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Comparative DSC kinetics of the reaction of DGEBA with aromatic diamines.

I. Non-isothermal kinetic study of the reaction of DGEBA with *m*-phenylene diamine

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Abstract

The reaction kinetics of different epoxy–aromatic diamine systems is a of great importance in the processing of the so called high-technology composite materials. Since the epoxy–amine reaction is strongly exothermic, at moderate and high temperatures it proceeds in significant gradient. Therefore, the processing requires substantial knowledge of the reaction kinetics under programmed temperature conditions.

Differential scanning calorimetry (DSC) is the only direct reaction rate method which operates in two modes: constant temperature or linear programmed mode. This permits two kinds of kinetic analysis to be performed. The second technique is simply known as non-isothermal kinetics. Up to now, it is not sufficiently elucidated with regard to the epoxy–amine reaction although highly reproducible experimental data are possible to acquire.

The first part of the present study concerns the non-isothermal reaction kinetics of an epoxy resin based on diglycidyl ether of bis-phenol A (DGEBA) with *m*-phenylene diamine (mPDA). In order to obtain reliable data, we performed a mechanistic-like four stage kinetic analysis consisting of: (i) multiple curve methods involving different heating rates (also known as isoconversional or apparent kinetic methods); (ii) analysis at the peak maximum of the DSC curves; (iii) integral and differential single curve methods; and (iv) modeling of the reaction and comparison of the model with the experiment.

The apparent activation energy, $E_{ap} = 52.3\ \text{kJ mol}^{-1}$, was calculated applying isoconversional methods. The analysis at the peak maximum temperatures of the DSC curves was carried out with the aid of E_{ap}. It validated the overall three molecular velocity equation of the reaction under programmed temperature regime rejecting other possible kinetic models – lower than three ‘overall reaction order’ autocatalytic and bimolecular non-catalytic ones. The velocity equation of the form: $d\alpha/dt = K_0 \exp(-E_a/RT)(B + \alpha)(1 - \alpha)^2$, was evaluated using single DSC curve methods, i.e. the activation energy, E_a, the pre-exponential factor, K_0, and the initial hydroxyl to epoxy ratio, B, were determined at different scanning rates. Modeling of the reaction in programmed temperature mode showed that reliable set of kinetic data, $E_a = 50.5\ \text{kJ mol}^{-1}$, was obtained at heating rates below $5\ \text{K min}^{-1}$.

The isoconversional methods indicated that side reaction at high degrees of conversion probably took place, whereas the single DSC curve kinetics exhibited non-typical false kinetic compensation effect above $5\ \text{K min}^{-1}$. The modeling predicted incomplete curing at the end of the scanning experiments which was supposed to be one of the reasons for the latest findings.

As a result, this four stage kinetic analysis enabled us to ascertain the three molecular autocatalytic model of the reaction between DGEBA and mPDA, as well as to measure its overall kinetic parameters under programmed temperature conditions.

Keywords: Epoxy–amine reaction; Non-isothermal DSC; Autocatalytic kinetics

1. Introduction

The study of Horie et al. [1] was the first important investigation on the isothermal DSC kinetics of the epoxy–amine addition. Assuming three molecular hydroxyl complex in transition state, the third-order autocatalytic kinetics of this reaction, first proposed by Smith [2], was confirmed and methods for processing of experimental, mostly DSC data, were developed. The approach of Horie et al. is widely used for solving the inverse kinetic problem of different epoxy–amine reactions and even HPLC, FTIR,

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