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Interpenetrating polymer networks of epoxy resin and urethane acrylate resin: 1. Kinetics of network formation

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Abstract

A series of simultaneous interpenetrating polymer networks composed of epoxy resin (epoxy) and urethane acrylate resin (UAR) with different compositions were synthesized and the polymerization kinetics of both network formations was monitored by using a Fourier transform infrared spectroscopy for the potential application in the reaction injection molding process to prepare the toughened epoxy materials. It was found that during the course of synthesis the polymerization rate for formation of both pure networks has almost no dependence on the concentration of reactants, especially at the early stage of reaction and the two pairs of reactants interfere with each other significantly, although they followed different polymerization mechanisms. All these unusual polymerization kinetics behaviors observed could be correlated well with the changes of viscosity and morphology of the systems.

1. Introduction

Interpenetrating polymer network (IPN) as one kind of polymer alloys consisting of two or more distinct crosslinked polymer networks held together by permanent entanglement [1] has been studied extensively. Frisch *et al.* [2] first reported simultaneous interpenetrating polymer networks (SINs) composed of polyurethane (PU) in combination with epoxy resin (epoxy), polyacrylate, or unsaturated polyester resin. Pernice *et al.* [3] pointed out that such SINs could be applied in the reaction injection molding (RIM). Since then SINs of PU and industrial unsaturated polyester resin have been paid more attention and investigated in detail [4–11]. However, no more information for preparing SIN composed of PU and epoxy was published in the literature, as most of the curing agents of epoxy or the secondary hydroxyl group existing in epoxy backbone will be very easy to react with isocynate [11], which is a main reactant for synthesizing PU, giving rise to hybrid structures and morphologies of such a SIN.

In our group, another kind of SINs consisting of PU and vinyl ester resin in which the main backbone of epoxy is still maintained has been synthesized and studied for the RIM process [12–17]. It is found that the kinetics of formation for the two networks depends on the morphology development and chemical binding between the two networks significantly during the formation of such SINs. Consequently, it directly responds to the different physical and mechanical properties of the IPN materials. In the present work, SINs composed of epoxy and urethane acrylate resin (UAR) with different compositions were synthesized, which could also be used for the RIM process to prepare the toughened epoxy materials, and the kinetics study of epoxy and UAR SINs with Fourier transform infrared (FTIR) spectroscopy at a temperature range from 60 to 90°C is reported.

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2. Experimental

2.1. Material

Difunctional poly(oxypropylene) polyol(NG-210, hydroxy number: 95 mg KOH/g) was supplied by Gao Qiao No. 3 Chemical Plant. Epoxy resin E-51 (diglycidyl ether of bisphenol-A, DGEBA, 0.50 epoxide equivalent/100 g resin) was provided by Shanghai Synthetic Resin Plant. Toluene diisocynate (2,4-TDI) was supplied by Shanghai no. 1 Reagent Plant. All other chemicals used in this study were standard laboratory reagents obtained from various manufacturers.

The polyol was dried at 80°C under vacuum for 12 h, then treated with 4 Å molecular sieves for over a week before use. Methyl methyacrylate (MMA) was dried with $MgSO_4$ for several days, then distilled under vacuum. 2,2′-Azobis-isobutyronitrile (AIBN) was filtered and recrystallized from hot ethanol and dried under vacuum at room temperature. Diethylene triamine (DETA) was distilled under vacuum before use. The free radical initiator AIBN for UAR was used at 2phr of UAR and the curing agent DETA for epoxy was used at 10.3phr.

2.2. Synthesis and characterization of urethane acrylate resin

UAR was first prepared by reacting polyol with TDI (molar ratio of TDI and polyol was at 2) at the temperature below 40°C. When the content of the -NCO group in the reaction medium decreased to half, which was measured according to ASTM D1638-74, the reaction temperature was raised to 55°C and hydroxyethyl methyacrylate (HEMA) containing a small amount of dibutyltin dilaurate (0.2 wt%) was added in drops to the system (molar ratio of HEMA and -NCO groups remained was at 1). When the concentration of -NCO group in the reaction mixture was below 0.2 wt%, the reaction was finished and the urethane acrylate oligomer (UAO) was obtained. MMA as comonomer was then introduced into this UAO (UAO/MMA = 66/34 by wt) to prepare UAR. The number average molecular weight of UAO was measured by using bromine addition method according to GB12005.3-89 and a Knauer-11.00 vapor pressure osmometer (VPO) and found to be at 1930 and 2150, respectively. Thus, the number average functionality (f) of such a UAO synthesized can be calculated at around $2.2(f = 2\,M_{\mathrm{vpo}}/\mathrm{M}_{\mathrm{c=c}})$. The viscosity of the final product (UAR) was measured by means of a NDJ-79 rotating viscometer and found to be at 0.24 Pas at 25°C.

2.3. Instrumentation and experimental routine

A Nicolet 5SX FTIR spectrometer at a resolution of 4 cm^{-1} in the transmission mode was employed for a kinetics study of individual components and SINs. To follow the reaction courses for all systems, the temperature chamber with two sodium chloride (NaCl) plates mounted was first heated to the desired temperature before any measurement. Ingredients of each component were weighed within a total weight from 10 to 20 g. All raw materials except DETA were then thoroughly mixed with a mechanical agitator at 1200 rpm for about 60 s and then DETA was quickly added into the mixture, which was pasted between the two NaCl plates. Three consecutive scans were taken at each sampling time, and their average was stored for later data analysis. All IR spectra for the kinetics studies were shown in the absorbance mode.

Infrared analysis is based on the fact that each chemical group in a sample absorbs infrared radiation with some characteristic frequencies. The use of the Beer–Lambert law allows the determination of the concentration of an absorbing species in the reception medium, if there exists an absorption peak that obeys the Beer–Lambert law,

$$A = \varepsilon c l \tag{1}$$

where A is the absorbance; ε the molar extinction efficient; c the concentration of the absorbing molecules, and l the thickness of the test specimen. To compensate thickness change in the sample during polymerization, a ratio is taken between the absorbance of the group of interest and that of an internal standard, i.e. a group whose concentration does not change during the reaction process. In this study, the C–H vibrating peak of CH_3 at 2970 cm^{-1} was chosen as the internal standard for epoxy and UAR as well as all SINs [16], respectively. The absorbance area determined by the tangent base-line method is used to calculate the reaction conversion from the change of the normalized absorbance,

$$\alpha = \frac{\dfrac{A_0}{A_{r0}} - \dfrac{A_t}{A_{rt}}}{\dfrac{A_0}{A_{r0}}} \tag{2}$$

where A_0 and A_t are the normalized absorbance of the reactant functional group and A_{r0} and A_{rt} are the normalized absorbance of the internal standard before the reaction and after a reaction time t, respectively.

A scanning electron microscopy (Stereoscan 250MK3, Cambridge) was used to characterize the morphology of SINs. These SIN specimens were prepared at 55°C for 2 h, 70°C for 5 h and 120°C for 2 h. Then, their tensile fractured surfaces were etched by dimethyl formamide (DMF) or acetone for 10 days, respectively. For the samples consisting of more UAR (UAR/epoxy > 1 by weight), they were etched using DMF, and for those containing more epoxy or same amount of epoxy and UAR (epoxy/UAR $\geq$ 1), they were etched with acetone. Finally the surface of the sample was coated with gold vapor before examining.

3. Results and discussion

It is clear that the curing reaction of epoxy with polyamine gives rise to epoxy network according to a step polymerization mechanism, while the UAR can be copolymerized with AIBN as initiator proceeding via a free radical polymerization. Thus, these two networks can be formed independently and simultaneously. The characteristic peaks at 913 cm^{-1} for epoxide group and 1640 cm^{-1} for double bond (-C=C-) existing in epoxy and UAR, respectively, are shown in Fig. 1, which were established in our laboratory and in the literature and found the validity of the Beer–Lambert law for these absorption peaks [16, 18–20].

3.1. Step polymerization of epoxy

Fig. 2 shows the relationship between the conversion of epoxide group (α) and time for epoxy curing reaction at different temperatures. It is interesting to find that a nearly linear correlation holds for conversion over the range up to ca. 40% (the linear coefficient is at around 0.99), i.e. the step polymerization rate exhibits almost no dependence on the concentration of reactants, and the conversion rate of overall epoxide groups ($\mathrm{d}\alpha/\mathrm{d}t$) can be estimated during this conversion range, as listed in Table 1. The gel time (t_g) for these epoxy/DETA systems was observed and their conversions at gel point (α_g) taken from Fig. 2 were found to be all at around 0.4. Furthermore, the apparent activation energy of 30.9 KJ/mol was obtained according to Arrhenius equation,

$$k = A\exp(-E/RT) \tag{3}$$

and the linear relationship between $\ln k(\mathrm{d}\alpha/\mathrm{d}t)$ and $1/T$ is shown in Fig. 3. All these kinetic parameters were also listed in Table 1.

Although the curing reaction mechanism of epoxy and polyamine has been studied extensively [19], it seems that in the case of epoxy/DETA system studied here the polymerization rate of the epoxide group strongly depends on the translational diffusion of reactants [21] before the network formation giving rise to the constant rate of polymerization. After gel point, the polymerization rate may result from segmental rearrangement diffusion [21], whose ability decreases with the increase of the viscosity of the system due to the formation of the network, so the polymerization rate decreases appreciably. The polymerization rate increases with the increase of temperature at early stage as consistent with increasing the translational diffusion rate of the reactants in these curing systems (see Table 1).

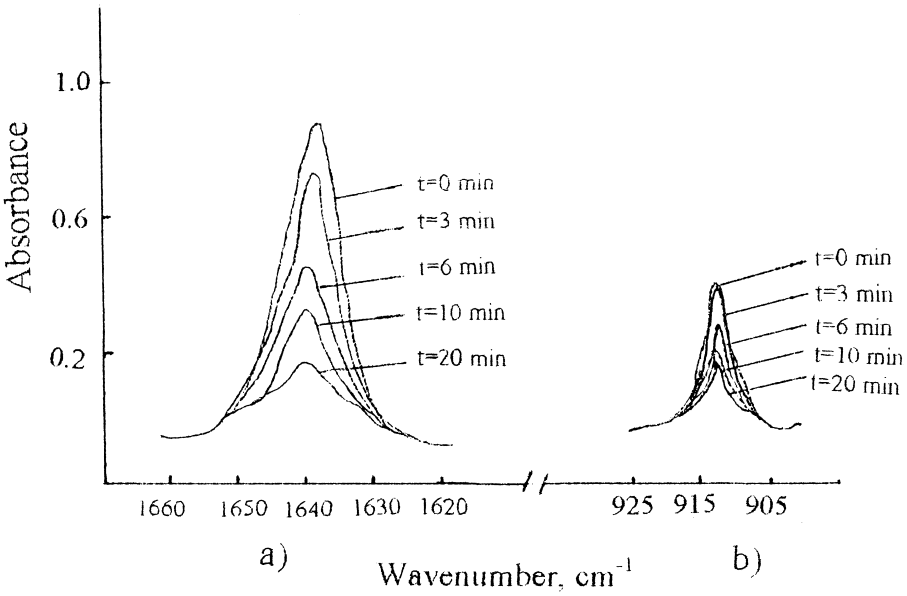

Fig. 1. Decrease of characteristic absorption peaks as the polymerization proceeds of epoxy/UAR (50/50) SIN at 80°C: (a) double bond in UAR at 1640 cm^{-1}, (b) epoxide group at 913 cm^{-1}.

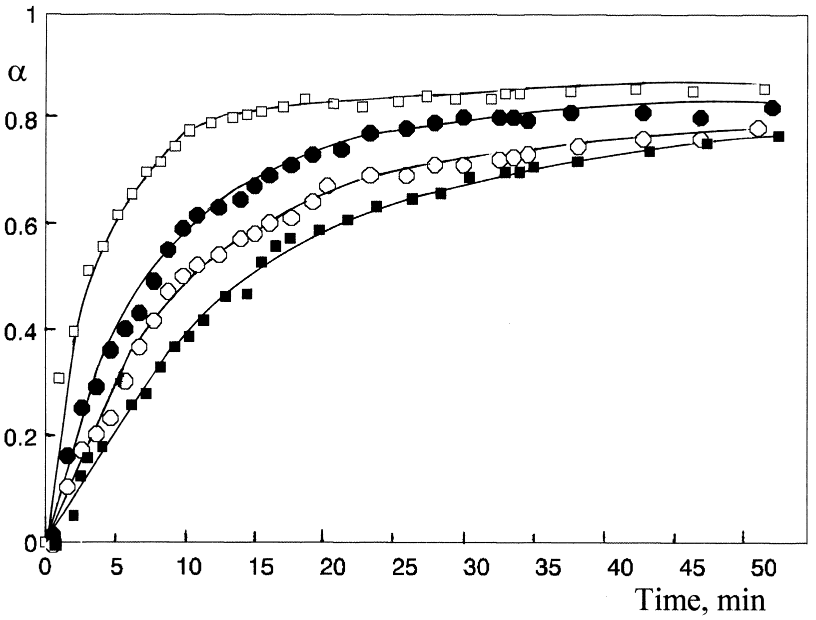

Fig. 2. Conversion of epoxide group vs reaction time for epoxy resin at different temperatures: (■) 60°C; (○) 70°C; (•) 80°C; (□) 90°C.

3.2. Free radical polymerization of UAR

Fig. 4 shows the copolymerization kinetics for UAR at various temperatures. The autoacceleration in the coplymerization rate of UAR was observed especially at 70°C. This phenomenon has been corresponded to diffusion-controlled termination of the propagating radicals leading to slower termination reaction and much faster propagation reaction for the free radical polymerization of vinyl monomers because of decreasing in segmental diffusion rate of polymer radicals [22a]. In this case, with increasing reaction temperature the lowering of viscosity of the system and the increase of both segmental diffusion and translational diffusion rate should be expected. Fig. 4 exhibits a linear relationship between the conversion and copolymerization time at 90°C over a wide conversion range up to ca. 70% instead of the autoacceleration behavior. In other words, the coplymerization rate shows no dependence on the concentration of reactants which must result from the increase of the segmental diffusion rate of the polymer radicals in such a system. A similar kinetics phenomenon in the copolymerization of vinyl ester resin [16] or in the copolymerization of some macromers with vinyl monomers in solution [23] was also observed.

Although the kinetics behavior of copolymerization for UAR at different temperatures reveals the versatility, at the early stage of copolymerization (the conversion of overall C=C bonds is less than ca. 20%) the copolymerization rate $k(\mathrm{d}\alpha/\mathrm{d}t)$ could be estimated from an almost linear relationship between the conversion and time (see Fig. 4) as listed in Table 1. According to the Arrhenius Eq. (3), the linear relation-

Table 1
Polymerization parameters of pure network formation at different temperatures

	Epoxy				UAR		
Temperature (°C)	$\mathrm{d}\alpha/\mathrm{d}t$ (min^{-1})	Conversion (at 30 min)	t_g (min)	α_g	Induction period (min)	$\mathrm{d}\alpha/\mathrm{d}t$ (min^{-1})	Conversion (at 30 min)
60	7.42×10^{-2}	0.63	12.4	0.41	7.1	1.46×10^{-2}	0.25
70	9.38×10^{-2}	0.72	9.6	0.44	4.3	2.01×10^{-2}	0.66
80	1.42×10^{-1}	0.78	6.8	0.41	4.1	7.21×10^{-2}	0.63
90	1.73×10^{-1}	0.84	3.0	0.38	1.5	1.37×10^{-1}	0.84

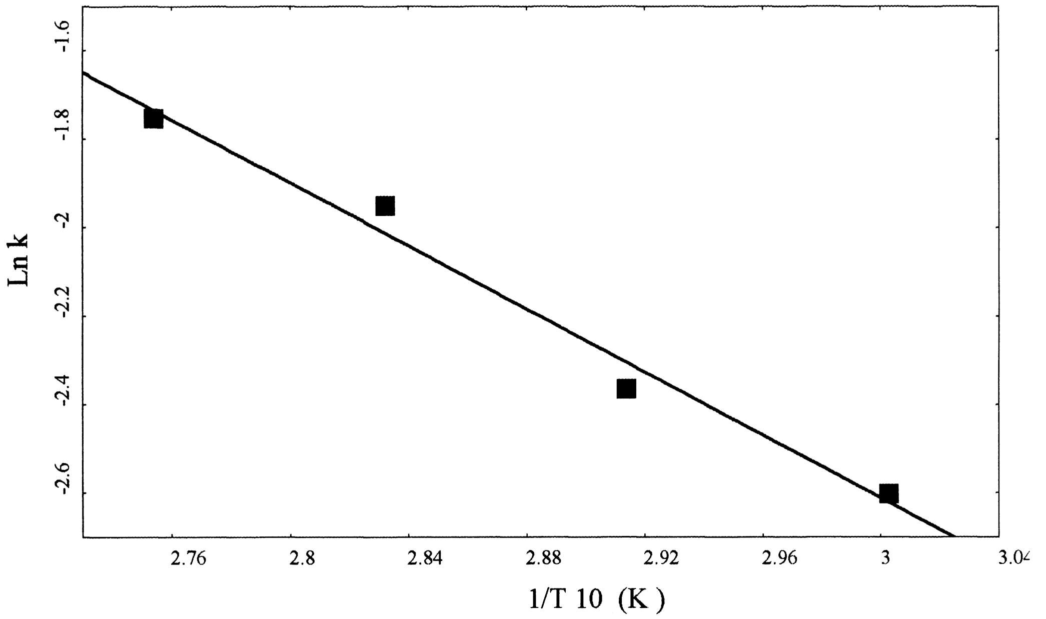

Fig. 3. Arrhenius plot of polmerization rate vs reciprocal of temperature for epoxy resin.

ship between ln k and $1/T$ is shown in Fig. 5 and an apparent activation energy of 132 KJ/mol is tested. It is well-known that the overall activation energy for most polymerization initiated by thermal initiator decomposition is only about 80–90 KJ/mol [22b]. Thus the higher apparent activation energy measured for the copolymerization of UAR could be correlated well with the strong diffusion effect existing in these copolymerization processes, as discussed before.

3.3. Polmerization kinetics of components in SINs

Figs. 6 and 7 show the reaction kinetics of epoxy in epoxy/UAR SINs having various compositions at 70

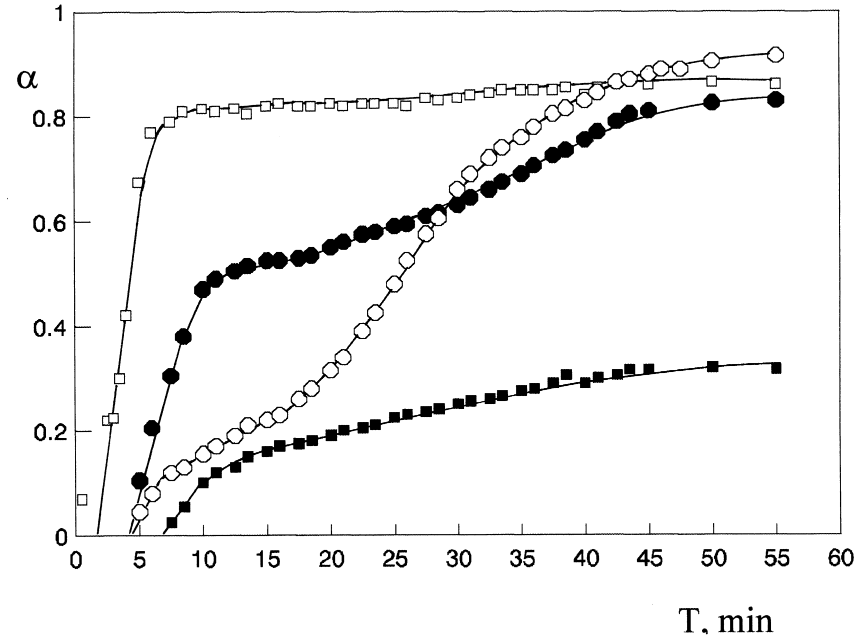

Fig. 4. Conversion of double bond vs reaction time for UAR at different temperatures: (■) 60°C; (○) 70°C; (●) 80°C; (□) 90°C.

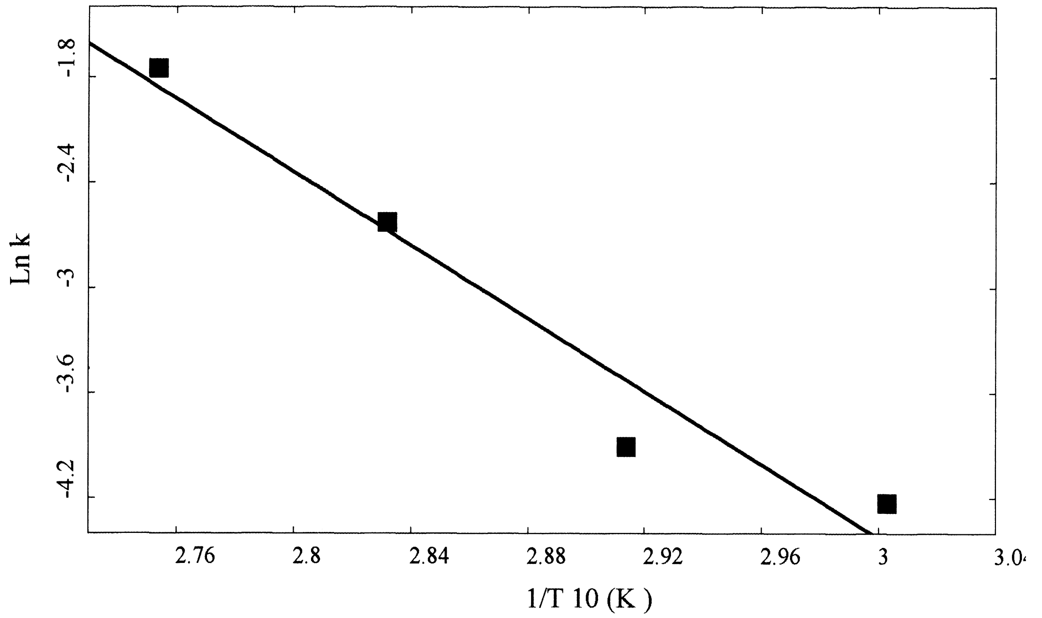

Fig. 5. Arrhenius plot of polymerization rate vs reciprocal of temperature for UAR.

and 90°C, respectively. A linear relationship between the conversion of epoxide group and polymerization time at both temperatures is also observed for these SINs below their gel points and the step polymerization rate of epoxy at early stage can be estimated, as listed in Table 2. Table 2 indicates that early step polymerization rate of epoxy increases with increasing temperature for the SIN containing more epoxy (epoxy/UAR ≥ 50 wt/wt), but it decreases while the SIN consists of less epoxy content (epoxy/UAR < 50/50). It was found that they all appear to be depressed in SIN formation compared with that in their pure sys-

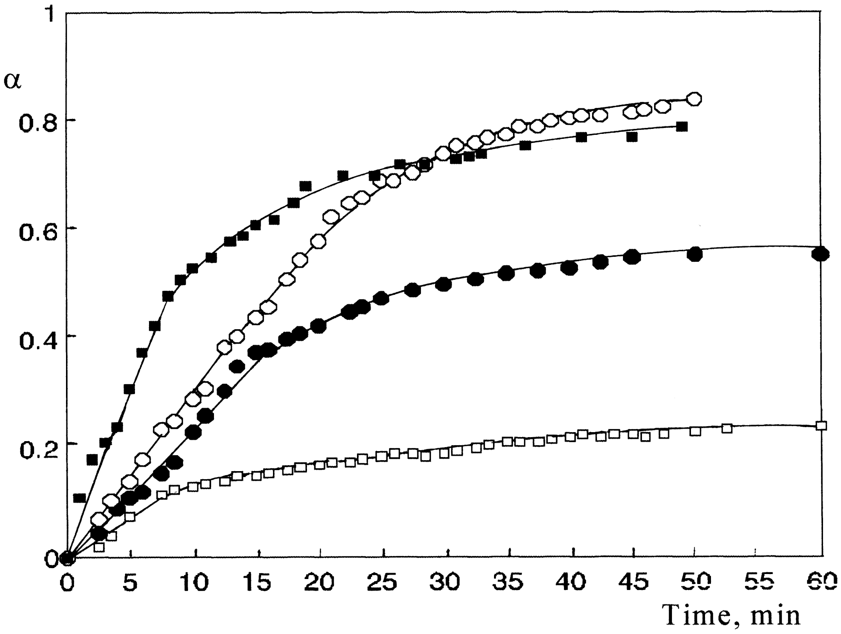

Fig. 6. Conversion of epoxide group vs. reaction time for epoxy/UAR SINs having various compositions at 70°C: (■) 100/0; (○) 80/20; (•) 50/50; (□) 20/80.

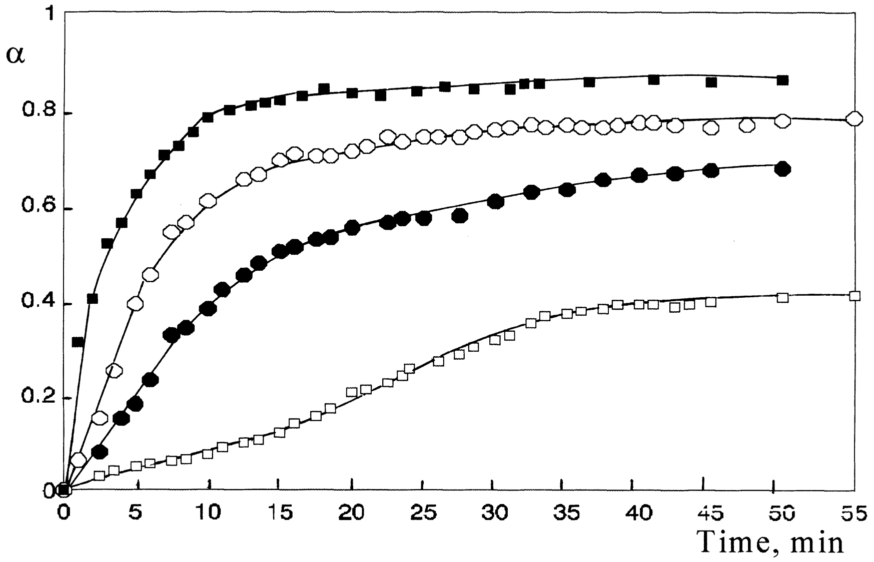

Fig. 7. Conversion of epoxide group vs. reaction time for epoxy/UAR SINs having various compositions at 90°C: (■) 100/0; (○) 80/20; (●) 50/50; (□)20/80.

tem at the same temperatures. The lowering of polymerization rate of epoxy in SIN should be expected because of the dilution effect of UAR reactants so as to reduce the concentration of epoxy and DETA in reacting mixture. However, for epoxy/UAR (80/20)and epoxy/UAR (50/50) SIN the concentrations of both reactants (epoxy and DETA) were only reduced by 20 and 50%, but the polymerization rate dramatically decreased by 3.0 and 4.1 times at 70°C as well as 2.3 and 4.5 times at 90°C, respectively. Thus the lowering of step polymerization rate in SIN formation could not be related only to the concentration of the reactants. As the viscosity of UAR is visually found to be much higher than that of epoxy/DETA mixture (the viscosity of epoxy/DETA is very difficult to measure at 25°C, but the viscosity of epoxy with 11 phr butyl glycidyl ether is only around 0.05 Pa.s [24]), the viscosity of the epoxy/DETA/UAR system will increase with the increase of UAR content. Thus, the reduction of polymerization rate of epoxy in SIN could be therefore attributed to the strong diffusion restriction resulting from the high viscous UAR. At higher temperature, i.e. 90°C, the viscosity of reactants in SIN should reduce appreciably compared with that at 70°C, but the step polymerization rate decreases by nearly the same times as that at 70°C for epoxy/UAR (50/50) SIN, which may correspond to fast copolymerization of UAR after the induction period so as to give rise to increase the viscosity of the reaction medium rapidly (see below).

For SIN consisting of less amount of epoxy (epoxy/UAR = 20/80), the epoxy network formation at different temperatures (70° and 90°C) was suppressed even more seriously than those containing more epoxy (epoxy/UAR $\geq$ 50/50). In this case, the early polymerization rate of epoxy decreases by 5.8 times at 70°C and as much as 16.9 times at 90°C, and the final conversion of epoxide is quite low compared with those for SINs (50/50) (see Table 2). These unusual experimental observation must result from the morphology development of these systems during the SIN formation. Fig. 8 presents the scanning electron microphotographs of the fracture surface of epoxy/UAR SIN at different compositions and clearly exhibits the phase separation between the two networks. For epoxy/UAR(20/80)SIN, the domains should be mainly formed by epoxy network, and the UAR network exists as matrix in the SIN. It is found that with increasing temperature, the induction period decreases and the copolymerization rate of UAR increases appreciably for this kind of SIN (see below). Thus, the fast formation of such a SIN should give rise to phase separation of the system at earlier stage so as to greatly suppress the early step polymerization rate of epoxy, because the reactant is too difficult to diffuse into the domains as consistently with the high value of apparent activation energy measured (see Table 2).

Figs. 9 and 10 show the reaction kinetics of UAR in SIN with different compositions at 70° and 90°C, respectively. The autoacceleration in the copolymerization of UAR was also observed at 70°C for SINs including more of UAR (UAR/epoxy $\geq$ 50/50). In this case the UAR network exists as a continuous phase in SINs, as shown in Fig. 8 (epoxy/UAR = 50/50 exhibits a co-continuous morphology), so it reveals a similar kinetics behavior to pure UAR. At 90°C the

Table 2
Polymerization parameters of epoxy/UAR SIN formation

Epoxy/UAR (wt/wt)	Epoxy					UAR						
	$d\alpha/dt$ (min^{-1})		Conversion (at 30 min)		E (kJ/mol)	Induction period (min)		$d\alpha/dt$ (min^{-1})		Conversion (at 30 min)		E (kJ/mol)
	70°C	90°C	70°C	90°C		70°C	90°C	70°C	90°C	70°C	90°C	
80/20	3.09×10^{-2}	3.51×10^{-2}	0.74	0.76	34.8	7.9	3.4	1.47×10^{-2}	1.94×10^{-2}	0.19	0.28	86.8
50/50	2.24×10^{-2}	3.82×10^{-2}	0.50	0.61	37.4	5.1	2.6	1.63×10^{-2}	4.82×10^{-2}	0.86	0.34	75.7
20/80	1.61×10^{-2}	1.02×10^{-2}	0.19	0.32	44.8	4.9	2.4	1.93×10^{-2}	6.95×10^{-2}	0.59	0.88	97.3

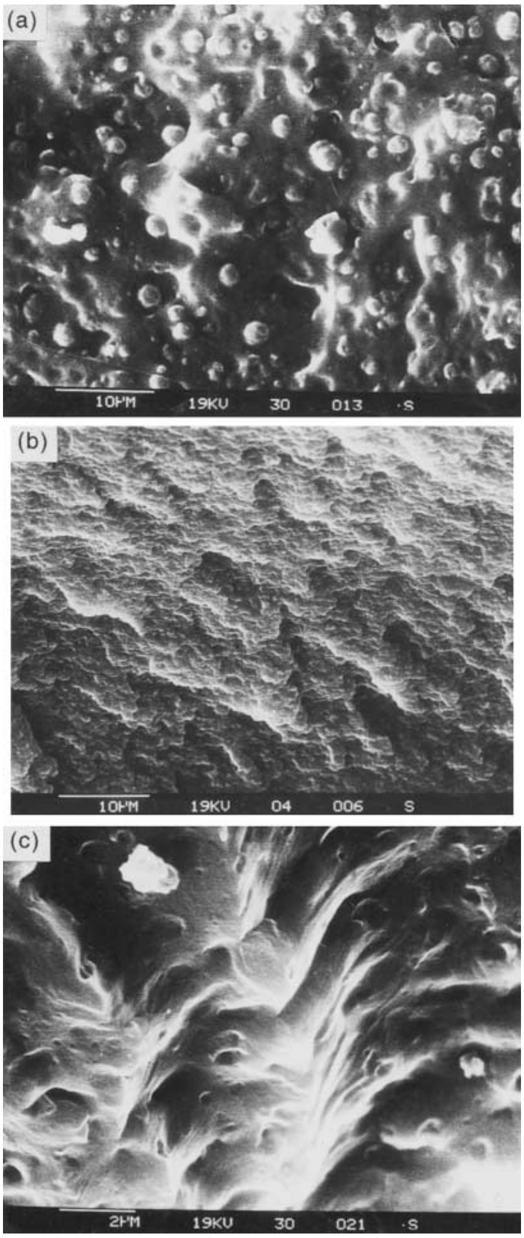

Fig. 8. Scanning electron microphotographs of fracture surface of epoxy/UAR SIN systems. Epoxy/UAR weight ratio: (a) 20/80; (b) 50/50; (c) 80/20.

autoacceleration disappears as the viscosity of reaction system reduces. For SIN consisting of less UAR (epoxy/UAR = 80/20) the ability of the UAR network formation appears to be dramatically depressed in either case at 70° and 90°C as UAR is the dispersing phase through the epoxy matrix (see Fig. 8), so as to decrease the translational diffusion rate of comonomer (MMA) into the domains as well as the copolymeriza-

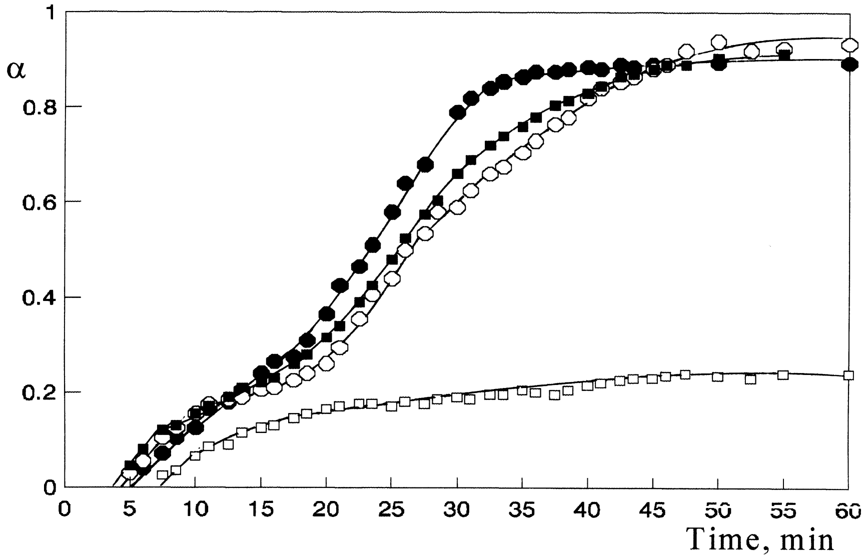

Fig. 9. Conversion of UAR vs reaction time for epoxy/UAR SINs having various compositions at 70°C: (□) 80/20; (•) 50/50; (○) 20/80; (■) 0/100.

tion proceeding of UAR. The copolymerization rate was estimated at an early stage for all these systems and is listed in Table 2.

Table 2 indicates that, just like the step polymerization of epoxy/DETA, the copolymerization rates of UAR are depressed in SIN formation compared with that in their pure systems at the same temperatures (see Table 1). However, the reducing extent of the polymerization rate for UAR is much less than that for epoxy/DETA system at the same compositions and temperatures. These experimental results could therefore be mainly attributed to the dilute effect of epoxy/DETA for UAR, especially at the beginning of the polymerization, because the viscosity of epoxy/DETA is less than that of UAR, as mentioned before. When the composition is at 50/50 in which UAR still exists in continuous phase, the dilution effect must be greater than others which also exist as a matrix, but its initial

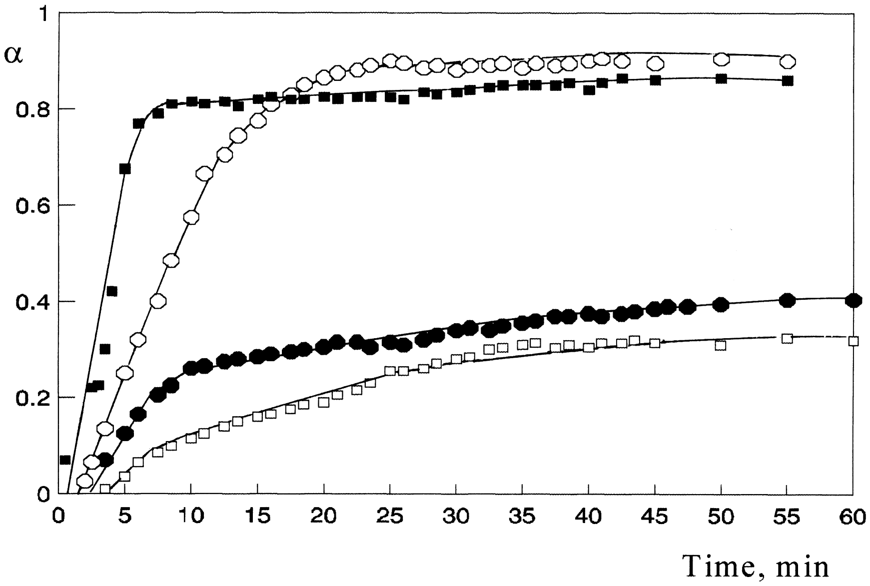

Fig. 10. Conversion of UAR vs reaction time for epoxy/UAR SINs having various compositions at 90°C: (□) 80/20; (•) 50/50; (○)20/80; (■) 0/100.

coplymerization rate is only a little lower than that of 20/80 SIN. This observation should not be due to the decrease of initial concentration of UAR in SIN, as the apparent activation energy measured at early stage of copolymerization for this SIN is less than that for 20/80 SIN, as listed in Table 2. For 80/20 SIN the higher apparent activation energy should be expected because of forming UAR domains and leading to stronger diffusion restriction.

Fig. 10 displays that for 50/50 SIN at 90°C, although the copolymerization rate of UAR at early stage is not too slow, it sharply reduces at around 10 min and the final conversion of total C=C groups is only at around 0.34 (see Table 2). It is interesting to find that at 10 min the conversion of epoxide groups is at around 0.4, i.e. gel point for epoxy (see Fig. 7). Thus, the unusual experimental behavior observed at 90°C may be related to the forced interpenetration between the two networks so as to suppress the formation of UAR network.

In conclusion, the polymerization kinetics of epoxy and UAR was monitored by using FTIR during formation of SINs. The unusual kinetics behaviors for both network formations were observed and could be correlated with the viscosity changes of the reaction system and the morphology development of the SIN. Although the mechanism of polymerization is very complicated, the polymerization rate for both network formations is mainly controlled by diffusion effect. Thus, the experimental results presented in this study should be useful to optimize the reaction conditions for preparing such SINs which could be used in RIM process, and to better understand the relationship between the morphology and physical and mechanical properties of these materials further. The morphologies as well as the physical and mechanical properties of such SINs have been studied and found to correlate well with their kinetics study and will be published elsewhere.

Acknowledgements

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