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Epoxy – diamine Thermoset / Thermoplastic blends: thermoset reactions and rheological evolutions during curing

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Summary: Isothermal rates of reaction during the cure of epoxy- amine/thermoplastic blends were studied. Epoxy-amine reaction induces a phase separation. Experimental results show that when TP concentration is higher than 30 wt % an increase of reaction rate is observed after phase separation. A modelling of the kinetics of each phase before and after phase separation, shows that in the epoxy-amine rich phase, gelation occurs for a conversion close to 0.6. Rheological behaviour was studied during the cure. The viscosity was found greatly dependent of the morphology, the epoxy amine conversion and of the evolution of the phase composition. Modelling of the viscosity using simple relations gives a good fit of the experimental results during the cure.

Introduction

Thermoset (TS)/Thermoplastic (TP) blends are materials resulting from the mixing of the TP polymer with the TS precursor (one or two monomers, a catalyst...) and the subsequent reaction of this precursor. Usually the initial mixture is homogeneous and due to the molar mass increase of the TS precursor a liquid-liquid phase separation occurs at a given conversion[1)]. The beginning of the phase separation process can be determined by light transmission (LT, in this case, the Cloud Point, Cp is characterized), light scattering (LS) or small angle X-ray scattering (SAXS). Depending on the technique used, the observation scales can be different. One important factor controlling the generated morphologies is the location of the composition of the initial blend, $\overset{\circ}{\phi}_{TP}$, with respect to the critical composition $\phi_{TP,crit}$. For TP with average molar masses between 10000-30000g/mol, $\phi_{TP,crit}$ in liquid epoxy and diamine monomers (as thermoset precursor) may be obtained from the Flory-Huggins model and is in the range of 10-15 wt% TP[1)]. In a previous study, E. Girard-Reydet et al.[2)] have demonstrated that for quantities of TP, if $\overset{\circ}{\phi}_{TP}$ is in the range of $\phi_{TP,crit}$, 10 wt% for example, phase separation during epoxy-amine reactions proceeds by spinodal dimixing (SD) and LT or LS give correct estimation of the beginning of the phase separation process. But for off-critical composition, typically TP ≥ 30wt% the second phase appears through nucleation and growth (NG) mechanism, and in this case SAXS is able to observe the beginning of the phenomena before LT or LS. It also has been shown that for TP ≤ 10 wt% the continuous phase is the epoxy-amine network, but for TP ≥ 30 wt% the continuous phase is the TP, and between 10-30 wt% more or less well defined bi-continuous structures are formed. One

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consequence is that TS-TP blends have been mainly studied for two reasons : i) modification of TS networks with high performance ductile TP$^{3)}$, or ii) new processing routes for intractable high-temperature resistant TP polymers$^{4-5)}$. For the first application the TP concentrations are generally lower than 15 wt% and for the second one higher than 30 wt%. Most of the studies on TS-TP blends are mainly focused on final morphologies and / or mechanical properties$^{1,3-6)}$. But the control of morphologies and properties requires a good knowledge of the different events occuring during the reaction of the TS precursor. Few studies try to investigate the effects of the TP on TS chemistry and rheology. The aim of this work is to propose a detailed analysis on the effect of a non functionalized thermoplastic, like commercial polyetherimide, PEI, on the epoxy-amine reaction on the basis of a previous complete description of the neat TS system$^{7)}$, but also the characterization of the different events occurring during the phase separation process. Taking into account all these parameters, kinetics and viscosity modeling during cure will be proposed.

Experimental

The TS precursor is an epoxy system based on classical liquid diglycidyl ether of bisphenol A, DGEBA $\bar{n} = 0.15$ and a liquid diamine, sterically hindered 4,4'- methylenebis [3-chloro 2,6-dianiline], MCDEA with a stoechiometric ratio equal to 1. The low reactivity of this hardener was chosen in order to follow carefully the phase separation process. Two TPs have been used, mainly PEI from GE (Ultem 1000) but also PS from Atochem (Lacqurene 1070N) for a comparison.The initial blends with low TP concentration ≤ 20 wt% were prepared in a two-stage process : TP was first dissolved at 140°C in the epoxy prepolymer, the diamine was then added at 90°C. For the initial blends with higher TP quantities, a co-rotating twin-screw extruder was used in a one-stage process, the TP was directly dissolved in the epoxy-amine mixture.Kinetic studies were conducted as described previously$^{7)}$. HPLC was used to measure the extent of epoxy-amine reaction. Gelation times were also obtained during HPLC measurements, it is considered to be the time at which the presence of an insoluble fraction is first observed.The morphology of blends was studied by transmission (TEM) or scanning (SEM) electron microscopies.Differential scanning calorimetry was used to measure the glass transition temperature, T_g and the change in heat capacity through the glass transition temperature, ΔC_p, a heating rate of 10°C/min was used. The viscoelastic properties were measured by shear rheology with a Rheometrix Dynamic Analyzer II.

Results and discussion

The experimental Cloud Point Curves (CPC) of PEI/DGEBA-MCDEA and PS/DGEBA-MCDEA blends before any reaction exhibit an UCST behaviour. PS is observed to be less soluble in epoxy TS precursor than PEI but at the selected curing temperature, T_i = 135°C both are soluble, and exhibit one T_g which can be measured or calculated by the help of Couchman equation[8]. In Figure 1 we can observed that during curing (at 135°C) the $T_g(x)$ of the homogeneous mixture increases due to the molar mass increase of the TS precursor, but after the CP two T_gs are observed, one higher and one lower than the $T_g(x)$ of the homogeneous phase.

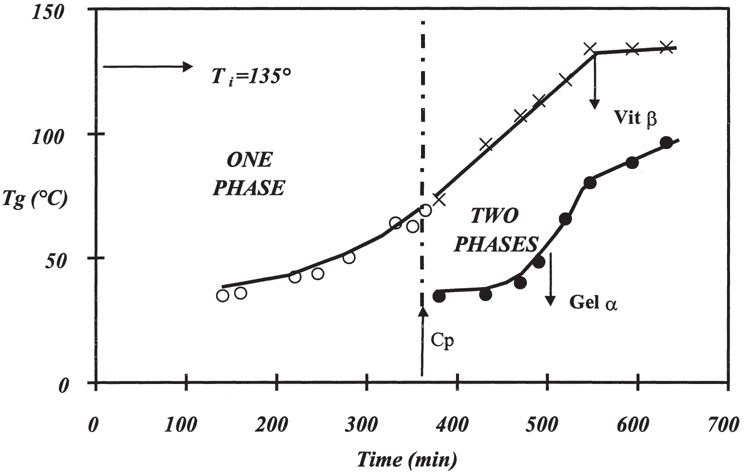

Fig. 1 : Tg evolution during the reaction of the PEI 48 wt%/DGEBA $\overline{n}$ = 0.15 - MCDEA blend cured at T_i = 135°C, (o) homogeneous phase, (●) α phase, (x) β phase.

The upper one, $T_{g\beta}$ is attributed to the PEI rich phase, the lower one, $T_{g\alpha}$ to the epoxy-amine rich phase. Both $T_{g\beta}$,ΔCp_β and $T_{g\alpha}$,ΔCp_α have different evolutions with curing time.The experimental evolutions of epoxy conversion, x, with curing time for DGEBA-MCDEA reactions with different TP concentrations have been measured. For all TP concentrations before phase separation, the addition of TP leads to a dilution of reactive groups. By taking into account the kinetic rate constants of the neat system previously[7] measured and the dilution effect induced by the presence of the TP, it was also possible to predict the behaviour of the blends, but in the one phase area only. Even if x vs time decreases with the increase of TP content, the real kinetic rate constants are not modified in the one phase area. For low TP concentrations ≤ 10 wt% the fitting is rather good during all the reaction. But when the TP concentrations ≥ 30 wt% a sudden increase of reaction rate is observed where the phase separation begins. This effect is stronger in the case of PS compared to PEI. When the phase separation occurs, the dilution ratio changes rapidly and differently for α and β phases. These new two dilution ratios also change with reaction times and x measured is $\overline{x}$, the average epoxy conversion. To model the behaviour after phase separation it is necessary i) to have the composition of α and β phases at each curing time, ii) to know the concentration of the dispersed phase. Microscopy and thermal measurements were performed on a blend with 48 wt% PEI to make an estimation of the composition of each phase, leading to kinetic prediction in both α and β phases. This prediction shows that gelation in the α phase occurs at x_α close to 0.6. This modeling is presents in Figure 2

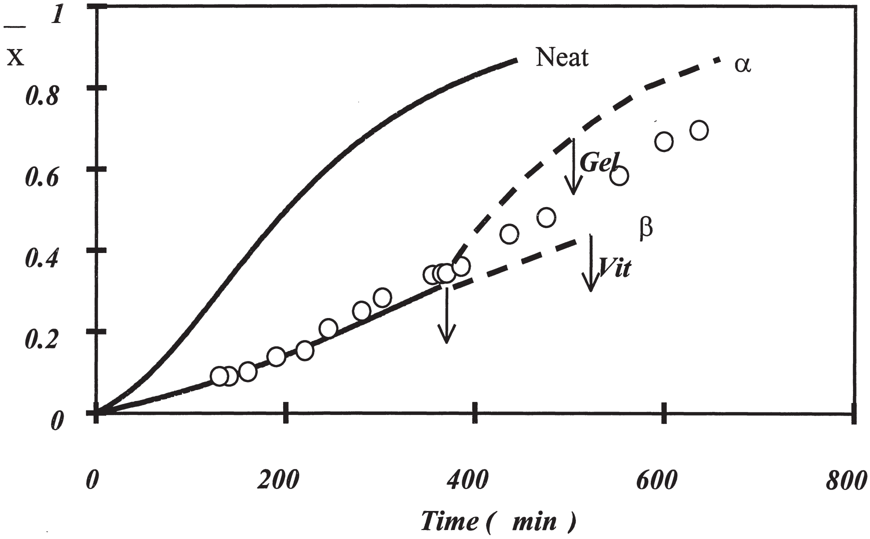

Fig. 2 : Kinetics of the epoxy-amine reaction in the blend with 48 wt% PEI at 135°C. (o) experimental points, and model taking into account only dilution effects for (———) one phase (— — —) two phases domains (o) experimental points (mean value, $\bar{x}$ after phase separation).

In figure 3, different behaviors can be observed.

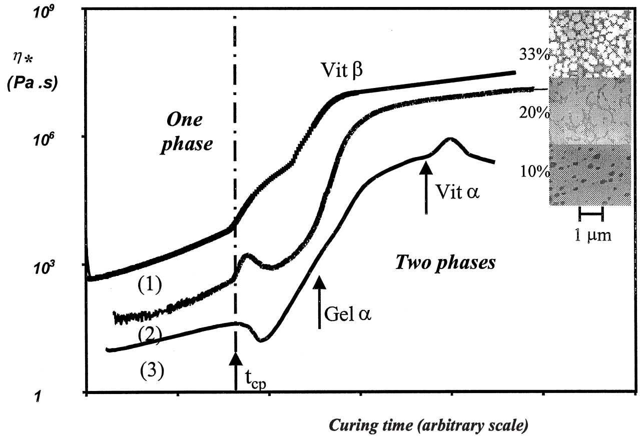

Fig. 3 : Influence of PEI concentration on the rheological behavior (1) 10 wt% (2) 20 wt% (3) 33 wt% . TEM micrographs illustrate the final morphologies obtained at T_i = 135°C after 5 hours and post cure at 220°C (during 7 hours).

When the TP concentration is lower than $\phi_{TP,crit}$ (10 wt%) phase separation at the CP is followed by a rapid decrease in viscosity. Gelation of the continuous α phase leads to an increase of G'. For longer times, vitrification of the α phase can be detected by a peak on δ and G' curves. When the TP concentration is slightly higher than $\phi_{TP,crit}$ the behaviour is more complex. In the beginning of the phase separation process a gradual increase in viscosity occurs due to the bicontinuous structure and the behaviour of the β phase. Then a decrease is observed due to the fact that the bicontinuous structure is destroyed and the α phase dominates. The amplitude of this phenomenon depends on the frequency[9]. When TP composition is high enough to ensure to have a continuous TP rich phase up to the end of the phase separation process (typically 30 wt%), the onset of phase separation is accompanied by a gradual increase in viscosity. For all TP compositions, before phase separation the viscosity of the homogeneous mixture can be described with the help of the composition and the viscosities of the two components. It increases due to the reaction and the increase of $\overline{M}_w$ of the TS precursor. After phase separation, Einstein relation can be used to describe the viscosity of a suspension taking in mind the same parameters than for kinetic modeling: phases composition and volume fraction of the dispersed phase. In the later stages of the reaction for TP concentrations ≥ 30 wt%, β phase behaviour dominates, and in the vicinity of its vitrification, WLF relation has to be used. Taking into account all these considerations, viscosity evolutions during cure of a blend with 33 wt% of PEI have been modeled. The result of the modeling is presented in Figure 4.

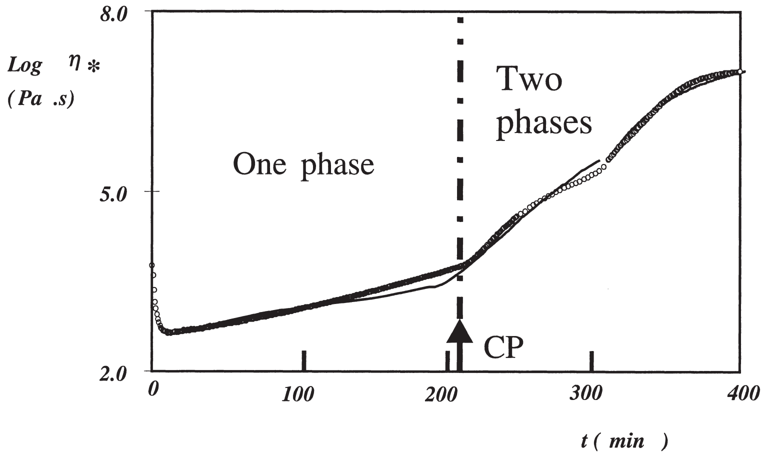

Fig. 4 : Simulation of the evolution of viscosity during the cure at 135°C of a reactive blend. DGEBA $\overline{n}$ = 0.15 – MCDEA with 33 wt% of PEI. (O) Experimental points, (—) modeling.

Conclusion

Phase separation in TS / TP blends was monitored using kinetic and rheological measurements. The main parameters for modeling are phase compositions and phase concentrations.

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