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MONITORING CURING WITH EPOXY POLYMERS USING DIELECTRIC MEASUREMENTS AND FREE KINETICS MODELS

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Abstract: Paper aims to present an applied modeling concept directed towards kinetic parameters' estimation during thermal curing on a commercial DGEBF epoxy polymer as retrieved from dielectric measurements. This dynamic process will be described by aid of few free kinetics models applied to a set of isothermal measurements at different frequencies thus enabling kinetic parameters retrieval (e.g. activation energy, glass temperature). The herein contribution is sought as an alternative to the familiar and yet classical approaches around data provided on scanning calorimetry measurements.
Keywords: thermo-kinetics, epoxy, polymer, glass temperature

1. INTRODUCTION

Technical literature provides numerous references on epoxy polymers, from synthesis to material characterization, individually or in the presence of various constitutive proven their versatility in engineering applications such as high-performance composites, aerospace, automotive and transport, electronic packaging or protective coating adhesives, etc. [1-2].

In addition, it is acknowledged that the properties of epoxy polymers, especially glass transition temperature (Tg), is generally influenced by the curing agents and other additives added to enhance their mechanical, thermal or chemical properties and to accelerate curing reactions [1]. Among the curing agents deployed with the epoxies, aromatic and aliphatic amines are the commonly used.

Dielectric properties of polymer resins are currently measured since the retrieved data enable insights in the relaxation phenomena and material heterogeneity [2, 3]. Besides dielectric spectroscopy other techniques such as thermally stimulated depolarization current (TSDC) or dielectric relaxation spectroscopy (DRS) were used to retrieve information on primary relaxation process associated with the glass-rubber transition, interfacial relaxation or ionic conduction process on epoxies [4, 5]. Activation energy retrieval was debated in numerous references [6-9]. A dependence on glass transition temperature (Tg) and Vogel temperature (Tv) which is found to be 30-40 °C below Tg [10].

The herein paper aims to provide a study on dielectric and conductive properties of a diglycidyl ether of bisphenol F (n. DGEBF) epoxy resin cured with an aromatic amine curing agent using a high-resolution impedance analyzer.

2. MATERIALS AND EXPERIMENTAL SETTING

The investigated epoxy polymer resulted from the curing of a diglycidyl ether of bisphenol F (n. DGEBF, trade name EPIKOTE 862 from Momentive) with an aromatic amine curing agent (trade name EPIKURE, same provider) carefully mixed to delivered a homogenous solution.

Dielectric measurements were carried out by means of a Novocontrol High Resolution Impedance Analyzer under controlled atmosphere within room to 120 °C temperature range and in the frequency interval 1- 10^7 Hz.

3. RESULTS AND DISCUSSIONS

Figure 1 shown a three-dimensional plot of the real (ε') part of dielectric permittivity as a function of frequency and temperature for DGEBF polymer under debate. As it can be seen from the figure, at low frequencies and

high temperatures the real dielectric permittivity reaches high values that are due to the elevated segmental mobility of the polymer molecules and orientation of dipoles in the direction of alternating field. The α relaxation process can be easily identified in the plot with increases of the frequencies.

In Figure 2 and Figure 3 are shown the isothermal variations of M' and M'' below and beyond Tg for the DGEBF resin. As it can be seen, two loss peaks are observed in the M''(f) spectrum at 40 °C, 60 ° and 120 °C respectively indicative of Maxwell-Wagner-Sillars (MWS) relaxation that appears in heterogeneous media due to the accumulation of charges at interfaces and α relaxation associated with the second peak. The latter is widely acknowledged as glass-rubber relaxation in literature [11].

The loss peak ascribed to the α relaxation can be seen at high both temperature and frequency, like mentioned above, and the conduction within these ranges is following a linear behavior (see Figure 3).
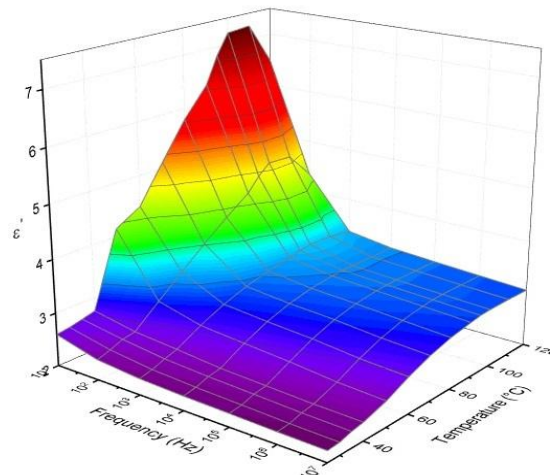

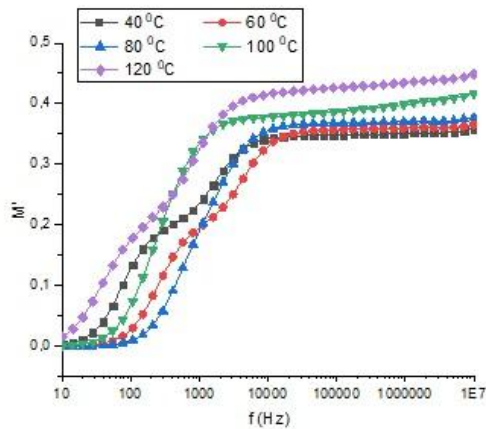**Figure 1:** Real part of dielectric permittivity as a function of frequency and temperature

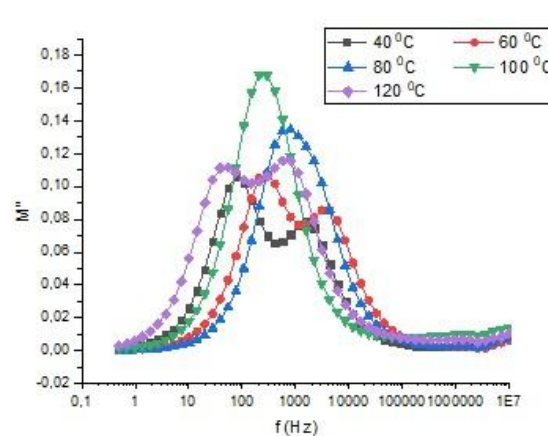**Figure 2:** Isothermal plots of real electric modulus **Figure 3:** Isothermal plots of imaginary electrical modulus

Theory of electrical conduction provide the expressions for the dielectric dependence in terms of complex electric modulus, such is $M^* = \dfrac{1}{\varepsilon^*}$, where the real and imaginary parts can be rewritten as following:

$$M^* = M' + iM'' \tag{1}$$

$$M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} \; , \; M'' = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} \tag{2}$$

where ε' and M' are the real components whereas ε'' and M'' are the imaginary components of dielectric permittivity and electric modulus, respectively.

If the relaxation time (τ) estimates plotted versus 1000/T in a semi-logarithmic scale reveals a linear behavior to the relation process, then the process can be described by the aid of Arrhenius law, such as following:

$$\tau = \tau_0 \exp\left(\frac{E_a}{k_B T}\right) \tag{3}$$

where τ_0 [s] is a pre-exponential factor, k_B is the Boltzmann constant, E_a [eV] is the activation energy of the relaxation process and T [K] is the absolute temperature. On the other hand, if the relaxation process is not following a linear dependence with 1000/T it has to be modeled using Vogel-Fulcher-Taman (VFT) equation, such as:

$$\tau(T) = \tau_0 \exp\left(\frac{B}{T - T_V}\right) \tag{4}$$

where B is a constant, T_V [K] is the Vogel temperature and T [K] is the absolute temperature. Additionally, according to Plazek et al. [12] the activation energy of α relaxation process can be estimated using the following expression :

$$\frac{E_a}{R} = \frac{B}{\left(1 - \dfrac{T_V}{T_g}\right)^2} \tag{5}$$

where E_a is the activation energy (eV), R is the gas constant and Tg [K] the glass transition temperature. The glass transition temperature has to be identified from differential scanning calorimetry (DSC) measurements since it is particular to individual polymer systems developed and proven the reliability of measurements.

The heterogeneity of the DGEBF system can be further exploited by plotting the real and imaginary components of the complex modulus using the well-known Haviliak-Negami approach for the MWS relaxation. Any departure for the ideal circular representation enable further insights in the epoxy resin behavior with frequency increases. It is beyond the purpose of herein paper to further investigate in the above issue.

4. CONCLUSION

The paper aimed to provide an insight with an epoxy system by the aid of dielectric relaxation occurring with this particular combination resin + hardener. The results show the presence of two relaxation peaks in the polymer, in accordance with other studies on similar epoxy systems cured with aromatic hardener revealing the importance of the hardener on the resin structure which in turn influences the dielectric properties under debate. In addition, the measurements show that the epoxy system developed is more suitable for applications as insulators for electrical equipment or optoelectronic devices due to its lower values found in the electrical conduction values.

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