Strain-rate dependence of interfacial adhesion in particle-reinforced polymers

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Glass beads not provided with a coupling agent debond from a polyamide-6 matrix during tensile deformation. The influence of the strain rate on the stress and strain at the debonding point has been examined using volume-strain and creep experiments. It was found that interfacial debonding takes place at a certain strain independent of the corresponding stress as long as all deformation is reversible. This 'critical strain criterion' is explained in terms of the generalized fracture mechanics theory.

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

INTRODUCTION

The mechanical properties of particle-reinforced polymers are highly dependent on the interfacial adhesion between filler particle and matrix polymer. This was illustrated in a previous paper with polyamide-6/glass bead composites[1]. The adhesion between polyamide-6 and glass can be improved significantly by applying an aminosilane coupling agent. The strength of the interfacial adhesion is determined with the volume–strain method[1,2]. This technique is able to detect the moment of interfacial debonding during a uniaxial tensile test by measuring the volume changes of the test bar. In this way a critical external stress and strain of the sample at debonding can be determined. The effects of filler concentration and the presence of a coupling agent have been reported in an earlier paper[1]. Models have been described in the literature to translate the externally measured stresses into local stresses arising around the filler particles. These theories, like that of Goodier[3] or Dekkers based on finite-element analysis[4], offer the possibility to calculate a local debonding stress. However, these models assume linear elastic behaviour of the matrix and neglect viscoelasticity in the case of a polymeric matrix. Mechanical properties of polymers are time-dependent. Young's modulus and yield strength generally increase with the rate of testing. Polyamide-6/glass bead composites were analysed with the volume-strain technique to study the influence of strain rate and time on the process of interfacial debonding.

MATERIALS AND METHODS

The polyamide-6 (PA-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^2) were injection-moulded after standard drying procedures (16 h at 110°C *in vacuo*). In the case of samples with coupling agent, 0.3% γ-aminopropyltriethoxysilane (γ-APS), obtained from Jansen Chimica, was added during extrusion. All tensile- 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[1,2]. A Zwick analogue extensometer was used to measure the elongational strain, and 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 since both relative transverse contractions are equal. Creep experiments were performed using equipment designed and built by TNO[5].

RESULTS

Stress–strain curves of PA-6 (dry as-moulded) recorded at different strain rates are shown in *Figure 1*. The E modulus increases slightly with the strain rate (*Table 1*), as expected on the basis of the time–temperature superposition principle for polymers. At strain rates of 5% min^{-1} or more, there is a maximum in the stress–strain curve, although not very pronounced. At lower strain rates the slope of the curve approaches zero, followed by a further increase in stress due to a partial orientation of the polymer chains (strain hardening). The yield point will be considered as either the maximum or the point where the slope is minimal. It appears that the yield stress (σ_y) increases linearly with the logarithm of the strain rate ($d\varepsilon/dt$) according to the well known equation[6]:

$$\sigma_y = \sigma_y^0 + K \log(d\varepsilon/dt) \qquad (1)$$

where K is a constant at fixed temperature and σ_y^0 is the yield stress when $d\varepsilon/dt = 1\%$ min^{-1} at the specified temperature (see *Figure 2*).

The strain at which yielding starts (ε_y) seems to be almost independent of the speed of testing (*Table 1*).

Polyamide-6 filled with 24 vol% glass beads with and without coupling agent (0.3% γ-APS) have been analysed with the volume-strain test using different strain rates. All samples have been conditioned at 23°C/50% r.h.

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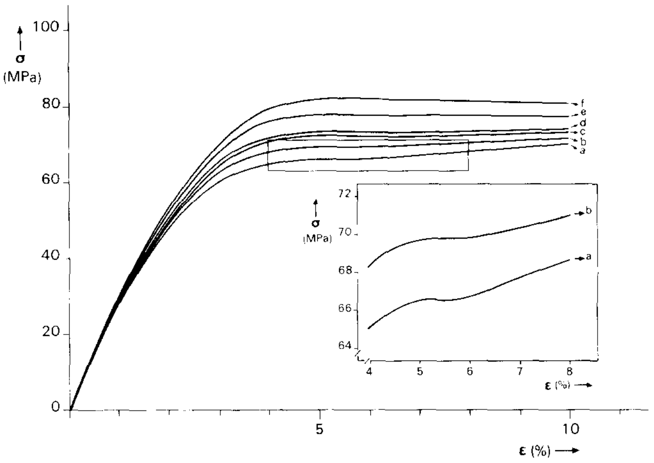

Figure 1 Tensile engineering stress–strain curves of PA-6 (dry as-moulded) at different strain rates: (a) 0.5, (b) 2, (c) 5, (d) 10, (e) 50, (f) 200% min^{-1}. Insert: magnification of detail

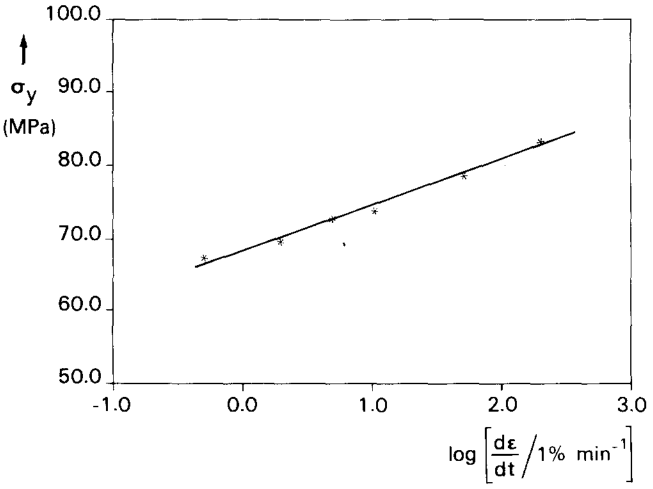

Figure 2 Yield stress of PA-6 (dry as-moulded) *versus* strain rate ('Eyring plot')

Table 1 Strain-rate dependence of the yield stress and yield strain of PA-6 (dry as-moulded)

$d\varepsilon/dt$ (% min^{-1})	E (GPa)	σ_y (MPa)	ε_y (%)
0.5	2.71	66.6	5.3
2	2.71	69.6	5.2
5	2.78	72.6	5.2
10	2.79	73.9	5.0
50	2.86	78.9	5.0
200	2.88	83.1	5.2

before testing. Stress–strain curves are shown in *Figures 3* and *4*. It appears that in the absence of a coupling agent the stress at elongations above 1–1.5% is significantly reduced. This is the result of the debonding of the glass beads as described earlier[1]. As in unfilled PA-6 the stress at any strain increases with the strain rate. Because no yield point can be observed, the curves are characterized by the stress at 8% strain (see *Table 2*). It is striking that the relative increase in stress is almost the same for the composite with well bonded filler particles as for the composite with debonded particles.

The corresponding volume-strain curves of the composite without silane are shown in *Figure 5*. All three curves recorded at a strain rate of 0.5, 5 and 50% min^{-1} respectively fully coincide. This implies that the debonding strain, which is defined as the elongation at which the volume starts to grow faster than predicted by the Poisson's ratio, is strain-rate-independent. Apparently the time necessary for the glass beads to debond is much shorter than the timescale of the experiment. The glass

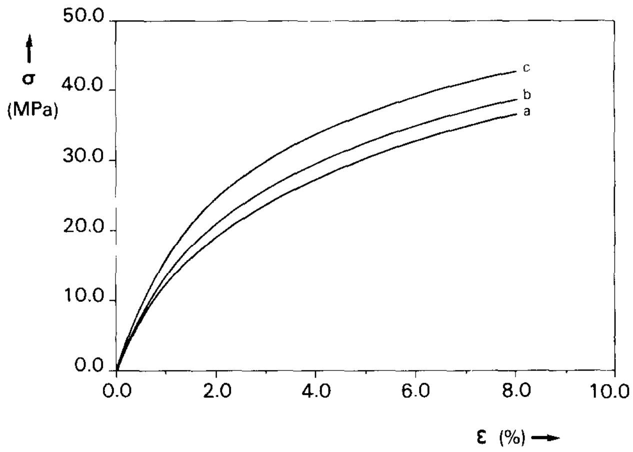

Figure 3 Tensile engineering stress–strain curves of PA-6 plus 24% glass beads plus 0.3% silane at different strain rates: (a) 0.5, (b) 5, (c) 50% min^{-1} (samples conditioned at 50% r.h.)

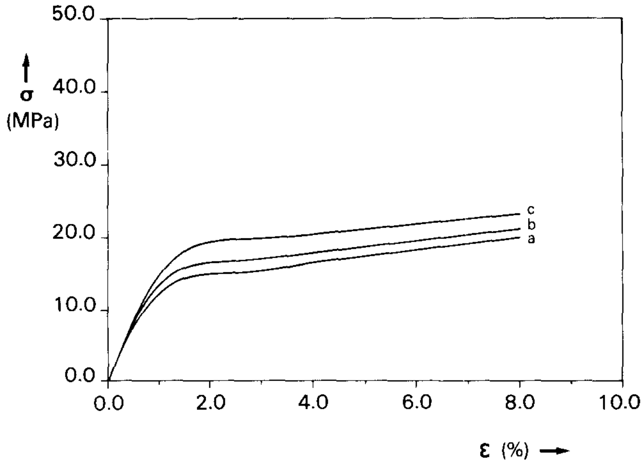

Figure 4 Tensile engineering stress–strain curves of PA-6 plus 24% glass beads (no silane) at different strain rates: (a) 0.5, (b) 5, (c) 50% min^{-1} (samples conditioned at 50% r.h.)

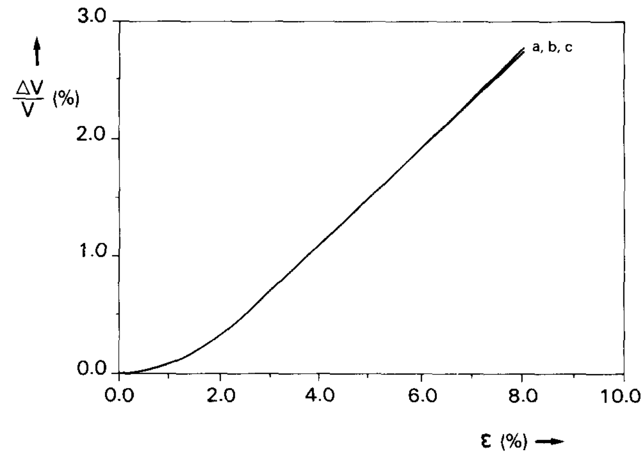

Figure 5 Volume-strain curves of PA-6 plus 24% glass beads (no silane) at different strain rates: (a) 0.5, (b) 5, (c) 50% min^{-1} (samples conditioned at 50% r.h.)

Table 2 Influence of the strain rate on the stress at 8% strain in PA-6 filled with 24 vol% glass beads (samples conditioned at 23°C/50% r.h.)

	σ ($\varepsilon = 8\%$) (MPa)	
$d\varepsilon/dt$ (% min^{-1})	No silane	0.3% silane
0.5	20.0	36.8
5	21.5	39.0
50	23.5	43.1

Table 3 Influence of the strain rate on the stress and strain at interfacial debonding in PA-6 filled with 24 vol% glass beads (no silane, samples conditioned at 23°C/50% r.h.)

$d\varepsilon/dt$ (% min^{-1})	$\sigma_{\text{debonding}}$ (MPa)	$\varepsilon_{\text{debonding}}$ (%)
0.5	13.4	1.15
5	14.4	1.15
50	16.0	1.10

beads always start to debond at the same strain. This means, however, that the stress at the moment of debonding is not constant but increases as the strain rate increases (see *Table 3*). This phenomenon of a varying stress at debonding is also illustrated with the following experiment. A tensile- and volume-strain test is performed with a strain rate of 0.5% min^{-1} until a stress of 11 MPa is reached. At that point the strain equals 0.9% and the volume-strain curve is still completely linear (no sign of debonding). Now a creep experiment is simulated by decreasing the strain rate in such a way that the stress remains 11.0 ± 0.1 MPa (see *Figure 6*). After 15 min the strain has increased to 1.2% and at that moment the volume strain starts to increase more rapidly (see *Figure 7*). After 2.5 h of creep the experiment is stopped. The volume-strain curve recorded in this way is exactly identical to the one obtained from an ordinary tensile test at constant rate.

The conclusion that can be drawn from these experiments is evident: the stress at which the glass beads start to debond is not constant but is highly dependent on the strain rate. The strain at debonding is almost insensitive to the rate of deformation.

It is not surprising that the process of debonding also has an influence on the creep rate. After debonding, all the stress has to be carried by the matrix, which will cause an accelerated creep of the composite. This can be seen in *Figure 8*, where the creep curves are plotted of PA-6 filled with 16 vol% glass beads with and without γ-APS. The creep stress (12 MPa) is well below the debonding stress as found in a 5% min^{-1} tensile test (18 MPa)[1], and so it is expected that the initial creep behaviour is the same in both materials. Nevertheless, after approximately 50 min the sample without γ-APS starts to creep with an increased rate and at the same time the samples show the whitening characteristic of the presence of interfacial voids. The compliance of the material at this point is 1.4 GPa^{-1} and so the strain at debonding $\varepsilon_b = 1.7\%$, which is almost identical to the strain at which debonding starts in a constant-rate tensile test (1.6%)[1], although the stress is significantly lower (12 MPa *versus* 18 MPa).

DISCUSSION

In linear elastic solids it is an arbitrary choice whether to speak about stresses or strains, since they are strictly connected to each other. The viscoelastic nature of polymers, however, makes it possible to change the stress in the material with constant strain or vice versa by adjusting a third parameter, time. We have used this

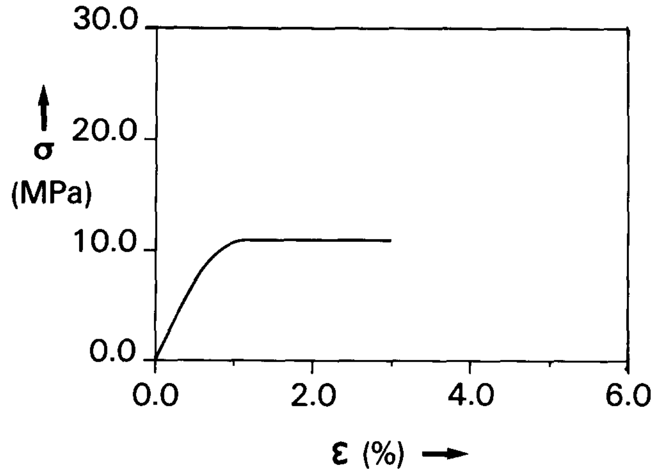

Figure 6 Tensile engineering stress–strain curve followed by a creep test at 11 MPa of PA-6 plus 24% glass beads (no silane)

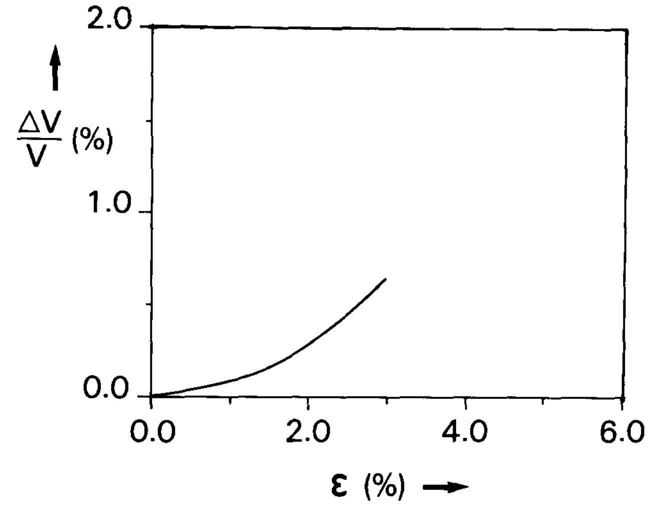

Figure 7 Volume-strain curve as recorded during the tensile creep test depicted in *Figure 6*

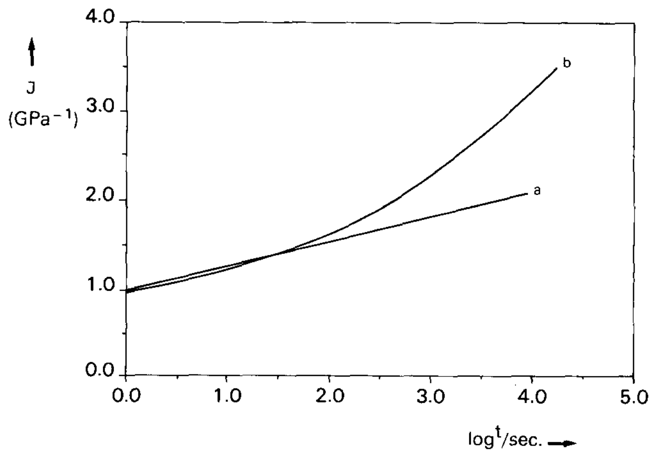

Figure 8 Compliance of PA-6 plus 16% glass beads (conditioned at 50% r.h.) as a function of time during a creep test at 12 MPa: (a) 0.3% silane, (b) no silane

phenomenon to determine which of them is the crucial parameter in the process of debonding of filler particles.

The experimental results are consistent and justify the conclusion that it is not possible to define a stress at which the filler particles will debond from the matrix in a given glass bead/polyamide composite. Depending on the rate of deformation, the debonding stress can vary significantly. It is shown that, even in a creep experiment in which the stress is kept constant, the state of bonding can change with time. The strain at which this debonding occurs is approximately constant and insensitive to the deformation rate.

The process of interfacial debonding is discussed in terms of the generalized theory of fracture mechanics as proposed by Andrews[7].

Kinetic theory of fracture

When a polymeric sample undergoes fracture, new surfaces are created involving the rupture of primary or secondary interatomic bonds. Griffith[8] used an energy balance approach to model the fracture process. He calculated the energy released by the growth of a sharp crack in a plate and related this to the energy required to create a new surface. The latter equals the surface free energy of the material.

Andrews[7,9–12] proposed a similar theory from a more atomistic viewpoint. This theory considers fracture as a kinetic phenomenon that is dependent on time and temperature. Moreover, the theory takes energy-loss processes in the material into account. The basic concept of considering bond rupture as an activated-rate process was developed by Coleman[13] and by Zhurkov *et al.*[14,15] using the Eyring theory of viscosity[16]. The concept is illustrated in *Figure 9*. State A represents an unbroken interatomic bond and state B the same bond broken. An activation energy G_{AB} must be supplied to obtain the transition A → B. The net rate at which bonds will break is given by:

$$r = r_0\{[A]\exp(-G_{AB}/kT) - [B]\exp(-G_{BA}/kT)\} \quad (2)$$

where r_0 is a temperature-independent constant, k is Boltzmann's constant and [A] and [B] are the concentrations of state A and B respectively. As long as the free energy of state B (G_B) is higher than that of state A (G_A), no net bond fracture will occur. However, if the material is under stress, and strain energy is stored in this bond, G_A increases, causing a decrease of the activation energy:

$$G_A^* = G_A + v\sigma \qquad G_{AB}^* = G_{AB} - v\sigma \quad (3)$$

where v is the so-called activation volume and σ is the stress on the bond. Eventually the stress-induced free energy of state A (G_A^*) will approach the free energy of the activated state ($G_{\max}$) and bond fracture will occur by direct mechanical action without the assistance of thermal fluctuations. If fracture occurs, the strain energy stored in the bond ($v\sigma$) is therefore a variable quantity with an upper and lower limit:

$$(G_B - G_A) < v\sigma < G_{AB} \quad (4)$$

Between these limits net bond fracture can occur under the applied stress but will do so at a rate controlled by the temperature.

This theory has been used to describe the dependence of the yield stress of polymers on strain rate and/or temperature[4,17] and gives satisfactory results. Zhurkov applied this theory to the process of molecular fracture in polymers[14,15]. This process can be observed by e.s.r. or i.r. spectroscopy[18,19]. Since interfacial debonding also involves primary or secondary bond rupture, the same kinetic model may be applied. For the initiation of processes like fracture or interfacial debonding, it is necessary that a sufficiently large number of bonds in the same area reach the debonded state (*Figure 9*) before the process will become catastrophic and an (interfacial) crack is created. So, depending on the level of the applied stress, debonding occurs after a certain amount of time. Moreover, the debonding stress as measured in a tensile test is not constant but increases with increasing strain rate since there is less time available.

The kinetic theory considers the material as completely

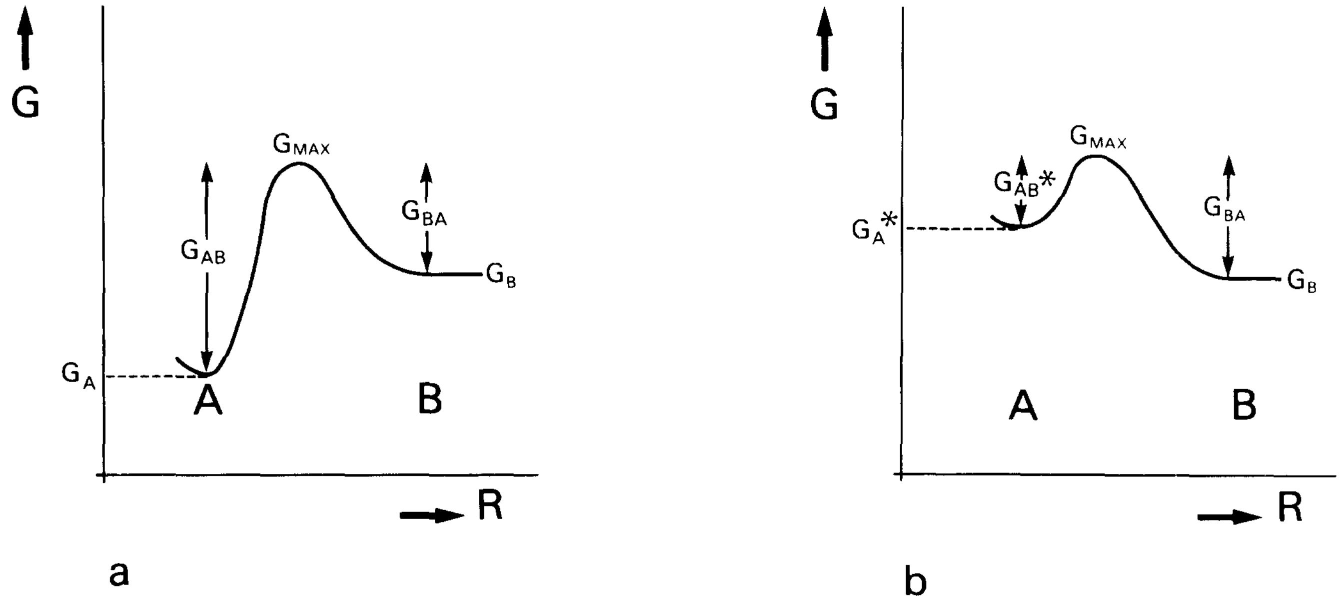

Figure 9 Free-energy diagrams for the activated fracture of an interatomic bond: (a) unstressed, (b) stressed. A is the bonded and B the debonded state; *R* on the horizontal axis represents the interatomic distance

elastic. The generalized theory of fracture mechanics[7] does not suffer from limitations as to linearity or elasticity of the deformation.

Viscoelastic losses

According to the generalized mechanics theory of Andrews[10,12], the fracture energy F of a solid (referred to unit area of fracture surface) is given by:

$$F = F_0\phi \qquad (5)$$

where F_0 is the energy required to fracture unit area of interatomic bonds across the fracture plane and ϕ is a loss function that takes into account all energy dissipated in the material due to, for example, viscoelastic losses and is also dependent on the local strain distribution.

Two different factors influence the debonding conditions: the value of F_0, which is dependent on time and temperature (kinetic theory), and the loss function, which is likely to dominate the rate and temperature dependence of the interfacial stress[10,12]. The loss function depends on the external stress and strain, the strain rate and the temperature. Thus F is not equal to F_0 plus lost energy but is also related to F_0 in a multiplicative manner. The loss function reduces to unity for a perfectly elastic solid.

The loss function is given by:

$$\phi = \frac{k_1}{k_1 - \frac{1}{2}\sum_{P_u}\beta g \delta V} \qquad (6)$$

where k_1 is a proportionality constant between the strain energy density (W) and F, which in the case of crack propagation reflects the geometry of the crack and therefore the volume of strained material that unloads as the crack propagates (k_1 is only a function of strain); g is a distribution function of the strain energy density throughout the specimen; δV is a volume element; P_u denotes the summation over points that unload as the interfacial crack propagates; and β is called the hysteresis ratio. So a summation of the strain energy losses takes place over that part of the matrix near the poles of the glass beads that unloads if the bead debonds.

The value of β will in general be a function of the local strain, strain rate and temperature. As a first approximation we can derive the value of β from the areas under the stress–strain curves for a uniaxial loading/unloading stress cycle (hysteresis loop) at constant temperature:

$$\beta(\varepsilon, \mathrm{d}\varepsilon/\mathrm{d}t) = (W - W_r)/W \qquad (7)$$

where the input energy density W is given by the area under the loading curve up to a particular strain ε and the recoverable energy density W_r by the corresponding area under the unloading curve.

Figures 10 and *11* show the hysteresis loops for the PA-6/glass beads composites (compare with *Figures 4* and *5*) at three different strain rates, and it appears that β increases with strain rate (see *Table 4*), which is in agreement with the results obtained for polyethylene and poly(vinyl chloride)[12]. It must be emphasized that the hysteresis ratio β involves loss processes in the non-linear region that are different from those responsible for the viscoelastic loss factor $\tan\delta$ $(=E''/E')$ as determined by dynamic mechanical analysis. In the linear viscoelastic region a loss modulus may be defined that is caused by the relaxation of side-chains and small backbone segments. However, the value of $\tan\delta$ in the solid state is very small, between 0.001 and 0.1 depending on temperature and frequency. At strains far beyond the linear viscoelastic region other deformation mechanisms appear to prevail, which cause the dissipation of a substantial fraction (even more than 50% as can be seen in *Figure 10*) of the work done by the external force. Tan δ depends on the rate of testing. At higher frequency tan δ increases if the material is tested above its glass transition temperature but it decreases if it is tested below T_g. The conditioned PA-6 specimens have a T_g of +15°C. All experiments presented in this section are performed at +20°C, just above T_g. However, similar experiments

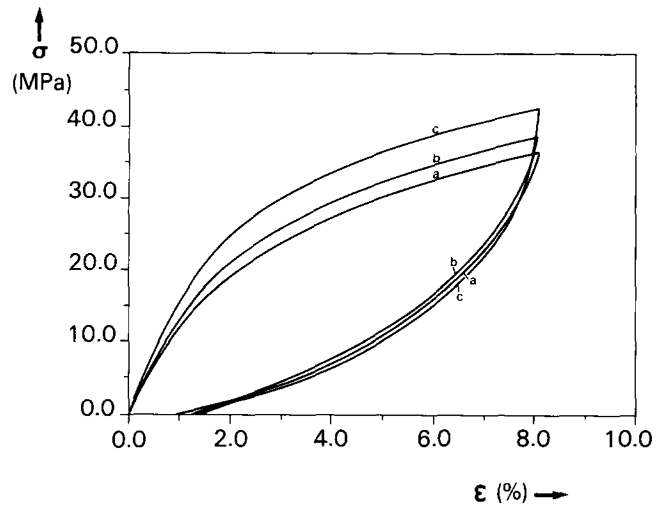

Figure 10 Cyclic loading/unloading tensile engineering stress–strain curves of PA-6 plus 24% glass beads plus 0.3% silane (conditioned at 50% r.h.) at different strain rates: (a) 0.5, (b) 5, (c) 50% min^{-1}

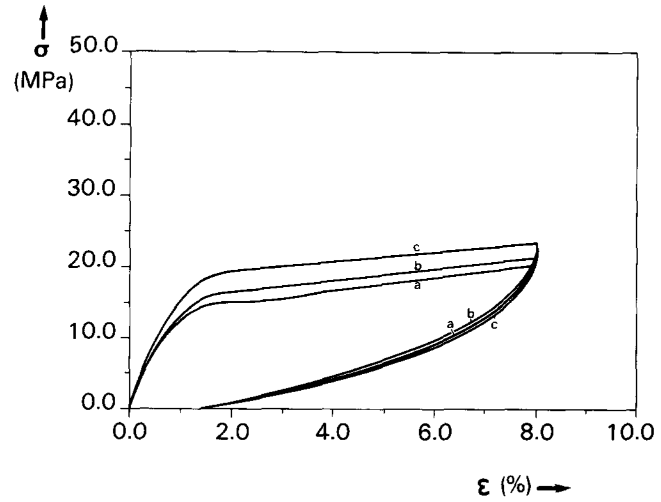

Figure 11 Cyclic loading/unloading tensile engineering stress–strain curves of PA-6 plus 24% glass beads (no silane) (conditioned at 50% r.h.) at different strain rates: (a) 0.5, (b) 5, (c) 50% min^{-1}

Table 4 The hysteresis ratio β of PA-6 filled with 24 vol% glass beads (conditioned at 23°C/50% r.h.) at different strain rates. Maximum strain 8%

	β ($\varepsilon = 8\%$)	
dε/dt (% min^{-1})	No silane	0.3% silane
0.5	0.64	0.60
5	0.65	0.62
50	0.72	0.68

have been performed just below T_g, at 8°C. It appeared that, although the mechanical properties (stiffness and strength) changed significantly, the same conclusions can be drawn below T_g. The strain at debonding and moreover the stored energy defined as the area under the unloading curve are independent of the strain rate. The stress at debonding and the dissipated energy increase with increasing strain rate. A more detailed study of the influence of temperature on the stress and strain at debonding is being performed and will be reported in a following paper.

The work needed to deform a polymer is partially stored as elastic (potential) energy in the deformed polymer chains and partially transformed into heat due to the viscous losses. According to the energy balance approach of fracture due to Griffith and Andrews[7-9], debonding will occur if the free surface energy can be compensated by the release of elastic energy stored in the matrix. The latter depends on the local stress state near the interface. However, the externally measured stress is also influenced by the time- and strain-rate-dependent viscous losses.

It appears from the cyclic experiments that at a given temperature the stored energy is independent of the strain rate and determined by the maximum imposed strain only. The energy balance will become favourable for debonding if this stored (recoverable) energy reaches a critical level. This leads to the assumption that debonding will occur at a more or less constant debonding strain but at different stress levels.

These results are in agreement with the experiments of Gent *et al.*[20,21]. They examined the resistance to separation of a viscoelastic adhesive spread on a rigid substrate and in particular the effect of the rate of detachment on the applied stress. It appeared that the failure energy varied strongly with the rate of extension, increasing with increasing deformation rate. The explanation was given in a similar way by dividing the apparent interfacial energy into two components: the reversible work of adsorption and the irreversible work of deformation of the adhesive (or, in general, polymer) in effecting separation.

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