Interfacial debonding in polyamide-6/glass bead composites

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Debonding of glass beads from a polyamide-6 matrix during tensile deformation has been studied using the volume–strain method. It is shown that stress and strain at the debonding point decrease with increasing filler concentration. Improvement of the interfacial adhesion by a coupling agent enhances the tensile strength but the elastic constants of the composite remain constant and can be described by existing theories. Cyclic tests show that both the E modulus and Poisson's ratio decrease sharply if debonding has taken place previously. A model is proposed which describes the elastic behaviour of a composite with both bonded and debonded filler particles.

(Keywords: polyamide-6; glass; composites; adhesion; silane; volume–strain)

INTRODUCTION

During the last few years there has been a rapid increase in the structural applications of filled thermoplastics, especially polyamides[1]. The presence of a filler can often lead to significant improvements in the load bearing capabilities of the polymer. The number of fillers available is extensive and ranges from cheap mineral fillers such as talc or glass beads to the advanced high-strength fibres such as carbon. The influence of the filler on the mechanical properties of the matrix is highly dependent on the quality of the adhesion between the two phases. This is illustrated here with a number of polyamide-6/glass bead composites. The interfacial adhesion between matrix and filler has been modified using an aminosilane, a well known coupling agent[2]. The effect on the mechanical properties of the composites has been examined using the volume strain method.

It has been observed by several authors[3–5] that coupling agents did not affect the elastic constants of composites and the conclusion has been drawn that the Young's modulus of a particle-reinforced polymer is not affected by the interfacial adhesion[1]. However, it is intuitively clear that a composite with fully debonded filler particles must have a lower modulus than a composite with a well bonded filler or than the unfilled matrix. This is confirmed here by measurements of the elastic constants of glass-bead-filled polyamide-6 which had been strained beyond the debonding point in a previous experiment. Moreover, a model is proposed which describes the E-modulus and Poisson's ratio of a matrix with both bonded and debonded rigid spheres.

MATERIALS AND METHODS

The polyamide-6 used was Akulon K123 from Akzo. The glass beads were Potters Ballotini 3000 without any surface treatment. The glass beads have a diameter between 20 and 50 μm. The samples were compounded on a Brabender single screw Stiftextruder. Dumbbell shaped tensile bars (ISO I, cross section 9.8 × 3.8 mm) were injection moulded after standard drying procedures (16 h at 110°C *in vacuo*). A series of composites have been prepared using four different concentrations of glass beads (approximately 10, 20, 30 and 40% by weight) either without coupling agent or with 0.3% γ-aminopropyl-triethoxysilane (γ-APS), obtained from Jansen Chimica. All tensile strain and volume strain experiments were performed on a Zwick 1474 tensile tester. The volume changes of the sample were measured by the continuous determination of the three dimensions of the test bar[6]. A Zwick analogue extensometer was used to measure the elongational strain. Two transverse strain sensors (Instron-2640) were used for monitoring the contraction of the width and the thickness of the sample. If the analysed material is isotropic, it is sufficient to use only one transverse extensometer, because both relative transverse contractions are equal. All tensile experiments were performed at a constant strain rate of 5%/min unless otherwise stated.

RESULTS

Tensile experiments

Stress–strain curves of polyamide-6 filled with different amounts of glass beads but without coupling agent are shown in *Figure 1a*. All test bars were dry as moulded. The figure shows that the maximum obtainable stress decreases with increasing volume fraction of the glass present in the samples (see *Table 1*). The opposite is true if 0.3% of the coupling agent γ-APS is added as can be seen in *Figure 1b*. In that case the tensile stress is increased by the addition of the glass beads. However, the γ-APS seems to have no influence on the Young's or E-modulus of the composite (i.e. the slope of the stress–strain curve at small strains). In both series of composites the E-modulus increases with the amount of glass beads according to the models of Kerner[7] and Chow[8]. This model has been compared with the experimental E_c values and the agreement is very good, irrespective of the presence of the silane (see *Tables 1* and *2*).

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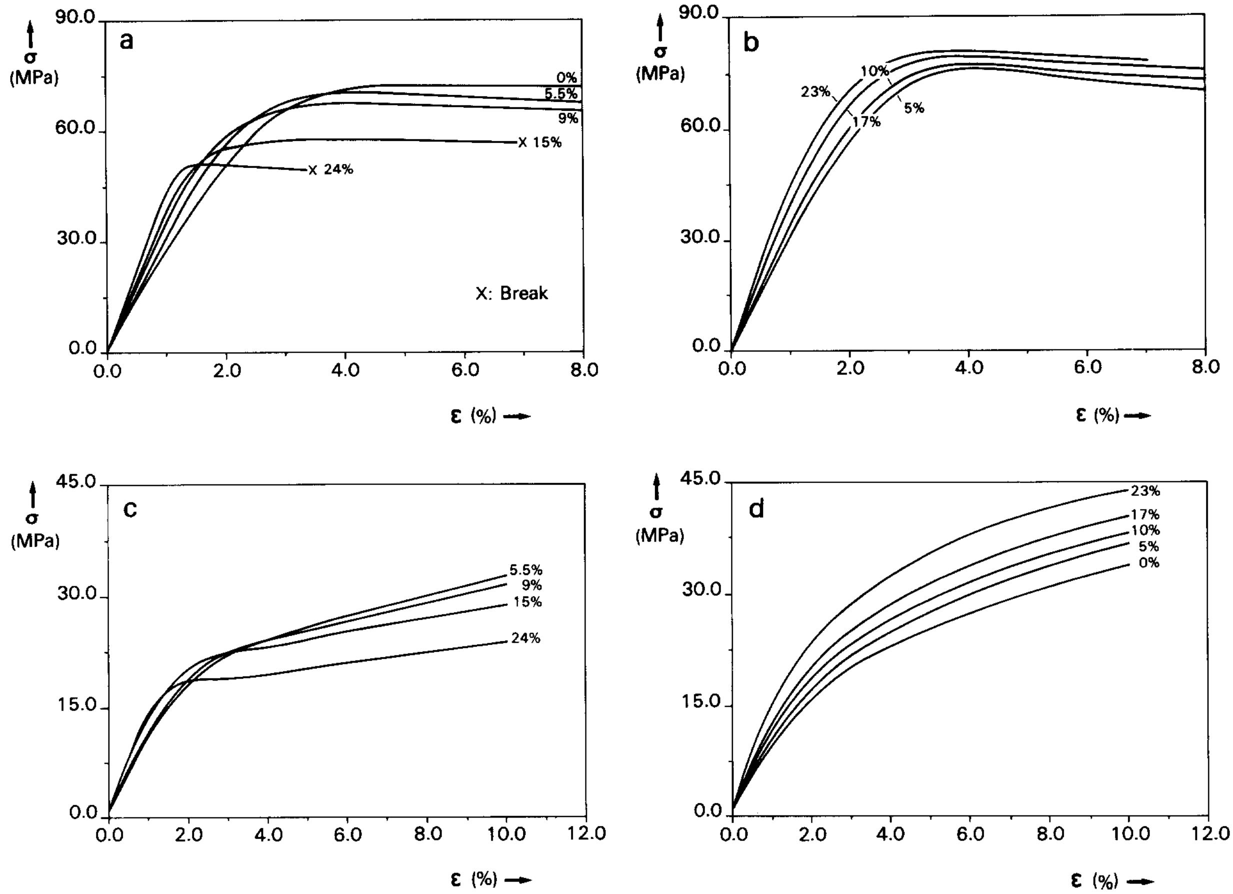

Figure 1 Tensile engineering stress–strain curves of PA-6 filled with different concentrations of glass beads. Dry as moulded: (a) no silane; (b) +0.3% silane. Conditioned at 23°C/50% r.h.: (c) no silane; (d) +0.3% silane

Table 1 Young's modulus and tensile strength of polyamide-6/glass bead composites. $E_{\text{theor.}}$ is the theoretical modulus of the composite using the Kerner–Chow equation[7,8]. Samples dry as moulded

Vol% glass beads	% γ-APS	E (GPa)	σ_y (MPa)	$E_{\text{theor.}}$ (GPa)
0	–	2.80	72.6	–
5.5	–	3.21	71.0	3.16
9.0	–	3.55	68.1	3.42
15.0	–	3.90	59.1	3.90
23.5	–	4.54	51.1	4.72
0	0.4	2.80	72.7	–
5.4	0.3	3.20	76.1	3.16
9.8	0.3	3.48	77.7	3.48
17.4	0.3	4.17	79.3	4.12
23.0	0.3	4.63	80.4	4.64

Table 2 Young's modulus and tensile strength of polyamide-6/glass bead composites. $E_{\text{theor.}}$ is the theoretical modulus of the composite using the Kerner–Chow equation[7,8]. Samples conditioned at 23°C/50% r.h.

Vol% glass beads	% γ-APS	E (GPa)	σ ($\varepsilon = 10\%$) (MPa)	$E_{\text{theor.}}$ (GPa)
0	–	0.98	34.0	–
5.5	–	1.13	32.6	1.12
9.0	–	1.24	31.5	1.21
15.0	–	1.54	28.7	1.40
23.5	–	1.73	23.7	1.71
0	0.4	0.98	34.1	–
5.4	0.3	1.02	36.8	1.12
9.8	0.3	1.25	38.3	1.24
17.4	0.3	1.38	40.5	1.48
23.0	0.3	1.73	44.0	1.69

It must be pointed out that it has been confirmed that γ-APS has no influence on the tensile properties of unfilled polyamide-6 in the absence of glass beads (*Tables 1* and *2*).

The mechanical properties of polyamide-6 are highly sensitive to the amount of water present in the sample[9–11]. The glass transition temperature as determined with dynamic mechanical analysis at 1 Hz decreases from +65°C in the dry state to +15°C if the sample has been conditioned at 50% r.h./23°C. Thus at room temperature the amorphous domains of the semicrystalline polyamide-6 change from the glassy state to domains with almost rubber-like behaviour. The effects of glass beads and γ-APS on the stress–strain curves of polyamide-6 in the conditioned state can be seen in *Figures 1c* and *1d*. Although the E-modulus and tensile strength of all samples are on a significantly lower level due to the plasticizing effect of the absorbed water, the same conclusions can be drawn as for the as-moulded state. The tensile strength of the matrix either increases or decreases with increasing concentration of glass beads depending on the presence of the coupling agent γ-APS. Again the E-modulus of the composite is not affected by the γ-APS and is in perfect agreement with the model of Chow[8]. Note that both the E-modulus and the Poisson's ratio of the matrix have changed as a result of the conditioning. E_m decreases from 2.8 GPa to 0.98 GPa and υ_m increases from 0.39 to 0.47, which reflects the more rubber-like behaviour of the amorphous part of the matrix in the conditioned state.

Volume–strain analysis

Volume–strain curves have been recorded for all composites mentioned before, both in the dry (*Figure 2a* and *b*) and conditioned (*Figure 2c* and *d*) state in order to detect the moment of debonding during the tensile test. A few samples showed nonhomogeneous deformation ('necking') beyond a certain strain level. This means, that at higher strains the volume of the test bar can no longer be determined using extensometers and, as a consequence, the experiment was stopped. These points have been marked in the figures.

It is striking that the initial slope of the volume–strain curve is hardly affected by the volume fraction of the filler. For isotropic materials $\Delta V/V=(1-2\upsilon)\varepsilon$ it appears that the Poisson's ratio of the composite is not very sensitive to the filler fraction, although the Poisson's ratio of glass and matrix are quite different ($\upsilon_f=0.25$, $\upsilon_m=0.39$ (dry) or 0.47 (conditioned)). However, because the glass is rigid compared to the polymer, υ_f only has a minor influence on υ_c, which is also predicted by Chow[8].

The volume–strain experiments make clear that it is the debonding of glass beads which is responsible for the lower stresses observed in the composites without γ-APS.

When two composites with the same volume fraction of glass beads with and without γ-APS are compared, they show the same stress–strain and volume–strain behaviour at low strains. This means that the elastic behaviour (*E* and υ) is not changed by the silane. However, at a certain elongational strain the volume–strain in the composite without γ-APS increases far more rapidly. This is coupled with a lower stress build-up. Apparently all the glass beads are initially well bonded but start to debond at a certain strain thereby creating interfacial voids. The stress and the strain at which the first signs of debonding can be observed are listed in *Table 3*. It appears that the stress as well as the strain at which debonding starts decreases when the filler fraction is increased. After conditioning of the composites at 50% r.h./23°C the same tendency can be observed although the stress at debonding is significantly lower. The debonding strain, however, is far less influenced.

It is known that water can influence the matrix–filler adhesion[2]. However, it appears that in the conditioned state, when the composites contain approximately 2.5% water the glass beads also remain bonded in the strain interval examined, provided that γ-APS was added. The

Table 3 Stress and strain at the moment the glass beads start to debond from the polyamide-6 matrix (no silane added)

Vol% glass beads	$\sigma_{\text{debonding}}$ (MPa)	$\varepsilon_{\text{debonding}}$ (%)
Samples dry as moulded		
5.5	57.4	2.0
9.0	55.0	1.75
15.0	48.1	1.35
23.5	45.9	1.10
Samples conditioned at 23°C/50% r.h.		
5.5	21.9	3.0
9.0	20.0	2.25
15.0	17.6	1.60
23.5	13.3	0.90

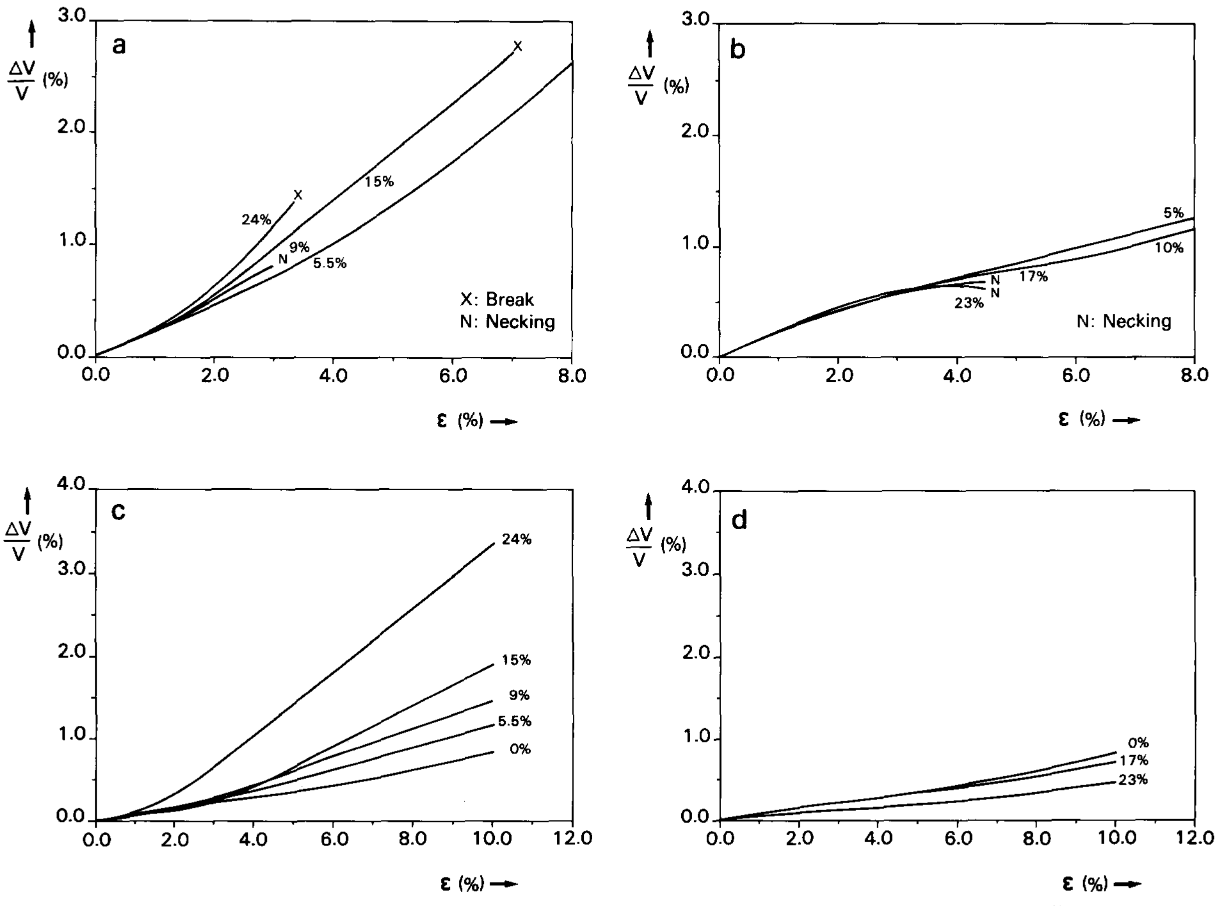

Figure 2 Volume–strain curves of PA-6 filled with different concentrations of glass beads. Dry as moulded: (a) no silane; (b) +0.3% silane. Conditioned at 23°C/50% r.h.: (c) no silane; (d) +0.3% silane

bare glass beads remain bonded as well, considering the measured E-modulus and Poisson's ratio, but they start to debond at about the same strain as in the dry state.

Cyclic experiments

The volume–strain curve of polyamide-6 filled with 16 vol% glass beads (conditioned at 50% r.h./23°C) is shown in *Figure 3* (curve a). No silane was added and debonding starts at approximately 2% strain causing an extra volume–strain. The experiment was stopped when the specimen was strained to 7% and afterwards the stress was removed. The sample was then allowed to relax. After 12 h there was still 1.8% strain left. This can be considered as permanent, irreversible strain. The volume–strain appears to be completely reversible, which means that the permanent strain does not cause any detectable volume change and can be considered to be the result of shear deformation[12]. Moreover, it appears that all the interfacial voids that have been created during the deformation have disappeared. The question arises as to whether the interfacial adhesion has been fully restored. This is definitely not the case, as can be concluded from a subsequent volume–strain test with the same specimen (*Figure 3*, curve b). There it appears that the slope of this curve is increased at low strains and equals the slope of the first volume–strain curve at higher strains which was characteristic for debonded glass beads. If we look at the corresponding stress–strain curves as shown in *Figure 4*, it also appears that the Young's modulus of the composite has decreased dramatically as a result of the first test.

On the basis of the same principle, we performed a number of subsequent cyclic volume–strain experiments. Starting with a new sample, the test bar was deformed to a fixed strain level and after removal of the stress the material was given 15 min to relax. The experiment was then repeated, so that each time the maximum extension is increased. Stress–strain as well as volume–strain curves were recorded continuously. In this way the dependence of the E-modulus and the Poisson's ratio on the prestrain (i.e. the maximum strain the sample has had during a previous experiment) can be determined.

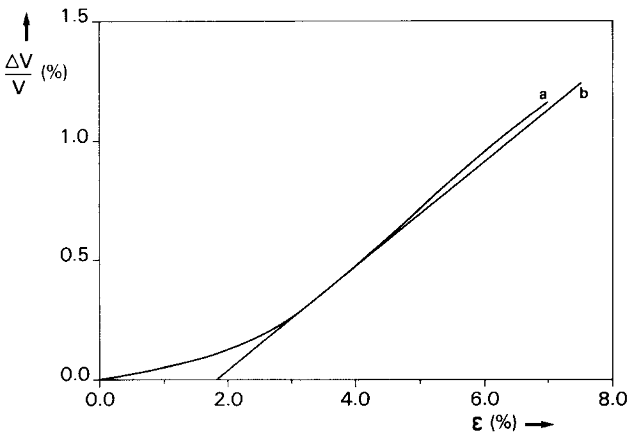

Figure 3 Two subsequent volume–strain curves of PA-6 filled with 16% glass beads (conditioned 50% r.h.). Curve a, new specimen, no strain history; curve b, subsequent test with same specimen (7% prestrain)

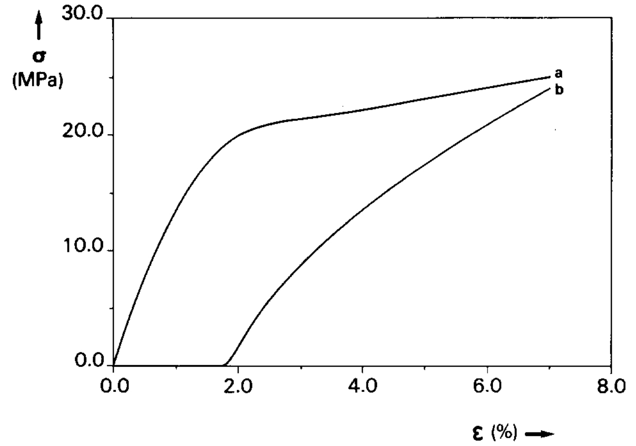

Figure 4 Two subsequent engineering stress–strain curves of PA-6 filled with 16% glass beads (conditioned 50% r.h.). Curve a, new specimen, no strain history; curve b, subsequent test with same specimen (7% prestrain)

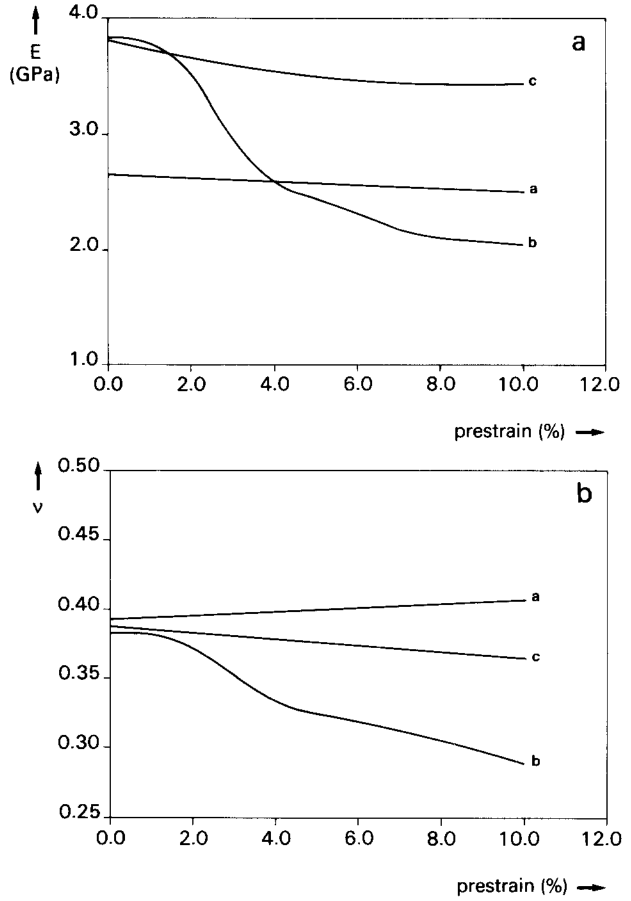

Figure 5 (a) Young's modulus and (b) Poisson's ratio as a function of prestrain of PA-6 composites (dry as moulded). Curve a, unfilled; curve b, filled with 16% glass beads; curve c, filled with 16% glass beads +0.3% silane

Unfilled polyamide-6 as well as polyamide filled with 16 vol% glass beads both without silane and with 0.3% γ-APS (all samples dry as moulded) have been analysed using these cyclic tests. Results are shown in *Figures 5a* and *5b*. The following conclusions can be drawn:

(1) Young's modulus and Poisson's ratio of unfilled polyamide-6 are hardly affected by a previous deformation.

(2) In the composite without silane a pronounced decrease of E and υ between 2% and 6% strain is observed. When the composite has been strained to more than 4% in a previous test, the E-modulus is even lower than the E-modulus of unfilled polyamide-6.

(3) The sharp decrease of both elastic constants is almost absent when a silane coupling agent is added.

Thus it appears that the elastic constants of a particle-filled composite are highly dependent on the interfacial adhesion. Once the filler particles are debonded they can not bear any stresses and therefore cause a reduction, rather than an increase, of the rigidity of the composite, which will almost behave like a polymer filled with pores. The decrease of the Poisson's ratio means that the regrowth of interfacial voids has already taken place at the beginning of the test at low strains, thereby creating an extra volume–strain.

The cube model

Mathematical models have been derived by Kerner[7] and Chow[8] which make it possible to calculate the elastic constants of a composite when the elastic constants of the two components and the shape and volume fraction of the filler are known. These models always assume perfect adhesion. We propose a simplified model that calculates the fraction of bonded and debonded (spherical) filler particles for a given E-modulus and the Poisson's ratio of the composite.

It is assumed that all filler particles can be divided into two groups: those that are firmly bonded to the matrix (φ_b) and those that are completely debonded (φ_d) and as a result are not able to carry any load. An illustration of this model is given in *Figure 6*. The composite is represented by a cube consisting of matrix polymer in which the well bonded beads are randomly dispersed. The debonded glass is thought to be situated in a small cube with volume fraction φ_d. When this imaginary composite is uniaxially strained, the cube φ_d and the column of material above will not support any load. In contrast a void will be created at the polymer/glass interface as is shown in *Figure 6b*. The elastic behaviour of the matrix filled with well bonded beads is described using the Chow model[8].

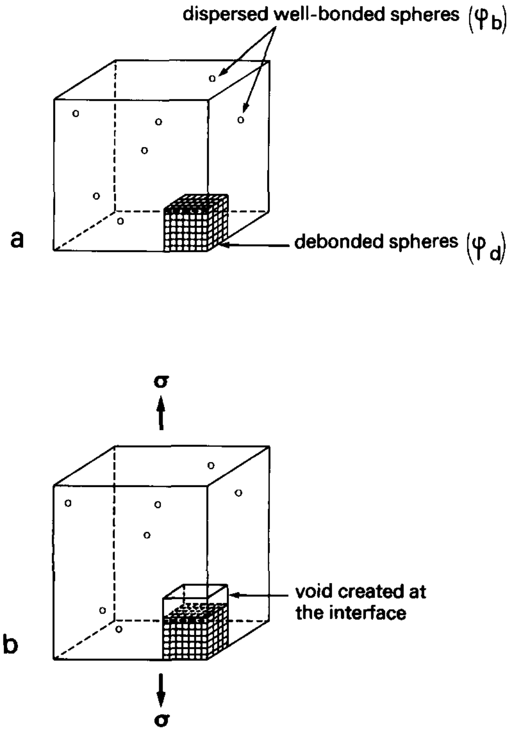

Figure 6 Schematic representation of the cube model describing the elastic behaviour of a composite with partially debonded rigid spherical filler particles

According to this model it follows that the entire stress (σ) must be carried by a reduced surface $1-\varphi_d^{2/3}$. Therefore the material experiences a higher effective stress (σ_{eff})

$$\sigma_{\text{eff}} = \frac{\sigma}{1-\varphi_d^{2/3}} \tag{1}$$

The E-modulus of the matrix filled with a fraction (φ_b) of well bonded glass beads is calculated using the Chow theory for rigid spheres ($E_f \gg E_m$) (ref. 8).

$$E(\varphi) = \left(1+\frac{\varphi_b}{\beta(1-\varphi_b)}\right)E_m \qquad \beta = \frac{8-10\upsilon_m}{15(1-\upsilon_m)} \tag{2}$$

where υ_m is the Poisson's ratio of the matrix.

The E-modulus of the entire composite (E_c) including the debonded beads, which is measured during a tensile test will be reduced accordingly:

$$E_c = (1-\varphi_d^{2/3})E(\varphi_b) \tag{3}$$

Further:

$$\varphi_b = \frac{\varphi_f-\varphi_d}{1-\varphi_d} \tag{4}$$

where φ_f is the total fraction of filler in the composite.

Because E_m, υ_m and φ_f are known constants for a given composite, the measurement of E_c is sufficient to calculate the fraction of glass beads that is debonded.

A similar calculation can be performed considering the volume–strain of the composite in the elastic region. The total volume–strain of the composite $(\Delta V/V)_c$ is the result of two mechanisms. First the matrix filled with the well bonded glass beads with Poisson's ratio $\nu(\varphi_b)$ is strained and will therefore cause a volume–strain:

$$\frac{\Delta V}{V}(\varphi_b) = (1-2\upsilon(\varphi_b))\varepsilon \tag{5}$$

The Chow theory[8] can again be used to calculate $\upsilon(\varphi_b)$:

$$\frac{1-2\upsilon(\varphi_b)}{E(\varphi_b)} = (1-2\upsilon_m)1\Big/\left[1+\frac{\varphi_b}{\gamma(1-\varphi_b)}\right]E_m \qquad \gamma = \frac{1+\upsilon_m}{3(1-\upsilon_m)} \tag{6}$$

Moreover, the interfacial void will cause an extra volume strain:

$$\left(\frac{\Delta V}{V}\right)_{\text{void}} = \frac{\varphi_d^{2/3}V_0\varepsilon}{V_0} = \varphi_d^{2/3}\frac{\sigma_{\text{eff}}}{E(\varphi_b)} \tag{7}$$

It follows:

$$\left(\frac{\Delta V}{V}\right)_c = \left(\frac{\Delta V}{V}\right)(\varphi_b) + \left(\frac{\Delta V}{V}\right)_{\text{void}} \equiv (1-2\upsilon_c)\varepsilon \tag{8}$$

Because E_m, υ_m and φ_f are known, the measurement of υ_c is sufficient to calculate the fraction of debonded filler particles together with equations (2) and (4).

The cyclic volume–strain and stress–strain experiments, described in the previous section produce values of the E-modulus and Poisson's ratio of the composite as a function of prestrain. Both quantities are determined independently, yet both must lead to the same value of φ_d. Thus we have a way to check whether this model gives a satisfactory description of a composite with a fraction of partially debonded glass beads.

Calculations of φ_d using the cube model

The results of the cyclic stress–strain experiments with polyamide-6/16 vol% glass beads with 0% and 0.3%

γ-APS (dry) as presented in *Figure 5* have been used to calculate the percentage of debonded glass beads in these composites as a function of prestrain. Calculations were performed according to the cube model as described above, using only the E-modulus of the composites. This was done with the help of a Fortran computer program running on a Harris H500 computer. The value of E_m used in the equations has been determined from the cyclic stress–strain experiment on the unfilled polyamide-6. The relative percentage of debonded glass ($\varphi_d/\varphi_f \times 100\%$) as a function of the maximum prestrain of these samples is presented in *Figure 7a*, together with the results for a conditioned sample of the same composite but without γ-APS. The curves show that in the unstrained samples all glass beads are still bonded. The two samples without γ-APS show debonding of most of the filler particles between 2% and 6% strain. In the composite which contains γ-APS the majority of the particles (80%) are still bonded. In *Figure 7b* results of similar calculations are shown but now based on the measured Poisson's ratio of the composites. In order for the cube model to give an adequate description, the curves of *Figure 7a* and *b* must coincide. However, due to experimental errors during the determination of E_c and υ_c deviations occur. Taking into account the relative error in both quantities, estimated to be 2% and 3%, respectively, we were able to calculate a best fit curve of φ_d/φ_f which is in agreement with both measured values E_c and υ_c. These results are presented in *Figure 7c*.

It appears that despite the few simplifying assumptions that were made the cube model is able to give a quantitative description of the debonding of rigid spherical filler particles.

Similar calculations were made for the composites containing different amounts of glass beads using the results of cyclic volume–strain experiments. The calculated curves are shown in *Figures 8a* and *8b*. Comparing the results for the dry and conditioned composites, they appear to be very similar, apart from the differences in elongation at break. However, if we consider the stresses at which debonding takes place there is a significant effect of the conditioning.

DISCUSSION

The stress–strain and volume–strain behaviour of polyamide-6 filled with different amounts of glass beads have been measured. In particular, the effect of γ-APS has been studied. It appears, that the E-modulus of all composites can be very well predicted using the models of Kerner[7] and Chow[8], which assume a perfect interfacial adhesion. Also the Poisson's ratio, and therefore the volume–strain, at low strains of the composite is not affected by the presence of the silane. It is the mechanical behaviour of the materials at higher elongations, which shows the importance of a good interfacial adhesion. The maximum stress which is reached during a tensile test is lowered, when the polyamide is filled with glass beads without the use of a silane. It was found that beyond the strain at which debonding of the glass beads starts, as detected by the volume–strain method, there is hardly any increase of the stress. The glass beads are not capable of carrying any stress once they become debonded and so the polymer matrix is weakened by the glass spheres. The stress and strain at which the debonding starts decreases with the volume fraction of the glass.

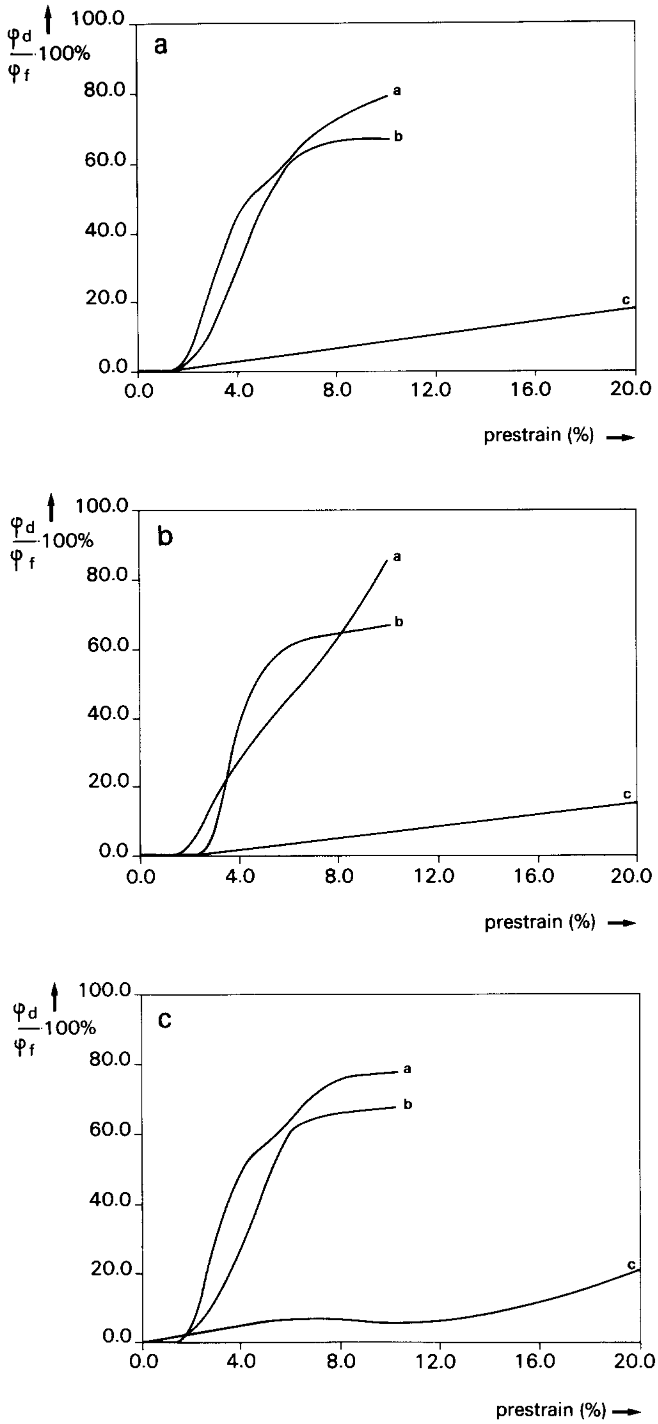

Figure 7 Fraction of debonded glass beads as a function of prestrain. (a) Calculations based on the E-modulus; (b) calculations based on the Poisson's ratio; (c) calculations based on the E-modulus and Poisson's ratio of the composites. Curve a, PA-6 + 16% glass beads (as moulded); curve b, PA-6 + 16% glass beads (conditioned at 50% r.h.); curve c, PA-6 + 16% glass beads + 0.3% silane (as moulded)

It is generally accepted that silane coupling agents can have a positive effect on the ultimate mechanical properties like tensile or impact strength. However, it is often thought that the elastic behaviour of composites is not influenced by the interfacial adhesion. We have found that in case of glass-bead-filled polyamide-6 the initial modulus and Poisson's ratio are indeed not influenced by the addition of the coupling agent γ-APS. However, this is only true for a freshly prepared composite which has not been strained before. Once the composite has

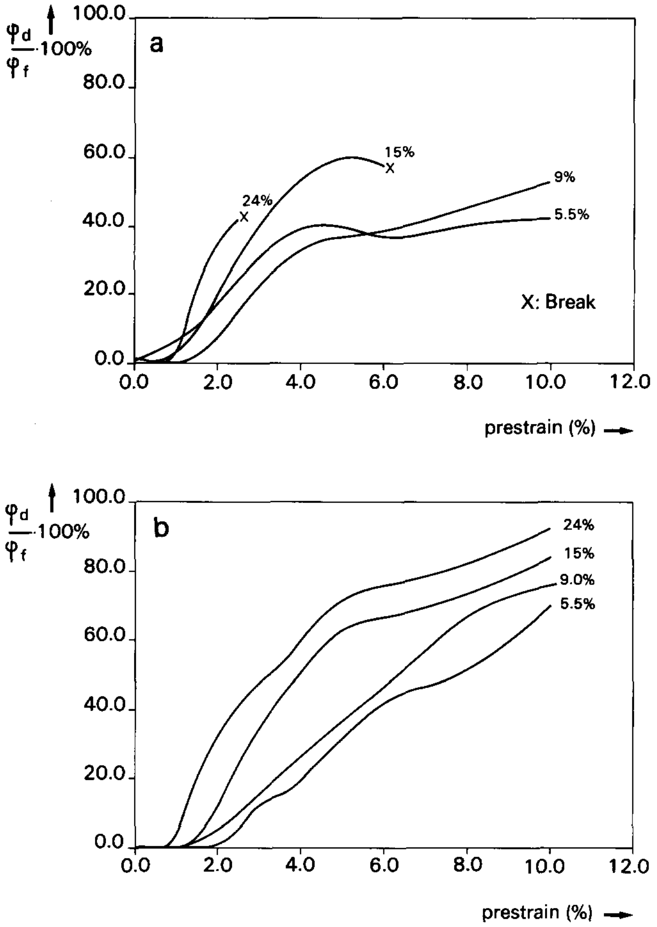

Figure 8 Fraction of debonded filler particles as a function of prestrain in PA-6 filled with different concentrations of glass beads. (a) Dry as moulded; (b) conditioned at 50% r.h.

been strained beyond the debonding point, the E-modulus of the material as measured in a second test decreases and can reach a value below the E-modulus of the unfilled sample. In that case most of the filler particles have become debonded. These particles cannot support any load and have about the same effect on the stiffness as pores. Bucknall[13] observed a similar effect, called strain damage, in case of high impact polystyrene.

In theory we could use the Kerner model[7] to calculate the modulus of a composite with partially debonded filler particles. We must consider the matrix to be filled with two different fillers: a fraction φ_b of rigid spheres ($E_f \gg E_m$) and a fraction φ_d of pores ($E_f \ll E_m$). If the Kerner equations[7] are used to calculate a value of φ_d from the measured E-modulus the results are very similar to those shown in *Figure 7c*. A difference is that at high prestrains the fraction of debonded glass approaches 100% instead of 80%, which may seem more realistic. However, this model is unable to describe the pronounced decrease of the Poisson's ratio with increasing φ_d. The low value of the Poisson's ratio is the result of the glass beads, which prevent lateral contraction of the voids. This creates a larger volume strain and so a lower Poisson's ratio. We propose the cube model, which is based on the Chow model[8] but takes into account the effects of debonded particles described above. The cube model gives, for all examined filler concentrations (5–24 vol%), an adequate description of the elastic behaviour of the polyamide-6/glass bead composites in different stages of debonding. This could also be checked by comparing the results of the calculations based on the measured E-modulus and those based on the Poisson's ratio. All deviations can be explained by the experimental error in the measurement of E_c and υ_c.

The cube model gives sensible results. It should be realized that the absolute values of the debonded fraction depend slightly on the shape of the debonded volume, which is chosen here as a cube. The model is based on the assumption that all filler particles are either perfectly bonded or fully debonded. It seems realistic to assume that there are grades in between, so that a glass bead can be only partially debonded (e.g. at the poles). The value of φ_d/φ_f, which is the fraction of the filler particles that are totally debonded, produced by the cube model can also be interpreted as the fraction of the projected glass surface which is debonded and unable to bear stresses. We analysed the effect of the debonding of the glass beads during uniaxial loading on the tensile properties in a direction normal to the testing direction. Therefore, we used a specimen as shown in *Figure 9*. Although this specimen is not suitable for an accurate determination of modulus and strength it can be used for a qualitative analysis of the effect of debonding on the transverse properties. First the specimen is strained in direction 1 far beyond the debonding strain. A second test in the same direction showed a sharp decrease in modulus similar to the results presented above (see *Figure 10a*). Next the specimen is tested in the direction 2 and it appears that the transverse modulus and tensile properties are affected to the same amount as those in direction 1 as can be seen in *Figure 10b*. A subsequent test in the 2-direction does not show any further decrease in mechanical properties.

Thus it can be concluded that if the glass beads are debonded in a uniaxial test, the entire surface is debonded. This results in the same lower modulus in all directions.

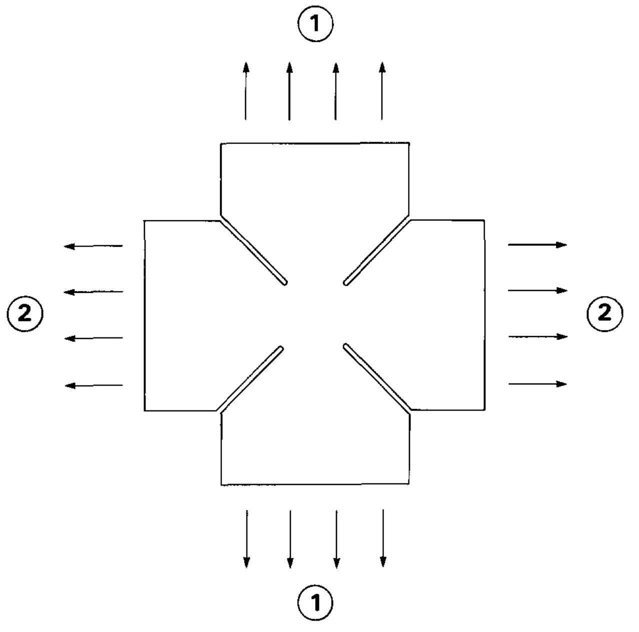

Figure 9 Specimen used to determine the transverse properties of a composite (direction 2) after interfacial debonding has occurred in a uniaxial test (direction 1)

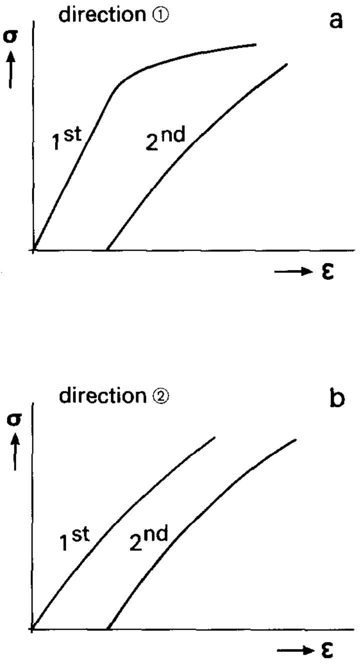

Figure 10 Four subsequent stress–strain tests performed with the specimen shown in *Figure 9*. (a) Two tests in direction 1 followed by (b) two tests in direction 2

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