

# Characterization of polyethylene/EPDM/silicon dioxide multicomponent composites by solid-state dynamic mechanical spectroscopy

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Various composites of polyethylene, ethylene propylene diene rubber (EPDM), and filler are milled and analysed by solid-state dynamic mechanical spectroscopy. The filler used is silicon powder with an oxidized surface. This filler is a model for materials with siliceous surfaces. The torsion pendulum measurements show that the multicomponent composites exhibited complex viscoelastic behaviour. For composites of polyethylene and silicon dioxide, there is evidence of particle–particle interactions. In composites which include polyethylene, rubber and filler, interactions of the polyethylene and especially of the rubber with the filler surface are significant. Treatment of the filler surface with gamma-aminopropyltriethoxysilane ( $\gamma$ -APS) or gamma-methacryloxypropyltrimethoxysilane ( $\gamma$ -MPS) has a significant influence on the resultant composite dynamic mechanical spectrum. Maleic anhydride grafting of the EPDM rubber also changes the character of the composites. These composites appear to exhibit complex morphologies, which may be controlled to a certain extent by filler surface treatment and grafting to the rubber. There is evidence for a chemical reaction between the maleic anhydride modification of the EPDM and  $\gamma$ -APS during processing on the roll mill. Prediction of the composite properties using the extended van der Poel model is qualitatively useful.

## 1. Introduction

Composites including high modulus particulates and rubbers have attracted increasing attention both industrially and academically over the past few years. It is well known that the addition of a high modulus component to a plastic matrix enhances the composite modulus, but generally results in increased brittleness. On the other hand, addition of a rubbery component often increases the impact strength but reduces the composite modulus. It is believed that careful incorporation of both high-modulus and rubbery materials in a composite could result in an improvement of both the modulus and impact strength. Only a few publications have been concerned with such systems [1–4].

Comitov *et al.* [2] studied multicomponent composites of calcium carbonate and styrene–butadiene–rubber or butadiene–styrene–latex in polypropylene. They found that the impact strength was increased with the addition of the rubber modifier. Pukanszky *et al.* [3] studied systems of EPDM and calcium carbonate in polypropylene. They measured the stress–strain behaviour, shear modulus, impact strength and dynamic mechanical properties of these composites. Dynamic mechanical spectra and scanning electron

micrographs (SEM) showed that in these systems the rubber partly covered the filler particles and/or filled in the voids in filler agglomerates. This morphology was critical in determining the properties of these composites. The addition of rubber was also found to restrain the deteriorating effect of the filler addition on composite impact strength. Pukanszky *et al.* [4] followed the torque and temperature against time curves during milling of PP/EPDM/CaCO<sub>3</sub> multicomponent composites.

Multicomponent composites incorporating a matrix, rubber and filler are expected to exhibit quite complex behaviour. Filler–matrix, filler–rubber and rubber–matrix interfaces and/or interphases may be involved. The use of coupling agents in such composites would result in the presence of even more interfaces/interphases. The morphology of these composites is also expected to be quite complex. Many different morphologies may be imagined. One possibility is a composite where the filler and rubber existed as separate, non-interacting particles within the matrix. Another morphology might involve filler particles encapsulated by the rubber inside the matrix. The composite properties of these two extreme cases

would certainly be different. There may be part of the matrix encapsulated in rubber particles. Agglomerations of filler in the matrix or within rubber particles may also be present.

The authors have conducted an exploratory study into the properties of multicomponent composites [5], and papers in preparation. Composites have been milled with a high density polyethylene (PE) matrix, EPDM and a maleic anhydride grafted EPDM rubber, and silicon dioxide and calcium carbonate fillers. These composites have been characterized by solid-state and melt-state dynamic mechanical spectroscopy, Izod impact testing, SEM of fracture surfaces, and Fourier transform infrared spectroscopy. The dynamic mechanical results were compared with predictions based on the extended van der Poel model.

This paper reports the solid-state dynamic mechanical properties of composites of PE, EPDM and oxidized silicon powder. Various amounts of rubber were applied to the filler from solution, for incorporation into composites by roll milling. Other composites were made with the rubber added directly on the mill. The effect of surface treatment of the oxidized silicon powder with two different coupling agents,  $\gamma$ -APS and  $\gamma$ -MPS, was investigated.

In this study, silicon powder with an oxidized surface was used as a model for fillers or reinforcements with siliceous surfaces. This powder has been used previously in model studies of silane coupling agents on such surfaces [6]. Henceforth, this powder will be referred to simply as "SiO<sub>2</sub>" in this paper. The weak infrared absorption of this powder makes it ideal for infrared diffuse reflectance studies of surface treatments or composites. Infrared spectra of the composites described here will be reported elsewhere [5].

The extended van der Poel model was used to predict dynamic mechanical properties of the composites for comparison with the experimental results. This model is described in detail elsewhere [7–9]. It allows prediction of the viscoelastic properties of composites from the properties of the pure constituent materials without the use of fitting parameters. The primary assumptions of this model are: non-interacting spherical inclusions in the matrix; continuity of stresses and displacements at the interfaces; linear viscoelastic behaviour; homogeneous and isotropic components; insignificant inertial forces; no cracking or crazing; and no thermal stresses.

## 2. Experimental procedure

Silicon powder (Aldrich Chemical Co., 325 mesh, 99%) was used as the filler to model an SiO<sub>2</sub> surface in this study. The powder surface was oxidized in an air oven for 1 h at 200 °C. The density of the oxidized material was assumed to be the same as that reported for the silicon by the supplier, 2.33 g cm<sup>-3</sup>. Before application of coupling agents or compounding into composites, the filler was dried overnight under vacuum at 80 °C. A Philips SEM 505 was used to obtain electron micrographs of the particles.

The surface of the SiO<sub>2</sub> powder was characterized with a X-ray photoelectron/Auger electron spectrometer, Leybold-Heraeus Type LHS-XPS/AES. This

instrument has a base pressure of  $1 \times 10^{-10}$  mbar maintained by a turbomolecular air pump. The radiation used was MgK<sub>α</sub> (1253.6 eV). Wide scans were taken with a retarding factor of three. High resolution scans were taken with  $E_0 = 50$  eV. The probing depth was estimated to be 2–20 atomic layers under these conditions. A Hewlett-Packard HP 1000 E Series computer was used for spectrometer control and data manipulation with software developed by the instrument manufacturer.

The Brunauer–Emmett–Teller (BET) surface area of the SiO<sub>2</sub> powder was measured with a Quantachrome Corporation Quantasorb. The powder was pretreated at 80 °C under helium atmosphere overnight. The measurement was made at –196 °C using a three-point dynamic system.

Coupling agents gamma-aminopropyltriethoxysilane ( $\gamma$ -APS) and gamma-methacryloxypropyltrimethoxysilane ( $\gamma$ -MPS) were obtained from Petrarch Systems and used as-received. They were applied to the SiO<sub>2</sub> powder from methanol solution by evaporation of solvent. The amount of coupling agent required to achieve an equivalent monolayer coverage on the SiO<sub>2</sub> was calculated assuming coverages of 353 m<sup>2</sup> g<sup>-1</sup> for  $\gamma$ -APS and 314 m<sup>2</sup> g<sup>-1</sup> for  $\gamma$ -MPS [10]. For application of the coupling agents, the amount of methanol (Merck, dried methanol, water content < 0.01%) used was 0.5 ml methanol g<sup>-1</sup> filler. Fifteen mol water per mol coupling agent were then added to the methanol. The coupling agent was added and the solution stirred at room temperature for 30 min. The coupling agent was applied to the SiO<sub>2</sub> by mixing the solution and powder in an open dish and stirring by hand under a hood at room temperature. The methanol evaporated and mixing was continued until the slurry became too solid for continued hand mixing to have any effect. The treated solid was then dried in an air oven at 80 °C for 1 h. Before milling into composites, the solid was dried under vacuum at room temperature overnight.

The polyethylene used was DSM Stamylen HDPE 9089F, with a nominal melt index of 8 dg min<sup>-1</sup>. This is a linear polyethylene with an approximate average molecular weight of 60 000 g mol<sup>-1</sup> and a density of 0.963 g cm<sup>-3</sup> at room temperature.

The EPDM rubber used was DSM Keltan 312, with a nominal Mooney viscosity ML(1 + 4) 125 °C of 33. Henceforth, this material will be referred to as "EPDM". For use in solution, the EPDM was dissolved at room temperature in *n*-hexane (Riedel-delta, AG, chemically pure). The gel content under these conditions was insignificant.

The modified EPDM rubber (EPDM-MA) was a specially made maleic anhydride modification of Keltan 312. It was reported to have 0.8% ( $\pm 0.1\%$ ) maleic anhydride modification as determined by infrared. During the modification of the Keltan 312, Irgonox 1076 was added (less than 0.5%) as a stabilizer. Talcum (less than 1.0%) was also added as a processing aid during modification. Infrared spectra of this material which are reported elsewhere [8] indicate that the material as-received had undergone significant hydrolysis of the anhydride functionality to

the acid form. For use in solution, the EPDM-MA was dissolved at room temperature in *n*-hexane and then centrifuged at 20 000 *g* for 1 h. The gel content under these conditions was less than 1.5%. The density of both the unmodified and modified rubbers was assumed to be 0.86 g cm<sup>-3</sup> at room temperature.

The EPDM and EPDM-MA were applied to SiO<sub>2</sub> from 4% *n*-hexane solution by evaporation of solvent. The filler and solution were mixed by hand in an open dish under a hood at room temperature until the mixture became too solid for continued hand mixing to have any effect. The treated fillers were then dried under vacuum at room temperature overnight for milling into composites the next day.

Composites were roll-milled on a Schwabenthan Polymix 80 T. This mill has rolls 8 cm in diameter and 30 cm long, with a roll ratio of 1:1.13. The nip distance was varied by the operator during milling, but averaged about 2 mm. The PE composites were milled at 170 °C; composites of rubber and SiO<sub>2</sub> were milled at 150 °C. The matrix was put on the mill for 5 min before the addition of any more constituents. In cases where one more component (such as a rubber or treated filler) was to be added, this component was added and worked for 10 min, after which the material was removed from the mill. In cases where the rubber and filler were added separately, the rubber was added first and worked for 2 min. Then the filler was added and worked for a further 8 min.

The milled composites were pressed on a Fontyne automatic press. A simple mould 15 cm square and 3 mm thick was used to make initial plaques. The PE composites and PE control were pressed at 190 °C. Samples of the modified and unmodified EPDM were pressed at 150 °C from the pellet form without prior milling. Each sample was heated between the press platens for 7 min under no pressure. The samples were then pressed with a total force of 1 kN for 5 min, 50 kN for 5 min, and 180 kN for 5 s. The samples were then cooled to room temperature under 180 kN force. The initial cooling rate was approximately 40 °C min<sup>-1</sup> and the entire cooling process took about 10 min. Plaques were stored under vacuum to prevent water absorption.

The dynamic mechanical measurements were made using a torsion pendulum designed at DSM. Pieces were cut from the pressed plaques and re-pressed under the same conditions as described above into samples approximately 5 × 1.25 × 0.2 cm. The moulding was done 1 week before testing in order to maintain a constant ageing time of 224 h. The torsion pendulum was operated at a frequency of 0.2153 Hz. Measurements were taken at approximately 2 °C intervals.

Model calculations were done based on the extended van der Poel model with double precision accuracy. Properties of the PE, EPDM, and EPDM-MA used as input for the calculations were obtained from the torsion pendulum results for the pure materials. The EPDM and EPDM-MA became too soft for accurate torsion pendulum results above about -35 °C. In order to extend the data above this temperature, composites of 0.50 volume fraction SiO<sub>2</sub>

in the rubbers were milled and analysed. These data were superimposed on the pure material data for extrapolation to higher temperatures. For the SiO<sub>2</sub>, a storage modulus (*G'*) of 2.8 × 10<sup>10</sup> Pa, and a loss modulus (*G''*) of 2.8 × 10<sup>7</sup> Pa were assumed. The Poisson ratios of the PE, rubber and filler were assumed to be constant real numbers with values of 0.4, 0.5, and 0.25, respectively.

Transmission electron micrographs of a PE/EPDM blend were taken with a Philips 420 TEM at 100 kV. The samples were first pre-cut to obtain a fresh surface. They were then treated in chlorosulphonic acid (ClSO<sub>3</sub>H) vapour for 3.5 h at 60 °C. The samples were then stained with uranyl acetate at room temperature. Slices for the TEM were cut with an ultramicrotome at room temperature.

### 3. Results and discussion

An SEM micrograph of the SiO<sub>2</sub> particles used in this study is given in Fig. 1. The particles are quite irregular in shape and the surfaces appear rough. A very broad distribution of particle size and shape is evident. Approximate particle diameters vary from 0.1 to 50 μm. The average particle size is about 5 μm diameter. The BET surface area was determined to be 2.5 m<sup>2</sup> g<sup>-1</sup>.

The surface atomic composition of the oxidized powder as determined by XPS is given in Table I. The estimated accuracy of the values is 10% relative error. These data confirm the oxidation of the powder surface.

The dynamic mechanical spectrum of the PE is given in Fig. 2, and those of EPDM and EPDM-MA in Fig. 3. The gamma transition of the PE occurs at -124 °C. The alpha transition peak begins to appear at -18 °C. The EPDM and EPDM-MA exhibit

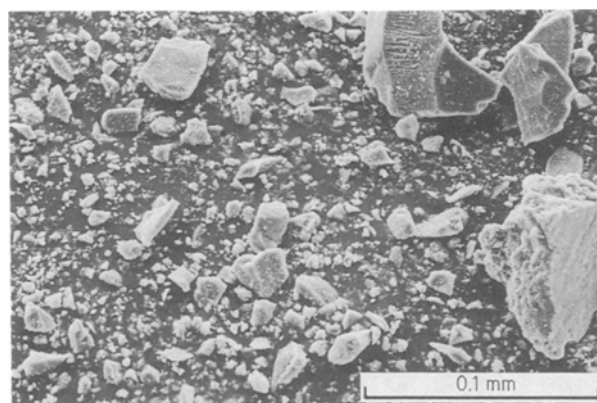


Figure 1 SEM micrograph of the oxidized silicon powder used for filler at × 330 magnification.

TABLE I XPS composition of oxidized silicon powder

Component	At %
Si (elemental)	35.5
Si (in SiO <sub>2</sub> )	18.0
O	42.5
C	4.5

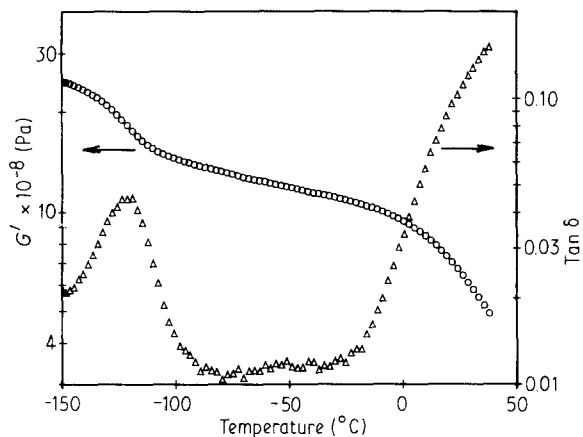


Figure 2 Dynamic mechanical spectrum of PE used, DSM Stamylan HDPE 9089F.

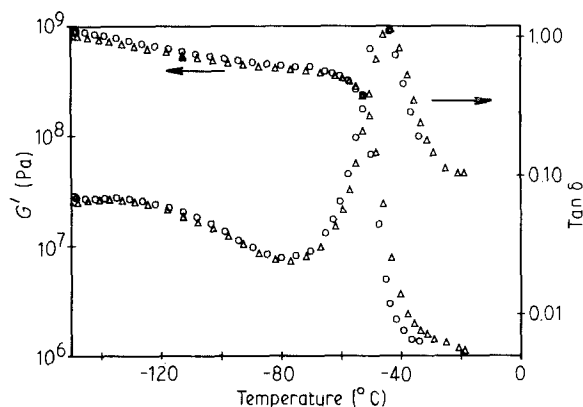


Figure 3 Dynamic mechanical spectra of the rubbers used: ○, EPDM; △, EPDM-MA.

glass transitions at  $-53$  and  $-50$  °C, respectively, as determined by the loss modulus  $G''$ . The higher glass transition temperature of the EPDM-MA is probably due to greater chain-chain interactions arising from the polar nature of the grafted moieties.

### 3.1. Composites of $\text{SiO}_2$ in PE

For composites of untreated  $\text{SiO}_2$ , the modulus enhancement factor  $G'_c/G'_m$  (composite storage modulus/matrix storage modulus) at  $-100$  and  $20$  °C are given as functions of  $\text{SiO}_2$  volume fraction along with the model predictions in Fig. 4. The experimentally observed enhancement is significantly greater than that expected from the constituent material properties assuming spherical particles. Possible reasons for this include immobilization of PE chains on the surfaces of the reinforcement, particle-particle interactions (including agglomerations), surface roughness, and non-spherical particle shape. In fact, several recent studies have focused on the presence of an interphase with properties different from those of the constituent materials in filled polyethylene composites. Dolakova and Hudecek [11] studied composites of glass beads, silica and kaolin in polyethylene. After fracture of these composites, they observed fibrillar links whose number depended on the filler used. Kendall and Sherliker [12] showed the presence of a bound polymer layer which could not be removed by solvent in

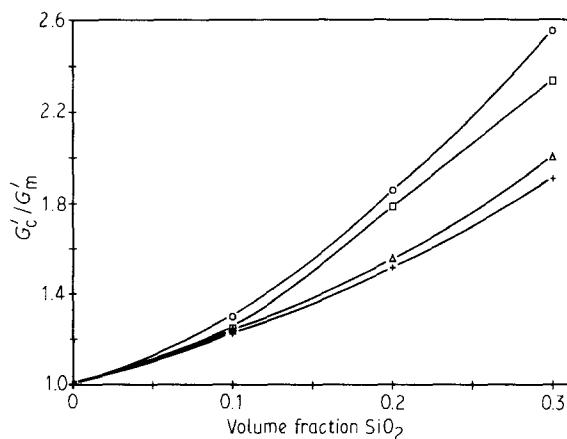


Figure 4 Values of the modulus enhancement factor  $G'_c/G'_m$  plotted as a function of filler volume fraction for composites of  $\text{SiO}_2$  in PE. ○, experimental at  $20$  °C; △, model prediction at  $20$  °C; □, experimental at  $-100$  °C; +, model prediction at  $-100$  °C.

silica-filled polyethylene. They modelled this as a uniform layer of polymer attached to the filler exterior, and estimated the layer to be  $2.0$  nm thick. Chacko *et al.* [13] observed a significant influence of filler on polymer morphology in PE/ $\text{CaCO}_3$  composites. Maurer *et al.* [14] studied the structure, thickness and properties of the interphase region in aerosil-filled polyethylene. They estimated the bound polymer layer thickness, described its mass distribution, measured its heat of fusion and calculated its dynamic mechanical properties. In another paper, Maurer *et al.* [15] studied the interphase region in kaolin-filled polyethylene. They determined the heat of fusion and correlated composite tensile strength with the undissolvable fraction of polyethylene on the filler surfaces.

The  $\tan \delta$  for these composites of  $\text{SiO}_2$  in PE is also significantly larger than that for PE over the temperature range  $-110$  to  $0$  °C. The effect increases with increasing volume fraction of filler. This is illustrated in Fig. 5. This type of loss is commonly attributed to particle-particle or particle-matrix friction [16, 17], different from the observed increased damping in kaolin-filled PE composites, which has been attributed to a disturbed polyethylene layer at the filler surface [15].

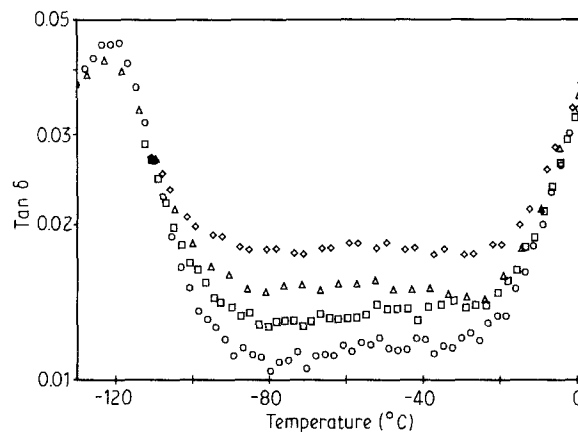


Figure 5  $\tan \delta$  for ○, polyethylene and composites with  $\text{SiO}_2$  volume fractions of □, 0.10; △, 0.20; and ◇, 0.30.

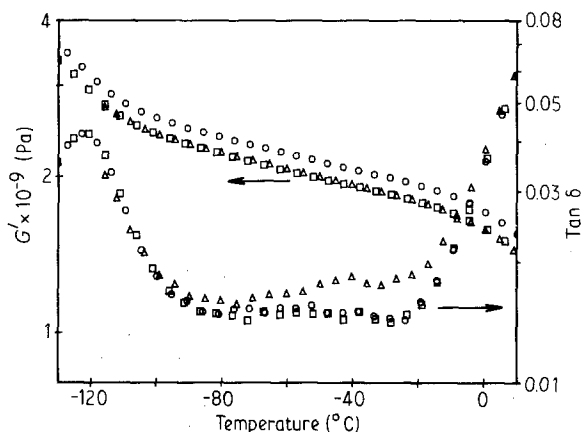


Figure 6 Effect of  $\gamma$ -MPS treatment on the dynamic mechanical properties of composites with 0.20 volume fraction  $\text{SiO}_2$ .  $\circ$ , Untreated filler;  $\square$ , one equivalent monolayer  $\gamma$ -MPS;  $\triangle$ , five equivalent monolayers  $\gamma$ -MPS.

The effect of surface treatment of the  $\text{SiO}_2$  was investigated for the case of 0.20 filler volume fraction in PE. At one equivalent monolayer coverage of  $\gamma$ -MPS, the storage modulus  $G'$  was reduced significantly and the  $\tan \delta$  reduced slightly compared to the untreated case. This is consistent with the above propositions of particle-particle interaction and friction. A thin layer of coupling agent reduces particle-particle interactions and friction, resulting in decreased  $G'$  and  $\tan \delta$  values. Reduced damping due to surface treatment has also been reported in the case of PE/calcium carbonate composites [18]. This is possibly due to improved particle dispersion. Surface treatment of fillers has often been found to improve dispersion in composites. Based on melt viscosity and mechanical property measurements in a variety of systems, coupling agents are often believed to improve the dispersion [19–21]. At five equivalent monolayer coverages of  $\gamma$ -MPS, the  $G'$  of the composite remains about the same as at one equivalent monolayer coverage but the  $\tan \delta$  increases beyond the level observed in the untreated composite. These effects are illustrated for  $\gamma$ -MPS in Fig. 6. At these higher coverages, the coupling agent probably forms a layer at the filler-matrix interphase. Formation of physically adsorbed low molecular-weight siloxane molecules have been observed previously on siliceous surfaces.

### 3.2. Blends of rubber in PE

The storage modulus and  $\tan \delta$  curves for blends of PE with 0.10 and 0.30 volume fractions EPDM are given in Fig. 7a. The results for composites with EPDM-MA are similar except for a shift of the loss peak 3 °C to higher temperatures, as was observed for the pure materials. Dynamic mechanical spectra for these composites, as predicted by the extended van der Poel model, are given in Fig. 7b. The unexpectedly broad glass-rubber transition of the EPDM to higher temperatures has been reported previously and attributed to phase intermixing of the PE and EPDM [22]. The area of the peak is significantly greater than expected at these volume fractions. This indicates that

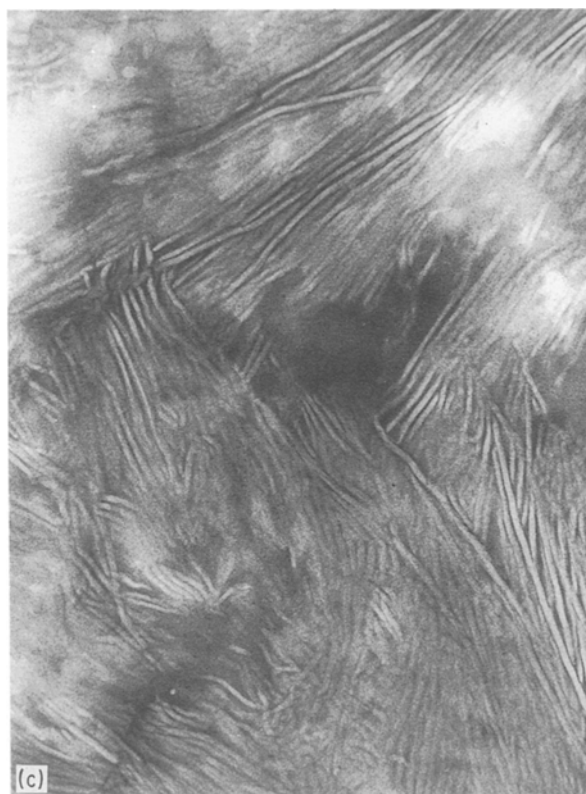
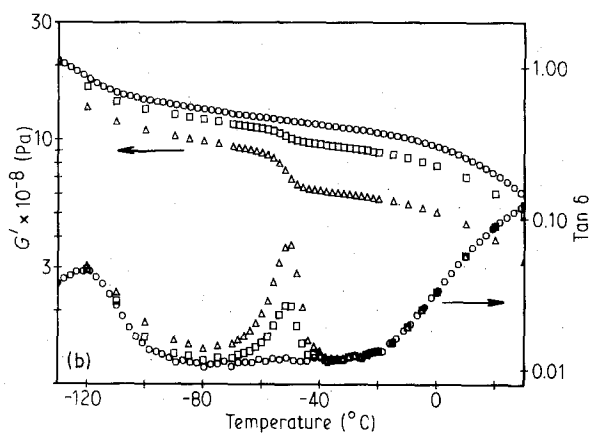
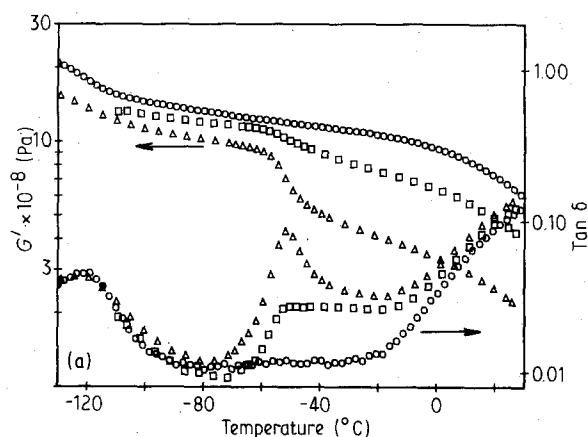


Figure 7(a) Dynamic mechanical properties of blends of EPDM in PE, with rubber volume fractions of  $\circ$ , 0;  $\square$ , 0.10  $\triangle$ , 0.30. (b) Predicted dynamic mechanical properties of blends of EPDM in PE based on the extended van der Poel model, with rubber volume fractions of  $\circ$ , 0;  $\square$ , 0.10;  $\triangle$ , 0.30. (c) Transmission electron micrograph of a blend of EPDM in PE. The EPDM has been stained dark. Magnification  $\times 52800$ .

the effective volume fraction of EPDM has been increased. It is not clear whether this is due to phase intermixing, inclusions of polyethylene in the rubber, or a possible reaction of the two components during processing. A shift in the polyethylene alpha transition peak to lower temperatures with the addition of the rubber is also observed. This has been attributed to a reduction in the lamella thickness due to the presence of the EPDM phase [22].

Transmission electron microscopy is used to obtain direct evidence for this phase intermixing. A TEM of a blend with 0.10 volume fraction EPDM in PE is given in Fig. 7c at 52 800 $\times$  magnification. The rubber has been stained a darker colour for the photograph. This micrograph clearly shows intermixing of the rubber and polyethylene: in several places, rubber can be seen between the lamellae of the polyethylene.

### 3.3. Composites of SiO<sub>2</sub> and rubber in PE

A series of composites was made with a 0.20 volume fraction of SiO<sub>2</sub> and rubber volume fractions of 0.001, 0.01, 0.03, and 0.10. The rubber was applied to the SiO<sub>2</sub> from *n*-hexane solution before milling, and both EPDM and EPDM-MA were used. The effect of residuals from solvent evaporation is not expected to be significant. For evaporation of the pure *n*-hexane, the concentration of residuals was found to be less than 0.004 wt %. This results in a solvent residuals volume fraction of less than about 0.0001 in the composites, involving evaporation of the largest amounts of solvent. The dynamic mechanical spectra of the EPDM series is given in Fig. 8. The experimental results again show a very broad glass-rubber transition of the EPDM. For an EPDM volume fraction of 0.10, the peak extends below -110 $^{\circ}$ C and above 5 $^{\circ}$ C, beyond which measurements were not made on this sample. Even in the case of an EPDM volume fraction of 0.001, the tan  $\delta$  peak is enhanced compared to the filled composite with no rubber. There are several possible reasons for this behaviour. These include the purely mechanical effect of a rubbery interlayer around the filler particles which broadens the transition to higher temperatures; broadening

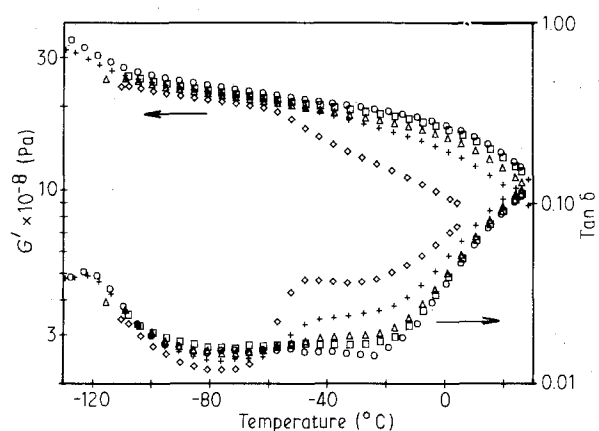


Figure 8 Dynamic mechanical properties of a series of multicomponent composites with SiO<sub>2</sub> volume fraction of 0.20 and EPDM volume fractions of  $\circ$ , 0;  $\square$ , 0.001;  $\triangle$ , 0.01; +, 0.03;  $\diamond$ , 0.10 deposited on the filler from solution before milling.

of the peak due to interaction of EPDM and PE (as observed in the case of the EPDM and PE blends); and immobilization of the rubber on the filler surface. Interpretation of these results is greatly complicated by the fact that the morphology is not known. SEM photographs of fracture surfaces indicate that there is at least some rubber near the surfaces of the filler particles (unpublished data). However, it is only possible to give qualitative information concerning the morphology at this point. In Fig. 9, the dynamic mechanical spectra of the EPDM-MA series are given.

Multicomponent composites were made with SiO<sub>2</sub> volume fraction of 0.20, rubber volume fraction of 0.10, with filler treatments of coupling agents  $\gamma$ -APS and  $\gamma$ -MPS, each in coverages of 1 and 5 equivalent monolayers. In these cases, the rubber and treated filler were added separately on the mill. The amount of silane present on the filler surface was not measured after treatment. Evaporation of the silanes during drying has been observed previously [23, 24]. Evaporation during addition on the roll mill is also possible and in fact was observed for the  $\gamma$ -MPS-treated fillers described here. Therefore the final surface coverage of the fillers in the composites is not accurately known. Infrared studies of the composites have confirmed the presence of  $\gamma$ -MPS in the final composites (unpublished data).

In composites of EPDM and SiO<sub>2</sub> with  $\gamma$ -APS surface treatment, there was essentially no difference in the dynamic mechanical spectra compared to the untreated filler, as shown in Fig. 10. However, significant changes resulted when EPDM-MA was used in combination with this surface treatment: these changes are shown in Fig. 11. In the case of one equivalent monolayer of  $\gamma$ -APS, the  $G'$  was essentially the same as that in the untreated case at temperatures below -55 $^{\circ}$ C. The composite  $G'$  was less than that in the untreated case for temperatures above the glass-rubber transition of the EPDM-MA. The shape of the tan  $\delta$  peak was also significantly changed. These changes may indicate that this surface treatment results in more rubber around the filler surface. With the use of five equivalent monolayers of  $\gamma$ -APS, more

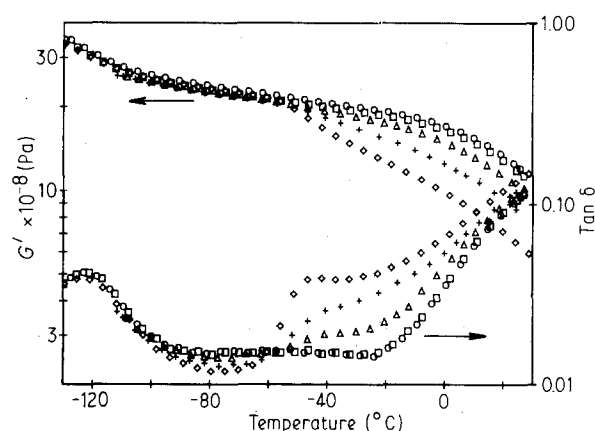


Figure 9 Dynamic mechanical properties of a series of multicomponent composites with SiO<sub>2</sub> volume fraction of 0.20 and EPDM-MA volume fractions of  $\circ$ , 0;  $\square$ , 0.001;  $\triangle$ , 0.01; +, 0.03;  $\diamond$ , 0.10 deposited on the filler from solution before milling.

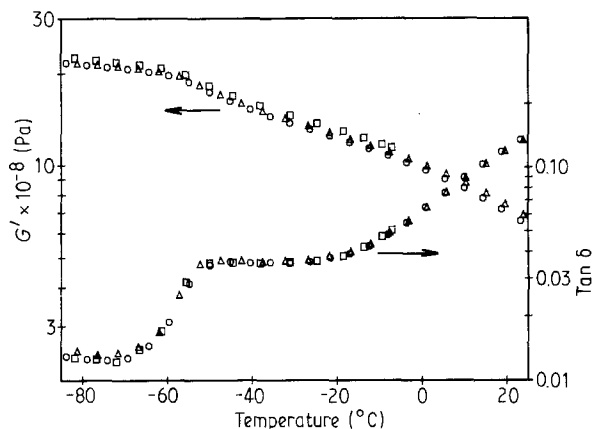


Figure 10 Effect of  $\gamma$ -APS treatment on composites with  $\phi_{\text{SiO}_2} = 0.20$  and  $\phi_{\text{EPDM}} = 0.10$ .  $\circ$ , Untreated filler;  $\square$ , one equivalent monolayer  $\gamma$ -APS;  $\triangle$ , five equivalent monolayers  $\gamma$ -APS.

changes result. The  $G'$  for five equivalent monolayers is less than that for one equivalent monolayer below the rubber transition, but they approach each other above the transition and become nearly the same near room temperature. The alpha transition of the polyethylene is also observed to shift to higher temperatures with the use of surface treatment. This may indicate that less rubber is available for phase intermixing with the matrix.

The results for composites including  $\gamma$ -APS and EPDM-MA should be interpreted in the light of possible interactions between their functionalities. The acidic nature of the maleic anhydride modification, and the basic nature of the amide functionality of the  $\gamma$ -APS, indicate that some interaction of these groups may be possible. This interaction could be simple hydrogen bonding, salt formation, acid-base interactions, or chemical reactions. Model studies in *n*-hexane solution also show that EPDM-MA and  $\gamma$ -APS will react at room temperature in dilute solution (unpublished data). No reaction was detected for EPDM under the same reaction conditions. There is infrared evidence for a reaction between these two species during processing on the roll mill (unpublished

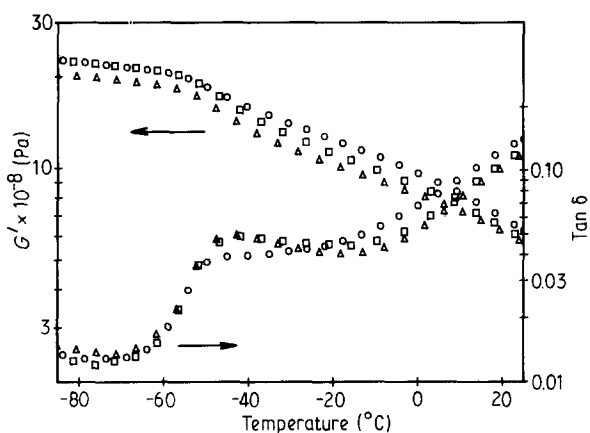


Figure 11 Effect of  $\gamma$ -APS treatment on composites with  $\phi_{\text{SiO}_2} = 0.20$  and  $\phi_{\text{EPDM-MA}} = 0.10$ .  $\circ$ , Untreated filler;  $\square$ , one equivalent monolayer  $\gamma$ -APS;  $\triangle$ , five equivalent monolayers  $\gamma$ -APS.

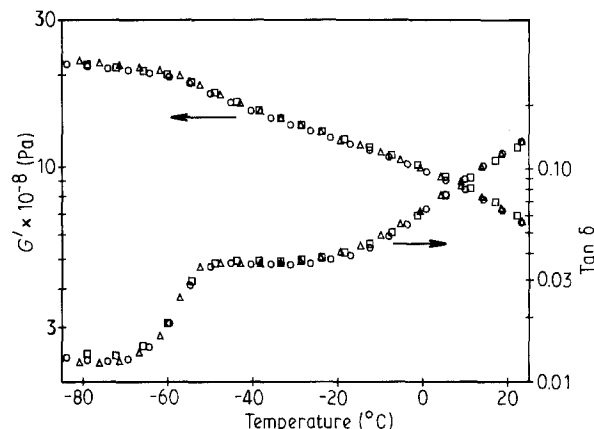


Figure 12. Effect of  $\gamma$ -MPS treatment on composites with  $\phi_{\text{SiO}_2} = 0.20$  and  $\phi_{\text{EPDM}} = 0.10$ .  $\circ$ , Untreated filler;  $\square$ , one equivalent monolayer  $\gamma$ -MPS;  $\triangle$ , five equivalent monolayers  $\gamma$ -MPS.

data). A band due to the cyclic imide formed from the reaction of  $\gamma$ -APS with the EPDM-MA has been detected in infrared spectra of the final composites. Assuming that the  $\gamma$ -APS and EPDM-MA may react during milling, the dynamic mechanical results may be interpreted as follows. This interaction increases the likelihood of more rubber surrounding the  $\text{SiO}_2$  particles during processing. Hence, compared to the untreated filler, the  $G'$  is nearly the same below the rubber transition but significantly lower above the transition. The shape of the  $\tan \delta$  peak is changed, and it is also shifted to higher temperatures. The presence of rubber around the filler particles is expected to broaden its glass transition and shift it to higher temperatures for purely mechanical reasons. The interpretation in the case of these composites is complicated by the phase intermixing between the PE and rubber. However, the shift of the  $\tan \delta$  peak at the rubber-glass transition point and the shift of the polyethylene alpha transition are clearly seen.

In composites of EPDM and EPDM-MA with  $\gamma$ -MPS, there is little change in the dynamic mechanical spectra compared to composites with untreated  $\text{SiO}_2$  surface, as shown in Figs 12 and 13. The effect of

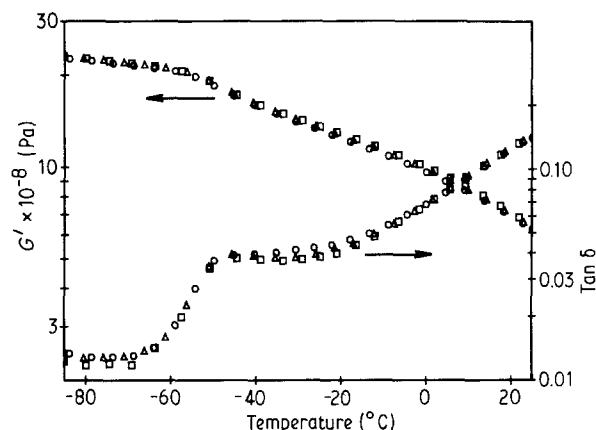


Figure 13 Effect of  $\gamma$ -MPS treatment on composites with  $\phi_{\text{SiO}_2} = 0.20$  and  $\phi_{\text{EPDM-MA}} = 0.10$ .  $\circ$ , Untreated filler;  $\square$ , one equivalent monolayer  $\gamma$ -MPS;  $\triangle$ , five equivalent monolayers  $\gamma$ -MPS.

coupling agent is much less significant than in the case of  $\gamma$ -APS. In the infrared study cited above, no reaction between  $\gamma$ -MPS and either EPDM or EPDM-MA was detected in the solution model study. This does not preclude the possibility of such a reaction under milling conditions, but it does indicate that such a reaction may be less likely than in the case of  $\gamma$ -APS. Changes in the compatibility of the filler surface and rubber may explain the small changes observed here.

### 3.4. Model calculations

The extended van der Poel model has been used to predict the composite dynamic mechanical spectra based on the properties of the constituent materials. Some results have been presented earlier in this paper.

For composites of matrix/rubber/filler, this model has been used to compare the expected dynamic mechanical spectra for two distinct morphologies: that with all the rubber around the filler particles, and that with the rubber and filler as separate particles in the matrix. The difference is shown in Fig. 14 for the case of  $\phi_{\text{SiO}_2} = 0.20$  and  $\phi_{\text{EPDM}} = 0.10$ . This morphological difference results in very significant differences in the spectra. Rubber around the filler instead of separate results in a lower  $G'$  over the entire temperature range shown, including a much more prominent modulus reduction after the EPDM glass-rubber transition. The  $\tan \delta$  peak is much larger and is also shifted from  $-50$  to  $-42^\circ\text{C}$ . The peak is also broadened toward higher temperatures. Note that this shift and broadening in the  $\tan \delta$  peak are purely mechanical effects.

Model predictions for composites with  $\phi_{\text{SiO}_2} = 0.20$ , and rubber volume fractions of 0.001, 0.01, 0.03, and 0.10 where the rubber is completely around the filler particles, are given in Fig. 15. Note that the  $\tan \delta$  peak due to EPDM glass-rubber transition shifts quite significantly and also broadens to higher temperatures. There are also two peaks predicted in the

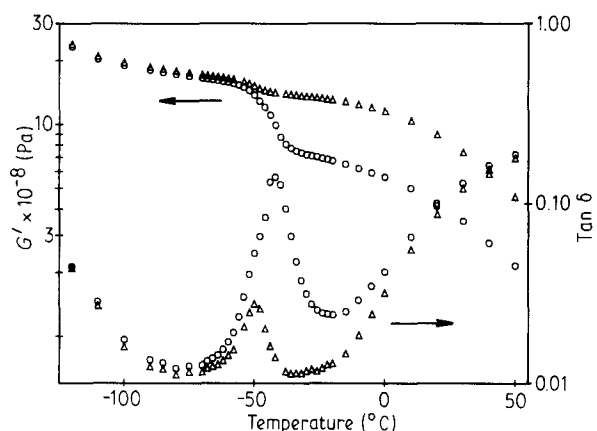


Figure 14 Dynamic mechanical property calculation based on the extended van der Poel model comparing two different morphologies.  $\circ$ , Rubber forming a layer around the filler particles;  $\Delta$ , rubber and filler particles as separate spheres in the matrix. Calculation is for a composite with  $\phi_{\text{SiO}_2} = 0.20$  and  $\phi_{\text{EPDM}} = 0.10$ .

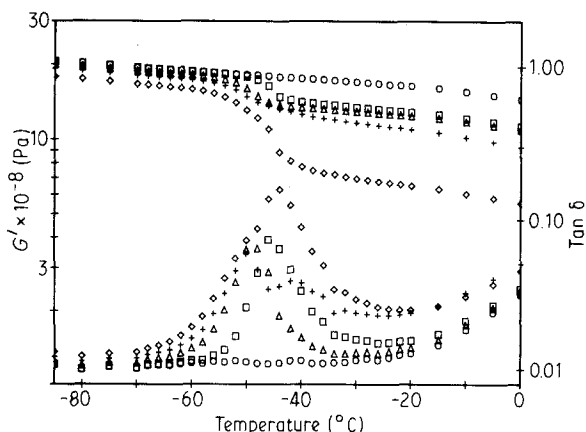


Figure 15 Predicted dynamic mechanical properties based on the extended van der Poel model of a series of multicomponent composites with  $\phi_{\text{SiO}_2} = 0.20$ . EPDM volume fractions,  $\circ$ , 0;  $\square$ , 0.001;  $\Delta$ , 0.01;  $+$ , 0.03;  $\diamond$ , 0.10 where the rubber exists as a layer around the filler particles.

EPDM glass-rubber transition region for the case of  $\phi_{\text{EPDM}} = 0.03$ .

## 4. Conclusions

The multicomponent composites in this investigation exhibit complex viscoelastic behaviour. Significant  $\text{SiO}_2$  particle-particle interaction has been postulated for PE/ $\text{SiO}_2$  composites. Phase intermixing of rubber and PE has been inferred from the dynamic mechanical spectra of PE/rubber blends. The phase intermixing was confirmed directly by TEM.

The surface character of the  $\text{SiO}_2$  filler has a very significant influence on the dynamic mechanical properties of the resulting composites. In composites of PE and  $\text{SiO}_2$  low coverages of coupling agent reduce particle-particle interactions and friction, resulting in reduced  $G'$  and  $\tan \delta$ . At high coverages, the coupling agent is expected to form an interlayer at the filler surface.

The morphology of the multicomponent composites could not be determined by the methods used here. In composites with rubber, surface treatment appears to influence the amount of rubber located around the filler particles. Specifically, the use of  $\gamma$ -APS with EPDM-MA appears to increase the amount of rubber around the particles most significantly. This may be attributed to interaction and possibly to reaction between the amine functionality of the coupling agent and the maleic anhydride modification.

The maleic anhydride modification of the EPDM significantly influences the properties of the resulting composites under certain conditions. This is most probably due to a change in the interaction of the rubber with filler surfaces, rather than due to changes in the dynamic mechanical properties of the rubber itself.

The extended van der Poel model is qualitatively useful for modelling these multicomponent composites. Major discrepancies with the experimental



results are due to phase intermixing of the matrix and rubber and filler–matrix and filler–filler interactions which are not accounted for in the model.

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