

Liquid crystalline and isotropic epoxy thermosets: Mechanism and kinetics of non-isothermal degradation

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Abstract

Thermal non-oxidative degradability of two epoxy thermosets was studied. Investigations were carried out on a non-commercial liquid crystalline structure and its isotropic homologue in order to provide further insight into the mechanism and kinetics of thermal degradation of the proposed systems. The studies were done by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). For the first time the degradation of a liquid crystalline epoxy was studied using an advanced isoconversional kinetic method. The results were used to predict the thermal stability of both types of epoxy networks. GC–MS analysis was applied on evolved gas during degradation to elucidate the degradation mechanism in accordance with the kinetic results. The liquid crystalline structure has a different mechanism of decomposition in comparison with its isotropic homologue. In spite of a higher T_g value, it shows a similar thermal stability but a lower release of degradation compounds. © 2007 Elsevier Ltd. All rights reserved.

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1. Introduction

Liquid crystalline epoxy thermosets (LCET) are an important challenge in epoxy science and technology. These materials show interesting theoretical aspects and offer new properties for possible applications: matrices for high performance composites, electronics packaging, insulating layers, nonlinear optics. Nematic and smectic networks, with high cross-linking density, high order parameter (S) and birefringence (Δn), reduced polymer shrinkage and good adhesion to substrates, can be produced by the polymerization of various liquid crystalline (LC) epoxy monomers in the mesomorphic state.

A very important aspect of the LCET study is the development of a correlation between chemical structure and molecular architecture, and their direct influence on macroscopic

properties, with emphasis on the location in the molecular edifice of the rigid units that generate the matrix orientation in the LC state. The statistical orientation of the mesophase in polydomains with different degrees of order has already been shown to be the key in controlling the behaviour of LCET [1–7]. Hence, a comparison with a commercial, isotropic, homologue is used to describe the thermal degradation phenomenon of these kinds of materials in a specific, quantitative way.

Thermal decomposition of thermoplastics is known to occur via initiation, followed by propagation and termination [8]. Peterson et al. [9] have shown that the initial rate of degradation of PMMA under nitrogen and air are, respectively, controlled by the unzipping of the polymer chain and by degradation initiated by random scission. The activation energy of the later stage of decomposition under nitrogen was estimated to be $\sim 230 \text{ kJ mol}^{-1}$. The understanding of the mechanisms of thermal decomposition of thermosets seems to be more difficult. In spite of a great number of works regarding the study of the epoxy/amine systems, literature data on mechanical and

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thermal properties of the LCET are very poor. It is common knowledge that generally, the epoxy resins show high glass transition temperatures and good thermal stability. In the case of degradation of epoxies cured with primary amines, high molecular weight fractions are degraded to liberate H_2 , CO , CH_4 , C_2H_4 , C_2H_6 , C_3H_6 and C_3H_8 [10].

Two epoxy monomers (with very close chemical structures and molecular weights) are studied as model compounds. One of the monomers is the most used and investigated commercial epoxy: the diglycidyl ether of bisphenol A (DGEBA). The other one, is a laboratory synthesized mesomorphic epoxy: the diglycidyl ether of 4,4'-dihydroxybiphenyl (DGEBP). The single difference between the two architectures is the existence of isopropylidene between phenolic aromatic rings in the isotropic structure. Both monomers were cured with the same curing agent, the 2,6-diaminopyridine (DAP), aromatic diamine. In this manner, by minimizing the chemical influences, we try to establish clearly the influence of an ordered organization, at both the molecular and supramolecular levels, on the thermal and mechanical performances of the models in question.

Thermal stability of DGEBA and DGEBP cured with DAP has been explored by thermogravimetric analysis (TGA). Weight loss information obtained is analyzed by an advanced isoconversional method to give a kinetic interpretation of thermal degradation of an isotropic resin and its mesomorphic homologue. Evolved degradation products are also analyzed by gas chromatography with a mass spectrometer detector (GC–MS) to identify chemical species and to establish the degradation pathways of both systems. Dynamic mechanical analysis (DMA) is also performed on the two cured epoxies, the results being used to compare their thermo-mechanical properties.

2. Experimental part

2.1. Materials

The chemical structures of epoxy monomers and of curing agent are shown in Fig. 1. The isotropic epoxy monomer, based on diglycidyl ether of bisphenol A (DGEBA), provided from Sigma Aldrich, has a molecular weight of about 355 g mol^{-1} , and an epoxy equivalent of about 176. This compound was used as delivered, without further purification. The mesomorphic epoxy monomer, diglycidyl ether of 4,4'-dihydroxybiphenyl (DGEBP), was synthesized according to the procedure already described [11]. It has a molecular weight of 313 and an epoxy equivalent of 155. The curing agent, 2,6-diaminopyridine (DAP), was purchased from Aldrich and used without further purification.

To prepare samples for thermal and mechanical experiments, stoichiometric amounts of epoxy and amine were placed in moulds and cured in an oven. The curing cycle was adapted to each system taking into account that the DGEBP/DAP system is more reactive than DGEBA/DAP: 165°C for 2 h and post-cured at 190°C for 2 h for DGEBP/DAP system, 140°C for 3 h and post-cured at 170°C for 3 h for DGEBA/DAP.

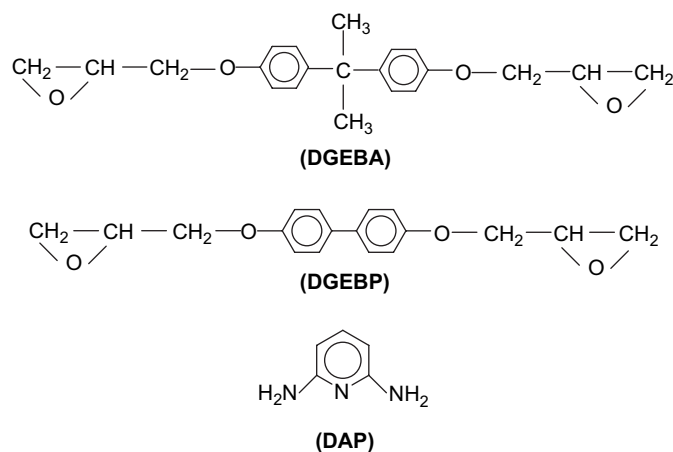


Fig. 1. Chemical structures of curing monomers.

2.2. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed using a Mettler-Toledo TGA/SDTA 851°. Samples of $14 \pm 3 \text{ mg}$ were placed in opened alumina pans. The experiments were carried out at five heating rates (5 , 10 , 15 , 20 and 25 K min^{-1}), in the temperature range 50 – 800°C , under non-oxidative atmosphere (80 mL min^{-1} flow of N_2).

2.3. GC–MS analysis

Evolved gases produced during thermogravimetric measurements at 10 K min^{-1} were investigated in terms of chemical composition. Each gas sample is transferred from the TGA furnace to the GC–MS by a heated transfer line (250°C). Gas samples are separated by an Agilent 6890 GC and analyzed by an Agilent 5973 Mass Selective Detector using a temperature scanning at 5 K min^{-1} from 60 to 250°C followed by an isothermal stage at 250°C for 24 min.

2.4. Dynamic mechanical analysis

The DMA measurements were conducted in a Bohlin Gemini rheometer in dual cantilever geometry. The DMA specimens were prepared in order to have free dimensions of $12 \times 4 \times 1 \text{ mm}^3$. The tests were carried out by heating the samples from 30 to 300°C at 2 K min^{-1} with a 1 Hz oscillating stress and a deformation of 0.3% . The storage (E') and loss (E'') Young moduli and loss tangent ($\tan \delta = E''/E'$) were determined.

2.5. Kinetics

Conversion of the global reaction of degradation can be written, in terms of weight loss of the sample, by the relationship:

$$\alpha = \frac{m_0 - m_\alpha}{m_0 - m_\infty} \quad (1)$$

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