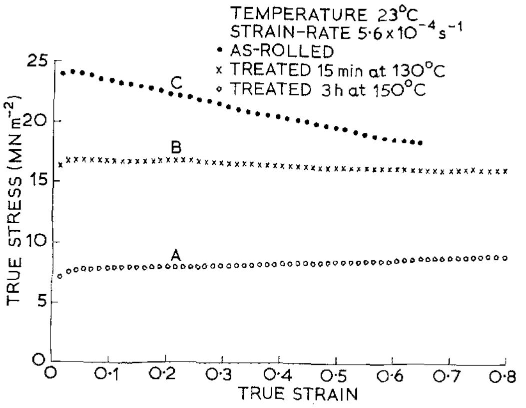

Figure 1

Curve "A" for as-rolled material tested immediately after preparation using a constant imposed strain-rate does indeed show strain hardening. Curve "B" for material produced by rolling and then annealing for 15 min (exactly) at 130°C, the condition most similar to the material used by Baudelet and Suery [1], and tested in our constant imposed strain rate device [2], shows flow which is very nearly strain independent. Curve "C" for material produced by rolling and then annealing for 3 h at 150°C shows pronounced strain softening. The condition of the material thus greatly affects both the character of the true stress – true strain behaviour and the level of the flow stress which is observed. We conclude that the difference between our results [2] and those of Baudelet and Suery [1] are explained entirely by the slight difference between the microstructure of the starting materials, and not by the form of the grips used in the two experiments. Subtle changes in the microstructure can significantly affect the mechanical properties observed, and therefore the characterization of the material is important.

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Growth of n-alkane crystals on graphite and on carbon-fibre surfaces

The growth of polymers, for which *n*-alkanes are models, on solid surfaces is a useful method of examining structure and interactions at solid/solid interfaces of relevance to adhesive systems and composite materials.

Fig. 1a shows a photograph, taken using incident polarized light, of crystals of *n*-hexatriacontane ($C_{36}H_{74}$) grown from amyl acetate solution on the basal plane of freshly cleaved Ticonderoga graphite. Three important features are evident: (i) the lozenge-shaped crystals are growing on an edge face; (ii) crystals grow independently without contact with one another; and (iii) crystals are oriented in three directions; the directions adopted by the largest visible dimension of the crystals are the $\langle 10\bar{1}0\rangle$ directions of hexagonal graphite as shown in Fig. 1b, and are the directions of the twin-boundaries used as crystallographic indicators [1, 2]. It is also noted that cleavage steps on graphite surfaces run in $\langle 10\bar{1}0\rangle$ and $\langle 11\bar{2}0\rangle$ directions [3]. Crystals grown from the melt showed similar orientation, but the mass in which they grew obscured details. The structures of several alkanes have been described by Keller [4], who found that the structure of $C_{36}H_{74}$ crystals depends to some extent on their method of preparation. In particular, those grown from petroleum ether are monoclinic when formed in suspension, and are orthorhombic when formed on evaporation of the solvent. Growth of the crystals, of which Fig. 1a is typical, was difficult to obtain by cooling the amyl acetate solution, and they were usually grown by evaporation. Also, it was found that the crystals much preferred to grow on edges of graphite flakes rather than on the basal plane. The question arises as to whether the parallel stacking of the hydrocarbon chains is perpendicular to (in which case the habit may be orthorhombic), or oblique to (when the habit is monoclinic or triclinic), the major faces of the crystals. Characterization of the crystals grown on graphite is obviously required, but on the supposition that the crystals are orthorhombic with parallel chains as in

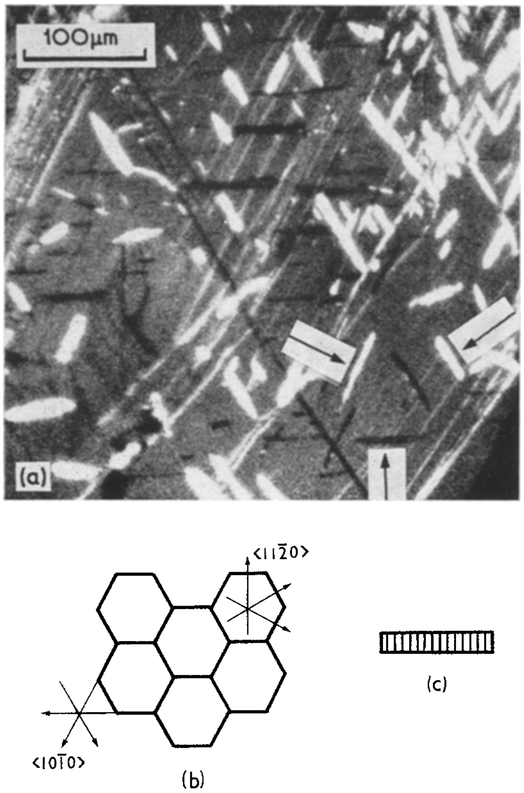

Figure 1 (a) Optical micrograph of hexatriacontane crystals on the basal plane of graphite (two light and one dark crystal are indicated by arrows), (b) crystallographic directions of the basal plane of graphite, (c) crystal of hexatriacontane indicating parallel packing of molecules.

Fig. 1c, the chains run in the $\langle 11\bar{2}0\rangle$ directions of the graphite. Crystal growth on a crystal edge with preferred orientation was *not* found in attempts to grow crystals with the graphite replaced by a glass slide, by a carbon-coated glass-slide, and by freshly cleaved mica.

In an electron microscope examination of polyethylene on the surface of graphite, Tuinstra and Baer [5] observed similar preferred directions of crystal growth, with the (100) face of the polyethylene in contact with the graphite. The directions of chain orientation for the alkane crystals are also those suggested by Groszek [6], in a study of dotriacontane adsorption from *n*-heptane solutions on powdered graphite samples, on the basis of the *hydrogen* atoms fitting over the hexagons forming the basal plane of graphite: there is no obvious short-range fit of the *carbon* atoms in the hydrocarbon over the hexagons. Poskus [7] informs us that in theoretical work involving the summation of pairwise interactions between adsorbate and adsorbent atoms, about one third of the interaction energy of ethane on graphite arises from hydrogen atoms nearest the surface, and about one half from the two carbon atoms. This suggests that any orientation effect might be dominated by interaction of the carbon atoms, rather than the hydrogen atoms, in the adsorbate (whether from vapour, liquid or solid) with the surface, although the energy barriers to motion parallel to the surface are expected to be the deciding factor.

The possibilities must not be overlooked that (i) the *nucleus* of the crystal may be oriented by the specific location at which it grows, e.g., by a dislocation, and it is this initial orientation which determines the preferred orientation of the macroscopic crystal, or (ii) that although the gross features (hexagonal structure) of the graphite basal plane determine the directions of crystal growth, the sites of growth are *not* randomly distributed over the surface. Growth-dissolution-growth cycles with photographs taken at intervals, and experiments in which crystals are removed and the graphite oxidized (to reveal non-basal plane dislocations [1]) should help to show whether crystals grow at special sites on the surface

Fig. 2 shows crystals of $C_{36}H_{74}$, grown by cooling amyl acetate solution, on graphitized carbon fibres of the high-modulus variety (made by pyrolysis of polyacrylonitrile [8]), which had been prewashed with amyl acetate. The shape of the crystals is not very evident, but they are plate-like with the fibre (diameter 8 to 10 μm)

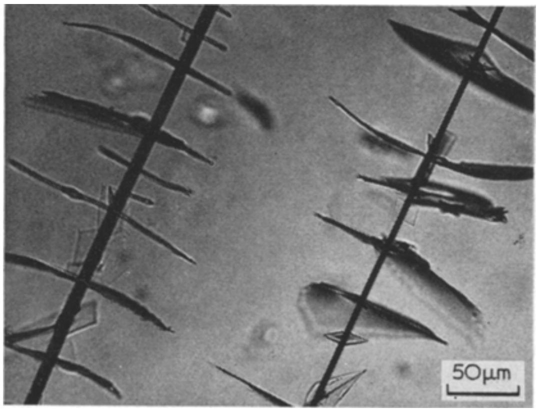

Figure 2 Crystals of hexatriacontane grown from amyl acetate solution on carbon fibres.

passing through them. It is clear that the crystals grow with the minimum paraffin/carbon contact area: this may arise merely from a preference of the molecules adjacent to the surface to lie parallel to it. The nature of carbon exposed at the surface of the fibres is not well characterized, although the internal structure of carbon fibres has been elucidated [9, 10]. The rather regular occurrence of crystals along the fibres suggests that even if grown on special sites on the fibres, and on the graphite, there might be many more sites than crystals, which, if this is the case, could make it difficult to detect the sites by repeated growth.

An implication of these observations is that oriented growth of polymer crystals on carbon can affect the structure of the polymer at distances much greater than 1 μm within the polymeric species, but this extended orientation must not be interpreted as arising from long-range forces. It is possible that in composites with a polymeric matrix, the matrix can be ordered by the surfaces of the reinforcing fibres. Studies of the kind reported here can be extended to involve the nucleation and growth of a principal species in the presence of an impurity species of lower molecular weight (this impurity could be coupling agents on the surface). Similar studies can also be used to find factors influencing the growth of biologically important polymeric materials on substrates such as those used as prostheses. Differences in principle between nucleation and growth of crystals from solution and from the melt have been pointed out by Hobbs [11], who found that nucleation from the melt of polypropylene was greater on the carbon fibre Morganite I than on Morganite II, which has a lower modulus and less well developed graphitic regions than I.

The carbon fibres used for these studies (PAN-based: obtained in the USA, but made under UK licence) were quite dirty: small particles of carbon could be washed off an untreated sample, and chemicals used for treatment could be washed off a surface-treated sample. It is suggested that were these fibres to be used without surface cleaning (e.g. by washing with solvent), a composite made from them would have inferior mechanical properties compared to one made with pre-cleaned surfaces.

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