

# Characterization of Interfacial Interactions in High Density Polyethylene Filled with Glass Spheres Using Dynamic-Mechanical Analysis

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## Synopsis

The dynamic-mechanical properties of high density polyethylene filled with 20% by volume of untreated glass spheres or glass spheres treated with a silane-based coupling agent were studied as a function of temperature and imposed tensile deformation. The coupling agent used is capable of providing covalent bonding between the polymeric matrix and the glass spheres. It is assumed that an interphase region is formed in the matrix around each filler particle with properties depending on the surface treatment of the filler, but different to that of the bulk matrix. It is shown how the mechanical loss factor can be used to characterize the properties of the interphase region and the degree of adhesion between the two phases, as affected by the surface treatment. We suggest that these kinds of measurements can be valuable when determining the effectiveness of various surface treatments of filler particles from a mechanical point of view.

## INTRODUCTION

The properties of filled polymers depend primarily on the corresponding properties of the constituents and on their volume fractions.<sup>1</sup> Also other factors, such as the size and the shape of the filler particles can be of significance, as well as the nature and properties of the interface between the two materials. Interactions at the interface, which can have a substantial effect on the mechanical, thermal, and other properties of the composite, have attracted much interest during recent years<sup>1-6</sup> due to the potential technical importance of these materials. On this basis, surface treatments of the filler particles are often used to optimize the properties of the composite in some required respect.

The amount of work relating to the viscoelastic properties of composites is rather limited compared to that of unfilled polymers. However, based on that work it is obvious that the nature of the interface plays an important role in this context (cf. Refs. 1-6). Interactions at the interface may lead to the formation of an interphase region close to the filler surface with properties different from that of the bulk polymer matrix. This in turn might influence the viscoelastic properties. The properties and the nature of the interphase are also in a rather natural way qualitatively connected to the degree of

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adhesion between the two phases. However, understanding of interfacial phenomena and their characterization and effect on the viscoelastic properties are still in a stage of development and more experimental work is required in this field.

In earlier work,<sup>7,8</sup> it has been shown that interfacial interactions can have a significant effect on the stress-relaxation and creep behaviors of high density polyethylene (HDPE) filled with inorganic fillers. The formation of an interphase region resulted in a decrease in macroscopic flow due to the restriction of macromolecular mobility close to the filler surface. This was very pronounced when covalent bonding between glass spheres and the HDPE matrix was achieved.<sup>8</sup> From stress-relaxation experiments it was also possible to estimate the extent of the interphase region.<sup>9</sup>

In this communication attention is focused on the dynamic-mechanical properties of HDPE filled with glass spheres. The nature of the interphase region is deliberately changed using controlled surface treatments of the glass spheres. The aim of the work is to demonstrate how dynamic-mechanical properties are affected by the properties of the interphase and to investigate to what extent such measurements can be used to characterize the interphase region and the degree of adhesion between the two phases. Following changes in the interphase region due to increasing levels of imposed deformation on the composite, using this technique is of special interest. The dynamic-mechanical analysis performed here may also provide a complement to the information provided by the stress relaxation and creep experiments reported on in Refs. 7-9.

## EXPERIMENTAL

### Materials

The high density polyethylene (HDPE) grade used in this work was Stamy-lan 9089F, DSM with a nominal density of 0.963 g/cm<sup>3</sup>, a melt flow index of 8 g/10 min and an average molecular mass ( $\bar{M}_w$ ) of  $6 \times 10^4$  g/mol. Two types of glass spheres from Potters Industries with differing particle diameters were used as fillers. The smaller glass spheres (No. 5000) had an average diameter of 10-13  $\mu$ m and the larger ones (3000 CP00) 30  $\mu$ m. The volume fraction of the filler in the composite was kept at 0.20 throughout this study.

### Sample preparation

HDPE and the glass spheres were compounded as described in Ref. 10 in an open two roll mill at 170°C for 15 min. Sheets with a thickness of 1.1 mm were produced from this mixture by compression molding between polished plates. From these sheets rectangular samples with a width of 6 mm and an effective length of 45 mm were cut and subsequently heat-treated at 110°C for 16 h. After this heat treatment the samples were slowly cooled (1°C/min) to room temperature. Unfilled HDPE specimens were prepared in an analogous way.

Some of the glass spheres were surface-treated with an azide functional alkoxysilane prior to compounding as a part of another investigation.<sup>10,11</sup> This silane is capable of providing a covalent bond between the glass spheres and HDPE (cf. Refs. 10 and 11). For the smaller glass spheres the amount of silane

used was 0.19% by weight, while for the larger ones two different amounts of silane were used, 0.0214 and 0.206%.

### Methods

The dynamic-mechanical properties were evaluated in the tensile mode using a mechanical analyzer (Dynastat, IMASS). The frequency of the forced oscillation was kept at 0.1 or 1.1 Hz.

## RESULTS AND DISCUSSION

### The Temperature Dependence of the Dynamic-Mechanical Properties

Figures 1 and 2 show the storage modulus  $E'$  and the mechanical loss factor  $\tan \delta$  for the unfilled material and the composite containing the smaller and the larger glass beads. Results for both untreated and surface-treated glass spheres are included. The data for the surface-treated larger glass spheres refers to a silane amount of 0.206%. The temperature range covered by the experiments was 25–125°C. When performing the measurements, the specimens were subjected to a constant tensile preload of 1 MPa. This corresponds to a short-term static deformation at 25°C of less than 0.04% for the unfilled HDPE and less than 0.03% for the composites. The imposed tensile periodic loading of the samples had a stress amplitude of 0.6 MPa. The data shown in Figures 1 and 2 were corrected for creep deformation and thermal expansion.

As expected, the addition of glass spheres to HDPE increases the storage modulus<sup>1</sup> and slightly higher  $E'$  values are noted when the glass spheres are

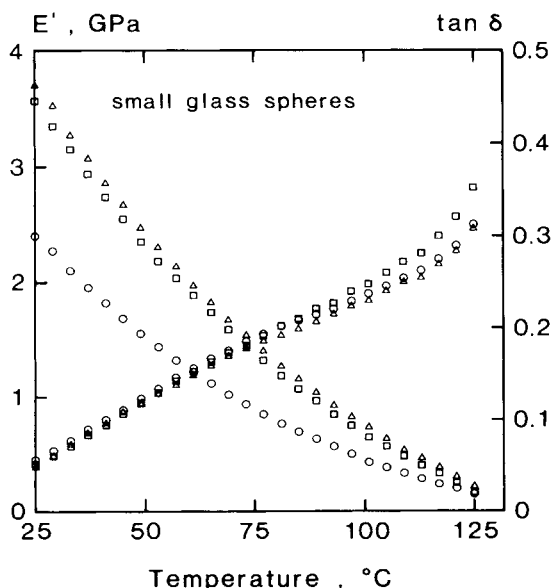


Fig. 1. The storage modulus  $E'$  and the mechanical loss factor  $\tan \delta$  vs. the temperature for (○) unfilled HDPE, (□) HDPE filled with small untreated glass spheres, and (△) HDPE filled with silane-treated small glass spheres. The frequency was 1.1 Hz.

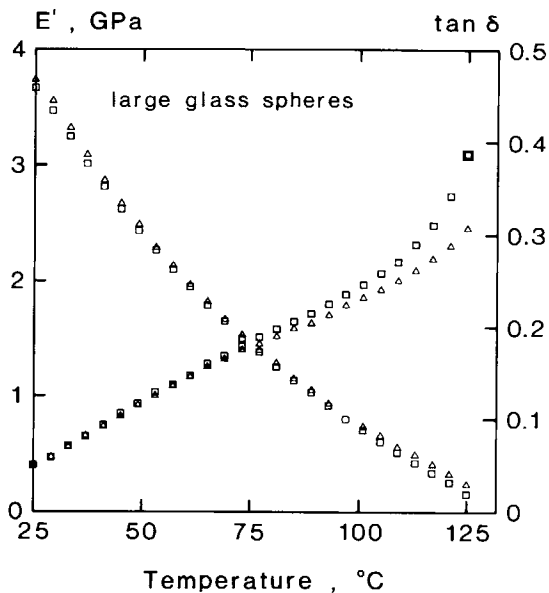


Fig. 2. Same as Figure 1 but for (□) HDPE filled with large untreated glass spheres and (Δ) HDPE filled with large glass spheres covered with 0.206% silane.

silane-coated. The difference in modulus between unfilled and filled HDPE decreases at higher temperatures. The mechanical loss factor  $\tan \delta$  for the composite containing the surface-treated glass spheres was somewhat lower than that for the unfilled polymer. The  $\tan \delta$  values for the composites containing the untreated glass spheres were similar to those of the unfilled HDPE at temperatures lower than about 70°C, but at higher temperatures the values increased. Without any covalent bonding, the adhesion between the glass spheres and the matrix is poor.<sup>8,10,12</sup> At lower temperatures contraction of the matrix around the filler particles produces  $\tan \delta$  values which are similar to those of the unfilled matrix (cf. Refs. 3 and 13). When the contraction is released by the increase in temperature, the loss factor for the composites containing untreated glass spheres is markedly increased presumably due to particle-matrix friction at the interface. When covalent bonding exists between the filler and the matrix no such increase is observed.

The radial compressive stress at the filler surface at room temperature can be estimated using the observation that the mechanical loss factors of the composites containing untreated and treated glass spheres start to deviate from each other at 70°C. The radial stress  $\sigma_r$  in the matrix outside a sphere can be written as<sup>14</sup>

$$\sigma_r = - \frac{2E_m \epsilon_{\text{misfit}}}{(2E_m/E_f)(1 - 2\nu_f) + (1 + \nu_m)} \left( \frac{r_f}{r} \right)^3, \quad r > r_f \quad (1)$$

where  $E$  is the elastic modulus,  $\nu$  Poisson's ratio,  $r_f$  the radius of the spheres, and  $r$  the distance from the center of the sphere ( $r > r_f$ ). The indices  $m$  and  $f$  relate to the matrix and filler, respectively. The factor  $\epsilon_{\text{misfit}}$  denotes the

difference in thermal expansion between the matrix and the filler at room temperature and 70°C. This strain can be estimated as

$$\epsilon_{\text{misfit}} = (\alpha_m - \alpha_f) \Delta T \quad (2)$$

where  $\alpha$  denotes the linear thermal expansion and  $\Delta T$  is the temperature difference (70 – 25°C = 45°C). Using reasonable values for the parameters of eqs. (1) and (2), i.e.,  $E_m = 2$  GPa,  $E_f = 70$  GPa,  $\nu_f = 0.25$ ,  $\nu_m = 0.35$ ,  $\alpha_m = 12 \times 10^{-5} \text{ K}^{-1}$ , and  $\alpha_f = 0.8 \times 10^{-5} \text{ K}^{-1}$ , gives a compressive stress of about 14 MPa at the filler surface at 25°C. This stress decreases sharply with increasing distance from the filler surface [cf. eq. (1)].

The results presented in the preceding section are in good agreement with stress relaxation and creep data,<sup>8</sup> which indicate a strong interaction between the treated smaller glass spheres and HDPE. The difference in  $\tan \delta$  between the composites containing untreated and silane-coated larger glass spheres is similar (Fig. 2) to that noted for the smaller spheres. When the amount of silane coating is decreased to 0.0214%, the corresponding  $\tan \delta$  curve approaches that of the composite containing untreated filler particles (not shown in Fig. 2), indicating that this amount is not sufficient to produce good adhesion between the phases. The same conclusions are arrived at in Ref. 12 when analyzing the creep and relaxation behaviors of these materials.

### The Mechanical Loss Factor as a Characteristic of the Interphase

The effect of an interphase region on the dynamic properties can be quantified in a rather straightforward way. As a first approximation, it can be assumed that the mechanical loss factor  $\tan \delta_c$  of the composite can be written (cf. Refs. 1 and 15)

$$\tan \delta_c = v_f \tan \delta_f + v_i \tan \delta_i + v_m \tan \delta_m \quad (3)$$

where the subscripts  $f$ ,  $i$ , and  $m$  denote filler, interphase, and matrix, respectively, and  $v$  is the corresponding volume fraction. It is quite obvious that eq. (3) does not provide a detailed prediction of the mechanical loss factor of the composite since it involves a combination of series and parallel coupling of the phases. Nevertheless, it will be useful as a starting point, as outlined below, when aiming at comparing the effect of different surface treatments on the state of adhesion between the phases. Assuming that  $\tan \delta_f \approx 0$  and that the volume fraction of the interphase is rather small, eq. (3) can be rearranged to give

$$\frac{\tan \delta_c}{\tan \delta_m} \approx (1 - v_f)(1 + A) \quad (4)$$

with

$$A = \frac{v_i \tan \delta_i}{1 - v_f \tan \delta_m} \quad (5)$$

Equation (4) can be rewritten as

$$A = \frac{1}{1 - \nu_f} \frac{\tan \delta_c}{\tan \delta_m} - 1 \quad (6)$$

Strong interactions between the filler and the matrix at the interface tend to reduce the macromolecular mobility in the vicinity of the filler surface compared to that in the bulk matrix. This reduces  $\tan \delta_i$  and thus  $A$ . A low value of  $A$  thus indicates a high degree of interaction or adhesion between the phases.

Figure 3 shows how the  $A$  factor varies with the temperature for the composites. When the glass spheres are surface-treated with silane (0.206% silane in the case of the larger glass spheres), the  $A$  value stays almost constant, independent of the temperature. This indicates that the adhesion between the two phases is rather good over this temperature interval. This is in contrast with the behavior observed when no covalent bonding exists between the HDPE matrix and the filler. In such a case, the  $A$  factor increases monotonically with temperature, which indicates a deterioration of the degree of adhesion. There is no marked difference between the composites containing the small or the large glass spheres with regard to the temperature dependence of  $A$ . Again, it is obvious that the  $\tan \delta$  values for the composites containing the untreated glass spheres deviate markedly from the values of the composites with the treated glass spheres only at temperatures exceeding 70°C. This occurs when the thermal contraction of the matrix around the filler particles has been released. The  $A$  value thus appears to provide a

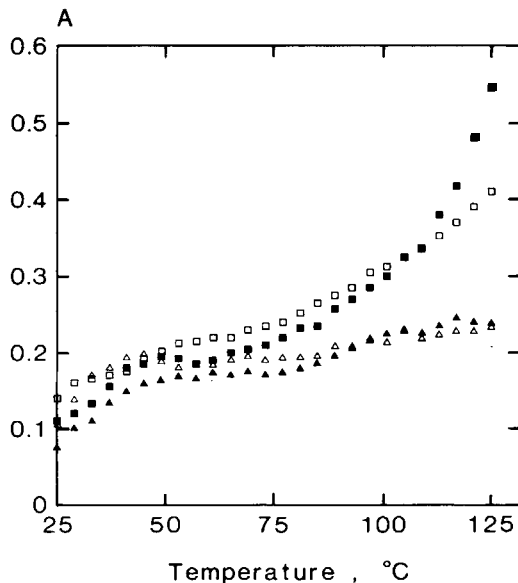


Fig. 3. The parameter  $A$  [eq. (6)] for HDPE containing ( $\square$ ■) untreated and ( $\triangle$ ▲) silane-coated glass spheres as a function of temperature. The filled symbols refer to the larger glass spheres (0.206% silane) and the unfilled ones to the smaller glass spheres.

convenient, although rather approximate, tool for describing how interfacial interactions respond to imposed changes.

If  $A = 0$ , eq. (4) reduces to

$$\frac{\tan \delta_c}{\tan \delta_m} = 1 - v_f \quad (7)$$

This relation is sometimes used when discussing the interactions between fillers and polymeric matrices.<sup>13,16</sup> However, in some cases it is observed that the decrease in  $\tan \delta_c$  due to filler adhesion is actually lower than predicted by eq. (7) (cf. Ref. 3), that is,  $A > 0$ .

### Description of the Results in Terms of the Concepts of Theocaris

The effect of an interphase on the dynamic-mechanical properties of particulate-filled and fiber-filled composites has also been discussed and modeled in a series of articles by Theocaris and co-workers (see, for example Refs. 17–20). It may therefore be worthwhile to interpret some of the results obtained in terms of the concepts used by them. They proposed that the modulus of the interphase region ( $E_i$ ) varied between that of the filler ( $E_f$ ) and the matrix ( $E_m$ ) from the filler surface and into the matrix. One way to express this relation is (cf. Ref. 18)

$$E_i(r) = E_m + E_f \left( \frac{r_f}{r} \right)^n - E_m \left( \frac{r_f}{r} \right) \quad (8)$$

Here  $r_f$  is the radius of the filler particle,  $r$  the distance in the matrix from the center of the filler particle ( $r > r_f$ ), and  $n$  a constant. The modulus of the interphase thus decreases from  $E_f$  at the filler surface to  $E_m$  at some distance from the filler. The higher the constant  $n$  is, the shorter the distance from the filler surface at which the modulus of the matrix is attained will be. That is, the higher the constant  $n$ , the thinner the interphase region around the sphere, or, almost equivalently, the poorer the degree of adhesion.

The real part of the dynamic compliance ( $D'_c$ ) for a composite containing particulate fillers with an interphase region [with the modulus given by eq. (8)] can be obtained from (cf. Ref. 18),

$$D'_c(1 - 2\nu_c) = \frac{v_f(1 - 2\nu_f)(\lambda'^2 - \lambda''^2)}{E_f} - \frac{v_f^2(1 + \nu_m)C_4}{2v_m^3} + \frac{(1 - 2\nu_m)C_6}{v_m} \quad (9)$$

with

$$\lambda^* = \lambda' - i\lambda''$$

$$= \frac{3E_f(1 - \nu_m)D_m^*}{2\nu_m(1 - 2\nu_f) + E_f D_m^* [1 + \nu_m + 2\nu_f(1 - 2\nu_m)]} \quad (10)$$

$$C_4 = D'_m - 2\lambda'D'_m + \lambda'^2 D'_m - \lambda''^2 D'_m + 2\lambda'' D''_m - 2\lambda'\lambda'' D''_m \quad (11)$$

$$C_6 = D'_m - 2\nu_f \lambda'D'_m + \nu_f^2 \lambda'^2 D'_m - \nu_f^2 \lambda''^2 D'_m + 2\nu_f \lambda'' D''_m$$

$$- 2\nu_f^2 \lambda'\lambda'' D''_m \quad (12)$$

Here  $D_m^* = D'_m - iD''_m$  is the dynamic compliance of the matrix, which includes the effect of the interphase region, that is,  $D_m$  is obtained using eq. (8),  $\nu_f$  is the volume fraction of the filler, and  $\nu_f$  is Poisson's ratio for the filler, and  $\nu_m$  is the corresponding parameter of the matrix, which is assumed to be constant, i.e., independent of the distance from the filler surface. The Poisson's ratio for the composite  $\nu_c$  is obtained from

$$\frac{1}{\nu_c} = \frac{\nu_f}{\nu_f} + \frac{1 - \nu_f}{\nu_m} \quad (13)$$

Using the temperature dependence of the dynamic properties of the unfilled HDPE, and choosing  $E_f = 70$  GPa and  $\nu_f = 0.25$ , eq. (9) can be fitted to the experimental dynamic-mechanical properties of the composites by choosing a proper value of  $n$ . In doing so, Poisson's ratio  $\nu_m$  for HDPE is assumed to vary with temperature as given by Schenkel.<sup>21</sup>

As shown in Figure 4, the  $n$  value increases with temperature for HDPE containing untreated or surface-treated glass spheres. The increase in  $n$  is especially marked at temperatures exceeding 80°C. This indicates that the thickness of the interphase region decreases with increasing temperature for both types of composites. This is indicated in the insert of Figure 4. In this sense the interaction between the phases can be said to decrease with increasing temperature. The  $n$  values for the composite containing untreated glass spheres are higher than those containing the surface-treated ones, which again indicates a weaker interaction or poor adhesion if no surface treatment is carried out (cf. the behavior of the  $A$  factor). The difference is especially pronounced at temperatures exceeding 80°C (cf. Fig. 4). In contrast to the  $A$  factor discussed above, the exponent  $n$  increases at higher temperatures, even when the spheres are surface-treated. This indicates a change of the interphase region as the temperature is increased also in this case. An analysis of dynamic-mechanical properties of the composites containing the larger glass spheres yields approximately the same dependence of  $n$  on temperature. However, the physical significance of such high values of the exponent  $n$  as 1000–1500 can, of course, be discussed.



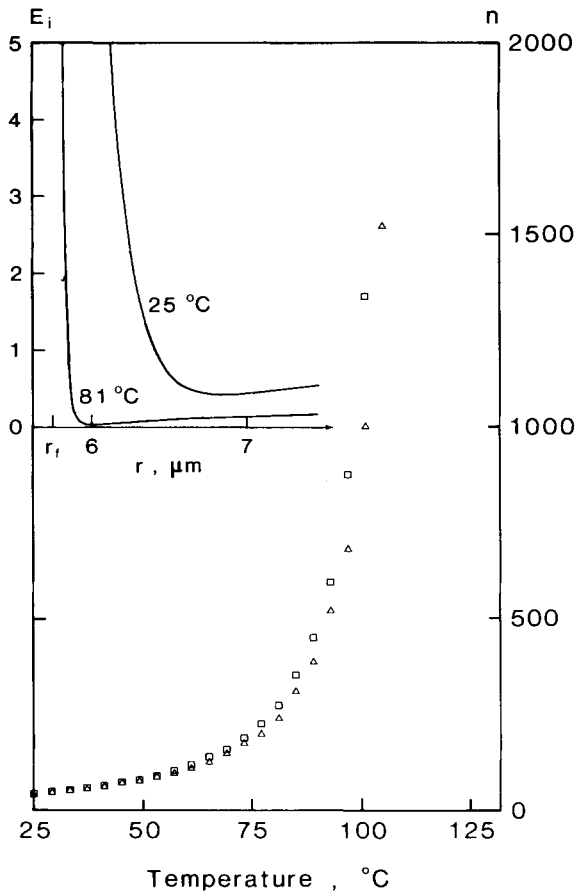


Fig. 4. The exponent  $n$  of eq. (8) for HDPE containing ( $\square$ ) untreated and ( $\Delta$ ) silane-coated small glass beads vs. temperature. The insert shows the variation of  $E_i$  with distance from the silane-treated glass surface according to eq. (8) at two temperatures.

### The Effect of the Strain Amplitude on the Dynamic-Mechanical Properties

From the result presented above it is clear that the adhesion or the nature of the interphase region has an effect on the dynamic-mechanical properties, primarily the mechanical loss factor. This can also be observed using another set of experiments. Intuitively, one would expect the losses in the material to increase when the amplitude of the imposed deformation increases if the interphase region is weak.

In a series of experiments using the composites containing the larger glass spheres, the specimens were subjected to a constant elongation (0.3%) and then a periodic deformation with varying amplitude was superimposed on that. This was done at room temperature (25°C) and the frequency was 0.1 Hz. Figure 5 shows how  $E'$  and  $\tan \delta$  vary with the amplitude,  $\epsilon_a$ , of the periodic deformation for the four types of HPDE materials considered here. The storage modulus  $E'$  decreases with increasing  $\epsilon_a$ . This is more pro-

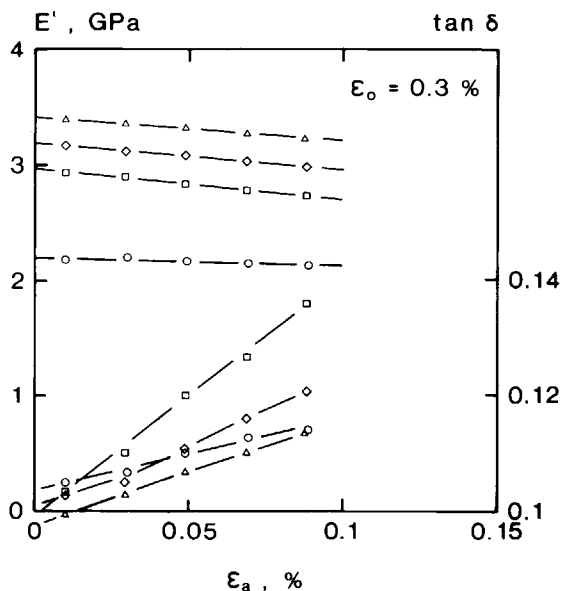


Fig. 5. The storage modulus  $E'$  and the loss factor  $\tan \delta$  as a function of the strain amplitude  $\epsilon_a$  for (○) unfilled HDPE, HDPE containing (□) untreated large glass spheres, (◇) large glass spheres with a thin silane layer, and (△) a thick silane layer. The static strain  $\epsilon_0$  was 0.3% and the frequency was 0.1 Hz.

nounced for the composites than for unfilled HDPE. There is no marked difference between the different composites in this respect.

The amplitude dependence of  $\tan \delta$  varies markedly, depending on the surface treatment. For the composite containing the untreated spheres, there is a significant increase in  $\tan \delta$  as the amplitude increases. In this case the interphase region is weak<sup>11</sup> and cannot withstand any substantial deformation without at least partially breaking. Then the marked increase in  $\tan \delta$  can possibly be associated with polymer-matrix friction as  $\epsilon_a$  increases (cf. Refs. 22 and 23). That friction is likely to be an important factor in this context is supported by the observation that the changes in  $\tan \delta$  are reversible with regard to changes in  $\epsilon_a$ . Improving the adhesion by a thin or thick silane coating on the glass spheres obviously reduces  $\tan \delta$  (cf. Fig. 5). It is to be expected that the thicker silane layer is more effective in this respect, since the creep tests reported in Ref. 12 showed that the best degree of adhesion was obtained at this silane content.

The effect of amplitude on the mechanical loss factor is enhanced when the static strain is increased up to 0.5% (cf. Fig. 6), but the same pattern of behavior is observed.

These experiments can also be interpreted in terms of Theocaris' concepts. Figure 7 shows how the amplitude affects the exponents  $n$  in eq. (8). First, it should be noted that at the strain levels discussed here there is a marked difference in  $n$  values between the composites even at room temperature. The highest  $n$  value is obtained when the composite contains untreated glass spheres, which indicates that the interphase is thin (and weak). The lowest  $n$  values are obtained when glass spheres coated with a thick silane layer are

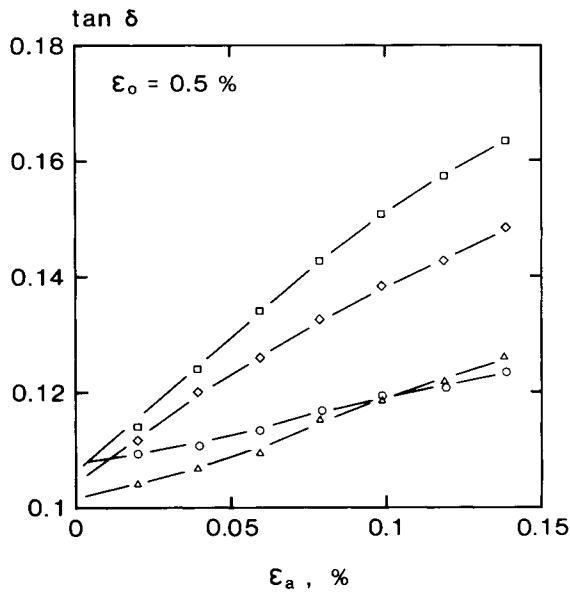


Fig. 6. The loss factor  $\tan \delta$  vs.  $\epsilon_a$  for the same samples as in Figure 5 but at a static strain of 0.5%.

used in the matrix. Second, the increase in the  $n$  value with increasing  $\epsilon_a$  is higher when no adhesion-promoting agent is used. The interphase region is probably, at least partially, then broken down as the imposed deformation increases. This increase in  $n$  is markedly reduced by the silane treatment, as shown in Figure 7.

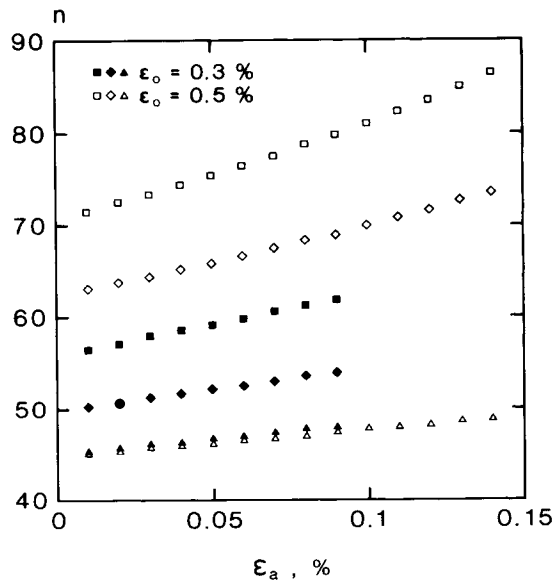


Fig. 7. The exponent  $n$  of eq. (8) vs.  $\epsilon_a$  for the same composites as in Figure 5.

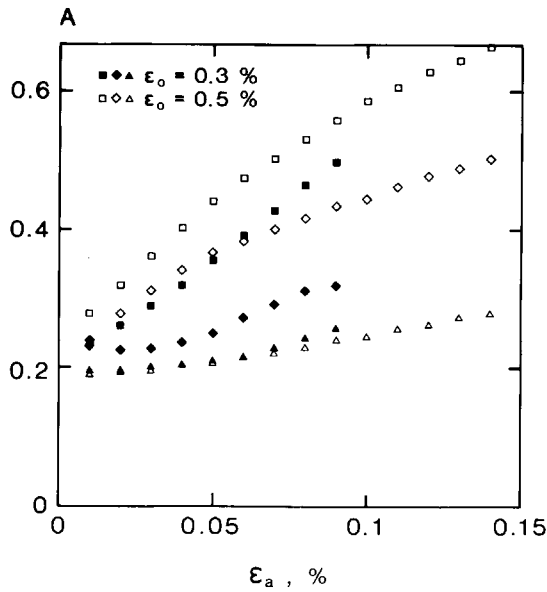


Fig. 8. The  $A$  factor, given by eq. (6), vs.  $\epsilon_a$  for the same composites as in Figure 5.

Figure 8 shows how  $A$ , given by eq. (6), depends on the applied amplitude  $\epsilon_a$  and the static strain  $\epsilon_0$  for the HDPE composites containing the larger glass spheres. The lowest value of  $A$  is noted for the composite containing glass spheres with the thick silane layer. The increase in  $A$  with  $\epsilon_a$  is not very pronounced in this case either. Decreasing the silane layer increases  $A$  as well as the strain amplitude dependence of  $A$  markedly. Except for the case when the glass spheres are covered with a thick silane layer, that is, the system with a satisfactory degree of adhesion, an increase in the static strain level  $\epsilon_0$  also brings about an increase in  $A$ , which again probably indicates a partial breakdown of the interphase region. Figure 8 represents an easy and sensitive method of judging the quality of an interphase region or the degree of adhesion using dynamic mechanical analysis.

## CONCLUSIONS

The most important conclusions can be summarized as follows:

1. Surface treatment of filler particles influences the mechanical loss factor.
2. The use of covalent bonding to improve adhesion can reduce the loss factor of HDPE composites at higher temperatures significantly, probably due to reduction of polymer-filler friction at the interface.
3. Measurements of the effect of temperature and the strain amplitude on the mechanical loss factor provides relevant information regarding the effectiveness of different surface treatments and the mechanical stability of the interphase region.

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