



The kinetic study and thermal characterization of epoxy resins crosslinked with amino carboxylic acids



Fanica Mustata*, Nita Tudorachi, Ioan Bicu

"P. Poni" Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda, No. 41 A, Iasi 700487, Romania

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ABSTRACT

The curing kinetics and thermal properties of two epoxy resins crosslinked with two amino acids (at molar ratio epoxy ring/amine or carboxylic proton 1/1), by non-isothermal differential scanning calorimetry (DSC) and simultaneous TG/FT-IR/MS analysis were studied. The kinetic analysis of the curing reactions was made using the variable peak exotherm methods of Flynn–Wall–Ozawa and Kissinger and multivariate non-linear regression. The most probable kinetic model and kinetic parameters of the degradation process using a multivariate non-linear regression program (Netzsch Thermokinetics software) were determined. The kinetic parameters and the thermal degradation mechanisms for crosslinked resins taking place in 2 and 3 steps, depending on the chemical structure of the sample were identified.

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1. Introduction

The epoxy resins are some of the first synthetic resins commercialized since 1946. These materials are among the most important thermosetting materials which after cure possesses important physico-chemical characteristics, as excellent mechanical strength, thermal, electrical and chemical behavior, coupled with good adhesion to various substrates (metal, ceramic, textile, and plastic materials) and moisture proof. These features allow their use in a very wide range of applications as: adhesives, civil construction composite materials, materials in machine building including automotive and ship, packaging materials for electronic devices, as well as in medicine or home fields [1–6].

Mainly, these compositions are based on various epoxy resins and various crosslinking agents, to which other materials (catalysts, polymeric or inorganic fillers, reactive organic diluents, colorants, etc.), with the purpose of inducing some specific properties are added. The ultimate properties of the crosslinked products depend both on the chemical composition of the mixture as well as the crosslinking conditions. Informations about the curing kinetics and thermal stability to achieve the desired characteristics are necessary. Epoxy resins with different kinds of curing agents can be cured. The usual curing agents used in the presence or absence of catalysts are aromatic or aliphatic amines and multifunctional acids or anhydrides [7]. Usually, the crosslinking agents are toxic

materials. *p*-Aminobenzoic acid (*p*AABA) and aspartic acid (ASA) are generally less toxic substances, suggesting safer operations with them, when are used as crosslinking agents for epoxy resins [8,9]. A survey of literature shows that only few articles are published, where the cross linking agents possess in their chemical structure both amine and acidic groups [10,11].

The main objective of the present article is to report the results of cure kinetics of two epoxy resins with two amino acids as hardeners, using non-isothermal DSC measurements and also the determination of the thermal degradation kinetic parameters of the cured products, using simultaneous TG/FT-IR/MS analysis.

2. Materials and methods

2.1. Materials

Triethylbenzylammonium chloride (TEBAC), *p*AABA and ASA were analytical grade products and used without being preliminary purified. The epoxy resins were diglycidyl ether of bisphenol A (DGEBA) (Sintofarm, Bucharest), commercial product with an epoxide number of 0.515 mol 100 g⁻¹ and diglycidyl ether of hydroquinone (DGEHQ) (synthesized as described in our previous published article [12]) with epoxide number of 0.757 mol 100 g⁻¹.

2.2. Preparation of the cured epoxy resins

The chemical structures of epoxy resins and curing agents are listed in Table 1. Epoxy resins and curing agents accurately weighed at 1/1 epoxy ring/amine or carboxylic proton molar

* Corresponding author. Tel.: +40 232 211299; fax: +40 232 211299.
E-mail address: fmustata@icmpp.ro (F. Mustata).

Table 1
Chemical structure of epoxy resins and curing agents.

Components	Chemical structures
Diglycidyl ether of bisphenol A	
Diglycidyl ether of hydroquinone	
<i>p</i> -Aminobenzoic acid	
Aspartic acid	

ratio, were manually homogenized in the presence of catalytic amount of TEBAC to form four mixtures DGEBA/*p*ABA, DGEBA/ASA, DGEHQ/*p*ABA and DGEHQ/ASA. After homogenization, the weighed samples having between 7 and 10 mg, were placed in aluminum crucibles and used to record DSC curves, in nitrogen atmosphere at the programmed heating rates. The remaining samples were cured at 100 °C for 1 h, at 120 °C for 1 h and post cured at 180 °C for another 4 h. The cured samples were ground as fine grains, in order to obtain specimens for thermal analysis.

2.3. Methods

The epoxide number was obtained by titration with hydrogen bromide in situ using ASTM D 1652-04 method and expressed in moles 100 g⁻¹ [13].

The extent of the curing reactions was carried out by means of DSC 912 Du Pont Instrument apparatus at different heating rates (5, 10, 15 °C min⁻¹), between 20 and 350 °C under nitrogen atmosphere (50 mL min⁻¹). A small quantity of sample was closed in the aluminum cell and heated in the presence of aluminum empty cell as reference, in order to cure the epoxy resins and recording the data for kinetic analysis. Kinetic parameters were estimated from DSC thermograms using the variable peak exotherm temperature method of Kissinger and Ozawa [14–16]. These methods permit to calculate the kinetic parameters using the fact that at the maximum reaction rate (at the peak temperatures), the degree of conversion is constant, independently of the heating rates. These assumptions are incorporated in the following equations:

$$E_K = \frac{-Rd[\ln(\frac{\beta}{T_M^2})]}{d(1/T_M)} \quad (1)$$

and

$$E_0 = -0.9505 Rd(\ln\beta)/d(1/T_M) \quad (2)$$

where E_K and E_0 represent the activation energy for the curing reactions obtained using Kissinger and Ozawa methods, A is the pre-exponential factor, β is the heating rate, C is a constant, T_M is the maximum exothermic peak temperature and R is the gas constant.

The activation energy and the pre-exponential factor for the curing reactions were obtained from the graphs $\ln\beta$ versus $1/T$ and $\ln(\beta \cdot T_M^{-2})$ versus $1/T$. The E values calculated with the Kissinger method show lower values than values calculated with Ozawa method. This fact is due to different approximation methods used to solve the initial equation.

The crosslinking reactions of the epoxy resins are complex reactions which occur in many steps. Because the DSC curves shape suggest the presence of several steps, the multivariate linear regression with non-Runge–Kutta of 6th degree process in a modified Marquardt procedure given in the “Thermokinetics 3” software, was used. In the first phase, this software allows the overlapping of the 16 incorporated formal kinetic models over the experimental data. In the second phase, complex kinetic models with two or multiple steps in the processing of the experimental data were used.

The thermal degradation measurements (simultaneous TG/FT-IR/MS analyses) were performed under dynamic conditions using STA 449 F1 Jupiter apparatus (Netzsch, Germany) at three heating rates (5, 10 and 15 °C min⁻¹) under nitrogen atmosphere at flow rate of 40 mL min⁻¹. The samples (10–15 mg) were placed in open Al₂O₃ crucibles and heated from 30 to 650 °C for each rate. The evolved gases were identified using the online connected FT-IR apparatus (Vertex 70) and Aeolus QMS 403C mass spectrometer (Netzsch, Germany). The FTIR transfer line (heated at 190 °C) is made of polytetrafluoroethylene tube with 1 m length and 1.5 mm diameter. The evolved gases are transferred in TGA-IR external modulus equipped with MCT detector (mercury cadmium telluride) cooled with liquid-nitrogen, the spectra being recorded on the range of 600–4000 cm⁻¹, with a resolution of 4 cm⁻¹. OPUS 6.5 software was used to acquire of the FT-IR 3D spectra. The gas transfer line to the mass spectrometer is made of quartz capillary, with 75 μm diameter and 2 m length, heated at 250 °C. The mass spectrometer works at 10⁻⁵ mbar vacuum and electron impact ionization energy of 70 eV. Aeolus® 3.2 software, in the range of $m/z = 1–200$, was used for the data acquisition.

In thermogravimetric analysis (TG) it can be considered that the materials decompose generally according to the next scheme:



The thermal degradation is an irreversible phenomenon, arising after a series of consecutive, competitive or parallel reactions. When TG is used for the kinetic study of thermal degradation, the rate of the release of degradation products is measured. The degree of conversion (α) as the mass loss is defined as the ratio of actual weight loss at time t to the total weight loss corresponding at the end of the degradation process (Eq. (4)):

$$\alpha = \frac{M_0 - M_t}{M_0 - M_f} \quad (4)$$

where M_0 – the initial weight of sample, M_t – the sample weight at time t and M_f is the sample weight after complete degradation.

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