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The preparation and characterization of hybrid materials composed of phenolic resin and silica

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Novel organic–inorganic hybrid materials were prepared by *in situ* polymerization of silicon alkoxide in a phenolic resin matrix. Very uniform hybrid materials composed of a phenolic resin and silica were obtained using varying amounts of silica. The transparency of the hybrid materials could be varied depending on the size of the resulting silica particles. SEM observations revealed that the hybrid materials consist of fine silica particles embedded in a phenolic resin matrix with good interaction at the interface. Density and ^{29}Si-NMR measurements indicate that the silica incorporated in the hybrid material has a high density and mainly Q4 chemical bonding environments. The hybrid material exhibits excellent mechanical improvements in modulus, strength, strain at break and impact strength. © *1998 Kluwer Academic Publishers*

1. Introduction

The preparation of organic–inorganic hybrid materials as new types of composite has attracted much interest in recent years. Of the several kinds of inorganic components, metal oxides such as silica [1, 2], alumina [3, 4] and titania [5–8] are the most prefered in hybrid materials because they are readily prepared *in situ* by the sol–gel process using the corresponding organic metal alkoxide. In particular, silicon alkoxide and silica therefrom are perhaps the most widely used for this purpose because the sol–gel reaction of silicon alkoxides is both mild and easily controlled.

The properties of the hybrids can be tailored by selecting an organic polymer and by varying the content of silica. The hybrid materials obtained can be classified into two types. The first is an organically modified hybrid containing an inorganic silica matrix [9–13] while the second contains an organic polymer matrix and a dispersion of inorganic silica. In the latter hybrid, one expects the mechanical properties of the organic polymer to be improved by the reinforcement resulting from the incorporation of silica. Organic polymers which have been used in this type of hybrid, include poly(dimethylsiloxane) [14,15], poly(methylmethacrylate) (PMMA) [16, 17], poly(hydroxyethylmethacrylate) [18, 19], poly(tetramethylene oxide) [20, 21], epoxy resin [22, 23], acrylic reactive microgel [24], poly(ether ether ketone) (PEEK) [25], polyamide [26] and polyimide [8, 15, 27–29]. However, in almost all of the hybrid materials mentioned, improvements in the mechanical properties have been limited. Strain at break was usually observed to decrease while strength was found to increase only slightly, especially in those organic polymers which possess a high glass transition temperature, such as polyimide, often decreased. In order to improve such mechanical properties, or achieve finer silica dispersions, the organic polymers were modified either by introducing silyl groups or by adding silane coupling agents to act as bonding agents between the inorganic and polymer phases [15, 21, 25, 29]. Although the interaction at the interface appears to increase by these treatments, the resulting improvements in the mechanical properties were found to be insufficient [15, 29].

In a previous letter [30], we briefly reported on novel organic–inorganic hybrid materials composed of phenolic resin and silica. In this paper, we describe the preparation of these hybrid materials, by the *in situ* polymerization of silicon alkoxides in phenolic resin matrix, in more detail. A combination of SEM, ^{29}Si-NMR, density and mechanical property measurements have been used to characterize the hybrid materials. We also report that these hybrid materials exhibit a uniform fine morphology and demonstrate a considerable improvement in their mechanical properties.

2. Experimental procedure

2.1. Materials

A resol-type phenolic resin, obtained from Dainippon Ink and Chemicals, Inc. was prepared from a 1.2 mole ratio of formaldehyde/phenol, ammonium catalyst

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(1 wt % of phenol) and a reaction temperature of 85 °C. The phenolic resin was soluble in solvents such as methanol, tetrahydrofuran (THF) and chloroform. Weight-average molecular weights, (M_w), were determined by gel permeation chromatography using THF as solvent. The molecular weight of the phenolic resin was 1700. Because the phenolic resin is synthesized in the presence of the ammonium catalyst, the pH of the phenolic resin/methanol solution (resin content = 40 wt %) was set at 8.3

Silicon alkoxide and tetramethylorthosilicate (TMOS) were obtained from Tokyo Kasei Co. All other reagents and solvents were reagent grade and used as-received.

2.2. Sample preparation

The basic procedure for the preparation of uniform hybrid materials is as follows. The TMOS solution, containing TMOS, and an almost equivalent amount of methanol, water and/or catalyst, was prepared at 25 °C with agitation. The H_2O to TMOS ratio varied in the range 0.5–8 mole. The acids HCl or CH_3COOH and the base NH_4OH were used as catalysts. The TMOS solution was mixed with the phenolic resin/methanol solution and stirred rapidly at 25 °C. The resin content ($= 100 \times$ resin/(resin + methanol)) in the overall solution was fixed at 40 wt % unless otherwise stated.

The resulting homogeneous solution was then coated on to clean glass substrates. For preparing hybrid samples for mechanical tests, the solution was poured into polystyrene dishes. The thickness of the resulting hybrid film was 0.5 or 0.7 mm. The consolidated hybrid precursor was obtained by removing the solvent (casting) at 25 °C over a period of 72 h and subsequently drying at 90 °C for 2 h. For samples deposited on polystyrene substrates, the hybrid precursor sample was placed on a glass plate after drying at 90 °C. They were finally heated to 150–250 °C for 1 h and the further polycondensations of both silicon alkoxide and phenolic resin proceeded simultaneously. Thus, hybrid materials composed of phenolic resin and silica were prepared by *in situ* polymerization of silicon alkoxides in phenolic resin. Silica content in the hybrid material was varied from 1–35 wt % by changing the amount of TMOS contained in the solution.

The starting composition and gelation time of the solution used to prepare hybrid samples for some morphological and mechanical analyses are listed in Table I. The nomenclature adopted herein specifies each sample as follows: J40-M20-4W-0.2A-25/150: J(resin content/wt %) – M(silica content/wt %) – (H_2O/TMOS mole ratio) W – (catalyst/TMOS mole ratio) (kind of catalyst; H = HCl, C = CH_3COOH, A = NH_4OH, N = none) – (casting temperature/ °C)/ (anneal temperature/°C). Here, the silica content quoted in the nomenclature is the calculated value, based on the assumption that the sol–gel reaction proceeds to completion.

2.3. Characterization

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were performed on a Seiko Instruments, Inc. TG/DTA instrument at a heating rate of 10 °C min^{-1} in air. Solution viscosities were measured using a Shibaura System Digital Vismetron VDA after keeping the solution in a closed vessel at a set temperature over a period of time.

Scanning electron microscopy (SEM) was performed using a Hitachi S-800 scanning electron microscope. The sample was broken at ambient temperature and the cross section observed after coating with platinum (5 nm). The sizes of silica particles incorporated in the hybrids were evaluated by averaging more than 50 measured diameters of silica from scanning electron micrographs.

Solid-state ^{29}Si-NMR spectra were recorded utilizing JEOL JNM-GSX-400 spectrometer, using the cross-polarization magic-angle spinning method, using polydimethylsiloxane (− 34 p.p.m) as the external standard.

The transmittance was obtained by measuring the overall light intensity at 600 nm using a Hitachi

TABLE I Starting composition and gelatin time of the solution

Hybrid samples	TMOS solution (g mol)				Phenolic resin solution (g)	Overall solution	
	THOMS	Methonol	H_2O	Catalyst	Resin methanol	(method + resin)	T_{gel}(25 °C)
J40-M10.5-4W-N	0.9 (0.006)	0.9	0.43 (0.024)	0	3 /3.6	0.4	28
J40-M10.5-4W-0.1C	1.8 (0.012)	1.8	0.86 (0.048)	AcOH: 1.2×10^{-3} mol	6/7.2	0.4	145
J40-M10.5-4W-0.2H	1.8 (0.012)	1.8	0.86 (0.048)	HCl: 2.4×10^{-3} mol	6/7.2	0.4	408
J40-M28-4W-0.05H	3 (0.020)	2.5	1.44 (0.080)	HCl: 1.0×10^{-3} mol	3/4.5	0.4	180

U-3500 spectrophotometer. Densities were measured by flotation at 25 °C using various water–salt solutions. Surface hardness was measured using a Shimadzu Dynamic Ultra Micro Hardness Tester DUH-200.

Flexural stress–strain curves were measured using a Shimadzu Autograph and rectangular samples (6 mm × 50 mm × 0.5 mm). The measurement conditions were 30 mm width between bars and the cross-head speed was 2 mm min^{-1}. Impact strengths were determined using a Custom Scientific Instrument, Inc. Mini Max Tensile Impact Tester, on a sample with dimensions of 10 mm × 50 mm × 0.7 mm (without notch).

3. Results and discussion

3.1. Gelation of the solution

Here, the gelation behaviour of the phenolic resin/silicon alkoxide solution was observed after keeping the solution in a closed vessel at a set temperature over a period of time. Gel formation is easily observed by viscosity measurement. The solution fluidity was rapidly lost and the apparent viscosity of the solution increased abruptly at the gel point, as shown in Fig. 1. After this point, the gel gradually hardens and becomes opaque. Fig. 1 shows the time dependence of viscosity of TMOS (A, B) and TMOS/phenolic resin (C, D) solutions with different compositions when kept at 25 °C. From the comparison of gelation times for solutions A–D, it was revealed that the gelation time decreased due to the coexistence of phenolic resin. This acceleration in gelation occurred by the coexistence of certain polymers was also observed in other systems containing functional groups such as poly(sodium styrenesulphonate)/silica and poly(acrylic acid)/silica systems [12, 31]. The significant enhancement in gel formation in the present system suggests that a considerable interaction exists between silicon alkoxide and the phenolic resin in the solution and the gel. However, it should be noted that, in gel samples prepared at 25 °C, for example, the phenolic resin is not chemically bonded with silicon oxide at the gel point, but weakly bonded. This is probably caused by hydrogen bonding, because the phenolic resin can be removed from the gel by repeated extraction using methanol at room temperature.

The gelation time of the TMOS/phenolic resin solution could be changed by more than three orders of magnitude, from less than 1 min to more than several hundred minutes, by changing the temperature, the pH(catalyst) and the H_2O/TMOS mole ratio, in addition to changing the concentrations of phenolic resin and TMOS in the solution. In general, the gelation time decreased with increases in the temperature, the concentration of phenolic resin and TMOS, the H_2O/TMOS mole ratio and pH, and vice versa. For example, Fig. 2 shows the effect of a catalyst on the gelation time.

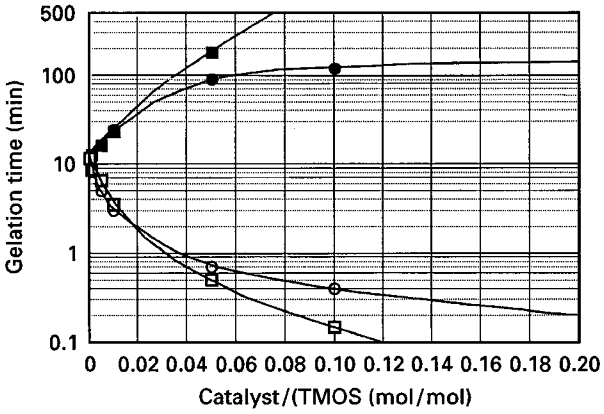

Figure 2 Effect of catalyst on gelation time of phenolic resin/TMOS solution (J40-M28-4W). Catalyst: (■) HCl, (●) CH_3COOH, (○) NH_4OH, (□) $C_2H_4(NH_2)_2$

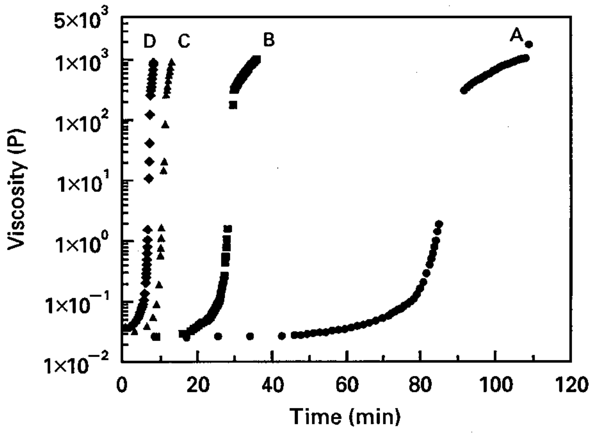

Figure 1 Time dependence of viscosity at 25 °C for solution with different compositions. A, MeOH = 8.55 g, TMOS = 3.42 g, H_2O/TMOS = 4, NH_4OH/TMOS = 0.002. B, MeOH = 5.13 g, TMOS = 3.42 g, H_2O/TMOS = 4, NH_4OH/TMOS = 0.002. C, J40-M28-4W-N (Resin = 3.42 g, MeOH = 5.13 g, TMOS = 3.42 g, H_2O/TMOS = 4. D, J40-M28-4W-0.002A (resin = 3.42 g, MeOH = 5.13 g, TMOS = 3.42 g, H_2O/TMOS = 4, NH_4OH/TMOS = 0.002).

3.2. Characterization of the hybrid materials

Homogeneous hybrid materials were obtained without heterogenities such as macroscopic phase separation or cracks. From TG analyses, it was found that the weight residue observed at 800 °C in air is almost consistent with the silica content calculated from the starting compositions, and from DTA analyses, it was found that silica incorporated in the phenolic resin scarcely affects the heat resistance of the phenolic resin.

3.3. SEM morphology

Uniform hybrid materials composed of phenolic resin and silica could be obtained for a wide range of silica contents. Fig. 3a shows the typical morphology of a fracture surface of the transparent uniform hybrid material (J40-M15-4W-N-25/150) observed by SEM. In Fig. 3a, the dispersion of fine silica particles, of less than 100 nm diameter, are observed while heterogeneous aggregations are not seen at all. The morphology of the conventional glass fibre-reinforced phenolic resin composite (GFRP), which was prepared by mixing with milled glass fibres of 20 μm diameter, is shown for comparison (Fig. 3). It is of interest that the overall images in Figs 3a and 3b are appreciably different from each other, although both composites contain the same quantity of silica (= 15 wt %); GFRP is opaque and non-uniform due to the large density difference of both components and its fracture surface is not as smooth as that of the hybrid material.

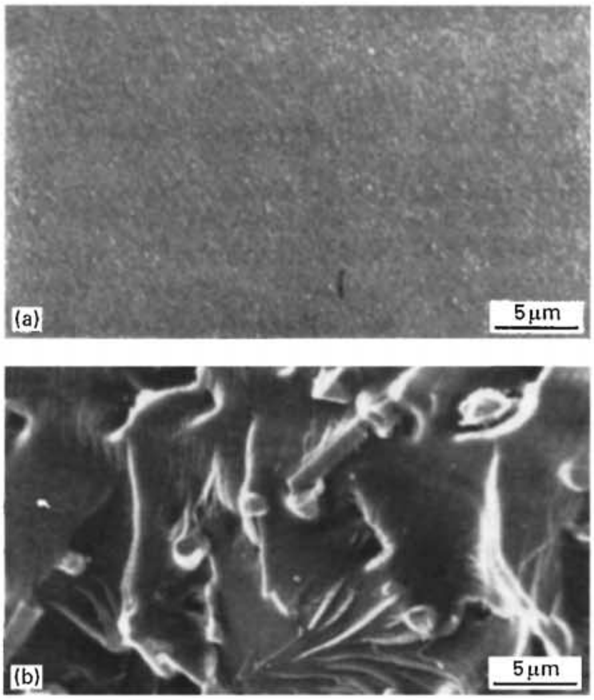

Figure 3 Scanning electron micrographs of phenolic resin/silica: (a) hybrid material (J40-M15-4W-N-25/150 × 2400); (b) phenolic resin/glass fibre (GF = 15 wt % × 240).

SEM observations of phenolic resin (Fig. 4a), silica glass (Fig. 4b) and transparent hybrid material (Fig. 4c and 4d) are shown at different magnifications. The transparent hybrid material has the same appearance as the phenolic resin itself and it is difficult to differentiate between them even by SEM observations at low magnification (× 2400), as shown in Fig. 4a and 4c. On the other hand, at high magnification (× 50 000), it is revealed that the silica glass consists of very fine silica particles of about 20 nm in size (Fig. 4b), and that the hybrid material contains similarly fine silica particles uniformly dispersed in the phenolic resin matrix (Fig. 4d).

The size of silica particle incorporated in the hybrid material can be controlled (Ca. 20 nm to several micrometers) by altering preparation conditions, such as pH, the H_2O/TMOS mole ratio and the casting temperature. In general, the size of silica particle increases by decreasing the pH, increasing the H_2O/TMOS mole ratio and decreasing the casting temperature. For example, transparent hybrid materials can be prepared in basic conditions at lower H_2O/TMOS ratios, typically less than 4.

In this connection it was revealed that the transparency of phenolic resin/silica hybrid materials can be varied depending on the resulting silica particle size. A plot showing how the transparency of the hybrid films (100 μm thick) varies with the size of the silica particles, is shown in Fig. 5. Here, the silica content was fixed at 10 wt % for all samples. Because transparency is little affected by silica content, hybrid materials

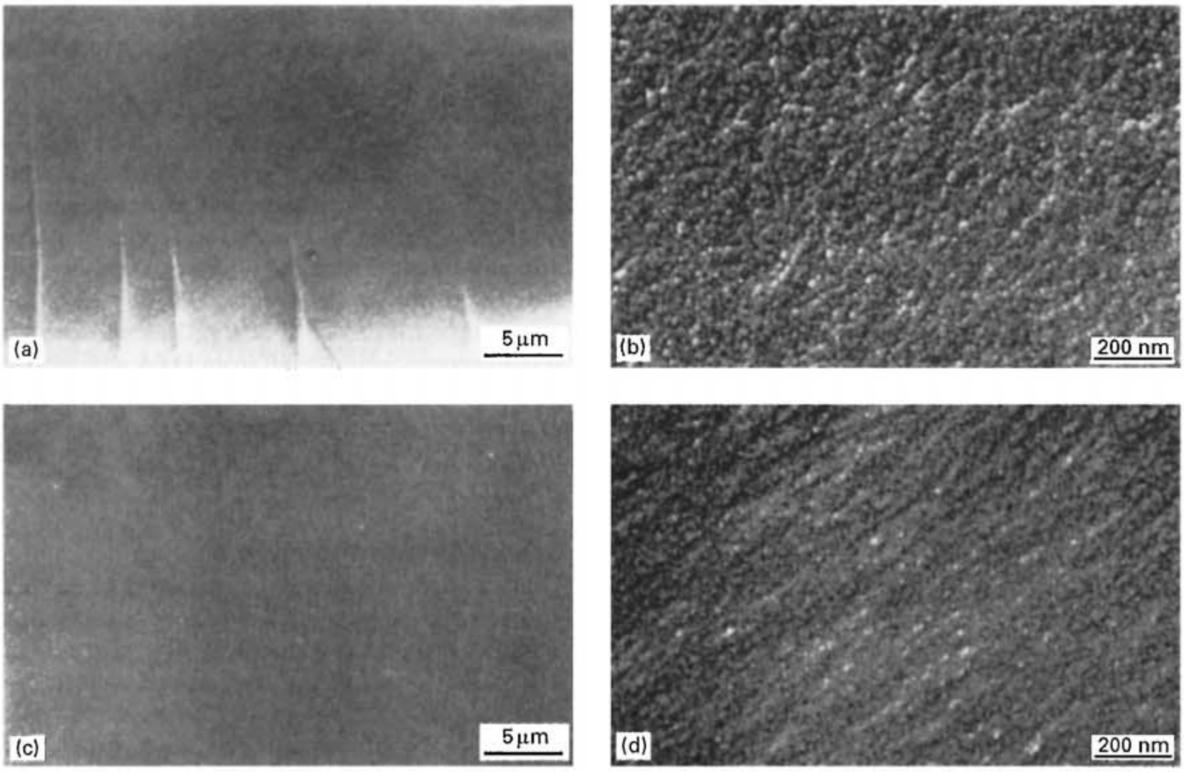

Figure 4 Scanning electron micrographs of phenolic resin, silica and hybrid material (J40-M15-4W-N-25/150) : (a) phenolic resin (× 2400); (b) silica glass (× 50000); (c) hybrid material (× 2400); (d) hybrid material (× 50000).

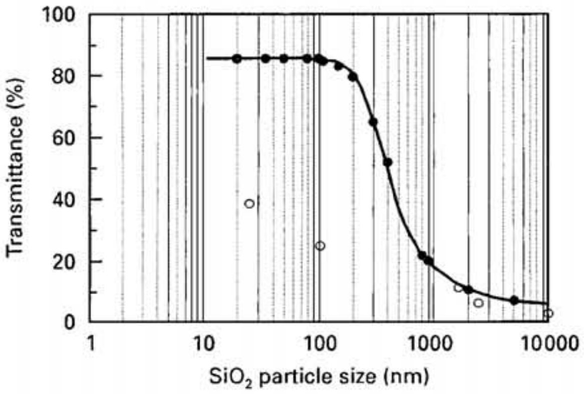

Figure 5 Transparency of hybrid films and conventinal composite films: (●) hybrids, (○) composites. $SiO_2 = 10$ wt%, film thickness = 100 μm, wave length = 600 nm.

with varied transparencies have been similarly prepared even in the case of 35 wt % silica content. On the other hand, conventional composites, prepared from the simple blending of phenolic resin and preformed silica, did not exhibit transparency even in the case of small particles of silica, as shown in Fig. 5, because of difficulties in forming uniform dispersions of silica.

In addition to the aforementioned silica particle size, the interface between silica and the phenolic resin matrix can also be changed by the preparation conditions. The most important factors affecting the interfacial morphology are the catalyst and the H_2O/TMOS mole ratio of the solution. Typical good interfacial morphology is shown in Fig. 6a for a hybrid sample prepared using slightly acidic conditions: J40-M28-4W-0.05H. Because the interfacial morphology is indistinguishable when very fine silica particles (less than 100 nm size) are used, hybrid samples having quite large silica particles (ca. 1 μm size) are adopted for measuring SEM. A poor (separated) interfacial morphology was obtained, for example, using a catalyst content higher than 0.1 H in the same system (Fig. 6b).

The interfacial morphology shown in Fig. 6a is superior to those of other hybrid materials reported previously. For example, a polyimide/silica hybrid material reported by Morikawa *et al.* [28] showed an interface with almost completely separated components. It is noteworthy that the phenolic resin in Fig. 6a looks to be strongly adhered to the silica surface, even though the phenolic resin is not chemically modified, by introducing silyl groups or silane coupling agents to improve the interface and/or the dispersion.

3.4. ^{29}Si-NMR spectrum measurements

When the silica glass was prepared by the sol–gel process at low annealing temperatures such as 150–200 °C, the characteristics of silica, evaluated using solid state ^{29}Si-NMR measurement, are strongly dependent on the preparation conditions such as pH and the H_2O/TMOS mole ratio. ^{29}Si-NMR spectra of the hybrid material and silica glass prepared in basic conditions (pH = 8.3) are shown in Fig. 7a and 7b, respectively. Only two kinds of silicon environments were observed, non-hydroxy (Q4) and mono-hydroxy (Q3) environments. In both the hybrid material and silica glass, the Q4 and Q3 environments are observed as main- and sub-peaks, respectively, where the Q3 intensity in the hybrid material is slightly larger than that observed in silica glass. Taking into account the good interface observed by SEM, it is proposed that some portion of the Q3 peak in the present hybrid material might be attributed to the existence of a Si–O–C species bonded to the phenolic resin.

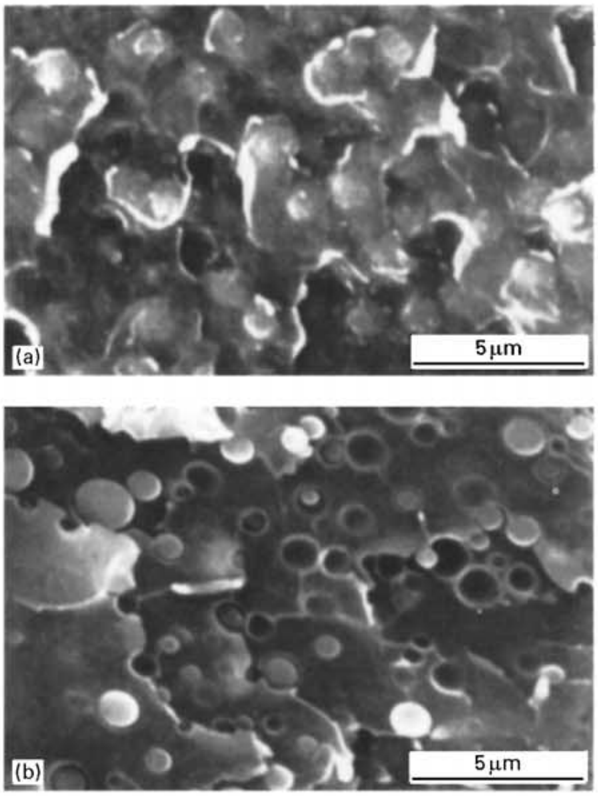

Figure 6 Scanning electron micrographs of phenolic resin/silica hybrid materials: (a) J40-M28-4W-0.05H, (b) J40-M28-4W-0.1H.

On the other hand, under acidic conditions, both silica glass and the hybrid material contain more larger intensities of the Q3 species, due to the characteristic sol–gel reaction process.

3.5. Density measurement

Fig. 8 shows the effect of the silica content on the density of hybrid materials. The silica density in the hybrid materials was evaluated to be 1.85 g cm^{-3} by extrapolation. This value is almost consistent with that of silica glass itself (1.85–1.90 g cm^{-3}), prepared by the sol–gel process under almost identical preparation conditions, pH, H_2O/TMOS mole ratio and annealing temperature. Therefore, it is concluded that the silica incorporated in hybrid materials by *in situ* polymerization has the same density characteristics and silicon chemical bonding environments as silica glass itself, and that the silica was embedded in the phenolic resin without any gaps at the interface. This result indicates a good interface between silica and phenolic resin, and is consistent with the results obtained from

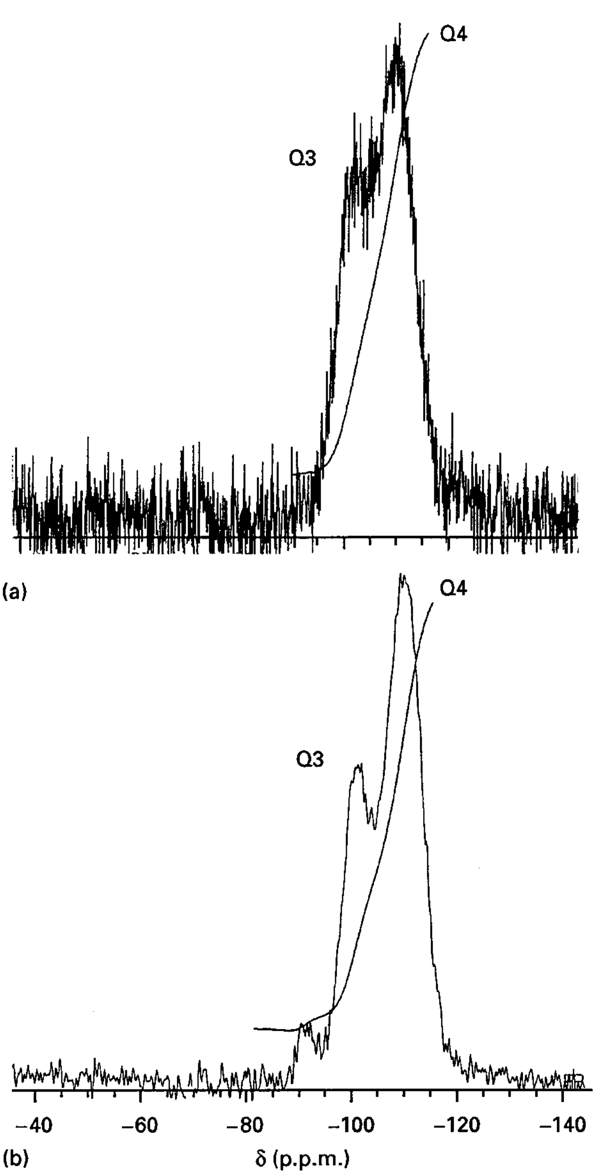

Figure 7 ^{29}Si-NMR spectra for the phenolic resin/silica hybrid materials and silica glass: (a) J40-M10-4W-N-25/150 (pH = 8.3), (b) J0-M100-4W-0.002A-25/150 (pH = 8.3).

SEM observation. For the polyimide/silica hybrid materials, prepared by annealing at 300 °C, it was reported that the density of silica was evaluated to be about 1.65 g cm^{-3} [2,28]. The reason why polyimide/silica hybrid materials give low silica density values, even when the annealing temperature was higher than that for the present hybrid material, may be attributed to the poor interface between silica and polyimide, as shown in the scanning electron micrographs in the literature.

The effect of the annealing temperature on the density of the hybrid material seems to be somewhat unique. Fig. 9 shows the effect of the annealing temperature on the densities of the hybrid material and the phenolic resin. As far as we know there is no report of a precise density change in the phenolic resin following heat treatment. Fig. 9 clearly shows that the density of the phenolic resin increases in the first stage of annealing and takes a maximum value of 1.273 g cm^{-3} at about 100–120 °C, and then decreases slightly with a further increase in the annealing temperature. For the hybrid material, although its absolute density is much higher than that of the phenolic resin, they both undergo very similar behaviour.

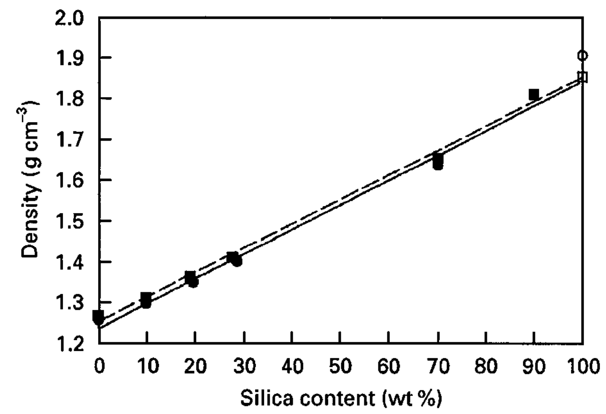

Figure 8 Dependence of hybrid material density on silica content. J40-MX-4W-N-25/*Y*: *X* = silica content, *Y* = annealing temperature. (■) *Y* = 150°C, (●) *Y* = 250 °C.

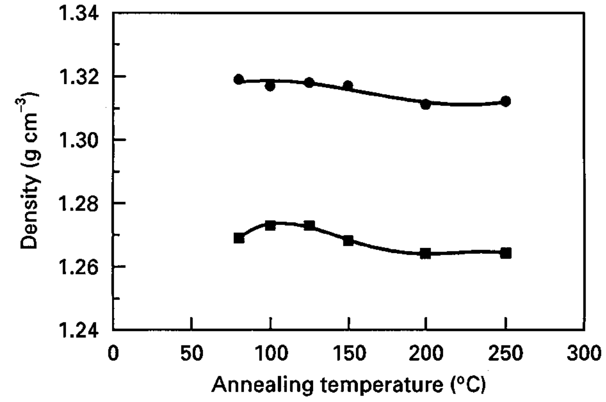

Figure 9 Effect of annealing temperature on densities of phenolic resin and hybrid material. J40-M10-4W-N-25/X : *X* = annealing temperature. (■) phenolic resin, (●) hybrid material (SiO_2 = 10 wt %).

3.6. Mechanical properties

3.6.1. *Surface hardness*

The effect of the silica, incorporated in the hybrid material, on the surface properties was examined by measuring the surface hardness. From the results obtained for various hybrid materials with different compositions it was concluded that the surface hardness increased with an increase in the H_2O/TMOS mole ratio and the annealing temperature, as well as an increase in the silica content. For example, the surface hardness was increased from 34 gf μm^{-2} (phenolic resin) to 51 gf μm^{-2} (hybrid material: SiO_2 = 28 wt%: J40-M28-4W-N-25/150), and from 42 gf μm^{-2} (J40-M28-1WN-25/150) to 54 gf μm^{-2} (J40-M28-8W-N-25/150). Also, it was found that the increase in surface hardness was independent of the indentation depth (0.1–2.1 μm depth).

3.6.2. *Flexural test*

The mechanical properties of the hybrid materials were examined by measuring their flexural mechanical properties. Typical stress–strain curves for the hybrid material and phenolic resin are shown in Fig. 10, where no yielding behaviour was observed and the stress–strain curve was simply extended to higher strain. The hybrid material exhibits a nearly two-fold increase in both flexural strength and strain at break. The mechanical properties for hybrid materials with various transparencies (i.e. different silica sizes) and phenolic resin itself are listed in Table II. It is especially interesting to note that the flexural modulus, flexural strength and strain at break are all improved simultaneously in the current hybrid materials.

The improved strain at break, as well as strength and modulus caused by the inclusion of hard silica is astonishing and of special significance. In conventional GFRP it was normally observed that the modulus and strength were increased by the presence of glass fibre, but that strain at break was decreased without exception. Even in the case of hybrid materials, similar behaviour to GFRP was usually observed. For example, in the case of rubbery polymer matrices such as poly(dimethylsiloxane) [14, 15], brominated butylrubber [31] or poly(vinyl acetate) [32], the mechanical properties of the resulting hybrid material were dramatically changed from elastomeric to high-modulus. That is, modulus and strength were increased but elongation at break was greatly decreased. In the case of non-rubbery polymer matrices, the changes in mechanical properties, resulting from the incorporation of silica, were less attractive, the strain at break was markedly decreased and the strength barely increased with increasing silica content. As a typical example, it was reported for polyimide/silica hybrid, materials [28] that both strength and strain at break decreased with increasing silica content, and that the strength was, to a considerable extent, recovered by modifying the chemical structure of polyimide to one containing silyl groups, but the strain at break still decreased with increasing silica content [29]. Other hybid materials such as PEEK, PMMA exhibited similar behaviour to the polyimide/silica hybrid system. Such remarkable mechanical improvements in the present hybrid material, which do not contain any silyl group, may be attributed to the homogeneous fine dispersion of incorporated silica and the good interaction at the interface between silica and the phenolic resin.

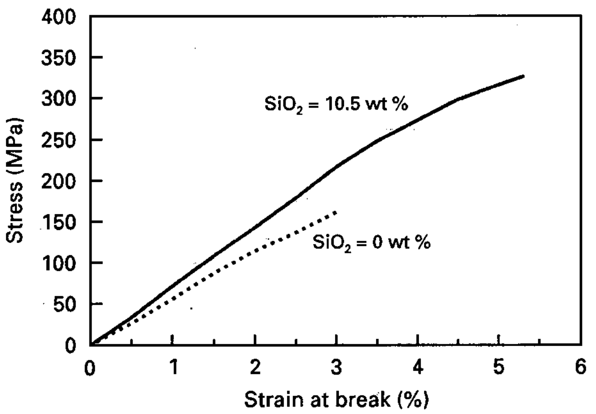

Figure 10 The stress–strain curves of phenolic resin/silica hybrid material (J40-M10.5-4W-N-25/150) and phenolic resin.

The improvements in mechanical properties of phenolic resin/silica hybrid materials were affected by silica particle size, silica content and other preparation conditions which affect the interfacial morphology. Concerning the effect of silica particle size on the mechanical properties, in general, the improvements are greater for transparent hybrid materials containing fine silica particles than for opaque ones. Examples of mechanical improvements for hybrid materials with various transparencies (different silica particle sizes) are shown in Table II.

Fig. 11 shows the effects of silica content on the flexural strength and strain at break of hybrid materials. It is evident that a silica content of between 8 and 12 wt % gives the greatest improvement in mechanical properties. This relatively low value suggests that the silica incorporated in the hybrid material acts as a very effective reinforcing material. In contrast to this, conventional GFRP usually contains about 30–40 wt % glass fibre in order to achieve the mechanical improvements for actual use. Because an ideal molecular composite, consisting of a molecularly-dispersed reinforcing material, would be expected to need a quite low content of reinforcing material [33], the present hybrid material is evaluated to be fairly close to the ideal molecular composite from the mechanical and morphological points of view.

Needless to say the mechanical properties are less improved or become worse for hybrid materials with poor interface and/or heterogeneities such as cracks or macroscopic phase separation.

3.6.3. *Impact strength*

When materials exhibit simultaneous mechanical property improvements in strength, modulus and strain,

TABLE II Mechanical properties of phenolic resin/silica hybrid materials

Sample[a]	SiO_2 (wt %)	Transparency	Flexural modulus (MPa)	Flexural strength (MPa)	Strain at break (%)	Izod impact (kJ m^2)
1	0	Transparent	5800	180	2.82	16.0
2	10.5	Transparent	7400	300	5.40	26.0
3	10.5	Translucent	7800	250	4.55	–
4	10.5	Opaque	7400	230	3.97	23.4

[a] 1. J40-M0-0W-N-25/150; 2. J40-M10.5-4W-N-25/150; 3. J40-M10.5-4W-0.1C-25/150; 4. J40-M10.5-4W-0.2H-25/150.

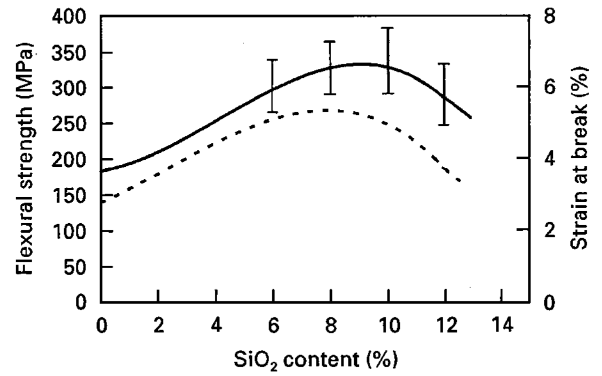

Figure 11 Effect of silica on flexural strength and strain at break for phenolic resin/silica hybrid materials. J40-MX-4W-N-25/150: X = silica content; (—) flexural strength, (- - -) strain at break.

it would be expected that the impact strength might also be improved. In Table II, it is shown that the impact strength of the hybrid material is considerably improved compared to that of phenolic resin. This result suggests two interesting features that should be noted. First, in the case of GFRP, it is generally observed that long glass fibres with high aspect ratio can increase the impact strength of the composite, but inclusions with low aspect ratio, such as glass beads and milled glass fibre, are inadequate as impact strength modifiers. However, in the present hybrid system, the impact strength was improved by incorporated fine silica particles. Second, tough composites with high impact strength were often obtained by inclusion of soft segments such as poly(dimethylsiloxane) and rubbers such as NBR and SBR. However, in the present hybrid material, the impact strength was improved by incorporation of hard silica components.

The mechanism of such improvements is definitely not explained by the simple blending of silica glass beads and phenolic resin. The most fundamental explanation should rest on the large interfacial area caused by the uniform dispersion of very fine silica particles, and also the presence of a remarkable interaction between silica and phenolic resin at the interface. This mechanism should be clarified from the physical and detailed morphological points of view in subsequent studies [35].

4. Conclusion

Novel organic–inorganic hybrid materials, composed of phenolic resin and silica, have been prepared by *in situ* polymerization of silicon alkoxide in a phenolic resin matrix. Uniform hybrid materials containing a wide range of silica contents were obtained. The transparency of these hybrid materials varied from transparent to opaque, corresponding to the size of the final silica particle resulted. SEM observations revealed that the hybrid materials consisted of silica particles embedded in a phenolic resin matrix with excellent interaction at the interface. It was observed by density and ^{29}Si-NMR measurements that the incorporated silica had a high density and Q_4 chemical bonding environments. The hybrid materials exhibited excellent improved mechanical properties, in which modulus, strength, strain at break and impact strength were improved simultaneously.

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