EFFECT OF PARTICLE SIZE DISTRIBUTION ON FRACTURE TOUGHNESS OF POLYMERS

Bernd Lauke
Mechanics and Fiber Formation, Leibniz Institute of Polymer Research Dresden
01069 Dresden, Hohe Str. 6, Saxony, Germany
+351/4658293, laukeb@ipfdd.de

Abstract. Fracture toughness of particle reinforced polymers is strongly affected by the particle size, respectively their size distribution. Toughness can be improved or reduced depending on the materials used, the volume fractions at which the values are compared as well by the bonding quality at the particle/matrix interface as the parameters of particle size distribution. Several dissipation mechanisms are responsible for the characteristic behavior, and particle debonding is one important process, which is considered herein. If only the adhesive energy per volume is considered it can be concluded that smaller particles are favorable to increase that value. But the product of this specific debonding energy with the dissipation volume is the decisive quantity that determines fracture toughness. Depending on the used debonding criterion, i.e. critical stress or critical energy, different conclusions can be drawn. The critical stress criterion applied to composites with particles of a Gaussian size distribution leads to the conclusion that the debonding processes inducing fracture toughness to increase with decreasing mean particle diameter, \( d_{p,\text{mean}} \). The increase is lower for larger standard deviations, \( s_d \), of the distribution. Contrary to this, the application of the energy criterion provides fracture toughness independent of mean particle size.

Keywords: particle composites, particle size distribution, crack resistance

1. INTRODUCTION

Throughout the last decades the subject of improving the mechanical properties of particle filled polymers received large attention and a bulk of publications exists. A survey about this development has been given recently and the reader is referred to Fu et al. (2008).

The fracture toughness behavior is rather complex and an increase of fracture toughness with increasing volume fraction of hard particles with a subsequent decrease is observed.

Interfacial debonding among others, as for example matrix yielding, determines the initiation and development of the damage process. For glass bead filled epoxies Lee and Yee (2001) observed that micro cracking is mainly caused by debonding. Recently Chen et al. (2007) examined the influence of particle size on damage dissipation in nanocomposites. They concluded on the basis of an energy debonding criterion that damage dissipation is strongly dependent on the size of particles and that smaller particles are favorable to increase material toughness. But dissipation energy per volume is only one side of the story. The other important point is: how large is the volume in front of the crack where debonding can be initiated, i.e.: where the stress or energy is high enough to debond the particles from the surrounding matrix. Evans and Faber (1981) developed a basic model for fracture toughness calculation, but basic equations are contradictory in the used approximations concerning the particle size dependence.

On the basis of the stress field solution of a single particle within an infinite matrix, i.e. particle-particle interaction is neglected, and a Gaussian particle size distribution the fracture toughness of particle composites is modeled.

2. FRACTURE TOUGHNESS

To initiate the propagation of an existing crack, energy must be available. The composite energy release rate \( G \) (available from the change of the elastic energy and the applied load for an increment of crack growth) must at least be equal to the energy necessary \( R_c \) (crack resistance) to initiate crack propagation. This is expressed usually as:

\[
G \geq G_c = R_c
\]
with $G_c$ as fracture toughness of the composite (all these quantities as energy per unit area of crack growth). In order to balance the effect of different structural changes on the crack resistance it is necessary to consider the processes near the crack tip in more detail. The fracture processes act in different zones: there are processes immediately near the crack surfaces, which is termed as process zone. The second group is the more extended structural processes, as for example particle/matrix debonding, which take place in the so-called dissipation zone. These zones are given in Fig. 1.

![Figure 1: Dissipation (debonding) and process zones in front of a crack; radius of debonding zone $\rho_d$, Gaussian particle size distribution.](image)

In the following only the debonding process is taken into account, for other possible mechanisms the same derivation can be used. The total crack resistance can be calculated by the separate contributions of the mechanisms in the process and dissipation zones, as:

$$R_c = R_{pz} + R_{dz} = R_{pz} + 2 \int_0^{\rho_d} \eta_d(\rho) \, d\rho \quad \text{or} \quad R_c = R_{pz} + 2\eta_d\rho_d$$

where $R_{pz}$ and $R_{dz}$ are the specific fracture energies of the process zone (as energy per unit area of crack and dissipation zone, respectively, $\eta_d$ is the volume density of debonding energy, $\rho$ is the distance from the crack tip, $\rho_d$ is the radius of debonding zone. For the special case that only debonding is considered and the volume specific debonding energy is independent of the distance to the crack tip, $\rho$, the integral can be carried out directly.

For the calculation of the radius of debonding zone the approximation for the plastic zone is extended to this mechanism:

$$\rho_d \cong \beta R_c E_c \frac{1}{(\sigma_c^d)^2} = \beta \frac{R_c}{E_c} \left(\frac{1}{(\varepsilon_c^d)^2}\right)$$

where $E_c$ is the Young’s modulus of the composite (assuming that it is not yet reduced by the debonding process), and $\varepsilon_c^d$ is the local strain in the composite in front of the crack when debonding is initiated, the parameter $\beta$ can be used as a fitting parameter. Inserting Eq. (3) into (2) provides for the crack resistance of the composite:
3. MICROMECHANICAL MODEL FOR THE STRESS FIELD, DEBONDING CRITERION

Incorporation of particles into a matrix causes stress concentrations in the neighborhood of the particle when the composite is under loading. The particle placed in an infinite matrix is a typical geometry that allows calculating the main features of the mechanical problem as was discussed in Lauke et al. (2000). A spherical particle placed within a matrix cylinder is considered. The geometry, loading direction and the coordinate system are shown in Fig. 2. The particle (index p) with diameter \( d_p = 2r_p \), consists of isotropic elastic material. The matrix material (index m) has elastic properties. The cylinder is under load in the \( z \)-direction, \( \sigma_c \), leading to stress concentrations, \( A_{ij}^k \),

\[
A_{ij}^k = \frac{\sigma_{ij}^k}{\sigma_c}
\]

with index \( k=p, m \) for the constituents and \( i, j = r, \theta, \phi \) for the spherical coordinates.

The stress concentration factors \( A_{ij}^k \) depend on the coordinates \( r, \theta, \phi \), the mechanical properties of the components and on the geometry parameters, as given in Lauke et al. (2000).

When the matrix stress (\( \sigma_m = \sigma_m^p = \sigma_m \)) reaches a critical value, debonding starts:

\[
\sigma_m = \sigma_d \quad \text{or as deformation} \quad \varepsilon_m = \varepsilon_d
\]

with \( \varepsilon_d \) as the debonding strain or \( \sigma_d \) the debonding stress (radial stress at the particle/matrix interface), respectively.

Nicholson (1976) considered the problem of particle debonding from a surrounding matrix. He obtained on the basis of an energy consideration (where the deformation energy of the particles is neglected) the following relation of the critical applied stress on a representative element for debonding at the particle/matrix interface:

\[
\sigma_{c,d} = \frac{1}{3(1 - \nu_m)} \sqrt{\frac{16\gamma_d E_m (1 + \nu_m)}{d_p}}
\]
with $E_m$ and $\nu_m$ as the matrix modulus and Poisson’s ratio, respectively, $2\gamma_d$, is the specific debonding energy for the two newly created surfaces.

For the determination of the debonding stress at the particle surface, the stress concentration: $\sigma_m = A_{ij}^m \cdot \sigma_c^d$ must be considered. This equation reveals that smaller particles demand higher local stresses for debonding to be initiated.

Thus, instead of the debonding stress criterion (6) the following energy criterion can be used:

$$\sigma_m = \sigma_d^\gamma$$

(8)

The main difference, which has considerable consequences on the structure of the modeled fracture toughness, is that Eq. (6) provides an experimentally determined value that is of course dependent on the debonding energy but no dependence on the particle diameter was observed until now in experiments. However, Eq. (8) with Eq. (7) is explicitly dependent on specific debonding energy, particle diameter and mechanical properties of the polymer.

If the relative frequency of particle size is symmetrically distributed around a mean diameter, $d_p,\text{mean}$, the normal distribution provides a mathematical description of the probability density, $f(d_p)$. The normal distribution in such cases describes more or less exact the measured values and it is given by:

$$f(d_p) = \frac{1}{s_N \sqrt{2\pi}} \exp \left( -\frac{1}{2} \left( \frac{d_p - \mu_N}{s_N} \right)^2 \right)$$

(9)

with $\mu_N$ as the expected value and $s_N$ as the standard deviation.

The particle diameter lies between the experimental determined limits $d_p,\text{min}$ and $d_p,\text{max}$. Consequently, the distribution function, $f_N$, is that one normalized within this region.

4. RESULTS OF FRACTURE TOUGHNESS MODELING

With the relation for the radial stress at the particle/matrix interface, Eq. (5), the dissipation zone radius is given by:

$$\rho_d = \frac{\beta E_c}{\sigma_d^d} \cdot R_c$$

with $A_{ij}^p = A_{ij}^m = k$

(10)

At first the simplest case of particles with the same diameter is considered.

In case that all particles have the same (mean) diameter, $d_p$, the volume specific debonding energy is given by the product of the particle density, $n_p$, ($n_p = \frac{6v}{\pi d_p^3}$, $v$: volume fraction), with the debonding energy of one particle, $W_d$, as:

$$\eta_d = n_p \cdot W_d = n_p \cdot 2\gamma_d \cdot A_d = \frac{6v}{\pi d_p^3} \cdot 2\gamma_d \pi d_p^2 = \frac{12 \gamma_d v}{d_p}$$

(11)

where it is assumed that all particles are able to debond that lie in distances $\rho \leq \rho_d$ from the crack tip. The specific debonding energy, $\gamma_d$, is multiplied by the factor 2 because two spherical surfaces, $A_d$, must debond. Inserting this energy and the radius of the debonding zone into Eq (4) provides for the specific debonding energy (energy per crack area):

$$R_d^0 = \frac{24 \gamma_d v \beta E_c}{\sigma_d^d} \cdot \frac{k^2}{d_p} \cdot R_c^0 = C_0 \cdot \frac{1}{d_p} \cdot R_c^0$$

(12)

If the particle diameter distribution function, $f_N$, is given, the individual surfaces of all particles within the dissipation zone must be summed up. It is assumed that the specific debonding energy, $\gamma_d$, is the same
independent of the particle size. The volume specific energy is thus given under consideration of
\[ W_d = 2 \gamma_d \cdot A_d \text{ as:} \]
\[ \eta_d = n_p 2\gamma_d \cdot A_d = 2\gamma_d \pi n_p \int_{d_{p,\text{min}}}^{d_{p,\text{max}}} f_N d_p^2 dd_p = 2\gamma_d \pi n_p \cdot S_f \]  
(13)

By inserting the particle density \( n_p \) the specific debonding energy is given by:
\[ R_d = C_0 \frac{S_f}{V_f} \cdot R_c \]  
(14)

The crack meets already debonded particles, moves around them and fractures the matrix bridges, leading to the following process zone energy:
\[ R_{p_z} = 2 \cdot \gamma_m \cdot (1 - v) \]  
(15)

Finally the fracture toughness is given in case of the stress criterion and particles of mean size, \( d_p \), by:
\[ R_c = \frac{2\gamma_m (1 - v)}{1 - C_0 \frac{s_f}{V_f}} \]  
(16)

For the case with a particle size distribution, \( f_N \), and the stress criterion one obtains:
\[ R_c = \frac{2\gamma_m (1 - v)}{1 - C_0 \frac{S_f}{V_f}} \]  
(17)

Applying the same procedure in case of the critical energy debonding criterion provides:
\[ R_{c,\text{en}} = \frac{2\gamma_m (1 - v)}{1 - C_{f,\text{en}}} \text{, with } C_{f,\text{en}} \text{ as a material parameter independent of the particle diameter.} \]

Now the proposed model is applied for glass sphere filled (\( v=0.1 \)) polyethylene with the following material properties of the spheres: elastic modulus \( E_p = 64 \times 10^3 \text{ MPa} \) and Poisson’s ratio \( \nu_p = 0.2 \). The properties of the polyethylene matrix are: \( E_m = 520 \text{ MPa, } \nu_m = 0.35 \text{ and } 2\gamma_m = 2.8 \text{ kJ/m}^2 \).

The specific debonding energy at the particle/matrix interface is: \( 2 \gamma_d = 10^{-2} \text{ kJ/m}^2 \) and the debonding stress is: \( \sigma_d = 10 \text{ MPa} \). For the composite modulus the value \( E_c = 640 \text{ MPa} \) is used, whereas: \( k=1.9 \). Only the particle diameter dependence is considered in the following. The results are shown in Fig. 3.

Applying the critical stress criterion of debonding provides an increasing fracture resistance of the composite with decreasing mean particle diameter. The increase is more pronounced for composites with a narrow particle size distribution and is highest for composites with particles of the same size.

However, if the energy criterion is applied the fracture resistance remains constant with changing mean diameter. This is caused by the fact that the increase in debonding energy density with smaller particles is canceled by the reduction of debonding zone size.

This general result is only valid, if debonding between particles and matrix and matrix fracture are the main dissipation processes.
Fig. 3. Normalized fracture toughness versus mean particle diameter for particles with constant particle diameter, $R_c^0$, and with a Gaussian particle size distribution, $R_c$, of standard deviation, $s_N=5$ µm and $s_N=10$ µm.

5. REFERENCES


6. RESPONSIBILITY NOTICE

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