Thermochimica Acta 599 (2015) 84–94

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Cure kinetics, thermal stability, and dielectric properties of epoxy/barium ferrite/polyaniline composites

Gamal R. Saad *, Adel A. Ezz, Hoda A. Ahmed

Department of Chemistry, Faculty of Science, Cairo University, 12163 Giza, Egypt

ARTICLE INFO

Article history:
Received 22 September 2014
Received in revised form 13 November 2014
Accepted 14 November 2014
Available online 18 November 2014

Keywords:
Epoxy
Ba ferrite/polyaniline
Composites
Cure kinetics
Dielectric properties
Electric modulus

ABSTRACT

Barium ferrite/polyaniline composites (Ba ferrite/PANI) were synthesized using in situ polymerization of different $BaFe_{12}O_{19}$/aniline weight ratios and dispersed in diglycidyl ether bisphenol-A/carboxylated polyester (DGEBA/CPE) hybrid powder coating system. The effects of heating rate, Ba ferrite/PANI compositions and their loading level on the curing process was investigated by differential scanning calorimetry (DSC) in the dynamic mode. The activation energy of the cure reaction was examined utilizing Kissinger–Akahira–Sunose (KAS) method. It was found that the activation energy of the cure reaction of the epoxy increases with increasing the content of the filler. The dielectric properties were studied using dielectric relaxation analysis over a range of frequency (0.2–100 kHz) at 30 °C. The obtained dielectric data were analyzed using complex permittivity and modulus formalisms, depending on the concentration of filler in the epoxy matrix.

1. Introduction

Polymer nanocomposites based on inorganic nanoparticles with an organized structure provide a new functional hybrid made from organic and inorganic materials for their potential applications in the fields of electronics, photonics, mechanics, and sensing [1–5]. In recent years, conducting polymers have attracted much attention due to their potential applications in various hi-tech aspects, such as in electrochemical displays, sensors, catalysis, redox capacitors, electromagnetic shielding, as well as in secondary batteries [6,7]. Polyaniline (PANI) and its derivatives are regarded as the most important conducting polymers due to their high conductivity, ease of preparation, and good environmental stability showing their potential in microwave fields [8–12]. However, because of the poor mechanical properties of PANI, it is necessary to blend it with a suitable matrix [13]. The dispersion of PANI filler in an insulating polymer changes the dielectric constant of the latter and produces a composite with a very high capacity to absorb or reflect electromagnetic radiation [14]. The microwave absorbing performance of PANI composites can be enhanced by incorporating magnetic materials such as barium ferrites. Recently, several attempts have been made toward the synthesis of conducting Ba ferrite/PANI nanocomposites [15–17].

Epoxy resins are selected, as a matrix of blending Ba ferrite/PANI composites, as it is the most widely applied thermosetting resins. It is usually used as coatings, structural adhesives, insulating materials, and polymeric composite materials, etc. However, new materials based on conducting polymer composites can combine the high-performance mechanical properties of epoxy with the electrical and magnetic properties of Ba ferrite/PANI. Thus, features and properties of epoxy composites not only depend on their chemical components and preparation procedure, but also depend on the type of curing agent and curing conditions. Kinetic studies are especially important when fillers are used to predict performances and design curing cycles for the epoxy composites. Different methods are used to determine the kinetic parameters of curing reaction. Among them, isothermal or dynamic differential scanning calorimetry (DSC) has been used extensively to characterize the cure kinetics of thermosetting systems for a wide variety of applications with regard to shelf-life predictions and the optimization of the processing conditions [18–21]. On the other hand, dielectric spectroscopy has been found to be a suitable technique for the study of the relaxation behavior and dielectric properties of thermosetting matrices and nanocomposites [22–27].

The present work aims to investigate the cure kinetics of diglycidyl ether bisphenol-A/carboxylated polyester DGEBA/CPE hybrid powder coating system dispersed within Ba ferrite/PANI composite. The cure kinetics of the studied systems is examined by non-isothermal differential scanning calorimetry (DSC) at different heating rates. Furthermore, the dielectric response of

* Corresponding author. Tel.: +2 2 35676626; fax: +2 2 356727556.
E-mail address: grsaad@yahoo.com (G.R. Saad).

http://dx.doi.org/10.1016/j.tca.2014.11.013
0040-6031/

the epoxy composites was studied in a frequency range 0.2–100 kHz and the obtained data were analyzed by electrical modulus formalisms.

2. Kinetic background

Commonly, the overall reaction rate could be described by the following equation:

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

where $d\alpha/dt$ is the reaction rate, α is the conversion degree, $k(T)$ is the rate constant, t is the time, T is the temperature, and $f(\alpha)$ is the reaction model. The change of the rate constant with temperature is assumed to have an Arrhenius type dependency as:

$$k(T) = A\exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

where E_a is the activation energy, A is the pre-exponential factor, and R is the gas constant.

In the nonisothermal conditions Eq. (1) could be written in the following form:

$$\frac{d\alpha}{dt} = \beta\frac{d\alpha}{dT} \quad (3)$$

where, β (=dT/dt) is the heating rate.

By using a linear heating rate β, Eq. (3) can be written as:

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

Kinetic parameters are calculated without any assumption on conversion-dependency. In this respect, Kissinger's equation [28] can be used. The integral form of the Kissinger equation is given as follows:

$$\ln\left(\frac{\beta}{T^2_p}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_p} \quad (5)$$

where T_p is the temperature corresponding to the maximum of the DSC peak.

According to the literature [29], isoconversional methods give more consistent results than those obtained by other methods, since E_α-dependency may reveal changes in the cure mechanisms, Eq. (5) can also be applied to different degrees of conversion and this method is known as the isoconversional Kissinger–Akahira–Sunose (KAS) method [29,30]. For each conversion (α), $\ln(\beta/T_\alpha{}^2)$ when plotted against $1/T_\alpha$ results in a straight line with slope ($-E_\alpha/R$), thus providing the activation energy as a function of conversion.

3. Experimental

3.1. Materials

Aniline (99%) was purchased from Aldrich, which was distilled before use. Dodecylbenzene sulfonic acid (DBSA), as a dopant, and ammonium persulfate (APS), as an oxidant, were obtained from Aldrich. $Ba(NO_3)_2$, $Fe(NO_3)_3{\cdot}9H_2O$ and citric acid were purchased from Merck. All reagents were used as received without further purification. The epoxy resin used was a diglycidyl ether of bisphenol-A (DGEBA), Araldite GT7013 (Jana co.) with an epoxide equivalent weight of 650–725. The curing agent used was carboxylated polyester resin (CPE), Crylcoat 1620-0 (Cytec resins co.) with an acid value 55–65.

3.2. Preparation of barium ferrite

Barium ferrite, $BaFe_{12}O_{19}$, was prepared by citrate sol gel auto combustion method [1]. In a typical procedure, 0.01 mol (26.13 g) of $Ba(NO_3)_2$ was added to 0.115 mol (46.46 g) of $Fe(NO_3)_3{\cdot}9H_2O$ in distilled water and heated gently to complete dissolution. An aqueous solution containing 12.5 mol (24.00 g) of citric acid was added to the resulting solution. The stoichiometric ratios of mixed solutions were 1:11.5:25 of Ba^{+2}:Fe^{+3}:citric acid, respectively. After complete dissolution of all starting materials in the least amount of distilled water, an appropriate amount of ammonia solution was added dropwise with agitation until the pH of the solution reaches 7, giving transparent dark green solution. The resulting solution was then allowed to evaporate at 90 °C until the transparent green solution turned to viscous brown gel. The viscous gel was then heated at 150 °C till spontaneous ignition occurs. The auto-ignition was completed within a few minutes, yielding a brown ash. This ash was crushed manually and ground thoroughly to give very fine powder. The powder was calcined (pre-sintered) at 450 °C for 3 h to remove carbonaceous materials and at 850 °C for 4 h to give the final formation of barium ferrite crystalline powder.

3.3. Preparation of PANI and Ba ferrite/PANI composites

PANI doped with dodecylbenzene sulfonic acid (DBSA) is synthesized in aqueous medium by the oxidative polymerization of aniline using APS as an oxidizing agent in the presence of DBSA as a dopant by the method described previously [31]. Thus, aniline 5.0 g (0.054 mol) and 56.1 g (0.161 mol) DBSA were dispersed in 500 ml distilled water. Vigorous stirring was applied until homogeneous solution was obtained. Then, 18.38 g (0.081 mol) of ammonium persulfate in 200 ml distilled water were added to the aniline solution with continuous stirring. The polymerization of PANI proceeded with stirring for 6 h at ambient temperature. The obtained final product was filtered, washed several times with water, and with acetone.

Barium ferrite/PANI composites with various compositions were prepared by in situ polymerization method [32]. The procedure is described as follows: 5 g of Ba ferrite powder were suspended in 200 ml of deionized water under vigorous stirring at room temperature for 1 h, producing a fine aqueous dispersion. Subsequently, an appropriate amount of aniline and DBSA, dissolved in 200 ml deionized, was added to the suspension and stirred for 3 h at room temperature then cooled to ~0 °C with stirring for 1 h. An aqueous solution of APS was added drop-wise during 6 h, with stirring, to initiate the polymerization. The

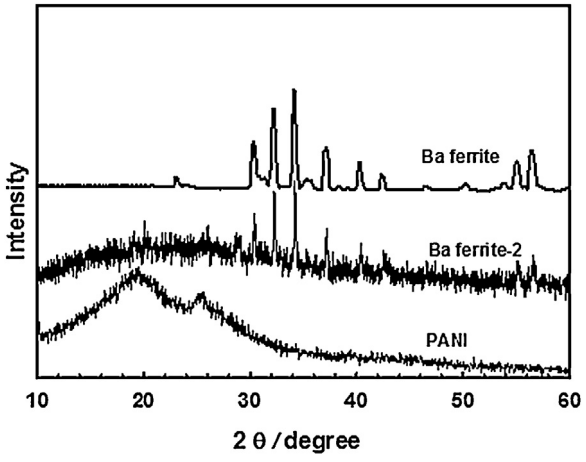

Fig. 1. X-ray diffraction for PANI, Ba ferrite and Ba ferrite-2.