

Cure kinetics, morphological and dynamic mechanical analysis of diglycidyl ether of bisphenol-A epoxy resin modified with hydroxyl terminated poly(ether ether ketone) containing pendent tertiary butyl groups

Bejoy Francis ^a, V. Lakshmana Rao ^{a,*}, Geert Vanden Poel ^b, Fabrice Posada ^b, Gabriel Groeninckx ^b, R. Ramaswamy ^a, Sabu Thomas ^{c,*}

^a *Polymers and Special Chemicals Division, Vikram Sarabhai Space Centre, Thiruvananthapuram, Kerala 695 022, India*

^b *Laboratory of Macromolecular Structural Chemistry, Department of Chemistry, Catholic University of Leuven, Celestijnenlaan 200F, 3001 Heverlee, Belgium*

^c *School of Chemical Sciences, Mahatma Gandhi University, Priyadarshini Hills P.O., Kottayam, Kerala 686 560, India*

Received 14 October 2005; received in revised form 13 May 2006; accepted 15 May 2006

Available online 16 June 2006

Abstract

Hydroxyl terminated poly(ether ether ketone) based on *tert*-butyl hydroquinone (PEEKTOH) was used to modify a diglycidyl ether of bisphenol-A epoxy resin. A diamine, 4,4'-diaminodiphenylsulfone was used as the curing agent. Isothermal differential scanning calorimetric measurements of the blends were carried out at 180, 165 and 150 °C. The extent of reaction was found to decrease with the addition of PEEKTOH. The phenomenological model developed by Kamal was used for kinetic analysis of curing reaction. The curing reaction followed autocatalytic mechanism regardless of the presence and amount of oligomer present in the epoxy resin. The experimental and theoretical reaction rates were in good agreement during the initial stages of the reaction. The experimental values were lower than theoretical rate during the final stages of reaction due to increase in the viscosity of the system. A semiempirical model was used to explain diffusion control during final stages of reaction. The cured blends exhibited two phase morphology at all the curing temperatures. A uniform particle size distribution was observed at all compositions. The domain size decreased slightly with increase in oligomer content and with decrease in curing temperature. Finally, the viscoelastic properties were analysed using dynamic mechanical thermal analysis. Two T_g s corresponding to epoxy rich and thermoplastic rich phases were evident from the dynamic mechanical spectrum.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Epoxy resin; PEEKTOH; Cure kinetics

1. Introduction

Epoxy resin/thermoplastic blends have been the focus of study for the last two decades. Commercially available thermoplastics as well as low molecular weight functionally terminated oligomers were used to modify epoxy resins [1–18]. Depending on the curing agent, curing conditions, composition, etc. a wide range of properties were achieved [19,20]. The ultimate morphology is strongly dependent of the curing

conditions used. Remiro et al. [21] found that the morphology of PMMA modified epoxy resin cured with DDM was strongly influenced by the curing condition. The curing conditions influence the morphology of epoxy resin blended with an amorphous PEEK, phenolphthalein polyether ether ketone (PEK-C), which was cured with DDM. In this case, homogeneous morphology was observed at low curing temperature [22] while a higher curing temperature favoured heterogeneous morphology [23]. An exceptional case was polyoxypropylene modified epoxy resin cured with a cycloaliphatic amine where the mechanical properties and fracture toughness do not depend on the precure temperature, but the domain size decreased slightly with increase in cure temperature [24].

The optimisation of curing conditions is necessary to achieve the desired properties. Curing reaction involves the liberation of heat and the amount of heat liberated is

* Corresponding authors. Tel.: +91 481 2730003; fax: +91 481 2731002.

** Tel.: +91 471 2564298; fax: +91 471 2706136.

E-mail addresses: rao_vl@rediffmail.com (V.L. Rao), sabut@sancharnet.in (S. Thomas).

proportional to the extent of curing. Since, differential scanning calorimetry (DSC) is an excellent tool for monitoring changes involving absorption or liberation of heat, curing reaction can be easily followed by this technique [25–31]. The advantage of DSC is that the measurements are sensitive to small changes in heat and requires specimens in milligram scale.

In this paper, we report on the cure kinetics, viscoelastic and morphology of an epoxy resin modified with hydroxyl terminated poly(ether ether ketone) with pendent *tert*-butyl group (PEEKTOH) cured with an aromatic diamine. PEEK is an engineering thermoplastic with excellent properties. Blending PEEK with epoxy resin is difficult due to its high molecular weight, semicrystalline nature, etc. Blends of epoxy resin with phenolphthalein polyether ether ketone [32–34] and amine terminated oligomers based on *tert*-butyl hydroquinone, methyl hydroquinone, hydroquinone and bisphenol-A based PEEK were reported [35]. In a previous publication, we reported that epoxy resin modified with random terminated PEEK based on *tert*-butyl hydroquinone cured with DDS followed autocatalytic mechanism [31]. The morphology and mechanical properties were investigated in detail. In the present study, PEEKTOH was used as a modifier for a difunctional epoxy resin. The oligomer was synthesised by the nucleophilic substitution reaction of 4,4'-difluorobenzophenone with *tert*-butyl hydroquinone in the presence of potassium carbonate at 200 °C. The cure kinetics, morphology and dynamic mechanical properties of the blends were investigated.

2. Experimental

2.1. Materials used

Commercially available 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 4,4'-diaminodiphenylsulfone (DDS, Aldrich). The materials were used as received without any further purification. Hydroxyl terminated poly(ether ether ketone) based on tertiary butyl hydroquinone was synthesized in the laboratory. The chemical structures of the epoxy resin, DDS and PEEKTOH are given in Fig. 1.

2.2. Blend preparation

The blends were prepared using a solventless mixing technique. PEEKTOH was dissolved in epoxy resin at 180 °C with constant stirring. The curing agent was dissolved in the blend at 180 °C in a short time span (40 s) to minimise the curing reaction during mixing and the mixture was immediately plunged into liquid nitrogen to quench the curing reaction. Blends with 0, 5, 10, 15 and 20 phr oligomer were prepared and the amine to epoxide ratio was one in all the systems studied.

2.3. Differential scanning calorimetric analysis

A power compensated type differential scanning calorimeter (Perkin Elmer Pyris 1) was used for dynamic and isothermal

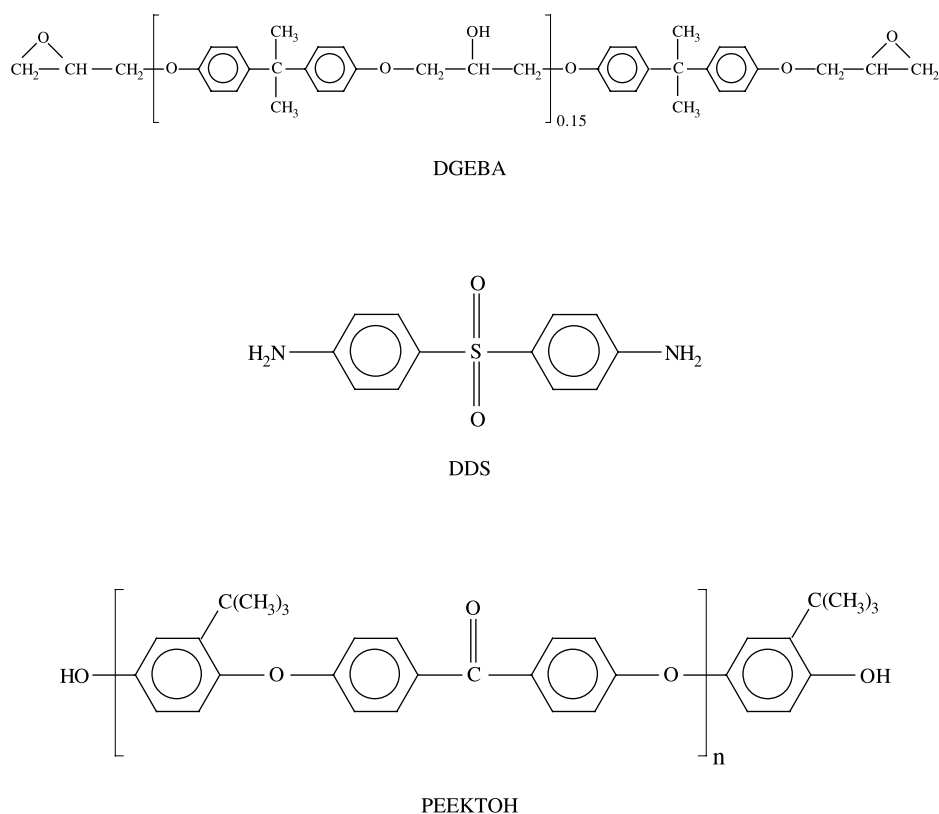


Fig. 1. Chemical structure of DGEBA, DDS and PEEKTOH.

DSC measurements. The instrument was calibrated with indium, tin and benzophenone standards. 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 in order to determine the total heat of reaction ΔH_{tot} . Isothermal measurements were done at 180, 165 and 150 °C, respectively. The curing reaction was assumed to be completed when the isothermal curve levelled off to a straight line. The area 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 $\alpha = \Delta H_t / \Delta H_{\text{tot}}$, 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.

2.4. Scanning electron microscopy

The morphology of the blends cured at 180, 165 and 150 °C were examined using 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 to remove the solvent. The fracture surfaces were sputter coated with gold before taking the micrographs.

2.5. Dynamic mechanical thermal analysis

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

3. Results and discussion

PEEKTOH was synthesised by the nucleophilic substitution reaction of 4,4'-difluorobenzophenone with *tert*-butyl hydroquinone in the presence of potassium carbonate and NMP as solvent. The oligomer was characterised by gel permeation chromatography (GPC), nuclear magnetic resonance spectroscopy (NMR), infrared spectroscopy (IR) and differential scanning calorimetry (DSC). The number average molecular weight was found to be 11,000 from GPC measurements and the glass transition temperature of the polymer was 171 °C.

3.1. DSC studies

Dynamic DSC measurements were done for 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

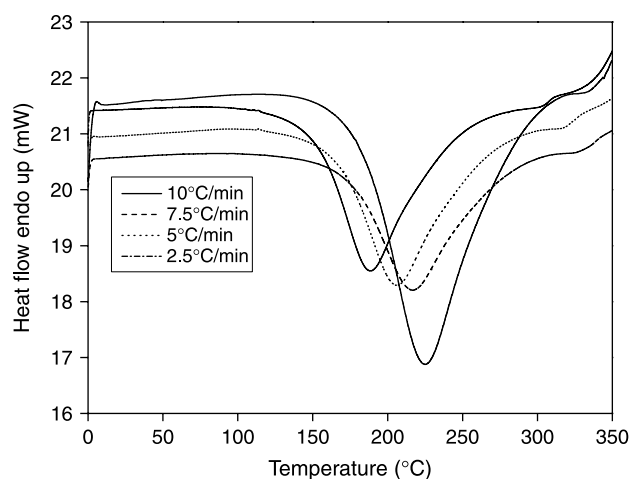


Fig. 2. Dynamic DSC scans of the neat resin at different heating rates.

average of the enthalpy values obtained at different heating rates. This value was taken as ΔH_{tot} for calculating the fractional conversion α at time, t [25,36].

The phenomenological model developed by Kamal [37] 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 [38–40].

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (1)$$

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 given in Eq. (2).

$$k_i = A_i \exp\left(\frac{-E_{ai}}{RT}\right) \quad (2)$$

where, A_i is the pre exponential constant, E_{ai} is the activation 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 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 [41]. 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 5, 10, 15 and 20 phr PEEKTOH were cured isothermally at three temperatures; 180, 165 and 150 °C. The rate of reaction $d\alpha/dt$ vs time plot for the blends cured at 180 °C is shown in Fig. 3. Similar curves were obtained for blends cured at 165 and 150 °C. The maximum rate was observed after the start of the reaction showing

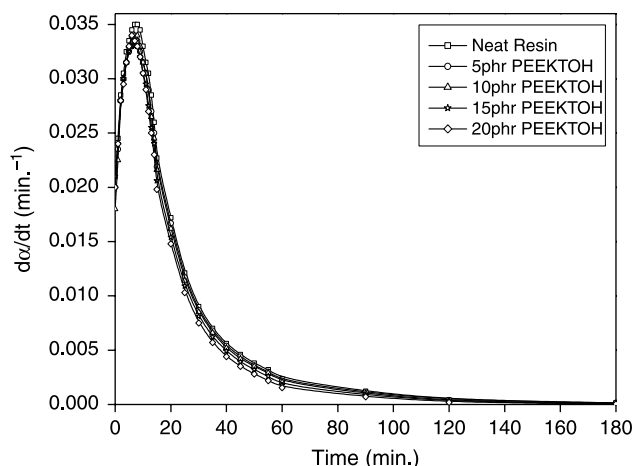


Fig. 3. Reaction rate vs time plot for neat resin and blends cured at 180 °C.

autocatalytic nature. The time required to attain maximum rate was found to increase with decrease in cure temperature. The rate of reaction was found to decrease with increase in PEEKTOH 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 at certain conversion. During phase separation some of the lightly crosslinked epoxy resin or DDS could be trapped in the separated out PEEKTOH phase leading to decrease in curing reaction. It could be better said that the probability for the reaction between epoxy resin and hardener is decreased as the thermoplastic content increased [42].

The kinetic parameters were determined according to 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 $\ln k_2$ against $1/T$. The slopes of these plots

were used to calculate the activation energies E_{a1} and E_{a2} , respectively. The activation energies for the curing of DGEBA/PEEKTOH blends exhibited higher values compared to the neat resin. This means that PEEKTOH hinders with the reaction between epoxide and amine.

The kinetic parameters obtained after considerable 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 15 phr PEEKTOH whereas 20 phr blends showed higher values for n .

Fig. 4 shows the plot of rate of reaction vs conversion for the neat resin as well as the blends cured at 180 °C. From the figure it was evident that the extent of conversion and the reaction rate decreased with increase in PEEKTOH 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 °C is given in Fig. 5. The experimental data agreed well with the model predictions at lower conversion, i.e. for the initial stages of cure and similar trend was observed at all other cure temperatures also. But at higher conversions, the values predicted by the model were high compared to the experimental data. This is due to the vitrification of the system. This meant that the cure reaction was controlled by diffusion during the final stages of cure. The difference from experimental data was greater at lower curing temperatures.

A semiempirical relationship based on free volume concept was used to explain diffusion control in cure reactions [43,44]. When the conversion reaches a critical value α_c , diffusion becomes the controlling factor and the rate constant k_d is given by

$$k_d = k_c \exp[-C(\alpha - \alpha_c)] \quad (3)$$

Table 1
Autocatalytic model constants for PEEKTOH ($\bar{M}_n = 11,000$) modified DGEBA epoxy blends

T (°C)	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/5 phr PEEKTOH									
180	0.97	2.62	3.59	20.6	191.18				
165	1.03	2.54	3.57	13.12	120.59	16.47	18.21	76.24	74.55
150	0.78	2.22	3.0	4.92	47.19				
Epoxy/10 phr PEEKTOH									
180	0.93	2.73	3.66	19.03	199.48				
165	0.87	2.51	3.38	8.94	90.48	12.13	18.34	60.80	75.27
150	0.93	2.48	3.41	6.02	48.23				
Epoxy/15 phr PEEKTOH									
180	1.07	3.08	4.15	21.4	257.03				
165	0.99	2.77	3.76	10.03	116.74	16.53	17.55	76.73	71.40
150	0.98	2.89	3.87	5.03	66.78				
Epoxy/20 phr PEEKTOH									
180	1.09	3.83	4.92	20.26	303.02				
165	1.20	3.36	4.56	10.98	179.18	22.77	22.71	99.92	89.66
150	0.81	3.16	3.97	3.1	56.37				

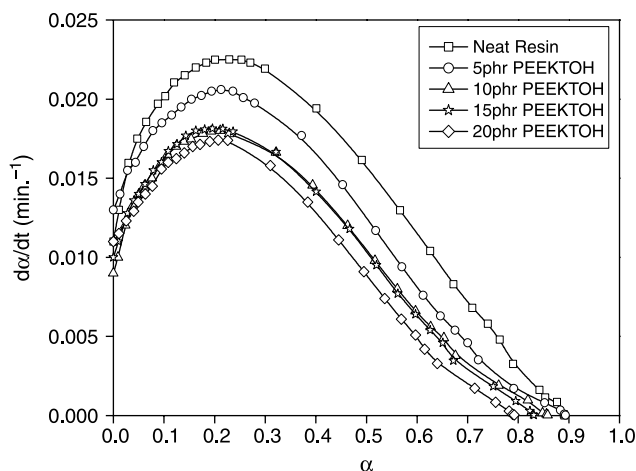


Fig. 4. Reaction rate vs conversion plot for neat resin and blends cured at 180 °C.

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 terms of k_d and k_c as follows

$$\frac{1}{k_e} = \frac{1}{k_d} + \frac{1}{k_c} \quad (4)$$

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

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

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 $f(\alpha)$ [45].

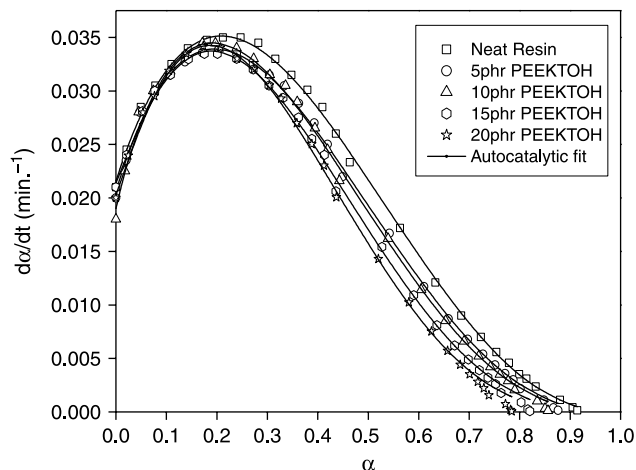


Fig. 5. Reaction rate vs conversion plot for experimental and autocatalytic fit for neat resin and blends cured at 180 °C.

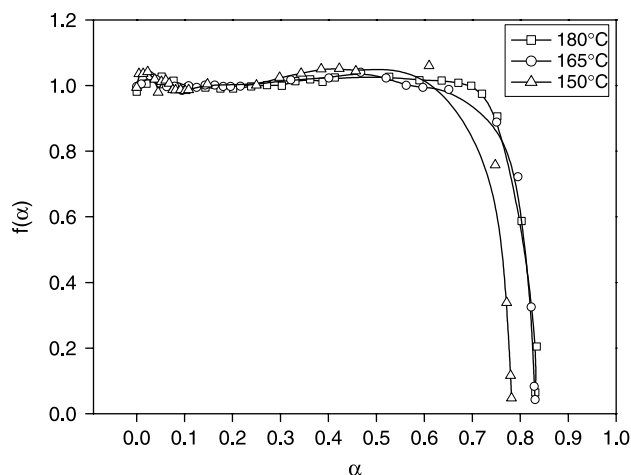


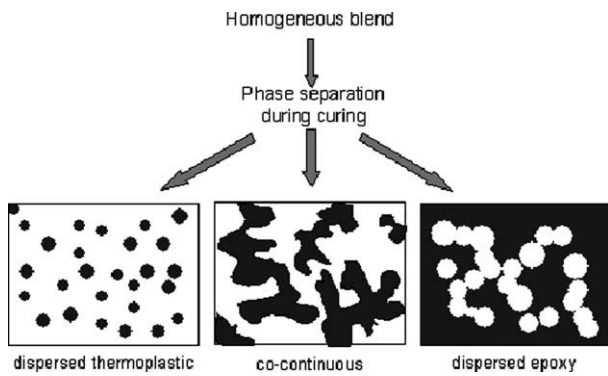
Fig. 6. Plot of diffusion factor $f(\alpha)$ against conversion at different curing temperatures for 15 phr blends.

The value of $f(\alpha)$ was taken as the ratio of the experimental reaction rate to the reaction rate predicted by 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 $f(\alpha)$ vs α for 15 phr blend is shown in Fig. 6. The decrease in $f(\alpha)$ and hence decrease in reaction rate due to diffusion control was evident from the figure. The other blends also showed the same trend. α_c gives the gradual change of the system from chemical control to diffusion control. The values of α_c and C are obtained by applying non linear regression to $f(\alpha)$ vs α data to Eq. (5). Table 2 gives α_c and C values for the blends cured at different temperatures. α_c values increased with increase in cure temperature, i.e. the change from chemical control to diffusion control occurred at higher conversions. The critical conversion was also affected by the composition of

Table 2

Values of critical conversion α_c and C parameters for epoxy/PEEKTOH $\bar{M}_n - 11,000$ 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/5 phr PEEKTOH		
180	0.86	107.43
165	0.89	284.91
150	0.85	67.26
Epoxy/10 phr PEEKTOH		
180	0.84	137.56
165	0.83	103.2
150	0.80	76.08
Epoxy/15 phr PEEKTOH		
180	0.79	49.27
165	0.80	81.87
150	0.76	96.20
Epoxy/20 phr PEEKTOH		
180	0.75	51.96
165	0.76	71.54
150	0.68	96.08



Scheme 1. Morphology evolution of epoxy/thermoplastic blends upon curing.

the blends. Compared to neat resin the change to diffusion control occurred at lower conversion for the blends. This is due to the increased viscosity of the system due to the addition of oligomer.

3.2. Morphological analysis

A typical characteristic of blends of epoxy resin is to undergo reaction induced phase separation upon curing. The morphology evolution on curing is shown in Scheme 1. Depending on the composition, dispersed, cocontinuous or phase inverted morphologies are generated. The initially miscible homogeneous mixture phase separates upon curing due to entropic and enthalpic contribution. Phase separation occurs unless there is strong interaction between epoxy and the

added second component. Exceptions are polycarbonate (PC)/epoxy and phenolphthalein polyether ether ketone (PEK-C)/epoxy blends cured with DDM at 80 °C [22]. The miscibility in the case of polycarbonate blends was attributed to the chemical reaction between PC and epoxy resin prior to cure. The blends we studied exhibited typical phase separated morphology. Irrespective of the curing temperature, all the blends had heterogeneous morphology as evident from the scanning electron micrographs of fracture surfaces etched with chloroform given in Fig. 7. No phase inversion was observed in the compositions we studied. The number of domains increased with composition and the dispersed domains have uniform particle size distribution. The domain diameters and polydispersity index were calculated for the blends using the following equations.

$$\text{Number average diameter, } \bar{D}_n = \frac{\sum n_i d_i}{\sum n_i} \quad (6)$$

$$\text{Weight average diameter, } \bar{D}_w = \frac{\sum n_i d_i^2}{\sum n_i d_i} \quad (7)$$

$$\text{Polydispersity index, } \text{PDI} = \frac{\bar{D}_w}{\bar{D}_n} \quad (8)$$

where, n_i is the number of domains having diameter d_i

Table 3 gives the domain size and polydispersity index of the dispersed phase measured using image analysis. The domain size decreased with increase in cure temperature. This is because gelation occurred in a shorter time due to the faster

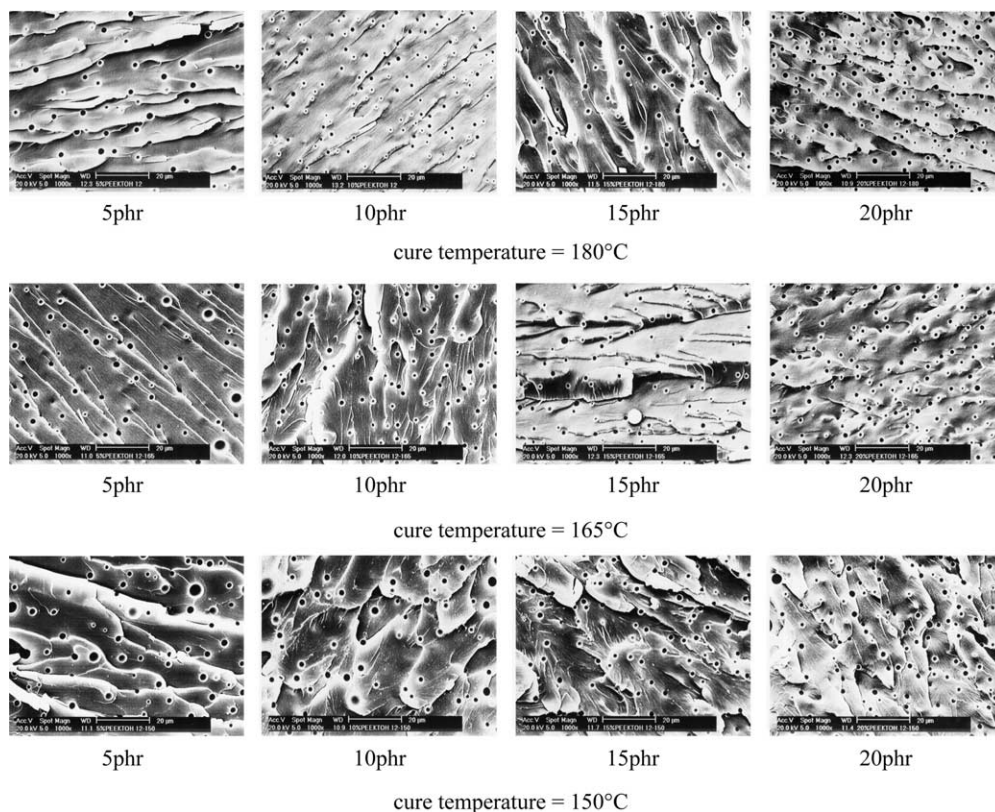


Fig. 7. SEM micrographs of the blends cured at different curing temperatures.

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

Curing temperature	PEEKTOH content (phr)	\bar{D}_n (μm)	\bar{D}_w (μm)	PDI
180 °C	5	1.56	1.71	1.09
	10	1.56	1.72	1.10
	15	1.20	1.32	1.10
	20	1.25	1.40	1.12
165 °C	5	1.49	1.61	1.08
	10	1.19	1.29	1.08
	15	1.12	1.23	1.10
	20	1.30	1.47	1.13
150 °C	5	1.37	1.54	1.12
	10	1.72	1.80	1.05
	15	1.42	1.47	1.04
	20	1.44	1.50	1.04

reaction rate with increase in cure temperature. An interesting phenomenon observed in the blends was the slight decrease in particle size with increasing PEEKTOH content. This is due to the increase in viscosity of the system. The addition of the PEEKTOH leads to increase in the viscosity of the system as a whole. As curing takes place, the viscosity of the system will increase with time and at a particular time gelation will occur and phase separation will stop. At higher PEEKTOH contents, gelation will occur earlier due to the higher system viscosity resulting in smaller domains.

The phase separation mechanism in epoxy resin/thermoplastic blends was studied extensively [46–49]. The phase separation mechanism was found to be dependent on the composition of the blends, nature of curing agent, curing temperature and secondary phase separation was observed in some cases. When the composition of the blend was near the critical composition, phase separation occurred by spinodal decomposition and at off critical compositions phase separation occurred by nucleation and growth mechanism. For thermoplastic with average molar mass between 10,000 and 30,000 g/mol, the critical concentration of thermoplastic was 10–15 wt%

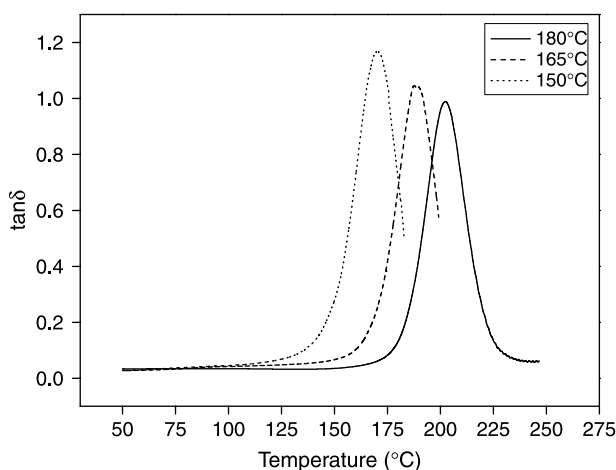


Fig. 8. $\tan \delta$ vs temperature plot for neat resin cured at 180, 165 and 150 °C.

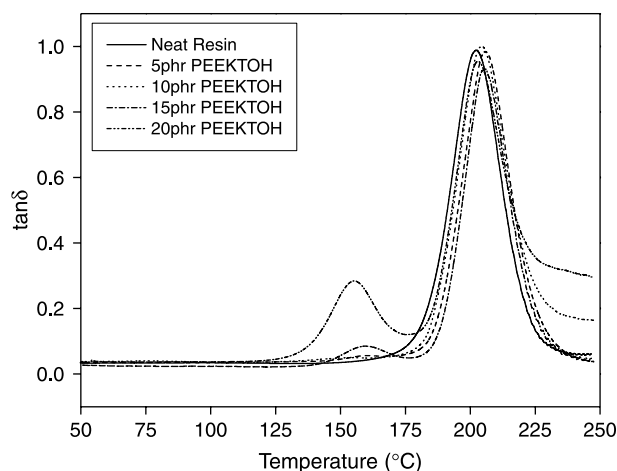


Fig. 9. $\tan \delta$ vs temperature plot for neat resin and blends cured at 180 °C.

in liquid epoxy and diamine monomer as calculated by Flory–Huggins model [50]. In the present study, the molecular weight of PEEKTOH is 11,000 g/mol. Hence, the critical concentration may be higher than the above mentioned range. Therefore, the phase separation was expected to occur by nucleation and growth mechanism.

3.3. Dynamic mechanical thermal analysis

The glass transition temperature of the unmodified epoxy resin decreased with decrease in cure temperature. The $\tan \delta$ vs temperature plot of unmodified epoxy resin cured at different temperatures are given in Fig. 8. The decrease in T_g was due decrease in crosslink density, which is evident from DSC studies where a decrease in the extent of cure reaction with lowering of curing temperature was observed. The height of $\tan \delta$ curve is more for epoxy resin cured at 150 °C. This is an indication of more damping characteristic or more flexibility. The typical dynamic mechanical spectrum of phase separated blends is given in Fig. 9. Two peaks were seen in the spectrum, the one at high temperature corresponds to the T_g of epoxy rich phase and the

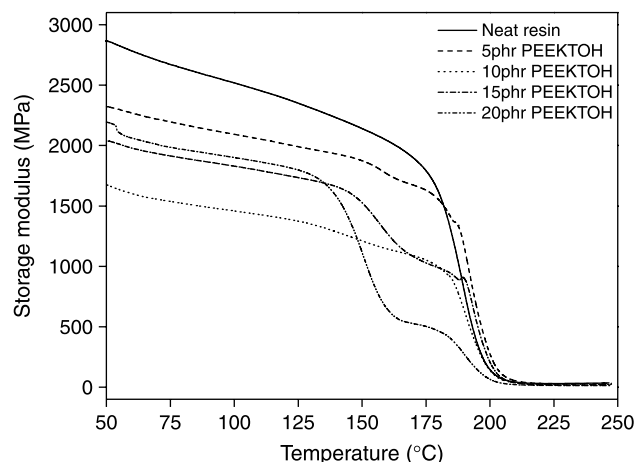


Fig. 10. Storage modulus vs temperature plot for neat resin and blends cured at 180 °C.

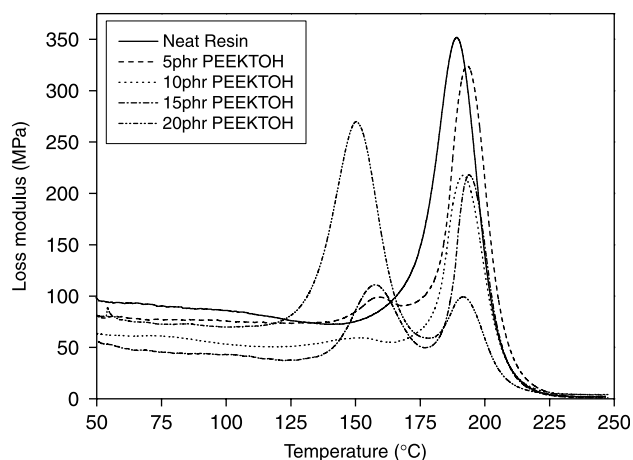


Fig. 11. Loss modulus vs temperature plot for neat resin and blends cured at 180 °C.

one at lower temperature is due to the T_g of thermoplastic rich phase in accordance with the two phase morphology observed in the scanning electron micrographs. The variation of storage modulus and loss modulus with temperature for the blends cured at 180 °C are shown in Figs. 10 and 11, respectively. The storage modulus decreased with temperature and after the glass transition region the values remained constant. The storage modulus of the blends was lower than that of the unmodified epoxy resin. The loss modulus vs temperature plot of the blends showed two peaks corresponding to epoxy rich and thermoplastic rich phases.

4. Conclusions

The effect of addition of hydroxyl terminated PEEK oligomers with pendent *tert*-butyl groups on the kinetics of cure of a DGEBA epoxy resin was investigated. Autocatalytic mechanism was found in the neat resin as well as the blends. The extent of reaction decreased with the addition of oligomers. The blends cured at various temperatures exhibited two phase morphology in which PEEKTOH domains were dispersed in the continuous epoxy matrix. The domain size decreased slightly with increase in composition. This is due to the increase in viscosity of the blends with increase in oligomer content. The domain size was not much affected by changing the curing temperature. The glass transition temperature of the unmodified resin from dynamic mechanical analysis decreased with decrease of curing temperature. This was due to the decrease in curing reaction at lower curing temperatures as evident from isothermal DSC studies. Two T_g s characteristic of heterogeneous morphology was evident from dynamic mechanical spectrum of the blends.

Acknowledgements

The authors thank the authorities of Vikram Sarabhai Space Centre for giving permission to publish this article. One of the authors (Bejoy Francis) is thankful to CSIR, New Delhi for

providing Senior Research Fellowship. Thanks are also due to Analytical and Spectroscopy Division, VSSC for analytical support.

References

- [1] Mimura K, Ito H, Fujikoa H. *Polymer* 2000;41:4451.
- [2] Min HS, Kim SC. *Polym Bull* 1999;42:221.
- [3] Varley RJ, Hodgkin JH, Simon GP. *Polymer* 2001;42:3847.
- [4] Cho JB, Huang JW, Cho K, An JH, Park CE. *Polymer* 1993;34:4832.
- [5] Reydet EG, Vicard V, Pacault JP, Sautereau H. *J Appl Polym Sci* 1997; 65:2433.
- [6] Bonnet A, Lestriez B, Pascault JP, Sautereau H. *J Polym Sci, Part B: Polym Phys* 2001;39:363.
- [7] Barral L, Cano J, Lopez J, Bueno IL, Nogueira P, Ramirez C, et al. *Thermochim Acta* 2000;344:137.
- [8] Liello VD, Martuscelli E, Musto P, Ragosta G, Scarinzi G. *J Polym Sci, Part B: Polym Phys* 1994;32:409.
- [9] Pearson RA, Yee AF. *Polymer* 1993;34:3658.
- [10] Iijima T, Fujimoto K, Tomoi M. *J Appl Polym Sci* 2002;84:388.
- [11] Jiang X, Huang H, Zhang Y, Zhang Y. *J Appl Polym Sci* 2004;92: 1437.
- [12] Jiang X, Huang H, Zhang Y. *J Polym Sci, Part B: Polym Phys* 2004; 42:1181.
- [13] Riccardi CC, Borrajo J, Meynie L, Fenouillot F, Pascault JP. *J Polym Sci, Part B: Polym Phys* 2004;42:1351.
- [14] Riccardi CC, Borrajo J, Meynie L, Fenouillot F, Pascault JP. *J Polym Sci, Part B: Polym Phys* 2004;42:1361.
- [15] Blanco I, Cicala G, Faro CL, Recca A. *J Appl Polym Sci* 2003;89:268.
- [16] Overbeke EV, Devaux J, Legras R, Carter JT, Mc Grail PT, Carlier V. *Polymer* 2003;44:4899.
- [17] Jainki W, Carlier V, Legras R, Morman W. *Macromol Symp* 2003; 198:323.
- [18] Cao Y, Shao Y, Sun J, Lin S. *J Appl Polym Sci* 2003;90:3384.
- [19] Crawford E, Lesser E. *J Polym Sci, Part B: Polym Phys* 1998;36:1371.
- [20] Shiraishi T, Motobe H, Ochi M, Nakanishi Y, Konoshi I. *Polymer* 1992; 33:2975.
- [21] Remiro PM, Marieta C, Riccardi CC, Mondragon I. *Polymer* 2001; 42:9909.
- [22] Zhang Z, Zheng S, Huang J, Cheng X, Guo Q, Wei J. *Polymer* 1998; 39:1075.
- [23] Guo Q, Huang J, Li B, Chen T, Zhang H, Feng Z. *Polymer* 1991;32:58.
- [24] Franco M, Corcuera MA, Gavalda J, Valea A, Mondragon I. *J Polym Sci, Part B: Polym Phys* 1997;35:233.
- [25] Naffakh M, Dumon M, Dupuy J, Gerard JF. *J Appl Polym Sci* 2005; 96:660.
- [26] Swier S, Mele BV. *Macromol Symp* 2003;198:367.
- [27] Swier S, Mele BV. *Macromolecules* 2003;36:4424.
- [28] Montserrat S, Roman F, Basany M, Colomer P. *Macromol Symp* 2003; 198:399.
- [29] Alig I, Jenninger W, Schawe JEK. *Thermochim Acta* 1999;330:167.
- [30] Wu SJ, Lin TK, Shyu SS. *J Appl Polym Sci* 2000;75:26.
- [31] Francis B, Vanden Poel G, Posada F, Groeninckx G, Rao VL, Ramaswamy R, et al. *Polymer* 2003;44:3687.
- [32] Song X, Zheng S, Huang J, Zhu P, Guo Q. *J Appl Polym Sci* 2001;79:598.
- [33] Zhong Z, Zheng S, Huang J, Cheng X, Guo Q, Wei J. *Polymer* 1998; 39:1075.
- [34] Guo Q, Huang J, Ge L, Feng Z. *Eur Polym J* 1992;28:405.
- [35] Bennet GS, Faris RJ, Thompson SA. *Polymer* 1991;32:1633.
- [36] Varley RJ, Hodgkin JH, Hawthorne DJ, Simon GP, McCulloch D. *Polymer* 2000;41:3425.
- [37] Kamal MR. *Polym Eng Sci* 1974;14:23.
- [38] Sourour S, Kamal MR. *Thermochim Acta* 1976;14:41.
- [39] Keenan MR. *J Appl Polym Sci* 1987;33:1725.
- [40] Horng TJ, Woo EM. *Angew Makromol Chem* 1998;260:31.
- [41] Ryan ME, Dutta A. *Polymer* 1979;20:203.
- [42] Chen JP, Lee YD. *Polymer* 1995;36:55.

- [43] Chern CS, Pohlein GW. *Polym Eng Sci* 1987;27:782.
- [44] Khanna V, Chanda M. *J Appl Polym Sci* 1993;49:319.
- [45] Reydet EG, Sautereau H, Pascault JP, Keates P, Navard P, Thollet G, et al. *Polymer* 1998;39:2269.
- [46] Barral L, Cano J, Lopez J, Bueno IL, Nogueira P, Abad MJ, et al. *Polymer* 2000;41:2657.
- [47] Yoon T, Kim BS, Lee DS. *J Appl Polym Sci* 1997;66:2233.
- [48] Blanco I, Cicala G, Motta O, Recca A. *J Appl Polym Sci* 2004;94:361.
- [49] Siddhamalli SK. *Polym Plast Technol Eng* 2000;39:699.
- [50] Bonnet A, Camberlin Y, Pascault JP, Sautereau H. *Macromol Symp* 2000;149:145.