DAMAGE DEVELOPMENT IN FILLED VISCOELASTIC MATRIX COMPOSITES

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SUMMARY: This paper deals with the stress-strain behavior of two viscoelastic polymers, polypropylene and polyamide 6, filled with rigid particles in the range of axial strain of 0 to 8%. These materials, when subjected to a constant strain rate test lose stiffness via two mechanisms: filler-matrix debonding and the viscoelastic softening of the matrix. A model which combines the concepts of damage mechanics and the time dependence of the interfacial strength is described and compared to the experimental results of polypropylene and polyamide 6 filled with up to 50 *vol.*% of untreated and silane treated glass beads. The matrix behavior is described in terms of an empirical equation selected to fit the stress-strain behavior of neat polymers in the range of strain rates between 0.12 and 0.5% s⁻¹ and strains between 0 and 8%. The stiffness of the damaged, partially debonded composite is calculated using the Kerner-Lewis equation assuming that debonded particles do not bear any load. The model is able to generate stress-strain curves which are in good agreement with the experimental data. The void volume attributable to debonding calculated using the model is much smaller than the experimental total determined void volume (which is a sum of several deformation mechanisms).

KEYWORDS: damage, interface, debonding, viscoelastic matrix

INTRODUCTION

When a second, rigid phase is dispersed in a polymer the most obvious effect is the substantial increase of the elastic (short term, small strain) stiffness. The effect on other properties is more complex to analyze. This is because, as a result of straining, the material properties change because of damage related to factors such as filler/matrix debonding but also due to the viscoelastic nature of the matrix. A number of attempts to model the debonding resulting from the tensile loading have been published (1). However, since only the rigid phase (the filler) is excluded from the load bearing as the debonding progresses, the material loses its stiffness not only from the reduction of the effective section but also from a reduction of the effective filler concentration in the remaining material [2,3].

This paper presents the model that can be used to calculate the stress-strain behavior of filled polymers, and to evaluate the debonding during the straining. The predicted results are compared to stress strain behavior of filled polypropylene and polyamide 6.

EXPERIMENTAL RESULTS

The materials investigated are polypropylene (PP) and polyamide 6 (PA6) filled with rigid particles (glass beads-GB, talc and calcium carbonate (CaCO₃). All the experimental details concerning the used, sample preparation and mechanical testing can be found in the previous paper [3].

Stress Versus Axial Strain Curves

Figure 1 shows the stress-strain curves of polypropylene and polypropylene filled with glass beads, talc and CaCO₃. In Table 1, the average values of several properties determined from the σ vs ε curves are listed: the initial modulus, E₀; the stress σ_0 and strain ε_0 at which the stress strain curve deviates from linearity; the stress and the strain at yield, (σ_v and ε_v).

The principal points of the experimental results are:

- All materials exhibit an elastic zone; the initial modulus E_o increases with the filler addition but is independent of the surface treatment for glass beads.
- The yield stress σ_y decreases with the filler addition: $\sigma vs \varepsilon$ curves of all composites except those containing talc fall below that of neat PP well before yield.
- Both the stress and the strain at which the material ceases to be elastic (σ_0 and ϵ_0) decrease with filler addition. The values of σ_0 and of ϵ_0 are higher with treated beads.
- The platy irregular shape of talc particles leads to a definite reinforcing effect in PP, as evidenced by the high initial modulus and yield stress.
- Although the transition between the linear (elastic) stage and the constant stress plateau starts at a higher strain with treated beads the yield stress is independent of the surface treatment.
- The composite with talc (20 vol.%) broke at a relatively low axial strain of about 5%.

Filled polyamide 6 also has a linear zone at small strains and the initial modulus is unaffected by the surface treatment. Besides these similarities, there are significant differences between filled polypropylene and polyamide 6 filled with untreated beads, on the one hand, and polyamide 6 filled with treated beads (Fig. 2 and Table 1). With untreated beads, the curves fall below that of neat polyamide 6 but at higher strains than in filled polypropylene. The departure from linearity in untreated glass-polyamide 6 composites follows a similar pattern as in filled polypropylene i.e., the strain ε_0 decreases with increasing glass concentration. However, the stress σ_0 increases slowly with filler content. With treated glass, the strain ε_0 appears to be independent of the filler content. In fact, it is very close to the ε_0 value of the neat polyamide 6. The stress σ_0 increases substantially with the treated glass content. The stress-strain curves of polyamide 6 composites containing treated beads remain above the neat polyamide 6 curve.

Polymer-filler- vol.%	E ₀ (GPa)	ε ₀ (%)	σ ₀ (MPa)	ε _y (%)	бу (MPa)
PP	1.57	0.75	11.9	7	32
PP-GB-20	2.4	0.30	7.3	4	22
PP-GB-20T	2.4	0.37	9.0	4	22
PP-Talc-20	4.96	0.24	11.9	2.4	30.7
PP-CaCO ₃ -20	3.1	0.20	6.2	2.9	22.7
PA6	0.92	0.73	6.8	2.7	18
PA6-GB-25	1.9	0.40	7.3	2.3	21
PA6-GB-25T	1.9	0.71	13.6	1.20	18

Table 1:Summary of tensile properties of filled polypropylene GB: glass beads (T: treated
beads)



Fig. 1: Stress σ vs axial strain ε curves of PP filled with 20 vol.% of: silane treated glass beads(1-T), untreated glass(NT), talc and CaCO₃. PP:unfilled polypropylene.



Fig. 2: PA6 filled with 25 vol.% glass beads. Stress σ and volume strain ζ vs axial strain ε (%). T- treated beads, dotted lines indicate dilational behavior(i.e. calculated using the initial Poisson ratio).

Tensile dilatometry

Figure 3 shows the volume strain versus axial strain (ζ vs ε) curves of polypropylene containing 0 and 20 *vol.*% of glass beads , talc and CaCO₃ respectively. The neat ζ *vs* ε polypropylene curve starts to deviate from linearity at about the same strain as the tensile stress-axial strain curve. The curves of filled polypropylene exhibit two linear parts, the first one being determined by the initial Poisson ratio, v_{0c} . Beyond the first stage the increasing volume is an indication of the onset of debonding. As shown by curve 2 The talc filler behaves differently: the perpendicular to stress oriented platelets in the sample core start to debond at very low strain. The volume strain *vs* axial strain curves of neat and filled polyamide 6 ($\phi = 0.25$) are shown in Figure 2. The behavior of neat polyamide 6 is similar to that of polypropylene. At small strains, the ζ *vs* ε curves of polyamide 6, filled with treated or untreated glass coincide up to $\varepsilon \approx 1.5\%$ (for $\phi = 0.25$). The curves then diverge, the volume of untreated glass composite increases at a much higher rate than that of treated glass. It indicates that the fully debonded state is not reached treated beads.



Fig. 3 Volume strain ζ vs axial strain ε of PP filled with 20 vol.% of : 1- glass beads, 2- talc and 3- CaCO₃. T: treated glass beads, dotted lines indicate dilational behavior

MODEL

The model is based on the following assumptions (see Fig. 4):

- Initially all filler particles (volume fraction ϕ) are well bonded to the matrix (bonded filler volume fraction $\phi_b = \phi$, Fig. 4a). The material behavior can be described by the Kerner-Lewis equation (see below).
- Upon straining the filler particles become progressively debonded ($\phi_b = \phi \phi_d$, ϕ_d being the debonded filler volume fraction). The debonded particles do not bear any load (Fig. 4b).
- The completely debonded composite (φ_b=0, φ_d=φ) behaves as a foam containing volume fraction of voids equal to φ_d (Fig. 4c). Its behavior can also be described by the Kerner-Lewis equation.
- The debonding rate $(d\phi_d/dt)$ depends on the applied stress and the number of particles available for debonding $(\phi-\phi_d)$ or (ϕ_b) .



Fig. 4 Schematic representation of a filled polymer subjected to uniaxial tension. a- wellbonded composite, b- partially debonded composite and c- fully debonded composite.

During the constant strain rate tensile test ($d\epsilon/dt = const$), the applied stress σ follows the relation:

$$\frac{d\sigma}{dt} = \frac{d(E_c \cdot \epsilon)}{dt} = \epsilon \cdot \frac{dE_c}{dt} + E_c \cdot \frac{d\epsilon}{dt}$$
(1)

where E_c is the secant modulus of the composite. The modulus (E) decreases as debonding progresses. The partially debonded composite containing a volume fraction ϕ of the filler (of which ϕ_d is debonded : $0 \le \phi_d \le \phi$) is considered to consist of three components:

- matrix (modulus E_m)
- bonded filler (volume fraction $[\phi \phi_d]$, modulus E_f)
- debonded filler each vacuole containing a debonded filler particle behaves as a void.

The modulus of such hybrid material can be described by the Kerner-Lewis equation [5]:

$$E_c = E_m \cdot E_1 \cdot E_2 \tag{2}$$

where E_1 represents the relative modulus of the still bonded filled material:

$$E_{1} = \frac{1 + A_{1} \cdot B_{1} \cdot (\phi - \phi_{d})}{1 - B_{1} \cdot \psi \cdot (\phi - \phi_{d})}$$
(3)

with $A_1 = (7 - 5\nu)/(8 - 10\nu)$, $B_1 = (E_f/E_m - 1)/(E_f/E_m + A_1)$ and $\psi = 1 + \phi (1 - \phi_m)/\phi_m^2$, ν is the Poisson ratio of the matrix, ψ is a "crowding factor" which depends on ϕ_m - the maximum packing fraction of filler. The modulus E_2 is the relative modulus of the foam with a void fraction equal to ϕ_d . E_2 is then given by:

$$E_2 = \frac{1 - \phi_d}{1 - B_2 \cdot \psi \cdot \phi_d} \tag{4}$$

with $B_2 = -1/A_1$. It is worth noting that the Kerner-Lewis equation and other expressions of this type have been successfully applied to hybrid materials [6] and to high density foams [7].

Considering the heterogeneous nature of materials under consideration it seems reasonable to adapt Bartenev's equation [8,9] for time to failure, t_p of a material subjected to an effective stress, \bar{o} . This equation, originally developed for materials containing defects, is written here in simplified form:

$$t_f = \frac{\exp(-B \cdot \overline{\sigma})}{K \cdot \overline{\sigma}}$$
(5)

The constants B and K depend on the temperature, the material molecular structure and the nature and number of defects. It should be noted that this and other equations (e.g. Zhurkov-Bueche [10]) relating the time to failure to the applied stress have a theoretical basis and are often considered as interpolation formulas of a semi-empirical nature - useful for the mathematical expression of experimental data. Applying the Bartenev concept to a filled material, we assume that the time to failure of the filler/matrix interface can be described by equation 5. The probability of debonding is proportional to $1/t_r$. The debonding rate $d\phi_d/dt$ is then considered to

be proportional to $K\bar{\sigma} \exp(B\bar{\sigma})$ (the constants K and B are related to the overall behavior of the filled material rather than only to that of single particle/matrix interface, $\bar{\sigma}$ is the effective stress - see below) and to $(\phi - \phi_d)$:

$$\frac{d\phi_d}{dt} = (\phi - \phi_d) \cdot K \cdot \overline{\sigma} \exp (B \cdot \overline{\sigma})$$
(6)

The effective stress, $\bar{\sigma}$, which acts only on the matrix and on the still bonded filler, can be related to the measured stress, σ (which is calculated using the entire sample cross section, including its debonded portion), using the strain equivalence principle [11]. A material containing a filler fraction ($\phi - \phi_d$) but no voids will have a modulus E'_c:

$$E'_{c} = E_{m} \cdot E_{1} \tag{7}$$

According to the strain equivalence principle:

$$\epsilon = \frac{\overline{\sigma}}{E'_{c}} = \frac{\sigma}{E_{c}}$$
(8)

This leads to:

$$\overline{\sigma} = \frac{\sigma}{E_2} \tag{9}$$

Since:

$$\frac{dE_c}{dt} = \frac{dE_c}{d\phi_d} \cdot \frac{d\phi_d}{dt}$$
(10)

a simultaneous solution of equations (1) and (6) can be obtained using known values of E_m , $d\epsilon/dt$ and ϕ , and using equations (2-4), (9) and (10). Solution of the equations (1) and (6) using the fourth order Runge Kutta method yields the value of the secant modulus E_c and of the debonded fraction ϕ_d . To determine the appropriate values of K and B, the calculated results are compared, with the help of the Marquardth-Levenberg algorithm, to the values of ϕ_d computed from the experimental stress-strain data using equation 2.

The volume increase due to debonding, ζ_d , can also be calculated assuming, for example, that each void created by debonding of a spherical particle (diameter d) is an ellipsoid with its two shorter axes equal to d and its longer axis equal to $d \cdot [1+(\epsilon - \epsilon_d)]$ where ϵ_d represents the strain at which the particle becomes debonded [2]. It follows that:

$$\zeta_d = \int_0^{\epsilon} \phi_d \ d\epsilon \tag{11}$$

RESULTS AND DISCUSSION

Having examined a number of more complex models for matrix behavior [4], we have finally adapted the following relation for the inelastic strain rate:

$$\dot{\varepsilon}_n = a \exp(b \sigma) + c\sigma + d = \dot{\varepsilon} - \frac{\dot{\sigma}}{E_{0m}}$$

with optimized constants a, b, c, d and E_{0m} .

The debonding process modeled with the help of equations 1, 2 and 6 using the materials constants of neat and filled polypropylene (Table 2) and several arbitrarily selected values of K and B leads to stress strain curves shown in Fig. 5. Two extreme cases are considered:

Table 2: Parameters used to calculate the initial composite modulus E_{0c} from equation 3. GB: glass beads.

Parameters PP/GB **PP/Talc** PP/CaCO₃ PA6/GB 1.71 0.88 E_{0m} (GPa) 1.62 1.71 1.68 5.62 2.60 1.90 A_1 B_1 0.85 1.48 1.21 1.03 0.60 0.33 0.58 1.04 Ψ



Fig. 5: Stress-strain curves calculated using equations 4.9 and 4.14 (see text): m: matrix, b: fully bonded composite, d: fully debonded composite. Curves 1 to 5 were calculated using following values of constants K and B, 1: K=3.04 10⁻² MPa⁻¹ s⁻¹, B= 0, 2: K= 2.03 10⁻³ MPa⁻¹ s⁻¹, B= 0, 3: K= 6.80 10⁻⁴ MPa⁻¹ s⁻¹, B= 0, 4: K= 1.2 10⁻⁴ MPa⁻¹ s⁻¹, B= 0 and 5: K=2.03 10⁻¹⁴ MPa⁻¹ s⁻¹, B= 1 MPa⁻¹.

When the value of the exponential term constant B is set to 0, the debonding rate is

proportional to the effective stress $\overline{\sigma}$. The measured stress $\sigma vs \varepsilon$ function deviates from that of the fully bonded composite at a relatively low strain and moves to the completely debonded state over a broad range of strains (see also Fig. 5 for the corresponding $\phi_d vs \varepsilon$ curves). With a high value of K (curve 1) the $\sigma vs \varepsilon$ curve of the composite will cross that of the matrix when the matrix is still elastic and join that of the debonded composite at a strain well below the yield. The value of K used to draw curve 2 in Fig. 5 was selected so that the debonding process would be complete in the range of strains studied experimentally (0 to 8%). In this case the stress strain curve reaches a maximum at about 1.5% strain when about a third of all filler particles have debonded.

With a very high value of B the debonding will occur at nearly constant effective stress ($\bar{\sigma}$). Curve 5 corresponds to this case. The stress strain curve ($\sigma vs \epsilon$) follows that of a well bonded

composite until the onset of debonding (with the combination of K and B used at $\sigma = \overline{\sigma} = 32$ MPa). With the reduction of the load bearing section the applied (measured) stress (σ)

decreases (while $\bar{\sigma} = \text{const}$) until the fully debonded state is reached at $\sigma = 18$ MPa and $\varepsilon = 6\%$). The apparent "yield" of the composite (maximum of the value $\sigma vs \varepsilon$ curve) corresponds to the onset of debonding rather than to the inherent yield of the matrix material. The corresponding $\phi_d vs \varepsilon$ curves are shown in Fig. 6.

The shapes of these curves suggest that the Bartenev type equation can cover the range of situations likely to occur in glass bead filled viscoelastic materials. The extreme case of the debonding occurring at constant effective stress (curves 5, Figs. 5-6) will certainly not be found in real materials where the dispersed phase distribution is at best uniformly random, particles are of different sizes, local stress fluctuations are caused not only by the material inherent heterogeneities but also by residual stresses which vary throughout the thickness, and where the debonding will therefore occur over a broader range of stress and strain.



Fig. 6 Debonded filler fraction ϕ_d calculated using equations 1 and 6 as a function of strain ε . The curves are numbered as in Fig. 5.



Fig. 7 Stress strain curves, predicted by the model and experimental (-----) of 20 vol. % filled PP. 1- glass beads, 2-talc and 3- CaCO₃. T- treated beads.



Fig. 8 Stress strain curves, predicted by the model and experimental (-----) of 25 vol. % filled PA6. T- treated beads.

The stress strain curve of filled material consisting of a matrix defined by equation 2 and undergoing the debonding process (eqs. 2 and 6) can be calculated and compared to experimental stress strain curves. Optimized values of K and B are listed in Table 3 for filled polypropylene and filled polyamide 6. The value of the constant K is affected by particle shape and traitment. On the other hand, the exponential term constant B also changes with the particle shape and treatment. The agreement between the experimental stress strain curves and those computed using the procedure described in this paper is quite good (Fig. 7 for polypropylene, glass beads, talc and CaCO₃, ϕ =0.2 and Fig. 8 for glass bead filled polyamide 6, ϕ =0.25). It confirms that the Bartenev equation can be used to describe the debonding process not only when the matrix is elastic [12] but also when the composite non-elasticity is caused by a combination of the debonding and of the matrix viscoelasticity. Moreover, the Bartenev equation appears to be able to cover the cases of both complete and partial debonding (polypropylene and polyamide 6 respectively).

Parameters	PP/GB		PP/Talc	PP/CaCO ₃	PA6/GB	
	NT	Т			NT	Т
$K \cdot 10^2$ (GPa ⁻¹ s ⁻¹)	4.3	3.10	0.163	0.36	1.8	1.4
$\begin{array}{c} \mathbf{B}\cdot10^2\\ (\mathbf{GPa^{-1}})\end{array}$	0.11	0.09	1.5	0.011	6.5	0.28

Table 3 : K and B values of 20vol. % filled polypropylene (PP) and25vol. % filled polyamide 6 (PA6) .T-treated beads.

CONCLUSION

The stress-strain behavior of filled polymer is modeled by using a Bartenev type relation for the time dependence of the filler matrix interface strength and by considering the gradual transformation of the initially well-bonded composite into foam which take account the matrix viscoelasticity. A good agreement was achieved between calculated and experimental data.

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