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The glass transition and interfacial layer in styrene-butadiene rubber containing silica nanofiller

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Abstract

The mechanical behaviour of a styrene-butadiene rubber, containing 23.5% styrene and filled with up to 55% by weight with silica nanoparticles, has been examined. The tan δ spectra of these composites show a second relaxation of relatively low intensity located about 40 °C above the main α relaxation, the glass transition T_g, which occurs at -34.5 °C in the unfilled polymer. This is attributed to an interfacial layer of polymer molecules whose chain relaxation dynamics have been altered by interaction with the filler surface. This is accompanied by a shift of the T_g itself to lower temperature when the filler surface is organophilic, but not when the filler surface is hydrophilic, and possible mechanisms for this are discussed. The amount of interfacial polymer can be quantified by resolving the glass transition and the second relaxation using a curve-fitting approach. A first-order treatment is presented which estimates the layer thickness to be of the order of a few nanometers.

Keywords: Nanofiller; Composite; Mechanical relaxation

1. Introduction

Improving the performance of polymer products by incorporating inorganic fillers has long been an important industrial activity, and traditionally this has been achieved by using materials such as carbon blacks, clays, talc and silica. More recently the modification of polymer composites using nanoscale fillers, with their high surface to volume ratios, has been of increasing interest. The presence of an interfacial layer between bulk polymer and the filler surface has been well-established by various techniques such as DSC [1], NMR relaxation measurements [2,3] and by neutron scattering studies [4–6], so consequently there is an expectation that nanofilled materials will offer significantly improved properties since the nature and behaviour of the filler-polymer interface will now exert a major influence on the macroscopic response. In particular, different segmental mobilities have been observed, where close to the filler surface, segmental relaxation times are significantly longer than those of the unfilled polymer [2–5].

Dynamic mechanical studies on nanofilled systems indicates the presence of a separate relaxation event which has been attributed to these less mobile chains within the interfacial region. In an extensive study, Tsagaropoulos and Eisenberg [7,8] reported that a range of vinyl polymers exhibit an additional maximum in tan δ about 50 °C above the main α relaxation occurring at the glass transition T_g, and similar behaviour has been observed also for poly(dimethylsiloxane) [9] and poly(vinylacetate) [10]. This additional relaxation was described by Tsagaropoulos and Eisenberg as a 'second glass transition' and the model they proposed to account for its presence, drawn from ionomer morphology, envisaged three regions around a nano particle; an inner tightly bound layer in which polymer motion is severely restricted by interactions with the surface, an intermediate but more loosely bound layer and finally the unrestricted bulk polymer. Such a 3-layer model is supported by NMR data [3], however neutron scattering experiments show only two relaxation times in filled systems [4,5]—a slow process, corresponding presumably to restricted mobility adjacent to the filler surface, and that

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of the bulk polymer which retains normal segmental dynamics. However nanofilling does not always result in a second distinguishable relaxation; adding nanofiller to poly(vinylalcohol) [10] and polyurethane [11,12] increases their T_g values, but there is no obvious additional above-T_g event. Interestingly, contrasting behaviour is found in the latter system where the filler increases the T_g of the elastomeric segment [12] but has little effect on the hard segment, whereas layered silica (montmorillonite) substantially increases the T_g of the hard segment phase [11]. Not surprisingly then, the nature of the interfacial interaction appears to be an important factor in determining behaviour. There is even a suggestion that the method of sample preparation can influence the mechanical behaviour of the final composite, as observed in the case of silica-filled poly(vinylacetate) [13].

Changes in relaxation behaviour have also been observed in filled rubbers [8,14] and in filled polyimide [15]. Mélé and co-workers [14], studying matrix reinforcement in SBR, were able to enhance the amount of bound material by treating their silica filler with a silane coupling agent. They also detected a decrease in the T_g of their SBR, a response they ascribed to an unspecified form of mechanical coupling between the rigid filler, the bound layer and the bulk rubber. Giunta [15] similarly noted a reduction in the glass transition of a polyimide containing TiO_2 as filler, and additionally inferred that the relaxation spectrum for the constrained phase was considerably broadened. Donth and co-workers [16], also studying SBR, determined the length of immobilised modes at the filler surface (in this case the nanofiller itself was a cured polybutadiene) and estimated the thickness of the immobilised layer to be ~1.5 nm. Complementary to these various experimental studies, the picture which emerges from a molecular dynamics simulation [17] of a nanoparticle in a polymer melt is one of a gradual change in dynamics as the surface is approached, in essence a many-layer model, with either an increase or a decrease in relaxation rate depending on the relative strength of filler-polymer interactions at the surface.

In this paper we examine the glass transition behaviour, and the applicability of the immobilised/bound layer model, by examining the dynamic mechanical (tan δ) response of a poly(styrene-*ran*-butadiene) elastomer filled with nanosilica particles with either a hydrophobic or a hydrophilic surface. The SBR used is of different styrene content (and lower T_g) from the sample examined by Tsagaropoulos and Eisenberg [8] and also differs from that used by Mélé [14] and co-workers where an oil extender was incorporated. Tsagaropoulos and Eisenberg reported a 'second T_g' for their SBR composite in contrast to the latter authors who analysed their data in terms of micromechanical models and did not note such a transition, at least within the temperature range examined. Here we report and analyse the isochronal relaxation (tan δ) behaviour of SBR, with filler contents up to 55 wt%, has been studied over the temperature range −80 to +100 °C.

2. Experimental

The poly(styrene-*ran*-butadiene) SBR elastomer was obtained from Enichem Elastomeri and had been prepared by radical emulsion polymerisation. NMR characterisation indicated a composition of 23.5% styrene and 76.5% butadiene (16% in the 1,2 form and 70% in the 1,4 form). The filler used was a precipitated amorphous silica (Degussa Ultrasil VN3) having specific surface area $\sim 160\ m^2\ g^{-1}$. For two of the SBR composites this was pretreated with bis(triethoxysilylpropyl)tetrasulphane (TESPT) to render the surface organophilic; for the remainder the filler was used untreated. In both cases the filler was first dispersed in the polymer for 1.5 min using a Banbury laboratory blender. 1.5 wt% of the cross-linking agent *tert*-butylcumylperoxide (Trigonox T, Akzo-Nobel) was then added and mixing was continued for 8 min at 120–150 °C. The material was next extruded at 150 °C followed by curing in a hot-press at 170 °C for 8 min to obtain crosslinked films of ca. 2 mm in thickness. The pressed films were stored in the dark at −5 °C until required for investigation. Sample identification with nominal weight percent filler contents are listed in Table 1.

Dynamic mechanical analysis was performed on cut strips 0.5 cm wide and 2 cm long using a TA Instruments DMA 2980 in the tension mode. The isochronal frequency employed was 1 Hz with a sample dynamic strain amplitude of 15 μm. The temperature was scanned within the temperature interval −80 to +100 °C at 2 °C min^{-1} using a dry nitrogen atmosphere. The mechanical stability of the test pieces was retained at temperatures significantly above-T_g with sample elongations at the end of each run being typically less than 2%.

3. Results and discussion

Fig. 1 shows the tan δ curves obtained for the SV series with up to 50 wt% of silica nanofiller and their T_g values, taken as the temperatures of the relaxation maxima, are collected in Table 1. The baseline values of tan δ at −80 °C and at +80 °C are essentially equal, and so the total area under each mechanical spectrum can be reliably computed.

These are included in column 4 of Table 1, as relative areas with respect to that of the unfilled SBR, and indicate that the increasing amounts of filler bring about a near linear reduction in the overall damping as the number of chains participating in the glass transition decreases.

Peak maxima in Fig. 1 can be located, at best, with a confidence of ±0.5 °C and, although the T_g of E-20-SV is lower than the others, the data in Table 1 show no distinct trend with increasing filler content. What is apparent however, is broadening of the T_g relaxation and the development of a shoulder between 0 and 20 °C. This is better seen in Fig. 2 which shows normalised tan δ data for the unfilled SBR and the two composites E-40-SV and E-50-

Table 1

Code[a]	Wt% filler	T_g (°C)	tan δ max	Relative tan δ area	Bound fraction	t (nm)
SBR	0	−34.5	1.74	1.00	0	–
E-10-SV	10	−34.0	1.48	~0.9[b]	–	–
E-20-SV	20	−36.0	1.22	0.87	0.11	2.0
E-30-SV	30	−34.5	1.02	0.78	0.13	2.1
E-40-SV	40	−34.0	0.85	0.71	0.20	1.8
E-50-SV	50	−34.5	0.64	0.62	0.23	1.6
E-30-SC	33	−37.5	1.33	–	~0.3	–
E-50-SC	55	−38.5	0.86	–	~0.5	–

[a] SV series are untreated silica, SC series are TESPT treated silica.

[b] The tan δ spectra of this sample differs only slightly from that of SBR and consequently this area is less well defined.

SV. For the last sample the shoulder is well-developed and evidences a relaxation which is associated with the presence of the filler but which is distinct from the main T_g event. The intensity of this relaxation is markedly lower than those reported by Tsagaropoulos and Eisenberg [8] for their composites, which were generally comparable with the intensity of the T_g relaxation itself. They also observed the size of the second peak to decrease and its maximum move to lower temperatures as the filler content increased. These trends, which are contrary to the pattern followed by our SBR samples, were interpreted in terms of the three-layer model in which the relative amounts of tightly bound and loosely bound polymer vary with the distance between filler particles. The second glass transition was ascribed to relaxation of the loosely bound regions; these are transformed to tightly bound as filler content increases and so the transition intensity will decrease with increasing filler content. Tightly bound material, i.e. in contact with the filler surface, was regarded as sufficiently immobile so as not to contribute to the observed relaxation dynamics.

The intensity of the above-T_g relaxation events here is, in direct contrast, an increasing function of filler content (bound fraction, Table 1), and so any interpretation according to the three-layer model as above would seem inappropriate. Nevertheless we can reasonably assume this relaxation is also due to the dynamics of surface-influenced polymer, although a two-layer picture would seem adequate here in which chains near the filler surface experience reduced freedom of movement—by constraints imposed by interactions with the nanoparticles and/or by confinement effects. The relatively low intensity of the transition could be taken to indicate a small change in mobility between interfacial and bulk polymer segments or, equally plausibly, a relatively small fraction of such polymer. In either case, the behaviour shown by the composites in Figs. 1 and 2 does not, to our minds, warrant the description of a second glass transition, certainly on the criterion of intensity. Furthermore, using differential scanning calorimetry, we have as yet been unable to detect any step-change or deviation in

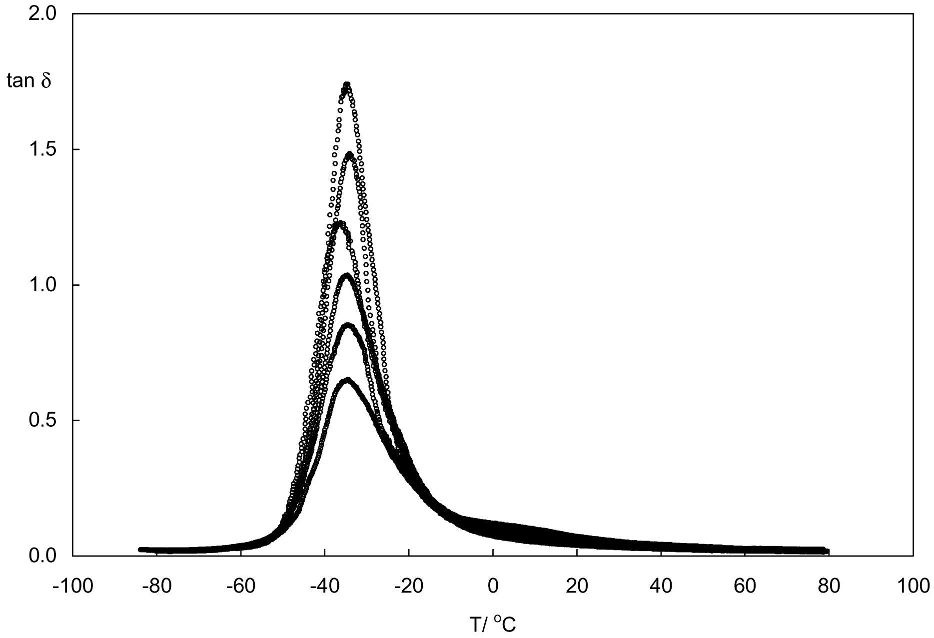

Fig. 1. Experimental tan δ vs. temperature behaviour for the SV series of composites. The upper curve is unfilled SBR and the increasingly lower curves are for composites E-10-SV through to E-50-SV.

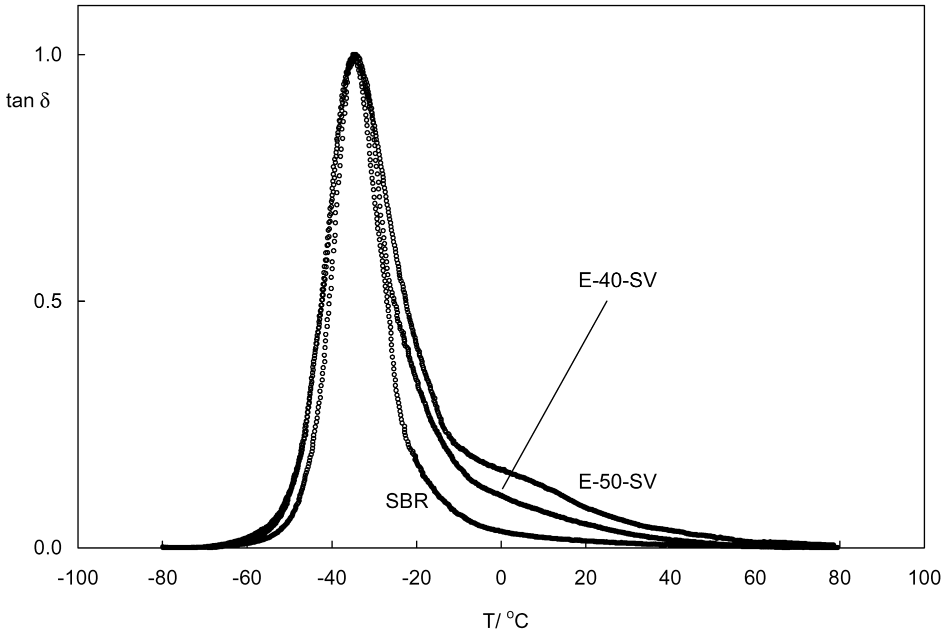

Fig. 2. Normalised tan δ data for the unfilled SBR (inner curve), for composite E-40-SV (middle curve) and for composite E-50-SV (outer curve).

the heat capacity that would provide the thermodynamic signature of a true devitrification transition.

The glass transition tan δ maxima, recorded in Table 1, are a decreasing function of the filler content and these data can provide some insight into the biphasic nature of the nanocomposite by applying the Takayanagi series-parallel phenomenological modelling approach [18]. According to this the viscoelastic response of a multicomponent system depends on the properties of the individual components, and on the manner by which these ‘couple’ to generate the overall behaviour. Neglecting here any differences between interfacial and bulk polymer, the complex tensile modulus ($E^* = E' + iE''$) of the composite depends on the two elements (A and B), arranged as shown in the inset of Fig. 3, such that:

$$E^* = E_B^*(1 - \lambda) + \frac{\lambda E_A E_B^*}{\phi E_B^* + (1 - \phi)E_A} \tag{1}$$

Here A is the silica filler with a purely elastic modulus $E_A \sim 70$ GPa, and B is the polymer having a complex viscoelastic modulus $E_B^* = E_B' + iE_B''$. The volume fraction of A + B in the series arm is λ, and the volume fraction of the filler A in the composite is $\phi\lambda$. The volume fraction of polymer B in the series arm (V_{BS}) is given by:

$$\phi = \frac{V_A}{V_A + V_{BS}} \tag{2}$$

An expression for tan δ of the composite may be derived, after some algebra, as:

$$\tan\delta = \frac{\tan\delta_B[\phi\alpha(1 + \tan\delta_B^2) + (1 - \phi)(2\alpha R + \beta R^2)]}{[(1 - \phi)\alpha(R - R\tan\delta_B^2) + \phi\alpha(1 + \tan\delta_B^2) + \phi\beta(R + R\tan\delta_B^2) + (1 - \phi)\beta R^2]} \tag{3}$$

where tan δ_B is the value of tan δ for the polymer, R is the filler/polymer modulus ratio E_A/E_B', and $\alpha = (\phi - \lambda\phi)$ with $\beta = (1 - \alpha)$. At the glass transition E_B' is $\sim$20 MPa, giving $R \sim 3000$ and leaving V_{BS} to be treated as an adjustable parameter. Allowing this to be a linear function of composition, Eq. (3) then provides a satisfactory description of the experimental tan δ data as shown by the minimised sum-of-squares best fit in Fig. 3. Cohen and Ramos [19] proposed that the degree of parallel coupling in the Takayanagi model can be expressed by $\phi(1 - \lambda)/(1 - \phi\lambda)$ and, for the fit shown in Fig. 3, this is 0.99 or greater for all the samples. Accordingly then, the coupling of filler and polymer in the SV composites is almost entirely parallel in nature and this can be interpreted, in terms of the macroscopic viscoelastic response, that the silica filler is dispersed with an element of connectivity between particles, similar to the picture envisaged by Mélé and co-workers [14].

Fig. 4 shows the normalised tan δ data for the composites containing organophilic surface-treated silica, samples E-30-SC and E-50-SC, with the unfilled SBR included for comparison. The glass transitions (Table 1) of these samples are now both moved to lower temperatures, an effect observed in several other filler-polymer systems [10–12,14, 15]. Comparing Figs. 2 and 4 shows another difference between the SV and SC fillers—both introduce an above-T_g

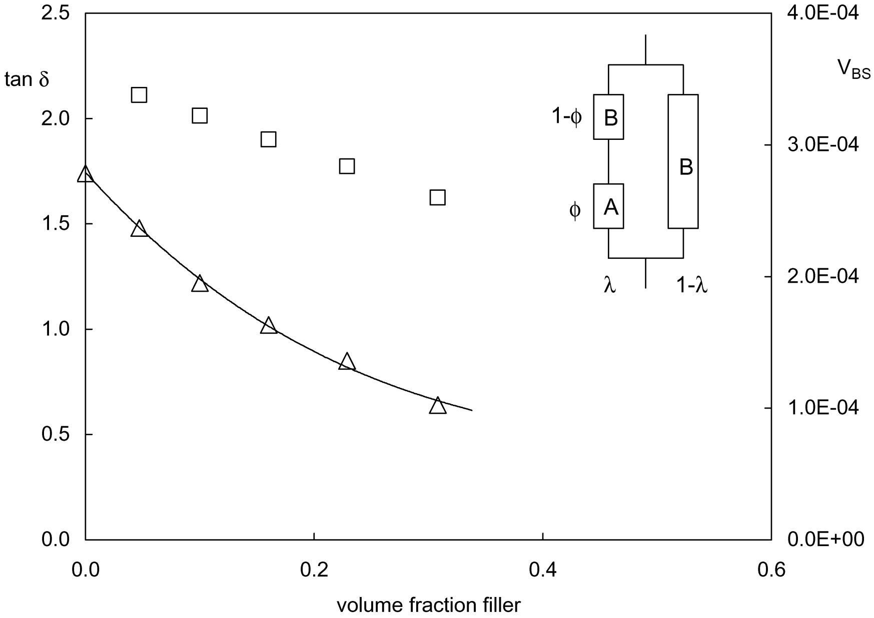

Fig. 3. Tan δ (at T_g) vs. filler volume fraction for the SV series of composites; Takayanagi model (—); experimental values (△). Polymer volume fractions in the series arm V_{BS} (□). The inset shows the Takayanagi model as described in text.

relaxation, but in the case of the organophilic filler this relaxation is much broader. A consideration of general behaviour at a surface readily allows for such differences: it is accepted that polymers are restricted close to a solid surface [20–22], where their conformation is determined by the energetics of their interaction with the surface, the cohesive energy in the bulk polymer, and by loss of entropy due to a decrease in the available configurations. This last effect is essentially an entropic force driving the chain away from the interface. Excluded volume effects in the bulk and, in particular, favourable interactions with the surface will promote the opposite trend. The interplay of these factors will thus determine the final structure, and the dynamics, so it seems reasonable to conclude that the difference between the SV and SC composites derives from more favourable interactions of the organophilic SC surface with the non-polar SBR chains.

However one aspect of this behaviour is rather puzzling. The T_g peaks for both composites in Fig. 4 move 'bodily' to lower temperature, with minimal broadening on either side, giving the impression that the overall relaxation behaviour of the bulk polymer has been modified. Why should the T_g in a filled system move to lower temperatures? And why should this occur for the SC composites where nominally

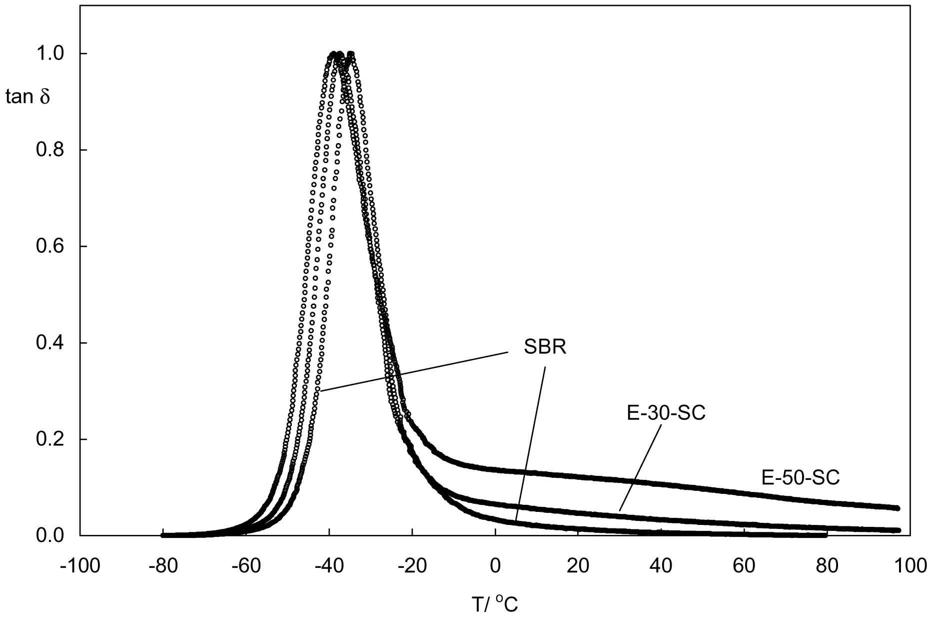

Fig. 4. Normalised tan δ data for the unfilled SBR (indicated), for composite E-30-SC (middle curve) and for composite E-50-SC (outer curve).

stronger surface interactions are present? Other instances have been noted [10–12,14,15] but, as yet, no convincing explanation appears to have been offered. The phenomenon does however invite comparison with the behaviour of ultrathin films where glass transitions significantly lower than the bulk value have been observed in both supported and in free-standing films [23,24]. This effect is now widely recognised [25] and a tentative explanation involving a ‘sliding’ mode of relaxation, only effective in thin films, has been suggested [26]. A parallel is seen in glass formers in nanoscopic environments, such as nanopore-confined solutions which can show two glass transitions [27,28], one at a lower temperature than the bulk state T_g and the other at a higher temperature. These observations lead to the suggestion of a two-layer model, with a ‘liquid’ in the centre surrounded by an interacting layer at the pore surface [28], and indeed some measure of justification for this view comes from recent thin film molecular dynamics simulations. Here dynamic inhomogeneities are found, with faster relaxations located in low density regions throughout the film, which are stabilized over extended time scales by the solid surfaces [29].

Both forms of confinement, thin film or nanopore, can be related to nanocomposite behaviour if the spatial confinement in these is quantified in terms of the mean distance L between statistically distributed nanoparticles of diameter d :

$$L = d[(F/v) - 1] \tag{4}$$

$F = 0.64$ is the packing factor for monodispersed spheres and v is their volume fraction [30]. Setting $d = 25$ nm (see below), we find $l = 34$ nm for the E-10-SV composite and $l = 7$ nm for the E-50-SV composite. Thus, the polymer chains are indeed confined to nanometer-scale volumes between the silica particles. The idea that nanofiller confinement could mimic thin film behaviour was put forward by Schadler and co-workers to explain the T_g of alumina/polymethylmethacrylate composites [31], although these authors did admit that their interparticle distances lay outside the limit for thin film effects. However this analogy does seem more appropriate for the present composites with their relatively high silica loadings and smaller interparticle distances. Especially so since the T_g shift is observed when the surface is organophilic, which is in line with the surface-driven two-layer mechanism suggested by Joon-Yong Park and McKenna [28]. Nevertheless, a full and satisfactory explanation of the lowered T_g in some nanocomposites is not yet extant and so this area invites further investigation, from both experimental and theoretical standpoints. What is evident however, is that the filler modifies not only the surface layer dynamics but influences also the behaviour of the so-called ‘bulk’ polymer.

Returning to the surface layer and its associated tan δ dispersion as shown in Figs. 1 and 2 and, if we assume that the intrinsic relaxation intensity for this process does not differ appreciably from that of the bulk polymer at the glass transition, which is quite likely for weak interactions, it is possible to estimate the relative volumes of bound and free polymer from their relative tan δ areas. Unfortunately these two relaxations are not resolved and so resort to curve fitting is unavoidable but, since there exists no theoretical expression or function to describe mechanical relaxation curves, an appropriate empirical choice has to be made. There are in fact few expressions which satisfactorily reproduce the asymmetry normally found in tan δ peaks, one such is the exponentially modified Gaussian (EMG) [32] used by Tsagaropoulos and Eisenberg [8], and by Cowie and co-workers [33]. However, this is unable to reproduce the low temperature flank of the present tan δ data and the alternative choice of the 3-parameter asymmetric double sigmoid (ADS) proved to be much more satisfactory. This has the form:

$$\tan\,\delta(T) = A(1 + \exp(a))^{-1}[1 - (1 + \exp(b))^{-1}] \tag{5}$$

where $a = (T - \mu)/\sigma_1$ and $b = (T - \mu)/\sigma_2$. When $\sigma_1 = \sigma_2$ the function is symmetric about μ, but is asymmetric otherwise. The peak height is determined by A. An advantage of our present data is the effectively constant baseline damping which can be removed without recourse to further curve fitting. By using non-linear techniques and sum of squares minimisation, the data can be satisfactorily fitted by two ADS functions as exemplified in Fig. 5, where the contributions from the bulk polymer and the surface layer are shown resolved. The amounts of bound and bulk polymer are assumed proportional to the areas under their respective ADS functions and the relative fractions of bound polymer are listed in Table 1 for the SV composites with 20–50 wt% filler. With some sensible further assumptions, these data can now be used to estimate the thickness of the bound layer.

We take the effective volume fraction of polymer (V_P) in a composite as being equal to its relative tan δ area also listed in Table 1, since this is a measure of the number of chains relaxing in each composite. The volume fraction of bound polymer (V_B) in a composite is given by the product of V_P and the relative fraction obtained from the ADS areas. If the filler is regarded as a quasi-spherical particle with radius r, so that the number of filler particles per unit volume is $N = (1 - V_P)/(4/3)\pi r^3$, the thickness ($t$) of the bound layer, again assuming a spherical geometry, follows from:

$$V_B = \left(\frac{4}{3}\pi(r + t)^3 - \frac{4}{3}\pi r^3\right)N \tag{6}$$

The filler diameter is stated as 9 nm, however it disperses in rubber as aggregates and agglomerates with sizes ranging between ~50 and ~500 nm [34]. Small-angle neutron scattering (SANS) measurements have been carried out on

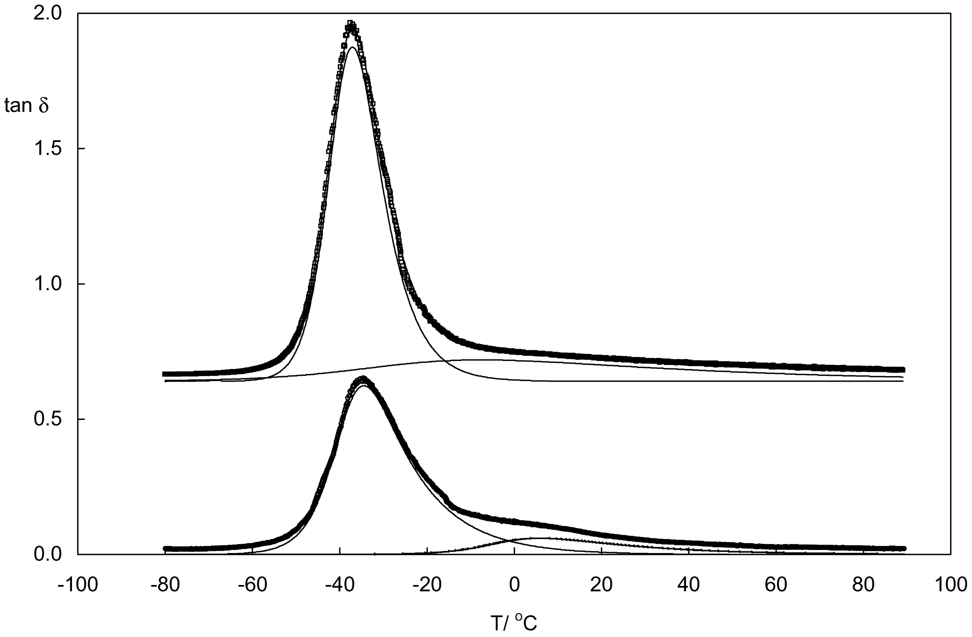

Fig. 5. Asymmetric double sigmoid fits to tan δ data for E-50-SV (lower curve) and E-30-SC (upper curve, displaced vertically for clarity).

this SBR-filler system [35], and these give the apparent diameter of the nanoparticles as 25 nm. Mélé and co-workers [14] have also measured the filler size distribution in an SBR with a slightly different styrene content and find the agglomerate fraction to be less than 7%, with mean aggregate diameters ranging from 25 to 44 nm depending upon composition. Neglecting then the presence of any larger agglomerates, and choosing the SANS-derived aggregate diameter of 25 nm to characterise the filler particle, leads us to the calculated the bound layers thickness shown in the last column of Table 1, giving an average and standard deviation of $t = 1.9 \pm 0.2$ nm for the SV series of composites.

It has been pointed out that the amount of surface-bound polymer in a composite will actually depend on the method which is used to probe it [36]. Donth and co-workers, using rheological data [16], estimate the thickness of the immobilised layer in SBR to be ~1.5 nm; from QUENS measurements on silica-filled poly(dimethylsiloxane) Arrighi and co-workers [4] find a layer thickness of ~5 nm, whereas Litvinov and Spiess [3] estimate 0.8 nm for this system using ^{2}H NMR as the probe. The value obtained here, from modelling of tan δ data in the manner described, is in satisfactory agreement with these other values. The bound polymer layer model thus provides an adequate description of the viscoelastic behaviour of these SBR nanocomposites, and also confirms that the influence of the filler is limited to a few nanometers.

A last observation, estimated bound fractions in the E-30-SC and E-50-SC composites are also shown in Table 1. However, the bound layer ADS functions extend beyond the experimental data range, which is used to obtain the fit and thus the result carries much less confidence. Nevertheless these indicate that the amount of bound material is greater than that in the SV series. This of course should logically follow from a more attractive surface potential, which also appears to generate a wider distribution of relaxation times and, speculatively, these effects could be due to a thicker surface layer.

4. Conclusions

The mechanical damping behaviour of silica nanofilled SBR has been examined. The macroscopic damping behaviour of these composites can be described by the two-component Takayanagi model of a composite, with a parallel coupling between the components which is taken to indicate a degree of continuity in the filler phase.

The tan δ spectra of the composites show a second relaxation, whose intensity increases with the filler content, at temperatures about 40 degrees above-T_g and which has been attributed to a surface layer of polymer with slower dynamics, as originally suggested by Tsagaropoulos and Eisenberg [8]. This is accompanied by a displacement of T_g to lower temperature when an organophilic filler is present, but not with untreated filler. Such behaviour may have the same origin as the T_g lowering in ultrathin films but, as yet, is incompletely understood. The surface layer can be quantified by resolving the above-T_g relaxations using a curve-fitting approach, and our simple first-order model then points to a value of the layer thickness of the order of a few nanometers, in satisfactory agreement with other estimates.

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