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Thermo-Mechanical/Thermal Properties of Photo-Cationic Polymerized Cyclo-Aliphatic Epoxy Hybrid Materials

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Abstract: Cyclo-aliphatic epoxy and methacrylate hybrimers were fabricated *via* the photocationic polymerization of cycloaliphatic epoxy oligosiloxanes and photoradical polymerization of methacrylate oligosiloxanes, respectively. The thermomechanical/thermal properties of these two hybrimers using different photo-polymerization mechanisms were compared. Although both oligosiloxanes showed similar degrees of condensation, siloxane network structures, and sizes, the cycloaliphatic epoxy hybrimer showed improved thermomechanical/thermal properties as compared to the methacrylate hybrimer. This was attributable to a highly crosslinked network structure developing from the living characteristics of photocationic polymerization and the short, compact organic chains of the cycloaliphatic epoxy hybrimer as compared to the methacrylate hybrimer.

Keywords: cyclo-aliphatic epoxide, hybrimer, sol-gel, photo-cationic polymerization, DMA.

Introduction

Photo-polymerization of various organic functional groups has been intensively studied due to its many advantages: rapid process, patternable property, low cost, low process temperature, and low energy consumption compared to thermal polymerization. On the basis of these merits, photo-polymerization has been applied to various industrial applications such as protective coatings, electronics, printing, optics, and so on.[1]

Photo-radical polymerization of methacrylates is one of the most commonly used technique for preparation of cross-linked materials, since photo-radical polymerization offers many advantages such as fast curing property, availability of various raw materials, and low cost of precursors. However, photo-radical polymerization is retarded by oxygen, which critically limits the practical processability. On the other hand, photo-cationic polymerization of epoxides has attracted considerable attention because of their superior insensitivity toward oxygen, living character, excellent adhesion on substrates by low shrinkage, and the generation of hydroxyl groups, compared to methacrylate systems. Notably, the products fabricated by photo-cationic polymerization of epoxides have higher cross-linking density compared to those of methacrylate systems due to their insensitivity toward oxygen and living character. However, their low curing speed, high cost of precursors, and limited variety of available raw materials restrict the expansion to their applications.[1,2]

Organic-inorganic hybrid materials (hybrimers) fabricated by photo/thermal polymerizations of various organic functional group have been actively studied in various application fields, as they have inherent advantages originating from their synergistically combined inorganic/organic networks.[3-10] Among these hybrimers, those fabricated by photo-radical polymerization of methacrylate exhibited excellent optical properties, a photo-patternable property, and easy processability to fabricate final products. Their applications could be further expanded to various application fields such as optics, displays, 3D patterning, *etc*..[5,6,9,10]

Recently, we reported on cyclo-aliphatic epoxy hybrimers fabricated by photo-cationic polymerization of sol-gel derived cyclo-aliphatic epoxy oligosiloxanes, which shows high transparency, a photo-patternable property, and excellent gas barrier properties.[11,12] However, the thermo-mechanical/thermal properties of cyclo-aliphatic epoxy hybrimers in comparison to those of methacrylate hybrimers have not been studied.

In this study, we fabricated cyclo-aliphatic epoxy and methacrylate hybrimers with photo-curable oligosiloxane resins synthesized by the same synthesis route. Their thermo-mechanical/thermal properties were measured to verify cross-linking density of the hybrimers. It was observed that the cyclo-aliphatic epoxy hybrimers have a higher storage modulus at a rubbery state, a lower coefficient of thermal expansion, and higher thermal stability than methacrylate hybrimers.

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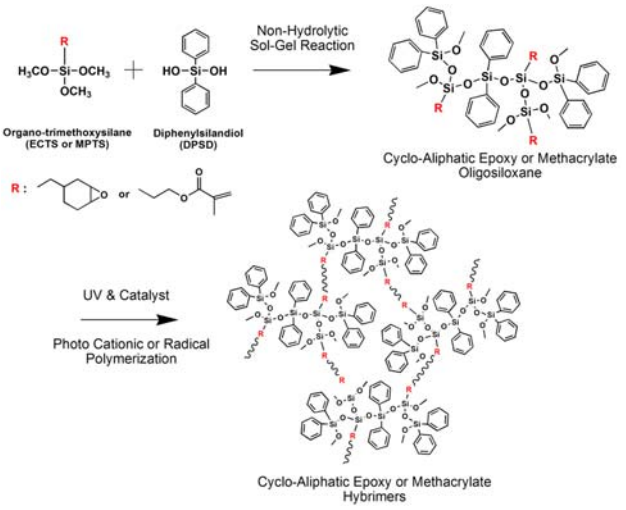
Experimental

Synthesis and Characterization of Cyclo-Aliphatic Epoxy and Methacrylate Oligosiloxane Resins. We synthesized cyclo-aliphatic epoxy oligosiloxane resin (ED) using a method described in a previous paper.[11] ED was synthesized by a simple sol-gel condensation reaction between 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (ECTS, Gelest), and diphenylsilanediol (DPSD, Gelest) at 80 °C for 4 h under N_2 purging. The molar ratio of ECTS and DPSD was 1 to 1. Barium hydroxide monohydrate ($Ba(OH)_2 \cdot H_2O$, 98%, Aldrich) was added as a catalyst to promote the reaction. Methacrylate oligosiloxane resin (MD) was also synthesized through the same procedures and with the same compositions using 3-(methacryloyloxy)propyltrimethoxysilane (MPTS, 98%, Aldrich) and DPSD. The synthesized resins were cooled to room temperature and filtered with a 0.45 μm-diameter Teflon filter to remove $Ba(OH)_2 \cdot H_2O$. The reaction schemes are shown in Scheme I.

The formation of siloxane networks in the synthesized resins was confirmed using ^{29}Si nuclear magnetic resonance (NMR) spectrometers (600 MHz, DMX600, Bruker). The samples for the ^{29}Si NMR measurement were prepared with 30 vol% resins in chloroform-d_6 added chromium(III) acetylacetonate with a concentration of 30 mg·L^{-1} as a relaxation agent of silicon. For determining the molecular weight distribution and structural analysis of oligosiloxanes in the resins, we examined matrix-assisted laser desorption and ionization time-of-flight mass spectrometry (MALDI-TOF MS) of each resin. MALDI-TOF MS spectra of each resin were evaluated with a Voyager-DE STR 4700 proteomics analyzer equipped with a nitrogen laser using a wavelength of 337 nm and a pulse width of 3 ns of PerSeptive Biosystems. 2,5-dihydroxybenzoic acid (DHB, Aldrich) and acetone were used as the matrix and solvent in the resins, respectively, to prepare measurement samples. The average size of the oligosiloxanes in each resin was measured using small-angle neutron scattering (SANS). The average size of the oligosiloxanes in each resin with a wide distribution of molecular weights was obtained from the radius of gyration (R_g) quantized by a Guinier plot of the SANS. SANS experiments were performed in the SANS instrument at the HANARO Reactor at the Korea Atomic Energy Research Institute (KAERI). The experimental conditions included a wavelength of 4.31 Å with a wavelength spread (FWHM) of 12%, and detector-sample distance of 2 m. The scattering vector ranged between 0.25 and 0.4 Å^{-1}. The resins were diluted to 10 wt% concentrations in acetone-d_6 to obtain good contrast between the resins and the solvent.



Scheme I. Fabrication of cyclo-aliphatic epoxy and methacrylate hybrimer using photo-cationic and radical polymerization.

Fabrication and Characterization of Cyclo-Aliphatic Epoxy and Methacrylate Hybrimers. Cyclo-aliphatic epoxy/methacrylate hybrimer were fabricated under polymerization conditions reported in a previous paper.[10,11] First, triarylsulfonium hexafluoroantimonate salts (Aldrich) were added as a photo initiator for photo-cationic polymerization of cyclo-aliphatic epoxy groups in the ED to fabricate the cyclo-aliphatic epoxy hybrimer. The content of photo initiator was 2 wt% in the resin. The prepared photo-sensitive ED was irradiated by ultraviolet (UV) light for 5 min using a Hg lamp (80 mW/cm^2, 365 nm, Oriel 97453) under the ambient atmosphere to fabricate samples for measurement of thermal/thermo-mechanical properties. Sequentially, the fabricated samples were thermally cured at 150 °C for 2 h under the ambient atmosphere to obtain further polymerized samples. Methacrylate hybrimer samples were fabricated by UV irradiation for 5 min under N_2 conditions. We used 2,2-dimethoxy-2-phenyl acetophenone (BDK, Aldrich) of 2 wt% as an initiator for photo-radical polymerization of MD. The fabricated methacrylate hybrimer samples were thermally cured at 150 °C for 2 h under the ambient atmosphere. The fabrication schemes are represented in Scheme I.

The dynamic mechanical responses of the hybrimers were recorded using a dynamic mechanical analyzer (DMA 2980, TA Instrument, Inc.). Storage modulus (E') and tanδ were measured within a temperature range from -50 to 150 °C at a ramp rate of 5 °C/min. The vibratory offset force was fixed at 0.01 N at a frequency of 1 Hz. The thermo-dilatometric responses of the hybrimers were assessed using a thermomechanical analyzer (TMA, EXTAR series TMA/SS 6100, Seiko Instruments, Inc.). The displacement was measured from -125 to 200 °C at a heating rate of 5 °C/min and the coefficients of thermal expansion (CTEs) were calculated from the displacement. Thermal stabilities of each hybrimer were checked *via* a thermogravimetric analysis (TGA, Q50, TA Instruments, Inc.) under a N_2 atmosphere. The temperature range was from 30 to 700 °C with a heating rate of 5 °C/min.

Results and Discussion

The siloxane network of organo-oligosiloxanes synthesized by a non-hydrolytic sol-gel reaction shows excellent structural reliability and reproducibility due to the absence of water which is usually introduced in the conventional hydrolytic sol-gel reaction. Through variation of the organic groups of organo-silanol and organo-alkoxysilane used as precursors, it is possible to synthesize various organo-oligosiloxanes with a similar siloxane network. Therefore, we investigated the siloxane network of cyclo-aliphatic epoxy and methacrylate oligosiloxanes formed by the non-hydrolytic sol-gel reaction in order to analyze the differences in the thermo-mechanical/thermal properties between cyclo-aliphatic epoxy and methacrylate hybrimer according to variation of the organic functional group.

Formation and Characterization of Cyclo-Aliphatic Epoxy and Methacrylate Oligosiloxanes. The formation of siloxane network of cyclo-aliphatic epoxy and methacrylate oligosiloxane in each resin was confirmed by ^{29}Si NMR experiments (Figure 1). Also, the degree of condensation (DOC) of the cyclo-aliphatic epoxy and methacrylate oligosiloxane resins was calculated using of D^n and T^n peak area of ^{29}Si NMR and with the following equation.[11]

$$\mathrm{DOC} = \frac{D^1 + 2D^2 + T^1 + 2T^2 + 3T^3}{2(D^0 + D^1 + D^2) + 3(T^0 + T^1 + T^2 + T^3)} \times 100$$

D^n and T^n denote the notation of Si from DPSD and ECTS or MPTS, respectively. The superscript "n" is the number of siloxane bonds of the Si atoms. As shown in the ^{29}Si spectra of each resin, cyclo-aliphatic epoxy and methacrylate oligosiloxane resins having the same synthesis methods and compositions show similar ^{29}Si NMR spectra regardless of their organic functional groups. Also, the calculated DOCs of cyclo-aliphatic epoxy and methacrylate oligosiloxane are 77% and 74%, respectively. Base on the similar ^{29}Si NMR spectra and DOC values, we confirmed that cyclo-aliphatic epoxy and methacrylate oligosiloxane in each resin have nearly same reaction degree of siloxane network in spite of each oligosiloxane having different organic functional groups.

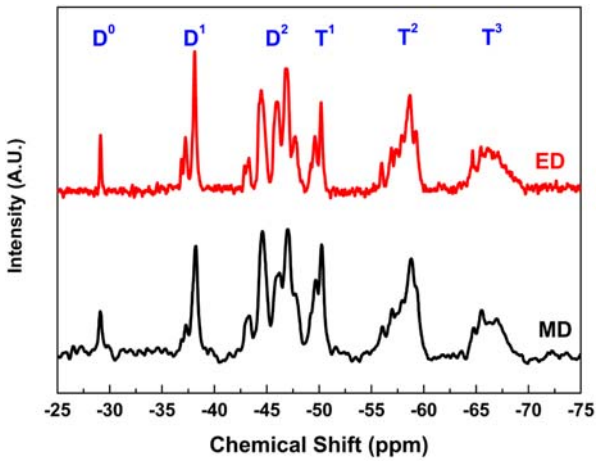


Figure 1. ^{29}Si NMR spectra of cyclo-aliphatic epoxy and methacrylate oligosiloxane resins.

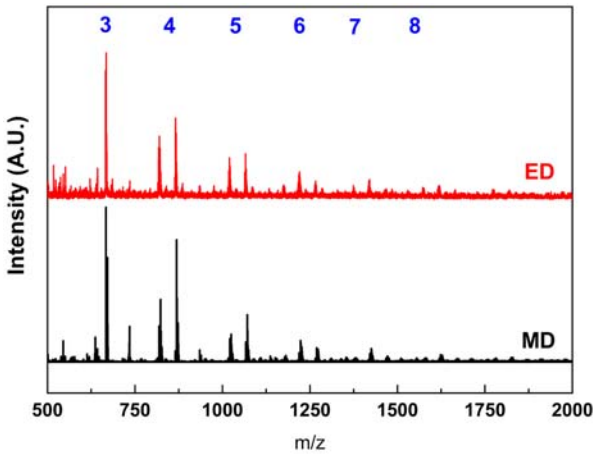


Figure 2. MALDI TOF spectra of cyclo-aliphatic epoxy and methacrylate oligosiloxane resins.

Siloxane Network Structural Analysis of Cyclo-Aliphatic Epoxy and Methacrylate Oligosiloxanes. To analyze the siloxane network structure of cyclo-aliphatic epoxy and methacrylate oligosiloxanes in each resin, we examined MALDI-TOF mass spectra of cyclo-aliphatic epoxy and methacrylate oligosiloxane resins. As shown in the MALDI-TOF mass spectra of Figure 2, the molecular distributions of cyclo-aliphatic epoxy and methacrylate oligosiloxanes in each resin are under 2,500 m/z. Since the molecular weights of the precursors ECTS and MPTS are 246.38 and 248.35 g/mol, respectively, cyclo-aliphatic epoxy and methacrylate oligosiloxanes have nearly the same peak position. Furthermore, the intensities of each peak corresponding to cyclo-aliphatic epoxy and methacrylate oligosiloxanes are similar due to the use of the non-hydrolytic sol-gel reaction, which yields siloxane networks with excellent structural reliability and reproducibility.

The empirically determined molecular weight of each peak originating from the cyclo-aliphatic epoxy and methacrylate oligosiloxanes is listed in Table I. Cyclo-aliphatic epoxy and methacrylate oligosiloxanes have nearly the same empirically determined molecular weight of each peak due to the similar molecular weights of the precursors. The molecular weights, calculated under the assumption that the siloxane network structures of cyclo-aliphatic epoxy and oligosiloxane have a linear structure, are also summarized in Table I. Through a comparison of the empirically determined molecular weight with the calculated molecular weight, siloxane network structures of cyclo-aliphatic epoxy and methacrylate oligosiloxanes can be defined. As shown in Table I, the peak positions of the empirically determined molecular weight are consistent with those of the calculated

Table I. Comparisons between the Empirically Determined Molecular Weights from the MALDI-TOF Mass Spectra and Calculated Molecular Weights of Cyclo-Aliphatic Epoxy or Methacrylate Oligosiloxane Obtained from Molecular Weights of ECTS or MPTS and DPSD

	Trimer	Tetramer	Pentamer
Calculated (m/z)	640 ~ 648	840 ~ 850	1,038 ~ 1,050
Practical (m/z)	663 ~ 671	815 ~ 870	971 ~ 1,068
	Hexamer	Heptamer	Octamer
Calculated (m/z)	1,236 ~ 1,250	1,434 ~ 1,450	1,632 ~ 1,650
Practical (m/z)	1,169 ~ 1,265	1,325 ~ 1,434	1,524 ~ 1,621

molecular weight. Therefore, it is reasonable to conclude that the siloxane network structures of the cyclo-aliphatic epoxy and methacrylate oligosiloxanes in each resin have identical linear structures.

Size Analysis of Cyclo-Aliphatic Epoxy and Methacrylate Oligosiloxanes. The radius of gyration (R_g) of cyclo-aliphatic epoxy and methacrylate oligosiloxanes can be obtained by SANS analysis.

The scattering intensity ($I(Q)$) is represented by the following equation according to the Guinier Law.

$$I(Q) = \rho_0^2 v^2 \exp\left(-\frac{1}{3}Q^2 R_g^2\right)$$

where $I(Q)$ is the scattering intensity, Q is the scattering vector, ρ_0 is the scattering length density of the resin, v is the molar volume of the resin, and R_g is the radius of gyration of the resin. R_g values of cyclo-aliphatic epoxy and methacrylate oligosiloxanes were calculated by the following equation from Guinier plots (scattered intensity ($I(Q)$ *vs.* Q^2) in the Guinier region ($0.1 < R_g \times Q < 1$).

$$\ln(I(Q)) = A - \frac{1}{3}Q^2 R_g^2$$

Figure 3(a) and (b) present an experimental SANS results of each resin and Guinier plots from Figure 3(a), respectively. The cyclo-aliphatic epoxy oligosiloxane resin has nearly the same Guinier plot gradients (-21.03) as those of methacrylate oligosiloxane resin (-19.29). The R_gs value of cyclo-aliphatic epoxy and methacrylate oligosiloxanes calculated from each slope are 0.79 and 0.76 nm, respectively. These similar R_gs of the two oligosiloxanes indicate that both of the oligosiloxanes have similar average molecular size.

Considering the ^{29}Si NMR, MALDI-TOF, and SANS results given above, both the cyclo-aliphatic epoxy and methacrylate oligosiloxanes showed similar degrees of siloxane condensation, structure, and radii of gyration. The results indicate that the two kinds of oligosiloxanes have similar siloxane networks. Therefore, it is expected that the thermo-mechanical/thermal properties of each hybrimer would be only dependent on the organic functional group of the oligosiloxanes and thus the overall organic network structure.

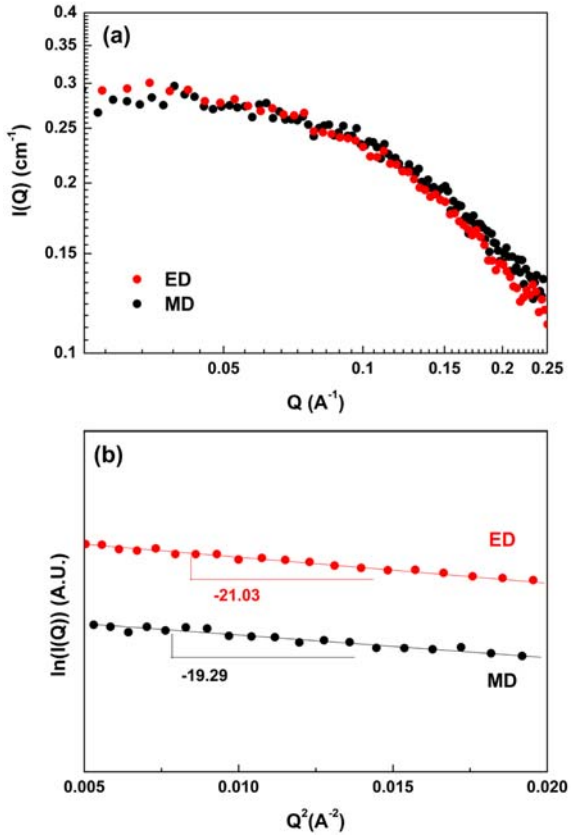


Figure 3. (a) Experimental SANS data of cyclo-aliphatic epoxy and methacrylate oligosiloxane resins (b) Guinier plots ($\ln(I(Q))$ *vs.* Q^2) of SANS data.

Thermo-Mechanical Properties of Cyclo-Aliphatic Epoxy and Methacrylate Hybrimer. The viscoelastic behavior of cyclo-aliphatic epoxy and methacrylate hybrimer was evaluated using a dynamic mechanical analyzer (DMA). Figure 1 displays the storage modulus and tan δ between cyclo-aliphatic epoxy and methacrylate hybrimer. As previously reported, the methacrylate hybrimer shows broad and weak glass transition behavior over a wide temperature range. This phenomenon is attributed to the high cross-linking density of methacrylate hybrimer, which is originated from the multi-functionality and the short siloxane chain of the oligosiloxanes.[10] As can be seen in Figure 4, the cyclo-aliphatic epoxy hybrimer has a similar glassy state storage modulus (~3,750 MPa) to that of the methacrylate hybrimer. On the other hand, the storage modulus at the rubbery state of the cyclo-aliphatic epoxy hybrimer (348 MPa) is higher than that of the methacryl hybrimer (280 MPa). In the case of the cyclo-aliphatic epoxy hybrimer, the maximum tan δ value is approximately 0.07. This tan δ value is lower than that of the methacrylate hybrimer which shows a maximum tan δ value of around 0.1. We also confirmed that the glass transition temperature (T_g) of cyclo-aliphatic epoxy hybrimer

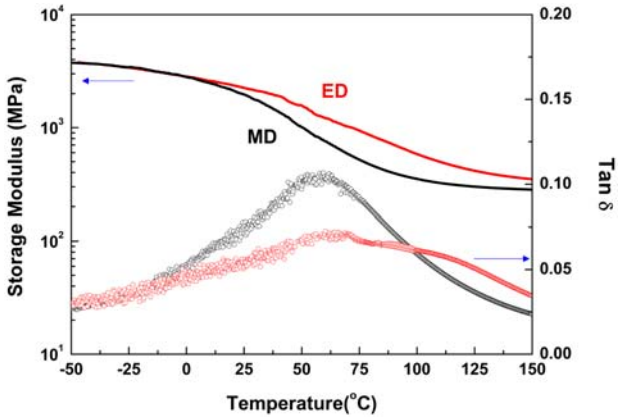


Figure 4. DMA results (storage modulus and tan δ) of cyclo-aliphatic epoxy and methacrylate hybrimer.

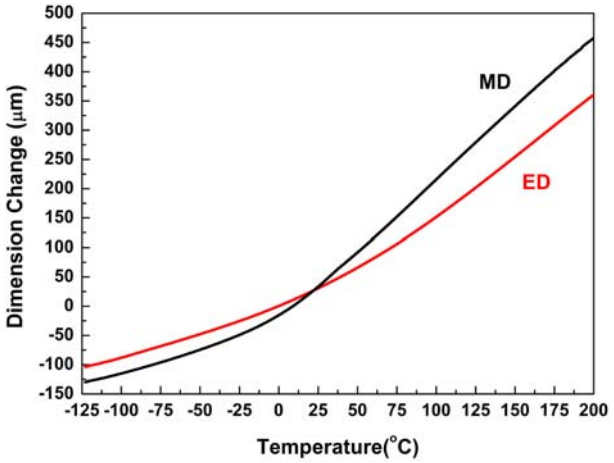


Figure 5. TMA results of cyclo-aliphatic epoxy and methacrylate hybrimer.

(65 °C) is higher than the methacrylate hybrimer (57 °C). These thermo-physical properties are summarized in Table II. The broader and weaker glass transition behavior over a wide temperature range of the cyclo-aliphatic epoxy hybrimer can be explained by the differences in the polymerization mechanism and the structure between cyclo-aliphatic epoxy groups and methacrylate groups. For the fabrication of the cyclo-aliphatic epoxy hybrimer, cyclo-aliphatic epoxy groups of oligosiloxanes are UV-cured by photo-cationic polymerization initiated by brönsted acids generated by photolysis of onium salt.[13-15] In general, the acid-based photo-cationic polymerizations have living characteristics without a termination step, in contrast with the photo-radical polymerization where radical terminations are usually involved.[2] Owing to the living characteristics of photo-cationic polymerization, the cyclo-aliphatic epoxy hybrimer has higher cross-linking density compared to the methacrylate hybrimer. Since the highly cross-linked organic network of the cyclo-aliphatic epoxy hybrimer effectively restricts thermal relaxation motion of organic chain segments by heat, the cyclo-aliphatic epoxy hybrimer has a higher storage modulus at the rubbery state, T_g, and a lower maximum tan δ value as compared to the methacrylate hybrimer.[10,16,17] In addition, since the short chain length and compact cyclo-hexane ring of the cyclo-aliphatic epoxy groups are expected to have weaker thermal relaxation motion, the cyclo-aliphatic epoxy hybrimer shows a lower maximum tan δ value.

The thermo-dilatometric responses of the cyclo-aliphatic epoxy and methacrylate hybrimers were measured using a thermomechanical analyzer (TMA) and the coefficient of thermal expansion (CTE) of the hybrimer was calculated from the TMA curves. Figure 5 shows the TMA results of the cyclo-aliphatic epoxy and methacrylate hybrimers. The CTEs before and after T_g calculated from the TMA results are listed in Table II. While the CTE$^{\alpha}$s do not vary regardless of the organic functional groups, the cyclo-aliphatic epoxy hybrimer has a lower CTE$^{\beta}$ value compared to the methacrylate hybrimer after glass transition behaviors. The lower CTE$^{\beta}$ of the cyclo-aliphatic epoxy hybrimer as compared to the methacrylate hybrimer is due to its higher cross-linking density and weaker thermal relaxation motions due to the short chain length and compact cyclo-hexane ring of cyclo-aliphatic epoxy groups.

Thermal Properties of Cyclo-Aliphatic Epoxy and Methacrylate Hybrimer. Thermal stability of the cyclo-aliphatic epoxy and methacrylate hybrimers was examined by a thermogravimetric analysis (TGA) (Figure 6). The 5% weight loss temperature of the cyclo-aliphatic epoxy and methacrylate hybrimers is 411 and 310 °C, respectively (Table II). The high thermal stability of the cyclo-aliphatic epoxy hybrimer is a reasonable result given the existence of thermally stable cyclo-hexane rings as compared to the methacrylate.[18,19] However, several noticeable features can be observed in the TGA results of the hybrimers. First, abrupt thermal decomposition of the methacrylate hybrimer occurs at two specific temperatures. The onset temperature of the

Table II. Thermo-Physical Properties of Cyclo-Aliphatic Epoxy and Methacrylate Hybrimer

	E'_g[a] (MPa)	E'_r[b] (MPa)	T_g[c] (°C)	CTE[d] (ppm/°C)		$T_{5\%loss}$[e] (°C)
				CTE$^{\alpha}$ (-120 ~ -100 °C)	CTE$^{\beta}$ (150 ~ 170 °C)	
Cyclo-Aliphatic Epoxy Hybrimer	3765	348	65	64.2	212.9	411
Methacrylate Hybrimer	3744	280	57	63.3	244.3	310

[a]E'_g: Storage modulus at glassy state. [b]E'_r: Storage modulus at rubbery state. [c]T_g: Glass transition temperature. [d]CTE: Coefficient of thermal expansion. [e]$T_{5\%loss}$: 5% loss temperature.

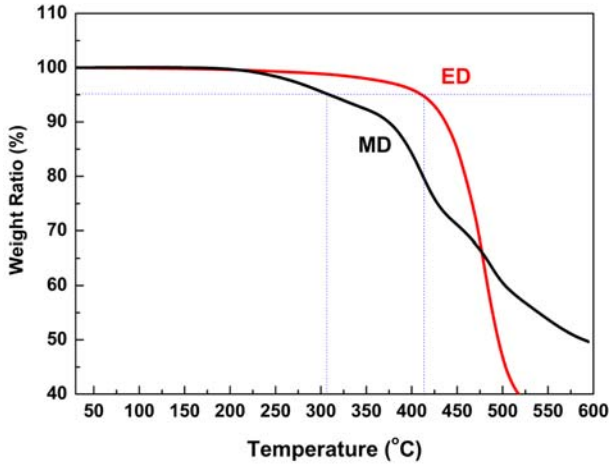


Figure 6. TGA results of cyclo-aliphatic epoxy and methacrylate hybrimer.

first and second abrupt thermal decomposition is 240 and 370 °C, respectively. Previously, we reported that the onset temperature of the first abrupt thermal decomposition originates from many unreacted methacrylate groups and the first abrupt thermal decomposition is suppressed by an increase of cross-linking density.[10] However, the cyclo-aliphatic epoxy hybrimer does not show the abrupt thermal decomposition arising from the unreacted cyclo-aliphatic epoxy groups.[16] Thus, it is reasonable to conclude that the cyclo-aliphatic epoxy hybrimer has relatively higher cross-linking density, originating from the living characteristics of photo-cationic polymerization, compared to the methacrylate hybrimer.

Conclusions

Cyclo-aliphatic epoxy and methacrylate oilgosiloxane resins having similar degrees of condensation, siloxane network structures, and radius of gyration were synthesized by a non-hydrolytic sol-gel reaction. Cyclo-aliphatic epoxy and methacrylate hybrimers were fabricated by photo-cationic polymerization and photo-radical polymerization of two oligosiloxanes, respectively. On the basis of the similar degrees of condensation, siloxane network structures, and radius of gyration of the two oligosiloxanes, the cyclo-aliphatic epoxy hybrimer has a higher storage modulus at the rubbery state, higher T_g, lower tan δ value, lower CTE, and higher thermal stability compared to those of the methacrylate hybrimer. The highly cross-linked organic network structure stemming from the living character of photo-cationic polymerization and short/compact organic group of the cyclo-aliphatic epoxy hybrimer was expected to be the major factors underlying these improved thermo-mechanical/thermal properties.

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