

Cite this: *J. Mater. Chem.*, 2011, **21**, 14941

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PAPER

Bimodal filler system consisting of mesoporous silica particles and silica nanoparticles toward efficient suppression of thermal expansion in silica/epoxy composites

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Received 29th May 2011, Accepted 21st July 2011

DOI: 10.1039/c1jm12405f

Here we propose a bimodal inorganic filler system consisting of mesoporous silica particles and fine silica nanoparticles to fabricate silica/epoxy composites with low thermal expansion property. Two types of inorganic fillers are mechanically mixed with epoxy resin firstly. Then, by adding a curing agent, silica/epoxy composites are prepared. From TEM observation, it is proved that both mesoporous silica particles and silica nanoparticles are well dispersed in the composites. Through the theoretical calculation, more than 90 vol% of the mesopores is estimated to be filled with the epoxy polymers. Various types of the composites are prepared by changing the amounts of doped silica nanoparticles. (The amounts of doped mesoporous silica particles are constant.) Their thermal expansion behaviours are systematically investigated by using thermal mechanical analysis (TMA). With the increase of the amounts of silica nanoparticles, the glass transition temperatures (T_g) are gradually shifted to the higher temperature range and the coefficient of linear thermal expansion (CTE) values are decreased. Thus, by utilizing the bimodal inorganic filler system, we can efficiently reduce thermal expansion in the silica/epoxy composites.

1. Introduction

Nowadays, epoxy resins have been widely mounted as circuit boards in various electronic devices, due to their superior electric isolation, good mechanical stability, easy handling, and low cost. For current miniaturization and multi-functionalization of the electronic devices, electronic circuits on the circuit boards are being highly complicated by connection with solder junctions. Thermal expansion of the electronic circuits mainly made of metals is generally much smaller than that of the circuit boards made of epoxy resins. Therefore, thermal stress at the solder junctions on the circuit boards often increases, causing the disconnection of the electronic circuits. To prevent such breakage and secure electrical bonding reliability, decreasing the coefficient of linear thermal expansion (CTE) of epoxy resins is indispensable.

It is well known that inorganic fillers such as particles,^{1–13} fibers,¹⁴ nanorods,¹⁵ nanotubes,^{16–18} graphite¹⁹ and clays^{20,21} show a beneficial effect on reduction in CTE of epoxy resin. Needless to say, as the amounts of the added fillers increased, the CTE values decreased due to enhanced restriction of the epoxy polymers. Very recently, we have focused on mesoporous silica particles as the next generation of inorganic fillers.^{22–24} The mesoporous silica can be spontaneously formed by utilizing the self-assembly of surfactants.^{25–34} Compared to other inorganic fillers reported previously,^{1–21} the mesoporous silicas have several more advantageous points. Firstly, the mesopore sizes are much larger than the width of the epoxy polymer (around 0.5 nm). A large amount of polymers can be easily penetrated into the mesopores due to capillary force. The polymers encapsulated by the silica walls show very high thermal stability. Secondly, unlike the other nanomaterials including nanotubes, mesoporous materials can be easily produced in large scale through several simple processes such as mixing, heating, filtration, and washing. Ton-scale plant for mesoporous silica production was already built at Mie prefecture in Japan. Currently, mesoporous silica becomes one of the commercially available materials. Thirdly, unlike nanosheets and nanotubes, the one-dimensional mesopore space is randomly oriented inside the composites (Fig. 1). Therefore, the anisotropy of CTE does not appear.

It has been generally known that the CTE values tend to decrease, as the amounts of added fillers increased. However, the viscosity of epoxy resins drastically increases and it becomes hard

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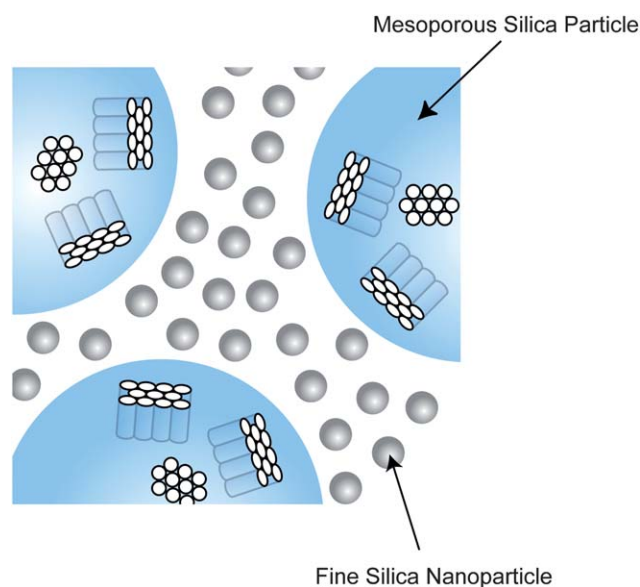


Fig. 1 Systematic illustration of the bimodal filler system. The silica nanoparticles are embedded at the gap among the mesoporous silica particles.

to uniformly mix epoxy resins with the fillers. This fact is a serious issue for industrial fabrication processing. Actually, in our previous work on mesoporous silica/epoxy composite, the maximum possible weight ratios of the added mesoporous silica (with a few hundred nanometres in diameter) are in the range from 25 wt% to 30 wt%.^{22–24} In order to achieve both an increase in filler amounts and a suppression of enhancement of epoxy resin viscosity, in this study we propose a bimodal filler system consisting of two types of fillers with different particle sizes. One is mesoporous silica particles with several hundred nm diameters, while the other is fine silica nanoparticles with around 20 nm in diameter. The systematic illustration of our idea is shown in Fig. 1. The fine silica nanoparticles can be effectively embedded in the gaps between large mesoporous silica particles. Here we successfully doped 40 wt% silica fillers in total in the composites without large enhancement of the viscosity of the epoxy resin. The polymers physically confined inside the mesopores are expected to show high thermal stability. Moreover, with the assistance of fine silica nanoparticles in the gaps, we can anticipate a superior interface effect between the silica nanoparticles and the epoxy resin, which will bring further improvement of thermal stability of the composites.

2. Experimental

2.1. Materials

Commercially available mesoporous silica particles with 2D-hexagonally ordered mesostructure (Taiyo-Kagaku mesoporous silicas, TMPS) were given from Taiyo Kagaku Co., Ltd. The particle size was distributed in a wide range from 100 nm to 3 μm and the average size was around 350 nm. 1,1,1,3,3,3-Hexamethyldisilazane (Sigma-Aldrich Inc.) was used for the surface modification of the mesoporous silica particles. Silica nanoparticles (YA010C-SP3) were obtained from Admatech Co. Ltd.

The average diameter of the fine silica nanoparticles was around 20 nm. The silica nanoparticles were modified by phenylsilane. Bisphenol A type epoxy resin and its curing agent (Ethacure 100) were obtained from Japan Epoxy Resins Co., Ltd and Albemarle Co., respectively. All chemicals were used without further purification in this study.

2.2. Preparation of silica/epoxy composites

Firstly, the mesoporous silica particles were organically modified to increase the affinity between the mesopore surface and the epoxy polymer. According to our previous paper,²² TMPS (10.0 g) and 1,1,1,3,3,3-hexamethyldisilazane (1.00 g) were mixed in a polypropylene bag. TMPS powders were subsequently treated at 120 $^{\circ}\text{C}$ for 24 h, and then organically modified TMPS powders (hereafter abbreviated as “TMS_TMPS”) were obtained.

TMS_TMPS (1.75 g), silica nanoparticles, and epoxy resin (4.38 g) were mechanically mixed under a reduced pressure condition by a THINKY vacuum mixer ARV-310 until bubble-free mixtures were prepared. Subsequently, the mixture was further mixed after the addition of the curing agent (0.870 g). All the mixing processes were conducted at room temperature. Finally, the mixture was heated at 120 $^{\circ}\text{C}$ for 2 h to obtain bubble-free silica/epoxy composites.

Several types of composites were prepared by varying the amounts of the fine silica nanoparticles, while the amounts of TMS_TMPS, epoxy resin, and curing agents were fixed. The detailed compositions were given in Table 1. Hereafter, each silica/epoxy composites was described as NS_ x ($x = 0\text{--}100$), where “ x ” indicates the weight ratios of silica nanoparticles to TMS_TMPS.

2.3. Characterization

The mesoporous structure of original TMS_TMPS was examined by low-angle XRD measurement and N_2 adsorption–desorption isotherm. The low-angle XRD was measured on a Rigaku RINT 2000/PC (Cu K α). The total pore volume of TMS_TMPS was estimated from the N_2 adsorption–desorption isotherm measured with BELSORP-mini II (BEL JAPAN) at 77 K. Prior to the measurement, a pre-treatment of the sample was conducted under vacuum at 100 $^{\circ}\text{C}$ for 24 h with BELPREP-vac II (BEL JAPAN). The density of synthesized silica/epoxy composites was determined by the Archimedeian method. The cross-sectional images of the composites were observed in an ultra-high resolution TEM (H-9000UHR, Hitachi). The FIB method was used for the TEM sample preparation. Thermal mechanical analysis (TMA) data of the composites were taken by a TMA-60 analyzer (Shimadzu). Prior to the measurement, rectangular specimens (10 mm \times 4.5 mm \times 4.5 mm) were prepared from the fabricated composites. The applied temperature was increased at a rate of 5 $^{\circ}\text{C min}^{-1}$ during the measurement. The obtained TMA charts were normalized by the original specimen length (10 mm). Linear regressions were conducted to estimate CTE values in different temperature regions. The temperature at which two regression lines crossed was considered as the glass transition temperature (T_g). The viscosity of the silica/epoxy composites before the addition of curing agents was

Table 1 Physical property of the synthesized silica/epoxy composites. Note that the amounts of TMS_TMPS and epoxy polymer are fixed to be 1.75 g and 5.25 g, respectively. The density of each composite is measured by the Archimedeian method. The dead pore ratios (vol %) are calculated by eqn (1) and (2). The inside polymer ratio (wt%) and outside polymer ratio (wt%) are calculated by eqn (3) and (4), respectively (inside polymer ratio (wt%) + outside polymer ratio (wt%) = 100 (wt%)). The outside polymer amount (wt%) is the relative weight ratio of epoxy polymer located outside the mesopores to the composite, which is calculated by eqn (5). The glass transition temperature (T_g) and the CTE values of the composites are estimated from the TMA charts

Sample	Amount of nonporous silica nanoparticles/g	Density/ g cm^{-3}	Dead pore ratio (vol%)	Inside polymer ratio (wt%)	Outside polymer ratio (wt%)	Outside polymer amount (wt%)	Glass transition temperature (T_g)/ $^{\circ}\text{C}$	CTE (above T_g)/ $\times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$
NS_0	0.000	1.293	95.4	32.0	68.0	51.0	92	135
NS_10	0.175	1.303	94.6	31.8	68.2	49.9	90	137
NS_20	0.350	1.313	93.9	31.5	68.5	48.9	96	131
NS_30	0.525	1.321	92.7	31.1	68.9	48.1	96	133
NS_40	0.700	1.332	92.4	31.0	69.0	47.0	97	134
NS_60	1.050	1.350	91.0	30.6	69.4	45.3	103	127
NS_80	1.400	1.365	89.0	29.9	70.1	43.8	112	123
NS_90	1.575	1.377	89.5	30.0	70.0	42.8	113	123
NS_100	1.750	1.381	87.6	29.4	70.6	42.3	122	122

measured by using a Rheosol-G1000 Rheometer. For the measurement of the viscosity, epoxy resins including TMS_TMPS and silica nanoparticles were prepared. Epoxy resin, TMS_TMPS, silica nanoparticles were mixed with a THINKY vacuum mixer ARV-310. Several epoxy resins were prepared by varying the amounts of silica nanoparticles, while the amounts of TMS_TMPS (2.10 g) and epoxy resin (33.3 g) were fixed. The weight ratios of added silica nanoparticles to TMS_TMPS were 0, 10, 20, 50 and 100 wt%.

3. Results and discussion

Before fabrication of silica/epoxy composites, we examined the mesoporous structure of the starting TMS_TMPS filler. Fig. 2a shows the low-angle XRD pattern of the organically modified mesoporous silica particles (TMS_TMPS). Several signals were observed, being assignable to (10), (11) and (20) diffractions of a well-ordered 2D hexagonal structure. The estimated d_{10} value was 5.0 nm. Therefore, the pore–pore distance was estimated to be 5.8 nm. The N_2 adsorption–desorption isotherms exhibited

type IV isotherms with a capillary condensation step (Fig. 2b). From the pore-size distribution calculated by the BJH method, uniform pore size was confirmed. Calculated BET surface areas, mean mesopore diameter, and total pore volume were $755 \text{ m}^2 \text{ g}^{-1}$, 3.7 nm, and $0.871 \text{ cm}^3 \text{ g}^{-1}$. Thus, the mesopore size estimated by the BJH method is expected to be sufficiently large for epoxy polymers to easily penetrate the internal mesospace. SEM image of TMS_TMPS is shown in Fig. 2c. The particle surface was very coarse and its particle diameter is a few hundred nanometres. The TEM image of the silica nanoparticles as the second filler is also displayed in Fig. 2d. The particle size was around 20 nm and each nanoparticle was dispersed well on the TEM grid.

For the fabrication of silica/epoxy composites, two types of silica fillers (mesoporous silica particle and silica nanoparticle) were mixed with the epoxy resin. The rheological property of the epoxy resin (before addition of curing agent) was examined to survey the processability of composites. Fig. 3 shows the viscosity of the epoxy resins with different amounts of silica nanoparticles. An epoxy resin itself showed Newtonian behaviour, because the viscosity was almost identical regardless of shear rate. Even after addition of silica nanoparticles, Newtonian behaviour was still observed (Fig. 3a). Although the viscosity increased monotonically with the increase of the added amounts of silica nanoparticles, the observed increase was moderate (Fig. 3b). This result is evidence that the silica nanoparticles are well dispersed without any aggregation in the epoxy resins.³⁵ If the aggregation of silica nanoparticles is occurring in the epoxy resin, the Newtonian region would completely disappear and the viscosity would be largely increased.³⁵ In contrast, in the present bimodal filler system, the hydrophobic modification on the silica surfaces may contribute to the prevention of their aggregation, leading to rather lower viscosity than we expected.^{36–38} Thus, the addition of silica nanoparticles did not seriously affect the enhancement of the viscosity, showing high processability.

By addition of curing agent, epoxy resins became rigid. The internal structures of the obtained silica/epoxy composites were examined by the cross-sectional TEM images. The embedded mesoporous silica particles (TMS_TMPS) were uniformly dispersed in the matrix (Fig. 4). Like our previous studies,^{22–24} any voids and cracks which seriously cause the distortion and/or breakage of the composite at high temperature were not observed at the silica/epoxy interfaces. In a highly magnified image (Fig. 4e

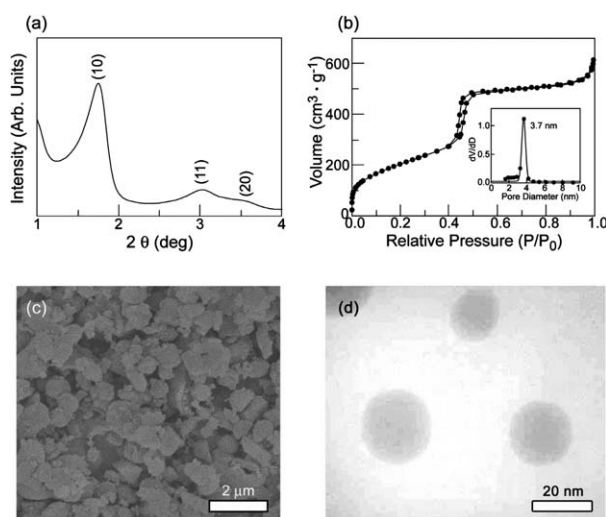


Fig. 2 (a) Low-angle XRD pattern, (b) N_2 adsorption–desorption isotherm (Inset image is the pore size distribution calculated by the BJH method.), and (c) SEM image of TMS_TMPS. (d) TEM image of silica nanoparticles.

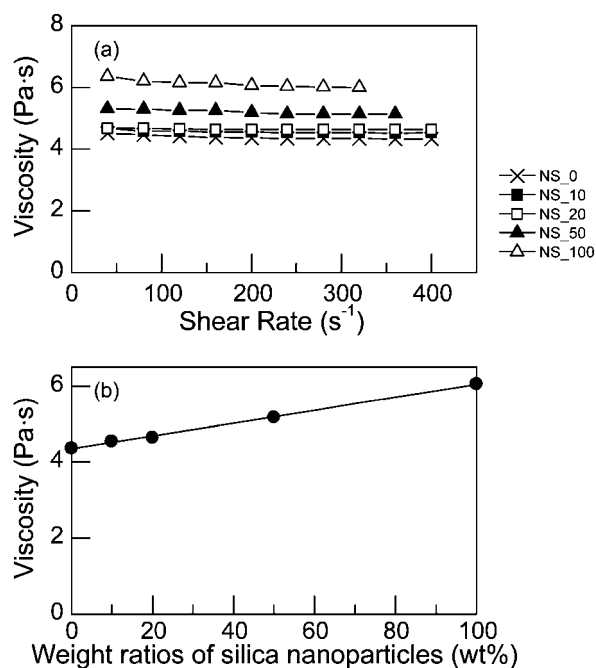


Fig. 3 (a) The relationship between the applied shear rates and the viscosity of epoxy resins containing different amounts of silica nanoparticles. (b) The relationship between the doped silica nanoparticle contents and the viscosity at constant shear rate (200 s^{-1}). The X-axis is the relative weight ratio of the added silica nanoparticles to mesoporous silica (TMS_TMPS).

and f), both tubular and honeycomb structures were observed, proving that the 2D hexagonally ordered mesostructures were well retained during the composite fabrication process. As assumed from the above viscosity data (Fig. 3), good dispersion of the silica nanoparticles in the epoxy matrix was also confirmed by cross-sectional TEM observation (Fig. 4e and f). Even when the amounts of the silica nanoparticle increased, any aggregations of silica nanoparticles were not observable (Fig. 4f). The silica nanoparticles were not introduced inside the mesopores of TMS_TMPS, because the particle diameter of silica nanoparticles (20 nm) is much larger than that of mesopores of TMS_TMPS (3.7 nm). It was understood that the mesopores were filled with the epoxy polymers, while the silica nanoparticles were located at the gap among the mesoporous silica particles.

To estimate how much percentage of the mesopores was filled with the epoxy polymers, we calculated the “dead pore ratio”.^{22–24} In this study, the amounts of TMS_TMPS and epoxy polymer were fixed to 1.75 g and 5.25 g, respectively, while only the amount of silica nanoparticle was varied (see Table 1). The remaining vacant mesopore volume (V , $\text{cm}^3 \text{ g}^{-1}$) per one gram of TMS_TMPS in the composite was calculated by eqn (1).

$$V = \frac{((5.25 + 1.75 \times (1 + x/100))/\rho) - (5.25/\rho_{\text{epoxy}}) - ((1.75 \times (1 + x/100))/\rho_{\text{silica}})}{1.75} \quad (1)$$

where x is the weight ratio (wt%) of doped silica nanoparticles to TMS_TMPS, and ρ , ρ_{epoxy} and ρ_{silica} are the densities of the composites, epoxy polymer (1.16 g cm^{-3}), and silica (2.18 g cm^{-3}),

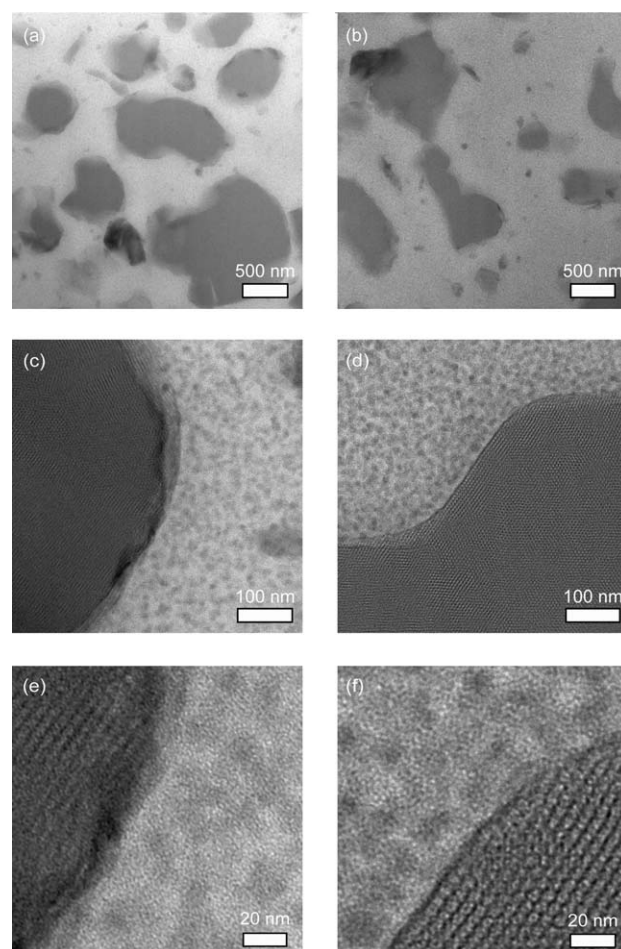


Fig. 4 Cross-sectional TEM images of (a, c and e) NS_20 and (b, d and f) NS_80. (e) and (f) are highly magnified images of (a) and (b), respectively.

respectively. Then, the dead pore ratios were estimated by eqn (2).

$$\text{Dead pore ratio (vol\%)} = \frac{V_0 - V}{V_0} \times 100 \quad (2)$$

where V_0 is the total pore volume of the original TMS_TMPS ($0.871 \text{ cm}^3 \text{ g}^{-1}$). If all the mesopores are perfectly filled with the epoxy polymer, the dead pore ratio is 100 vol%. In contrast, if all mesopores completely remain, it is 0 vol%. The estimated dead pore ratios of all the composites are listed in Table 1. The dead pore ratios were around 90 vol% or higher, indicating that most of the mesopores were filled with the epoxy polymer. The dead pore ratios slightly decreased with the increase of doped amounts of silica nanoparticles. This would be caused by a little increase of the viscosity of epoxy resins (Fig. 3).

The length-normalized TMA charts for all the silica/epoxy composites are summarized in Fig. 5. Broad inflection points (*i.e.*, glass transition temperature, T_g) were observed in all the charts.

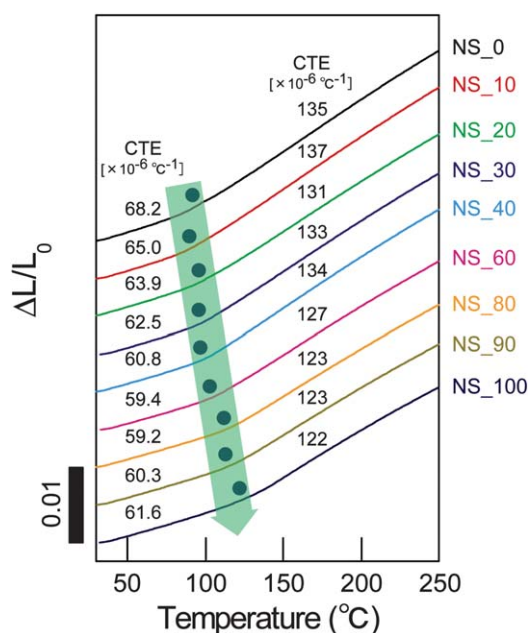


Fig. 5 TMA charts of the fabricated silica/epoxy composites. Filled circles indicate the glass transition temperature (T_g) of each composites. CTE values of both below and above T_g are also indicated.

The T_g values of mesoporous silica/epoxy composite without silica nanoparticles (NS_0) were observed at 92 °C. As listed in Table 1 and Fig. 6, the T_g gradually increased up to 122 °C with the increase of amounts of silica nanoparticles. It is well known that effective interaction at polymer–substrate interface induces enhancement of T_g , delaying induction for the thermal mobility.^{39,40} Also, there have been several reports on the critical effect of functional groups on T_g enhancement in silica/epoxy composites.⁴¹ In the present system, the used silica nanoparticles were modified by hydrophobic phenyl groups. Therefore, it is expected that π – π interaction exists between the silica nanoparticles and the epoxy resin. Such a strong interaction can cause the increase of the T_g values.

To clarify the effect of the doped silica nanoparticles on the thermal expansion of the composites, the CTE values were

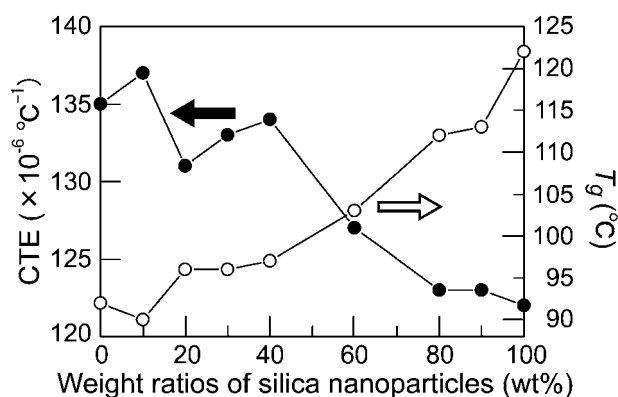


Fig. 6 The glass transition temperature (T_g) (open circles) and CTE values above T_g (filled circles) as a function of the weight ratios of the added silica nanoparticles. The X-axis is the relative weight ratio of the added silica nanoparticles to mesoporous silica (TMS_TMPS).

examined for all the silica/epoxy composites. The CTE values were calculated from the slope of the thermal mechanical analysis (TMA) chart. The CTE values above T_g largely reduced by adding higher amounts of silica nanoparticles, although the CTE values below T_g were not so changed (Fig. 5 and 6).

To further understand the above phenomena, we calculated the amounts of epoxy polymers outside the mesopores by eqn (3)–(5).

Inside polymer ratio(wt%) =

$$\frac{V_0 \times 1.75 \times (\text{dead pore ratio}(\text{vol}\%)/100) \times \rho_{\text{epoxy}}}{5.25} \times 100 \quad (3)$$

Outside polymer ratio (wt%) = 100 – inside polymer ratio (wt%)
(4)

Outside polymer amount(wt%) =

$$\frac{5.25 \times (\text{outside polymer ratio}(\text{wt}\%)/100)}{5.25 + 1.75 \times (1 + x/100)} \times 100 \quad (5)$$

where V_0 is the total pore volume of the original TMS_TMPS ($0.871 \text{ cm}^3 \text{ g}^{-1}$), x is the weight ratio of doped silica nanoparticles to TMS_TMPS, ρ_{epoxy} is the density of the epoxy polymer ($1.156 \text{ g} \cdot \text{cm}^{-3}$).

The calculated inside and outside epoxy amounts were summarized in Table 1 and their relationship to CTE (above T_g) are shown in Fig. 7. For comparison, the CTE values of mesoporous silica/epoxy composites (without silica nanoparticles) are also shown.²² In our previous study, the same epoxy resin was mixed with various amounts of mesoporous silica particles to prepare mesoporous silica/epoxy composites.²² In this case, the CTE values were proportionally decreased with the decrease of the epoxy amounts located outside the mesopores, as plotted in Fig. 7. This result indicated that the physically confined epoxy polymers inside the mesopores showed very high thermal stability and did not contribute to the thermal expansion at all. In

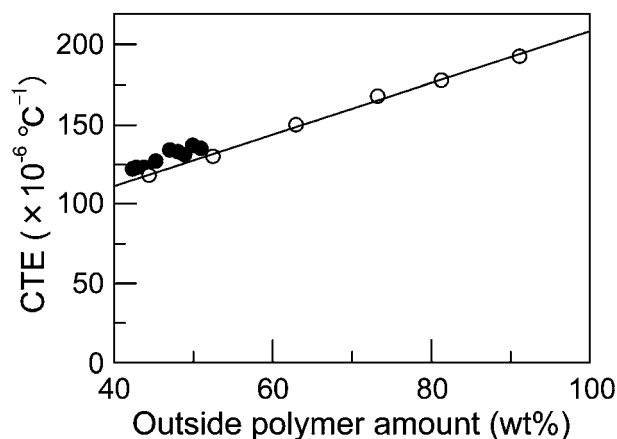


Fig. 7 The relationship between the CTE values (above T_g) and the outside polymer amounts (wt%). The X-axis is the relative weight ratio of the epoxy polymer located outside the mesopores to the composite, which is calculated by eqn (5). The filled circles indicate the silica/epoxy composites containing both mesoporous silica particles and silica nanoparticles (this study), while the open circles indicate the silica/epoxy composites containing mesoporous silica only (ref. 22).

other words, only the epoxy polymers outside the mesopores thermally expanded, thereby contributing to the CTE values.

If the interaction between the epoxy resin and the silica nanoparticle plays an important role as the significant effect for reducing CTE values, a large difference must be observable between the present and previous studies (Fig. 7). However, the relationship between the CTE values and outside epoxy amounts was almost identical, regardless of whether the epoxy composites contain the silica nanoparticles or not. From this result, we can conclude that the silica nanoparticles did not reduce the CTE values of the composites.

From the above results, it should be importantly noted that the silica nanoparticles have a large effect on T_g values, although they contribute less on lowering CTE values. As described above, the π - π interaction existing between the silica nanoparticles and the epoxy resin can delay induction for the thermal mobility of the epoxy polymers, thereby causing the increase of the T_g values.^{39,40} However, once the epoxy polymer thermally expanded, the CTE values were determined by the amounts of the epoxy polymers outside the mesopores, regardless of whether the silica nanoparticles were included in the composites.

TMA charts for three samples (NS_100, mesoporous silica/epoxy composites (with 30 wt% doped mesoporous silica),²² and neat epoxy polymer without silica fillers) are shown in Fig. 8. Both NS_100 and mesoporous silica/epoxy composite showed smaller CTE values than neat epoxy polymer. The epoxy polymer amount outside the mesopores in the mesoporous silica/epoxy composite²² is almost the same as that in NS_100. Therefore, no large difference of the CTE values between them was confirmed. However, the T_g value was largely shifted in the higher temperature range by the addition of silica nanoparticles. The T_g of NS_100 (122 °C) showed a much higher value than that of the mesoporous silica/epoxy composite (88 °C)²² and neat epoxy polymer (96 °C).

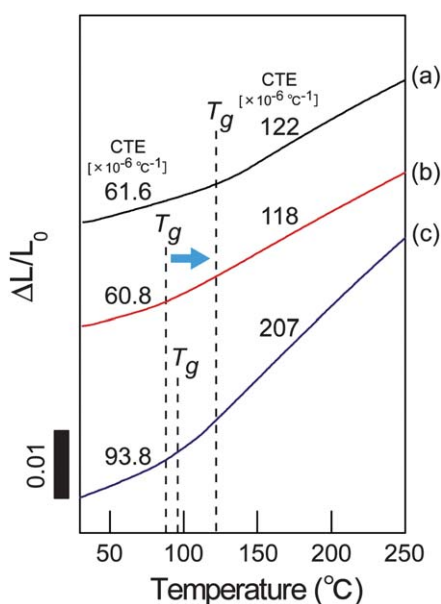


Fig. 8 Comparison of TMA charts (a) silica/epoxy composite with silica nanoparticles (NS_100), (b) mesoporous silica/epoxy composite with 30 wt% TMS_TMPS (in ref. 22), and (c) neat epoxy polymer. The CTE values and the glass transition temperatures (T_g) are also noted.

As a result, the total expansion volume of NS_100 could be decreased by 7.1% in comparison with mesoporous silica/epoxy composite,²² when the applied temperature was increased up to 250 °C. Compared to neat epoxy polymer, the total expansion volume of NS_100 was decreased by 45.3%, due to the increase of the T_g value as well as the reduction of CTE value.

4. Conclusion

We proposed a bimodal filler system consisting of mesoporous silica particles and fine silica nanoparticles to fabricate silica/epoxy composites with superior low thermal expansion property. In the case of NS_100, the addition of 40 wt% silica was achieved without causing any drastic increase of the viscosity of the epoxy resin. From the systematic study on the thermal expansion of the composites, it was clarified that the silica nanoparticles located at the gap among the mesoporous silica particles played an important role for increasing T_g values. The physical confinement of the epoxy polymers inside the mesopores was quite effective for the decrease of CTE. By blending mesoporous silica particles and silica nanoparticles, both increase of T_g and reduction of CTE could be realized, showing outstanding low thermal expansion. Our concept reported here is widely applicable for various polymers and also will be a key technique to establish a more complicated multi-scale filler system toward perfect low thermal expansion materials, which will be reported in the near future.

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