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Thermal properties of epoxy resin/filler hybrid composites

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ABSTRACT

Epoxy resin/filler hybrid composites were prepared by the melt blending of diglycidylether of bisphenol-A (DGEBA), as the epoxy resin, with nano-Al_2O_3 or nano-SiC particles, as the nanoscaled fillers. The thermal properties, such as the curing behavior, thermal stability, dynamic mechanical properties, and thermal mechanical properties of the DGEBA/nano-Al_2O_3 and DGEBA/nano-SiC composites were examined using a range of techniques. As a result, the DSC curve peak temperature of both composites decreased with increasing filler content. The integral procedure decomposition temperature increased from 630 °C to 853 °C for DGEBA/nano-Al_2O_3 composite and 858 °C for DGEBA/nano-SiC composite. The char yield at 800 °C increased from 14.3% to 26.2–26.6% for both composites. Both composites had a 10 °C higher glass transition temperature than the neat epoxy resin. The coefficient of thermal expansion of both composites at the glassy and rubbery regions decreased with increasing filler content.

1. Introduction

Inorganic fillers are added to the epoxy formulations to form organic–inorganic composites to improve the thermal stability, glass transition temperature, and dimensional stability of epoxy resins. Nanoscale fillers, such as nano-particles, nano-tubes, and layered silicate clays, are used widely in the preparation of epoxy composites [1–3]. Directly blending the epoxy resins and nanoparticles provides a convenient route to form epoxy resin-inorganic hybrid composites [4].

Several studies have examined the preparation and thermal characterization of epoxy resins using a range of inorganic fillers. Tarrío-Saavedra et al. fabricated epoxy resin/fumed silica composites to improve the thermal stability of the epoxy resin [5]. These results suggest that the thermal stability of the epoxy resin was improved and the mass loss rate was reduced by the addition of fumed silica. Kuan et al. examined the flame retardance and thermal stability of the carbon nanotube/epoxy composites prepared using sol–gel method [6]. They concluded that the glass transition temperature (T_g) and integral procedural decomposition temperature (IPDT) were increased from 118 to 160 °C and from 890 to 1571 °C, respectively. Macan et al. investigated the thermal degradation of epoxy/silica organic/inorganic hybrid materials [7]. The resulting hybrid materials exhibited higher thermal stability, such as the temperature of the maximum degradation rate (T_{max}) and the IPDT, compared to the neat epoxy resin. Chiang et al. studied the thermal stability and degradation kinetics of novel organic/inorganic epoxy hybrid composites containing nitrogen/silicon/phosphorus [8]. The thermal stability of the hybrid composites increased with increasing content of inorganic components. Liu et al. investigated the thermal stability of epoxy/silica hybrid materials by thermogravimetric analysis (TGA) [4]. Their results suggested that the thermal stability and weight loss rates of the epoxy resins were improved by introducing nanoscale colloidal silica to form epoxy-silica nanocomposites.

In this study, epoxy resin/filler hybrid composites were prepared from diglycidylether of bisphenol-A (DGEBA), as the epoxy resin, and nano-Al_2O_3 and nano-SiC particles, as the nanoscaled fillers. The thermal properties, such as the curing behavior, thermal stability, dynamic mechanical properties, and thermal mechanical properties of the DGEBA/nano-Al_2O_3 and DGEBA/nano-SiC composites were investigated by a differential scanning calorimetry (DSC), TGA, dynamic mechanical analysis (DMA), and thermal mechanical analysis (TMA).

2. Experimental

2.1. Materials

The diglycidylether of bisphenol-A (DGEBA, Kukdo Chem. of Korea) had an epoxide equivalent weight of 185–190 g/eq and a density of approximately 1.16 g/cm^3 at 25 °C. 4,4′-Diaminodiphenyl

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methane (DDM, Aldrich Chem.) was selected as a curing agent. The nano-Al_2O_3 (γ-Al_2O_3) particles were obtained from Nanjing High Technology Nano Material Co. in China. The grain size and specific surface area of the nano-Al_2O_3 particles were 20 nm and 160 m^2/g, respectively. The nano-SiC particles were supplied by Xuzhou Hongwu Nano Materials INC of China. The diameter of the nano-SiC particles was $<$100 nm.

2.2. Sample preparation

The weight content of the fillers was varied from 5 to 15 wt%. The desired amounts of DGEBA and filler were mixed with a magnetic stirring bar at 80 °C for 1 h and treated ultrasonically for 30 min. Subsequently, DDM was added to the mixture. The bubble-free mixture was poured into a preheated mold, which had previously been sprayed with a mold release agent. Initial cure temperature and final cure temperature of DGEBA/DDM system was 102.5 and 224.6 °C, respectively. The curing cycle used in this study was determined according to the curing characteristics. Curing was performed at 110 °C for 1 h, at 140 °C for 2 h, and at 170 °C for 1 h in a convection oven.

2.3. Characterization and measurements

The cure behavior of DGEBA/nano-Al_2O_3 and DGEBA/nano-SiC samples was examined by a DSC (NETZSCH, DSC 200 F3) at a heating rate of 10 °C/min from 30 to 300 °C under a nitrogen flow of 30 ml/min.

Dispersion state of nano-particles in epoxy matrix was investigated using a Field Emissio-Transmission Electron Microscope (FE-TEM, JEM2100/JEOL) with an accelerating voltage of 200 kV.

The thermal stability of the DGEBA/nano-Al_2O_3 and DGEBA/nano-SiC composites was analyzed with TGA (NETZSCH TG 209 F3) at a heating rate of 10 °C/min from 30 to 850 °C under a nitrogen atmosphere.

The dynamic mechanical properties of the composites were determined by DMA (RDS-II, Rhemetrics Co.) at a frequency of 1 Hz, temperature range from 35 to 250 °C, and heating rate of 5 °C/min. The specimen dimensions were 2 mm × 12 mm × 35 mm.

The coefficient of thermal expansion (CTE) of the composites was determined by TMA (RDS-II, Rheometrics Co.) with an applied a force of 0.05 N at a heating rate of 5 °C/min under a nitrogen atmosphere. The CTE was calculated using the following equation:

$$\alpha = \frac{1}{L_0}\frac{\Delta L}{\Delta T} \tag{1}$$

where L_0 is the initial length, ΔL is the change in length, and ΔT is the temperature range.

3. Results and discussion

3.1. Curing behavior

The effect of fillers, nano-Al_2O_3 and nano-SiC particles, on the curing behavior of the DGEBA epoxy resin cured with DDM was examined by DSC, and the dynamic DSC thermograms are shown in Fig. 1. The peak maximum temperature (T_p) and reaction enthalpy (ΔH) were calculated from the thermograms, and the results are summarized in Table 1. The T_p of DGEBA/nano-Al_2O_3 and DGEBA/nano-SiC composites shifted towards a lower temperature with increasing filler content. The T_p decreased from 163.4 to 147.1 °C for the DGEBA/nano-Al_2O_3 composites and 158.5 °C for the DGEBA/nano-SiC composites. These results suggest that the nano-Al_2O_3 and nano-SiC particles have a catalytic effect on the curing reactions of the epoxy resins [9,10]. The T_p of DGEBA/nano-Al_2O_3 composites is lower than that of the DGEBA/nano-SiC composites under similar conditions, which due to acceleration of the amine–epoxide reaction by traces of hydroxyl groups in the nano-Al_2O_3 surfaces.

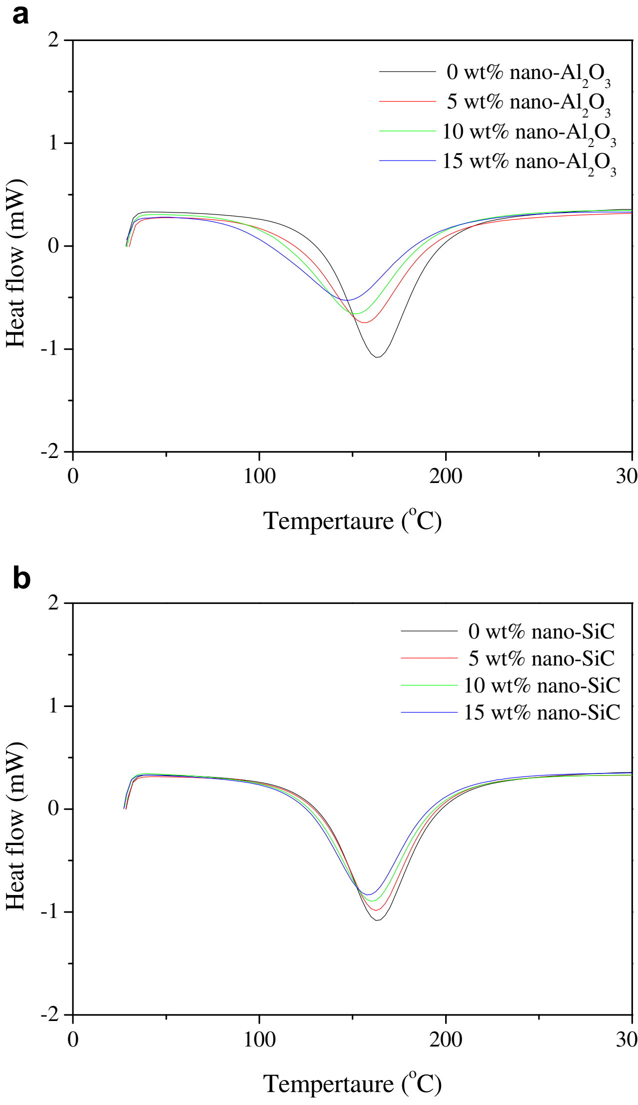

Fig. 1. DSC thermograms of (a) DGEBA/nano-Al_2O_3 and (b) DGEBA/nano-SiC composites.

As shown in Table 1, the ΔH based on epoxy of the DGEBA/nano-Al_2O_3 composites was lower than that of the DGEBA/DDM sample and the ΔH based on epoxy of the DGEBA/nano-SiC composites was

Table 1
Peak maximum temperature (T_p) and reaction enthalpy (ΔH) of DGEBA/nano-Al_2O_3 and DGEBA/nano-SiC composites.

Al_2O_3 content (wt%)	SiC content (wt%)	T_p (°C)	ΔH (J/g-sample)	ΔH (J/g-epoxy)
0	0	163.4	406.7	549.6
5	0	156.5	365.6	529.9
10	0	151.8	346.5	541.4
15	0	147.1	316.0	535.6
0	5	162.5	387.0	560.9
0	10	160.5	374.0	584.4
0	15	158.5	363.7	616.4

higher than that of the DGEBA/DDM sample. This means that the nano-Al_2O_3 particles in the epoxy network structure absorb heat and act as a heat sink in the composites [11]. The ΔH of the DGEBA/nano-Al_2O_3 composites was lower than that of the DGEBA/nano-SiC composites under the same conditions.

Fig. 2 shows the morphology of the DGEBA/nano-Al_2O_3 and DGEBA/nano-SiC composites examined by TEM. As can be seen, the nano-Al_2O_3 and nano-SiC particles are well dispersed in the epoxy matrix.

3.2. *Thermal stability*

The thermal stability of the DGEBA/nano-Al_2O_3 and DGEBA/nano-SiC composites was measured by TGA at a heating rate of 10 °C/min under a nitrogen atmosphere. The results are shown in Fig. 3. The degradation of the composites exhibited a two-stage process. The first stage occurs at the temperature between 35 and 360 °C, which was due to the breaking of unreacted epoxy resin or other impurity traces apart from the cured epoxy resin. The second stage takes place from 360 to 450 °C, corresponding to thermal degradation of the cured epoxy network [12,13].

The thermal stability factors, including the IPDT, activation energies for decomposition (E_t), and char yield at 800 °C, can be determined from the TGA thermograms [12,14]. The IPDT proposed by Doyle correlates the volatile parts of the polymeric materials and has been used to estimate the overall inherent thermal stability of the polymeric materials in the degradation process [15–17]. The IPDT was calculated from the TGA curves using the following equation:

$$\text{IPDT} = A^* K^* \left(T_f - T_i\right) + T_i \tag{2}$$

$$A^* = (S_1 + S_2)/(S_1 + S_2 + S_3) \tag{3}$$

$$K^* = (S_1 + S_2)/S_1 \tag{4}$$

where A^* is the area ratio of the total experimental curve divided by the total TGA thermogram, K^* is the coefficient, is T_i is the initial experimental temperature (35 °C in this study), and is T_f is the final experimental temperature (800 °C). S_1, S_2, and S_3 are the areas of the three regions into which the TGA plot had been divided, as shown in Fig. 4.

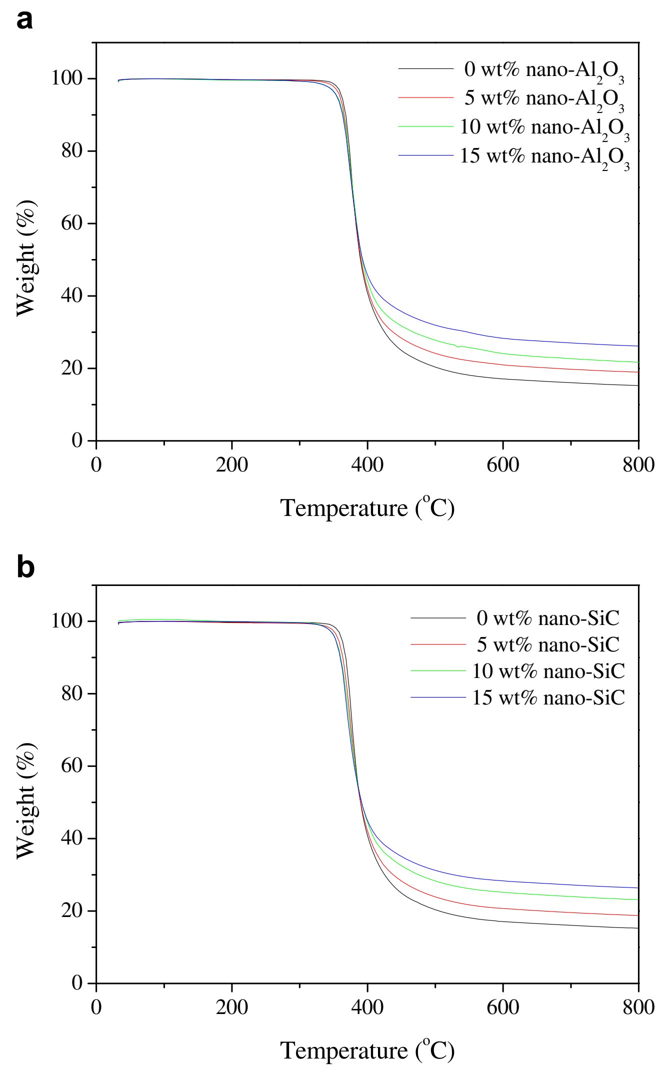

Fig. 3. TGA thermograms of (a) DGEBA/nano-Al_2O_3 and (b) DGEBA/nano-SiC composites.

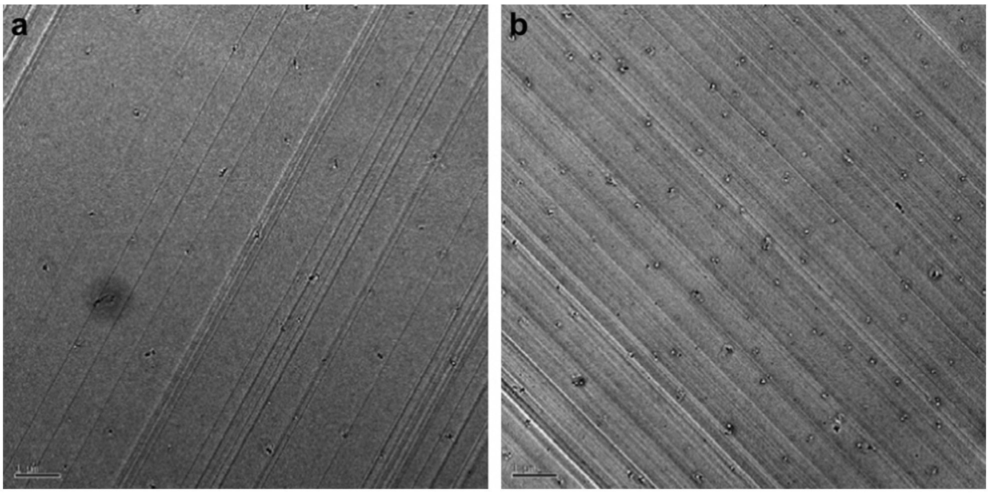

Fig. 2. TEM images of (a) nano-Al_2O_3 and (b) nano-SiC particles in epoxy matrix.

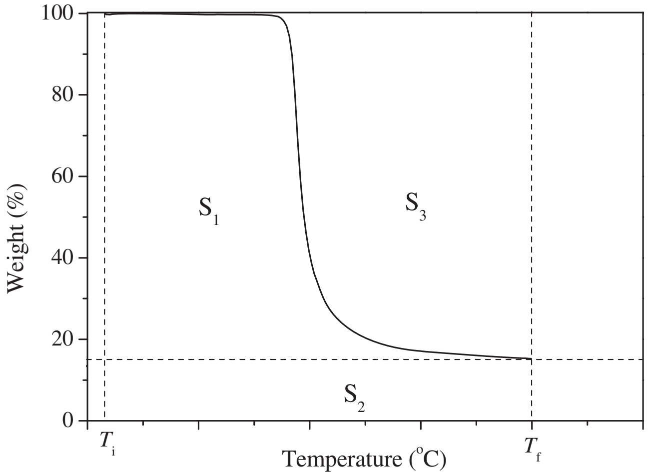

Fig. 4. Schematic representation of S_1, S_2, and S_3.

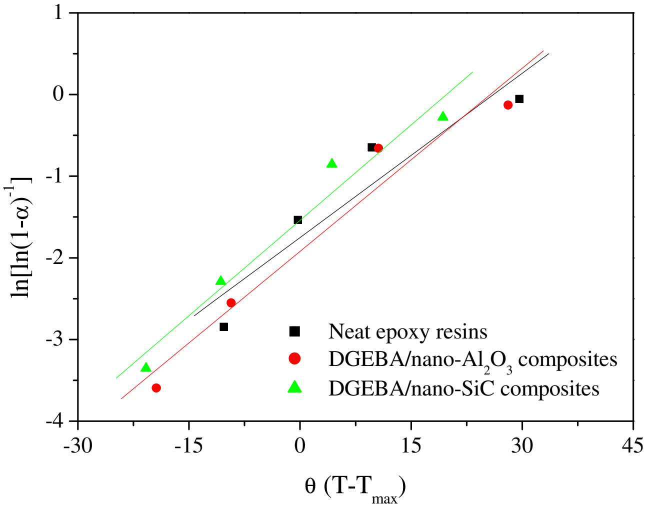

Fig. 5. Plots of $\ln[\ln(1-\alpha)^{-1}]$ vs. θ for DGEBA/nano-Al_2O_3 and DGEBA/nano-SiC composites.

The E_t was calculated from the TGA curves using the integral method reported by Horowitz and Metzger according to the following equation [18,19].

$$\ln\left[\ln(1-\alpha)^{-1}\right] = \frac{E_t\theta}{RT_{\max}^2} \tag{5}$$

where α is the decomposed fraction, $T_{\max}$ is the temperature at the maximum rate of weight loss, $\theta = T - T_{\max}$, and R is the gas constant.

Table 2
Thermal stability of DGEBA/nano-Al_2O_3 and DGEBA/nano-SiC composites obtained from TGA thermograms.

Al_2O_3 content (wt%)	SiC content (wt%)	IPDT (°C)	E_t (kJ/mol)	Char yield at 800 °C (%)
0	0	630.1	77	14.3
5	0	692.0	87	18.9
10	0	750.5	97	21.7
15	0	853.3	96	26.2
0	5	688.3	91	18.8
0	10	781.4	99	23.2
0	15	858.1	102	26.4

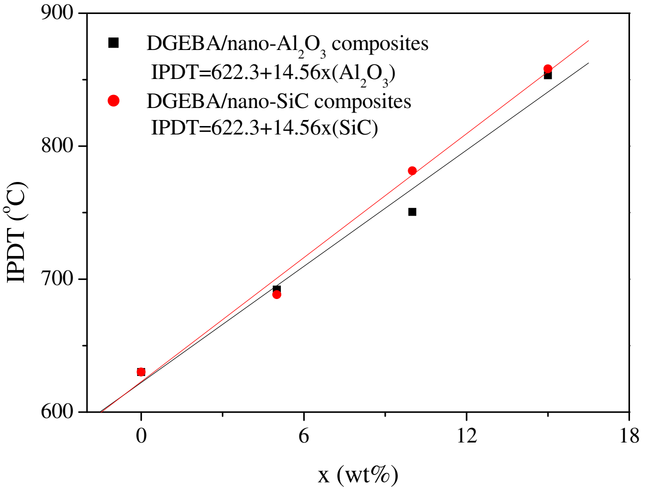

Fig. 6. Linear dependence of IPDT on filler content in DGEBA/nano-Al_2O_3 and DGEBA/nano-SiC composites.

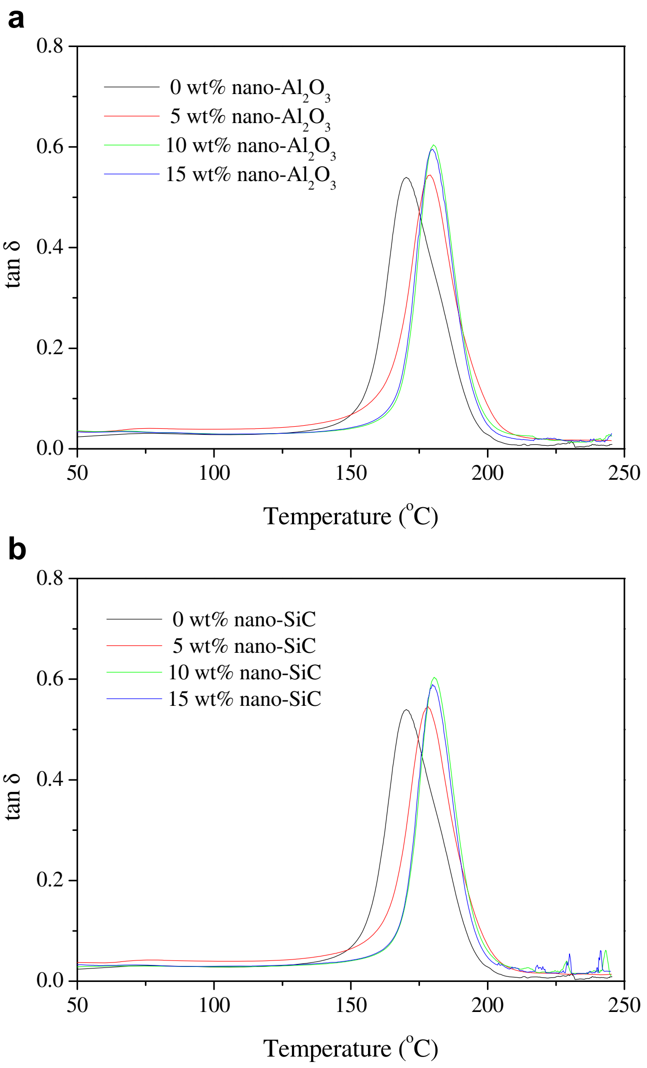

Fig. 7. tan δ of (a) DGEBA/nano-Al_2O_3 and (b) DGEBA/nano-SiC composites as a function of temperature.

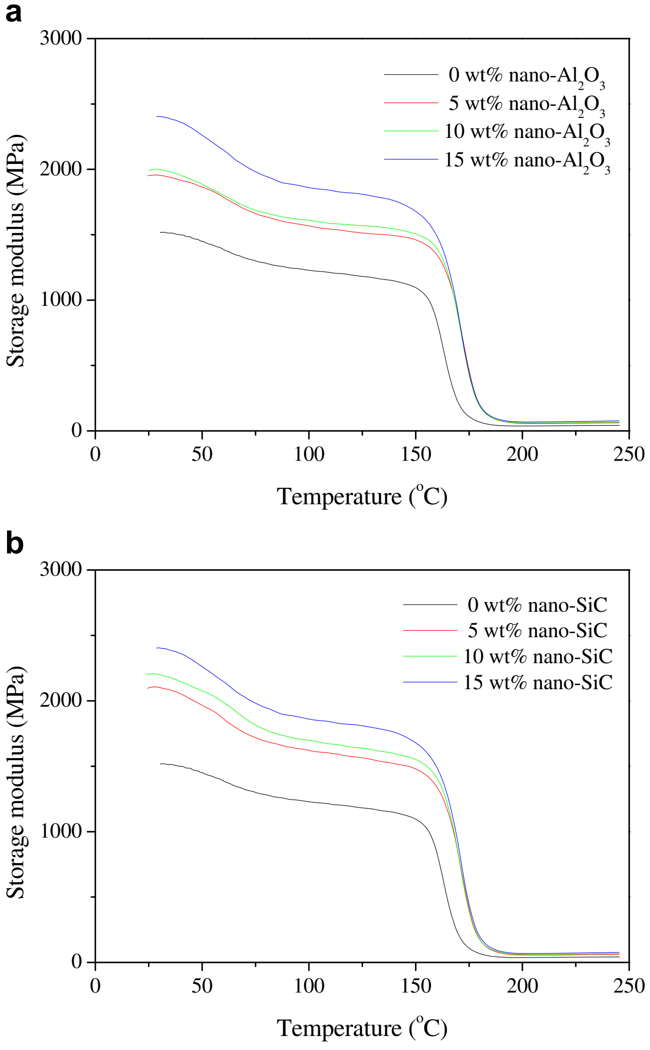

Fig. 8. Storage modulus of (a) DGEBA/nano-Al_2O_3 and (b) DGEBA/nano-SiC composites as a function of temperature.

Fig. 5 shows the plots of $\ln[\ln(1-\alpha)^{-1}]$ vs. θ. The E_t of the both composites was calculated from the slope of the straight lines using Eq. (4). Table 2 lists the thermal stability of both composites at different filler contents. From Table 2, the IPDT of the pure epoxy resin, DGEBA/nano-Al_2O_3 composites, and DGEBA/nano-SiC composites was 630 °C, 692–853 °C, and 688–858 °C, respectively. The thermal stability of both composites increased linearly with increasing filler content in the composites, as shown in Fig. 6.

The E_t of the DGEBA/nano-Al_2O_3 and DGEBA/nano-SiC composites increased from 77 to 97 kJ/mol and 102 kJ/mol, respectively. Furthermore, the char yield at 800 °C of both composites increased gradually with increasing filler content. This was attributed to the formation of char by the Al_2O_3 or SiC layers, retarding degradation in the second stage. This suggests that the nano-Al_2O_3 and nano-SiC particles can improve the thermal stability of the neat epoxy resin. Liu and Tarrío-Saavedra et al. reported similar observations using the epoxy/silica hybrid composites [4,5].

Table 3
Glass transition temperature (T_g) and storage modulus of DGEBA/nano-Al_2O_3 and DGEBA/nano-SiC composites obtained from DMA results.

Al_2O_3 content (wt%)	SiC content (wt%)	T_g (°C)	Storage modulus (MPa)	
			Glassy region[a]	Rubbery region[b]
0	0	170.2	1513	37.7
5	0	178.7	1938	56.5
10	0	180.4	1980	61.5
15	0	179.8	2386	68.8
0	5	178.0	2082	55.8
0	10	180.7	2178	61.6
0	15	180.0	2386	68.9

[a] Storage modulus at 35 °C.
[b] Storage modulus at $T_g + 30$ °C.

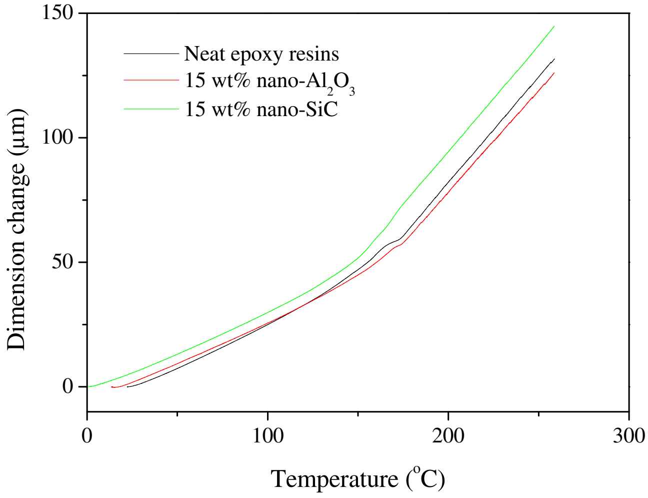

Fig. 9. Dimensional change of DGEBA/nano-Al_2O_3 and DGEBA/nano-SiC composites as a function of temperature.

3.3. Dynamic mechanical properties

The dynamic mechanical properties of the DGEBA/nano-Al_2O_3 and DGEBA/nano-SiC composites were examined by DMA over a range of temperatures. Figs. 7 and 8 show the tan δ and storage modulus of both composites as a function of temperature. The glass transition temperature (T_g) was derived from the DMA results by examining the α-relaxation temperatures. Table 3 lists the T_g and storage modulus. The T_g of the DGEBA/nano-Al_2O_3 and DGEBA/nano-SiC composites increased from 170.2 °C to 180.4 °C and 180.7 °C, respectively. Both composites had a 10 °C higher T_g than the neat epoxy resin. This can be interpreted in terms of the addition of nano-Al_2O_3 or nano-SiC particles to the epoxy resins, which can decrease the free space between the macromolecules, resulting in a decrease in rotation or movement in the composites [2,20].

The storage modulus in the glassy and rubbery regions of both composites increased with increasing filler content. These composites have good heat resistance by the addition of nano-Al_2O_3 and nano-SiC particles [21]. Kuan et al. reported a similar observation using carbon nanotube/epoxy composites [6].

Table 4
Coefficient of thermal expansion of DGEBA/nano-Al_2O_3 and DGEBA/nano-SiC composites.

Al_2O_3 content (wt%)	SiC content (wt%)	CTE (10^{-6} °C)	
		Glassy region	Rubbery region
0	0	78.8	177.1
5	0	76.2	176.8
10	0	75.9	175.3
15	0	70.4	166.2
0	5	76.1	174.9
0	10	75.6	174.0
0	15	73.5	173.2

3.4. Thermal mechanical properties

Fig. 9 shows the dimensional changes in the DGEBA/nano-Al_2O_3 and DGEBA/nano-SiC composites as a function of temperature under a nitrogen atmosphere. Table 4 lists the CTE values. The CTE of the both composites at the glassy and rubbery regions decreased with increasing nano-Al_2O_3 or nano-SiC content. This might be caused by the decreased motion of segments of the macromolecules by the addition of nano-Al_2O_3 or nano-SiC particles to the epoxy resin as well as the increased interfacial adhesion between these nano-particles and the epoxy matrix. Shi et al. reported a similar observation using nano-Al_2O_3 particles-modified epoxy composites [22].

4. Conclusions

The thermal properties of the organic-inorganic hybrid materials based on DGEBA epoxy resin and nano-Al_2O_3 or nano-SiC particles were examined using a range of techniques. The T_p of the DGEBA/nano-Al_2O_3 and DGEBA/nano-SiC composites shifted towards a lower temperature with increasing filler content, i.e., nano-Al_2O_3 or nano-SiC content. The thermal stability and char yield at 800 °C of both composites increased linearly with increasing filler content. The T_g of both composites was 10 °C higher than that of the neat epoxy resin. The storage modulus in the glassy and rubbery regions of both composites increased with increasing filler content. On the other hand, the CTE of the both composites at the glassy and rubbery regions decreased with increasing filler content. These results suggest that the thermal stability of the epoxy resin was improved by the addition of nano-Al_2O_3 or nano-SiC particles.

Acknowledgments

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