The Novel Organic-Inorganic Hybrid Materials Composed of Phenolic Resin and Silica

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Organic-inorganic hybrid materials composed of phenolic resin and silica were prepared by *in-situ* polymerization of silicon alkoxides in phenolic resin matrix. The hybrid materials showed uniform morphology with very fine dispersion of silica. The transparency of the hybrid, the size of incorporated silica particles and its interface with matrix resin could be controlled. The uniform hybrid materials showed excellent improvements in mechanical properties.

Hybrid materials composed of organic and inorganic polymers have recently received considerable attention as a new type of composite. Among the several kinds of inorganic component used for the hybrid such as clay materials,[1] metal oxides[2] and imogorite,[3] metal oxides prepared by sol-gel process were most preferably used as an inorganic component, because the inorganic metal oxide can be readily prepared with its associated mild condition from the corresponding organic metal alkoxide. In seeking for the hybrid materials with outstanding characteristics, various combinations of organic polymers and metal oxides were examined so far.[4-7] However almost all of hybrid materials did not show the useful improvement in mechanical properties. For example, polydimethylsiloxane/silica hybrid materials showed very different mechanical behavior by incorporating silica but the property just varied greatly from elastomeric rubbers to high modulus materials.[8] In the case of polyimide/silica hybrid[9] the change of mechanical property was less attractive. This paper describes the novel organic-inorganic hybrid materials having the excellent improvements in mechanical properties.

Uniform hybrid materials composed of phenolic resin and silica were prepared by *in-situ* polymerization of silicon alkoxides in phenolic resin matrix. Throughout the preparation the gelation and the macrophase separation in a solution state should be avoided by controlling the preparation conditions, otherwise heterogeneous samples having wrinkles, cracks or large domains of silica aggregation were obtained. The basic procedures are as follows; After the silicon alkoxide was partially hydrolysed and polycondensed in the solution containing silicon alkoxide, solvent, water and/or catalyst at 20~70 °C, the solution was mixed with phenolic resin and stirred for some time. Then, the resulting very fine silicon alkoxide oligomers should be frozen in the phenolic resin matrix by removing the solvent. The further polycondensations of both silicon alkoxide and phenolic resin proceeded by heating to 150~200 °C. Here,we used tetramethylorthosilicate(TMOS) as a silicon alkoxide, resol-type phenolic resin (Mw=1700), H_2O/TMOS=0.2~8 (mol ratio), pH=1~ 14 , and methanol as a solvent. The silica content in the hybrid material was varied from 1 to 50 wt%.

The uniform hybrid materials were obtained over the entire range of silica contents and they showed the morphology in which incorporated silica particles were dispersed homogeneously in phenolic resin matrix. Figure 1 shows a typical morphology of fracture surface of the phenolic resin/silica hybrid material (silica content=15wt%) observed by scanning electron microscopy (SEM). Although the transparent hybrid material had the same appearance with phenolic resin itself, it was shown by SEM observation at higher magnification that it had similar fine morphology to silica glass itself prepared by sol-gel process.

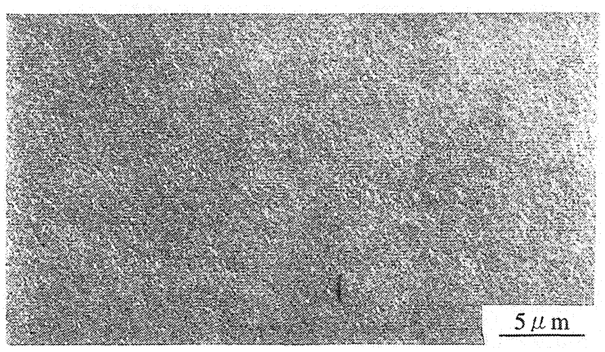

Figure 1. Scanninig electron micrographs of phenolic resin/silica hybrid.

The transparency of phenolic resin/silica hybrid materials can be controlled from transparent to opaque. The transparency is little affected by silica content but mainly changed by the silica partile size. Figure 2 shows the variation in transparency of the hybrid, where the silica partilce size was controlled by mainly pH and H_2O ratio from nearly 10 nanometers to several micrometers, whereas the silica content was fixed at 10 wt% for all samples.

The interface between silica particle and phenolic resin matrix can be also changed by pH and H_2O ratio. The different phenolic resin/silica interfaces prepared by pH=6.5 and 3.5 are shown in Figures 3(a) and (b), respectively. Here, the silica particle size was controlled to be ca.0.5~1 micrometer in order to make the interfacial differences clear. These different interfaces should significantly affect on the mechanical properties of the hybrid.

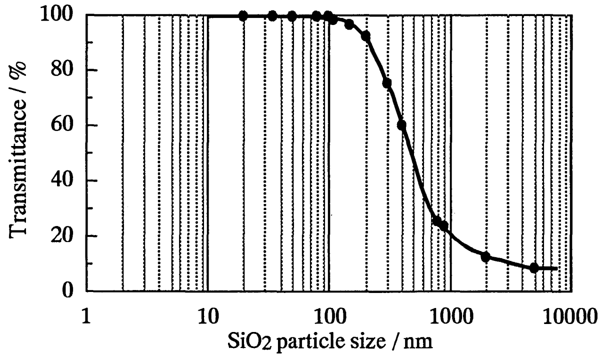

Figure 2. Transparency of phenolic resin/silica hybrid films with various silica particle sizes (SiO_2=10wt%).

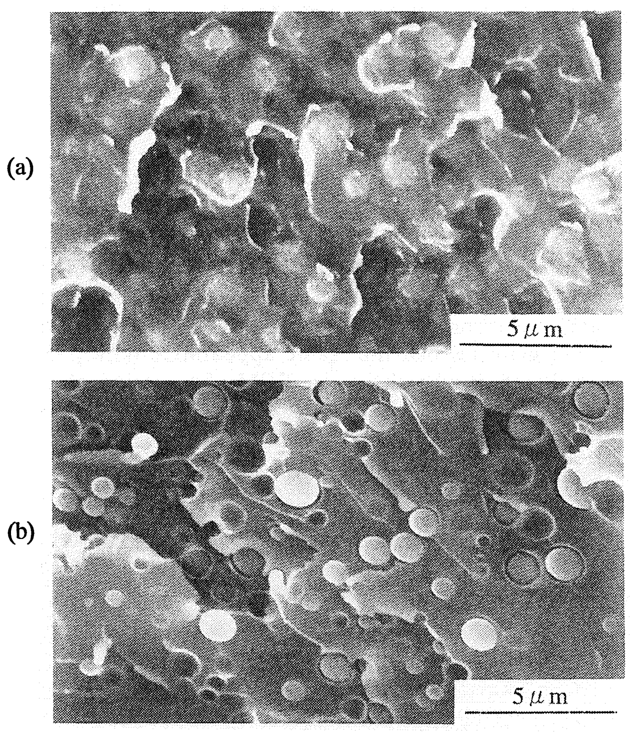

Figure 3. Scanning electron micrographs of phenolic resin/silica hybrids.

In general, the silica glass prepared by the sol-gel process and annealed at quite low temperature had not sufficient quality as a silica glass. The ^{29}Si-NMR spectrum for the present hybrid material is shown in Figure 4. Although the anneal temperature of 150 °C is quite low, the silica incorporated in the hybrid material was composed of only Q4 and Q3 environments, and Q2 or lower ones were not observed at all. Therefore the silica incorporated in the hybrid material was evaluated to be quite good in terms of local bonding structure.

As expected by its compositions higher surface hardness was observed for the hybrid materials. Furthermore, the uniform hybrid materials with good interface showed the excellent improvements in mechanical properties.

In Table 1 it was shown that the flexural modulus, flexual strength and strain at break of the hybrid material (H_2O ratio = 4 , pH=8.3 : transparent and 6 : opaque) were all improved simultaneously in comparison with those of phenolic resin. The results were quite different from those for the conventional blends of phenolic resin and silica glass beads, nor for hybrid materials reported so far.[4,6,9] It was normally observed that the strain at break was decreased with increasing silica content. Further, in the case of polyimide/silica hybrid both strength and strain at break were decreased, unless polyimide is modified to contain some silyl groups.[10,11]

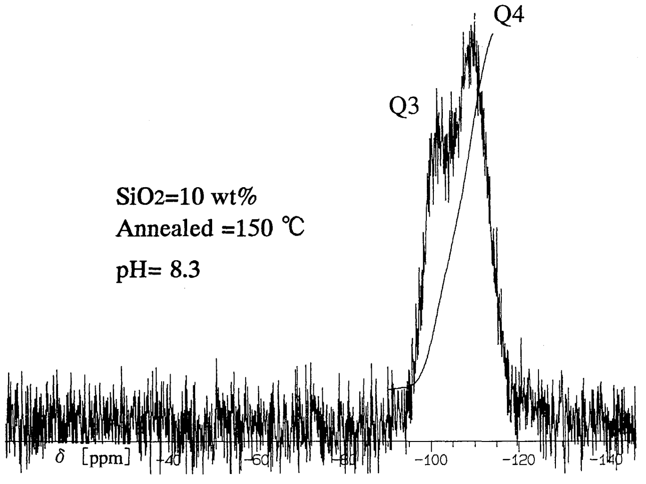

Figure 4. ^{29}Si-NMR spectrum of phenolic resin/silica hybrid.

Table 1. Mechanical properties of phenolic resin/silica hybrids

SiO$_2$ wt%	transparency	Flexural Modulus	Flexural Strength	Strain at break	Izod Impact
		kgf mm^{-2}	kgf mm^{-2}	%	kgf•cm cm^{-2}
0	transparent	595	18.8	2.82	16.34
10.5	transparent	780	38.0	5.61	26.60
10.5	opaque	751	23.3	3.97	-

The degree of mechanical improvements of phenolic resin /silica hybrid materials varied with silica particle size, namely transparency as shown in Table 1, and silica content. Concerning the effect of silica content on the mechanical properties ca. 10 wt% of silica content gave the highest mechanical strength for the present hybrid materials.

As expected by the results of flexural test the impact strength of the hybrid material was also improved compared to that of phenolic resin (Table 1). It is worthwhile to remark that the impact strength of phenolic resin is improved by the inclusion of hard silica component instead of the soft rubbery component. It is also of interest that the phenolic resin/silica hybrid materials seem to be one of the ideal nanocomposites from the mechanical and morphological points of view.

The mechanism of such mechanical improvements should be elucidated from now on but they are definitely not explained by the simple blending mechanism of silica glass beads and phenolic resin. We presume that the effective improvements may be due to the large interfacial area caused by the uniform dispersion of very fine silica particles and also due to the presence of interfacial bonding of silica and phenolic resin.

References and Notes

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