Water diffusion and swelling stresses in highly crosslinked epoxy matrices

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A B S T R A C T

The present work investigates the swelling induced stresses arising in two epoxy systems during water uptake. The analysed systems are two epoxy resin based on DGEBA monomer and DGEBF monomer respectively, both fully cured by DDS amine. The systems achieve different cross-link density degrees, and are characterised by high glass transition temperatures ranging between 200 and 230 °C. Both epoxies have been conditioned in deionized water baths at two different temperatures (50 °C and 80 °C). A desorption process at room temperature in a dry airborne environment was performed after saturation. Dynamic Mechanical Thermal Analysis, carried out at the various stages of hydrothermal conditioning, has allowed to characterise the modifications occurring in the network structures during aging. Photoelastic Stress Analysis is adopted to monitor the evolution of stresses on rectangular beam samples during absorption and desorption of water. Correlation of water uptake, dynamic mechanical behaviour and transitory stress fields, has allowed to make some assumptions about the influence of the epoxy network on the swelling behaviour.

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1. Introduction

Thermoset resins are widely used as matrices for composites, adhesive bonding or coating materials in structural applications. Solvent uptake is a natural and common aging process for such thermosets, leading to a change of thermal resistance (Glass Transition Temperature, T_g) and mechanical behaviour (strength, toughness, etc …), and to the development of internal stresses caused by the swelling action of the absorbed solvent [1]. These changes can have a severe influence on highly constrained structures presenting interfaces between materials with strong properties mismatches (e.g. matrix/fibre interfaces, structural hybrid joints, etc.).

Studies so far have evidenced the presence of many concurrent phenomena influencing the diffusion kinetics and the amount of absorbed water at equilibrium in epoxy based resins. It is commonly accepted that the absorbed water is in part filling the free volume (free water) and in part chemically reacting with the epoxy network forming polar bonds (bonded water) [2—4]. The relative amount of bonded and free water and the role of each type of water in both swelling and degrading phenomena is though much more complex to establish. This is due to the mutual influence of various factors. In fact the formation of bonded water may change the network structure, and in particular its flexibility and free volume [5]. All these effects lead to a final modification in the properties of the aged material difficult to predict [6].

Water diffusion can influence structural properties of the material such as its T_g, which generally decreases with water uptake, and fracture toughness [7,8]. These changes are primarily associated to a plasticization of the material as extensively reported in the literature [1,8—12].

Among the transformations activated by water absorption, one particularly difficult to assess is swelling. Such hydrostatic volume change is usually proportional to the amount of absorbed water. During the transitory from water ingress to saturation a non-uniform distribution of water is responsible for the development of internal stresses, due to non-uniform swelling. Only a few works have attempted the evaluation of such transitory stages, due to the intrinsic difficulty to make an effective full field evaluation of the stress/strain fields [13,14]. Recently the authors have proposed a

new approach to evaluate the transitory swelling stresses arising during absorption/desorption, which uses Photoelastic Stress Analysis [1]. The method has proven to be robust and easy to implement on transparent and birefringent resin systems, providing a very high sensitivity, sufficient to detect swelling stresses arising also in small sample coupons. The authors have also successfully used the method to investigate the influence of swelling stresses on cracked materials, and to interpret the influence of hydrothermal aging on the material fracture toughness [15,16].

The present work exploits the Photoelastic technique to correlate the evolution of swelling stresses with the network structure of glassy polymers. Two highly crosslinked epoxy resin systems based on DGEBA and DGEBF monomers respectively are compared. These resin systems have been cured with amine DDS, achieving different values of T_g. By analysing the evolution of swelling stresses during absorption and desorption, it has been found that the two considered resin systems achieve a similar stress distribution, with comparable swelling stresses peaks, but the kinetic of the stress evolution is instead different and influenced by the network structure.

2. Experimental procedure

2.1. Materials and sample preparation

The epoxy systems analysed in this work are 2,2-bis[4-(glycidyloxy)phenyl]propane (DGEBA), (epoxide equivalent weight, 172–176, Sigma Aldrich, Italy) and Araldite PY 306 CH (purity almost 100%, Huntsman Advanced Materials, Belgium) based on bis(4-glycidyloxyphenyl)methane (DGEBF); the curing agent is a 4,4′ diamino-diphenyl sulfone (DDS) (Sigma Aldrich, Italy). The chemical formula of the relative monomers are reported in Fig. 1.

The DGEBA and DGEBF resins have been prepared by mixing a stoichiometric amount of DDS to the epoxy at 80 °C, fully dissolved after mechanical stirring for 30 min at 130 °C. The resin blends have then been casted into an aluminium open mould flat plate, having a smooth finish. This made possible to manufacture panels with good thickness control, smooth surface finish and adequate transparency, all necessary features to implement Photoelastic Stress Analysis [1].
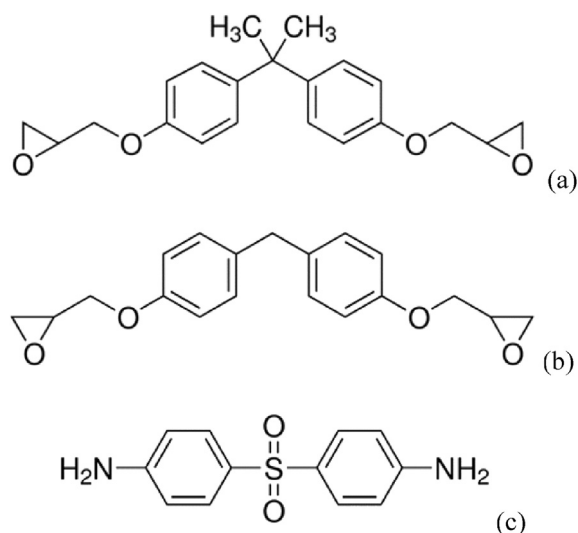

Fig. 1. Molecular structure of monomers DGEBA (a), DGEBF (b) and curing agent DDS (c).

DGEBA and DGEBF based systems have been cured in three steps: the first one consisted of a temperature gradient of 2 °C/min from room temperature to 180 °C, resting at this temperature for 2 h, and cooling at the same rate to room temperature. After this first cure process, beam samples of nominal dimension of $36 \times 8 \times 3$ mm have been cut from the cured panels and post-cured.

In the following the two cured systems will be indicated as DGEBA and DGEBF resins respectively.

The post-curing process has been different for DGEBA and DGEBF resins, due to their different cross-linking network: the former has been post-cured at 200 °C for 2 h followed by a slow cooling to room temperature in 24 h, while the latter has been post-cured at 180 °C for 2 h followed by the same cooling rate applied for DGEBA. The previous treatments were able to provide fully cured and dry samples, without any significant residual stresses left from sample cutting and ambient humidity absorption.

2.2. Hydrothermal conditioning

Hydrothermal aging has been carried out in two baths of deionized water at controlled temperature of 50 °C and 80 °C. Desorption has been performed at room temperature in a recipient with a calcium chloride salt to assure a dry airborne environment. Samples aged at 80 °C have been also subjected to the desorption process.

2.3. Gravimetric and dynamical-mechanical-thermal analysis

The specimens have been taken out of the bath at short time intervals, shorter in the initial stages of absorption and desorption. The samples have then been wiped off of surface water and, after a sufficient time to reach thermal equilibrium with the ambient, weighted on a 10^{-5} g resolution electronic balance. Results have been plotted in terms of percentage of mass uptake M_r versus time t, according to the follow equation:

$$M_r(t) = \frac{M(t) - M(0)}{M(0)} \tag{1}$$

where $M(t)$ is the weight at the time t, $M(0)$ is the initial weight before the hydrothermal aging.

The gravimetric analysis, in the absorption and desorption process, has been carried out until it was not observed a significant mass change.

The glass transition temperature, T_g, has been determined by Dynamical Mechanical Thermal Analysis (DMTA), performed on a Rheometrics DMTA V in a single cantilever beam arrangement at a heating rate of 10 °C/min, frequency of 1.8 Hz and elongation of 0.02%. The temperature corresponding to the tanδ curve peak has been assumed as the value of T_g.

DMTA has been carried out for each hydrothermal conditioning, at four different stages of aging:

1) initial not aged post-cured samples;
2) under maximum swelling stresses, as detected by photoelasticity;
3) at saturation (water uptake equilibrium);
4) at desorption equilibrium (for systems aged at 80 °C).

2.4. Photoelastic stress analysis

The photoelastic technique is able to reveal the average distribution of hygroscopic in-plane stresses arising in the sample, when