Comparison of kinetic and rheological evaluation of gel time for an amine–epoxy system

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For tetrafunctional formulations, Flory's classic analysis yields the value of 58% for conversion at gel point. This study utilizes a recently developed mechanistic kinetic model for epoxy–amine reactions to calculate the time needed to reach 58% conversion. That time was then compared to the gel time determined from rheological measurements and the two were found to be in superb agreement.

(Keywords: epoxy–amine; cure; modelling; kinetics; rheology)

Introduction

We have recently reported the results of a comprehensive investigation of modelling of the reaction mechanism of epoxy–amine systems, using both model compounds and polyfunctional formulations[1,2]. A mechanistic reaction scheme was put forward, involving the initial formation of hydrogen bond complexes which, via intermediary transition complexes, lead to the reaction products by three major routes. From the proposed set of equations we were able to derive all significant kinetic parameters. The observed agreement between the model predictions and the experimental results was superb. We showed unambiguously that the kinetic mechanism was characterized by a temperature-dependent negative substitution effect on the amine nitrogen.

In this work, we utilized our kinetic model in the following way. Using Flory's classic approach we first determined the theoretical conversion at gelation. The obtained value was substituted into our kinetic model and the corresponding 'kinetic' gel time was calculated for a series of isothermal conditions. We then proceeded to make use of recently performed rheological measurements, on the same polyfunctional formulation, from which we calculated 'rheological' gel times corresponding to the asymptotic value of viscosity as it tends to infinity.

The main objective of this communication is to contrast the values of kinetic and rheological gel times, evaluated from kinetic and rheological measurements, respectively.

The results presented herein are part of a comprehensive investigation of the chemorheology of epoxy–amine cure aimed at correlating the results of a gamut of experimental techniques (calorimetric, spectroscopic, chromatographic, dielectric and viscoelastic), currently underway at the University of Naples and the Polytechnic University.

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Experimental

The resin formulation consisted of the stoichiometric amounts of diglycidyl ether of bisphenol A (DGEBA) epoxy resin (Epon 825), and 4,4′-methylene dianiline (MDA) curing agent (Aldrich). Structure and properties of both components are reported elsewhere[2].

Kinetics of cure of the DGEBA–MDA formulation were investigated in a series of isothermal tests at temperatures between 90 and 120°C. Twenty glass vials, each containing 50 mg of the formulation, were placed inside an oil bath. The temperature of the bath was controlled with an Omega CN 2010 controller coupled with an RTD temperature sensor, and verified with a thermocouple. At desired time intervals a sample was removed from the bath, quenched to arrest the progress of reactions, and analysed by spectroscopic and rheological measurements. Fourier transform infra-red (*FT*i.r.) spectra were generated on a Bio-Rad Digilab Division FTS 60 spectrometer. Each spectrum was averaged over 32 scans. A Brookfield viscometer was used for rheological measurements. Further details of the experimental procedures have been published elsewhere[1–3].

Results and discussion

The starting point in this investigation was our mechanistic model for epoxy–amine reaction kinetics, based on the existence of different transition complexes

Table 1 A comparison of gel times obtained by kinetic and rheological methods

Temperature (°C)	Time to 58% conversion (from kinetics) (min)	Time to gel (from rheology) (min)
90	54	54
100	31	30
110	20	21
120	14	15

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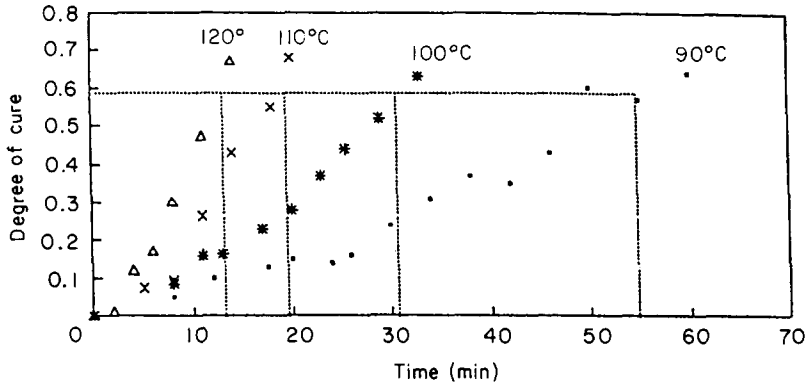

Figure 1 Degree of cure as a function of time with temperature as a parameter

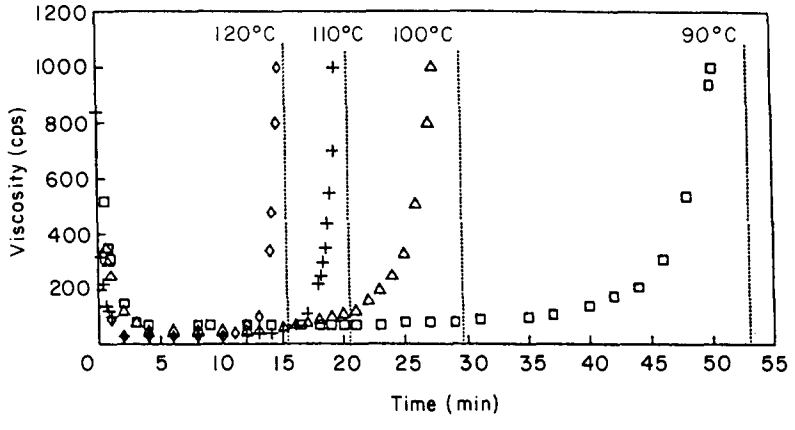

Figure 2 Viscosity as a function of time with temperature as a parameter

during the course of epoxy–amine cure[1–3]. Degree of conversion in our model is related to the time and temperature of cure by the following expressions for the rate of disappearance of primary amine (1) or the rate of production of the tertiary amine (2):

$$-\frac{d[PA]}{dt} = -\left(\frac{d[PA]_a}{dt} + \frac{d[PA]_b}{dt} + \frac{d[PA]_c}{dt}\right)$$
$$= W_1 k_{a1}[Ep][PA]^2 + W_2[Ep][PA](k_{b1}[CO] + k'_{b1}[OH]) + W_3\left(k_{c1}[Ep][PA][OH] + \frac{[PA]}{[OH]}\frac{d[OH]}{dt}\right) \quad (1)$$

$$\frac{d[TA]}{dt} = \frac{d[TA]_a}{dt} + \frac{d[TA]_b}{dt} + \frac{d[TA]_c}{dt}$$
$$= W_1 k_{a2}[Ep][SA]^2 + W_2[Ep][SA](k_{b2}[CO] + k'_{b2}[OH]) + W_3\left(k_{c2}[Ep][SA][OH] + \frac{[SA]}{[OH]}\frac{d[OH]}{dt}\right) \quad (2)$$

where [Ep], [PA], [SA] and [TA] represent concentrations of epoxy, primary amine, secondary amine and tertiary amine groups, respectively. Other kinetic parameters of equations (1) and (2) are defined elsewhere[1–3].

Since the *FT*i.r. analysis yields results in terms of epoxy and primary amine groups and our model requires as input the concentrations of reactants and products, i.e. [Ep], [PA], [SA] and [TA], the last two terms had to be calculated from mass balances[2,3]. We then continued our analysis using Flory's classic expression[4] for the degree of cure at gelation in a formulation with the same number of reactive groups (here, epoxy and amine hydrogens):

$$\alpha_c = \sqrt{1/(f-1)} \quad (3)$$

where f is the functionality of the branching unit, here equal to four, and hence the predicted degree of cure is 0.58, or 58%. We then determined the degree of cure for our formulation from *FT*i.r. analysis, and plotted it as a function of time with temperature as a parameter, as shown in *Figure 1*. The time necessary to reach the 58% conversion, termed 'kinetic' gel time, was calculated for each temperature and the result superposed on the conversion curves of *Figure 1*. A series of rheological measurements was performed next. Viscosity was calculated and plotted as a function of time with temperature as a parameter, as shown in *Figure 2*, from which the corresponding rheological gel times were evaluated. A comparison of the kinetic gel time, needed to reach 58% conversion, with the 'rheological' gel time, at which viscosity tends to infinity, is presented in *Table 1*. An excellent agreement is apparent.

We maintain that the observed agreement provides further support for the accuracy and validity of our

kinetic analysis. Our present research efforts are aimed at developing fundamental correlations between kinetic and rheological measurements on the one hand, and dielectric and spectroscopic measurements on the other hand. The importance of such research stems from a considerable interest in the use of dielectric and fibre optic sensors for *in situ* monitoring of processing.

References

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