

# Interfacially induced micromechanical transitions in BaSO<sub>4</sub>-filled poly(styrene-co-acrylonitrile)

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A poly(styrene-graft-ethylene oxide) (P(S-g-EO)) graft copolymer affects the dynamic mechanical properties of a random poly(styrene-co-acrylonitrile) (SAN) copolymer filled with barium sulphate (BaSO<sub>4</sub>) through the location of the graft copolymer as an interphase between the filler and the SAN matrix. The addition of the graft copolymer results in a new transition, positioned at a lower temperature than the glass transition of SAN. The new transition is caused by the temperature-dependent change in relative dynamic mechanical properties of the components in the filled polymer blend and is called a micromechanical transition. It is shown that the new transition does not originate from a molecular transition in any of the constituents. The measured properties are compared with calculations using an interlayer model. The effects of the interlayer increase with the thickness of the interphase. The dynamic shear modulus decreases, and the micromechanical transition is positioned at a lower temperature as the concentration of the graft copolymer is increased. © 1998 Elsevier Science Ltd. All rights reserved.

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## INTRODUCTION

One of the most useful ways to alter the properties of a thermoplastic polymer is the incorporation of an inorganic filler<sup>1</sup>. Stiffness will usually be increased, while the impact properties<sup>2,3</sup> often decrease. A boundary or interphase layer between the filler and the polymer has been described by several authors<sup>4–6</sup>, Lipatov having put this in the perspective of colloid chemistry<sup>7</sup>. Maurer<sup>8,11</sup> and Friedrich *et al.*<sup>9</sup> investigated the effect of glass sphere-filled polymers with chemically bound polymer layers. Maurer developed an interlayer model<sup>10,11</sup> to analyse a filled poly(styrene-co-acrylonitrile) polymer, and Friedrich *et al.* studied polystyrene (PS) filled with glass beads with PS grafted to the surface, which results in an additional relaxation in the melt state. Tsagaropoulos and Eisenberg<sup>12,13</sup> identified two tan  $\delta$  peaks for a number of amorphous polymers filled with very fine silica particles, one related to the usual polymer glass transition, while the other, occurring at a higher temperature, was assigned to the glass transition of regions containing polymer chains of reduced mobility. The properties of filled polymers with strong interactions between matrix and filler have been studied extensively in the past, especially in the rubber field. Another area concerning heterogeneous systems with interlayer effects is compatibilized blends of immiscible polymers: Eklind and Maurer<sup>14–16</sup> describe how the dynamic mechanical properties of a poly(2,6-dimethyl-*p*-phenylene oxide) (PPO) and poly(methyl methacrylate) (PMMA) blend are affected by a (P(S-g-EO)) graft copolymer used as a compatibilizer in the immiscible blend. The addition of the P(S-g-EO) results in a reduction of the domain size and a new tan  $\delta$  peak occurring at a lower temperature than the glass

transition of PMMA. The new transition is caused by the change in relative dynamic mechanical properties of the components in the blend as a function of temperature and frequency and not by a transition in any of the components in the blend, as shown by dynamic mechanical measurements. The new transition is therefore called a micromechanical transition. It is theoretically shown that the new transition does not originate from a molecular transition in any of the constituents. Experimentally, the micromechanical transition can be observed as a shoulder on the PMMA glass transition tan  $\delta$  peak on the lower temperature side. The micromechanical transition, tan  $\delta$  peak, decreases in temperature position with increasing amount of compatibilizer. Theoretically, using the interlayer model<sup>10,11</sup>, the micromechanical transition is simulated and becomes a separate tan  $\delta$  peak. It is also argued and shown by transmission electron microscopy (TEM) that the interlayer in this case is diffuse and that it contains not only the graft copolymer, but also homopolymers with different concentration profiles.

In this paper, our aim is to demonstrate that the micromechanical transition can also be observed in a filled polymer system below the glass transition temperature of the matrix when applying an interfacial layer of specific properties. We will show this by investigating how a P(S-g-EO) graft copolymer, similar to the one used by Eklind *et al.*<sup>17</sup>, affects the dynamic mechanical properties of a random poly(styrene-co-acrylonitrile) copolymer filled with barium sulphate. The most important differences compared with the blends investigated by Eklind *et al.* are the expected sharper concentration gradient at the filler surface of the graft copolymer, the larger difference in the mechanical properties of the BaSO<sub>4</sub> filler and the polymeric constituents and the P(S-g-EO)/matrix polymer negligible interaction. It should be possible to simulate the properties with the

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interlayer model if the P(S-g-EO) graft copolymer is located as an interphase between the filler and the SAN matrix. In this study, we will investigate the dynamic mechanical properties in the solid state of SAN/BaSO<sub>4</sub> blends with a systematic variation of the volume share graft copolymer P(S-g-EO) and compare the experimental results with calculations made with the interlayer model. The partial miscibility between the different parts of the graft copolymer and the polymers in the PMMA/PPO blend in Eklind's study motivate further investigation of the cause of the micromechanical transition. The experimental conditions in this study, with negligible polymer miscibility and an inactive solid filler, should further strengthen the conclusion on the origin of the micromechanical transition.

## EXPERIMENTAL

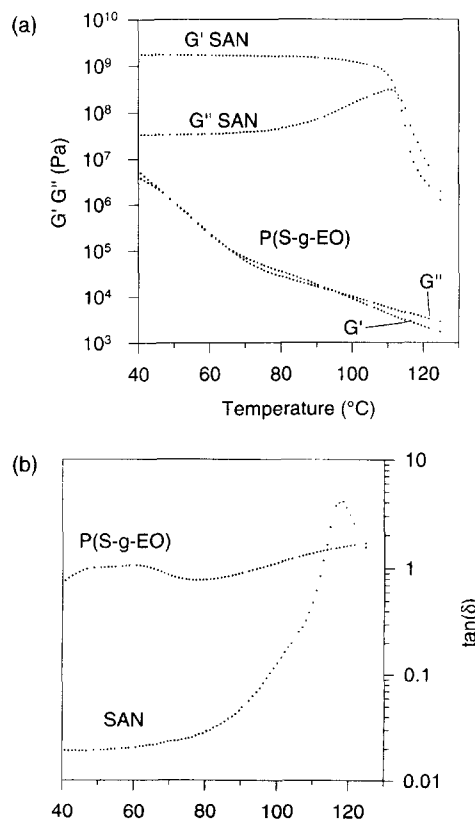
The SAN, Luran 368R, was supplied by BASF, and had a melt index of 10 ml/10 min (220°C/10) according to the manufacturer. The BaSO<sub>4</sub>, Blanc Fixe F, precipitated mineral filler with an average particle size of 1 μm was delivered by Sachtleben. The poly(styrene)-poly(ethylene oxide) graft copolymer consists of a main chain PS-acrylamide copolymer, which was polymerized with a free radical mechanism. The amine groups were then initiation sites for the PEO side chains, formed by a base-catalyzed ring opening polymerisation of ethylene oxide, commonly called ethoxylation. The main chain originally had a molecular weight of 80 kg mol<sup>-1</sup> and the PEO grafts 1.3 kg mol<sup>-1</sup>. The PEO content was 39% by weight and the acrylamide content in the backbone was 5 mol.%. The synthesis of the P(S-g-EO) was performed by Jannasch and Wesslén<sup>18</sup>. The graft copolymer used by Eklind and co-workers as a compatibilizer of PPO/PMMA blends was from a different batch than the one used in this study. To investigate whether any crystallization of the PEO side chains in the graft copolymer takes place upon cooling from 105 to 40°C, differential scanning calorimetry (d.s.c.) was performed on a Perkin-Elmer 7 DSC. The d.s.c. cooling rate was 10°C min<sup>-1</sup> and started from 170°C after maintaining the sample at this temperature for 5 min. The molecular mass of the SAN polymer was determined by size-exclusion chromatography, calibrated with narrow poly(styrene) standards. The SAN had an  $M_n$  of 98 kg mol<sup>-1</sup> and an  $M_w$  of 205 kg mol<sup>-1</sup>. Melt mixing in a Brabender AEV 330, with a batch volume of 50 ml, was preceded by drying overnight under vacuum at 60°C. The SAN and graft copolymer were first preblended for 5 min with an additional 10 min melt mixing with the BaSO<sub>4</sub> filler added. The mixing was performed at 40 rpm and a melt temperature of 190°C. The filled polymer composites were then pressed at 190°C to samples for dynamic mechanical tests. These were carried out in the linear viscoelastic region on a Rheometrics Dynamic Analyzer RDAII in the melt and solid state. The measurements made in the melt state were necessary to obtain SAN and P(S-g-EO) data over a large temperature range. Scanning electron microscope (SEM) analysis was performed with a Zeiss DSM 940A apparatus on samples fractured at liquid nitrogen temperatures. The densities used to estimate the volume fractions were 1080 kg m<sup>-3</sup> for the SAN polymer, 1110 kg m<sup>-3</sup> for the P(S-g-EO) graft copolymer and 4400 kg m<sup>-3</sup> for the BaSO<sub>4</sub> filler. The SAN and BaSO<sub>4</sub> volume relations were kept constant at 70 and 30 volume parts each, and 1, 2, 5 or 10 parts P(S-g-EO) were then additionally added to the thermoplastic composite.

## THEORETICAL APPROACH

The interlayer model<sup>10,11</sup> is used to simulate the dynamic mechanical properties of the filled SAN. The model is derived from the van der Poel model<sup>19</sup> corrected by Schwarzl<sup>20</sup>, Schwarzl and van der Eikhoff<sup>21</sup> and Smith<sup>22</sup>. The representative volume element in the interlayer model has the geometry of a sphere covered by a shell of interlayer, which in turn is surrounded by a shell of matrix material. Finally, there is a homogeneous phase with properties equivalent to those of the heterogeneous dispersion surrounding the sphere. The model assumes a perfect spherical particle in the matrix without taking any interactions, particle size or particle size distribution into account. The method accounts only for the pure mechanical-geometrical effect of the presence of the particle and layers. The most important conditions are that the representative volume element reacts to external stresses as a cube of homogeneous composite material and that displacements and radial and tangential stresses are continuous at the boundaries of the phases. With these limiting prerequisites, a set of linear equations is obtained as a result of the continuity conditions in a rotationally symmetrical shear stress field. The determinants of the coefficients of the linear equation system should be zero to obtain a solution that is not trivial with which to calculate the shear modulus. This leads to a quadratic equation with the following form:

$$40 \left( \frac{G_c}{G_m} \right)^2 |X| + \left( \frac{G_c}{G_m} \right) (2|Y| + 8|Z|) - 5|T| = 0 \quad (1)$$

$G_c$  and  $G_m$  are the shear moduli for the composite and matrix, respectively, and  $|X|$ ,  $|Y|$ ,  $|Z|$  and  $|T|$  are



**Figure 1** The dynamic mechanical properties of SAN and P(S-g-EO) measured as a function of temperature at 1 rad s<sup>-1</sup>. In (b) the ordinate is  $\tan \delta = G''/G'$ . (a) Shows the shear storage and loss modulus and (b) the  $\tan \delta$

tenth-order determinants of the  $10 \times 10$  matrixes,  $X$ ,  $Y$ ,  $Z$  and  $T$ , respectively. The determinants depend on the shear modulus, Poisson ratios and the volume fractions of the substrates. The extension of the elastic solution for equation (1) to a viscoelastic solution is made on the basis of the correspondence principle<sup>11,23</sup>. A more detailed description of the interlayer model is presented and the elements of the determinants are listed in a recent paper<sup>14</sup>.

The dynamic mechanical properties of the polymers used in the model as the constitutive materials are shown in *Figure 1a,b*. In the calculations of the mechanical properties of the SAN/P(S-g-EO)/BaSO<sub>4</sub> system, SAN was always used as the matrix polymer, i.e. the outer shell with the above terminology, P(S-g-EO), was the interlayer shell when included in the calculations, and the BaSO<sub>4</sub> filler was the inner model sphere. The theoretical volume relations for the SAN and BaSO<sub>4</sub> were kept to a 70/30-parts relation, and additional 1, 2, 5 and 10 parts of P(S-g-EO) were included in the calculations. The aim was to simulate the measurements with the same volume shares of the constituents.

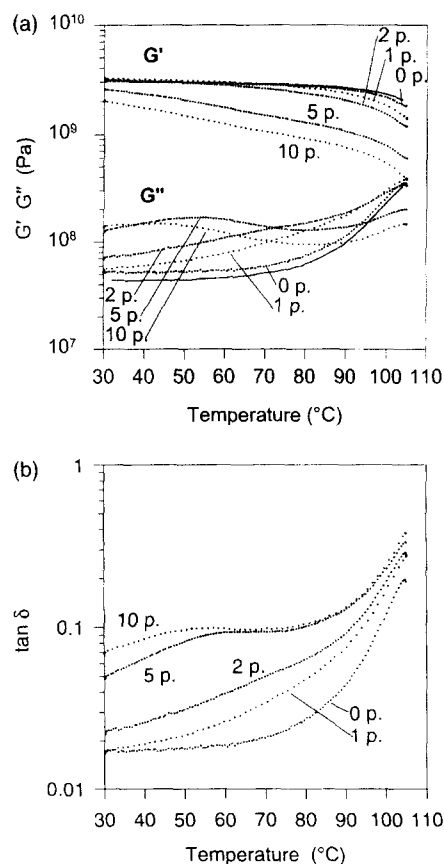
The model is sensitive to the Poisson's ratio of the interlayer<sup>16</sup> but, to avoid different calculated properties depending on varying Poisson's ratios, SAN and P(S-g-EO) have a chosen Poisson's ratio of 0.5 in the calculations. The Poisson's ratio for the BaSO<sub>4</sub> filler<sup>24</sup> is 0.3, and the dynamic shear modulus,  $G_d$ , for BaSO<sub>4</sub> is calculated<sup>24</sup> at a value of  $1.15 \times 10^{10}$  (Pa). The filler is considered in the simulations to be pure elastic, i.e. the dynamic shear loss modulus,  $G''_{\text{filler}} = 0$ .

## RESULTS AND DISCUSSION

Dynamic mechanical spectroscopy, compared to steady shear measurement in the melt state, is a suitable method for the analysis of filled polymers and immiscible polymer blends, or multicomponent systems in general. The reason is that transitions can be studied and small deformations can be applied without disrupting any filler network structure or polymer blend morphology. Because of this, structural changes as a function of time, composition or temperature, for example, can be monitored.

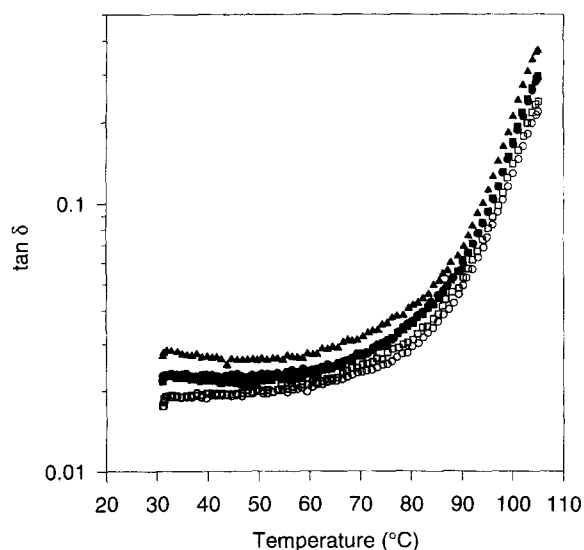
The dynamic mechanical data of the pure polymer constituents used in the thermoplastic composites and in the calculations are shown in *Figure 1a,b*. *Figure 1a* plots the shear storage modulus,  $G'(T)$ , and shear loss modulus,  $G''(T)$ , as a function of temperature, and *Figure 1b* plots the corresponding  $\tan \delta$  value. The latter parameter is sensitive in particular to molecular transitions. The measurements of the P(S-g-EO) graft copolymer were made starting from higher and going towards lower temperatures, at  $2^\circ\text{C min}^{-1}$ , to avoid crystallisation in the PEO side chains in the graft copolymer<sup>25</sup>. The d.s.c. measurements did not indicate any crystallisation in this temperature interval. It must be pointed out that the measurement values below  $47^\circ\text{C}$  for the P(S-g-EO) graft copolymer are uncertain since the modulus begins to reach the upper limit in the measurement window for the DMA fixture. As concerns the SAN polymer, the temperature ramps ( $2^\circ\text{C min}^{-1}$ ) started from  $105^\circ\text{C}$  in the solid state, after a specified hold at this temperature to be close to the  $T_g$  of SAN and to ensure sufficiently high mechanical properties of the samples to carry out correct measurements. The measurements in the melt state regarding the temperature range over the  $T_g$  of the SAN copolymer started at  $170^\circ\text{C}$ .

The measurements of the SAN/P(S-g-EO)/BaSO<sub>4</sub> system, with  $70/x/30$  volume parts and  $x = 0, 1, 2, 5$  and



**Figure 2** (a) Dynamic shear moduli,  $G'(T)$  and  $G''(T)$ , at  $1 \text{ rad s}^{-1}$  for the SAN/BaSO<sub>4</sub> (70/30 volume fraction) blends with different additional volume parts P(S-g-EO) and (b),  $\tan \delta$  from the same measurements. The solid lines represent the theoretical calculations of the SAN/BaSO<sub>4</sub> (70/30 vol.%) system

10 additional volume parts, were performed from  $105^\circ\text{C}$  towards lower temperatures with a ramp rate of  $2^\circ\text{C min}^{-1}$ . The results are depicted in *Figure 2a,b*; in *Figure 2a*, the shear storage modulus,  $G'(T)$ , shows lower levels and a steeper slope as the concentration of P(S-g-EO) is increased. This is consistent with the addition of a constituent with low modulus and a less regular morphology, deviating from the core shell assumptions, when the concentration of the graft copolymer is increased<sup>26-28</sup>. The introduction of P(S-g-EO) does not change the slope and level of  $G'(T)$  in *Figure 2a* very much when 1 and 2 parts of P(S-g-EO) were added to 100 parts of SAN/BaSO<sub>4</sub>, but 5 and 10 parts result in a marked change. The measurements in *Figure 2a,b* show a broadening or a shoulder on the SAN glass transition peak on the low temperature side for both the  $G''(T)$  and  $\tan \delta$  curves. This is a micromechanical transition, as described by Eklind and Maurer<sup>14-16</sup>, and it should be caused by the change in relative modulus of the constituents in the SAN/P(S-g-EO)/BaSO<sub>4</sub> system and not by a transition in any of the constituents. D.s.c. measurements made by Jannasch and Wesslén<sup>25</sup> and in this study show no transition in the temperature range of the micromechanical transition for the pure materials. The broadening or shoulder peak is present only when P(S-g-EO) is added to the BaSO<sub>4</sub>-filled SAN copolymer, indicating that the graft copolymer is the reason for the micromechanical transition. Measurements, depicted in *Figure 3*, of the  $\tan \delta$  of binary blends of SAN and P(S-g-EO) consisting of 100 parts SAN and 1, 2, 5 and 10 parts P(S-g-EO) do not indicate any miscibility or any additional



**Figure 3** The  $\tan \delta$  as a function of temperature at  $1 \text{ rad s}^{-1}$  for pure SAN and SAN/P(S-g-EO) binary blends with 100 volume parts SAN (○) and 1 (□), 2 (●), 5 (■) and 10 (▲) additional volume parts P(S-g-EO). The curves overlap at some points, but the trend is clear with increased  $\tan \delta$  values with higher concentrations of P(S-g-EO). The curve with the lowest values is the pure SAN and the uppermost curve represents the SAN/P(S-g-EO) blend of 100/10 volume parts

transition. The  $\tan \delta$  values are slightly increased with increasing volume fraction of P(S-g-EO), but this is consistent with an increased inclusion of the immiscible graft copolymer with high  $\tan \delta$  values compared with the SAN matrix, as can be seen in *Figure 1b*. The results very strongly indicate that the two polymers are immiscible and that an interlayer in a multicomponent system is a prerequisite for the micromechanical transition.

A calculated layer thickness in the SAN/P(S-g-EO)/BaSO<sub>4</sub> systems of the graft copolymer around the filler particles would be 5.5, 11, 26 and 46 nm for 1, 2, 5 and 10 parts P(S-g-EO), respectively, if all particles were spherical with a diameter of  $1 \mu\text{m}$ , and if all the graft copolymer is located at the polymer–filler interface as an interlayer. The calculated interlayer thickness can be compared with the size of a random polymer coil,  $r$ , which is a measure of the chain end-to-end distance calculated from the relation:

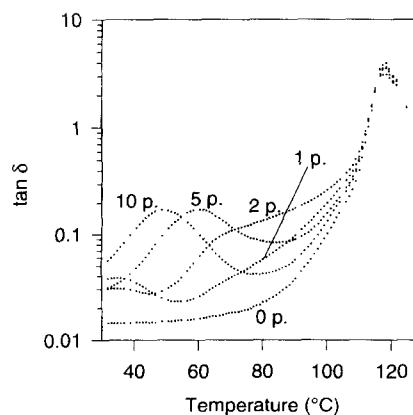
$$\langle r^2 \rangle = Cnl^2$$

where  $C$  is a constant that depends on the nature of the polymer,  $n$  is the number of main chain bonds and  $l$  is the bond length ( $1.54 \text{ \AA}$ ). Since the backbone of the graft copolymer is polystyrene with a molecular weight of  $80 \text{ kg mol}^{-1}$ , this was used in the calculation as a measure of the size of the P(S-g-EO).  $C$  is set to a value of 10 in accordance with data regarding PS presented by Flory<sup>29</sup>. The result of the calculation of the end-to-end distance is:  $r = 19 \text{ nm}$ . This value indicates the interlayer minimum thickness without conformational changes and is exceeded at 5 parts P(S-g-EO). This exercise and the results from the measurement of  $G'(T)$  of the SAN/P(S-g-EO)/BaSO<sub>4</sub> system indicate that the graft copolymer first forms an interlayer around the filler particles, and the structure then becomes less ideal. This is also supported to some degree by SEM micrographs, not presented here. Once the P(S-g-EO) interlayer is formed and becomes thicker, as in the case with 5 and 10 parts graft copolymer, the impact on the storage shear modulus,  $G'(T)$ , and  $\tan \delta$  in *Figure 2* is severe, primarily from the soft interlayer, but also probably

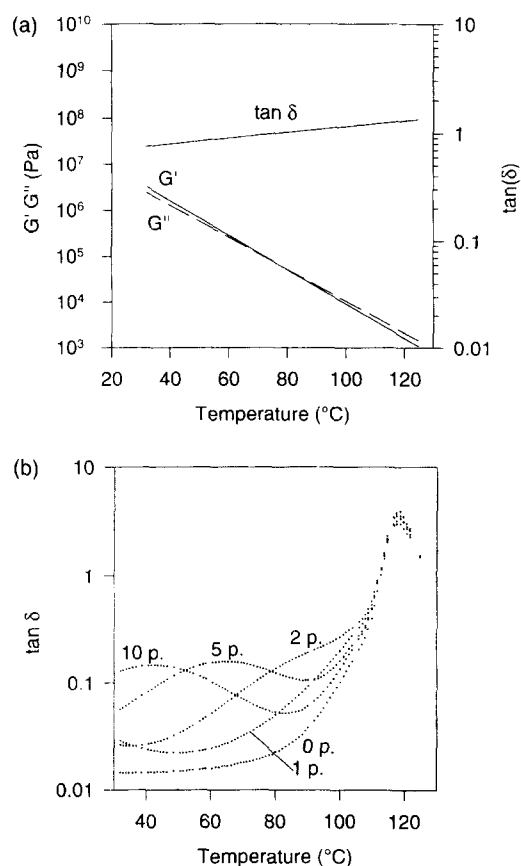
from a separate P(S-g-EO) phase after the interlayer is formed. The filler particles are unable to change in shape and cannot deviate from their shape, but the P(S-g-EO) has a very low modulus compared to the SAN matrix and can easily be deformed to its own phase domains by shear forces at the blending procedure. Agglomeration of filler particles or a separate filler plus graft copolymer phase is unlikely, since the BaSO<sub>4</sub> filler has low interaction capabilities<sup>30–32</sup> and the graft copolymer has a relatively low molecular mass and low mechanical properties during blending conditions. Similar findings are reported by Scott et al.<sup>4</sup>, who investigated polyethylene/EPDM/calcium carbonate composites where rubber–filler interactions caused by maleic anhydride-modified rubber resulted in a large influence on the dynamic mechanical properties. Rösch<sup>53</sup> investigated PP/elastomer/polyamide (PA) blends of core shell morphology and found how small amounts of soft elastomer interlayer (EPM-g-MA) around the PA particles caused a dramatic modulus decay, while a stiffer interlayer of maleinated poly(styrene-block-(ethylene-co-but-1-ene)-block-polystyrene) resulted in a blend with much better mechanical properties. Kolarik et al.<sup>34</sup> also describe how ternary systems consisting of PP/EPDM elastomer/CaCO<sub>3</sub> show an increase in the  $\tan \delta$  peak at the glass transition of EDM rubber by incorporated filler particles, which are encapsulated by the rubber.

#### THEORETICAL CALCULATIONS

*Figure 4* shows the results of calculations made with the interlayer model using the properties of the constitutive materials shown in *Figure 1a* and the properties of the BaSO<sub>4</sub> filler described under Section 3. At 1 and 2 parts P(S-g-EO), the  $\tan \delta$  peak connected with the glass transition of SAN broadens or shows a shoulder, but a separate peak is visible at higher graft copolymer concentrations. In *Figure 1b*, a small increase of the  $\tan \delta$  values of P(S-g-EO) below  $74^\circ\text{C}$  can be seen. A simulation was made to theoretically evaluate whether the theoretical micromechanical transition could be the result of the dynamic mechanical properties of the P(S-g-EO) graft copolymer in this temperature interval. The properties of the SAN copolymer and the BaSO<sub>4</sub> filler were kept constant as compared with the original calculations, but the properties of the P(S-g-EO) used in these simulations were altered and are shown in *Figure 5a*. The dynamic storage and loss modulus are the result of a linear



**Figure 4** The calculated  $\tan \delta$  values, using the measured properties of the polymer constituents, as a function of temperature for SAN/BaSO<sub>4</sub> blends (70/30 volume parts) at and below  $T_g$  of SAN with different additional volume parts P(S-g-EO) in the calculations



**Figure 5** (a) Modified dynamic mechanical properties of the P(S-g-EO) graft copolymer. The lines in the figure are the result of linear regression of the measurement results regarding the P(S-g-EO) depicted in Figure 1. (b) Depicts the calculated  $\tan \delta$  values as a function of temperature for SAN/BaSO<sub>4</sub> blends (70/30 volume parts) at and below the  $T_g$  of SAN with different additional volume parts of P(S-g-EO) in the calculations. The P(S-g-EO) values from (a) are used in the calculations

regression of the measured values for the graft copolymer in Figure 1. This was done to avoid a theoretical influence from the increase in the  $\tan \delta$  curve of P(S-g-EO) below 74°C. The results of these simulations are shown in Figure 5b, which theoretically demonstrates that the micromechanical transition is not a result of the increase of the  $\tan \delta$  of the P(S-g-EO) graft copolymer in this temperature interval. The theoretical simulations support our findings that the phenomenon of the micromechanical transition is a result of the change in relative modulus of the constituents in the SAN/P(S-g-EO)/BaSO<sub>4</sub> system and not of a transition in any of the constituents.

#### COMPARISON BETWEEN MEASUREMENTS AND THEORETICAL CALCULATIONS

For the SAN/P(S-g-EO)/BaSO<sub>4</sub> system, the measurements and theoretical calculations indicate that a P(S-g-EO) interlayer between the SAN matrix and the filler is formed at low concentrations of the graft copolymer and that the micromechanical transition is caused by the change in relative dynamic mechanical properties of the components in the blend. One of the strongest arguments for this is the presence of the micromechanical transition in both the measurements and the theoretical calculations, in which the interlayer can be included or excluded. The complete absence of any shift, shoulder or extra  $\tan \delta$  peak in the temperature region of the micromechanical transition

temperature,  $T_{mm}$ , in the binary SAN/P(S-g-EO) blend also lends strong support to our argumentation, since this excludes the possibility for the micromechanical transition to be caused by SAN and P(S-g-EO) interactions. The SAN/BaSO<sub>4</sub> (70/30 vol.%) system was able to be treated in the model with satisfying results in spite of the high degree of filling. The comparison between theory and experiment is shown in Figure 2a. Deviations between theory and measurements should, in the light of this, originate mainly from the interlayer phase or deviations from the ideal core shell morphology assumed in the theoretical model. The measured micromechanical transition,  $\tan \delta$  peaks, are broader than the corresponding theoretical peaks or have the form of a plateau, probably owing to deviations from ideal morphology and not because of any miscibility between the polymer phases. The experimental shape of the  $\tan \delta$  curves for the binary blends of SAN/P(S-g-EO) in Figure 3, on the lower temperature side of the glass transition of SAN, contradicts any miscibility between the two polymers, as mentioned previously. The increased  $\tan \delta$  values of the binary SAN/P(S-g-EO) blends compared with the SAN copolymer are consistent with an increased amount of an immiscible and almost Newtonian graft copolymer second phase.

The peak temperatures in Figure 4,  $T_{mm}$ , for the theoretical micromechanical transition for BaSO<sub>4</sub>-filled SAN with 5 and 10 additional volume parts P(S-g-EO) are 61 and 49°C, respectively. The theoretical  $T_{mm}$  regarding 5 parts P(S-g-EO) is positioned at the same temperature as the  $\tan \delta$  plateau for the corresponding measurement in Figure 2b. In the measurement of the system containing 10 parts P(S-g-EO) in Figure 2b, a peak can be detected at 57°C; this is only 8°C higher than the theoretical  $T_{mm}$ . This deviation is small compared with Eklind and Maurer's result<sup>15</sup> for the PMMA/P(S-g-EO)/PPO (70/10/30 vol. parts), where the measured  $T_{mm}$  is 37°C higher than the theoretical value. The shape of the measured and calculated  $\tan \delta$  curves in Figure 2b and Figure 4 has the same tendencies for 1 and 2 volume parts P(S-g-EO). These correlations between measurements and theory are interpreted as a theoretical indication of a micromechanical transition, as described by Eklind and Maurer<sup>14</sup>, but in this case in the SAN/P(S-g-EO)/BaSO<sub>4</sub> systems investigated here. The larger deviations between theoretical calculations and measurements found in Eklind and Maurer's study were influenced by some miscibility between the different parts of the P(S-g-EO) graft copolymer and the different polymers in the PPO/PMMA blend. This would affect the dynamic mechanical properties of the interlayer and cause deviations compared with the theoretical calculations, using the pure constitutive materials. In our study, we did not see these large deviations with respect to the  $T_{mm}$ , and this is consistent with the conditions of our system; the graft copolymer shows no signs of miscibility with the SAN copolymer, and the BaSO<sub>4</sub> filler is considered as inactive and most probably has weak interactive capabilities with the P(S-g-EO) interlayer. As a result, the concentration gradient at the SAN/P(S-g-EO) interface and property gradient at the P(S-g-EO)/BaSO<sub>4</sub> interface are very sharp, as in the theoretical model. A word of caution may be merited regarding the position of the theoretical,  $\tan \delta$ , peak temperature position,  $T_{mm}$ , which turned out to be very sensitive for the Poisson ratio. This sensitivity could naturally be a factor in the deviations between measurements and calculations; the effects of varying Poisson ratio are further described by Eklind and Maurer<sup>14</sup>.

## CONCLUSIONS

The P(S-g-EO) graft copolymer in a SAN/BaSO<sub>4</sub> thermoplastic composite of 70/30 volume parts acts as an interlayer between the BaSO<sub>4</sub> filler and the SAN matrix. We have shown theoretically that, also for a mineral-filled polymer with an interlayer, a new transition, the so-called micromechanical transition, is a result of the change in relative dynamic mechanical properties of the substances in the multicomponent system and does not originate from a molecular transition in any of the constituents. Experimentally, we have shown that the micromechanical transition is not caused by interactions of the polymers. The effects of the interlayer become stronger when the interlayer thickness is increased. Increased concentrations of P(S-g-EO) also result in a less ideal structure. The conditions of the system investigated in this work, with immiscible polymers and a stiff mineral filler with low interactive capabilities, result in smaller deviations between measurements and theoretical calculations, as compared with Eklind's study regarding micromechanical transitions in a compatibilized polymer blend. The fact that the micromechanical transition is present in this study with the mentioned prerequisites strengthens the conclusion made by Eklind on the origin of the micromechanical transition.

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