

KINETICS STUDIES OF THE EFFECT OF PPSU ON THE CURING OF AN EPOXY/AMINE RESIN

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Introduction

The modification of epoxy networks with high-performance ductile thermoplastics has been studied as an alternative to reactive rubbers for improving their toughness without sacrificing other useful properties such as glass transition temperature and stiffness. Most of the studies on thermoplastic/thermoset blends are mainly focused on their mechanical properties and final morphologies. Although, recently, some authors have investigated the effect of the modifier on the kinetics of curing. Curing kinetics of epoxy resins has been studied with different techniques, such as differential scanning calorimetry (DSC). In this contribution, we use one isothermal model to study the cure kinetics of an epoxy system containing diglycidyl ether of bisphenol-A (DGEBA) and diamino diphenyl methane (DDM) as curing agent, and its blends with the thermoplastic, polyphenylsulfone (PPSU) at 5, 10 and 15 phr (where phr represents the number of parts by mass quantity of PPSU per hundred parts of DGEBA epoxy resin).

Experimental Details.

The epoxy resin used here was diglycidyl ether of bisphenol-A (DGEBA), and the hardener used was 4,4' diamino diphenyl methane (DDM) and the thermoplastic modifier was polyphenylsulfone (PPSU); all materials were supplied by Aldrich Chemical Co. The thermoplastic-modified mixtures were prepared in the following way. First, the

corresponding weighted amount of PPSU was dissolved in dichloromethane, the DGEBA was then added and stirred until complete dissolution of the resin. The solvent was removed afterwards by heating at 80 °C *in vacuo*; and DDM, in a stoichiometric epoxy/amine ratio, was added at 100 °C, and dissolved by continuously stirring the mixture for 2 min. Differential scanning calorimetry (DSC) dynamic and isothermal modes were carried out in a *TA Instruments* DSC model 2920 (in a dry nitrogen atmosphere). Runs at different heating rates (2.5, 5, 10, 15 and 20 °C/min) in a temperature range from 30 to 250 °C, for dynamic measurements; and runs at several temperatures, for isothermal measurements were performed.

Results and Discussion.

Figure 1 shows the time dependence of heat of reaction of the DGEBA/DDM networks and DGEBA/DDM/PPSU semi-IPNs during isothermal curing at different temperatures. For all the samples, the rate of the exothermic epoxy/amine reaction increases first and get a maximum in the exothermic heat flow, and it is indicative of an auto-acceleration in the rate-reaction which arises from autocatalysis of the epoxy/amine reaction by hydroxyl groups formed during the amine reaction [1]. It can be seen that for semi-IPNs this maximum is shifted to longer curing times. Also, the width of the maximum increases with increasing content of PPSU which reflects a slower reaction rate and it can be explained by the decreasing of reacting groups

concentration and/or by a decrease of the diffusion coefficient due to the presence of PPSU.

A well detailed description for the epoxy/amine reaction in terms of a mass-controlled autocatalytic reaction can be made with the autocatalytic model, which is a phenomenological approach developed by Kamal [2]. The general equation assumed for the curing process is:

$$\frac{d\alpha}{dt} = (k_1 + k_2 \alpha^m)(1 - \alpha)^n$$

where α is the conversion, k_1 and k_2 are the rate constants with two different activation energies; m and n are the kinetic exponents of the reactions, and $m + n$ the overall reaction order.

For the determination of the curing kinetics by means of an autocatalytic model, first, the isothermal curing is carried out at several temperatures, then the experimental rate equation (α , $d\alpha/dt$) is determined for the complete course of the reaction, and finally, the experimental results are adjusted with the kinetic equation. Thus, the reaction orders and the rate constants are obtained for each temperature. In this study, the parameters m , n , k_1 , and k_2 were estimated using the least-squares method.

Plots of the isothermal conversion, α , as a function of curing time at various PPSU content, at 80°C, are shown in Figure 2. As can be seen, they all exhibit a rapid increase in conversion, early in the cure, followed by a cessation of reaction as the material vitrifies. The kinetics parameters, obtained by fitting the isothermal data with non-linear least-squares procedures at 80 °C, are shown in Table 1. It can be seen that k_1 values are small compared with those obtained for k_2 , which is associated with proton donors that are produced during cure. The overall reaction order, $m + n$, lies in the range 2.4 ~ 2.9.

Table 1. Kinetic parameters for PPSU-modified DGEBA epoxy blends.

PPSU (phr)	k_1 (s ⁻¹)	k_2 (s ⁻¹)	m	n	$m + n$
0	0.014	0.12	1.73	1.14	2.87
5	0.013	0.15	1.52	1.35	2.87
10	0.014	0.10	1.37	1.09	2.46
15	0.010	0.10	1.29	1.09	2.38

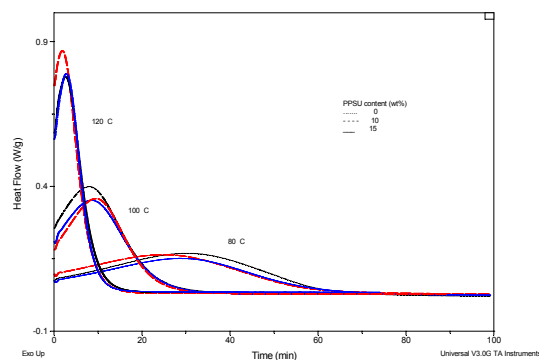


Figure 1. Curing time dependence of the heat flow during the isothermal reaction for neat system and for the semi-IPNs containing 10 or 15 phr PPSU measured by conventional DSC. The curing temperatures are indicated.

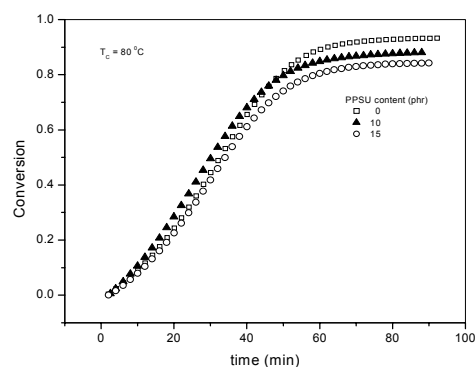


Figure 2. Curing time dependence of conversion, α , obtained from the data in Figure 1 at 80 °C.

References.

- [1] Horie K. And Hiura H., *J Polym Sci (Part A-1)* **8**: 1537 (1970).
- [2] Jungang G. and Yanfang L., *Polymer Int* **49**: 1591 (2000).