

Effect of acetic acid content on in situ preparation of epoxy/zirconia hybrid materials

Mitsukazu Ochi · Daisuke Nii · Miyuki Harada

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Abstract Epoxy/zirconia hybrid materials were synthesized via in situ polymerization of acetic acid-modified zirconium alkoxide. The reactivity of acetic acid-modified zirconium alkoxide changed with the amount of acetic acid added. In the hybrid materials, the phase structure varied between the homogeneous phase and nanophase separation as the reactivity of zirconium alkoxide changed. At the molecular level, the storage modulus in the rubbery region significantly increased and the peak area of $\tan \delta$ in the glass-transition temperature region decreased with increasing zirconia contents in the hybrid dispersed zirconia. Additionally, the optical properties of the hybrid materials in the homogeneous phase were better than those in the system with nanophase separation.

Introduction

Organic–inorganic hybrid materials have recently attracted increasing attention because of their unique physical and chemical properties, which result from the combination of organic and inorganic materials in a single compound. These materials possess enhanced mechanical, magnetic, and optoelectronic properties [1–4]. Hybrid materials can be prepared by incorporating, on molecular or nanometer scale, inorganic nanoparticles or fillers into the polymer matrix. The sol/gel process is a method for preparing inorganic polymers at low temperature. Using the sol/gel process, we were able to combine organic substances that

would be decomposed at a relatively low temperature with inorganic substances that have a high-heat resistance. We previously reported the preparation of epoxy/silica hybrid materials from an epoxy resin and silane alkoxide via a sol–gel process, demonstrating that these hybrid materials had a good thermal property [5, 6].

Light emitting diodes (LEDs) have also generated considerable interest in terms of their application to products such as traffic signals, outdoor displays, and back lighting in liquid–crystal displays. Thus, transparent materials with a high-refractive index are desirable for the encapsulation of the LED [7–12]. 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. Titania (TiO_2) and zirconia (ZrO_2) are widely used as dopants for modification of the properties of optical materials due to their exceptional properties, such as their high-refractive index and excellent chemical and mechanical stability [9, 13–16]. However, the rates of the sol–gel reaction of titanium and zirconium alkoxides are significantly different from that of silane alkoxide. Specifically, titanium and zirconium alkoxides are generally highly reactive with water, thus it is difficult to prepare hybrid materials containing these compounds without the formation of clusters. We previously reported that epoxy/zirconia hybrid materials with high thermal properties and a high-refractive index were synthesized via in situ polymerization using acetic acid-modified zirconium alkoxide [17]. In addition, acetic acid could be used to control the reaction rate of the sol–gel reaction in zirconium alkoxide to be much faster than that of epoxy curing.

In this study, epoxy/zirconia hybrid materials were synthesized via in situ polymerization using zirconium

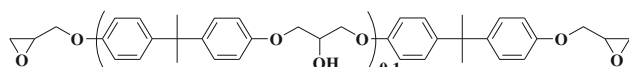
M. Ochi (✉) · D. Nii · M. Harada
Faculty of Chemistry, Materials and Bioengineering,
Kansai University, 3-3-35 Suita-shi, Osaka 564-8680, Japan
e-mail: mochi@ipc.ku.kansai-u.ac.jp

alkoxide that was modified with different amounts of acetic acid. Moreover, the effects of acetic acid content on the thermal and optical properties and the phase structure of the hybrid materials were investigated in detail.

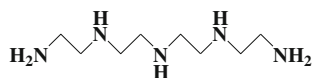
Experimental procedure

Materials

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



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



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., Japan).

Preparation of acetic acid-modified zirconium alkoxide

Acetic acid was mixed with zirconium-tetra-*n*-propoxide at different mol ratios up to 1.5 per zirconium alkoxide (hereafter abbreviated as *n*). The mixtures were then stirred at room temperature for 1 h to promote the reaction. An exothermic reaction occurred, and a clear solution was obtained.

Preparation of epoxy/zirconia hybrid materials

The acetic acid-modified zirconium alkoxide solution was added to DGEBA as the inorganic source while stirring at 40 °C. In addition, two moles of H₂O per mole of zirconium alkoxide and a stoichiometric amount of TEPA as the curing agent for the epoxy group were added, after which the mixtures were stirred to obtain homogeneous solutions that were subsequently poured into an aluminum container to prepare the epoxy/zirconia hybrid plates. The compounds were then precured to remove the by-products at 80 °C for 4 h in vacuo. Then, the compounds were cured at 100 and 150 °C for 4 h during each curing step. Table 1 lists the starting composition and percentage of zirconia (wt%) in the hybrid materials as determined by TGA (described below).

Measurement

The weight percentage of zirconia in the hybrid materials was determined by TGA (TG/DTA 6200, Seiko Instruments Co., Ltd.) via heating in the air from 100 to 800 °C at a rate of 20 °C min⁻¹. Because the organic component appeared 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 reaction products were conducted by FT-IR (Spectrum 2000, Perkin-Elmer Co., Ltd.) measurements.

The ultra-thin 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 nonresonance forced vibration viscoelastometer (DVE-V4, Rheology Co., Ltd.)

Table 1 Compositions 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

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 $250 \text{ }^\circ\text{C}$ and the heating rate was $2 \text{ }^\circ\text{C min}^{-1}$.

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

The UV-vis spectra of the hybrid materials were obtained using an ultraviolet-visible spectrophotometer (LAMBDA 650, Perkin Elmer Co., Ltd.).

Results and discussion

Preparation of acetic acid-modified zirconium alkoxide with different acetic acid contents

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 characteristic bands of C=O stretching (monomer) around 1756 cm^{-1} , and C=O stretching (dimer) around 1725 cm^{-1} . The reaction product from the above compounds exhibited a new set of bands around 1560 and 1460 cm^{-1} that were ascribed to the

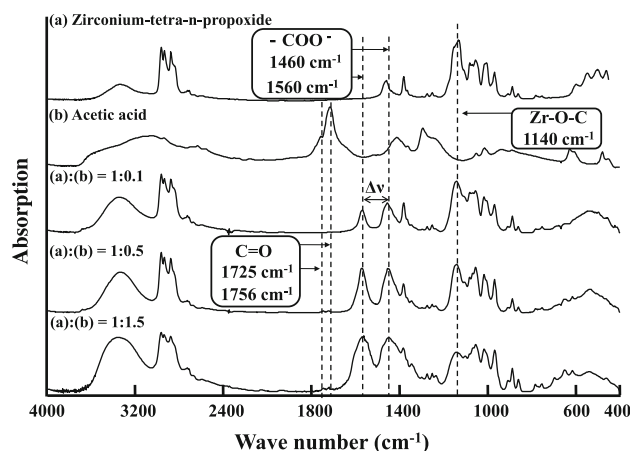
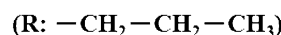


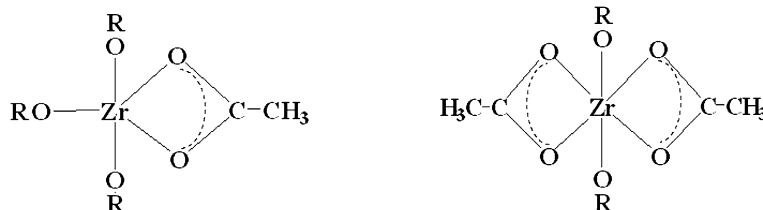
Fig. 1 FT-IR spectra of zirconium alkoxide, the modifier, and their reaction product

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 CH_3COO^- acts as a bidentate chelating coordination mode [18]. 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 as the acetic acid content increased. These results suggested that the added acetic acid reacted completely with the zirconium alkoxide as follows:

Reaction of zirconium alkoxide and acetic acid



Coordination mode



acetate ligand because the antisymmetric stretching of the $-\text{COO}^-$ vibration (ν_{asym}) at 1560 cm^{-1} and the symmetric stretching of the $-\text{COO}^-$ vibration (ν_{sym}) at 1460 cm^{-1} corresponded to the bidentate acetate ligand linked to the zirconium. In addition, the intensity of these bands increased as the amount of acetic acid added increased. These results suggested that the amount of acetate ligand was increased in the reaction products. The acetate group

Chelating ligands could link more strongly to zirconium than to the alkoxide group; thus, the coordination with acetic acid could decrease the reactivity of the zirconium. Additionally, acetic acid can substitute up to two alkoxy groups of the zirconium alkoxide molecule [19]. As a result, the reaction product is a mixture of monosubstituted and disubstituted derivatives, and the ratio of these two derivatives changes with the amount of acetic acid added.

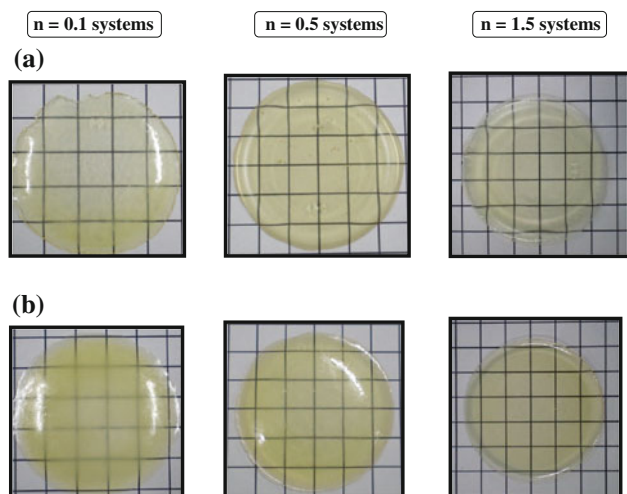


Fig. 2 Optical photographs of the epoxy/zirconia hybrid systems. ZrO_2 content (wt%): **a** 13 and **b** 18.4

Effect of acetic acid content on the morphology of epoxy/zirconia hybrid materials

Figure 2 shows the optical photographs of the epoxy/zirconia hybrid materials with different acetic acid contents (one grid is $10\text{ mm} \times 10\text{ mm}$ and thickness of all samples is 1.5 mm). In the case of $n = 0.1$, opaque hybrid materials were obtained. However, the prepared hybrid systems with $n = 0.5$ or 1.5 exhibited an excellent optical transparency, regardless of the zirconia contents. Generally, the transparency of the hybrid materials is affected by the dimension of the inhomogeneity; therefore, the acetic acid content might affect the dispersibility of the zirconia network.

To investigate the phase structure in detail, the hybrid materials with different acetic acid contents were used as samples for the TEM observations. Figure 3 shows the morphology of the hybrid materials identified by TEM. In the case of $n = 0.1$, dark aggregates (approximately 60 nm) in which the zirconia network was highly concentrated were observed. When the dimension of the inhomogeneity is larger than one-tenth of the wavelength of light, i.e., approximately 50 nm, the hybrid materials become opaque. Therefore, hybrid materials with $n = 0.1$ have poor transparency (Fig. 2). As the acetic acid content increased, the size of the aggregates decreased. In the case of $n = 1.5$, the hybrid system showed a homogeneous phase structure over the entire area, regardless of the zirconia contents. These results indicate that the zirconia network is uniformly dispersed in the epoxy matrix at the molecular level.

In a previous study [17], we reported that the alkoxide group of zirconium alkoxide had such high reactivity that a zirconia network formed before epoxy curing, and that the epoxy curing and sol–gel reaction could proceed at the same time by reducing the reactivity of the alkoxide group.

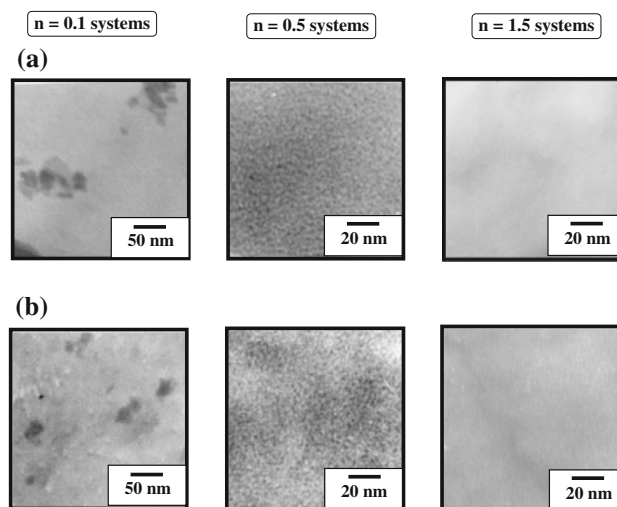


Fig. 3 TEM images of epoxy/zirconia hybrid systems. ZrO_2 content (wt%): **a** 13, **b** 18.4

Figure 4 shows the FT-IR spectra of the hybrid systems before curing. A set of bands around 1560 and 1460 cm^{-1} corresponding to the bidentate acetate ligand linked to zirconium increased as the acetic acid content increased. On the other hand, the band around 1140 cm^{-1} corresponding to the Zr–O–C vibrations of alkoxy groups directly bonded to zirconium was not observed in any systems. In addition, the intensity of a broad band at 460 cm^{-1} corresponding to Zr–O–Zr decreased as the acetic acid content increased from 0.1 to 1.5. These results indicated that the amount of Zr–O–Zr network before curing was changed by the acetic acid content. Therefore, formation of zirconia aggregations was prevented by the increasing acetic acid content. In other words, the dispersibility of the zirconia network was controlled by suppressing the reactivity of the zirconium alkoxide with acetic acid during the in situ polymerization.

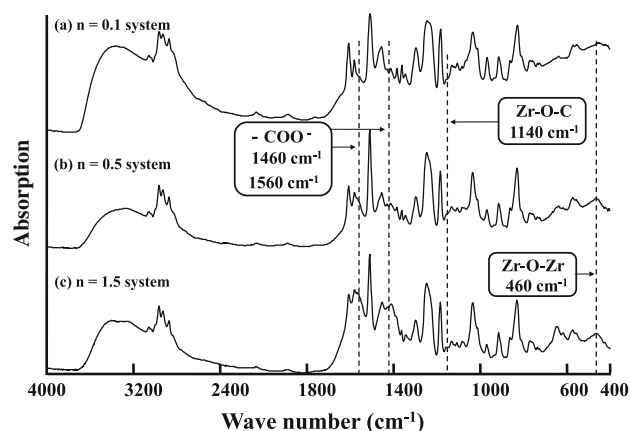


Fig. 4 FT-IR spectra of epoxy/zirconia hybrid systems before curing (ZrO_2 content 18.4 wt%)

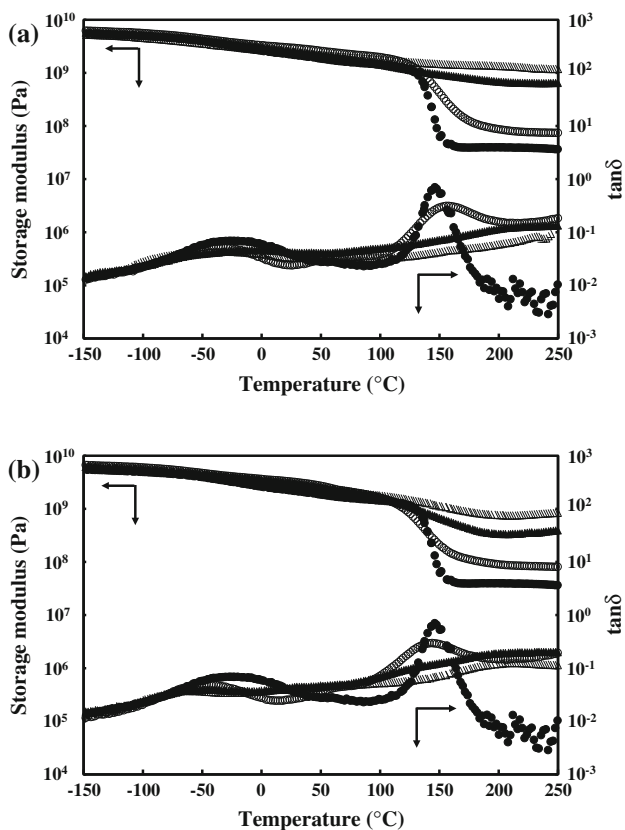


Fig. 5 **a** Dynamic mechanical properties of epoxy/zirconia hybrid systems ($n = 1.5$). ZrO_2 content (wt%): filled circle, 0; open circle, 6.9; filled triangle, 13.0; and open triangle, 18.4. **b** Dynamic mechanical properties of epoxy/zirconia hybrid systems ($n = 0.1$). ZrO_2 content (wt%): filled circle, 0; open circle, 6.9; filled triangle, 13.0; and open triangle, 18.4

Thermal properties of epoxy/zirconia hybrid materials

The temperature dependence of the dynamic mechanical properties of the epoxy/zirconia hybrid materials is shown in Fig. 5(a, b). In the system without zirconia, the storage modulus clearly decreased in the glass-transition (T_g) region and showed a very low 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 hybrid systems, the modulus in the rubbery region increased as the zirconia contents increased, regardless of the acetic acid contents, which led to the glass-transition behavior becoming indistinct. This result shows that the micro-Brownian motion of the epoxy network is strongly restricted by hybridization with the zirconia network. The storage modulus of hybrid systems with over 13.0 wt% zirconia showed no decrease in glass transition and was maintained at a high value, even at temperatures over 200 °C. This means that the heat resistance of the cured epoxy resin is significantly improved by hybridization with the zirconia network and that the hybrid

materials could maintain a glassy state up to their decomposition temperature.

It is well known that cured epoxy resin clearly shows a large $\tan \delta$ peak in the glass-transition region. In addition, the unmodified epoxy system showed a large $\tan \delta$ peak in the glass-transition region in this study. 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 and that the motion of the network chains is strongly restricted in the epoxy/zirconia hybrids.

In addition, the system without zirconia clearly exhibited β relaxation around -30 °C. This relaxation can be attributed to the motion of the hydroxyether portion that is formed by the ring-opening of epoxy groups during curing of the epoxy resin [20]. Moreover, the relaxation around -30 °C decreased in the hybrid systems, which indicates that in the hybrid systems the zirconia network interacts with the hydroxyl groups in the hydroxyether portion through a condensation reaction with the alkoxide group. Conversely, the storage modulus of hybrid systems with $n = 0.1$ (Fig. 5b) decreased at lower temperatures when compared with that of the system with $n = 1.5$ (Fig. 5a). As previously indicated, the nanometer-order inorganic phase was clearly separated in the epoxy resin matrix. Therefore, the portion of the epoxy network restricted by zirconia was less than that in the hybrid materials containing zirconia that was dispersed at the molecular level. For this reason, the hybrid materials containing zirconia dispersed at the molecular level have a better transparency and thermal properties.

Optical properties of epoxy/zirconia hybrid materials

Figure 6 shows the refractive indices and Abbe’s number of the epoxy/zirconia hybrid materials containing different amounts of acetic acid. The refractive indices increased linearly as the zirconia contents increased, regardless of the

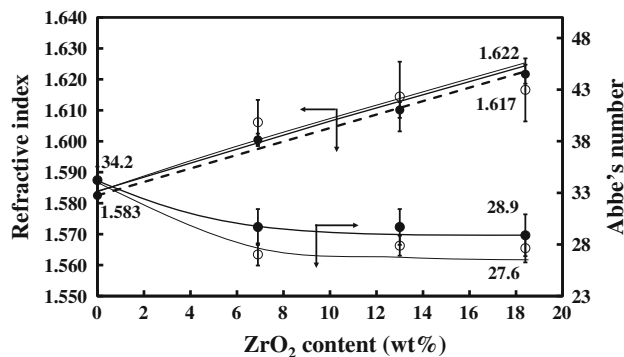


Fig. 6 Refractive indices and Abbe’s number of epoxy/zirconia hybrid systems. (Dotted lines) Values calculated on the basis of the additive law. Filled symbol: $n = 1.5$ systems, open symbol: $n = 0.1$ systems

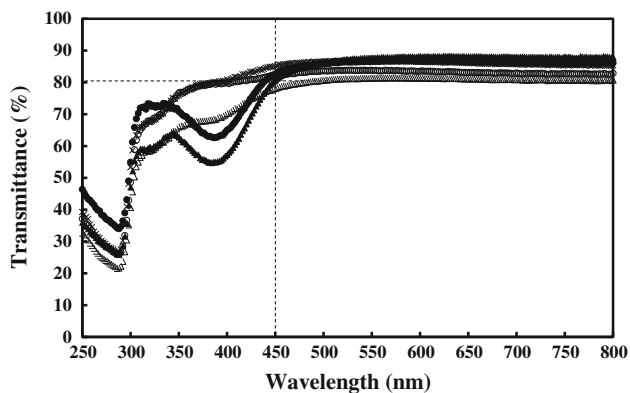


Fig. 7 UV-vis spectra of the epoxy/zirconia hybrid systems. ZrO_2 content (wt%): *times symbol* 0; *circle*, 6.9; and *triangle*, 18.4. *Filled symbol*: $n = 1.5$ systems, *open symbol*: $n = 0.1$ systems

acetic acid contents, with levels of 1.62 at 18.4 wt% eventually being obtained. The amorphous zirconia prepared via the sol-gel reaction has a refractive index of about 1.8 [21]. The increase in the refractive index in response to hybridization with the zirconia network is due to the dispersed zirconia network, which has a high-refractive index in the epoxy matrix. In addition, the increasing rate of the refractive index agreed well with the theoretical value based on the additive law. Also, in case of $n = 1.5$, transparent hybrid materials could be prepared over 20 wt%. However, by-products of sol-gel reaction remaining into epoxy matrix, negatively affect properties of the hybrid materials, are increased and refractive index of the hybrid material was lower than theoretical value based on the additive law. Thus, there was not a great difference in the refractive index as a result of changing the phase structure.

On the other hand, Abbe's number, which is the dependence of the refractive index on the measuring frequency, decreased with increasing zirconia content. This can be attributed to the fact that zirconia has a high dispersibility. In addition, the reduction rate of Abbe's number differed greatly between the hybrid materials with a homogeneous phase structure ($n = 1.5$) and those with a nano separation structure ($n = 0.1$). Lee and Chen found that optical dispersion was significantly influenced by the size of the inorganic segment [11]. In case of $n = 1.5$, the zirconia network is uniformly dispersed in the epoxy matrix at the molecular level; therefore, the reduction rate of Abbe's number was smaller than in case of $n = 0.1$. These results suggest that the optical properties of the prepared hybrid materials can be tuned through their phase structure and molecular compositions.

Figure 7 shows the UV-Vis transmittance spectra of the epoxy/zirconia hybrid materials with different acetic acid contents. In the near-ultraviolet range (300–450 nm), the

transmittance of the hybrid materials decreased with increasing zirconia contents, regardless of the acetic acid contents. These findings indicate that amorphous zirconia introduced into the epoxy matrix had an absorption band at 300–450 nm [22]. In fact, the hybrid systems with $n = 1.5$ had an absorption band at about 382 nm, which corresponded to coordination of the acetic acid to zirconium [23]. These results suggest that some acetate ion coordinated to zirconium remained in the hybrid systems. For this reason, the hybrid materials were stained slightly yellow (Fig. 2). However, in the field of LED encapsulation, wavelengths greater than 450 nm are more important. Only in the hybrid systems with a homogeneous phase structure ($n = 1.5$) was the transmittance at wavelengths higher than 450 nm greater than 80%. This is attributed to the fact that zirconia is uniformly dispersed in the epoxy matrix at the molecular level.

Conclusions

The effects of acetic acid content on the in situ preparation of epoxy/zirconia hybrid materials were investigated in this study. The dispersibility of the zirconia network in the epoxy matrix was controlled by changing the amount of acetic acid added during in situ polymerization. This was attributed to the amount of residual alkoxide groups that developed during the sol-gel reaction to form a three dimensionally bridged gel before epoxy curing. Moreover, the thermal and optical properties of the hybrid materials were affected by their phase structure. When compared with the nano phase separation structure, the hybrid materials containing zirconia dispersed at the molecular level maintained a high storage modulus in the rubbery region at higher temperatures. In addition, the reduction rate of transmittance and Abbe's number was suppressed, even though a great difference in the refractive index was not observed.

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