Catalytic Effect of 2,2′-Diallyl Bisphenol A on Thermal Curing of Cyanate Esters

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ABSTRACT: Cyanate esters are a class of thermal resistant polymers widely used as thermal resistant and electrical insulating materials for electric devices and structural composite applications. In this article, the effect of 2,2′-diallyl bisphenol A (DBA) on catalyzing the thermal curing of cyanate ester resins was studied. The curing behavior, thermal resistance, and thermal mechanical properties of these DBA catalyzed cyanate ester resins were characterized. The results show that DBA is especially suitable for catalyzing the polymerization of the novolac cyanate ester resin (HF-5), as it acts as both the curing catalyst through depressing the exothermic peak temperature (T_{exo}) by nearly 100°C and the toughening agent of the novolac cyanate ester resin by slightly reducing the elastic modulus at the glassy state. The thermogravimetric analysis and dynamic mechanical thermal analysis show that the 5 wt % DBA-catalyzed novolac cyanate ester resin exhibits good thermal resistance with T_d^5 of 410°C and the char yield at 900°C of 58% and can retain its mechanical strength up to 250°C. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1775–1786, 2006

Key words: 2,2′-diallyl bisphenol A; DBA; cyanate ester; novolac cyanate ester; catalytic effect; thermal curing

INTRODUCTION

Recent developments in electronic circuitry, wireless communications,[1–3] and also aerospace structural composites[4–7] have pushed the demands for new materials that are lightweight and yet possess a combination of excellent mechanical properties, good thermal stability, and retention of these mechanical properties at high temperatures. To this end, epoxy, Bismaleimide (BMI), and recently cyanate ester-based resins and composites have emerged as excellent materials to fulfill these increasing technological demands.[8] Epoxy resins boast easy processibility, thus making it attractive in industrial scale processes. However, epoxy resins retain their mechanical properties only up to 150°C, which makes them unsuitable for aerospace applications. BMI-based resins are, to date, the best choice of thermal resistant polymers for their ease in processing, good thermal stability, fire resistance, and long-term usage at elevated temperatures up to 230°C. However, they suffer from brittleness, due to the stacking of the polymer chains affected by the polarity of the carbonyl groups and their high crosslinking density.[4] Thus, toughening additives, such as 2,2′-diallyl bisphenol A (DBA), are often employed to improve the toughness and processibility

while maintaining good mechanical properties at elevated temperatures.[9,10] In addition, the polar carbonyl groups in BMI results in relatively high dielectric constants that limits their application in electronics and wireless communications. To this end, cyanate ester resins have emerged as a promising candidate that combines the advantages of both epoxy and BMI resins to meet the technological needs.

Cyanate ester resins possess good mechanical properties at elevated temperatures up to 250°C. In addition, they possess low dielectric constant (ε = 2.8–3.2) and dielectric loss, relatively low moisture absorption and toxicity as compared with BMI resins, making them ideal for electrical insulation for electronic devices as well as wireless communications. Cyanate ester resins polymerize through cyclotrimerization of three cyanate groups to form triazine linkages[8] that result in the strong crosslinking, leading to their excellent thermal and mechanical properties. The triazine ring promotes low dielectric constant and low moisture absorption because of its symmetric structure. However, this crosslinking via cyclotrimerization requires high steric specificity for the cyanate groups to come in close proximity for the reaction to take place, and thus, this thermal-initiated curing reaction typically requires high temperatures above 250°C. In fact, pure cyanate ester has been shown[11] not to cure at all, and such so-called noncatalytic curing is due to adventitious impurities present in the cyanate ester, from either hydrogen donating impurities or reaction by-products.
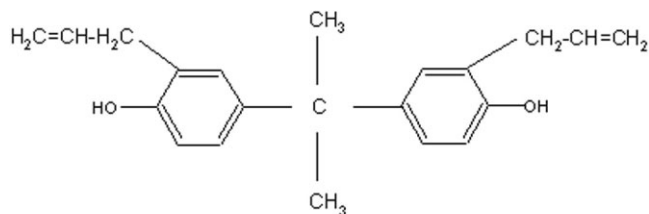
Figure 1 Chemical structure of 2,2′-diallyl bisphenol A (DBA).

To increase the practical processibility of cyanate resins, catalysts are often added. Previous work[12–15] has identified metal complexes, organometallic salts, and hydrogen donors (e.g., nonyl phenol) as suitable catalysts for polymerization of cyanate esters. It is well established[8,16] that the metal ion complexes with the cyanate groups bring them into close proximity for cyclotrimerization. Cyclotrimerization is eventually promoted by hydrogen donors, such as adventitious impurities or by incorporation of a cocatalyst, for example, nonyl phenol. Thus, cocatalyst blends, typically metal acetylacetonate/nonyl phenol blends, have also been investigated with considerable success.[12–15]

Recently, works on BMI-cyanate ester and polyimide-cyanate ester interpenetrating polymer networks[17,18] suggested that DBA (Fig. 1), added as the toughener for BMI and polyimides, could also catalyze the cyclotrimerization of cyanate esters by its hydrogen-donating phenol groups through the formation of the reactive imidocarbonate intermediate. In

this work, we study the catalytic effect of DBA on the cyanate esters and its potential toughening effect on the rigid novolac cyanate ester.

EXPERIMENTAL

Raw materials

The two cyanate ester resins, 2,2′-bis(4-cyanatophenyl)-ethylene (HF-9) and novolac cyanate ester (HF-5), were supplied by Shanghai Huifeng Technology and Business (China). 2,2′-Diallyl bisphenol A (DBA) was purchased from Laiyu Chemical (China). Copper (II) acetylacetonate (CuAt) and nonyl phenol (NoP) were obtained from Aldrich and were used without further purification.

Formulation and curing

The novolac cyanate ester, HF-5, is a highly viscous liquid at room temperature and is difficult to be processed. It was heated to around 80°C to reduce its viscosity for easy handling. HF-5-based samples were formulated by homogeneously mixing HF-5 with the calculated amount of catalyst, followed by vacuum degassing for 30 min to remove the trapped air bubbles before curing. HF-5 was mixed with the catalyst at the weight ratio of 0.5–50 wt % for DBA, 0.1–1.0 wt % for CuAt, and 0.3–6.0 wt % for NoP. The catalytic effect of the cocatalyst (0.5 wt % CuAt and 5 wt % NoP) was also studied for comparison with DBA.

As HF-9 is a moderately viscous liquid at room temperature, it can be easily processed at room temperature. Similarly, HF-9-based samples were formu-
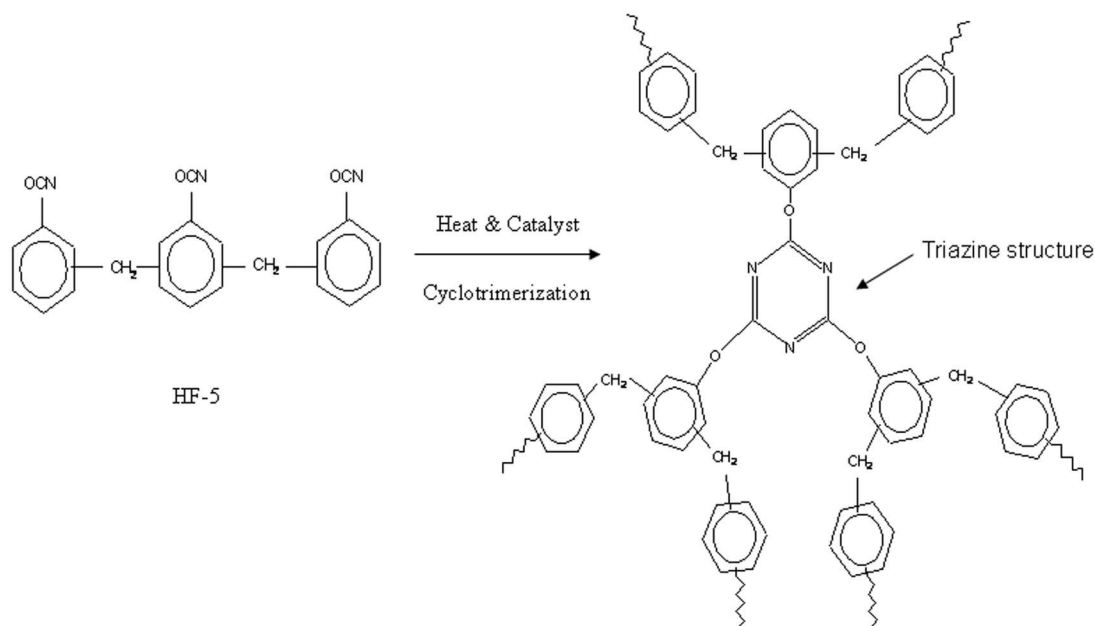

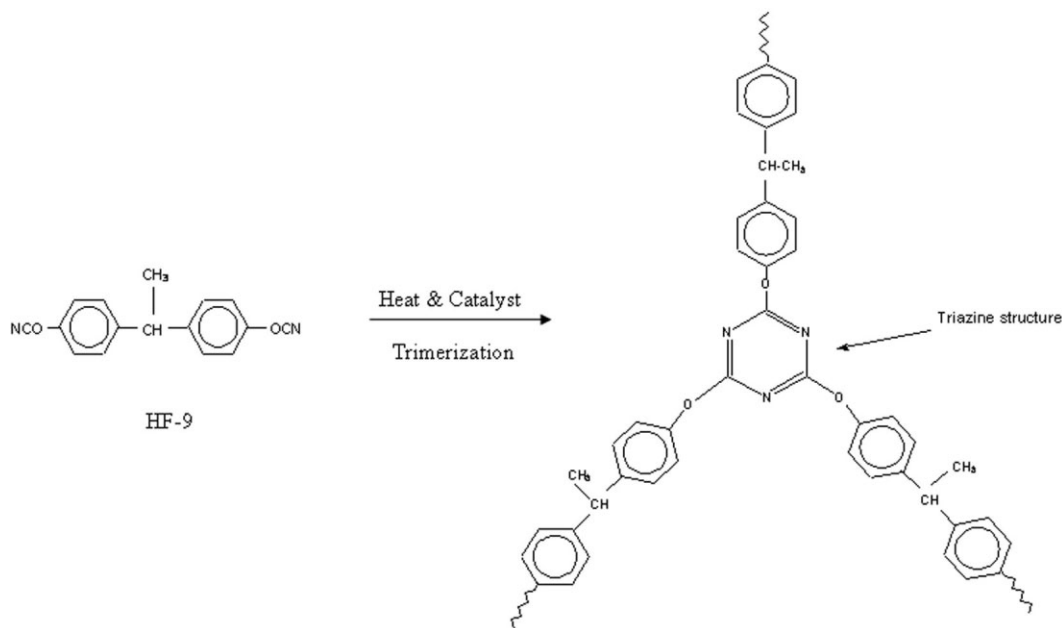**Figure 2** Cyclotrimerization of trifunctional novolac cyanate ester (HF-5).

Figure 3 Cyclotrimerization of difunctional bisphenol E cyanate ester (HF-9).

lated through incorporation of the same amount of catalysts as those of HF-5-based samples.

The formulated cyanate ester resins were cured at 120, 140, and 160°C consecutively each for 2 h in an air-circulated oven. The cured cyanate ester samples form light brown transparent solids and need further postcuring to achieve maximum conversion of cyanate groups into crosslinked triazine structures. Postcuring was subsequently done at 250°C for 4 h in an air-circulated oven. Cyanate ester samples after postcuring are dark brown in color due to the thermal oxidation.

The curing mechanism of both the trifunctional novolac cyanate ester (HF-5) and the difunctional bisphenol E cyanate ester (HF-9) were sketched in Figures 2 and 3. It is expected that the cured HF-5 should have higher glass transition temperature than the corresponding cured HF-9 because of the relatively higher crosslinking density of the former.

Characterization

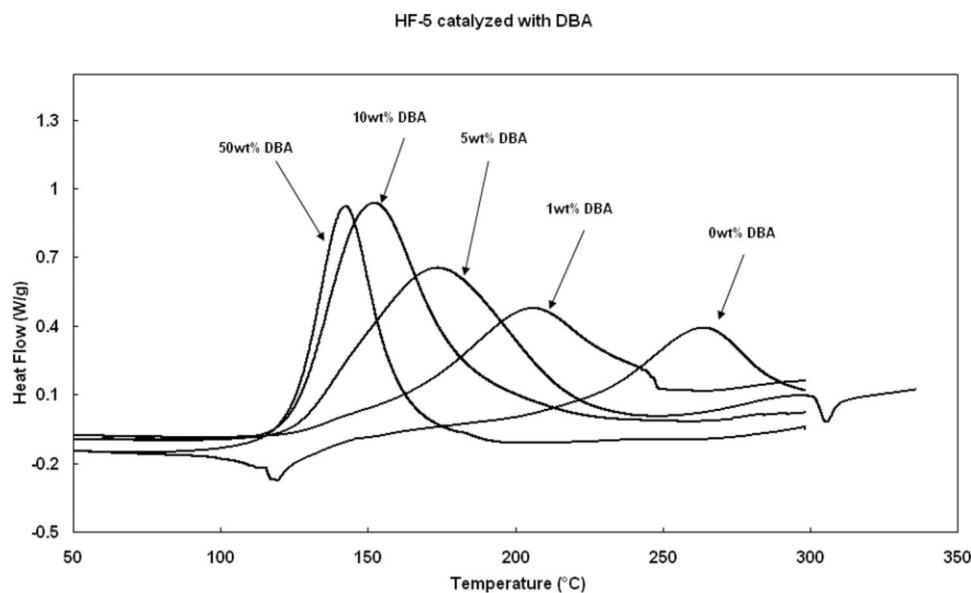The infrared spectra of cyanate ester resins at different curing stages were recorded on a Fourier Transform

Figure 4 DSC curves of the cyanate ester samples of HF-5 with DBA ranging from 0 to 50 wt %.

TABLE I
DSC Data of Cyanate Ester Resins of HF-5 Catalyzed with Different Amounts of DBA

DBA (wt %)	T_{exo} (°C)	ΔH (J/g)
0	271.6	106.4
1	204.8	302.7
5	173	492
10	152.2	333.8
50	142.38	318

Infrared Spectrophotometer (FTIR), FTIR-8201PC (Shimadzu, Japan). The obtained infrared spectra were averaged over 30 scans from 4800 to 500 cm^{-1} with the resolution of 2 cm^{-1}. The FTIR samples were prepared by sandwiching the cyanate ester resin in 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} indicate the cyclotrimerization of the cyanate ester resins.

The viscosity–time curves of the formulated cyanate ester resins were measured on a Brookfield DV-II+ viscometer at 80–100°C.

The differential scanning calorimetry (DSC) curves (heat flow versus temperature) of the cyanate ester resins were acquired on a DSC 2962 differential scanning calorimeter (TA Instruments, USA). The testing temperature ranges from 30 to 350°C, with a temperature ramping rate of 5°C/min under N$_2$ purge. The DSC curves were used to study the curing behavior of these DBA-catalyzed cyanate esters based on the exothermic peak temperature (T_{exo}) and the heat of polymerization (ΔH).

The thermogravimetric curves (weight loss versus temperature) of the cyanate ester samples were measured by a SDT 2960 Simultaneous DSC-TGA (TA Instruments, USA). The testing temperature range is 40–900°C, with the temperature ramping rate of 10°C/min under N$_2$ purge. The thermogravimetric curves were employed to determine the thermal stability of the cured cyanate ester resins in terms of the decomposition temperature at 5% weight loss (T_d^5) as well as the char yield of the resin at 900°C.

The thermal mechanical properties of the cyanate ester resins were characterized by a Rheometric DMTA 3E dynamic mechanical thermal analyzer (DMTA) using the three point bending mode. The cyanate ester samples were measured at the temperatures ranging from 40 to 350°C, with the temperature ramping rate of 3°C/min at 1 Hz. This is to characterize the mechanical strength retention at elevated temperatures and the corresponding glass transition temperatures (T_g) of the cyanate ester samples at different curing conditions.

RESULTS AND DISCUSSION

DSC analysis

DSC is an ideal technique to characterize the curing behavior of cyanate ester resins through analyzing the exothermic peak corresponding to the cyclotrimerization of cyanate ester resins in DSC curves. Figure 4 and Table I illustrate the DSC curves and the resulted DSC data of the cured novolac cyanate ester (HF-5) catalyzed with different amounts of DBA. Upon adding 1 wt % DBA into HF-5, the exothermic peak temperature (T_{exo}) is reduced by 67°C, and the heat of
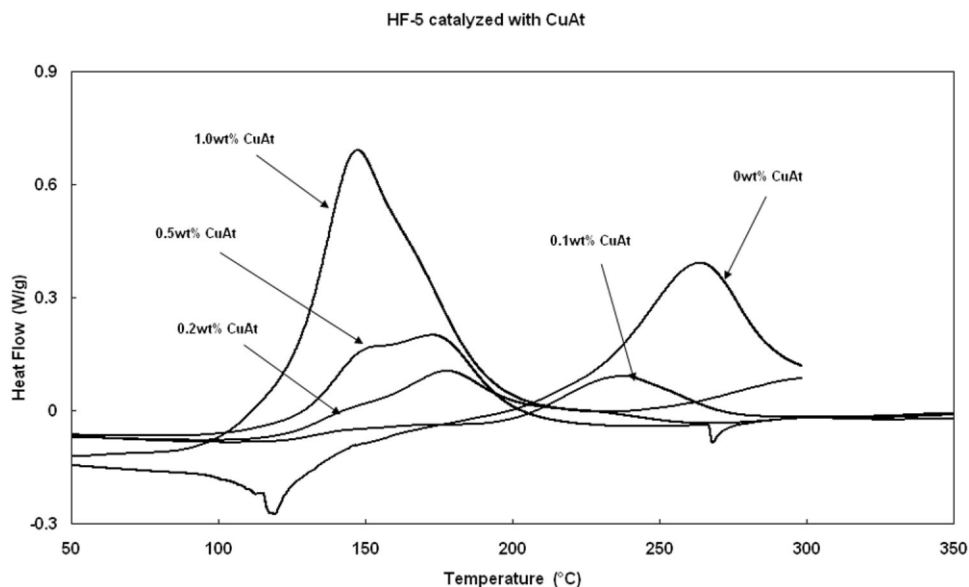

Figure 5 DSC curves of the cyanate ester HF-5 catalyzed with different amounts of CuAt.

TABLE II
DSC Data of the Cyanate Ester HF-5 Catalyzed with Different Amounts of CuAt

CuAt (wt %)	T_{exo} (°C)	ΔH (J/g)
0	271.6	106.4
0.2	177.4	116.2
0.5	173.8	167
1	147.3	404.7

TABLE III
DSC Data of the Cyanate Ester HF-5 Catalyzed with Different Amounts of NoP

NoP (wt %)	T_{exo} (°C)	ΔH (J/g)
0	271.6	106.4
0.3	267.5	136.8
3	240.1	137.7
6	169.2	123.4

polymerization (ΔH) increases by around three folds, clearly showing the effectiveness of DBA in catalyzing the cyclotrimerization of HF-5. Further increasing the DBA content to 5–10 wt %, the T_{exo} is further reduced to 173 and 152°C, respectively, and the corresponding ΔH value is further increased, demonstrating the increased catalyzing effect. It becomes undesirable to further increase the DBA content, as only 10°C drop in T_{exo} is observed for the cyanate ester sample of HF-5 catalyzed with 50 wt % DBA. The above results show that 5–10 wt % of DBA is adequate in catalyzing the curing of novolac cyanate ester HF-5. Excess amount of catalyst may also adversely catalyze the thermal oxidative degradation under high temperature postcuring.[8,19]

For comparison, the catalytic effect of the conventional cyanate ester catalysts, including CuAt, NoP and their combination, on the cyclotrimerization of the novolac cyanate ester HF-5 was also studied. It is found that it is quite difficult to uniformly disperse more than 1 wt % of CuAt into HF-5. Accordingly, the CuAt content is limited within 0.1–1 wt % of HF-5. As displayed in Figure 5 and Table II, increasing the CuAt content results in a decrease in T_{exo} and an increase in

ΔH, especially at higher CuAt levels. Accordingly, the optimal CuAt content in catalyzing the curing of HF-5 is 0.5 wt %, when considering both the catalytic efficiency in initializing the curing of cyanate esters and the negative side effect in catalyzing the thermal oxidation at the postcuring stage.

NoP is a well-known hydrogen donor, by virtue of its phenolic group. The NoP content is within 0.3–6 wt %, in accordance with the literature-reported values.[12–15] NoP is expected to catalyze the curing reaction of cyanate ester via aiding the formation of the intermediate imido-carbonate, similar to that of DBA. As shown in Figure 6 and Table III, the addition of 0.3 wt % of NoP into HF-5 does not shift the exothermic peak of the cyclotrimerization of HF-5, indicating poor catalyzing effect at low catalyst content. When increasing the NoP content to 3 wt %, the exothermic peak broadens significantly, showing the improved catalytic efficiency. When the NoP content reaches 6 wt %, the exothermic peak is shifted to the lower temperature (169°C) by around 100°C, confirming that the literature-reported value of NoP is adequate to catalyze the curing reaction of cyanate ester resins.
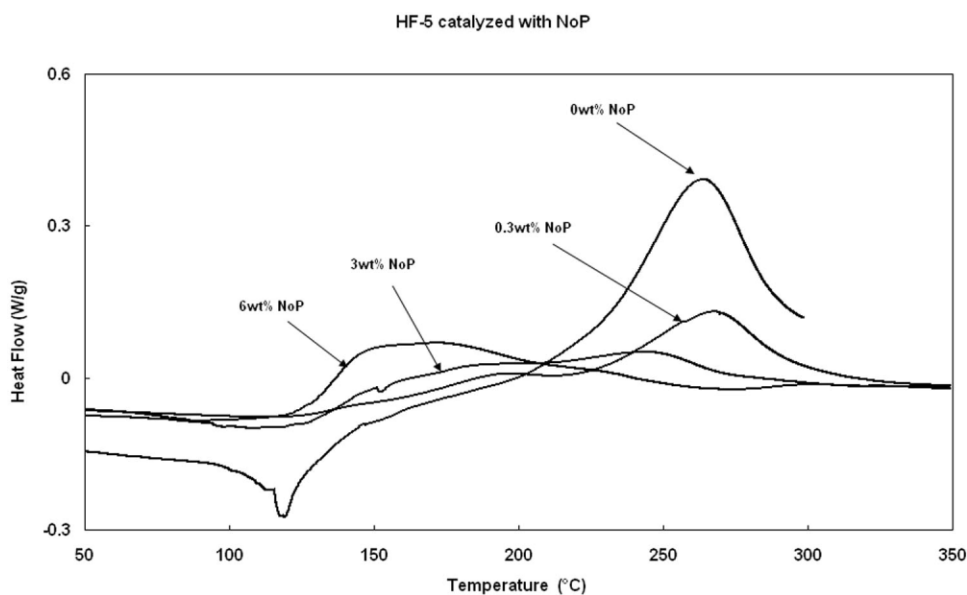

Figure 6 DSC curves of the cyanate ester HF-5 catalyzed with different amounts of NoP.
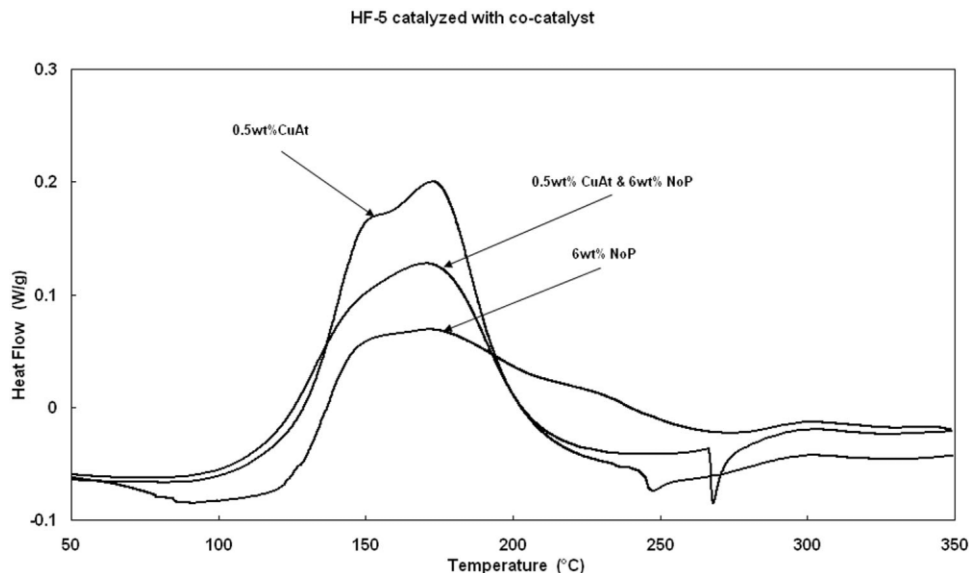
Figure 7 DSC curves of the cyanate ester HF-5 catalyzed by the cocatalyst of CuAt/NoP, compared with its component catalysts.

The catalytic effect of the cocatalyst composed of 0.5 wt % CuAt and 6.0 wt % NoP, both experimentally determined optimal ratios, on catalyzing the cyclotrimerization of cyanate ester groups in HF-5 was also investigated in accordance with the previously reported work.[20] As shown in Figure 7 and Table IV, there is no synergistic effect observed by combining both catalysts as one might expect from the improved steric specificity offered by the complexation with CuAt and subsequent hydrogen donation of the NoP. The T_{exo} and ΔH values of the cocatalyst-catalyzed HF-5 are more close to those of the pure CuAt-catalyzed HF-5, suggesting that CuAt plays the main role in catalyzing the curing of HF-5.

It is interesting to note that the DBA-catalyzed cyanate ester HF-5 shows a much higher heat of polymerization as compared with those of CuAt, NoP, and the cocatalyst of CuAt/NoP-catalyzed HF-5, clearly demonstrating its excellent catalytic effect in initializing the cyclotrimerization of the novolac cyanate ester HF-5. This might be due to the synergetic contribution of the phenol catalyzed cyclotrimerization of cyanate esters and the thermal-initiated self-crosslinking of allyl groups.

The catalytic effect of DBA in catalyzing the cyclotrimerization of the difunctional cyanate ester, bisphenol-E cyanate ester (HF-9), was also characterized by DSC measurement. As shown in Figure 8, the exothermic peak of the pure HF-9 is located at around 270°C. Upon the addition of 5 and 10 wt % of DBA, the exothermic peaks shift to 230 and 210°C, respectively, indicating the effectiveness of DBA in catalyzing the curing reaction of the difunctional cyanate ester HF-9. However, the heat of polymerization does not change much, in contrary to the situation of the trifunctional novolac ester HF-5.

The above results show that DBA is very effective in catalyzing both the difunctional and trifunctional cyanate esters as evidenced by the exothermic peaks shifting to lower temperature region and the sharpening of the peaks, indicative of a short temperature range whereby gelation and vitrification occurs.

FTIR measurement

FTIR spectroscopy is another effective means in monitoring the polymerization level of cyanate ester resins.[21] Figure 9 depicts the FTIR spectra recorded before curing, after curing, and after postcuring of HF-5

TABLE IV
DSC Data of the Cyanate Ester HF-5 Catalyzed with the Cocatalyst of CuAt/NoP, Compared with Its Component Catalysts

Catalysts	T_{exo} (°C)	ΔH (J/g)
No catalyst	271.6	106.4
0.5 wt % CuAt	173.8	167
6 wt % NoP	169.2	123.4
0.5 wt % CuAt and 6 wt % NoP	170.5	164.9

TABLE V
DSC Data of the Difunctional Cyanate Ester HF-9 Catalyzed with Different Amounts of DBA

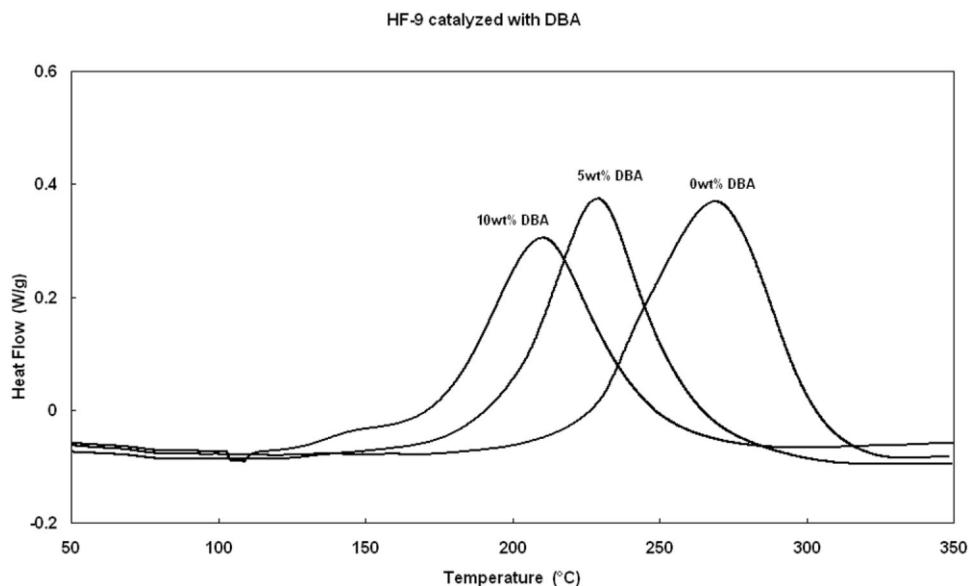| DBA (wt %)	T_{exo} (°C)	ΔH (J/g)
0	269.3	278.3
5	229.2	265.2
10	210.5	225.9

HF-9 catalyzed with DBA

Figure 8 DSC curves of the difunctional cyanate ester HF-9 catalyzed with different amounts of DBA.

catalyzed with 5 wt % DBA. It is clear from Figure 9 that the curing reaction took place during the course of curing and postcuring as evidenced by a gradual decrease of the cyanate ester group absorption peak at 2230 cm^{-1} and a gradual emergence of the two triazine peaks at 1370 and 1560 cm^{-1}. It is also observed that the allyl absorption peak at around 1640 cm^{-1} is gradually reduced after curing and finally disappears after postcuring, confirming the assumption that the thermal-induced self-crosslinking of allyl groups occurred.

To quantitatively monitor the polymerization level of cyanate esters during curing and postcuring, the phenyl absorption peak at 1500 cm^{-1} is used as the internal reference peak for quantitative comparison between different FTIR spectra, as the phenyl groups remain 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 is used to represent the polymerization level. Figure 10 illustrates the polymerization level of the novolac cyanate resin HF-5 catalyzed with different amount of DBA during the course of curing and postcuring. When cured at 120°C for 2 h, the polymerization level of the pure HF-5 is below 10%, while around 50% of cyanate estergroups in HF-5 samples catalyzed with 5–10 wt % of DBA are con-
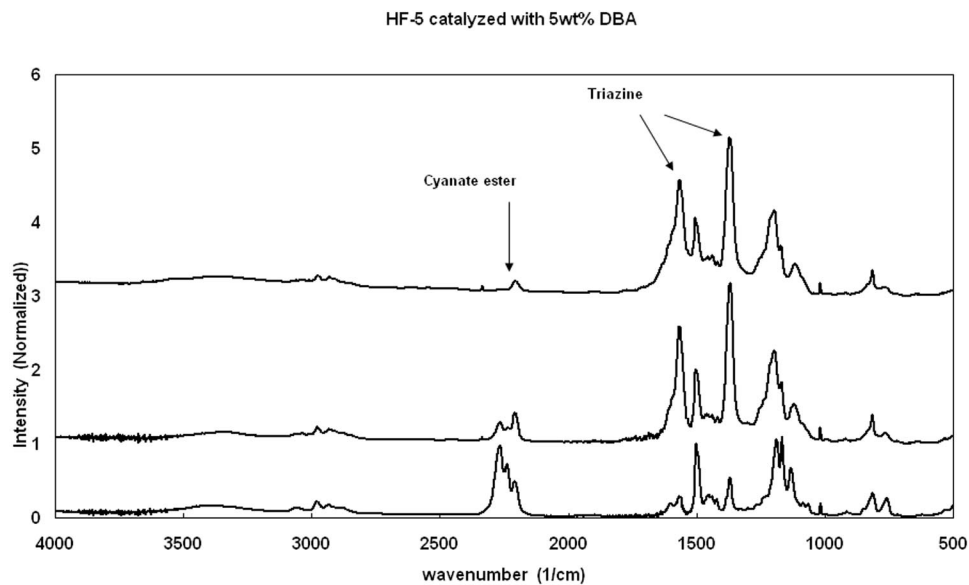
HF-5 catalyzed with 5wt% DBA

Figure 9 FTIR spectra of the cyanate ester HF-5 with 5 wt % DBA recorded before curing, after curing, and after postcuring.
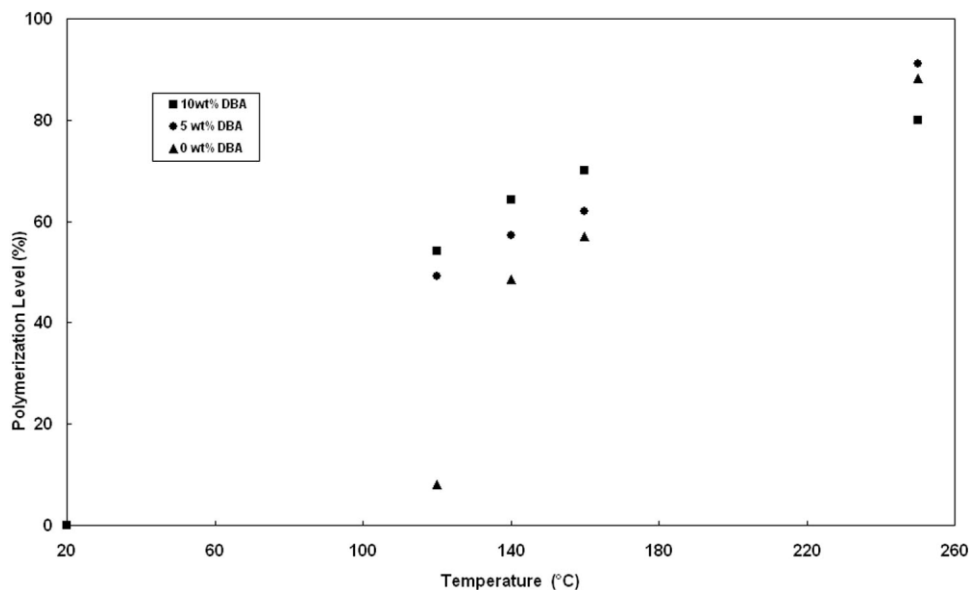
Figure 10 Polymerization level of the cyanate ester HF-5 with varying amounts of DBA as a function of curing temperature.

verted into triazine structures, clearly showing the catalytic efficiency of DBA. Upon further curing at 140°C for 2 h and 160°C for 2 h, the polymerization level of the catalyzed HF-5 gradually increases to 60–70%, and the pure HF-5 gradually reaches the polymerization level of the catalyzed HF-5. It is assumed that at lower curing temperatures (120–140°C), the curing kinetics is catalytically controlled, which explains why the cyanate ester resin with higher catalyst content has a higher polymerization level. Upon reaching the polymerization level of around 50–60%,

the curing kinetics become diffusion controlled, as the significant crosslinking hinders the unreacted cyanate ester groups from further cyclotrimeriztion.[8] As a result, postcuring at a higher temperature (250°C) is required to achieve higher level of polymerization (>80%). It is also observed that it is difficult to achieve full polymerization of cyanate ester resins upon postcuring at 250°C for 4 h. This might be due to the fact that the residue cyanate groups are trapped into the crosslinked triazine cages at this high level of polymerization and cannot come into contact with the
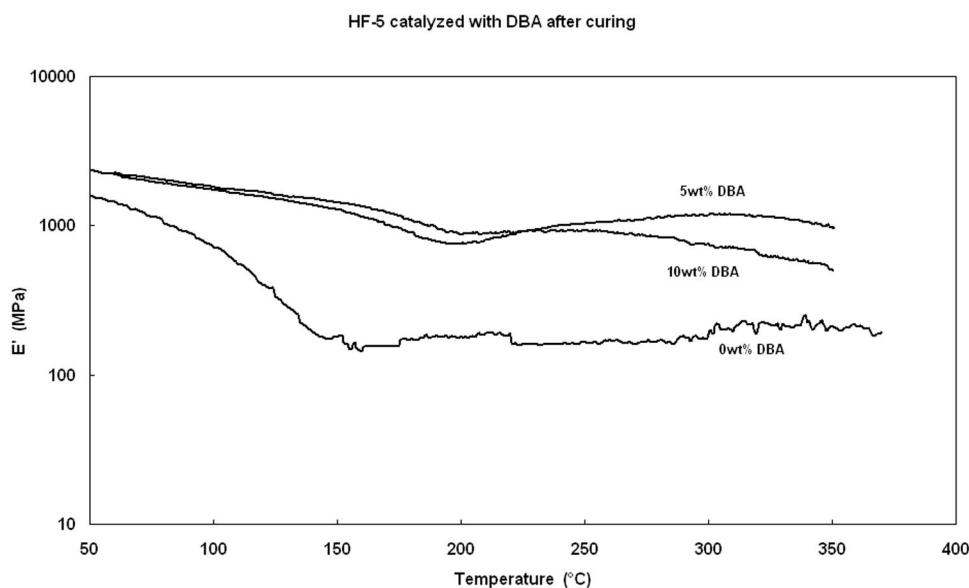

Figure 11 Elastic modulus (E')–temperature (T) curves of HF-5 catalyzed with 0, 5, and 10 wt % of DBA after curing at 120, 140, and 160°C each for 2 h.
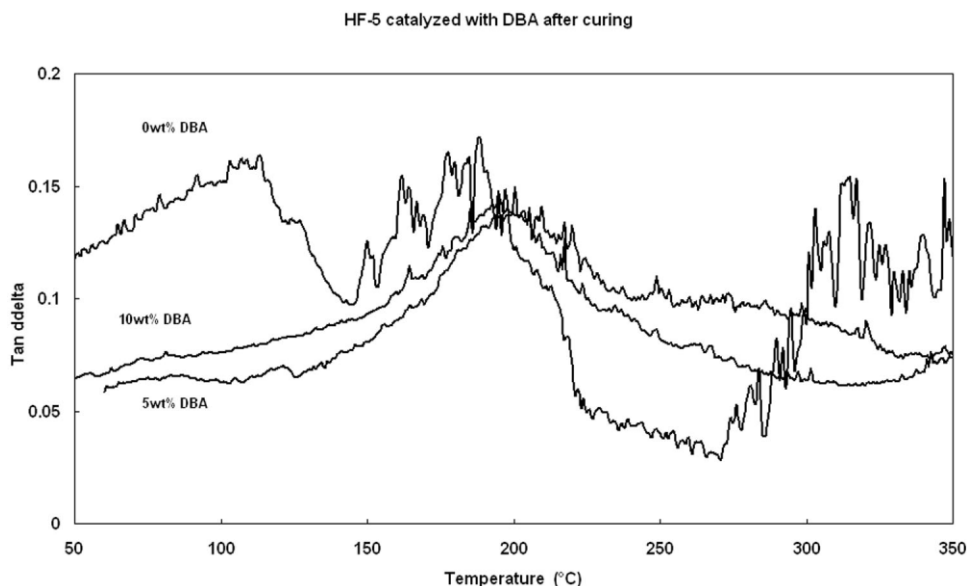
HF-5 catalyzed with DBA after curing

Figure 12 Loss factor (tan δ)–temperature (T) curves of HF-5 with 0, 5, and 10 wt % of DBA after curing at 120, 140, and 160°C each for 2 h.

adjacent cyanate groups for cyclotrimerization. To further increase the polymerization level, even higher postcuring temperature (above T_g) is required to reactivate these cyanate ester groups. But, under such postcuring condition (>250°C), the resulted cyanate ester resin will be heavily oxidized.

Thermal mechanical properties

Figures 11 and 12 illustrate the elastic modulus (E')–temperature (T) curves and the corresponding loss factor

(tan δ)–temperature curves of the pure HF-5 and the DBA-catalyzed HF-5 after cured 120, 140, and 160°C each for 2 h. The DBA-catalyzed HF-5 samples exhibit higher elastic modulus than the pure HF-5 sample throughout the whole measured temperature range and their T_g values (around 200°C) are remarkably higher than that of the pure HF-5 sample (around 100°C), demonstrating the catalytic effectiveness of DBA. It is also observed that there is not much difference in both the E'–T and tan δ–T profiles between the 5 and 10 wt %
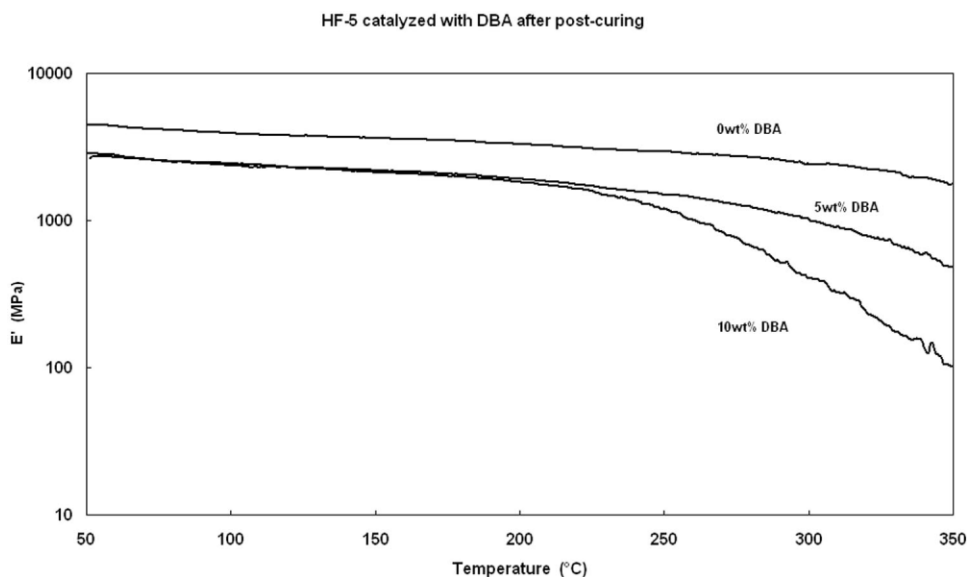
HF-5 catalyzed with DBA after post-curing

Figure 13 Elastic modulus (E')–temperature (T) curves of HF-5 with 0, 5, and 10 wt % of DBA after postcured at 250°C for 4 h.
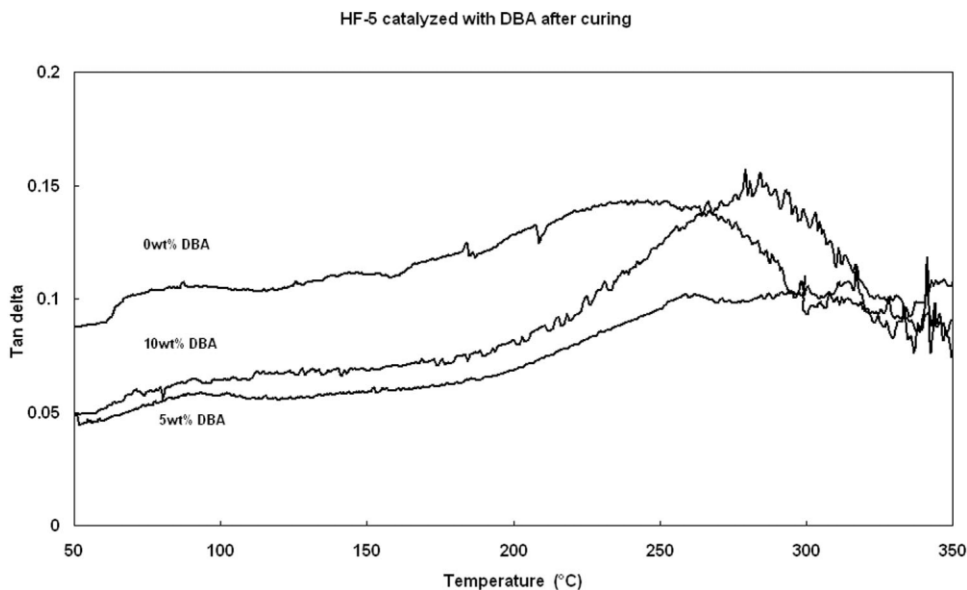
HF-5 catalyzed with DBA after curing

Figure 14 Loss factor (tan δ)–temperature (*T*) curves of HF-5 with 0, 5, and 10 wt % of DBA after postcured at 250°C for 4 h.

DBA-catalyzed HF-5 samples, indicating that 5 wt % DBA is enough to catalyze the curing of HF-5.

Figures 13 and 14 show the $E'–T$ and tan δ–*T* curves of the pure HF-5 and the DBA-catalyzed HF-5 after postcured at 250°C for 4 h. Upon postcuring, the elastic moduli of both the pure HF-5 and the two DBA-catalyzed HF-5 samples increase at the higher temperature region, and their corresponding T_g values shift from the original 100–200°C to 250–300°C range, indicating the higher conversion of cyanate ester groups into crosslinked triazine structure. This result is in consistent with the findings drawn from the DSC and FTIR measurements. As shown in Figure 13, the two DBA-catalyzed HF-5 samples have slightly lower elastic modulus at the glassy state region than the pure HF-5, clearly showing the toughening effect of DBA on the novolac cyanate ester HF-5. When the two DBA-catalyzed HF-5 samples are compared, the one with 5 wt % DBA has a higher elastic modulus at the high temperature region than the one with 10 wt % DBA. To get better mechanical strength retention at high temperature, 5 wt % DBA is more appropriate in catalyzing the curing reaction of cyanate ester resins.
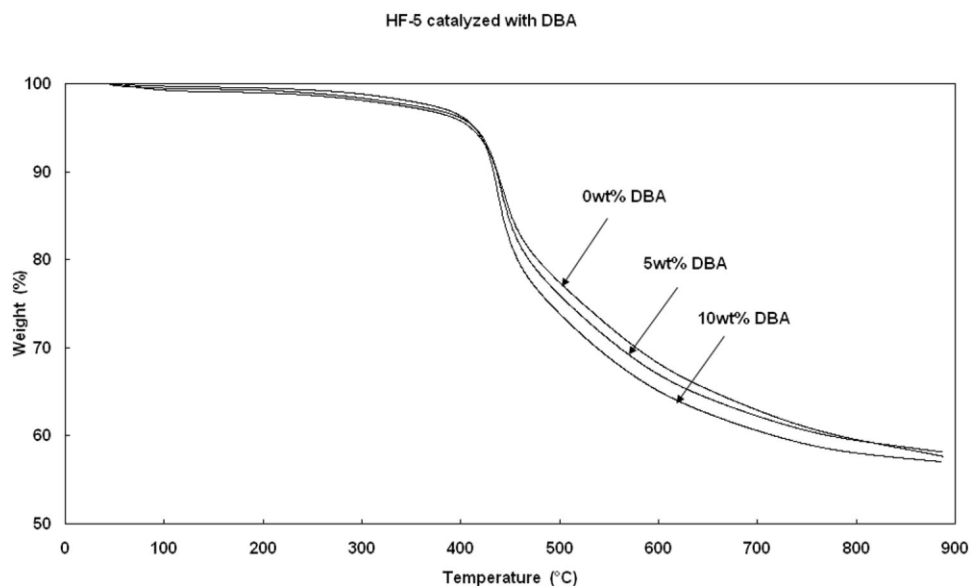
HF-5 catalyzed with DBA

Figure 15 TGA curves of HF-5 with 0, 5, and 10 wt % of DBA measured under nitrogen purge.
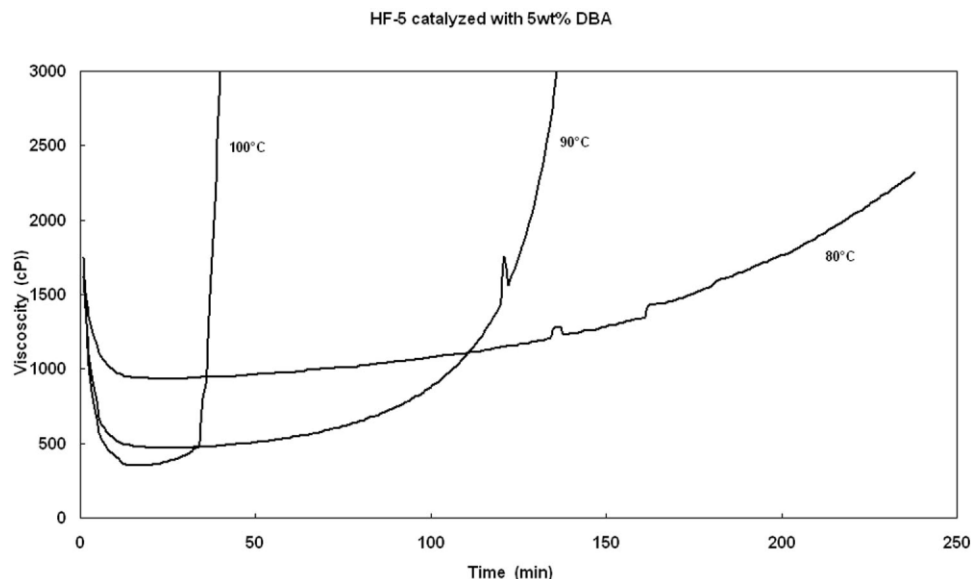
Figure 16 Viscosity–time curves of HF-5 catalyzed with 5 wt % DBA at 80, 90, and 100°C.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out for the novolac cyanate ester HF-5 with 0, 5, and 10 wt % DBA. As shown in Figure 15, all the three cyanate ester samples exhibit the similar TGA profile with the decomposition temperature at 5 wt % weight loss (T_d^5) of around 410°C and the char yield at 900°C of around 57–58 wt %, showing their good thermal stability.

Viscosity measurement

The rheology and initial curing behavior of the DBA-catalyzed novolac cyanate ester HF-5 were studied by monitoring their viscosity response with time at the processing temperatures (80–100°C). The obtained data are important in determining the processing parameters in fabricating fiber reinforced cyanate ester composites. Figure 16 displays the viscosity–time curves of the selected cyanate ester formula, HF-5 catalyzed with 5 wt % DBA, at 80, 90, and 100°C. At 80°C, the cyanate ester resin is quite stable and its viscosity slowly increases with time. If the pot life of the cyanate ester resin is defined as the time needed to reach the viscosity of 1500 cPs at the measured temperature, the pot life of the 5 wt % DBA-catalyzed HF-5 at 80, 90, and 100°C is around 170, 120, and 30 min, respectively. The results show that the pot life (>120 min) at 80–90°C of the 5 wt % DBA-catalyzed HF-5 is long enough for the convenient resin transform molding process.

CONCLUSIONS

The catalytic effect of DBA on the thermal curing of cyanate esters was studied. When compared with the conventional cyanate ester catalysts, DBA exhibits stronger catalytic effect in initiating the cyclotrimerization of cyanate esters, as evidenced by the lower exothermic peak temperature (T_{exo}) and the higher heat of polymerization (ΔH) due to the synergetic contribution of the phenol-catalyzed cyclotrimerization of cyanate esters and the thermal-initiated self-crosslinking of allyl groups. DBA is especially suitable for catalyzing the polymerization of the trifunctional novolac cyanate ester (HF-5), as the former acts as both the curing catalyst and the toughening agent of the latter. The TGA and DMTA show that the 5 wt % DBA-catalyzed HF-5 has good thermal resistance with T_d^5 of 410°C and the char yield at 900°C of 58% and can retain its mechanical strength up to 250°C.

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