

# Binary and Ternary Particulate Composites.

## I. Viscoelastic Behavior

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Received 4 March 1996; accepted 26 June 1996

**ABSTRACT:** Dynamic mechanical behaviors of binary and ternary particulate composites are investigated to test for the influence of the nature of a polymeric adduct, i.e., maleated styrene ethylene-*co*-butylene styrene (SEBS) or styrene-*co*-methacrylic acid (SAMA) copolymers, at the polystyrene (PS)/glass-beads interface on the mechanical coupling and the adhesion quality between phases. Then, to separate the influence of these two causes, a rigorous modeling of the viscoelastic properties of ternary particulate composites is proposed. Thus, by comparing experimental and theoretical data, it is concluded that the rubbery and rigid adducts both induce a change in the magnitude of the mechanical coupling between phases. It is shown, however, that the SAMA coupling agent exhibits a better compatibility with the PS matrix than that of maleated SEBS. This could result from the difference in the wt % of styrene segments between these two copolymers. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1029–1040, 1997

### INTRODUCTION

Micromechanical behavior of polymers reinforced by particles is governed by the properties of both matrix and inclusions and by other factors such as the volume fraction of inclusions, the presence of clusters of particles, and the quality of the adhesion between phases.<sup>1–10</sup> Changes, then, in viscoelastic behavior of the polymer matrix induced by fillers can be due to the two following causes:

1. the mechanical coupling effect between phases, which can be enhanced by the formation of the clusters of fillers<sup>8–10</sup>; and
2. the presence of physicochemical interactions at the polymer matrix/inclusions interface which can lead to a decrease in the

molecular motion ability of the matrix chains.<sup>1,2,5–7</sup>

To separate the influence of these two origins in binary composites and then to give evidence of the quality of adhesion between phases, we have developed an original modeling of the viscoelastic behavior, well-suited over a wide range of volume fractions of fillers.<sup>10</sup> Such a self-consistent scheme is based on the definition of a representative morphological motif taking into account the eventual local-phase inversions occurring for volume fractions of fillers higher than the clustering threshold of particles.

To improve, for example, the impact toughness of composites, particles can be coated by various coupling agents giving rise to an interphase.<sup>2,11,12</sup> In such ternary particulate composites, changes in viscoelastic behavior of the polymer matrix could also result from both an improvement of the

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**Table I Characteristics of the Polymers Used in This Study as Matrix and/or Polymeric Adduct**

Polymer	Styrene (wt %)	$\bar{M}_w$	$I_p^a$
PS	100	260,000	2.9
SAMA	87	184,000	2.0
SEBS	30	—	—

<sup>a</sup>  $I_p$ , polydispersity degree.

mechanical coupling because of the presence of a third phase, and the reducing of the molecular mobility of the polymer chains because of additional interactions at the interfaces. The aim of this paper, then, is to distinguish the respective contribution of these two causes through an improved modeling of the micromechanical behavior of ternary particulate composites. Theoretical data predicted for two kinds of interlayer, i.e., a rubbery or a rigid coupling agent, at the polystyrene (PS)/glass-beads interface are compared to experimental data to evaluate the compatibility between PS and coupling agents.

Based on such an approach, tensile mechanical behaviors of binary and ternary particulate composites will be investigated in the Part II of this paper.

## MATERIALS AND METHODS

### Materials

The unfilled polymers used as matrices, i.e. PS homopolymer and a styrene-*co*-methacrylic acid copolymer (SAMA) were provided by ELF/ATOCHEM Company (CERDATO, Serquigny, and GRL, Pau, France), respectively. Their characteristics are reported in Table I.

Glass beads sized by a silane agent were provided by the Sovitec Company (Belgium). The size

distribution ranges from 2 to 44  $\mu\text{m}$  (average diameter  $\approx 26 \mu\text{m}$ ). The weight fraction of coupling agent deposited on the glass beads is estimated at 0.2 wt % by burning glass beads at 873 K for 30 min.

To create ternary composites, the two following coupling agents were used:

1. a rubbery adduct, i.e., a maleated styrene ethylene-*co*-butylene styrene copolymer (maleated SEBS) provided by Shell Company, and
2. a rigid adduct, i.e., SAMA.

Their characteristics are reported in Table I.

### Sample Preparation

Table II lists the characteristics of the binary and ternary particulate composites used in this study.

Unfilled PS and SAMA samples were molded at 463 K under high pressure (200 Pa) and then cooled to room temperature.

Two kinds of particulate composites were prepared:

1. Binary composite samples constituted by PS or SAMA matrix reinforced by 15 vol % of sized glass beads, i.e., by a volume fraction of fillers lower than the clustering threshold.<sup>10</sup> Such binary composites were prepared by mixing the polymer resin and coated glass beads in a twin-screw extruder (Haake-Rheocord 40) at 463 K.
2. Ternary composite samples were prepared in the same way, by mixing the PS and the silane sized glass beads coated either by the maleated SEBS or by the SAMA adduct. The volume fractions of coating agents are, respectively, 14 and 6%.

**Table II Characteristics of Binary and Ternary Particulate Composites**

Materials		$V_f^a$ (vol %)	$V_i^a$ (vol %)	Surface Treatment of Fillers
Binary composites	PS/glass beads	15	0	Silane coating
	SAMA/glass beads	15	0	Silane coating
Ternary composites	PS/SEBS/glass beads	15	14	Silane coating
	PS/SAMA/glass beads	15	6	Silane coating

<sup>a</sup>  $V_f$  and  $V_i$  are the volume fractions of fillers and polymeric adducts, respectively.

**Table III DSC Characteristic Values of the Materials Used in This Study**

Materials		$T_g$ (K)	$\Delta C_p$ (J g <sup>-1</sup> K <sup>-1</sup> )
Unfilled polymers	PS	373	0.26 ± 0.03
	SAMA	402	0.31 ± 0.03
Binary composites	PS/glass beads	373	0.26 ± 0.03
	SAMA/glass beads	403	0.28 ± 0.03
Ternary composites	PS/SEBS/glass beads	373	0.28 ± 0.03
	PS/SAMA/glass beads	375	0.26 ± 0.03

Both adducts are assumed to form a regular and homogeneous interlayer at the PS/glass-beads matrix interface.

The molded samples were finally cut (20 × 4 × 5 mm) for dynamic mechanical analysis. The volume fractions of fillers, reported in table II, are determined from the residue of specimens burned out at 873 K.

### Test Procedure

Differential scanning calorimetry (DSC) was carried out over the temperature range from 300 to 473 K at 10 K/min by using a Perkin Elmer DSC7 instrument purged with nitrogen. To give the same thermal history at each sample, specimens were heated at a temperature higher than their glass transition ( $T_g$ ) and cooled at room temperature at the same cooling rate. Then, on the second heating run,  $T_g$  of the various samples were determined from the change in the slope of the baseline. For composite materials, the specific heat jump ( $\Delta C_p$ ) related to  $T_g$  is evaluated per gram of polymer matrix.

Dynamic mechanical measurements were performed using a Viscoanalyser (Metravib, France). This setup provides the real ( $E'$ ) and imaginary ( $E''$ ) parts of the dynamic Young's modulus and the damping factor  $\tan \delta$  ( $=E''/E'$ ) as a function of the temperature (for one or several frequencies) or of the frequency (under isothermal conditions). Thus, isochronal scans were performed at three frequencies (5, 10, and 30 Hz) and at a heating rate of 1 K/min from 300 to 473 K. Only data recorded at 10 Hz are reported in this work.

## RESULTS AND DISCUSSION

### Binary Particulate Composites

The characteristic values determined from the thermograms of polymers (PS and SAMA) reinforced by silane-coated glass beads are listed in Table III.

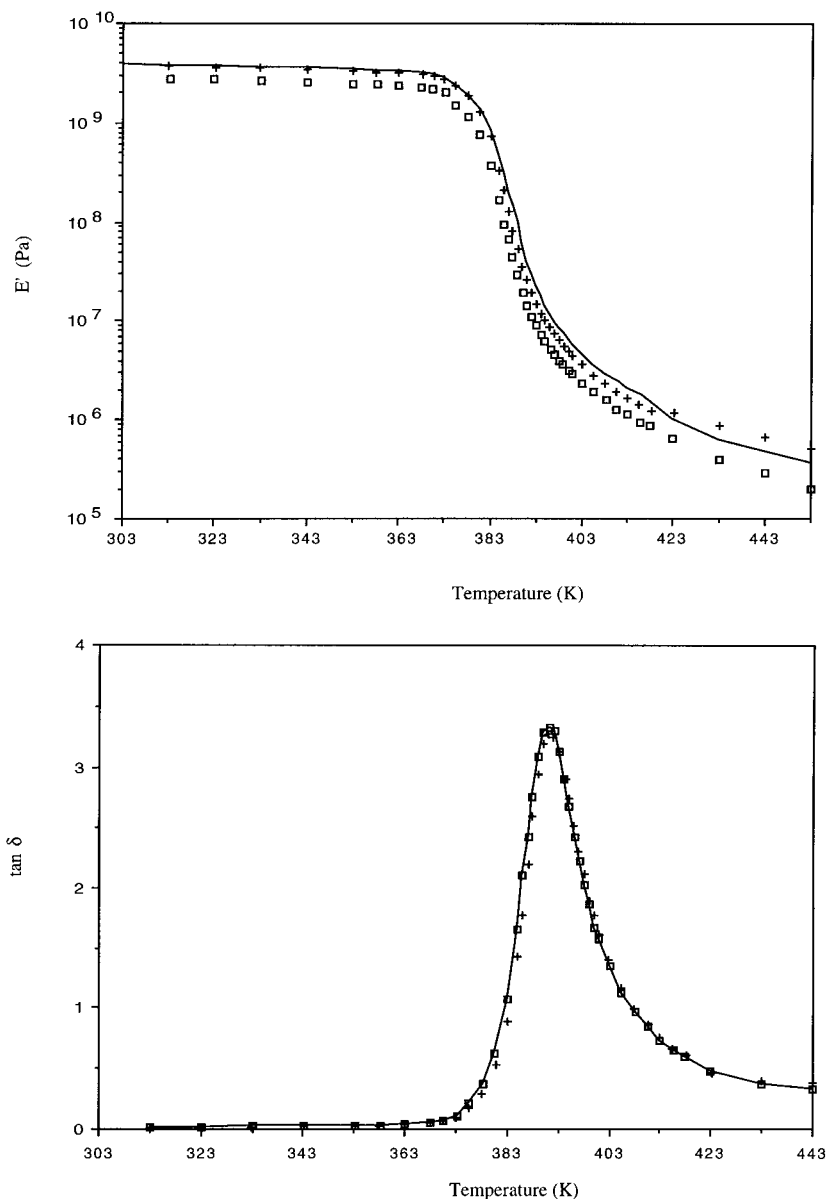
Unfilled SAMA exhibits a glass transition located at a higher temperature than that of the unreinforced PS. This is consistent with the presence of hydrogen bonds between methacrylic acid units acting, in SAMA, as physical ties hindering the molecular motions.<sup>6</sup>

The reinforcement of the PS matrix by the glass beads does not induce changes either in the glass temperature location or in the magnitude of the specific heat jump related to  $T_g$  of PS. It can be concluded, then, that interactions at the PS/glass-beads interface are weak and do not induce a significant decrease in the molecular motion ability of PS chains.

SAMA filled by glass beads exhibits a weak increase in the temperature location of  $T_g$ . This could be due to additional specific interactions between sized glass beads and SAMA matrix.

Figure 1 shows  $E'$  and  $\tan \delta$  spectra recorded at 10 Hz in the temperature range from 300 to 463 K for unfilled PS and PS reinforced by glass beads. It can be observed that the presence of glass beads does not induce a significant change either in the temperature location of the mechanical relaxation related to  $T_g$  or in its magnitude. Only a weak increase in the real part of Young's modulus, over the analyzed temperature range, can be detected. Then, in agreement with results of DSC analysis, it can be concluded that interactions at the PS/sized-glass-beads interface are weak.

Figure 2 displays  $E'$  and  $\tan \delta$  spectra recorded at 10 Hz in the same temperature range for unfilled SAMA and SAMA reinforced by glass beads sized by the silane coupling agent. The main relaxation, related to  $T_g$  of unfilled SAMA, is located at a temperature higher than that of the unreinforced PS. Moreover, its magnitude is significantly reduced. Such changes in the dynamic mechanical behavior induced by the presence of methacrylic acid groups are consistent with conclusions from the calorimetric analysis. Thus, hydrogen bonds between methacrylic acid groups in SAMA copolymer hinder molec-



**Figure 1** Plots of (a)  $E'$  and (b)  $\tan \delta$  at 10 Hz versus temperature of PS ( $\square$ ) reinforced by (+) 15 vol % of glass beads. Theoretical data (—) are superimposed for comparison.

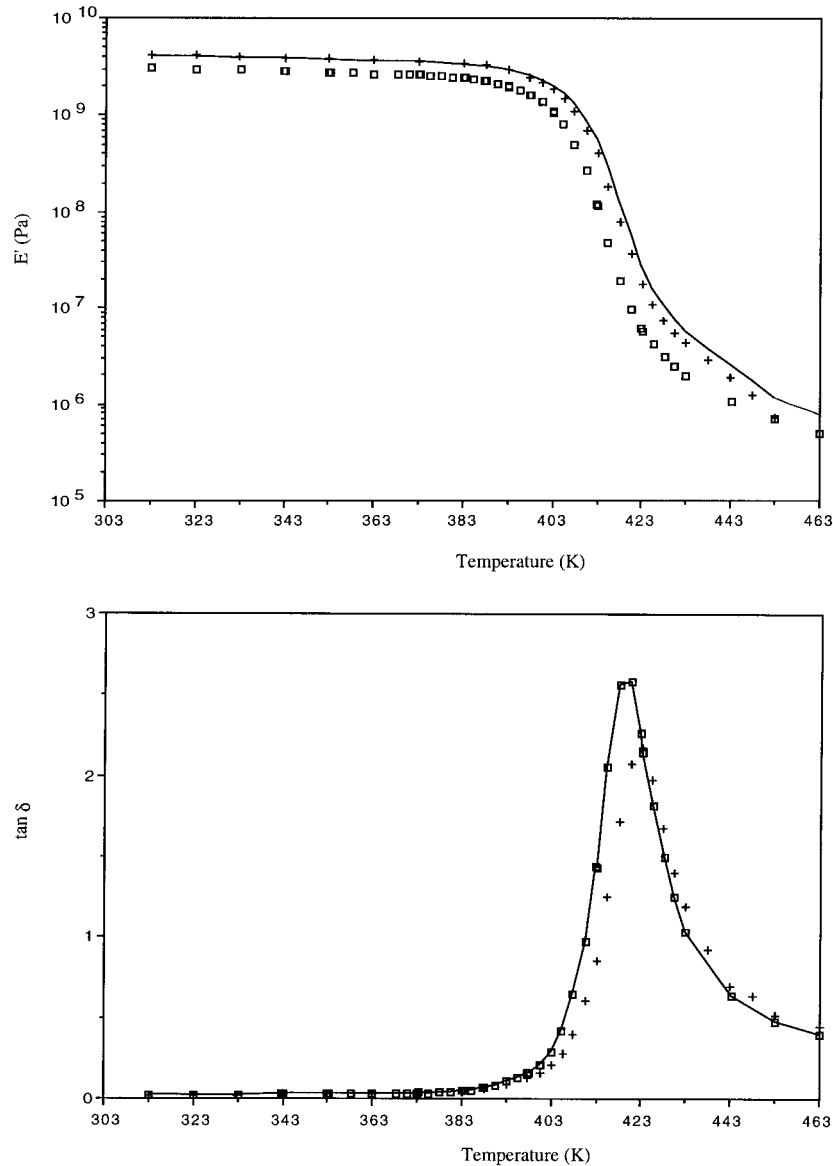
ular motions.<sup>6</sup> The main relaxation related to  $T_g$  of SAMA reinforced by coated glass beads is located at a higher temperature than that of unfilled polymer. Moreover, the magnitude of the mechanical relaxation is decreased and the modulus is increased over the analyzed temperature range, particularly in the rubbery state.

Accordingly, it could be of interest to evaluate the respective contribution of (i) the mechanical coupling between phases and (ii) the interface ef-

fects on the dynamic mechanical behavior of particulate-filled SAMA.

To separate these two causes, dynamic mechanical behavior of such binary particulate composites can be predicted by the well-known Christensen and Lo model<sup>13</sup> extended to describe the viscoelastic properties of these binary composites through the correspondence principle.<sup>14</sup>

Such a modeling is based on the following assumptions:



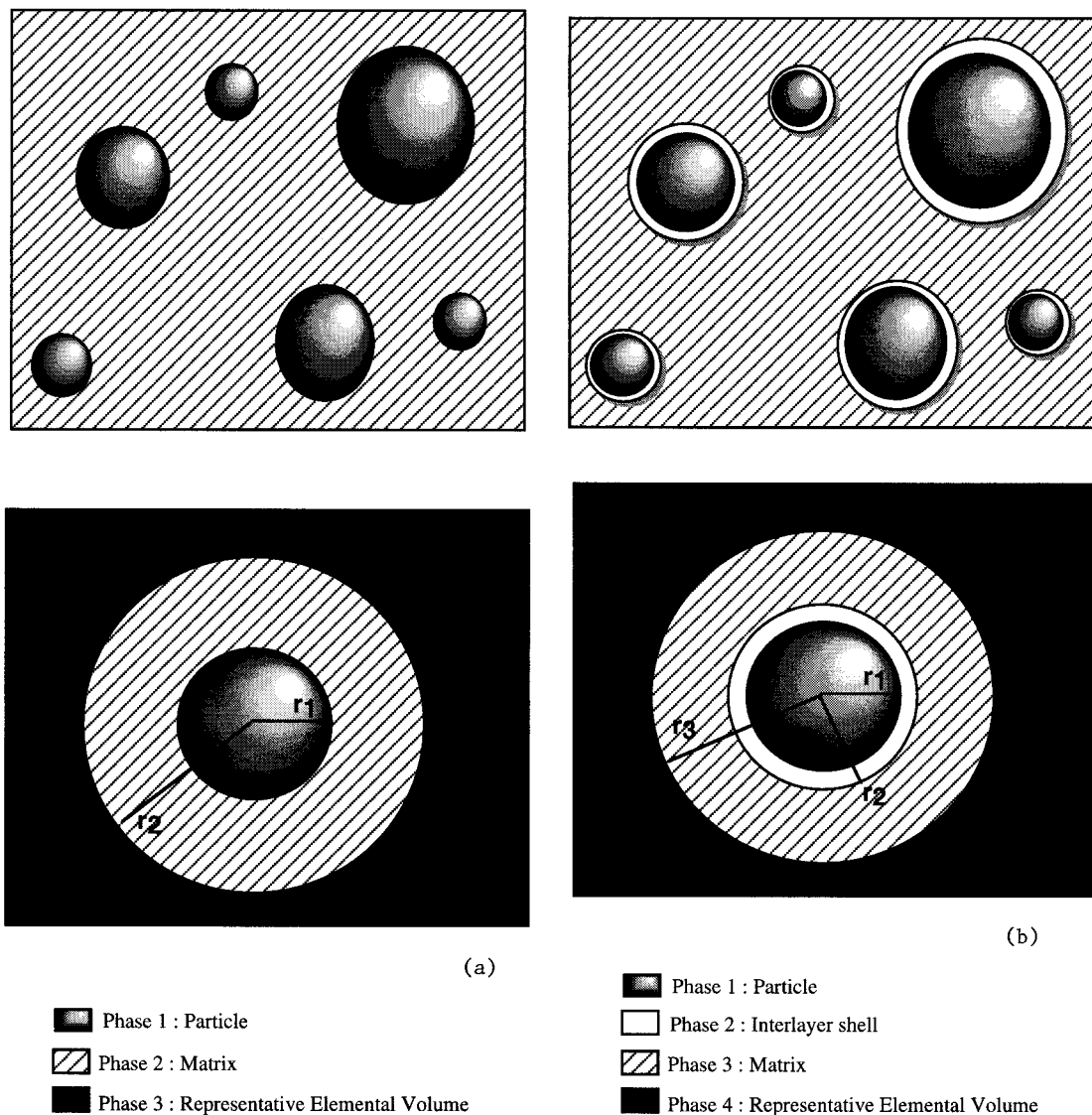
**Figure 2** Plots of (a)  $E'$  and (b)  $\tan \delta$  at 10 Hz versus temperature of SAMA copolymer ( $\square$ ) reinforced by (+) 15 vol % of glass beads. Theoretical data (—) are shown for comparison.

1. Fillers are assumed to be randomly dispersed in the matrix. Such an hypothesis is verified in this study because the volume fraction of fillers is lower than the clustering threshold.<sup>10</sup>
2. Perfect bonding is considered at the interface.
3. Each phase is assumed to be homogeneous and isotropic.

Moreover, for this modeling, it is considered a rep-

resentative elemental volume (REV) constituted by a two-concentric-sphere composite embedded in an homogeneous medium [Fig. 3(a)]. Phase 1, the central core is constituted by the glass beads with the radius  $r_1$ . Phase 2, the matrix shell, is limited by the spheres with the radii  $r_1$  and  $r_2$ . The ratios of radii are defined as follows:

$$\frac{r_1^3}{r_2^3} = V_f \quad (1)$$



**Figure 3** The “representative elemental volume”: (a) For binary composites: a two-concentric-sphere composite embedded in an equivalent homogeneous medium. Phase 1 is the filler phase and phase 2 is the matrix shell. (b) For ternary composites: a three-concentric-sphere composite embedded in an equivalent homogeneous medium. Phase 1 is the filler phase, phase 2 is the interlayer shell, and phase 3 is the polymer matrix.

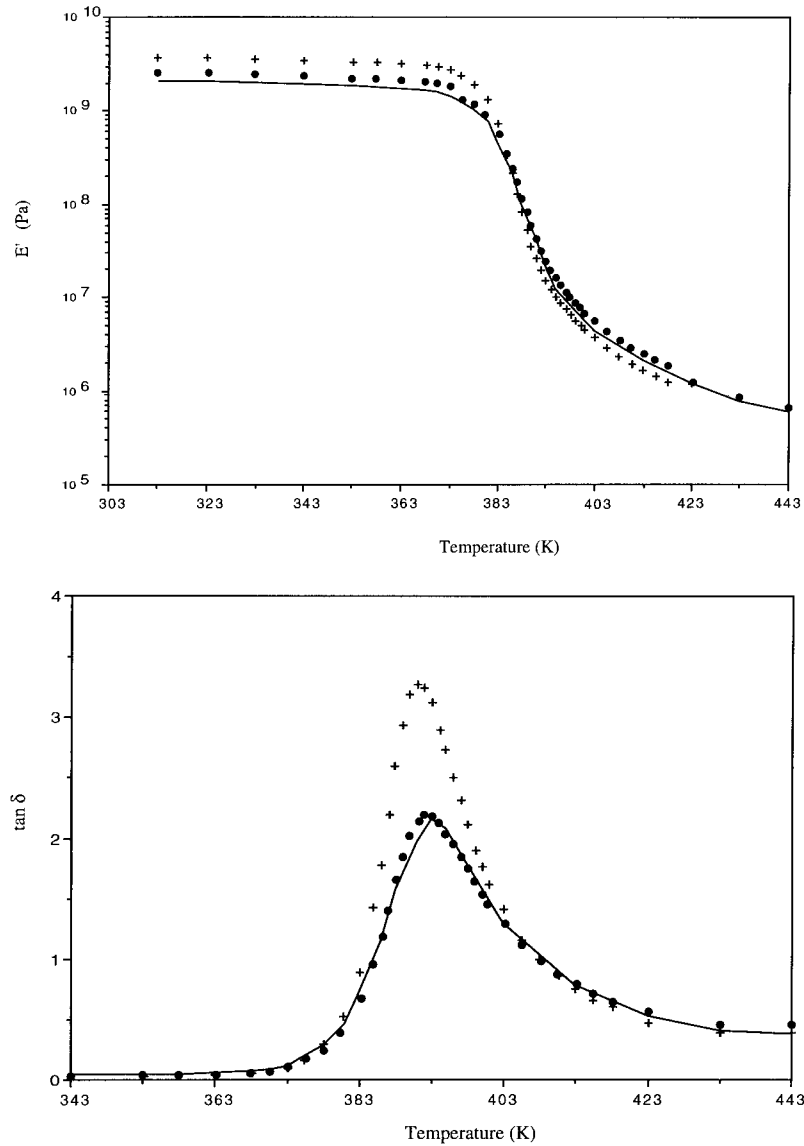
$$1 - \frac{r_1^3}{r_2^3} = V_m = 1 - V_f \tag{2}$$

Finally, the elastic bulk ( $K$ ) and shear ( $\mu$ ) moduli and the corresponding viscoelastic parameters,  $K^*$  and  $\mu^*$  of the binary particulate composites can be predicted through Christensen and Lo’s model. To allow comparison with experimen-

tal data recorded in tensile mode, the theoretical complex Young’s modulus is determined by the following well-known equation:

$$E^* = \frac{9K^*\mu^*}{\mu^* + 3K^*} \tag{3}$$

The modeling of the viscoelastic properties re-

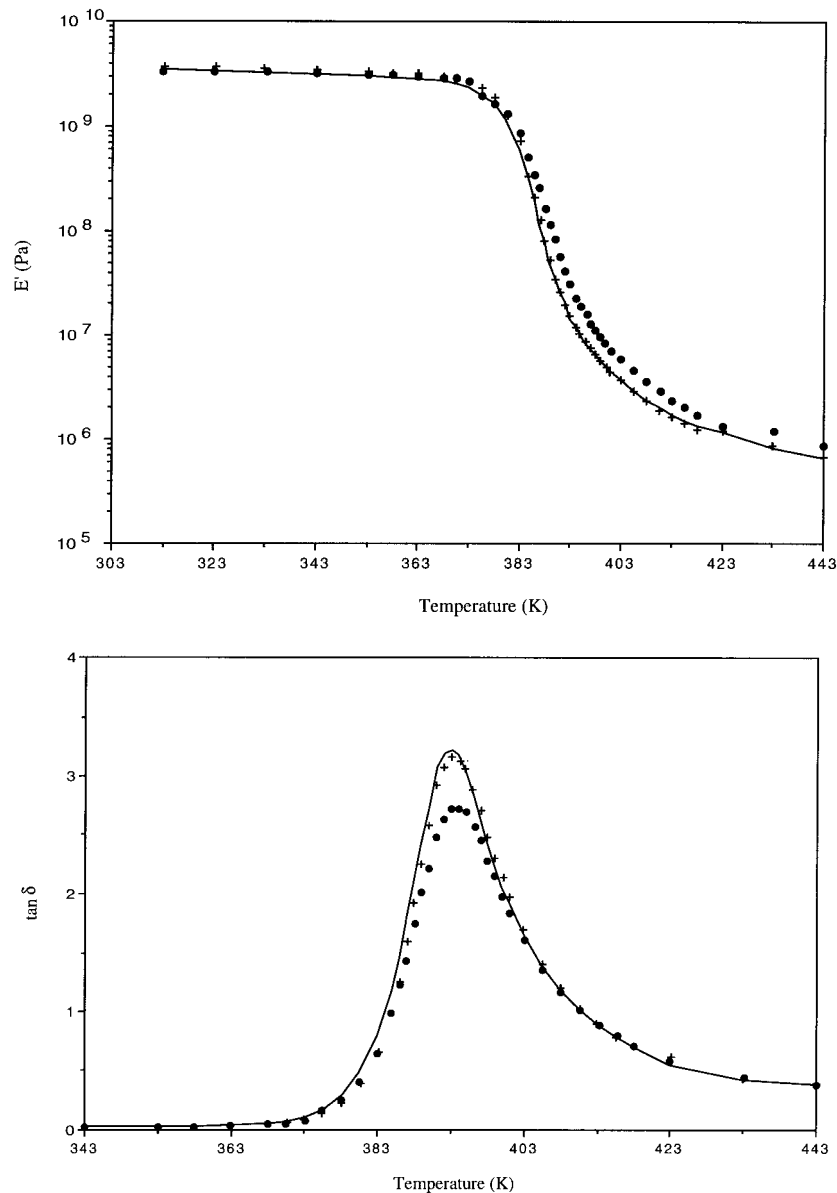


**Figure 4** Plots of (a)  $E'$  and (b)  $\tan \delta$  at 10 Hz versus temperature of PS/glass-beads binary composite (+) and of the ternary composite showing an elastomeric adduct (SEBS) at the PS/glass-beads interface (●). Theoretical data (—) are superimposed for comparison.

quires the knowledge of the mechanical properties of each phase. Thus, the complex Young's moduli of PS and SAMA copolymer, respectively used as the matrix, are experimentally measured. Glass beads have an elastic behavior over the analyzed temperature range. Poisson's ratio and Young's modulus of the fillers are respectively 0.2 and 70 GPa. Moreover, the prediction of the viscoelastic behavior also requires knowledge of the evolution of Poisson's ratio of the polymers used as the matrix. To account for the vitreous-rubbery transi-

tion undergone by the polymers through their glass transition, we assumed an S-shaped variation of Poisson's ratio, assumed to be a real parameter, versus temperature (or frequency). This can be expressed as follows:

$$\nu_m(T) = \nu_m(T_g) \left[ 1 - (1 - 2\nu_m(T_o)) \frac{E'_m(T)}{E'_m(T_o)} \right] \quad (4)$$



**Figure 5** Plots of (a)  $E'$  and (b)  $\tan \delta$  at 10 Hz versus temperature of PS/glass-beads binary composite (+) and of the ternary composite showing a rigid interphase (SAMA) at the PS/glass-beads interface (●). Theoretical data (—) are superimposed for comparison.

where  $\nu_m(T_o)$  and  $E'_m(T_o)$  are, respectively, Poisson's ratio and the real part of Young's modulus of the polymer matrix at room temperature ( $T_o$ ). From ultrasonic measurements,  $\nu_m(T_o)$  is evaluated to be 0.33 for the two polymers;  $\nu_m(T_g)$  is Poisson's ratio of the polymers at their respective  $T_g$ . It is chosen to be about 0.50 for both polymers

used as matrix.  $E'_m(T)$  and  $\nu_m(T)$  are, respectively, the real part of the complex Young's modulus and Poisson's ratio of the matrix at any temperature higher than room temperature ( $T_o$ ).

Figures 1 and 2 show theoretical plots of  $E'$  and  $\tan \delta$  versus the temperature at 10 Hz exhibited respectively by PS and SAMA polymers filled by



glass beads. It can be observed that dynamic mechanical behavior displayed by PS filled with coated glass beads is well predicted by the mechanical modeling. In contrast, for SAMA/glass-beads composites, the theoretical magnitude of the main relaxation is significantly overestimated with respect to the experimental one. Moreover, the weak shift of the  $\tan \delta$  peak toward the higher temperatures is not shown by the modeling.

It can be concluded, then, that the changes in the dynamic mechanical behavior of SAMA induced by the presence of coated glass beads result not only from a mechanical coupling between phases as for PS/glass-beads composites but also from interface effects which are not accounted for by the mechanical modeling.

### Ternary Particulate Composites

Characteristics values from DSC analysis of PS reinforced by silane-sized glass-beads composites showing an interlayer, either maleated SEBS or SAMA adduct at the fillers/polymer interface, are reported in Table III.

No significant change is detected, either in the location of  $T_g$  of the PS matrix or in the specific heat jump, whatever the kind of adduct.

Figures 4 and 5 exhibit  $E'$  and  $\tan \delta$  spectra versus temperature at 10 Hz of particulate composites showing, respectively, a SEBS or SAMA interlayer at the PS/sized-glass-beads interface.

Over the analyzed temperature range, it can be observed that Young's modulus displayed by the ternary PS/SEBS/glass-beads composite is decreased with respect to that exhibited by the binary composite material. In contrast, no significant change in the modulus is induced by the SAMA interphase.

Compared to the  $\tan \delta$  spectrum displayed by the binary PS/sized-glass-beads composites, the presence of the interlayer at the interface between phases leads to a significant decrease in the magnitude of the mechanical relaxation related to  $T_g$  of PS, whatever the kind of adduct. Such changes in the  $\tan \delta$  spectrum detected for ternary particulate composites could result from the following two origins: (i) an improvement of the mechanical coupling between phases because of the presence of a third phase, and (ii) the presence of additional specific interactions between the PS matrix and the interlayer leading to a decrease in the molecular motion ability of PS chains.

The respective contributions of these two origins can be separated through a modeling of the viscoelastic behavior, which can give evidence for the mechanical coupling between the phases. This modeling is based on the  $(n + 1)$  phase self-consistent scheme<sup>15</sup> and is applied for a three-layered phase-concentric sphere, extended to predict the dynamic mechanical behavior of these ternary particulate composites.

Thus, by assuming a perfect bonding between neighboring phases, a REV characteristic of the three-phase composite can be defined [Fig. 3(b)]. Phase 1, the central core is constituted by the particle with the radius  $r_1$ . Phase 2, the interlayer shell, is limited by the spheres with the radii  $r_1$  and  $r_2$ . Phase 3, the PS matrix, overlying the shell, is limited by the spheres with the radii  $r_2$  and  $r_3$ .

The ratios of radii are defined as follows:

$$\frac{r_1^3}{r_3^3} = V_f \quad (5)$$

$$1 - \frac{r_2^3}{r_3^3} = V_m \quad (6)$$

$$\frac{r_2^3 - r_1^3}{r_3^3} = V_i \quad (7)$$

with

$$V_f + V_m + V_i = 1 \quad (8)$$

and where  $V_f$ ,  $V_i$ , and  $V_m$  are the volume fractions of glass beads, i.e., 15 vol %; polymeric adduct, i.e., 14 and 6 vol % of maleated SEBS and SAMA copolymers, respectively; and PS matrix, i.e., 71 and 79 vol % for composites showing, respectively, maleated SEBS and SAMA coupling agents.

Then, as for the usual self-consistent schemes, the prediction of elastic and viscoelastic properties of the ternary particulate composites is based on the derivation of the elastic strain or stress field in an infinite medium constituted of a three-layered inclusion embedded in a matrix submitted to uniform stress or strain at the infinity. The four-phase model derived from Hervé and Zaoui's approach<sup>15</sup> is applied to predict the viscoelastic behavior of such a composite sphere.

Finally, the complex bulk ( $K^*$ ) and shear ( $\mu^*$ ) moduli of ternary particulate composites can be expressed as follows:

$$K^* = K_m^* + \frac{(3K_m^* + 4\mu_m^*)r_i^3((K_f^* - K_i^*)r_f^3(3K_m^* + 4\mu_i^*) + (K_i^* - K_m^*)r_i^3(3K_f^* + 4\mu_i^*))}{3(K_i^* - K_f^*)r_f^3(r_i^3(3K_m^* + 4\mu_i^*) + 4r_m^3(\mu_m^* - \mu_i^*))} + (3K_f^* + 4\mu_i^*)r_i^3(3r_i^3(K_m^* - K_i^*) + r_m^3(3K_i^* + 4\mu_m^*)) \quad (9)$$

$$A \left[ \frac{\mu^*}{\mu_m^*} \right]^2 + B \left[ \frac{\mu^*}{\mu_m^*} \right] + C = 0 \quad (10)$$

where the subscripts  $m$ ,  $i$ , and  $f$  refer to the matrix, the polymeric adduct, and the fillers, respectively. The calculation of the constants  $A$ ,  $B$  and  $C$  is given by Alberola and colleagues<sup>10</sup> and Hervé and Zaoui.<sup>15</sup>

To allow comparison with experimental data, complex Young's modulus is determined through the well-known eq. (3).

Moreover, the theoretical determination of the viscoelastic behavior of the ternary particulate composites requires the knowledge of the mechanical characteristics of each phase over the analyzed temperature range. Thus, viscoelastic behavior of both the PS matrix and the SAMA copolymer used as the coupling agent are experimentally determined. Mechanical properties of glass beads are known (see BINARY PARTICULATE COMPOSITES). To predict the dynamic mechanical properties of the other ternary composite material, i.e., PS/SEBS/glass beads, the viscoelastic properties of the SEBS copolymer are experimentally measured in the same conditions as those used for the other materials (Fig. 6).

Furthermore, the modeling of the mechanical behavior of ternary particulate composites also requires knowledge of Poisson's ratios of the different polymers and their evolution versus temperature. Thus, the Poisson's ratio evolution versus temperature of PS was previously defined. In the analyzed temperature range, Poisson's ratio of the SAMA copolymer is assumed to be constant and about 0.33. Poisson's ratio of the elastomeric adduct is assumed to be constant and equal to 0.49 over the analyzed temperature range.

Figures 4 and 5 show theoretical variations of  $E'$  and  $\tan \delta$  versus temperature at 10 Hz of the ternary particulate composites.

For PS/SEBS/glass-beads composites, a good agreement can be observed between experimental and theoretical spectra. Thus, for such particulate composites, it can be concluded that changes in the dynamic mechanical properties induced by the presence of the rubbery adduct are mainly due to a mechanical coupling effect between phases.

Accordingly, the coating of the glass beads by this coupling agent does not induce changes in the molecular motions of PS chains and then the compatibility between PS and maleated SEBS could be poor. The presence of such an interphase, then, would not significantly improve the transfer load between the fillers and the PS matrix.

For PS/SAMA/glass beads, mechanical modeling tends to overestimate the magnitude of the relaxation related to  $T_g$  of PS. Thus it can be concluded that the decrease in the maximum of  $\tan \delta$  results not only from an improvement in the mechanical coupling but also from a decrease in the molecular motions of PS chains. Accordingly, it could be concluded that such an interphase shows a better compatibility with the PS matrix than with the rubbery adduct. This could result from the difference in the weight content of styrene segments between these two copolymers. As a matter of fact, SAMA copolymer exhibits a higher weight fraction of styrene segments, i.e., 87 wt %, than that of SEBS copolymer, i.e., 30 wt % (see Table I in Part I).

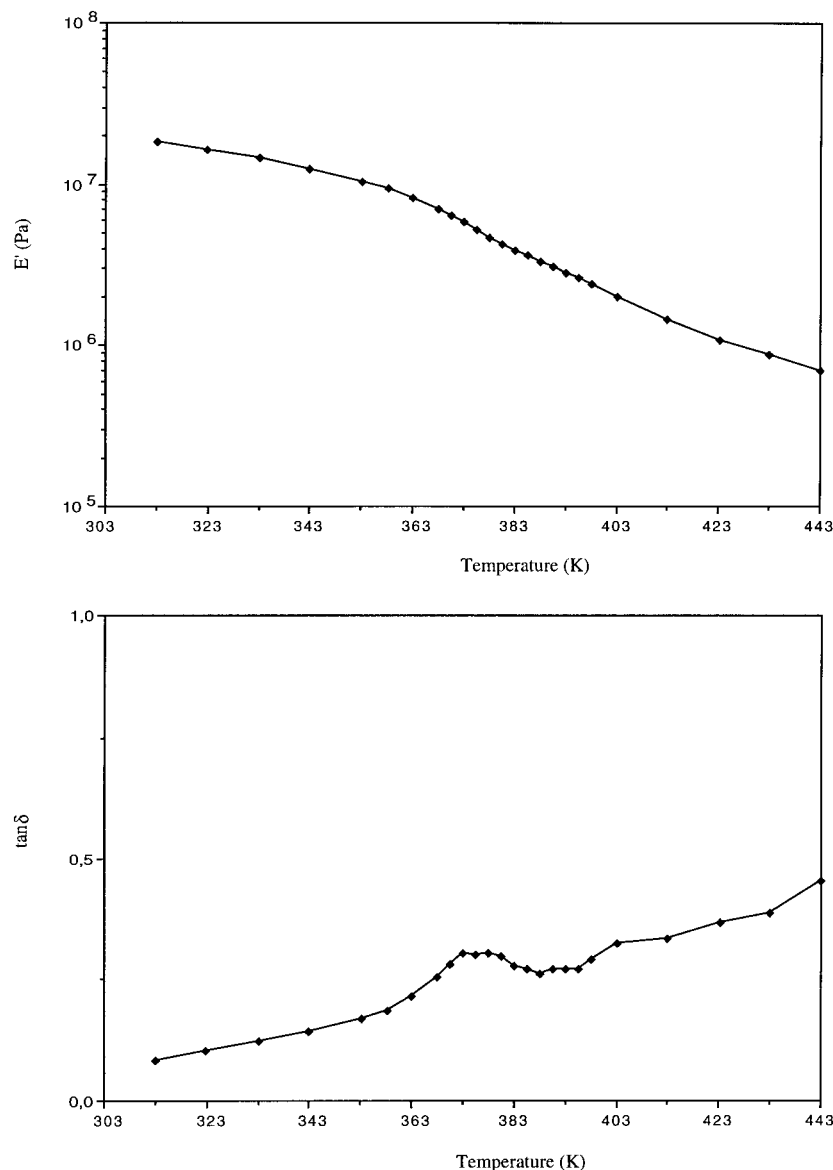
## CONCLUSIONS

Dynamic mechanical behaviors displayed by binary particulate composites, i.e., PS or SAMA reinforced by glass beads sized by a silane coupling agent, were analyzed over a temperature range from 30 to 200°C.

Based on the modeling of the mechanical properties of these binary composites, it was shown that changes in viscoelastic behavior of the polymer matrix induced by fillers originate (i) mainly from mechanical coupling between phases when PS is used as the matrix and (ii) from an additional cause resulting from interactions at the interface when SAMA is used as the continuous phase.

In a second step, the influence of the presence of two kinds of polymeric adduct, i.e. rubbery (maleated SEBS) or rigid (SAMA) interlayer at the PS/glass-beads interface, was investigated in the same temperature range.

To separate the respective contributions of the improvement in the mechanical coupling effect



**Figure 6** Plots of (a)  $E'$  and (b)  $\tan \delta$  at 10 Hz versus temperature of SEBS copolymer in the  $T_g$  region of PS.

from that resulting from an enhancement in the quality of adhesion between phases, a mechanical modeling of the viscoelastic properties of such ternary composites was developed. This self-consistent scheme allows rigorous prediction of viscoelastic properties of such three-phase materials, knowing the micromechanical properties of each component.

Then, by comparing experimental and theoretical data, it was concluded that for composites showing the rubbery interphase, changes in the mechanical behavior of composites re-

sults mainly from a change in the mechanical coupling between phases. Thus the presence of this coating agent does not enhance the adhesion quality between fillers and matrix. When glass beads are coated by the SAMA coupling agent, changes in the viscoelastic behavior of composites result not only from an improvement in the mechanical coupling between the phases but also from a decrease in the molecular mobility of the matrix chains. This could result in a better transfer load between glass beads and matrix.

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