Reaction Kinetics and Thermal Properties of Cyanate Ester-Cured Epoxy Resin with Phenolphthalein Poly(ether ketone)

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ABSTRACT: This article describe the influence of phenolphthalein poly (ether ketone) (PEK-C) on the cure behaviors and thermal properties of the diglycidyl ether of bisphenol A (DGEBA) epoxy resin with cyanate ester as curing agent. The curing kinetics and reaction pathways were monitored using dynamic differential scanning calorimeter and Fourier transform infrared spectroscopy. The dependence of activation energy on the conversion degree for all the studied systems was calculated in the light of Ozawa-Flynn-Wall method. Furthermore, the thermomechanical properties and the thermal stability of the cured resins were also evaluated by dynamic mechanical analysis and thermogravimetric analysis, respectively. Conclusions can be drawn as follows: the main reaction pathways did not vary with the inclusion of PEK-C, but the reaction rate of the blend was found to be higher than that of the neat epoxy. The glass transition temperature of the blend was not changed by the addition of PEK-C, while the initial decomposition temperature slightly decreased with increase in PEK-C content. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 2590–2596, 2009

Key words: blends; DSC; FT-IR; thermodynamics; thermogravimetric analysis

INTRODUCTION

Cyanate ester-epoxy resins have been well applied in both the aerospace and the electronic industry because of low moisture absorption, excellent electrical properties, good flammability characteristics, and high performance/cost ratio.[1–5] However, these thermosets are generally brittle because of high crosslink densities. Most of the studies are mainly focused on the toughening of cyanate or epoxy resins. Few reports on the toughening modification of cyanate ester-epoxy systems are seen.[3–5]

Toughening epoxy resins using rubbers has been known for a considerable time.[6–8] However, the use of rubber as toughening agent results in a significant decrease in modulus, yield strength, and glass transition temperature (T_g) of the cured epoxy resins. Therefore, toughening of highly crosslinked thermosets was explored by blending with high modulus, high glass transition temperature thermoplastics.[9–15]

It is known that the cure of epoxy resins involves conversion of liquid monomers or prepolymers into crosslinked solid. Thereby thermoplastic resins are thought to affect the cure kinetics of thermosetting polymers. On one hand, kinetic parameters, such as the cure extent,[16] the time of cure, and the cure temperature, control the physical properties and T_g of the cured products. On the other hand, the cure rate determines the phase morphologies of the blends, which directly effects the improvement in toughness. For this reason, a clear understanding of the cure mechanism and the reaction kinetic are essential. Differential scanning calorimerty (DSC) and Fourier transform infrared spectroscopy (FTIR) are widely used to characterize the cure kinetics of thermosetting systems.[16–21]

In this study, a thermoplastic phenolphthalein poly (ether ketone) (PEK-C) was used to modify the diglycidyl ether of bisphenol A (DGEBA) epoxy cured with cyanate ester. The cure kinetics of the neat epoxy and its blend with PEK-C were investigated by DSC and FTIR, to see the effect of the thermoplastic resins on the curing rate and chain structure. Thermomechanical properties and thermal stability were also determined by dynamic mechanical analysis (DMA) and thermogravimetric analysis
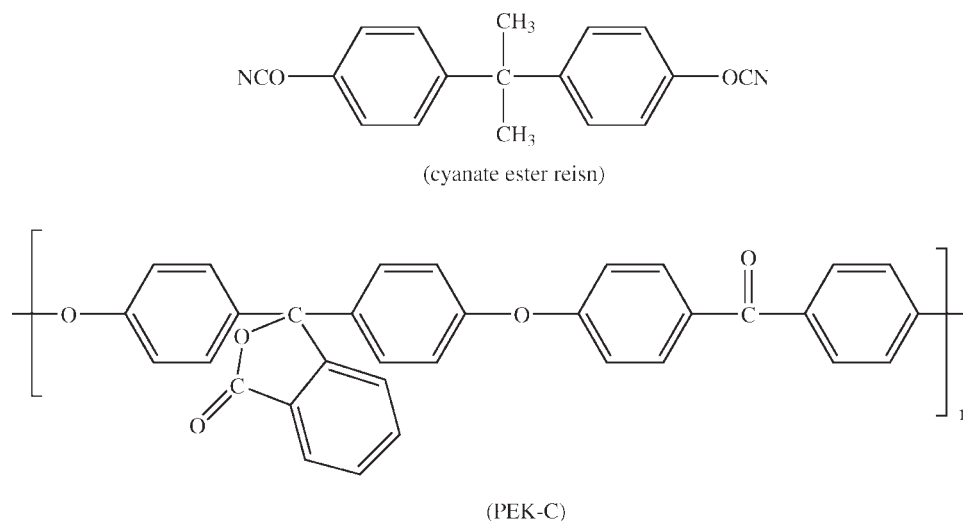
Figure 1 Chemical structures of cyanate ester resin and PEK-C.

(TGA), to confirm thermal properties of the epoxy/PEK-C blends.

EXPERIMENTAL

Materials

The thermoplastic resin used was phenolphthalein PEK-C with an intrinsic viscosity of 0.81 dL g^{-1} measured in chloroform at 25°C. It was purchased from Xuzhou Chemical Factory, China. The DGEBA, E-51, with epoxy equivalent 185–210, was supplied by Wuxi Resin Works, China. The hardener used was bisphenol A dicyanate provided by Shanghai Huifeng Science and Trading Company (Shanghai, China). All reagents were used as received. The chemical structure of cyanate ester resin and PEK-C is given in Figure 1.

Blend preparation

The thermoplastic resin was first dissolved in the epoxy resin at 150°C with constant stirring. Then the curing agent was dissolved in this blend at 150°C in less than 1 min to minimize the curing reaction during the mixing for DSC and FTIR measurements. Samples for the DMA and TGA tests were prepared by molding of the mixture in Teflon molds and cured according to 150°C/4 h + 200°C/2 h + 230°C/4 h. Blends with 0, 5, 10, or 15 wt % PEK-C were prepared, and the ratio of cyanate to epoxide was one in all cases.

Differential scanning calorimetry

Cure kinetics of the blends was carried out using differential scanning calorimetry (DSC, Perkin–Elmer Diamond). About 5 mg of each resin system was sealed in aluminum pans and heated at rates of 5, 10, 15, and 20°C min^{-1} for dynamic DSC scanning. The reaction was considered complete when the DSC thermogram leveled off to the baseline. The heat of reaction, ΔH, could be calculated from the area under the exothermic peak in a DSC curve. The heat of cure is directly proportional to the area under the DSC cure.[16] Thus, the fractional extent of conversion, α, at a given temperature T can be expressed as

$$\alpha = \frac{\Delta H_T}{\Delta H}$$

where ΔH_T is the heat of reaction of partially cured samples heated up to the temperature T, ΔH is the total heat of the cure reaction.

Fourier transform infrared spectroscopy

A Nicolet-20DXB FTIR spectrometer was used to follow the cure reaction of the neat epoxy and the blend. For unreacted solution, thin films for FTIR studies were obtained by casting solutions onto KBr disk. Sample at certain curing time was pressed into a pellet together with KBr and used for the measurements.

Dynamic mechanical analysis

DMA was carried out on a TA Q800 instrument. A single cantilever mode was used to produce bending deformation in the samples. The frequency was 1 Hz and the heating rate was set at 5°C min^{-1}. The specimen dimension was 31 × 10 × 3 mm^3.

Thermogravimetric analysis

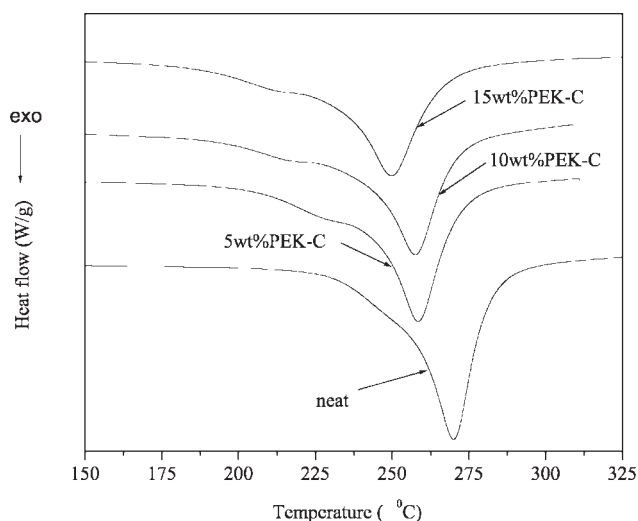TGA was performed with A Netzsch Instruments model TG209C thermal analyzer. The samples were

Figure 2 Dynamic DSC thermograms of epoxy/PEK-C blends at 10°C/min.

Figure 3 Fractional conversion as a function of temperature for various composites.

heated from room temperature to 600°C at a heating rate of 10°C min^{-1} in nitrogen atmosphere.

RESULTS AND DISCUSSION

DSC analysis

Figure 2 shows the dynamic DSC thermograms of all the systems investigated at 10°C min^{-1}, and the corresponded characteristics of the cure were listed in Table I. The DSC curves all produced a broad exothermic peak at higher temperature with a small shoulder at lower temperature. These results indicated that two or more successive reactions took place and that the addition of PEK-C did not change the reaction mechanisms between epoxy and cyanate ester. However, the initial temperature (T_i) and the peak temperature (T_p) shifted to low temperature region with an increase of PEK-C content, which means that the reaction rate of the blend was enhanced by the presence of PEK-C. This could be attributed to the presence of the PEK-C phenolic end-groups, which accelerated the trimerization

TABLE I
Curing Characteristics of the Blends Evaluated from DSC Curves

PEK-C content (wt %)	T_i (°C)	T_p (°C)	T_f (°C)	ΔH (J g^{-1})
0	221.5	270.0	296.5	723
5	194.1	258.5	286.3	675
10	187.7	257.5	285.4	637
15	185.4	249.8	280.8	615

reaction of cyanate monomers, and resulted in a fast curing rate of the epoxy resins.

Furthermore, as it can be seen from the data appeared in Table I, reaction heat (ΔH) of the blends was reduced when PEK-C content increased. It is noted that calculation of the heats of reaction for the blends was based on the net weight of the cyanate ester-epoxy resin in the blends with the weight of PEK-C in the epoxy blends being discounted. The decrease of ΔH with the increase in PEK-C should not be taken as a result of the PEK-C weight in the blend. Rather, this was the result of the steric and diffusional limitations imposed by the PEK-C on the formation of the crosslink network[3] as well as the reaction of cyanate ester with phenolic end-groups.

Figure 3 shows the variation of the fractional conversion (α) as temperature in all the four studied systems. It is clear that all the α values increased very slowly at the beginning of curing. When the samples were heated to given temperatures, the α values appeared to leapingly increase to over 90% and then leveled off. Moreover, to obtain the same conversion value, the required temperature was reduced with increase in the PEK-C content, which further suggested the acceleration effect of PEK-C for the curing reaction. All of the curves showed s-shape and shifted to right hand side at the elevated temperature.

It is well known that the polymerization mechanism of cyanate ester-epoxy resin system is very complex. Thus, a single value of Arrhenius parameters is not appropriate choice to describe the epoxy cure. The Ozawa-Flynn-Wall method based on Doyle's approximation is used to obtain the activation energies (E_a) for different conversion levels (a) and is expressed as follows[18,19]:
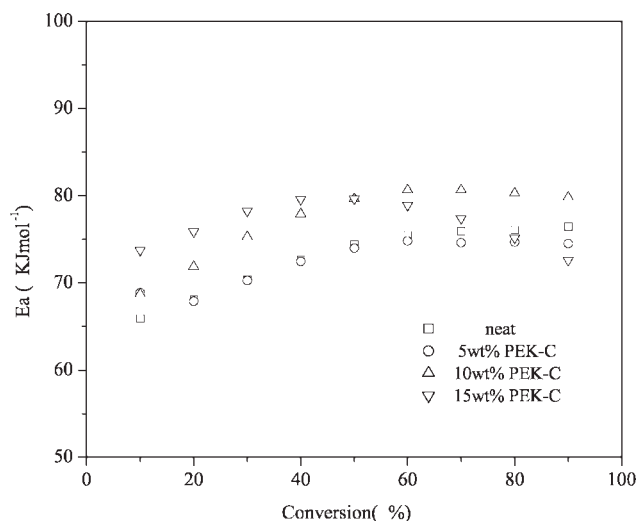
Figure 4 The activation energy as a function of the conversion for epoxy/PEK-C blends.

$$\log(\beta) = \log(AE_a/R) - \log[g(a)] - c - l(E_a/RT)$$

where, β is the heating rate, c and l are couple tabulated coefficients and $g(a)$ is integrated form of the conversion dependence function. The main problem of the Ozawa-Flynn-Wall method consists in the accurate setting of the coefficients c and l. The most frequently used values are: $c = 2.313$ and $l = 0.4567$ if $E_a/RT = 28$–50, or $c = 2.000$ and $l = 0.4667$ if $E_a/RT = 18$–30.[18] The analysis of the reaction of epoxy with cyanate ester shows that the relation $E_a/RT = 13$–20 is significantly less and the values of the coefficients c and l differ from the universal ones, viz. $c = 1.600$ and $l = 0.4880$.[19]

Figure 4 shows the variation of E_a for all the studied samples as a function of the fractional conversion. It can be observed that E_a first exhibited the slight increase in the conversion interval $0.1 \leq a \leq 0.6$, then E_a tends to be constant in the final stage of the reaction, indicating different steps in the curing process. With some exceptions, E_a for the blend with 15 wt % PEK-C suggest a slight tendency to decrease in the range of $0.5 \leq a \leq 0.9$. Although a reasonable explanation has not been found yet, some deviations are probably due to the errors in the baseline approximation for peak tails.

FTIR analysis

The curing of the cyanate ester-cured epoxy and its blend with 10 wt % PEK-C was also investigated by FTIR measurements carried out at 150°C/4 h + 200°C/2 h. Figure 5 is the plots of FTIR spectrum for the blend with 10 wt % PEK-C. The neat sample shows similar plots and is not presented. The resid-

ual of cyanate and epoxide groups at different time, $X(t)$, was calculated as[2,20,21]:

$$X(t) = (H_i/H_{2965})_t / (H_i/H_{2965})_{t=0}$$

where H_i is the peak height at $i = 2270$ or $i = 915$ cm^{-1} for cyanate and epoxide groups, respectively. The evolution of the other groups appearing with the cure was followed by normalizing their corresponding peak height to that of the methyl group at 2965 cm^{-1}. The evolution of main groups in the neat system and the blend with 10 wt % PEK-C was quantified in Table II.

Similar to the neat cyanate ester-epoxy resin system, the first reaction in the modified sample was still the trimerization reaction of the cyanate monomers to form a triazine. Then epoxy groups reacted with cyanate monomers or triazine to form oxazolidinone at 1758 cm^{-1}. The other reaction included the etherification of epoxy and hydroxyl groups. Moreover, from Table II, it can be clearly seen that the disappearing rate of both cyanate and epoxy groups was faster than that of the neat sample. This result is consistent with DSC analysis. Observing the percentage of main products (triazine and oxazolidinone) at the end of heat treatment, it is found that the quantities of triazine in neat epoxy and the blend were nearly equal; while the oxazolidinone amount in the modified system was clearly lower than that in the unmodified system. Similar result has been reported by Wu in cyanate ester-cured epoxy blend with PPO.[4] As stated earlier, the consumption of epoxy groups at early stage was accelerated by PEK-C. Thus the relative content of epoxy, which can further coreact with cyanate monomers or triazine at later stage of cure, was reduced. This is probably the
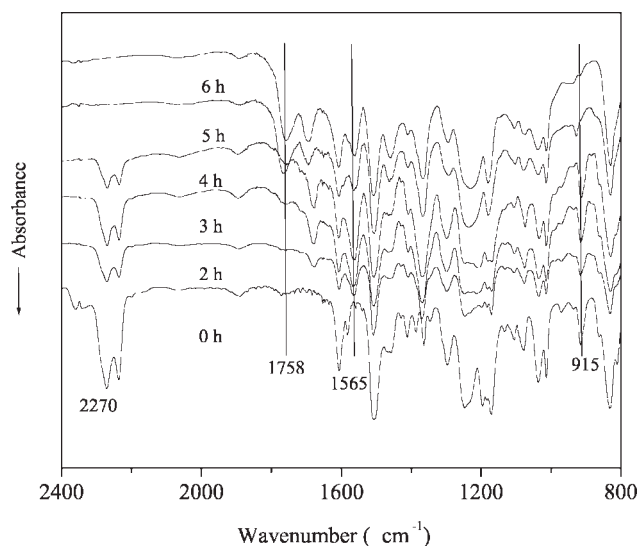

Figure 5 Change in the FTIR spectrum with cure at 150°C/4 h + 200°C/2 h in the cyanate ester-cured epoxy/PEK-C(10 wt %) system.

Time (h)	Neat				The blend			
	Epoxide $X(t)$	Cyanate $X(t)$	Triazine H_{1565}/H_{2965}	Oxazolidinone H_{1758}/H_{2965}	Epoxide $X(t)$	Cyanate $X(t)$	Triazine H_{1565}/H_{2965}	Oxazolidinone H_{1758}/H_{2965}
$t = 0$	1	1	0	0	1	1	0	0
1	1.05739	0.93076	0.21521	0	0.89433	0.73418	0.91153	0
2	0.95641	0.61441	1.14634	0	0.87506	0.57183	1.07553	0.08269
3	0.91500	0.45287	1.27557	0	0.81082	0.33545	1.43384	0.01159
4	0.865	0.30694	1.58521	0.20988	0.77123	0.19853	1.60124	0.04253
5	0.38867	0	1.32743	0.82837	0.10285	0	1.30066	0.33243
6	0	0	1.12682	0.86284	0	0	1.19265	0.35037

main reason for the reduction of copolymerization product (oxazolidinone) in the blend with PEK-C.

Dynamic mechanical analysis

To investigate the effect of PEK-C on the viscoelastic properties, the pure epoxy and modified epoxy networks were investigated with dynamic mechanical analysis. Plots of tan δ and the storage modulus versus the temperature for these systems are given in Figure 6. The T_g of the epoxy phase was observed near 232°C in the dynamic mechanical spectrum. No distinct peak was observed in the tan δ curves of the blends because of the proximity of the T_g of PEK-C[22] (235°C, by DMA) and that of the neat epoxy resin. Correspondingly, it can be confirmed that the T_g of the blends was very close to that of the unmodified resin, as shown in Table III. However, in all the blends, the storage modulus was lower than that of the pristine resin below the T_g of the system and continued to be the same in the rubbery region.

The crosslinking density of a cured network can be approximated with the theory of rubber elasticity as[11,23]

$$M_c = \frac{3\rho RT}{E}$$

where E is the elastic modulus, R is the universal gas constant, ρ is the density, M_c is the average molecular weight of the chain segments between crosslink points, and T is the absolute temperature. By assuming that ρ is constant for all composites, we can consider E to be inversely proportional to M_c. Thus, the lower value of storage modulus of the blends in the plateau region is an indication of the decrease in crosslink density. That is, the addition of PEK-C slightly reduced the crosslink density of the cured resin.

Thermal degradation

The degradation temperature and kinetic parameters of the reaction, such as initial decomposition temper-

ature (*IDT*), temperature of the maximum rate of degradation (T_{max}), and the activation energy of decomposition (*Et*) are important in expressing the thermal stability of a material and can be
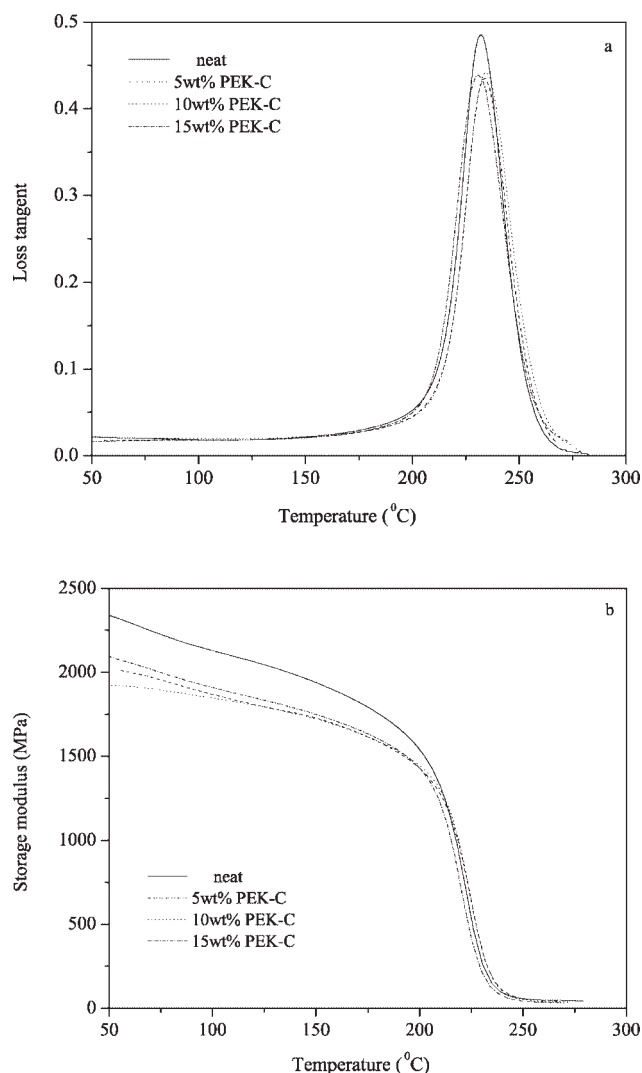

Figure 6 DMA curves of epoxy/PEK-C blends: (a) tan δ; (b) storage modulus.

TABLE III
Dynamic Mechanical Properties
of DGEBA/PEK-C Blends

PEK-C content (wt %)	T_g (°C)	E (Pa)	
		60°C	270°C
0	232	2.30×10^9	46.76
5	234	2.00×10^9	43.12
10	234	1.92×10^9	37.72
15	231	2.06×10^9	32.95

TABLE IV
Thermal Stability Factors of DGEBA/PEK-C Blends

PEK-C content (wt %)	IDT (°C)	T_{max} (°C)	E_t (kJ mol^{-1})
0	360	397	174
5	351	400	158
10	350	400	158
15	353	395	154

determined from the TGA thermograms. Figure 7 shows TGA thermograms of the neat and modified samples obtained in a nitrogen atmosphere. All the samples underwent the degradation mainly as a one-stage process. Using the integral method of Horowitz and Metzger,[24] one calculates the activation energy for the decomposition of the cured resin from TGA thermograms according to the following equation:

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

where α is the decomposed fraction at T, E_t is the activation energy for decomposition, T_{max} is the temperature at the maximum rate of weight loss, $\Theta = T - T_{max}$, and R is the gas constant. The results of the IDT, T_{max}, and E_t of the blends with varied PEK-C contents are listed in Table IV. As results, the values of IDT and E_t were little decreased by the increase of PEK-C content, whereas the value of T_{max} was constant. It can be confirmed that the thermal stability of the blends was little decreased with increase in PEK-C content, which was attributed to the reduced crosslinking density of the epoxy network, as evident from DMA studies, where M_c calculated from storage modulus in the rubbery plateau region increased.

CONCLUSIONS

All DSC curves for the cyanate ester-cured epoxy and its blend with PEK-C exhibited two overlapped peaks. DSC and FTIR results showed that the cure rate of both cyanate and epoxy was increased by PEK-C because of the PEK-C reactive chain ends. Similar to the neat system, the main reaction in the blend still included: cyclotrimerization of cyanate ester to produce triazine rings; coreaction of epoxy and triazine rings to form oxazolidinone rings and etherification of epoxy. The incorporation of PEK-C had no significant effect on the T_g of the blends, while it leaded to a slight reduction of the storage modulus in the glassy and rubbery state. The value of the initial decomposition temperature was little decreased by the increase of PEK-C content, whereas temperature of the maximum rate of degradation was almost constant.
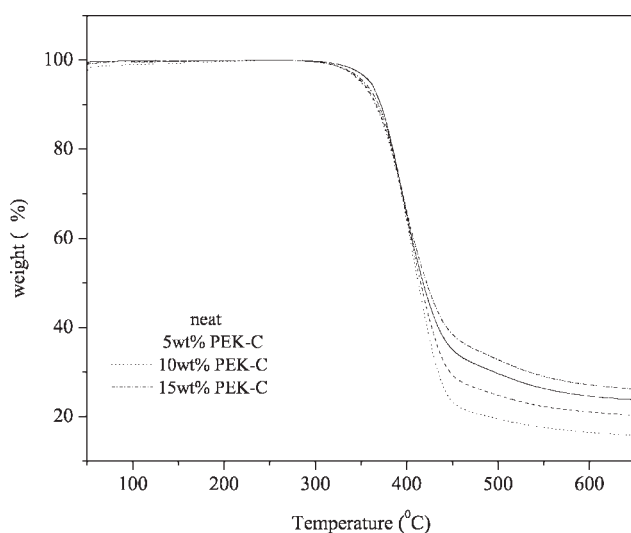

Figure 7 TGA thermograms of epoxy/PEK-C blends.

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