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Cure kinetics and morphology of blends of epoxy resin with poly (ether ether ketone) containing pendant tertiary butyl groups

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Abstract

The cure kinetics and morphology of diglycidyl ether of bisphenol-A (DGEBA) epoxy resin modified with a poly (ether ether ketone) based on tertiary butyl hydroquinone (PEEK-T) cured with diamino diphenyl sulphone (DDS) were investigated using differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and dynamic mechanical thermal analysis (DMTA). The results obtained from DSC were applied to autocatalytic and diffusion controlled kinetic models. The reaction mechanism broadly showed autocatalytic behaviour regardless of the presence of PEEK-T. At higher PEEK-T concentration, more diffusion controlled mechanism was observed. The rate of curing reaction decreased with increase in thermoplastic content and also with the lowering of curing temperature. The activation energies of the blends are higher than that of the neat resin. The blends showed a phase separated morphology. The dispersed phase showed a homogeneous particle size distribution. The T_g of the neat resin decreased with the decrease in cure temperature. Two T_g's corresponding to the epoxy rich and thermoplastic rich phases were observed in the dynamic mechanical spectrum. The storage modulus of 10 and 20 phr PEEK-T blends are found to be greater than the neat resin.

Keywords: Epoxy resin/poly (ether ether ketone) blends; Cure kinetics; Morphology

1. Introduction

Among the thermosetting polymers used, epoxy resins find a wide range of applications as adhesives, coatings, sealant, in aerospace industry, etc. The wide range of applications arise from the properties like easy processability, good chemical and corrosion resistance, good adhesion to various substrates, easy cure, etc. [1,2]. But due to the inborn brittle nature of the epoxy resin owing to the high crosslink density, it is necessary to improve the toughness for its use in many end use applications. Considerable efforts have been made in the past to improve the toughness by blending with reactive liquid rubbers [3–6]. Improvement in toughness was achieved with the lowering of other good properties like glass transition temperature (T_g), thermal and oxidative stability. Studies had revealed that blending with engineering thermoplastics such as polyethersulphone [7–9], polyetherimide [10–13], polycarbonate [14], polyphenyleneoxide [15,16] and poly ethylene terephthalate [17,18] could enhance the fracture toughness without sacrificing strength, stiffness, T_g or any other desirable properties. The ultimate properties of the cured resin as well as the blends depend on various factors such as the nature of curing agent, curing conditions (time, temperature), chemical interactions between component polymers etc. Blending epoxy resins with functionally terminated polymers has been a recent focus on the toughness enhancement. The functional groups were so selected that there is some interaction between the components to have better properties.

The kinetics of cure of epoxy resin has been studied by different techniques [19–24]. The reaction mechanism was found to be autocatalytic. Relatively few systematic studies

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were done on the cure kinetics of blends of epoxy resins with thermoplastics. It has been found that the reaction mechanism remained autocatalytic irrespective of the addition of thermoplastic [25–30].

Poly (ether ether ketone) (PEEK) is a tough, semi crystalline high performance thermoplastic polymer with good thermo mechanical properties. Because of its semi crystalline nature, it is difficult to blend this with epoxy resins. Hence only few literatures are available on blends of epoxy resins with PEEK type polymers.

Since the processing was difficult, amorphous PEEK like phenolphthalein poly (ether ether ketone) (PEK-C) or functionally terminated PEEK with bulky pendant groups was used for modifying epoxy resin [31–36]. Bennet et al. [37] investigated the fracture toughness and mechanical properties of blends of diglycidyl ether of bisphenol-A (DGEBA) epoxy resin with amine terminated tertiary butyl hydroquinone, methyl hydroquinone and bisphenol-A based PEEK oligomers. In another study, Song et al. [31] found that amorphous PEEK, PEK-C formed homogeneous blends with tetrafunctional epoxy resin. The fracture toughness decreased slightly with increase in PEK-C content. The effect of curing agent and curing conditions on the morphology was also investigated. According to Zhang et al. [32] lowering of cure temperature favoured homogeneous morphology in amine cured DGEBA + PEK-C blends. But Guo et al. [33] obtained heterogeneous blends at higher cure temperature. Also Guo et al. [34] found that the morphology of epoxy + PEK-C blends depend on the nature of curing agent used. The phthalic anhydride cured system gave homogeneous morphology while maleic and hexahydrophthalic anhydride cured systems gave heterogeneous morphology. Recently efforts were made by Brostow et al. [38,39] to develop low friction epoxy by the addition of fluorinated PEK. They obtained 30% reduction in friction by the addition of 10% fluorinated PEK and also the properties depend strongly on the morphology.

From the above discussion, it is clear that the processing of blends could be improved by using PEEK with terminal functional groups and also with bulky pendant groups. The final properties were dependent on the morphology developed, which in turn was dependent on the type of curing agent and curing conditions. Also to our knowledge no work has been reported on the kinetics of cure in epoxy + PEEK blends. In the present work, DGEBA epoxy resin was modified with poly (ether ether ketone) based on tertiary butyl hydroquinone. As a result of the presence of the bulky tertiary butyl groups on the polymer chain, the crystallinity was reduced and as a consequence the processability was greatly improved. We investigated in detail the effect of curing conditions and composition of the blends on the curing kinetics and morphology with a diamine curing agent.

2. Experimental

2.1. Materials used

A diglycidyl ether of bisphenol-A (DGEBA) epoxy resin (LY 556, Ciba Geigy) with an epoxide equivalent weight of 188.68 was used. The curing agent used was diaminodiphenyl sulphone (DDS, Aldrich). The materials were used as received without any further purification. The thermoplastic modifier, poly (ether ether ketone) based on tertiary butyl hydroquinone (PEEK-T) was synthesised in the laboratory. The structure and molecular weight were characterized by IR and GPC measurements. The chemical structures of the epoxy resin, DDS and PEEK-T are given in Fig. 1.

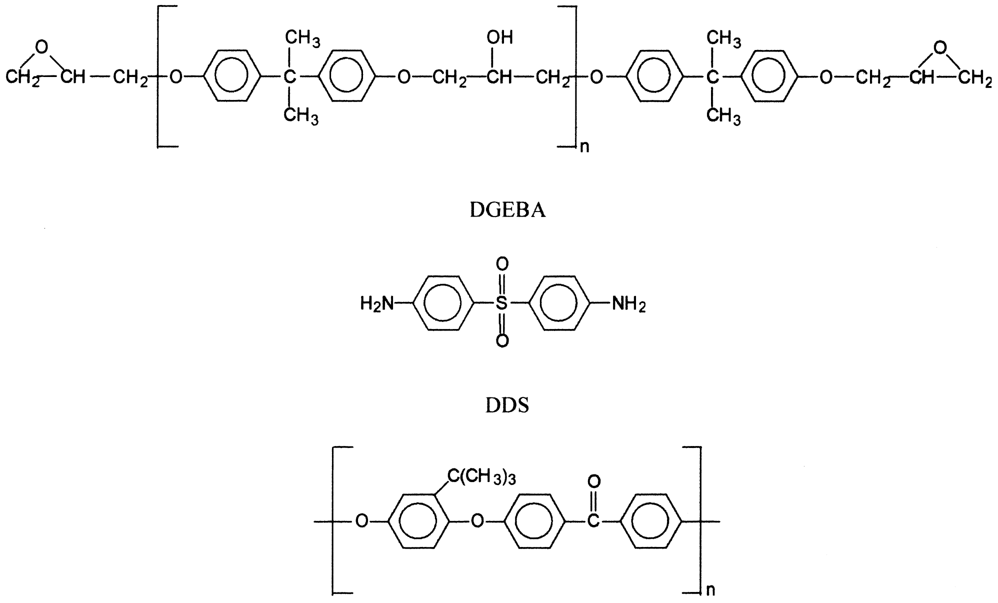


Fig. 1. Chemical structures of DGEBA, DDS and PEEK-T.

2.2. Blend preparation

The blends were prepared using a solventless mixing technique. The thermoplastic modifier was dissolved in epoxy resin at 180 °C with constant stirring. The curing agent was dissolved in the blend at 180 °C in less than 40 s to minimize the curing reaction during mixing and the mixture was immediately plunged into liquid nitrogen to freeze the curing reaction. Blends with 0, 10, 20, 30, 40 and 50 phr thermoplastic were prepared. The amine to epoxide ratio was one in all the cases.

2.3. DSC analysis

A power compensated type differential scanning calorimeter (Perkin Elmer Pyris 1) was used for dynamic and isothermal DSC measurements. The instrument was calibrated with indium, tin and benzophenone standards before starting the measurements. Nitrogen was used as the purge gas and samples of 5–10 mg were used for the measurements.

Dynamic DSC measurements were carried out at 10, 7.5, 5 and 2.5 °C/min for the neat epoxy resin/DDS mixture. Isothermal measurements were done at 180, 165 and 150 °C. The curing reaction was assumed to be complete when the isothermal curve leveled off to a straight line. The areas of the peak under the isothermal curve at various times were used to determine the conversion (α) at various times. The conversion α at time t was defined as $\alpha = \Delta H_t / \Delta H_{tot}$, where ΔH_t is the heat of cure at time t and ΔH_{tot} is the total heat of cure of the neat epoxy resin alone.

2.4. Scanning electron microscopy

The morphology of the blends cured at 180, 165 and 150 °C were examined using a Philips XL 20 scanning electron microscope. The samples were fractured in liquid nitrogen. The fracture surfaces were etched with chloroform at room temperature to remove the thermoplastic phase. The specimens were kept overnight in vacuum oven to remove the remaining solvent. The fractured surfaces were sputter coated with gold before taking the SEM micrographs.

2.5. Dynamic mechanical thermal analysis

The viscoelastic properties of the blends as well as the neat resin cured at various temperatures were measured using TA instruments DMA 2980 dynamic mechanical thermal analyzer. The samples were cured at 180, 165 and 150 °C and the analyses were done in three point bending mode. The samples were heated from 50 to 250 °C at the heating rate of 3 °C/min. The frequency used was 10 Hz.

3. Results and discussion

3.1. DSC studies

Dynamic DSC measurements were done for the DGEBA + DDS mixture at 10, 7.5, 5 and 2.5 °C/min. The dynamic heating curves at various heating rates are shown in Fig. 2. It was observed that peak maximum shifted towards the lower temperature side as the heating rate is lowered. The total heat of reaction ΔH_{tot} for the neat epoxy system was taken as the average of the enthalpy values

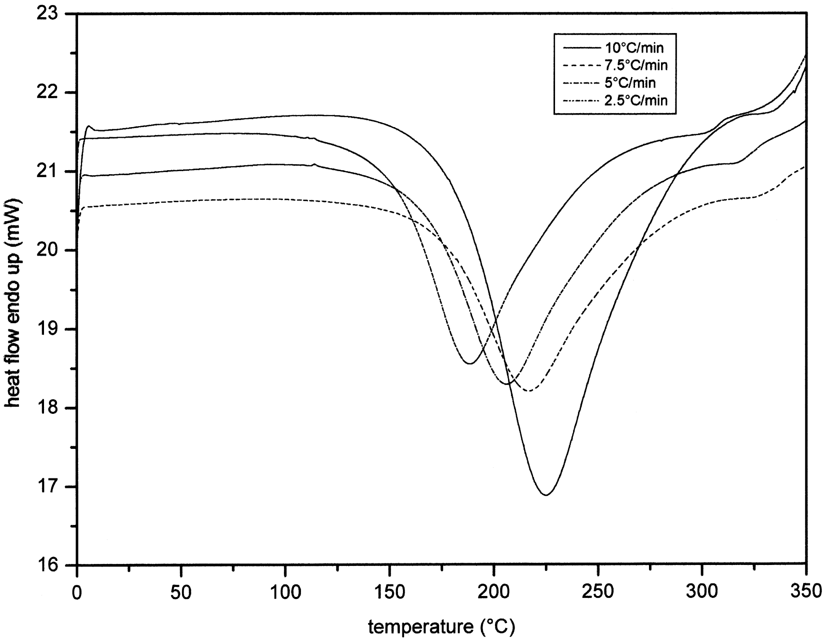


Fig. 2. Dynamic DSC scans of the neat resin at different heating rates.

obtained at different heating rates. This value was taken as ΔH_{tot} for calculating the fractional conversion α at time t [40,41].

The phenomenological model developed by Kamal [42] was used for isothermal kinetic analysis. The amine epoxide reaction was found to be autocatalytic in nature. The general equation assumed for the curing reaction of epoxy–amine system is given below [43–45].

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = (k_1 + k_2\alpha^m)(1-\alpha)^n \tag{1}$$

where α is the fractional conversion at time t, k_1 and k_2 are the rate constants with two different activation energies, m and n are the kinetic exponents of the reaction and $m+n$ gives the overall reaction order. The constant k_1 can be calculated if the initial rate at $\alpha = 0$ can be estimated.

The kinetic constants k_1 and k_2 depend on temperature according to Arrhenius law

$$k_i = A_i \exp(-E_{\mathrm{a}i}/RT) \tag{2}$$

where A_i is the pre exponential constant, $E_{\mathrm{a}i}$ is the activation

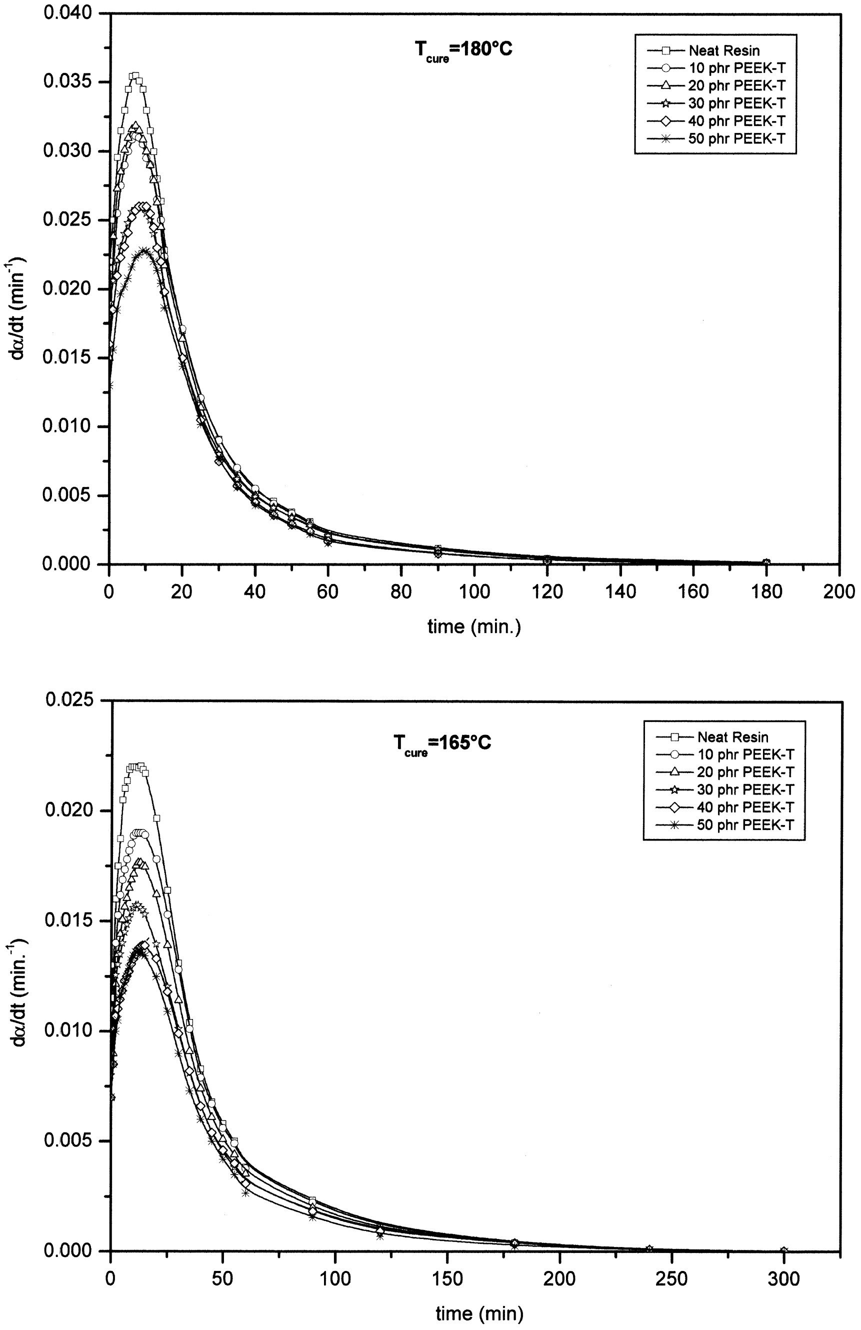


Fig. 3. (a) Reaction rate vs time plot for neat resin and blends cured at 180 °C. (b) Reaction rate vs time plot for neat resin and blends cured at 165 °C. (c) Reaction rate vs time plot for neat resin and blends cured at 150 °C.

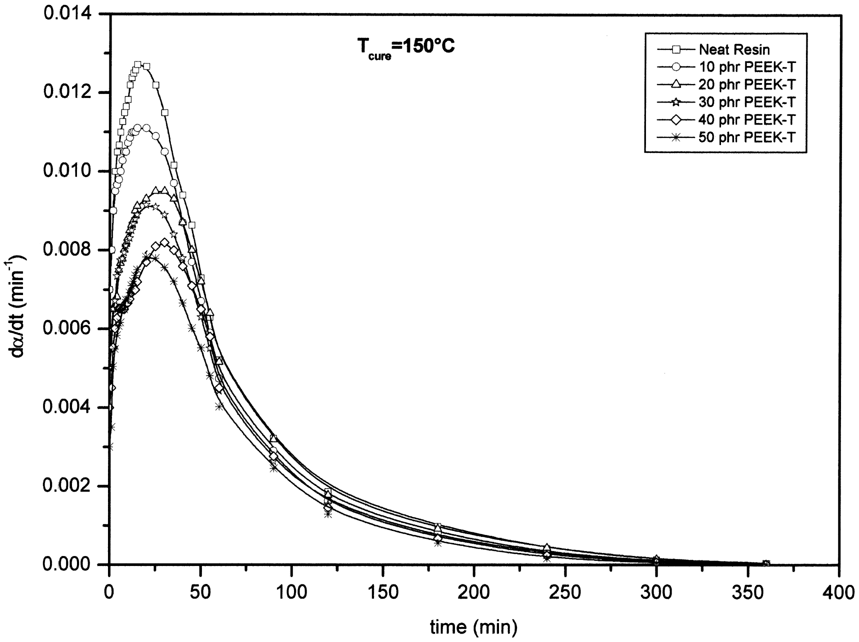


Fig. 3 (*continued*)

energy, R is the gas constant and T is the absolute temperature.

In order to investigate the cure kinetics, isothermal DSC measurements were done at three curing temperatures. The experimental value of conversion α and the reaction rate for the complete course of reaction were then determined and adjusted with the kinetic equation. The activation energies and frequency factors were determined for each curing temperature. Several methods were available for the calculation of parameters of Eq. (1) from isothermal DSC curves [46]. In our study the parameters k_1, k_2, m and n were determined without any constraints on them.

The neat resin and its blends with 10, 20, 30, 40 and 50 phr PEEK-T were cured at three isothermal temperatures; 180, 165 and 150 °C. The rate of reaction $\mathrm{d}\alpha/\mathrm{d}t$ versus time plots are shown in Fig. 3(a)–(c). The maximum rate is observed after the start of the reaction showing autocatalytic nature. The reaction mechanism remained the same even after the addition of the thermoplastic. The rate of reaction was found to decrease with increase in PEEK-T content and also with decrease in the isothermal cure temperature. A possible explanation could be given on the basis of phase separation. As the curing reaction proceeds, the thermoplastic component will phase separate out. The separated out thermoplastic can hinder the curing reaction. It could be better said that the probability for the reaction between epoxy resin and hardener is decreased [47].

The kinetic parameters were determined according to the autocatalytic model. Since there are two kinetic constants k_1 and k_2, two activation energies E_{a1} and E_{a2} could be obtained by plotting $\ln k_1$ and $\ln k_2$ versus $1/T$. The slopes of these plots were then used to calculate the activation energies E_{a1} and E_{a2}, respectively. The activation energies for the curing of DGEBA + PEEK-T blends exhibits higher values compared to the neat resin. This means that PEEK-T hinders the reaction between epoxide and amine.

The kinetic parameters obtained after a large number of iteration are given in Table 1. The overall reaction order $m+n$ was in the range 2.5–3.5. The value m was in the range 0.6–1.2 for the neat resin as well as the blends. The values of n range from 1.7 to 2.7 for the neat resin and blends up to 20 phr PEEK-T. Above 20 phr the blends showed higher values for n.

Fig. 4 shows the plot of rate of reaction ($\mathrm{d}\alpha/\mathrm{d}t$) versus conversion ($\alpha$) for the neat resin as well as the blends. From the figure it is evident that the extent of conversion and the reaction rate decreased with increase in PEEK-T content. The neat resin as well as the blends cured at 165 and 150 °C showed similar behaviour.

The plot of the experimental data and the data obtained by autocatalytic model for the neat resin and blends cured at 180, 165 and 150 °C are given in Fig. 5(a)–(c). The experimental data agrees well with the model predictions at lower conversion, i.e. for the initial stages of cure. But at higher conversions, the values predicted by the model are high compared to the experimental data. This is due to the vitrification of the system. This means that the cure reaction was controlled by diffusion during the later stages. The differences from experimental data were greater at lower curing temperatures. That is the reaction became more diffusion controlled.

A semi empirical relationship based on free volume concept was used to explain diffusion control in cure reactions [48–49]. When the conversion reaches a critical value α_c, diffusion becomes the controlling factor and the

Table 1
Autocatalytic model constants for PEEK-T ($\bar{M}_n$—5400) modified DGEBA epoxy blends

	m	n	$m+n$	$k_1 \times 10^{-3}$ (min^{-1})	$k_2 \times 10^{-3}$ (min^{-1})	ln A_1	ln A_2	E_{a1} (kJ mol^{-1})	E_{a2} (kJ mol^{-1})
Neat epoxy									
180	0.97	2.42	3.39	22.0	187.1				
165	0.67	1.76	2.83	10.9	66.1	12.06	20.29	59.99	83.00
150	0.69	1.93	2.62	7.0	38.6				
Epoxy/PEEK-T (10 phr)									
180	0.93	2.63	3.56	18.1	170.8				
165	0.81	2.37	3.18	9.2	89.7	9.04	17.37	50.21	72.33
150	0.79	2.37	3.16	7.0	44.1				
Epoxy/PEEK-T (20 phr)									
180	0.85	2.70	3.55	15.98	169.7				
165	0.74	2.67	3.41	7.1	82.7	12.8	16.23	62.50	67.98
150	0.81	2.52	3.33	4.9	45.3				
Epoxy/PEEK-T (30 phr)									
180	1.28	3.90	5.18	19.0	346.47				
165	0.86	3.41	4.27	8.3	99.9	14.36	24.43	69.28	96.58
150	0.99	3.43	4.42	5.3	72.9				
Epoxy/PEEK-T (40 phr)									
180	1.22	4.12	5.34	16.2	365.9				
165	0.90	3.69	4.59	7.2	102.7	15.67	24.73	74.71	97.14
150	0.98	3.66	4.64	4.0	71.6				
Epoxy/PEEK-T (50 phr)									
180	1.27	4.76	6.03	13.5	417.8				
165	0.94	4.33	5.27	7.1	123.9	17.24	28.34	81.08	110.48
150	0.68	3.69	4.37	2.9	41.6				

rate constant k_d is given by

$$k_d = k_c \exp[-C(\alpha - \alpha_c)] \tag{3}$$

where k_c is the rate constant for chemical kinetics and C is a parameter. Eq. (3) corresponds to an abrupt change from chemical control to diffusion control of the curing reaction when conversion reaches α_c. But the onset of diffusion control is gradual and there is a region where both diffusion and chemical factors are controlling. The overall rate constant can be expressed in

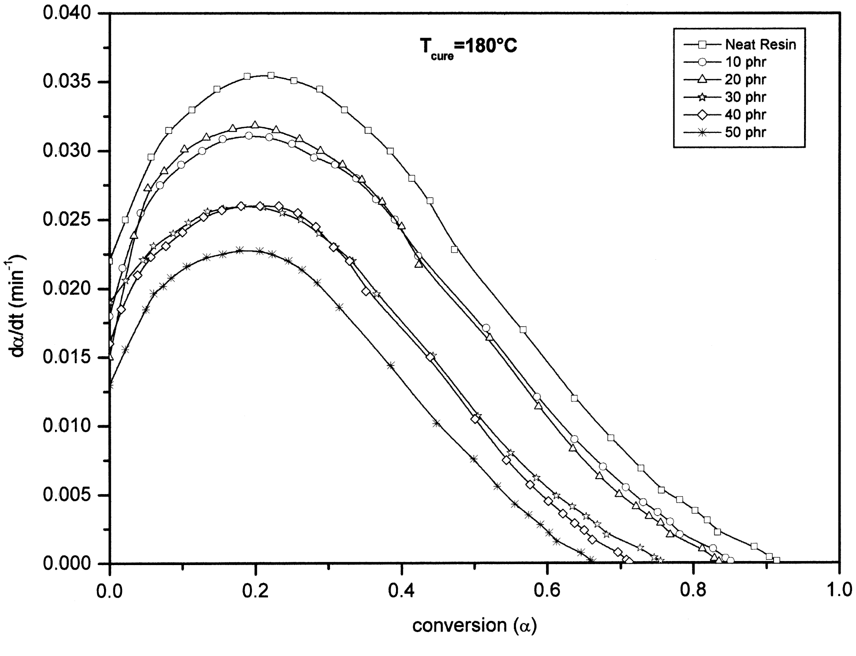


Fig. 4. Reaction rate vs conversion plot for neat resin and blends cured at 180 °C.

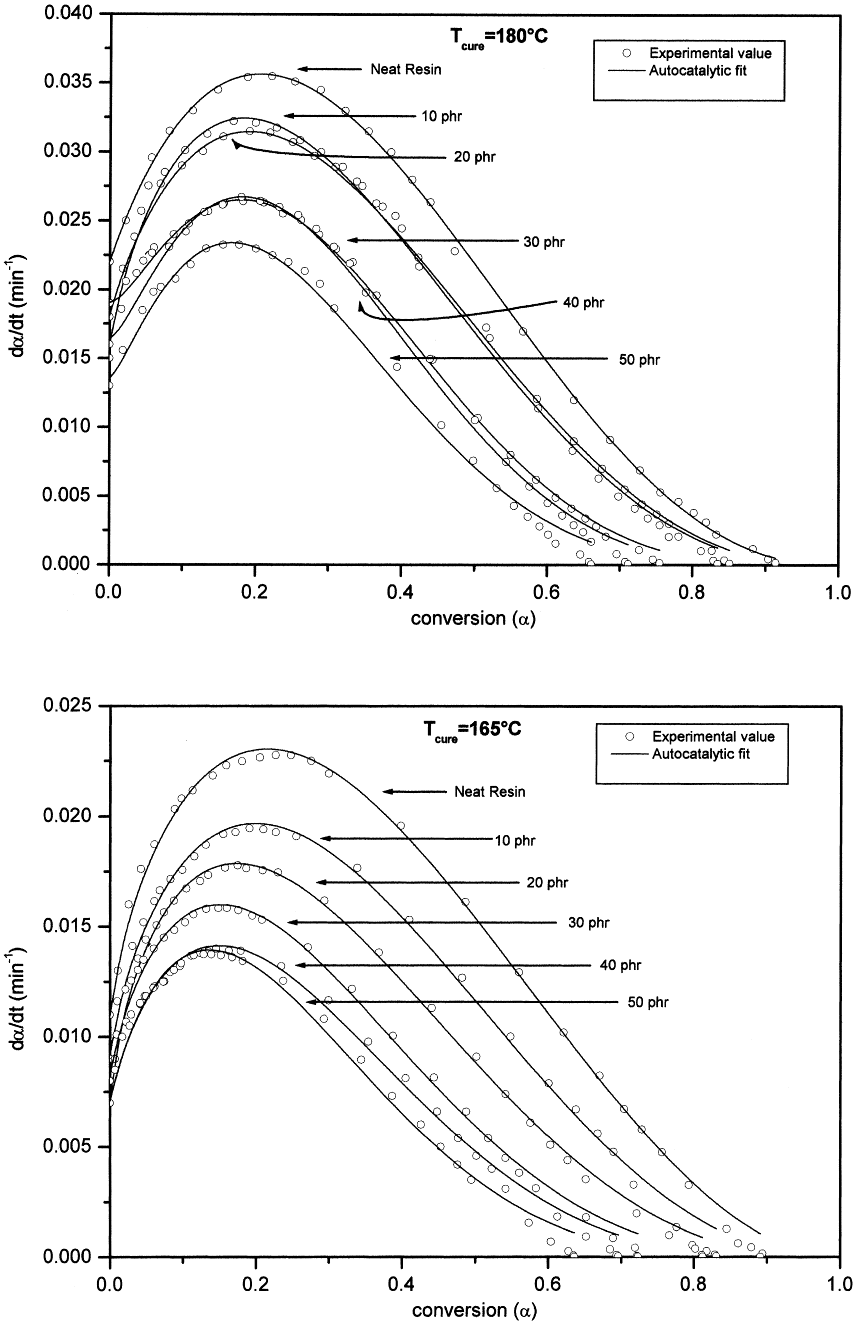


Fig. 5. (a) Reaction rate vs conversion plot for experimental and autocatalytic fit for neat resin and blends cured at 180 °C. (b) Reaction rate vs conversion plot for experimental and autocatalytic fit for neat resin and blends cured at 165 °C. (c) Reaction rate vs conversion plot for experimental and autocatalytic fit for neat resin and blends cured at 150 °C.

terms of k_d and k_c as follows

$$\frac{1}{k_e} = \frac{1}{k_d} + \frac{1}{k_c} \tag{4}$$

This equation combined with Eq. (3) gives the diffusion factor $f(\alpha)$

$$f(\alpha) = \frac{k_e}{k_c} = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \tag{5}$$

When α is much smaller than α_c, $\alpha \ll \alpha_c$, $f(\alpha)$ is approximately unity and the reaction is kinetically controlled and the diffusion effect is negligible. As α increases, $f(\alpha)$ decreases and will approach zero where the reaction effectively ceases. The effective reaction rate at any conversion is equal to the chemical reaction rate multiplied by $f(\alpha)$ [50].

The value of $f(\alpha)$ was taken as the ratio of the experimental reaction rate to the reaction rate predicted by

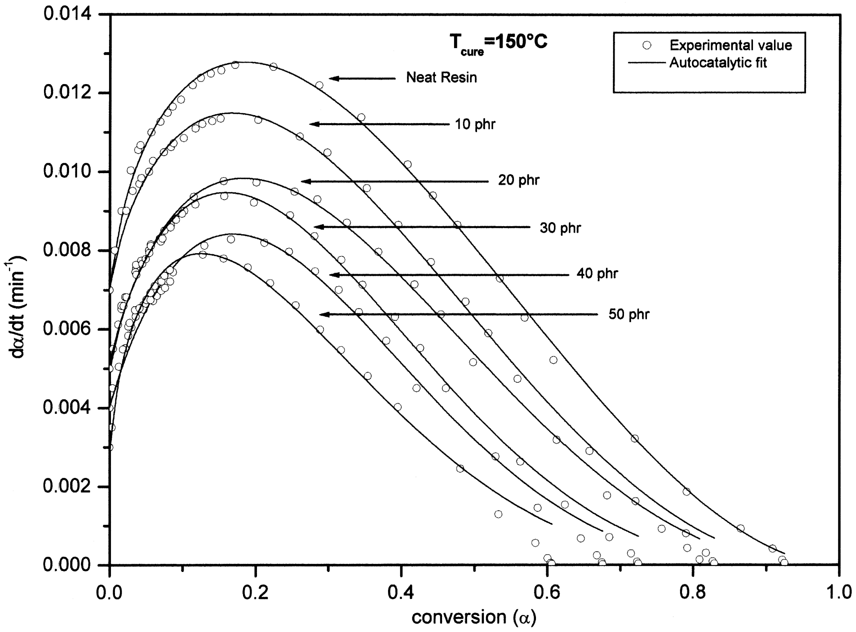


Fig. 5 (*continued*)

the autocatalytic model. The value of $f(\alpha)$ was around one during the early stages of cure. As the curing reaction proceeds further $f(\alpha)$ decreases markedly due to the onset of diffusion control. The plot of $f(\alpha)$ versus α for 20 phr blend is shown in Fig. 6. The decrease in $f(\alpha)$ and hence in effective reaction rate due to diffusion control is evident from the figure. The other blends also showed the same trend. The value of α_c and C is obtained by applying non linear regression to $f(\alpha)$ versus α data to Eq. (5). The values of α_c and C are given in Table 2. The value of α_c is increased slightly as the cure temperature increased. α_c gives the state of the system at which the curing reaction became more diffusion controlled. But it cannot be said exactly that at this particular conversion diffusion control begins, as the change from chemical control to diffusion control is a gradual process.

3.2. Morphology

The scanning electron micrographs of the blends cured at 180, 165 and 150 °C are shown in Fig. 7. A phase separated morphology was observed in all cases. The thermoplastic

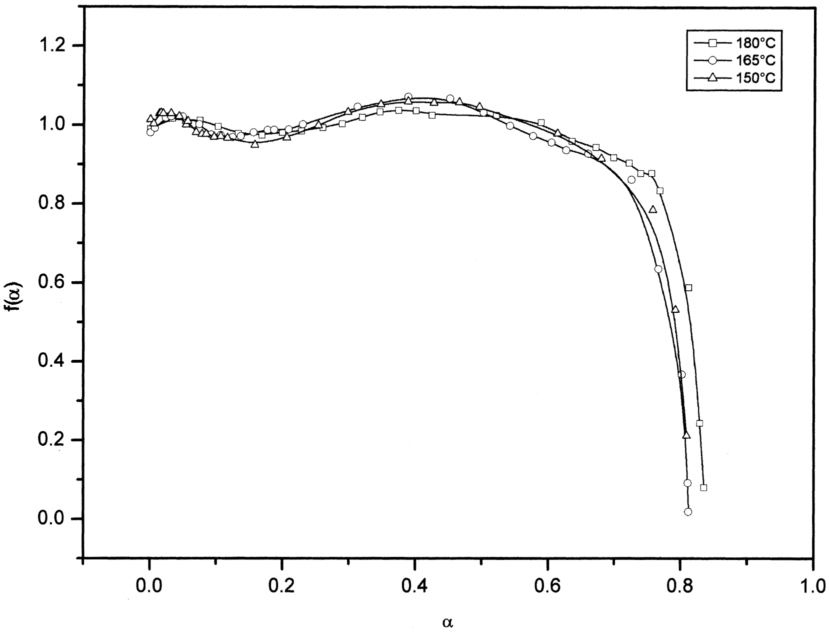


Fig. 6. Plot of diffusion factor $f(\alpha)$ against conversion at different curing temperatures for 20 phr blends.

Table 2
Values of critical conversion α_c and C parameters for epoxy + PEEK-T ($\bar{M}_n$—5400) blends cured at different temperatures

T (°C)	α_c	C
Neat epoxy		
180	0.91	142.55
165	0.87	110.31
150	0.90	118.67
Epoxy/PEEK-T (10 phr)		
180	0.83	94.58
165	0.88	73.72
150	0.80	65.33
Epoxy/PEEK-T (20 phr)		
180	0.81	64.40
165	0.77	
0.78	48.70	
47.41		
150		
Epoxy/PEEK-T (30 phr)		
180	0.74	81.34
165	0.68	31.90
150	0.67	54.36
Epoxy/PEEK-T (40 phr)		
180	0.68	51.88
165	0.66	47.21
150	0.65	84.85
Epoxy/PEEK-T (50 phr)		
180	0.62	44.88
165	0.59	57.00
150	0.56	46.03

rich phase was dispersed in epoxy rich phase at all the curing temperatures up to 30 phr blends. The particle size was measured using image analyzer. The dispersed particle size is in the range 1.6–2.6 μm. The dispersed particle size was observed to increase with the lowering of curing temperature and also with increase in thermoplastic content. At high cure temperature, the rate of curing reaction is high. Hence time for gelation is less, which will result in smaller particle size. Also with the progress of the curing reaction, viscosity of the system will increase. As a result the probability of the dispersed phase to coalesce decreases. A homogeneous particle size distribution was observed at higher curing temperatures but the polydispersity increased with the lowering of curing temperature. The data are summarised in Table 3. It is also important to add that unlike thermoplastic + thermoplastic, uncrosslinked rubber + rubber and thermoplastic + uncrosslinked rubber blends, coalescence is really suppressed in epoxy + thermoplastic blends. This is associated with the high viscosity of the epoxy matrix as a result of gelation and vitrification upon curing. We have observed similar results in the case of epoxy + rubber blend systems [51].

3.3. Dynamic mechanical thermal analysis

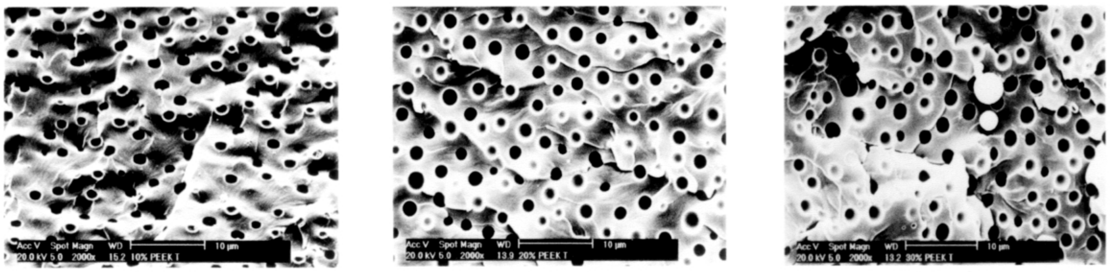
The tan δ versus temperature plots for the neat resin cured at 180, 165 and 150 °C are shown in Fig. 8. The glass transition temperature (T_g) decreased with decrease in curing temperature. The decrease in T_g was due to the reduced conversion as a result of the lowering of curing temperature.

The blends showed two peaks corresponding to the T_g's of epoxy rich and thermoplastic rich phases in the tan δ versus temperature plots. The tan δ versus temperature plots for the blends cured at 180 °C is given in Fig. 9. The T_g of the blends cured at various temperatures is given in Table 4. For the blends cured at 180 °C, the T_g values of both phases remain close to that of the pure components. At lower curing temperatures the T_g values of the two phases are less compared to that of the pure components. This is due to the presence of partially cured or uncured epoxy in both the phases. At all curing temperatures the T_g of the thermoplastic rich phase decreases continuously with its increasing concentration. This clearly indicates that epoxy molecules get into thermoplastic phase, which acts as a plasticizer.

The storage modulae of the neat resin and the blends cured at 165 °C is shown in Fig. 10. The storage modulus of 10 and 20 phr blends are greater than that of the neat resin whereas that of 30 phr blends is lower than the neat resin. At lower concentrations, PEEK-T acted as reinforcement to the epoxy. At higher concentrations the phase separated PEEK-T contain uncured or partially cured epoxy which acted as a plasticizer which resulted in lowering of cross link density. In fact we have PEEK-T rich phase and epoxy rich phase in the system. The lowering of cross link density and the plasticization effect by the uncured or partially cured epoxy led to decrease in the storage modulus.

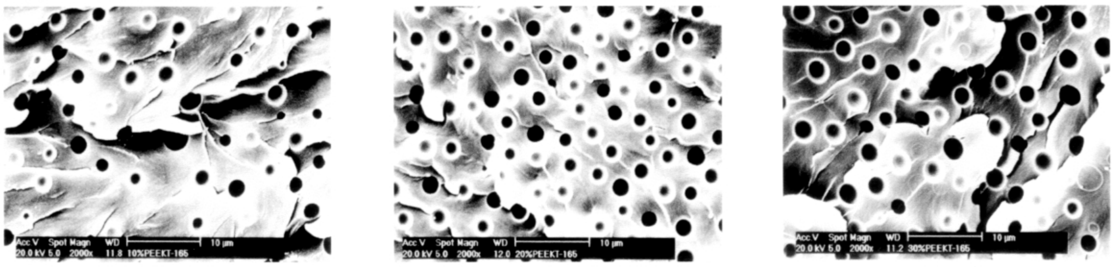
Table 3
Dispersed particle size and polydispersity of the blends cured at different temperatures

Composition	Curing temperature (°C)								
	180			165			150		
	$\bar{D}_v$ (μm)	$\bar{D}_n$ (μm)	PI	$\bar{D}_v$ (μm)	$\bar{D}_n$ (μm)	PI	$\bar{D}_v$ (μm)	$\bar{D}_n$ (μm)	PI
10	1.69	1.68	1.07	2.26	1.87	1.08	2.54	2.53	1.06
20	1.9	1.91	1.09	2.32	2.32	1.07	2.63	2.62	1.12
30	1.98	1.97	1.06	2.72	2.72	1.08	2.65	2.64	1.15



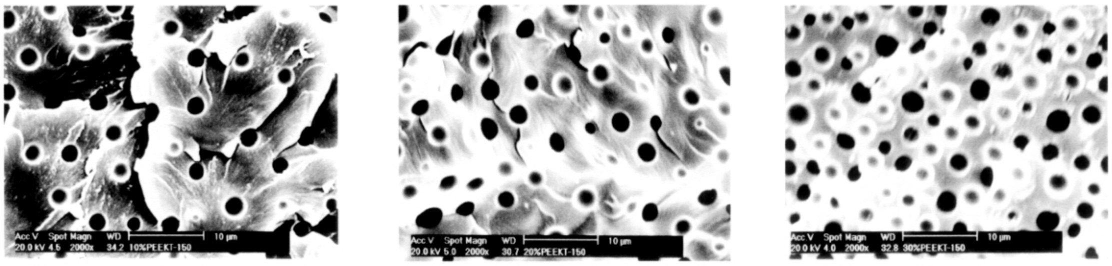
10 phr 20 phr 30 phr

curing temperature 180°C



10 phr 20 phr 30 phr

curing temperature 165°C



10 phr 20 phr 30 phr

curing temperature 150°C

Fig. 7. SEM micrographs of the blends cured at different curing temperatures.

4. General discussion and concluding remarks

A DGEBA epoxy resin was modified with poly (ether ether ketone) based on tertiary butyl hydroquinone using DDS as curing agent. Autocatalytic model was used for the kinetic analysis. Diffusion control was used to explain the conversion during the final stage.

The curing reaction was followed with DSC. It was found that the addition of PEEK-T did not affect the reaction mechanism. The neat epoxy resin as well as the blends exhibited autocatalytic mechanism. The extent and rate of the reaction decreased with the lowering of cure temperature and also with the increase in thermoplastic content.

The kinetic parameters were determined using auto-

Table 4
T_g of the blends cured at different temperatures

Composition PEEK-T (phr)	Curing temperature (°C)					
	180		165		150	
	Epoxy rich	Thermoplastic rich	Epoxy rich	Thermoplastic rich	Epoxy rich	Thermoplastic rich
0	202	–	183	–	169	–
10	202	138.9	178.9	131.3	161.9	–
20	202.4	135.1	183.5	130.5	165.1	125.0
30	201	133.1	180.7	127.2	166.3	124.0

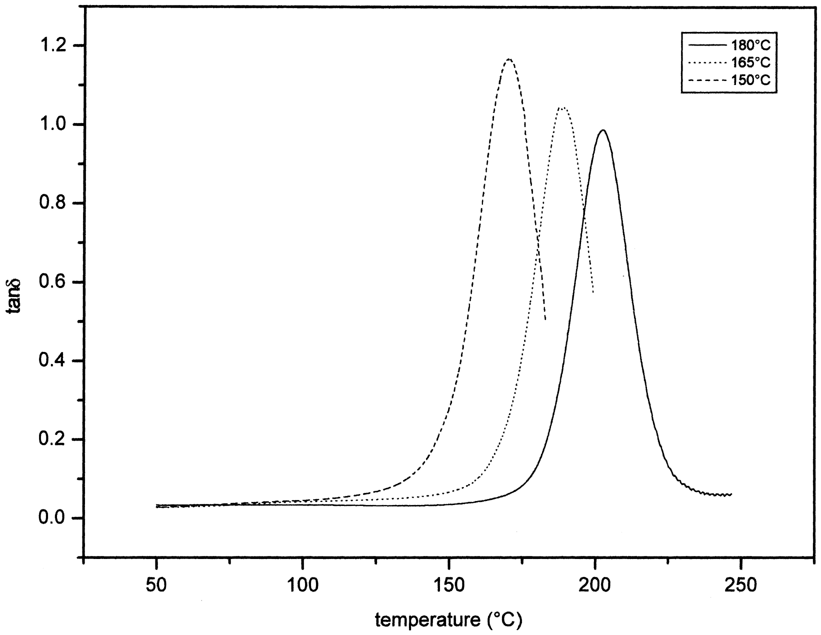


Fig. 8. tan δ vs temperature plot for neat resin cured at 180, 165 and 150 °C.

catalytic model. The autocatalytic model agrees well with the experimental data up to the vitrification point and afterwards the reaction became diffusion controlled. A diffusion factor was introduced to explain the reaction during the later stages of cure. The kinetic data fit well with the inclusion of diffusion factor.

The SEM studies revealed heterogeneous morphologies for the blends. The dispersed particle size increased slightly with the lowering of curing temperature and also with the increase in PEEK-T content. Homogeneous particle size distribution was observed for all the blends. Compared to thermoplastic + thermoplastic blends the dispersed phase size was low in our system due to the suppression of coalescence.

Dynamic mechanical thermal analysis of the cured resin revealed that the T_g decreased with the decrease in cure temperature due to the lower conversion as a result of vitrification. The blends gave two T_g's corresponding to the epoxy rich and thermoplastic rich phases in the dynamic mechanical spectrum. The storage modulus values of 10 and 20 phr blends cured at 165 °C are greater than that of the neat resin. The storage modulus decreased at 30 phr PEEK-T

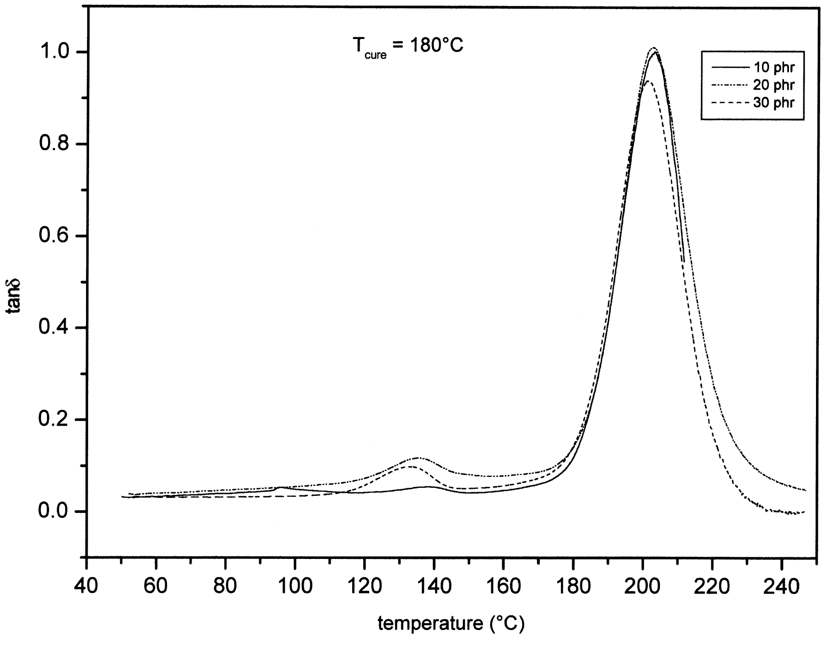


Fig. 9. tan δ vs temperature plot for the blends cured at 180 °C.

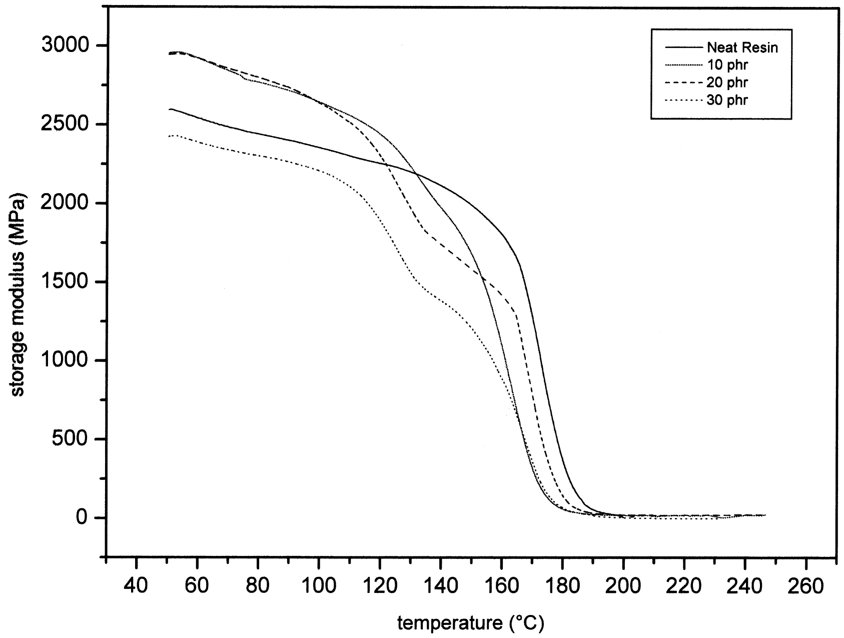


Fig. 10. Storage modulus vs temperature plot of the blends cured at 165 °C.

due to the decrease in crosslink density and also due to the presence of uncured or partially cured epoxy in the thermoplastic rich phase. Finally it is important to add that blends of modified PEEK and epoxy resin are extremely important for generating new class of high performance materials.

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