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# On Modulus and Fracture Toughness of Rigid Particulate Filled High Density Polyethylene\*

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A Kaolin-filled, high-density polyethylene (HDPE) system was used to illustrate the influence of particulates on modulus and toughness of the bulk material. A variation of filler content, particulate size and coupling quality for two HDPE-matrix systems with different viscosity led to a strong dependency of elastic modulus and fracture toughness under various testing conditions, *e.g.* static loading, fatigue and impact.

A stiffness improvement with increasing filler content was achieved by all coupling qualities. The developed Kaolin reinforcement of HDPE with optimised coupling offers an improvement of the stiffness and toughness under all investigated loading conditions. The degree of improvement depends on the particulate size and matrix viscosity. The energy dissipation mechanisms were investigated by fractographic analysis.

**Keywords:** Particulate; HDPE; coupling agent; stiffness; fracture toughness

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\*One of a Collection of papers honoring Yuri S. Lipatov on the occasion of his 70th birthday, 10 July 1997. Parts of this paper were presented at the following symposia:

- 1) *Fracture and Durability of Polymers and Composites*, Qingdao, China, 28 September 1994,
- 2) *Interfacial Materials Science in Composites (SIMS-V)*, Fukuoka, Japan, 15 May 1996.

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## INTRODUCTION

Studies over the last 10–15 years of the structure and properties of polymer composites with dispersed, particulate fillers have shown that interfacial phenomena at the solid-polymer interface are an important factor in determining the composite properties. Lipatov [1,2] has pointed out that these phenomena produce major changes in physical and chemical properties of the border or interphase layer (interlayer) near the interface. As a result, the structure of a filled composite can be represented in terms of three components: the solid phase (filler), the interphase layer and the polymeric matrix. The properties of the interlayer can be distinguished from the matrix properties because of the effect of the phase border.

Addition of mineral filler has represented a common practice for improving the cost/performance balance of polyolefins, with particular reference to the increase of stiffness and temperature resistance, and to the reduction of creep, shrinkage, warpage and thermal expansion. In general, it can be stated that the mechanical properties, and in particular impact strength and toughness, can be drastically varied, depending on matrix characteristics, type and content of filler, and the adhesion between filler and matrix.

Some characteristic features in these respects have been studied on various HDPE systems, in particular to improve their stiffness properties without losing their intrinsic toughness properties [3–7]. Experimental activities of this investigation were focused on a newly-developed Enichem HDPE/Kaolin system, which contains a proprietary coupling agent, effective also for  $\text{CaCO}_3$ , talc and mica. The experimental investigation was concentrated on stiffness and toughness improvement under different loading conditions (*e.g.* impact, static and fatigue). Microscopic characterization should lead to a better understanding of the fundamental failure mechanisms.

## EXPERIMENTAL

The materials used as matrix were HDPE for injection molding applications and HDPE for blow molding. The latter requires a higher molecular weight, which is reflected here in a lower melt flow index

MFI (Tab. I). Furthermore, blow molding can generate a degree of molecular biorientation that would enhance the strength and decrease the failure strain.

The crystallinity was obtained by DSC traces. Both matrices offer a crystallinity of 60–65% which is independent of the filler content. Reinforcement was obtained by Kaolin particulates (China clay) with a density of 2.63 g/cm<sup>3</sup> and two different equivalent spherical diameters. The equivalent spherical diameter is defined as the diameter of a sphere with the same volume as that of an irregularly-shaped particulate. The data in Table I represent average values. Kaolin has the formula Al<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub>·2H<sub>2</sub>O and is widely used, but its applications in polymers have been limited to those that utilize its very small particle size and plate-like shape. Their crystalline structure can be altered to an amorphous form by calcination above 400°C where water is removed and the surface catalytic activity is improved [8]. Of all mineral fillers except mica, Kaolin has the highest surface area [9]. This offers the ability for a superior load transfer to the rigid particulates if a proper coupling is achieved. By a modification of the coupling system a tailored interphase for very stiff/strong, respectively tough/yieldable, bonding is possible. Although any other rigid additive that bonds well to the polymer matrix would also have an effect on the properties, Kaolin is, in addition to its other advantages, a rather cheap filler material and was, therefore, preferred to be used in this study.

The filler content was varied from 10 to 30% by volume. Compounding, with and without coupling agent, was carried out by the

TABLE I Investigated material combinations. The size is given in equivalent spherical diameter

<i>Matrix HDPE</i>		<i>+ Filler Kaolin + Content Vol%</i>		<i>Coupling Agent</i>	
			<i>Size [μm]</i>		
Injection molding		10	0.80 1.40	yes	no
		15	0.80 1.40	yes	no
Density	0.953	20	0.80 1.40	yes	no
MFI [g/10 min]	4.00	30	0.80 1.40	yes	no
Blow molding		10	0.80	yes	
		15	0.80	yes	
Density	0.953	20	0.80	yes	
MFI [g/10 min]	0.27	30	0.80	yes	

manufacturer on a twin-screw extruder, so as to distinguish materials with a “good coupling” and with a “poor coupling”. The effects of particulate size and coupling quality were investigated only for the injection molding matrix. To demonstrate the influence of the matrix material, injection-molded samples made of either the injection-molding type or the blow-molding type of matrix were compared on the basis of various filler volume fractions (but the same filler size of 0.8  $\mu\text{m}$ , having good coupling quality).

Mechanical characterization was carried out by the use of both razor-blade-notched compact tension specimens and tensile test bars. The loading direction of the specimens was in both cases parallel to the injection molding direction. Stiffness and fracture toughness data were determined under a constant loading speed of 10 mm/min. If a deviation from the general trend was observed two additional samples were tested. The evaluation of the static fracture toughness,  $K_{Ic}$ , was carried out along two lines:

- (1) The maximum of the load-displacement curve was used to calculate a maximum toughness value,  $K_{Ic, \text{max}}$ .
- (2) A force,  $F_Q$ , determined by a line with 95% of the initial load-displacement curve was used to calculate a critical stress intensity factor,  $K_{Ic}$ .

Procedure (2) is typical for specimens in which a portion of plane stress conditions at the crack tip causes some degree of plastic deformation during failure of the material. Typical load-displacement curves for an unfilled and two filled (poorly and well bonded) systems are represented in Figure 1. From the curves it can be expected that, in some cases, the conditions of these tests might have exceeded the limits of the linear fracture mechanics application (*e.g.* that both the crack size and the specimen width must be greater than 2.5 times the plastic zone size). In spite of this invalidity, the tests were evaluated according to the given procedures, so as to get some feeling for the resistance against crack growth of the various materials under the given conditions of testing and materials' availability.

Impact toughness data were determined by an instrumented Izod hammer with an impact velocity of 3.5 m/sec. The dynamic fracture toughness,  $K_{Ic, d}$ , was calculated from 5 samples with different razor notch lengths [10].

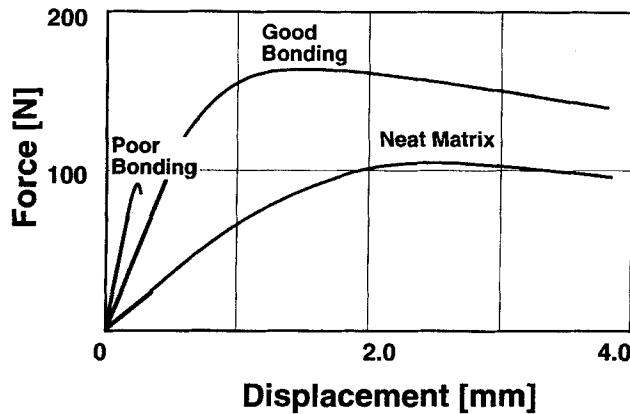


FIGURE 1 Schematic drawing of the force-displacement curves used for the fracture toughness evaluation: Poor bonding in 30 vol% Kaolin/HDPE, good bonding in 30 vol% Kaolin/HDPE; neat HDPE matrix.

The influence of the specimen thickness on the toughness of the injection-moulding matrix with and without coupling agent was investigated under cyclic load. Due to the limited amount of testing material each test condition was applied to three samples. Fatigue crack propagation measurements were carried out with compact tension specimens under uniaxial tension-tension with a min./max. load ratio of  $R = 0.1$  (at a frequency of 5 Hz). Failure mechanisms were studied by fractographic analysis of gold-coated specimens in the SEM. The shape of the neat Kaolin particulates and the distribution quality was analyzed by SEM as well.

## RESULTS

In the micrographs of Figure 2 a clear difference in the size is visible. Due to the platelike shape, the thickness of which is much lower than width and length, the particulates seem to be larger than the listed equivalent diameter value. An important parameter for the efficiency of the reinforcement by particulates is the quality of the distribution in the matrix. Agglomeration of particulates leads to a reduction of the mechanical properties [11]. Figure 3 shows excellent distribution without any agglomeration for 10 and 30 vol% filler content. Neither

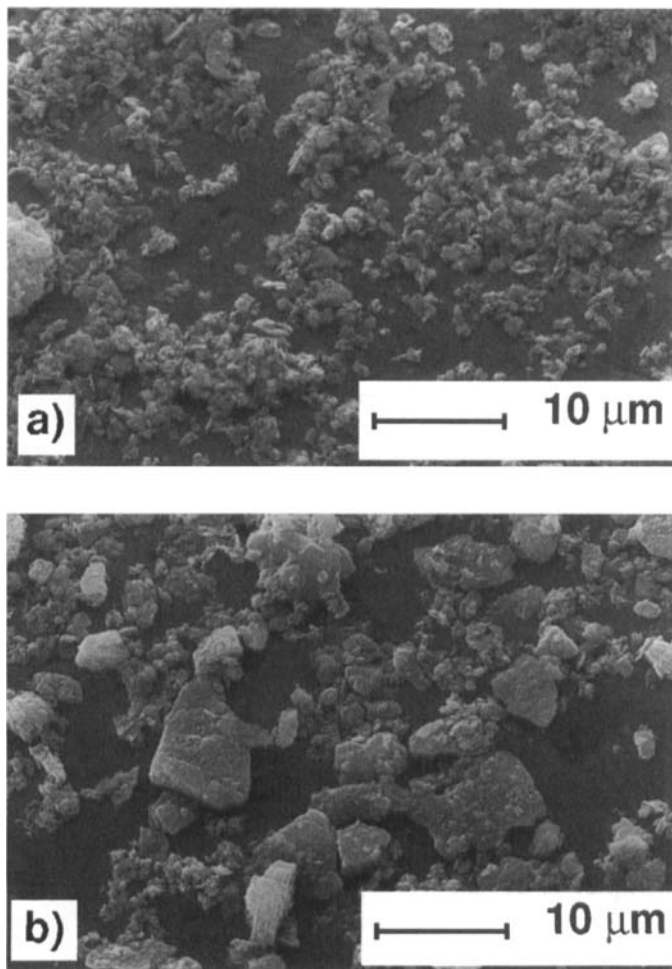


FIGURE 2 Micrographs of neat Kaolin particulates with a) 0.8 µm and b) 1.4 µm equivalent spherical diameter.

the combination with coupling agent nor the particulates without coupling agent show any agglomeration tendency.

The tensile modulus *versus* the Kaolin volume content is presented in Figure 4 for the materials investigated. The stiffness of the neat matrices shows no differences. A continuous improvement with increasing Kaolin content is visible for both matrix systems. Surprisingly, a

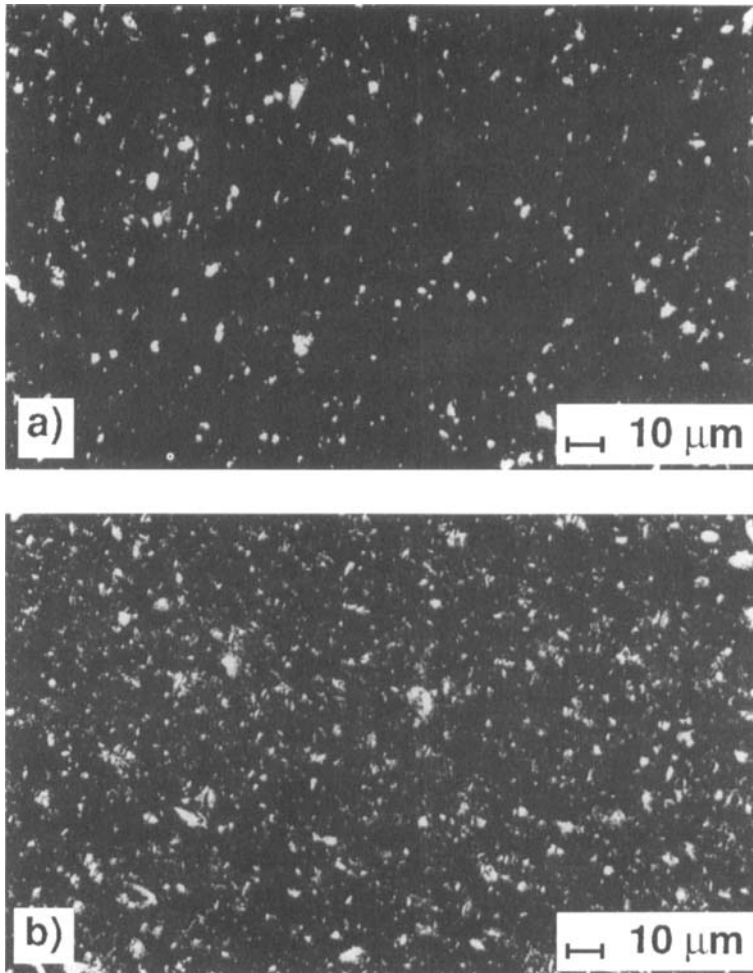


FIGURE 3 Distribution of Kaolin particulates with  $0.8\ \mu\text{m}$  equivalent spherical diameter and a filler content of a) 10 vol%, b) 30 vol% in HDPE for injection molding.

better coupling system leads to lower values. A comparison of the particulates with coupling agent shows no significant effects of molecular weight of the matrix or the size of the particulates.

Further results of the tensile tests (Figs. 5 and 6) show that the coupling quality influences the values of strength and the strain to break. The strength improvement of the blow-molding matrix is more



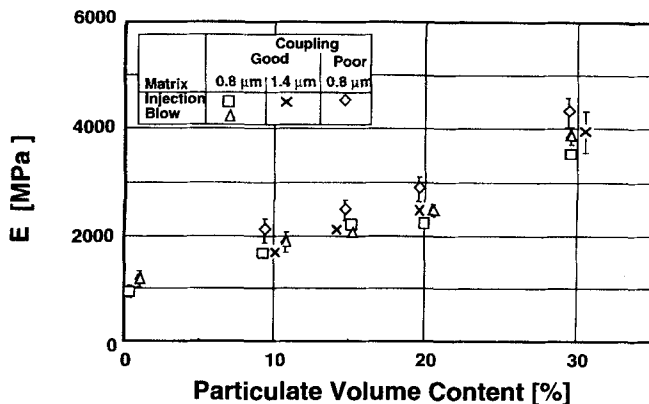


FIGURE 4 Tensile modulus of samples with 3 mm thickness and different coupling qualities, matrix viscosity and particulate size *versus* Kaolin content.

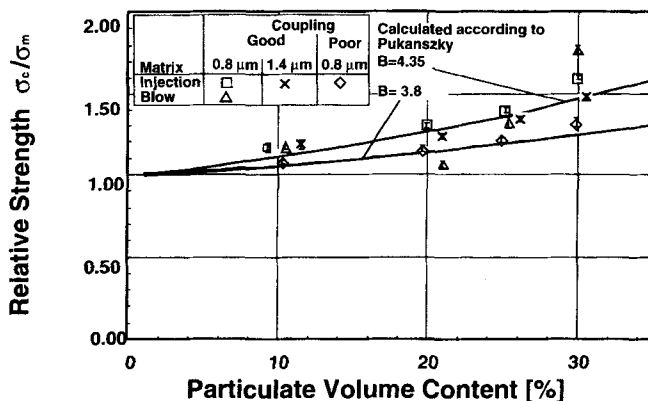


FIGURE 5 Relative strength of samples with 3 mm thickness and different coupling qualities, matrix viscosity and particulate size *versus* Kaolin content. Lines represent calculated values. Matrix strength = 21.5 MPa.

pronounced than that of the injection-molding matrix. The incorporation of smaller particulates in this matrix does not lead to significantly higher strength values, except for the case of 30 vol% filler content. For the strain-to-break values a clear effect of the matrix type is visible. The injection-molding grade fails at a strain that is three times higher than measured for the blow-molding matrix. This

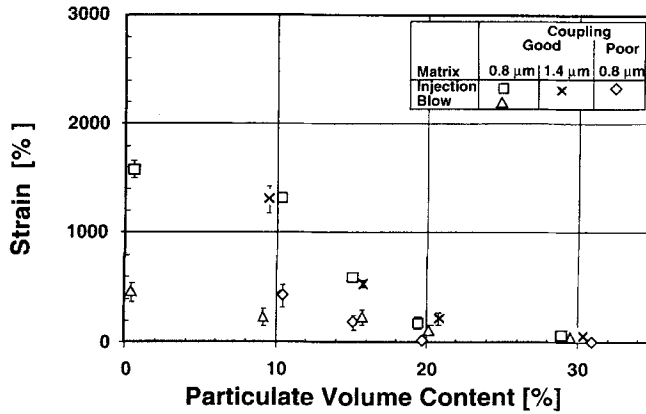


FIGURE 6 Strain-to-break of samples with 3 mm thickness and different coupling qualities, matrix viscosity and particulate size *versus* Kaolin content.

may, however, be due to the injection molding processing of the two types of matrices, because other studies on compression molded samples at Enichem, Italy, have provided a slightly different trend [12]. But no final clarification of these differences could be made within this study.

As expected, incorporated particulates decrease the strain-to-break values for all materials tested. The decrease is, however, not as pronounced when a good coupling agent is applied, especially not for the materials with only 10% particulates. But here also, when reaching filler volume fractions of 20% or more, there is a substantial decrease of the strain-to-failure values down to approximately 10% of the neat matrix values. The size of the particulates shows no significant differences.

The courses of  $K_{\max}$  and  $K_Q$  in Figures 7 and 8 illustrate the influence of the filler content, coupling quality, type of matrix (as based on their different molecular weight) and particulate size on the materials' fracture toughness. The toughness maxima,  $K_{\max}$ , show a clear effect of the good bonding and equal values for the neat matrices. The incorporation of filler without coupling agent decreases the toughness. A slight increase was measured for 1.4  $\mu\text{m}$  particulates with a filler content of 20 and 30 vol%. A more pronounced increase was found for the smaller particulates in the injection molding matrix and the

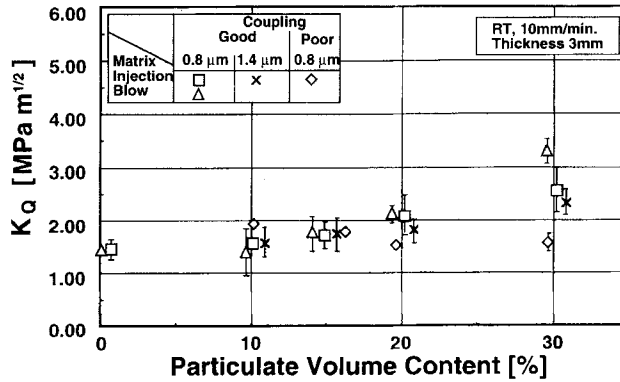


FIGURE 7 Fracture toughness calculated from the force of 95% initial slope ( $K_Q$ ) as a function of Kaolin content, different coupling qualities, matrix viscosity and particulate size.

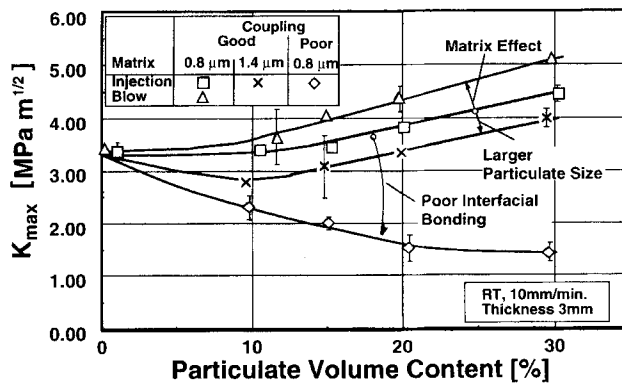


FIGURE 8 Fracture toughness calculated from the load maximum ( $K_{max}$ ) as a function of Kaolin content, different coupling qualities, matrix viscosity and particulate size.

highest improvement of the values is in the curve of the blow-molding matrix. A volume content of only 10% leads to a significant toughness increase. For volume contents of 20 and 30 vol% a higher toughness than that of neat HDPE was determined for all small particulates with coupling agent.

The  $K_Q$  data represent a more conservative toughness value which is not yet related to stable crack growth in the samples under plane stress conditions. However, the same trends are visible as for the  $K_{max}$

values. In general, the  $K_Q$  values of the neat matrix and of the well-bonded particulate composites are much lower than the corresponding  $K_{max}$  data. This clearly shows the high toughening efficiency of the well-bonded particulates. The fact that  $K_Q$  of the blow-molding matrix represents a clear increase for 30 vol% could be related to an optimized stress distribution for localized yielding and strain hardening in front of the crack tip. This mechanism might also be the reason for the high strength of this material. On the other hand, there are no differences between  $K_Q$  and  $K_{max}$  detectable in the case of more than 15 vol% of the poorly-bonded particulates, *i.e.*  $F_Q$  was identical to  $F_{max}$ , referring to a brittle failure behavior if poorly-bonded particulates are incorporated in the ductile HDPE matrix.

The notched Izod data were analyzed according to a fracture mechanics approach.  $K_d$  values determined by the method of Plati and Williams [10] give evidence that (Fig. 9) the good coupling results in similar toughness improvements with increased filler content.

Studies on the fatigue crack propagation (FCP) were carried out only on selected samples, in order to illustrate the principal effects of bond quality, filler content and specimen thickness. Figure 10 summarizes the various FCP-data, from which the following conclusions can be drawn:

- (1) An increase in specimen thickness shifts the FCP curves to the left, *i.e.* for a given stress intensity factor range,  $\Delta K$ , at the crack tip,

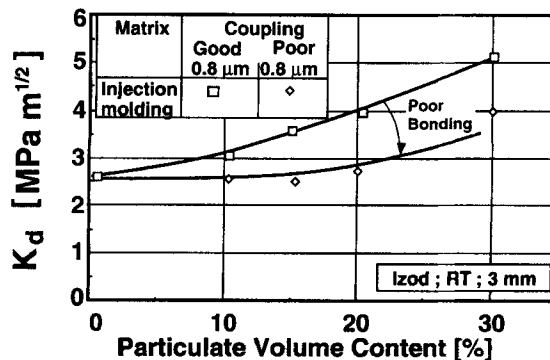


FIGURE 9 Dynamic fracture toughness calculated from instrumented Izod impact tests as a function of Kaolin content, different coupling qualities and particulate size.

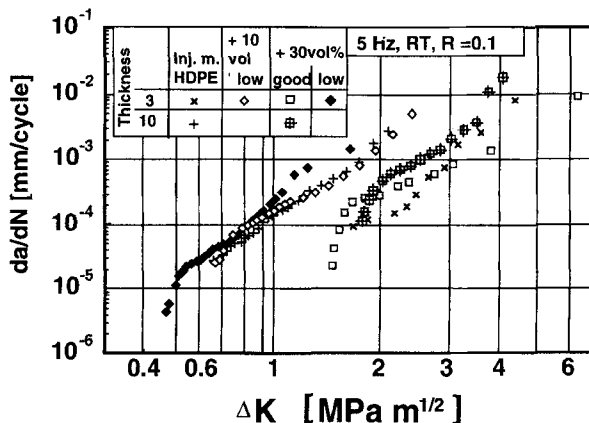


FIGURE 10 Influence of coupling quality, sample thickness and particulate content on the relationship between crack speed and stress intensity factor  $\Delta K$ . Tests under sinusoidal load at room temperature and a max. force/min. force ratio of 0.1.

cracks propagate faster in the thicker specimens (as demonstrated for both the neat matrix material (crosses) and the 30 vol%, well-bonded particulate composite system (crossed and unfilled squares).

- (2) In the thicker samples, well-bonded, rigid particles are much more effective in improving the FCP resistance of HDPE than in the 3 mm thick specimens. This trend also corresponds to the greater difference between the  $K_{\max}$  values of the 30% Kaolin *vs.* the neat HDPE in the case of the 10 mm relative to the 3 mm thick samples.
- (3) For the 3 mm thick specimens it is shown that the permanent reduction in fracture toughness,  $K_{\max}$ , due to the addition of poorly-bonded, rigid particles (*i.e.* matrix *vs.* 10 vol% *vs.* 30 vol% Kaolin filler content) leads to a drastic increase in FCP rate within the particulate-filled materials. This is in agreement with the trend observed for the  $K_{\max}$  values measured for these materials.
- (4) In addition, it can be stated that the threshold values for initiation of fatigue crack propagation in the various materials are clearly lower in the poorly-bonded composites and in the thick matrix plates than in those materials that exhibit a tendency to form a large plastic zone prior to crack propagation, *i.e.* the thin matrix plates and the specimens containing well-bonded Kaolin particles.

Table II compares the value of the stress intensity factor range,  $\Delta K$ , necessary to propagate a fatigue crack under a speed of  $2 \times 10^{-3}$  mm/cycle through the various materials.

## DISCUSSION

The morphology of a semicrystalline matrix with a rigid filler is dependent on the whole system of individual properties of each component and their interactions during the combination and processing cycle. The HDPE/Kaolin systems investigated either possess an injection-molding matrix with a medium viscosity or a higher viscosity blow-molding grade; in addition, they contain particulates with a high nucleation activity that can be further improved by coupling agents. Therefore, the requirements for a localized crystalline growth of lamellae on the particulate surfaces that were found for PE/CaCO<sub>3</sub> [13] and different other PE/filler combinations [14] are fulfilled. In agreement with other investigations [15, 16] a non-dissolvable PE layer on the Kaolin surface was also found here but could not be quantified. But in spite of this microscopic observation, no influence of the type of coating on the global degree of crystallinity could be found, at least based on the DSC measurement performed. The results of the mechanical tests have to be interpreted by differences of the particulate-interphase-matrix morphology and the interactions between the particulates. Various failure mechanisms were observed depending on the morphology, particulate content and size [17–22].

The increase of the stiffness with higher filler content is obviously due to the much higher modulus of the particulates ( $E_{PE} = 1100$  MPa;  $E_{Kaolin} = 200$  GPa). The determination of the modulus is based on the

TABLE II Stress intensity factor range,  $\Delta K$  [MPa m<sup>1/2</sup>], corresponding to a fatigue crack speed of  $2 \times 10^{-3}$  mm/cycle

Thickness [mm]	Neat HDPE	Particulate Composites		
		- poor bonding - 10%	30%	- well bonding - 30%
3	3.4	2.2	1.8	4.3
10	2.0	%	%	2.9

linear slope of the stress-strain curve which was in a range of low stress. In this low stress region the poor coupling seems to be stiffer than the interphase with good coupling, which may be due to the fact that the more-complex, toughness-improving interphase, *i.e.* the formation of a relatively compliant layer at the interface, masks the stiffness of the filler particles. In this way, a complete stress transfer between particles and matrix is hindered. The same modulus was determined for the different neat matrices. The incorporation of larger particulates shows no significant variation of the stiffness behavior. In agreement with existing models, the filler content and the modulus of the filler are the dominant parameters for stiffness improvement by rigid particulates. On the other hand, the size and shape of particulates is of lower influence [23, 24]. In the case of a pronounced interphase around the particulate the modulus could be drastically reduced, as *e.g.* by an elastomeric shell as used in ternary PP systems [25]. A good prediction of these trends can probably be carried out by applying Privalko's SSA-Model [26, 27] to these data. In fact, this will be carried out in future work by the authors.

Calculations of the strength of particulate filled materials are carried out according to Pukánszky. In these equations microstructural parameters are related to the strength of the composite [28, 29]:

$$\sigma_{yc} = \frac{1 - V_p}{1 + 2,5 \cdot V_p} \sigma_{ym} \cdot e^{(B \cdot V_p)} \quad (1)$$

$$B = (1 + l \cdot A_p \cdot \rho_p) \cdot \ln \cdot (\sigma_i / \sigma_{ym}) \quad (2)$$

$\sigma_{yc}$ : Yield strength of composite

$\sigma_{ym}$ : Yield strength of matrix

$V_p$ : Volume content of filler

$B$ : Parameter related to load bearing area,  
including interphase properties

$l$ : Interface thickness

$A_p$ : Specific particulate surface

$\rho_p$ : Particulate density

$\sigma_i$ : Interface strength

A systematic variation of the value of the parameter  $B$  gives a correlation to the microstructure. Calculated data with a value of  $B = 3.8$  show good agreement with measured data of the injection-molding HDPE filled with poorly-coupled particulates (Fig. 5). For the blow-molding grade a value of  $B = 4.35$  leads to acceptable results except for a volume content of 30%. These values are in agreement with the reported data of HDPE with  $\text{CaCO}_3$  or Talc as filler [28]. The described correlation of an increased parameter  $B$  for a larger surface area, respectively smaller particulate size, is also observed for HDPE and Kaolin filler. The microstructural parameters (Eq. (2)) which are related to the parameter  $B$  are constant in this investigation except for the strength and thickness of the interface. The micrographs of fracture surfaces clearly show different interphases for particulates with or without coupling agent. A quantitative determination is not yet possible. The large deviation in the calculated values of the 30 vol% content of the blow-molding grade could be an effect of the nonlinear behavior of the interphase strength due to homogeneous stress conditions and improved local yielding of the matrix between the particulates nucleated by the interphase.

The fracture behavior of the neat matrices (Fig. 11) shows a failure under plane stress conditions for the blow-molding matrix and a mixed failure mode for the injection-molding matrix. In the center of the sample, plane stress leads to localized matrix deformation and the near-surface layers fail under plane stress conditions with macroscopic yielding.

For the toughening of a semicrystalline material two basic mechanisms can be responsible:

- 1) The strength increase in front of the crack tip leads to a higher bearable stress intensity.
- 2) The building of a larger process zone with extensive crazing and/or yielding is absorbing energy.



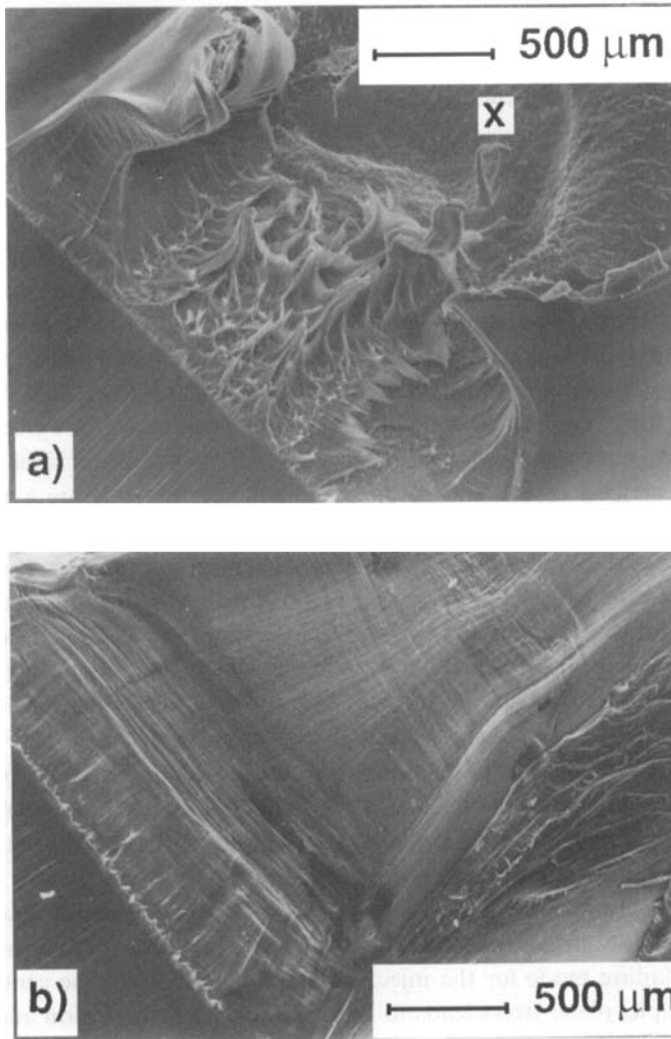


FIGURE 11 Overview of fractured neat HDPE CT specimen under static loading with 10 mm/min. a) Injection-molding grade, b) Blow-molding grade, (*X* = Brittle fracture under liquid nitrogen).

A crack propagation model based on the fractographic results is shown in Figure 12. The low crack speed during the static fracture toughness test leads to extensive yielding. On the fracture surface of the material with well-bonded particulates of 0.8 μm no particulates

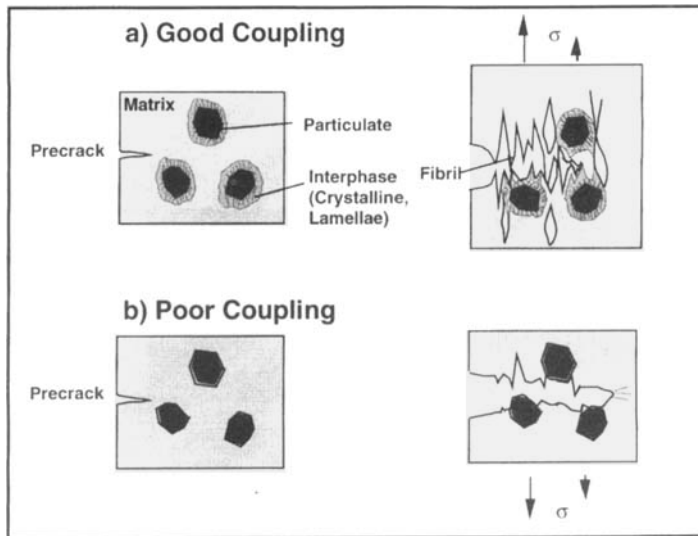


FIGURE 12 Schematic drawing of crack growth in a ductile matrix with rigid filler particulates and a) good coupling or b) low coupling.

are visible (Fig. 13a). In the sample containing 30 vol% particulates of 1.4  $\mu\text{m}$  a few large particulates can be observed in the range of the starting crack (Fig. 13b). The failure mainly occurs through the matrix under energy absorption by fibrillation and yielding. The increase of the viscosity, respectively the molecular weight, leads to higher deformed matrix tips for 30 vol% Kaolin (Fig. 13c).

The energy absorption in the plastic zone in front of the crack leads to higher nonlinear behavior and is quantitatively reflected in the  $K_{\text{max}}$  data. Due to the plane stress in thin samples, yielding is induced even with lower particle volume content if a proper coupling is applied. The samples with 10 mm thickness include more plane strain conditions where yielding is hindered. Due to the advantage of good bonding and increasing filler content a local yielding and fibrillation process is supported and the overall fracture toughness is much higher than the corresponding matrix value. For the blow-molding matrix the stress state changed, due to the incorporated filler, from a complete plane stress in the neat matrix to a localized plane strain mode. The favorable behavior of the filled blow-molding grade exhibits, beside these

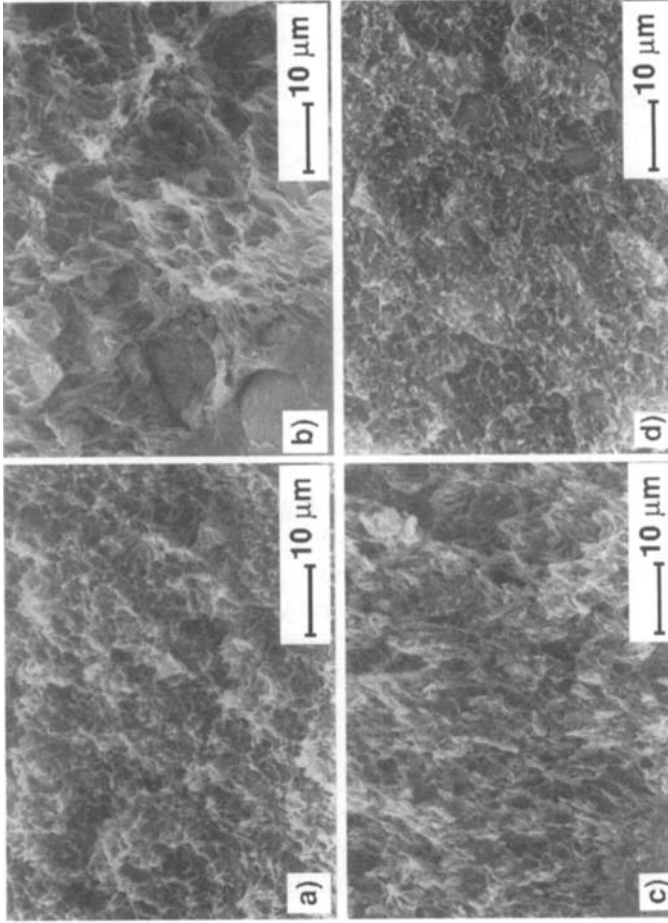


FIGURE 13 Micrographs of fractured CT specimen under static loading with 10 mm/min. a) Injection molding HDPE + 30 vol% particulates  $\phi$  0.8  $\mu\text{m}$ , good coupling ( $K_{\text{max}} = 4.44 \text{ MPa}\cdot\text{m}^{1/2}$ ), b) Injection molding HDPE + 30 vol% particulates  $\phi$  1.4  $\mu\text{m}$ , good coupling ( $K_{\text{max}} = 3.97 \text{ MPa}\cdot\text{m}^{1/2}$ ), c) Blow molding HDPE + 30 vol% particulates  $\phi$  0.8  $\mu\text{m}$ , good coupling ( $K_{\text{max}} = 5.10 \text{ MPa}\cdot\text{m}^{1/2}$ ), d) Injection molding HDPE + 30 vol% particulates  $\phi$  0.8  $\mu\text{m}$ , poor coupling ( $K_{\text{max}} = 1.56 \text{ MPa}\cdot\text{m}^{1/2}$ ).

mechanisms, an improved  $K_Q$  value which might be related to the potential of strength increase that was also found in the tensile tests.

On the fracture surface of the material with poor bond quality some particulates covered with only slightly-yielded PE material were found (Fig. 13d). The Kaolin particulates seem to have a negative influence as stress concentrators and do not nucleate a yielding of the surrounding matrix. The crack propagates along the particulate surface or along the thin interphase. The plastic deformation in front of the crack tip is small and the crack propagates under plane strain conditions. The toughness reduction by embrittlement with increasing filler content is compensated by the stiffness and strength improvement. Higher magnifications (Fig. 14) show, for the well-coupled 1.4  $\mu\text{m}$  particulates, yielded matrix material on the surface and the edges of the single particulate, which leads to increased energy absorption. In this range, as stated by Lipatov [1], the work of adhesion is determined thermodynamically not by the cohesion energy of the matrix but by the cohesion energy of the interphase material. On the particulates with poor coupling, less and not yielded PE is visible, and the surrounding matrix tips have a poor adhesion to the particulates.

In the fatigue experiments the same effects of energy absorption are found due to a matrix deformation in front of the crack tip (Fig. 15). A clear improvement of the crack resistance by an optimized coupling system is realized. The extensive matrix deformation of the unfilled HDPE is changed to a high number of small but highly deformed areas. This nucleation of local matrix deformation in front of the crack tip might be enhanced by the tough connection between interphase and matrix. During the slow cyclic crack propagation a more extensive yielding and strain hardening of the yielded fibrils takes place.

## CONCLUSIONS

The determined stiffness-toughness profile of the HDPE-Kaolin composite investigated is shown in Figure 16. A stiffness improvement with increasing filler content is achieved by all coupling qualities. The poor coupling quality follows, at the same time, the traditional trend, namely, a simultaneous reduction in toughness. The well-coupled materials, on the other hand, and in particular the blow molding

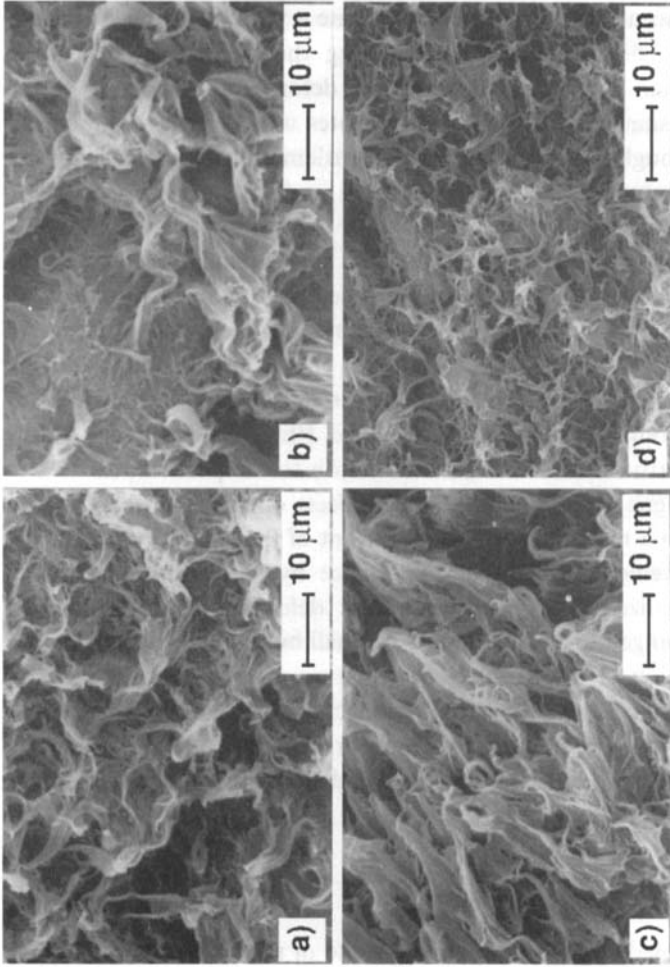


FIGURE 14 Details of fracture surfaces of CT specimen under static loading with 10 mm/min. a) Injection molding HDPE + 30 vol% particulates  $\phi 0.8 \mu\text{m}$ , good coupling ( $K_{\text{max}} = 4.44 \text{ MPa}\cdot\text{m}^{1/2}$ ), b) Injection molding HDPE + 30 vol% particulates  $\phi 1.4 \mu\text{m}$ , good coupling ( $K_{\text{max}} = 3.97 \text{ MPa}\cdot\text{m}^{1/2}$ ), c) Blow molding HDPE + 30 vol% particulates  $\phi 0.8 \mu\text{m}$ , good coupling ( $K_{\text{max}} = 5.10 \text{ MPa}\cdot\text{m}^{1/2}$ ), d) Injection molding HDPE + 30 vol% particulates  $\phi 0.8 \mu\text{m}$ , poor coupling ( $K_{\text{max}} = 1.56 \text{ MPa}\cdot\text{m}^{1/2}$ ).

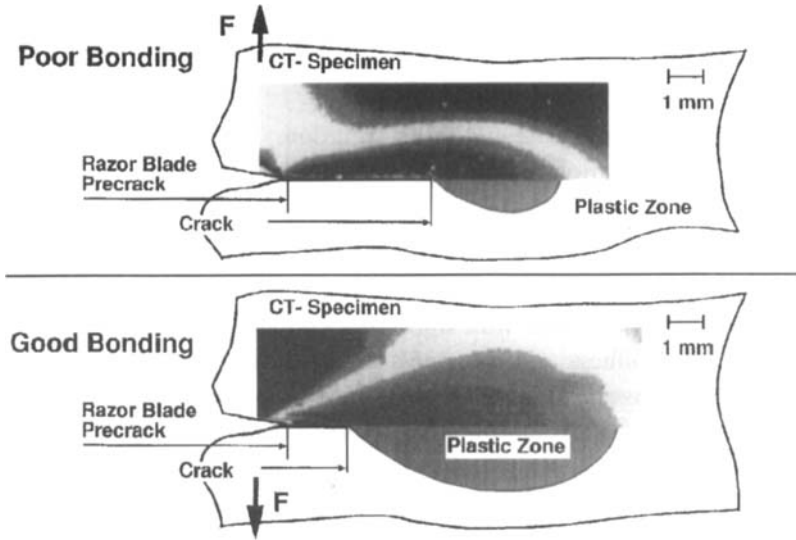


FIGURE 15 Size of the plastic zone in front of a propagated crack determined by a surface topography quantification with a laser profilometer.

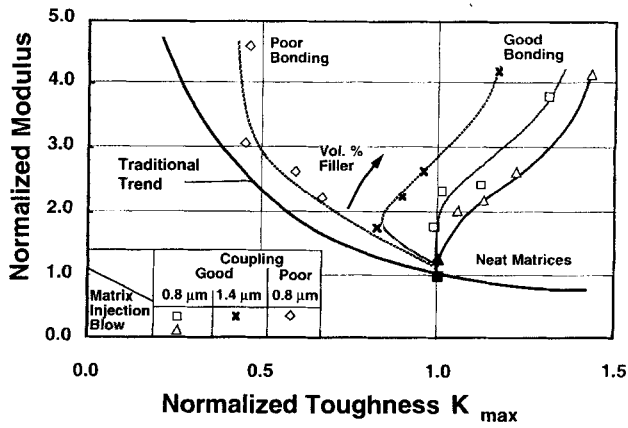


FIGURE 16 Influence of the Kaolin particulate reinforcement, the coupling quality, the matrix viscosity and the particulate size on the normalized stiffness and normalized toughness properties of HDPE under static load.

material with good coupling, small particulates and a vol. content of 30%, show also a certain amount of toughness improvement under all loading conditions investigated. The energy dissipation mechanisms

were investigated by fractographic analysis and, in agreement with [13, 14], three dominating mechanisms were found for materials with good coupling and high toughness:

- Non-linear viscoelastic matrix deformation,
- Plastic deformation of matrix bridges,
- Fracture of fibrils.

Particulates with poor bond quality show a brittle fracture surface with local microscopic matrix deformation. The developed Kaolin reinforcement of HDPE with optimized coupling offers an improvement of the stiffness and toughness under static, impact and fatigue loading. The investigation of different matrix viscosities and molecular weights shows a more pronounced improvement for the matrix with the higher molecular weight. A variation of the particulate size leads to a slightly lower stiffness/toughness profile. The investigation of different sample thicknesses shows an increase of the toughness under plane strain and plane stress conditions. The problem of previous filler systems, where a strength and stiffness increase by strong coupling was accompanied by reduced toughness, is solved by using a coupling that supports the building of an interphase. Due to this interphase the stiffness at low strain is improved; on the other hand, energy absorption by local yielding and strain hardening is induced for higher deformations in front of a propagating crack. A comparison of the filled HDPE with PP matrices shows that many mechanical properties are competitive. The HDPE systems can be tailored to applicational needs without loss of favourable properties like blow-moldability and low-temperature impact resistance.

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