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Composition dependence of the fracture toughness of heterogeneous polymer systems

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A brief literature survey is presented on the models predicting the composition dependence of fracture properties of heterogeneous polymer systems. Some of the models cannot predict composition dependence properly or are limited to a narrow composition range, while more exact ones are difficult to use because of their complexity. A different approach is presented, which takes into consideration matrix characteristics, component interaction, changing stiffness and the decrease of matrix cross-section due to modification. Particulate filled and elastomer modified polypropylene blends and composites were prepared in the 0–0.3 volume fraction composition range, and strain energy release rate as well as notched Izod impact strength were determined. The proposed model proved to be valid for the studied blends and composites and revealed that the major energy absorbing process is the plastic deformation of the matrix, which, in the studied case, is enhanced by the presence of the second component. Data taken from the literature for the most diverse systems from elastomer modified thermoplastics to particulate filled epoxy resins were analysed in the same way and the approach proved to be valid in most cases. A correlation was found between fracture characteristics and yield stress of the systems. The structure of composites is an often neglected factor; orientation of anisotropic particles as well as aggregation strongly influence both the absolute values and composition dependence of fracture resistance.

(Keywords: fracture toughness; blends; particulate filled polymers)

INTRODUCTION

The introduction of a second component into polymers is an accepted and frequently used method to modify their properties and to obtain new materials with improved characteristics[1–4]. Modification may be required to improve one or more properties, develop special characteristics like flame retardancy or conductivity[5,6], or simply to reduce price. Some of the second components which are often added are fillers to increase stiffness and dimensional stability, elastomers to improve fracture toughness and impact resistance and fibres to increase stiffness and strength. Fracture and impact properties have special significance in practice, simultaneous improvement of stiffness and impact resistance is very often the main goal of research and development[7–9]. Introduction of a second component modifies all characteristics of the polymer, therefore a balance of properties must be achieved, which is usually attained at a given optimum composition.

In order to find the optimum amount of second component to be introduced, properties must be studied as a function of composition. Models predicting the composition dependence of properties help the development of new materials enormously, since they reduce the number of necessary experiments, point out the most important factors influencing properties, describe the response of the material to the effect of the environment and often indicate the most advantageous way to improve performance. There are many models describing the composition dependence of modulus[3,10,11], while there are only a few predicting the correlation of yield properties with composition[12–14]. Very few models exist which describe the composition dependence of ultimate properties of blends and composites[15]. In spite of their importance, only a few correlations can be found which give any information on the effect of a second component on the fracture and impact properties of heterogeneous polymer systems.

There are a number of reasons for the lack of models on failure. One of the main goals of fracture studies was to develop techniques which give reliable, size independent fracture characteristics[16,17]. Even during fracture of a homogeneous polymer, numerous processes can take place (crack initiation, propagation, yielding, crazing,

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etc.), the number of which is further increased by the introduction of a second component (cavitation, voiding, debonding, etc.). Heterogeneities induce stress concentrations in the material and modify the stress field before the crack. Models which try to describe composition dependence of failure properties based on a single deformation mechanism often fail. Micro- and macromechanical deformation processes may change as a function of composition, and evaluation is often complicated by morphological changes as well (aggregation, orientation of anisotropic particles, phase inversion, development of interpenetrating network structures, etc.).

The aim of this study is to shed more light on the question of composition dependence of fracture characteristics. First a brief survey is given about the existing models, then a new correlation will be proposed. The model is applied for the description of the composition dependence of impact properties of particulate filled and elastomer modified polypropylene, but its general validity is verified by the analysis of the most diverse fracture characteristics of both thermoplastics and thermosets taken from the literature. Special attention is paid to the comparison to other mechanical properties and also to structure, a subject very often neglected in the investigation of fracture toughness of heterogeneous polymer systems.

EXISTING MODELS

Since in foams during fracture all the energy is absorbed by the matrix and voids reduce the effective area of the fracture surface, Bucknall[18] has proposed the use of the effective area model, developed by Ishai and Cohen[12] and also by Nicolais and Narkis[13], for the prediction of the strain energy release rate (G_{Ic}) of foams:

$$G_{\mathrm{Ic}} = G_{\mathrm{Ic}_0}(1 - 1.21\varphi^{2/3}) \tag{1}$$

where G_{Ic} and G_{Ic_0} are the fracture energy of the foam and the matrix, respectively, and φ is the volume fraction of the voids. Although he found good agreement with the prediction in the case of HIPS structural foams, contradictory results were published as well[19]. Assuming that unbonded beads have a similar effect on the constraints at the crack tip and thus on fracture resistance as voids, Bucknall[18] used equation (1) to analyse the composition dependence of G_c of some poly(phenylene oxide)/glass composites measured by Trachte and DiBenedetto[20]. Although the trends in the measured and predicted values were the same, significant differences existed in the actual values. Moreover, the application of equation (1) implies that the crack propagates through the minimum cross-section of the matrix; the filler/matrix interaction does not influence fracture and the filler does not induce any additional deformation processes[18]. According to literature data none of these assumptions is valid, thus, although a decrease of matrix cross-section seems to influence fracture resistance, the equation is not adequate in most heterogeneous polymer systems.

Analysing the fracture of a polyethylene filled with colloidal silica and carbon black, Kendall[21] developed a correlation which takes into account the fracture energy of the interface, i.e. the interaction:

$$R_c = R_0(1 - k\varphi) + R_i n k\varphi \tag{2}$$

where R_c, R_0 and R_i are the fracture resistance of the composite, matrix polymer and interface, respectively, $k\varphi$ is the fracture surface volume fraction, which depends on the path of the crack across the specimen, and n takes into account the extra path around the particles. Measurement of the adhesion strength between polyethylene and silica indicated that R_i is practically zero, and thus could be neglected.

Friedrich and Karsch[22] used basically the same principles to describe G_c of a silica filled polypropylene:

$$G_c = R_0(\varphi)(1 - k\varphi) + R_i n k\varphi \tag{3}$$

with the exception that they assumed that fracture resistance of the matrix depends also on filler content. At higher filler content the matrix cannot resist crack growth because strain at break is reduced by the coalescence of holes around the filler particles. This results in a decrease in the size of the plastic zone in which matrix resistance can develop to its maximum value. They expressed the composition dependence of R_0 as:

$$R_0 = R_0(0)[2 - \exp(\varphi)] \tag{4}$$

They also neglected the effect of interfacial fracture resistance (R_i) in analysing their data. Denault and Vu-Khanh[23] suggested a similar correlation to describe the composition dependence of maximum crack growth resistance ($K_{R_{\max}}$):

$$K_{R_{\max}} = K_{R_0}(\varphi) + [K_{R_i} - K_{R_0}(\varphi)]\varphi \tag{5}$$

They did not define the composition dependence of K_{R_0}, i.e. $K_{R_0}(\varphi)$, and assumed that the contribution of K_{R_i} is positive, but did not check the prediction against their experimental data.

The above equations contain components related to matrix properties, specimen cross-section (fracture surface) and filler/matrix interaction. They assume, however, that with increasing interaction (adhesion) fracture resistance increases. This approach is strongly criticized by Chen *et al.*[24] and is not in agreement with numerous experimental data which indicate that decreasing adhesion results in an increase of fracture energy or toughness[25–27]. Moreover, validity of these correlations seems to be limited to the cases they were developed for and they have not found wide application yet.

Rigid particles often increase the fracture resistance of polymers. The most diverse fracture properties have shown a maximum in their composition dependence both in thermosets and thermoplastics[27–33]. One approach to explain this phenomenon was proposed by Lange[34], who assumed that the propagating crack is pinned by the particle and increased stress, and thus energy, is needed to make the crack bow out between particles and propagate further. According to his theory the most important factor determining fracture resistance is the interparticle distance, C, and it is inversely proportional to the fracture energy:

$$G_{\mathrm{Ic}} = G_{\mathrm{Ic}_0} + \frac{T}{C} \tag{6}$$

where T is the line energy per unit length of crack front. Particle spacing can be expressed as:

$$C = \frac{2d(1 - \varphi)}{3\varphi} \tag{7}$$

where d is the size of the particles. To obtain a more exact solution Evans[35] and later Green *et al.*[36,37] carried out stress analysis to determine the stress necessary to propagate the secondary cracks bowing out between the obstacles. They found that the ratio of particle size to particle distance and not particle spacing was the determining factor. These more exact solutions could not always be expressed in an analytical form and they are further complicated by the interaction of secondary cracks, penetration of the obstacles, overlapping of strain fields and plastic deformation of the matrix.

Many attempts were made to use the line tension (crack-pinning) concept for the explanation of increasing toughness in particulate filled thermosets[27,33,38–41] and also in thermoplastics[42]. Although in most cases good agreement was claimed between theory and experiments, applicability was confined to a limited composition range and in some cases the model could not be used at all[27]. Moreover, Evans[35] concluded from his analysis that line energy has any importance only in the case of a rigid matrix filled with impenetrable, rigid particles in brittle fracture and whenever additional micromechanical deformations, e.g. debonding, fibre pull-out, plastic deformation, take place, the contribution of the line energy can be neglected.

The influence of plastic deformation, however, is significant in most cases, including thermosets. By comparing the fracture of an elastomer modified epoxy with that of the unmodified matrix Kinloch *et al.*[43,44] have shown that increased fracture toughness was a consequence of the plastic deformation initiated by the second phase even when specimens prepared both from the unmodified and the modified resin fractured in plane strain and fulfilled linear elastic fracture mechanics (LEFM) conditions. Significant plastic deformation was observed also in particulate filled polymers[22,26–28,45–47]. Debonding and microcracking of the polymer result in a changing stress field which in turn initiates enhanced plastic deformation of the matrix[45]. This is reflected by the inelastic character of the deformation and the hysteresis of the stress *versus* strain curve. Evans *et al.*[45] carried out an analysis of this non-linear stress–strain relation and concluded that fracture toughness is determined by the 'degradation' of matrix material due to filling and by the plastic deformation during flow. By combining the two effects they arrived at the correlation:

$$J_c = J_{c_0}\left[1-\varphi+\frac{2^{(n+2)}}{n+1}\frac{\ln(h/R)}{I_n}\right] \tag{8}$$

where J is the path independent line integral, n is the work hardening rate of the polymer, I_n is a function of n, h is the width of the plastically deformed zone and R is the radius of the particles. Since h is not known, it must be approximated. This can be done by:

$$h \simeq \left(\frac{EJ_c}{\sigma_y^2}\right)g(n) \tag{9}$$

where E is the Young's modulus, σ_y is the yield stress of the composite and $g(n)$ is a function of n. Assuming $n=0.2$ for epoxy resins they obtained the final correlation:

$$\frac{J_c}{J_{c_0}} = 1-\varphi+0.8\ln\left(\frac{EJ_c}{4\sigma_y^2 R}\right) \tag{10}$$

which is the upper bound toughness. A more complete solution for steady-state toughening can also be obtained, but it is even more complicated. They found good agreement with their experimental data, but used relative values based on the argument that the deformation mechanism is different in the composite and the matrix, i.e. $J_{c_0} \neq J_{c_{\text{polymer}}}$. In spite of the agreement, the necessity to know n, to determine I_n and $g(n)$, as well as the approximation of h make the application of the model quite cumbersome.

A different approach was suggested recently by Jančař *et al.*[48]. Accepting the reasoning of Fernando and Williams[49] they expressed fracture toughness as a combination of a plane strain and a plane stress component. Using the principles of LEFM to define the correlation between K_c and G_c and giving the relation of plane strain (G_{1c}) and plane stress (G_{2c}) fracture energies as:

$$G_{1c} = G_{2c}(1-2\nu)^2 \tag{11}$$

they arrived at the final correlation:

$$(G_c')^{1/2} = \left(\frac{G_{1c}}{1-\nu^2}\right)^{1/2} + \frac{EG_{2c}}{\pi B\sigma_y^2}\left[G_{2c}^{1/2} - \left(\frac{G_{1c}}{1-\nu^2}\right)^{1/2}\right] \tag{12}$$

where G_c' is the strain energy release rate of the composite, ν is Poisson's ratio and B is the thickness of the specimen. Composition dependence is expressed indirectly through E and σ_y. They used the Lewis–Nielsen (Kerner–Nielsen or modified Kerner)[3] equation for the description of the composition dependence of the modulus and a set of equations to give the upper and lower bounds for that of the yield stress in the case of perfect and zero adhesion[50]. In this way they arrived at an upper and lower bound of G_c, which corresponded well to the experimental data on polypropylene/$CaCO_3$ composites. Aside from the fact that the approach of Fernando and Williams[49] was criticized at that time by Bucknall[18] as having no theoretical justification, upper and lower bounds are not always helpful in research and development and the indirect composition dependence as well as the application of several equations make the model difficult to use, just as in the previous case.

THE PROPOSED APPROACH

The above approaches either do not correspond to the experimental results or the theoretically more perfect solutions are difficult to use because of their complexity. Analysis of the models and the experimental data, however, show that the major factors in determining fracture toughness and fracture energy are the properties of the matrix, decrease of matrix material due to the introduction of the second phase and interaction of the matrix and the dispersed component. It is also clear that the most important energy absorbing process is plastic deformation. The stress field in the front of the crack results in a debonding of the particles[45], or cavitation in the case of an elastomer modified polymer[43,44], thus changing stress distribution and constraint. These result in a significant plastic deformation of the matrix. Adhesion or interdiffusion of the components leads to increased debonding stress and changing matrix or, more exactly, interphase properties.

Taking into account these considerations matrix properties are expressed by G_{c_0}, as in some of the previous cases, and decrease of the energy absorbing material (matrix) by the changing of the effective load bearing area. Since the Nicolais–Narkis[13] equation considers only one specific spatial arrangement of the particles and gives zero matrix cross-section at $\varphi<1$, which is physically impossible, we use the expression developed earlier[51], i.e. $A=(1-\varphi)/(1+2.5\varphi)$. Analogously to our earlier treatment of yield stress[14] and tensile strength[15], we assume that property changes due to interaction are proportional to the actual value of the given property:

$$\frac{dG_c}{d\varphi}=B_f G_c \tag{13}$$

where B_f is a proportionality constant, and thus we arrive at the final correlation:

$$G_c=\frac{G_{c0}}{E/E_0}\,\frac{1-\varphi}{1+2.5\varphi}\exp(B_f\varphi) \tag{14}$$

where E/E_0 takes into consideration the resistance of the matrix material against plastic deformation. It has been shown that B is related to the stress carried by the minor phase and depends on the size of the interface and on the strength of the interaction[14,15,52,53]. The correlation can be applied to all fracture characteristics related to the energy dissipated in fracture, i.e. G_c, J_c or any of the standard impact tests (Izod, Charpy).

If valid LEFM conditions prevail, using the usual correlations between G_c and K_c

$$K_c^2=G_cE \tag{15}$$

for the plane stress and

$$K_c^2=\frac{G_cE}{1-\nu^2} \tag{16}$$

for plane strain conditions, the composition dependence of the critical stress intensity factor can be given with the correlation as well:

$$K_c^2=K_{c0}^2\frac{1-\varphi}{1+2.5\varphi}\exp(B_f\varphi) \tag{17}$$

Equations (14) and (17) express direct composition dependence and using reduced, $G_{c_{red}}=G_c\,(1+2.5\varphi)/(1-\varphi)$, or relative, $G_{c_{rel}}=G_{c_{red}}/G_{c0}$, variables linear correlations should be obtained in a semi-logarithmic plot.

EXPERIMENTAL

A polypropylene homopolymer (PP) was used as matrix polymer. Two different particulate fillers, a $CaCO_3$ and a talc were applied to prepare the composites. Elastomer modification was made with an ethylene–propylene copolymer (EPR). The most important characteristics of the materials used in the experiments are listed in *Table 1*. Composition of the blends and composites changed between 0 and 0.3 volume fraction in 0.05 volume fraction steps.

Table 1 Characteristics of the investigated polymers and fillers

Type	Density ($g\,cm^{-3}$)	Particle size (μm)	Specific surface ($m^2\,g^{-1}$)	Melt flow index (g/10 min)
PP	0.90			10.0[a]
$CaCO_3$[b]	2.70	1.0	11.0	
Talc	2.78	3.4	8.0	
EPR	0.87			1.1[c]

[a] 230°C, 21.6 N
[b] Surface treated with 0.9 wt% stearic acid
[c] 190°C

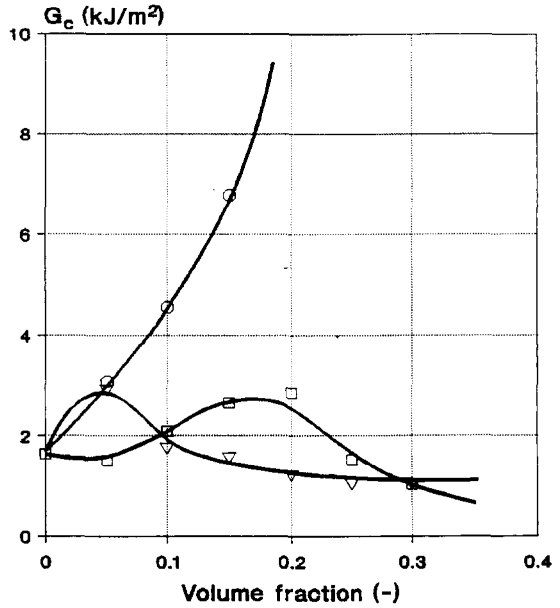

Figure 1 Composition dependence of strain energy release rate of PP blends and composites determined on small (4 × 10 × 80 mm) SEN specimens: (○) EPR; (□) $CaCO_3$; (▽) talc

Homogenization was carried out in a Brabender DSK 42/7 twin screw compounder; the blends and composites were cooled in a water bath and pelletized. Specimens were prepared by injection moulding. An Engel ES 330/65 reciprocating screw machine was used to prepare dog-bone type tensile specimens of 4 mm thickness. Large 10 × 15 × 140 mm bars were injection moulded on a Battenfeld BSKM 100 B machine.

Tensile testing was carried out at $50\,mm\,min^{-1}$ cross-head speed. Young's modulus (E), yield (σ_y, ε_y) and ultimate (σ, ε) properties were determined. Izod testing was carried out according to ASTM D 256 on standard specimens with a notch radius of 0.25 mm. Fracture mechanics tests were carried out on small (4 × 10 × 80 mm) and large (10 × 15 × 140 mm) specimens with the technique introduced by Plati and Williams[54]. The relative length of the notch (a) to the width of the specimen (D) changed between 0.25 and 0.75 a/D, the ratio of span ($2L$) to thickness was 4 and the impact rate was $2.9\,m\,s^{-1}$. Notches were cut by a thin saw and then sharpened by a razor blade. Scanning electron microscopy (SEM) was used to characterize fracture surfaces.

VERIFICATION OF THE APPROACH

Composition dependence of the strain energy release rate of the PP blends and composites is given in *Figure 1*. G_c was determined with the small, three point bending specimens. Composition dependence of the blends is quite different from that of the composites, the former increases continuously, while the latter passes through a maximum, a phenomenon shown many times in the most diverse systems[27–33]. Composition dependence of notched Izod impact strength is similar, as shown by *Figure 2*. To check the validity of equation (14) reduced values of *Figure 1*

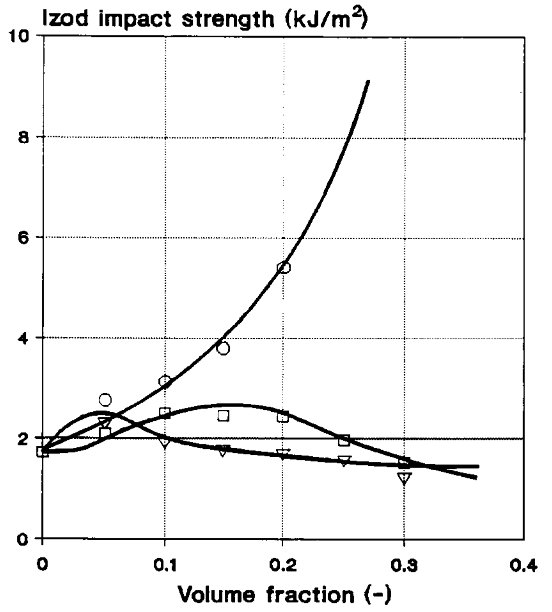

Figure 2 Notched Izod impact strength of PP blends and composites plotted as a function of composition. For symbols, see *Figure 1*

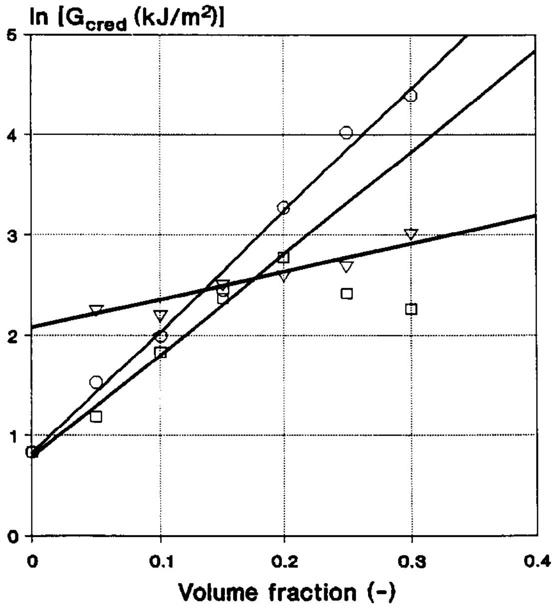

Figure 3 Reduced strain energy release rate of PP blends and composites plotted in a linearized form according to equation (14). For symbols, see *Figure 1*

($G_{c_{red}}$) are plotted as a function of composition in a semi-logarithmic form in *Figure 3*. Very good linear correlations are obtained in all three cases, with only a few points deviating from the straight lines. These deviations, as it will be shown, can be explained by considering the structure of the composites. The deviations are caused by the anisotropy of the particles in the composites containing talc and by aggregation in the $CaCO_3$ filled system.

The unexpectedly good correlations prove that component interaction, plastic deformation of the matrix, and changing effective matrix cross-section are the most important factors in impact modification. Plastic deformation of the matrix is the main energy consuming process during fracture both in blends and composites. This is amply proven by the fact that composition dependence of both the blends and composites could be described in the same way, although the primary data have shown completely different characteristics. The linear correlations properly reflect the effect of all the relevant factors. The effect of decreasing matrix cross-section can be separated and the primary effects can be clearly seen. It is obvious that the main effect of elastomer modification comes from the decreasing modulus, at least in the studied PP blends. Debonding and the subsequent plastic deformation are major factors in the $CaCO_3$ filled composites. The technique makes possible the study of the effect of changing structure as well. Equation (14) was fitted to all the data obtained on the three systems with the three different specimen configurations and the results are compiled in *Table 2*. It is clear that the linear fit is excellent, the treatment can be applied in all cases.

In spite of the good agreement between the experimental data and equation (14), this might be limited to the studied PP systems. Some data found in the literature were therefore analysed for a greater variety of systems. The composition dependence of the notched impact strength of poly(vinyl chloride)/$CaCO_3$ composites[32] is presented in *Figure 4* and the linear representation of the data in

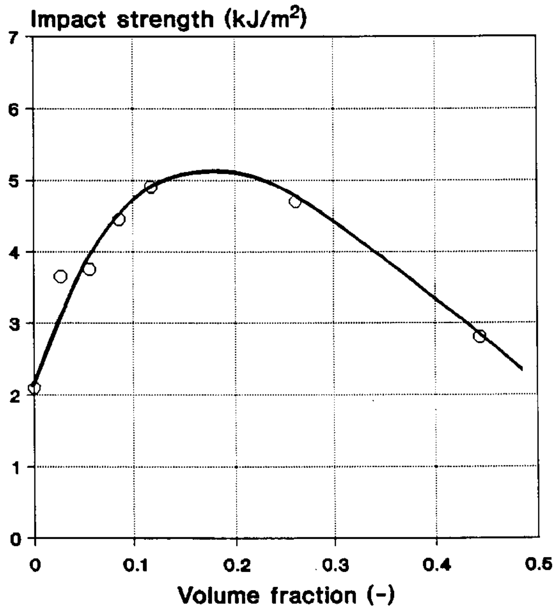

Figure 4 Composition dependence of the notched impact strength of poly(vinyl chloride)/$CaCO_3$ composites[32]

Table 2 Parameters determined from the impact properties of PP blends and composites according to equation (14)

Second component	Technique	G_{c0} (kJ m^{-2})	G'_{c0}[a] (kJ m^{-2})	B_f	r[b]
	G_c, small	1.64	1.55	10.18	0.995
$CaCO_3$	G_c, large	2.10	2.33	7.50	0.971
	Izod	1.73	1.96	8.54	0.986
	G_c, small	1.64	5.29	3.07	0.957
Talc	G_c, large	2.10	10.44	3.06	0.945
	Izod	1.73	4.63	4.73	0.981
	G_c, small	1.64	1.63	12.10	0.996
EPR	G_c, large	2.10	2.22	8.27	0.995
	Izod	1.73	1.56	9.01	0.978

[a] Calculated from the linear fit of equation (14)
[b] Regression coefficient

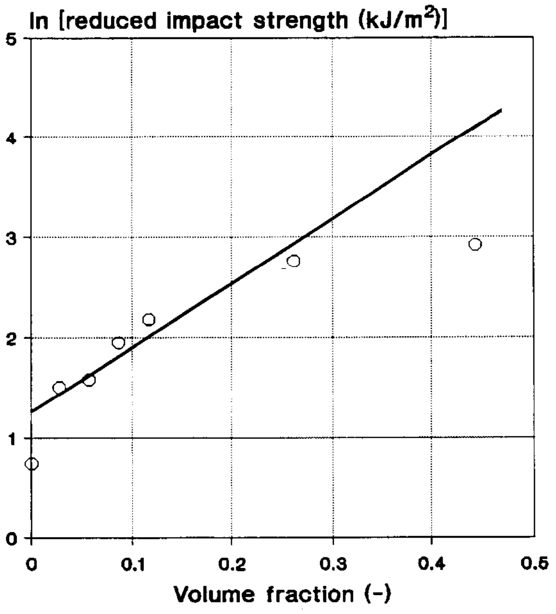

Figure 5 Reduced impact strength of poly(vinyl chloride)/$CaCO_3$ composites plotted in a linearized form according to equation (14)

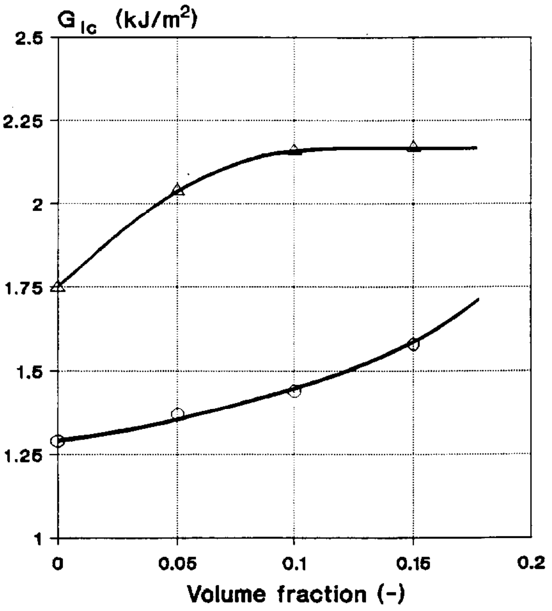

Figure 6 Strain energy release rate of CTBN modified epoxy resins filled with glass beads as a function of composition: (○) 10 phr CTBN; (△) 15 phr CTBN[40]

Figure 5. The agreement is acceptable again with two deviating points. Deviation at high filler content can undoubtedly be explained by aggregation, while in the case of the matrix property only speculations can be made. Poly(vinyl chloride) has a peculiar globular morphology which breaks down during processing. Presence of the filler might change the extent of fusion, but it is also possible that the mechanism of deformation changes from the matrix to the composite, as was suggested by Evans *et al.*[45].

Strain energy release rate measured on a completely different system is presented in *Figure 6*. A carboxyl-terminated butadiene–acrylonitrile rubber modified epoxy resin was filled with glass beads by Zhang and Berglund[40]. *Figure 7* shows that the linear fit is perfect for both levels of elastomer content.

According to our reasoning presented in the previous section the approach should be valid also for K_c. In *Figure 8* K_{Ic} values measured on a glass bead filled epoxy resin by Spanoudakis and Young[38] are presented as a function of composition. Using the linearized form of equation (17) we obtain excellent fit again (*Figure 9*). Success of the treatment in completely different systems from PP blends to glass filled epoxy seems to prove its validity sufficiently. More experiments have to be carried out to establish its credibility further and to obtain sufficient information on the physical meaning of parameter B and on its relation to component properties and structure.

Calculations carried out on widely differing systems make it possible to compare different properties of these blends and composites. Study of earlier theories, analysis of micromechanical deformation processes and the

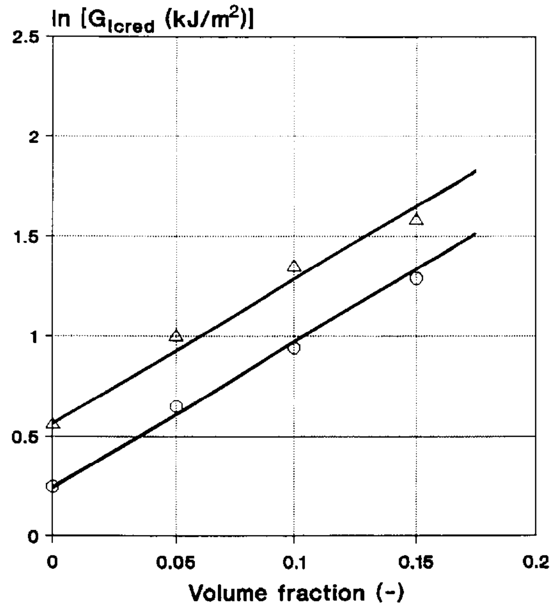

Figure 7 Linearized plot of the reduced values of *Figure 6*

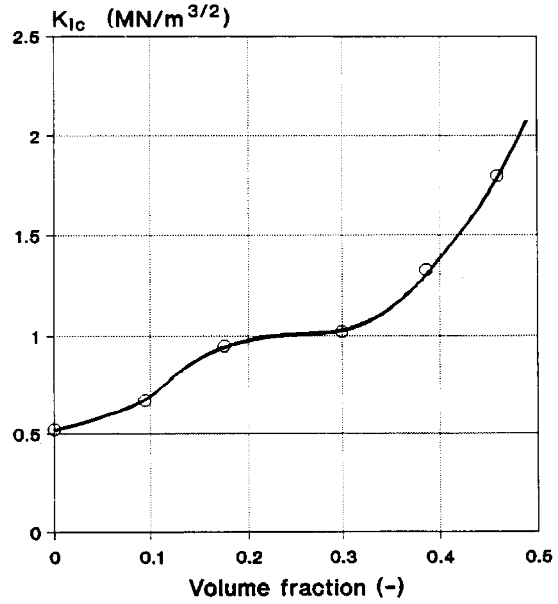

Figure 8 Critical stress intensity factor of epoxy/glass bead composites plotted as a function of composition (particle size 47 μm)[38]

experimental data indicate the importance of plastic deformation and especially yielding. Correlation of B parameters determined from fracture properties (B_f) and from yield (B_y) (strength data obtained in flexure on unnotched specimens were taken from ref. 39) is presented in *Figure 10.* The significance of the symbols, the characteristics from which the parameters were calculated and some other details are collected in *Table 3.* An unambiguous correlation seems to exist between the two quantities, but a separate one for thermosets (i.e. epoxy) and thermoplastics. Without bestowing too much importance onto the correlations of *Figure 10* it is clear that interactions which improve strength properties result in decreased fracture resistance both in thermoplastics and thermosets. Further experiments have to be carried out to prove the existence and the real character of the indicated correlations.

STRUCTURE

During the evaluation of our own and some literature data the crucial role of structure became evident. This emphasized again the advantages of the approach, on the one hand, and drew attention to the necessity of proper sample preparation and characterization, on the other. Orientation of anisotropic particles during injection moulding is a well known fact. In our talc modified composites we have proved the existence of orientation with SEM studies and measured average orientation quantitatively by an e.s.r. technique[55]. Comparison of these results with some other properties unambiguously proved that the deviation between the calculated and measured matrix property is caused by orientation.

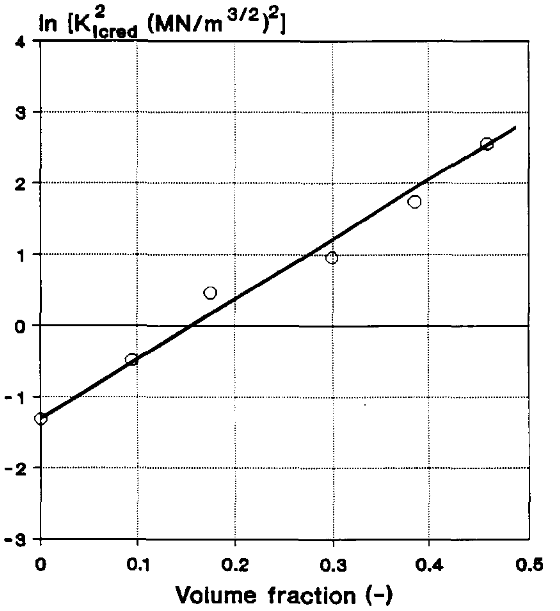

Figure 9 Composition dependence of $K_{Ic_{red}}$ plotted in the linearized form according to equation (17)

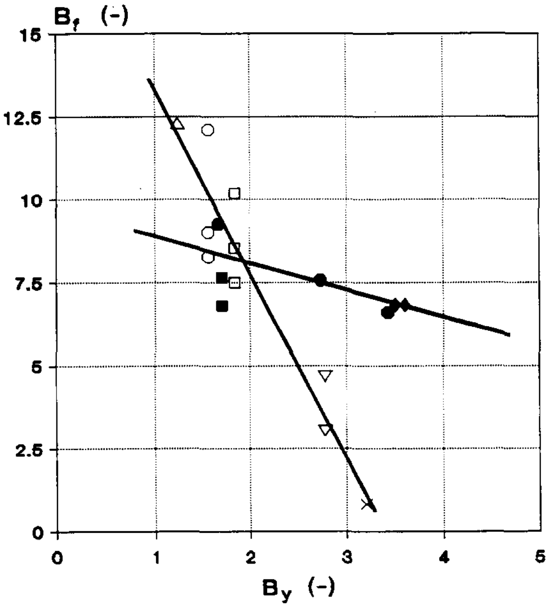

Figure 10 Correlation of interaction parameters determined from fracture (B_f) and yield or strength (B_y) properties with the help of equations (14) and (17). (Open symbols) thermoplastic; (filled symbols) epoxy matrices (see *Table 3*)

Table 3 Components, characteristics, determination methods, significance of symbols and other details of the blends and composites of *Figure 10*

Symbol	Matrix polymer	Second component	Fracture	Yield	Variable	Ref.
■	Epoxy	Glass	J_c		Particle size	45
◆	Epoxy	Glass	G_c DT[a]	Compression	CTBN content	40
●	Epoxy	Glass	K_c DT[a]	Strength, flexure	Adhesion	39
△	PP	EPR	G_c impact	Tensile	–	30
×	Polyethylene	Kaolin	a_t tensile impact	Tensile	–	56
○	PP	EPR	G_c impact	Tensile	Size, technique	This work
□	PP	$CaCO_3$	G_c impact	Tensile	Size, technique	This work
▽	PP	Talc	G_c impact	Tensile	Size, technique	This work

[a] Double torsion

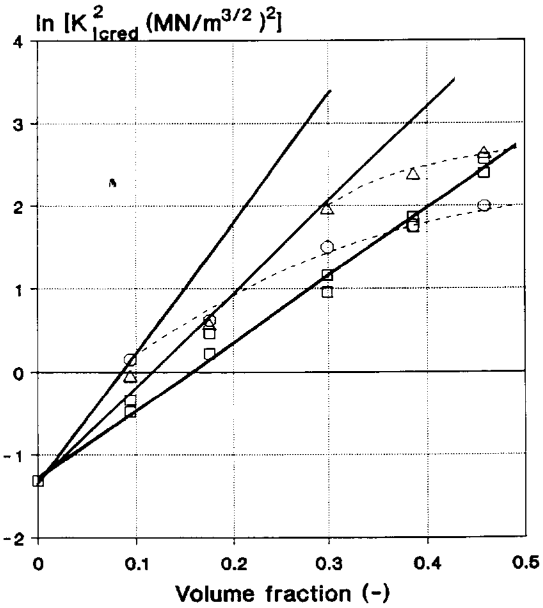

Figure 11 Effect of particle size on the aggregation tendency of epoxy/glass bead composites shown by the linear representation of reduced $K_{\mathrm{Ic_{red}}}$. Particle size: (□) 62 and 47 μm; (△) 32 μm; (○) 4.5 μm[38,39]

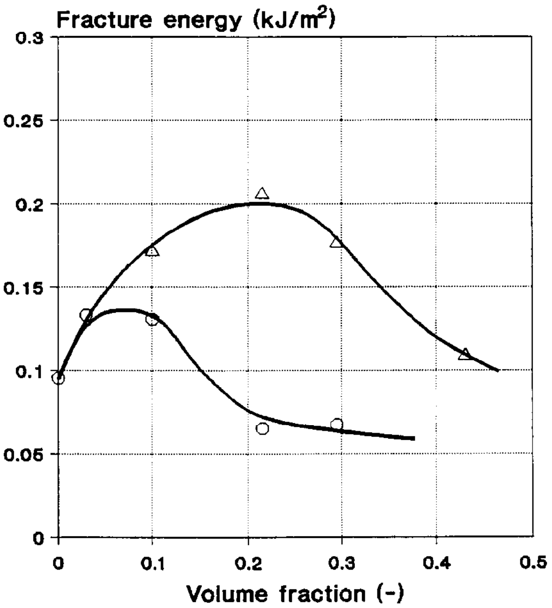

Figure 12 Composition dependence of fracture energy in epoxy/Al(OH)$_3$ composites. Particle size: (○) 1 μm; (△) 8 μm[33]

It is also known that filler particles interact with each other and form aggregations. The detrimental effect of aggregations on fracture and impact properties has been shown several times[56–59]. The CaCO$_3$ filler used in our experiments has a relatively small average particle size and large specific surface area (*Table 1*). Such an average particle size means the presence of some smaller particles as well (~0.1 μm), which undoubtedly form aggregates prevailing under the very severe shear conditions of injection moulding. This is the most probable reason of the smaller impact resistance at high filler content (*Figure 3*). This reasoning is further corroborated by *Figure 5*. In the poly(vinyl chloride) composite the same filler was used as in our PP. The significantly larger viscosity of poly(vinyl chloride) resulted in a more homogeneous composite even under the milder conditions of extrusion; the deviation from the linear correlation occurs at a significantly higher filler content.

The significance of sample preparation and aggregation is even greater in thermosets. Because of the very low viscosity of the resin, small particles cannot be evenly distributed even with high speed mixers, as shear stresses are not sufficiently high. In *Figure 11* $K_{\mathrm{c_{red}}}$ values of Spanoudakis and Young[38,39] are plotted against composition in a linearized form. They studied the effect of particle size and prepared epoxy/glass composites with particles with diameters of 4.5–62 μm. Values of composites prepared with 62 and 47 μm diameter particles give linear correlations, and the treatment is valid. With decreasing particle size, however, a deviation is observed from the straight line, which starts at lower filler contents with its extent becoming increasingly larger. Composites containing a filler with 32 μm particle size are not completely homogeneous. It is obvious that fracture properties measured on such materials are not characteristic of the composite, but depend on the homogeneity of the sample.

The maximum in fracture energy presented by Lange and Radford[33] (*Figure 12*) created much speculation and the results were used to support the line tension (crack pinning) mechanism of impact resistance improvement[33–35]. Linearized representation of the data clearly indicates that the composites are not homogeneous (*Figure 13*). Comparing the shape of the curves to previously presented ones and considering that 1 μm particles could not be homogeneously distributed even in PP and poly(vinyl chloride) under melt processing conditions, where shear stresses orders of magnitude higher prevail, it is clear that serious aggregation must take place in these materials. Although all the data and considerations presented in this section verify the explanation given of the role of structure on fracture properties, the evidence is indirect. More experiments must be carried out to determine the effect of filler anisotropy and aggregation on the properties in question.

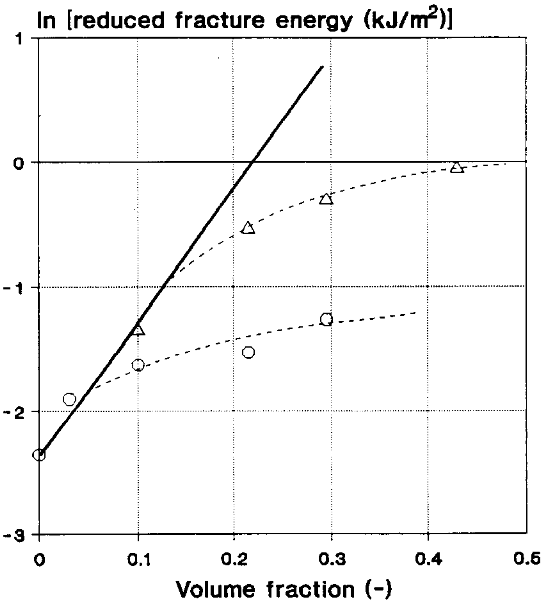

Figure 13 Reduced fracture energy of epoxy/Al(OH)$_3$ composites of *Figure 12* plotted in a linearized form according to equation (14)

CONCLUSIONS

A literature survey on the models describing composition dependence of fracture characteristics of heterogeneous polymer systems has been presented. Most of the models do not describe the experimental data or are too complicated to use. A simpler approach is proposed which takes into account fracture resistance of the matrix, its change with composition, the decrease of effective matrix cross-section and interaction. The approach proved to be valid for particulate filled and elastomer modified PP blends and composites, it properly describes the composition dependence of strain energy release rate and Izod impact strength as well. Its validity could be verified also in the case of the most diverse properties (notched impact strength, G_c, K_c, J_c) measured on a variety of samples from elastomer modified thermoplastics to particulate filled thermosets. A correlation was found between the parameter calculated from the composition dependence of fracture properties and that obtained from yield stress. Analysis of the data has shown that fracture resistance decreases, while strength increases with component interaction. The structure of the composites is a major factor in fracture testing, orientation of anisotropic particles and especially aggregation may influence the measured values significantly. Proper analysis of the results clearly reveal such effects.

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