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Thermo-stimulated creep analysis on the effect of water in glass bead-reinforced composites

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Thermo-stimulated creep analysis is performed to characterize the effect of water on the anelastic properties of the model system: epoxy resin–glass beads. The changeable parameter is the nature of the interfacial region. The behaviour of filled composites after water exposure is compared for composites filled with raw beads, beads treated with silane coupling agent, and beads coated with elastomeric adduct (tailoring interphase). Both the glassy region and the glass transition region are investigated. Specific behaviours are reported in the case of epoxy reinforced with silane-treated beads and coated beads.

(Keywords: glass–epoxy composite; thermo-stimulated creep; water absorption)

INTRODUCTION

Water penetration and its effect on thermoset-based composites is of major interest for determining the stability and ultimate use of these materials. Moisture is an important element affecting the mechanical, electrical and various physical properties of glass-reinforced composites[1], especially at higher temperatures.

There are essentially two kinds of theories in the field of water absorption and diffusion in themosetting epoxy resin. The first ones, labelled 'voluminal', attach importance to the concepts of density or compaction[2], free volume[3], expansion[3,4] and possibly physical morphology[5] (in other words, spatial fluctuations of voluminal features). The second kind of theories, called 'interactional', refer to the existence of strong interactions by hydrogen bonding[6,7] between the water molecules and particular segments or polar groups, such as hydroxyl or amine, present in the polymer[8].

Both free volume and type and concentration of polar groups play an important part in determining the degree of water absorption[2]. According to Diamant *et al.*[5], the coefficient of moisture diffusion into epoxy resin depends on four main factors as follows: (i) the polymer network structure; (ii) the polymer polarity, determining polymer–moisture affinity; (iii) the physical morphology of the polymer (e.g. a two-phase structure); and (iv) the development of microdamage under severe humidity conditions.

The interface in composite materials is known to play an important role in its properties. In the present study, different interphase regions are deliberately formed by means of a silane coupling agent and an elastomeric adduct covering the glass spheres. The molecular mobility of both dry and wet glass-bead-reinforced epoxy is evaluated via low- and high-temperature thermo-stimulated creep (TSCr) spectroscopy. Water absorption experiments on the matrix and on the composites have been performed in order to separate the effect of interfacial character from that of water-induced plasticization.

The main interest in making these studies was to understand how the relaxation processes in the composite interrelate with moisture sorption depending on the interface nature.

EXPERIMENTAL

Materials

The specimens investigated in this study were supplied by 'Laboratoire des Matériaux Macromoléculaires et Composites' of 'Institut National des Sciences Appliquées', Lyon (France). A summary of the sample codes used is presented in *Table 1*. The details of the materials used, together with their respective references, molecular weight ($\overline{M_n}$) and functionality ($\overline{F_n}$) are listed in *Table 2*. The structures of diglycidyl ether of bisphenol A (DGEBA) epoxy resin, dicyandiamide (DDA) curing agent, γ-aminopropyltriethoxysilane (γ-APS) coupling agent and carboxy-terminated butadiene–acrylonitrile (CTBN), used in the elastomeric adduct coating, are shown in *Figure 1*. The glass-bead-reinforced composites were prepared following a procedure previously described[9]. However, the essential details of the experimental system are as follows.

Epoxy matrix. The mixing of diglycidyl ether of bisphenol A ($n = 0.14$) (DGEBA$_{0.14}$) and dicyandiamide

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(DDA, curing agent) was carried out with an amine/epoxy ratio of 0.6 in the presence of benzyldimethylamine (BDMA, catalyst). The components were mixed using mechanical stirring under vacuum for 1 h at 60°C. The mixture was then transferred to a mould and the resin was cured in an oven for 1 h at 120°C followed by a postcure for 1 h at 180°C. The density of the epoxy network at room temperature is 1.3 kg m^{-3}.

Filler. Glass bead-reinforced composites that were manufactured using the above-mentioned system were also examined. Glass beads, with a density at room temperature of 2.45 kg m^{-3}, were supplied by Sovitec (France). The volume fraction of filler was 20 wt% and the size distribution of the beads ranges from 4 to 44 μm with an average particle diameter of 26 μm.

Table 1 Summary of identification codes used

Code	Sample
(M)	Matrix (DGEBA$_{0.14}$–DDA)
(M+RB)	Matrix + 20% raw glass beads
(M+SB)	Matrix + 20% silane (A-1100) treated glass beads
(M+EB)	Matrix + 20% elastomeric adduct coated glass beads

Table 2 Details of the materials used including molecular weight ($\overline{M_n}$) and functionality ($\overline{F_n}$)

Material	Reference	$\overline{M_n}$ (g mol^{-1})	$\overline{F_n}$
DGEBA ($\bar{n}$ = 0.14)	Bakelite E0164 (Union Carbide)	380	2
DDA	VE 2560 Bakelite (Union Carbide)	84	4
γ-APS	A1100 (Union Carbide)	221.3	2
CTBN	Hycar 1300 × 8 (Goodrich)	3600	1.8

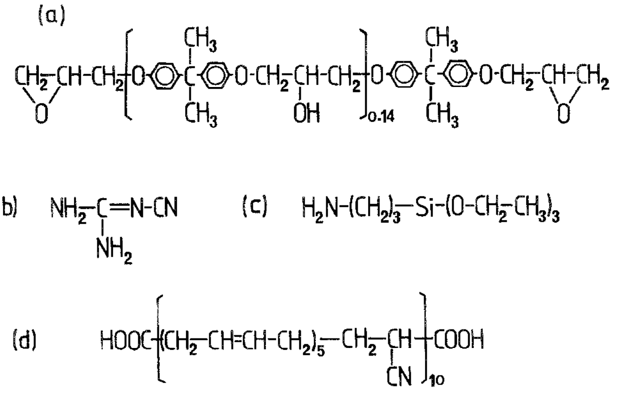

Figure 1 Structures of (a) diglycidyl ether of bisphenol A (DGEBA), (b) dicyandiamide (DDA), (c) γ-aminopropyltriethoxysilane (γ-APS) coupling agent, and (d) carboxy-terminated butadiene–acrylonitrile (CTBN)

Table 3 Weight change in the specimens after 6 months exposure to distilled water at room temperature

Sample	M	M+RB	M+SB	M+EB
Apparent change in weight (%)	+3.2	+3.3	+2.0	+3.4
Actual change in weight (%)	+3.2	+5.1	+3.0	+5.2

Silane treatment. The silane coupling agent used for the surface treatment was γ-aminopropyltriethoxysilane (A-1100, Union Carbide). The coupling agent was used in a solution of ethanol and water (95:5 v/v). The amount of coupling agent was controlled to give 0.5 wt% silane on the filler basis. The glass beads were first washed in isopropanol, and then added to the silane solution. The liquid was removed under vacuum for 12 h at 95°C.

Elastomeric adduct coating. In order to synthesize an elastomeric adduct, DGEBA and carboxy-terminated butadiene–acrylonitrile (CTBN) prepolymers were mixed at 85°C under mechanical stirring and inert atmosphere (N_2) with a carboxy/epoxy ratio of 0.5. Triphenylphosphamine (TPP) was used as catalyst. After 20 h of reaction, liquid diamine (isophorone diamine (IPD, 3-aminomethyl-3,5,5-trimethylcyclohexylamine)) was added in an amine/epoxy ratio of 2; the reaction was run for 30 h at 120°C. It was established[10] that DGEBA was totally modified and that epoxy groups were still present in the final adduct. These were capable of reacting with amine groups in the epoxy matrix.

Adduct was deposited by adding the glass beads to an elastomer solution of methyl ethyl ketone (MEK, 2 wt% of adduct). The solution was stirred for 20 min, and removal of solvent (MEK) was effected under vacuum at room temperature. The beads were then placed in an oven for 12 h at 120°C to ensure crosslinking of the adduct and evaporation of residual solvent. The presence of the elastomeric adduct on the surface of the beads was verified by infra-red spectroscopy (*FT*i.r.) and scanning electron microscopy (SEM). The thickness of the elastomeric adduct on the glass bead surface has been determined by thermogravimetric analysis. It has been found to be 0.55 μm[10], i.e. 4.2% of bead radius.

Water absorption

The specimen used in TSCr experiments is a thin rectangular strip with dimensions of 60 mm × 7 mm × 500 μm. After weighing the samples, they were conditioned by immersion in distilled water. They were exposed to water at room temperature for 6 months to ensure that moisture absorption had reached equilibrium. The water temperature was maintained at 25 ± 0.5°C.

In order to evaluate the water uptake of our composite materials, we have measured the increase in weight after exposure to water on a four-digit analytical balance. Changes in weight are compiled in *Table 3*. The weight percentage increase was calculated as follows:

$$\text{weight change } (\%) = \frac{m_f - m_i}{m_i} \times 100 \qquad (1)$$

where m_f and m_i are the final and initial weights, respectively, of the sample. The apparent value refers to the composite weight, whereas the actual value refers to the epoxy weight. Indeed, despite the fact that other sorption processes might be generated, water is unable to soak into glass beads, and epoxy is the main part of the system likely to absorb water. So, it is necessary to remove the glass weight from the whole composite weight in order to determine the weight fraction of absorbed water.

Thermo-stimulated creep (TSCr)

The TSCr principle and the experimental apparatus used in this study have been described elsewhere[11–13]. Only a brief outline is given here:

A static mechanical shear stress σ was applied to the sample at a temperature T_σ for a time allowing complete orientation of the mobile units that one wishes to consider. The out-of-equilibrium configuration (resulting viscoelastic strain $\leq 10^{-3}$) is then frozen in by a rapid quench to a temperature $T_0 \ll T_\sigma$ where any molecular motion is completely hindered. The release of the frozen-in strain is then monitored as the specimen is heated at a controlled rate: the most convenient heating rate throughout the experiments was found to be $7°\mathrm{C\,min^{-1}}$.

Thus, the frozen-in strain $\gamma(t)$, its time derivative $\dot{\gamma}(t)$, and the temperature (T) are simultaneously recorded as functions of time. The plot of the recovery rate $\dot{\gamma}$ (normalized to the stress σ) *versus* temperature represents the TSCr spectrum. In fact, this spectrum is complex and corresponds to a distribution of retardation times.

The experimental set-up used for TSCr experiments was designed and carried out in our laboratory[11]. It consists of a torsional pendulum placed in a cell that could be cooled by external nitrogen gas circulation and heated in a controlled helium atmosphere. The specimen was located in the lower part of the cryostat and maintained in a vertical position by two clamps, the upper one rigidly bound to the pendulum rod and the lower one fixed to the bottom of the cryostat. The actual specimen temperature is measured during the experiment using a thermocouple located quite near the sample. As the sample was heated, the release of the uncovered frozen-in strain stimulated the rotation of the diaphragm above the photocell yielding $\gamma(t)$ and $\dot{\gamma}(t)$. A more complete description of the experimental set-up can be found in ref. 13.

RESULTS AND DISCUSSION

Glassy region

The low-temperature or secondary TSCr retardation spectra are shown in *Figures 2* to *5* for the epoxy matrix (M) and the three composites, i.e. the epoxy resin filled with raw beads (M+RB), silane-treated beads (M+SB) and elastomeric adduct-coated beads (M+EB) respectively. A shear stress $\sigma = 2.0$ MPa was applied to the samples for 2 min at $T_\sigma = 47°\mathrm{C}$. The temperature was then lowered to $T_0 = -183°\mathrm{C}$ and the stress was removed. The samples were subsequently heated at a rate of $7°\mathrm{C\,min^{-1}}$ up to 70°C. This controlled increase of the temperature induces the release of the frozen-in strain so that the mobile units could return at random. The strain γ and its time derivative $\dot{\gamma}(t)$ were recorded. The plot of the recovery rate $\dot{\gamma}$ (normalized to the stress σ) *versus* temperature represents the TSCr spectrum. In fact, this spectrum is complex and corresponds to a distribution of retardation times. *Figures 2* to *5* show the normalized magnitude $|\dot{\gamma}/\sigma|$ *versus* temperature.

The results related to the dry materials were reported and discussed in detail elsewhere[14]. The shoulder at −160°C was attributed to the γ relaxation of the epoxy network. This relaxation is generally associated either with the motion of a polymethylene sequence consisting of at least four carbon atoms in systems crosslinked by an aliphatic amine[15–17] or, in the case of aromatic amines, with rotational motions of unreacted epoxy groups[18]. The major glassy region retardation mode, labelled β, around −75°C was considered as the addition of two sub-modes: one at low temperature associated with motions of diphenylpropane units and the other with crankshaft rotational motion of hydroxy ether groups (at higher temperature). Owing to the broadness of this complex retardation mode, no difference was distinguished in its temperature position in the presence of beads, and whatever the surface of the filler may be. On the other hand, the magnitude was depressed by the presence of fillers in the epoxy network. It was assumed that the intensity of the relaxation peak in the composite depends on the volume fraction of the resin, which is responsible for damping properties. Indeed, damping values are found to decrease with filler content, but the relative damping should not be related simply to the filler volume fraction, as indicated by Nielsen[19]. In addition, a retardation mode, labelled α_e, appears at −50°C in the coated beads composite (see *Figure 5*). This mode was assigned to the anelastic manifestation of the glass transition of the elastomeric interlayer[14].

The hydration of the epoxy matrix (see *Figure 2*) induces a significant decrease of the magnitude of the γ shoulder and of the β peak. The temperature at the maximum of the spectrum is slightly lowered from −75°C to −80°C. This last result is indicative of the plasticization effect induced by water on the β relaxation, also observed by Keenan[20] with a tetraglycidyldiaminodiphenylmethane–dicyandiamide (TGDDM–DDA) network. Inversely, i.e. after vacuum dehydration at room temperature of diglycidyl ether of bisphenol A–diaminodiphenylmethane (DGEBA–DDM) networks, Boye[21] reported a shift of the β peak to higher temperature and an increase of its magnitude. Another peak appears around 60°C in the wet sample. It corresponds to a partial contribution of the mode associated with the glass transition of the epoxy network. This peak, widely dependent on the loading programme

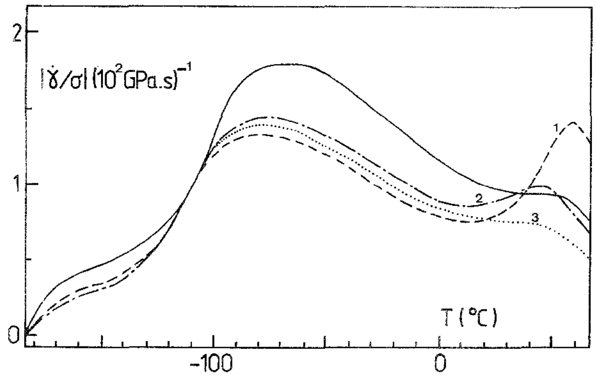

Figure 2 Complex TSCr spectra of DGEBA–DDA matrix in the glassy region: (——) dry state; (- - - -) wet state, first scan; (—•—) wet state, second scan; and (······) wet state, third scan

conditions, will not be taken into account here. Indeed, this peak will grow and shift to higher temperature as the temperature of stress application T_σ is increased. This evolution stops as soon as T_σ reaches the actual relaxation process temperature position.

Although it represents localized motions of the polymeric chains, the fact that the β mode occurs at low temperatures (below 0°C) guarantees that the sample's internal morphology is preserved during testing and that the changes observed can be directly attributed to that morphology. The moisture sorption of epoxy resin systems is shown to be related to its specific volume and hence to its fractional free volume. It has been reported[4] that, in the glassy state, the free volume is apparently in the form of frozen 'voids', and moisture sorption/desorption at this temperature is of the Langmuir, void-filling, type with little or no bond formation.

The magnitude and the temperature position of the β retardation mode do not vary appreciably during three successive temperature scans on the wet network (see *Figure 2*). The general aspect of the spectrum is not altered, contrary to the raw beads filled composite (*Figure 3*).

The raw beads filled material when soaked in distilled water is strongly altered. The mode previously labelled β, and which was a broad peak for the dry specimen, occurs in the shape of two separate shoulders for the wet composite. Moreover a small narrow peak around 0°C is detected and vanishes during three successive temperature scans. Subsequent temperature scans do not modify the last recorded spectrum. The complex character of the β retardation mode, previously observed by applying 'fractional stresses'[14] in the dry state, is displayed by its splitting in the wet state. These two sub-modes, indistinguishable on the complex spectrum in the initial state, are partially resolved in the presence of water.

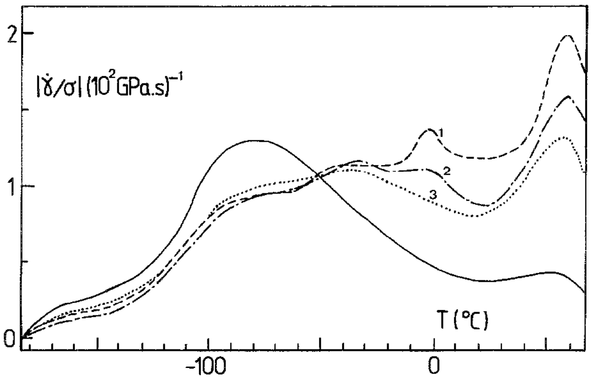

Figure 3 Complex TSCr spectra of the (M+RB) composite in the glassy region: (——) dry state; (- - - -) wet state, first scan; (—•—) wet state, second scan; and (·······) wet state, third scan

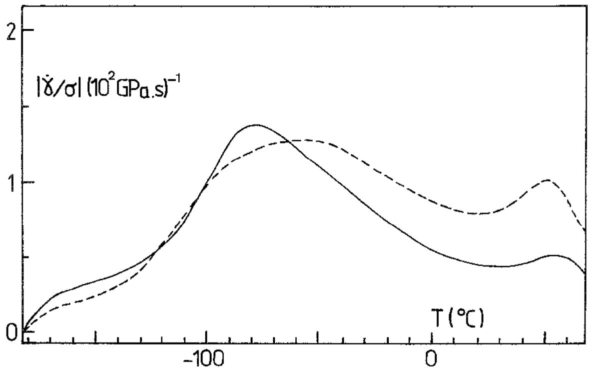

Figure 4 Complex TSCr spectra of the (M+SB) composite in the glassy region: (——) dry state; and (- - - -) wet state

Water molecules can exist in a polymeric medium in two states: unbound as well as bound to the polymer molecules[5]. The unbound molecules are contained in the free volume; they are relatively free to travel through the voids and do not cause swelling. The bound water molecules are immobilized and are responsible for the dimensional increase of the polymer.

Moreover, the interface between matrix and fillers is a rather ill-defined but extremely important part of the composite, which can easily allow the absorption of moisture[22]. The amount of moisture content in the system and the high cohesive energy of water lead to the phenomenon of clustering in the composite. Therefore, a model that considers the composite material as a homogenized material in which moisture diffusion is controlled only by the matrix seems to be insufficient. It is clear that the matrix material itself is an inhomogeneous medium towards water diffusion, because there are a number of factors which matter: e.g. extent of homogeneity of the cure, stoichiometry of the reactants, the stress system in the resin, etc. In addition, the matrix/filler interface appears as a strong discontinuity with regard to the moisture diffusion. Indeed, according to the difference in thermal expansion coefficient of the filler and the matrix, residual stresses are induced in interphase regions after curing. It is evidenced from the amount of moisture content in our systems (see *Table 3*). Indeed, the raw beads composite, when immersed in liquid water at room temperature, sorbs 5.1% of water, which is much higher than for the unfilled epoxy resin (3.2%). The splitting of the β peak is only observed in the raw beads filled composite, and not in the epoxy matrix material. Then, this phenomenon is undoubtedly associated with the presence of beads in the network. Moreover, the filled epoxy exhibits a more significant water uptake. It is likely that the excess of absorbed water in the raw beads filled composite with respect to the unfilled epoxy matrix is associated with the splitting observed for the β peak in this specimen.

It seems from *Figure 3* that the 'low temperature' component is unaffected, with regard to its temperature position, whereas the 'high-temperature' component shifts to higher temperatures. Indeed, in the (initial) 'dry' state, these two sub-modes are displayed as a single broad peak around −75°C, whereas in the wet state the 'low-temperature' sub-mode appears as a shoulder around −75°C and the 'high-temperature' sub-mode is located near −35°C. This last sub-mode was assigned to crankshaft motions of strongly polar hydroxy ether groups and shown to be very sensitive to changes in local morphology around the filler particles and to the volume of 'constrained' epoxy matrix at the interfaces relative to unconstrained epoxy[14]. In this previous work[14], concerning the dry materials, the 'high-temperature' component was found to be almost unaffected by the presence of raw beads. The thickness of the immobilized polymer layer around glass beads was estimated from the relative magnitude of the primary or α retardation mode, and was found to be 0.48 mm, i.e. around 3% of bead radius[9]. Accordingly, the splitting could be attributed to the presence of an excess of water in microvoids at the filler/matrix interface. It results in a decrease of the mobility of these segments, which are constricted by water molecules. Indeed, the beads have some hydrophilic species at the surface, like hydroxyl groups. These groups are able to react with polar water molecules. Moreover, the disturbance induced by the embedded glass beads could also break the network structure in the vicinity of the interface, and release some unreacted groups. Water is bonded at polar sites and can act as a nucleus for cluster formation. Water molecules may be interacting with adjacent bond sites, so that hydroxy ether rotational movements become hindered. Successive temperature scans reduce the distinctness of the β mode resolution, while retaining a significant broadness.

Owing to its temperature position, the small narrow peak at 0°C for the raw beads filled composite (see *Figure 3*) is probably related to a transition from solid to liquid water at the interface. This peak does not appear for the other composites (neither the silane-treated nor the coated beads composite). Thus it is associated with an interfacial phenomenon. Since the expansion coefficients of rigid inclusions and the soft matrix will be expected to be different, biaxial stresses can develop in the matrix, which, at lower temperatures, can result in expansion of the matrix in the immediate vicinity of the rigid phase and creation of voids into which moisture can enter. This peak could display clusters of water molecules at the interface between the epoxy matrix and the glass beads, which could be due to the presence of voids or microcavities. Dielectric loss measurements have also displayed a similar water trapping in glass fibre–epoxy composites[23]. The disappearance of this peak during thermal cycles is likely to be due to the delocalization of this trapped water as a consequence of the heating during the TSCr spectra experiment. It is likely that, in the high-temperature part of the scan, the sample dries out during the course of the experiments. There is no possibility to control the moisture content in the experimental set-up and then to prevent the water from leaving the sample while the test is being run. There is also no direct possibility to measure how much water was lost per scan.

If we assume that the excess of water absorbed by the raw beads filled composite is located in the vicinity of the glass beads/epoxy resin interface, it is possible to estimate an average water layer thickness around each particle, assuming a monodisperse distribution of beads (taking the average diameter as 26 μm). The result is a thickness of about 0.68 μm.

The peak at 0°C does not appear on the TSCr spectrum for the soaked composite where the beads were silane-treated (see *Figure 4*). This figure includes a single TSCr spectrum for the wet sample because no significant change has been observed during subsequent temperature scans. Calorimetric studies of water–polymer systems have shown that complex thermal behaviour is often observed for the water in strongly interacting systems[24,25]. Lee *et al.* noted similarly the absence of solid–liquid phase transitions for the water in low-water-content synthetic hydrogels[25]. This effect is generally attributable to the immobilization of water molecules within the polymer. The water that becomes 'bound' to the polymer does not aggregate sufficiently to permit the observation of a normal phase transition. The water cannot diffuse in sufficient concentrations across the interphase to create a water clustering at the filler/matrix interface. The treatment is expected to protect the filler/matrix interface from penetration of water molecules and to be resistant to an interface failure caused by the swelling stresses generated in the epoxy resin. In this case, decoupling at the interface does not appear to occur. Such a protection from permanent water damage in the interphase region provided by silane coating has been observed [26]. It has been stated that in the glass/silane coupling agent interface, a monolayer of silane agent chemically bonded to the glass is resistant to water; but successive outer layers become less ordered and less resistant to water[27,28].

Previous work[9,14] performed on this composite in the dry state has displayed an increase of the crosslink density and the stiffness of the interfacial region with respect to the raw beads filled composite. This phenomenon was due to the existence of strong linkages created in the silane coupling agent between the filler and the matrix. The thickness of the immobilized polymer layer around each particle was found to be 1.75 mm, i.e. 13% of bead radius[9]. By comparing the actual amount of moisture content in the raw beads composite (M+RB) (5.1%) and in the silane-treated beads filled epoxy (M+SB) (3.0%) (see *Table 3*), it is clear that the interfacial nature has a major influence. This effect could be associated with changes in crosslink density and stiffness of the interfacial regions, which prevent water from diffusing across the interphase. Indeed, a strong dependence of the sorption behaviour of water as a function of crosslink density was reported[29]. The sorption behaviour of the silane-treated beads filled composite (M+SB) is therefore equivalent to the unfilled epoxy matrix (M) one, as displayed by the actual water uptake (3.2% for (M) and 3.0% for (M+SB); see *Table 3*). A broadening of the β mode towards higher temperatures is observed in *Figure 4*, for the soaked sample (broken curve), without splitting of the two sub-modes.

Figure 5 shows the TSCr complex spectra obtained for the elastomeric adduct-coated beads composite, i.e. the (M+EB) sample, in both the dry and wet states. The appearance of the TSCr spectrum does not change after the second temperature scan for the wet specimen. In

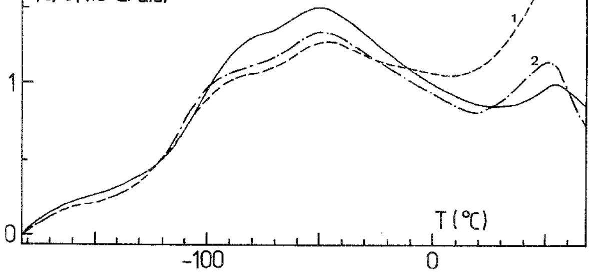

Figure 5 Complex TSCr spectra of the (M+EB) composite in the glassy region: (——) dry state; (- - - -) wet state, first scan; and (–•–) wet state, second scan

examining the influence of moisture on the TSCr spectrum of this composite, no pronounced changes or trends were observed, except a slight decrease of the magnitude, despite the extent of moisture content for this sample, which was 5.2% (see *Table 3*). It may be recalled that the behaviour in the high-temperature region is not taken into account owing to its dependence on the loading programme conditions. The effect of soaking on the viscoelastic properties of this composite seems to be annihilated by the presence of the elastomeric interphase.

Glass transition region

The high-temperature or primary TSCr retardation spectra are shown in *Figures 6* to *9* for the epoxy matrix and for the three composites respectively over the temperature range from 40 to 180°C. A shear stress $\sigma = 0.40$ MPa was applied to the samples for 2 min at $T_\sigma = 177$°C. A lower shear stress was chosen for the high-temperature data compared with the low-temperature experiments, owing to its viscoelastic behaviour as a function of temperature. The loading programme, and in particular the temperature of stress application, T_σ, was experimentally determined using dry materials as follows: T_σ was increased until its variation induced no further temperature position evolution of the α retardation mode. The so-defined value of T_σ corresponds to about $T_g + 30$°C. In order to run the experiment, the temperature was then lowered to $T_0 = 25$°C, where any molecular motion is completely hindered and the stress was removed. The specimens were subsequently heated and scans were made at 7°C min^{-1} heating rate. The strain γ and its time derivative $\dot{\gamma}$ were recorded. *Figures 6* to *9* show the normalized magnitude $|\dot{\gamma}/\sigma|$ *versus* temperature. Although different stresses were applied in the low- and high-temperature experiments, the results are still comparable. Examination was also made for non-linear effects.

Each spectrum was characterized by: its normalized magnitude $|\dot{\gamma}/\sigma|$, which depends on the number of relaxing species; the half-height width, which accounts for the degree of homogeneity of the network; and T_α, the temperature at the maximum of the peak.

The high-temperature results connected to the dry materials were examined in an earlier paper[9]. This single retardation mode, labelled α and whose narrowness is typical of amorphous materials around their glass transition temperature, was assigned to the anelastic manifestation of the glass transition of the DGEBA–DDA network. It has been experimentally resolved into elementary processes by using the technique of 'fractional stresses'[9]. The experimental resolution has not been carried out on the wet samples owing to the hydration state changes that would be induced by this technique, during the successive temperature scans. This mechanism involves cooperative motions of long chain sequences.

We observe for all samples that the sorbed moisture

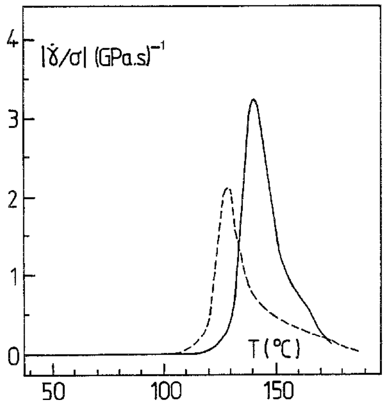

Figure 6 Complex TSCr spectra of DGEBA–DDA matrix around the glass transition: (——) dry state; and (- - - -) wet state

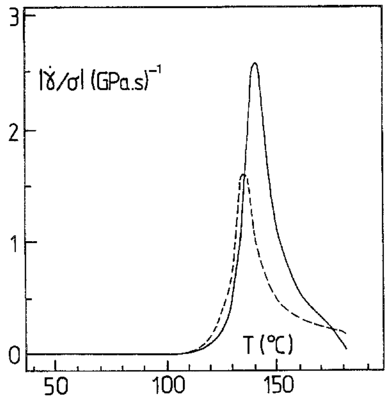

Figure 7 Complex TSCr spectra of the (M+RB) composite around the glass transition: (——) dry state; and (- - - -) wet state

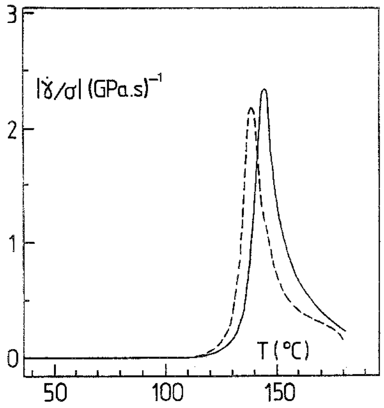

Figure 8 Complex TSCr spectra of the (M+SB) composite around the glass transition: (——) dry state; and (- - - -) wet state

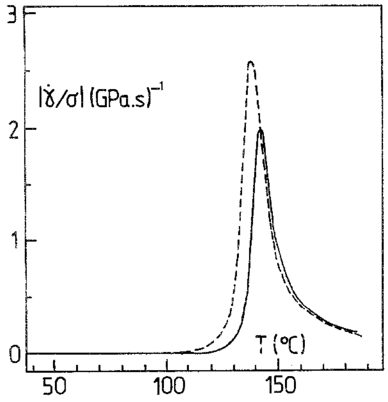

Figure 9 Complex TSCr spectra of the (M+EB) composite around the glass transition: (——) dry state, and (- - - -) wet state

Table 4 Temperature (T_α) and magnitude (I_α) of the α modes corresponding to the DGEBA–DDA maxtrix (M) and to the (M+RB), (M+SB) and (M+EB) composites in both dry and wet states

	Dry state		Wet state		
Sample	T_α (°C)	I_α (GPa s)$^{-1}$	T_α (°C)	I_α (GPa s)$^{-1}$	ΔT_α (°C)
M	142	3.3	128.5	2.2	13.5
M+RB	141	2.6	134.5	1.6	6.5
M+SB	145	2.35	139	2.2	6
M+EB	139	2.0	136	2.6	3

plasticizes the epoxy resin with a resultant depression of the α retardation mode temperature. This plasticization effect of water on epoxy systems has been reported by several authors[6,8,29]. It results in a decrease of performance characteristics, and this ageing effect, being mostly irreversible, can cause a premature fracture in a stressed composite structure. It may be attributed to a strong interaction between the dispersed water and some specific segments or groups in the polymer[29]. However, the depression of T_α is expected to be dependent upon the interface nature. Indeed, moisture absorption is always accompanied by matrix swelling. The rigid fillers restrain the swelling at the interface, thereby inducing a high stress at the filler/matrix interface.

The amplitude I_α of the TSCr spectrum is a measure of the intensity of the relaxation. For both dry and wet materials, T_α and I_α values, as well as the temperature depression $\Delta T_\alpha = T_\alpha(\text{dry}) - T_\alpha(\text{wet})$, are listed in *Table 4*. For the unfilled epoxy network, a significant shift of the maximum of the TSCr retardation mode towards lower temperatures is clearly observed as the sample is soaked. The shift is slighter for the composites, especially in the case of the elastomeric adduct-coated beads composite. It is probably due to the preferential water clustering in the vicinity of the glass beads surface.

It is seen that the magnitude of the peak (I_α) decreases for the wet epoxy resin (M) and raw beads filled composite (M+RB). This means a decrease in the number of mobile units. On the other hand, there is no significant change in the I_α value for the dry and wet sample when the beads are silane-treated. This result is in good agreement with the previous conclusions and displays the protection from water ingress provided by this treatment. In the case of the coated beads composite, the soaked sample exhibits a larger magnitude than the dry sample. The marginal behaviour of this composite may be due to the strong interaction between water and elastomeric adduct. Indeed, considerable visual dimensional damage and swelling were observed for the adduct alone upon exposure to distilled water, so that no TSCr measurement was possible.

Previous work[9] for the dry state had shown an increase of the activation entropy. The motions of mobile units in the vicinity of the glass/resin interface have therefore more accessible sites and are thereby easier. We had suggested the presence of a weakly crosslinked region around each coated filler particle and a partial miscibility of the elastomer in the epoxy matrix. The swelling, ascribable to the water, increases the free volume fraction in the interphase. This results in an increase of the magnitude of the cooperative movements liberated at the glass transition. Such a looser network in the interfacial region might be expected to provide greater access to water as evidenced by the moisture content of this composite in *Table 3*.

In order to examine the reversible or irreversible feature of the hydration imposed to the materials investigated in this study, the epoxy matrix and the three composite materials were subjected to a drying regime. The samples were subjected to heating at $T_g + 20$°C for 15 min followed by vacuum dehydration for a further 15 min. This procedure was repeated four times. TSCr experiments were subsequently carried out on these samples. No evolution with respect to the initial wet material was observed on the silane-treated and elastomeric adduct-coated beads composites. For the unfilled epoxy matrix and raw beads composite, the temperature position of the α peak (T_α) was unaffected by this dehydration attempt. However, an increase of the magnitude of the α retardation mode was noted, which remains nevertheless lower than those of the initially dry samples.

Carfagna *et al.*[30] explain this phenomenon in terms of microvoid nucleation during the sorption process, which is favoured at high relative humidities by the tendency of water to cluster. It is particularly evident for the epoxies, in which the glassy and crosslinked stiff structure does not allow the matrix to relax after the microvoids have been formed. Moreover the fact of decay temperature through 0°C during low-temperature experiments allows the solidification of water clusters, which increases the volume and induces mechanical stresses in the polymer. Therefore, stress leads to delamination and microcracking in the bulk composite. These authors[30] report that defects persist and do not disappear.

CONCLUSIONS

Using TSCr spectroscopy, an investigation of the effect of modifying the nature of the interface on moisture uptake has been performed. From these results, the following conclusions are obtained:

In the soaked unfilled epoxy resin, a decrease of the magnitude of the TSCr spectrum has been observed in both the glassy region and glass transition region. This means a reduction in the number of mobile units. The plasticization effect of water has been evidenced by the resultant depression of the α mode temperature.

The low-temperature spectrum of the raw beads reinforced composite is highly altered, when soaked in distilled water. A splitting of the β mode, ascribable to a decrease in the mobility of hydroxy ether segments, has been reported. Evidence for clusters of water molecules at the interface due to the presence of microcavities has been realized through the appearance of a small narrow peak at 0°C, assigned to a solid–liquid phase transition of water. This residual water in the interphase region and at the interface is expected to weaken the phase boundary.

The silane coating provides protection from water damage in the interphase region. It appears to provide good bonding between matrix and filler and less water-permeable interphase boundaries. Indeed, broadening of the β mode has been observed, without splitting. Moreover, the magnitude of the α retardation mode is unaffected by the presence of moisture.

No significant change is noted for the elastomeric adduct-coated beads reinforced network, when wet in distilled water, despite the extent of the moisture content within this composite. However, an increase of the magnitude of the cooperative movements liberated at the glass transition is ascribed to a strong swelling of the elastomeric interphase.

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REFERENCES

1 Hoeve, C. A. J. in 'Water in Polymers' (Ed. S. P. Rowland), ACS Symp. Ser. 127, American Chemical Society, Washington, DC, 1980, p. 135
2 Enns, J. B. and Gillham, J. K. *J. Appl. Polym. Sci.* 1983, **28**, 2831
3 Johncock, P. and Tudgey, G. F. *Br. Polym. J.* 1986, **18**(5), 292
4 Gupta, V. B., Drzal, L. T. and Rich, M. J. *J. Appl. Polym. Sci.* 1985, **30**, 4467
5 Diamant, Y., Marom, G. and Broutman, L. J. *J. Appl. Polym. Sci.* 1981, **26**, 3015
6 Moy, P. and Karasz, F. E. in 'Water in Polymers' (Ed. S. P. Rowland), ACS Symp. Ser. 127, American Chemical Society, Washington, DC, 1980, p. 505
7 Fuller, R. T., Fornes, R. E. and Memory, J. D. *J. Appl. Polym. Sci.* 1979, **23**, 1871
8 Carfagna, C., Apicella, A. and Nicolais, L. *J. Appl. Polym. Sci.* 1982, **27**, 105
9 Dufresne, A. and Lacabanne, C. *Polym Compos.* 1993, **14**, 238
10 Amdouni, N. PhD Thesis, INSA Lyon, France, 1989
11 Monpagens, J. C., Chatain, D., Lacabanne, C. and Gautier, P. C. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 767
12 Monpagens, J. C., Chatain, D., Lacabanne, C. and Gautier, P. C. *Solid State Commun.* 1976, **18**, 1611
13 Dufresne, A. PhD Thesis, INSA Toulouse, France, 1991
14 Dufresne, A. and Lacabanne, C. *Polymer* 1993, **34**(15), 3173
15 Delatycki, O., Shaw, J. C. and Williams, G. J. *J. Polym. Sci. (A-2) Polym. Phys.* 1969, **7**, 753
16 Ochi, M., Okazaki, M. and Shimbo, M. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 689
17 Charlesworth, J. M. *Polym. Eng. Sci.* 1988, **28**(4), 221
18 Oleinik, E. F. *Adv. Polym. Sci.* 1986, **80**, 49
19 Nielsen, L. E. *Appl. Polym. Symp.* 1969, **12**, 249
20 Keenan, J. D., Seferis, J. C. and Quinlivan, J. T. *J. Appl. Polym. Sci.* 1979, **24**, 2375
21 Boye, J. PhD Thesis, Toulouse, France, 1990
22 Favre, J. P. and Dewas, J. N. 'JNC4, Quatrièmes Journées Nationales sur les Composites, AMAC,' (Ed. G. Verchery), Pluralis, Paris, 1984, pp. 615–30
23 Doukkali, K. and Segui, Y. *J. Appl. Polym. Sci.* 1990, **41**, 1533
24 Haly, A. R. and Snaith, J. W. *Textile Res. J.* 1967, **39**, 907
25 Lee, H. B. Jhon, M. S and Andrade, J. D. *J. Colloid Interface Sci.* 1975, **51**, 225
26 Bian, X. S., Ambrosio, L., Kenny, J. M., Nicolais, L. and Dibenedetto, A. T. *Polym. Compos.* 1991, **12**(5), 333
27 Antoon, M. K. and Koenig, J. L. *J. Polym. Sci., Polym. Phys. Edn.* 1981, **19**, 1567
28 Ishida, H. and Koenig, J. L. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 1931
29 Moy, P. and Karasz, F. E. *Polym. Eng. Sci.* 1980, **20**(4), 315
30 Carfagna, C. and Apicella, A. *J. Appl. Polym. Sci.* 1983, **28**, 2881