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Polycarbonate/epoxy semi-interpenetrating polymer network: 1. Preparation, interaction and curing behaviour

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An epoxy based on the diglycidyl ether of bisphenonl-A (DGEBA) has been modified with polycarbonate (PC) and cured with 4,4′-diaminidiphenylsulfone (DDS) and maleic anhydride (MA). The chemical interaction between the PC and epoxy resin during the melt-mixing process and its effects on the physical characteristics of the PC have been investigated prior to the curing process. The curing kinetics of the neat resin and of PC/epoxy blends were analysed in detail by dynamic differential scanning calorimetry. The results showed that the PC usually has no effect or has promoting effects on the curing reaction for amine hardener because of the *in situ* curing mechanism, except for diffusion control. The presence of quaternary ammonium salts catalysing the PC–epoxy reaction resulted in a two-step curing behaviour, but its curing kinetics are similar to those of the neat resin. For MA curing systems, a different effect caused by PC and catalyst is associated with a different interaction among the reactants. Copyright © 1996 Published by Elsevier Science Ltd.

(Keywords: PC-modified epoxy; chemical interactions; cure kinetics)

INTRODUCTION

Epoxy resins are the desired materials for many important applications such as adhesives, semiconductor encapsulants and structural matrices, due to their high thermal resistance, high tensile strength and modulus, and good chemical resistance. However, their widespread use is limited in many high-performance applications because of their inherent brittleness. Several methods have been proposed to increase the toughness of epoxy resin, with rubber modification of epoxy resin being a well-known technology. Traditional modifiers include functionalized rubbers such as carboxy- or amino-terminated butadiene–acrylonitrile copolymers which are soluble in the uncured resin[1–4]. Basically these are two-phase systems in which relatively small rubber particles are dispersed in and bonded to an epoxy matrix, owing to a chemical reaction between the rubber end groups and the epoxy. In most instances a significant increase in toughness is achieved, but the presence of the rubber phase usually results in a lowering of effective properties such as glass transition temperature T_g, elastic modulus, yield strength and creep resistance. Moreover, rubber modification fails to produce a desirable level of toughening in highly crosslinked systems because the ability of the epoxy matrix to deform by shear yield is reduced[5,6].

To overcome the above drawbacks, many more recent studies have concentrated on improving the toughness of epoxy resin by the incorporation of high-performance engineering thermoplastics such as poly(ether sulfone) (PES)[7,8], polysulfone (PSF)[9], poly(ether ketone) (PEK)[10] and poly(ether imide) (PEI)[11]. The degree of toughening obtained in these systems is relatively modest compared with networks modified by carboxy-terminated butadiene–acrylonitrile, but the enhanced toughness is achieved with the retention of a high modulus and thermal stability. The results of previous studies conducted on thermoplastic/epoxy blends indicated the necessity of establishing strong adhesion at the interface. Van der Waals' bonding is usually not adequate, and therefore introducing reactive groups into the modifier that can react with the epoxy resin becomes more important. It is worth mentioning that significant progress has been achieved in thermoplastic-toughened epoxies by chemically reacting a thermoplastic polymer into an epoxy network. In these investigations, either phenolic hydroxyl- or aromatic amine-terminated poly-(arylene ether sulfone)[12] or polysulfone[13] oligomer was pre-reacted with a large excess of epoxy resin. The resulting networks with a two-phase morphology showed significantly enhanced fracture toughness arising from the polysulfone particles, which plastically deformed upon fracture as well as induced a local plastic deformation in the epoxy matrix.

We have taken a somewhat similar approach except that we have used commercial polycarbonate resins as modifer[14]. Bisphenol-A polycarbonate is easily dissolved in epoxy resin based on the diglycidyl ether of bisphenol-A (DGEBA) by the melt-blending process. The carbonyl

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groups in PC chains and the hydroxyl or amine groups in epoxy resin can interact via hydrogen bonding, which will induce strong interface adhesion. Diepoxides and in-chain carbonate groups react readily in the presence of quaternary ammonium salts, which gives an opportunity to chemically react PC into an epoxy resin network by a simple physical blend method. As part of our composite research programme, we describe in this paper the characterization (by infra-red spectroscopy and thermal analysis) of PC and epoxy resin that have been recovered from melt blend to illustrate the chemical interactions taking place between the two components during the melt-blending process. The influence of the addition of PC and a carbonate–epoxide reactive catalyst on the curing behaviour of the epoxy resin with amine or anhydride hardener have been investigated by differential scanning calorimetry (d.s.c.). The aim of this work was to reveal the network structure of PC/epoxy blends developed during the curing process and investigate factors affecting its control, the latter providing the basis for control of phase separation and morphology, and consequently fracture toughness.

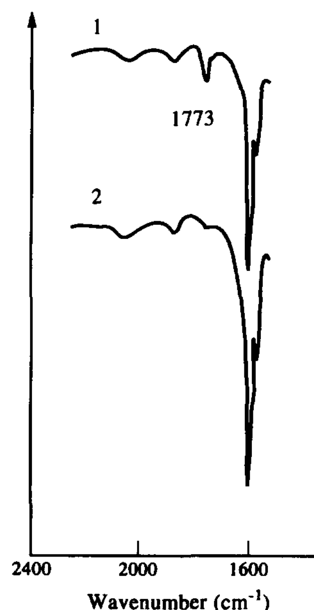

Figure 1 *FT*i.r. spectra of epoxy resin recovered from PC/epoxy melt mixture (1) and pure resin (2) at 2400–1600 cm^{-1}

EXPERIMENTAL

Materials

The DGEBA epoxy resin was a product of commercial grade obtained from Gangzhou East Chemistry Company (E51, molecular weight = 392 g mol^{-1}). The polycarbonate was supplied by Shun De Resin company (it was a powder with $M_w = 4.13 \times 10^4$). 4,4′-Diaminiodiphenylsulfone (DDS) and maleic anhydride (MA) were used as curing agents. Tetramethyl ammonium iodide (TMAI) was used as a catalyst for inducing reaction between PC and epoxy resin.

Techniques

An MS-x infra-red spectroscope was used to measure Fourier transform infra-red (*FT*i.r.) spectra. Thermal analysis of uncured mixtures and components was performed with Perkin–Elmer DSC 2 and CDR-1 differential scanning calorimeters, as well as a Perkin–Elmer TGS 2 thermogravimeter. Dynamic mechanical measurements were carried out with a Rheovibron DDV-II viscoelastometer. Density was measured by gravity bottle.

A certain amount of PC was dissolved in the epoxy resin at 180°C for 20 min and 200°C for 10 min to give a clear homogeneous mixture. Both components were selectively separated from the mixture by dissolving the mixture in toluene; the precipitated PC was recovered by filtration. Any possible epoxy resin remaining in the precipitated PC powder was removed by extracting the powder with acetone in an extractor for 5 h.

To study the kinetics of the curing process, the above PC/epoxy resin mixture was mixed with the required amount of DDS or TMAI at 130°C for 10 min to ensure complete mixing of components, and then the uncured mixture was quenched and stored in a sealed container at about −10°C. The dynamic scans were taken at temperatures of up to 300°C at different heating rates ranging from 5 to 40°C min^{-1}. The d.s.c. runs were made in duplicate and the reproducibility of kinetic data was found to be very good. For anhydride hardener, MA was mixed with the mixture at 60°C; the other measuring steps for the kinetic studies were the same as those for DDS curing systems.

RESULTS AND DISCUSSION

Characterization of PC and epoxy resin separated from PC/epoxy melting mixture

The fact that chain scission can occur in PC by the hydrolysis of carbonate groups during the high-temperature dissolution process has been demonstrated by Abbate *et al.*[15]. The epoxy resin used in this work contained 0.3×10^{-3} mol g^{-1} of hydroxyl groups. Therefore the in-chain carbonate groups of PC were able to react with the hydroxyl groups at high temperature, as shown in *FT*i.r. spectra (*Figure 1*). A sharp peak at 1773 cm^{-1}, not present in the starting epoxy resin, is evident in the resin recovered. This band can readily be ascribed to the stretching vibrations of carbonyl groups, and reveals the occurrence of the PC chain scission process because the shorter chains favour dissolution of PC in toluene. The degree of chemical interaction between the two components was not sufficient to make any obvious difference between the *FT*i.r. spectra of pure PC and recovered PC, a finding that is associated with the lower mixing temperature and shorter mixing time compared with ref. 15. In this situation, the hydroxyl-terminated PC chains formed by chain scission scarcely react with the epoxy groups to form epoxy-terminated PC chains.

However, the PC chain scission still has an important influence on the crystallization of PC as shown in the d.s.c. traces (*Figure 2*). The pure PC used in this work is a semicrystalline polymer with a crystallinity of 32.5% and melting point of 24.0°C. The PC recovered from the PC/epoxy mixture also possesses crystallinity, but has a lower value of 27.3% and a lower melting point of 228.8°C, which is related to the lowering of molecular weight. This effect is also evident in *Figure 3*, which

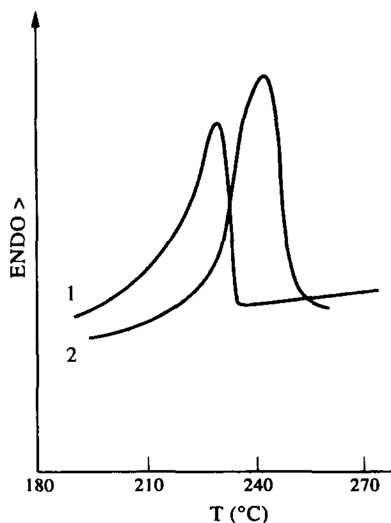

Figure 2 D.s.c. thermograms of PC recovered from PC/epoxy melt mixture (1) and pure PC (2)

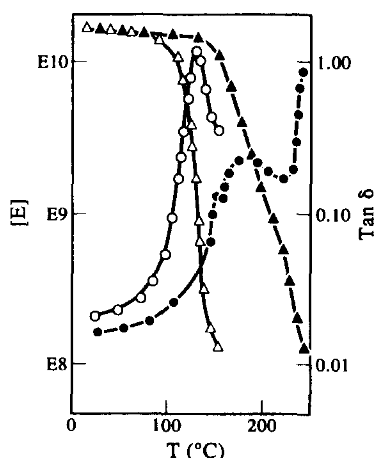

Figure 3 Dynamic mechanical spectrum of PC cast film for: PC recovered from PC/epoxy melting mixture (○, △); pure PC (●, ▲)

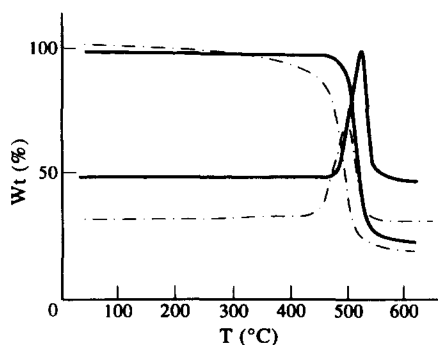

Figure 4 Thermogravimetric spectra of PC recovered from PC/epoxy melting mixture (– – –) and pure PC (——)

shows the dynamic mechanical properties of samples cast from CH_2Cl_2 solution. Showing features typical of a semicrystalline polymer the pure PC has a broad α transition, with a peak temperature T_α of 181.2°C and a full width at half-maximum W_α of 75°C, and a maximum $\tan\delta$ value, $(\tan\delta)_{max}$, of 0.24; all these data are consistent with ref. 16. By comparison the recovered PC possesses a narrower α transition peak, with T_α of 130.8°C, W_α of 21°C and $(\tan\delta)_{max}$ of 1.18, indicating the amorphous nature of this fraction and its plasticizing effect on molecular motion.

The existence of hydroxyl-terminated PC chains formed by chain scission decreased the thermal stability as demonstrated by thermogravimetric analysis (t.g.a.) (*Figure 4*), which shows a decrease of 20°C for the d.t.g. peak temperature. Therefore, mixing of PC and epoxy resin at high temperatures for a long time is not advisable; mixing times should be kept as short as possible to maintain the thermal stability of PC.

Influence of PC on the curing behaviour of epoxy/DDS systems

From the characteristic d.s.c. scans, the temperature at which the curing reaction started (T_i), attained the maximum (T_p), and completed (T_f), the overall reaction heat (ΔH) and the fractional conversion (α_p) at T (defined as the ratio of partial heat ΔH_p to the overall heat) are presented in *Table 1*. The exotherm peak temperature (T_p) varied in a predictable manner with the heating rate (ϕ). Addition of PC (10 phr) to the resin mildly affected the temperatures T_p and T_f, but greatly decreased T_i. The higher values of ΔH for the neat epoxy represent a higher exotherm and final conversion was observed. However, the lowering of ΔH was not evident for samples with low content of PC (5–15 phr).

Conversion *versus* temperature curves at different heating rates for the neat resin and blend are reported in *Figure 5*. When $\phi = 20°C\,min^{-1}$ the addition of PC tended to shift the curve to lower temperature (curve II) and therefore, at the same temperature, the system containing PC attained greater conversion. When $\phi = 5°C\,min^{-1}$ the two curves with and without PC intersect at point A (curve I), corresponding to the temperature T_A of 215°C. So, there is an inverse effect of PC on the kinetics of the curing process depending on the temperature, $T < T_A$ or $T > T_A$.

A simple and accurate relationship between activation energy E, heating rate ϕ, pre-exponential factor ln A and peak exotherm temperature T_p is given by the Kissinger[17] equation in the form

$$-\ln(\phi/T_p^2) = E/RT_p - \ln(AB/E)$$

The values obtained from this equation for the blends with different PC contents are presented in *Table 2*. It is noticed that the addition of 10 phr PC decreases the activation energy by 20%, while for a higher content of PC (20 or 30 phr) the E remains unaffected by blend composition. The kinetic data seem to indicate that the presence of PC in the system does not alter the overall reaction mechanism. The decrease of the pre-exponential factor and consequently the rate constant with increasing PC content can tentatively be ascribed to an increase of the bulk viscosity of the system caused by the presence of PC, i.e. diffusion control which results in low conversion of the reactants.

Figure 6 presents Arrhenius plots of rate constant ln K against reciprocal temperature for blends with various amounts of PC. The results show that the system with 10 phr PC has a larger rate constant than the neat resin over the experimental temperature range of 60–400°C. Thus it can be considered that, at low levels of incorporation, PC usually has a promotive effect on the

Table 1 Curing characteristics of neat resin and PC/epoxy blend with DDS hardener

System	ϕ (°C min^{-1})	T_i (°C)	T_p (°C)	T_f (°C)	ΔH (J g^{-1})	α_p (%)
Neat resin	5	148	213	289	314	46
	10	158	236	313	352	51
	20	176	258	337	339	53
	40	202	283	357	281	64
PC/epoxy = 10/100	5	93	208	299	322	51
	10	113	231	324	318	58
	20	135	259	330	281	57
	40	194	296	367	214	63

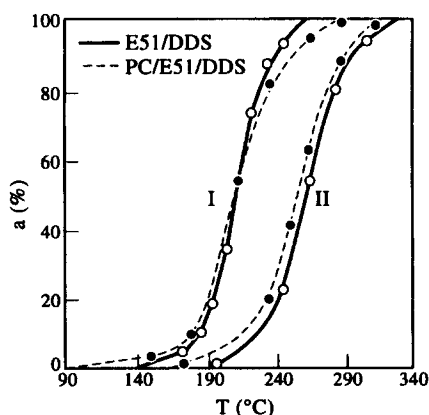

Figure 5 Temperature dependence of conversion rate for neat resin (——) and PC/epoxy 10/100 system (- - -): (I) $\phi = 5\,\mathrm{K\,min^{-1}}$; (II) $\phi = 20\,\mathrm{K\,min^{-1}}$

Table 2 Kinetic parameters of DDS cured systems obtained by d.s.c. data according to Kissinger equation

System	ln A	n	E (kJ mol^{-1})
Neat resin	12.3	1.5	57.6
PC/epoxy = 10/100	10.6	2.0	46.2
PC/epoxy = 20/100	4.8	2.2	52.0
PC/epoxy = 30/100	6.7	2.1	58.3

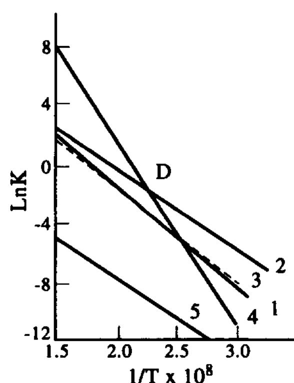

Figure 6 Temperature dependence of rate constants for DDS curing systems: (1) neat resin; (2) PC/epoxy 10/100; (3) PC/epoxy/TMAI 10/100/0.4; (4), (3) without DDS; (5) PC/epoxy 20/100

curing reaction but the effect will become less obvious as the temperature increases. The combination of this variation and higher viscosity can explain the appearance of intersection A in *Figure 5*, curve I. For a higher heating rate T_i and T_p will be shifted to higher temperature and cause the viscosity to decrease; as a result there is no intersection in curve II. *Figure 6* also reports the decrease of the rate constant for the system with 20 phr PC owing to diffusion control.

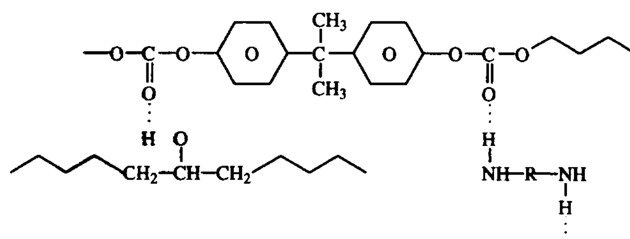

Figure 7 Schematic diagram of hydrogen bonding between in-chain carbonyl and amine or hydroxyl groups

It is generally agreed that the reaction mechanism for the addition of amine to epoxy takes into account the phenomenon of catalysis by hydrogen bond donors. Shechter *et al.*[18] suggested that the mechanism of this catalytic effect is via hydrogen bonding of the hydroxyl group to the oxygen of the glycidyl ether in the transition state. Therefore the phenomenon that PC, as a hydrogen bond acceptor, does not hinder the reaction offers some insight into the special reaction mechanism for the PC/epoxy blend. It should be realized that PC can interact with the resin or amine or newly formed network via hydrogen bonding (*Figure 7*). The formation of an epoxy resin network in the presence of PC may follow a special mode: the reaction of epoxide and amine may take place along the PC chain, namely via an *in situ* curing mechanism. Hydrogen bonding between carbonyl and hydroxyl groups is unfavourable for the curing reaction, while the interaction of carbonyl and amine favours the curing reaction. In this case, kinetic studies showed that PC usually remains unaffected or has a promoting effect on the curing reaction, which is not consistent with a conventional mechanism. However, hydrogen bond formation and dissociation in a polymer are thermally reversible. At an elevated temperature at which a larger proportion of hydrogen bonds have dissociated, the two systems with and without PC tend to have the same curing behaviour as shown in *Figure 5* by the nearing of curve I and curve II with increasing temperature.

It is a reasonable hope that semi-interpenetrating polymer networks (semi-IPNS) with molecular-level entanglement of segments could be formed by this method. For systems with a high content of PC (> 20 phr), although the final conversion of reactants is lower, the entanglement structure between the PC and epoxy resin network resulting from an *in situ* curing

Table 3 Density of PC-modified epoxy resin cured with DDS

PC content (phr)	Measured density ρ_m ($g cm^{-3}$)	Calculated density ρ_c ($g cm^{-3}$)	$\rho_m - \rho_c$
0	1.2389	–	–
5	1.2696	1.2374	0.0322
10	1.2780	1.2361	0.0432
15	1.2866	1.2348	0.0518
20	1.2472	1.2336	0.0136
25	1.2571	1.2325	0.0246

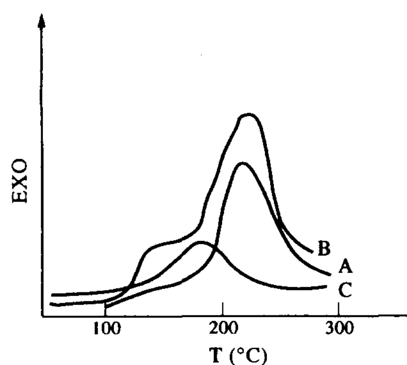

Figure 8 Dynamic d.s.c. scans for the mixture with 32 phr DDS at heating rate of 5°C/min: (A) PC/epoxy 10/100; (B) PC/epoxy/TMAI 10/1000/0.4; (C) (B) without DDS

mechanism will be compensated by the loss of crosslink density, which is consistent with the IPN principle. The Binder Frisch[19] theory predicts that the entanglements in a semi-IPN will give an important contribution to its elasticity when the crosslink density of the network is not very low. The density–composition data (*Table 3*) showed increased density in all systems containing PC, maxima occurring at PC incorporation of 15 phr. The increased density of IPNs can be explained qualitatively by means of chain entanglement at the domain boundaries[20].

Kinetics of PC/epoxy/DDS/TMAI systems

In the presence of TMAI (0.4 phr), d.s.c. scanning of the PC/epoxy mixture revealed an exothermic peak (*Figure 8*, curve C); when the same sample was scanned again by d.s.c. the exothermic peak disappeared indicating the completion of the reaction. Although the exotherm began at a comparatively low temperature, the heat of reaction was much less than that of the epoxy resin cured with DDS, especially for those runs carried out at high heating rate (*Table 4*). The high activation energy obtained by the Kissinger equation and consequently the low rate constant account for the low conversion of epoxide groups at high heating rate ϕ; the higher ϕ, the less time available for the reaction. The increase in viscosity by adding high-molecular-weight PC may result in the system quickly attaining the gel point, which can partially explain the overall low conversion compared with the oligomer PC/epoxy/catalyst system in ref. 21. For the system cured for 4 h at 160°C, the stretching band of epoxide groups at 960 cm^{-1} still remained in the *FT*i.r. spectra (*Figure 9*). The Arrhenius relationship of $\ln K$ against $1/T$ for this system is reported in *Figure 6*, in which a sharp dependence of $\ln K$ on temperature can be observed. At temperatures $T > T_D$ (197°C), the rate constant of the PC–epoxy reaction is even higher than that of the epoxy–DDS reaction.

Cure studies on the effect of addition of catalyst (TMAI) to the PC/epoxy/DDS system are reported in *Table 4*, the results showing a significant diminution of the exotherm initiation temperature T_i while T_p and T_f remain nearly unchanged. The reaction between PC and epoxy resin tends to increase the entire activation energy to a value near that of the neat resin. The relationship of $\ln K$ against $1/T$ in *Figure 6* shows nearly the same behaviour as the neat resin. The decrease of the reaction heat ΔH is readily ascribed to the occurrence of PC–epoxy reaction, leading to a quick attainment of gel point. Comparison with the system without TMAI (*Figure 8*) evidences the occurrence of a two-step reaction during the d.s.c. scanning process. Both reactions of PC–epoxy and epoxy–DDS can take place simultaneously in this system; nevertheless, based on the fact that T_i is very close to that of the PC/epoxy/TMAI system, the PC–epoxy reaction may occur first and bring about a viscosity enhancement, even though the rate constant of the epoxy–DDS reaction is higher than that of the PC–epoxy reaction at low temperature (<197°C).

Influence of PC and TMAI on curing behaviour of the epoxy/MA system

The observed data by d.s.c. scans (*Table 5*) indicate a different curing behaviour caused by PC and TMAI in the anhydride curing system than in the amine curing system, implying a variation in the reaction mechanism related to the interaction among the reactants. For neat resin cured with MA, the exotherm peak initial

Table 4 Curing characteristics of DDS-cured systems containing 0.4 phr catalyst TMAI and their kinetic parameters obtained from Kissinger equation

System	ϕ (°C min^{-1})	T_i (°C)	T_p (°C)	T_f (°C)	ΔH (J g^{-1})	$\ln A$	n	E (kJ mol^{-1})
PC/epoxy = 10/100	5	70	177	205	15.0			
	10	80	190	212	6.7			
	20	138	202	226	3.1	27.1	1.6	106.5
without DDS	40	175	215	240	2.4			
PC/epoxy = 10/100	5	75	218	263	52.0			
	10	96	238	309	56.0			
	20	107	263	311	43.0	11.6	1.8	54.9
with DDS	40	147	292	327	25.0			

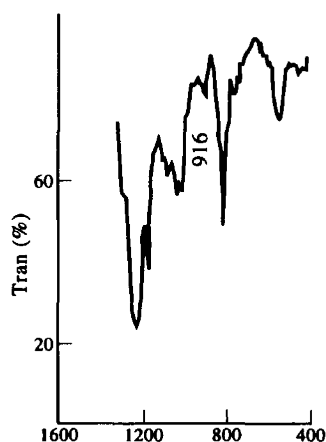

Figure 9 *FT*i.r. spectrum of the stiochiometric mixture of PC/epoxy catalysed by TMAI cured for 4h at 160°C at 1600–400 cm^{-1}

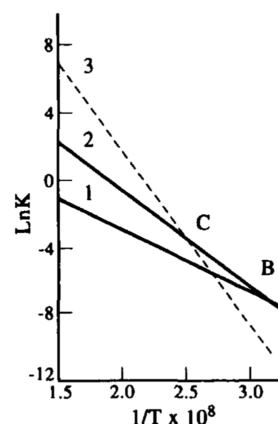

Figure 10 Temperature dependence of rate constant for MA curing systems: (1) neat resin; (2) PC/epoxy 5/100; (3) PC/epoxy/TMAI 5/100/0.4

temperature T_i, reaction heat ΔH and activation energy E are lower than those of DDS curing systems. The addition of 5 phr PC to the neat resin does not evidently alter T_i, T_p and T_f but activation energy E and pre-exponential factor $\ln A$ were increased. The reaction of anhydride with epoxide is associated with the opening of cyclic anhydride caused by the interaction between anhydride and hydroxyl groups. Therefore, PC as a hydroxyl acceptor should hinder the curing reaction. However, from the relationship of $\ln K$ and $1/T$ in *Figure 10*, it can be concluded that PC has a promoting effect on the MA curing reaction, the effect becoming less obvious with decreasing reaction temperature. The higher values of $\ln A$ above can partly explain the promoting effect, which may be associated with a concentration increase of reactants in a microdomain brought about by adding high-molecular-weight polymer, even though the viscosity is increased. On the other hand, the carbonate groups in the PC chain as nucleophilic groups may have the effect of promoting the opening of cyclic anhydride, similar to tertiary amines.

The appearance of PC–epoxy reaction catalysed by TMAI tended to lower T_p and T_f but increase the T_i at low heating rate, as well as increase ΔH at high heating rate (*Table 5*). The dramatic enhancement of both E and $\ln A$ ascribed to the PC–epoxy reaction lead to a sharp relationship between $\ln K$ and $1/T$ as shown in *Figure 10*. When $T > T_c$ (137°C), the higher rate constant K of the system with TMAI, which brings about an additional exotherm in the PC–epoxy reaction, may constitute the whole ΔH for runs carried out at a higher heating rate. At low heating rate (1–2°C min^{-1}), since there is enough for the more reactive reaction of epoxy with anhydride, the exotherm contributed by the PC–epoxy reaction becomes less obvious.

CONCLUSION

The PC chain scission process caused by the reaction between carbonate and hydroxyl groups during high-temperature mixing processes influences the properties of the PC recovered from PC/epoxy melt mixtures, such as crystallization, dynamic mechanical properties and thermal stability. The decrease of melting point, α transition temperature and thermal stability are associated with the low-molecular-weight fraction of PC produced by the chain scission process, which will further alter the properties of PC/epoxy semi-IPNs.

PC/epoxy semi-IPNs formed by a melt-blending process displayed unusual curing behaviour, depending on intermolecular interaction. The curing behaviour of epoxy resin in the presence of PC, which can interact

Table 5 Curing characteristics of MA-cured systems and their kinetic parameters obtained from Kissing equation

System	ϕ (°C min^{-1})	T_i (°C)	T_p (°C)	T_f (°C)	ΔH (J g^{-1})	$\ln A$	n	E (kJ mol^{-1})
Meat resin	1	43	168	219	48.5			
	2	45	203	283	55.2			
	5	81	250	290	10.4	4.13	1.45	30.4
	10	154	293	317	17.3			
PC/epoxy = 5/100	1	48	194	250	55.6			
	2	50	217	276	34.3	10.8	1.16	47.8
	10	148	283	312	9.8			
PC/epoxy/TMAI = 5/100/0.4	1	72	143	175	55.8			
	2	83	154	200	58.2			
	5	77	170	235	52.1	22.3	1.05	87.4
	10	116	182	249	45.4			

with resin or hardener or newly formed network via hydrogen bonding, may follow a special mode in which the reaction of epoxide and amine groups takes place along the PC chains, i.e. an *in situ* curing mechanism. It is not a typical mechanism of matrix polymerization because the crosslink density is too high to form a polymer complex; PC/epoxy semi-IPNs formed by *in situ* cure are probably composed of a high degree of interpenetrating molecules rather than complexes. The reaction kinetics studies showed that PC usually remains ineffective or has a promotive effect on the curing reaction for amine hardener according to the activation energy data, which is not consistent with a hydrogen catalysis mechanism. Therefore the influence of kinetic effects may be in two directions, acceleration or deceleration, mainly through diffusion control. At low incorporation of PC (10 phr), PC usually has a promoting effect, but the effect can vary with temperature. At higher incorporation (>20 phr), a significant decrease of the frequency factor leading to a lower rate constant was observed because of the great increase of viscosity.

The reaction of high-molecular-weight PC with epoxy resin catalysed by TMAI possesses a high activation energy, leading to a sharp relationship of rate constant against reciprocal temperature and low conversion. The addition of TMAI to PC/epoxy/DDS systems causes a two-step curing behaviour, in which the reaction of PC with epoxy resin occurs first and brings about a decrease of conversion. However, its curing kinetics are similar to those of neat resin.

For the anhydride curing system, the different behaviour caused by PC and TMAI is related to different interactions between the components. Ordinarily, PC has a promoting effect on the MA curing reaction over the experimental temperature range. The occurrence of the PC–epoxy reaction catalysed by TMAI leads to a sharp relationship of the rate constant and reciprocal temperature.

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