

Photocurable Transparent Cycloaliphatic Epoxy Hybrid Materials Crosslinked by Oxetane

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ABSTRACT: Organic/inorganic hybrid materials (hybrimers) were fabricated by the photocationic polymerization of sol-gel-derived cycloaliphatic epoxy oligosiloxane (CAEO)/oxetane blends. The CAEO/oxetane blends showed faster photocationic polymerization rates compared to a CAEO resin. The CAEO/oxetane hybrimers showed a high crosslinking density and flexibility with the addition of oxetane monomer. The increased crosslinking density improved the insulation properties and lowered

their dielectric constant. The CAEO/oxetane hybrimer with a substantial thickness of 2 mm showed high transparency (>90%) in the visible range. On the basis of these properties, the CAEO/oxetane hybrimers could be applied to various applications, including optics and display fields. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: cationic polymerization; curing of polymers; oligomers; monomers; glass transition

INTRODUCTION

The photocationic polymerization of epoxides has two distinct features compared to the photoradical polymerization of acrylates: a lack of sensitivity toward oxygen and a living character. Also, crosslinked polymers prepared by the photocationic polymerization of epoxides have outstanding properties, including a low shrinkage, high thermal capability, excellent adhesion to various substrates, and good chemical resistance, compared to those fabricated by the photoradical polymerization of acrylates. To exploit these advantages, the photocationic polymerization of epoxides has been applied in various industrial fields. However, their application fields have been limited because of their relatively low curing speed, high cost of precursors, and limited variety of raw materials. In particular, the low curing speed of the photocationic polymerization of epoxides has been seen as an obstacle for new application fields.¹ To date, there have been extensive studies in the search for new catalysts, additives,

and intermediates to overcome this low curing speed.^{2–14}

Oxetanes have a high ring strain, similar to that of epoxides, and their heterocyclic oxygens have a higher basicity compared to the oxirane oxygens in epoxides.¹⁵ The higher basicity of the heterocyclic oxygen in oxetane makes the oxetanes more reactive than epoxides during photocationic polymerizations. However, despite the high reactivity, oxetanes are generally used with epoxides because of their long induction period compared to epoxides in the early stage of polymerization.¹⁶ Given this theoretical background, improved curing speeds in epoxide/oxetane hybrid systems have been reported by many researchers.^{12,13}

Recently, we reported an organic/inorganic hybrid material (hybrimer) fabricated by the photocationic polymerization of sol-gel-derived cycloaliphatic epoxy oligosiloxane (CAEO) resins with a high viscosity. Because of the high transparency, photopatternability, and excellent gas barrier properties, CAEO hybrimers have been used in manifold applications, such as encapsulants for organic light-emitting diodes.^{17–19} However, the low photocationic polymerization speed of cycloaliphatic epoxy groups and the limited crosslinking density of CAEO hybrimers, originating from the high viscosity of the CAEO resin, can degrade the basic physical properties of CAEO hybrimers.

In this study, we investigated the photocationic polymerization behavior of CAEO resins with the addition of a difunctional oxetane monomer to study the effects on the photocationic polymerization speed. The addition of the difunctional oxetane

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TABLE I
Formations and Notations of the CAEO/DOX Resins

Sample	Weight ratio (equivalent molar ratio)		Catalyst content (to mixed resin)
	CAEO	DOX	
CAEO	1.0 (1.00)	0.0 (0.00)	2 wt %
CAEO/DOX10	1.0 (0.71)	0.1 (0.29)	
CAEO/DOX20	1.0 (0.56)	0.2 (0.44)	
CAEO/DOX30	1.0 (0.45)	0.3 (0.55)	
CAEO/DOX100	1.0 (0.20)	1.0 (0.80)	
DOX	0.0 (0.00)	1.0 (1.00)	

monomer into the CAEO hybrimer was expected to provide enhancements not only in the overall curing efficiency but also in the characteristic properties of the CAEO hybrimer. Multiple tools, such as a dynamic mechanical analyzer, a room-temperature mechanical bending test, a source measure unit, and an impedance/gain analyzer, were used to check variations in the thermophysical and electrical properties of the CAEO hybrimer in the presence of oxetane monomer. On the basis of these improved properties, we confirmed that the CAEO hybrimer could be used in various application fields.

EXPERIMENTAL

Preparation of the CAEO/DOX resins

CAEO/DOX resins were prepared to evaluate the photosensitivity and viscosity of the resins. The CAEO resin was synthesized via a nonhydrolytic sol-gel reaction between 0.01 mol of 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (Gelest, Morrisville,

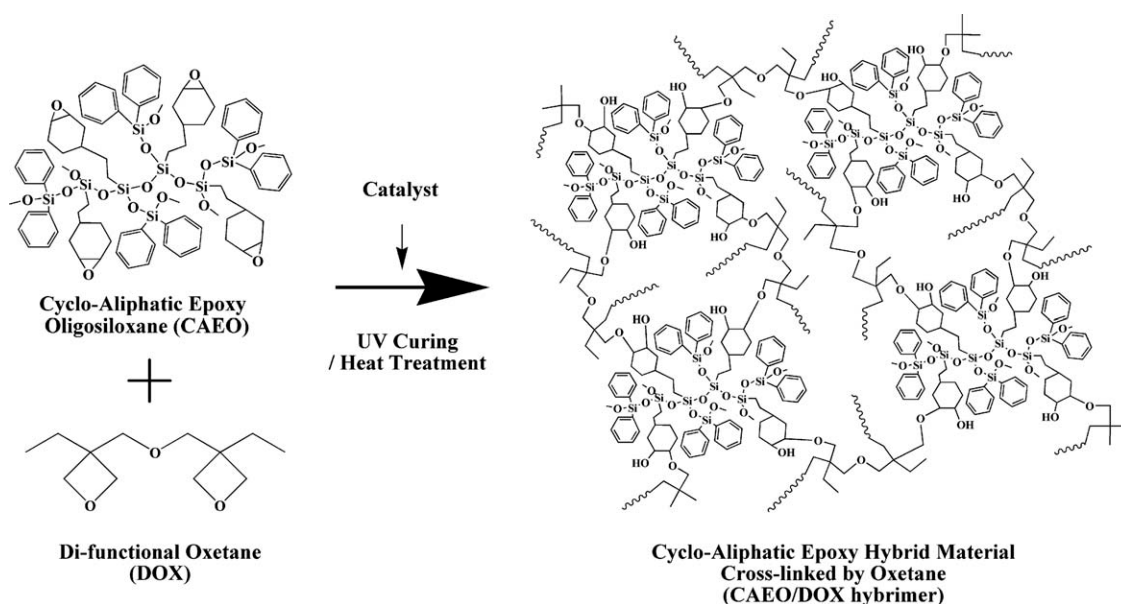
PA) and 0.01 mol of diphenylsilanediol (Gelest) with a previously reported synthesis method.¹⁷ 3-Ethyl-3{[(3-ethyloxetane-3-yl)methoxy]methyl} oxetane (DOX; Toagosei, Tokyo, Japan) was mixed with the CAEO resin, and the weight ratio between the CAEO resin and DOX is listed in Table I. Triarylsulfonium hexafluoroantimonate salts of 2 wt% (Aldrich, St. Louis, MO) was added as a catalyst for the photocationic polymerization. The formulations and notations of each resin are summarized in Table I.

Characterization of the CAEO/DOX resins

The viscosity of the resins was measured at 25°C with a rheometer (DV-III+, Brookfield Engineering Laboratories, Inc., Middleboro, MA). The photosensitivity of each resin was characterized by a differential scanning calorimeter (DSC Q2000, TA Instruments, New Castle, DE) equipped with a photocalorimeter accessory (high-pressure mercury lamp, TA Instruments). Each sample (3–4 mg) was loaded to an aluminum pan and irradiated by ultraviolet (UV) light under a dry-air atmosphere. The light intensity was adjusted to 20 mW/cm², and a light wavelength of 250–650 nm was transformed to a wavelength of 250–450 nm with a UV broadband filter.

Fabrication of the CAEO/DOX hybriders

The CAEO/DOX hybriders were fabricated by the photocationic polymerization of CAEO/DOX resins. The CAEO/DOX resins were irradiated with UV light for 10 min with a Hg lamp (80 mW/cm², 365 nm, 97453, Oriel Instruments, Stratford, CT) under an air condition to obtain samples with various



Scheme 1 Fabrication of the CAEO/DOX hybrid material by photocationic polymerization.

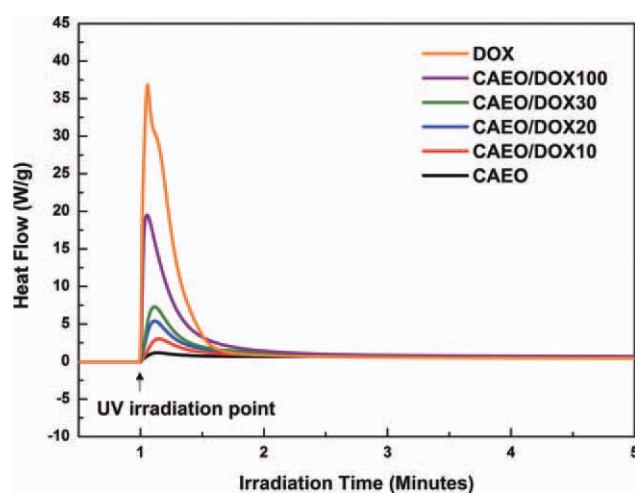


Figure 1 Photo DSC exothermic curves of the CAEO/DOX resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dimensions for the measurements of various physical properties. Sequentially, the UV-cured samples were thermally cured at 150°C for 2 h under an air condition for the promotion of polymerization. The fabrication scheme is shown in Scheme 1.

Characterization of the CAEO/DOX hybrimers

The dynamic mechanical responses of the fabricated samples were assessed with a dynamic mechanical analyzer (DMA 2980, TA Instruments). The storage modulus (E') and $\tan \delta$ were measured within a temperature range of -70 to 200°C at a ramp rate of $5^\circ\text{C}/\text{min}$. The vibratory offset force was fixed at 0.01 N at a frequency of 1 Hz. A three-point loading test of the fabricated samples was carried out in the atmosphere at a temperature of $23 \pm 2^\circ\text{C}$ and a humidity of $50 \pm 5\%$. The crosshead speed and support span of the testing machine (5583, Instron Co., Norwood, MA) were 0.8 mm/min and 25 mm, respectively. The sample dimensions for the three-point loading test were determined by ASTM D790-92. Also, the stress-strain curves of the fabricated samples were obtained from load-deflection curves plotted from the results of the three-point bending test. The electrical properties of the fabricated samples, including the leakage current density and dielectric constant, were measured with Au/sample film/indium tin oxide structures with a Keithley 237 source measure unit (Keithley Instruments, Inc., Cleveland, OH) and an HP4194A impedance/gain analyzer (Agilent Technologies, Santa Clara, CA). CAEO and the CAEO/DOX20 resins were diluted with propylene glycol methyl ether acetate (98%, Aldrich) to fabricate thin-film samples. The thickness of each film was approximately 300 nm. The transparency of a 2 mm thick CAEO and the CAEO/

DOX20 hybrimers was measured in a wavelength range between 300 and 800 nm with a UV-visible-near infrared spectrophotometer (UV3101PC, Shimadzu, Kyoto, Japan).

RESULTS AND DISCUSSION

Photosensitivity of the CAEO/DOX resins

Photo differential scanning calorimetry (DSC) characterization of the CAEO/DOX resins as a function of the DOX content, as shown in Figure 1, was performed to confirm the photocationic polymerization behavior of the resin. The CAEO resin without the addition of DOX showed a very small exothermic energy (14.33 J/g) in the early stage of irradiation, which, thereby, lasted for a long period of irradiation during photocationic polymerization. This weak and broad exothermic peak originated from the degraded mobility of the cycloaliphatic epoxy groups because of the high viscosity of the CAEO resin ($\sim 43,750$ mPa s at 25°C). On the other hand, the exothermic curves and exothermic energy of the CAEO/DOX resins became sharper and larger with increasing DOX content, respectively (Table II), and the exothermic curves decreased smoothly after the maximum exothermic peak point. In the case of the CAEO and CAEO/DOX20 resins, the exothermic energy (106.4 J/g) in the early stage of irradiation was much larger than that of the CAEO resin (14.33 J/g), despite the equilibrium weight formation between the CAEO resin and DOX in the CAEO/DOX20 resin. This indicated a faster photocationic polymerization speed of the CAEO/DOX resins with the addition of DOX. This result was due to the high basicity of the oxetane ring and the high mobility of the cycloaliphatic epoxy groups, which resulted from the low viscosity of the CAEO/DOX resins (Table II).

Physical properties of the CAEO/DOX hybrimers

Generally, most organic polymers have a drastic change in their glass-transition behaviors with heating compared to inorganic materials. In particular, when organic polymers are integrated with

TABLE II
Values of Exothermic Energy from Photo DSC and Viscosity of the CAEO/DOX Resins

Sample	Exothermic energy (J/g)	Viscosity (mPa s at 25°C)
CAEO	14.4	43,750
CAEO/DOX10	48.4	7,722
CAEO/DOX20	114.3	2,730
CAEO/DOX30	147.5	1,482
CAEO/DOX100	363.4	152
DOX	494.0	12

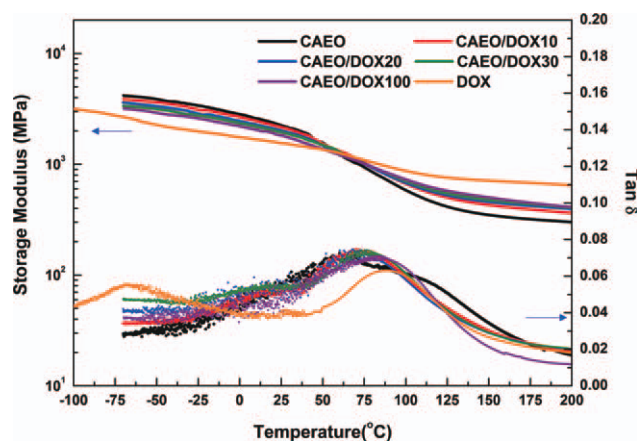


Figure 2 Storage modulus and $\tan \delta$ change values of the CAEO/DOX hybriders depending on the DOX content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

inorganic materials for practical applications, this drastic glass-transition change of organic materials can give rise to serious problems, such as delamination, which is related to the compatibility with the inorganic materials.

The glass-transition behavior of the CAEO/DOX hybriders was measured with dynamic mechanical analysis (DMA). Figure 2 and Table III present the storage modulus and $\tan \delta$ values of the CAEO/DOX hybriders of various compositions. DOX polymer fabricated with DOX, had two glass-transition temperatures (T_g 's), -68 and 90°C ; these corresponded to the β (or γ) transition and α transition of the DOX polymer, respectively.^{20,21} In particular, the DOX polymers showed a broad and weak glass-transition behavior over a wide temperature range before/after T_g , and a high storage modulus in the rubbery state. These DMA results of the DOX polymers indicated that the DOX polymers had a high crosslinking density, originating from the difunctional structure and low molecular weight of the DOX.^{22,23} Similarly, the CAEO hybrimer also showed broad and weak glass-transition behaviors over a wide temperature range; this was attributed to their high crosslinking density because of the

multifunctional structure and short siloxane chain of the CAEO.²⁴ It had two T_g points, which appeared at about 20 and 65°C ; these were correlated with the siloxane networks and the α transition of the organic networks, respectively. On the basis of the viscoelasticity of the two materials, noticeable features in these DMA results could be observed in the T_g and storage modulus values of the CAEO/DOX hybriders. As summarized in Figure 2 and Table III, the CAEO/DOX hybriders had a single T_g (α transition) in the temperature range between the T_g 's of the CAEO hybrimer and DOX polymer. This indicated that the CAEO/DOX hybriders had a homogeneous organic network, despite cationic polymerization between the different organic functional groups. Also, the CAEO/DOX hybriders showed a higher storage modulus at the rubbery state compared to the CAEO hybriders, regardless of their composition. This meant that the crosslinking density of the CAEO/DOX hybriders was enhanced compared to that of the CAEO hybrimer.^{22,23} Because the CAEO resin had a high viscosity and because of the low photocationic polymerization rate of the cycloaliphatic epoxy groups, unreacted cycloaliphatic epoxy groups could exist in the organic networks of the CAEO hybriders, despite the living characteristics of the cationic polymerization. On the other hand, DOX, which assisted the fast curing of the epoxides and had a low viscosity, led to the removal of these unreacted cycloaliphatic epoxy groups of the CAEO hybrimer. Therefore, the CAEO/DOX hybriders showed a higher storage modulus, originating from their higher crosslinking density, than the CAEO hybriders. The addition of the DOX broadened and weakened the glass-transition behaviors of the CAEO hybrimer.

Cycloaliphatic epoxy resins were introduced to satisfy other requirements of different properties compared to glycidyl ether epoxy resins. Polymers fabricated with cycloaliphatic epoxy resins are expected to have greater compressive and tensile strengths than those fabricated with glycidyl ether resins because of their rigid and rather brittle structure; this originates from the compact ring of

TABLE III
Thermomechanical/Mechanical Properties of the CAEO/DOX Hybriders

	E'_g (MPa)	E'_r (MPa)	T_g ($^\circ\text{C}$)	r (mm/mm)	S (MPa)	E (MPa)
CAEO	4165	302	65	0.025	38.09	1533.64
CAEO/DOX10	3855	364	73	0.025	38.90	1608.61
CAEO/DOX20	3600	397	73	0.028	43.19	1660.29
CAEO/DOX30	3371	406	76	0.034	47.47	1500.36
CAEO/DOX100	3182	409	83	0.037	49.40	1453.38
DOX	2666	648	90	0.096	64.71	937.73

E'_g , storage modulus in the glassy state (at -70°C); E'_r , storage modulus in the rubbery state (at 200°C); r , yield strain; S , yield stress; E , flexural modulus.

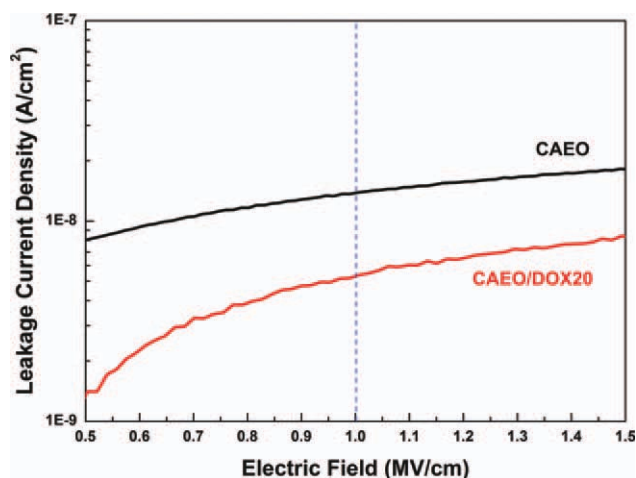


Figure 3 Leakage current density of the CAEO/DOX hybrimer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cycloaliphatics. However, the polymers fabricated with cycloaliphatic epoxy resins displayed lower flexural strengths relative to those fabricated with glycidyl ether resins because of the existence of compact rings.²⁵ Their low flexural strengths could lead to practical problems, such as cracks, when they are used in various applications, such as optics and displays. Oxetane monomers, having a structure comprised of a long chain and a difunctional group, such as DOX, can resolve the problem of low flexural strength.²⁶ The yield strain, yield stress, and flexural modulus values obtained from the stress-strain curves of the three-point bending test are listed in Table III. The higher yield stress and lower flexural modulus of the DOX polymer indicated that they had greater flexibility, which originated from the long chain of DOX. Therefore, as presented in Table III, the CAEO/DOX hybrimers showed

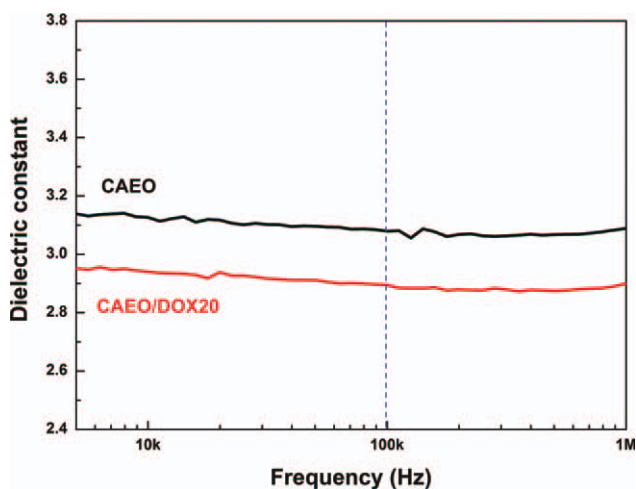


Figure 4 Dielectric constant of the CAEO/DOX hybrimer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

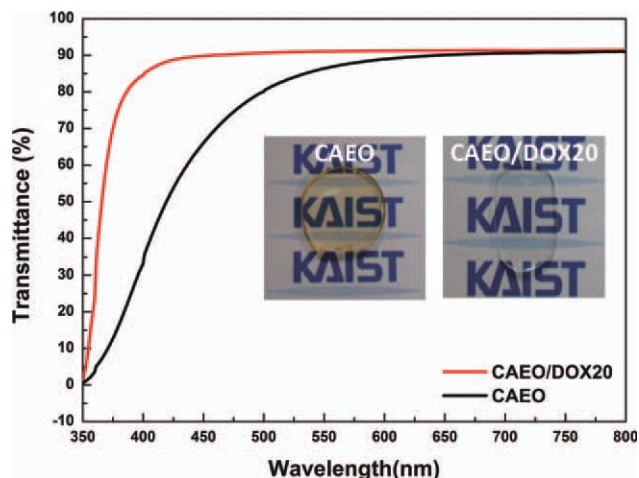


Figure 5 Transparency and photograph of the CAEO/DOX hybrimers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increased flexibility with DOX contents. Another noticeable feature was the increase in the flexural modulus of the CAEO/DOX10 and CAEO/DOX20 hybrimers, even with small amounts of DOX. The CAEO hybrimers feasibly would have had unreacted cycloaliphatic epoxy groups in the matrix because of the slow cationic polymerization by the high viscosity of the resin. These unreacted cycloaliphatic epoxy groups in the matrix would have degraded the original flexural modulus of the CAEO hybrimer. DOX, which increased the crosslinking density of CAEO hybrimer, eliminated the unreacted cycloaliphatic epoxy groups from the matrix and increased the flexural modulus of the CAEO hybrimer. In the case of the CAEO/DOX hybrimer with a higher DOX content than CAEO/DOX20 hybrimer, the flexural modulus decreased with increasing DOX. This was because the role of DOX as a flexibilizer was dominant in these hybrimers. Thus, the addition of DOX led not only to increased flexibility of the CAEO hybrimer but also to the removal of unreacted cycloaliphatic epoxy groups from the CAEO hybrimer.

Dielectric materials used as gate insulators or passivation layers in thin-film transistors (TFTs) must have good insulation properties to realize TFTs with high performance and reliability.^{27,28} Thus, we examined the leakage current density of the CAEO/DOX hybrimer. Figure 3 shows the variation of the leakage current density of the CAEO hybrimer and the CAEO/DOX20 hybrimer depending on the applied electric field. The leakage current densities of the CAEO hybrimer and the CAEO/DOX20 hybrimer at 1 MV/cm were 13.8 and 5.2 nA/cm², respectively. Because the addition of DOX led to a more highly crosslinked organic network, the CAEO/DOX20 hybrimer showed enhanced insulating properties compared to the CAEO hybrimer. The

leakage current density of the CAEO/DOX20 hybrimer was even lower than that of previously reported solution-processed siloxane dielectric materials.²⁸

Among the dielectric materials applied in TFTs, the passivation layer, in particular, should have a low dielectric constant to improve the performance of the TFT by a reduction of the capacitive coupling in the dielectric material.^{28–31} Figure 4 presents the variation of the dielectric constants of the CAEO and CAEO/DOX20 hybridizers as a function of frequency. Their dielectric constants at 1 kHz were 3.08 and 2.89, respectively, which were lower than that of SiO₂ (~ 3.9). The lower dielectric constant of the CAEO/DOX20 hybridizer relative to that of the CAEO hybridizer could be explained by the following Clausius–Mossotti relationship:³²

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{\rho N_0}{M 2\epsilon_0} (\alpha_d + \alpha_i + \alpha_e)$$

where ϵ_r is the dielectric constant, ρ is the density, N_0 is Avogadro's number, M is the molecular weight, ϵ_0 is the vacuum permittivity, and α_d , α_i , and α_e are the dipolar, ionic, and electronic polarizability, respectively.

From the Clausius–Mossotti relationship, the dielectric constant of a material decreases with decreasing polarizability of the material. As previously reported, CAEO resin with an equivalent molar ratio of 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane to diphenylsilanediol had unreacted diphenyldimethoxysilane.¹⁷ Also, the CAEO hybridizer was expected to have unreacted cycloaliphatic epoxy groups because of its low crosslinking density. The unreacted diphenyldimethoxysilane during the non-hydrolytic sol–gel reaction and cycloaliphatic epoxy groups during cationic polymerization acted as a source of dipolar polarization against alternating electric fields with a given frequency. The dipolar polarization increased the dielectric constant of the CAEO hybridizer according to the Clausius–Mossotti relationship. Thus, the lower dielectric constant of the CAEO/DOX20 hybridizer compared to that of CAEO hybridizer was believed to originate from effective motion restriction of the unreacted diphenyldimethoxysilane and cycloaliphatic epoxy groups by a high crosslinking density.

To facilitate their use in various applications, such as in optics and display fields, the CAEO/DOX hybridizers needed high transparency without discoloration. We fabricated CAEO and CAEO/DOX20 hybridizer bulks with 2 mm thicknesses to check their transparency. For fabrication of the CAEO and CAEO/DOX20 hybridizer bulks, CAEO and CAEO/DOX20 resins were irradiated by UV light for 10 and 1 min, respectively, because of the difference in

their photosensitivity. The UV-cured sample was then heat-treated at 150°C for 2 h to promote cationic polymerization. Figure 5 shows the transparency and photograph of the CAEO and CAEO/DOX20 hybridizers. Despite the substantial thickness of the hybridizer, the CAEO/DOX20 hybridizer fabricated by a short UV irradiation time exhibited excellent transmittance, exceeding 90% in the visible range, and was also colorless. On the other hand, the transparency of the CAEO hybridizer bulk was degraded by yellowness generated by a long UV irradiation time. This discoloration of the CAEO hybridizer could be explained to originate from free radicals generated by the photolysis reaction of onium salts used as a catalyst for the photocationic polymerization and the oxidative degradation reaction of the organic part in the CAEO hybridizer activated by free radicals and UV.^{2,33} Therefore, the high transparency of the CAEO/DOX20 hybridizer bulk originated from DOX, which facilitated the fast photocationic polymerization and, thereby, allowed a short UV irradiation time.

CONCLUSIONS

The low photocationic polymerization rate of a highly viscous CAEO resin was improved by the introduction of DOX. The increased photocationic polymerization speed of the CAEO/DOX resin originated from both the increased mobility of the cycloaliphatic epoxy groups because of the decreased viscosity of the resin and the high basicity of the heterocyclic oxygen in the oxetane. The CAEO/DOX hybridizers had a higher crosslinking density than the CAEO hybridizer with the addition of DOX. The increased crosslinking density resulted in improved mechanical/electrical properties in the CAEO hybridizer. Also, because of the fast photocationic polymerization of the CAEO/DOX system, the fabrication of a transparent hybridizer bulk, even with large dimensions, was straightforward. Given these properties, the CAEO/DOX hybridizers are expected to be used in various applications, including optics and display fields.

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