Polymer Testing 55 (2016) 97–100

Contents lists available at ScienceDirect

Polymer Testing

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

Short Communication: Test Equipment

Rheological testing of a curing process controlled by Joule heating

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ARTICLE INFO

Article history:
Received 13 July 2016
Accepted 17 August 2016
Available online 18 August 2016

Keywords:
Curing
Joule heating
Electro-rheology

ABSTRACT

A multi-walled carbon nanotubes (MWCNT)/epoxy system was cured through direct application of a DC electric field while rheological properties were measured. Therefore, rheological testing was performed simultaneously to the curing reaction. Each plate was electrically connected to either pole of a DC power supply so that, by means of the Joule effect, heating was controlled by application of an electric potential. The plates were also connected to the poles of an LCR meter in order to perform dielectric analysis to evaluate the initial conductivity of the sample. The temperature of the sample was measured by a thermographic camera connected to a PID control unit used for adjusting the electric potential according to the heating program. It was observed that wt 3% of MWCNTs and 1 A current allowed reaching 200 °C, a sufficiently high temperature to fully cure most thermoset systems.
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1. Introduction

Curing of thermosets has been extensively studied, since thermosets are produced and widely used in many industrial applications. The curing process is typically driven by heat. UV curing is of interest in some cases, albeit its use is limited to relatively thin parts [1]. Nevertheless, an important limitation of the use of UV curing lies in the low penetration index of UV light, which becomes problematic in the curing of large samples. Other curing methods which have been garnering increasing attention in recent years include the use of microwaves and radio waves [2–4].

Joule heating is the process by which the passage of an electric current through a conductor releases heat. Heating by the Joule effect can be used to promote curing reactions, an approach which is receiving a degree of attention by the scientific community. As seen below, the amount of heat resulting from the Joule effect, namely Q, is directly proportional to the square of the current intensity, I:

$$Q \propto I^2 \cdot R \cdot t \tag{1}$$

where R is the resistance and t, the time.

Carbon fibres present in some aeronautic composites allow heat to be produced through the Joule effect [5,6]. However, the heat generated from carbon fibres would be more or less homogeneously distributed depending on the distribution of the carbon fibres along the thermosetting matrix. Additionally, the need for carbon fibres would constitute an important limitation in many composites where this type of reinforcement would not be necessary.

Other approaches to Joule effect curing consist of incorporating nano-sized conductive fillers, such as carbon black and carbon nanotubes (CNT), in order to provide electrical conductivity to the polymeric matrix [7–9]. These nano-sized, electrically conductive fillers should be present in sufficient amount, adequately dispersed and homogeneously distributed in volume to achieve homogeneous heat generation.

CNTs at concentrations close to and over the percolation threshold have been used for thermoset curing using the heat obtained by the Joule effect [10]. The resistivity value was used to track the curing reaction. The application of an electrical field induces the formation of a CNT network. The structure of that network is affected by the electrical field [11,12].

In the present work, CNTs will also be used for the conductive network that will allow for Joule effect heating, but the curing reaction of the system will be tracked by measuring its viscoelastic properties. In order to perform these experiments, a specific device was developed which basically consists of a rheometer with its parallel plate geometry connected to a DC electrical source which is governed by a controller unit. This controller unit receives the temperature reading of the sample from an infrared camera. Although the viscoelastic characterization may provide an

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http://dx.doi.org/10.1016/j.polymertesting.2016.08.015
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interesting insight on the structure of the network formed due to the application of the electrical field, such a point falls outside the scope of the present work. An important feature of the experimental device is that the heating rate can be controlled by adjusting the electric field through a PID control loop.

2. Experimental

An epoxy system was subjected to curing by means of controlling the application of a DC electric field while rheological properties were measured. This requires the incorporation of conducting particles into the thermoset, as well as using a specific device for simultaneous application of the DC electric field and rheological testing. In order to evaluate the initial conductivity of the sample so as to properly adjust the DC electric field, a dielectric analysis was performed using a LCR unit, which was also connected to the rheometer plates.

2.1. Materials and sample preparation

Multi-walled carbon nanotubes (MWCNT)/epoxy mixtures containing wt 3% of MWCNTs were prepared for the purpose of studying their curing reaction.

The epoxy system, BEPOX 1622, was provided by Spanish vendor Gairesa. It is an epoxy resin with average molar mass below 700 g/mol and a trimethylolpropane poly(oxypropylene) triamine-based hardener. MWCNTs of purity higher than 95%, with external diameter between 6 and 9 nm and 5 μm in length, were purchased from Sigma-Aldrich; their average diameter is 6.5 nm. MWCNTs were mixed with the resin by manual stirring. The mixture was homogenized for 2 min using a Heidolph DIAX 900 homogenizer. Then, the hardener was incorporated into the resin containing the MWCNTs, and the mixture was homogenized again for 1 min. Independently of the MWCNT content, resin and hardener were used at the stoichiometric proportion, as per the manufacturer's recommendation (hardener:resin = 1:2.38).

2.2. Instrument layout

The experiments were performed on a TA Instruments Discovery Hybrid Rheometer DHR2 furnished with a DC power supply, a dielectric analysis (DEA) accessory and an infrared camera for temperature measurement. The DEA accessory basically consists of an Agilent E4980A Precision LCR Meter, with frequency and electric potential ranges from 20 Hz to 2 MHz and from 0.005 to 20 V, respectively. Its maximum output intensity is 200 mA, which is not enough to heat the sample at the heating rate chosen in this work. The sample testing geometry consisted of two 25 mm-diameter disposable aluminum plates. The LCR meter was connected to both rheometer plates, which were mechanically attached to the rheometer through a series of electrically insulating parts. The LCR was disconnected once dielectric measurements were finished. The power supply, which was permanently connected to the plates through two thin electrical wires, was programmable and could output 0–75 V at 0–5 A, with a maximum power output of 350 W. The sample temperature was continuously measured using a FLIR E50 infrared camera, which was connected to a computer running Matlab software on which a PID close loop was implemented in order to control the heating rate of the sample. The values used for PID control were P = 0.05, I = 0.01, and D = 0.01. Temperature was used as the control variable, and voltage as an output signal.

2.3. Testing procedure

2.3.1. Measuring conductivity

DEA was performed on the fresh mixture and on a fully cured sample to evaluate its electrical conductivity, which includes both electronic and ionic components. A fresh, unfilled sample was also tested to better understand the contribution of MWCNTs to the electrical conductivity of the sample. The method has been reported by some of the authors [13]. Accordingly, the complex dielectric constant of a material, ε^*, can be separated into its real and imaginary parts:

$$\varepsilon^* = \varepsilon' - \varepsilon'' \tag{2}$$

where ε' is the permittivity (real part) and ε'' is the loss factor (imaginary part).

There are two possible contributions to the loss factor: relaxation and conductivity,

$$\varepsilon'' = \varepsilon''_{rel} + \sigma/(\omega \cdot \varepsilon_0) \tag{3}$$

where σ is the conductivity of the sample, ω is the measuring frequency and ε_0 is the vacuum permittivity. Direct testing of the sample at a given temperature and a high enough frequency will provide measurements exempt from any relaxation process and, therefore, the conductivity factor would be the only contribution to the loss factor. The testing parameters used for DEA were 0.02 V amplitude and frequency sweep from 10^2 to 10^6 Hz. Such a small amplitude was chosen in order to prevent significant heating of the sample. Although DEA can be used to study polymer transformations, its purpose in the present work was confined to the study of electric conductivity, thus leaving all analysis of the curing process to rheology.

2.3.2. Joule heating and rheological testing

Using the aforementioned instrument layout, the sample temperature was controlled through the software so that the electric field was continuously adjusted in order to keep specific heating rates according to each experimental setup. In order to check the heating rate control system based on the Joule effect on a sample mounted between the rheometer plates, a 2 °C/min ramp was programmed. Additionally, rheological testing was performed according to the following experimental conditions:

Strain of 0.1% for all the experiments, at all times. This value was checked to be into the linear viscoelastic range.

Experiment no. 1: 1 Hz frequency, 17.5 °C/min heating rate from room temperature to 65 °C; then, 0.05 °C/min from 65 °C to 76 °C.

Experiment no. 2: A 1/(2π), 2/(2 π) and 5/(2 π) Hz multi-frequency experiment was performed with the following thermal program: 2 °C/min heating rate from room temperature to 90 °C; then, isothermal at 90 °C for 30 min.

3. Results and discussion

Fig. 1 shows plots of the conductivity observed versus the frequency for samples filled and non-filled with MWCNTs. The more or less constant conductivity regions of the curves imply the absence of relaxation phenomena —and show that conductivity is the only contribution to the loss factor. That is basically what happens in the fully cured composite. On the other hand, both uncured samples, especially the unfilled one, show an important increase in conductivity at medium frequencies. This is an indication of relaxation phenomena, which, in addition to ionic conductivity, contributes to the total electric conductivity. With regard to performing the curing by the Joule effect, the great increase of

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