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Epoxy−Aromatic Diamine Kinetics. 2. Influence on Epoxy−Amine Network Formation

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ABSTRACT: From the complete description of neat systems and the determination of phase diagrams, the influence of a nonfunctionalized initially soluble thermoplastic on epoxy−amine kinetics was discussed, considering the dilution effect induced by the additive. The initially soluble thermoplastic, a poly(ether imide), PEI, can act as a catalyst when the initial reactivity of the epoxy−amine system is very low. The conversion, x_{cp}, at which phase separation occurs depends on the initial miscibility of PEI in the mixture of monomers. Both structural transformations, gelation and vitrification, were found to be affected by the phase separation process because of the induced fractionation phenomena. The evolution of phase diagrams which cure was also considered and temperature−conversion−transformation (*TxT*) diagrams were presented.

Introduction

The modification of epoxy networks with high-performance ductile thermoplastics has been studied as an alternative to reactive rubber for improving their toughness without sacrificing other useful properties such as glass transition temperature and stiffness.

During the isothermal copolycondensation of an initially miscible thermoplastic−monomer(s) mixture, three transformations are expected to occur: (i) phase separation which results from the increasing molar mass of the epoxy−hardener copolymer; (ii) gelation; (iii) vitrification of the matrix. Newly developped temperature−time or conversion−transformation diagrams[1,2] are very useful ways for summarizing all these physical changes.

Most of the studies on thermoplastic/thermoset blends are mainly focused on mechanical properties and final morphologies.[3−19] Only a few of them try to investigate the effect of the modifier on kinetics.[1,20−22] Additives such as high-T_g thermoplastics may still have an influence on the reaction rates and structural transformations. The phase separation process may also affect the stoichiometry of the system. Unfortunately, none of these questions is clearly answered. Only the reaction rate in modified systems is qualitatively discussed. When the rate is reported to be lower than in the neat system,[1] the restricted molecular mobility resulting from the increase of viscosity caused by the modification is put forward. Overall, it can be expected that no rule exists and that the evolution depends on the chemistry and the reactivity of the additive.

The aim of this work is to propose a much detailed analysis of the effect of a nonfunctionalized poly(ether imide) on the epoxy−amine kinetics from a complete description of neat systems[23] and the determination of phase diagrams.

Experimental Section

Materials. A classical epoxy prepolymer, diglycidyl ether of Bisphenol A (DGEBA), with a low polydispersity index ($\bar{n}$ = 0.03) was used.

Two aromatic diamines were studied: 4,4′-diaminodiphenyl sulfone (DDS), M = 248 g·mol^{-1} and 4,4′-methylenebis[3-chloro-2,6-diethylaniline] (MCDEA), M = 380 g·mol^{-1}.

Poly(ether imide) (PEI), mass average molar mass 50 000 g·mol^{-1} with a polydispersity index of 1.92, was supplied by General Electric.

The PEI-modified mixtures were prepared in a two-step process: PEI was first dissolved at 140 °C in the epoxy prepolymer; the diamine was then added at 135 °C for DDS and 90 °C for MCDEA. The hardeners were used at the stoichiometric ratio.

Techniques. Kinetic studies were conducted in a regulated oil bath at two temperatures, 80 and 135 °C. Two PEI concentrations 10% and 20% by weight were studied.

Size exclusion chromatography (SEC) was employed to measure the extent of epoxy−amine reactions. The eluent used was tetrahydrofuran (THF). The extraction of soluble products was conducted in two steps: first in dichloromethane at 10% by weight which was found to dissolve both PEI and epoxy−amine copolymer, thereafter in THF at 1% by weight to make PEI precipitate. A complete extraction of residual epoxy monomer was then possible even if phase separation has occurred.

Epoxy conversion x_e is given by

$$x_e = 1 - \left(\frac{h_t}{h_0}\right)^{1/2} \tag{1}$$

where h_t/h_0 is the ratio of the actual peak of epoxy monomer with respect to the initial one.

The glass transition temperatures, T_g, were determined by differential scanning calorimetry (DSC) at a heating rate of 10 K·min^{-1}.

Cloud points were determined with a light transmission device,[24] a technique which begins to detect particles when average diameters are on the order of 0.1 μm. The cloud-point times, t_{cp} and the cloud-point temperatures, T_{cp}, were respectively determined as the onset time and the onset temperature where a decrease in the transmitted-light intensity was recorded. The cloud-point conversions, x_{cp}, (corresponding to t_{cp}) were measured by SEC.

Modeling of a Dilution Effect on Epoxy−Amine Chemical Kinetics.

Considering both the catalytic mechanism (rate constants k_1, k_2) and noncatalytic mechanism (rate constants k'_1, k'_2) and if etherification reactions are neglected, the chemical kinetics for a stoichiometric epoxy−amine system may be expressed

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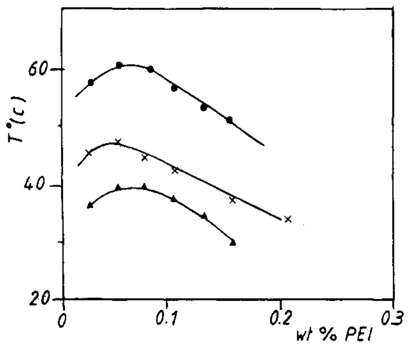

Figure 1. Initial cloud-point curve (CPC) for (×) DGEBA/PEI, (●) DGEBA–DDS/PEI, and (▲) DGEBA–MCDEA/PEI.

by[25]

$$\frac{dx_e}{dt} = (1 - x_e)[K'_1 + K_1F(\alpha)][2(1 - r)\alpha + r\alpha^{r/2}]/(2 - r) \quad (2)$$

$$\frac{d\alpha}{dt} = -2\alpha(1 - x_e)[K'_1 + K_1F(\alpha)] \quad (3)$$

where

$$F(\alpha) = 1 + \frac{(OH)_0}{e_0} - [(1 - r)\alpha + r\alpha^{r/2}]/(2 - r) \quad (4)$$

and $x_e = (e - e_0)/e_0$, $\alpha = a_1/e_0$, e is the concentration of epoxy equivalents, a_1 is the concentration of primary amino hydrogens, (OH) is the concentration of hydroxyl groups, $K_1 = k_1e_0^2$, $K'_1 = k'_1e_0$, and $r = k_2/k_1$ is the ratio of secondary to primary amino-hydrogen rate constants.

If the addition of an additive only leads to a dilution of reactive functions, the rate constants of the neat system (k_N, k'_N) and the rate constants of the modified system (k_M, k'_M) must be the same:

$$k'_N = k'_M \quad \text{gives} \quad K'_{1M} = K'_{1N}\frac{e_{0M}}{e_{0N}} \quad (5)$$

$$k_N = k_M \quad \text{gives} \quad K_{1M} = K_{1N}\frac{e_{0M}^2}{e_{0N}^2} \quad (6)$$

The ratio e_{0M}/e_{0N} can be expressed as a function of ω (the mass fraction of additive), and ρ_p (the density of the epoxy–amine copolymer), and ρ_M (the density of the additive) by

$$\frac{e_{0M}}{e_{0N}} = 1 + \frac{\omega}{1 - \omega}\frac{\varrho_N}{\varrho_M} \quad (7)$$

If the kinetic rate constants of neat systems are known, it is thus possible to predict the kinetics of modified systems by considering the dilution effect induced through eqs 5 and 6.

Results and Discussion

Epoxy–Amine Kinetics. In a previous paper,[23] the kinetics of the neat systems DGEBA–DDS and DGEBA–MCDEA were studied at various temperatures. The ratios of rate constants were determined for both diamies. The overall reactions were then modeled, and the chemical rate constants were expressed.

Initial Phase Diagrams. The cloud-point curve (CPC) of the DEGBA/PEI quasi-binary system is shown in Figure 1. It is typical of a system exhibiting upper critical solution temperature (UCST) behavior.

The addition of a diamine is known to turn the system at time $t = 0$ (no reaction) into a quasi-ternary mixture.[26] Then, any quantitative thermodynamic treatments necessitate knowing the cloud-point curves of DGEBA/diamine/PEI blends before any reaction has taken place. Such experimental determinations require systems of low reactivity and low temperature threshold. This was actually the case. However, SEC measurements realized after the cloud-point determinations ($T < 70$ °C) have confirmed epoxy conversions close to zero. The CPCs of initial systems are compared to the DGEBA/PEI CPC on the same Figure 1. The addition of the diamines (at the ratio 1 mol of diamine for 2 mol of DGEBA) actually modifies the quasi-binary phase diagram: MCDEA increases the miscibility of DGEBA/PEI blends whereas DDS decreases it. The modeling of the curves and the determination of the interaction parameters χ will be the subject of another publication.[27]

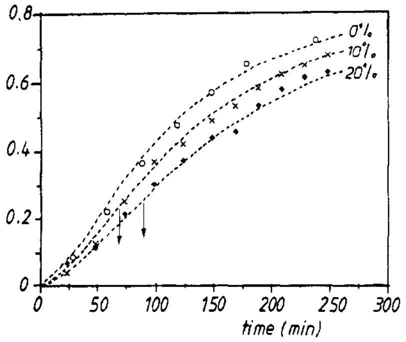

Figure 2. Epoxy conversion x_e versus time at $T_i = 135$ °C for neat and modified DGEBA–DDS systems: (○) neat; (×) 10 wt % PEI; (◆) 20 wt % PEI; (- - -) kinetic prediction. Arrows (↓) indicate cloud-point times.

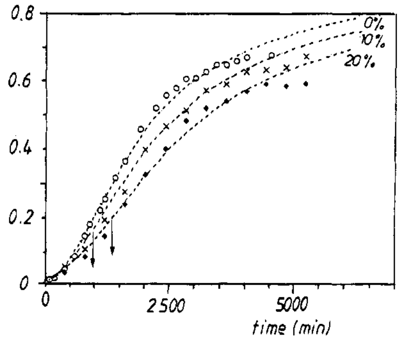

Figure 3. Epoxy conversion x_e versus time at $T_i = 80$ °C for neat and modified DGEBA–DDS systems: (○) neat; (×) 10 wt % PEI; (◆) 20 wt % PEI; (- - -) kinetic prediction. Arrows (↓) indicate cloud-point times.

Influence of PEI on the Reaction Rates. The experimental evolutions of epoxy conversion with time for modified systems are presented and compared to the neat system in Figures 2–5 for each diamine at 80 and 135 °C. On the same figures are given the kinetic modeling of the neat systems and the kinetic predictions of modified systems by taking into account only the dilution effect induced by the presence of PEI. The etherification reactions were not considered in the kinetic model because of the range of conversions studied ($x_e < 0.7$) and low curing temperatures used.

Cloud-point times, t_{cp}, are indicated by an arrow. Resulting conversions, x_{cp}, are listed in Table 1. For the same conditions of temperature and concentration of PEI, x_{cp} was always higher in the case of MCDEA. This is consistent with initial CPCs in that the DGEBA–MCDEA system was found to be a better solvent of PEI than the DGEBA–DDS system.

If we first consider results involving DDS (Figures 2 and 3), it appears that before phase separation the addition of PEI only leads to the dilution of reactive

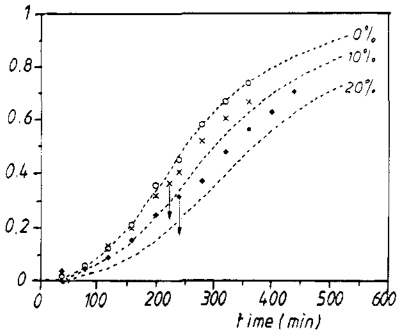

Figure 4. Epoxy conversion x_e versus time at T_i = 135 °C for neat and modified DGEBA–MCDEA systems: (○) neat; (×) 10 wt % PEI; (◆) 20 wt % PEI; (- - -) kinetic prediction. Arrows (↓) indicate cloud-point times.

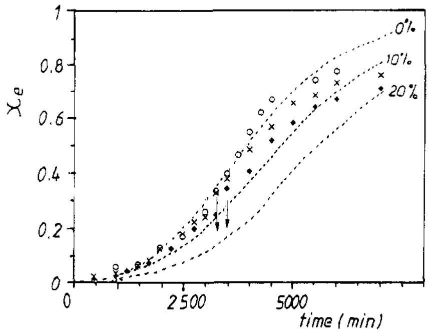

Figure 5. Epoxy conversion x_e versus time at T_i = 80 °C for neat and modified DGEBA–MDCEA systems: (○) neat; (×) 10 wt % PEI; (◆) 20 wt % PEI; (- - -) kinetic prediction. Arrows (↓) indicate cloud-point times.

Table 1. Cloud-Point Conversion, x_{cp}, as a Function of the Diamine, the Concentration of PEI, and Cure Temperature

	DGEBA–DDS		DGEBA–MCDEA	
T_{cure} (°C)	10 wt % PEI	20 wt % PEI	10 wt % PEI	20 wt % PEI
80	0.10	0.11	0.29	0.26
135	0.28	0.26	0.38	0.38

epoxy–amine functions. Even if the extent of reaction with time decreases with PEI content, the real kinetic rate constants are not modified. After phase separation, measured epoxy conversions include both epoxy groups in the epoxy rich phase and epoxy groups in the PEI rich phase. Moreover, developed kinetic models cannot be applied anymore since two phases coexist with unknown concentrations in each phase. It is then difficult to clearly conclude in which degree phase separation affects the epoxy–amine kinetics. However, no sudden change of reaction rates is observed at the cloud points. Predictions fit even experimental results after phase separation. It looks as if the epoxy and amine-hydrogen concentrations were not modified by phase separation.

The situation is different in the case of MCDEA (Figues 4 and 5). Whatever the temperature, 80 or 135 °C, in the one-phase window, the predictions based on a dilution effect underestimate experimental conversions. The reactions were thus faster in the presence of PEI. The difference between experimental and calculated values tends to increase with the initial concentration of additive. PEI may act as a catalyst of DGEBA–MCDEA reactions. In any case, this is supported by the kinetic curves obtained at 80 °C where (i) before phase separation, the evolutions of conversions with time are nearly the same and (ii) the reaction rates suddenly decrease in modified systems just after cloud-point times when most of the PEI has been excluded from the epoxy-rich phase. The DGEBA–MCDEA system is, however, weakly reactive, and the reactions can thus easily be catalyzed by an additive (the tertiary nitrogen from PEI for example) or any impurities present in this additive.

Table 2. Gel Conversions, x_{gel}, for Neat and Modified Systems at 80 and 135 °C

	neat		10 wt % PEI		20 wt % PEI	
epoxy system	80 °C	135 °C	80 °C	135 °C	80 °C	135 °C
DGEBA–DDS	0.61		0.58	0.58	0.55	0.56
DGEBA–MCDEA	0.61		0.59	0.59	0.55	0.57

Table 3. Vitrification Times, t_{vit} (min), for Neat and Modified System

	neat		10 wt % PEI		20 wt % PEI	
epoxy system	80 °C	135 °C	80 °C	135 °C	80 °C	135 °C
DGEBA–DDS	3300	375	3400	375	3600	375
DGEBA–MCDEA	5300	650	5500	650	5500	650

Influence of PEI on the Structural Transformations. The gel conversion results are presented in Table 2. The modified systems exhibit lower gel conversions which tend to decrease when the cure temperature decreases and/or the concentration of PEI increases. This evolution of x_{gel} is not consistent with an eventual modification of the epoxy–amine stoichiometry induced by phase separation, as it could be obtained in some rubber-modified epoxy networks.[28] Such an effect would have led to an increase of x_{gel}. On the other hand, this evolution can be the result of a fractionation phenomena which occurs during the phase separation process. During reaction the initially one-phase system is turned into a two-phase system. In a recent publication,[29] the composition and conversion of both phases were calculated when complete equilibrium is reached at any conversion level. It was shown that the conversion of epoxy groups in the modifier rich phase is significantly lower than the overall conversion of epoxy (and amine) groups. This decrease results from the preferential segregation of monomers and low molar mass species in the modifier rich phase. In our case, a sharp decrease of the mass transfer is expected as the thermoplastic rich phase vitrifies. Therefore it is assumed that, at 80 and also 135 °C, epoxy–amine species with low molar masses and low functionalities remain trapped in the thermoplastic rich phase, leading to an increase of the second moment of average functionality distribution, $\bar{f}_w$ in the epoxy rich phase and consequently to a decrease of x_{gel}.

The complete extraction of soluble products is difficult for high reaction extents after gelation and, consequently, the vitrification conversions, x_{vit}, could not be experimentally measured. However, the vitrification times, t_{vit}, of neat and modified systems (epoxy rich phase), listed in Table 3, were measured to be nearly the same. On the basis of kinetic studies, equal times of reaction mean lower epoxy conversions in the modified systems. These PEI-modified systems probably vitrify for lower conversions because of some PEI (the lower molar masses) kept dissolved in the epoxy rich phase which then increases the glass transition temperature of this phase.

Evolution of Phase Diagrams. Systems are regarded as a solution of the thermoplastic in the growing thermosetting copolymer. The increase of the molar mass of the epoxy–amine copolymer with conversion

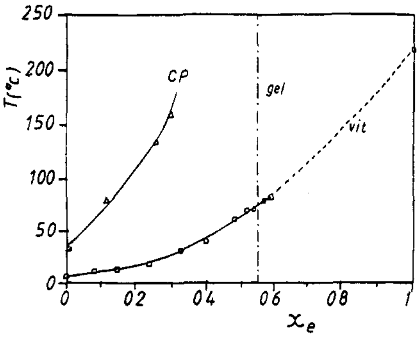

Figure 6. Experimental phase diagram temperature versus conversion for the DGEBA–DDS/20 wt % PEI blend: (Δ) cloud points; (□) vitrification, (–•–) gelation. (For the sake of clarity, the possible evolution of x_{gel} with temperature is not considered.)

obviously modifies the phase diagrams of blends. The evolution of cloud-point temperatures, T_{cp}, versus conversion, x_{cp}, was studied with 10% and 20% by weight of PEI. The increase of the T_g of the epoxy rich phase with conversion was also followed. All the experimental results can be plotted on the same temperature–conversion–transformation (*TxT*) diagram, as shown in Figure 6 for the DGEBA–DDS/20 wt % PEI blend, by integrating phase separation (T_{cp}, x_{cp}), gelation (x_{gel}), and vitrification (T_g, x). T_{cp} increases with conversion which agrees with the UCST-type initial phase diagram. It appears that x_{cp} is always lower than x_{gel} and that T_{cp} is always higher than $T_g(x)$ at a given overall conversion. In other words, phase separation occurs before the vitrification of the epoxy–amine copolymer during the isothermal cure of blends and before gelation if gelation occurs. The boundary is defined by gel T_g = 75 °C for DGEBA–DDS and gel T_g = 54 °C for DGEBA–MCDEA.

These phase diagrams are very useful for controlling the curing of the blends.

Conclusion

The DGEBA/PEI blends exhibit upper critical solution temperature (UCST) behavior. The addition of the diamine was found to modify the quasi-binary phase diagram, and the resulting quasi-ternary initial phase diagrams were then determined: at the stoichiometric ratio of amino-hydrogen to epoxy, MCDEA increases the miscibility whereas DDS decreases it.

From the complete description of the neat systems, the influence of poly(ether imide) on the epoxy–amine kinetics was investigated. Before phase separation, the DGEBA–DDS kinetics could be described considering only the dilution effect induced by the presence of the additive. The kinetic rate constants were not modified. After phase separation, the kinetic models could not be applied, but no sudden change of reaction rates was observed. Differently, PEI acts as a catalyst of DGEBA–MCDEA reactions.

The gel conversions were found to be lower in the modified systems. This could not result from a modification of the stoichiometry. On the other hand, the decrease from x_{gel} may result from some monomers, or low polymerized species, kept dissolved in the PEI rich phase. The presence of some PEI in the epoxy rich phase can explain the decrease of the vitrification conversions.

Temperature–conversion–transformation (*TxT*) diagrams were introduced to describe the evolution of phase diagrams with cure and kinetic results. During an isothermal cure, phase separation always occurs before gelation and vitrification.

With the help of these kinetic results and phase diagrams, it is now possible to control the curing of the blends with appropriate precuring and postcuring schedules in order to control subsequent morphologies and mechanical properties.

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