

The Effect of Epoxy Excess on the Kinetics of an Epoxy-Anhydride System

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ABSTRACT: The uncatalyzed cure of a commercial tetrafunctional epoxy monomer TGDDM (*N,N,N',N'*-tetraglycidyl-4,4'-diaminodiphenylmethane) with hexahydrophthalic anhydride (HHPA), using variable stoichiometric ratios is reported. The reaction was followed by differential scanning calorimetry (DSC). Two kinds of experiments were performed: (1) fresh samples were run at several heating rates, and (2) samples, precured a certain time in an oil bath at constant temperature (i.e., 80 to 120°C), were run at 10°C/min. Two peaks were observed in the case of the epoxy excess but only one for the stoichiometric formulation: the peak at low temperature was attributed to the epoxy copolymerization with the anhydride while the peak at high temperature was attributed to the epoxy homopolymerization. The catalytic effect of the OH groups present in the epoxy monomer on the copolymerization reaction was demonstrated by the decrease in the activation energy of the propagation step when increasing the epoxy excess. There is a catalytic effect of the copolymerization product on the homopolymerization reaction. Our simplest model, proposed previously for a catalyzed epoxy/anhydride system [*J. Polym. Sci. Part B: Polym. Phys. Ed.*, **37**, 2799 (1999)], can be used to fit both isothermal and dynamical kinetic data. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2342–2349, 2002

INTRODUCTION

A simple kinetic model was recently proposed to study epoxy/anhydride polymerization initiated by tertiary amines.¹ It enabled us to provide an explanation of the inconsistencies found in previous kinetic studies. These inconsistencies may be summarized as follows: (a) first-order kinetics can fit both dynamic and isothermal differential scanning calorimetry tests, but with significantly different values of the apparent activation energy,^{2–5} and (b) phenomenological autocatalytic kinetic expressions with different orders can also be used to fit kinetic results under both isothermal

and nonisothermal conditions, using a single value of the apparent activation energy.^{6–8} The simplest polymerization model consists of two relevant steps: a reversible reaction transforming an inactive species (*i*) into an active one (*i**), and the usual propagation step where the monomer, *m*, reacts with the active specie. In this case *m* represents a couple of epoxy and anhydride groups because, once formed, the active epoxides at chain ends react almost immediately with anhydride monomers.^{9,10} It was also assumed that the chain transfer step regenerated the active species.

In a previous study of a tetrafunctional epoxy monomer with hexahydrophthalic anhydride (HHPA), it was pointed out that OH groups, present as impurities in the technical epoxy, catalyze the epoxy-anhydride copolymerization, and that the epoxy homopolymerization reaction be-

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comes significant in formulations containing epoxy excess. Although first-order kinetics can fit both isothermal and nonisothermal experiments, there was no coincidence between the calculated activation energy values.¹¹

The aim of this article is to present and discuss experimental results related to the cure of a commercial tetrafunctional epoxy monomer with HHPA anhydride, using variable stoichiometric ratios, applying the model previously described and introducing the homopolymerization reaction in the kinetic model.

EXPERIMENTAL

Materials

The epoxy monomer used consisted mainly of *N,N,N',N'*-tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM, Ciba-Geigy MY-720). The mass per epoxy group was 120.1 g, as determined by titration with perchloric acid. The theoretical value for pure TGDDM was 105.5 g, meaning that a significant amount of impurities is present in the commercial product. These have been identified as chlorohydrins, glycols, dimers, trimers, and higher oligomers.^{12,13} The presence of a broad band at 3500 cm⁻¹ in the FTIR spectra showed that the product contains a significant concentration of OH groups. The mass per epoxy equivalent is 60.05 g/eq.

The commercial anhydride used in this study was hexahydrophthalic anhydride (HHPA, Fluka) that had a melting point of 30–32°C and a theoretical mass per anhydride equivalent equal to 77 g/eq.

Techniques

Sample Preparation

Before mixing with anhydride, the epoxy monomer was degassed under vacuum for about 10 min at 50°C. The stoichiometric ratio was defined as:

$$r = \text{anhydride equiv/epoxy equiv}$$

Samples with *r* equal to 1, 0.7, 0.5, and 0.1 were analyzed. TGDDM-HHPA samples were prepared by mixing both components for about 10 min at 50°C. The solution remained homogeneous at room temperature, meaning that HHPA crystallization was inhibited upon cooling. It was veri-

fied that the reaction was not advanced during the mixing period.¹¹

Differential Scanning calorimetry (DSC)

DSC measurements were performed under nitrogen atmosphere with a Shimadzu DSC-50, calibrated by standard procedures. Two kinds of experiments were performed: (1) fresh samples were run at different heating rates, *q*, varying between 0.5 and 20°C/min, and (2) samples with *r* equal to 0.5 and 0.7 precured a certain time in and oil bath at constant temperature (i.e., 80 to 120°C), were run at 10°C/min. Total and residual heat were obtained from these thermograms. Also, in both cases, the glass transition temperature, *T_g*, was measured in a second scan at 10°C/min.

Dynamic-Mechanical Thermal Analysis (DMTA)

Plaques for subsequent dynamic mechanical characterization were obtained in a mold consisting of two glass plates coated with siliconized paper, spaced by a 2.5 mm rubber cord, and held together with clamps. The cure cycle employed was 2 h at 120°C and 2 h at 200°C. Specimens with dimensions 20 × 3.3 × 2.5 mm, were machined from the plaques. Dynamic mechanical spectra were obtained with a Perkin-Elmer DMA-7 system, operating at 1 Hz in the three-point mode at a heating rate of 10°C/min.

Fourier-Transformed Infrared Spectra (FTIR)

Filings of the plaques obtained for dynamic mechanical characterization were used to prepare KBr pellets of materials with *r* ≤ 1. Fourier-transformed infrared spectra were obtained in a Mattson Genesis II device in the 400–4000 cm⁻¹ range with a resolution of 2 cm⁻¹.

RESULTS AND DISCUSSION

DSC scans of fresh samples prepared with different *r* ratios were made at several heating rates. Thermograms of samples prepared with epoxy excess (*r* < 1) and cured at *q* < 10°C/min show a shoulder at high temperatures. Figure 1 allows us to compare the symmetric aspect of the curve corresponding to the stoichiometric sample with the two peaks scan obtained with the epoxy excess. Bouillon et al. observed two peaks in the case of the epoxy excess but only one for *r* ≥ 1, in