NANOCOMPOSITE DESIGN OF SILICA/EPOXY RESIN SYSTEM WITH LOW THERMAL EXPANSION COEFFICIENT VIA UNIFORM DISPERSION OF HYDROPHILIC COLLOIDAL SILICA NANOSPHERES

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Abstract

The aim of the present study is to elucidate the possibility of fabricating the silica/epoxy resin nanocomposites with a coefficient of thermal expansion (CTE) lower than the conventional type of the epoxy nanocomposites with the scope of examining the effects of hydrophilic nature of surfaces of dispersed colloidal silica nanospheres on thermal expansion behavior of silica-loaded epoxy resin. The authors have fabricated the epoxy nanocomposites, wherein silica nanoparticles without surface modification using hydrophobic surface modifiers such as silanecoupling agents were dispersed through the breakdown of loose agglomerates of colloidal silica nanospheres in an epoxy resin solution. It was found that a chemical interaction derived from hydrogen bonds occurring between the hydroxyl groups on hydrophilic surfaces of dispersed colloidal silica nanospheres and cross-linked epoxy polymer networks in this designed nanocomposite system might restrict strongly thermal molecular motion of the epoxy polymer chains, resulting in considerable reduction in CTE of the nanocomposite.

1. Introduction

Epoxy resins are widely used to encapsulate electronic circuits. In order to raise the reliability of electronic circuits, the interfacial failures among dissimilar materials caused by the mismatch of their mechanical and/or thermal properties including CTE need to be prevented. Since many electrical/electronic materials are of particularly low CTEs, or at least lower than the CTEs of encapsulating epoxy resins, drastic reduction in the CTE of epoxy resin by filling inorganic nanoparticles would be one of the solutions to the above-mentioned issue. In this study, the effects of hydrophilic nature of surfaces of dispersed silica nanoparticles on thermal expansion behavior of silica-loaded epoxy resin (silica/epoxy resin nanocomposite) has been investigated.

Silica/epoxy resin nanocomposites have be fabricated conventionally utilizing a blending method with an enhancement wettability of silica nanofiller against epoxy resin as a polymeric matrix via surface treatment using silane coupling agents, resulting in a reduction in interfacial activity between silica nanofillers and epoxy polymer networks. The interfaces between silica nanofiller and epoxy resin matrix phase formed in a conventional type of this nanocomposite system are so limited that interactions occurring there is difficult to be utilized positively for designing advanced functional nanocomposites. For example, the effects of volume fraction of dispersed nano-silicas on CTE of the

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conventional type of silica/epoxy resin nanocomposite fabricated via a blending method with surface modification on nano-silicas using organosilane was obeyed approximately the simple rule of mixture (ROM) and Kerner model [1] (see Fig. 8 (b) in the later section 4.4.) [2]. It is predicted from the results obtaind in this previous study [2] that silica volume fraction required to reduce CTE to a level of dissimilar materials such as a copper wiring (~ 20 ppm $^{\circ}C^{-1}$) reaches over 70 vol%. Form the viewpoint of this issue, the present study was conducted to elucidate the possibility of fabricating the silica/epoxy resin nanocomposites with low thermal expansion coefficient, which is applicable to an encapsulating material that enable prevention of the interfacial failures among dissimilar materials caused by the mismatch of their CTEs to raise the reliability of electronic circuits.

2. Strategy for Designing and Fabricating Silica/Epoxy Resin Nanocomposite System in the Present Study

The strategy for designing new silica/epoxy resin nanocomposite with much lower CTE than conventional type of this nanocomposite system are explained using Fig. 1. In the present study, the chemical interaction derived from hydrogen bonds at huge interfacial area between epoxy polymer networks and dispersed silica nanofillers having hydrophilic surfaces. If this type of nanocomposite could be fabricated, this chemical interaction will be able to restrict the chain motion in epoxy networks, resulting in drastic reduction in CTE of epoxy resin.

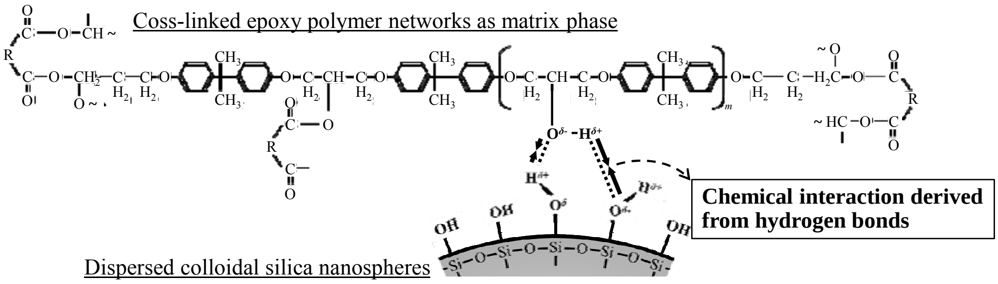

Figure 1. Conceptual diagram illustrating nanocomposite system designed in the present study on the basis of effective utilization of huge interfacial area between epoxy polymer networks and dispersed colloidal silica nanospheres having hydrophilic surfaces.

In order to utilize chemical interaction derived from hydrogen bonds at the interface between silica nanofiller and epoxy resin matrix, silica nanofillers having hydroxyl-rich surfaces have to be dispersed in epoxy resin without any chemical modification of their silica filler surfaces. In general, it is extremely difficult to achieve nanodispersion of silica fillers with hydrophilic surfaces in polymeric matrix because of a poor wettability between fillers and matrix phase. Recently, the present authors and coworkers have proposed a novel blending method for fabricating various types of the silica/thermoplastics nanocomposite systems which does not depend upon the surface modification technique [3-7]. For the proposed method, isolated primary nanoparticles of hydrophilic colloidal silica without surface modification can be dispersed uniformly through mechanical breakdown of loosely packed agglomerates of colloidal silica pre-controlled with low fracture strength in a polymer melt during direct melt-compounding. A reduction in fracture strength of the agglomerates of colloidal silica before the melt-compounding process is one of the key strategies for obtaining a uniform dispersion of the silica nanoparticles in this method.

In the present study, an attempt to fabricate the designed silica/epoxy resin nanocomposite systems has been made by the use of solution-mixing method on the basis of the same strategy. According to the Rumpf's equation regarding the fracture strength of the packing structure of spherical particles, σ_t, with a diameter of d_p and a surface energy of γ [8,9]:

$$\sigma_t = \frac{(1-\varepsilon_p)\cdot N_C(\varepsilon_p)\cdot\gamma}{d_p}, \tag{1}$$

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the fracture strength can be reduced by increasing the volume fraction of void spaces between primary particles, ε_P and by decreasing the coordination number of primary particle (number of interparticle contacts per unit primary particle), $N_C(\varepsilon_P)$. This equation indicates that numerous nanospaces generated as defects in packing structure of silica nanospheres can reduce drastically its fracture strength, resulting in achievement of uniform dispersion of hydrophilic silica nanospheres during mixing process with epoxy resin solution.

3. Experimental Details

The method to realize the silica/epoxy resin nanocomposite system designed by the present authors is illustrated in Fig. 2. The method for fabrication of the silica/epoxy resin nanocomposite systems consists of two stages. The first stage involves pre-control of the packing structure in agglomerates of silica nanopheres, and the second one involves blending of epoxy resin solution with the loose silica agglomerates prepared in the first stage. In the first stage, the colloidal silica nanospheres with a primary diameter of 190 nm coagulate in an aqueous solution of colloidal silica (silica sol solution) destabilized by pH control from initial state (~ 9.3) to 4 and the addition of KBr (salt concentration in the solution, [KBr] = 2.6 M), resulting in the formation of random loose packing structure of colloidal silica nanospheres. Evaporating off the water yielded lumps of precipitated agglomerates of silica nanospheres contaminated with deposited salt. The resultant granular samples were immersed in hot water (~ 80 ˚C) to leach the salt phase acting as a template for generation of nano-sized void spaces between silica nanospheres. Finally, loose agglomerates of colloidal silica nanospheres having arrangement structure with large amounts of nano-sized void spaces were obtained by drying the sample at 120 ˚C. In the second stage, the epoxy resin solution were mixed with appropriate amounts of the prepared loose silica agglomerates in a planetary centrifugal mixer (AR-250, THINKY CORP.) for 50 min at a revolution/rotation speed of 2000 rpm/800 rpm. The epoxy resin solution by dissolving 30 % of solid component of bisphenol A-type epoxy resin and acid anhydride curing agent into acetone have been used as a matrix component. Through the curing process of the expxy matrix by heating at a temperature range from 60 to 150 ˚C under a reduced pressure, silica/epoxy resin nanocomposites were fabricated for a range of silica volume fraction, V_f from 0 to 34 %.

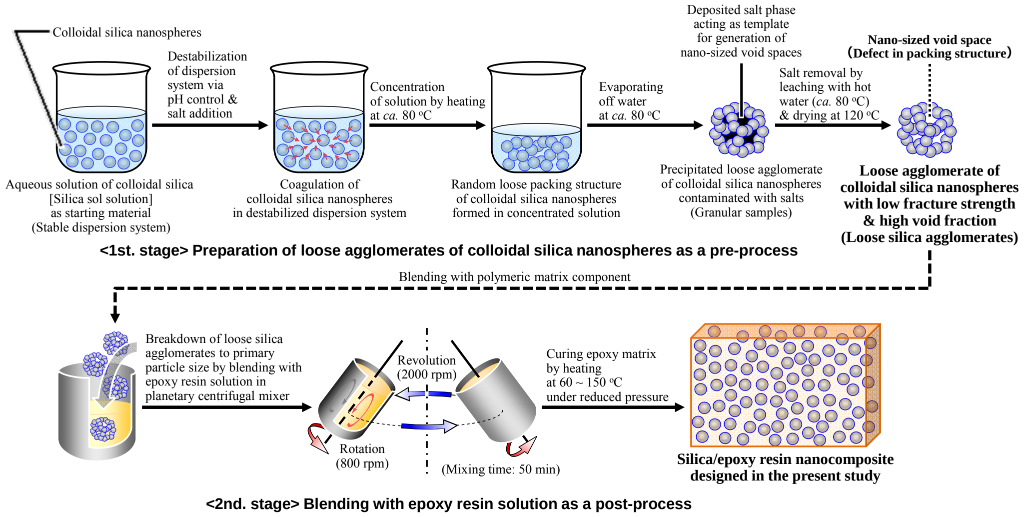

Figure 2. Process flow illustration for fabrication of silica/epoxy resin nanocomposite by solution-mixing method combined with process for pre-control of packing structure in agglomerates of silica nanopheres as inorganic fillers that enable acceleration of breakdown their agglomerates via blending with epoxy resin solution.

The arrangement structures and pore size distribution in the agglomerates of colloidal silica nanospheres prepared in the first stage were characterized, respectively, by a scanning electron microscope (SEM) and mercury intrusion porosimetry. A microcompression test (MCT-W500,

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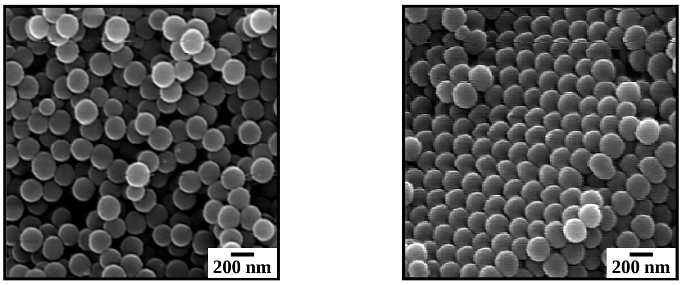
Shimadzu Co.) was conducted to evaluate the fracture strength of the agglomerates. In addition, a solid state silicon-29 nuclear magnetic resonance spectroscopy (^{29}Si NMR) were employed to evaluate the amounts of hydroxyl groups on surfaces of colloidal silica nanospheres formed the loose silica agglomerates. Dipolar decoupling, magic-angle spinning (DD-MAS) NMR spectra were recorded under the conditions of a pulse width of 4.50 μs and a delay time of 60 s. All spectral shifts were recorded relative to hexamethylcyclotrisiloxane.

On the other hand, the fabricated silica/epoxy resin nanocomposite samples were subjected to assessment of the dispersion state of silica nanospheres by SEM observation and characterization of the themal expansion property by thermomechanical analysis (TMA) at a compression mode with a load of 0.49 N under air atmosphere, according to JIS K 7197. The CTEs of the nanocomposite samples below a glass-transition temperature of the epoxy matrix phase were determined from the TMA data oftained under the conditions of the scanning temperature range from 50 to 70 ˚C at a heating rate of 0.083 ˚Cs^{-1}.

4. Results and Discussion

4.1. Characterization of agglomerates of colloidal silica nanospheres prepared in first stage

Figure 3 (a) shows SEM micrographs of an example of arrangement structures in the agglomerates of colloidal silica nanospheres prepared from the silica sol with pH control and salt addition. In comparison with the regular close packing structure in the silica agglomerates prepared from the same sol solution without pH control or salt addition as a control silica agglomerate sample, shown in Fig. 3 (b), large amounts of nano-sized void spaces could be generated in the silica agglemerates shown in Fig. 3 (a).



(a) with pH control from initial state to 4 and salt addition ([KBr] = 2.6 M)

(b) without pH control (initial state: pH 9.3) or salt addition ([KBr] = 0 M)

Figure 3. SEM micrographs showing arrangement structures of colloidal silica nanospheres in two types of agglomerates prepared from (a) silica sol solution with pH control and salt addition and (b) same sol solution without pH control or salt addition.

The fracture strength, σ_t, and void fraction, ε_P, of the silica agglomerates having two different arrangement structures of colloidal silica nanospheres shown in Fig. 3 (a) and (b) were determined from a microcompression test [10] and mercury intrusion porosimetry of their agglomerates, respectivery. The relationship between σ_t and ε_P are shown in Fig. 4, which indicates that the fracture strength of silica agglomerate reduced drastically with increasing its void fraction in accordance with Eq. 1. This implies that the arrangement structure and fracture strength of the agglomerate of colloidal silica nanospheres can be controlled by destabilizing the dispersion system in the silica sol solution used as starting material via pH control and salt addition.

4.2. Dispersion state of silica in silica/epoxy resin nanocomposites fabricated using loose agglomerates of colloidal silica nanospheres

The loose agglomerates of colloidal silica nanospheres with low fracture strength and high void fraction having the arrangement structure shown in Fig. 3 (a) have been used as fillers for the

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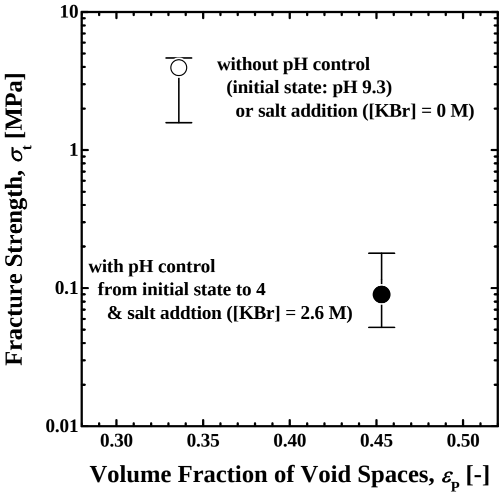

Figure 4. Relationship between fracture strength of prepared agglomerates of colloidal silica nanospheres and its void fraction.

silica/epoxy nanocomposite system designhed strategically in the present study. Figure 5 is anexample of the SEM micrographs showing distributon of colloidal silica nanospheres in the silica/epoxy resincomposite sample fabricated by blending 34 vol% loose silica agglomerates with the epoxy resin solution. This micrograph clearly show that isolated primary particles of colloidal silica with a diameter of 190 nm are dispersed uniformly in the cured epoxy resin matrix phase. It was found that the proposed method using the loose silica agglomerates enables a successful fabrication of the silica/epoxy resin nanocomposites without any hydrophobic treatment of colloidal silica surfaces even at silica volume fraction much higher than 30 vol%.

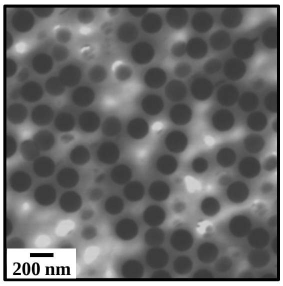

Figure 5. SEM micrographs showing an example of distribution of primary silica particles having hydrophilic surfaces with a diameter of 190 nm in epoxy resin highly filled with 34 % colloidal silica.

4.3. Effects of hydroxyl groups on surfaces of dispersed colloidal silica nanospheres on thermal molecular motion of polymer chains in the epoxy matrix

In order to examine the effects of hydroxyl groups on surfaces of dispersed silica nanospheres on the thermal expansion behavior of the designhed silica/epoxy resin nanocomposite system, the values of CTE of the nanocomposite samples fabricated by mixing epoxy resin solution with the prepared loose agglomerates of colloidal silica having different hydrophilicity on their surfaces. In the present study, the hydrophilicity on the surfaces of the loose silica agglomerates has been controlled by varing the conditions of the drying process of the prepared agglomerates in the first stage. As shown in Fig. 2, the drying of the agglomerates at 120 ˚C for 24 hours under atmospheric pressure (~ 10^5 Pa) was used as a standard condition. A typical example of the ^{29}Si NMR spectra for the loose silica agglomerates obtained after the above-mentioned drying process is shown in Fig. 6 (b). This figure (b) shows that the ratio of signal intensity of Q^3 with chemical shift $\delta \approx -108$ ppm characteristic for $Si(SiO)_3(OH)$ to that of Q^4 with chemical shift $\delta \approx -116$ ppm characteristic for $Si(SiO)_4$, Q^3/Q^4, which indicates

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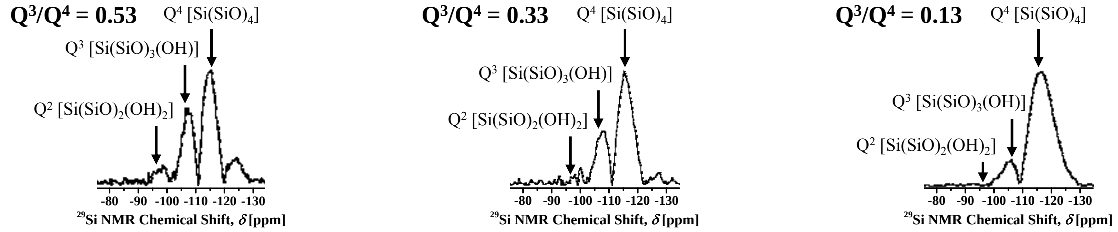
amounts of hydroxyl groups on silica surfaces, was about 0.33. It was found from Fig. 6 (a) ~ (c) that amounts of hydroxyl groups on surfaces of the obtained loose silica agglomerates was a medium level between those of the agglomerates dried under the following two controlled conditions (1) and (2). As the controlled condition (1), the prepared loose silica agglomerates were dried at 80 °C for 24 hours under a reduced pressure (< 30 Pa). In this case, since dehydrocondensation of hydroxyl groups on colloidal silica surfaces was suppressed during those drying process, the ratio of Q^3/Q^4 was reduced to 0.13 as shown in Fig. 6 (a). As the controlled condition (2), the prepared loose silica agglomerates were dried by heating at 600 °C for 24 hours under atmospheric pressure to accelerate dehydrocondensation of hydroxyl groups on silica surfaces. Figure 6 (c) indicates that the ratio of Q^3/Q^4 in this case was the largest value (0.53) in these three conditions. The results of these 29Si NMR spectra reveal that the largest amounts of hydroxyl groups on silica surfaces was the agglomerates dried under the controlled condition (1), followed in order by the agglomerates dried under the standared condition and those dried under the controlled condition (2).



(a) Loose agglomerate of colloidal silica nanospheres dried under controlled condition (1)

(b) Loose agglomerate of colloidal silica nanospheres dried under standard condition

(c) Loose agglomerate of colloidal silica nanospheres dried under controlled condition (2)

Figure 6. ^{29}Si NMR (DD-MAS) spectra of loose agglomerates of colloidal silica nanospheres having different amounts of hydroxyl groups on their surfaces.

Using these three types of the loose silica agglomerates, the silica/epoxy resin nanocomposites were fabricated, respectively, for a volume fraction of nano-silica, V_f, being 25 %. Almost the same dispersivity of isolated primary particles of colloidal silica were observed in all three nanocomposite samples. The CTE values, α, of these nanocomposites are plotted in Fig. 7 against the ratio of the signal intensity, Q^3/Q^4, in the NMR spectra for the silica agglomerates used for the filler component of each nanocomposite. The value of CTE of epoxy resin is reduced by filling silica into the resin. In comparison with the result for the case of Q^3/Q^4 being 0.13, the value of CTE for the case of Q^3/Q^4 being 0.33 was successfully reduced as shown in this figure. A comparison between these two results revealed that an effective restraint of thermal expansion of epoxy resin could be realized by strategy for designing and fabricating new silica/epoxy nanocomposite utilizing strong interaction between epoxy polymer network and dispersed nano-silica with hydrophilic surface. However, an increase of hydroxyl groups on surfaces of the dispersed colloidal silica more than the intensity ratio of Q^3/Q^4 being 0.33 seems to be ineffective against further reduction in CTE of the nanocomposite system.

4.4. Effects of volume fraction of dispersed colloidal silica nanospheres on CTE of silica/epoxy resin nanocomposite

The values of CTE, α, of the nanocomposites fabricated using the loose agglomerates of colloidal silica nanospheres having surfaces with Q^3/Q^4 being 0.33 were plotted in Fig. 8 (a) against silica volume fraction. As shown in Fig. 8 (a), the silica/epoxy resin nanocomposite with much lower CTE than the simple rule of mixture (ROM):

$$\alpha = \alpha_f V_f + \alpha_m (1 - V_f) \tag{2}$$

and Kerner model [1]:

$$\alpha = \alpha_f V_f + \alpha_m (1 - V_f) + (\alpha_f - \alpha_m) V_f (1 - V_f) \cdot \frac{1/K_m - 1/K_f}{(1 - V_f)/K_f + V_f/K_m + 3/(4G_m)} \tag{3}$$

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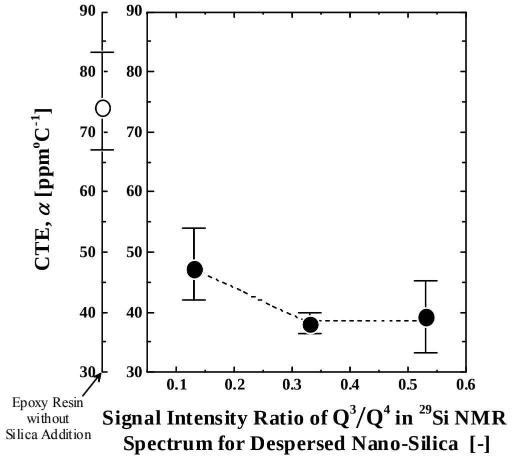
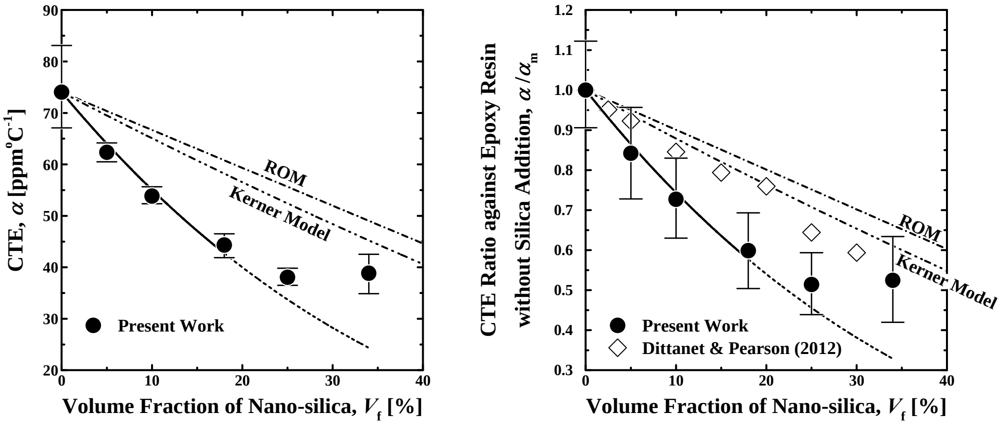


Figure 7. Relationship between coefficient of linear thermal expansion (CTE) of silica/epoxy resin nanocomposite fabricated for V_f being 25 % and amounts of hydroxyl groups on surfaces of colloidal silica nanospheres dispersed in epoxy resin matrix phase.



(a) CTE, α (b) CTE ratio, α/α_m

Figure 8. Effects of volume fraction of dispersed colloidal silica nanospheres on thermal expansion behavior of silica/epoxy resin nanocomposite fabricated using loose silica agglomerates dried under the standared condition: (a) Results of CTE values and (b) CTE ratio against epoxy resin without silica addition.

could be fabricated successfully according to design principle utilizing strong attractive chemical interaction, that might be hydrogen bond, occurring via hydroxyl groups on epoxy polymer chains and hydrophilic surfaces of dispersed colloidal silica nanospheres. Here, in Eqs. 2 and 3, α is CTE, V is volume fraction, K is bulk modulus, G is shear modulus, the subscripts, f and m, denote filler and matrix, respectively. However, thermal expansion of epoxy resin could not be suppressed by adding up to 30 vol% colloidal silica nanospheres. Under these high V_f condition, huge amount of colloidal silica nanospheres with a diameter of 190 nm added as filler might obstruct crosslinking reaction among epoxy polymer chains in the epoxy resin solution during its curing process, resulting in formation of epoxy resin matrix phase with a poor themal properties.

As shown in Fig. 8 (b), the CTE value of the silica/epoxy resin nanocomposite fabricated without surface modification of colloidal silica nanospheres in the present study is much lower than that of conventional type of the nanocomposite fabricated using nano-silicas with surfaces modified by organosilane [2]. The results plotted in this figure (b) reveals that a chemical interaction derived from hydrogen bonds occurring at hydrophilic colloidal silica/epoxy resin interfaces in this designed nanocomposite system might restrict strongly thermal molecular motion of the epoxy polymer chains, resulting in considerable reduction in CTE of the nanocomposite.

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5. Conclusions

The present study was conducted to elucidate the possibility of fabricating the silica/epoxy resin nanocomposite system with CTE lower than the conventional type of this nanocomposite system with the scope of examining the effects of hydrophilic surfaces of dispersed colloidal silica nanospheres on thermal expansion behavior of silica-loaded epoxy resin. The obtained results are summarized as follows:

- Practical technique that enables to achieve a uniform dispersion of isolated primary nanoparticles of colloidal silica with hydrophilic surfaces into epoxy resin at a silica volume fraction higher than 30 vol% could be developed successfully.
- New silica/epoxy resin nanocomposite system with much lower CTE than conventional this nanocomposite system could be fabricated according to design principle utilizing chemical interaction occurring via hydroxyl groups on epoxy polymer chains and surfaces of dispersed hydrophilic colloidal silica nanospheres.

Acknowledgments

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