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The concept of one polymer composites modelled with high density polyethylene

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One polymer composite materials have been prepared using a difference in melting points between the components. This depends on the fact that aligned and extended chains provide thermodynamically more stable crystals, which thus will have higher melting points than conventionally crystallized melts. The growth of transcrystalline regions in the melt matrix at the interface plus an observed partial melting between fibre and matrix are indications of a strong and intimate interfacial bond with a gradient in morphologies for the system studied, high-density polyethylene. The pull-out test is a simple and adequate method for evaluating the interfacial shear strength of one polymer composites. The value for the high-density polyethylene composite falls between the strengths for glass-reinforced polyester and epoxy resins. However, the interfacial strength in the polyethylene composites is due mainly to the unique epitaxial bonding rather than the radial forces from compressive shrinkage. The low critical aspect ratio for the filaments in these polyethylene composites suggests possible advantageous uses as short fibre-reinforced materials where the interfacial strength is a controlling factor.

1. Introduction

The interest in the use of polymers as replacements for other materials such as metals, wood and ceramics has increased markedly in the last decades. However, bulk plastics have the limitation of relatively low elastic moduli which restricts competition for many novel metallurgical products and applications. The key to enhanced strength and stiffness in polymeric materials is their ability to be structurally reinforced. A multitude of alternatives has been used to improve their mechanical properties. Fibrous and particulate reinforcement, polymer blending, crystallization and orientation by various processes are among common examples not yet exhaustively explored.

The achievement of a strong and stable interface between composite components has been a classical problem for fibre and particle reinforced materials. Since filler and matrix are, in general, chemically different, the corresponding distinct surface energies and the characteristic individual properties impede direct bonding. In some cases, for example for glass-reinforced polymeric resins, coupling agents are generally required to attain an adequate interfacial strength [1–3]. For fibrous composites, properties such as tensile and comprehensive strength, work-to-fracture and creep and fatigue resistance are controlled mainly by the interfacial bond strength [4].

The effort here is to present a novel idea in reinforced polymeric materials, the one polymer composite. This corresponds to a composite in which the matrix and reinforcement are made from different morphologies of the same polymer. As a model case, polyethylene has been used through this study; the results, nonetheless may be generally extended to other semicrystalline thermoplastics.

High-modulus polyethylene fibre and film strips have been prepared in this laboratory by a solid-state (crystal–crystal) transformation, under a sensitive set of operational conditions, in an Instron Capillary Rheometer [5]. The resulting

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morphology has been subjected to intense characterization [6–9]. Important characteristics of these fibres and film strips are their optical transparency and their high and time and temperature insensitive Young's moduli [5]. Their moduli, about 7×10^{11} dyn cm^{-2}, are similar to that of glass fibres. The extreme polyethylene crystal orientation, indicated by an X-ray orientation function of 0.9960 [6] and the presence of extended chain crystals [9], contributes to the clarity and pronounced mechanical anisotropy.

The high-modulus polyethylene filaments and film strips have a higher melting point, 5 to 9° C higher, than the same polyethylene conventionally crystallized. Typical melting endotherms for the oriented fibre and the starting polyethylene, as measured by differential scanning calorimetry, are shown in Fig. 1. Conventional melting of high-density polyethylene is exhibited by the non-oriented sample whereas the ultra-oriented filament of the same polymer shows a notably higher melting temperature and, from the endotherm shape, a higher percent crystallinity and narrower perfection range.

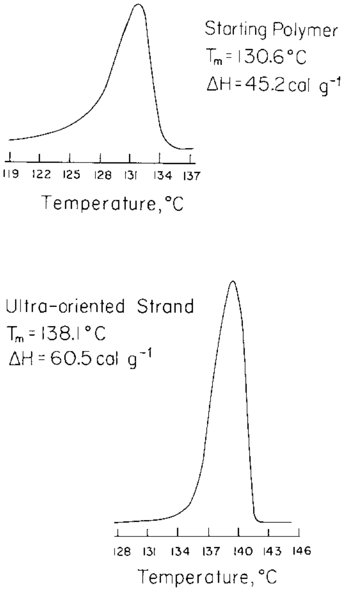

Figure 1 Differential scanning calorimetry for a high-density polyethylene, tests at 5° C min^{-1}.

The melting point difference between the fibre and matrix is the defining feature for the one polymer composite. Advantage is taken of this difference to obtain unique interfacial properties in the composite. The melting point difference makes possible the dispersion of the polyethylene fibres in the melt of the polyethylene matrix. Either low- or high-density polyethylene and a range of molecular weights can be used as the matrix.

It is, of course, known that intimate contact is essential for the firm union of materials [10]. Since the viscosity of the polymer melt increases markedly with its molecular weight, a relatively low molecular weight matrix is chosen to achieve a good contact between phases. The molecular weight must not be so low, however, as to seriously reduce the adhesion. For the reinforcement fibre, the melting point increases with molecular weight [11]. The polyethylene used to make the fibres should thus have the highest molecular weight compatible with the fibre preparation method. Polyethylenes with molecular weights below the characteristic entanglement value of about 4000 are likely to be unsuitable for both matrix and fibre.

HDPE DuPont Alathon 7050 and 7026 were selected, respectively, as matrix and fibre materials for initial tests of the concept of a one polymer composite. These polymers are in the low and high molecular weight range, respectively, of the Alathon linear polyethylene series. This selection gives the largest feasible melting point difference between the composite components and also the lowest convenient matrix melt viscosity.

Interfacial bonding of the polyethylenes is enhanced here by partially melting the outer sheath of the high modulus fibres into the matrix melt. This is aided by the fact that the outer sheath of the polyethylene fibre has been found to have a slightly lower melting point and perfection than the fibre core.

2. Experimental

An embedding technique for the fibres in the matrix was developed using a Differential Scanning Calorimeter, Perkin-Elmer DSC-1B. The goal was to achieve a well-bonded interface between the spherulitic (matrix) and fibrillar (reinforcement) morphologies. Polyethylene Alathon 7050 was melted and set up at various embedding temperatures in a non-volatile DSC aluminium sample pan. A polyethylene fibre was then introduced into the molten matrix and the system cooled down to ambient. The samples were then microtomed to a 30 μm thickness and observed in a polarizing microscope. The time–temperature condition for achieving a good interface were thus determined.

The composite samples for mechanical testing were prepared in an Instron Rheometer. The material used for the filaments was Alathon 7026, $M_w = 128\,000$. Details on the fibre preparation method are described elsewhere [5].

Briefly, the filaments were extruded at 140° C and 2 400 atm. A polished and Teflon-lubricated, 20° entrance angle, brass capillary was used with a length and diameter of 1 cm and 0.13 cm, respectively. The fibre melting point measured by the DSC-1B at the lowest scanning rate (0.625° C min^{-1}) was 140.1° C. Before embedding, the strands were cleaned and degreased by immersion in boiling acetone for 5 min, then dried in a vacuum oven at 60° C for 15 min and stored in a vacuum desiccator. The material used for the matrix was Alathon 7050, $M_w = 52\,500$. The melting point, at the same conditions as before is 131.1° C. No pretreatment was performed on this matrix polyethylene.

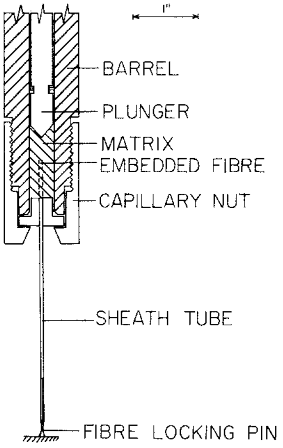

Figure 2 Fibre embedding system.

For the composite sample preparation in the Instron Rheometer, a special fibre support, shown in Fig. 2, was used in lieu of a capillary. The matrix is melted and heated up to 190° C, then cooled down to 139° C and left for 10 min to equilibrate the temperature. The fibre is then introduced through the lower sheath tube, see Fig. 2, locked into the molten matrix and left 5 min, still at a controlled temperature of 139° C. The heaters are then shut off and the composite cooled at a rate of ~ 1° C min^{-1}. A small force (30 to 40 kg) is maintained on the sample so that the plunger will follow the volume changes due to matrix crystallization and cooling. When the temperature reaches ~ 100° C, the force is released and the sample taken out.

The matrix-embedded fibres were subjected to tensile testing at a constant rate of strain in the Instron. The purpose was to measure the strength of the matrix–fibre interface. The pull-out stresses were measured on fibres which were embedded to various lengths.

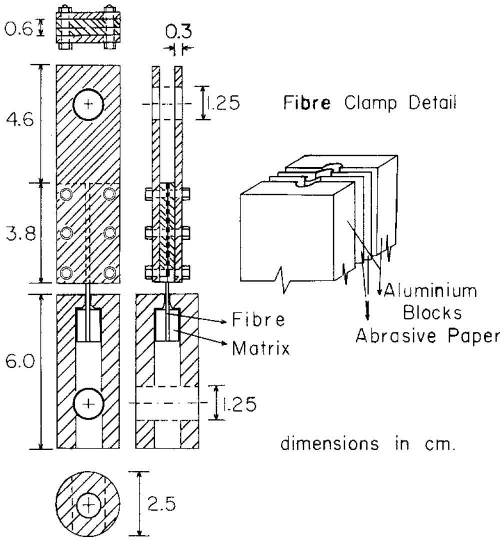

Figure 3 Clamping system.

Fig. 3 shows the gripping technique used for the pull-out tests. On the fibre side, a sandwich-like assembly is used. As can be seen in the detail of Fig. 3, the parts, from the outside, are: two aluminium blocks with axial semicircular grooves of the same diameter as the fibre; two pieces of silicon carbide paper (20 μm grain size); and, in the centre, the fibre. This arrangement prevents slippage out of the jaws [5]. On the composite side, the matrix is held from its front face, as seen in Fig. 3. The hollow-flanged cylinder resists tensile stresses without imposing compressive radial forces on the matrix. Both ends are fixed to the heads of the Instron by regular pins. The tensile tests were performed at an Instron cross-head speed of 0.05 cm min^{-1}.

3. Results and discussion

The presence of low mechanical strength regions at the surface is common for polyethylene and other polymers crystallized from the melt [10, 12]. These defect regions are developed when the

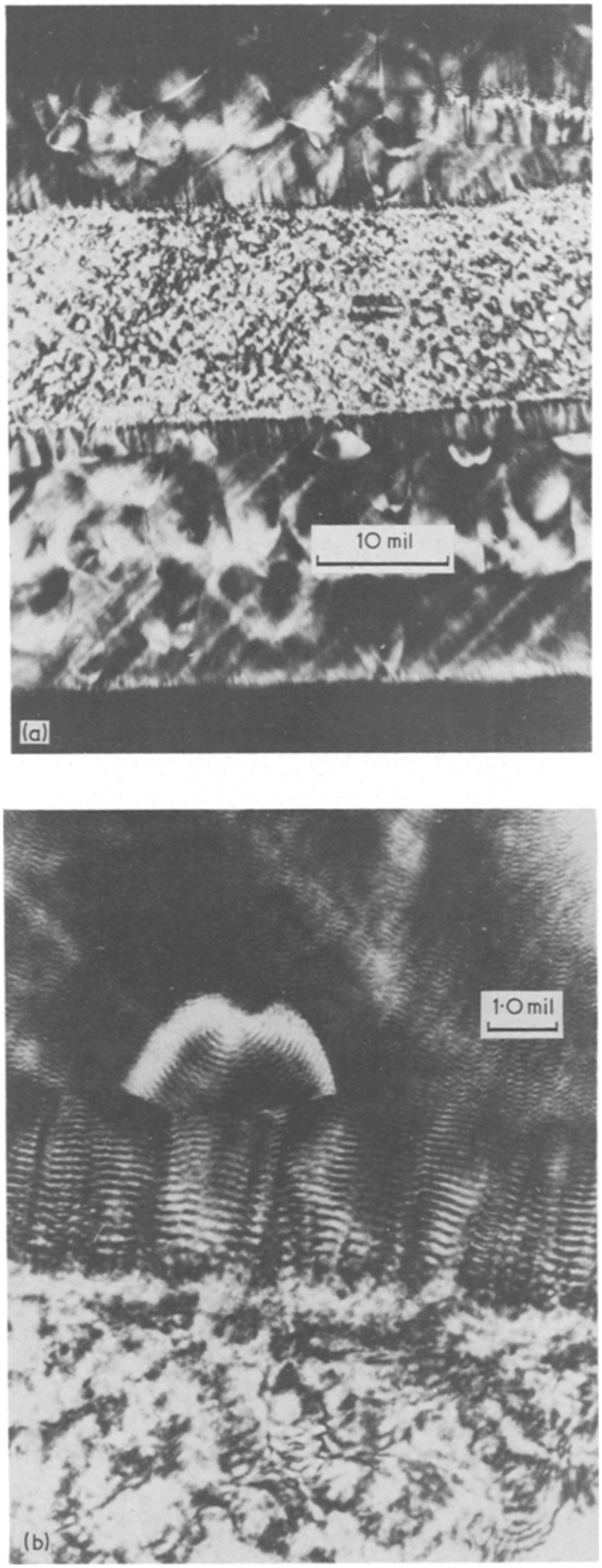

Figure 4 Light microscope picture of cross-section for composite formed from two morphologies of high-density polyethylene. (a) Low magnification; (b) high magnification. 1 mil = 10^{-3} in.

polymer crystallizes against a non-nucleating solid The rate of crystallization is greater in the bulk than at the surface and the polymer that cannot be accommodated in the main crystal structure is segregated at the polymer–solid interface. The bonding potential is further reduced by concentration at the interface of impurities and low molecular weight chains excluded from the crystals. On the other hand, if the surface is nucleating (i.e. of high surface energy), the nucleation velocity of crystal from the melt is greater at the interface and the segregation does not occur at the surface. The result, in this case, is a defect-free interface [12]. This has been achieved here with polyethylene as illustrated in Fig. 4a and b. Growth of interfacial, transcrystalline regions can be seen in two enlargements. They are a microphotograph from an oriented film embedded in a matrix of the same Alathon 7050 in a DSC-1B. The sample was maintained 45 min at 134° C and then cooled to room temperature. The microtome cut in Fig. 4 is normal to the fibre axis. One is thus looking end on at 100 and more magnification at the microfibrils that make up the film strip. The high modulus film strip used in these composites is 0.017 in. x 0.164 in. in end dimensions.

The type of structure and the thickness of the interface region resembles the results by Schornhorn for polyethylene crystallized on clean aluminium surfaces [13]. This suggests that the polyethylene fibres behave as a high surface energy material promoting nucleation, epitaxial crystal growth from the melt, and high mechanical strength at the interface. Also the desired effect of partial melting between fibre and matrix can be observed in Fig. 4 as a diffuse separation between the two phases. Thus produced is not only a good interface but a gradient of changing morphology between reinforcement and matrix. This should be a virtually ideal arrangement for maximum mechanical properties.

A simple system has been devised for studying the interfacial strength of a fibre partially embedded in the matrix. Fig. 5 shows samples having four different lengths for fibre embedments. This arrangement is convenient for relatively large diameter fibres. Since the low lateral to cross-sectional area ratio allows the use of longer embedments, greater accuracy can be achieved in the length measurement. The strength of the matrix–fibre interface is measured by fibre pull-out experiments at a constant rate of strain. In this cylindrical geometry, the tensile stress on the fibre is gradually transferred to the matrix through the interface which undergoes a shear deformation. Therefore, there is a stress decay in the fibre, along the embedded length, and a consequent interface shear stress distribution. The pull-out stresses were measured on fibres embedded to various lengths. The subsequent extrapolation to zero length gives the maximum shear strength of the interface. In Fig. 6 the average shear stress, τ_{av} (pull-out force/fibre lateral area), is plotted against the embedded length. This indicates a maximum interfacial shear strength of 1.7×10^8 dyn cm^{-2}. This distinctive parameter is comparable to the literature values for commonly-used composite materials. Table I shows typical interfacial shear strength values for epoxy and polyester–glass fibre-reinforced matrices [14] along with the value for these polyethylene composites. The interfacial strength

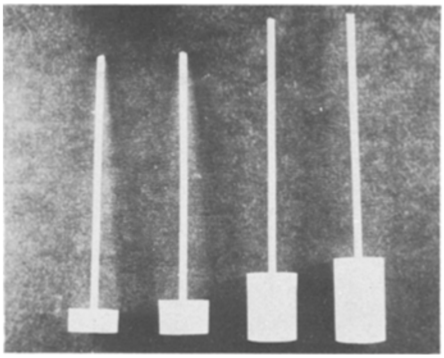

Figure 5 Cylindrical composite samples – different lengths for pull-out tests.

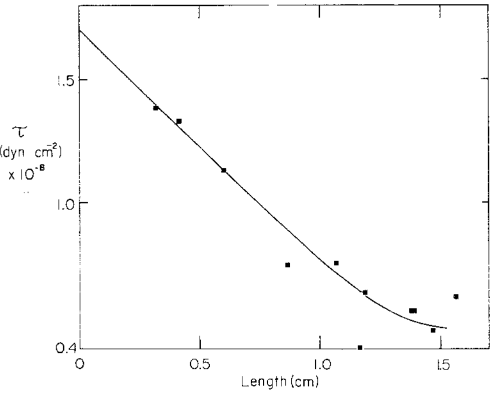

Figure 6 Interfacial shear strength – pull-out test.

TABLE I A comparison of mechanical properties of composites

Test method	Materials	Fibre treatment	Interfacial strength (10^{-8} dyn cm^{-2})
Lap joint	Polyester resin–soft glass	Vinyltrichlorosilane	0.26
Rod-disc (push test)	Polyester resin–glass rod	Acetone cleaned	0.42
Rod-disc (push test)	Polyester resin–glass rod	Vinyltrichlorosilane	0.47
Trapezoidal fibre (compression)	Polyester resin–E glass	Acetone cleaned	0.69
Partially-embedded fibre (pull-out)	Polyethylene–polyethylene	Acetone cleaned	1.7
Trapezoidal fibre (compression)	Epoxy–resin–E glass	Acetone cleaned	2.01–2.42

obtained from pull-out tests for the single polymer composite exceeds that for reported glass-reinforced polyester and falls below that for epoxy composites. Moreover, the compression type test for the trapezoidal fibre, used by others, seems to give higher values of interfacial strength than the rod-disc type tests, similar to the partially embedded fibre used in the present work. This can be observed by comparing the polyester composite tested both by a rod-disc and a trapezoidal fibre geometry. As seen in Table I, for the same fibre treatment, the values for rod-disc and trapezoidal fibre tests are 4.2×10^7 and 6.9×10^7 dyn cm^{-2}, respectively.

The relative contributions of mechanical friction and adsorptive bonding to the interfacial strength may be related to the composite resistance to environmental conditions. With conventional reinforcement, weakening by water absorption is common. Interfacial bonds attained mainly by adsorptive interaction between fibre and matrix should be more stable than a bonding derived predominantly from radial compression stresses as developed by shrinkage in thermosetting resins.

The contribution of friction to the interfacial strength is comparatively low for these one polymer composites. It is about 10% of the total strength, as measured from the residual stress after interface failure during the pull-out tests. That is, most of the strength is due to an intimate epitaxial bonding between fibre and matrix. This is not the case for glass fibre-reinforced polyesters where friction contributes up to 94% of the interfacial strength [15]. Epoxy resins also generate large frictional forces because of residual stresses induced by shrinkage due to cross-linking [14].

The interfacial shear strength is also the basis for the estimation of the critical fibre length in short fibre composites – that is, the shortest fibre in which the reinforced material fails by fibre fracture rather than by interfacial debonding. Since injection moulding is the most common method for processing thermoplastics, it is clear that short fibre systems are very important for thermoplastic composites. Hence the interest in the critical fibre length estimation for these polyethylene composites.

For the case of a fibre of diameter d embedded in the matrix to a length l, the critical aspect ratio is simply [16]

$$\left(\frac{l}{d}\right)_c = \frac{1}{4}\,\frac{\sigma_f}{\tau_i} \qquad (1)$$

where σ_f is the tensile strength and τ_i the interfacial shear strength.

The ultimate tensile strength for the polyethylene filaments used is $\sigma_f = 6.2 \times 10^9$ dyn cm^{-2} [11] and the interfacial strength $\tau_i = 1.7 \times 10^8$ dyn cm^{-2}, the critical aspect ratio is thus $(l/d)_c = 9.0$.

Equation 1 shows the importance of bonding, since the fibre length necessary to transfer the stresses between fibres is inversely related. The effect of the critical fibre length on the composite tensile strength has been pictured as follows for the modified rule of mixtures model for short fibre composites [17]

$$\sigma_c = V_f\left(1 - \frac{l_c}{2l}\right)\sigma_f + (1 - V_f)\sigma_m \qquad (2)$$

where σ_c is the composite tensile strength, V_f the fibre volume fraction and σ_m the matrix tensile strength.

The factor $(1 - l_c/2l)$ relates the actual fibre length to the degree of reinforcement that can be achieved. The greater the interfacial strength the smaller the critical length l_c and the ratio l_c/l tends to 1 with the composite tensile strength approaching the theoretical value for continuous fibre reinforcement. For example, assuming 0.051 cm fibre length, 0.0013 cm diameter and 30% fibre volume fraction, the tensile strength for the one polymer composite of high-density polyethylene calculated from Equation 2 is 1.8×10^9 dyn cm^{-2}. The fibre diameter and the volume fraction adopted are similar to values for discontinuous glass fibre-reinforced plastics [18]. The fibre length, however, is an average value which results after pelleting and mixing of 0.64 cm chopped glass fibres [19]. For this condition, the factor $1 - l_c/l = 0.89$ indicates that even for very short fibres a large proportion (89%) of the fibre capacity will be used. In contrast, a tensile strength value of 7.6×10^8 dyn cm^{-2} has been reported for glass fibre reinforced linear polyethylene with 30% fibre volume fraction [19]. The poor utilization of the glass strength, in this case, reduced drastically the composite tensile strength. One probable reason is a weak interfacial bond resulting from a low interaction with the polyethylene chains.

Acknowledgement

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