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Micromechanical interpretation of fracture toughness of particulate-filled thermoplastics

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The toughness behaviour of particulate-filled thermoplastics is determined by different failure mechanisms in the plastic zone and fracture process zone in front of the macrocrack such as particle–matrix debonding, shear processes or crazing and fracture of matrix fibrils. Theoretical expressions describing the critical strain causing microcrack initiation as well as the critical crack opening and the critical *J* integral value for unstable crack initiation are derived on the basis of a micromechanical analysis. Matrix properties, particle diameter, filler content and phase adhesion are taken into account. Critical particle contents and diameters caused by matrix morphology are discussed. Model calculations are compared with experimental results from acoustic emission analysis and dynamic fracture mechanics tests on PS, PVC and HDPE filled with $CaCO_3$ or SiO_2 particles.

1. Introduction

The development of composites with definite properties assumes the analysis of microscopic deformation and fracture processes determining the macroscopic strength and toughness level. Composite behaviour is influenced by a number of parameters such as matrix structure, nature and morphology of filler particles as well as characteristics of phase interactions between particles and polymer matrix. Only theoretical models of the strength and toughness behaviour based on a micromechanical analysis give an understanding of the effective macroscopic composite behaviour. Estimates concerning structurally or morphologically caused limits of property improvements and of weakest composite regions are of special interest. At present only a few theoretical approximations defining toughness behaviour of particulate-filled composites exist [1–4]. Fracture mechanics based toughness characteristic of polymers and their composites correspond with the aim of modern materials testing to assess the quality and performance of the products by methods well founded in materials science. As shown [5–10] only elastic–plastic fracture mechanics gives realistic values for toughness characteristics of thermoplastics.

2. Damage zone at the crack tip

Assuming elastic–plastic fracture behaviour, the stress concentration ahead of the crack tip results in a plastic zone (see Fig. 1). The physical fracture process, however, happens in a much smaller area near the crack tip – the fracture process zone [6]. Lauke *et al.* [9, 11, 12] analysed and modelled such zones and the processes of energy dissipation within these zones under a micromechanical approximation for short-fibre reinforced thermoplastics. The size of the plastic zone thought to be circular and depending of the respective microstructure can be estimated by

$$r_D^{(i)} = \beta_{(i)}(\delta_c)_C \frac{E_C}{(\sigma_c)_{(C)}^{(i)}} \qquad (1)$$

where $(\delta_c)_C$ is the critical crack opening, E_C is Young's modulus and $(\sigma_c)_C^{(i)}$ is the critical composite stress of the failure process (i). Values given for $\beta_{(i)}$, a factor specific for each mechanism, differ between $1/2\pi$ [5, 6, 12, 13], 0.036 to 0.157 [14] and $\pi/16$ [15–18].

Acoustic emission analysis has been used to determine critical composite stresses and actual failure mechanisms in composites experimentally [19–22]. Representative damage states were related to a dominant failure mechanism in connection with finite-element calculations of local stress–strain distributions in the composite.

It was shown that the energy criteria defining the critical composite strain $(\varepsilon_c)_C$ for the particle–matrix debonding

$$(\varepsilon_c)_C = \frac{1}{\alpha_\varepsilon \alpha_0 E_C}\left(\frac{12\gamma_{T/M}E_M}{D_T}\right)^{1/2} \qquad (2)$$

is in a good agreement with experimental results [21] (see Fig. 2). In Equation 2 $\gamma_{T/M}$ the specific debonding energy of particle–matrix interface, E_M and E_C are Young's moduli of matrix and composite, D_T is the mean particle diameter and α_ε the strain concentration factor around the particles, α_0 is the additional stress concentration in crazing polymers which support the

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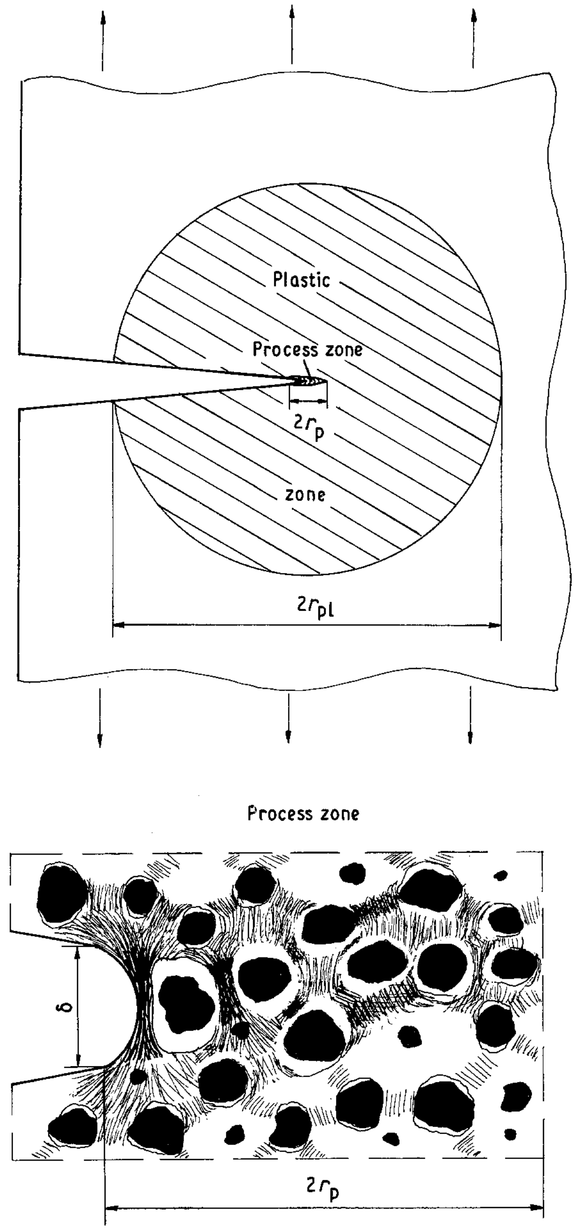

Figure 1 Damage zone ahead the macrocrack of a particulate-filled thermoplastic material.

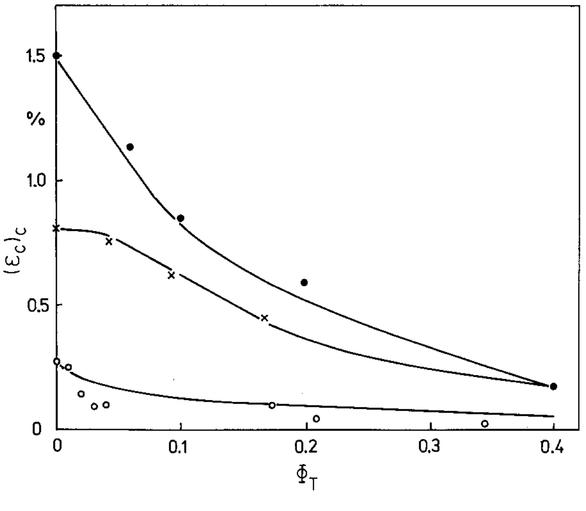

Figure 2 Critical strains from acoustic emission analysis of tensile test experiments at $T = 295$ K, $v_T = 1$ mm min^{-1} for PS (○) $D_T = 1$ μm and $v_T = 10$ mm min^{-1} for PVC (×), $D_T = 2$ μm and HDPE (●), $D_T = 2$ μm (theoretical approximation after Equation 2).

craze formation like surface scratches

$$\alpha_0 = 1 \qquad \text{for shear yielding}$$

$$\alpha_0 = \left(\frac{R_m}{\sigma_{cAE}}\right)_M \qquad \text{for craze mechanism}$$

where R_m is the ultimate fracture strength and σ_{cAE} is the crazing stress of the polymer matrix. This stress level is also determined by means of acoustic emission analysis for thermoplastic matrices as well as short-fibre reinforced thermoplastics [21].

3. Nature and energy of dissipation mechanism

In different zones the following energy dissipation mechanisms are detected in particulate-filled thermoplastics.

(i) Particle–matrix debonding ($w_{T/M}$, plastic zone)

(ii) Non-linear viscoelastic matrix deformation leading to microshear bands or crazes (w_s, plastic zone)

(iii) Plastic deformation of matrix bridges (w_{pl}, fracture process zone)

(iv) Fracture of matrix fibrils (w_f, fracture process zone).

Fig. 3 demonstrates the influence of filler particles on thermoplastic fracture behaviour.

Using the energy criteria and expressions derived by Pompe and Lauke [16, 18], the total fracture energy can approximately be formulated as

$$J_C = (1 - \Phi_T)J_{M*} + \sum_i r_D^{(i)} w_{(i)} \qquad (3)$$

where J_C and J_{M*} are the J integral values of the composite and modified matrix, $w_{(i)}$ is the volume-specific energy dissipation of failure mechanism (i), $r_D^{(i)}$ are extensions of the corresponding failure subzones and Φ_T is the particle volume content.

The specific energy results from

$$w_{(i)} = \frac{W_{(i)}}{(D_T + \lambda_T)^3} \qquad (4)$$

where $W_{(i)}$ is the deformation or fracture energy, D_T is the mean particle diameter and λ_T is the spatial particle distance.

A micromechanical approach for individual dissipation mechanisms leads to the following specific deformation and fracture energies (Table I). To calculate the composite fracture energy now the critical composite crack opening $(\delta_c)_C$ is to be known or to be eliminated. The critical crack opening as a true toughness parameter itself characterizes the deformation state ahead the crack tip at crack initiation.

A crack opening δ directly at the crack tip of an unfilled matrix initiates crack propagation if the rupture strain of the fibrils is reached. It can, therefore, be estimated considering the rupture length

$$\delta_R = l_0(1 + \varepsilon_R) \qquad (5)$$

with deformation length $l_0 = 2 \times$ crack tip radius. This means that the critical crack opening in the case of dynamic crack initiation experimentally measured

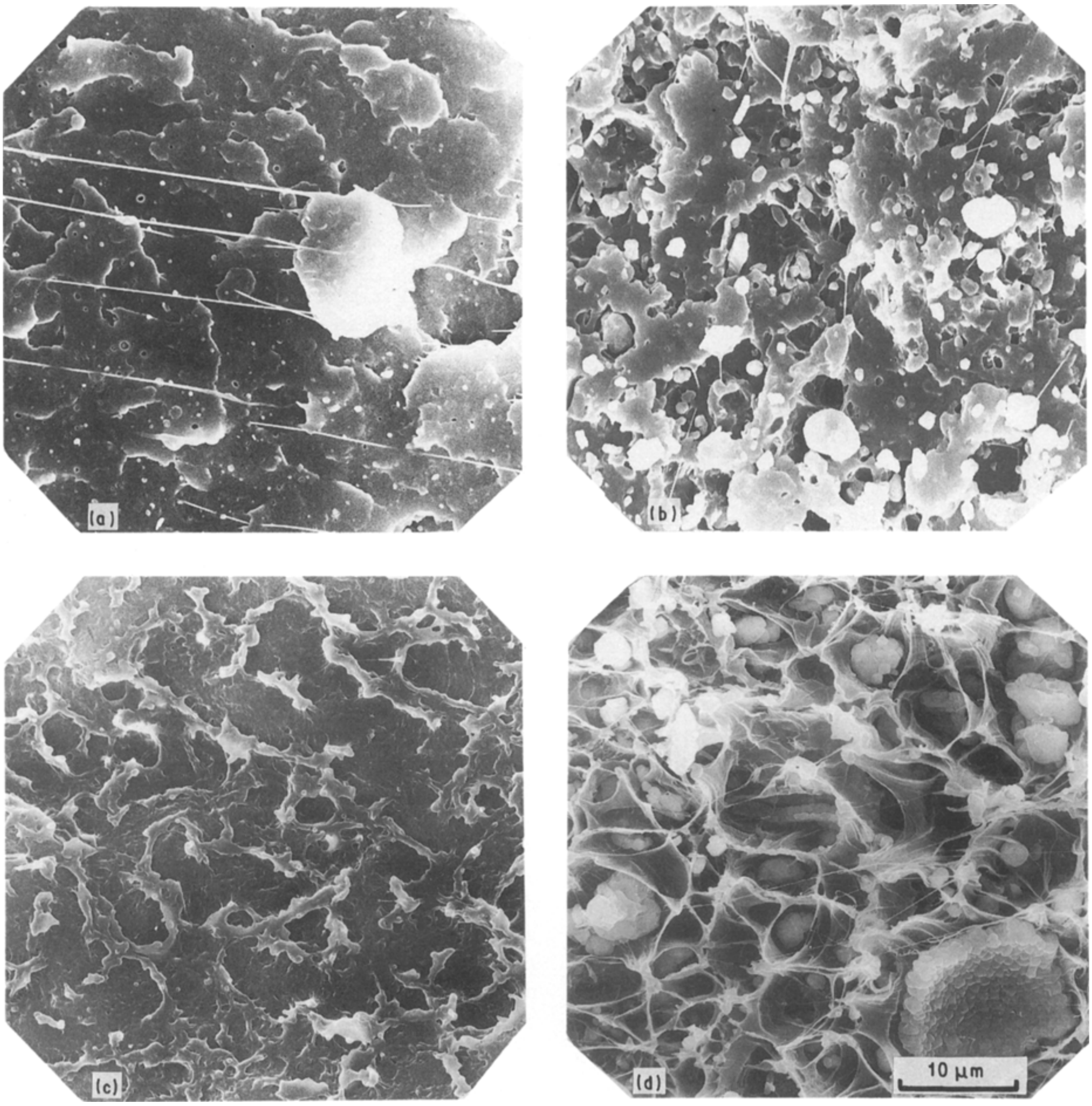

Figure 3 SEM of fracture surfaces (a) unfilled PVC, (b) chalk-filled PVC (10 vol %), (c) unfilled HDPE, (d) chalk-filled HDPE (20 vol %) (regions of "stable" crack growth).

by maximum test piece deflection equals

$$\delta_{\mathrm{Id}} = \beta\delta_{\mathrm{R}}\frac{E}{R_{\mathrm{e}}} \qquad (6)$$

where R_e is the yield strength of the material.

The J integral can be found according to the known expression as

$$J_{\mathrm{Id}} = mR_{\mathrm{e}}\delta_{\mathrm{Id}} \qquad (7)$$

The material-specific parameter $m \geqslant 2$ corresponds to the planar strain state including strain-hardening processes [5, 6]. In accordance with finite-element calculations the value $m = 2$ was confirmed experimentally for chlorinated PVC [23].

In Equation 7 R_e is to be replaced by tensile strength R_m for materials failing through crazing. The results shown in Table II confirm this model for different thermoplastics.

In composites the radius of the failure zone is increased by an earlier onset of energy dissipation. The critical composite crack opening should be increased proportionally to $(\varepsilon_c)_{M*}/(\varepsilon_c)_C$. Experimental results, however, point to a composite embrittlement above a critical matrix-specific filler content. Obviously this is true if

$$\frac{\lambda_{\mathrm{T}}}{D_{\mathrm{T}}} < \frac{\lambda^*}{D_{\mathrm{T}}}$$

The critical particle distance λ^* can be traced back to a minimum microcrack distance depending on the microcrack size (resp. particle size)

$$\lambda^* \sim 2\beta\left(\frac{J_{\mathrm{Id}}E}{\sigma_{\mathrm{c}}^2}\right)_{\mathrm{M}*} \qquad (8)$$

This distance characterizes the case of overlapping the plastic zones of neighbouring microcracks. Based on experimental results received on PVC–matrix composites the critical morphological conditions of "ductile-to-brittle" transition have been calculated for different composite matrices (Table III; loading

TABLE I Volume-specific energies of dissipation mechanisms

Plastic zone	(a) particle–matrix debonding: $w_{T/M} = \frac{6\Phi_T}{D_T}\gamma_{T/M}$
$r_{pl.} = m\beta(\delta_c)_C\frac{E_C}{(\sigma_{cAE})_C}$	(b) craze or microshearband formation: $w_s = \frac{\Phi_T}{2}(C\varepsilon_y^{(1+n)} - \sigma_{cAE}\varepsilon_{cAE})_{M*}$
Fracture process zone	(c) plastic deformation of matrix bridges: $w_{pl} = \Phi_T\left(\frac{\sigma_R(\varepsilon_R - \varepsilon_y)}{1 + \tilde{\varepsilon}}\right)_{M*}$
$r_P = m\beta(\delta_c)_C\frac{E_C}{R_C}$	(d) fracture of stretched matrix fibrils: $w_f = \frac{3\Phi_T\lambda_T^2}{D_T^3}\gamma_f$

$\gamma_{T/M}$	specific debonding energy of particle–matrix interface,	
$\varepsilon_{cAE}/\sigma_{cAE}$	critical matrix strain–stress determined by acoustic emission	of the modified matrix $M*$
ε_y	yield strain	
$\tilde{\varepsilon}$	strain in the true stress–strain relation at which the necking process is stabilized [10, 16]	
ε_R/σ_R	rupture strain–stress	
C/n	constant-strain-hardening coefficient in the true stress–strain relation	
γ_f	specific fracture energy of fibrils	
$(\sigma_{cAE})_C$	critical composite stress determined by acoustic emission	
R_C	yield strength (shearband deformation) or fracture strength (craze deformation) of the composite	

conditions see Table II). It was supposed that above a critical particle content the geometrically caused decrease of matrix bridge elongation under an identical local rupture strain is proportional to (λ_T/λ^*).

Then the critical composite crack opening can be calculated as

$$(\delta_c)_C = A\left(\frac{(\varepsilon_c)_{M*}}{(\varepsilon_c)_C}\right)_{AE}(\delta_c)_{M*} \quad (9)$$

where

$$A = 1 \quad \text{for } \lambda_T/D_T \geqslant \lambda^*/D_T$$
$$A = \lambda_T/\lambda^* \quad \text{for } \lambda_T/D_T < \lambda^*/D_T$$

In Equation 9 $(\varepsilon_c)_{M*}$ and $(\varepsilon_c)_C$ are critical strains of the modified matrix and of the composite measured by acoustic emission tests and $(\delta_c)_{M*}$ is the critical crack opening of the modified matrix. In case of a dynamic crack initiation δ_c corresponds to δ_{Id}.

The concept of a "modified" composite matrix considers the fact that besides the above discussed phase interactions in the failure process structural interactions between particles and matrix can also happen in the manufacturing process. These interactions depend on the particle surface activity (surface treatment), the matrix reactivity, as well as on the particle content, their shape and specific surface. These modifications can result in defined interphases but also in structural or morphological changes of the whole matrix. The effect of interphases was not considered in this model. Such a matrix modification leads to significant changes in the relaxation behaviour measured by dynamic mechanical analysis. In the case of chalk-filled thermoplastics the filler surface was modified by stearic acid. Changes of the relaxation spectra of chalk-filled PVC compared with the unfilled matrix indicate a stiffening of interphase molecules around the particles. Chalk-filled HDPE, however, shows a higher damping in the temperature range of β relaxations. This effect results from the softening of intercrystalline amorphous regions near the particle surface by stearic molecules. Silica filler was used without surface treatment.

TABLE II Theoretical and experimental critical crack opening and J integral values under dynamic crack initiation at $T = 295$ K ($v_H = 1.5\ \text{m s}^{-1}$ for PVC and HDPE, $v_H = 1.0\ \text{m s}^{-1}$ for PS, $l_0 = 0.4\ \mu\text{m}$)

Polymer matrix	E (GPa)	R_e (MPa)	ε_R Local	δ_R (μm)	δ_{Id} (μm)	J_{Id} (N mm^{-1})	δ_{IdK} (μm)	J_{Id} (N mm^{-1})
				Theory			Experiment	
PVC	2.70	51	1.1	0.84	17	1.9	20	1.7
HDPE	1.00	27	8.0	3.60	52	2.8	49	2.7
PS	3.19	(32) (R_m)	2.0	1.20 (with $\beta = \pi/8$, $m = 2$)	47	3.0	35	2.7

TABLE III Morphological conditions for a "ductile-to-brittle" transition at dynamic crack initiation

Polymer	λ^*/D_T	Φ_T^*
PVC	0.87[a]	0.080
HDPE	2.07[b]	0.020
PS	4.68[b]	0.003

[a] Experimental.

[b] Theoretical.

The relaxation spectra of such composites show remarkable interactions between the matrix and filler phase (see Fig. 4). These results can be interpreted with a strongly influenced crystallization process of HDPE in the direction of a higher disorder. On the one hand PVC molecules seem to be partly immobilized, on the other a thermal stress induced higher free volume support relaxation mechanisms.

The failure mechanism of a composite matrix can vary as a result of strong interactions or large filler contents causing changes in local stress distribution.

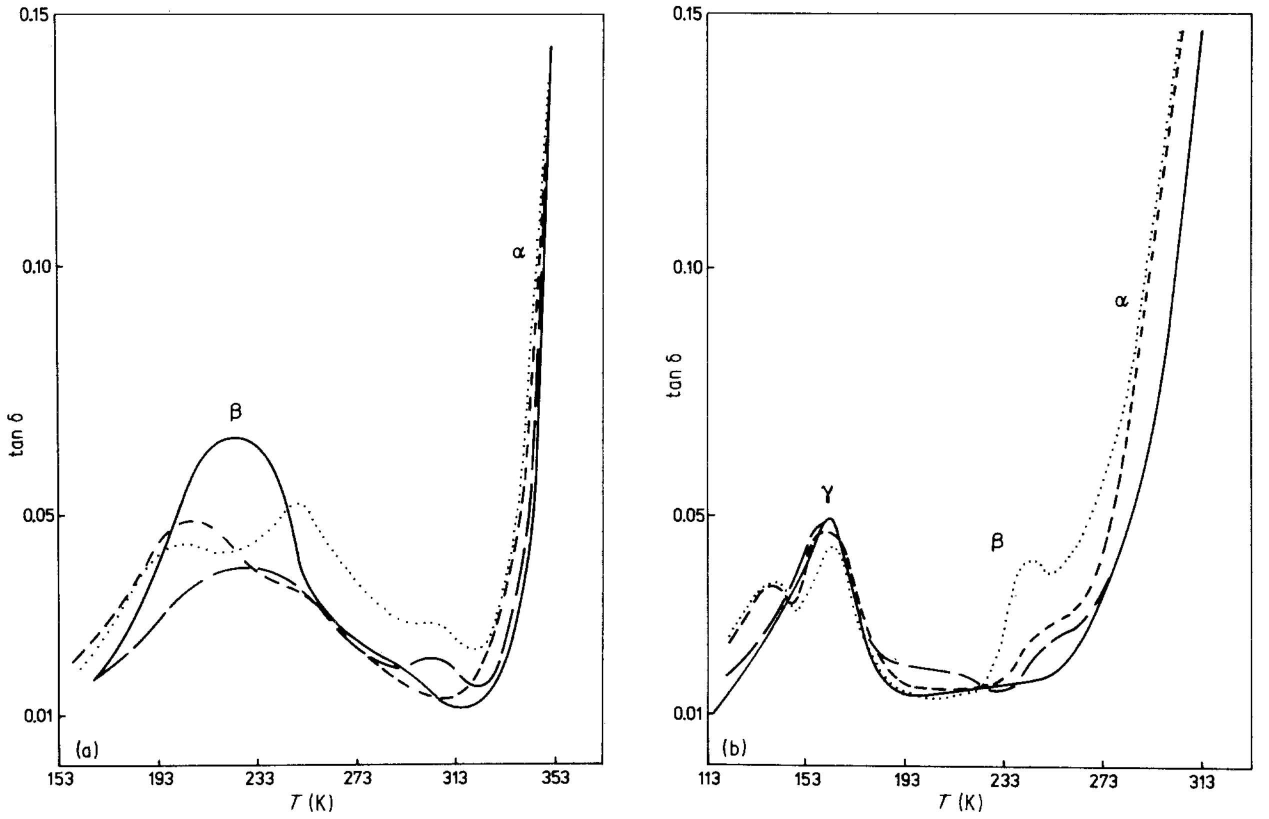

Figure 4 Relaxation spectra of unfilled and silica-filled thermoplastics ($f \approx 1$ Hz) (a) (—— PVC, — — PVC/SiO$_2$ ($\Phi_T = 0.06$), - - - PVC/SiO$_2$ ($\Phi_T = 0.14$), ... PVC/SiO$_2$ ($\Phi_T = 0.22$)) (b) (—— PE, — — PE/SiO$_2$ ($\Phi_T = 0.05$), - - - - PE/SiO$_2$ ($\Phi_T = 0.10$), ... PE/SiO$_2$ ($\Phi_T = 0.15$)).

The composite matrix fails in a structurally caused brittle manner. There is also another effect producing embrittlement. The interaction between neighbouring microcracks in the process zone leads above critical crack densities to instability of the matrix bridges and therefore promotes macrocrack growth earlier [24–26].

The total fracture energy of composites can thus be expressed as

$$BJ_C = (1 - \Phi_T)J_{M*} + m\beta(\delta_c)_C E_C \times \left(\frac{w_{T/M} + w_s}{(\sigma_{cA\dot{E}})_C} + \frac{w_{pl} + w_f}{R_C} \right) \qquad (10)$$

where $m \geqslant 2$, $\beta \leqslant \pi/16$ and B considering the effect of matrix bridge instability

$$B = 1 \qquad \text{for } \lambda_T/D_T \geqslant \lambda^*/D_T$$

$$B = (\lambda_T/\lambda^*)^2 \qquad \text{for } \lambda_T/D_T < \lambda^*/D_T$$

4. Discussion

Results calculated by the model described are compared with experimental data in Figs 5 and 6. In these calculations a poor phase adhesion and an unchanged deformation and fracture behaviour of the composite matrix compared with the unfilled matrix was supposed. Experimental data differing from theoretical calculations are caused by particle agglomeration effects above 10 vol % or by a filler surface treatment. In silica-filled thermoplastics a satisfactory agreement between theoretical and experimental results can be found only supposing extended phase interactions degreasing the fracture energy of the modified matrix. As shown the relaxation spectra point to such an explanation. The filling of thermoplastic matrices with spherical, high-modulus particles thus increases in the case of undercritical filler contents the J integral towards instable crack initiation. The relative improvement in toughness is the higher the lower the composite matrix toughness. This phenomena is related to the discussed critical particle distance λ^* and the resulting increase of the critical filler content in brittle matrices.

The dominant additional energy dissipation takes place in the fracture process zone as a result of a particle-initiated microshearband or craze multiplication (w_{pl}).

The composite toughness is determined by the matrix toughness, the filler volume, the particle diameter and the phase adhesion. On the one hand these parameters determine the critical strain and stress levels causing dissipation processes (plastic zone size), on the other they limit the critical particle content, that is, the maximum of the composite J integral. Obviously, the optimum particle diameter is comparable with the size of naturally, matrix-specific microcracks. Particle size distributions with a mean value above the size of stable grown matrix cracks lead to a geometrically caused instability. As expected the critical microcrack length measured by SEM on fracture surfaces is in good correspondence with the matrix toughness (Table IV).

Results also indicate that there is a certain relation-

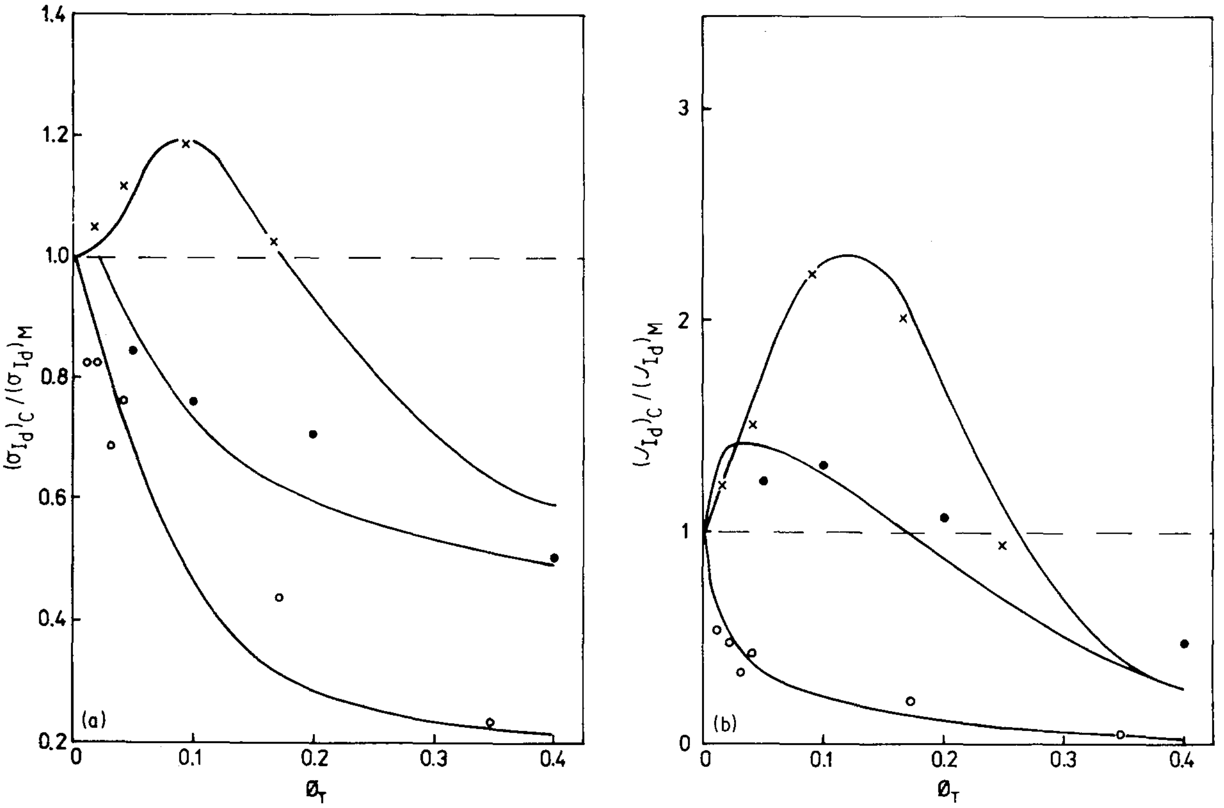

Figure 5 Fracture toughness behaviour of chalk-filled thermoplastics under dynamic loading. (● PE, D_T = 1.8 μm; × PVC, D_T = 1.8 μm, ○ PS, D_T = 1.0 μm, —— theory).

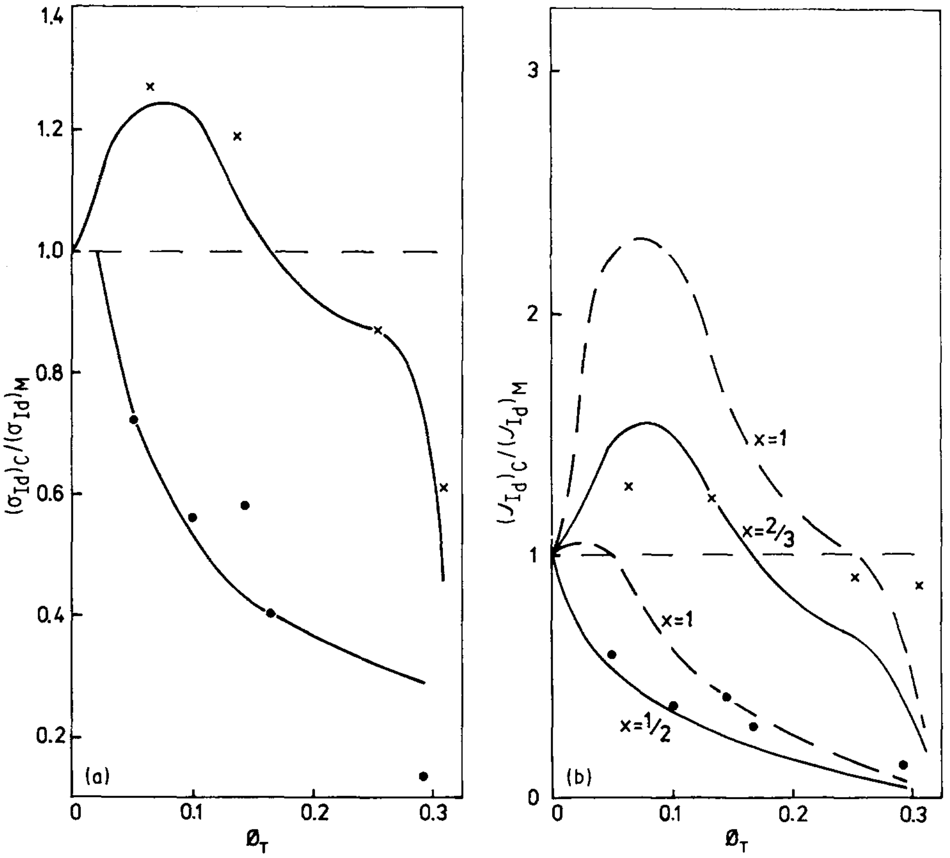

Figure 6 Dynamic fracture toughness of silica-filled thermoplastics. (● PE, × PVC, theory; D_T = 0.4 μm, ——— $J_{M*} = J_M$, ——— $J_{M*} = xJ_M$).

ship between the microcrack size and the size of morphological units such as agglomerates of PVC-primary particles (≤ 5 μm) or spherulites in HDPE (4–8 μm).

Much smaller particles (< 1 μm) with large and active surfaces lead to a structurally caused matrix embrittlement.

It is thought that extremely small particles raise the

TABLE IV Maximum size of stable grown microcracks

Polymer	$(2 \cdot a_c)_{max}$ (μm)
PVC	4–6
HDPE	6–8
PS	8–10

network density and restrict the chain mobility in boundary layers of amorphous thermoplastics. In semicrystalline polymers they promote the formation of transcrystalline regions. To increase toughness it is recommended that an optimum is achieved and not maximum phase adhesion using coupling agents. This can be reached by boundary layers capable of relaxation processes which increase the rupture strain of the modified matrix and thus the energy term w_{pl}. "Ideal" phase adhesion prevents interphase boundary failure and leads to a triaxial stress state inside the composite matrix and consequently to brittle fracture behaviour. In fracture mechanics tests investigating the influence of silanes and other coupling agents, it was often found that there was no unstable crack propagation [27]. To describe such a fracture behaviour in further models, quantities and mechanisms of stable crack propagation are to be considered.

References

1. K. FRIEDRICH and U. A. KARSCH, *J. Mater. Sci.* **16** (1981) 2167.
2. A. C. MOLONEY, H. H. KAUSCH and H. R. STIEGER, *ibid.* **18** (1983) 208.
3. *Idem., ibid.* **19** (1984) 1125.
4. K. KENDALL, *Brit. Polymer J.* **10** (1978) 35.
5. H. H. KAUSCH, "Polymer Fracture" (Springer, Berlin, 1987).
6. H. BLUMENAUER and G. PUSCH, "Technische Bruchmechanik" (VEB Deutscher, Leipzig, 1987).
7. W. DOELL, L. KOENCZOEL and L. BEVAN, "Encyclopedia of Polymer Science and Engineering", Vol. 9, 2nd Edn (John Wiley, New York, 1987).
8. W. GRELLMANN and J.-P. SOMMER, "Fracture Mechanics, Micromechanics and Coupled Fields" Vol. 17 (FCM, Berlin, 1985) p. 48.
9. W. GRELLMANN, S. SEIDLER and B. LAUKE, *Polym. Compos.*, to be published.
10. W. GRELLMANN and S. SEIDLER, in Proceedings of 7th European Conference on Fracture, Budapest 19.-24.9.1988, Vol. I, p. 517.
11. B. LAUKE and B. SCHULTRICH, *Compos. Sci. Technol.* **26** (1986) 1.
12. M. PARVIN and J. G. WILLIAMS, *Int. J. Fracture* **11** (1975) 963.
13. D. T. READ and R. P. REED, *ibid.* **13** (1977) 201.
14. N. LEVI, P. V. MARCAL, W. I. OSTERGREEN and J. R. RICE, *ibid.* **7** (1971) 143.
15. J. P. EILINCK, J. C. BAUWENS and G. HOMES, *ibid.* **7** (1971) 277.
16. B. LAUKE and W. POMPE, *Compos. Sci. Technol.* **26** (1986) 37.
17. B. BUDIANSKY, J. HUTCHINSON and J. C. LAMBROPOULOS, *Int. J. Solid Structures* **19** (1983) 337.
18. W. KREHER and W. POMPE, *J. Mater. Sci.* **16** (1981) 694.
19. G. LEPS, J. BOHSE and M. MAY, *NDT Int.* **19** (1986) 387.
20. J. BOHSE and G. KROH, *Plaste und Kautschuk* **34** (1987) 376.
21. J. BOHSE, Dr sc techn. Thesis, Technical University Leuna-Merseburg, Merseburg, FRG, (1989).
22. J. BOHSE and G. KROH, *J. Mater. Sci.*, to be published.
23. W. GRELLMANN, Dr sc techn. Thesis, Technical University Leuna-Merseburg, Merseburg, GDR, 1985.
24. H.-J. WEISS, *Plaste und Kautschuk* **24** (1977) 684.
25. W. POMPE, *Neue Huette* **23** (1978) 321.
26. G. GILLE, in Proceedings of VI International Pulvermetallurgische Tagung, Dresden 1977, FRG, p. 9-1.
27. S. SEIDLER, Dr.-Ing. Thesis, Technical University Leuna-Merseburg, Merseburg, FRG, (1989).

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