

# A study of the interphase in styrene–methacrylic acid copolymer/glass bead composites

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The influence of filler loading, size and surface treatment on the dynamic mechanical behaviour and thermal properties of styrene–methacrylic acid copolymer/glass bead composites is analysed. A theoretical approach to quantifying molecular mobility is proposed to explain the decrease in molecular motion due to strong matrix–filler linkages. The higher the filler content and the smaller the particle size, the greater the number of anchored bonds. This effect is enhanced for beads coated by silane or an elastomeric agent. In the latter case, the reduction in molecular motion is less evident owing to an increase in the mobile sequence length, which induces greater mobility. Copyright © 1996 Elsevier Science Ltd.

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## INTRODUCTION

For any composite applications, the coupling of the filler with the surrounding matrix is required. It is well known that the quality of the adhesion between phases governs the static and dynamic mechanical properties. Therefore, the interfacial adhesion between filler and matrix is optimized for a great many commercial composites.

Coupling agents are used to promote adhesion between organic polymers and inorganic reinforcements such as glass<sup>1</sup>. The most commonly used are organofunctional silanes. It has been observed that an understanding of the mechanism of coupling through silanes should clarify the general concept of adhesion. It is widely acknowledged that such coupling agents contain chemical functional groups which can react with the silanol groups on glass. Attachment to the glass can thus be made by covalent bonds. In addition, such coupling agents contain at least one other type of functional group which can coreact with the resin. Coreaction of the organofunctional groups of coupling agents with thermosetting resins is easily achieved during cure; nevertheless, only reactive thermoplastics undergo chemical reactions during moulding and forming operations. Hence, the coupling agent may act as a bridge to bond the glass to the resin. This could be expected to lead to a stronger interfacial bond, giving improved adhesion and better macroscopic mechanical properties. Therefore, the coating must be thin enough to allow the particles to reinforce the material and thick enough to create a stress field. Matonis and Small<sup>2</sup> considered the coating thickness to be the most important parameter. Other authors<sup>3</sup> have shown that the difference between the thermal expansion coefficients of the filler and the matrix

may lead to thermal residual stresses near the interface. Di Benedetto and Nicolais<sup>4</sup> observed that the introduction of an elastomeric interphase can relieve these stresses in interphase regions after cure.

A wide range of adhesion tests have been performed including contact angle measurements<sup>5</sup>, tests of compression of a polymer containing a single fibre<sup>6</sup>, single-fibre pull-out tests<sup>7</sup> and tensile tests. Other tools recently used to probe the adhesion quality in polymer composites include solid-state n.m.r. techniques<sup>8</sup>. Gambogi and Blum<sup>8</sup> made an original characterization of the adsorption of silane coupling agents onto silica surfaces and of the interaction of these functional silanes with a bis(maleimide) resin. These authors quantitatively described the interface of the composite using realistic models of molecular motion.

Otherwise, the advent of dynamic mechanical instruments has brought powerful tools to the correlation of viscoelastic behaviour to macromolecular structure and motion, as already shown in a previous paper for the case of amorphous polymers reinforced by untreated fillers<sup>9</sup>. The influence of filler addition<sup>10,11</sup>, orientation<sup>12</sup> and surface treatment<sup>12</sup> has been studied by means of viscoelasticity measurements.

The purpose of the present investigation is two-fold: first, to find out the effects of different filler surface treatments and filler sizes on the viscoelastic properties of styrene–methacrylic acid copolymer/glass bead composites; and second, to suggest a theoretical approach that can be used to quantify molecular mobility.

## EXPERIMENTAL

### Materials

*Matrix.* Two amorphous polymers provided by Elf-Atochem (France) were investigated as the matrix

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**Table 1** Characteristics of the polymers used as matrices

Polymer	Methacrylic acid content (wt%)	Methacrylic acid content (mol%)	$M_w$	$M_w/M_n$
PS	0	0	200 200	1.7
SMAA15	12.8	15	183 630	2.0

polymers: an atactic polystyrene (PS) and a random styrene-methacrylic acid copolymer (SMAA15). Their characteristics are reported in *Table 1*. The methacrylic acid molar fraction contained in SMAA15 was determined by titration. The mean molecular weight ( $M_w$ ) and the polydispersity ( $M_w/M_n$ ) were measured by gel permeation chromatography (g.p.c.).

**Filler.** The volume fraction of filler determined from the residues of burned specimens was up to 50%. Two size distributions of beads were used: the first ranged from 1 to 10  $\mu\text{m}$  with an average particle diameter of 5  $\mu\text{m}$ , and the second ranged from 1 to 45  $\mu\text{m}$  with an average particle diameter of 20  $\mu\text{m}$ .

The silane coupling agent used for the surface treatment was  $\gamma$ -methacryloxypropyltrimethoxysilane (A174, Union Carbide), designated by S.

The amount of coupling agent was controlled to give 0.2 wt% silane on the filler basis by burning the glass beads at 600°C for 30 min. The average thickness of the coating was estimated to be about 16 nm. The silane coating was supplied by Sovitec (Belgium).

Two elastomeric adducts were deposited on the glass beads by Sovitec: (1) a styrene-acrylic acid copolymer (Glascal LS26), designated by SAA, and (2) a maleic anhydride-butadiene copolymer (Maldene 286), designated by MAB.

The amount of coupling agent was controlled to give 0.9 wt% styrene-acrylic acid copolymer (thickness of 74 nm) and 0.6 wt% maleic anhydride-butadiene copolymer (thickness of 47 nm) on the filler basis.

#### Sample preparation

The unfilled polymer samples were moulded at 200°C under pressure and then cooled to room temperature.

The composite specimens were prepared by mixing the polymer resin and glass beads in a twin-screw extruder at 200°C so that the glass beads were homogeneously distributed in the polymer matrix. The extruded samples were then moulded like polymer specimens.

*Table 2* lists the characteristics of the composites used in this study and gives the theoretical filler contents and the effective contents. The effective contents were determined from the residues of burned samples. The void content was negligible in all materials.

#### Test procedures

**Differential scanning calorimetry (d.s.c.).** D.s.c. measurements were performed using a Perkin-Elmer DSC7. The glass transition temperature for a heating rate of 10°C min<sup>-1</sup> was determined from the change in the heat capacity baseline. All specimens were first heated above their glass transition temperatures and then cooled to ambient (heating and cooling rates of 10°C min<sup>-1</sup>) in order to give them the same thermal history.

**Table 2** Characteristics of the polystyrene and SMAA15 composite materials used for this study

Polymer	Surface treatment	Filler size ( $\mu\text{m}$ )	Filler content (vol%)	Effective content (vol%)
PS	None	20	50	48.5
		5	50	48.4
	S	20	21	16.4
		50	50	40.8
		5	21	19.1
		50	50	47.9
SAA	20	50	47.4	
	MAB	20	50	47.1
SMAA15	None	20	50	44.6
		5	50	51.9
	S	20	21	18.4
		50	50	46.9
		5	21	21.3
		50	50	50.4
	SAA	20	50	48.1
	MAB	20	50	45.8

**Dynamic mechanical spectrometry.** The set-up used for this study was a Metravib viscoanalyser, which provided the real ( $E'$ ) and imaginary ( $E''$ ) parts of the dynamic stress modulus and the internal friction factor  $\tan \phi$  ( $= E''/E'$ ) as a function of temperature (under isochronal conditions) or frequency (under isothermal conditions).

Each specimen was rectangular (20 × 4 × 5 mm). Each was placed in a thermal jacket where the temperature varied from 50 to 200°C with a heating rate of about 1°C min<sup>-1</sup>. Spectra were determined for several frequencies over the range from 5 to 100 Hz.

**Microscopy.** Microscopy was performed for metalized samples by Sovitec using a JEOL scanning electron microscope (operating voltage of 25 kV).

## RESULTS AND DISCUSSION

#### D.s.c. measurements

*Table 3* shows the  $T_g$  values for two filler contents (0 and 50 vol%), two filler sizes (20 and 5  $\mu\text{m}$ ) and various filler surface treatments (no treatment, silane agent, SAA and MAB elastomers).

For the polystyrene-reinforced matrix, no significant influence of such parameters on the  $T_g$  value was detected.

**Table 3** D.s.c. results (heating rate of 10°C min<sup>-1</sup>) for composites: influence of the filler content, size and surface treatment on  $T_g$ 

Filler content (vol%)	Filler size ( $\mu\text{m}$ )	Surface treatment	$T_g$ (°C)		
			PS	SMAA15	
0			102	131	
50	20	None	100	131	
		S	102	141	
		SAA	99	137	
		MAB	104	133	
		5	None	102	147
			S	100	155

For SMAA15 copolymer reinforced matrix, the results were as follows.

1. A shift in  $T_g$  towards higher temperatures was observed with increasing filler content only for composites reinforced by 5  $\mu\text{m}$  diameter raw glass beads.
2. A shift in  $T_g$  towards higher temperatures was observed for coated glass beads whatever their diameter. The greater shifts in  $T_g$  were observed for silane treatment, namely +10°C for 20  $\mu\text{m}$  diameter glass beads and +24°C for 5  $\mu\text{m}$  diameter glass beads compared to the matrix. For SAA treatment, the shift in  $T_g$  was smaller but still significant (+6°C). For MAB treatment, no significant variation in  $T_g$  was detected.
3. A significant shift in  $T_g$  towards higher temperatures was observed for the smallest glass beads, regardless of the surface treatment.

As  $T_g$  remained constant for composite materials reinforced by 20  $\mu\text{m}$  diameter particles, it can be suggested that the molecular mobility of the chains is not significantly changed by the new interactions promoted between the filler and the matrix. However, when smaller glass beads (5  $\mu\text{m}$ ) were used, the number of interactions increased, and thereby  $T_g$  was greatly increased.

The effect of filler surface treatment on  $T_g$  may depend on the compatibility between the coupling agent and the polymer matrix. By comparing the treatments applied, we can see that the silane agent is a better coupling agent for glass beads than the other two coupling agents. The presence of methacrylic acid units in the matrix could promote new specific interactions with the glass beads.

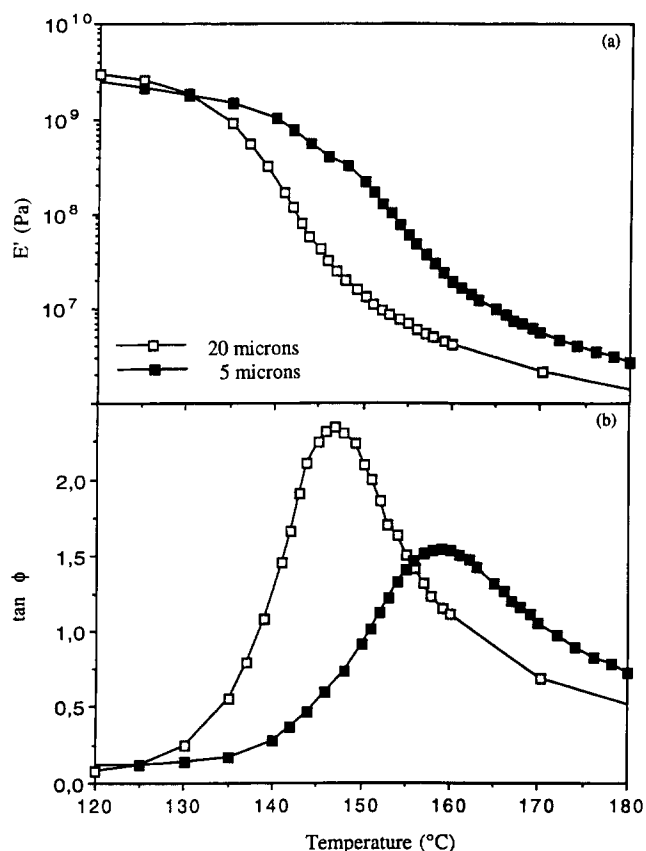
#### Dynamic mechanical spectrometry

*Influence of the filler content.* A study of the influence of the filler content in composites reinforced by raw glass beads has been described in a previous paper<sup>9</sup>. The following conclusions were given.

1. For composites using polystyrene or SMAA15 copolymer as the matrix reinforced by particles of 20  $\mu\text{m}$  diameter, the magnitude of the main mechanical relaxation related to  $T_g$  ( $\alpha$ -relaxation) decreased with increasing filler content.
2. However, no significant change in the temperature of this main relaxation ( $T_\alpha$ ) with the volume fraction of particles was detected. This last result agrees with previous d.s.c. measurements.

These observations could be the results of two factors: the reinforcement effect on the matrix from the filler and the changes in the molecular mobility of the polymer adsorbed on the filler surface. As a matter of fact, adsorption of polymer segments onto a surface restricts the molecular motion of the segments and modifies the density of packing of the polymer chains near the filler surface. These two factors have up to now been confused.

*Influence of the filler size.* For a polystyrene matrix, experimental dynamic mechanical data (plots of  $\log E'$  and  $\tan \phi$  versus temperature for a given frequency) have shown that the filler size has no significant influence on the viscoelastic behaviour.



**Figure 1** Plots of (a)  $\log E'$  and (b)  $\tan \phi$  versus temperature at 5 Hz for SMAA15 copolymer reinforced with 21 vol% of raw glass beads of (□) 20  $\mu\text{m}$  and (■) 5  $\mu\text{m}$  diameter

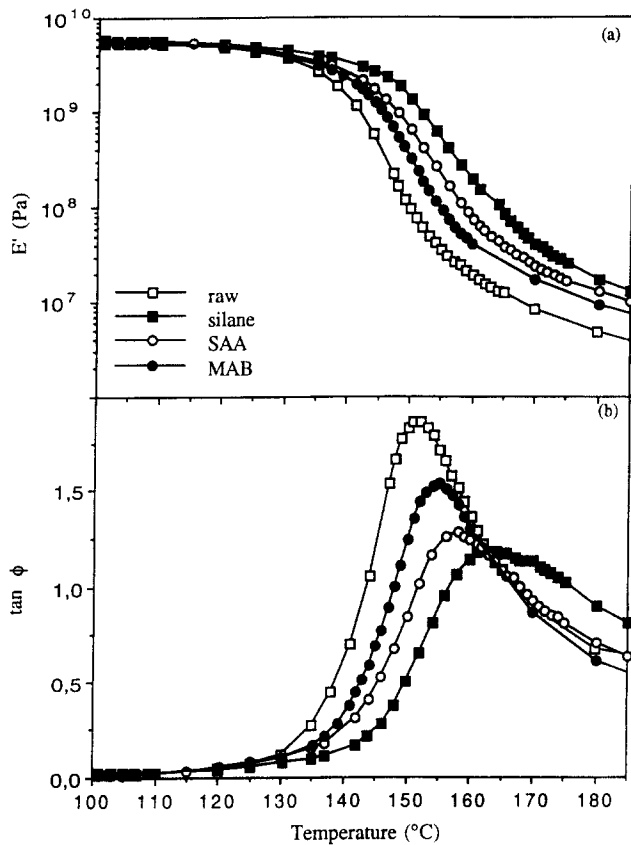
Figure 1 shows  $\log E'$  and  $\tan \phi$  spectra at 5 Hz in the temperature range from 120 to 180°C for SMAA15 copolymer reinforced by 21 vol% of raw glass beads of two different sizes (20 and 5  $\mu\text{m}$  diameter). For an SMAA15 copolymer matrix, a decrease in the filler diameter leads to a decrease in the  $\alpha$ -peak magnitude and to a shift of this peak towards higher temperatures whatever the surface treatment.

*Influence of the surface treatment.* For a polystyrene matrix, no significant influence of the surface treatment of the filler was detected from experimental dynamic mechanical data ( $\log E'$  and  $\tan \phi$  spectra).

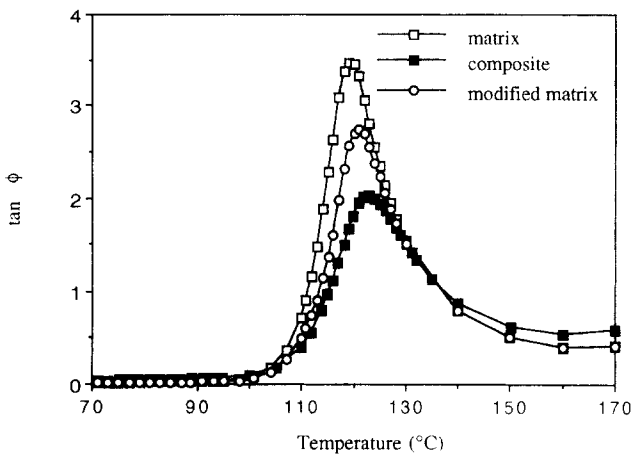
Figure 2 shows  $\log E'$  and  $\tan \phi$  spectra at 5 Hz for SMAA15 copolymer reinforced by 50 vol% of raw and coated glass beads of 20  $\mu\text{m}$  diameter. It can be seen that for an SMAA15 copolymer matrix, the mechanical behaviour of the composite depends on the surface treatment of the glass beads.

The presence of coupling agents induces a decrease in the damping peak, showing that the surface treatment may enhance the particle-polymer interactions. Our results are in agreement with those of Malik *et al.*<sup>13</sup> on the rheological properties of carbon black filled polyethylene. Their results were correlated with the interfacial conditions in the filled compounds.

Changes in the dynamic mechanical properties of a polymer reinforced by a filler could result from both mechanical coupling and changes in the molecular mobility of the polymer matrix. Accordingly, in order to give evidence for the presence of additional specific



**Figure 2** Plots of (a)  $\log E'$  and (b)  $\tan \phi$  versus temperature at 5 Hz for SMAA15 copolymer reinforced with 50 vol% of 20  $\mu\text{m}$  (□) raw glass beads, (■) silane-coated glass beads, (○) SAA-coated glass beads and (●) MAB-coated glass beads



**Figure 3** Plots of  $\tan \phi$  versus temperature at 5 Hz for (□) polystyrene, (■) polystyrene reinforced with 50 vol% of raw glass beads and (○) the separated matrix of this composite

interactions through physical modelling<sup>14,15</sup>, we propose first to remove the reinforcement effect induced by the elastic particles on the matrix.

*Physical modelling of the interphase*

*Removal of the reinforcement effect.* The removal of the reinforcement effect due to the filler was carried out by means of mechanical models as described in a previous paper<sup>16</sup>. Figure 3 displays the results of this

mechanical separation and shows  $\tan \phi$  versus temperature for the polystyrene matrix, for polystyrene reinforced with 50 vol% of raw glass beads and for the separated matrix of this composite.

It can be seen that the magnitude of the main relaxation is lower for the separated matrix relative to the unfilled matrix, even if the reinforcement effect or the mechanical coupling has been removed. This suggests that microstructural changes have occurred in the matrix because of the presence of the filler.

*Physical model.* In this section, the  $\alpha$ -relaxation of the so-separated matrix is described by means of a molecular model for the deformation of an amorphous polymer near  $T_g$ . Such models have been extensively described and applied elsewhere to amorphous<sup>17-20</sup> and semicrystalline<sup>21</sup> polymers and to composites<sup>22</sup>. Thus, the complex modulus  $E^*$  can be expressed by

$$E^* = E_r + \frac{E_u - E_r}{1 + H(i\omega\tau_{mr})^{-h} + (i\omega\tau_{mr})^{-k}} \quad (1)$$

where  $\omega$  is the pulsation, and  $E_u$  and  $E_r$  are the unrelaxed and the relaxed modulus, respectively. The expression for  $\tau_{mr}$  is

$$\tau_{mr} = \left( \frac{\tau_0}{t_0^{1-k}} \right)^{1/k} \quad (2)$$

where  $\tau_0$  is the mean time for an elemental microscopic molecular movement. It has been suggested that  $\tau_0$  be identified as the relaxation time related to the first subglass transition (the  $\beta$ -relaxation), and it can be expressed by

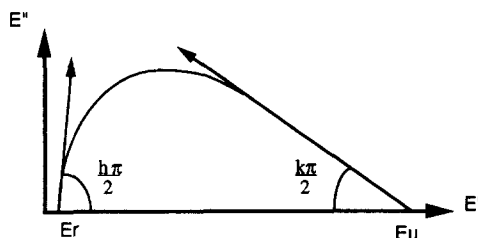
$$\tau_0 = \tau_\beta \exp\left(\frac{U_\beta}{RT}\right) \quad (3)$$

where  $\tau_\beta$  is the Debye time ( $\sim 10^{-13}$  s) and  $U_\beta$  is the activation energy of the subglass relaxation ( $\sim 80$  kJ mol<sup>-1</sup> for polystyrene and SMAA15 copolymer). The time  $t_0$  is an adjusting parameter and may vary from  $\tau_\beta$  to  $\tau_0$ .  $H$  is a function of  $h$ ,  $k$  and  $K_u$ .

The parameter  $k$  ( $0 < k < 1$ ) is consistent with the local motional ability of the chains and therefore with the material density. At  $T < T_g$ ,  $k$  is constant because the motions are frozen. At  $T > T_g$ ,  $k$  increases with increasing temperature.

The parameter  $h$  ( $0 < h < 1$ ) is related to the presence of junction points (i.e. inclusions or chemical and/or physical crosslinks) hindering the molecular motion on a large scale. For a macromolecular system showing physical and chemical crosslinks,  $h$  varies from 0.60 to 0.90.

To determine the characteristic values of the different parameters, we smoothed the experimental Cole-Cole data (plots of  $E''$  versus  $E'$ ) through a computational method developed elsewhere<sup>17</sup>. Here,  $h$  and  $k$  were obtained from the slopes of the Cole-Cole diagrams corresponding respectively to lower temperatures and higher temperatures, i.e. they were obtained from the angles ( $\theta_u, \theta_r$ ) between the tangent and the  $E'$  axis.  $E_u$  and  $E_r$  were obtained by extending this tangent onto the  $E'$  axis to lower and higher temperatures, respectively. The way to determine each of these parameters is indicated in Figure 4:  $k = 2\theta_u/\pi$  and  $h = 2\theta_r/\pi$ .



**Figure 4** Determination of  $h$ ,  $k$ ,  $E_u$  and  $E_r$  by means of Cole–Cole diagrams

**Table 4** Parameter values determined for the two reference matrices

Matrix	$h$	$k$	$E_u$ (GPa)	$E_r$ (MPa)	$\tan \phi_m$	$T_m$ (°C)
PS	0.89	0.31	2.8	1.5	3.5	119
SMAA15	0.86	0.25	2.8	2.4	2.7	147

**Table 5** Parameter values determined for matrices reinforced with 50 vol% of glass beads of 20  $\mu\text{m}$  diameter

Matrix	Surface treatment	$h$	$k$	$E_u$ (GPa)	$E_r$ (MPa)	$\tan \phi_{mm}$	$T_{mm}$ (°C)
PS	None	0.89	0.22	2.7	4.3	2.8	121
	S	0.89	0.22	2.9	3.8	2.8	119
	SAA	0.89	0.21	2.9	3.5	2.5	121
	MAB	0.86	0.22	3.2	4.2	2.6	122
SMAA15	None	0.81	0.21	2.5	2.8	2.0	150
	S	0.68	0.12	2.5	3.2	1.2	157
	SAA	0.75	0.14	2.6	4.0	1.5	154
	MAB	0.79	0.17	2.2	2.8	1.9	150

**Physical modelling of the interphase.** In this section, the data issued from the physical model when applied to the two reference materials, i.e. polystyrene and SMAA15 copolymer, are shown. The parameter values are listed in *Table 4*;  $\tan \phi_m$  is the height at 5 Hz of the main relaxation and  $T_m$  is the temperature at which this relaxation peak occurs.

The presence of methacrylic acid units leads to a decrease in both  $h$  and  $k$ . Here,  $h$  decreases from 0.89 to 0.86 and  $k$  from 0.31 to 0.25 on going from polystyrene to SMAA15 copolymer. Such variations could be related to a physical network that is fluctuant because of additional physical ties such as hydrogen bonds between methacrylic acid groups<sup>17,18</sup>. Furthermore, such a decrease in the molecular motion could also result from the existence of a stable network of chemical crosslinks induced by the formation of anhydrides during SMAA15 copolymer processing<sup>18</sup>.

*Table 5* gives the parameter values for composites reinforced by 50 vol% of particles of 20  $\mu\text{m}$  diameter;  $\tan \phi_{mm}$  is the height at 5 Hz of the  $\alpha$ -relaxation of the separated matrix of the composite and  $T_{mm}$  is the temperature at which this relaxation peak occurs. These results can be compared with those listed in *Table 4*.

For a polystyrene matrix, no significant variation in  $h$  is detected, while  $k$  and  $\tan \phi_{mm}$  (related to the relaxation intensity) decrease. These trends suggest that only a low number of additional specific interactions could occur because of the low polarity of the polystyrene units.

For an SMAA15 copolymer matrix, the results show a decrease in  $h$  from 0.86 for the unfilled matrix to 0.81 for

the composite reinforced by 50 vol % of raw glass beads. There is an accompanying decrease in both  $k$  and  $\tan \phi_{mm}$ . The  $\alpha$ -relaxation tends to be shifted towards higher temperatures as the filler content increases.

According to experiments reported in the literature, the introduction of a reinforcing filler into a polymeric matrix can induce different effects.

1. In some cases,  $T_\alpha$  (or  $T_g$ ) was found to remain constant whatever the concentration of filler<sup>23–26</sup>.
2. In other cases, an increase in  $T_\alpha$  (or  $T_g$ ) was observed with increasing filler content. Some authors<sup>27–31</sup> attributed this result to the loss of degrees of freedom and to motional hindrance. Yim *et al.*<sup>32</sup> explained it in terms of the polymer–filler interaction energies, which were measured as the heats of adsorption. An increase in compacity and a restriction in the short range molecular motions of the adsorbed polymers are the proposed origins. The increase in the rotational and translational energy barriers of the adsorbed species is obvious and makes clear that, at least in the first layers adsorbed on the surface, the beginnings or ordering occur in the polymer structure, thus giving increased close packing. The thickness of the layer of low molecular mobility is a much-discussed subject. According to the literature, it can be of the order of the range of the surface force field ( $\sim 30 \text{ \AA}$ ), although a thickness of several hundred angstroms has also been suggested. This latter value is very high, but it gains some credence in macromolecular systems because of the fact that all rotational and translational motions require cooperative motion.
3. In contrast, a decrease in the  $\alpha$ -relaxation temperature was reported by Chauchard *et al.*<sup>33</sup> for epoxy/glass fibre composites and by Gérard<sup>34</sup> for epoxy/carbon fibre composites. From the concept of the interphase, an origin for this anomalous behaviour of  $T_\alpha$  (or  $T_g$ ) was derived. As a matter of fact, these authors assumed that the composite was composed of two well-separated regions, the matrix material and the interphase, such that the combination of the glass transitions determined the total glass transition of the composite.

However, some caution must be exercised when interpreting the above three cases. These approaches have all led to physical conclusions without having first removed the reinforcement effect. Therefore, the  $T_\alpha$  variations observed by these authors should be due to the presence of both physical and/or chemical coupling and mechanical coupling.

*Table 6* gives the parameter values for composites reinforced by 21 vol % of silane-coated glass beads;  $\tan \phi_{mm}$  and  $T_{mm}$  are as previously defined.

**Table 6** Parameter values determined for matrices reinforced with 21 vol% of silane-coated glass beads

Matrix	Filler size ( $\mu\text{m}$ )	$h$	$k$	$E_u$ (GPa)	$E_r$ (MPa)	$\tan \phi_{mm}$	$T_{mm}$ (°C)
PS	20	0.89	0.23	2.9	3.2	3.2	121
	5	0.88	0.22	2.9	3.8	3.2	120
SMAA15	20	0.79	0.19	2.7	2.8	2.1	153
	5	0.70	0.12	2.9	3.5	1.3	156

For a polystyrene matrix, no significant variation in  $h$  or  $k$  is detected, showing that the filler size does not modify the polymer–particle interactions for 21 vol% reinforced compounds.

For an SMAA15 copolymer matrix, the results show a decrease in  $h$  from 0.79 for 20  $\mu\text{m}$  beads to 0.70 for 5  $\mu\text{m}$  beads accompanying a decrease in both  $k$  and  $\tan \phi_{\text{mm}}$ . Since the interactions can only occur at the particle surface, it is not surprising that a greater effect is detected for very small particles exhibiting large surface area. The most likely reason is that the presence of filler hinders the rotation of the segments of the polymer network with respect to one another. The smaller the particles, the greater the number of anchored bonds. Thus, the distance between them becomes shorter and hence an increasing amount of polymer appears in the range of the anchoring effect of the surface-bonded segments. Nielsen<sup>35</sup> has also suggested the possibility of cluster formation. The probability of cluster formation should increase with decreasing filler size. Microscopy has shown that the glass beads are quite well dispersed in the polymer matrix.

The interparticle distance can be calculated by assuming that the glass beads are homogeneously distributed in a given volume of polymer. Calculation of the number of glass beads in this given volume then leads to the interparticle distance. For example, for composites reinforced by 21 vol% of glass beads, this distance is about 7.12  $\mu\text{m}$  for 20  $\mu\text{m}$  diameter beads and 1.78  $\mu\text{m}$  for 5  $\mu\text{m}$  diameter beads. For 50 vol% reinforced compounds, the corresponding distances are about 0.31 and 0.08  $\mu\text{m}$ , respectively. Other experiments<sup>10,36</sup> on epoxy resin/particle composites are in good agreement with these results.

This interparticle distance can be compared to the effective thickness of the particle–matrix interphase evaluated from empirical relations using dynamic mechanical<sup>23,27</sup> and calorimetric<sup>35</sup> measurements. Boluk and Schreiber<sup>23</sup> have attempted to estimate the interphase thickness from damping values through

$$\tan \phi_c = (1 - Bv_f) \tan \phi_m \quad (4)$$

where  $\tan \phi_c$  and  $\tan \phi_m$  are the damping values of the composite and the matrix, respectively. The filler volume fraction is  $v_f$  and  $B$  is related to the interphase thickness through

$$B = \left(1 + \frac{\Delta R}{R}\right)^3 \quad (5)$$

where  $R$  is the particle radius and  $\Delta R$  is the interphase layer thickness. For composites loaded with 21 vol% of particles 5  $\mu\text{m}$  in diameter, this thickness is about 1.45  $\mu\text{m}$ . Other empirical relations lead to a thickness of about 1  $\mu\text{m}$ . These values are in good agreement with the estimated interparticle distance.

As shown in Table 5, no significant variation in the parameter values is detected for a polystyrene matrix, showing that the surface treatment does not sufficiently modify the polymer–particle interactions. This could be a result of the low reactivity of polystyrene with the coupling agents.

For an SMAA15 copolymer matrix, the results show a significant decrease in  $h$  from 0.81 for raw glass beads to 0.75 for styrene–acrylic acid copolymer (SAA) sized glass beads and to 0.68 for silane-coated glass beads. The

decrease in  $h$  is associated with a decrease in both  $k$  and  $\tan \phi_{\text{mm}}$ . It is also accompanied by a shift towards higher temperatures of the  $\alpha$ -peak from 150°C for raw glass beads to 154°C for SAA-sized beads and to 157°C for silane-coated beads. The presence of maleic anhydride–butadiene elastomer (MAB) on the glass beads does not influence  $h$ .

In the present study, the presence of the silane or SAA induces a decrease in the motional ability of the matrix. The results probably stem from a lowering of the filler surface energy upon addition of the coupling agent and hence an enhancement in the polymer–particle interactions. These effects illustrate the stiffness of the interfacial region caused by the existence of strong linkages created by the coupling agent between the filler and the matrix. It can be assumed that a matrix of constricted chain mobility is formed which differs from the bulk matrix. The coupling agent used is capable of creating covalent bonds between the polymeric matrix and the particles strong enough to reduce the number of accessible sites. The decrease in the number of accessible sites is responsible for the modification of the kinetics of the retardation process; that is, it has an inhibiting effect on intramolecular motion. A tendency towards compression of the network can occur, so that the motion of mobile units in the vicinity of the glass–matrix interface therefore has fewer accessible sites. The spectrum of relaxation times must be wide because of the non-uniformity of the matrix microstructure in the region of defects. The entanglement junction could confine the diffusion of a chain molecule. It acts as a crosslink, restricting the slippage of chains during deformation under applied stress.

In contrast, many authors<sup>24,34,37</sup> in the case of epoxy composites have observed that the presence of an elastomeric adduct on the beads makes the motion of macromolecular segments easier around the glass transition temperature. Such authors suggest that the polyepoxy network is consequently slightly ‘plasticized’ by the elastomer, which is in agreement with the observed  $T_g$  shift towards lower temperatures. The discrepancy with the present investigation could be related to two factors. First, in this study, the elastomer could have partially diffused into the polymeric matrix during the processing of the composite. Second, it is more likely that the conclusions of the previous authors are based on the spectra of composites that included the mechanical coupling effect.

Nevertheless, the decrease in mobility when glass beads are sized by an elastomer could originate from two competitive factors: a decrease in the number of mobile units, inducing a lowered mobility because of the additional specific interactions; and an increase in the length of the mobile sequences, leading to a greater flexibility.

For SAA elastomer, the first factor predominated, inducing a global decrease in mobility and also better glass–matrix adhesion. For MAB elastomer, the two factors are in competition, and no global change in mobility was detected. Since the reactivity of SAA elastomer seems to be greater than that of MAB elastomer with styrene–methacrylic acid copolymer, the SAA coating is capable of more specific interactions and contains fewer mobile sequences than the MAB elastomer. Therefore, for MAB elastomer, the increase in length due to the presence of long anchored blocks at the glass surface balances the other factor.

To support these results, we examined the fracture surfaces of the composites by scanning electron microscopy. The fracture surface of SMAA15 copolymer reinforced with 50 vol% of silane-coated glass beads showed particles covered with a layer of resin. However, smooth, uncoated glass beads were observed for composites reinforced with raw particles. This difference stems from the improvement in matrix–filler adhesion brought about by the silane coupling agent.

## CONCLUSIONS

Characterization of the interphase of particulate composites was carried out by means of differential scanning calorimetry and dynamic mechanical spectrometry. According to the nature of the matrix, the conclusions are as follows.

1. Changes in thermal and dynamic mechanical behaviour observed when using polystyrene as the matrix mainly result from mechanical coupling between the phases. Just a few specific interactions could occur because of the low polarity of the polystyrene units.
2. The results can be summarized as follows for an SMAA15 copolymer matrix.
  - a. Dynamic mechanical spectrometry data show a decrease in the magnitude of the main mechanical relaxation with increasing filler content. This decrease is enhanced for very small particles and for coated fillers embedded in the SMAA15 matrix. It is accompanied by a shift of the main relaxation towards higher temperatures. This shift is in good agreement with the d.s.c. measurements of  $T_g$ .
  - b. After removing the reinforcement effect induced by the filler (by means of mechanical models), we can interpret the above experimental data in terms of changes in molecular mobility through a physical approach. Thus, this approach gives evidence for a decrease in mobility which could result from physical and/or chemical crosslinks created by additional specific interactions between the filler and SMAA15 copolymer. The number of anchored bonds increases with increasing filler content and decreasing particle size. This effect is enhanced for glass beads coated with a silane coupling agent or an elastomeric adduct. However, in the latter case, the motional restriction is counterbalanced by an increase in length of the mobile units, leading to a greater flexibility and hence a greater mobility. All these changes in motional ability are in agreement with the adhesion quality observed through microscopy.

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