a good interfacial adhesion was maintained in the specimens with the hybrid containing 14 wt% silica even at 120°C, the mechanical properties of the silicone rubber substrate itself decreased in this temperature region. Thus the large decrease in the bonding strength observed in the

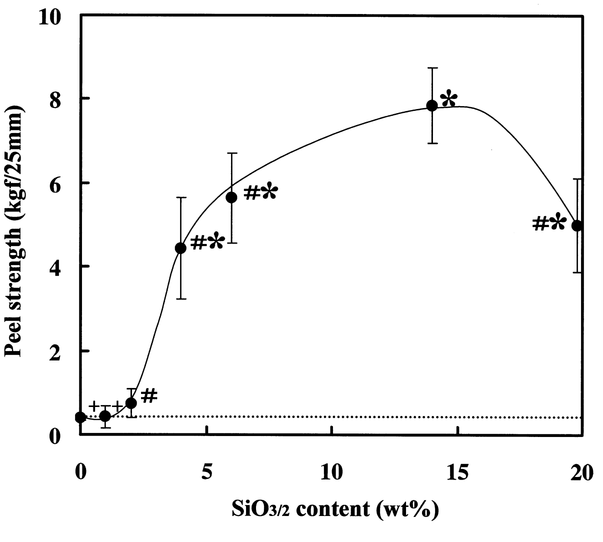


Fig. 6. Peel strength of epoxy/silica hybrids with GPTMS. (···) Unmodified epoxy resin; (+) contact failure; (#) cohesive failure; (*) adherend failure.

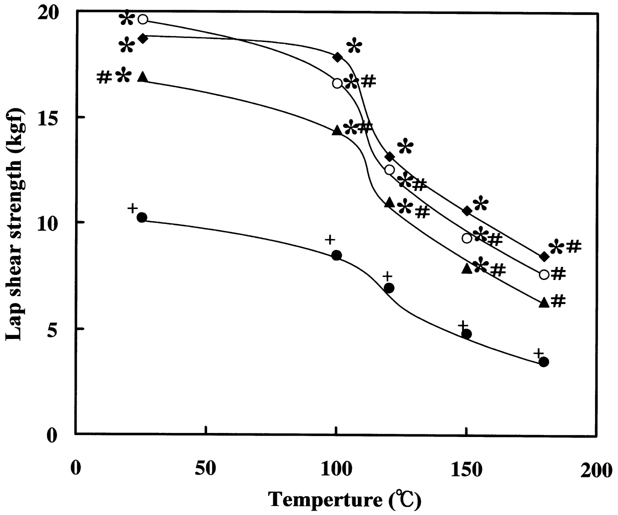


Fig. 7. Temperature dependence of lap shear strength of epoxy/silica hybrids with GPTMS. Symbols as in Fig.4; (+) contact failure; (#) cohesive failure; (*) adherend failure.

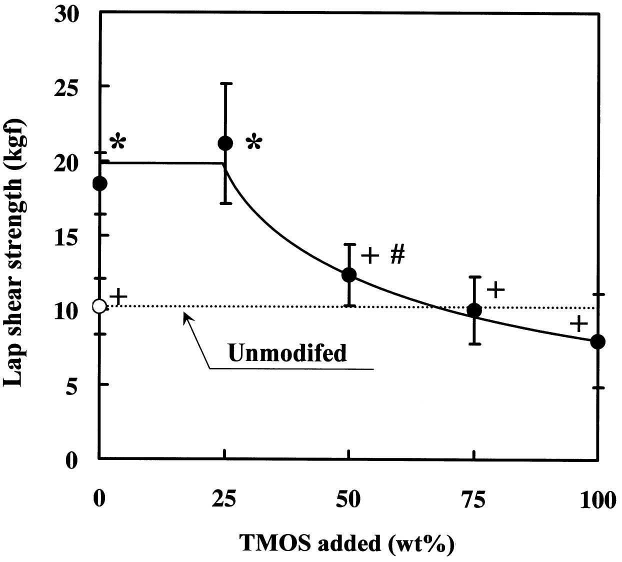


Fig. 8. Lap shear strength of epoxy/silica hybrids prepared from the mixture of TMOS and GPTMS. (○) Unmodified epoxy resin; (+) contact failure; (#) cohesive failure; (*) adherend failure. Total silica content: 6 wt%.

100–120°C region should result from the heat degradation of the silicone rubber substrate. In other words, this result shows that these hybrid materials have a high bonding strength for silicone rubber even in the high temperature region, and the bonding strength of the joints heavily depends on the thermal stability of the silicone substrate in the region over 120°C.

The lap shear strengths of the silicone rubber joints bonded with the hybrids containing 6 wt% silica prepared by changing the fractions of GPTMS and TMOS are shown in Fig. 8. In this figure, the dotted line shows the lap shear strength of the joints bonded with an unmodified epoxy resin. The contact failure was observed in the specimens bonded with an unmodified epoxy resin and some hybrids containing more than 50 mol% TMOS, and the lap shear strength decreased with an increase in the addition of TMOS. In addition, the value of the bonding strength in the specimen bonded with the hybrid prepared from the mixture of GPTMS and TMOS in the ratio of 25:75 was almost the same as that with the unmodified epoxy resin. It is clear that the improvement in bonding strength of the silicone rubber joints was not achieved in the hybrids prepared with TMOS. Thus, it is important for improving the bonding strength between the epoxy resin and silicone rubber that the silane alkoxides containing the functional (epoxy) group that react with the organic component are used as the inorganic component to form the interaction between the organic and inorganic phases.

To reveal the bonding mechanism between the silicone rubber substrate and the hybrids with GPTMS as the inorganic component, the Si concentration of adhesive layer was measured by XMA as shown in Fig. 9. The Si concentration was analyzed along the solid line, and the result is the wavy line. This result shows that in the adhesive joint of the silicone rubber, the silica network was concentrated in the interfacial area. However, a relatively uniform morphology was observed in the hybrid materials as shown in Fig. 3. Thus, in the DGEBA/GPTMS hybrids prepared with an aluminium mold, the heterogeneity of the Si concentration was not observed as shown in the XMA result (Fig. 9). These results show that the silica component migrated from the inside of the adhesive layer to the interfacial area during the formation of the adhesive bonding between the DGEBA/GPTMS hybrids and the silicone rubber substrate. From this result, it is easily expected that the GPTMS and its network have a good affinity to silicone rubber and the migration of GPTMS to the interfacial area may result from their good affinity. Thus the affinity of DGEBA itself, and the mixture of DGEBA and GPTMS to the silicone rubber substrate, was evaluated by measuring the swelling ratio of the silicone rubber. A piece of silicone rubber ($20 \times 10 \times 5\ \mathrm{mm}^3$) was immersed in DGEBA or a mixture of DGEBA and GPTMS which contain a different silica content from 6 to 19.8 wt% at 60°C for 3 days. In these swelling tests, a curing agent was not added to all the mixtures. The degree of silicone rubber swelling is shown

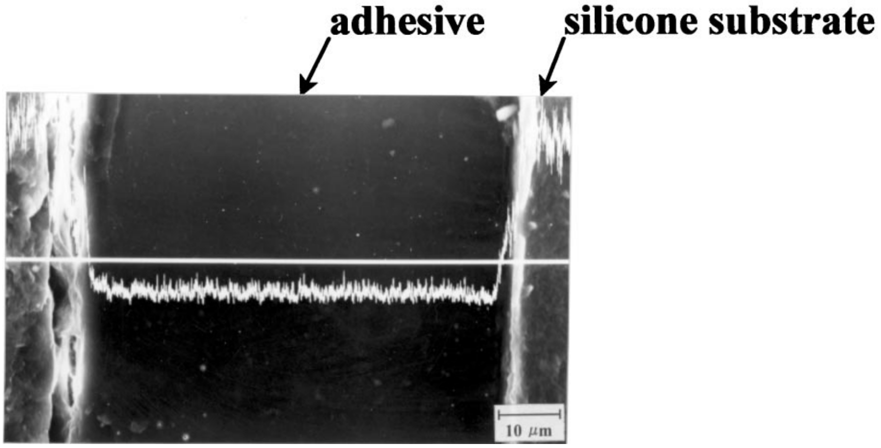


Fig. 9. Distribution of Si-concentration in the epoxy/silica hybrid adhesive layer observed by the XMA line profile. Total silica content: 6 wt%.

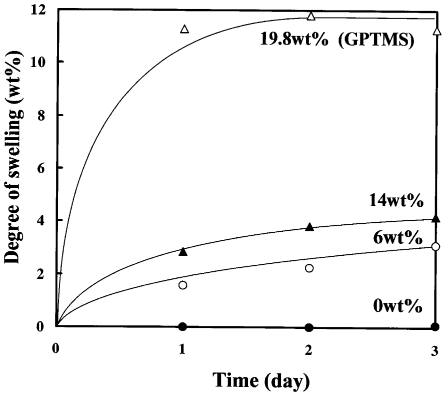


Fig. 10. Swelling ratio of silicone rubber substrate with GPTMS at 60°C/.

in Fig. 10. The silicone rubber was not swollen by the unmodified epoxy resin at all, and the degree of swelling increased with the increasing GPTMS content in the mixture. It is clear that the addition of GPTMS plays a major role in the swelling of the silicone rubber with the mixture of DGEBA and GPTMS. From these results, it is considered that the GPTMS molecules in the hybrid materials should penetrate into the silicone rubber substrate at the interface due to the good affinity between the silicone rubber and GPTMS. The GPTMS molecules should react with each other in the inner surface of the substrate to form the silica networks. As the GPTMS has a functional (epoxy) group, the silica networks formed on the surface of the substrate could be bonded with the epoxy networks at the interface between the adhesives and substrates. This is shown by the dramatic improvement in the bonding strength in the silicone rubber joints with the addition of GPTMS to the epoxy adhesives is due to the formation of interfacial bonding between the silica networks constructed on the surface of the silicone rubber substrate and the epoxy network formed in the adhesive layer.

4. Conclusion

Epoxy/silica hybrids containing from 4 to 19.8 wt% of silica were synthesized from DGEBA and GPTMS or TMOS by utilizing a sol–gel process. In the DGEBA/GPTMS hybrids, the storage modulus in the rubbery region increased and the peak area of the tan δ curves in the glass transition region decreased with the hybridization of small amounts of silica. This may result from the suppression of the epoxy network moiety with the incorporation of a silica network containing a functional (epoxy) group which can react with the organic component. TEM observations revealed that silica networks were uniformly dispersed in the hybrids.

The hybrids containing GPTMS showed a very high bonding strength for the silicone rubber compared with that of the unmodified epoxy resin, but this improvement in the bonding strength was not observed in the hybrids with TMOS. It is concluded from the XMA analysis results of the silicone rubber joints and the swelling test of the silicone rubber with the mixture of DGEBA and GPTMS that the high bonding strength observed in the DGEBA/GPTMS hybrids was due to the formation of the interfacial bonding between the silica networks formed on the surface of the substrate and the epoxy networks in the adhesive layer.

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