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# The effect of fillers on the interfacial polymer properties from cryogenic dynamic mechanical measurements

ROGER J. MORGAN
*McDonnell Douglas Research Laboratories, McDonnell Douglas Corporation, St. Louis, Missouri, USA*

Dynamic mechanical measurements were used to study the effect of high surface area carbon black and fused silica fillers and a number of simple organic diluents on the SBR (31.6 mol% styrene) $\beta$ peak, which is associated with small main chain motions of trans polybutadiene units. The amount of molecular motion eliminated from the glassy state by carbon black was greater than fused silica, indicating stronger polymer-filler interaction. The degree of interaction between polymer and filler at the interface affects polymer motion further removed from the filler surface. The reasons for this phenomenon are discussed. It is proposed that dilatational stresses resulting from the mismatch in the coefficients of expansion of filler and matrix are the cause of shifts in relaxation spectra to lower temperatures, which are more pronounced when polymer-filler interaction is weak. The toughness of the matrix near the interface is discussed in terms of polymer-filler interaction, the dilatational stresses and resulting shifts in the relaxation spectra. The effect of diluents on polymer motion in relation to diluent structure show no significant trends and is difficult to interpret without information on the percentage of diluent molecules existing in diluent clusters.

## 1. Introduction

The nature of the interface in fibre composites plays an important role in the failure criteria, particularly in the growth of early damage regions via interfacial failure from the high shear stresses associated with fibre ends. The fracture process often occurs within the resin adjacent to the interface when there is strong interaction between matrix and fibre. Hence, in glassy polymer composites the strength of interaction between the polymer and filler and the nature of the adjacent polymer layers are important parameters that affect the ease of crack growth along the interface. In addition, it has been shown that both the small main chain molecular motions associated with secondary glass transitions and the free volume of a polymer glass strongly affect the polymer fracture toughness [1]. Hence, we investigated the effect solid fillers have on the intensity of these secondary glass transitions, with the aim of understanding the properties of the glass in the vicinity of the interface. Dynamic mechanical rather than NMR measurements were preferred in this investigation, because the latter spectra are distorted by the presence of paramagnetic impurities in the filler [2] or free radicals on the filler surface [3].

In previous work on the dynamic mechanical properties of composites, Nielsen [4] noted that if damping in the filled polymer originates only from the same mechanisms which produce the damping in the unfilled matrix, then the following relationship holds,

$$\Delta_{\mathrm{FI}}/\Delta_{\mathrm{UF}} = (1 - \phi_{\mathrm{F}}) \quad (1)$$

where $\Delta_{\mathrm{FI}}$ and $\Delta_{\mathrm{UF}}$ are the damping values of the filled matrix, at filler volume fraction $\phi_{\mathrm{F}}$, and unfilled matrix respectively. This relationship, which assumes negligible damping from the filler and volume additivity of the matrix damping, has been found to hold when additional damping mechanisms within the composite such as filler-filler interaction, polymer-filler interaction and/or a polymer rich skin on the specimen surface are small [5, 6]. For example Nielsen and Lee report that damping values for polystyrene containing 13% volume fraction salt follows Equation 1 from 25 to 65°C [5]. Filler-filler interaction, producing additional damping, is most likely to occur when the filler particles exist as weakly interacting agglomerates and at high filler volume fractions. Polymer-filler interaction can cause additional damping within a rubbery matrix by polymer chain segments moving past the solid filler surface for the case of no adhesion or past the rigid polymer at the filler surface for good adhesion. For example Kardos *et al.* [7] observe the damping, normalized for volume fraction of filler, increases with filler content for a rubbery matrix, despite good adhesion and minor filler-filler interaction. For a glassy state matrix the polymer-filler interaction from molecular frictional effects at the filler surface is expected to be small as only small localized motions occur in the polymeric glass. However, mechanical friction at the interface could be significant due to the rigid nature of the two constituents, particularly if there is no interaction between filler and matrix. The damping values of a particulate composite can be distorted by a polymer rich skin which is produced by the inability of the filler particles to protrude through the sample surface during preparation, as they are restricted by walls of the mould [6]. This phenomenon will be more pronounced with larger sized particles. As the stress is a maximum at the surface in torsion or flexure, this skin will distort experimental results.

In the case of semi-crystalline or crystallizable matrices, the filler surface may induce morphological changes in the polymer. For example it has been reported that polycarbonate crystallizes at the surface of graphite [8] and glass beads [9]. In addition, the damping of filled polyethylene normalized for filler volume fraction is greater at 60°C than 20°C [4]. This phenomenon cannot be explained by the deviations discussed above but would indicate a shift in the relaxation spectra in the region approaching the melting point of the matrix, which could be due to morphological changes induced by the filler.

Most of the literature data compare damping values over a limited temperature range and hence is sensitive to shifts in the relaxation spectra. This problem can be eliminated if the spectrum intensity is compared over a large temperature range, particularly down to low temperatures, as it will then only be sensitive to shifts into the main glass transition. There has been little work on the effect of fillers on secondary glass transitions. NMR and dielectric studies by Lipatov and Fabulyak [10] and NMR studies by Stejskal *et al.* [2] involve relaxations that either were associated with side group motions or distorted by filler impurities. Dammont and Kwei [11] have examined the effect of fillers on the $\gamma$ transition in epoxies; however, their data show considerable scatter when the area under this peak is plotted against volume fraction, probably because of inconsistent sample preparation.

For this investigation SBR (31.6 mol% styrene) was chosen as the polymer matrix. This material exhibits a large secondary glass transition ($\beta$ peak) near 125 K ($\sim$ 5 Hz) associated with main chain localized segmental motion of the trans polybutadiene units, enhanced by a unique crackshaft structure [12]. (Since this polymer is an elastomer at room temperature, many of the problems of incorporation and dispersion of the filler are minimized compared with other glassy matrices.) In addition, the random nature of this co-polymer eliminates induced crystallization at the filler surface as observed in the case of polycarbonate [8, 9]. The fillers chosen were high surface-area carbon black and fused silica, which had surface areas $10^2$ to $10^3$ times greater than the normal fibres utilized in fibrous polymer composites. (These filler particles exist as aggregates in which some polymer will be occluded in a composite. However, this occluded material should still contribute to the measured dynamic mechanical properties in the glassy state, although this is not true in the rubbery state [13].) The approach used was to determine the effect these fillers ($\leqslant \sim 25\%$ volume fraction) had on the area and shape of the SBR (31.6 mol% styrene) $\beta$ peak, from 80 to 180 K, and if the subsequent damping-volume fraction relationship deviated from Equation 1. This technique is sensitive to the elimination of molecular motions that have been moved into or above the main glass transition. The shift of any molecular motions from lower temperatures into the 80 to 180 K region by interaction at the filler interface for SBR (31.6 mol% styrene) is expected to be insignificant [12].

In addition to the carbon black and fused silica fillers, the effect of size, shape, and dipole moment of the diluent molecule on the $\beta$ peak in SBR (31.6 mol% styrene) was studied. Thus the effect of carbon tetrachloride (spherical), 1,1,1 trichloroethane (spherical with strong dipole), benzene, mesitylene (symmetrical), and toluene (asymmetrical) diluents on the SBR (31.6 mol % styrene) $\beta$ peak were investigated in $\sim$ 25% by volume diluent range, with the aim of determining if there were any distinguishable differences in the interaction of these molecules with the trans polybutadiene units associated with the polymer motion. From studies of the effect of diluents on the mechanical spectra of polystyrene [14, 15] it was suggested that part of the diluent molecules within the glassy polymer existed in small clusters ($\sim$ 100 molecules); asymmetric molecules exist in the amorphous state within the clusters as evidenced by their characteristic glass transition temperatures, whereas symmetrical and spherical molecules exist in a more-ordered, probably crystalline state. (Of the diluents investigated, only toluene was an asymmetric molecule, and this diluent produces a strong absorption peak near 90 K associated with the glass transition temperature of the toluene clusters [15]). These clusters may well interact with the polymer in a manner analogous to the fused silica and carbon black fillers. Hence the effect of benzene through a range of volume fractions on the SBR (31.6 mol % styrene) $\beta$ peak was investigated. This diluent molecule was chosen as it did not exhibit a strong absorption associated with the glass transition temperature of diluent clusters in the region of the $\beta$ peak.

## 2. Experimental

### 2.1. Materials

The characterization and purification of the SBR elastomer (American Synthetic Rubber Co, ASRC 3043) have been described elsewhere [12, 16]. Its microstructure (moles) is as follows: 31.6% styrene units and 48.1% *trans*, 9.9% *cis* and 10.4% vinyl butadiene units. The carbon black (Statex 160, Cities Service Co) and fused silica (Cab–O–Sil M–5, Cabot Inc) have average particle diameters of 190 and 150 Å, respectively, and surface areas of 155 and 200 $m^2\ g^{-1}$, respectively [17-19]. The diluents used were high purity grade.

### 2.2. Sample preparation

The fillers were incorporated into the elastomer by milling for 15 min at 50°C. Samples approximately 10.0 cm long, 1.0 cm wide and 0.1 cm thick were moulded at 100°C from the milled composite. The diluents were introduced into the elastomeric sample by immersion in the diluent for 15 min followed by exposure to an atmospheric of the diluent for 2 h. (The weight of the diluent in the polymer determined before and after the experimental run never differed by more than 0.25%.)

### 2.3. Dynamic mechanical measurements

A freely vibrating reed apparatus [20] was used to determine the dynamic mechanical properties of the composites from 77 K to the glass transition temperature, $T_g$. The experimental procedure and the method of introduction of elastomers into the apparatus have been described elsewhere [20, 12]. The frequencies of measurement were in the 5 to 15 Hz range, with an approximate 4 Hz change occurring over the temperature range investigated. (It should be noted the frequency will increase with increasing filler or diluent volume fraction due to modulus increases. This will result in a slight shift in the relaxation spectra of generally less than 1 K. The largest shift of 3 K is only expected when the unfilled and highest filled systems are compared in the lowest activation energy region. These small relaxation spectra shifts do not affect our subsequent analysis, as the data are averaged over the whole filler volume fraction range.)

## 3. Results

Representative plots of the damping expressed in terms of the logarithmic decrement $\Delta$ versus temperature from 77 K to $T_g$ are shown in Figs. 1 to 3 for the carbon black, fused silica, and benzene filled SBR (31.6 mol % styrene) systems, respectively. Similar plots, at one diluent concentration, are shown in Fig. 4 for the toluene and mesitylene filled systems. From data similar to those shown in Figs. 1 to 4, the average intensity of the $\beta$ peak from 80 to 180 K was determined. In the case of the diluent-filled systems, the average intensity was determined

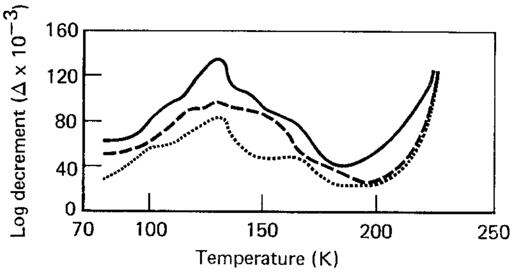

*Figure 1* Damping ($\Delta$) versus temperature for SBR (31.6 mol % styrene) containing 0% (——), 8.7% (- - - -), and 26.8% (· · · ·) by vol % carbon black.

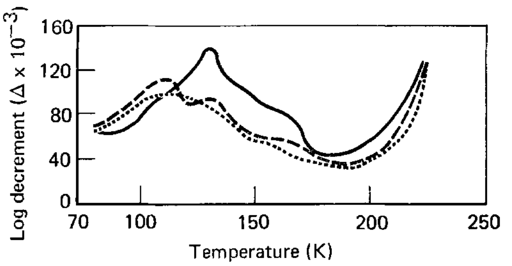

*Figure 2* Damping (Δ) versus temperature for SBR (31.6 mol% styrene) containing 0% (——), 7.8% (– – – –), and 20.6% (· · · ·) by vol% fused silica

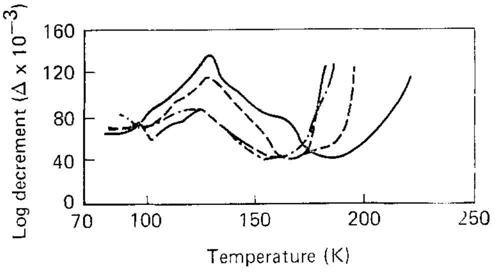

*Figure 3* Damping (Δ) versus temperature for SBR (31.6 mol% styrene) containing 0% (——), 6.5% (– – – –), 12.9% (— · —) and 23.9% (— — —) vol% benzene

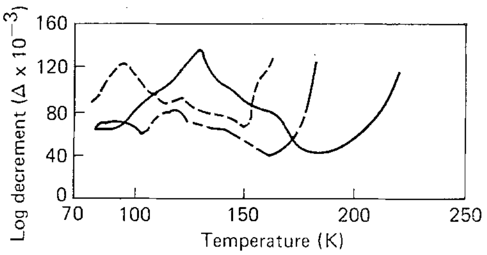

*Figure 4* Damping (Δ) versus temperature for SBR (31.6 mol% styrene) containing 0% (——), 32.2% (– – – –) toluene, and 23.7% (— — —) mesitylene by vol%

from 80 to ($T_g - 25$) K, as the glass transition temperature was depressed by the diluent. The volume percentage of diluent was determined using the density of the liquid phase of the diluent. In the case of toluene, the damping associated with the glass transition temperature of the diluent clusters at ~ 90 K was subtracted from the total measured damping using data associated with the glass transition temperature of toluene clusters in polystyrene [15]. Plots of this average intensity as a function of the volume fraction of the filler or diluent are shown in Figs. 5 to 7 for the carbon black, fused silica, and diluent filled systems, respectively. The upper line represents Equation 1 in these figures. These plots are approximately linear for the carbon black and fused silica filled systems but have a lower gradient than that predicted by Equation 1. The benzene-polymer data fall below the line representing Equation 1 at low volume fractions (< 20%), and rise above this line at high volume fractions as do the other diluent data points.

## 4. Discussion

The discussion will be divided into two parts, the

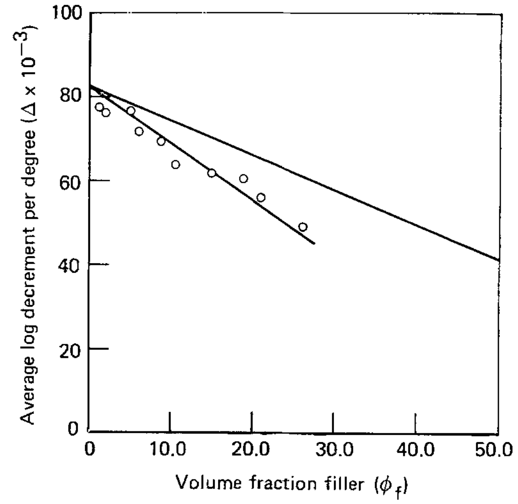

*Figure 5* Average damping Δ versus vol% filler for SBR (31.6 mol% styrene)-carbon black composite.

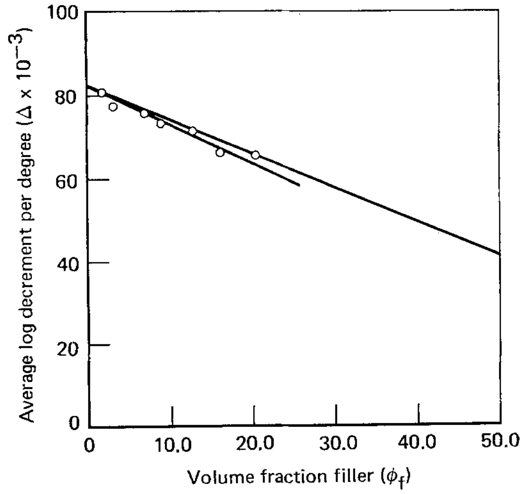

*Figure 6* Average damping Δ versus vol% filler for SBR (31.6 mol% styrene)–fused silica composite.

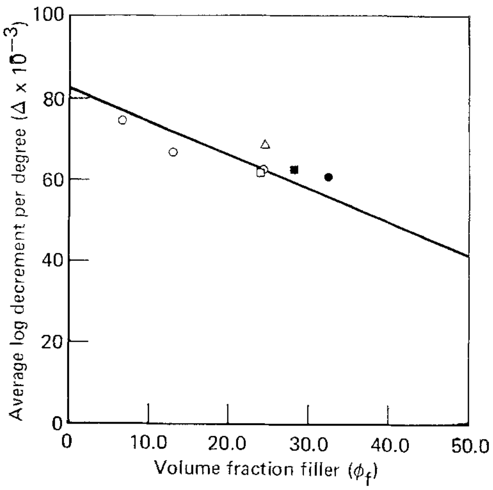

*Figure 7* Average damping versus volume percentage diluent for SBR (31.6% mol% styrene) containing benzene (○), toluene (●), mesitylene (■), carbon tetrachloride (△), and 1,1,1 trichloroethane (□).

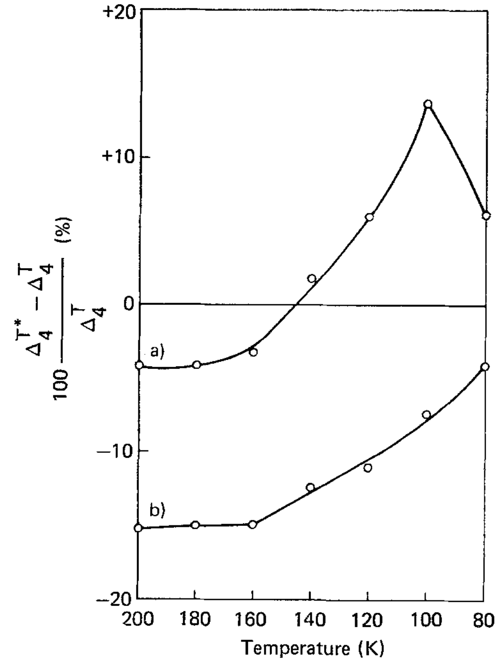

*Figure 8* Parameter $100(\Delta_4^{T*} - \Delta_4^{T})/\Delta_4^{T}$ versus temperature for (a) SBR (31.6 mol % styrene)–fused silica composite and (b) SBR (31.6 mol % styrene)–carbon black composite.

first will deal with the carbon black and fused silica filled systems and the second with the diluent filled systems.

The damping intensities for the fused silica and carbon black filled systems fall below those predicted by Equation 1, indicating that the additional damping mechanisms discussed earlier are small. In Figs. 5 and 6, the plots of the average damping intensities versus volume fraction of filler are approximately linear in the volume fraction range investigated, thus indicating minor filler-filler, and polymer-filler frictional effects which, if significant, would cause an upturn in these plots with increasing filler volume fraction. The filler particles exist as fused aggregates 0.5 to 5 μm in size, which are made up of essentially spherical particles approximately two orders of magnitude smaller. As these aggregates are filled with polymer, the ratio of specimen thickness to particle size can be taken as $\sim 5 \times 10^4$, which according to the analysis of Nielsen and Lee [6] would result in a negligible polymer rich skin.

In the light of the negligible additional damping mechanisms discussed above, the data will now be analysed to determine quantitative differences resulting from the two types of fillers. The nature of these differences and the phenomenon effecting the relaxation spectra of a glassy composite will then be discussed.

The amount of small main chain motions taking place in the glassy state at temperature $T$, as measured by the total damping from 4 K to $T(\Delta_4^{T})$ has been shown to directly affect the toughness of the polymer matrix used in this study [12]. Fig. 8 shows a plot of $100(\Delta_4^{T*} - \Delta_4^{T})/\Delta_4^{T}$ versus temperature for both types of composites, where $\Delta_4^{T*}$ is the total damping from 4 K to $T$ originating from the matrix of the composite corrected for volume fraction of filler via Equation 1. The parameter $\Delta_4^{T*}$ was averaged at each temperature from damping values normalized (using Equation 1) for each filler volume fraction. The small amount of damping from 4 to 80 K [12] was taken as a constant for this analysis. Two significant phenomena are evident from these plots. (1) For both types of composites, $100(\Delta_4^{T*} - \Delta_4^{T})/\Delta_4^{T}$ is negative and constant in the 160 to 200K temperature region, with that value for the carbon black composites exhibiting the larger negative value. (Any changes in this low intensity damping region have an insignificant effect on the total damping compared to the larger changes taking place at lower temperatures.) (2) For both types of composites the values of $100(\Delta_4^{T*} - \Delta_4^{T})/\Delta_4^{T}$ become less negative at lower temperatures. In the case of the fused silica composites there is a pronounced maximum in the damping ratio near 100 K. The significance of these phenomena will now be discussed.

The negative values of the parameter $100 (\Delta_4{}^{T*} - \Delta_4{}^T)/\Delta_4{}^T$ in the 160 to 200 K range would indicate that part of the motion taking place in the polymer glass has been eliminated by the presence of the fillers. This would suggest a modification of the state of the polymer glass at the filler surface. In fact our data can be represented by a model that assumes there is a shell of polymer glass surrounding each filler particle within an aggregate, with modified properties such that no small main chain motions occur. For such a model Equation 1 is modified to:

$$\Delta_{\mathrm{FR}}/\Delta_{\mathrm{UF}} = 1 - \frac{(r + t)^3}{r}\phi_{\mathrm{F}} ,$$

where $\Delta_{\mathrm{FR}}$ is the damping originating from the unmodified matrix, $r$ is the radius of the filler particles (assuming approximately spherical particles) and $t$ is the thickness of the immobilized polymer shell. The plots in Figs. 5 and 6, which are for the total damping in the glassy state, fit this equation for the carbon black and fused silica filled systems, and according to this model the layers of modified matrix surrounding the carbon black and fused silica particles are 17 ± 1 Å and 5 ± 1 Å respectively. This would indicate that the strength of polymer-filler interaction is greater at the carbon black than the fused silica interface. However, one has to be cautious in interpreting these damping intensity changes unless (1) the phenomena allowing molecular motion to take place in the glassy state and (2) the mechanism by which such motions absorb energy from the applied oscillatory stress field, are understood.

The nature of main chain motions in the glassy state depend on a number of molecular parameters. Only certain units which occur in favourable conformations with respect to their surroundings, because of a distribution in the packing and conformations in the glassy state, can undergo these motions [12]. All other units are frozen in until the temperature is near the main glass transition temperature. The volume swept out by the moving unit in relation to the local free volume determines if the motion occurs. Co-operative local main chain torsional motions are favoured by (1) structures that sweep out small volumes (i.e. consecutive trans or extended configurations without side groups), (2) low energy differences between rotational isomers and (3) collinear bonds. The magnitude and frequency of occurrence of intermolecular interactions along the polymer chain are also significant parameters that affect these motions. Hence any phenomena that modifies the rotational isomeric configurations and/or intermolecular interactions will affect the amount of molecular motion occurring in the glassy state and, hence, the damping intensity. However, damping changes cannot quantitatively be related to molecular motion changes until the mechanism causing these motions to absorb energy from the applied oscillatory stress field is understood. This mechanism, however, should not be modified in the elastic region by the presence of fillers in the polymer matrix, which essentially is the basis of Equation 1. The most plausible explanation of this mechanism would involve a coupling of the applied oscillatory stress field and the molecular motion when their frequencies coincide resulting in resonance and hence energy absorption from the applied field. Irrespective of the uncertainty of the nature of the energy absorbing mechanism, which will be the same for both composites and also the unfilled polymer glass in the elastic region, it is evident from the simple shell model that carbon black inhibits more molecular motion from the glassy state than fused silica. In addition the polymer-filler interaction apparently affects the properties of the matrix at distances greater than the first interfacial monolayer. The nature of these observations will now be considered in terms of changes in intermolecular interactions and rotational isomeric configurations.

It is well established that the presence of double bonds in polymer chains leads to strong interaction with many types of carbon black, whereas saturated elastomers exhibit less interaction [21]. This interaction occurs between the $\pi$ electrons of the double bond and the free radicals on the surface of the carbon black. The surface interaction for fused silica is much less: infra-red data indicate no surface interaction between the double bond of the butadiene portion of an acrylonitrile-butadiene co-polymer with an untreated silica surface [22]. Hence, it is reasonable to assume that the degree of rigidity of the trans polybutadiene units in the SBR co-polymer will be much greater at the carbon black surface than at the fused silica surface. At both the carbon black and fused silica surfaces (even if there were no strong polymer-filler interactions), the surface geometry [10] and its rigid nature in relation to the unfilled polymer will enforce entropic restrictions on the polymer conformations, decreasing polymer chain flexibility. In the case of carbon black, however, additional restrictions on molecular motion occur from the strong interactions between the polymer $\pi$ bonds and the surface free radicals, which also distort the normal rotational-isomeric configurations of the polymer chains in this surface monolayer. The degree of rigidity of the polymer monolayer at the filler surface influences the molecular mobility of adjacent layers via entropic restrictions on the polymer conformations. For example, Kumins and Roteman noted "Adsorption of the polymer molecule on a surface decreases the number of degrees of freedom for oscillatory motion which then interferes with the movement of adjacent molecules or portions thereof" [23]. In addition, for the case of the carbon black filler the distortion of the rotational isomeric configurations influences the packing of adjacent layers. These phenomena would be expected to decrease as a function of distance from the interface, which is consistent with recent NMR observations by Kaufman *et al.* [17] who report a completely immobilized and a partially immobilized layer of elastomer surrounding each carbon black particle. Additional evidence of the effect of fillers on the properties of the surrounding glassy matrix is found from diffusion and solubility studies of low molecular weight molecules in particulate filled glassy polymers, which has led a number of workers to propose the existence of ordered layers surrounding filler particles [23-25]. It is important to note that as the interaction between matrix and filler at the interface becomes stronger, which will inhibit dewetting under applied stress, the adjacent polymer matrix becomes more brittle.

We will now consider the phenomena that cause the parameters 100 $(\Delta_4^{T*}-\Delta_4^{T})/\Delta_4^{T}$ to become less negative at lower temperatures for both types of composites. The changes in these parameters indicate that less molecular motion is eliminated at lower temperatures and for the fused silica composites it is evident that there is a pronounced shift in the relaxation spectra to lower temperatures. We associate the shift in the relaxation spectra to lower temperatures and any enhancement of molecular motion in relation to the unfilled state with the stress fields that develop in the matrix because of the mismatch in the coefficients of expansion of the matrix and filler. The polymer matrix surrounding a filler is in a state of biaxial tension tangentially and is in compression normal to the filler surface [26]. Since Poisson's ratio for glassy polymers is less than 0.5, the biaxial tension produces dilatation in the matrix. This effect is greatest at the interface and decreases as a function of distance from the interface. In addition, these stresses, and hence the dilatation, increase linearly as the temperature is lowered below $T_g$ [26]. The increase in the parameter 100 $(\Delta_4^{T*} - \Delta_4^{T})/\Delta_4^{T}$ at lower temperatures for both filled composites is consistent with the expected dilatational effects, allowing greater freedom in molecular motion. This effect is greater for the fused silica filled system than for the carbon black, despite the dilatational stresses being essentially the same for both systems. This observation could be explained by the fact that the polymer surrounding the fused silica is less constrained by polymer-filler interaction than for the case of carbon black, and hence is more susceptible to the dilatational effects of these stresses. (It should be noted that the $\beta$ peak is a composite of two peaks, which we have suggested originates from two different rotational isomeric configurations of the trans polybutadiene units [12]. It is possible, therefore, that the fillers could change the contributions of these two components, in addition to the shifts in the relaxation spectra. However, such a phenomenon seems unlikely, particularly as changes in the relaxation spectra are more pronounced for the fused silica than for the carbon black composites, whereas larger rotational isomeric changes are expected for the carbon black composites.)

The approximate linearity of the amount of damping eliminated from the glassy state versus volume fraction of filler for these composites would suggest that these dilatational effects in addition to the surface adsorption effects are proportional to the filler volume fraction. Nielsen and Lewis have derived expressions which show that the average dilatational stresses in a composite are not proportional to filler volume fraction except at very low filler concentrations [27]. Hence this would imply that the dilatational stresses are primarily causing a shift in the relaxation spectra to lower temperatures and any enhancement of motion (i.e. motion shifted out of the main glass transition temperature into the glassy state), is only occurring, if at all, in a few monolayers adjacent to the filler surface. Any significant shifts of motion out of the main glass transition temperature into the glassy state further away from the interface would result in a non-linear relationship between the total damping in the glassy state and filler volume fraction. The toughness of a polymer glass near the interface of a filler is, therefore, modified by both polymer-filled interaction, whose strength will determine the amount of molecular motion moved into the main glass transition temperature, and the dilatational stresses which primarily cause a shift in the relaxation spectra to lower temperatures. The influence of the dilatational stresses on the relaxation spectra appear to depend on the strength of the polymer-filler interaction.

In the case of the polymer-diluent systems interpretation of the results is difficult. The average damping of the SBR (31.6 mol% styrene)-benzene system below ~ 20% by volume benzene falls below the damping predicted from Equation 1, which could be caused by either interaction between the trans polybutadiene units and individual benzene molecules and/or benzene clusters. (The latter interaction could occur in a manner analogous to that discussed for the carbon black and fused silica fillers.) Above ~ 20% by volume diluent, where clustering is expected to be greater [15], the damping is equal to or greater than that predicted from Equation 1. It is not clear why the diluent clusters should produce additional damping in addition to that associated with their glass transition temperatures or melting points. However, from investigation of the mechanical spectra of polystyrene-diluent systems, numerous other small peaks of unknown origin were found [14, 15].

In the ~ 25% by volume diluent range there is no clear distinction between the effect of different diluents on the average damping of the SBR (31.6 mol% styrene) $\beta$ peak (Fig. 7) which allows an interpretation in terms of shape, size, or dipoles of the diluent molecules. Any such effect could be masked by the diluent clustering phenomena.

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