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Effect of curing on activation energy and dielectric properties of carbon black–epoxy composites at different temperatures

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ABSTRACT

The effect of curing on activation energy and dielectric properties of carbon black–epoxy (CB–EP) composites has been reported at different temperatures and frequencies. The activation energy was found to be higher for the room temperature cured CB–EP samples as compared with the thermally cured CB–EP samples. Curing behavior of epoxy nanocomposites prove that epoxide molecules contribute to the curing reaction and reacted with them to form a cross-linked network. Dielectric constants of thermally cured CB–EP samples were higher than the room temperature cured samples. The results showed that activation energy, decreased with an increase in the concentration of carbon black in the composite, which may be due to an increase of polarization energy and/or charge carrier density leading to a decrease of the domain boundary potential of carbon black aggregates into the epoxy matrix. At room temperature, the electrical conductivity is due to electron tunneling and hopping. Dielectric constant of the CB–EP composite increase with increase in temperature and decreases with an increase in frequency from 0.5 kHz to 10 kHz for both room temperature cured and thermally cured specimens. The peak height of the dielectric constant curve of both cured samples decreases with increasing frequency.

1. Introduction

Development of nanocomposites is a fast growing field owing to the excellent properties at low concentration of filler. Epoxy based nanocomposites have attracted much interest, as there is an enhancement in the physical properties of epoxy composites due to dispersion of conducting particles within an insulating matrix [1–6]. Epoxy resin a thermosetting material is widely used in advanced structures of composite materials. This is because of the attractive physical and chemical properties. It contains two or more oxirane rings or epoxy groups in their molecular structure. The performance of an epoxy-based nanocomposite significantly depends on its curing circumstance. Studies on curing behavior of epoxy based nanocomposites conclude that epoxide molecules contribute to the curing reaction and react with themselves to form a cross linked network and/or with other reactive molecules whether a catalyst is used or not [7]. Curing of epoxy plays a vital role in its composite properties. The electrical, mechanical, and chemical properties possessed by the epoxy-based composites are due to the curing reaction. Curing refers to an irreversible exothermic chemical reaction by which the composite is transformed from a soft, multi-layered mixture of resin to a hard structural component [8]. During curing low molecular weight, resin is converted to an infinite molecular weight polymer with a three-dimensional network structure through chemical reaction or physical interlocking or both. Hence, the study of cure behavior of epoxy composites is significant for the design and analysis of processing parameters [9].

The electrical properties of such systems are dependent on various factors like the curing of composites, the degree of dispersion, the interaction between components, the volume fraction of the filler and percolation [10–14]. Electrical conductivity of polymer nanocomposites strongly depends on the filler content and can be explained in terms of the percolation theory. Below the percolation threshold, the electrically conducting composite materials behave either as insulators or semiconductors, whereas the raise in conductivity with increase of temperature is determined by thermally assisted hopping or, possibly, charge tunneling between the conducting particles [15].

Among the available fillers, carbon black (CB) has been widely used because of its ability to give high electrical conductivity to an insulating polymer at relatively low filler content. Conductivity of an insulating polymeric material using CB as filler is enhanced by free electron transport through a continuous network in the polymer matrix. Carbon black as filler is used to reduce the tunneling distance and increase the number of tunneling contacts, which have to be overcome by charge carriers, determining the overall conductivity [16–18].

The dependence of conductivity σ on temperature can be explained by Arrhenius equation. It expresses the dependence of the conductivity

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σ over a wide range of temperatures in terms of two parameters, first is the preexponential factor A depending on mobilities of charge carriers and second is the experimental activation energy E_a in joules [19]. The equation is given by

$$\sigma = A \exp\left(\frac{-E_a}{K_B T}\right) \quad (1)$$

where K_B is the Boltzmann's constant; and T is the temperature in Kelvin.

Recent investigation has shown that epoxy/nanocomposites exhibit some advantages for both mechanical and dielectric properties when compared with pure resin system [10,20–22]. An enhancement in the electrical properties of the epoxy nanocomposites can be attributed to the relaxation processes. The relaxation processes correlate to dipolar orientation effects or space charge migration [23,24]. The dielectric effect of the epoxy nanocomposites is due to the charge mobility and interfacial polarization. At lower temperatures, polar side groups enhance the electrical performance of the system. Interfacial polarization is the result of the heterogeneity of the system e.g., mobile charges assembled at the polymer–filler interface form large dipoles. The volume concentrations of the conductive charges are proved crucial parameter governing the electrical behaviour of the polymer composites [25]. When the filler content is low, the mean distance between charge particles or clusters is large and conductance is limited due to the presence of the dielectric polymer matrix. At a critical volume fraction (or percolating threshold) of the filler, a physical path is formed in a way that the current can flow, percolating the whole system [26].

The effect of CB on the network structure of epoxy composites, like volume fraction of the network, the extent of CB reinforcing, and the interparticle distance between conductive particles, has been investigated in detail for thermally cured and as prepared samples. It is found that the conductivity of an insulating epoxy matrix increases continuously with CB content and is well explained by percolation theory. The temperature dependence of the dielectric response has been analyzed below and at near the epoxy glass transition temperature for various CB concentrations.

The aim of the present study is to obtain new information on the curing effect on the activation energy and dielectric properties of CB–epoxy composite under different conditions of different temperatures and frequencies. In addition, we attempt to give extensive experimental results that may lead to a better understanding of network structure and electrical properties of carbon black–epoxy (CB–EP) composites for practical applications as heating devices and/or conducting composites.

2. Experimental details

2.1. Materials

The carbon black used in this study was Ketjenblack EC-600 JD (Supplied by Akzonoble) with a total surface area, BET 1400 m^2/g, diameter 36 nm, apparent bulk density 0.12 g/cm^3, iodine absorption 1000–1100 mg/g, pore volume DBP 480–510 ml/100 g and ash content < 0.1 (as specified). The thermosetting matrix used in this study was unmodified epoxy resin provided by Atul Pvt. Ltd. Valsad, India. Fig. 1 (a, b) shows the structure of unmodified epoxy prepolymer resin and structure of a hardener. The density of the resin, cured at room temperature was 1.15 g/cm^3.

2.2. Composite preparation

Composite was prepared using a resin/hardener ratio of 10:1. Carbon black was first heated to 60 °C for 30 min in order to remove the moisture. The carbon black–epoxy (CB–EP) composite samples of 0.5, 1, 1.5, 2, 2.25, and 2.5 w/v % respectively were prepared. For the proper dispersion of the CB, initially the resin was heated at 60 °C for 30 min for reducing the viscosity of resin and then the weighed amount of CB was mixed with the resin. The mixture was then sonicated for 30 min using an ultrasonic bath sonicator. The mixture was again heated for 15 min and sonicated for another 30 min. This dispersed mixture of CB and epoxy resin was then stirred for 1 h with 50 °C temperature using a hot plate stirrer. After cooling, hardener was added to the mixture in the abovementioned ratio and then stirred for complete mixing. For preventing air entrapment in the prepared mixture, vacuum mixing was used and the mixture was then poured in the mould for making the sheets. The sample sheet was cured at room temperature for 7 days and another set of samples having a same w/v % was cured at 125 °C for 1 h.

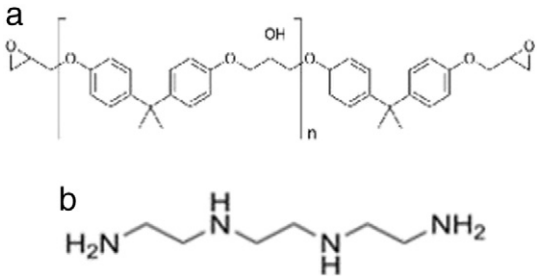

Fig. 1. (a) Structure of unmodified epoxy pre-polymer resin. (b) Structure of a hardener.

2.3. Preparation of test sample

Sample sheets of 0.5, 1, 1.5, 2, 2.25, and 2.5 w/v % of CB–EP composite cured at room temperature and at 125 °C were prepared. Test samples, are then cut from the sheets in a square, having the each side of 9 mm and with 2 mm thickness. Uniformity of surface was obtained by polishing the sample. Both surfaces of the sample were coated by air-drying conducting paint in such a way that both the surfaces should not connect electrically with each other. The test samples were then heated at 60 °C for 10 min, to remove the solvent of the silver conducting paste.

3. Characterization

3.1. Activation energy

The Arrhenius equation plays a dominant role in classical studies of chemical kinetics. E_a is in practice taken as the slope of an Arrhenius plot of ln (σ) versus $1/T$ in Kelvin [27,28]. The term $(-E_a/K_B T)$ is the slope and Eq. (1) can be rewritten as

$$\ln(\sigma) = \ln(A) Slope\left(\frac{1}{T}\right). \quad (2)$$

Now the value of the slope can be computed from the linear graph of ln (σ) V/s $1/T$ in Kelvin as follows [15]:

$$\text{Slope} = \frac{\Delta \ln(\sigma)}{\Delta\left(1/T\right)}. \quad (3)$$

The activation energy (E_a) is now calculated as

$$E_a = -K_B \times \text{slope}. \quad (4)$$

The slope being negative, a positive value of E_a is obtained [19].

3.2. Dielectric measurements

Dielectric constant (ε') refers to the measure of the reduction of coulomb interaction between the ion pairs in polymer electrolytes.