

Morphological investigation of hybrid materials composed of phenolic resin and silica prepared by *in situ* polymerization

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Morphological investigations for hybrid materials composed of phenolic resin and silica, prepared by *in situ* polymerization of silicon alkoxide, were performed using TEM. Irregularly shaped silica particles a few tens of nanometres in size, composed of hyper-fine particles, are homogeneously dispersed in the transparent hybrid materials forming a partial or uniform silica network depending on the silica content. In the translucent hybrid materials, the dispersion of complex silica aggregates (*ca.* 100 nm) were observed uniformly throughout the sample. In the opaque hybrid materials, silica particles of micrometre range were found to be incorporated uniformly, although the interface was uneven. Such large silica particles embedded in the hybrid material contain both silicon oxide and phenolic resin in an interpenetrating network of both components. It was considered that these different morphologies observed in transparent~opaque hybrid materials are caused by freezing-in the silica aggregation at different stages in the course of phase-separation between phenolic resin and silica formed *in situ*. These morphological characteristics were also compared with those of conventional phenolic resin/silica glass composites. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Organic–inorganic hybrid materials prepared via the sol–gel technique have attracted substantial attention as new types of composites^{1–3}. In particular hybrid materials consisting of an organic polymer matrix and a metal oxide dispersion are widely used with a view to obtaining mechanically improved polymer materials^{4–9}. As a metal oxide, silica prepared by *in situ* polymerization of silicon alkoxide is most commonly utilized because of the associated mild conditions for preparation. However, in most hybrid materials composed of polymer matrix and silica dispersion, the resulting mechanical improvement is not sufficient and is particularly poor when the matrix polymer has a high glass transition temperature such as polyimide^{10–12}.

We have recently reported that a hybrid material composed of phenolic resin and silica prepared by *in situ* hydrolysis and polycondensation of silicon alkoxide exhibits excellent improvements in mechanical properties^{13,14}. Mechanical improvements have been achieved in strength, strain at break and impact strength as well as modulus. These results were somewhat astonishing in the following points; firstly, modulus, strength and strain at break are all improved by a hard silica inclusion. Secondly, the impact strength is also improved not by inclusion of soft rubbery materials but by hard silica components. Therefore it would be presumed that the mechanism for the mechanical improvements is quite different from that of conventional simple blending of phenolic resin and pre-formed silica beads or fibres. Such remarkable effects of a silica inclusion should be attributed to the morphological characteristics of silica including its microstructure, level of dispersion and the interface. It is important therefore to examine the

morphology in more detail to shed light on factors from which the improvement may arise.

In the preceding papers^{13,14} it was found that the hybrid materials were uniform and exhibited different features from transparent to opaque depending upon the size of resulting silica inclusion. Furthermore, it has been revealed by scanning electron microscope (SEM) observations that the silica incorporated interacted well with phenolic resin matrix at the interface.

In this report we investigate the fine morphology of the hybrid materials by using a transmission electron microscope including an electron energy loss spectrum measurement. Thus, it is revealed that the hybrid material shows a distinct fine morphology which is very different from that of conventional phenolic resin/silica glass composites.

EXPERIMENT

Materials

The hybrid materials composed of phenolic resin and silica were prepared by *in situ* polymerization of silicon alkoxide in phenolic resin matrix. A scheme for the preparation is shown in *Figure 1*. In this preparation, the TMOS solution, containing TMOS and an almost equivalent amount of methanol, water and/or catalyst, was prepared and rapidly mixed with a phenolic resin/methanol solution at 25°C with agitation. The resin content (= 100 × resin/(resin + methanol)) in the final solution was fixed at 40 wt.%. The resulting homogeneous solution was then coated onto clean glass substrates. After casting the solvent for 72 h at 25°C and drying at 90°C for 2 h, the resulting consolidated hybrid precursor was then heated to 150°C for 1 h. The thickness of the hybrid film was fixed at 0.5 mm^t. The silica content can be varied by changing the weight ratio of silicon alkoxide to phenolic resin. The resulting

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silica particle size in the hybrid material could be varied by controlling the preparation conditions, such as mole ratio of water/silicon alkoxide, the type of raw material of silicon alkoxide, catalyst and temperature. The synthetic method and preparation conditions for the hybrid materials are the same procedures as described in the preceding paper¹⁴.

Resol-type phenolic resin (formaldehyde/phenol ratio, 1.2; catalyst, ammonium salt; $M_w = 1700$) was obtained from Dainippon Ink and Chemicals, Inc. Silicon alkoxide, tetramethylorthosilicate (TMOS), was obtained from Tokyo Kasei Co. Pre-formed silica particles of 25 nm and 1.5 μm (average) were obtained from Nihon Aerogel Inc. (Aerogel[®]70) and Mitsubishi Kagaku Inc. (MKC silica SS15), respectively. The preparation conditions for each hybrid used in the present study are shown in its nomenclature as follows.

J40-M20-4W-C0.2-260-25/150: J (resin content (wt.%)–M (silica content (wt.%)–(H₂O/TMOS mol ratio) W–(kind of catalyst; H = HCl, C = CH₃COOH, A = NH₄OH, N = None) (catalyst/TMOS mole ratio)–(gelation time of solution (min))–(casting temperature(°C))/ (annealing temperature (°C)). Here, the silica content in the nomenclature is the calculated value assuming that the sol–gel

reaction proceeded completely, which is consistent with the observed value. During the solvent-casting process some samples became turbid due to the phase separation of silica. In such cases, it was also observed that this turbidity reaches a saturation point within the solvent casting at 25°C and barely changes during additional heating. This indicates that the phase separation morphology freezes during the first casting process.

Measurements

Morphological observations by transmission electron microscopy (TEM) were performed using a JEM-200CX instrument at 100 kV. The hybrid sample for TEM observation was prepared by cutting the material, embedded in epoxy resin, with an ultra-microtome (Reichert Ultracut S). Thin samples of ca. 30 nm thickness were mounted onto holey microgrids. The fine morphologies of hybrid materials were observed at 10 000–500 000 magnification.

The measurement of electron energy loss spectrum (EELS) was performed using a Gatan Model 666 PEELS and a Hitachi HF-2000 at 200 kV with the same thin samples described above.

The morphology of fracture surfaces of hybrid materials were observed by scanning electron microscopy (SEM)

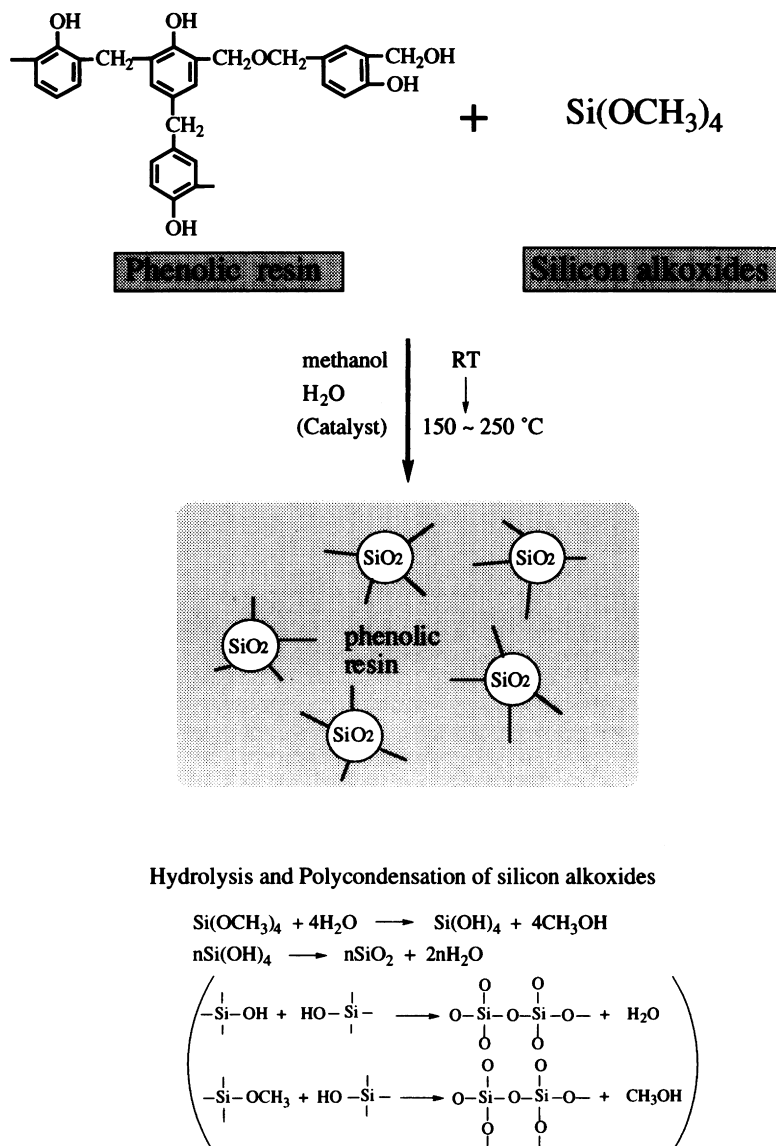


Figure 1 Scheme for the preparation of hybrid material

(Hitachi S-800). Samples were prepared by breaking the hybrid materials in liquid nitrogen and observing the cross-section after coating Pt at 3 nm.

RESULTS

Morphology of transparent hybrid materials

Several transparent hybrid materials with different silica contents from 5 to 30 wt% were used for the TEM observation: all samples were uniform and exhibited high transparency with transmittances of about 95% (wave length = 750 nm).

Figure 2 shows the morphology identified by TEM for a hybrid material containing 12 wt.% of silica (J40-M12-4W-N-22-25/150). It is observed that a partial silica network seems to have formed throughout the hybrid sample. It can be seen in *Figure 2* that the silica incorporated in the hybrid material is about 10–30 nm in size and that it is not in the form of spherical particles, but is very irregular in form. Also, such fine silica is homogeneously dispersed in the resin matrix and no large spherical agglomerations of the silica are observed. *Figure 2* shows that such fine silica inclusions consist of even finer units, hyper-fine particles, having sizes less than 5 nm.

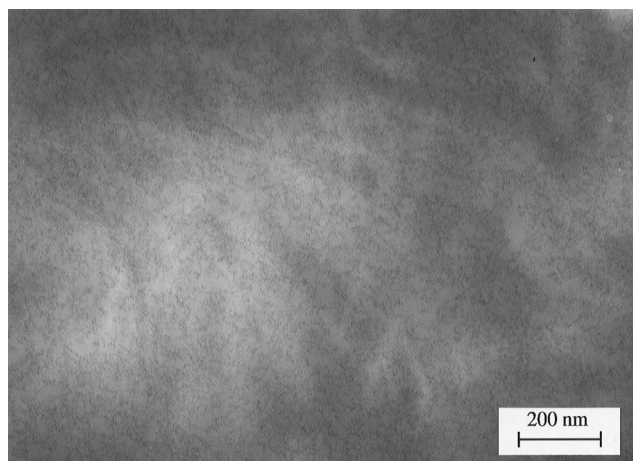


Figure 2 Transmission electron micrograph of a transparent phenolic resin/silica hybrid material with 12 wt.% silica (J40-M12-4W-N-22-25/150), at a magnification of 100 000

Probably these hyper-fine particles correspond to the primary particles of silica gel which form in the very early stages of the sol-gel process.

The fact that defects, such as void or cleavages at the interface between silica and phenolic resin matrix, are not observed throughout the sample (*Figure 2*) indicates that the silica inclusions are well mixed with the phenolic resin with a fairly good interaction.

The aforementioned fine morphology in the hybrid materials is not dependent on the amount of silica present, since many similar morphologies are observed for hybrid materials containing larger quantities of silica (~30 wt.%). The difference between these hybrids lies only in the concentration of the silica network. As expected from the composition, the high content of silica results in a silica network of greater density, which suggests that the uniformly grown silica network interpenetrates with the phenolic resin.

The morphology of the present hybrid materials is apparently different from those of conventional composites with the same silica content, prepared by simple blending of phenolic resin and pre-formed silica glass beads and/or fibres having sizes in the micrometre range (*Figures 6, and 10*). Even in the case of finer pre-formed silica particles of

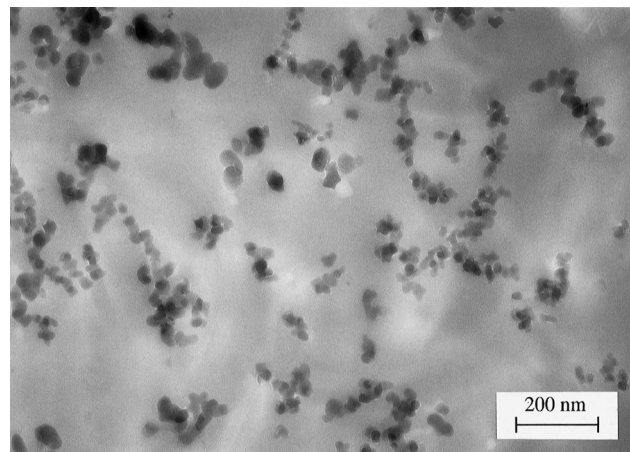


Figure 4 Transmission electron micrograph of a phenolic resin/pre-formed silica composite mixed with 10 wt.% silica, at a magnification of 100 000

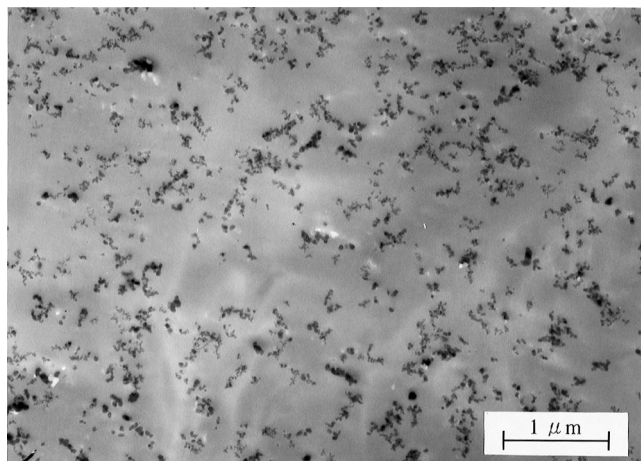


Figure 3 Transmission electron micrograph of a phenolic resin/pre-formed silica composite mixed with 10 wt.% silica, at a magnification of 25 000

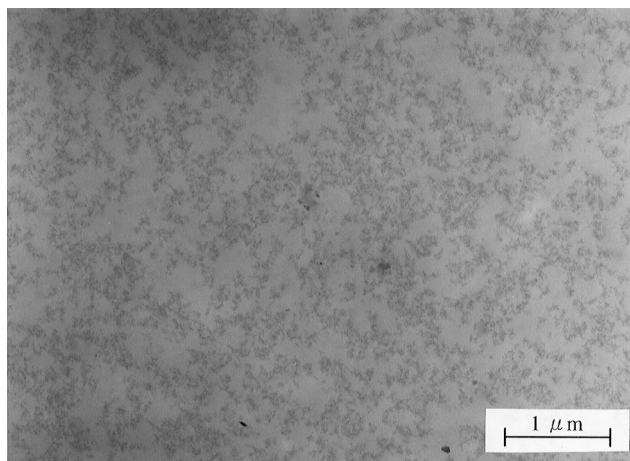


Figure 5 Transmission electron micrograph of a translucent phenolic resin/silica hybrid material with 10 wt.% silica (J40-M10-4W-C0.12-153-25/150), at a magnification of 25 000

nanometre size, the morphology of the composite is also very different from that of the hybrid material. *Figures 3 and 4* show the morphologies observed by TEM for the conventional composite composed of phenolic resin and pre-formed fine silica particles (25 nm size) produced by vapour-phase methods using silicon tetrachloride. The composite was prepared by mixing the fine silica powders with phenolic resin solution at 10/90 weight ratio of silica/phenolic resin, followed by solvent casting and subsequent annealing at 150°C. *Figures 3 and 4* show that fine silica particles of about 25 nm in diameter were not dispersed as monoparticles but formed aggregates with several to tens of silica particles, which is the usual problem in conventional blend composites. It is also shown that the interface between pre-formed silica particles and phenolic resin is clearly distinguished and that separation has occurred at some of the interfaces (*Figures 3 and 4*). Furthermore some of the silica particles are missing, which probably occurs during the process of sample preparation for TEM measurement due to lack of sufficient interfacial strength. The composites shown in *Figures 3 and 4* did not exhibit as good transparency nor such good improvements in mechanical properties as the hybrid material shown in *Figure 2*.

Thus, we conclude that the morphology shown in *Figures 3 and 4* is not responsible for effective mechanical improvement, and that the morphology shown in *Figure 2* is necessary to give rise to good transparency and improvement in mechanical properties.

Morphology of translucent hybrid materials

Figure 5 shows a typical morphology of the optically translucent hybrid material (J40-M10-4W-C0.12-153-25/150; 55% transmittance). In *Figure 5*, the silica is dispersed uniformly throughout the sample and the silica shape is not spherical but very complex, like an arborescent tree-like pattern composed of hyper-fine particles. Thus the fine morphology of silica in the translucent hybrid sample is similar to that of the transparent hybrid sample except for the size of silica aggregates. The silica size is estimated to be about 100 nm, although it is not easy to define the size because of its irregular form. The size is consistent with that predicted from optical transparency, that is, the dispersion of particles of 100 nm size gives rise to translucency.

For comparison the morphology of a conventional composite composed of phenolic resin and pre-formed

silica particles having the same size (100 nm) is shown in *Figure 6*. The weight ratio (10/90 = silica/phenolic resin) is also the same as that in *Figure 5*. However, the morphological differences between *Figures 5 and 6* are obvious. The composite exhibits uneven distributions in both millimetre and micrometre scales. In *Figure 6* it is observed that spherical silica particles aggregate irregularly and some of those detach.

The detailed microstructure of the hybrid shown in *Figure 7* indicates that the silica is composed of aggregated hyper-fine particles. Also, it is worth noting that the microstructure of the arborescent pattern is similar to the fractal pattern¹⁵ made by branching of polyfunctional monomers with functionality greater than 2.

It may be concluded that the morphologies in *Figure 2* reflect the formation of a silica network in the matrix resin without pronounced progressive aggregation of the silica, and those of *Figures 5, and 7* reflect aggregation of an early stage, probably caused by phase separation. Sample transparency decreases gradually as phase separation progresses, consistent with the resulting average size of the silica aggregates. At the end of the aggregation process denser and more spherical large silica particles appear, as shown in the next section.

Morphology of opaque hybrid materials

The morphologies in *Figures 2–7* do evidently show the characteristic differences between hybrid materials and conventional composites, which contain *in situ* polymerized fine silica and the pre-formed particles of 10–100 nm size, respectively. However, there is still a question about the morphology of hybrid materials containing silica particles of greater than 1 µm in size. In mechanical property measurements hybrid materials containing such large silica inclusions still give improved results in comparison with those of conventional composites. Therefore, it is necessary to reveal the differences which exist between *in situ* polymerized silica and pre-formed silica in hybrid and composite materials, although similar sizes and spherical shapes of inclusions were observed by SEM measurements^{13,14}.

Figure 8 shows the morphology of optically opaque hybrid materials (J40-M10-4W-H0.2-408-25/150: 15% transmittance). It is found that spherical silica particles of about 1 µm in diameter are dispersed quite uniformly in the

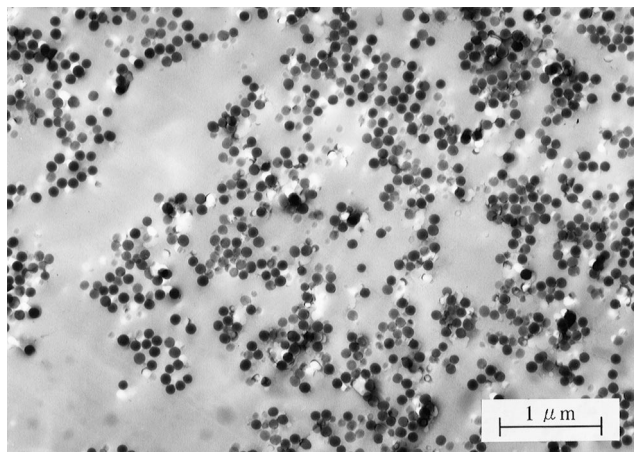


Figure 6 Transmission electron micrograph of a phenolic resin/pre-formed silica composite mixed with 10 wt.% silica, at a magnification of 25 000

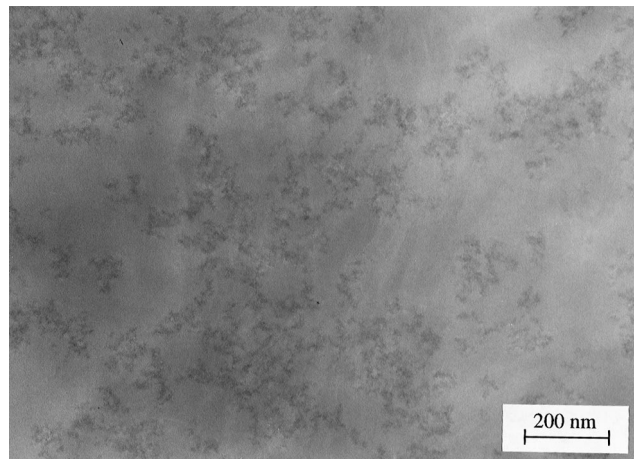


Figure 7 Transmission electron micrograph of a translucent phenolic resin/silica hybrid material with 10 wt.% silica (J40-M10-4W-C0.12-153-25/150), at a magnification of 100 000

phenolic resin matrix for both samples. The size of silica particles observed here is consistent with the result of SEM observation. The overall morphology shown in *Figure 8* seems to be superficially same as that of conventional composites containing silica particles of about $1\ \mu\text{m}$ size (*Figure 10*). However, the detailed microstructure of the silica and its interface in the hybrid material, as clearly shown in *Figure 8*, are distinctly different from those of silica particles in conventional composites. It was found that the exterior of the spherical silica in the hybrid material is not smooth but complex with interpenetration, like an indented coastline. In the interfacial region the silica and phenolic resin matrix appear to strongly interact with each other. Also, it is observed that a few spherical particles are just coalescing to form larger particles, and that surrounding the spherical particles there exist more finer silica aggregates. Such a morphology, including the microstructure of coalescing silica and the fine surrounding silica, may reflect the state of aggregation in the course of the phase separation process.

Figure 9 shows the morphology of a fracture surface observed by SEM for the same sample as in *Figure 8*. It is observed in *Figure 9* that the silica size is about $1\ \mu\text{m}$, which is consistent with the result of TEM observation, and the silica surface is wetted very well with phenolic resin; the surface also looks to be complex and composed of finer

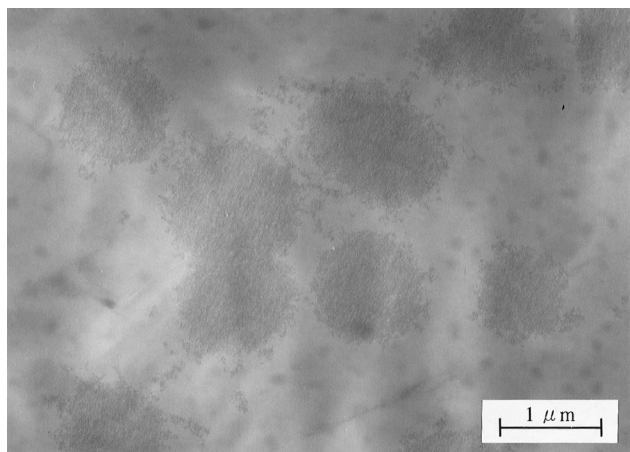


Figure 8 Transmission electron micrograph of an opaque phenolic resin/silica hybrid material with 10 wt.% silica (J40-M10-4W-H0.2-408-25/150), at a magnification of 25 000

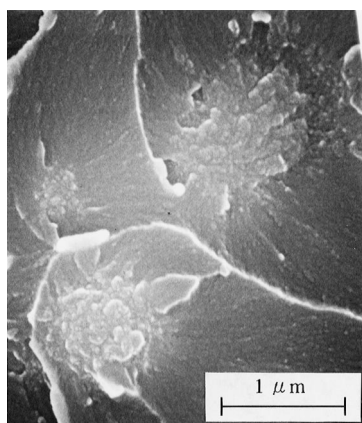


Figure 9 Scanning electron micrograph of a opaque phenolic resin/silica hybrid material with 10 wt.% silica (J40-M10-4W-H0.2-408-25/150), at a magnification of 30 000

particles. These surface features should reflect the microstructure at the interface shown in *Figure 8*.

In contrast to *Figure 8*, very spherical silica particles having a clear exterior surface are observed in *Figure 10*, which was obtained by TEM observation of the conventional composite prepared by simple blending of pre-formed silica particles of $1.5\ \mu\text{m}$ (average) and phenolic resin. In *Figure 10*, the silica is fractured into several parts by the stress applied during sample preparation, which indicates the brittle nature of the silica; some parts of the silica are separated from the matrix resin, probably because of the weak interfacial strength. Thus the morphologies of silica particles in optically opaque hybrid materials (*Figure 8*) and conventional composites (*Figure 10*) are so different from each other that the effects on the mechanical properties should be very different.

Further analysis of silica inclusion

As described above, it has been revealed that silica incorporated in the present hybrid materials exhibits a morphology which is distinct from that of conventional composites over the entire range of silica size.

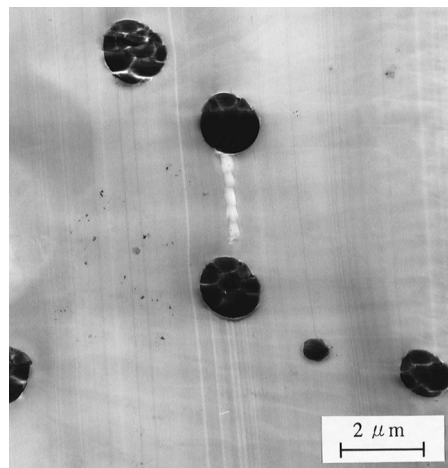


Figure 10 Transmission electron micrograph of a phenolic resin/pre-formed silica composite mixed with 10 wt.% silica, at a magnification of 25 000

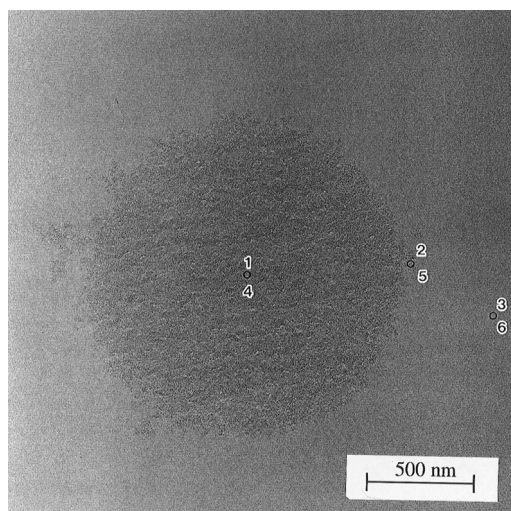


Figure 11 Transmission electron micrograph of an opaque phenolic resin/silica hybrid material with 10 wt.% silica (J40-M10-4W-H0.18-252-25/150), at a magnification of 75 000

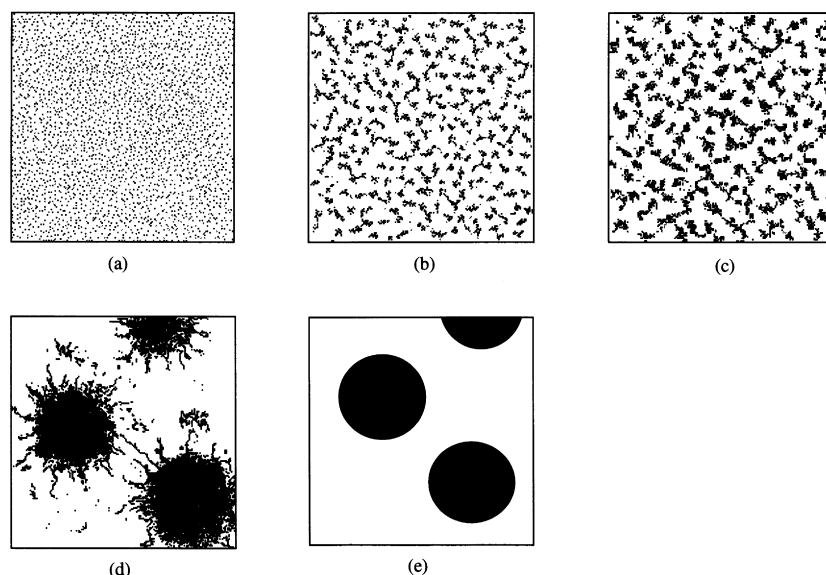


Figure 12 Schematic structures for various silica aggregation stages in phenolic resin/silica hybrid materials

Table 1 Results of EELS measurements of an opaque phenolic resin/silica hybrid material with 10 wt.% silica

EELS analysis point	Atomic species (at.%)		
	C	O	Si
Centre of silica part			
No. 1	56	27	17
No. 4	54	29	17
Edge of silica part			
No. 2	67	24	9.1
No. 5	75	17	8.1
Resin part			
No. 3	95	4.8	0.7
No. 6	96	4.0	0.0

Here we employed a new analytical method, electron energy loss spectroscopy (EELS), for further identification of the silica in the hybrid material. *Figure 11* shows a spherical silica particle of about $1.5 \mu\text{m}$ in diameter observed in an opaque hybrid material (J40-M10-4W-H0.18-252-25/150). Numbers from 1 to 6 in *Figure 11* indicate actual points at which EELS analysis was performed. The analytical results of EELS measurements, which were conducted twice at every point, are summarized in *Table 1* where it is shown that the silica sphere contains quite large quantities of carbon and hydrogen. This indicates that the silica particle in *Figure 11* is composed of not only silicon oxide but also fairly large quantities of phenolic resin, which was not expected from the previous studies. The weight ratio of organic phenolic resin to silica component inside the spherical particle was evaluated as 58/42. It is supposed that appreciably homogeneous interpenetrating networks of both components form in the silica sphere.

On the other hand, since the result of EELS measurements for the outer (resin) part is consistent with the result of conventional elemental analysis of phenolic resin itself, it is concluded that no silicon oxide is included in the phenolic resin matrix. Also, data obtained for the interfacial region show intermediate values. From these analyses it is concluded that the spherical silica particles formed in the present hybrid material have quite different characteristics from the pre-formed

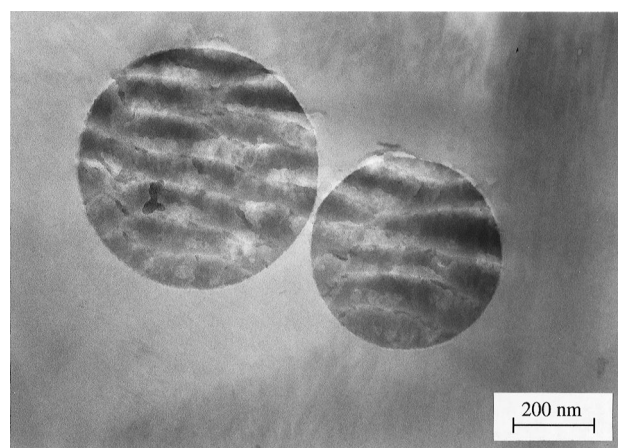


Figure 13 Transmission electron micrograph of a phenolic resin/silica hybrid material with 28 wt.% silica (J40-M28-4W-H0.1-1000-25/150), at a magnification of 100 000

silica particles, not only in morphology but also in composition.

DISCUSSION

It was shown that silica incorporated in the present hybrid materials exhibits very different features in microstructure and size which relate to the transparencies of hybrid materials, as shown in *Figures 2–8*. It would be reasonable to consider that such morphological changes are caused by freezing-in the silica aggregation at different stages in the course of phase separation. Generally speaking, the aggregation of silica in the hybrid system mainly arises from an increase in molecular weight of silica which induces phase separation. If the mobility of the system is lost rapidly by, for example, the formation of a gel network of silica, the morphology is frozen during the course of phase separation. Nakanishi and co-workers reported, for gelling silica-poly(sodium syrenesulfonate) or polyacrylic acid or poly(ethylene oxide) solution systems, that various silica gel morphologies were obtained by freezing at different stages of the phase separation and subsequent

removal of organic polymer^{16–18}. In the present study the preparation conditions are different, in that solvent casting is performed parallel to the *in situ* polymerization of silicon alkoxide and also the organic polymer (phenolic resin) can be thermoset.

Since the transparency of the hybrid material barely alters during the two heating processes (90 and 150°C), the thermosetting of the phenolic resin has negligible effects on the phase separation of silica. Therefore, the sharp decrease in mobility of the system, by which the morphological quenching takes place, results from gel formation of the silica and/or from evaporation of the solvent. Consequently, the resulting morphology is dependent on the relative rates of phase separation and freezing. The times for the onset of phase separation (t_p) and the apparent freezing (t_f) are roughly estimated from the continuous measurement of the turbidity for each casting sample. Consequently, t_p and t_f can be determined from the time when the turbidity starts to increase and saturate, respectively. In the present study, t_p occurred after 20–50 min, while t_f occurred approximately 10 min later. The resulting morphology was determined from the extent of the phase separation during t_f . Further analyses for the phase separation mechanism will be reported in a forthcoming paper.

When the relative rates of both phenomena are changed arithmetically, the resulting morphologies can be predicted easily, as depicted in *Figure 12a–e*. Very early freezing of the system caused by very quick solvent casting in which phase separation does not proceed at all should give rise to homogeneous hyper-fine dispersions of silica, probably less than of 5 nm size (*Figure 12a*), although this was not observed in the present study. In the case that the freezing takes place in the initial stages of phase separation, a fine dispersion of silica a little larger than 5 nm would be obtained while a homogeneous silica dispersion is maintained (*Figure 12b*), which corresponds to *Figure 2*. Here, no large scale agglomeration is detected, but it is observed that fine silica (10–30 nm) is dispersed homogeneously throughout the hybrid sample. Further, the shape of the silica is not spherical but of arborescent form which consists of linked hyper-fine silica units.

The longer we delayed the freezing step the more aggregation of silica occurred in accordance with the micro-phase separation principle. The sizes of the silica particles vary from tens of nanometres to several micrometres, according to the degree of phase separation which occurs before the morphology freezes. *Figure 12c* and *Figure 12d* illustrate such morphologies for different states of aggregation, corresponding to *Figures 5*, and *8*, respectively. Since the silica content is minor in the present hybrid materials, the shape of the silica aggregates should become spherical and, at equilibrium, perfect spherical silica particles would be obtained. *Figure 12e* shows the morphology at near equilibrium of the separated phase and the silica is expected to be perfectly spherical. *Figure 13* shows a TEM micrograph of such spherical silica particles which were prepared by very slow freezing relative to the rate of *in situ* polymerization of silicon alkoxide (J40–M28–4W–H0.1–1000–25/150). In *Figure 13* perfect spheres with smooth outward surfaces are observed. The spheres exhibit a brittle nature and some interfacial separation. Since the hybrid material shown in *Figure 13* did not exhibit improved mechanical properties, such spherical inclusions are not adequate for that purpose.

So far, there have been some reports on fine morphologies of silica domains in hybrid materials. The domain sizes and

morphologies seem to be different in each system and experiment. For example Mark and co-workers^{9,19,20} reported that silica or complex metal oxide particles of 20–30 nm or several tens of nanometres are formed with very little particle aggregation in poly(dimethylsiloxane) hybrid systems. Landry *et al.*²¹ reported that silica clusters of 1–5 μm were formed by agglomeration of spherical silica particles of 0.2–1 μm size in the poly(methyl methacrylate)/silica system. In the case of polyimide/silica hybrid materials, Nandi *et al.*²² reported very fine nanoclusters of 1–1.5 nm or large particles of 1 μm (1000 nm) and Morikawa *et al.*¹¹ reported that silica particles of 0.5–7 μm in diameter were observed for opaque samples but no particles were observed in transparent samples.

In comparison with the results cited above, we have shown that various sizes of silica inclusion, from several nanometres to micrometres, can be realized in the present hybrid system and the present study most clearly shows the detailed fine silica morphology available in organic polymer/silica hybrid systems. It is also shown that the morphology should reflect the freezing-in of different stages of silica aggregation during the course of phase separation.

Concerning the microstructures of the resulting silica inclusions, it was found that they consist of hyper-fine silica particles and exhibit complicated non-spherical shapes like an arborescent pattern. Even in the case of spherical particles, the surfaces exhibit an interpenetration like that of an indented coastline. It was also found that the silica spheres include large quantities of phenolic resin which is probably mixed at a molecular level. According to a morphological model of microstructure proposed by Betrabet and Wilkes *et al.*²³ for a functionalized oligomeric poly(tetramethylene oxide) (PTMO)/silicon oxide system, the silicon oxide species were included in an oligomer-rich matrix phase in addition to the spherical silica phase. In the present system the silicon oxide species was not observed in the phenolic resin matrix, although phenolic resin may have good affinity with silicon alkoxide. Instead, quite large amounts of phenolic resin species are observed in the interior of the spherical silica phase, which suggests the IPN of silicon oxide and phenolic resin.

In addition to characteristic sizes and microstructures of silica, no gap or cleavage between the silica components and the phenolic resin matrix was observed in any sample by either TEM or SEM observations. This indicates that a strong interaction exists between silica and matrix resin. Such fine silica dispersions and morphological characteristics, including interfacial features, could be responsible for the excellent improvements in mechanical properties exhibited by the present hybrid materials.

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