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Curing kinetics of solid epoxy/DDM/nanoclay: Isoconversional models versus fitting model

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ABSTRACT

The curing behavior and kinetics of epoxy nanocomposites based on solid epoxy, diaminodiphenyl methane (DDM) and nano organoclay were studied. The curing kinetics of epoxy nanocomposites was elucidated by non-isothermal differential scanning calorimetry. The fitting model was used to calculate the kinetic parameters. The kinetics of the curing reaction was also evaluated by two different isoconversional models. The kinetic parameters calculated from fitting model were almost the same for neat epoxy system and nanocomposite systems indicating that the curing kinetics was not affected by the presence of nanoclay particles. However, the isoconversional models showed that the incorporation of nanoclay particles into the epoxy/DDM system had a significant effect on the trend of activation energy during the curing process. Therefore, it can be concluded that using isoconversional models would be a preferred method to elaborate the effect of nanoparticles on the curing mechanism of nanocomposite systems.

1. Introduction

Epoxy resins have substantially used in different industries because they outperform most other resin types in great chemical, moisture and solvent resistances, good thermal and dimensional stabilities and a high adhesive strength to most substrates [1–3]. Besides the properties of epoxy resin, elucidation of the reaction mechanisms of epoxy-amine cure is still a subject of great interest for both fundamental and applied reasons [4]. Reactions of epoxy resin with amines are widely used for thermoset systems but the curing mechanisms are still not completely understood. This complexity makes difficult the kinetic approach to the reactions. For these reasons, epoxies have been the subject of many theoretical and experimental investigations. These studies have a great importance for both challenging questions about very basic knowledge of curing aspects and also obtaining useful information for the production of epoxy materials with improved properties. Particularly, the influence of side reactions such as etherification or homopolymerization has been the subject of numerous contradictory results. Competitive chemical reactions accompanied by complex physical phenomena occur during curing, when the system passes from a mixture of linear and branched oligo- and polymers into a single three-dimensional macromolecule [5–7]. These reactions would be more complicated when solid epoxy was used, specifically in the presence of nanoparticles such as nanoclay and nano silica. These nanoparticles are usually used to improve the mechanical, thermal and chemical properties of epoxy resins. Several researchers have studied epoxy/clay nanocomposite systems. One of the main important steps in epoxy–clay nanocomposite synthesis consists of organophilication of the clay in order to improve the compatibility of nanoclay particles with epoxy resins. The most popular intercalants are compounds based on onium ions, which contain an amine cation and a long hydrocarbon chain [8]. There is a possibility that the presence of intercalants may affect on the curing process, therefore a deep understanding of curing mechanism for these systems is necessary. Worth mentioning that cure kinetics is the key for obtaining an optimal temperature program for the curing process which allows one to model the reaction process as accurately as possible [9]. Becker et al. [10] studied the curing kinetics of different epoxy resins with various functionalities (i.e. triglycidyl p-amino phenol (TGAP), diglycidyl ether of bisphenol A (DGEBA) and tetraglycidyl diaminodiphenyl methane (TGDDM)) in the presence of an organoclay using differential scanning calorimetry. It was shown that the organoclay particles influenced the epoxy self polymerization and this effect was more drastic in DGEBA system comparing to the others. The curing of trifunctional epoxy nanocomposites was investigated by Pages et al. [11] by means of FTIR spectroscopy. They demonstrated that the onium ions catalyzed the intragallery epoxide polymerization process. The curing study of the DGEBA with Jeffamine D-230 was carried out by Brnardic et al. [12]. They observed that the total heat of reaction

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decreased with the increasing of clay content. Lelli et al. [9] have investigated the modeling of the chemo-rheological behavior of the epoxy/cycloaliphatic amines/montmorillonite system. In addition, the effect of nanoclay concentration on the cure behavior of epoxy/aromatic amine was investigated using an on-line dielectric cure monitoring technique [13]. Xu et al. [14] studied the curing kinetics of epoxy/imidazole nanocomposites in isothermal mode and analyzed the results by the modified Avrami equation. In all the above mentioned studies a liquid epoxy resin was used and the curing reaction was evaluated using only one kinetic approach.

The aim of this work was to investigate the curing kinetics of a solid epoxy/DDM/clay using two different approaches, i.e. model free kinetics and fitting model kinetic. For this purpose two different organically modified nanoclay particles were employed. In addition, the structure of nanocomposites was studied by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The differential scanning calorimetry technique was employed to study the cure mechanism and the cure kinetics of the nanocomposites.

2. Kinetic analysis

The reaction rate equations based on power law model usually consist of two different independent functions, namely temperature function ($k(T)$) and fractional conversion function ($f(\alpha)$) as showed in Eq. (1) [15],

$$\frac{d\alpha}{dt} = f(\alpha)\cdot k(T) \tag{1}$$

The dependency of the rate constant, k, on temperature is traditionally described by Arrhenius equation. The function of fractional conversion ($f(\alpha)$) is usually estimated by terms of an autocatalytic mechanism for the curing of epoxy resins [16,17]. Therefore the autocatalytic rate expression is proposed as in Eq. (2) [18]:

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E}{RT}\right)\alpha^m(1-\alpha)^n \tag{2}$$

where A is the pre-exponential factor, E is the activation energy, R is the universal gas constant, T is the absolute temperature, m and n are reaction orders. To take into account the autocatalytic behavior, i.e. the initial reaction rate of the autocatalytic reaction is not zero, Kamal proposed the generalized expression that is shown in Eq. (3) [19]:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)\cdot(1-\alpha)^n \tag{3}$$

where

$$k_1 = A_1\exp\left(\frac{E_1}{RT}\right) \tag{4}$$

$$k_2 = A_2\exp\left(\frac{E_2}{RT}\right) \tag{5}$$

In addition, isoconversional methods are usually used to study the activation energy behavior of curing reactions precisely. These models allow us to evaluate the effective activation energy as a function of the extent of reaction (i.e. α). If changes in the cure mechanism are associated with the changes in the activation energy, they can be detected using an isoconversional method [20,21]. The isoconversional principle states that the reaction rate at a constant extent of conversion is only a function of temperature [22]. Isoconversional models can be treated in two different ways namely differential method and integral method [23]. In differential method, the common equation proposed by Friedman can be expressed as in Eq. (6) [24]:

$$\ln\left(\beta\frac{d\alpha}{dT}\right)_{\alpha,I} = \ln[A_\alpha f(\alpha)] - \frac{E_\alpha}{RT_{\alpha,i}} \tag{6}$$

Table 1
Samples' code and their specifications.

Code	Epoxy resin (g)	DDM (g)	Clay content (phr)	Clay type
ED	100	7.6	0	NA
ED-3I	100	7.6	3	I.30 E
ED-5I	100	7.6	5	I.30 E
E-3I	100	0	3	I.30 E
E-5I	100	0	5	I.30 E
ED-3C	100	7.6	3	Closite 30B
ED-5C	100	7.6	5	Closite 30B
E-3C	100	0	3	Closite 30B
E-5C	100	0	5	Closite 30B

where β is the heating rate, the subscript i denotes to the ordinal number of non-isothermal experiments conducted at different heating rates and the subscript α denotes the quantities evaluated at a specific conversion degree. In this method E_α is calculated from the slope of $\ln(\beta\, d\alpha/dT)$ versus $1/T$ plot at a specific value of α.

On the other hand, one of the most accurate equations based on integral method is the Advanced isoconversional method which is proposed by Vyazovkin [6,25]. In this method, the reaction model is assumed to be independent of the heating program. According to this assumption, the J-integrals in each value of α are equal for all experiments that carried out under different arbitrary temperature programs, $T_i(t)$. The E_α value is determined as a value that minimizes the function $\varphi(E_\alpha)$ (i.e. Eq. (7)),

$$\varphi(E_\alpha) = \sum_{i=1}^{s}\sum_{j\neq i}^{s}\left[\frac{J(E_\alpha, T_i(t_\alpha))}{J(E_\alpha, T_j(t_\alpha))}\right] \tag{7}$$

where

$$J(E_\alpha, T_i(t_\alpha)) = \int_{t\alpha-\Delta\alpha}^{t\alpha}\exp\left[-\frac{E_\alpha}{RT_i(t)}\right]dt \tag{8}$$

where the subscript i and j denote different heating rates, s is the total number of heating rates [22].

3. Experimental

3.1. Materials

The main materials used in this investigation were a solid DGEBA-based epoxy resin (with EEW=650 g/mol) and diaminediphenylmethane (DDM) as curing agent. The epoxy resin and DDM were obtained from Huntsman and BASF, respectively, and used as received. Two organically modified nanoclay recommended for use with amine-cured epoxy systems, namely Nanomer I.30E (montmorillonite treated with octadecyl amine, a primary amine base) and Nanomer Closite 30B (montmorillonite treated with methyl tallow bis-(2-hydroxyethyl) quaternary ammonium) from Nanocor were used.

3.2. Preparation of Samples

The appropriate amounts of organoclay particles and epoxy resin were mixed in an internal mixer at 80 °C for 10 min. Then the sample was cooled and the stoichiometry amount of DDM was added into them and milled for 30 min. The nanoclay content in the epoxy resin was chosen to be 3 and 5 phr based on the epoxy resin. Samples specifications and their codes are given in Table 1.

3.3. Measurements

X-ray diffractometer (Philips Xpert) was used to analyze the nanostructures of the epoxy/clay nanocomposites. The XRD