Slow crack growth in blends of HDPE and UHMWPE

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Slow crack growth rates were measured in blends of UHMWPE particles in a matrix of HDPE. Microscopic examinations of the growing crack showed how the UHMWPE particles bridge the crack while it propagated in the HDPE matrix. The rate of crack propagation was related to the volume fraction of the UHMWPE particles by the equation $\dot{\delta}_p = \dot{\delta}_p(0)[1 - (\sigma_f/\sigma)C]^{4.5}$, where C is the volume fraction and σ_f/σ is the ratio of the counterstress exerted by particles with respect to the applied stress and the power n comes from the empirical observation that $\dot{\delta}_p \sim \sigma^{4.5}$. From the data $\sigma_f = 3\sigma$.

(Keywords: blends; slow crack growth; HDPE; UHMWPE)

INTRODUCTION

The present authors[1] measured the effect of molecular weight on the rate of slow crack growth in homopolymers of polyethylene (PE). $\bar{M}_n$ was nearly constant. The rate of slow crack growth obeyed the relationship:

$$\dot{\delta} = \frac{A}{\bar{M}_w - 18\,000} \tag{1}$$

where A was a constant for a given stress intensity and temperature. This equation was based on values of $\bar{M}_w$ up to 158 000. However, the slow crack growth rate of UHMWPE was about 10^2 times slower than the value predicted by equation (1) (*Figure 1*). Therefore it was interesting to determine the slow crack growth behaviour of blends of UHMWPE and a relatively lower molecular-weight resin.

Whether the blends would or would not be miscible was an important question. Since the components of the blend have greatly different values of *MI* and diffusivity, it seemed that they would not be miscible at the molecular level unless the temperature was very high. Also, work by Zachariades and Kanamoto[2] showed that UHMWPE does not disentangle at temperatures below about 220°C. Nevertheless, it was decided to blend at about 210°C, which is the usual extrusion temperature of HDPE. The materials were passed through the extruder twice to enhance the possibility of achieving miscibility. The resulting blend indicated practically no mixing at the molecular level and was essentially a composite of particles of UHMWPE in a matrix of HDPE. From the scientific point of view this morphology was most interesting because it provided a new insight into the mechanism of slow crack growth in PE.

Recent work by Ree *et al.*[3] showed that blends of LDPE and LLDPE were not miscible in that each component essentially separated during crystallization. However, the blend of LLDPE and HDPE used by Hu *et al.*[4] co-crystallized. Wright and Bowman[5] measured the lifetime under slow crack growth of blends of HDPE and LLDPE and blends of an ethylene–octene and ethylene–hexene copolymer. They found a monotonic change in lifetimes for blends of composition up to about 20%. The general trend for the additions of HDPE to the LLDPE gas-pipe resin was to decrease the lifetime. The general explanation of the results was based on the assumption that the HDPE produced less tie molecules than the number in the pure LLDPE pipe-grade material. The addition of the ethylene–octene pipe-grade resin to the ethylene–hexene pipe-grade resin had practically no effect on the lifetime.

Spenadel[6] measured the environmental stress crack resistance of a blend of rubber particles in matrices of LDPE and HDPE matrix. The effect of the rubber particles depended on the type of rubber. He found that the resistance to crack growth increased linearly with the percentage by weight of butyl rubber in the LDPE matrix: 10% butyl rubber increased the lifetime by about 200 times in Igepal at 50°C for an unnotched specimen under a constant stress of 600 psi (≈4.14 MPa). Spenadel[6] did not make a morphological study of the fracture process so that the role of the rubber particles was not elucidated. In this paper the microscopic details of the fracture process are presented so that we have a clear picture of how the particles of UHMWPE increase the resistance to slow crack growth.

EXPERIMENTAL

Pellets of linear HDPE ($\bar{M}_w = 106\,000$ and $\bar{M}_n = 20\,300$) were blended with a powder of UHMWPE ($M_w \approx 10^6$). The compositions of the blends were 0, 1%, 3%, 6% and 12% by weight of UHMWPE. The pellets and powder were first mixed manually and then blended in a twin co-rotation screw extruder (Werner and Pfleiderer 25K-30, $L/D = 29/1$) at a feed rate of 21 lb h^{-1}

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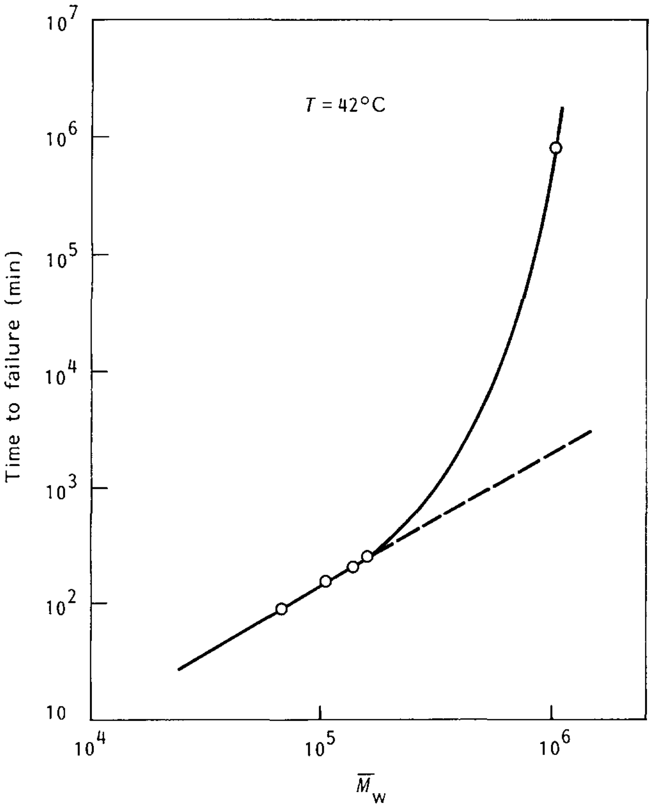

Figure 1 Time to failure *versus* molecular weight

Table 1 Characterization of blends

Composition	Density^a	MI (g (10 min)$^{-1}$)^b
0	0.9714	0.61
1	0.9708	0.52
3	0.9697	0.27
6	0.9684	0.24
12	0.9640	0.06
100	0.9335	

[a] Compression-moulded–slow-cooled
[b] 190°C; 2.16 kg; ASTM D1238

(≈ 9.5 kg h^{-1}). The screw speed was 150 rev min^{-1}, the temperature in the screw ranged from 140 to 210°C and the head pressure was 210–320 psi (≈ 1.45–2.21 MPa). The material was run through the blender twice. The blends were characterized as shown in *Table 1*. Differential scanning calorimetry (d.s.c.) could not detect phase separation. The melting point of all blends and for 100% UHMWPE is 135°C. The crystallinity of the blends as measured by d.s.c. is about 73%. The crystallinity of pure UHMWPE is about 50%. The specimens were machined from compression-moulded slow-cooled plaques of 10 mm thickness.

Slow crack growth was measured on notched tensile specimens whose geometry is shown in *Figure 2*. The notching procedure was very carefully controlled by slowly pressing a fresh razor blade into the specimen. The specimen was designed to produce pure plane strain fracture. The crack opening displacement was measured with an optical microscope having a filar eyepiece and by looking directly into the mouth of the notch (*Figure 2*). The stress level in all experiments was sufficiently low, less than one-half the yield point, to ensure that all fractures were of the purely brittle type. The temperature of the tests was 35 ± 0.5°C.

The experimental scatter in the lifetimes was about ±40%. This value is greater than that for unblended resins because of the variations in the distribution of the particles in the matrix.

RESULTS

Morphology of blend

Figure 3c shows the particles of UHMWPE before blending. The particles were equiaxed and varied from about 180 to about 500 μm in size in the unblended state. *Figure 3a* and *b* show the fractured surface of the compression-moulded material of 0% and 6% composition after fracturing in liquid nitrogen. The particles of UHMWPE appear darker than the HDPE matrix because they scatter fewer of the incident electrons by virtue of having a lower crystallinity. The particles in the compression-moulded plaque appear elongated because they were flattened during compression and the normal to the fractured surface in *Figure 3b* is perpendicular to the compression direction. The area fraction of the particles was measured by superposing a fine grid over the fractured surface. The results are shown in *Table 2*. It is to be noted that the area fraction of the particles is equal to the volume fraction. This result is expected for a random array of particles. It also signifies that practically none of the UHMWPE particles dissolved in the matrix. The linear fraction of the front row of fibrils of UHMWPE was measured from micrographs like *Figure 7*. The theoretical value of the linear fraction as measured by the intercepts of a random line in the material should equal the volume fraction. However, the experimental values in *Table 2* are somewhat greater because the experimental method involved a strip instead of a line, where the width of the strip is determined by the depth of focus of the optical microscope.

Stress–strain behaviour

Figure 4 shows the stress–strain curves of pure HDPE and pure UHMWPE. The stress–strain curves of all the blends were practically identical to the pure HDPE curve. The most interesting difference between the two curves is in the behaviour beyond the yield point. After yielding the HDPE draws at a stress well below the yield point, whereas the UHMWPE strain hardens. This difference is reflected in their behaviour during craze growth, where

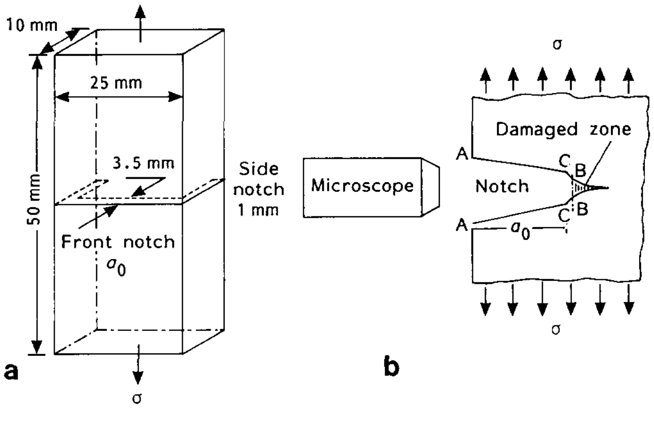

Figure 2 (a) Specimen geometry and (b) experimental method

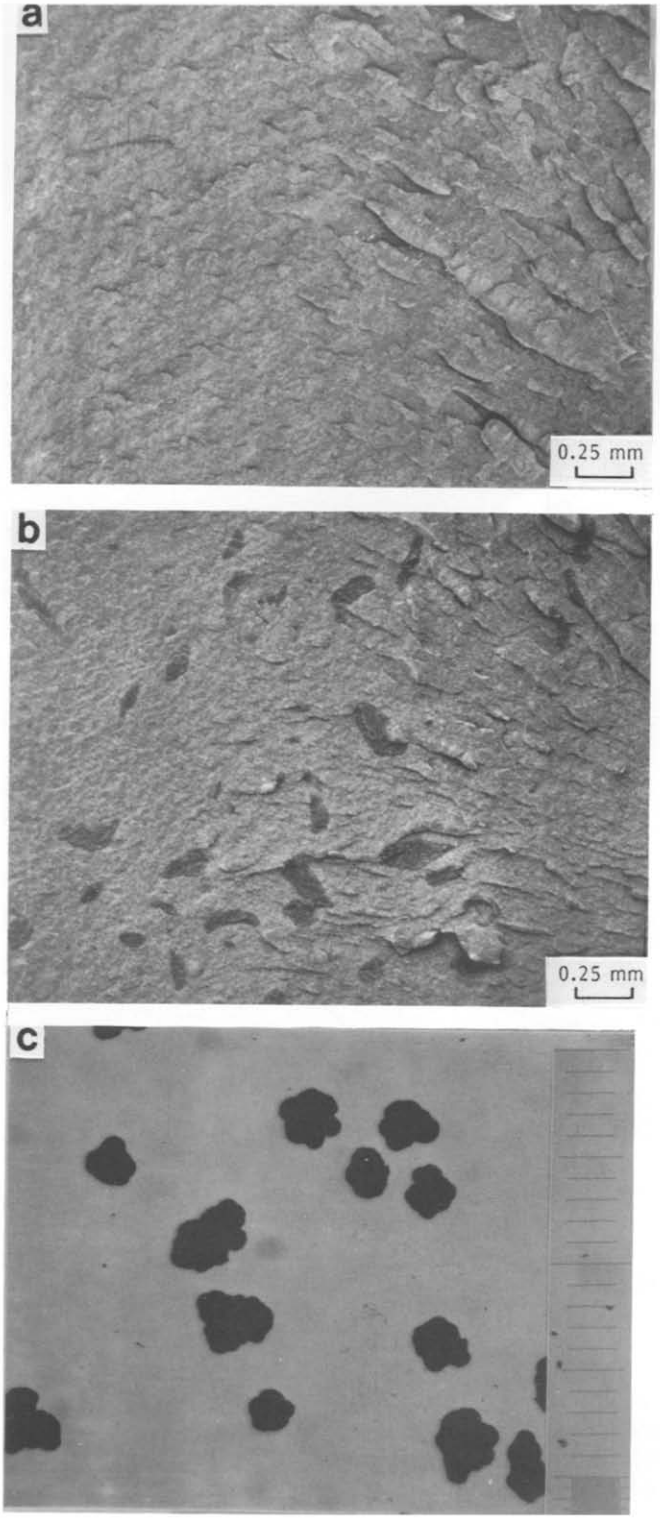

Figure 3 (a) Fractured surface of 0% and (b) 6% blend, which were fractured in liquid nitrogen; (c) unblended particles of UHMWPE. The normal to the surface is perpendicular to the direction of compression during moulding

the UHMWPE particles can sustain a higher stress than the fibrils of HDPE.

Kinetics of slow crack growth

Figure 5 shows the crack-opening displacement *versus* time for each blend. Fracture occurs in the HDPE matrix while the UHMWPE particles bridge the crack and slow down the rate of fracture. First note the kinetics of slow crack growth in the pure HDPE. A craze forms upon loading the specimen. Its size is approximately predicted by the Dugdale theory and varies inversely as the square of the yield point. The craze growth until the *COD* is about 75 μm and then fracture initiates in the HDPE fibrils at the base of the craze. The crack propagates to a point corresponding to a *COD* of about 250 μm, after which time the final phase of failure involves rapid yielding in the remaining ligament.

Now it is interesting to observe how the particles of UHMWPE modify the fracture process of pure HDPE. The initial *COD* of the blends is about the same as for the pure HDPE because the yield points are about the same. The rate of craze growth before crack initiation is only slightly decreased as the percentage by weight of UHMWPE is increased.

After crack initiation, the effect of the blend is more prominent with regard to its effect on the rate of crack propagation. As will be shown below, during crack propagation the matrix fractures, but the fibrils of UHMWPE remain intact and retard the opening of the crack. The retardation of crack propagation by the UHMWPE fibrils is clearly exhibited, given by the slope of the *COD versus* time curve just beyond the point of crack initiation. This slope will be called $\dot{\delta}_p$, the initial rate of crack propagation in the matrix. *Table 3* lists values for $\dot{\delta}_p$ and the time for complete failure for each

Table 2 Volume, area and linear fractions of UHMWPE particles

Volume fraction	Area fraction	Linear fraction of front row
0	0	0
0.01	0.013	0.022
0.03	0.032	0.048
0.06	0.060	0.078
0.12	0.14	0.17

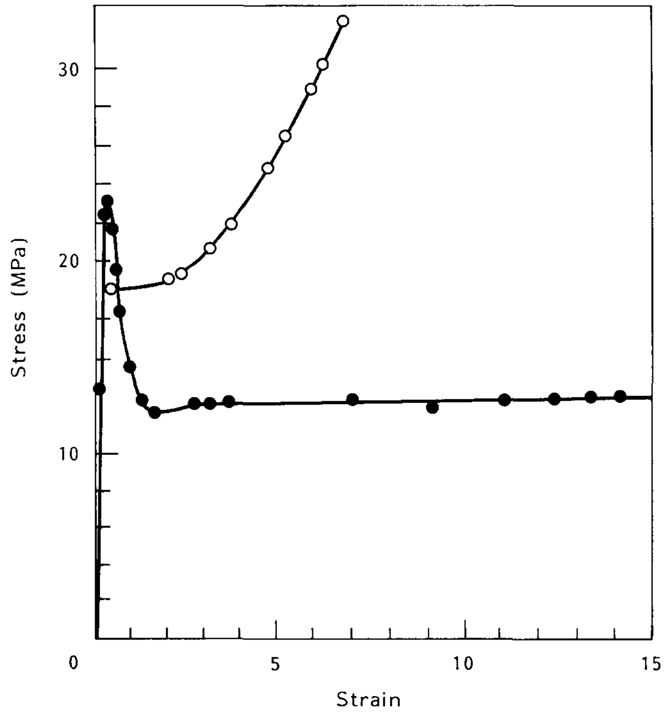

Figure 4 Tensile stress–strain curves of HDPE (●) and UHMWPE (○) at 42°C: $\dot{\varepsilon}$, 0.4 min^{-1}; strain values are based on overall displacement

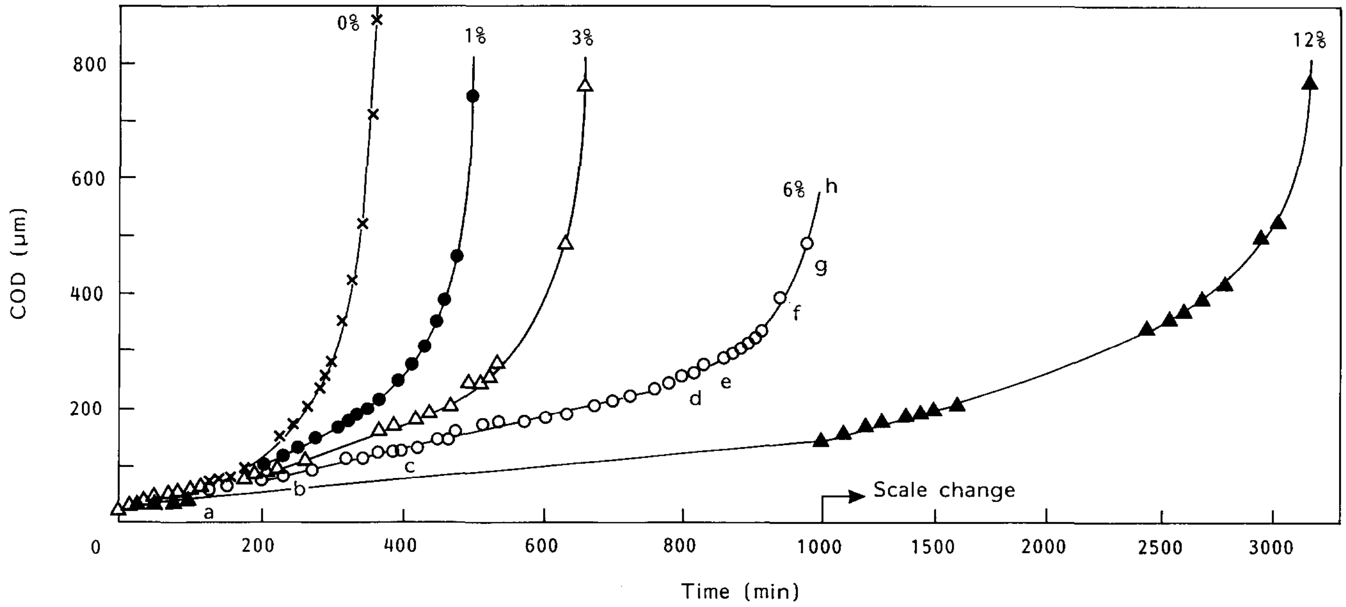

Figure 5 *COD versus* time for the various blends: σ, 3 MPa; notch depth, 3.5 mm; 35°C; crack initiation occurs at *COD* ≈ 75 µm

Table 3 Rate of crack propagation and failure time *versus* composition

UHMWPE (wt%)	$\dot{\delta}_p$ (µm min^{-1})[a]	Time to failure (min)
0	0.8	400
1	0.66	525
3	0.41	712
6	0.30	1050
12	0.12	2775

[a] $\dot{\delta}_p$ = rate of notch opening at crack initiation

composition. As expected, the time for complete fracture increases with composition and the rate of crack propagation decreases with composition, as shown in *Figure 6*.

The dependence of $\dot{\delta}_p$ on composition is amenable to analysis, especially when the initial rate of crack propagation is considered. However, the time for complete fracture is a more complex quantity because it involves the periods of crack initiation, crack propagation and the final yield process in the remaining ligament.

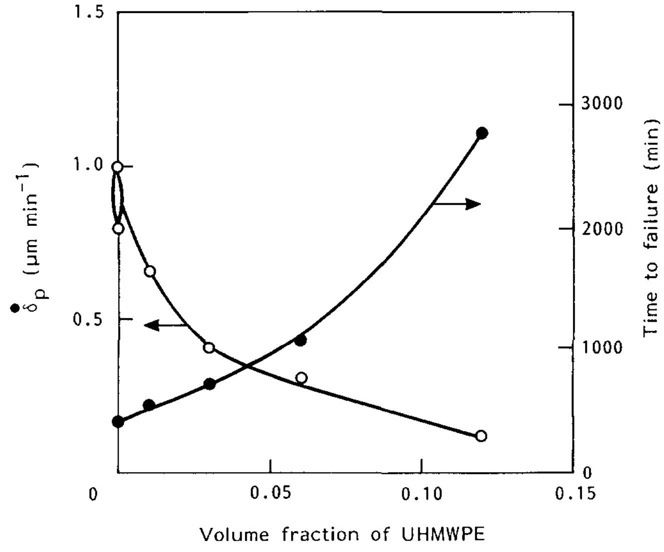

Figure 6 Rate of crack propagation, $\dot{\delta}_p$, when crack initiates in the HDPE matrix, and time to failure *versus* volume fraction of UHMWPE

Morphology of the fracture process

Figure 7 shows the bottom of the notch while looking into the mouth of the notch with the optical microscope for the 6% blend. The time increases from *Figure 7a* to *h* and the corresponding times are designated from *a* to *h* on the 6% blend curve in *Figure 5*. *Figure 7b* shows crack initiation. As the crack propagates in the matrix, the fibrils of UHMWPE extend, as shown in *Figure 7b–h*. In *Figure 7h* the UHMWPE is about to fracture. So, it is seen that the UHMWPE fibrils counteract the applied stress, which causes the crack to propagate. The concentration of fibrils is sufficiently low that it appears that each fibril produces the same force that counteracts the applied stress, so the total counterforce by the fibrils is simply proportional to the area fraction of fibrils on the plane of fracture. The force exerted by the individual UHMWPE fibril no doubt varies with the extension of the fibril as determined by the *COD*. Based on the stress–strain behaviour of UHMWPE in *Figure 4* and the change in fibril diameter in *Figure 7*, it appears that the force exerted by the fibril reaches a maximum value. This maximum probably occurs at a *COD* of 250 µm, where the *COD versus* time curve undergoes a marked acceleration.

Figure 8 shows side views of the fracture process for blends of 0, 3 and 6% for a *COD* of 100 µm, which is just after crack initiation. The crack in the matrix simply propagates between UHMWPE fibrils. *Figure 9* shows optical micrographs of a thin section in reflected and transmitted light. The purpose is to show the connection of the UHMWPE fibrils to the UHMWPE particles in the matrix. *Figure 9a* is by reflected light, where the UHMWPE fibril is bright because it is more porous than the matrix. *Figure 9b* is by transmitted light, so the porous fibril is dark. However, the UHMWPE particles in the matrix are brighter than the matrix because bulk UHMWPE is more transparent than bulk HDPE. The UHMWPE fibrils that bridge the crack are only a small

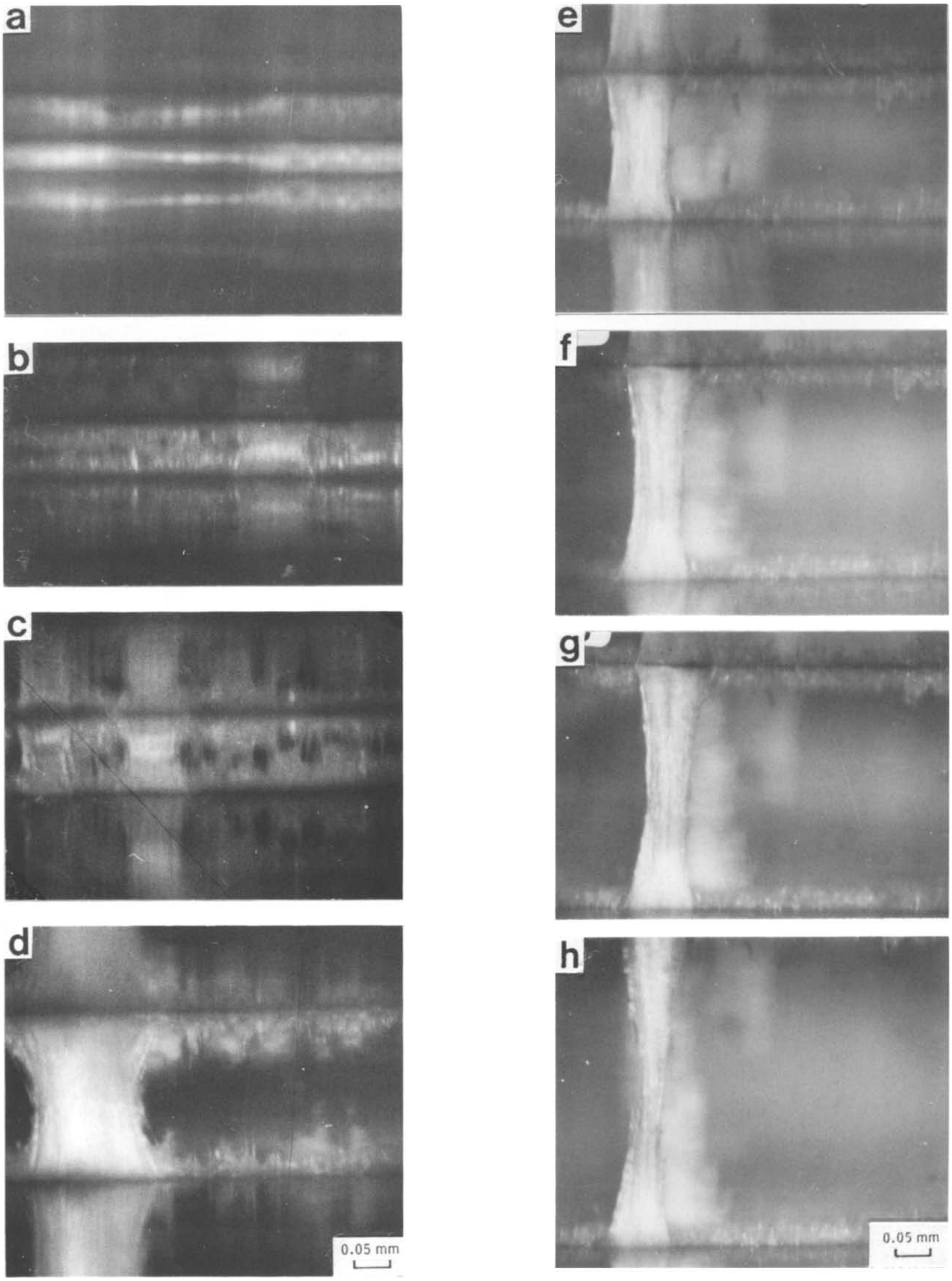

Figure 7 Optical view of bottom of notch: time increases from (a) to (h); (b) corresponds to crack initiation (note fine fibrils of matrix compared to the coarse UHMWPE fibril); (d) and (e) are different locations at the same *COD*

fraction of the bulk particle from which it formed. Note that the ends of the bridging fibrils that are within the matrix also are porous, as indicated by their dark contrast. Also note in *Figure 9b,c* that the UHMWPE fibrils are much coarser than the fibrils that form from the HDPE matrix. It is generally observed that the thickness of fibrils in PE increases with the strength of the fibrils, as reflected by their rate of disentanglement. The present authors[7] have shown that there is a systematic increase in fibril thickness as the resistance to slow crack growth of a PE resin increases.

Figure 10 shows the fractured surface in the area of slow crack growth for various blends. Most of the UHMWPE fibrils have fractured, but a small fraction were pulled out of the matrix, as indicated by the holes. Fracture of the UHMWPE fibrils is expected rather than pull-out because the fibril consists of a small fraction of the embedded particle. It has been determined that the amount of resin in the bridging fibrils is only about 10% of that in the embedded particle.

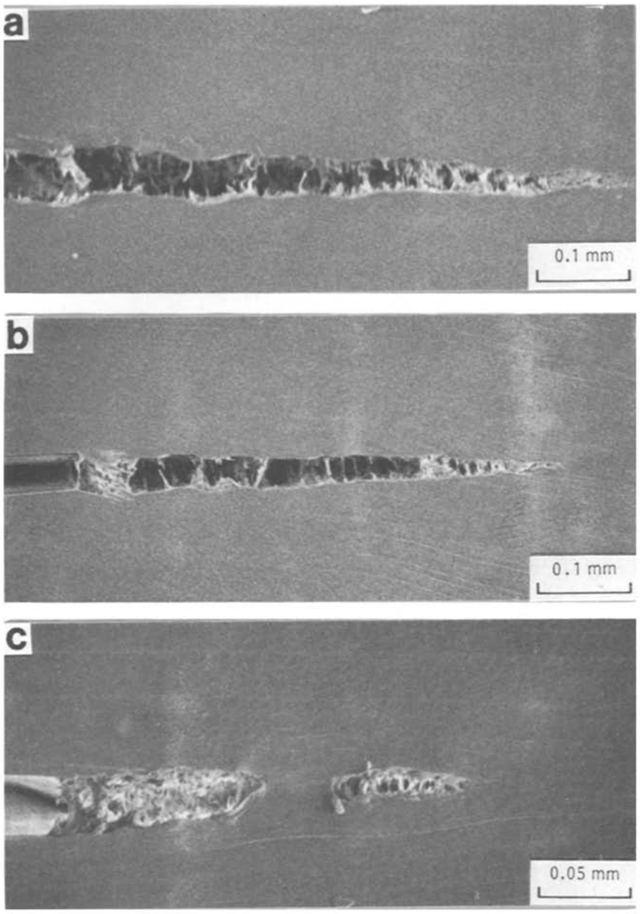

Figure 8 S.e.m. micrographs of fracture in: (a) 0%; (b) 3%; and (c) 6% blends

The effect of stress

Figure 11 shows stress *versus* time to failure in the brittle regime for all blends. The data show:

$$t_f = C\sigma^{-4.5} \qquad (2)$$

for all blends where C depends on the composition. For pure UHMWPE, Huang[8] found that

$$t_f \sim \sigma^{-2} \qquad (3)$$

The difference in exponents of the stress indicates that for the blends the fracture process involves only the HDPE material and the UHMWPE fibrils only act to counteract the applied stress. For slow crack growth in pure UHMWPE, another exponent of the stress occurs, which is characteristic of the UHMWPE fracture process.

ANALYSIS

The way the UHMWPE fibrils retard the slow crack growth process is very clear, as illustrated by *Figure 12*. Immediately after loading, the size of the initial craze is independent of the composition of the blend because the yield point, which is about the same for all blends, governs the size in accordance with the Dugdale theory. Before the initiation of fracture the structure is illustrated by *Figure 12b*. The rate of craze growth is only slightly affected by the UHMWPE fibrils because they are working together with the HDPE fibrils in resisting the widening of the craze. Especially at low values of the *COD*, the stress exerted by the UHMWPE fibrils may not be appreciably greater than that exerted by the HDPE fibrils. Once fracture occurs, as illustrated in *Figure 12c*, the rate of crack propagation is strongly influenced by the UHMWPE fibrils for two reasons: (1) the opening of the crack area is only being counteracted by the UHMWPE fibrils; and (2) with the greater *COD*

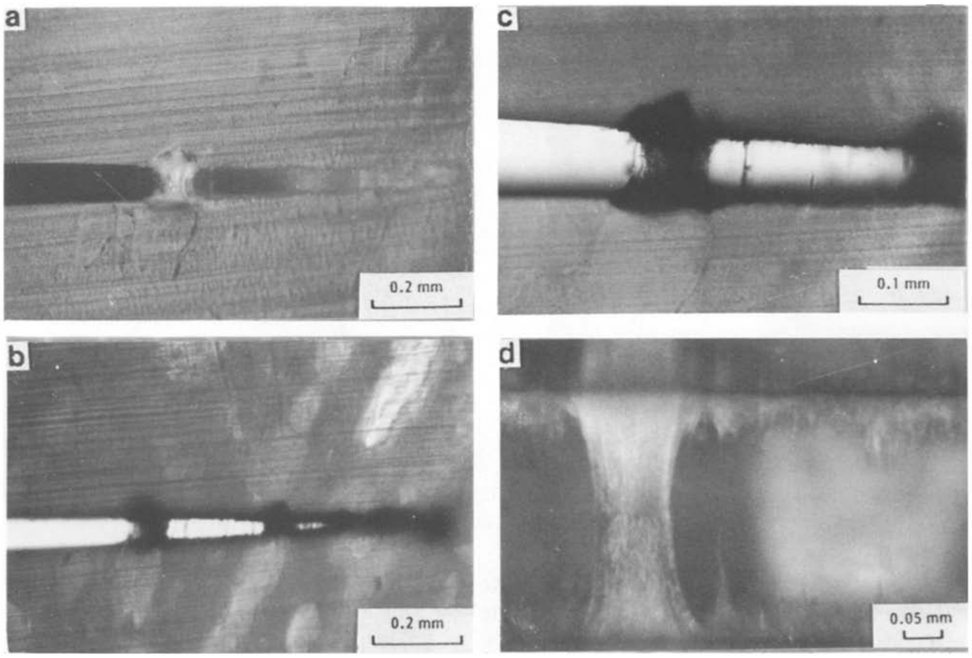

Figure 9 Optical micrographs of thin sections: (a) reflected light; (b) transmitted light (light areas are particles of UHMWPE); (c) same as (b) at higher magnification; (d) further extension of UHMWPE particle

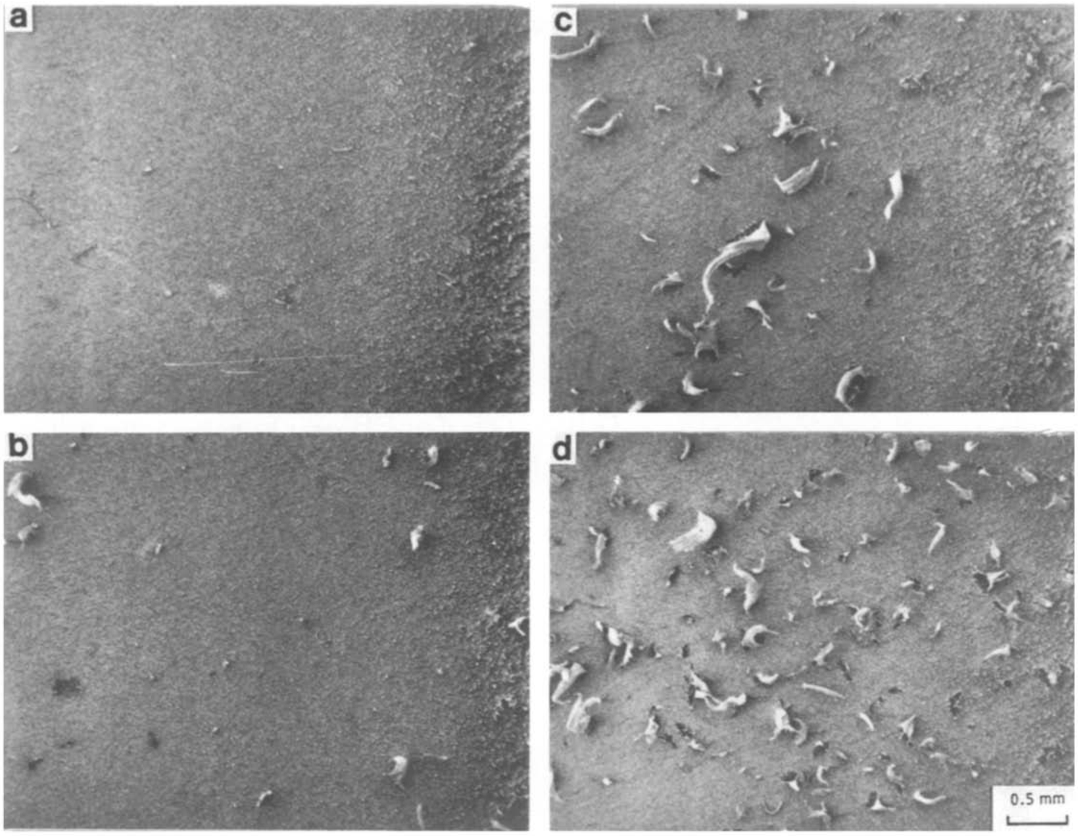

Figure 10 Fractured surface in the area of slow crack growth. Most fibrils have fractured but some have pulled out as indicated by the dark holes: (a) 0%; (b) 1%; (c) 3%; (d) 6%

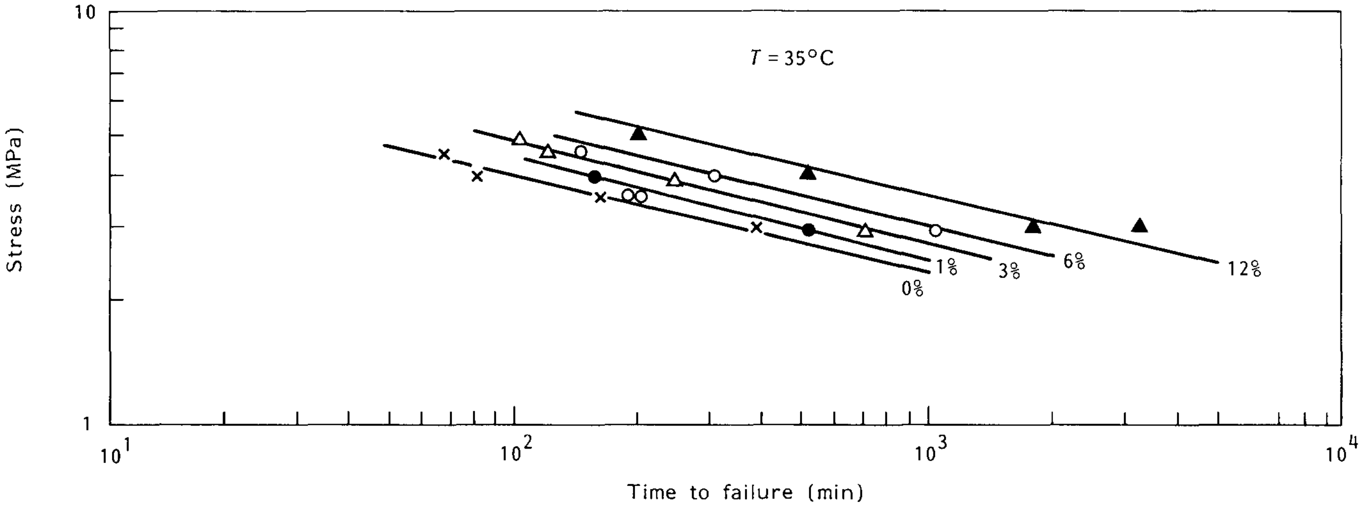

Figure 11 Stress *versus* time for brittle failure for each blend at 35°C (slope = 4.5)

the stress exerted by the UHMWPE fibrils is relatively greater with respect to the stress exerted by the HDPE fibrils. So even though the HDPE matrix fractures, the stress intensity does not increase appreciably in the blend, whereas it does in the 0% blend, whose *COD versus* time curve continuously accelerates after crack initiation. The rate of crack notch opening, $\dot{\delta}_p$, is nearly constant in each blend after crack initiation. The relationship between $\dot{\delta}_p$ and the composition of the blend can be described by a simple theory.

The UHMWPE particles decrease the rate of crack opening simply by forming fibrils that bridge the crack and thus produce a counterstress with respect to the applied stress. Thus the effective stress that causes the crack to propagate is given by:

$$\sigma_{\mathrm{eff}} = D(\sigma - \sigma_f A) \tag{4}$$

where σ is the applied stress, σ_f is the stress exerted by a UHMWPE fibril and A is the area fraction of the fibrils on the plane of fracture. A is the same as the volume fraction and practically the same as weight fraction C. D is a stress concentration factor which can be considered to be a constant.

The rate of slow crack growth in all PEs varies with

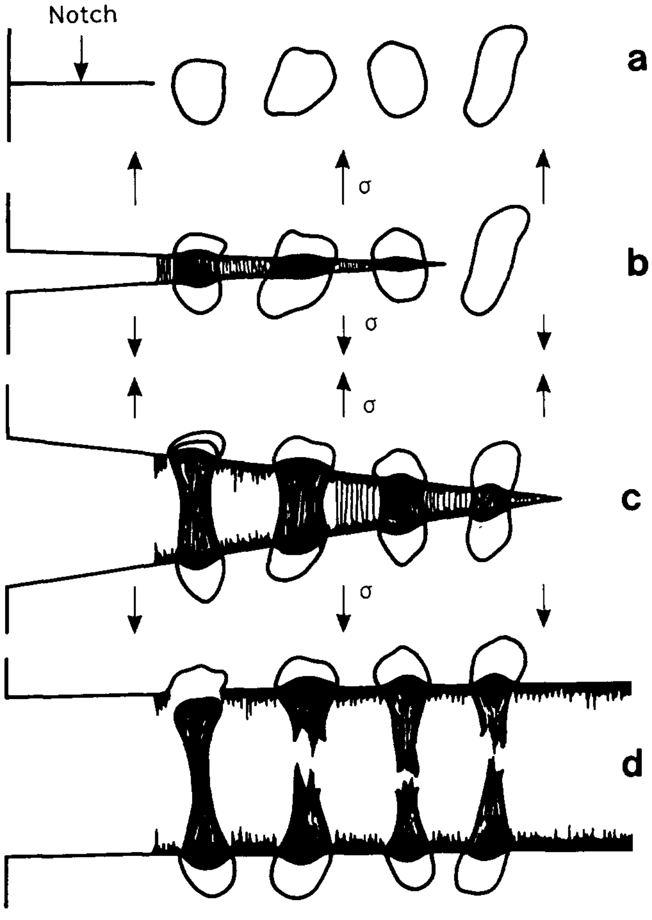

Figure 12 Illustration of the failure process: (a) before loading; (b) before crack initiation; (c) after crack initiation; (d) after complete fracture

stress according to the general equation:

$$\dot{\delta}_p = B\sigma^n \qquad (5)$$

as shown by the extensive research by Brown and co-workers[9], where B and n depend on the resin. Also, the time to failure varies as:

$$t_f \sim \sigma^{-n} \qquad (6)$$

where for a given resin, n is the same in equations (5) and (6). The results in *Figure 11* show that n is the same for all compositions of blends. Therefore:

$$\dot{\delta}_p = B(\sigma - \sigma_f A)^n \qquad (7)$$

The value of $\dot{\delta}_p$ at 0% is given by:

$$\dot{\delta}_p(0) = B\sigma^n \qquad (8)$$

Therefore

$$\dot{\delta}_p/\dot{\delta}_p(0) = \left(1 - \frac{\sigma_f}{\sigma}A\right)^n \qquad (9)$$

Equation (8) is a general equation for all blends with a PE matrix. The value of n would depend on the matrix and not on the reinforcing particles.

In our case $n = 4.5$. In order to determine σ_f/σ, the ratio of the counterstress of the UHMWPE particles with respect to the applied stress, equation (8) is given the form:

$$1 - \left[\frac{\dot{\delta}_p}{\dot{\delta}_p(0)}\right]^{1/4.5} = \frac{\sigma_f}{\sigma}C \qquad (10)$$

since C is equal to A for these blends. Equation (10) is plotted in *Figure 13*; the slope is $\sigma_f/\sigma = 3.0$. This is a reasonable result considering the way that the UHMWPE strengthens as it deforms (*Figure 4*). Note that the value of σ_f/σ was obtained without any adjustable constants. In essence the theory is based on the microscopic observations that the UHMWPE fibrils bridge the crack while it propagates and thus exert a counterstress to the applied stress.

SUMMARY

(1) UHMWPE particles are not miscible in a HDPE matrix after blending at 210°C.

(2) The UHMWPE particles are well bonded to the matrix.

(3) During slow crack growth the HDPE matrix fractures between the UHMWPE fibrils, which do not fracture except toward the very end of the fracture process.

(4) The UHMWPE fibrils slow down the rate of crack propagation by exerting a counterforce to the applied stress that opens the crack.

(5) The counterforce of the UHMWPE fibrils is proportional to their area fraction, which is the same as the volume fraction.

(6) Time to failure $t_f = D\sigma^{-4.5}$, where D is a function of the composition of the blend.

(7) The theoretical relationship between the composition of the blend and the initial rate of crack propagation is given by:

$$\dot{\delta}_p = \dot{\delta}_p(0)\left(1 - \frac{\sigma_f}{\sigma}A\right)^{4.5}$$

where $\dot{\delta}_p(0)$ is the rate for pure HDPE, σ is the applied stress, σ_f is the counterstress exerted by the UHMWPE fibril and A is the area fraction of the UHMWPE fibrils on the fracture surface. Based on the data, this equation gives a value for σ_f which is 3.0σ.

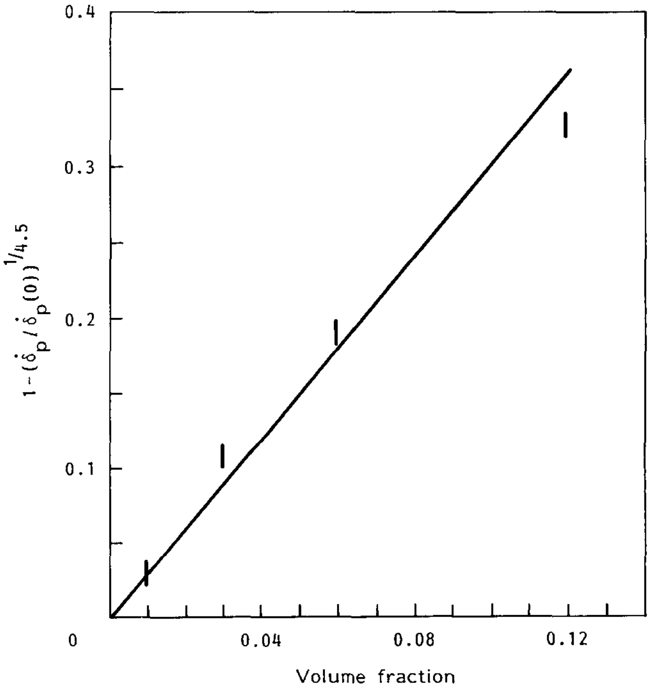

Figure 13 Plot of equation (10) (slope = $\sigma_f/\sigma = 3.0$)

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