

Curing Behavior and Thermal Mechanical Properties of Cyanate Ester Blends

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ABSTRACT: Cyanate esters are a class of important thermally resistant polymers. To tailor their processability and thermomechanical properties, a series of cyanate ester blends based on a trifunctional novolac cyanate ester (HF-5), a difunctional bisphenol E cyanate ester (HF-9), and a reactive catalyst [2,2'-diallyl bisphenol A (DBA)] were formulated. The effect of the blend composition on the rheology and curing behavior of these cyanate ester blends and the corresponding thermal and mechanical properties of the cured cyanate ester blends was studied. The results showed that HF-5 contributed to good mechanical property retention at high tempera-

tures because of its trifunctionality, whereas HF-9 imparted processability by reducing the viscosity and extending the pot life of the formulated cyanate ester blends at the processing temperature. On the basis of the results, an optimal cyanate ester blend suitable for resin transfer molding was determined: the HF-5/HF-9/DBA weight ratio of 80 : 15 : 5 exhibited good processability and thermomechanical properties. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4284–4290, 2006

Key words: blends; curing of polymers; mechanical properties; thermal properties

INTRODUCTION

Cyanate ester resins possess many attractive properties. They polymerize through the cyclotrimerization of three cyanate groups to form triazine linkages¹ that result in strong crosslinking, leading to their excellent thermal and mechanical properties as well as good adhesion to metal substrates. Moreover, the symmetric structure of the triazine ring promotes a low dielectric constant (2.8–3.2) and dielectric loss and low moisture absorption of cyanate esters. All these factors make them ideal for electrical insulation for electronic devices^{1–5} and high-temperature matrix materials for fiber-reinforced structural composites.^{6–9}

The curing reaction of cyanate esters usually occurs at high temperatures as it requires high steric specificity for the cyanate groups to come in close proximity for cyclotrimerization. In fact, pure cyanate ester has been shown not to cure at all, and such noncatalytic curing is due to adventitious impurities present in the cyanate ester from either hydrogen-donating impurities or reaction byproducts.¹⁰ For this reason, catalysts are usually used to reduce the curing temperature and time. It has been reported that metal complexes, organometallic salts, and hydrogen donors (e.g., nonyl phenol) are suitable catalysts for the polymerization of cyanate esters.^{11–14} The metal cations can form complexes with the cyanate groups, bring-

ing them into close proximity for cyclotrimerization.^{1,15} Cyclotrimerization is eventually promoted by hydrogen donors, such as adventitious impurities, or by the incorporation of a cocatalyst, such as nonyl phenol. The cocatalyst blends, typically metal acetylacetonate/nonyl phenol blends, have also been investigated with considerable success.^{11–14} Recently, work on bismaleimide (BMI)/cyanate ester and polyimide/cyanate ester interpenetrating polymer networks^{16,17} has suggested that 2,2'-diallyl bisphenol A (DBA; Fig. 1), added as a toughener for BMI and polyimides, can also catalyze the cyclotrimerization of cyanate esters by its hydrogen-donating phenol groups through the formation of the reactive imidocarbonate intermediate.

In our previous work,¹⁸ the catalytic effect of DBA on two cyanate esters (Fig. 1), trifunctional novolac cyanate ester (HF-5) and difunctional bisphenol E cyanate ester [i.e., 2,2'-bis(4-cyanatophenyl)ethylene (HF-9)], and its potential toughening effect on the rigid novolac HF-5 were studied. The results demonstrated that DBA is especially suitable for catalyzing the polymerization of HF-5, as it acts both as a reactive curing catalyst by depressing the exothermic peak temperature (T_{exo}) by nearly 100°C and as a toughening agent of HF-5 by slightly reducing its elastic modulus (E') in the glassy state. The addition of 5 wt % DBA to cyanate esters is adequate to catalyze the curing reaction of cyanate ester resins.

Although DBA-catalyzed HF-5 exhibits good thermal and mechanical properties, its viscosity at the processing temperature (80°C) is still high (>1000 cP) for employing resin transfer molding (RTM) to fabricate fiber-reinforced polymer composites. To improve

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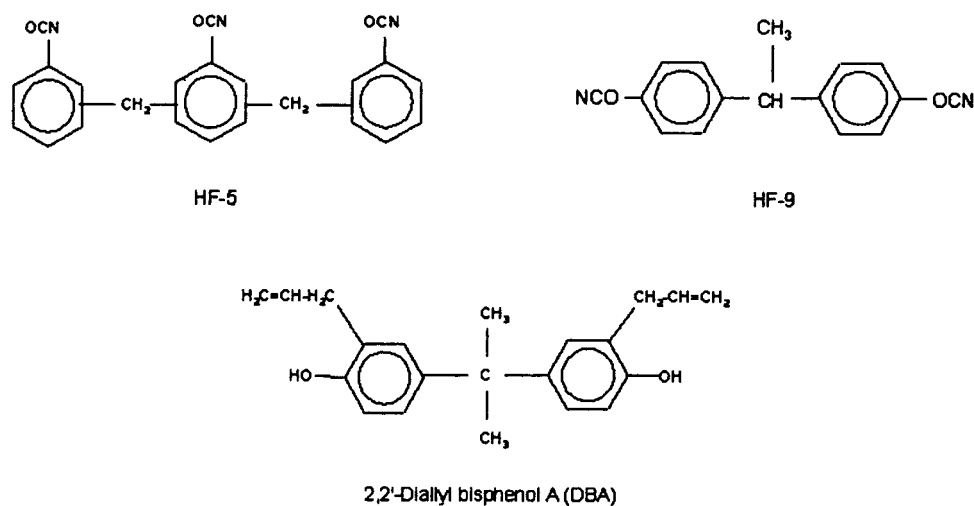


Figure 1 Chemical structures of HF-5, HF-9, and DBA.

the processability, it is preferred that the viscosity of the cyanate ester resin at the processing temperature (80–90°C) be further reduced below 600 cP and that the corresponding pot life be greater than 2 h. To this end, this research was directed to study DBA-catalyzed cyanate ester blends based on trifunctional HF-5 and difunctional HF-9. The effects of the blend composition on the rheology and curing behavior of these cyanate ester blends and the corresponding thermomechanical properties of the cured cyanate ester blends were investigated. On the basis of the results, an optimal cyanate ester blend formula suitable for the RTM process with a satisfactory viscosity, pot life, and thermomechanical properties was identified.

EXPERIMENTAL

Raw materials

The two cyanate ester resins, HF-9 and HF-5, were purchased from Shanghai Huifeng Technical & Business Co., Ltd. (Shanghai, China). DBA was supplied by Laiyu Chemical Co., Ltd. (Laizhou City, China). All the materials were vacuum-dried around 80°C before use.

Formulation and curing

The cyanate ester blends were formulated by homogeneous mixing of the three components, two cyanate esters (HF-5 and HF-9) and their catalyst (DBA), followed by vacuum degassing for 30 min to remove the trapped air bubbles before curing. As HF-5 is a highly viscous liquid at room temperature, the formulated cyanate ester blends were usually heated to around 80°C for easy mixing and degassing.

The formulated cyanate ester blends were consecutively cured at 120, 140, and 160°C (each for 2 h) in an air-circulated oven. The cured cyanate ester samples formed light brown, transparent solids and needed

further postcuring to achieve the maximum conversion of cyanate groups into crosslinked triazine structures. Postcuring was conducted at 250°C for 4 h in an air-circulated oven. The cyanate ester blend samples after postcuring were dark brown because of the thermal oxidation. The curing mechanism of the cyanate ester blends based on trifunctional HF-5 and difunctional HF-9 was sketched in Figure 2.

Characterization

The differential scanning calorimetry (DSC) curves (heat flow vs temperature) of the cyanate ester blends were acquired on a DSC 2962 differential scanning calorimeter (TA Instruments, New Castle, DE). The testing temperature ranged from 30 to 350°C with a temperature ramping rate of 5°C/min under a purge of N₂. The DSC curves were used to study the curing behavior of these cyanate ester blends based on T_{exo} and the heat of polymerization (ΔH) obtained by integration of the exothermic curing peak.

The infrared spectra of cyanate ester blends at different curing stages were recorded on an IRPrestige-21 Fourier transform infrared (FTIR) spectrophotometer (Shimadzu, Japan). The obtained infrared spectra were averaged over 64 scans from 4800 to 500 cm⁻¹ with a resolution of 4 cm⁻¹. The FTIR samples were prepared by the sandwiching of the cyanate ester blends between two KBr crystal discs. The gradual disappearance of the cyanate ester group absorption peak at 2230 cm⁻¹ and the gradual emergence of the triazine absorption peaks at 1370 and 1570 cm⁻¹ indicated the cyclotrimerization of the cyanate ester blends.

The rheology of the formulated cyanate ester blends in terms of the viscosity–time curves was characterized with a Brookfield DV-II+ viscometer at 80 and 90°C.

The thermogravimetric curves (weight loss vs temperature) of the cyanate ester blends were measured with an SDT 2960 simultaneous DSC/thermogravi-

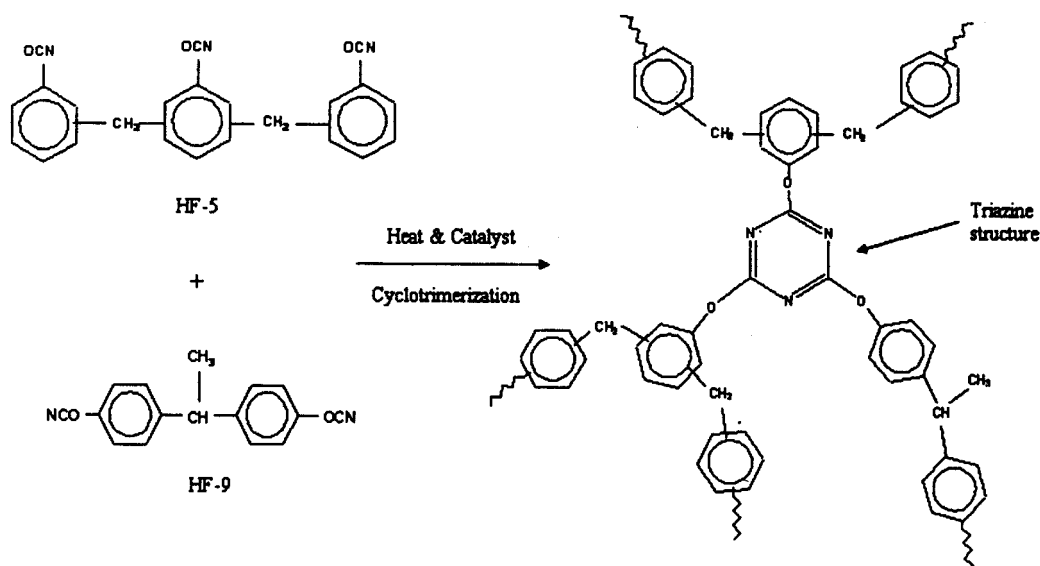


Figure 2 Curing mechanism of cyanate ester blends.

metric analysis (TGA) instrument (TA Instruments). The testing temperature range was 40–900°C with a temperature ramping rate of 10°C/min under a purge of N₂. The thermogravimetric curves were used to evaluate the thermal stability of the cured cyanate ester blends in terms of the decomposition temperature at 5% weight loss (T_d^5) as well as the char yield of the cyanate ester blends at 900°C.

The thermomechanical properties of the cyanate ester blends were characterized with a Rheometric DMTA 3E dynamic mechanical thermal analyzer in the three-point-bending mode. The cyanate ester blends were measured at temperatures ranging from 40 to 350°C with a temperature ramping rate of 3°C/min at 1 Hz. The measured E' /temperature curves and the loss factor ($\tan \delta$)/temperature curves were used to characterize the mechanical property retention at elevated temperatures and the corresponding

glass-transition temperatures (T_g 's) of these cured cyanate ester blends.

RESULTS AND DISCUSSION

Curing behavior

DSC is an effective technique for characterizing the curing behavior of cyanate esters as the exothermic peak corresponding to the cyclotrimerization of cyanate esters can be observed in DSC curves. In our previous studies on the catalytic effect of DBA on the thermal curing of cyanate esters,¹⁸ the optimal amount of the catalyst for cyanate esters was determined to be 5 wt % of DBA as the T_{exo} values of pure HF-5 and HF-9 were remarkably reduced by around 100 and 40°C upon the addition of 5 wt % DBA. In this work, all the cyanate ester blends were formulated by the incorporation of

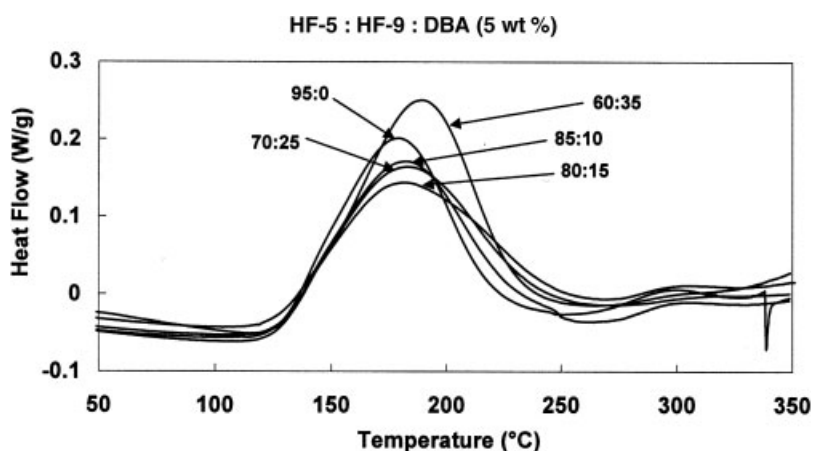


Figure 3 DSC curves of HF-5/HF-9 cyanate ester blends catalyzed with 5 wt % DBA.

TABLE I
C Data for Cyanate Ester Blends

HF5/HF-9/DBA (wt %)	T_{exo} ($^{\circ}\text{C}$)	ΔH (J/g)
95:0:5	177.5	161.6
85:10:5	181.1	173.7
80:15:5	177.3	151.0
70:25:5	180.7	160.5
60:35:5	187.9	198.4

5 wt % DBA as a catalyst. Figure 3 illustrates the DSC curves of the formulated cyanate ester blends with different HF-5/HF-9 weight ratios, and Table I lists their corresponding DSC data. Because the same amount of the catalyst was used, the exothermic peaks of these cyanate ester blends were located in the same temperature region in the DSC curves, with T_{exo} within 177–187 $^{\circ}\text{C}$. In addition, ΔH of these cyanate ester blends was on a similar level, suggesting that the change in the HF-5/HF-9 weight ratio did not significantly influence the curing behavior of these cyanate ester blends. According to the temperature range of these exothermic peaks in Figure 3, curing at 120–160 $^{\circ}\text{C}$ and postcuring at 250 $^{\circ}\text{C}$ are appropriate for curing these cyanate ester blends.

FTIR is another means of studying the curing behavior of cyanate esters¹⁹ through the monitoring of the cyanate ester group absorption peak around 2230 cm^{-1} and the two triazine absorption peaks at 1370 and 1560 cm^{-1} during the course of curing and postcuring. Figure 4 depicts the FTIR spectra recorded before curing, during curing, and after postcuring of the cyanate ester blend with the HF-5/HF-9/DBA weight ratio of 80 : 15 : 5. As shown in Figure 4, the curing reaction took place during the course of curing and postcuring, as evidenced by a gradual reduction of the cyanate ester group absorption peak around 2230 cm^{-1} and a gradual emergence of the two triazine absorption peaks at 1370 and 1560 cm^{-1} .

To quantitatively monitor the polymerization level of these cyanate ester blends during curing and postcuring, the phenyl absorption peak at 1500 cm^{-1} was used as the internal reference peak for a quantitative comparison between different FTIR spectra, as the phenyl groups remained unreacted throughout the curing reaction. The ratio of the area reduction of the cyanate ester absorption peak at 2230 cm^{-1} at a certain curing stage to its original peak area was used to calculate the polymerization level. Figure 5 displays the polymerization level of the cyanate ester blends based on different ratios of trifunctional HF-5 to difunctional HF-9 catalyzed with 5 wt % DBA at different curing stages. Figure 5 shows that all four cyanate ester blends had similar curing profiles. With curing at 120 $^{\circ}\text{C}$ for 2 h, the polymerization level of these cyanate ester blends was around 49–58%. Upon further thermal curing at 140 $^{\circ}\text{C}$ for 2 h and at 160 $^{\circ}\text{C}$ for 2 h, the polymerization level of these cyanate ester blends gradually increased to 62–67 and 67–75%, respectively. It is believed that when a polymerization level of around 50–60% is reached, the curing kinetics become diffusion-controlled, as significant crosslinking hinders the unreacted cyanate ester groups from coming into close proximity for further cyclotrimerization.¹ Accordingly, postcuring at the higher temperature (250 $^{\circ}\text{C}$) was required to achieve a higher level of polymerization (> 90%). Similarly to our previous findings,¹⁸ it was difficult to achieve full polymerization of these cyanate ester blends even after postcuring at 250 $^{\circ}\text{C}$ for 4 h, and their respective polymerization level was within 89–95%.

It is generally believed that polymer resins should be postcured at temperatures above their T_g 's to achieve full polymerization through increased mobility of the unreacted functional groups. To confirm this assumption, two cyanate ester blend samples with the HF-5/HF-9/DBA weight ratios of 70:25:5 and 60:35:5 were further postcured at 300 $^{\circ}\text{C}$ for 4 h, as

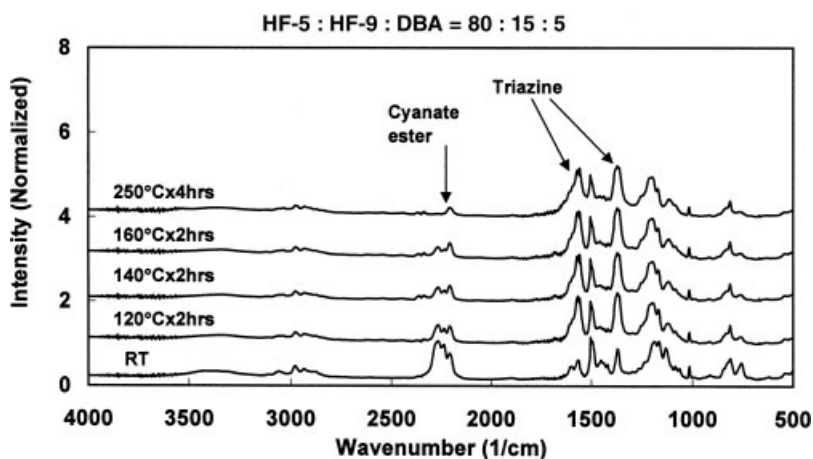


Figure 4 FTIR spectra of a cyanate ester blend (HF-5/HF-9/DBA = 80:15:5) recorded at different curing stages.

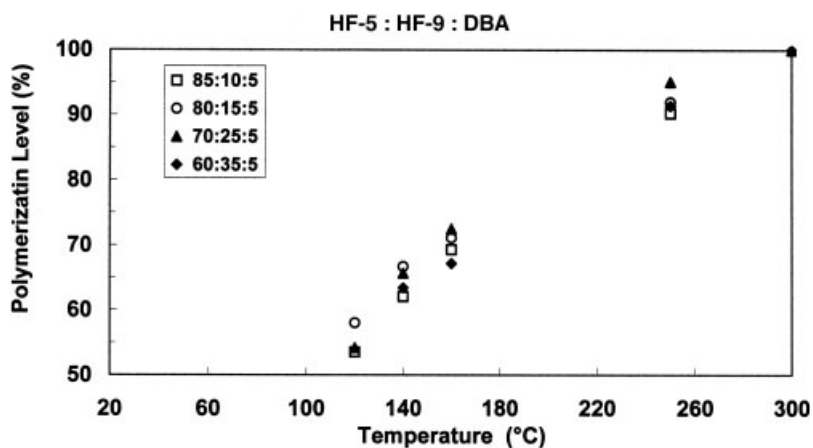


Figure 5 Polymerization level of cyanate ester blends at different curing stages.

their T_g 's were around 290°C (obtained by the thermomechanical property characterization discussed later in this article). As shown in Figure 5, upon post-curing at 300°C for 4 h, all the cyanate ester groups in these two cyanate ester blends were converted into a crosslinked triazine structure. Under such a postcuring condition (300°C), the resultant cyanate ester resin will be adversely oxidized.

Rheology

The rheology of the formulated cyanate ester blends was studied by the monitoring of their viscosity response with time at 80 and 90°C. It is important to know the initial curing behavior of these cyanate ester blends to determine the processing parameters for fabricating fiber-reinforced polymer composites. Figure 6 shows the viscosity–time curves of the formulated cyanate ester blends with different HF-5/HF-9 weight ratios at 80°C for around 2 h and at 90°C for around 1 h. At 80°C, these cyanate ester blends were quite stable as their viscosity was marginally in-

creased within 2 h. Then, with heating to 90°C, the viscosity of these cyanate ester blends was remarkably reduced and increased faster with time than at 80°C, especially for those blends with lower difunctional HF-9 contents (0–10 wt %). Accordingly, the optimal processing temperature of these cyanate ester blends was 80°C as a longer pot life (> 2 h) was expected. It was also observed that increasing the content of difunctional HF-9 could effectively reduce the viscosity and extend the pot life of the formulated cyanate ester blends. To employ the RTM technique to process these cyanate ester blends, the resin viscosity should be kept as low as possible (< 600 cP) for at least 2 h at 80°C. According to this guideline, suitable cyanate ester blends are those with an HF-9 concentration of 15–35 wt %.

Thermal stability

TGA was carried out for the cured cyanate ester blends in a nitrogen purge. As shown in Figure 7, all four cyanate ester samples exhibited similar TGA pro-

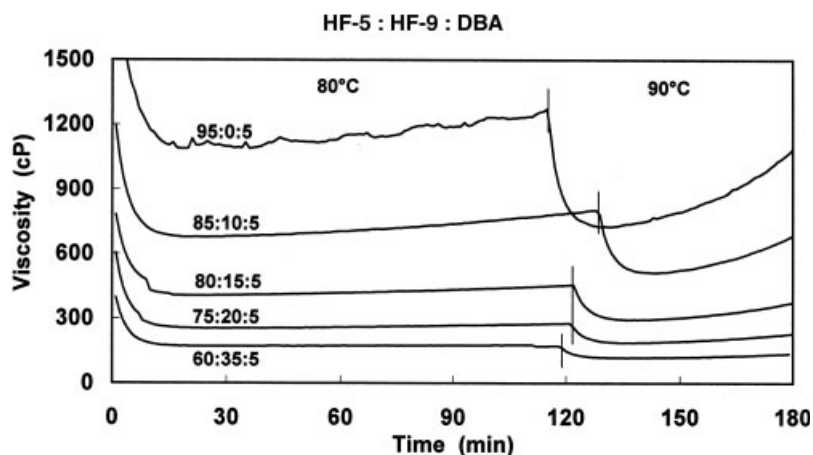


Figure 6 Viscosity–time curves of cyanate ester blends at 80°C for around 2 h and at 90°C for around 1 h.

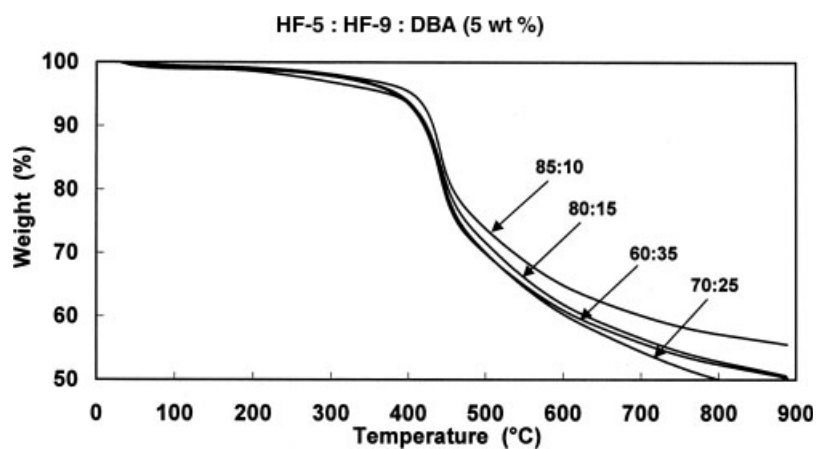


Figure 7 TGA curves of cyanate ester blends measured under a nitrogen purge.

files with T_d^5 around 430°C and a char yield at 900°C around 53–58 wt %, indicating their good stability against thermooxidative degradation. Increasing the difunctional HF-9 content in the blends caused a decrease in weight retention in the high temperature region (400–900°C), and a slightly lower thermal resistance was shown.

Thermomechanical properties

Figures 8 and 9 show the E' /temperature and corresponding $\tan \delta$ /temperature curves of the cyanate ester blends after postcuring at 250°C for 4 h. All four cyanate ester blends had similar E' values at room temperature and maintained their E' values up to 250°C. In the higher temperature region (250–350°C), E' of these cyanate ester blends started to gradually degrade as the temperature increased. The higher the HF-9 content was in the blend, the heavier the degradation was in E' . Figure 9 shows that the T_g 's of these cyanate ester blends were around 290°C. In addition, their $\tan \delta$ peaks became gradually prominent as the HF-9 content increased in the blends. These results

indicated that the addition of difunctional HF-9 to trifunctional novolac HF-5 resulted in a decrease in the mechanical property retention in a higher temperature region (250–350°C). For this reason, the processability and thermomechanical properties have to be compromised in formulating cyanate ester blends. On this basis, the optimal cyanate ester blend suitable for the RTM process, with good processability (low viscosity and long pot life at 80°C) and satisfactory thermal and mechanical properties, was determined to have an HF-5/HF-9/DBA weight ratio of 80:15:5.

CONCLUSIONS

A series of cyanate ester blends based on two cyanate esters, trifunctional HF-5 and difunctional HF-9, and their catalyst, DBA, were formulated. Their curing behavior, rheology, and thermomechanical properties were characterized. DSC and FTIR measurements showed that these cyanate ester blends had similar curing behaviors, as evidenced by their similar exothermic peaks in DSC curves corresponding to the

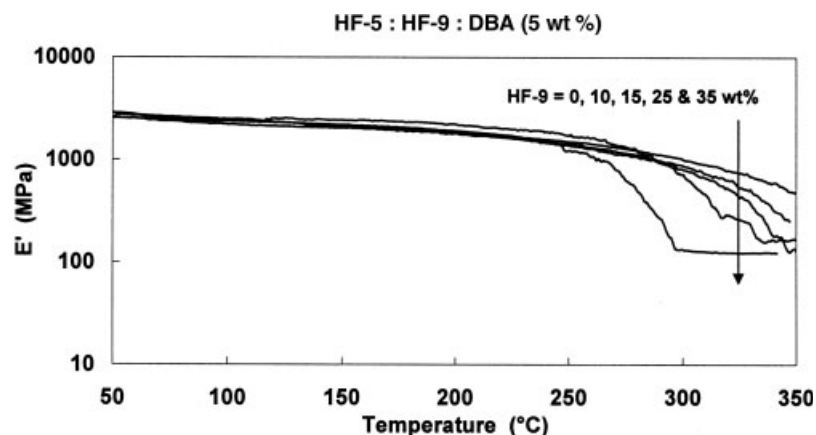


Figure 8 E' /temperature curves of cured cyanate ester blends.

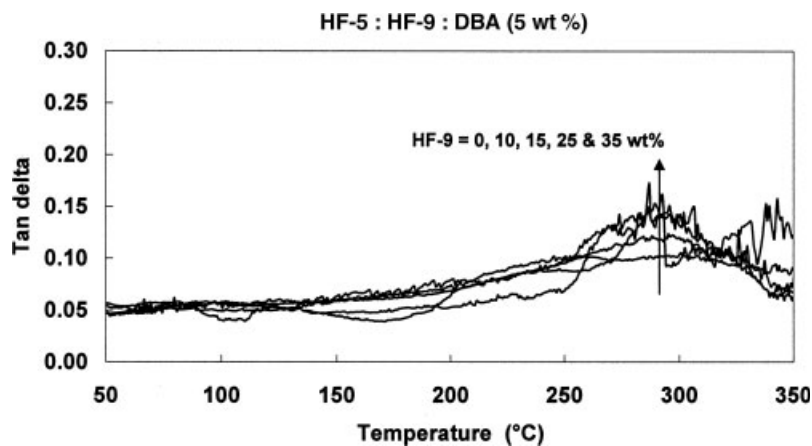


Figure 9 Tan δ /temperature curves of cured cyanate ester blends.

cyclotrimerization of cyanate ester groups and their similar polymerization levels at different curing stages derived from FTIR spectra. The rheology and thermomechanical property characterization of these cyanate ester blends indicated that increasing the difunctional HF-9 content in the blends caused a decrease in the viscosity at 80°C and degraded mechanical property retention in a higher temperature region (250–350°C). On the basis of these results, the optimal cyanate ester blend suitable for the RTM process, with good processability as well as good thermal and mechanical properties, was determined to have an HF-5/HF-9/DBA weight ratio of 80:15:5.

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