The Reactivity of Epoxy/Polycarbonate/BF₃- MEA System

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Abstract: The cationic reaction of an epoxy/BF₃-MEA system occurs between the oxirane group and the oxonium group. The addition of polycarbonate to the system does not cause a transesterification reaction between the carbonate group and the oxonium group, thus the molecular weight of the PC is unchanged during the reaction. PC crystallization is observed in the cured system because the epoxy monomer accelerates the PC crystallization. The epoxy/BF₃-MEA and epoxy/PC/BF₃-MEA systems all follow the first order reaction. The PC modified systems show lower activation energy, a lower pre-exponential factor and a higher reaction rate constant.

Keywords: Epoxy, Polycarbonate, Boron trifluoride complex, Kinetic parameter.

Introduction

In the past, many studies reported on the use of epoxy to graft (or crosslink) with polyamide and polyester. For example, Gorton [1] studied the interaction of polyamides with epoxy resins in adhesive blends. Komarova et al. [2] used epoxy to cure polyester of different structures. Most of these thermoplastic-modified epoxies show higher thermal, mechanical and physical properties than the original systems did. Studies on modifying crosslinked epoxy resins by thermoplastics have been intensifying during the last two decades [3]. The incorporation of a ductile thermoplastic in an epoxy network tends to make the energy dissipative processes more complicated than that of the unmodified resin matrix [4,5]. Although certain thermoplastics can react with epoxy during curing by means of their functional end group, most thermoplastics do not react with epoxy during curing or postcuring procedure. However, the polycarbonate (PC) is an exceptional case; its carbonate group in the backbone is reactive in the epoxy system. When an aliphatic amine is used as a curing agent in epoxy/PC blends, it will transamidate with polycarbonate to yield carbamates and ureas immediately [6-8].
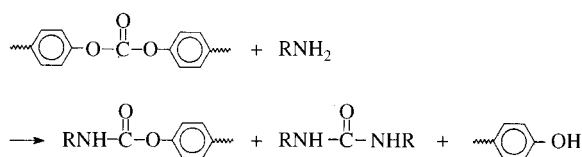
The carbonate group of PC can also react with the hydroxyl group formed from the ring opening reactions of the oxirane with the hardner. This phenomenon is especially pronounced in the postcuring stage of the epoxy/PC/aromatic amine system [9,10].
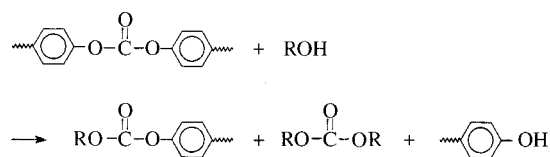
Our previous study demonstrated that the carbonate group reacts with epoxy in the presence of tertiary amine [11]. IR spectra show that these transesterification reactions convert the original aromatic/aromatic carbonate into aromatic/aliphatic and aliphatic/aliphatic carbonates. The epoxy cured by anhydride hardner is similar to that cured by tertiary amine; the transesterification between the oxirane and carbonate group also occurs [12]. The transesterification is believed to undergo an alkoxide

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anion of the zwitter ion composed of oxirane and tertiary amine that attacks the carbonate group of the PC.
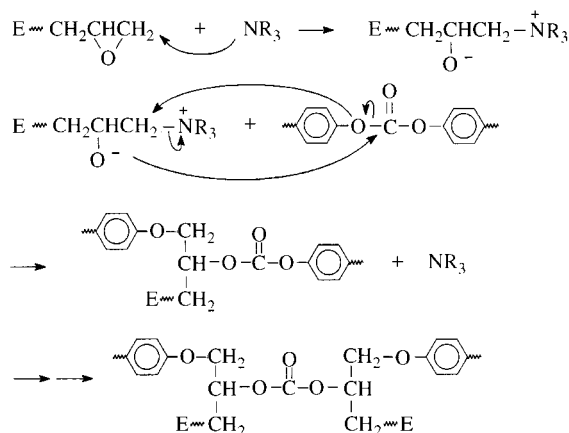
IR spectra show an unknown structure formed during the later stages of the transesterification reaction [12]. A model reaction was designed to identify the unknown structure. A five-member ring structure is formed from the cyclization reaction and the following mechanism is proposed [11].
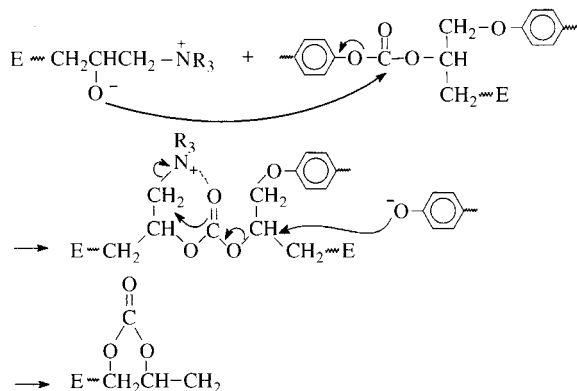

Due to the occurence of transamidation, transesterification and cyclization, it is difficult to maintain the unreacted and original PC chains in these epoxy/PC blends during the curing or postcuring procedures. In order to obtain a truly non-reactive epoxy/PC blend, curing by a boron trifluoride monoethyl amine complex (BF$_3$-MEA) has been investigated. The amine-boron trihalide complex can initiate the cationic polymerization of the epoxide and thus avoids the occurrence of transesterification between oxirane and carbonate.
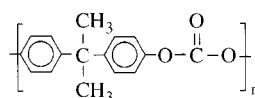
Experimental

1. Materials

Calibre 301-15, a bisphenol-A based natural

grade polycarbonate (PC) with a melt flow rate of 15 used in this study, was from the Dow Chemical Company. DER332, an epoxy prepolymer of low molecular weight liquid diglycidyl ether of bisphenol-A (DGEBA) with epoxide equivalent weights of 182, DER332, was also purchased from the Dow Chemical Company. The boron trifluoride monoethyl amine complex (BF$_3$-MEA) was supplied from the Allied Chemical Company, U.S.A. The model compounds, phenyl glycidyl ether (PGE) and diphenyl carbonate (DPC), were purchased from Merck Co. The chemical structures of PC, epoxy, BF$_3$-MEA, PGE and DPC are illustrated as follows:
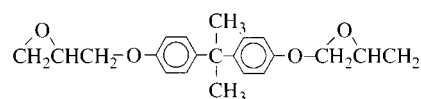
Diglycidyl ether of bisphenol-A (DER 332)

Bisphenol-A based polycarbonate

BF_3-$C_2H_5NH_2$
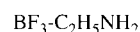
Boron trifluoride monoethly amine complex
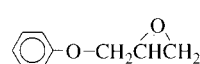
Phenyl glycidyl ether
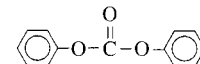
Diphenyl carbonate

2. Procedures and instrumentation

2.1 Experimental techniques

The experimental procedure to prepare the model reaction was carried out by dissolving DPC (30 g) and BF$_3$-MEA (1.4 g) into PGE (70 g) at 120 °C. This clear and homogeneous solution was heated at various temperatures and time periods, and samples were taken for IR and GPC analyses.

The blends of PC and epoxy were dehydrated at 120 °C for 24 hours under a vacuum. The mixtures of PC (10 g) in epoxy (70.46 g) were prepared by dissolving the PC in the epoxy monomer at 200 °C under dry nitrogen gas for 2 hours; this transparent solution was quenched to room temperature to prevent PC crystallization [10].

Another epoxy monomer (17.77 g) was heated to 120 °C, then BF$_3$-MEA (1.77 g) was added. The mixture was stirred until it became homogeneous, and then it was quenched in a cold water bath to prevent curing of the epoxy. Then these two solutions (epoxy/PC and epoxy/BF$_3$-MEA) were mixed at ambient condition to obtain a blend system with 10% PC content. The notation and composition of the study is listed in Table I.

The curing temperatures were set from 110 to 170 °C. The mold or specimen holder was preheated to the setting temperature, then the mixture was poured into the specimen holder. All speci-

Table I. Composition[a] and notation of the study.

Notation	PC4%	PC8%	PC10%	PC12%
PC	4	8	10	12
Epoxy resin	94.12	90.20	88.23	86.27
BF_3-MEA	1.88	1.80	1.77	1.73

(a) The weight ratio of epoxy/BF_3-MEA is 100/2 in all systems.

mens prepared for mechanical property tests had been postcured at 200 °C for 5 hours under vacuum to minimize possible degradation.

2.2 Fourier transformed infrared spectroscopy (FT-IR)

One drop of the epoxy/PC blend was pasted into a thin film between two sodium chloride plates and then mounted on a sample holder located in an FT-IR instrument. Infrared spectra were obtained on a Perkin-Elmer 842 Infrared Spectrometer with a resolution of 2.4 cm^{-1} in the transmission mode.

2.3 Gel permeation chromatography (GPC)

Tetrahydrofurane (THF) was added to the epoxy/PC blend to prepare a 1 % solution. The solvent utilized for GPC analysis was THF at a flowing rate of 1.0 mL/min using a Waters Associates GPC equipped with a Waters-R410 refractometer.

2.4 Differential scanning calorimetry (DSC)

The kinetic parameters were calculated by a TA Instruments DSC 2010 with heating rates of 2.5, 5, 10, and 20 °C/min from 50 to 300 °C. The DSC profile contained several exotherm peaks; only the major exotherm was considered. The high temperature minor exotherm may come from the degradation of the system.

Results and Discussion

1. Mechanism of epoxy cured by BF_3-MEA complex

Lewis acids such as BF_3 always conjugate with a protogen to initiate the cationic polymerization of the epoxy resin. The boron trifluoride monoethyl amine complex (BF_3-MEA) is the most commonly used epoxy curing agent which is activated by heating to 80-100 °C [13]. The activated mechanism of the BF_3-MEA complex is very complicated. Smith et al. [14-16] utilized the fluorine-19 NMR to investigate the system and discovered that the BF_3-MEA breaks down rapidly into HBF_4 at 80 °C and above. Kamon et al. [17] also studied epoxy cured by BF_3-MEA. Their DTA thermogram shows that one of

the exothermic peaks of the curing system is almost identical to the peak cured by the $BF_4NH_3C_2H_5$. Both reports revealed that the BF_3-MEA is not a catalyst in such a system; instead, the HBF_4 serves as the catalyst. Smith et al. [14-16] analyzed the HBF_4 curing system and found the HBF_4 can come from any of the following three means,

(1) Commercial BF_3-MEA has 5-10% HBF_4
(2) Hydrolysis of BF_3-MEA obtains the HBF_4

$$BF_3 \cdot X + H_2O \longrightarrow HBF_3OH$$

$$HBF_3OH + H_2O \longrightarrow HBF_2(OH)_2 + HF$$

$$2HBF_3OH \longrightarrow HBF_4 + HBF_2(OH)_2$$

$$2HBF_2(OH)_2 \longrightarrow HBF_4 + B(OH)_3 + H_2O$$

where X is the donor molecule and can be epoxy, ether, or alcohol.

Equilibrium may exist between these different complexes and boron-amine complexes. Hydrolysis of BF_3-MEA is the most probable source of the HBF_4 in this study. The BF_3-MEA disappears within 5 min and only HBF_4 and HBF_3OH can be detected at 100 °C.

(3) Nonhydrolysis of BF_3-MEA to yield the HBF_4

$$2BF_3 \cdot NHR_2 \longrightarrow BF_4^-N^+H_2R_2 + BF_2^+N^-R_2$$

$$BF_4^-N^+H_2R_2 \longrightarrow HBF_4 + NHR_2$$

Kamon et al. [17] reported that the BF_3-MEA reacts with equal eqivalence of the epoxy group to form the $BF_4NH_3C_2H_5$ at the initiating temperature of the curing exotherm peak. Happe et al. [18] proposed that BF_3-MEA reacts with oxirane slowly and converts into a tetrafluoroborate salt with a loss of fluoride at 85 °C.

$$BF_3NH_2C_2H_5 + E \sim CH_2\overset{O}{\overset{\diagup\diagdown}{CH}}CH_2$$

$$\longrightarrow E \sim CH_2\overset{OBF_2}{\underset{|}{CH}}CH_2-NH_2C_2H_5 + HF$$

$$BF_3NH_2C_2H_5 + HF \longrightarrow BF_4^-N^+H_3C_2H_5$$

This mechanism illustrates the formation of the epoxy-MEA adduct during curing. The epoxy-amine adduct produced in the epoxy system was confirmed by the ^1H NMR spectrum [19,20].

Although the processes that yield the HBF_4 are complicated and uncertain, the curing mechanism by cationic polymerization can be simplified by donating a proton from the HBF_4 to the oxirane to form a tertiary oxonium ion. This oxonium ion is stabi-

Figure 1. Carbonyl stretching of PGE/DPC/BF$_3$-MEA = 70/30/1.4 by heating 2 hr at different temperatures: (a) 25 °C/2 hr, (b) 120 °C/2 hr, (c) 150 °C/2 hr and (d) 180 °C/2 hr.
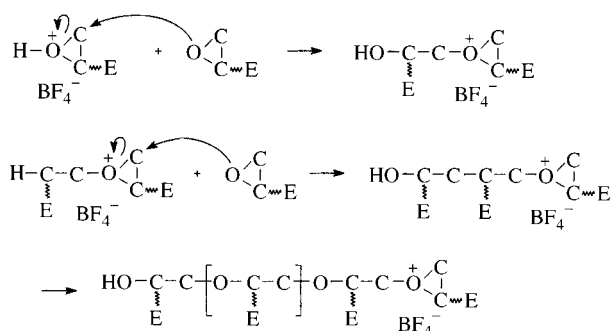

Figure 2. GPC diagrams of PGE/DPC/BF$_3$-MEA before and after different heat treatments: (a) 25 °C (before reaction), (b) 120 °C/2 hr (c) 150 °C/2 hr, (d) 180 °C/2 hr and (e) 200 °C/5 hr.

lized by a counterion.
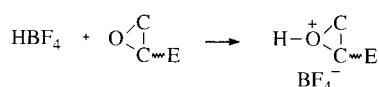
Propagation of polymerization undergoes a nucleophilic attack of the oxirane on the electron-deficient α-carbon of the oxonium ion [21].

As shown in the above mechanism, the nucleophilic reagent in the cationic curing system is the oxirane. The nucleophilicity of oxirane is strong enough to attack the electron-deficient α-carbon of the oxonium ion. However, it is still too weak to react with the carbonate group of PC. Consequently, the oxirane does not participate in the nucleophilic substitution reaction with carbonate that has been demonstrated in our previous studies [6]. In addition, the nucleophilic carbonate may attack the oxonium ion during the cationic curing in the epoxy/PC/BF$_3$-MEA system [22-27]. In order to elucidate the re-

action mechanism of the epoxy/PC/BF$_3$-MEA system, PGE, DPC and BF$_3$-MEA were chosen to carry out the model reaction. Curves (a), (b), (c) and (d) of Figure 1 represent the carbonyl absorption band (υ = 1775 cm^{-1}) of the products from the PGE/DPC/BF$_3$-MEA = 70/30/1.4 composition cured at 25, 120, 150 and 180 °C for 2 hrs, respectively. These curves reveal that the carbonyl group absorption does not change noticeably. Figure 2 presents the GPC chromatographies of the same model reaction at various temperatures and time periods. This figure shows that the concentration of DPC remains nearly unchanged during heating. Both IR and GPC results confirm that the carbonate does not involve the cationic polymerization of the oxirane. In other word, the model reaction indicates that the PC polymer chains will not be scissored during cationic curing in this cationic polymerization system.

2. Crystallization of PC

Figure 3 represents the infrared absorptions of this PC10% system in the carbonyl region cured at 110 °C after different time periods. Before curing, the absorption at υ = 1775 cm^{-1} corresponds to the amorphous PC (Gaussian bandshape). This carbonyl peak gradually shifts to a lower wavenumber and eventually locates at υ = 1768 cm^{-1} after 140 minutes. This lower wavenumber corresponds to the carbonyl stretching band from the crystalline PC (Lorenzian bandshape) [28], implying that part of the PC is crystallized during the process of curing. Figure 4 shows the DSC thermogram of the speci-
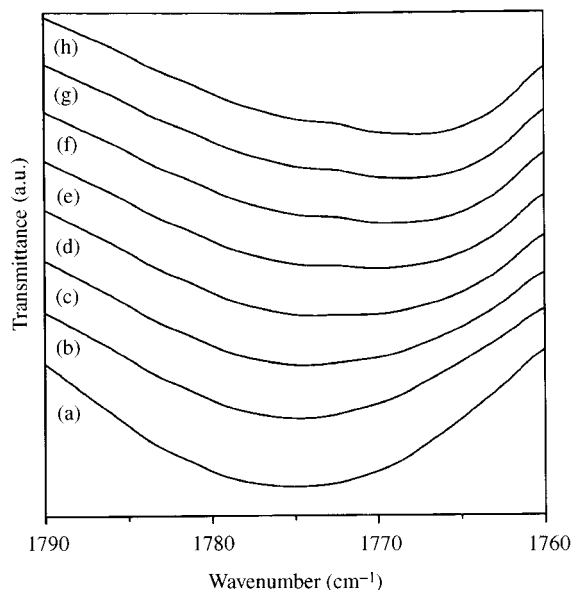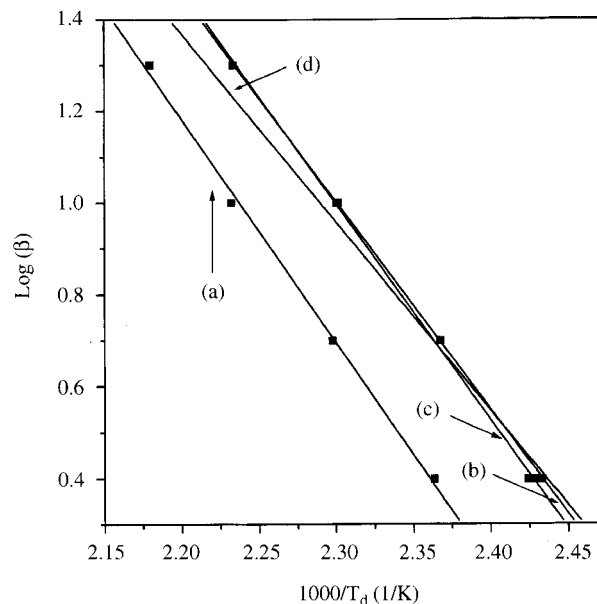
Figure 3. Carbonyl stretching of the PC10% system cured at 110 °C after different time periods: (a) 0 min, (b) 20 min, (c) 40 min, (d) 60 min, (e) 80 min, (f) 100 min, (g) 120 min and (h) 140 min.

Figure 5. Plots of log(β) versus 1000/T_d for PC modified systems: (a) PC4%, (b) PC8%, (c) PC10% and (d) PC12%.
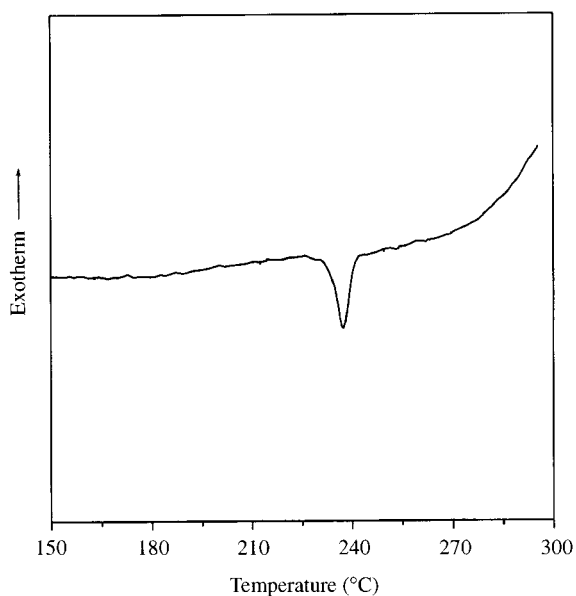
Figure 4. DSC thermogram of the PC10% system cured at 110 °C.

men after isothermal annealing at 110 °C for 5 hours. The endotherm peak at 235~250 °C comes from the melting of PC crystals. The integral of the melting peak is 5.3 cal/g, and the heat of fusion of 100% crystalline PC is about 26.5 cal/g [29,30]; thus the crystallinity of 20% is obtained. A similar result was also reported by Jonza and Porter [31] by recovery from acetone solution to increase the PC crys-

tallinity up to 22%. This result implies that the epoxy resin can also act as a solvent in the system to promote PC crystallization even though the annealing temperature (110 °C) is lower than the T_g of the PC (150 °C).

3. Kinetics of the system

The kinetic parameters of the epoxy/BF_3-MEA system were reported in our previous study [32]. The ASTM E 698 method is used to analyze the system since the cationic polymerized epoxy resin system has multiple exotherm profiles and an irregular baseline. This method assumes (1) the extent of the reaction at the exotherm peak, α_p, is constant and independent of heating rate, β, (2) the reaction rate constant obeys the Arrhenius equation [$k = A \cdot \exp(-E_a/RT)$], and (3) the reaction is first order [$d\alpha/dt = k (1 - \alpha)$]. This ASTM method requires several DSC scans at different heating rates. Based on the obtained linear relationship between the reciprocal of the exotherm peak temperature ($1/T_P$) and the logarithm of the heating rate ($\log\beta$), the Ozawa method [33,34] can be used to calculate the activation energy (E_a) of the system as follows:

$$E_a \cong -2.19R[d(\log \beta)/d(1/T_d)]$$

The pre-exponential factor (A) can then be evaluated,

$$A \cong \beta E_a \times \exp(E_a/RT_d)/RT_d^2$$

Figure 5 shows plots of the logarithm of the heating rate ($\log\beta$) versus the reciprocal of the analyzed tem-

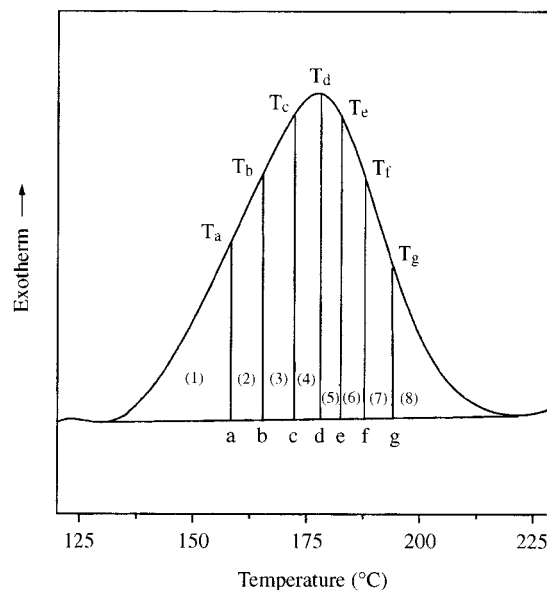**Table II.** Kinetic parameters of the system based on the exotherm temperature.

Items system	Activation energy (KJ/mol)	Pre-exponential factor	Reaction rate constant at 130 °C (1/min)
Unmodified	97.96	2.00×10^{11}	0.041
PC4%	88.81	1.21×10^{10}	0.038
PC8%	85.77	1.11×10^{10}	0.085
PC10%	84.18	7.78×10^{9}	0.087
PC12%	82.59	4.46×10^{9}	0.089
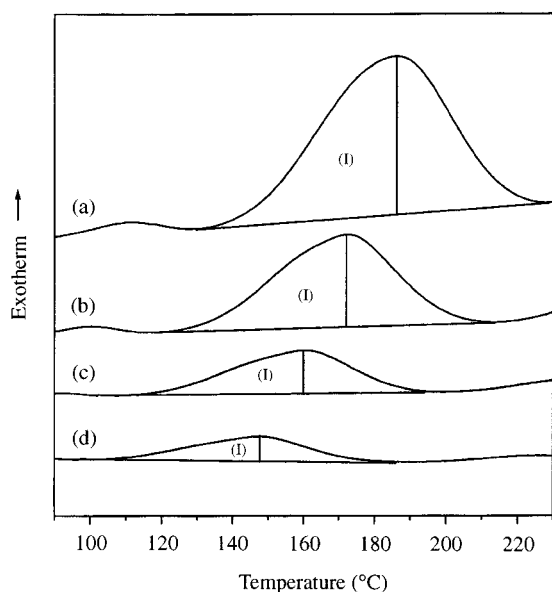
Figure 6. DSC thermogram of PC10% system at different heating rates: (a) 20 °C/min, (b) 10 °C/min, (c) 5 °C/min and (d) 2.5 °C/min.

Figure 7. Diagram of separated area of the exotherm curve conversion: (1) 13.75%, (2) 27.5%, (3) 41.25%, (4) 55% (5) 66.25%, (6) 77.5%, (7) 88.75% and (8) 100%.

perature ($1/T_d$) for this study and results in high linearity, meaning that the ASTM E 698 is applicable in this system and the calculated kinetic parameters of this system, which are summarized in Table II, should be valid. The activation energy is lower in the higher PC content system, and the pre-exponential factor is also lower in PC-modified systems because the higher viscosity of these systems tends to decrease the mobility of the epoxy monomer and results in lower collision frequency. However, at 130 °C, the reaction rate constant is increased at the higher PC content system. Indicating meaning that the activation energy shows a more significant effect than the collision factor.
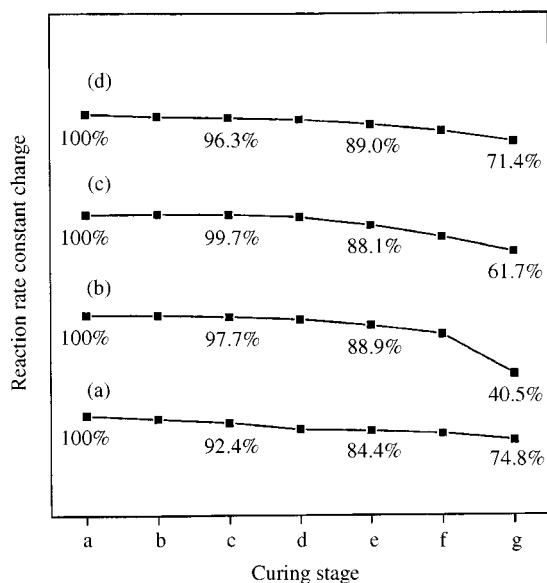
4. Change of reaction rate constant during reaction

Normally the first order reaction rate constant remains constant before gelation, and decreases

gradually at later stages of the reaction because the monomer concentration is lower and the viscosity of the system is higher. In the previous report [34], the ASTM rule is deduced to the whole reaction stage through modification by an Arrhenius factor. According to the assumption (1) of the ASTM E 698, the extent of reaction at the exotherm peak is identical, as shown in Figure 6. The close area (I) at different heating rates (from 2.5 to 20 °C/min) is similar, the conversion is about 60%. Figure 7 depicts four equally divided areas (1), (2), (3) and (4) in area (I); each area implies a 15% conversion. Therefore the corresponding temperatures T_a, T_b, T_c, and T_d all can be fitted to assumption (1) of the ASTM E 698. The complementary area (II) is also divided into four equal parts and temperatures of T_e, T_f, and T_g can also be analyzed by this method. The kinetic parameters were modified by a factor that is based on the Arrhenius rule because the temperatures of T_a to T_g are different. Figure 8 shows the 130 °C reaction rate constant of the study. The data remained fairly constant before reaching the exotherm peak (point d), implying that the system follows the first order reaction before gelation. The observed lower reaction rate constant at late stages of the reaction is caused by the lower diffusion coefficient.

Conclusions

The reaction mechanism of the epoxy/PC/BF₃-

Figure 8. Reaction rate constant change of the system at different curing stages: (a) PC4%, (b) PC8%, (c) PC10% and (d) PC12%.

MEA system has been analyzed by FT-IR and GPC. The only possible reaction involved is the reaction between the oxirane group from epoxy resin and the oxonium group from the BF_3-MEA activated epoxide group. GPC confirms that the molecular weight of PC remains constant during the curing process. The transesterification reaction of the carbonate group from the PC does not occur. The FT-IR and DSC measurements confirm that the PC10% system shows a 20% crystallinity during the 110 °C curing process. The high crystallinity is attributed to the epoxy monomer increasing the mobility of the PC chains. The kinetic parameters are obtained by the ASTM E 698 method and the epoxy/BF_3-MEA system follows the first order reaction. The PC modified system shows lower activation energy and a lower pre-exponential factor at higher PC content. The higher reaction rate constant is observed at higher PC content, which implies that the activation energy factor is more significant than the collision frequency. The PC modified system also follows the first order reaction. The reaction rate constant decreases at the late curing stages (conversion exceeds 60%) because of the diffusion controls of the system.

Acknowledgements

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