

Thermal and optical properties of epoxy/zirconia hybrid materials synthesized via in situ polymerization

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Abstract Epoxy/zirconia hybrid materials were synthesized from a bisphenol-A type epoxy resin, zirconium-tetra-*n*-propoxide and acetic acid via in situ polymerization. Acetic acid was used to control the hydrolysis and condensation reaction of the zirconium-tetra-*n*-propoxide. As a result, the zirconia produced by the in situ polymerization was uniformly dispersed into the epoxy matrix on a nano scale or less, and the hybrid materials exhibited an excellent optical transparency. With the increasing zirconia contents, the storage modulus in the rubbery region increased and the peak area of $\tan\delta$ in the glass transition temperature region decreased. These results indicate that their heat resistance of the hybrid materials could be improved by hybridization with zirconia. Furthermore, the refractive indices of the hybrid materials were significantly improved with the increasing zirconia contents.

Introduction

Organic polymers usually have some superior characteristics with respect to their toughness, flexibility, and processability, while inorganic polymers have a high heat resistance and good mechanical and optical properties. Recently, organic/inorganic hybrid materials have been investigated as promising materials by combination of the superior properties of both the organic and inorganic polymers [1–3]. The sol/gel process is a method for preparing inorganic polymers at low temperature. By using

the sol/gel process, we could combine the organic substances, which would be decomposed at a relatively low temperature, with inorganic substances, which have a high heat resistance. Also, we previously reported [4, 5] the preparation of epoxy/silica hybrid materials from an epoxy resin and silane alkoxide via a sol–gel process, showing that these hybrid materials had a good thermal property.

On the other hand, as light emitting diodes (LED) have become popular, the transparent and high refractive index materials have attracted considerable interest in the encapsulation of the LED [6–11]. If an encapsulating resin with an index of 1.80 or more can be prepared, the light extraction efficiency will be greatly enhanced due to internal reflection phenomena occurring at the interface between the light emitting semiconductor layer and the resin. Also, titania (TiO_2) and zirconia (ZrO_2) can be embedded in a polymer matrix via the sol–gel process to form high refractive index materials. However, the reaction rate of the sol–gel reaction of Ti and Zr alkoxides are significantly different from silane alkoxide. Titanium and zirconium alkoxide are generally highly reactive with water, thus it is difficult to prepare the hybrid materials without the formation of clusters. Phase separation of the TiO_2 and ZrO_2 easily occurs which seriously reduces the transparency of the hybrid materials.

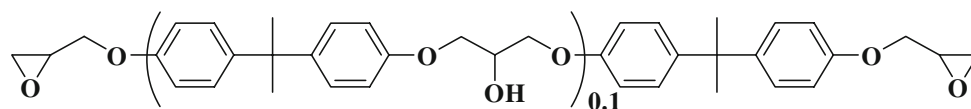
In this study, epoxy/zirconia hybrid materials were synthesized via in situ polymerization for improving the thermal property and refractive index of the epoxy resin. The reaction rate of the sol–gel reaction in zirconium alkoxide, that is much faster than that of epoxy curing, was controlled by the modification with acetic acid through the formation of a coordination structure [12–16]. The thermal and optical properties and the phase structure of the hybrid materials were investigated in detail.

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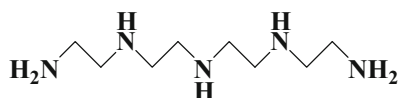
Experimental

Materials

The epoxy resin used in this study was a commercial grade of the diglycidyl ether of bisphenol-A (DGEBA; jER 828, epoxy equivalent: 190 ± 5 ; Japan Epoxy Resin Co., Ltd.).



The curing agent used was tetraethylene pentamine (TEPA; extra-grade, Kanto Chemical Co., Ltd.).



The zirconium alkoxide used as the inorganic source was zirconium-tetra-*n*-propoxide (ZTNP; 23–28 wt% free alcohol, Stream Chemicals (USA)), and the modifier of the zirconium alkoxide was acetic acid (extra-grade, Wako Pure Chemical Co., Ltd.).

Preparation of acetic acid-modified zirconium alkoxide

The acetic acid was mixed with zirconium-tetra-*n*-propoxide in the mol ratio of 1.5 per zirconium alkoxide. The mixtures were then stirred at room temperature for 1 h. An exothermic reaction occurred and a clear solution was obtained.

Preparation of epoxy/zirconia hybrid materials

Two mol H₂O per mol of zirconium alkoxide was added to DGEBA with stirring at 40 °C. In addition, a stoichiometric amount of TEPA as the curing agent for the epoxy group and the acetic acid-modified zirconium alkoxide solution as the inorganic source were added, and then the mixtures were stirred to obtain homogeneous solutions. The resulting homogeneous solutions were poured into an aluminum container in order to prepare the epoxy/zirconia hybrid plates. The compounds were pre-cured to remove the by-products at 80 °C for 4 h in vacuo. Then, that finally cured 100, 150 °C for 4 h during each curing step. Table 1 shows the starting composition and percent zirconia (wt%) of the hybrid materials determined by TGA.

Measurement

The weight percentage of zirconia in the hybrid materials was determined by TGA (TG/DTA 6200, Seiko Instruments

Co., Ltd.) via heating in air from 100 to 800 °C at the rate of 20 °C min⁻¹. Because the organic component seems to have almost completely decomposed in the temperature region around 800 °C, the values of the residual weights were used as the zirconia contents in the hybrid materials.

Confirmations of the epoxy curing and sol-gel reaction were carried out by FT-IR (Spectrum 2000, Perkin Elmer

Co., Ltd.) measurements. The intensity of the adsorption peak at 1180 cm⁻¹, which is the characteristic peak at the para-substituted benzene C=C stretching vibration, was used as the internal standard adsorption peak.

The ultrathin sections of the hybrid materials were observed using a transmission electron microscope (TEM; JEM-1210, JEOL Co., Ltd.) to study the microphase structure of the hybrid materials. The specimens for the TEM observations were prepared using an ultramicrotome (REICHEART ULTRACUT E, Leica Co., Ltd.) with a diamond knife. Prior to the TEM observations, the specimens were stained with RuO₄.

The dynamic mechanical properties of the cured hybrid materials were determined using a non-resonance forced vibration viscoelastometer (DVE-V4, Rheology Co., Ltd.) in air. The frequency and amplitude of the vibration were adjusted to 10 Hz and $\pm 5 \mu\text{m}$, respectively. The temperature range was from -150 to 250 °C and the heating rate was 2 °C min⁻¹.

The refractive index measurement of the hybrid materials were carried out using a refractometer (NAR-2T, Atago Co., Ltd.) with Na monochromatic light source (589.3 nm). The contact liquid was methylene iodide containing sulfur ($n_D = 1.7800$).

Table 1 Composition of the monomer mixtures and the cured hybrid systems

Sample code	Amount of monomers (g)			Zirconia content in cured hybrids	
	DGEBA	TEPA	ZTNP (23–28% free alcohol)	wt% (calc) ^a	wt% (expt) ^b
1	3.00	0.44	–	0.0	0.0
2	3.00	0.44	0.92	6.9	6.7
3	3.00	0.44	1.83	13.0	13.5
4	3.00	0.44	2.75	18.4	18.3

^a Calculated from reactant stoichiometry

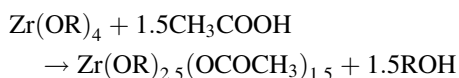
^b Experimentally determined from TGA measurements at 800 °C in air

Results and discussion

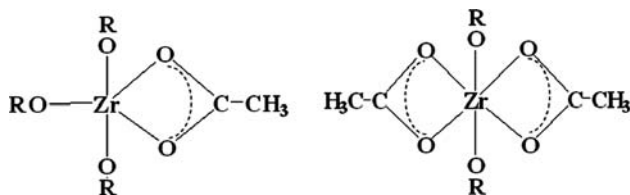
Reaction of zirconium alkoxide with acetic acid

Figure 1 shows the FT-IR spectra of zirconium-tetra-*n*-propoxide, acetic acid, and their reaction product. The zirconium alkoxide (Fig. 1a) exhibited a sharp band around 1140 cm⁻¹ corresponding to the Zr–O–C vibrations of the alkoxy groups directly bonded to the zirconium. Acetic acid (Fig. 1b) exhibited the characteristic bands of the C=O stretching (monomer) around 1756 cm⁻¹, C=O stretching (dimer) around 1725 cm⁻¹. The reaction product (Fig. 1c) from the above compounds exhibited a new set of bands around 1560 and 1460 cm⁻¹. These new bands were ascribed to the acetate ligand because the antisymmetric stretching of –COO⁻ vibration (ν_{asym}) at 1560 cm⁻¹ and symmetric stretching of –COO⁻ vibration (ν_{sym}) at 1460 cm⁻¹ corresponded to the bidentate acetate ligand linked to the zirconium. The acetate group has various modes of coordination such as monodentate and bidentate (chelating or bridging). The small frequency separation ($\Delta\nu = 100 \text{ cm}^{-1}$) between the ν_{sym} and ν_{asym} suggested that CH₃COO⁻ acts as a bidentate chelating coordination mode [17]. In addition, a band at 1725 cm⁻¹ corresponding to free acetic acid could not be identified and a band at 1140 cm⁻¹ corresponding to the Zr–O–C vibrations of the alkoxy groups directly bonded to zirconium decreased. These results suggested that added acetic acid completely reacted with the zirconium alkoxide as follows:

Reaction of zirconium alkoxide and acetic acid (R: –CH₂–CH₂–CH₃)



Coordination mode



Chelating ligands could link more strongly to zirconium when compared to the alkoxide group. Thus, the coordination with acetic acid could decrease the reactivity of the zirconium. Also, acetic acid can substitute up to two alkoxy groups of the zirconium alkoxide molecule [12], but the excess addition of acetic acid increases the by-product of the sol–gel reaction. Therefore, the acetic acid was mixed in a mol ratio of 1.5 per zirconium alkoxide to control the reactivity of the zirconium alkoxide. Thus, the reaction

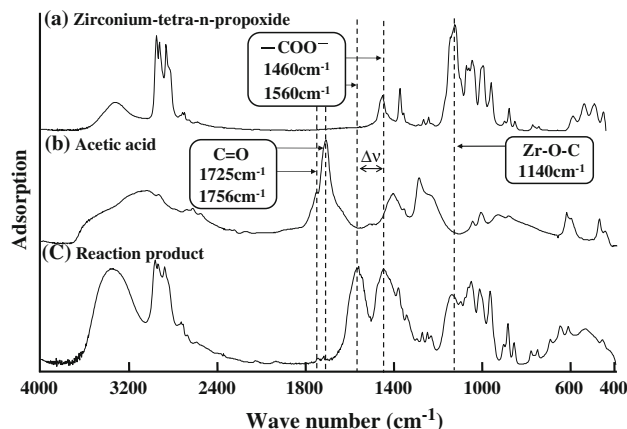


Fig. 1 FT-IR spectra of zirconium alkoxide, modifier, and their reaction product

product is a mixture of monosubstituted and disubstituted derivatives.

Reaction mechanism of epoxy/zirconia hybrid materials

We investigated the reaction mechanism of the in situ polymerization using the acetic acid-modified zirconium alkoxide. Figure 2a and b shows the epoxy resin (DGEBA)/curing agent (TEPA) mixture and acetic acid-modified zirconium alkoxide, respectively. Figure 2c shows the FT-IR spectra of the prepared hybrid systems before curing. The band of the acetic acid-modified zirconium alkoxide was not observed in Fig. 2a. However, in the last spectra, a set of bands around 1560 and 1460 cm⁻¹, corresponding to the bidentate acetate ligand linked to zirconium, was observed. On the other hand, the band around 1140 cm⁻¹ corresponding to the Zr–O–C vibrations of the alkoxy groups directly bonded to zirconium was not observed in this system, though the adsorption peak is clearly observed in Fig. 2b. In addition, a broad band at 460 cm⁻¹ corresponding to the Zr–O–Zr bond was already

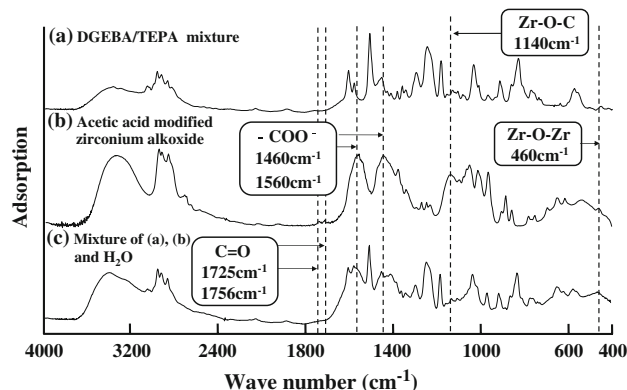
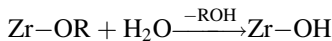


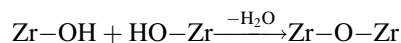
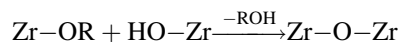
Fig. 2 FT-IR spectra of epoxy/zirconia hybrid systems before curing (ZrO₂ content 18.4 wt%)

confirmed even during the no-curing stage of the epoxy resin. This result indicates that the alkoxide group with a high reactivity already initiated a hydrolysis reaction and some of them initiates a condensation reaction as follows:

Hydrolysis reaction of OR group



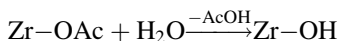
Condensation reaction of OR group



Also, the characteristic bands of the C=O stretching around 1725 or 1756 cm^{-1} corresponding to the free acetic acid, should be generated as a by-product due to the result of the sol-gel reaction of the acetate group, was not observed. This result indicates that the sol-gel reaction of the stabilized acetate group does not proceed before curing of epoxy resin.

Figure 3 shows the epoxy conversion (910 cm^{-1}) and peak intensity of the acetate ligand (1560 cm^{-1}) and Zr-O-Zr bond (460 cm^{-1}) based on the FT-IR measurement during the curing process. As a result, a change in the peak intensity corresponding to Zr-O-Zr and reduction of the peak intensity corresponding to the acetate ligand to zirconium was observed. This means that the acetate group remaining before curing proceeds sol-gel reaction as follows:

Hydrolysis reaction of OAc group



Condensation reaction of OAc group

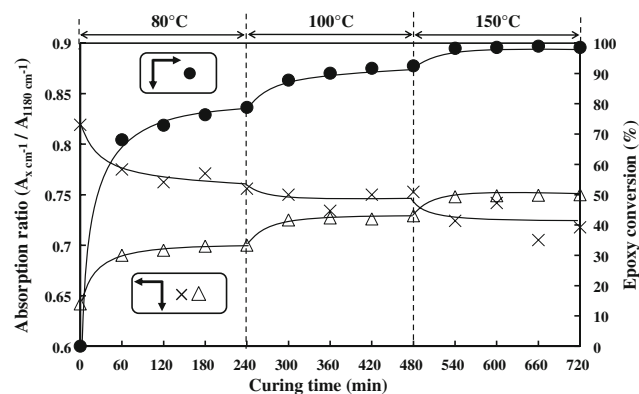
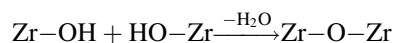
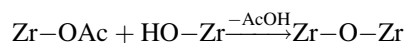
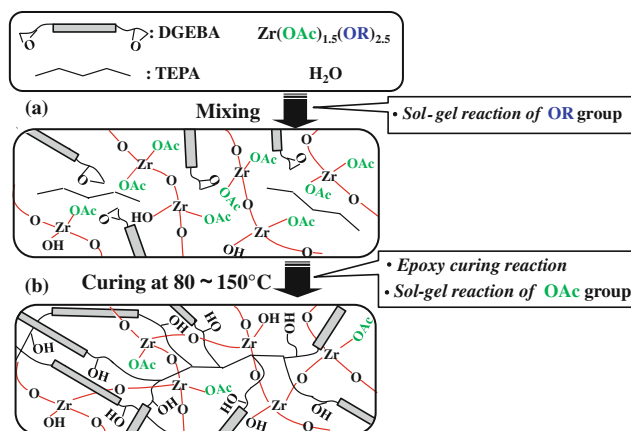


Fig. 3 Epoxy conversion and peak intensity change in the epoxy/zirconia hybrid systems based on the FT-IR spectra in the curing process. Filled circle epoxy conversion, cross $-\text{COO}^-$, triangle Zr-O-Zr



Scheme 1 Contemplated reaction of epoxy/zirconia hybrid systems

Moreover, the conversion of the epoxy group increased with the curing reaction. This means that the epoxy and zirconia network were almost simultaneously constructed to form the hybrid systems.

The following is qualitatively predicted by result of FT-IR measurement. The acetic acid-modified zirconium alkoxide has two different kinds of side chain group, OR and OAc. Before curing, the alkoxide group with a high reactivity already initiated the sol-gel reaction. However, the formation of zirconia agglutination is prevented by the presence of the coordinated group (acetate group) with a low reactivity (Scheme 1a). In the high temperature curing process, the sol-gel reaction of the acetate group and epoxy curing reaction proceed at the nearly same time. It seems that the formation of the epoxy network should prevent the agglutination of only the zirconia network.

Morphology of epoxy/zirconia hybrid materials

Figure 4 are optical photographs of the epoxy/zirconia hybrid materials. The prepared hybrid materials using the unmodified zirconium alkoxide caused a macrophase separation, i.e., large zirconia particles. This result is due to agglutinate zirconia before the epoxy curing reaction. On the other hand, the hybrid materials prepared using the acetic acid-modified zirconium alkoxide exhibited an excellent optical transparency regardless of the zirconia contents. Generally, to prepare transparent hybrid materials, the dimension of the inhomogeneity needs to be less than one-tenth the wavelength of light, i.e., about 50 nm. For this reason, it is expected that the prepared hybrid materials in this report do not exhibit a separated structure exceeding 50 nm.

To investigate the phase structure in detail, unmodified epoxy resin and several hybrid materials with different zirconia contents from 6.9 to 18.4 wt% were used as

Fig. 4 Optical photographs of epoxy/zirconia hybrid systems. ZrO₂ content (wt%); **a** 0, **b** 6.9, **c** 13.0, **d** 18.4

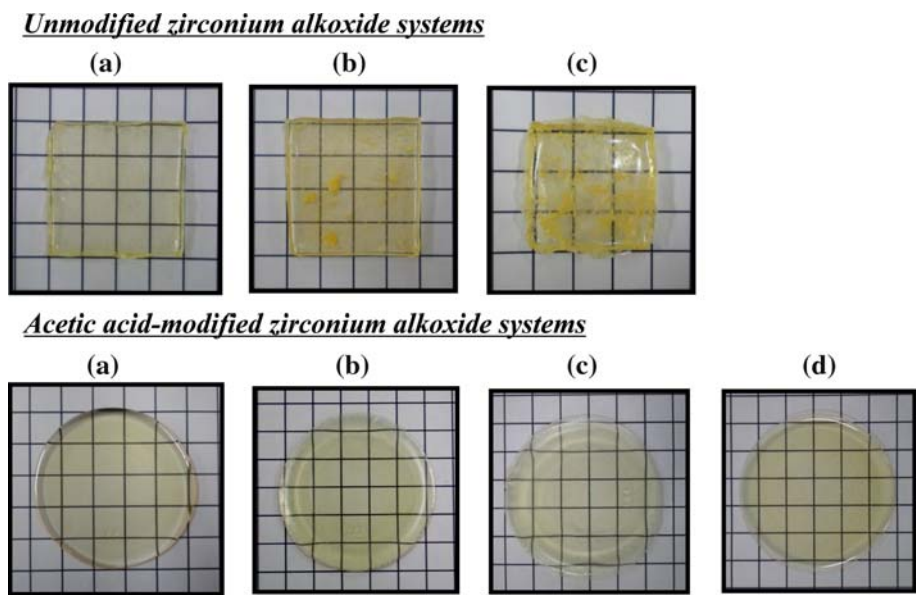
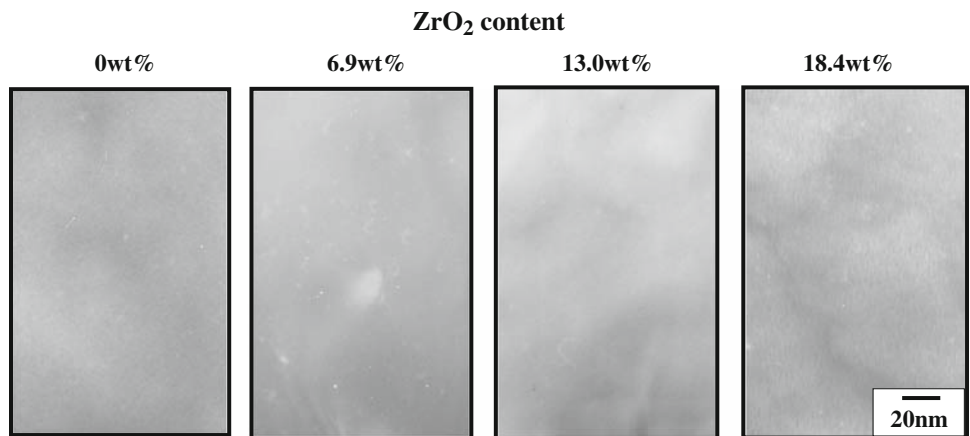


Fig. 5 TEM images of epoxy/zirconia hybrid systems



samples for the TEM observations. Figure 5 shows the morphology of the hybrid materials identified by TEM. All systems showed a homogeneous phase structure over the entire area regardless of the zirconia contents. This result means that the zirconia network is uniformly dispersed in the epoxy matrix on a molecular level. Namely, the dispersibility of zirconia was improved by controlling the reactivity of the zirconium alkoxide with acetic acid during the in situ polymerization, thus the aggregate of zirconia was not formed in the epoxy/zirconia hybrid materials synthesized from the coordinated zirconium alkoxide.

Thermal properties of epoxy/zirconia hybrid materials

The temperature dependence of the dynamic mechanical properties of the epoxy/zirconia hybrid materials containing different amounts of zirconia is shown in Fig. 6. In the unmodified system, the storage modulus clearly decreased in the glass transition region (T_g) and showed a very low

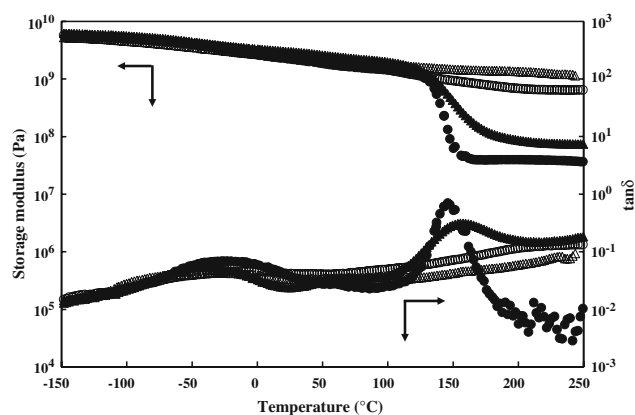


Fig. 6 Dynamic mechanical properties of epoxy/zirconia hybrid systems. ZrO₂ content (wt%); filled circle 0, filled triangle 6.9, open circle 13.0, open triangle 18.4

value in the rubbery region. It is well known that the decrease of the modulus in the T_g region is due to the micro-Brownian motion of the network chain. However, in

the hybrid systems, the modulus in the rubbery region increased with an increase in the zirconia contents and thus the glass transition behavior became indistinct. This result shows that the micro-Brownian motion of the epoxy network is strongly restricted by the hybridization with the zirconia network. The storage modulus of the hybrid systems with over 13.0 wt% zirconia showed no decrease in the glass transition and maintained at a high value even in the high temperature region over 200 °C. This means that the heat resistance of the cured epoxy resin is significantly improved by hybridization with the zirconia network and the hybrid materials could maintain the glassy state up to their decomposition temperature.

It is well known that the cured epoxy resin clearly shows a large $\tan\delta$ peak in the glass transition region. Also, in this study, the unmodified epoxy system showed a large $\tan\delta$ peak in the glass transition region. However, the peak area of $\tan\delta$ at the glass transition temperature decreased and shifted to a high temperature in the hybrid systems. These results show that the zirconia network coexists with the epoxy network on a molecular level and the motion of the network chains is strongly restricted in the epoxy/zirconia hybrids.

In addition, the unmodified epoxy system clearly exhibited β relaxation around -30 °C. This relaxation is attributed to the motion of the hydroxyether portion that is formed by the ring-opening of epoxy groups that occurred in the curing process of the epoxy resin [18]. On the other hand, the relaxation around -30 °C decreased in the hybrid systems. This result means that, in the hybrid systems, the zirconia network interacts with the hydroxyl groups through the condensation reaction with the alkoxide group.

Optical properties of epoxy/zirconia hybrid materials

Figure 7 shows the refractive indices and abbe's number of the epoxy/zirconia hybrid materials prepared at different zirconia contents. The refractive indices linearly increased

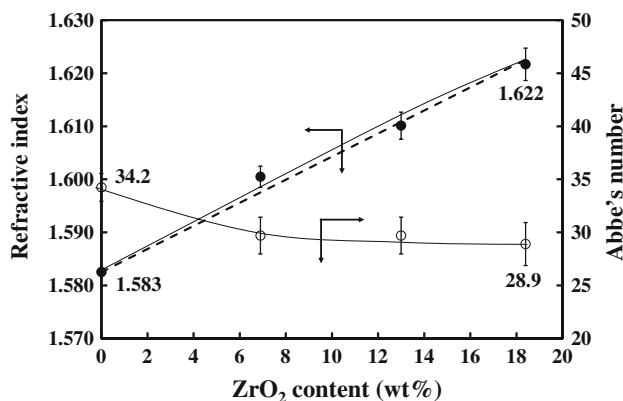


Fig. 7 Refractive indices and abbe's number of epoxy/zirconia hybrid. *Dashed line* calculated line based on the additive law

with an increase in the zirconia contents, and achieved 1.621 at 18.4 wt%. The amorphous zirconia prepared via the sol–gel reaction has a refractive index of about 1.8 [19]. The increase in the refractive index by the hybridization with the zirconia network is due to the homogeneously dispersed zirconia network, which has a high refractive index in the epoxy matrix. In addition, increasing the rate of the refractive index well agreed with the theoretical value based on the additive law.

On the other hand, abbe's number, which means the dependence of the refractive index on the measuring frequency, decreased from 34.2 to 28.9 with the increasing zirconia content. This is attributed to the fact that zirconia has a high dispersibility of the refractive index. Lee et al. [10] described that the optical dispersion is significantly affected by the size of the inorganic segment. In the prepared hybrid materials, the zirconia network is uniformly dispersed in the epoxy matrix on molecular level. Therefore, the reduction rate of abbe's number was small, and the measured value of the hybrid materials was indicated to be close to the required value of 30 for commercial application [20].

Moreover, the relationship between the refractive index and the zirconia content is the reverse of the trend for abbe's number. This suggests that the optical properties of the prepared hybrid materials can be tuned through their molecular compositions.

Conclusions

Novel epoxy/zirconia hybrid materials were synthesized via in situ polymerization using the acetic acid-modified zirconium alkoxide. The epoxy curing and sol–gel reaction proceed at the same time by reducing the alkoxide group with a high reactivity. Thus, the agglutination of only the zirconia network was prevented and the zirconia network was uniformly dispersed in the epoxy matrix on molecular level. Also, the motion of network chains is strongly restricted in the epoxy/zirconia hybrids by dispersing the zirconia network on a molecular level. As a result, with the increasing zirconia contents, the storage modulus in the high temperature region increased and the glass transition temperature of the hybrid materials shifted to a higher temperature. Moreover, the refractive indices of the hybrid materials achieved 1.621 at 18.4 wt%. This result is due to the uniform dispersion of the zirconia network.

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