Polymer Degradation and Stability 144 (2017) 137–145

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

Water diffusion and swelling stresses in ionizing radiation cured epoxy matrices

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ARTICLE INFO

Article history:
Received 18 May 2017
Received in revised form
13 July 2017
Accepted 10 August 2017
Available online 12 August 2017

Keywords:
Epoxy resins
Radiation curing
Hydrothermal aging
Swelling
Dynamic mechanical thermal analysis
Photoelastic Stress Analysis

ABSTRACT

In this work a DGEBF epoxy monomer was cured by electron beam radiation in the presence of an iodonium salt and the obtained system was hydrothermally aged as such and also after a thermal treatment, in order to obtain two systems having different uniformity in the cross-linking degree. On both systems, the transient stress field arising from swelling was measured and monitored by an optical Photoelastic technique and the results were commented with reference to a thermally cured epoxy system containing the same monomer and already discussed in a previous work. Beam samples with identical dimensions, obtained from the irradiated systems, have been aged at 80 °C in water, and characterised by Gravimetric and DMTA tests. The results are compared also with already reported swelling behaviour of similar thermally cured systems. It is observed that the different curing techniques (radiation curing, radiation curing followed by thermal curing and thermal curing) determine a different network structure and a different water chemical affinity, which influence the amounts of absorbed/desorbed water, and the relative amounts of bonded/free water. Such differences affect the swelling behaviour, and then the transient stress field. Photoelastic Stress Analysis has allowed to evaluate the evolving stress field, providing a different point of view on the investigation of the material transformations associated to water diffusion.

1. Introduction

Thermoset resins are used in various structural applications such as matrices for composites, adhesive joining and coatings. Traditional manufacturing processes use thermal curing of epoxy monomers and/or oligomers in presence of various curing agents [1–4], with a certain ability to tailor physical/mechanical properties such as glass transition temperature, toughness and strength [4–7].

Alternative to thermal process, curing by interaction of ionizing radiation with apt epoxy formulations has been studied [8–13], due to some potential advantages with respect to the more traditional thermal process. In fact, ionizing radiation curing of epoxy resin can be an environmentally friendly process, due to the possibility to work at mild temperatures and without the use of organic solvents. Furthermore, also the mechanical properties can be improved due to the reduced presence of thermally induced stresses during curing processing.

An important requirement of epoxy resins based materials for structural applications is their ability to maintain the properties within a fixed range during their operative life, i.e. to show significant resistance to the external aging factors such as thermal cycles, water or in general solvents absorption and desorption, etc. [14–18]. Among them, one of the more frequent ageing conditions is hydrothermal ageing, due to both temperature cycles and water absorption-desorption. In fact, water absorption induces some important transformation in the mechanical behaviour of epoxies. These include plasticization and degradation of the network structure, which may affect the strength and fracture toughness [19,20], and swelling, which may induce important internal stresses [21].

It is accepted that the absorbed water is partly filled in the polymer free volume and partly chemically bonded to the matrix [22]. The relative amount of bonded and free water and the role of each type of water in both swelling and degradation phenomena is more complex to establish due to the mutual influence of several factors. Some authors have suggested that the bonded water is the main responsible for swelling [22–24], since such bonds are usually bulkier than normal interchain hydrogen bonds [23], and Type I hydrolysis decreases Van Der Waals interchain forces [22]. On the

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http://dx.doi.org/10.1016/j.polymdegradstab.2017.08.009
0141-3910/

other hand, the formation of bonded water may induce changes in the network structure of the resin, which may also affect the free volume, and then the free water [4,25]. This changing scenario leads to modifications in water absorption which may affect the transitory as well as the final (equilibrium) properties of the aging material in ways that are difficult to predict [17].

The concurrent mechanisms of swelling/un-swelling during water absorption/desorption cycles are also particularly difficult to investigate, due to the several mutual effects occurring, and to a lack of reliable and simple measuring techniques. Hence, only few works in the scientific literature have attempted to investigate such transitory stages [21,25,26]. Some of the authors have recently proposed a new approach to evaluate the transitory swelling/un-swelling stresses, by means of Photoelastic Stress Analysis [21,27]. This technique, applied on thermally cured and differently cross-linked epoxy resin systems, has resulted in a robust method able to detect and monitor swelling stresses arising in transparent and birefringent samples. In this way, it is possible to evaluate the material in terms of its propensity to swell and to develop internal stresses, correlating this property to the kinetics of water uptake and to the thermal and mechanical properties of epoxy resin systems [27]. Furthermore, Photoelasticity is an ideal tool for evaluating the aptitude of a thermoset resin system to develop hygroscopic internal stresses from non-uniform swelling distributions, as can exist in water transport transients, or at the interface of different materials/phases.

The present work performs the Photoelastic analysis on two epoxy resin systems made with the same DGEBF monomer, subjected to hydrothermal aging up to equilibrium, followed by desorption in a room temperature dry airborne environment. Both monitored systems are cured by ionizing radiation, and one is further treated with a thermal post-cure. These different preparations determine different network structures, and then different water physical/chemical affinities, which influence the amounts of water absorbed/desorbed, and the relative amounts of bonded/free water. Such differences affect the swelling behaviour, and the relative transient stress fields. Results are then compared with the photoelastic response of the same monomer cured by traditional thermal curing and already presented in a previous study [27].

2. Experimental procedure

2.1. Materials and sample preparation

The epoxy monomer is based on Bis(4-glycidyloxyphenil) methane (DGEBF), (epoxide equivalent weight, 160–170), provided by Sigma Aldrich. For radiation curing an onium salt, cumyltolyliodonium tetra(pentafluorophenil) borate (Rh 2047) supplied by Rhodia Silicones, was used as initiator. The chemical formula of the relative components are reported in Fig. 1.

The epoxy monomer was compounded with 0.1 phr of the iodonium salt at 60 °C and stirred for about 30 min until the initiator was dissolved in the resin. E-beam irradiation was carried out, in steel moulds 150 × 150 mm, at the ISOF-CNR laboratory in Bologna, Italy, with the 12 MeV Vickers type linear accelerator whose technical characteristics are reported elsewhere [28]. The irradiation dose rate was 80 kGy/h and the total dose was 100 KGy. The resin blend was casted into an aluminium open mould flat plate, having a smooth finish needed for preserving the sufficient optical transparency required by the photoelastic analysis. During irradiation the temperature of the polymerizing resin has been recorded through a thermo resistor wired to a data acquisition system interfaced to a computer. The thermal profile, here not reported, revealed a temperature during irradiation always lower than 60 °C.

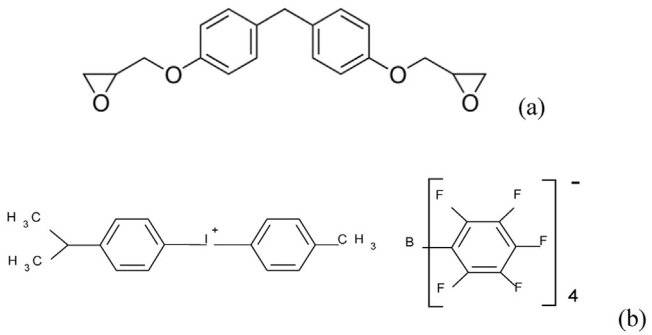

Fig. 1. Molecular structure of DGEBF monomer (a), Rh initiator (b).

After radiation cure, beam samples with nominal dimension of 36 × 8 × 3 mm were cut from the cured panels. Two lots of beam samples were considered, one radiation cured (DGEBFirr) and another thermally post cured in oven at 120 °C for 2 h after irradiation (DGEBFirr-pc). The choice of the DGEBF monomer is made in order to compare the outcomes of the present characterisation with the results from Ref. [27], where the same monomer is used and equivalent sample beams prepared by thermal curing (hereinafter referred as DGEBFt). DGEBFt was obtained curing the monomer by a tertiary ammine in a thermal cycle at high temperature and post curing the product material at 180 °C for 2 h. These treatments give rise to a highly crosslinked structure.

Care was taken in order to prepare and pre-condition all sample batches in a most similar way. Photoelastic Stress Analysis (see section 2.4) was used throughout each preparation step, to monitor the potential rise of internal stresses during cutting operations or while exposing the samples to the working environment before starting the hydrothermal aging. The following preparation procedure was in particular implemented:

1) Cured panels of all three batches were cut into beam sample shape on a table saw;
2) DGEBFirr-pc and DGEBFt beam samples were post-cured in a controlled oven. After the maximum post-cure temperature was reached, samples were brought back to room temperature with a very slow cooling of 24 h to avoid thermally induced residual stresses;
3) The three batches of samples (the two post-cured and the one simply cured), were then left for at least 24 h in a sealed container containing calcium chloride salt, before entering the hydrothermal aging bath.

Photoelasticity revealed that no meaningful internal stresses were introduced at the end of each of the three steps mentioned above.

2.2. Hydrothermal conditioning and gravimetric analysis

Hydrothermal aging of all cured samples has been carried out in deionised water at controlled temperature of 80 °C for a total time of about 1530 h. Desorption has been performed at room temperature (maintained almost constant at 25 °C) in a small sealed recipient (about 10^3 cm^3) with a relatively high content of calcium chloride salt to assure a dry airborne environment. In fact, in this condition, the atmospheric moisture is not in equilibrium, since the water vapour present in the air is not sufficient to the deliquescence of calcium chloride.

For the photoelastic and gravimetric characterizations, the specimens have been temporarily taken out of the bath a number of