

# A study of interphase in model composites via low temperature thermo stimulated creep spectroscopy

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Thermo stimulated creep analysis is performed to characterize the anelastic properties in the glassy state of the epoxy resin-glass bead model system. Different interphase regions have been deliberately formed by means of a silane coupling agent and an elastomeric adduct coating. By applying 'fractional stresses', with a convenient choice of the loading programme, the complex  $\beta$  peak is experimentally resolved and local changes of morphology in the interphase zone are evidenced in terms of mobility.

(Keywords: composite; thermo stimulated creep; interphase; epoxy; low temperature relaxation)

## INTRODUCTION

Mechanical properties of a filler-matrix composite depend not only on the properties of each primary component but also on the nature of the filler surface, the nature of the bonds between filler and resin, and the mechanism of load transfer at the interface. The inherent problem of these multiphase material systems is the filler-matrix interface which is the critical link providing the structural integrity of these materials. Conventionally, the interface is considered to have zero thickness and results from interactions between matrix and filler surface. However, the presence of a rigid surface can influence the structure of the matrix near the filler surface and the local mobility. These changes in local morphology may lead to the formation of an interphase around the filler particles with properties different from those of the bulk matrix, i.e. the composite can be regarded as a three-phase material. The formation of such an interphase is expected to influence the viscoelastic properties. Drzal<sup>1</sup> suggests that the interphase exists from some point in the filler where the local properties begin to change from the filler bulk properties through the interphase into the matrix where the local properties again equal the bulk properties. This interphase can in many cases be the controlling element in composite performance.

Application of silane coupling agents to glass fillers used in reinforced polymers results in improved composite properties. This improvement has been most notable in the ability of the composite to retain its strength under conditions of severe exposure to moisture. It has been observed<sup>2</sup> that the coupling agent forms a chemical bond with the surface of glass through one

functional group, while another functional group on the same molecule chemically bonds to the resin. Adhesion of the resin to glass is therefore strengthened through a bridge of chemical bonds connecting the two phases.

However, this improvement involves a decrease of impact strength: impact strength varies inversely with the filler-matrix adhesion. Theoretical studies<sup>3</sup> have shown that insertion of an interphase (tailoring interphase) can improve impact strength without decreasing the elastic mechanical properties of the composite. Broutman and Agarwal<sup>3,4</sup> showed that composite strain energy displayed a maximum for an interphase with a lower modulus than that of the matrix. Di Benedetto and Nicolais<sup>5</sup> showed that, according to the difference in the thermal expansion coefficient of the filler and the matrix, the introduction of an elastomeric interphase can relieve residual stresses in interphase regions after curing<sup>6</sup>. These two concepts show the existing interest in modification by tailoring of the interphase. In this treatment the most important parameter is the thickness of the coating<sup>7</sup>. It must be thin enough to allow the particles to reinforce the material and thick enough to create a stress field similar to those existing around elastomeric particles.

In the present work, different interphase regions are deliberately formed by means of a silane coupling agent and an elastomeric adduct covering the glass spheres, and the viscoelastic properties in the glassy state are evaluated via thermo stimulated creep (TSCr) spectroscopy.

## THERMO STIMULATED CREEP

### Principle

The principle of this technique and the torsion pendulum used for this work have been extensively

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described elsewhere<sup>8</sup>. In brief:

- The sample is subjected to a static mechanical stress  $\sigma$  at a given temperature  $T_e$  for a time allowing complete orientation of the mobile units to be considered.
- The resulting viscoelastic strain ( $\gamma \leq 10^{-3}$ ) is then frozen by quenching the sample to a temperature  $T_0 \ll T_e$  where any molecular motion is completely hindered. The stress is then removed.
- The sample is subsequently warmed up at a controlled rate so that the mobile units can return at random. The response  $\gamma$ , its time derivative  $\dot{\gamma}$ , and the temperature are simultaneously recorded *versus* time  $t$ .

If the recovery behaviour can be described by a Kelvin–Voigt model, the mechanical retardation time  $\tau$  can be deduced from measurements of  $\dot{\gamma}(T)$  and  $\gamma(T)$ :

$$\tau(T) = \frac{|\dot{\gamma}(T)|}{|\gamma(T)|} \quad (1)$$

Thermally activated states theory predicts that  $\tau(T)$  follows the Arrhenius equation:

$$\tau(T) = \tau_0 \exp\left(\frac{\Delta H}{kT}\right) \quad (2)$$

where  $\tau_0$  is the 'pre-exponential' factor,  $\Delta H$  is the activation enthalpy and  $k$  is Boltzmann's constant.

The Eyring equation allows us to define the activation entropy  $\Delta S$  from  $\tau_0$ :

$$\tau_0 = \frac{h}{kT} \exp\left(-\frac{\Delta S}{k}\right) \quad (3)$$

where  $h$  is Planck's constant.

$\Delta S$  provides then the number of accessible sites  $W$  from Boltzmann's equation:

$$\Delta S = k \ln W \quad (4)$$

In polymers, the model of a single retardation time must be generalized in order to obtain a good fit between theory and experiment; this is generally done by using a distribution of retardation times. The great advantage of the TSCr technique is that it allows a detailed study of this distribution.

## EXPERIMENTAL

### Equipment

The specimen was a thin rectangular strip (60 mm  $\times$  7 mm  $\times$  500  $\mu\text{m}$ ). It was subjected to a shear stress by a torsional balance. The deformation was determined by observing the variation of an electrical current collected by photovoltaic cells. The sample was placed in a thermal jacket whose temperature could vary over a temperature range from that of liquid nitrogen to 500 K. In all experiments, the heating rate was 7 K  $\text{min}^{-1}$ . The strain  $\gamma$  and the temperature  $T$  were simultaneously recorded *versus* time. By taking the time derivative of the strain, the rate of strain  $\dot{\gamma}$  was obtained with an accuracy of 5%. A more complete description of the experimental set-up can be found in reference 9.

### Materials

The samples studied were supplied by the Laboratoire des Matériaux Macromoléculaires et Composites of the

**Table 1** Coding of the samples

Code	Sample
M	Matrix (DGEBA <sub>0.14</sub> -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

Institut National des Sciences Appliquées (Lyon, France). The components are described below. Four samples were chosen for this study (see *Table 1*).

**Epoxy matrix.** The mixing of diglycidyl ether of bisphenol-A ( $n=0.14$ ) (DGEBA<sub>0.14</sub>) and dicyandiamide (DDA, curing agent) was carried out with an amine/epoxy ratio of 0.6 and in presence of benzyl dimethyl amine (BDMA). The trade name of the resin used for synthesis of the epoxy matrix was DGEBA 0164 Bakelite and its average molecular weight was  $\sim 380 \text{ g mol}^{-1}$ . The components were mixed under mechanical stirring and vacuum during 1 h at 60°C. The mixture was then moulded in an oven, cured for 1 h at 120°C and postcured for 1 h at 180°C.

**Filler.** Glass bead reinforced composites obtained from this matrix system were also examined. The volume fraction of filler was 20 wt% and the size distribution of the beads ranged from 4 to 44  $\mu\text{m}$  with an average particle diameter of 26  $\mu\text{m}$ .

**Silane treatment.** The silane coupling agent used for the surface treatment was  $\gamma$ -aminopropyltriethoxysilane (A-1100, Union Carbide). Its average molecular weight was 221.3  $\text{g mol}^{-1}$ . The coupling agent was used as a solution in 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 liquid was removed under vacuum.

**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 ( $\text{N}_2$ ) with a carboxy/epoxy ratio of 0.5. Triphenylphosphamine (TPP) was used as a catalyst. After 20 h of reaction, liquid diamine (IPD) was added in an amine/epoxy ratio of 2; the reaction was run for 30 h at 120°C. It was established<sup>10</sup> 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.

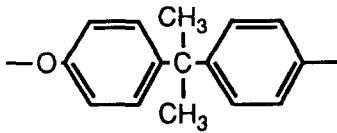
Adduct was deposited by adding the glass beads to an elastomer solution of methyl ethyl ketone (MEK, 2 wt% of adduct). The solution was stirred for 20 min and removal of solvent (MEK) was effected under vacuum at room temperature. The beads were then placed in an oven for 12 h at 120°C to ensure crosslinking of the adduct took place. The thickness of the elastomeric adduct at the glass bead surface has been found<sup>10</sup> to be 0.55  $\mu\text{m}$ , i.e. 4.2% of the bead radius.

## RESULTS AND DISCUSSION

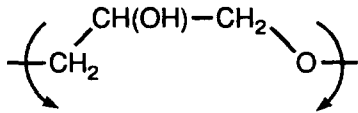
## Reference matrix

We present in this section the results obtained with the reference material, i.e. the epoxy matrix.

**Complex TSCr spectrum.** Figure 1 shows as a solid line the TSCr spectrum obtained with the epoxy matrix (DGEBA-DDA) alone over the temperature range from  $-180$  to  $60^\circ\text{C}$ . A shear stress  $\sigma$  of  $2.0\text{ MPa}$  is applied for 2 min at  $T_\sigma = 47^\circ\text{C}$  and removed gradually over a period of 2 min at  $T_0 = -183^\circ\text{C}$ . We observe a shoulder around  $-160^\circ\text{C}$  and a maximum around  $-75^\circ\text{C}$ . The shoulder at  $-160^\circ\text{C}$  is attributed to the  $\gamma$  relaxation of the epoxy network. This relaxation is generally associated with the motion of a polymethylene sequence consisting of at least four carbon atoms<sup>11,12</sup>. The major low temperature relaxation peak at  $-75^\circ\text{C}$  is generally considered as the addition of two relaxations: one at low temperature associated with motions of diphenylpropane units:



and the other with motions of hydroxyether groups (at higher temperature)<sup>11,13</sup>:



**Fine structure of the TSCr spectrum.** By a convenient choice of the parameters (temperature and time) defining the loading programme, fractional stresses are applied to the samples. The following procedure is used for the experimental resolution of the complex TSCr spectra<sup>14</sup>:

- the stress is applied at the temperature  $T_{\text{son}}$  for 2 min in order to allow the mobile units with a retardation time lower than  $\tau(T_{\text{son}})$  to orientate;
- the temperature is lowered to  $T_{\text{soff}} = T_{\text{son}} - 5^\circ\text{C}$  at which the stress is removed. The temperature is maintained constant for 2 min in order to randomize the units having a retardation time shorter than  $\tau(T_{\text{soff}})$  and the viscoelastic strain is then frozen by quenching the sample to a temperature  $T_0 \ll T_{\text{son}}$ .

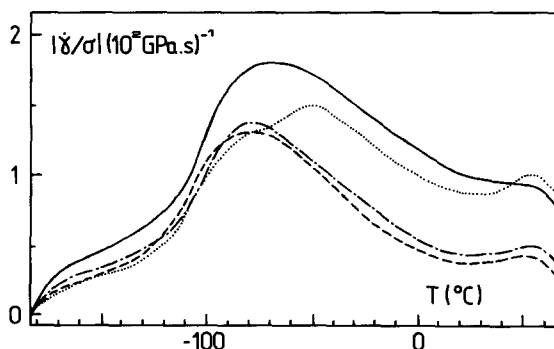


Figure 1 Complex TSCr spectra of DGEBA-DDA matrix M (—) and of (M+RB) (---), (M+SB) (-·-) and (M+EB) (···) composites in the glassy state

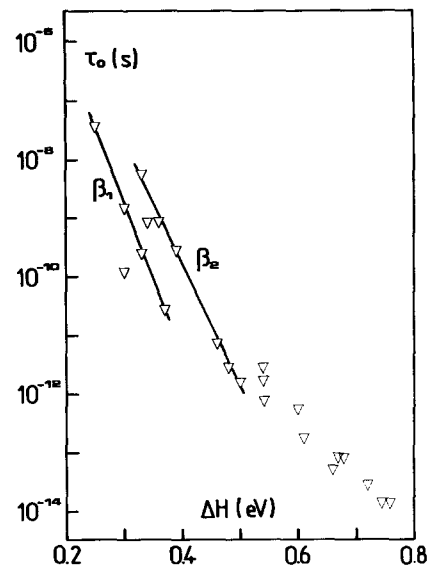


Figure 2 Compensation diagram of the DGEBA-DDA matrix

Table 2 Activation parameters of the low-temperature peak of the DGEBA-DDA matrix. Each row of values corresponds to an elementary process whose TSCr has its maximum at  $T_m$  and whose retardation time follows a compensation law

	$T_m$ ( $^\circ\text{C}$ )	$\Delta H$ (eV)	$\tau_0$ (s)
$\beta_1$	-136.5	0.25	$3.8 \times 10^{-8}$
	-131	0.30	$1.5 \times 10^{-9}$
	-126	0.33	$2.5 \times 10^{-10}$
	-121	0.37	$2.7 \times 10^{-11}$
$\beta_2$	-108	0.33	$5.6 \times 10^{-9}$
	-104	0.36	$9.1 \times 10^{-10}$
	-99.5	0.39	$2.9 \times 10^{-10}$
	-90	0.46	$7.6 \times 10^{-12}$
	-88	0.48	$2.9 \times 10^{-12}$
	-85	0.50	$1.6 \times 10^{-12}$

For the next fractional loading programme, the stress is applied at  $T_{\text{son}} + 5^\circ\text{C}$ . By varying  $T_{\text{son}}$  in the temperature range, the whole complex TSCr spectrum can be resolved into 'elementary' TSCr peaks that can be analysed by making the hypothesis of a single retardation time  $\tau(T)$  given by equation (1).

In such a case the retardation times can be described by the Arrhenius equation [equation (2)]. The corresponding parameters  $\tau_0$  and  $\Delta H$  are obtainable from the semi-logarithmic plot of  $\tau(T)$  versus  $1/T$ . Figure 2 shows the variation of  $\ln \tau_0$  versus  $\Delta H$  for the TSCr peak represented in Figure 1 (epoxy matrix DGEBA-DDA). The stress application temperature  $T_{\text{son}}$  varies from  $-148$  to  $-38^\circ\text{C}$ . For some consecutive experimental points the relationship between  $\ln \tau_0$  and  $\Delta H$  is linear. They are well described by a line whose equation is:

$$\tau(T) = \tau_c \exp \left[ \frac{\Delta H}{k} \left( \frac{1}{T} - \frac{1}{T_c} \right) \right] \quad (5)$$

These particular elementary peaks have the same retardation time  $\tau_c$  at a 'compensation temperature'  $T_c$ . In other words their activation entropy varies linearly with the activation enthalpy. The corresponding parameters  $\tau_0$  and  $\Delta H$  are listed in Table 2 for the epoxy

matrix system. The temperature  $T_m$  corresponds to the maximum temperature of each TSCr elementary peak whose retardation time  $\tau$  follows a compensation law.

Two compensation phenomena labelled  $\beta_1$  and  $\beta_2$  are observed for the epoxy matrix, for which the parameters are:

$$T_{c1} = -84^\circ\text{C} \quad T_{c2} = -24^\circ\text{C}$$

$$\tau_{c1} = 1.4 \times 10^{-1} \text{ s} \quad \tau_{c2} = 1.9 \times 10^{-2} \text{ s}$$

The temperature ranges of these two compensation phenomena indicate that they concern the  $\beta$  retardation mode and not the  $\gamma$  mode. Thus, the complex  $\beta$  mode is resolved into two sub-modes (labelled  $\beta_1$  and  $\beta_2$ ). The low values of  $\tau_c$  are characteristic of localized movements.

The upper limit of the temperature  $T_m$  range for the  $\beta_1$  sub-mode is  $-121^\circ\text{C}$  (cf. Table 2). The activation enthalpy  $\Delta H$  varies from 0.25 to 0.37 eV. This low enthalpic dispersion is probably the sign of steric restriction of mobile units. Thus, the  $\beta_1$  sub-mode is attributed to the motions of diphenylpropane units. The temperature range of the processes describing the  $\beta_2$  compensation phenomenon extends from  $-108$  to  $-85^\circ\text{C}$ . The upper limit is close to the maximum of the complex  $\beta$  retardation mode. The contribution of crankshaft motions of hydroxyether groups to the  $\beta$  relaxation in epoxy networks takes place in this temperature range<sup>15</sup>. Thus, the  $\beta_2$  sub-mode is associated with motions of hydroxyether groups.

#### Composite systems

**Complex TSCr spectra.** Figure 1 shows the TSCr spectra obtained for 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). The same experimental conditions as previously described for the matrix are used for these samples. The spectrum corresponding to the DGEBA-DDA matrix is shown in Figure 1 as a reference system.

It is obvious that the same retardation modes ( $\gamma$  and  $\beta$ ) are observed for the composites as for the matrix. The broadness of the  $\beta$  mode does not allow any difference in its temperature position to be distinguished. On the other hand, its magnitude is depressed by the presence of fillers in the epoxy network. This depression can be explained by the decrease of the amount of epoxy in the composite, i.e. there are less mobile units.

In the coated beads composite, the elastomeric interphase is evidenced *in situ* by a retardation mode,

**Table 3** Activation parameters of the low-temperature peak of raw bead filled composite. Each row of values corresponds to an elementary process whose retardation time follows a compensation law

	$T_m$ ( $^\circ\text{C}$ )	$\Delta H$ (eV)	$\tau_0$ (s)
$\beta_1$	-123.5	0.26	$6.9 \times 10^{-8}$
$T_{c1} = -52^\circ\text{C}$	-119	0.28	$2.9 \times 10^{-8}$
$\tau_{c1} = 7.4 \times 10^{-2} \text{ s}$	-112	0.33	$2.9 \times 10^{-9}$
	-107	0.36	$3.8 \times 10^{-10}$
	-91.5	0.37	$3.6 \times 10^{-9}$
$\beta_2$	-88.5	0.41	$5.6 \times 10^{-10}$
$T_{c2} = 30^\circ\text{C}$	-84	0.43	$2.9 \times 10^{-10}$
$\tau_{c2} = 4.4 \times 10^{-3} \text{ s}$	-78.5	0.45	$1.7 \times 10^{-10}$
	-70.5	0.49	$2.8 \times 10^{-11}$

**Table 4** Activation parameters of the low-temperature peak of silane treated bead filled composite. Each row of values corresponds to an elementary process whose retardation time follows a compensation law

	$T_m$ ( $^\circ\text{C}$ )	$\Delta H$ (eV)	$\tau_0$ (s)
	-129	0.22	$1.7 \times 10^{-6}$
$\beta_1$	-123.5	0.26	$2.3 \times 10^{-7}$
$T_{c1} = -84^\circ\text{C}$	-119	0.27	$8.6 \times 10^{-8}$
$\tau_{c1} = 7.3 \times 10^{-1} \text{ s}$	-114.5	0.32	$4.7 \times 10^{-9}$
	-108	0.37	$1.5 \times 10^{-10}$
	-102.5	0.38	$2.4 \times 10^{-10}$
$\beta_2$	-99	0.42	$3.9 \times 10^{-11}$
$T_{c2} = -13^\circ\text{C}$	-93.5	0.45	$1.1 \times 10^{-11}$
$\tau_{c2} = 5.3 \times 10^{-3} \text{ s}$	-89.5	0.48	$2.9 \times 10^{-12}$
	-85	0.50	$1.1 \times 10^{-12}$
$\beta'$	-65	0.53	$8.1 \times 10^{-12}$
$T_{c3} = 73^\circ\text{C}$	-62	0.56	$1.7 \times 10^{-12}$
$\tau_{c2} = 3.2 \times 10^{-4} \text{ s}$	-54.5	0.61	$3.1 \times 10^{-13}$
	-50	0.66	$9.4 \times 10^{-14}$

labelled  $\alpha_e$ . This mode is assigned to the anelastic manifestation of the glass transition of the elastomeric interlayer. It appears at  $-50^\circ\text{C}$  and consequently in the same temperature range as the secondary retardation mode of the epoxy network. Assuming that apparent activation energies of  $\alpha_e$  (elastomeric interphase) and  $\beta$  (epoxy) modes are not very different, the distinction between  $\alpha_e$  and  $\beta$  is only possible because of the low effective frequency ( $10^{-3} \text{ Hz}$ ) of the TSCr spectroscopy. This result suggests that the elastomeric adduct is effectively localized around the glass beads and proves the three-phase character of this composite. Dynamic mechanical measurements have provided a similar result for an epoxy resin-elastomeric adduct coated carbon fibre system<sup>16</sup> and for an epoxy resin-glass bead model system covered with PBMA<sup>17</sup>.

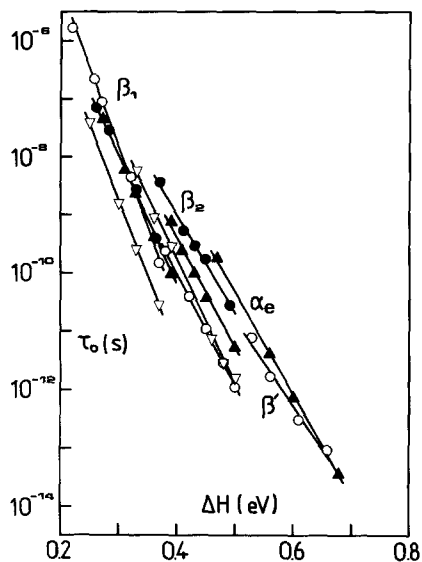
**Fine structure of the TSCr spectra.** Fractional stress programmes are applied to resolve experimentally the complex  $\beta$  TSCr spectra. The temperature steps between loading and unloading are  $5^\circ\text{C}$  and  $-153^\circ\text{C} < T_{\text{son}} < -13^\circ\text{C}$ . The analysis of each elementary peak has provided the activation parameters  $\tau_0$  and  $\Delta H$ . The plot of  $\ln \tau_0$  versus  $\Delta H$  reveals some compensation phenomena. The parameters corresponding to elementary processes whose retardation times follow a compensation law are presented in Tables 3, 4 and 5 for the raw, silane treated and coated bead reinforced epoxy resin, respectively. The compensation parameters are also reported. Figure 3 shows the variation of  $\ln \tau_0$  versus  $\Delta H$  for the three composites and for the DGEBA-DDA matrix reference.

All the samples exhibit the two sub-modes ( $\beta_1$  and  $\beta_2$ ) previously observed for the matrix alone. They were associated with motions of diphenylpropane units ( $\beta_1$ ) and hydroxyether groups ( $\beta_2$ ). Moreover, the silane surface treatment and the elastomeric adduct coating are evidenced by the presence of a third retardation mode, labelled  $\beta'$  and  $\alpha_e$ , respectively.

The filler presence and its surface treatment have no significant effect on the activation enthalpy range of the  $\beta_1$  process. On the contrary, for a given  $\Delta H$ , the pre-exponential factor  $\tau_0$  shifts to higher value when the network is reinforced whatever the surface treatment may

**Table 5** Activation parameters of the low-temperature peak of adduct coated bead filled composite. Each row of values corresponds to an elementary process whose retardation time follows a compensation law

	$T_m$ (°C)	$\Delta H$ (eV)	$\tau_0$ (s)
$\beta_1$ $T_{e1} = -42^\circ\text{C}$ $\tau_{e1} = 2.9 \times 10^{-2}$ s	-124.5	0.27	$4.6 \times 10^{-8}$
	-119	0.31	$5.9 \times 10^{-9}$
	-113.5	0.33	$2.3 \times 10^{-9}$
	-109	0.36	$4.0 \times 10^{-10}$
$\beta_2$ $T_{e2} = 13^\circ\text{C}$ $\tau_{e2} = 3.3 \times 10^{-3}$ s	-104.5	0.39	$1.0 \times 10^{-10}$
	-99.5	0.38	$7.8 \times 10^{-10}$
	-95	0.405	$2.4 \times 10^{-10}$
	-91	0.43	$1.0 \times 10^{-10}$
$\alpha_e$ $T_{e3} = 11^\circ\text{C}$ $\tau_{e2} = 4.2 \times 10^{-2}$ s	-86.5	0.45	$3.9 \times 10^{-11}$
	-82	0.50	$5.4 \times 10^{-12}$
	-67	0.47	$1.9 \times 10^{-10}$
	-62	0.56	$4.5 \times 10^{-12}$
	-57	0.60	$7.6 \times 10^{-13}$
	-52.5	0.68	$3.8 \times 10^{-14}$



**Figure 3** Compensation diagram of DGEBA-DDA matrix M ( $\nabla$ ) and of (M+RB) ( $\bullet$ ), (M+SB) ( $\circ$ ) and (M+EB) ( $\blacktriangle$ ) composites

be. In other words, there is a decrease of the activation entropy  $\Delta S$  [equation (3)], i.e. a decrease of the number of accessible sites to mobile entities [equation (4)]. Indeed, motions of diphenylpropane units are not affected ( $\Delta H$  constant) but their kinetics are different.

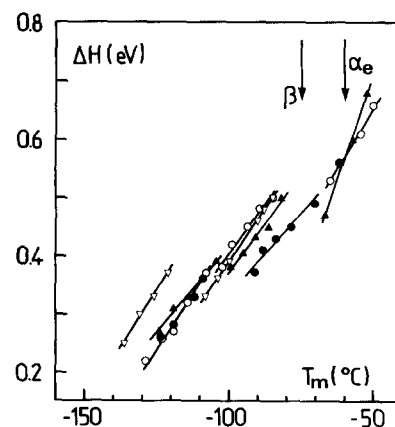
The behaviour is quite different for the  $\beta_2$  sub-mode. This process seems to be indeed unaffected by the presence of beads when these are silane treated or adduct coated. However, in the presence of raw beads the compensation line corresponding to the  $\beta_2$  sub-mode shifts to higher values of  $\tau_0$ , i.e. to lower values of  $\Delta S$  for a given  $\Delta H$ . Moreover, the upper limit of the  $T_m$  range differs for this last sample. We suggest assigning the  $\beta_2$  process of the raw bead reinforced network to the crankshaft motions of hydroxyether groups both in bulk matrix and in the interphase zone. The kinetics of these motions is affected by changes in local morphology around the filler particles.

The  $\beta'$  sub-mode is evidenced only in the silane treated bead reinforced epoxy. Thus, it is associated with an

interfacial phenomenon. The elementary peaks whose retardation time follows this compensation law have their maxima between  $-65^\circ\text{C}$  and  $-50^\circ\text{C}$ . The activation enthalpy of these elementary processes varies from 0.53 to 0.66 eV. These movements entail therefore a larger energy than the previous ones. We suggest that motions of hydroxyether groups in the surface treated glass composites result in the presence of two separate compensation phenomena. The first one ( $\beta_2$  sub-mode) is attributed to motions of hydroxyether in the bulk matrix, and the second one ( $\beta'$  sub-mode) to motions of these groups in the immobilized layer of polymer surrounding the particles, i.e. in the interphase. This effect evidenced the stiffness of the interfacial region due to the existence of strong linkages created out of the silane coupling agent between the filler and the matrix. This effect was reported elsewhere<sup>18</sup>; it has been found that the interphase thickness is much larger in the presence of silane treated beads than in the presence of raw beads. Thus, the occurrence of two well-separated sub-modes associated with the motions of hydroxyether groups depends upon the amount of 'modified' matrix compared to the bulk matrix.

The specific character of the  $\alpha_e$  compensation process corresponding to the elastomeric adduct coated bead reinforced DGEBA-DDA network allows us to consider it as a purely interfacial phenomenon. The  $T_m$  and  $\Delta H$  ranges of elementary processes involved in the  $\alpha_e$  and  $\beta'$  modes appear to be similar. However, despite these analogies,  $\alpha_e$  and  $\beta'$  have different origins that are revealed by differences in the compensation parameters. Moreover the temperature  $T_m$  of the last elementary peak whose retardation time follows the  $\alpha_e$  compensation law ( $T_m = -52^\circ\text{C}$ ) is very close to the temperature corresponding to the mode assigned to the elastomer glass transition. The  $\alpha_e$  mode is attributed to the anelastic manifestation of the glass transition of the elastomeric interlayer.

The activation enthalpy for each temperature window is plotted versus the maximum temperature of each elementary TSCr spectrum whose retardation time follows a compensation law in Figure 4. The result shows that the activation enthalpy is distributed and generally rises with increasing temperature. Each curve can be divided into two or three regions depending on the sample with a break in the general rise separating each region.



**Figure 4** Activation enthalpy  $\Delta H$  versus the temperature maximum of each elementary process  $T_m$  whose retardation time follows a compensation law. DGEBA-DDA matrix M ( $\nabla$ ) and (M+RB) ( $\bullet$ ), (M+SB) ( $\circ$ ) and (M+EB) ( $\blacktriangle$ ) composites

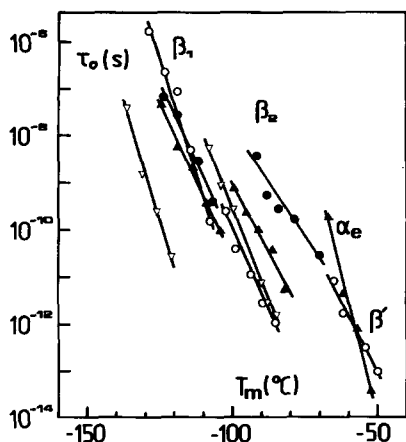


Figure 5 Variation of the pre-exponential factor  $\tau_0$  versus the temperature maximum of each elementary process  $T_m$  whose retardation time follows a compensation law. DGEBA-DDA matrix M ( $\nabla$ ) and (M+RB) ( $\bullet$ ), (M+SB) ( $\circ$ ) and (M+EB) ( $\blacktriangle$ ) composites

These regions correspond, with increasing temperature, to the  $\beta_1$ ,  $\beta_2$ , and  $\beta'$  or  $\alpha_e$  peaks. The arrows in Figure 4 are located at the peak temperature for the  $\beta$  and  $\alpha_e$  modes observed on the complex spectra. The enthalpy values corresponding to the various plateaux are in good agreement with those reported in the literature<sup>19-22</sup> for the  $\beta$  relaxation in polyepoxy networks.

The pre-exponential factor  $\tau_0$  of the Arrhenius equation is plotted against the maximum temperature of each elementary process,  $T_m$ , in Figure 5. Although it is often assumed  $\tau_0$  is constant for each type of motion, there is no a priori reason that it should be. Clearly  $\tau_0$  is not constant; instead of two or three plateaux depending on the considered sample, the results show two or three distinct groups of data points. In each group,  $\tau_0$  decreases with increasing temperature. This representation displays the  $\beta_1$ ,  $\beta_2$  and  $\beta'$  sub-modes and the  $\alpha_e$  mode.

## CONCLUSIONS

TSCr spectroscopy has been applied to the characterization of interphase in model composites in the glassy region. From these results, the following conclusions are obtained:

1. In the temperature range  $-180$  to  $60^\circ\text{C}$ , complex TSCr peaks were observed in all samples, namely around  $-160^\circ\text{C}$  for the  $\gamma$  mode and around  $-75^\circ\text{C}$  for the  $\beta$  mode.
2. By applying 'fractional stresses', with a convenient choice of the loading programme, the complex  $\beta$  peak has been experimentally resolved. Two components can be distinguished in all samples: the 'low temperature' component or  $\beta_1$  sub-mode is characterized by mechanical retardation times following a compensation law. It has been attributed to motions of diphenylpropane units; and the 'high

temperature' component or  $\beta_2$  sub-mode which is influenced by interphase morphology and has been assigned to motions of hydroxyether groups.

3. Evidence for elastomeric interphase in the coated glass bead reinforced matrix can be realized by TSCr measurements because of the low effective frequency of this technique, although the coating represents  $<1$  wt% of the whole composite. The formation of an elastomeric interphase (tailoring interphase) has been established with its own retardation mode.
4. In the coupling agent treated bead reinforced network, an interfacial polymer layer surrounding the filler particles has been evidenced. The interphase region is thick enough to provide two separate compensation phenomena associated with motions of hydroxyether groups. In this layer, the mobility of hydroxyether groups is constricted by the silane agent. Motions of these groups are displayed by an additional retardation mode labelled  $\beta'$ .

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