Epoxy Composites Based on Glass Beads. I. Viscoelastic Properties

N. AMDOUNI, H. SAUTEREAU, and J. F. GERARD*

Laboratoire des Matériaux Macromoléculaires, URA CNRS n° 507, Institut National des Sciences Appliquées de Lyon, 20, Avenue A. Einstein, 69621 Villeurbanne Cedex, France

SYNOPSIS

The viscoelastic behavior of glass beads composites are studied. Untreated, silane-treated and elastomer-coated glass beads were used, dispersed in a DGEBA–DDA–BDMA epoxy matrix. Using low frequency experiments, the three-phase structure of coated glass bead composites is demonstrated. The characteristics of both the α and β relaxations of the epoxy networks are analyzed and discussed. The β relaxation is independent of volume fraction and glass treatment. On the contrary, the position of the α relaxation increases strongly with glass volume fraction and silane treatment. The introduction of the elastomer as a thin layer at the filler/matrix interface induces a large chain mobility, thus decreasing the temperature position of the α peak. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Much work has been done on the dynamic mechanical properties of particulate or fibrous composite materials with two objectives. First, viscoelastic studies has been used to display the chemical or physical modifications of the matrix induced by the introduction or and surface treatment of the filler. Second, the dynamic mechanical behavior of the composite has been studied as a function of the properties of each phase. In this case, model composites and mechanical predictions were developed and frequently an additional term was added corresponding to the interphase to fit the model to experimental data.

Generally, the introduction of a filler in a polymeric matrix leads to a reduction of the mobility of the macromolecular chains in the vicinity of the filler surface,[1-6] by adsorption or chemical bonding. This conclusions results from the increase in the temperature of the main relaxation, associated with the glass transition, with increasing the volume fraction of filler in the case of epoxy[1,4,6] or thermoplastic[2,3,5] matrices. In many cases the filler is glass,[1-4,6] car-

bon,[7] or metallic.[5] Many studies conclude that an interphase with properties different than the bulk matrix is created near the filler surface. Some authors have attempted to compute the thickness of this interlayer.

The effect of the filler surface treatment on the viscoelastic properties depends on the nature of the reinforcement. For example, in the case of glass fibers in a polyester matrix, the dynamic mechanical spectra in the glass transition region of the matrix is greatly influenced by the nature of the organosilane used.[8]

Previous studies have shown the interest of the use of an interphase with controlled properties on the mechanical behavior of particulate or fibrous composites. The introduction of a crosslinked elastomeric interlayer with a controlled thickness during the processing leads to an increase in impact and fracture properties without decreasing the Young's modulus and glass transition temperature T_g.[9-11] Some studies have been done on the viscoelastic properties of such composites with coated particles or fibers. Generally, the introduced interphases have glass transition temperatures lower than that of the matrix.[9-14] For these composites, dynamic mechanical spectroscopy has two objectives: (1) to display the three-phase structure of the composite by the evidence of the relaxation of the interfacial

---

layer;[13,15,16] (2) to characterize the modifications induced by the coating treatment on the viscoelastic behavior of each phase (matrix and interlayer).[11,15,16] When the mechanical relaxation associated with the T_g of the interphase is not in the same temperature range as the relaxations of the matrix, the distinction can be made easily.[13] In some cases, the coating around particles displays its relaxation in the same range as the secondary relaxation of the matrix, and only a viscoelastic in a large frequency range can lead to a distinction.[11,16] From the dynamic mechanical behavior, Lipatov et al.[12] concluded that a thin interlayer of poly(butyl methacrylate) reduces the stress concentration at the interface of glass beads reinforcing an epoxy matrix.

The aim of this work is to study the viscoelastic properties of composite materials based on untreated, silane-treated, or elastomer-coated glass beads. The characteristics of each relaxation are determined using different models. Activation energies and C_1, C_2 WLF coefficients are computed and discussed in connection with the volume fraction and surface treatments of the filler.

EXPERIMENTAL

Materials

Epoxy Matrix

The chemical formulae of the different components used in the synthesis of the matrix of composites are described in Table I. The chemical character-

ization, mechanical and viscoelastic properties of such a DGEBA-dicy-BDMA matrix were described in previous papers.[17,18]

The stoichiometric ratio (amine-to-epoxy) was equal to 0.6 and the cure schedule was 1 h at 120°C followed by 1 h at 180°C. Rotated PTFE-coated molds were used to prevent dicy(DDA) or glass bead precipitation in the first stages of cure.
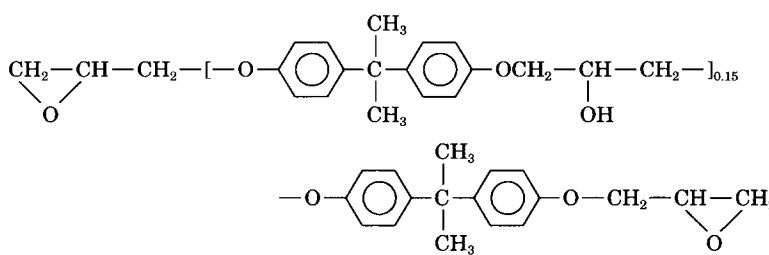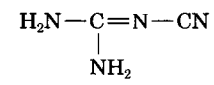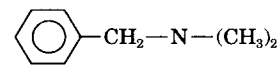
Glass Beads—Surface Treatments

Glass beads from Sovitec (A050) with particle sizes ranging from 4 to 44 μm (average particle diameter 26 μm) were used. Three kinds of surface treatments were performed:

—no treatment (noted untreated glass beads in this paper)
—adduct coating with different amounts of a crosslinked elastomer to obtain different thicknesses of rubbery interlayer on glass surface
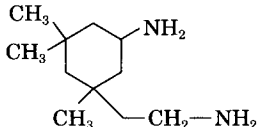
The synthesis of this rubbery coating was based on a previous paper.[16] In this study, the liquid diamine IPD replaced the previously used diamine (MNDA 1,8 p-menthane diamine) for reasons of purity.

This elastomer was prepared in a two-stage process from a carboxy-terminated butadiene acrylonitrile copolymer (CTBN), an epoxy prepolymer (DGEBA—diglycidylether of bisphenol-A), and a liquid hardener (IPD—isophorone diamine) (Table II). This adduct was dissolved in methyl-ethyl-ke-

Table I Chemical Reagents for Epoxy Matrix Synthesis

Product	Supplier	Formulae
DGEBA (epoxy prepolymer)	Bakelite 0164	$CH_2-CH-CH_2-[-O-\langle\bigcirc\rangle-\underset{CH_3}{\overset{CH_3}{C}}-\langle\bigcirc\rangle-OCH_2-\underset{OH}{CH}-CH_2-]_{0.15}$
		$-O-\langle\bigcirc\rangle-\underset{CH_3}{\overset{CH_3}{C}}-\langle\bigcirc\rangle-O-CH_2-CH-CH_2$
		Diglycidyl ether of bisphenol A: $\overline{M_n}$ = 380 g
DDA (dicy) dicyandiamide	VE 2560 Bakelite	$H_2N-\underset{NH_2}{\overset{}{C}}=N-CN$
BDMA (Catalyst)	Aldrich	$\langle\bigcirc\rangle-CH_2-N-(CH_3)_2$

Table II   Chemical Formulæ of Reagents for Elastomeric Adduct Synthesis and Silane Treatment

Name	Chemical Formulæ	Supplier
DGEBA (epoxy prepolymer)	(see Table I) $\overline{M_n}$ = 380 g	Bakelite 0164
CTBN (liquid rubber)	HOOC $\text{-}[(\text{CH}_2\text{CH}=\text{CH}-\text{CH}_2)_5(\text{CH}_2-\overset{\vert}{\underset{\text{CN}}{\text{CH}}})]_{10}$ —COOH $\overline{M_n}$ = 3500 g	Goodrich Hycar 1300 × 8
IPD (liquid hardener)	$\begin{array}{c}\text{CH}_3\\\text{CH}_3\end{array}\!\!\searrow\!\!\!\bigcirc\!\!\!-\text{NH}_2$ $\begin{array}{c}\text{CH}_3\end{array}\!\!-\text{CH}_2-\text{NH}_2$	Hüls
γ-APS	$\text{H}_2\text{N}-(\text{CH}_2)_3\text{Si}-(\text{OCH}_2\text{CH}_3)_3$	Union Carbide A1100

tone (MEK) and deposited onto glass beads by a solvent coating process. After removal of the solvent by heating at 120°C, crosslinking of this elastomer occurred around glass particles (occurred by means of a reaction between secondary amine and epoxy groups). Different coating thickness were obtained by changing the amount of elastomer in MEK. e/r ratios (thickness of the interlayer to radius of the beads) were computed from thermogravimetric analysis (TGA at 625°C), taking into account the distribution of glass beads diameters;

The glass transition temperature of this adduct was about −55°C (determined by DSC).

Silane-Treated. γ-Aminopropyltriethoxy silane (γ-APS or A1100) (Table II) was applied after removal of any contamination by isopropyl alcohol at reflux, by immersion in 0.5% vol solution of ethanol : water (95 : 5 vol) at pH > 4.

Composite Materials

Composite materials were made from untreated, silane-treated, and elastomer-coated glass beads with different volume fractions (from 0 to 30% vol) of glass. The same cure schedule as for the pure epoxy matrix was used (1 h at 120°C followed by 1 h at 180°C). The various filler volume fractions were checked by burning off the resin at 625°C.

The influence of the interlayer thickness on the dynamic mechanical behavior was studied for materials with the same filler content (20% vol). A previous work[10] showed that fracture properties reached maximum values for this volume fraction. The interlayer thickness varied from 0 (untreated) to 6.5% of the radius of the glass beads.[10]

Dynamic Mechanical Measurements

Analytical

Two kinds of dynamic mechanical analyzers were used. A viscoelasticimeter RDA 700 Rheometrics was used for recording the dynamic mechanical spectra G', G'', and tan δ versus temperature at a frequency of 10 Hz in torsion mode and in the temperature range −150/250°C. In the low temperature region (−100/20°C), the complex modulus E^* was recorded at seven frequencies: from 0.033 to 30 Hz using a dynamic mechanical thermal analyzer (DMTA) from Polymer Laboratories. In this case, samples were tested in a single cantilever bending with a fixed displacement (±16 μm) in a frequency/temperature sweep mode.

Data Treatment

Dynamic Mechanical Spectra—Characteristics of the Relaxations. From dynamic mechanical spectra, i.e., G', G'', and tan δ versus temperature at a fixed frequency, different parameters could be determined (Fig. 1):

● The various characteristics of the relaxations (α and β) of the epoxy matrix at this frequency (temperature, position, and width at the half-height of tan δ peaks).

● The values of the real parts of the moduli in the glassy and rubbery states. The modulus at room temperature was also determined.

From multifrequency experiments in the low temperature range (β secondary relaxation zone), the
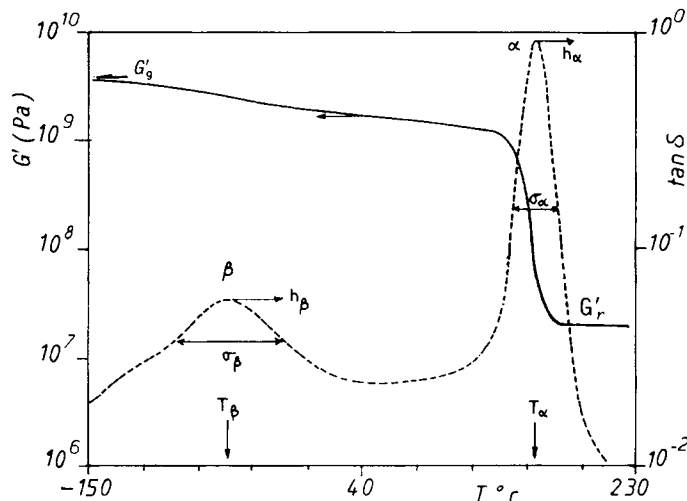
Figure 1 Dynamic mechanical spectrum at 10 Hz in torsion mode for a composite material based on silane treated glass beads (20% vol fraction).

apparent activation energy of this β peak ($E_{a\beta}^{\neq}$) was determined using Arrhenius law:

$$\ln \nu = -E_{a\beta}^{\neq}/RT_m + cst$$

where R is the gas constant and T_m the temperature position of the tan δ peak at the frequency ν. From the WLF constants, C_1 and C_2, the activation energy of the α relaxation could be also computed (see below).

Time–Temperature Superposition Principle. In the α transition zone of the epoxy matrix, the time–temperature principle (WLF principle) could be applied and by shifting the curves of the storage modulus vs. frequency, the "master curve" reduced to a reference temperature could be obtained[19] [Fig. 2(b)]. From the shift factors ^aT determined at various temperatures around the reference temperature [Fig. 2(a)], the constants C_1^g and C_2^g were computed:

$$\log \, ^aT = \frac{-C_1^g(T - T_{\text{ref}})}{C_2^g + (T - T_{\text{ref}})}$$

This shifting and calculation procedure is to be made in the same manner to compare the results obtained on the various materials.[20] The values of C_1^g and C_2^g were verified by applying the same shift factor on the G'' vs. frequency curves at various temperatures.

From these constants, the apparent activation energy of the α relaxation was calculated:[19]

$$E_{a\alpha}^{\neq} = 2.303 R \cdot C_1^g \cdot T_{\text{ref}}^2/C_2^g$$

Rheological Model. The dynamic mechanical behavior of the matrix or composites could be modeled by a rheological model such as a limited biparabolic one:[21]
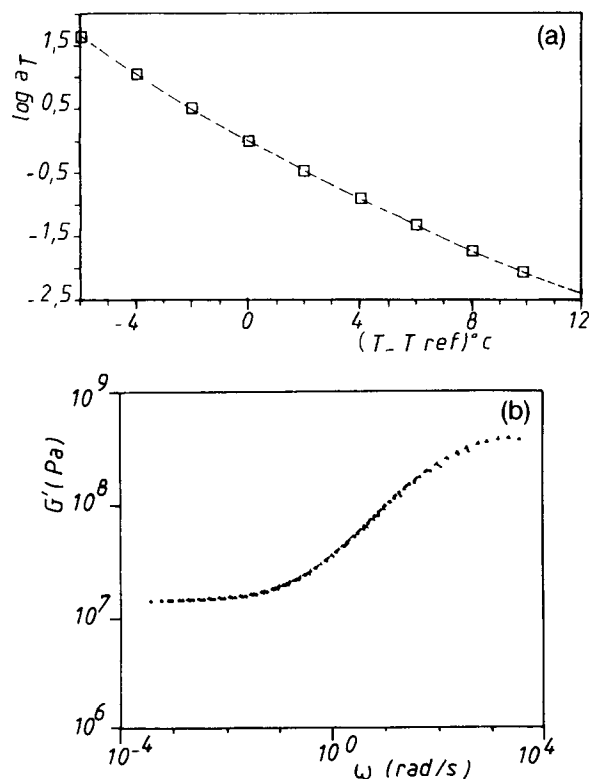
Figure 2 (a) Determination of the shift factors a_T on the storage modulus G' vs. frequency for preparing the "master curve" (b) at a temperature reference of 152°C for a composite material based on untreated glass beads (20% vol fraction).
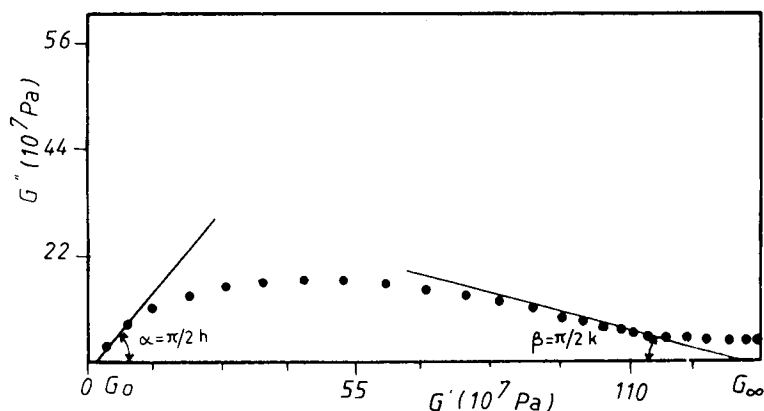
Figure 3 Cole–Cole plot and determination of the parameters of the rheological model (G_0, G_∞, h, and k) for a composite based on untreated glass beads (20% vol fraction).

$$G^* = G_0 + (G_\infty + G_0)/[1 + (i\tau_1)^{-h} + (i\tau_2)^{-k}]$$

where $h > 0$ and $k > 1$, h and k parameters, respectively, corresponding to long times (low ν and high temperatures) and short times (high ν and low temperatures). τ_1 and τ_2 are the relaxation times ($\tau_1/\tau_2 = \text{const}$). G_0, G_∞, h, and k were determined on a Cole–Cole diagram.[22] In fact, in such a representation, all the experimental points were on the same curve in accordance with the time–temperature principle. For the long times or high temperatures, the curve tended to G_0, which is the modulus of the relaxed material. At short times or low temperatures, the curve tended to G_∞ corresponding to the instantaneous modulus (Fig. 3).

## RESULTS AND DISCUSSION

Relaxations of the Pure Epoxy Network

The dynamic mechanical spectrum (see Fig. 1 as an example) clearly displays the two relaxations of the DGEBA–DDA–BDMA network.

—The main relaxation (denoted α) with the maximum temperature T_α near 160°C at 10 Hz associated with the glass transition of the epoxy network.

—A secondary relaxation (denoted β) with the maximum temperature T_β (near −55°C at 10 Hz) associated with motions of parts of the macromolecular chains. Generally, the β-relaxation is epoxy networks is associated with motions of hydroxyoether groups and other parts of the network.[23,24]

The viscoelastic properties of the DGEBA–DDA–BDMA matrices as functions of the cure cycle have been developed in previous papers.[17,18] With de-

creasing precure temperature, the α transition shifts to a higher temperature and the rubbery modulus increases, indicating that additional crosslinking points are created via an etherification reaction between the epoxy and hydroxyl groups. This phenomenon was verified by ^{13}C-NMR CP–MAS.[17] The β-relaxation is not affected in its temperature position when the precure temperature decreases, but its amplitude decreases confirming the etherification. This study is important for understanding the viscoelastic properties of composite materials made from this matrix because the presence of glass modifies the temperature in the mold. In fact, the reaction between DGEBA and *dicy* is very exothermic and glass filler can absorb a part of the heat developed.

Viscoelastic studies allow us to determine the effect of the introduction of glass beads or the surface treatment of glass on the behavior (both α- and β-relaxations) of the epoxy matrix used. But in the
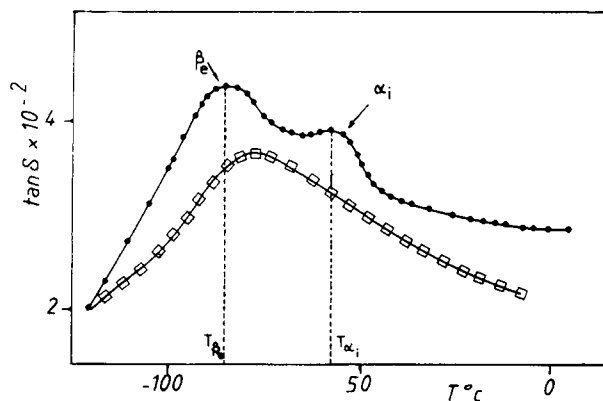
Figure 4 Dynamic mechanical spectra at low temperatures (at 0.033 Hz) for composites based on untreated glass beads (□) and elastomer coated (●) [thickness-to-radius $(e/r) = 6.5\%$] glass beads (20% vol fraction).
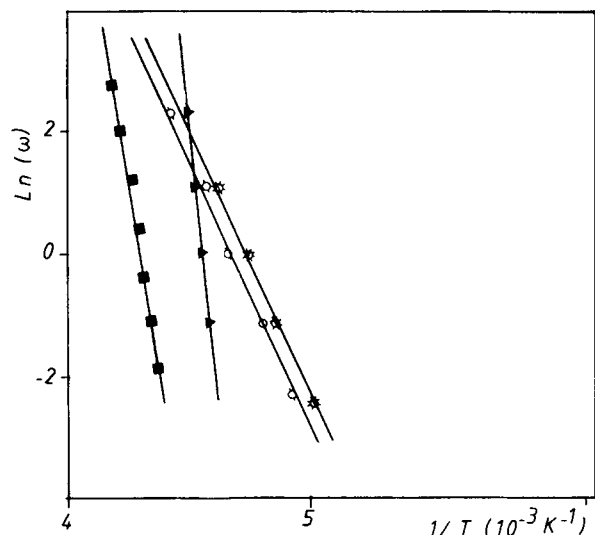
Figure 5   Arrhenius plot for the determination of apparent activation energies of the secondary relaxation, β, of DGEBA-$dicy$-BDMA matrix [($\bigcirc$) unreinforced matrix; ($\varoslash$) composite with 20% vol fraction of untreated glass] and of α_i, main relaxation of elastomer [($\blacktriangleright$) as an interphase in a composite based on 20% vol fraction of coated glass beads (e/r = 6.5%); ($\blacksquare$) pure elastomer].

first part of this paper, dynamic mechanical measurements can be used to control the three-phase structure of the coated glass bead composites.

Evidence of the Three-Phase Structure in the Case of Coated Glass Bead Composites

The elastomeric interlayer is displayed *in situ* by its main relaxation associated with its glass transition

temperature (α_i) at $-57°C$ (for a frequency of 0.033 Hz) as a shoulder of β_e relaxation peak of the DGEBA-$dicy$-BDMA matrix (Fig. 4). This evidence of α_i confirms the three-phase structure of the composite material (epoxy matrix/elastomer/glass). The elastomer is located at the interface since the elastomer is crosslinked around the glass beads.

Other authors[12,13] used such viscoelastic studies to display thin layers deposited on a filler, but, in these cases, the mechanical relaxation of the interlayer does not occur in the same zone as the secondary relaxation of the matrix. In this work the distinction between the secondary relaxation β_e and α_i is only possible at low frequencies (Fig. 5). This observation was previously made in a studies of coated-carbon fiber-based unidirectional composites[11] and glass bead composites.[16] Thus, the difference between the apparent activation energies of β_e (63 kJ mol^{-1} for the pure matrix) and α_i of the elastomer (29.7 kJ mol^{-1}) explains the possibility of distinguishing the two peaks at low frequencies. The apparent activation energy of the elastomer located at the interface (297 kJ mol^{-1}) is higher than for the pure elastomer (200 kJ mol^{-1}) as a plate prepared under the same cure conditions as the composites. The increase in apparent activation energy is attributed to the reduction of chain mobility due to the interactions with the glass surface and to the compressive stresses developed during curing. This fact demonstrates that the separated elastomer is really localized around the glass particles. This conclusion was also made by Lipatov and colleagues[12] by studying the viscoelastic prop-
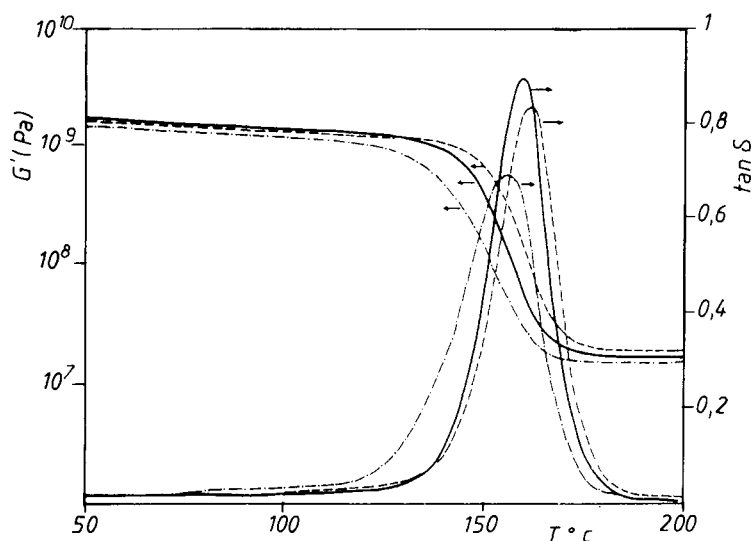
Figure 6   Dynamic mechanical spectra of composite materials based on (——) untreated, (- - -) silane-treated, (- · - · -) elastomer-coated (e/r = 4.2%) glass beads (20% vol fraction) at 10 Hz.

Table III   Dynamic Mechanical Characteristics of Composite Materials Based on Different Volume Fractions of Untreated and Silane-Treated Glass Beads (at 10 Hz)

Material	G'_g [a] (GPa)	G'_r [b] (MPa)	T_α (°C)	σ_α [c] (°C)	tan δ_{max_α}
Epoxy matrix	0.95	7.2	156	17	1
10% vol untreated	1.4	11.4	158	16	0.94
20% vol untreated	1.7	17.2	159	16	0.9
30% vol untreated	2	29.05	162	17	0.85
10% vol silane-treated	1.3	10	159	17	0.93
20% vol silane-treated	1.6	19	162	17	0.84
30% vol silane-treated	2	25.5	164	18	0.78

[a] At 40°C.
[b] At 200°C.
[c] Width of the α peak (see Fig. 1).

erties of composites based on an epoxy resin and glass beads covered with poly(butyl methacrylate).

Relaxations of the Epoxy Network Used as the Matrix

Figure 6 displays the dynamic mechanical spectra of composites based on 20% vol fraction of glass beads with various surface treatments. The characteristics of these spectra (moduli and characteristics of α transition) are listed in Tables III and IV.

The introduction of glass beads in the epoxy matrix affects significantly the viscoelastic behavior of the epoxy network. With increasing the filler content for untreated and silane-treated glass, the loss factor peak shifts to higher temperature (Fig. 7) and its amplitude is reduced proportionally to the volume fraction of the matrix. This effect could be attributed to: (1) the specificity of DGEBA-*dicy*-BDMA system, or (2) the decrease in chain mobility due to the adsorption or interactions with the glass surface.[1-8,25]

In a previous paper, we show that the glass transition temperature of DGEBA-*dicy*-BDMA networks increases with decreasing precure temperature.[17] In the case of the composite, the maximum temperature, reached in the mold and due to the exothermicity of the system, decreases with increasing volume fraction of filler. This phenomenon can explain the increase observed on our composites. As a matter of fact, when covalent bonds are created between glass surfaces (silanol groups) and epoxy functional groups using a γ-amino propyltriethoxy-silane (A1100), the position of the α peak, associated with glass transition, increases (for the same volume fraction) (Fig. 7). Thus, the increase in T_α with increasing volume fraction of filler could be attributed to: (1) changes in the chemistry of the epoxy matrix or (2) the creation of interactions or adsorption of macromolecular chains with the glass surface, especially in the case of silane treatment.

The reduction of matrix chain mobility in the vicinity of glass particles and particularly when a

Table IV   Dynamic Mechanical Characteristics of Composite Materials Based on Glass Beads (20% vol fraction) Coated with Various Thickness of Elastomer (at 10 Hz)

Thickness of Elastomeric Interlayer[a] (%)	G'_g [b] (GPa)	G'_r [c] (MPa)	T_α (°C)	σ_α [d] (°C)	tan δ_{max_α}
0	1.7	17.2	159	16	0.9
2.8	1.6	16.6	154	18	0.79
4.2	1.5	15.6	155	22	0.69
6.5	1.4	14	154	25	0.69

[a] Thickness to radius.
[b] At 40°C.
[c] At 200°C.
[d] See Figure 1.
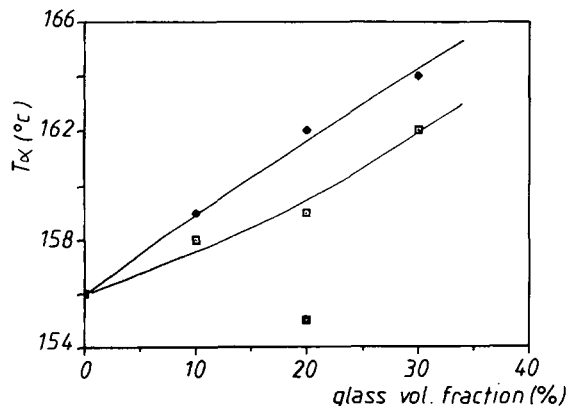
Figure 7 Position of the maximum tan δ peak at the α relaxation vs. the volume fraction of glass beads (($\square$) untreated; ($\blacklozenge$) silane treated; ($\blacksquare$) elastomer coated (e/r = 4.2%)).

coupling agent is used also explains the decrease in the amplitude of the a peak in agreement with other studies.[26,27] Another parameter, G'_r, the modulus in the rubbery state, is also affected by other existence of additional interactions or chemical bonds between the epoxy matrix and the glass surface (Table III). The increase in G'_r with a silane treatment confirms the existence of an "immobilized" layer of polymer in the vicinity of glass microspheres.[5,26] Some authors[5,28] have proposed calculating the thickness of this polymer layer around the particles using an empirical equation. In our cases, this thickness is about 0.5 μm (thus 3.5% of the particle radius) for

the untreated glass beads and about 1.4 μm (thus 10.6% of the particle radius) for the silane-treated beads. Iisaka and colleagues[28] found thicknesses from 1 to 1.4 μm for polystyrene or poly(methyl methacrylate)/glass beads (20–60 μm) composites. The rubbery modulus can be plotted versus interparticle distance ($\overline{D_S}$)[29]:

$$\overline{D_S} = 2d(1 - \phi_g)/3\phi_g$$

where d is the average particle diameter and ϕ_g the glass volume fraction (Fig. 8). For 30% volume fraction of glass, the distance between particles becomes very low and the interactions between the glass beads are important. Thus, for high glass contents, the additional decreasing of mobility due to the silane presence is less pronounced. When glass beads are coated with the elastomer, the position of the α peak is slightly reduced (about 4°C when the thickness represents 4.2% of the average particle radius) (Table IV).

In fact, the epoxy network is plasticized by the elastomeric interlayer. For the same volume fraction of glass (20%), the storage modulus in the rubbery state, G'_r, is also reduced. The increase in the width of α peak indicates a lower homogeneity of the epoxy matrix network. In the case of coated carbon fiber unidirectional epoxy composites, Gérard[11] reported the same trends. This phenomenon is confirmed by the decrease in rubbery modulus, G'_r, for the highest thicknesses ($e/r \geq 4.2\%$) (Table V). The storage
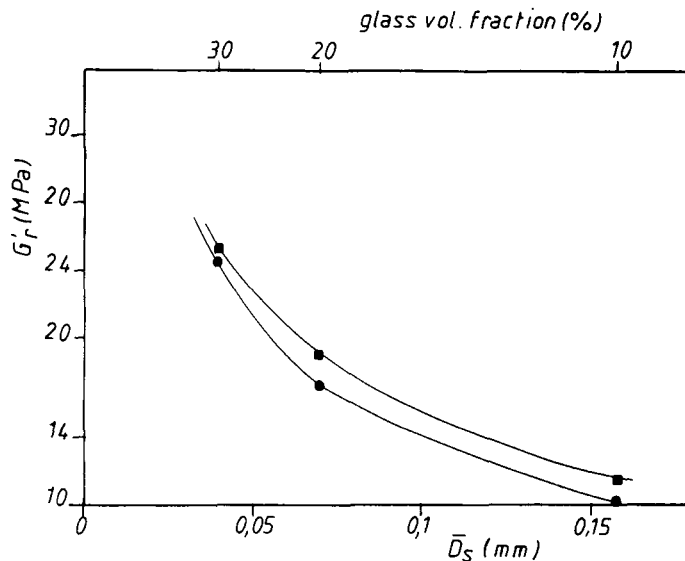
Figure 8 Storage modulus G'_r in the rubbery state vs. interparticle distance for composite materials based on untreated ($\bullet$) and silane-treated ($\blacksquare$) glass microspheres.

Table V   WLF Coefficients and Apparent Activation Energy $E_{a\alpha}^{\neq}$ for the α-Process Computed from WLF Parameters (a) and from Arrhenius Law (b)

Material	T_{ref} (°C)	C_1^g	C_2^g (K)	$E_{a\alpha}^{\neq}$ (a) (kJ mol^{-1})	$E_{a\alpha}^{\neq}$ (b) (kJ mol^{-1})
Epoxy matrix	146	11.2	45	825	666
10% vol untreated	151	12.6	52	826	800
20% vol untreated	152	15.2	63	833	21
30% vol untreated	155	18	80	790	828
20% vol silane-treated	155	20	76	928	—

modulus near room temperature, G'_g, also decreases slightly with increasing e/r. The effect of interlayer thickness on the mechanical properties of composite materials is discussed in other papers.[9,10] The increase in width of the α peak at half-height with increasing interlayer thickness could be attributed to the interdiffusion of the interphase and epoxy matrix networks.

WLF Parameters (C_1^g, C_2^g) and Apparent Activation Energies of the α_e Relaxation
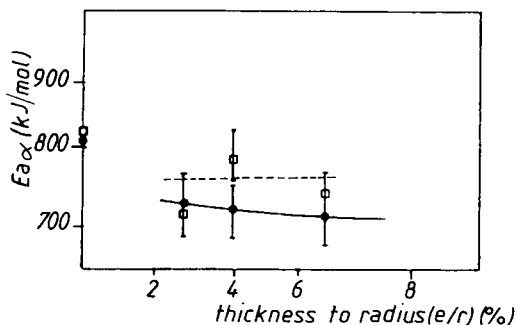
In agreement with other studies on the viscoelastic properties of particulate composites,[30,31] the time (frequency)-temperature superposition principle can be applied on the composites in this study (Fig. 2). C_1^g and C_2^g cannot be easily discussed for these composites. Thus, in this paper, C_1^g and C_2^g values are only used to compute the apparent activation energies, $E_{a\alpha}^{\neq}$ of α process in the various composites (Tables V and VI). As a matter of fact, the WLF coefficients are generally used for unreinforced polymers to determine the free volume fraction characteristics through the Doolittle equation. There is no significance of such an approach on composite materials. Nevertheless, the C_1^g and C_2^g parameters are very sensitive to the volume fraction and surface treatments of the glass. Also, $E_{a\alpha}^{\neq}$ values are calcu-

lated considering that the α-relaxation obeys an Arrhenius process, and these values are also reported in Tables V and VI. Considering the lack of precision for the C_2^g parameter, the error in the determination of apparent activation energies could be very high, but, generally, the values obtained using the two types of analyses are in agreement. The increase in $E_{a\alpha}^{\neq}$ with increasing volume fraction of glass or with treating the glass surfaces with a coupling agent (at the same volume fraction) confirms the reduction in mobility of macromolecular chains at the glass surface. The introduction of an elastomer at the glass/epoxy matrix interface induces, as previously shown, a larger mobility since the apparent activation energy decreases significantly.

The presence of the elastomer on the glass surface prevents the interactions between the epoxy matrix and glass. The dependence of $E_{a\alpha}^{\neq}$ with interlayer thickness (e/r) (Fig. 9) shows that the activation energy is roughly constant when e/r varies from 2.8 to 6.5%. However, a large difference exists between the composite with untreated glass beads and the composite with the thinner elastomeric interlayer (2.8%). This phenomenon can be explained by the fact that the chain mobility of the matrix is reduced since the epoxy matrix is in contact with the glass surface. This hypothesis is confirmed by the constant temperature T_α of the α peak observed for all

Table VI   WLF Coefficients and Apparent Activation Energy $E_{a\alpha}^{\neq}$ for the α-Process Computed from WLF Parameters (a) and from Arrhenius Law (b)

Thickness of the Elastomer Interlayer (e/r)	T_{ref} (°C)	C_1^g	C_2^g (K)	$E_{a\alpha}^{\neq}$ (a) (kJ mol^{-1})	$E_{a\alpha}^{\neq}$ (b) (kJ mol^{-1})
0	152	15.2	63	833	821
2.8	148	14.4	68	720	729
4.2	150	13.7	60	792	721
6.5	147	13.2	60	749	712

Figure 9 Apparent activation energies of the α-process vs. interlayer thickness for composite materials based on 20% vol fraction of coated glass beads [($\square$) from C_1 and C_2; ($\bullet$) from an Arrhenius analysis].

the composites based on coated glass beads ($T_\alpha \approx 154°C$ at 10 Hz) whatever the thickness of the interlayer.

The application of the rheological model confirms all these conclusions on the dependence of chain mobility and the nature of the surface treatment (Tables VII and VIII). The parameters h and k, associated respectively with short time and long time behavior of the epoxy chains, are approximately constant with increasing the volume fraction of untreated glass beads. But, when the glass surface is treated with the coupling agent γ-APS, h decreases, indicating an additional reduction of the mobility for long times.

For the elastomer coated glass bead composites, the rubbery interlayer induces a larger mobility for long times, but the increase is very low. The slight variations in h and k for all of the composites with the different surface treatments or volume fractions of filler, indicates that the bulk epoxy matrix is not greatly affected. This effect was also observed by Gérard[11] on unidirectional carbon epoxy composites for which the carbon fibers were coated with a similar elastomer. The moduli G_0 and G_∞, the modulus of the relaxed material and the instantaneous mod-

Table VIII **Parameters for Biparabolic Rheological Model Applied to Composite Materials Based on Coated Glass Beads (20% Vol Fraction) with Various Thickness**

Thickness of Elastomeric Coating (%)	h	k	G_0 (MPa)	G_∞ (GPa)
0	0.57	0.14	17	1.4
2.8	0.55	0.14	16	1.4
4.2	0.53	0.15	16	1.3
6.5	0.52	0.14	14	1.2

ulus, respectively, can be discussed as the rubbery modulus and the modulus in the glassy state.[25]

Secondary β_e Relaxation in the Epoxy Matrix Used in Composites

As mentioned previously, the secondary relaxation β_e, of the epoxy network occurs in the low temperature region. The characteristics of this β_e peak can be studied: position, width, and apparent activation energy $E_{\alpha\beta}^{\neq}$ are listed in Tables IX and X. These characteristics are quite constant with increasing filler volume fraction, indicating that the motions responsible for the β_e relaxation are not greatly modified by the presence of the filler. A noticable increase in the apparent activation energy is noted only for the silane treatment of the glass in comparison with the untreated glass bead composites. Thus, the conclusions are the same as in the glass transition region of the matrix network. Reduction of mobility through interactions or chemical coupling between the epoxy chains and the glass surface by silane could be involved. For the coated glass beads based composites, a decrease in $E_{\alpha\beta}^{\neq}$ with increasing the interlayer thickness is observed, but the determination of these values is greatly affected

Table VII **Parameters for Biparabolic Rheological Model Applied to Composite Materials**

Material	h	k	G_0 (MPa)	G_∞ (GPa)
Matrix (pure)	0.58	0.13	9	0.8
10% vol untreated	0.57	0.12	12	1.1
20% vol untreated	0.57	0.14	17	1.4
30% vol untreated	0.6	0.15	26	1.6
20% vol silane-treated	0.5	0.14	21	1.3

Table IX **β Relaxation Characteristics (at 10 Hz) for Composite Materials Based on Coated Glass Beads with Various Interlayer Thickness**

Thickness of Elastomeric Interlayer (%)	T_β (°C)	$\tan \delta_{max}$ (at T_β)	σ_β[a] (°C)	$E_{\alpha\beta}^{\neq}$ (kJ mol^{-1})
0	−55	0.052	58	70
2.8	−55	0.055	55	68
4.2	−55	0.056	55	65
6.5	−55	0.063	64	61

[a] Width of β peak (see Fig. 1).

by the superposition of the β_e peak and the main relaxation of the elastomer α_i (Fig. 10).

A similar agreement may be made if we consider the apparent increase in the tan δ_{max} peak. The increase could be attributed to the surimposition of the α_i peak and the β_e secondary relaxations.

CONCLUSION

The viscoelastic behavior of glass bead composites were studied. The effect of glass bead volume fraction and silane or coating treatments were studied.

In the case of coated glass beads, the dynamic mechanical technique allowed us to demonstrate the three phase structure of these composites. This elastomer phase was observable, only at low frequencies, superimposed onto the β-relaxation of the epoxy network.

The main relaxation, α, of the network was very sensitive to the introduction of glass beads. We noticed an increase of T_α with ϕ_g and with the silane treatment due to the reduction of mobility induced by the filler. The introduction of an elastomer coating favors the mobility in the vicinity of the glass beads and to decrease in $T_{g\alpha}$ is noted, associated with a decrease in the rubber modulus. The use of the WLF theory and Arrhenius plots allows us to determine the apparent activation energies, of the relaxations of the epoxy network.

The β-relaxation seems independent of filler content and surface treatment while the α-relaxation depends strongly of the introduction of the filler. The reduction in mobility with increasing volume fraction or with the silane treatment induces an increase in $E^{\neq}_{\alpha\beta}$. The influence of interlayer thickness is not very sensitive for a ratio thickness of the interlayer to radius of glass beads, e/r, over 2.8%. The application of the limited biparabolic rheological model leads to the same conclusions.

Table X β **Relaxation Characteristics (at 10 Hz) for Composite Materials Based on Untreated and Silane-Treated Glass Beads**

Material	T_β (°C)	tan δ_{max} (at T_β)	$\sigma_\beta{}^a$ (°C)	$E^{\neq}_{\alpha\beta}$ (kJ mol^{-1})
Epoxy matrix	−55	0.069	60	70
10% untreated	−55	0.056	58	71
20% untreated	−55	0.052	58	73
30% untreated	−56	0.051	58	71
20% silane-treated	−52	0.058	72	80

^{a} Width of β peak (see Fig. 1).
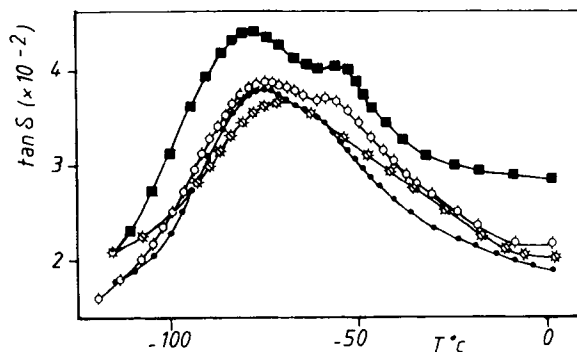
Figure 10   Dynamic mechanical spectra at a low frequency (0.033 Hz) and in the β relaxation zone for composites with 20% vol of glass beads coated at various thicknesses: (■) 6.5%; (✡) 4.2%; (●) 2.8%; (◇) 0%.

REFERENCES

1. T. B. Lewis and L. E. Nielsen, *J. Appl. Polym. Sci.*, **14**, 1449 (1970).
2. D. H. Droste and A. T. Di Benedetto, *J. Appl. Polym. Sci.*, **13**, 2149 (1969).
3. G. J. Howard and R. A. Shanks, *J. Macromol. Sci. Phys.*, **B19**(2), 167 (1981).
4. Z. Petrovic and N. Stojakovic, *Polym. Compos.*, **9**(1), 42 (1988).
5. M. Y. Boluk and P. H. Schreiber, *Polym. Compos.*, **7**(5), 295 (1986).
6. J. A. Manson and E. H. Chiu, *J. Polym. Sci., Symp.*, **41**, 95 (1973).
7. T. Hirai and D. E. Kline, *J. Compos. Mater.*, **8**, 27 (1974).
8. P. S. Chua, *Polym. Comp.*, **8**(5), 308 (1987).
9. J. F. Gérard, N. Amdouni, H. Sautereau, and J. P. Pascault, in *Controlled Interphases in Composites Materials*, H. Ishida, Ed., Elsevier, New York, 1990, p. 441.
10. N. Amdouni, H. Sautereau, J. F. Gérard, F. Fernagut, G. Coulon, and J. M. Lefebvre, *J. Mater. Sci.*, **25**, 1435 (1990).
11. J. F. Gérard, *Polym. Eng. Sci.*, **28**(9), 568 (1988).
12. S. Yu Lipatov, V. F. Rosovitsky, and B. V. Babich, *J. Appl. Polym. Sci.*, **25**, 1029 (1980).
13. B. Schlund and M. Lambla, *Polym. Compos.*, **6**(4), 272 (1985).
14. D. G. Peiffer and L. E. Nielsen, *J. Appl. Polym. Sci.*, **23**, 2253 (1979).
15. M. Kodama, I. Karino, and K. Kobayashi, *J. Appl. Polym. Sci.*, **33**, 361 (1987).
16. Y. G. Lin, J. F. Gérard, J. Y. Cavaillé, H. Sautereau, and J. P. Pascault, *Polym. Bull.*, **17**, 97 (1987).
17. N. Amdouni, H. Sautereau, J. F. Gérard, and J. P. Pascault, *Polymer*, **31**, 1245 (1990).
18. Y. G. Lin, J. Galy, H. Sautereau, and J. P. Pascault,

in *Crosslinked Epoxies*, B. Sedlacek, Ed., de Gruyter, Berlin, 1987, p. 148.

19. J. D. Ferry, in *Viscoelastic Properties of Polymers*, 3rd ed., Wiley, New York, Chap. 11, 1980.

20. J. F. Gérard, J. Galy, J. P. Pascault, S. Cukierman, and M. Halary, *Polym. Eng. Sci.*, **31**(8), 615 (1991).

21. C. Huet, *Ann. Ponts Chaussées*, **VI**, 373 (1965).

22. K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).

23. A. Pogany, *Polymer*, **11**, 66 (1970).

24. S. Pangrle, C. S. Wu, and P. H. Geil, *Polymer Comp.*, **10**(3), 173 (1989).

25. C. Migliaresi, L. Nicolais, L. Nicodemo, and A. T. DiBenedetto, *Polym. Compos.*, **2**(1), 29 (1981).

26. J. Chauchard, B. Chabert, P. Jeanne, and G. Nemoz, *J. Chim. Phys.*, **84**(2), 239 (1987).

27. P. S. Chua, *42nd Ann. Conf., Compos. Inst. SPI, Feb. 2-6*, **21A**, 1 (1987).

28. K. Iisaka and K. Shibayama, *J. Appl. Polym. Sci.*, **22**, 3135 (1978).

29. F. F. Lange and K. C. Radford, *J. Mater. Sci.*, **6**, 1197 (1971).

30. C. Migliaresi, in *The Role of the Polymeric Matrix in the Processing and Structural Properties of Composite Materials*, J. C. Seferis and L. Nicolais, Eds., Plenum, New York, 1983, p. 357.

31. Y. S. Lipatov, V. F. Babich, and J. Rosovizkyu, *J. Appl. Polym. Sci.*, **8**, 1213 (1974).