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Electrochemical impedance spectroscopy (EIS): An efficiency method to monitor resin curing processes

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ABSTRACT

Electrochemical impedance spectroscopy (EIS) is widely used to characterize the charge carrier transfer and charge storage process. Charge carrier transfer process may be affected by the media viscosity. Here, EIS was used to monitor the curing processes of epoxy/amine blends for the first attempt, and a new equation was proposed to character the curing process and estimate the curing degree of resins, while, resins, curing agents and the curing processes have significant effect on product properties. Monitoring curing processes of certain resin/curing agent system is very helpful to design an appropriate formulation. The epoxy/amine blends, the model system, were prepared with Diglycidyl ether of bisphenol-A as epoxy resin and different ratio of phenalkamine modified with cardanol as curing agent. The curing processes of epoxy/amine were also investigated by differential scanning calorimetry (DSC), which was employed as a comparative method to verify the EIS results. A good agreement is obtained between the two methods, especially under higher curing temperature condition, which demonstrates the great promise to monitor the curing processes using EIS. The EIS results were also modeled to equivalent electrical circuits (EEC) by Z_{Simple}Win software for the further analysis. These results might provide some insights on optimizing the epoxy/amine ratio and the performance of cured epoxy resin and monitoring some process related to viscosity change.

1. Introduction

Electrochemical impedance spectroscopy (EIS), a powerful technique to investigate the charge transfer and charge storage processes, has been known for more than a century. When EIS measurement is conducted, a sinusoidal AC potential with small amplitude is applied, which producing measurable electric signal (impedance and phase angle) at the given frequency range. EIS, as an sensitive tool to for investigating electrochemical systems, has the advantage of separating interfacial processes at different frequency domain, and it is useful to analyze the reaction mechanism of the electrode system [1–4]. Its applications are close related to sensors, catalysts, solar cells, supercapacitors, corrosion science, etc [5–9]. Analysis of EIS spectra with equivalent electrical circuits (EEC) can help quantify the various contributions to the overall impedance, such as charge transfer resistance, solution resistance, double layer capacitance and so on. Viscosity and conductivity are two important parameters during the entire curing processes of resins, which are related to the resistance of a sample, therefore impedance modules obtained from EIS measurement can be used to track the curing processes and the curing degree of resins.

Resins, curing agents and the curing processes have significant effect on product properties. Monitoring curing processes of certain resin/curing agent system is important to optimize the product performance and choose appropriate curing condition. Different technologies including differential scanning calorimetry (DSC), dielectric analysis (DEA), Raman spectroscopy and thermogravimetric analysis (TGA) have been utilized to characterize the curing processes and the curing degree [10–12]. DSC analysis, based on the enthalpy released during polymerization reactions of a sample, has been extensively used to monitor the curing processes of

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thermosetting resins [13]. However, DSC results are easy to be affected by other heat-related events, such as solvent evaporation [14]. DEA analysis, based on variation of dielectric properties (such as dielectric constant and dielectric loss factor) of a sample, is highly affected by ions movement and dipoles alignment [15]. Although DEA analysis is more sensitive to small variation of sample properties in studying the curing degree, it requires plenty of preliminary experiments to ensure accuracy [12,16]. Raman spectroscopy detects chemical bonds and their variation during polymerization without special sample preparation, however, it may be influenced by the refractive index, colour and fluorescence characteristics of a sample [12]. Besides, measurements using these technologies mentioned above would be disturbed by solvent volatilization, and thus they may be not suitable for a thin film. As a consequence, a new analytical method is required for monitoring curing processes conveniently and precisely.

As one of the most popular thermosetting resins, epoxy resin shows distinct advantages over other resins [17,18]. It has been widely used as protective coatings, insulating materials, adhesives and casting materials owing to its superior properties, such as excellent chemical and corrosion resistance, strong adhesion, good mechanical properties, dielectric properties and lower cost [17–21]. Diglycidyl ether of bisphenol-A (DGEBA) is the most commercially available epoxy resin [22]. Nevertheless, epoxy resin has almost no practical value until it is converted into three dimensional networks in the presence of curing agents. Phenalkamineis a commonly used curing agent due to its applicability at low temperature and excellent comprehensive performance [23]. In recent years, phenalkamine curing agent modified with cardanol has attracted great attention, because cardanol is renewable sources derived from cashew nut shells and shows good flexibility [18].

Generally, two curing reactions occur in the epoxy/amine system. The first one is the polymerization reaction between epoxy groups and amino groups, and the second one is the polymerization reaction between epoxy resin molecules under the alkaline condition [24]. The curing reactions are complex processes, along with the variation of viscosity, conductivity, dielectric properties and so on. As is known, the performance of the cured epoxy resin depends on its structure, curing degree, curing conditions and the choice of curing agent. Ineffective or inadequate cure of epoxy resin always have significant negative impact on its mechanical properties and heat resistance [20]. As a result, it is necessary to figure out the curing degree of epoxy resin in order to optimize the comprehensive performance of curing products [13].

In the present work, curing process of DGEBA by cardanol-modified phenalkamine was monitored by electrochemical impedance spectroscopy (EIS) technique for the first attempt. A new equation, using the impedance modules as variable, was proposed to calculate the EIS curing degree. And the DSC analysis was employed as the comparative method to demonstrate the potentialities of EIS to investigate the curing processes and curing degree.

2. Experimental

2.1. Materials

The epoxy (diglycidylether of bisphenol A, 0.41–0.47 eq/100 g) serving as matrix component was obtained from Wuxi Phoenix resin Ltd. Co., China, and the cardanol modified phenalkamine curing agent (270–310 mg KOH/g) from Shanghai Meidong Biomaterials Co., China. Anhydrous alcohol and acetone applied as solvent are purchased from Tianjin Jiangtian Reagent Ltd. Co., China. Carbon steel plates (N80, $50 \times 10 \times 3$ mm in dimensions) used as parallel-plate electrodes were manufactured by Shandong Shengxin Technology Ltd. Co., China. All chemicals are analytical and used without any further purification prior to application.

2.2. Sample preparation

The electrodes were cleaned and degreased in anhydrous alcohol prior to the experiment. Epoxy solution was prepared by mixing epoxy resin with anhydrous alcohol and acetone. Cardanol modified phenalkamine was diluted with acetone firstly and then with anhydrous alcohol to form amine solution. The solvent was in 30 wt% relative to epoxy resin or phenalkamine. Then epoxy solution was blended with calculated amount of amine solution by stirring evenly. The blend was brushed onto the electrodes to form 1 cm^2 testing area for EIS characterization. The epoxy resin samples with different curing agent loading were characterized and designated as sample A (epoxy/amine 100/70, wt./wt.) and sample B (epoxy/amine 100/90, wt./wt.).

2.3. EIS measurements

EIS measurements were employed to investigate the curing processes of epoxy/amine system at two isothermal curing temperatures (20 °C and 40 °C). All EIS measurements were conducted on an electrochemical workstation (VersaSTAT, USA) using two electrode electrochemical cell composed of two parallel carbon steel plates with certain gap, called the working electrode (WE) and the counter electrode (CE), respectively. The uncured sample was filled into the gap (about 30 μm) of the two parallel electrodes. The scheme of the electrode and electrochemical cell is presented in Scheme 1. During the testing procedure, the cell was placed in a Faraday cage in order to minimize Coulombic fields. All the EIS measurements were conducted under sinusoidal ac voltage with amplitude of 10 mV in a wide range of frequency from 10^{-2} Hz to 10^5 Hz (ten points per decade were recorded). The impedance modulus at different curing period was collected with respect to frequencies. The experimental results of EIS were presented in terms of Bode plots (logarithm of the impedance modulus vs. the logarithm of the frequency) and Nyquist plots (imaginary impedance z" vs. real impedance z'). The curing degree was estimated from EIS method and compared to DSC results. Furthermore, the EIS data were analyzed and modeled into equivalent electrical circuits (EEC) with Z_{Simple}Win software.

2.4. DSC analysis

DSC analysis was employed to verify the EIS results. The isothermal DSC analysis was performed on METTLER DSC1-500. Approximately 20 mg uncured sample were sealed into DSC pan and then put in the DSC cell. The DSC cell was held at constant temperature (20 °C and 40 °C) in a nitrogen atmosphere. The heat released of reaction during curing processes was obtained by means of integrating over the exothermic peak as function of curing time.

3. Results and discussion

3.1. EIS measurements and EEC evaluation

A series of monitors were carried out during the whole curing period of the epoxy/amine blend. The EIS results of sample A and B, in terms of Bode plots, are presented in Fig. 1. As the curing reaction goes on, three-dimensional network of epoxy forms and get insoluble in solvent. The solvent evaporates through the gap between the two electrodes and the epoxy/amine system turns from viscosity fluid into porous solid, leading to restriction of ions mobility and dipoles alignment. Hence the ionic conductivity decreases and the impedance modulus increases over the curing time. Fig. 1(a)