Particle size dependence of the Young's modulus of filled polymers: 1. Preliminary experiments

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Experimental results are reported from which it appears that in the case of polymer filled with silane-treated glass beads the Young's modulus is, in accordance with present theory, independent of the particle size of the filler. However, if pure glass beads are used as filler, the Young's modulus appears to be significantly dependent on the particle size. Different explanations for this behaviour have been discussed, of which all but one could be ruled out. The remaining explanation is based on the assumption of a particular morphology of the polymer surrounding untreated filler particles.

(Keywords: composites; filler particle size; Young's modulus; morphology)

INTRODUCTION

According to present theory, the Young's modulus of a composite, consisting of an isotropic and homogeneous matrix material and a dispersed phase of solid spherical particles, is independent of the dimension of the dispersed phase. The local stresses in the composite under load are only dependent on the ratios of the distance between the particles of the dispersed phase to the dimensions of these particles. At a certain volume fraction of dispersed phase and for a certain spatial distribution of the particles in the matrix, this ratio is constant[1–4].

For this reason the Young's modulus of a composite should only depend on the Young's moduli and Poisson's ratios of the filler and the polymer, and on the volume fraction of the spherical particles[4–8]. A parameter that therefore plays no role in all the equations is the particle size of the filler.

Although this theory often appears to be valid, data have been reported in the literature which show that in particular cases the Young's modulus tends to increase with decreasing particle size of the filler[7,9–16]. Most of these studies, however, were concerned with the effects of submicrometre filler particles, and no satisfactory explanation was given for the observed phenomenon.

In the present investigation the effects of the filler particle size on the Young's modulus of composites were studied for a broad range of particle sizes: five types of filler materials were applied, with diameters ranging from 0.035 to 100 μm. To extend the scope of this investigation, four different polymers were applied as matrix materials. As a third parameter the surface treatment of the filler was involved in this study.

EXPERIMENTAL

The materials that were used as the constituents of the composites are listed in *Table 1*. The mean particle size and the range of the particle size distribution of the rather small alumina beads were determined with a Philips 515 scanning electron microscope. For the glass beads, these data were obtained with a Cambridge MK2A scanning electron microscope.

Because of the rather broad particle size distribution of the 4 μm glass beads, these particles were also analysed with a Coulter counter. The agreement between the results of the SEM and the Coulter counter was satisfactory.

The different polymers and fillers were mixed on a two-roll mill. The filler content was varied in the range of 0 to 25 vol%. In order to diminish mixing problems and to improve the dispersion of the alumina beads, master batches of the polymers filled with 30 vol% of alumina beads were mixed with the unfilled polymers on the mill to obtain the desired composites.

The master batches were made in the following way. A certain amount of polymer was dissolved in a slightly polar solvent. The 30 vol% of alumina beads was added and the mixture was stirred for a few hours. The mixture was poured on to a large surface, and the solvent was allowed to evaporate overnight. Finally the master batch was dried at 100°C under vacuum.

The solvent used for polystyrene (PS) and styrene–acrylonitrile copolymer (SAN) was ethylene acetate, and methylene chloride was applied to dissolve polycarbonate (PC). Because of the absence of an easy to use, slightly polar solvent for polypropylene (PP), no alumina composites of this material were produced.

Owing to the non-polar character of PS and PP the interfacial adhesion between these polymers and the filler is very poor. In the case of SAN and PC a noticeable physical interfacial adhesion is present. For this reason separate experiments were performed in which the adhesion between the polymers PC and SAN and the filler was decreased by a pretreatment of the glass beads with siloxane DF 1040 (General Electric Plastics). The procedure to apply this coating was similar to a procedure reported elsewhere[17].

In another series of experiments with PC and SAN

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Table 1 Applied matrix and filler materials. The processing temperature of the polymers is indicated as T_p. The mean diameters of the filler particles are given, as well as the range of particle sizes

Matrix materials		T_p (°C)
Polystyrene	Styron 634 (Dow Chemical)	190
Polystyrene	XZ 86609.02 (Dow Chemical)	190
Styrene–acrylonitrile copolymer	Tyril 867E (Dow Chemical)	190
Polycarbonate	Makrolon 2405 (Bayer)	240
Polypropylene	HM6100 (Shell)	190

Filler materials	Diameter (μm)	Range (μm)
Alumina beads (Buehler)	0.035	0.03–0.04
Alumina beads (Buehler)	0.4	0.1–0.7
Glass beads (Louwers)	4	1–10
Glass beads (Tamson)	30	10–50
Glass beads (Tamson)	100	80–110

extremely good interfacial adhesion was obtained by the use of coupling agents. In the case of PC γ-aminopropylsilane (Union Carbide, A-1100)[17] was applied. The following pretreatment with vinylbenzyltrimethoxysilane (Dow Corning, Z-6032)[18] was performed in the case of SAN.

To a suspension of 100 g of glass beads in 200 ml of methanol, 30 ml of Z-6032 and 2 ml of concentrated hydrochloric acid were added. This mixture was stirred for 1 h, after which it was centrifuged to obtain a sediment of glass beads. The sediment was washed with 200 ml of methanol, centrifuged again and pre-dried at room temperature. The glass beads were dried for 1 h under vacuum at 130°C.

Tensile bars were machined from compression-moulded sheets, in accordance with ASTM D638. The tensile tests were performed on an Instron tensile tester, which was equipped with an extensometer ($l_0 = 50$ mm), at a strain rate of $0.02\,\mathrm{min}^{-1}$. The polystyrene, the styrene–acrylonitrile copolymer and the polycarbonate composites were annealed for 24 h at 80°C.

Micrographs of fracture surfaces were taken with a Cambridge scanning electron microscope (SEM) in order to check the dispersion of the alumina beads.

RESULTS AND DISCUSSION

Dispersion of alumina beads

The presence of agglomerates of filler particles can have an enormous effect on the Young's modulus of a composite material[7]. In the case of inclusion of matrix material by the agglomerates, the apparent volume fraction of the filler will be much higher than the actual filler content. For this reason extra attention was paid to the dispersion of the filler materials in the different polymers, resulting in a special mixing method for the alumina beads (see 'Experimental' section).

The dispersion of the alumina beads was checked by taking micrographs of fracture surfaces with the SEM. A micrograph of polycarbonate filled with 0.035 μm alumina beads is shown in *Figure 1*. In this case, as well as in all other cases, the dispersion was excellent.

Young's modulus

The experimentally determined Young's moduli of the different composites are plotted as a function of the volume fraction of the filler in *Figures 2–9*. In these plots the predictions according to the modified Kerner equation are represented as broken curves. The modified Kerner equation is expressed as:

$$E_c = E_1 \frac{1 + AB\phi}{1 - B\psi} \qquad (1)$$

with

$$A = \frac{7 - 5\nu_1}{8 - 10\nu_1} \qquad B = \frac{(E_2/E_1) - 1}{(E_2/E_1) + A}$$

$$\psi = 1 - \exp\left(\frac{-\phi}{1 - (\phi/\phi_m)}\right) \qquad (2)$$

where E is Young's modulus; the subscripts c, 1 and 2 refer to the composite, the polymer and the filler, respectively; ν is Poisson's ratio; ϕ is the volume fraction of the filler; and ϕ_m is the maximum packing density.

The data needed for the calculations are listed in *Table 2*. As the Young's moduli of glass and alumina are both very large compared to the moduli of the polymer matrices, the differences in the calculations with respect to the two filler materials are negligible.

It is quite obvious from *Figures 2, 4* and *5* that in the case of PS, PC and PP composites containing pure glass and alumina beads, there is a strong tendency of the Young's modulus to increase with decreasing particle size of the filler. As the 95% accuracy interval of each data

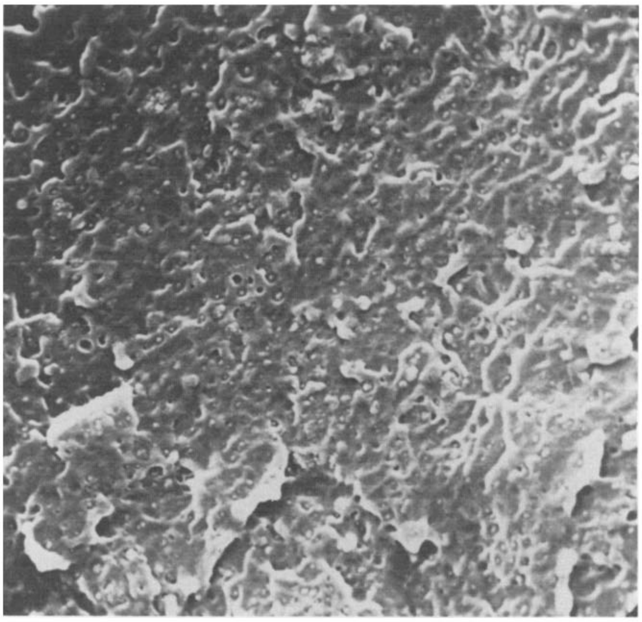

Figure 1 Fracture surface of polycarbonate filled with 0.035 μm alumina beads

Table 2 Data needed for the calculations with the modified Kerner equation

Material	Young's modulus (MPa)	Poisson's ratio
PS	3 450	0.34
SAN	3 800	0.33
PC	2 150	0.38
PP	1 560	0.42
Glass	70 000	0.22
Alumina	200 000	0.22

Maximum packing density $\phi_m = 0.64$ (random close packing)

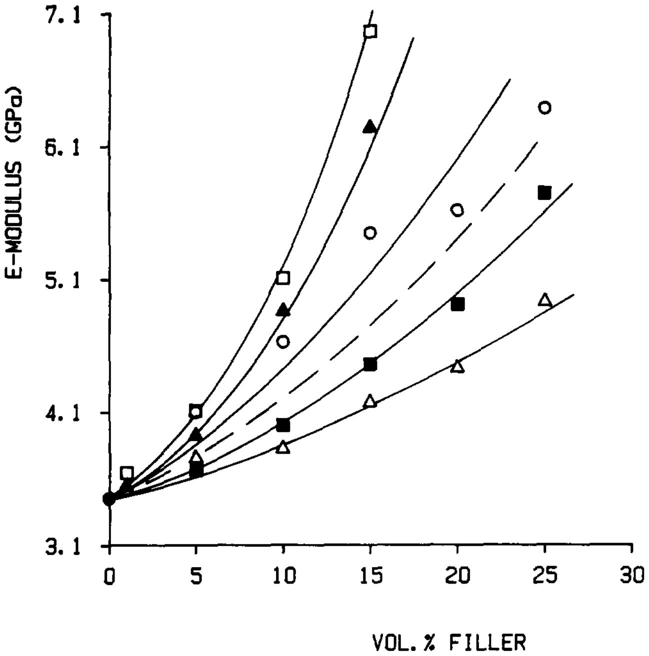

Figure 2 The Young's modulus of PS filled with 0.035 μm (□), 0.4 μm (▲), 4 μm (○), 30 μm (■) and 100 μm (△) particles as a function of the filler content. The broken curve represents the calculations according to the modified Kerner equation. Pure PS is indicated as ●

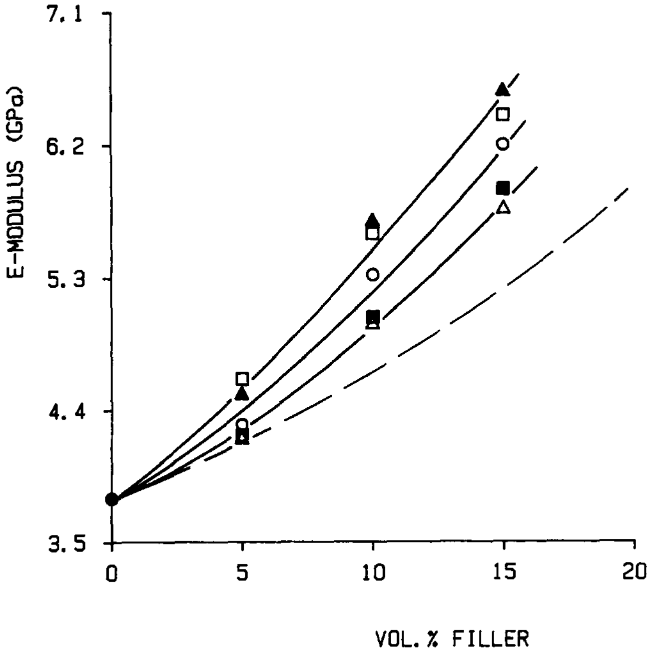

Figure 3 The Young's modulus of filled SAN. Points as in *Figure 2*

point is about ±5% of the measured value, this tendency certainly cannot be explained by experimental errors.

From comparison with the model predictions it appears that in the case of the 30 μm beads the agreement is fair, but smaller filler particles render much higher values, and larger filler particles render lower experimental values.

In the case of the SAN composites the particle size dependence of the Young's modulus is much less strong, but still noticeable. From this it can be concluded that the observed tendency is a common feature of all four examined polymers in the case of untreated fillers. However, *Figures 6, 7, 8* and *9* clearly show that the particle size dependence is absent in the case of either perfect or very poor adhesion, resulting from a silane pretreatment.

A number of explanations have been reported in the literature[17,19–21] that deal with a particle size dependence of the Young's modulus. These explanations will be discussed below.

Adsorption of additives. Commercial polymers generally contain mineral oils and other low-molecular-weight materials (additives), which have the effect of

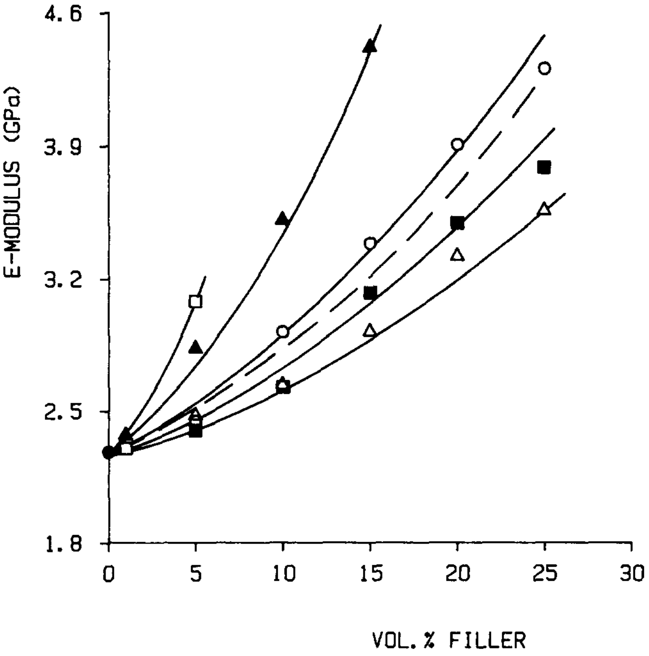

Figure 4 The Young's modulus of PC filled with 0.035 μm (□), 0.4 μm (▲), 4 μm (○), 30 μm (■) and 100 μm (△) particles as a function of the filler content. The broken curve represents the calculations according to the modified Kerner equation. Pure PC is indicated as ●

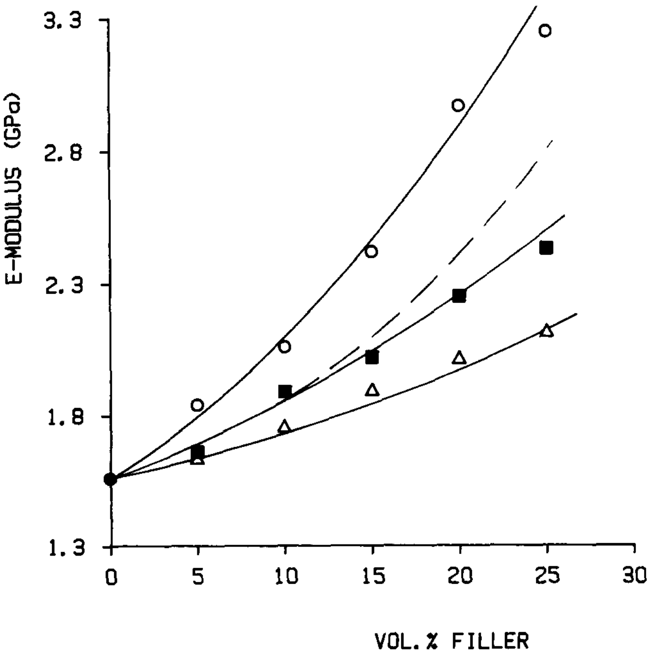

Figure 5 The Young's modulus of filled PP. Points as in *Figure 4*

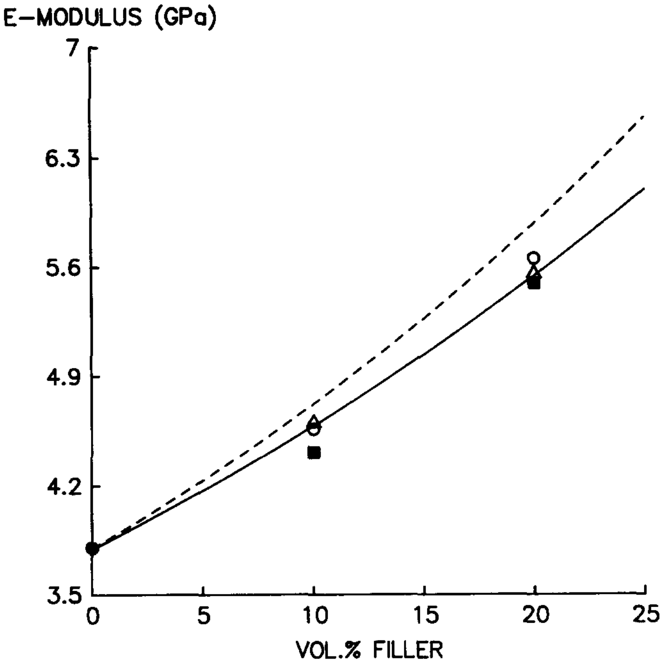

Figure 6 The Young's modulus of SAN filled with excellently adhering glass beads: 4 μm (○), 30 μm (■) and 100 μm (△). The broken curve represents the calculations according to the modifier Kerner equation. Pure SAN is indicated as ●

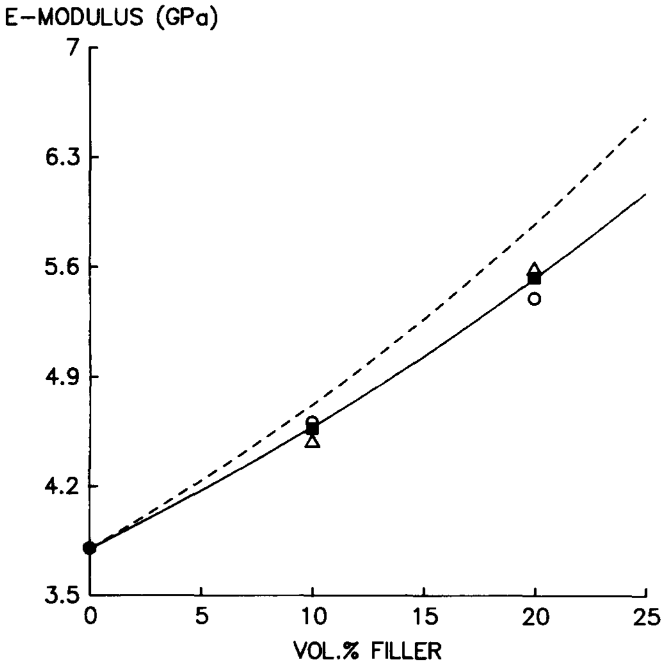

Figure 7 The Young's modulus of SAN filled with poorly adhering, DF 1040 treated, glass beads. Points as in *Figure 6*

diminishing the Young's modulus of the polymer as a whole. If these additives were extracted from the polymer matrix because of adsorption at the free surface of the filler particles, the Young's modulus of the polymer matrix would increase. As the specific surface is inversely proportional to the radius of a filler particle, the effect of the extraction and adsorption would increase with decreasing filler particle size. For this reason a higher Young's modulus would be obtained in the case of smaller filler particles.

In order to check if this hypothesis forms an explanation for the observed experimental results, a series of separate experiments was performed. In this case a special batch of polystyrene (XZ 86609.02, Dow Benelux), which contains no additives but is otherwise identical to Styron 634, was used as the matrix material. As clearly appears from *Figure 10*, where the Young's modulus of this special PS filled with 4 and 100 μm glass beads is plotted as a function of the filler content, in this case the same particle size dependence is also present. Therefore, an explanation based on the adsorption of additives can be ruled out.

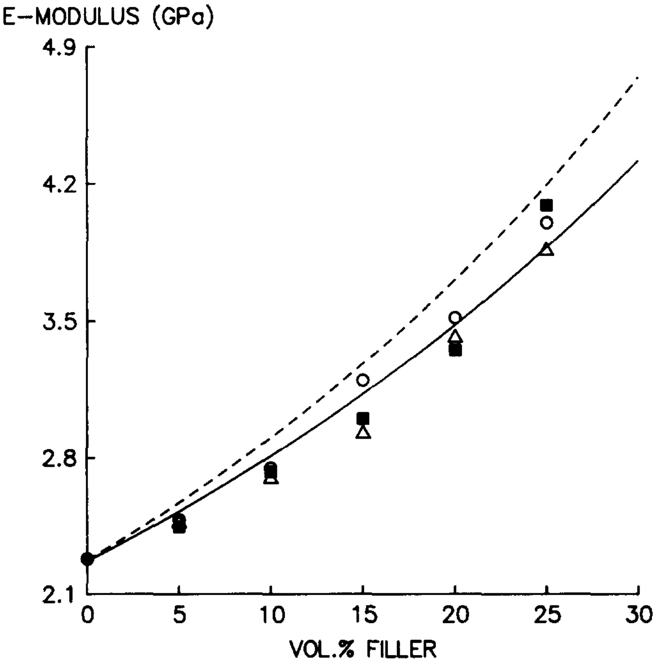

Figure 8 The Young's modulus of PC filled with excellently adhering glass beads: 4 μm (○), 30 μm (■) and 100 μm (△). The broken curve represents the calculations according to the modified Kerner equation. Pure PC is indicated as ●

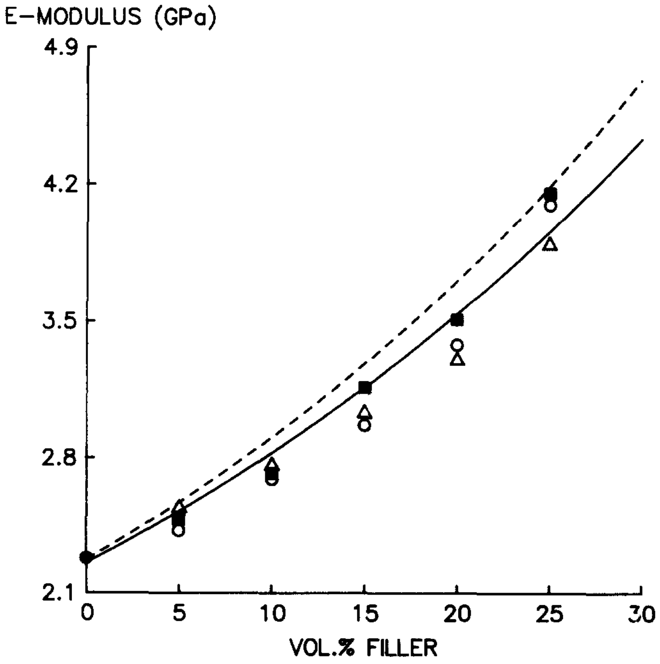

Figure 9 The Young's modulus of PC filled with poorly adhering, DF 1040 treated, glass beads. Points as in *Figure 8*

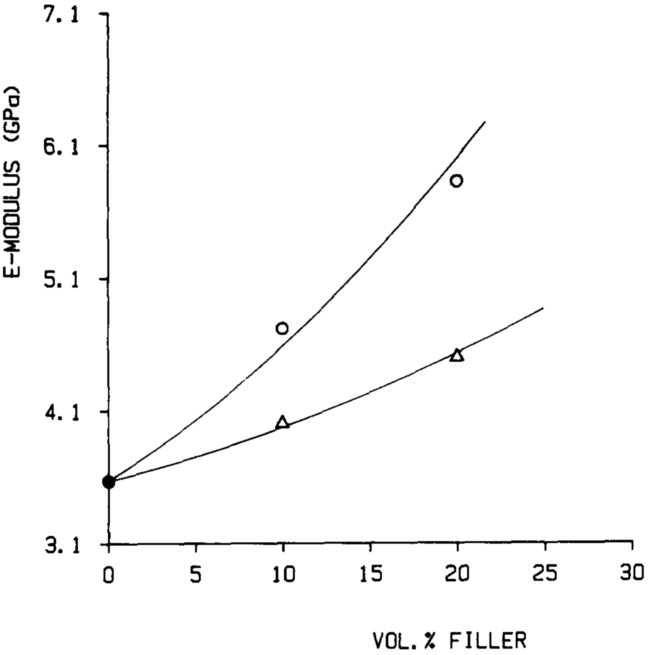

Figure 10 The Young's modulus of 'special PS' (PS that contains no additives) filled with 4 μm (○) and 100 μm (△) glass beads as a function of the filler content

Particle size distribution[7]. The parameter that is affected by the particle size distribution of the filler is the maximum packing fraction ϕ_m. A narrow particle size distribution leads to a lower value of ϕ_m than a broad particle size distribution. Nielsen and Lewis have derived an equation that links ϕ_m to the Young's modulus of a composite[7]. However, as the composites were prepared from the same feedstocks of fillers in the case of both pure as well as surface-treated beads, it can be concluded that the particle size distribution cannot be responsible for the anomalous behaviour of the Young's modulus.

Dewetting. As has been reported in a previous study[22], in the case of poor adhesion between the filler and the polymer, the dewetting stress depends on the particle size of the filler. From this point of view it could be argued that in the case of the larger filler particles the measurement of the Young's modulus is confused due to the fact that in a very early stage of the tensile test the process of dewetting takes place.

However, as also mentioned in that report, even in the case of the largest filler particles (100 μm) the stress at which dewetting occurs could easily be determined from the stress–strain diagram and the Young's modulus was measured below the dewetting stress. Besides, if this explanation were to be valid, the experimentally determined Young's moduli of SAN and PC containing extremely poor adhering glass beads should also be dependent on the filler particle size. As appears from *Figures 8* and *9*, this is not the case.

Morphology of the matrix. As has been reported by other investigators[20,21,23–29] there is reason to believe that the morphology of the polymer matrix is affected by the presence of pure filler particles. In the present study, that the free surface of an inorganic substance is responsible for the observed effects is indicated by the absence of modulus variation when the glass beads are treated with silanes. Although the possibility of molecular order in amorphous polymers has been the subject of extensive debate[30], in a recent report Cervinka *et al.*[31] conclude from neutron scattering results of amorphous PC that a large portion of roughly parallel short sequences exists in the bulk amorphous state. If it is assumed that the local parallelization of polymer molecule segments is favoured at the pure, untreated filler surface, the following explanation could be derived.

When a thermoplastic is cooled down from the melt a solidification process will take place. If it is assumed that the polymer adjacent to the embedded particles contracts in an earlier stage of the process because of a more favourable orientation of the molecules than the material in the bulk, a zone with a higher density will be formed around the particles. Owing to transportation processes a depletion zone with a relatively low density will be created surrounding the high-density zone. According to Van Krevelen[32] the density (ρ) is correlated to the Young's modulus (E):

$$E \propto \rho^7 \tag{3}$$

This means that the starting zones, which have a higher density, have a higher Young's modulus, and the depletion zones, which have a lower density, have a lower modulus.

The filler particles can act as initiation sites of the solidification process, and for this reason they could be surrounded by an enriched layer of polymer with an increased modulus (high-modulus layer), around which a zone of material with a lower modulus (low-modulus zone) is found.

The effects of this morphology on the Young's modulus of a filled polymer with respect to the filler particle size will be explained by discussing the two extremes: very large filler particles and very small filler particles. Of course, an intermediate particle size will cause a combination of both effects.

Figure 11 gives a representation of the morphology surrounding a large filler particle. The effect of the high-modulus layer is that the volume fraction of the filler is apparently increased. But, because of the fact that the thickness of the layer is very small compared to the

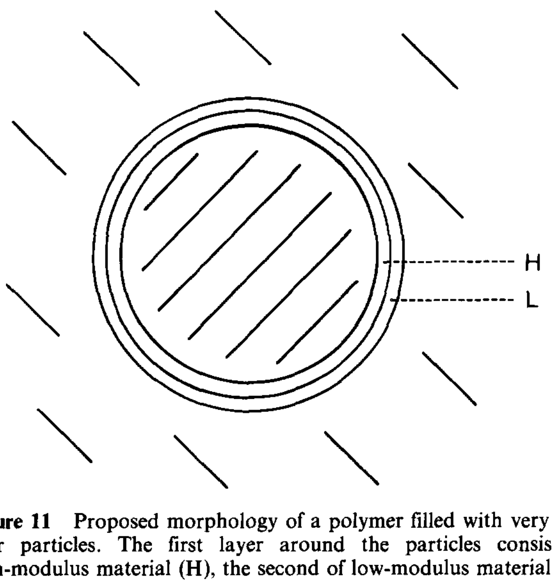

Figure 11 Proposed morphology of a polymer filled with very large filler particles. The first layer around the particles consists of high-modulus material (H), the second of low-modulus material (L)

radius of the filler particle, this increase in volume fraction is negligible.

On the other hand, from calculations of Matonis and Small[33] it appears that even a very thin layer of low-modulus material surrounding a filler particle has a significant lowering effect on the Young's modulus of the composite.

A combination of these two effects leads to the conclusion that in the case of large filler particles the described morphology has a decreasing effect on the Young's modulus of the material.

When very small particles are applied as a filler material, a gigantic number of starting points for the thermal contraction process is present. In that case this process takes place more or less homogeneously and a nearly homogeneous, high-modulus material is created.

For this reason a very high Young's modulus is obtained in the case of a composite filled with very small filler particles.

In order to find out if this hypothesis explains not only qualitatively but also quantitatively the observed differences in the Young's moduli, some calculations were performed, using filled PS as an example.

If it is assumed that the situation of a nearly homogeneous high-modulus matrix material is reached in the case of the composites filled with the untreated 0.035 μm alumina beads, it is possible to make an estimation of the Young's modulus of this high-modulus material. With the modified Kerner equation it can be calculated that in order to obtain a Young's modulus of about 7000 MPa in the case of PS filled with 15 vol% of 0.035 μm alumina beads, the Young's modulus of the polymer matrix, which is assumed to be the high-modulus material, has to amount to about 6000 MPa. From equation (3) it appears that the density of the high-modulus material should therefore be approximately 10% higher than the density of 'normal' PS. The density of the material in the depletion zones in the case of PS filled with large filler particles (e.g. the 100 μm glass beads) should therefore be 10% lower than the density of 'normal' PS, which results in a Young's modulus of about 1700 MPa for this material.

If it is assumed that the thickness of the two layers adjacent to the filler particles is of the order of magnitude of 1 to 5 μm, a Young's modulus of an apparent filler, consisting of 100 μm glass beads surrounded by a high- and a low-modulus layer of which the thickness is 3 μm, can be calculated with the simple series model[34].

The Young's modulus of this layered system appears to be about 15000 MPa, which is considerably lower than the 70000 MPa of pure glass. Owing to the presence of the two layers the volume fraction of the apparent filler is slightly higher than that of the pure glass beads, but this may be compensated by a small increase in the maximum packing fraction because of the more deformable character of the apparent filler. For this reason the volume fraction of the 100 μm glass beads and the volume fraction of the apparent filler are considered to be identical.

The Young's moduli of PS filled with pure glass beads ($E = 70000$ MPa) and of PS filled with the layered system ($E = 15000$ MPa) are calculated with the modified Kerner equation. In *Figure 12* the calculated values are shown and from comparison with the experimental results of PS filled with untreated 100 μm glass beads it appears that the agreement between the experimental results and the calculated values on the basis of the two-layer system is very satisfactory. In fact the calculated values approximate the experimental results within the limits of the experimental error (about 5%).

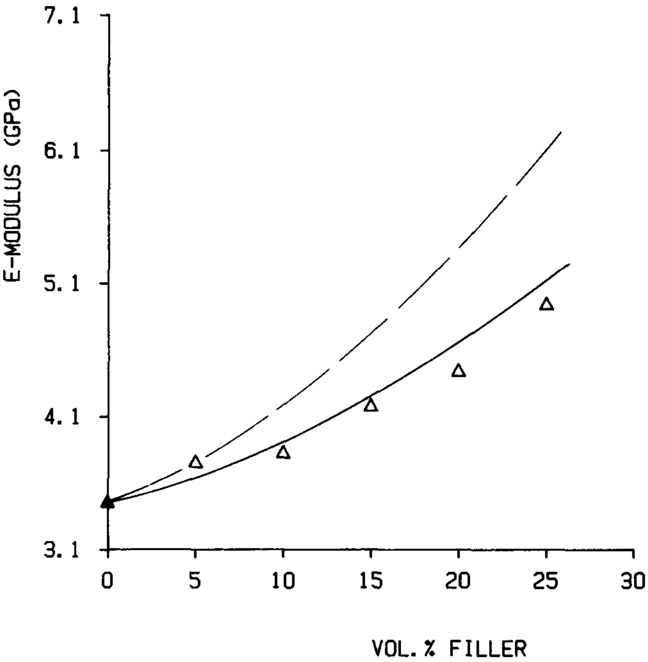

Figure 12 The calculated Young's moduli of PS filled with pure glass beads ($E = 70000$ MPa), indicated as the broken curve, and of PS filled with the layered system ($E = 15000$ MPa), indicated as the full curve, compared with the experimental results of PS filled with 100 μm glass beads (△)

From the calculations it appears that the hypothesis of the special morphology caused by the presence of pure filler particles could explain the experimentally observed behaviour, but it has to be stated that it is still based on speculations. In the next report, experimental results sustaining this hypothesis will be discussed.

CONCLUSIONS

The Young's modulus of four polymers (PS, SAN, PC and PP) filled with pure, untreated glass or alumina beads appeared to be dependent on the particle size of the filler. The effect of the particle size is considerable: at a constant volume fraction of filler the difference between the increase in Young's modulus caused by the smallest applied particles (0.035 μm) compared to the increase caused by the largest applied particles (100 μm) could amount to 300%. However, experimentally a particle-size-independent Young's modulus was found when the surface of the filler particles was pretreated with a silane compound (causing either excellent or very poor adhesion).

Four different explanations for this behaviour, which is in contradiction with all the models and equations proposed in the literature, have been discussed. Three of the explanations could be ruled out. The remaining explanation is that the solidification of the matrix is locally activated at a free filler particle surface. This hypothesis is still speculative, and therefore further research is necessary upon this subject.

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