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Modeling and simulation of curing kinetics for the cardanol-based vinyl ester resin by means of non-isothermal DSC measurements

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ABSTRACT

The cure kinetics of vinyl ester–styrene system was studied by non-isothermal differential scanning calorimetric (DSC) technique at four different heating rates. The kinetic parameters of the curing process were determined by isoconversional method for the kinetic analysis of the data obtained by the thermal treatment. Activation energy ($E_a = 56.63$ kJ mol^{-1}) was evaluated for the cure process and a two-parameter (m, n) autocatalytic model was found to be the most adequate to describe the cure kinetics of the studied cardanol-based vinyl ester resin. Non-isothermal DSC curves, as obtained by using the experimental data, show good agreement with the DSC curves obtained by theoretically calculated data.

1. Introduction

Worldwide potential demands for replacing petroleum derived raw materials with renewable plant based products in the production of polymers are quite significant in the social and environmental viewpoint. Due to increasing concern about the tight legislation on the maintenance of greenness in industry processes led us to develop a method using a material that is less hazardous, non-toxic, cheap, and benign to the environment, in the last few years. Cashew nut shell liquid (CNSL) has gained importance in the development of sustainable material which acts as an excellent monomer for thermosetting polymer production [1,2].

Cardanol (*Anacardium occidentale* L.), a phenol derivative having a meta substituent of a C_{15} unsaturated hydrocarbon chain with one to three double bonds, is a major component of CNSL [3,4]. Because of this phenolic nature, cardanol reacts with formaldehyde to form both base-catalysed resoles and acid-catalysed novolacs [1–9]. The cardanol based novolac-type phenolic resins may be modified to develop epoxy resins with epichlorohydrin to enhance the performance of such resins in various fields [10–16]. The introduction of unsaturation at the end of the epoxy resin backbone by the reaction with acid functional acrylic/methacrylic monomer can produce an eco-friendly vinyl ester resin system [17–19].

Vinyl ester resins (*VERs*) are free-radical polymerizing thermosets, which are structurally similar to unsaturated polyester resins (*UPE*) with developed to overcome chemical resistance shortcomings of *UPE* resin. As a result of this relationship due to *UPE* resins have been studied in greater depth than *VERs*, numerous characteristics of the *UPE* cure have been attributed to *VER* cure as well. In conventional polyester resins, the ester groups and C–C double bonds are located along the polymer chains and are distributed randomly in the polymer network formed after copolymerization and cross-linking with styrene. In *VERs*, the ester units and methacrylate type double bonds are located only at the end of vinyl ester monomers. Its resistance to degradation by corrosive and hostile environment leads to the use of *VERs* in many applications, such as: in swimming pools, sewer pipes and solvent storage tanks, and thus *VERs* are of considerable interest [20–23]. Vinyl ester systems can be cured at room or elevated temperatures [24].

Curing of *VERs* is a free-radical induced process [25,26] and it starts as the initiator thermally decomposes, releasing free radicals in the system. The role of free-radicals is to link two adjacent vinyl esters to extend the chain by connecting styrene molecules via inter- and intra-molecular reactions. The long chain formed is supposed to have a spherical structure which is due to intramolecular bonding between the C=C bonds of the vinyl ester molecules [25]. In such reactions it is very interesting to follow the progress of the reaction to reach optimal curing. This is due to the fact that any residual unsaturation is considered as a site for degradation or oxidation. Selection of cure conditions is motivated by processing and economic considerations.

Studying the cure behavior begins with studying the cure kinetics of the resins. Vital clues regarding the structure of the network

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can be obtained from the kinetics of cure, which is believed to have significant effect on the development of the network and the resulting material behavior [27]. It is difficult to model the cure kinetics of cross-linking free-radical polymerization [28] because of the competing reactions among the initiators, inhibitors, and comonomers, the heterogeneities during network formation and diffusion limitations. It is of great practical importance to understand the cure kinetics of such systems, to which several reports have been devoted [29–35]. At present, there are primarily two kinds of models used to simulate the reaction rate profiles of *VERs*: autocatalytic models [36–38] and mechanistic models [39–41]. Mechanistic models have many parameters and are not easy to use in process simulations [42]. The autocatalytic models developed by Kamal and Sourour [42] have been used by many researchers to simulate the reaction rate. The literature on cure kinetics and the applications of kinetic models are still untouched for cardanol-based *VERs* inspite of its growing use in various applications.

Differential scanning calorimetry (DSC), which measures the heat flow of the sample as function of temperature and time, has extensively been used to study the cure kinetics of various thermosetting polymers [43–49]. An optimal curing process depends on understanding the curing kinetics, the curing mechanism and accurate modeling of the curing process. This modeling includes determination of the mechanism, or appropriate kinetic equation for an analyzed system, measurement of reaction order and activation energies of the reaction. By assuming that the heat evolved during cure is proportional to the extent of the reaction, the kinetic parameters have been determined by fitting the experimental rate data to the kinetic model using a linear or non-linear regression method. The regression techniques require detailed information relating to the reaction rate as a function of time at any given temperature. In fact, the success and convergence of many regression schemes depends critically on the boundary conditions and the initial assumed values [50,51].

An appropriate method must be used to measure accurately the cure kinetics parameters viz., the degree of conversion (α), conversion rate ($d\alpha/dt$) and the apparent activation energy (E_a). The rate of conversion can, therefore be defined as follows:

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_{Rxn}} \tag{1}$$

where ΔH_{Rxn} is the total heat of reaction.

The present paper reports the cure kinetics of the cardanol-based vinyl ester/styrene system and determination of the kinetic parameters of the cure reaction from non-isothermal DSC measurements, applying the simple and consistent method [52,53] on kinetic analysis of the data obtained by the thermal treatment. The used method allowed us to select the most convenient model for the curing reaction (Šesták–Berggren equation) of the studied system [54].

2. Experimental

2.1. Materials

Cardanol (M s^{-1} Dheer Gramodyog Ltd., Kanpur), formaldehyde (40% solution from M s^{-1} Qualikem Industries, New Delhi), *p*-toluene sulphonic acid (*PTSA*) obtained from M s^{-1} E. Merck, New Delhi, Methanol (BDH), epichlorohydrin (M s^{-1} Ranbaxy Laboratories Ltd., Punjab), sodium hydroxide, methacrylic acid and triphenylphosphine (from M s^{-1} CDH Pvt. Ltd., New Delhi), styrene, benzoyl peroxide and hydroquinone (from M s^{-1} E. Merck, New Delhi) were used during the investigation.

2.2. Synthesis of cardanol-based vinyl ester resin

Cardanol-based vinyl ester resins (*CNEVERs*) were prepared by using 1:0.9 mol ratio of indigenously synthesized cardanol-based epoxidised novolac resin [3] and methacrylic acid. The reaction was carried out in the presence of triphenylphosphine (TPP) catalyst (1 phr by weight of the resin) and hydroquinone (200 ppm as inhibitor) at 90 °C in nitrogen atmosphere, and the progress of the reaction was monitored by determining the acid value intermittently by the method of Ogg et al. [55]. In order to remove the free methacrylic acid, the prepared resin was dissolved in benzene and treated with potassium carbonate, stirring for 2 h at 30 °C. The acid – in the form of an acid salt – was extracted by water and benzene was evaporated using a Rotovap^{TM} evaporator under vacuum [56]. The resin was characterized for their structures by FTIR spectroscopy (PerkinElmer FTIR, RX-1 spectrophotometer). This was investigated in our previous publication [57] and the structure of cardanol-based vinyl ester resin was elucidated as given in Scheme 1.

2.3. DSC measurements

Cardanol-based vinyl ester resin, styrene, and benzoyl peroxide were mixed in the ratio of 10:4:0.2, at room temperature and stored at −13 °C. The weighed samples (20–30 mg) was placed in the DSC cell and analyzed at the various heating rates of 2.5, 5.0, 7.5 and 10 °C min^{-1} as per ASTM E-698 method. The data of thermal curing were obtained by means of a TA Instrument, USA; Model DSC 2920 heated from 35 °C to 200 °C with different heating rates in nitrogen atmosphere. Pure indium was used as a standard for calorimetric titration. An identical empty aluminium hermetic pan was taken as reference. The heat flow data, as a function of temperature and time, were obtained using the area under the peak of the exotherm. These were processed further to obtain the fractional conversion (α) and the rate of reaction ($d\alpha/dt$).

The rate of the kinetic process can be described by Eq. (2) [43,53]:

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \tag{2}$$

where $K(T)$ is a temperature-dependent reaction rate constant and $f(\alpha)$ a dependent kinetic model function. There is Arrhenius type dependence between $K(T)$ and temperature according to Eq. (3).

$$K(T) = A\ \exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

where A is the pre-exponential factor and E_a is the apparent activation energy.

For non-isothermal conditions, when the temperature varies with time at constant heating rate ($\beta = dT/dt$), Eq. (2) is modified as follows:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\ \exp\left(-\frac{E_a}{RT}\right)f(\alpha) \tag{4}$$

Usually, E_a values were determined using the integral forms of Eq. (4), the most popular derivative modes being those proposed by Ozawa [58], Flynn and Wall [59], and Doyle [60], which gave E_a from the plot $\ln\beta_i$ against $T_{\alpha,i}^{-1}$ (i is the ordinal number of DSC runs performed at different heating rates, β_i). Generally, the E_a values found by these equations require further corrections [61], which could be avoided using the methods suggested by Coats–Redfern approximation [62], according to which the E_a was evaluated from the plot $\ln(\beta_i/T_{\alpha,i}^2)$ against $T_{\alpha,i}^{-1}$ where $T_{\alpha,i}$ were the temperatures corresponding to different values of α. The experimentally evaluated values of E_a were used to find the appropriate kinetic model which best described the conversion function of the process studied.

The kinetic parameters of the curing process were determined by the isoconversional method given by Málek [52,53]. Once E_a has