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Mechanical properties of intercalated cyanate ester–layered silicate nanocomposites

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Abstract

Cyanate ester resins are among the most important engineering thermosetting polymers and have received attention because of their outstanding physical properties such as low water absorptivity and low outgassing. However, like most thermosets their main drawback is brittleness. Nanocomposites of cyanate esters were prepared by dispersing organically modified layered silicates (OLS) into the resin. Inclusion of only 2.5% by weight of OLS led to a marked improvement in physical and thermal properties (Coefficient of thermal expansion, T_g and effective thermal stability). Most impressively, a 30% increase in both the modulus and toughness was obtained.

Keywords: Cyanate esters; Nanocomposites; High temperature thermosets

1. Introduction

Cyanate esters are currently finding widespread use in high performance electronic and aerospace applications because of their high thermal stability, low outgassing, and radiation resistance [1]. These properties are accompanied by low dielectric (2.5–3.1), dimensional stability at solder temperatures (T_g: 250–290 °C) and low moisture absorption (0.6–2.5%). Cyanate ester homopolymers absorb less water at saturation than epoxy, bismaleimide (BMI), and polyimide resins. Unfortunately, highly cross-linked thermosets, such as cyanate esters, tend to be brittle and to have reduced impact resistance. Although a cured cyanate resin has a relatively higher toughness than a cured BMI or a cross-linked epoxy resin, it still requires suitable modification to improve toughness without reducing the intrinsic physical strength for structural applications.

To improve the toughness of a cured cyanate resin, approaches such as the preparation of flexibilized cyanate resins, the incorporation of monocyanates, the utilization of rubber toughening technologies, and the preparation of semi-interpenetrating networks (SIPNs) have proven useful [2]. However, toughening usually occurs at the expense of other characteristics of the cyanate ester resin. Note that a few examples of utilization of thermoplastic modifiers to improve mechanical properties without sacrificing toughness do exist, such as Pearson and Yee's investigations of DGEBA epoxies [3], but attempts to provide a broad understanding to enable generalization to various thermoset systems have been unsuccessful.

Interest in the addition of nanoscale fillers, such as layered silicates and clays, to polymers as an approach to enhance performance has substantially increased recently [4]. Polymer–clay nanocomposites were first reported in the literature as early as 1961, when Blumstein demonstrated polymerization of vinyl monomers intercalated into montmorillonite clay [5]. Numerous methods to prepare polymer–clay nanocomposites have recently been developed by several groups [6–8]. For example, Pinnavai et al. have achieved exfoliated morphologies using epoxy resins [6]. This is presumably due primarily to the relatively high polarity of these systems, which promotes diffusion into the clay galleries. The acidity of the alkylammonium ions is thought to catalyze homopolymerization of DGEBA epoxy resins. The maximum layer expansion is obtained when

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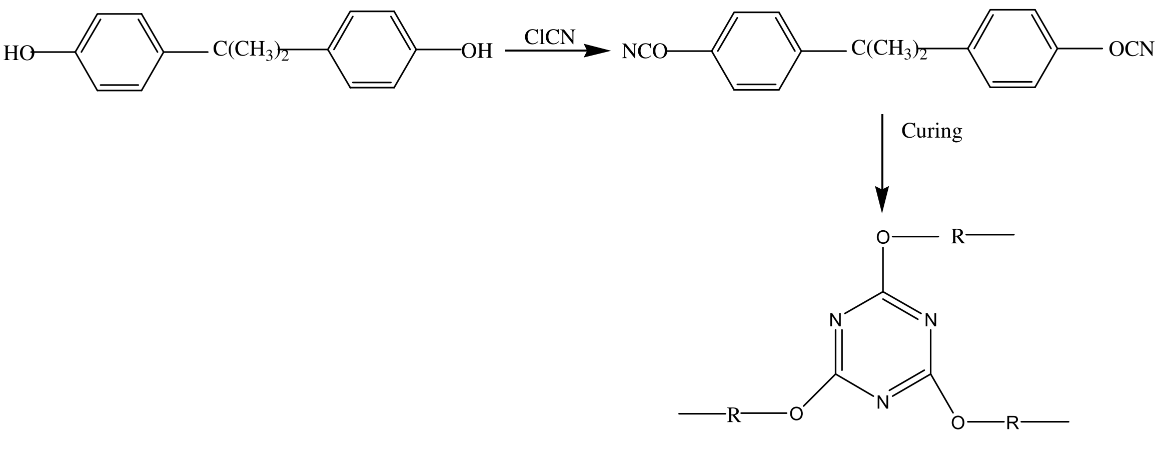

Fig. 1. Network formation of triazines from cyanate esters where $R = C_{15}H_{14}$.

intragallery polymerization rates exceed that in the extragallery regions allowing exfoliation before gelation. A balance between these rates must be maintained in order to insure a homogeneous, three-dimensional network is formed.

In some instances, polymer nanocomposites have demonstrated enhancements in mechanical properties without sacrificing toughness. Several such studies on thermoset-based nanocomposite have been recently reported [6] but primarily focus on epoxy resins, which exhibited T_gs of 110 °C and less. Only a few examples of nanocomposites from high performance thermosets such as PMR-15 (high performance polyimide, T_g: -330 °C [9]) can be found.

Herein fabrication, morphological characterization and properties of cyanate ester montmorillonite nanocomposites are discussed.

2. Experimental

A phenolic-based cyanate ester resin, RS9RTM, was supplied by YLA Inc., Cloisite 30B modified montmorillonite was obtained from Southern Clay Products. The cyanate ester resin was placed in a ceramic crucible maintained at a temperature of 60–65 °C using a hot plate. A high-shear mixing blade was placed into the resin and stirred at 52 rad/s (500 rpm) and Cloisite 30B was slowly added (1, 2.5, 5 and 10%) and mixed for 15 min. The mixture was then sonicated using an ultrasonic probe for 2 min. Sonication was necessary to visibly disperse the Cloisite 30B. The cure schedule was: heat to 110 °C over 120 min under vacuum, then ramp to 188 °C at 5 °C/min and hold for 120 min; then cool to 30 °C over 60 min. The sample was then postcured at 250 °C for 180 min.

Thermogravimetric analysis (TGA) was performed using a TA Instruments TGA 2950 at 10 °C/min in air. The glass transition temperature (T_g) of the cured samples was obtained using a TA Instruments DMA 2980 in the single cantilever mode (strain amplitude of 40 μm, oscillatory frequency of 1 Hz, heating rates of 3 °C/min). Coefficients of thermal expansion (CTEs) were determined using a TA Instruments TMA 2940 in the expansion mode.

A MINIMAT mechanical tester from RSI Inc. was used to determine the mechanical properties. The three-point bend mode was used. An aspect ratio of 7:1 was maintained for all the samples to ensure that the samples were in the plane stress regime. Fracture toughness experiments were conducted using a single edge notched bend specimen according to ASTM method E-399.

Wide angle X-ray scattering (WAXS) measurements were performed on a Bruker D8 Discover system with Eulerian 1/4 cradle, GADDS software and Cu Kα radiation (40 kV, 40 mA). The samples (thickness = 0.14 mm) were run in transmission with the detector (sample to detector distance of 15 cm) centered at $2\theta = 22°$. Patterns, collected for 20 min, were radially integrated (60°). Additional scans were conducted on a Rigaku RU200 rotating anode generator equipped with a Statton camera. Nickel filtered Cu Kα radiation was used at an accelerating voltage of 50 kV/170 mA. The data was collected on phosphor image plates and digitized using a Molecular Dynamics scanner.

3. Results and discussion

3.1. Fabrication

The curing behavior of cyanate ester systems is markedly different from that of an epoxy resin. A typical reaction involves forming an oligomer (molecular weight ~ 2000 g/mol) by reacting a di-functional phenol with a halogen cyanate [10]. The oligomer cures via cyclotrimerization of the cyanate groups to form triazine rings. The cure reaction for the cyanate esters used in this study is shown in Fig. 1.

In the present study, nanocomposites are formed via diffusion of the oligomeric prepolymer into the interlayer regions, followed by cross-linking. The evolution of the morphology during this process was studied by X-ray diffraction, Fig. 2. Cloisite 30B has an interlayer spacing of

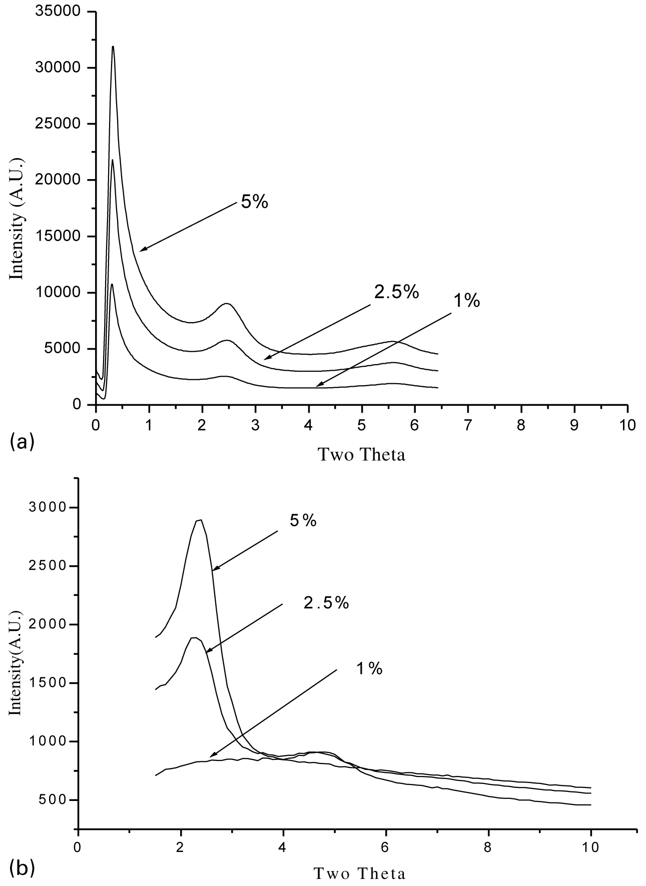

Fig. 2. (a) X-ray diffraction patterns for the uncured cyanate ester systems. (b) X-ray diffraction patterns for the cured cyanate ester systems.

17.83 Å ($2\theta = 4.950$) [9]. This spacing increases to 35 Å ($2\theta = 2.50$) upon addition of the prepolymer. When the sample is cured, the spacing increases to ca. 40 Å ($2\theta = 2.20$) indicative of a small degree of mass transfer into the galleries. Presumably, the OLS surfaces catalyze the curing process, leading to rapid gelation, which retards diffusion of the prepolymer into the galleries and inhibits extensive layer separation [6]. In contrast to the previously examined two-phase epoxy-amine thermoset systems, the cyanate ester is a one-phase thermoset. Nevertheless, while the chemical makeup of the cross-links may not suffer from stoichiometric imbalances due to partitioning of the various components at the silicate surface and within the clay galleries, the cross-link topology (number of unreacted isocynate groups/cross-link) is likely not spatially homogenous.

Note that the cure temperature (188 °C) and the postcure temperature (250 °C) is comparable to the onset of modifier degradation in Cloisite 30B [9]. The extent of the modifier decomposition that occurs during elevated temperature processing and its effect, if any, on the polymer–silicate interface and resulting properties is currently unknown [11]. However, significant improvements in properties have been obtained for both thermosets and thermoplastics inspite of this [5].

Table 1
Physical properties for cyanate ester/layered silicate nanocomposites

	Neat	Cloisite 30B		
		1%	2.5%	5%
K_{1C}[a] (MN/m$^{3/2}$)	0.62	0.72	0.85	0.89
E (GPa)[b]	2.9	3.7	4.5	4.3
Strength (MPa)[c]	173	179	185.2	186
T_g (°C)[d]	305	329	378	390
CTE (μm/m °C)[e]	60	50	46	44
T_D (°C)[f]	334	384	385	395

[a] Stress intensity factor derived by SENB test mode.
[b] Flexural modulus derived by three point bend mode.
[c] Ultimate strength derived from the three point bend test.
[d] Glass transition temperature derived from the DMA test.
[e] Coefficient of thermal expansion (linear), derived from the TMA.
[f] Onset of thermal decomposition derived from the TGA run in air.

3.2. Physical properties

Dynamic mechanical analysis of the neat resin and the nanocomposites are shown in Fig. 3. From the onset of the decrease in the storage modulus curves, the T_g, of the neat resin increases significantly from 305 to 390 °C for the 5% nanocomposite. These values are summarized in Table 1. Additional insight on the nature of the cross-link topology is evident in the loss modulus curves, shown in Fig. 3(b). The neat resin exhibits a single relaxation centered at ca. 300 °C while the nanocomposites exhibit multiple, broad relaxations, indicative of a more heterogeneous cross-link topology [4].

Fig. 4 shows the non-isothermal decomposition of the neat cyanate ester and its nanocomposites. The neat resin exhibits an initial weight loss at ca. 400 °C, which is due to thermoxidative degradation of the ether oxygen bond between the phenyl and triazine rings [4]. A slight increase in the temperature of the weight loss is observed upon addition of clay. The second weight loss, may be due to the breakdown of the triazine ring occurs at ca. 550 °C for the neat resin [4], and shifts to a maximum of ca. 600 °C for the highest clay loading. In addition, the rate of the mass loss decreases with increasing clay loading, presumably indicative of char formation. It is noted that the residual char correlates with the respective clay contents (minus the organic modifier).

The results of the mechanical tests are listed in Table 1. CTE exhibit a 26% decrease for 5% 30A. Overall, the nanocomposites exhibited increase in modulus, strength and toughness. Modulus and toughness increased by 30%, while the improvement in strength was minimal, only 7%. The toughness as measured by the stress intensity factor increased from 0.62 to 1.44 MN/m$^{3/2}$. While the improvement in toughness is not as large as that obtained using n-phenyl–maleimide styrene copolymers [12], deterioration of other properties such as modulus, strength and T_g did not occur. It has been postulated that toughening effects in

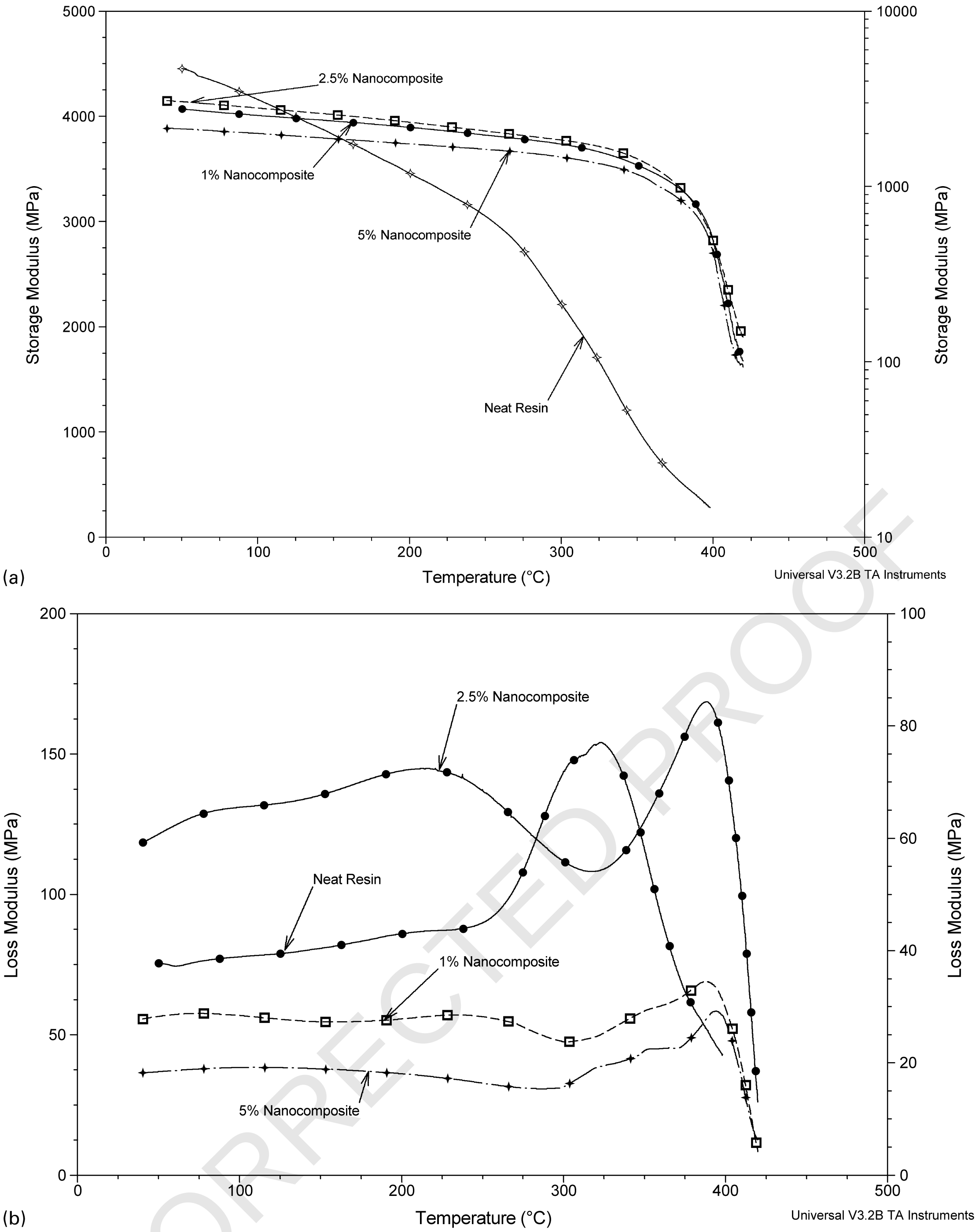

Fig. 3. (a) Storage modulus versus temperature for cyanate ester/layered silicate nanocomposites. (b) Loss modulus versus temperature for cyanate ester/layered silicate nanocomposites.

epoxy nanocomposites may arise from plasticization by the oninium ions. [6]. However, the DMA results did not indicate a decrease in the T_g of the cyanate ester nanocomposites associated from plasticization. The T_g increased with increasing clay content, indicative of an increase in the cross-link density, mechanical reinforcement arising from a percolated clay morphology, and/or restriction of segmental relaxation of chain segments near the clay layers. An increase in cross-link density though is usually accompanied by a decrease in toughness. Thus, the toughening effect must be directly attributed to the presence of the clay and not its effect on network topology.

4. Conclusions

Cyanate ester/layered silicate nanocomposites have been synthesized. In addition to increased onset of

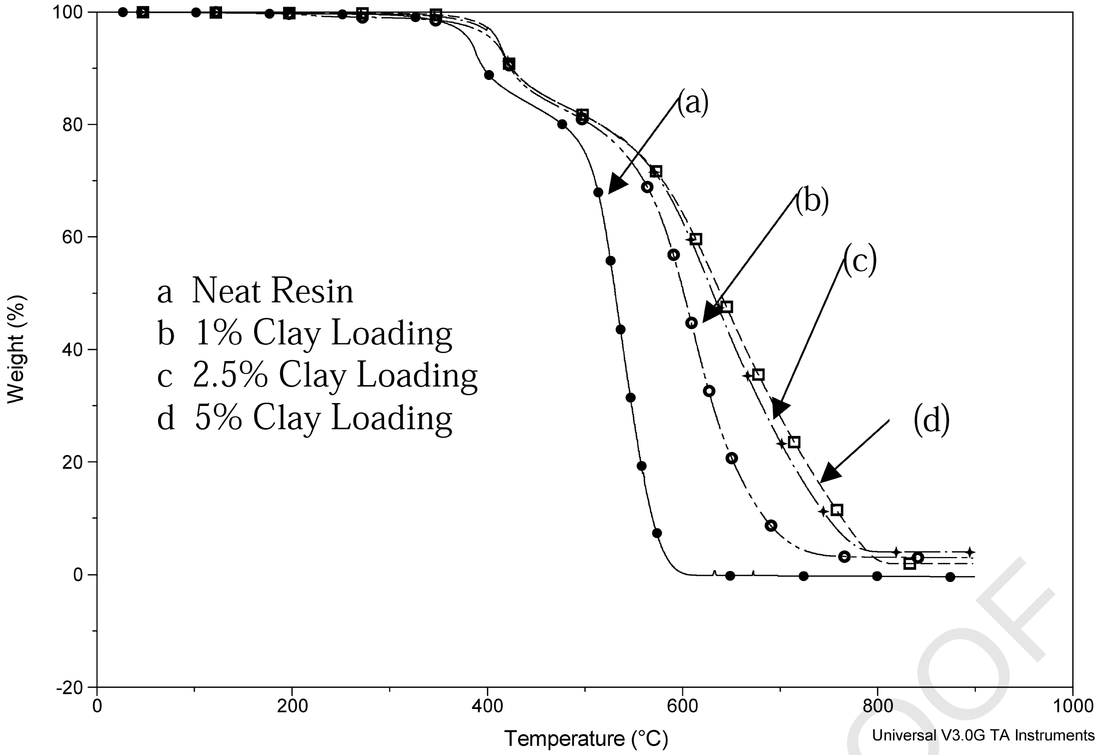

Fig. 4. TGA scans for cyanate ester/layered silicate nanocomposites.

non-isothermal decomposition, the T_g improved from 354 °C for the neat resin, to 387 °C for 2.5% loading. The fracture toughness and the flexural modulus were found to increase by 30% as the clay loadings increased to 5%. Optimization of the mechanical properties and associated cure cycle for these materials will depend on understanding the interplay of cure chemistry, resin–clay interface and cross-link topology on the toughness, rheology and modulus.

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