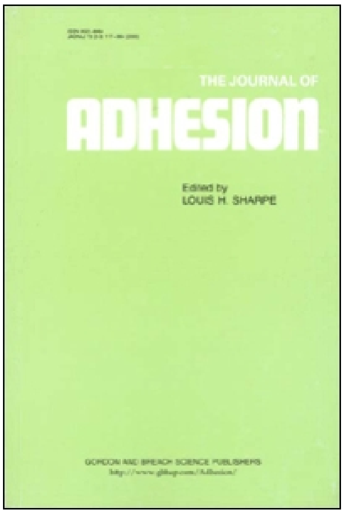

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Use of dielectric spectroscopy to assess adhesively bonded composite structures, Part I: Water permeation in epoxy adhesive

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USE OF DIELECTRIC SPECTROSCOPY TO ASSESS ADHESIVELY BONDED COMPOSITE STRUCTURES, PART I: WATER PERMEATION IN EPOXY ADHESIVE

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This three-part series of papers describes studies on water penetration into epoxy resins and the use of low- and high-frequency dielectric spectroscopy as a method of monitoring the health of adhesive bond lines in bonded epoxy/graphite composite structures. The first paper is concerned with an investigation of the effect of water ingress into the epoxy adhesive resin used in the manufacturing of the adhesive bond. This study reports a dynamic mechanical thermal analysis (DMTA) and gravimetric analysis of the effects of water uptake and interprets the data in terms of various processes that can occur within the adhesive. Surprisingly high values of water absorption were observed in samples where the edges were unconstrained and presented direct access to the fibre matrix for the moisture. The study demonstrated the effects of postcure and leaching on the sorption and desorption processes and provided background data, which are necessary for the interpretation of the study described in Parts II and III of this series of articles.

Keywords: Epoxy resin; Moisture; Thermal and dynamic properties

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INTRODUCTION

The sorption process in an epoxy resin is complex and seems to vary with the time of exposure to a hot/wet environment. The mechanisms associated with the process have been investigated extensively. Apicella et al. [1] proposed that there are 3 modes of sorption: 1) bulk dissolution of water in the polymer network, 2) moisture absorption onto the surface of vacuoles that define the excess free volume of the glassy structure, and 3) the occurrence of hydrogen bond formation between polymer hydrophilic groups on the polymer chain and water molecules. Adamson [2] postulated that the transport of moisture below T_g is a 3-stage process in which the absorbed water initially occupies the free volume present in the form of voids. In the second stage, water becomes bound to network sites causing swelling. Finally, it enters the densely crosslinked regions.

It has been proposed that the water equilibrium concentration is mainly governed by the available free volume in the resin [2, 3] or that water molecules occupy what are essentially microvoids and other morphological defects [4–7]. It is probable that much of the water is bound to hydroxyl and other polar groups, rather than being in the free, unbound state [4]. Spectroscopic investigation suggests that water molecules are linked by strong hydrogen bonds to some hydrophilic groups [8, 9], mainly hydroxyl [10] or amine groups [11]. When exposed to hygrothermal environments, epoxy composites undergo degradation, which manifests itself in terms of reduced structural performance [12–14] and anomalous moisture diffusion behaviour. Degradation can lead to sorption-desorption hysteresis and 2-step absorption. The absorbed moisture allows relaxation of polymer chains leading to changes in the residual stress and the formation of microvoids and/or microcracks in the resins [15, 16]. An important mechanism for the loss of mechanical properties in a moist-rich environment is the formation and growth of cracks in the material. The crack growth is often aided by localised chemical bond hydrolysis or chain scission at the crack tip. The formation of microcracks increases the equilibrium moisture content. Morgan and Mones [17] concluded that sorbed moisture enhances the craze cavitation and propagation processes in amine-cured epoxy resins. The initial stages of failure enhance the accessibility of moisture to the sorption sites within the epoxy resin. The later stages of failure may, however, just involve crack propagation.

A review of sorption processes in composite materials by Lee and Peppas [18] explained that moisture sorption induces micromechanical damage in the epoxy resin and/or at the epoxy-fibre interface as well as internal stresses, relaxation of mechanical properties, and plasticisation. Some of these degradations or physical ageing processes are closely linked to the swelling processes. Hahn [19] showed that the absorbed water produces relatively little swelling until a critical amount of water has been absorbed, and subsequent absorption leads to the resin sample increasing its volume proportionally to the additional water content absorbed. He also indicated that hygrothermal degradation is a result of matrix plasticisation, microvoid, and microcrack formation. Halpin [20] observed that the rates of the apparent diffusion process and the magnitude of the equilibrium weight gain are accelerated by the presence of cracks and voids in a laminate.

In this paper, a study of the dynamic mechanical thermal analysis (DMTA) and gravimetric behaviour of a widely used epoxy resin system exposed to relatively high temperatures and humidity levels is reported. The results obtained from this study will, in a subsequent paper, be correlated with parallel dielectric measurements.

EXPERIMENTAL PROCEDURE

Materials

The overall study is concerned with polymeric materials and thick adhesively bonded structures; however, this work presents results obtained for the adhesive material. The adhesive film used is supported by a polymeric woven film and is a blend of approximately 70% of bis[2-chloro-N,N-bis(2,3epoxypropyl)-4-aminophenyl]methane and 30% of diglycidylether of bisphenolA which was cured with about 3–7.0% of dicyandiamide and between 0.5–1.5% of (N,N′-(methyl-1,3-phenylene)bis(N,N′dimethylurea)). The samples required for the experiments were created by curing 6 layers of the adhesive film between metal plates, using a temperature of 125°C for a period of 1 h. A set of samples was postcured for 8 h at 145°C.

Gravimetric Measurements

Immediately after manufacture, all of the samples (films of 78 × 10 × 1 mm) were placed in a dessicator at room temperature in order to avoid absorption of moisture prior to the start of the experiments. Gravimetric measurements were performed by immersion of the samples in a water bath held at a constant temperature of 60°C. The weight of the sample was recorded after the excess moisture had been removed by rapidly blotting with tissue paper, using an electronic balance (Mettler AJ100) with an accuracy of ±0.1 mg. The time required for weighing the sample was assumed to be sufficiently short so as not to influence the values of the mass measured.

Dynamic Mechanical Thermal Analysis

A Polymer Laboratories Dynamic Mechanical Thermal Analyser MkIII was used to test the epoxy adhesive. The single cantilever mode operating at a frequency of 1 Hz was applied during the measurements with a 64 μm peak-to-peak displacement and a rate of heating of 5°C/min over the temperature range considered. The tests were performed on samples of dimensions $26 \times 10 \times 1$ mm.

RESULTS AND DISCUSSION

To understand the effect of moisture on the adhesive resin in terms of sorption and induced degradations, two sets of adhesives samples were produced. The first one was cured and postcured (Group A), whereas a second set of samples was not postcured (Group B). From each group, different types of sample were manufactured. Specimens were cut from a large plate, creating rough surfaces on the edges and direct access for the water to the polymeric woven film support (indexed 1). It is possible that some near-surface cracks were also induced. The other specimens were manufactured as single samples, and all the edges were sealed with no direct access to the support film (indexed 2). Comparison of the sorption results between these two sets of samples will indicate the effect of exposing the support film directly to water.

Gravimetric Measurements

All the specimens were immersed in water at 60°C for 10,900 h, followed by 3,243 h at 60°C in an air-ventilated oven. Figures 1a and 1b present the sorption and desorption data for groups A and B, respectively, as a function of the square root of time divided by the thickness. It is interesting to notice that the groups having rough edges (groups A1 and B1) have an equivalent final equilibrium value for the sorption process of around 26%, independent of the manufacturing process. This observation would suggest that the sorption is mainly driven by water ingress by capillary processes *via* the support film. Moreover, the film being based on highly hydrophilic polymeric materials, water clusters are created around the carrier, increasing the water content in the epoxy adhesive.

The sorption equilibrium achieved at long exposure time can be best described as a pseudo-equilibrium. The water entering the structural adhesive is equilibrated with the leaching of low molecular weight species associated with uncured resin components, degradation of the film support, and/or polymeric materials constituting the epoxy network.

In the case of the resin-sealed edges, the sorption process is purely a function of the manufacturing process and is not influenced by the accessibility of the fibre. The nonpostcured specimens reach an equilibrium value of 12.2%, whereas the postcured specimens equilibrate at 7.6%. The lower value in the case of the postcured material reflects the more highly cross-linked matrix formed and a greater rigidity of the matrix. Lack of accessibility to the fibre matrix greatly reduces the amount of water absorbed by capillary action, and the sealed edges reduce capacity of the resin to swell and absorb moisture.

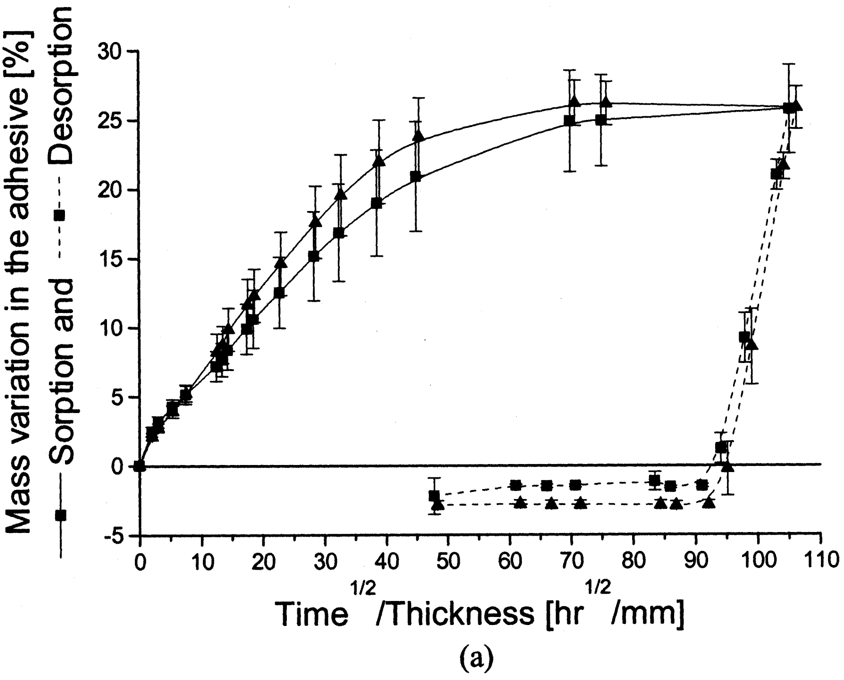

FIGURE 1 (a) Sorption (—) and desorption (----) processes for (■) group A1 and (▲) group B1; (b) sorption (—) and desorption (----) processes for (■) group A2 and (▲) group B2.

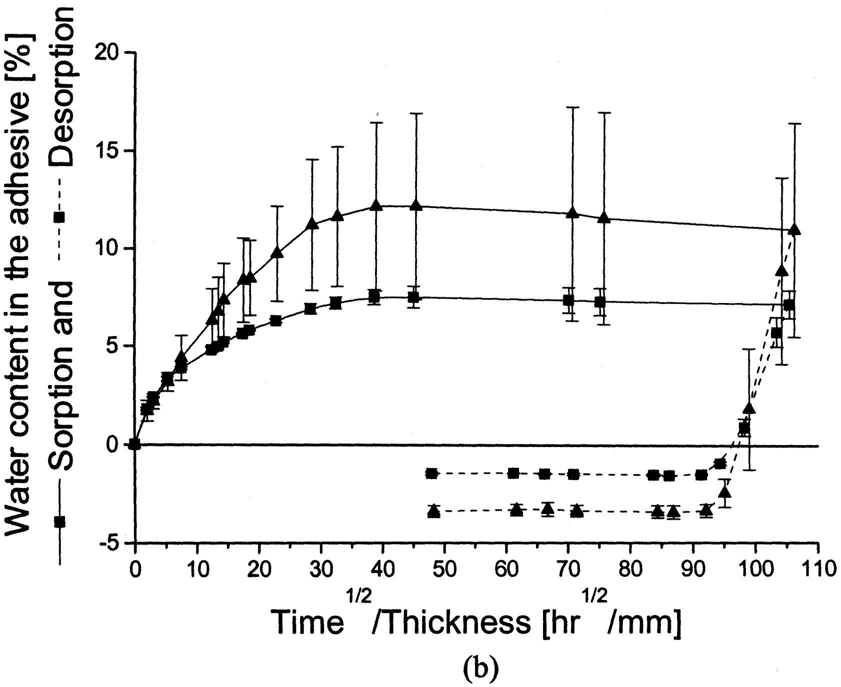

FIGURE 1 (*Continued*).

In all the cases studied, the amount of material leached, as indicated by the difference between the sorption and desorption values, is almost constant at about 2.3%. This would imply that the process is related to low molar mass extractable materials and is not a consequence of degradation or densification. The latter processes might be expected to be sensitive to the thermal history of the sample. The possible leaching of the unreacted dicyandiamide curing agent has been previously observed by Saunders et al. [21] and will be a contributing factor in this system. The formulation used contains approximately 3–7.0% of dicyandiamide and between 0.5–1.5% of (N,N′-(methyl-1,3-phenylene)bis(N,N′dimethylurea)). These low molar mass components will segregate to the surface of the resin during the cure process. The extent of segregation may be expected to be approximately the same in both cases and, hence, the extent of the amount of the extractable material appears to be insensitive to the fabrication or sample preparation process. The sealing of the edges appears to influence the final water uptake value and reflects whether or not capillary diffusion along the fibres is a dominant mechanism in the particular

TABLE 1 Diffusion Data for the Structural Adhesive

Identification	Equilibrium sorption value (%)	Equilibrium desorption value (%)	Variation (%)
Group A1	25.8	28	+ 2.2
Group A2	7.6	8.8	+ 2.2
Group B1	26.2	28.8	+ 2.6
Group B2	12.2	14.5	+ 2.3

case studies. Table 1 presents the diffusion information for all the specimens.

When the sample is cut from a large plate, it can be represented as a shish kebab or parallel multilayer system, (Figure 2a). Thus, when the water penetrates the adhesive, it swells the polymeric materials, pushing apart the epoxy network from the polymeric woven film support. This process creates water cluster areas around the woven film, which generate the high water content. In the case of samples manufactured with a continuous resin coating (Figure 2b), the epoxy resin network on the edges counterbalances the swelling effect. The energy necessary to break covalent bonds of the epoxy network is higher than the energy involved in the separation and swelling of the layers. Figure 2 is a schematic representation of the possible process. Figure 3 represents the normalised mass variation of the adhesive during the sorption and desorption process as a function of the square

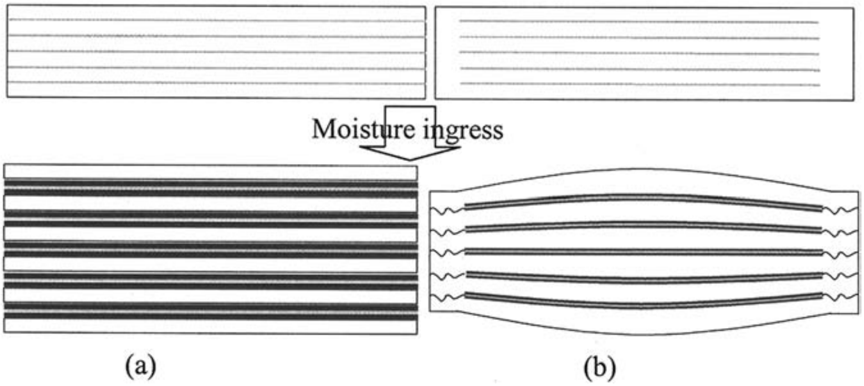

FIGURE 2 Schematic representation of moisture ingress in (a) rough-edge samples and (b) glassy-edges samples (see Color Plate I).

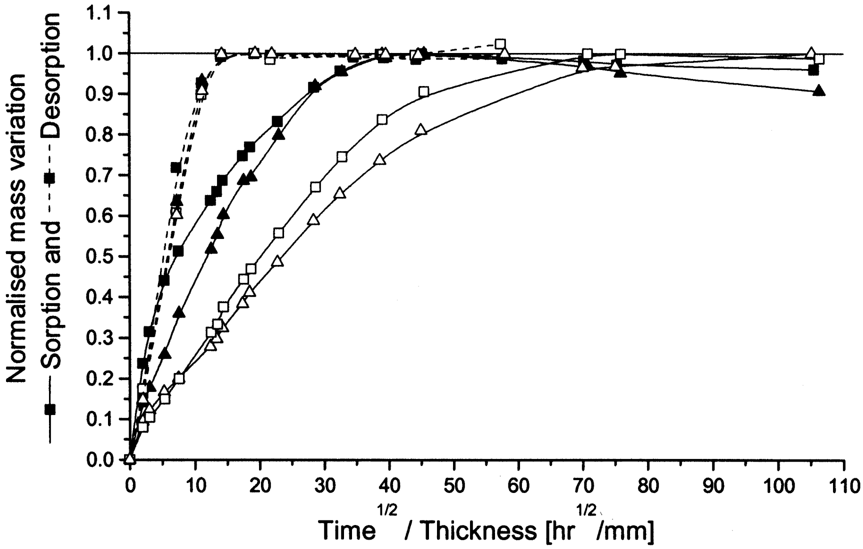

FIGURE 3 Normalised mass variation during (—) sorption and (----) desorption for (□) Group A1, (Δ) Group B1, (■) Group A2 and (▲) Group B2.

root of time divided by the thickness. Table 2 gives the diffusion data for the different samples.

Dynamic Mechanical Thermal Analysis (DMTA)

DMTA measurements were performed on samples of the resin sampled during the water uptake process. At fixed times, samples were removed from the hot/wet environment and tested from 50°C to 145°C. The results are presented in Figure 4.

TABLE 2 Diffusion Coefficient for the Structural Adhesive During the Sorption and Desorption Processes

	Diffusion coefficient [mm^2/h]	
Identification	Sorption process	Desorption process
Group A1	$0.715 \pm 0.5 \times 10^{-4}$	$13.0 \pm 0.5 \times 10^{-4}$
Group A2	$4.41 \pm 0.5 \times 10^{-4}$	$14.8 \pm 0.5 \times 10^{-4}$
Group B1	$1.00 \pm 0.5 \times 10^{-4}$	$13.2 \pm 0.5 \times 10^{-4}$
Group B2	$2.78 \pm 0.5 \times 10^{-4}$	$14.2 \pm 0.5 \times 10^{-4}$

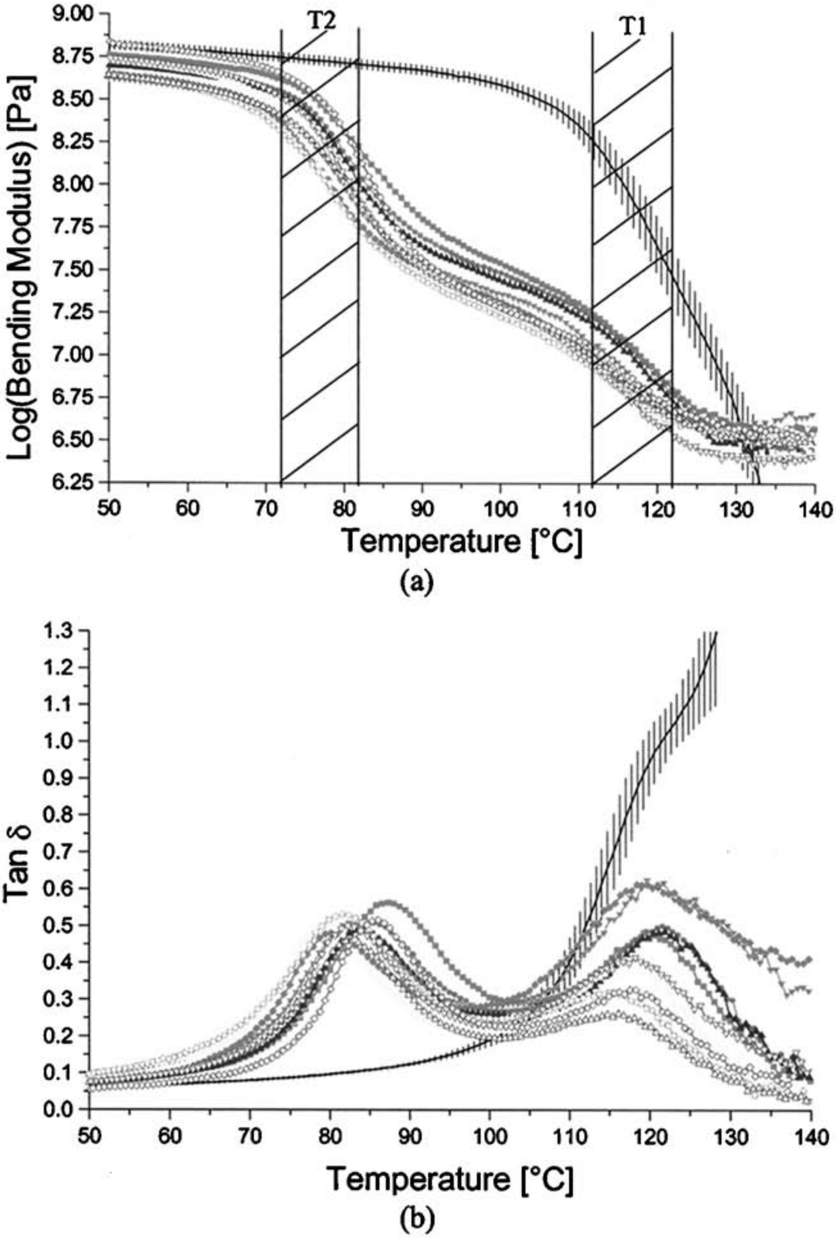

FIGURE 4 Effect of water on (a) the bending modulus and (b) the dynamic loss of postcured adhesive, (—) as manufactured, after (—■—) 24 h, (—●—) 50 h, (—▲—) 121 h, (—▼—) 240 h, (—◆—) 408 h, (—□—) 672 h, (—○—) 867 h, (—△—) 1,369 h, (—▽—) 2,713 h, and (—◇—) 3,890 h (see Color Plate II).

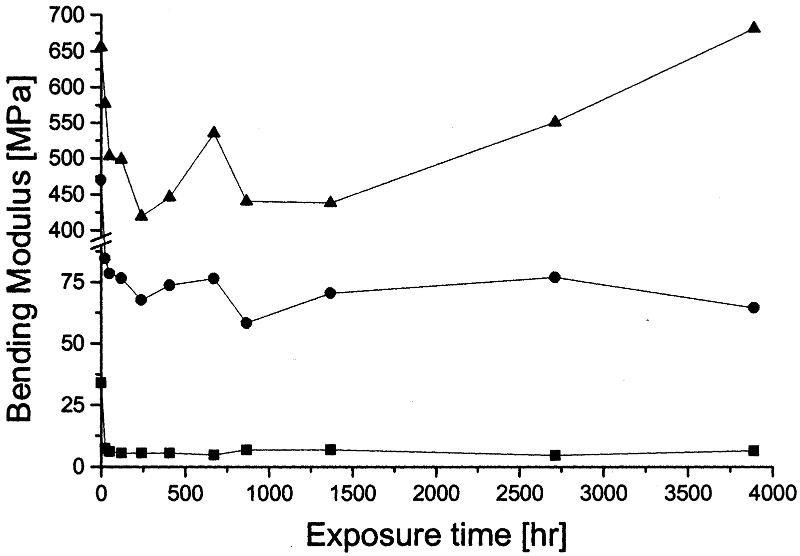

FIGURE 5 Effect of water on the bending modulus of postcure adhesive at (▲) 50°C, (●) temperature of transition 2 and (■) temperature of transition 1.

As shown in Figure 4, a dramatic change of the bending modulus in the glassy state region occurs almost as soon as the sample is exposed to water. The overall variation is presented in Figure 5, where values of the bending modulus are measured for three different temperatures: temperature of transition T_1 (120°C, assimilated to the glass

TABLE 3 Loss in the Bending Modulus Due to Water Sorption

	Loss in bending modulus		
Ageing time in water at 60°C (h)	At T_1 (%)	At T_2 (%)	At 50°C (%)
24	−84.5	−84.2	−24.1
50	−83.4	−82.6	−25.9
121	−88.3	−81.8	−20.6
240	−86.2	−81.8	−25.9
408	−85.5	−83.8	−25.9
672	−86.6	−83.0	−18.7
867	−83.4	−85.5	−32.4
1,369	−83.0	−85.2	−27.6
2,713	−86.5	−83.6	−17.1
3,890	−86.8	−85.9	−4.5

transition temperature), temperature of transition T_2 (80°C) and low temperature (50°C). The loss in bending modulus is presented in Table 3.

After a dramatic fall in the bending modulus after just a few hours of exposure in the hot/wet environment, the bending modulus is stable at a lower value equal to 83–85% of the original bending modulus value between the temperatures T_1 and T_2. The combined effect of the increased free volume due to plasticisation, leaching of small unreacted components, and/or hydrolysis releases the stresses generated by the penetrant into the matrix and produces a steady decrease of the modulus. As plasticisation takes place, relaxation of stresses induced during the manufacturing process can occur, leading to the creation of local densification of the matrix and an overall toughening effect of the composite structure.

It appears that the glass transition temperature, T_g, is not significantly decreased during exposure to hot/wet environment. However, more importantly, a second peak appears and stabilises around 82°C. These phenomena have been described previously [22]. Kaelble et al. [23] showed that in optimum conditions, the epoxy resin forms a perfect 3D network structure. However, in real epoxy system manufacturing all the conditions are seldom achieved and areas with different crosslink density are formed inside the neat resin. Similar ideas have been proposed by Mijović and Tsay [24] and Dušek et al. [25]. The dense crosslinked areas correspond to more completely formed crosslinked structures that are connected by less completely formed regions. At a molecular level the resin is a composite structure in which the rate of water uptake differs from place to place according to the perfection of the extent of crosslinking. Thus, less plasticisation occurs in the densely crosslinked phase, producing only a small reduction of the temperature of glass transition T_g, around 5°C after 867 h. However, in the more lightly crosslinked regions the ingress of water produces a greater degree of plasticisation, resulting in a new relaxation appearing around 40°C lower than the T_g. Figures 6a and 6b represent the recovering effect of the epoxy adhesive system when the water is removed from the sample.

The water desorption is achieved by testing the sample in the DMTA apparatus for several consecutive runs from 50°C to 145°C. These measurements show clearly the reversibility of the ageing process at low temperature which is characteristic of a simple plasticisation. Desorption of the water decreases the free volume of the system, resulting in the restoration of the constraint imposed by the dense crosslinked areas and, consequently, increasing the bending modulus. However, after 5 runs complete water desorption would be

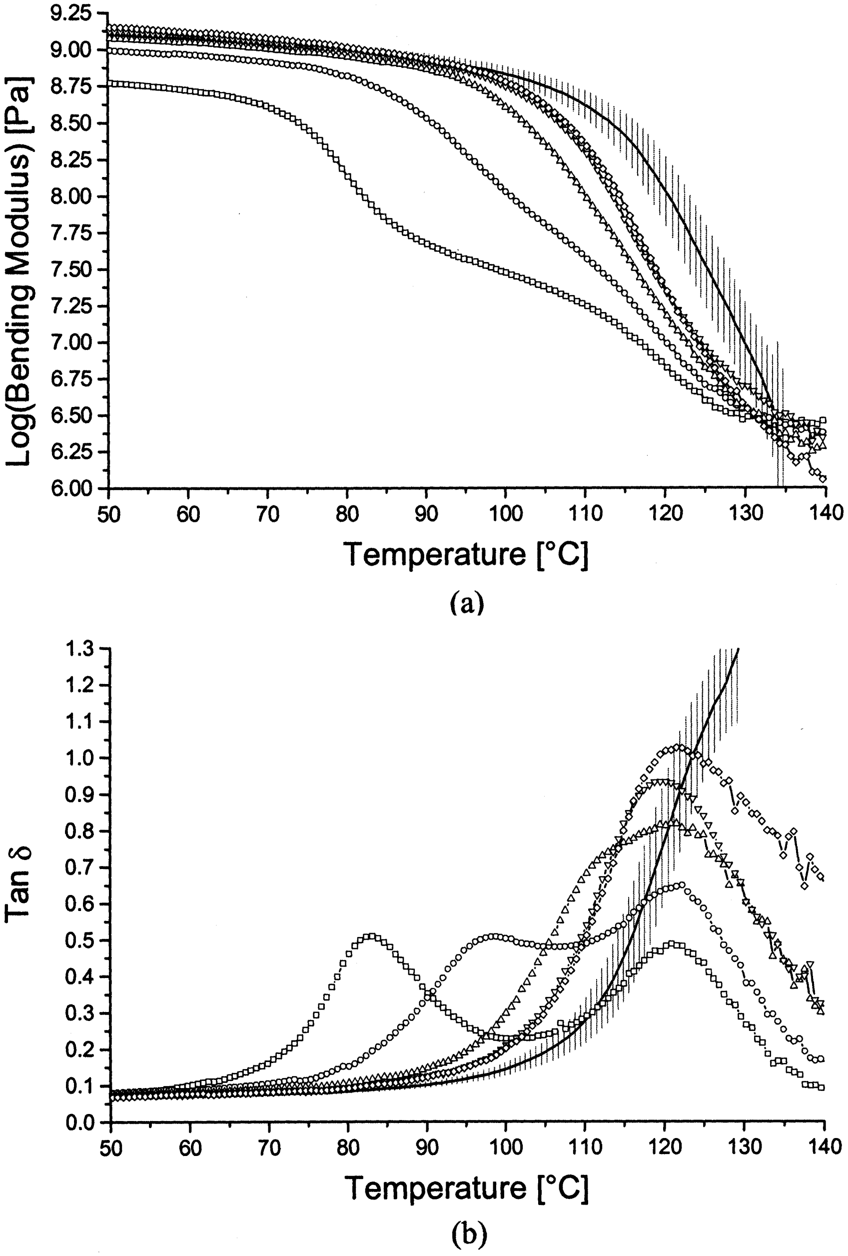

FIGURE 6 Effect of water desorption on (a) the bending modulus and (b) the dynamic loss of postcured adhesive: (—) unaged and after (—□—) run 1, (—○—) run 2, (—△—) run 3, (—▽—) run 4, and (—◇—) run 5 from 50°C to 145°C.

expected, but the initial glass transition temperature of the system is not observed to be fully recovered. The relaxation of the stresses originally created by the fabrication process and possibly chain scission can account for these irreversible changes. Similar phenomena have been observed previously [22, 26] and have been attributed to hydrolysis. Partial recovery of the T_g may also be the result of the presence of bonded water molecules at hydrophilic sites [7, 27, 28] that need higher energy to be removed from the polymeric network [29]. Some physical ageing may also be part of the process, as the specimens have spent over 3,000 h in a warm environment.

CONCLUSION

This study demonstrates the complexity of the water absorption process in a typical structural adhesive. Most epoxy resins will achieve increases of around 4 to 7% in weight, and therefore it was very surprising to observe values of up to 26%. The higher values are associated with the unconstrained absorption of water where capillary effects can play an important role. The dynamic mechanical properties are largely reduced by moisture in the glassy stage of the adhesive. Up to 85% decrease of the initial strength is observed after more than 10,000 h immersion in hot water. The DMTA measurements have shown that the adhesive presents areas of different crosslinking density. Two relaxations have been observed, the glass transition temperature at around 120°C and another relaxation at lower temperature (80°C), both associated with the areas of different crosslinking density—high and low density, respectively.

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