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Molecular dynamics of an epoxy resin studied by Thermally Stimulated Depolarization Currents

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ABSTRACT

The Thermally Stimulated Depolarization Current (TSDC) technique has been used to study the molecular mobility of diglycidyl ether of bisphenol-A (DGEBA) in the temperature range from −160 °C up to 10 °C. The molecular mobility in the glassy state and in the supercooled liquid was then characterized. Two secondary relaxations were detected, one of them partially disguised by the main α-process. Differential Scanning Calorimetry (DSC) was used to analyse the dynamics of the structural relaxation around T_g (from the heating rate dependence of the onset temperature of the glass transition signal). The values of the fragility index obtained in this work by TSDC and DSC are compared with the values reported in the literature obtained from other experimental techniques. A relaxation above the glass transition temperature was also observed. The controversy about the attribution of this upper-T_g mobility at the molecular level is reported.

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1. Introduction

It is well established that glass-forming systems present different relaxation processes in the glass transition temperature region and below. In order to characterize this mobility in the amorphous solid state and in the supercooled liquid, several techniques (for example DMA, DSC, and NMR) have been used. The technique of Thermally Stimulated Depolarization Currents (TSDC) was also used in this context, and the large number of published results reflects the success of its contribution to the understanding of the glass mobility. The narrow frequency range of this technique when compared with Dielectric Relaxation Spectroscopy (DRS) is counterbalanced by the high resolution shown in the study of secondary processes. Another important advantage of this technique is the possibility of experimentally separating a broad relaxation into its individual relaxation modes using the so-called partial polarization (PP) procedure.

In this work, we used TSDC to analyse the molecular mobility of diglycidyl ether of bisphenol-A (DGEBA), a monomer largely used to obtain polymeric materials for an extensive variety of applications [1,2]. The results of a study of DGEBA by dielectric spectroscopy and time domain Brillouin spectroscopy [3–5] were at the centre of a discussion on the physical nature of the glass transition: kinetic event or true phase transition? The ability of this substance to prevent crystallization when it is cooled down from the melt makes it a good glass-forming system. Its glass transition temperature, T_g, detected by Differential Scanning Calorimetry is 255 K (at 10 °C min^{-1}) [6]. Different studies have been published to date describing the dielectric behaviour of this material in the bulky state, varying temperature or pressure conditions [7], upon polymerization [8,9], etc. The more relevant findings concerning the molecular dynamics of the pure compound studied by DRS is the detection of three relaxation processes: the main relaxation related to the glass transition, and two secondary relaxations with lower intensity and located below T_g [10,11].

The γ-relaxation, detected at lowest temperatures, is such that its temperature/frequency location is influenced neither by pressure variations nor by changes in the degree of polymerization [12,13]. This behaviour suggests that this motional process involves motions of only a part of the molecule decoupled from the main process, specifically the motions of the epoxide end groups.

In contrast, the β-relaxation, visible at higher temperatures and weaker than γ, is sensitive to pressure [14] and chemical changes [12] showing a clear tendency to follow the changes induced in the main relaxation process. These observations lead to identify the β process to a Johari–Goldstein relaxation, i.e. to a mobility of the molecule as a whole, acting as a precursor of the α-relaxation [15,16].

In the present work, we provide a detailed study of the molecular mobility in DGEBA by Thermally Stimulated Depolarization Currents,

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and compare our results with those supplied by different techniques, especially by Dielectric Relaxation Spectroscopy. The Differential Scanning Calorimetry (DSC) technique was also employed to complement this study.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol-A (DGEBA) was purchased from Sigma-Aldrich (CAS number 1675-54-3). The empirical formula is $C_{21}H_{24}O_4$ (molecular weight $M=340.41$ g mol^{-1}), the chemical structure is shown in Fig. 1 and it was used as received.

2.2. Techniques

Differential Scanning Calorimetry (DSC) measurements were performed with a 2920 MDSC system from TA Instruments Inc. Samples of ~5–10 mg were introduced into aluminium pans and hermetically sealed using a sample encapsulating press. The measuring cell was continually purged with high purity helium gas at 30 mL min^{-1}. An empty aluminium pan, identical to that used for the sample, was used as reference. Details of the calibration procedures are given elsewhere [17].

Thermally stimulated depolarization current (TSDC) experiments were carried out with a TSC/RMA spectrometer (TherMold, Stamford, CT, USA) covering the range from −170 to +400 °C. For TSDC measurements, the sample was placed between the electrodes of a parallel plane capacitor with an effective area of ~38 mm^2 (thickness of ~0.5 mm). The sample was immersed in an atmosphere of high purity helium (1.1 bar). In TSDC, the polarization induced in the sample at a temperature is retained by cooling the sample keeping the electric field applied. The depolarization current measured in a heating ramp, allows extract information about the molecular motions previously immobilised.

To analyse specific regions of the TSDC spectrum, different methods of polarizing the sample can be used, namely the so-called TSDC global polarization experiment and the partial polarization (PP) experiment (often called thermal sampling or windowing or cleaning). The PP method, where the polarizing field is applied in a narrow temperature interval, enables to resolve a global peak into its individual relaxation modes [18]. This partial polarization procedure allows the retention (or freezing) of a polarization that arises from a narrow variety of dipolar motions. A review paper is available on TSDC applications [19]. More information about the TSDC technique can be found in [20–23]. Particularly, supporting materials attached to ref. [23] can be useful to readers not familiar with the TSDC technique.

3. Results and discussion

3.1. Differential Scanning Calorimetry

The glass transition temperature of DGEBA was determined by DSC as the temperature of the onset, T_{on}, of the glass to supercooled liquid transition signature, obtained with a heating rate of 10 °C min^{-1} (the sample was previously cooled at the same rate). The DSC thermogram shows a glass transition signal with the onset at $T_g=255.3\pm0.1$ K $=-17.9\pm0.1$ °C in very good agreement with the values of 255 K reported in the literature from calorimetric measurements [6,7] and 254 K obtained from Dielectric Relaxation Spectroscopy (temperature at which the relaxation time is $\tau=100$ s) [11]. The heat capacity jump, ΔC_P, of the calorimetric glass transition is $\Delta C_P=(0.51\pm0.06)$ J K^{-1} g^{-1} (average of 46 determinations), where the uncertainty indicated corresponds to the standard deviation of the mean.

The technique of Differential Scanning Calorimetry was also used to estimate the activation energy of the structural relaxation and the fragility index. One of the methods of thermal analysis allowing the determination of glass-former fragility is precisely based on the scanning rate dependency of T_g [24,25]. In this method, the activation energy is calculated from the relationship [26]

$$\frac{d\ln|r|}{d\left(1/T_g\right)}=-\frac{E_a}{R} \tag{1}$$

where r is the heating rate, E_a the activation energy for the relaxation times controlling the structural relaxation, and R is the perfect gas constant. By using the definition of the fragility index proposed by Angell [27], i.e. the slope at the T_g of any dynamic property in an Arrhenius plot, where the abscissa is scaled to the T_g of the material, the value of m is obtained from:

$$m=-\frac{E_a\left(T_g\right)}{2.303RT_g}. \tag{2}$$

In this work, two different protocols were used: 1) cooling the sample from the supercooled liquid at the constant rate $r_c=-5$ °C min^{-1}, and varying the heating rate, r_h, from 2 to 20 °C min^{-1}, and 2) heating the sample at a rate with an absolute value equal to the rate of the previous cooling ($r_c=r_h$) , both varying from 2 to 20 °C min^{-1}. In the former case the glassy state obtained is always the same, while it is different in the latter one. The corresponding activation energies calculated from a linear fitting of the data presented in Fig. 2 were 292 ± 15 kJ mol^{-1} ($r_c=5$ °C min^{-1}) and 375 ± 10 kJ mol^{-1} ($r_h=r_c$) respectively. The corresponding fragility indexes were respectively 60 and 77.

As shown in Fig. 2, the onset temperature, T_g, of the calorimetric glass transition signal is higher for protocol 1 (constant r_c) compared with protocol 2 ($r_c=r_h$) for the same heating rate, and the difference increases as the ratio r_h/r_c increases.

A similar behaviour was found by Simatos et al. [24] in their careful study of sorbitol and fructose, and also in other materials [28]. It was rationalized [24] considering that, when the heating rate is significantly higher than the previous cooling rate (high r_h/r_c ratio), the time for the important structural recovery is too short, giving rise to an important hysteresis between the cooling and re-heating enthalpy curves.

3.2. Thermostimulated Depolarization Currents

Fig. 3 presented the result of a TSDC global experiment carried out on DGEBA in the temperature region between −90 and 20 °C and it also included the base line ($E_P=0$ V mm^{-1}). The more intense peak

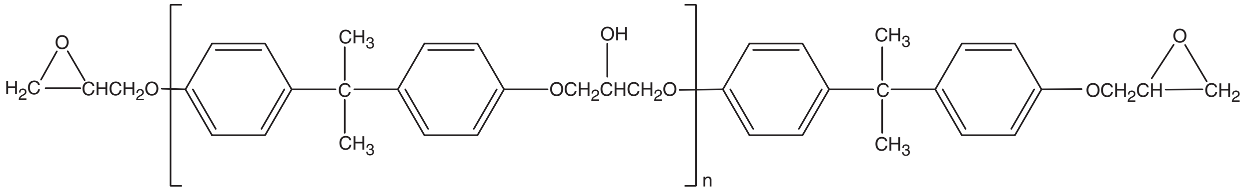

Fig. 1. Molecular structure of bisphenol A diglycidyl ether, DGEBA.

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