Macromol. Symp. ***2001,*** *169, 79-87*

Deformation and Fracture Mechanisms in Filled Polymers

H. H. Kausch, Ph. Béguelin
Materials Department, Swiss Federal Institute of Technology Lausanne
CH-1015 Lausanne/Switzerland

ABSTRACT: As fillers are traditionally designated those finely divided solids which are added to a polymer matrix in relativly large amounts to modify its properties and/or to reduce the price of the resulting compound. Generally a filler material is stiffer than the matrix and depending on their origin, shape and treatment fillers are reinforcing or not. In this presentation the authors will briefly review the characteristic mechanical effects on small strain behaviour, structure and time-dependent properties of filled polymers stemming from the addition of more or less " spherical " fillers such as calcium carbonate, quartz flour, silica or glass spheres. The effect of such fillers on yield deformation, the nature of possible damage preceeding fracture and their effect on the toughness of particulate filled thermoplastics and thermosets will be discussed in more detail.

IMPORTANT CHARACTERISTICS OF FILLING MATERIALS

More or less equiaxed mineral fillers or *extenders* are primarily added to improve dimensional stability (heat distortion temperature, shrinkage, thermal expansion), sample stiffness and compressive strength. They also improve the ultimate electrical properties of such systems. A concise description of mineral and organic fillers is given in many handbooks and encyclopediae (see for instance [1-5]). The most important filler parameters influencing the structure and the properties of a polymer are particle composition, size, size distribution (*top-cut*) and average interparticle distance, aspect ratio (spherical, fibrous, plate-like), particle surface properties (type of bonding that can be engaged with the matrix, affinity to humidity, but also nucleation and catalytic activities), hardness and abrasive action during processing of the compound, dispersion behaviour and influence on processing. It should also be mentioned that the composition of polymeric compounds is more complex than simply consisting of filler and polymer, they also contain stabilisers, compatibilisers and pigments, which may modify the action of the filler particles or *be modified by them* (due to unwanted adsorption at the filler-matrix interface of water or additives such as stabilisers or cross-linking agents). Depending on their chemical composition, fillers may catalyse secondary or degradative reactions which influence the molecular structure and stability of the surrounding matrix; on the other hand, finely ground $CaCO_3$ may also adsorbe and deactivate remnants of catalysts and thus increase the thermal stability of a filled polymer [2, 6].

EFFECT OF THE ADDITION AND PRESENCE OF FILLER PARTICLES ON THE STRUCTURE AND *SMALL STRAIN* PROPERTIES OF FILLED POLYMERS

The presence of filler particles influences the density, stiffness and viscoelastic behaviour of a compound in a fairly straightforward manner. It has been shown by Nielsen that the *static* elastic moduli (shear, Young's or bulk) of a filled polymer are well represented by a modified Kerner equation [7]. The - otherwise highly important - surface treatment of filler particles has generally little direct influence on the short time moduli. The combined effects of *time* and *presence of fillers* on the *viscoelastic behaviour* are frequently considered separately. Thus the *time-dependent* compliance $D_c(t)$ of a particulate composite is to a first

CCC 1022-1360/00/$ 17.50+.50/0

approximation proportional to the matrix creep deformation ε_m and the ratio of the elastic moduli E_m / E_c :

$$\sigma_o D_c(t) = \varepsilon_c(t) = \varepsilon_m(t) E_m / E_c \qquad (1)$$

where σ_o is the applied uniaxial stress, E is Young's modulus and the subscripts c and m refer respectively to the filled polymer and the matrix. It should be noted that the creep compliance $D_c(t)$ can often be reduced by time-temperature-stress superposition (TTSS) to a single creep-compliance master curve [8, 9]. In a similar way the shear modulus, G(t), can be represented.

The most notable effect concerning the *dynamic* response of filled polymers is their greater sensitivity to strain amplitude; thus the tanδ increases non-linearly with extension due to strain concentration at and between particles and to dewetting (or decohesion) at particle-matrix interfaces [6, 7]. The above small strain effects are rather similar for a wide range of thermoplastic and thermosetting matrices.

The effect of solid particles on the *crystallisation* behaviour and the ensuing morphology of semi-crystalline thermoplastics is also well understood. The presence and homogeneous distribution of a large number of crystallisation nuclei leads to a higher crystallisation temperature and a much finer spherulitic structure. The overall crystallinity x_c is influenced in different manners. Glass beads in sPP [10] lead to a decrease of x_c since the total interspherulitic or *impingement area* (which has a lower degree of crystallinity) is increased. $CaCo_3$ in PP [11] has very little influence on x_c and talc-filled composites show a diverging behaviour [10,11]). Evidently, for a given filler, nucleation effects should be proportional to the total interface area. However, there seems to be a lower limit to particle size. Very small particles in a coarse spherulitic material have been observed to congregate in the interspherulitic regions giving rise to brittle interspherulitic fracture [12].

It is also known that surface treated particles can promote the selective formation of a given crystal phase with respect to another (thus the β-crystallisation of polypropylene is favoured by the presence of surface treated calcium carbonate [13, 14]). Whereas these elements of sample morphology have a modest effect on the *small strain* properties, they influence more strongly the deformation mechanisms and thus the yield stress and toughness of a filled polymer. Concerning these latter properties fillers have quite different effects on thermoplastic and thermosetting resins which have to be discussed separately, therefore.

DEFORMATION AND FRACTURE MECHANISMS IN THERMOSETTING RESINS

Damage mechanisms

As an example we will analyse the deformation mechanisms of a quartz-flour filled epoxy resin[1]. As shown by Smith [8] there are essentially two local deformation mechanisms, *particle-matrix debonding* and *micro-shear banding.* Depending on the sensitivity of the matrix to crack extension there are three modes of fracture. At low temperatures (and high stresses) *a single debonding event* can already give rise to rapid brittle fracture. The main sample volume remains essentially undamaged. At intermediate temperatures *a limited number of debonding events* occur before the inception of crack propagation (in this case there is limited volume damage). The crack then jumps from one debond to the other more or less

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[1] A difunctional hydantoin-based epoxy resin (CY 225 from Ciba-Geigy cured with anhydride hardener Hy 925) filled with varying degrees of quartz-flour (W10 from Quarzwerke Frechen/Germ.)

within a plane and a smooth sub-critical crack zone is formed (and well visible on the final fracture surface). It should be pointed out that there is a rather good correlation between stress intensity factor and crack speed which can be used to evaluate the expected lifetime of a loaded sample [15]. The third fracture mode occurs at high temperatures when the matrix is less brittle and extensive volume damage is done before the crack propagates by void coalescence which involves further ductile matrix deformation (micro-shear banding). This mechanism leads to a rather rough zone of sub-critical crack growth. It is of particular significance that a single TTSS-compliance master curve can be constructed where the different mechanisms are associated with different regions of the master curve [8]. These different mechanisms are schematically represented in Fig.1.

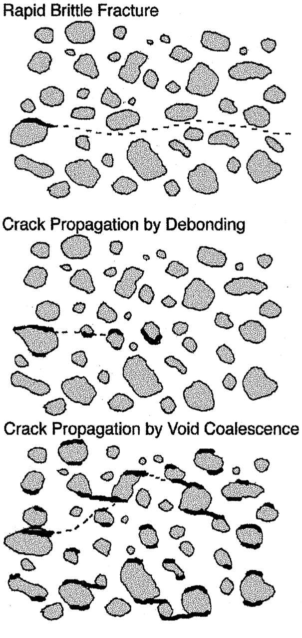

Fig. 1: Schematic representation of crack propagation mechanisms in a highly filled epoxy resin (after Smith [8]).

In compressive loading (of the same quartz-flour filled epoxy resin) one observes (in this order) matrix shear, particle-matrix debonding, particle fracture and matrix micro-cracking by linking up of debonded zones. The latter three mechanisms are irreversible, they create the *volume damage* which is first observed close to the yield point.

Estimation of brittle fracture strength

In tension, most particulate filled cross-linked resins and rigid thermoplastics break in a brittle manner before reaching the yield point. Brittle fracture is generally triggered by the appearance and/or activation of a critical defect. Several criteria have been proposed to estimate the brittle strength of such composites.

a) Critical matrix strain ε_{mb} in the stress direction

Provided there is good adhesion between a rigid matrix and filler particles, it can be assumed [1, 6, 7, 16] that the composite breaks when the average matrix ligament in the stress direction attains its ultimate failure *strain* ε_{mb}. The overall composite strain ε_{cb} at this moment is:

$$\varepsilon_{cb} = \varepsilon_{mb}(1 - \sqrt[3]{\frac{3}{\pi}}\Phi_f^{1/3}). \tag{2}$$

The composite breaking stress σ_{cb} then equals $\varepsilon_{cb} \cdot E_c$. In most – but not all - composites σ_{cb} decreases with increasing filler contents and average particle size. The above approach suffers from the fact that the ligaments which break first are not *average ligaments*, that ligament fracture is in competition with interfacial debonding and micro-shearbanding (see below) and that the composite can most probably tolerate several interfacial debonding events.

Much more than Young's modulus, composite strength is sensitive to the quality of adhesive bonding, to particle size and distribution, to the presence of defects (inherent flaws) and to matrix properties (see b).

For a system with *no* particle-matrix adhesion Nicolais and Narkis [17] have obtained a similar relation (Eq.3) based on the failure *stress* of the load carrying ligaments in a cross-section perpendicular to the principal stress direction:

$$\sigma_{cb} = \sigma_{mb}(1 - 1.21\Phi_f^{2/3}). \tag{3}$$

Their estimate can be considered as the lower bound of tensile strength data, as confirmed by differently treated fillers in epoxy resins (Fig.2).

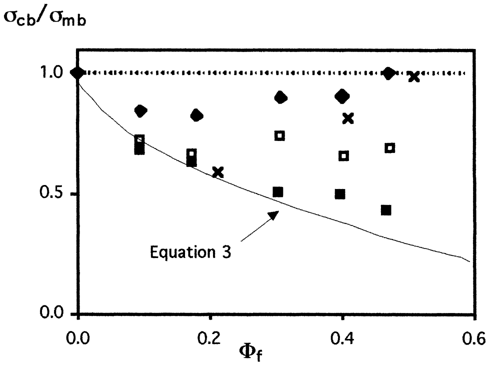

Fig. 2: Tensile strengths of differently filled epoxy resins; x 50 μm-silica particles [30]; 62 μm-glass beads: ◆ A 187-treated; ■ treated with release agent; □ untreated (after [6] using data from the literature [16, 18]).

b) Inherent flaws

Using a linear elastic fracture mechanics approach, brittle fracture of any material containing a defect of size *a* can be related to the toughness K_{Ic} of the material through:

$$\sigma_{cb} = K_{Ic} / (Y\sqrt{a}) \qquad (4)$$

The limited strength of a homogeneous material is then explained through the existence of inherent flaws, of which the size *a* has been related to that of pre-existing heterogeneities or defects such as the particle diameter, poorly bonded or weak particles, or flaws generated during sample preparation. Unfortunately, the resulting values of *a* turn out to be systematically too large (e.g., for epoxy resins filled with particles of between 5 and 50 μm, the values of *a* range between 36 and 522 μm [18, 19]).

Filler effects on fracture toughness K_{Ic} of thermosets

The presence of well bonded particles influences macroscopic fracture - and thus the toughness K_{Ic} - positively (by crack pinning and bowing, void formation, and crack bridging). For many systems K_{Ic} was seen to increase linearly with filler volume fraction V_p. At equal volume fractions the toughening efficiency increases from that of surface treated glass beads to alumina and silica particles and that of silicon carbide (Fig. 3).

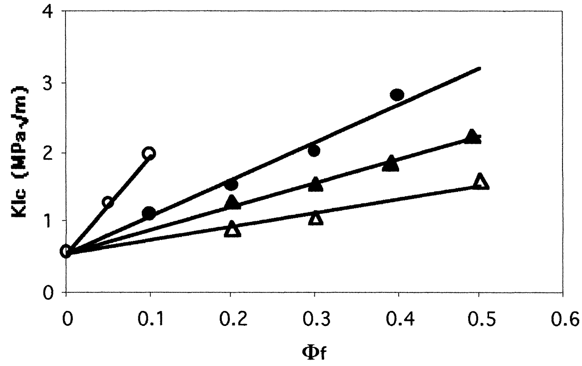

Fig. 3: Stress intensity factor as a function of volume fraction Φ_f of different fillers: ▲, alumina and silica particles; Δ, A187 treated glass beads; • silicon carbide; o short glass fibres (indicated for comparison); after [18].

In the case of rather weak filler materials (such as dolomite) toughening will be limited by particle fracture. In addition to the above parameters it should be mentioned that the particle size, the ratio of particle size and interparticle distance, the rate of loading and the quality of the used precrack have an influence on the toughness K_{Ic}. [6, 18, 20]. The observed trends caused by these parameters are summarized in the following table (see also the standard references such as [1-5]).

Table 1. Observed trends of mechanical property modification by spherical fillers (after [1, 16, 18])

Change in filler property and/or test condition	Effect on modulus	on Toughness K_{IC}	on Flexural strength
volume fraction increases	increases	increases	is limited to the matrix value
particle size increases	constant	slight decrease	decreases
strength and modulus of filler increase	increases	increases	increases
improved adhesion	constant	increases	decreases
embedded in tougher matrix	small decrease	increases	decreases
rate of loading increases	slight increase	increase followed by plateau	slight increase

DEFORMATION AND FRACTURE MECHANISMS IN FILLED THERMOPLASTICS

Damage mechanisms

In semi-crystalline thermoplastics several new phenomena have to be considered which are partly stemming from the two-phase nature of semi-crystalline thermoplastics (the reinforcing action of the crystal lamellae and of the fibrils which are formed during their microplastic deformation), partly from the interaction between the filler particles and the polymer (nucleation of particular crystalline phases, effect on sample crystallinity). The main deformation mechanisms of an unfilled semi-crystalline thermoplastic are dilatation - and eventually cavitation - of the amorphous regions and concomitantly crystal plastic deformation (fine shear, bloc shear, decrystallisation). We wish to emphasise that the continued lamellar fragmentation beyond cavitation and fibrillation of such thermoplastics as high density polyethylene (HDPE), low density polythylene (HDPE), polypropylene and polyoxymethylene leads to the incorporation and alignment of crystal blocks into the structure of the formed fibrillar deformation zones. The latter are additionally hardened by strain induced crystallisation of the oriented amorphous and/or decrystallised matrix material.

The essential point in filling a semicrystalline thermoplastic *is to improve its toughness* by favouring microplastic deformation. This requires firstly good adhesion of the matrix to the filler particles so as to initiate the above deformation mechanisms. This can be obtained from adhesion promoters, surface treatment or by increasing the amorphous component of the polymer - which often adheres more easily to mineral substrates [1,2,5,10]. Secondly particle size and volume fraction should be controlled so as to avoid stress concentration and thus premature brittle fracture. The concept of a critical interparticle distance which has proven valid in many rubber reinforced systems seems to apply in mineral filled polymers as well (see below).

The first sign of damage observed when straining a *thermoplastic* composite containing *weakly (or non-)adhering* particles is particle-matrix debonding (dewetting) leading either to the formation of stable voids (which manifests itself as a knee in the stress-strain curve) or directly to fracture. When voids are created from *large* particles or aggregates they are likely to form a critical crack, which will initiate brittle fracture. On the other hand, small, well dispersed and weakly adhering particles initiate a large number of small and stable voids which permit further deformation of the matrix ligaments between particles. However, if the matrix has a limited extensibility brittle fracture can not be avoided even after generation of many, well distributed voids (unplastizised amorphous PVC charged with 40 % by weight of chalk breaks at 10 % ultimate strain). Non-adhering particles in a *ductile* matrix have little influence on the yield and fracture behaviour. Thus plastizised PVC shows up to 35% by weight of $CaCo_3$ no change in ε_{cb} (about 365%) and tensile strength σ_{cb} (19.5 MPa) [7].

Interfacial void formation in composites with *well adhering fillers* requires larger strains. The stability of the strained composite then depends on particle size and ligament properties. Again, large particles are susceptible to act as defects and will give rise to brittle fracture – at a much higher stress though than the non-adhering particles. Small particles may retard void formation to such a stress level that the first debonding event gives rise to brittle fracture. In order to avoid that, *the formation of voids should be well distributed in space and time.* Generally the toughest material is obtained with not completely mono-disperse medium sized particles.

Estimation of the strength of a filled thermoplastic

As indicated above, filled thermoplastics could behave in a brittle or ductile manner. The limiting stress of a specimen, its *strength,* is therefore either given by its brittle strength, σ_{cb}, or by its yield strength σ_{yt}. For the estimation of the *brittle strength* of a filled thermoplastic the same models as for thermosetting matrices have been used. Again we have to draw attention to the fact that the brittle strength of a specimen depends on various extrinsic parameters (such as sample geometry, temperature and loading conditions to name just the three most important ones). At this point we have to discuss how to predict the yield strength σ_{yt}.

Any homogeneous or filled (polymer) specimen yields if and when local shear deformation initiates and extends sufficiently far before *crazing* and/or *fracture* dominate the deformation behaviour. In the simplest model it is considered that the stresses are transmitted by the matrix and by inclusions *in proportion to their effective cross-sections.* In tension, the composite yields (at a stress σ_{yt}) when the average matrix stress reaches the matrix yield stress σ_{ym}. Stress concentration (caused by unbonded inclusions or aggregates) are taken into account through a factor S < 1 and the quality of bonding and possible effects on the surrounding matrix material by the stress component σ^* transmitted through the particles [6, 17, 21]:

$$\sigma_{yt} = \sigma_{ym}\left(1 - 1.21\Phi_f^{2/3}\right)S + \sigma^* \, 1.21\Phi_f^{2/3}. \qquad (5)$$

For unbonded particles, σ^* is zero. The then remaining term corresponds to Eq. (3) and indicates the lower bound of σ_{yt}. Syndiotactic polypropylene (sPP) of low stereoregularity filled with 5 μm-size glass beads and LDPE and PVC filled with 3.6 μm-size $CaCo_3$ filler particles comply quite well to the upper bound of the above equation.

Considering the composition-dependence of tensile yield stress including crystallinity, crystal size, possible filler anisotropy, and the quality of adhesion Pukanszky et al. [11] arrive at the following relation:

$$\sigma_{yt} = \sigma_{ym}\frac{1-\Phi_f}{1+2.5\Phi_f}\exp\left(B\Phi_f\right) \qquad (6)$$

where B is an empirical parameter characterising the degree of particle-matrix interaction (it increases with the specific surface area and the adhesive strength of the interphase).

A number of semicrystalline matrix materials gave a surprising response. The recent studies of Bartczak et al. [22] have shown that the toughness of a calcium carbonate filled HDPE increased dramatically once the thickness of the ligament between particles (average interparticle distance) had dropped to below 0.6 μm (Fig. 4).

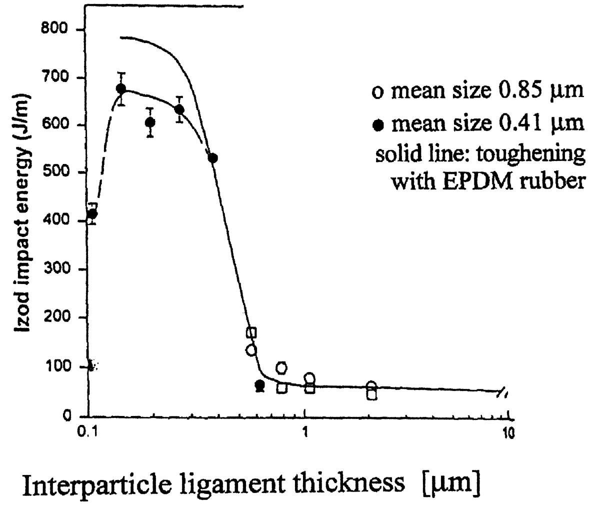

Fig. 4: Izod impact toughness as a function interparticle ligament thickness for samples of calcium carbonate filled HDPE (from Bartczak et al. [22]).

As toughening mechanism the authors proposed the reduced plastic shear resistance of the oriented layers of crystal lamellae which had grown radially outward from around the CaCo$_3$-particles to a characteristic small thickness of 0.3 to 0.4 μm. The extensibility of the ligaments increased enormously once the interparticle volume essentially consisted of such oriented material. The concept of *a critical interparticle* distance which has proven valid in many rubber reinforced systems seems to apply in mineral filled polymers as well. A similar enhancement of toughness by small, well-bonded particles was found by Walter et al. [23] for HDPE filled with 30% by vol. of Kaolin. They interpreted the observed fibrillar deformation of the ligaments - and subsequently of the bulk matrix - by the formation of an *interphase* around the particles. The formed fibrillar deformation zones strongly resembled craze-like structures as they are observed in elastomer modified semi-crystalline thermoplastics.

CONCLUSION

The formation of composites by blending filler particles of low aspect ratio with thermoplastic and thermosetting polymers leads to several beneficial effects. Young's moduli are considerably increased through active fillers of large specific surface area and through their influence on the structure of the surrounding matrix material (crystallinity, density). Time-dependent moduli can be derived from static ones by the separation of variables. The creep resistance is significantly increased, and the time-temperature-stress reduction principle has been applied successfully. To produce composites with adequate strength, fillers must show good bonding, but even then strength generally decreases with filler content. On the other hand, toughness is less sensitive to the quality of adhesion, such that particle-matrix debonding (causing void formation) can be tolerated provided the formation of voids is well distributed in space and time. Apart for cost reduction fillers are advantageously used if high strength, dimensional stability and/or special thermal, optical and electrical performances are required. Automotive and tribological components, light-weight garden furniture, opalescent packaging films, and high-voltage circuit breakers are some descriptive examples.

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