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Phthalonitrile-based resin for advanced composite materials: Curing behavior studies

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Phthalonitrile-based resins play important roles in advanced materials due to their outstanding properties, which would be determined by the curing process and curing mechanisms. Thus, in this work the curing behaviors of phthalonitrile-based resin containing benzoxazine were investigated and the kinetic parameters were determined by non-isothermal differential scanning calorimetry (DSC) at various heating rates. Sequential double exothermic thermograms were separated by PeakFit v4.12 and analyzed as independent reaction processes. The kinetics model of each reaction was evaluated by multi-heating-rate DSC methods assisted with the iso-conversion method, and an autocatalytic model for the curing reaction of BA-ph resin was confirmed. The curing kinetics parameters including activation energyE_α, pre-exponential factor A, reaction orders m and n were evaluated and calculated. The activation energies for reactions of benzoxazine and nitrile groups were 102.2 and 90.6 kJ/mol with reaction orders approximately 1.8 and 2, respectively. Additional, the predicated mathematical models for curing reactions of benzoxazine and nitrile groups were obtained and fitted well with the experimental data derived from the non-isothermal DSC thermograms.

1. Introduction

Phthalonitrile-based resins continue to play an important role in several key industries including aerospace, ships and warships, microelectronics and optoelectronics because of their outstanding thermal and mechanical properties, as well as the versatility in tailoring desired properties [1,2]. As a novel phthalonitrile-based resin, phthalonitrile containing benzoxazine (BA-ph) has attracted increasing interesting both in academic and manufacture, due to its self-curing polymerization and outstanding processability and thermal stability [3–6]. In order to make on optimum use of this kind of phthalonitrile-based resin, understanding and accurate controlling of the curing process is a pre-condition to select the suitable process parameters and obtain the optimum properties [7,8]. The curing reactions, especially for the thermosetting resins, are very complex processes because many reactive processes occur simultaneously [9,10]. Also, the final properties of the crosslinked phthalonitrile-based resins depend significantly on the curing kinetics of the polymerizations concerned with the extent of curing degree, the curing conditions and so on [11,12]. Therefore, the study of the curing kinetics of phthalonitrile-based resins contributed to both a better knowledge of process development and the nature of their curing process, the structure of the cured material, and how its kinetic parameters can be influenced by temperatures, etc.

Several techniques have been utilized to examine curing kinetics of phthalonitrile-based resins including differential scanning calorimetry (DSC) [13,14], Fourier Transform Infrared Spectroscopy (FTIR) [9] and rheokinetic measurements [15]. Among these, the DSC techniques have been the most utilized methods to determine the curing kinetics parameters and rate equations of the polymerization of phthalonitrile-based resins [14,16,17]. In general, the kinetic parameters estimated from DSC dynamic experiments were reported to agree well with those estimated by other techniques. As a precise measure, non-isothermal DSC method has been carried out at various heating rates to evaluate the curing kinetic parameters [9]. Due to the fact that the kinetic data can be obtained in a relatively short period of time, the method has attracted increasing interesting [7,18]. Therefore, in this work, curing kinetics of phthalonitrile-based resin containing benzoxazine was studied via the non-isothermal DSC technique, assisted with the peak-fitting method. Additional, the non-isothermal DSC thermograms were

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verified and confirmed by the predicated curves, which were derived from the kinetics parameters and rate equations.

2. Experiment

2.1. Materials

The phthalonitrile-based resin containing benzoxazine (BA-ph) based on bis-phenol A, formaldehyde and 3-aminophenoxyl-*o*-phthalonitrile was synthesized with 1, 4-dioxide and Methylbenzene as the solvent. Bis-phenol A and formaldehyde were obtained from Chengdu Kelong chemicals Co. Ltd, Chengdu, China. 1, 4-dioxide and Methylbenzene were purchased from Shanghai Bodi chemical Co. Ltd, Shanghai, China. 3-aminophenoxyl-*o*-phthalonitrile was obtained from Chengdu Dymatic fine chemical co., Ltd, Chengdu, China. The chemical structures of the initial materials and BA-ph were shown in Fig. 1.

2.2. DSC measurements

A differential scanning calorimeter model 2910 from TA Instruments was employed to study the exothermic curing reaction of phthalonitrile-based resin. The samples were scanned by non-isothermal method from 50 to 350 °C at various heating rates of 5, 10, 15 and 20 °C/min under a constant flow of nitrogen at 50 mL/min.

2.3. Kinetic analysis

Kinetic analysis of non-isothermal resin-cured system is based on the rate equation

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

Where, $k(\mathrm{T})$ is a temperature-dependent reaction rate constant, $f(\alpha)$ is the differential conversation function depending on the curing mechanisms. The rate constant$k(\mathrm{T})$, is temperature dependent according to Arrhenius law shown as follows

$$k(\mathrm{T}) = \mathrm{A}\exp\left(\frac{-E_\alpha}{\mathrm{RT}}\right) \tag{2}$$

As reported previous, the mechanisms of the curing reaction of thermoset resins usually possess two general kinetic reactions, a *nth*-order and an autocatalytic reaction [9,19]. In case of the *nth*-order reaction:

$$f(\alpha) = (1-\alpha)^n \tag{3}$$

And in the case of autocatalytic reaction:

$$f(\alpha) = \alpha^m(1-\alpha)^n \tag{4}$$

For non-isothermal reaction conditions, the activation energy can be calculated by various integral iso-conversional methods, including Friedman method, Flynn-Wall-Ozawa method and Kissinger method, among these the Straink method offers a significant improvement in the accuracy of the E_α values [7,20]. The equation of Straink method is as follows:

$$\ln\frac{\beta_i}{T_{\alpha,\mathrm{i}}^{1.92}} = \mathrm{Const} - 1.0008\left(\frac{E_\alpha}{RT_\alpha}\right) \tag{5}$$

where, $T_{\alpha,\mathrm{i}}$ is the temperature at an equivalent conversion at various heating rates.

3. Results and discussion

The phthalonitrile-based resin containing benzoxazine (BA-ph) was prepared from an amino-substituted phthalonitrile monomer and bisphenol A at the presence of paraformaldehyde in the solvent of 1, 4-dioxane [21]. The Scheme of the synthetic route is shown in Fig. 1.

The heat flow of BA-ph from conditional DSC mode is shown in Fig. 2. The information about the nature of the curing reaction such as initial curing temperature, peak temperature, and the curing range of the resin at different scan rates could be derived, which are

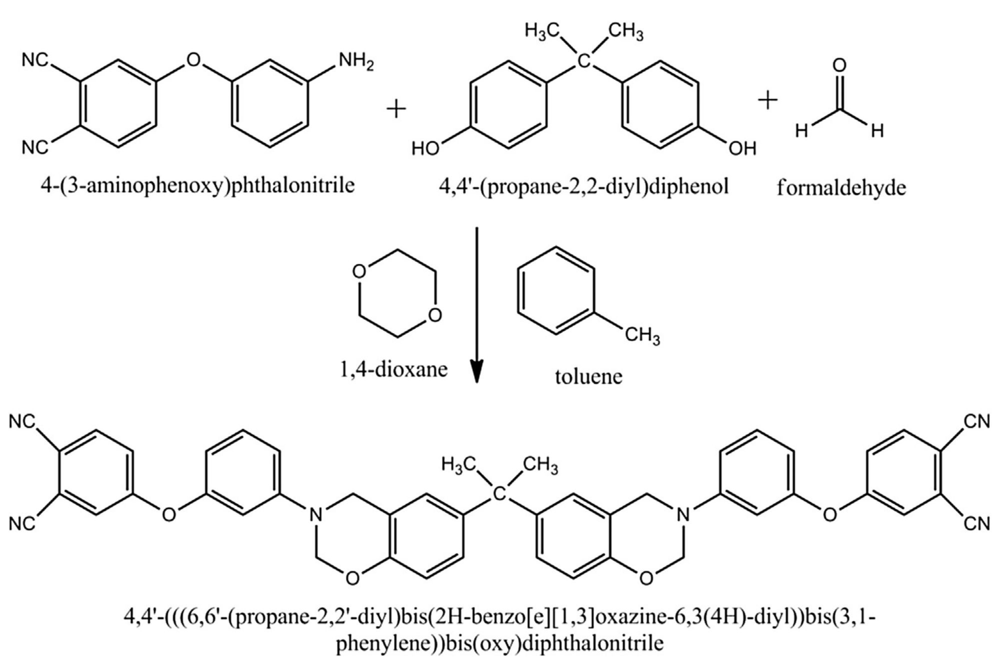

Fig. 1. Synthetic route of phthalonitrile containing benzoxazine monomer (BA-ph).