Plasma etching of polypropylene films and fibres*

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The introduction of a ~1000 Å scale corrugated structure, aligned perpendicular to the filament axis, into oriented semi-crystalline polymers on plasma etching is shown to result from restructuring of the partially etched surface and not, as has previously been proposed, to correspond to morphological detail in the unetched material. The detail exposed on plasma etching polypropylene is shown to vary extensively with the etching conditions used. The exposed surface is compared with those resulting from peeling and chromic acid etching. Plasma etching is, however, shown to be useful in exposing coarse morphological detail such as spherulites, and in providing a convenient route for rapidly stripping the polymeric sample. The restructured partially etched surface may then be removed easily by, for example, a brief chromic acid treatment, exposing the sample interior to microscopic examination.

1. Introduction

The etching of polymers by activated gaseous species is a commonly used technique in the preparation of samples for electron microscopy [1, 2]. Because of the differing resistance of morphological structures to etching, morphological detail can be exposed and so rendered accessible to examination by electron microscopy. Microscopy may involve either making a surface replica or examining directly by scanning electron microscopy (SEM).

The exact nature of the activated gaseous species varies with the etching conditions used. Inert gases, typically argon, may be activated either by high voltages (ion or sputter etching) or in a radio-frequency plasma. The resultant transient high energy ions can then break covalent bonds on the polymer surface, eventually rendering the polymer decomposition products volatile. Alternatively, activated oxygen, usually generated in a radio-frequency plasma, may be used. In this case the nature of the etchant will depend on the distance of the sample "downstream" from the plasma because of the varying lifetimes of the activated species (e.g. oxygen ions, atomic oxygen, etc.)

There have been many reports in the literature concerning the etching of oriented semi-crystalline polymers by these methods. These reports appear to fall into two categories. The first involves correlation of the observed morphological features (markings 50 to 200 Å in diameter oriented perpendicular to the draw axis) with the long period as determined by small angle X-ray scattering (SAXS) [3–6]. Other workers, however, report the observation of much larger (~1000 Å) morphological features again oriented perpendicular to the draw direction and infer from these observations that such units form an integral part of the microstructure of oriented semi-crystalline polyers [7–9]. The purpose of this paper is to demonstrate that these larger structures can be artifacts of the activated gas-etch process resulting from the restructuring of partially etched material. The significance of the results from this and other methods of etching fibrillar structures is discussed.

Polypropylene filaments were chosen for this study because their morphology is comparatively well understood and is not prone to restructuring with storage and exposure to moisture (cf. polyamides).

2. Experimental

The etching procedure used here is of the activated oxygen type with the sample sufficiently far "downstream" that the active species is probably atomic oxygen [1]. A continuous stream of activated oxygen was produced by the passage of oxygen at low pressures (typically $100\,\mu$m Hg) through an inductively coupled radio-frequency coil (~ 40 MHz 20 mA discharge current). Polymer samples were placed in a Pyrex boat 20 cm downstream from the plasma, so as to be partially shielded from the gas flow (reducing gas stream related etching effects) and shielded from the far u.v. irradiation emitted from the plasma. The parameter most useful in describing the etching conditions is the etching rate itself. Under our chosen conditions the etching rate was typically $< 0.1\,\mathrm{mg\,cm^{-2}\,h^{-1}}$. This compares with values of $\sim 1\,\mathrm{mg\,cm^{-2}\,h^{-1}}$ reported by Fischer and Goddar [10] (polyethylene), $0.4\,\mathrm{mg\,cm^{-2}\,h^{-1}}$ reported by Hansen *et al.* [11] (polypropylene), $0.24\,\mathrm{mg\,cm^{-2}\,h^{-1}}$ by Chalykh *et al.* [3] (polypropylene) and $0.05\,\mathrm{mg\,cm^{-2}\,h^{-1}}$ by Reneker and Bolz [12] (polyethylene). Relative to these data the chosen etching parameters correspond to comparatively mild etching conditions.

Polymer weight loss was measured after etching using a Cahn Electrobalance. In preparation of the samples for electron microscopic examination it was found that brief washing with acetone was effective in removing surface debris, which partially obscured the regular substructure, without otherwise altering the appearance of the surface being studied. Polymer samples were mounted on aluminium stubs, gold coated and examined in a Cambridge Mk IIA SEM. Samples were generally

viewed at an angle of $45°$ to the incident electron beam.

Polymer samples studied here include chill-roll cast film (Enjay), commercial hot drawn filaments (Amtech Inc.), and filaments prepared in our laboratories.

3. Results

The usefulness of plasma etching in exposing gross morphological detail such as spherulites is shown in Fig. 1. Closer examination of these etched samples, however, revealed that the spherulites were highly pitted, obscuring the fine detail within the spherulite. The corresponding unetched polypropylene filament (prepared in our laboratories by extruding slowly with a low spinline tension [13]), had a comparatively featureless surface texture at these low magnifications.

The reliability of plasma etching in exposing more subtle morpholgical detail was examined using a commercial, chill-roll cast, polypropylene film. This sample was expected to be devoid of morphological detail on a level greater than a few hundred Angstroms because of the rapid cooling involved in its manufacture, with the implication that any surface texture seen after etching must result from the non-uniformity of the etching process. The etching conditions were systematically varied (duration, oxygen pressure, r.f. coil power, and distance from plasma) and the resultant surface features examined in the SEM. It was found that, even using the mildest etching conditions ($< 0.1\,\mathrm{mg\,cm^{-2}\,h^{-1}}$), severe pitting occurred after prolonged etching (Fig. 2). This masked the observation of any other morphological detail. The use of more severe etching conditions (increasing the
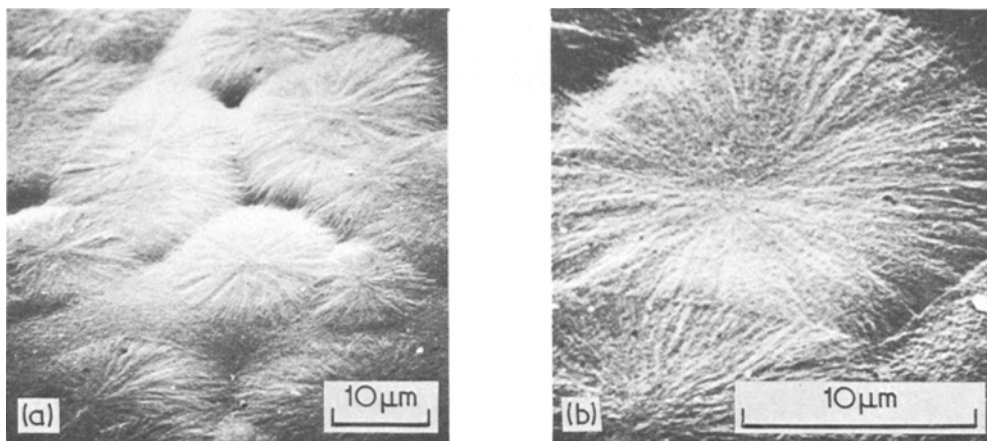

Figure 1 Spherulitic polypropylene fibre after 1 h plasma etching. Conditions as in text.
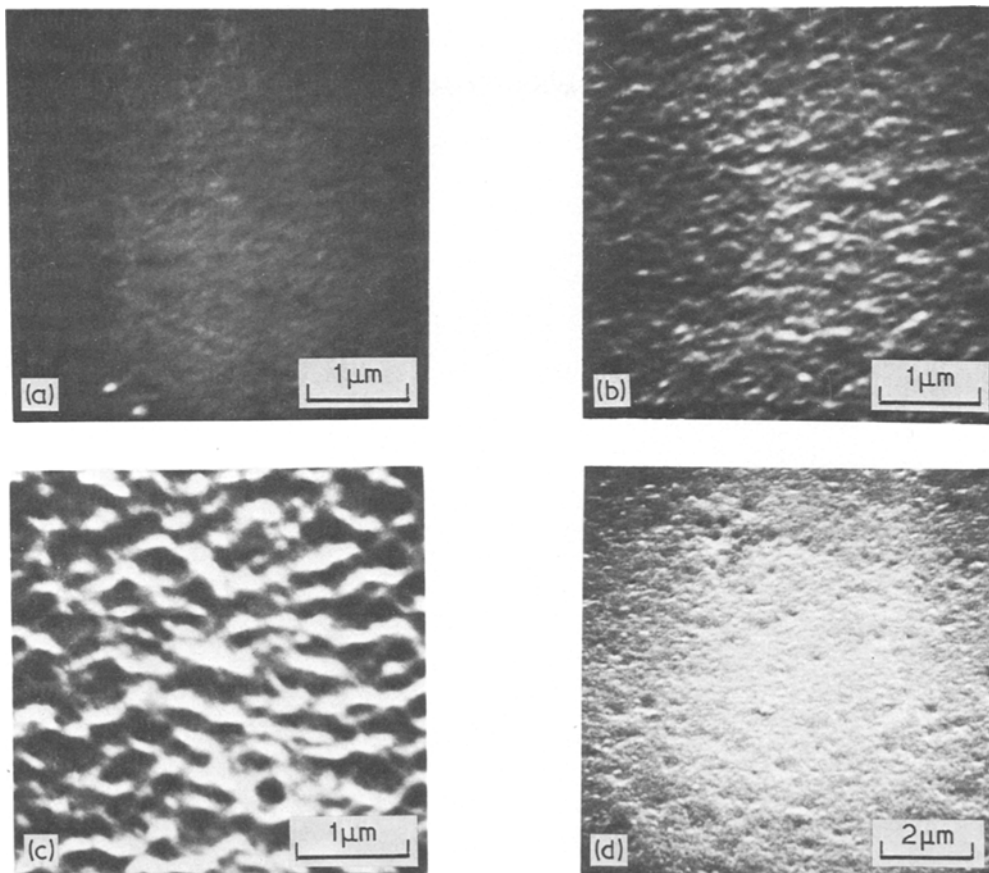
Figure 2 Etching of chill-roll cast polypropylene film (25 μm thick) (a) 0.3% weight loss, 1 h etch; (b) 3% weight loss, 4 h etch; (c) 12% weight loss, 16 h etch; and (d) 10% weight loss, 1 h etch at high (~ 300 μm) oxygen pressure.

etching rate) resulted in the occurrence of pitting at lower degrees of etching.

Fig. 3 shows the etching characteristics of an oriented fibre sample (a commercial, hot drawn, polypropylene filament, Amtech Inc., Maryland). During the early stages of the plasma etching, a regular corrugated substructure of 500 to 700 Å periodicity was observed at very high magnification. The long axes of these features were oriented largely perpendicular to the fibre axis. Electron beam sensitivity of polyolefin samples such as these limited photography to a magnification of × 15 000 making resolution of this detail indistinct. On more prolonged etching (~ 10% weight loss) these corrugations increased in size and became less elongated (Figs. 3a and b). The features visible in Figs. 3a and b appear to be identical to the "sea-shore" structures noted by several authors [7–9]. Continued etching resulted in a further coarsening of the surface texture with the indentations becoming almost circular.

In Fig. 4 the results of four different methods of examining the structure of an oriented filament are compared. Chord peeling [14] (Fig. 4a) revealed what is conventionally called a fibrillar structure. The reproducibility of the detailed surface texture between different portions of the peel was poor, presumably because of differing geometries and rates of peeling. Chromic acid etching [15] revealed a somewhat similar structure (Fig. 4b). At higher magnifications, however, the chromic etched surface appeared virtually featurless indicating that the fibrillar elements shown in Fig. 4b had no discernable fine structure. Plasma etching of the same filament produced a corrugated structure (Fig. 4c) with the corrugations elongated perpendicular to the filament axis, the size of the exposed morphological detail again varying with the etching con-
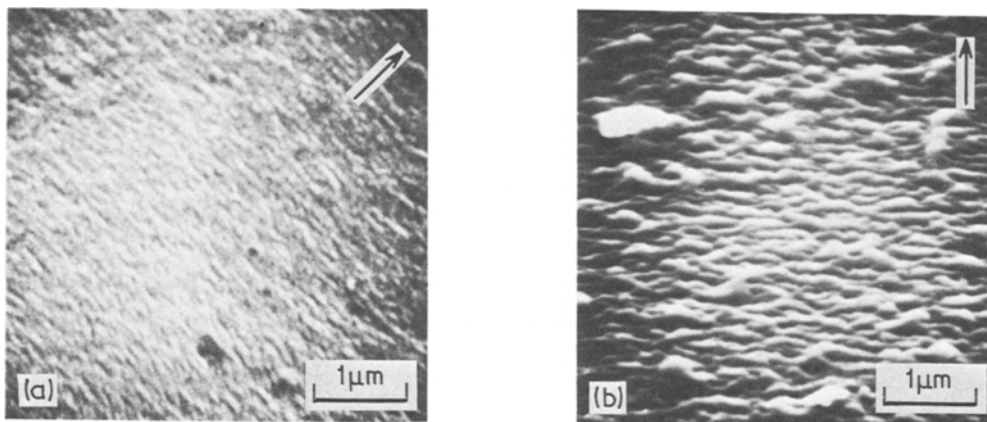
Figure 3 Plasma etching of oriented polypropylene filament (150 μm diameter). Arrows show fibre axis. (a) 9% weight loss; (b) 12% weight loss.
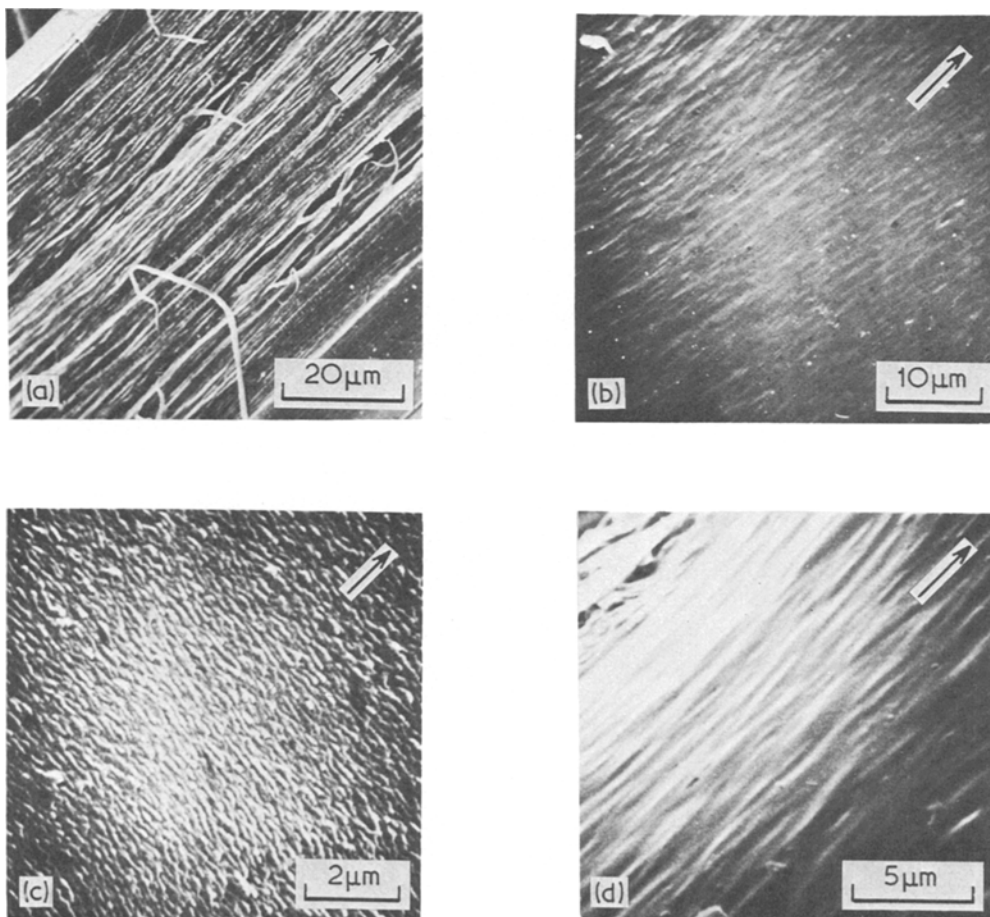

Figure 4 Comparison of different techniques of exposing morphological detail. Oriented 152 μm diameter polypropylene filament. Arrows show fibre axis. (a) Chord peeled; (b) chromic acid etch (72 h) 6% weight loss; (c) plasma etch 12% weight loss; (d) plasma etch (as c) and chromic acid etch (16 h).

ditions used (compare with Fig. 3). Subsequent chromic acid etching of this plasma etched filament resulted in the morphology reverting to that typical of conventional chromic acid etching (compare Figs. 4b and d).

The weight loss on such brief chromic acid etching will be small. It therefore seems unlikely that the difference between Figs. 4c and d is the result of the exposure of different structures within the filament to observation.

4. Discussion

It is clear from the time dependence of the exposed morphological detail (Fig. 3) and a comparison of the morphological features exposed by various sample preparation techniques (Fig. 4) that, contrary to earlier reports [7—9], the "sea-shore" appearance of plasma etched oriented fibres does not correspond to any morphological feature in the unetched material. It probably results from restructuring and shrinkage of the partially degraded surface layer. Plasma etching is, however, useful in exposing morphological detail in samples which are less prone to restructuring (e.g. spherulitic samples, Fig. 1), although finer detail present even on these samples may be an artefact.

Ideally an etching agent should satisfy several criteria.

(a) The etching action should be selective, i.e. it should differentiate between morphological features by, for instance, differences in density or permeability. In such a way, etch resistant morphological detail will be exposed.

(b) The decomposition products of the etched material should be cleanly removed.

(c) The etchant should not cause extensive restructuring of the surface under study. This can occur either by restructuring of the partially degraded material prior to its removal or by interaction with the undegraded material, e.g. swelling by a solvent.

Plasma etching appears to satisfy the first criterion in that the amorphous component of the semicrystalline structure is preferentially etched (Fig. 1). The high reactivity of the activated gaseous species, in this case probably atomic oxygen, will, however, restrict the extent of the selectivity because of the limited degree of migration that can occur into the sample surface before reaction takes place. This should be contrasted with, for example, the chromic acid etching of a crazed polypropylene filament [15], where the voided zones of the filament were almost totally removed while the unvoided zones were untouched as a result of the differences in permeability of the structures to chromic acid. The selectivity of plasma etching may then largely result only from density differences and so will be effective for spherulites (Fig. 1) but less so for fibrillar structures where density fluctuations will be smaller.

If the plasma etching conditions are chosen correctly the second criterion, concerning the clean removal of the final etch products, can be satisfied. Slow etching rates and rapid removal of gaseous products by a high pumping rate should reduce the deposition of etch products as "ash". That some slight redeposition did occur is indicated by the effects of a brief washing with a solvent (acetone) which will not restructure the polymer. This wash removed the bulk of the surface debris, without altering the underlying surface morphology.

Plasma etching can, however, be most heavily criticized because of its failure to meet the final criterion in that certain morphologies are extensively restructured during the etch. Artefacts caused by surface heating and directional effects of the activated gas flow have been adequately described by Warner et al. [7]. We described here the introduction of artefacts not directly caused by the etchant itself but presumably caused by restructuring of partially etched material. A highly oriented "fibrillar" structure is clearly entropically unfavourable. Restructuring is only prevented by the presence of tie molecules in the amorphous phase. Etching will occur in the amorphous phase fracturing these tie molecules. This, combined with the mobilizing effect of molecular weight reduction and possibly some surface heating will lead to extensive restructuring of the surface unless the partially degraded material is rapidly removed. Relaxation of the oriented polymer will therefore occur resulting in longitudinal shrinkage and as a consequence the appearance of a corrugated structure oriented perpendicular to the filament axis. This behaviour is not apparently restricted to activated oxygen etch systems. Similar "sea-shore" structures have been reported to be formed on treatment with argon plasmas [7—9].

It should be noted that the use of another chemical etchant, which, unlike chromic acid, did

not cleanly remove partially etched material, would also be likely introduce a corrugated substructure into such samples.

The etching of fibrillar polymers therefore presents special problems. The development of a suitable etching technique is, however, necessary to substantiate the often reported existence of morphological structures exposed on peeling samples (Fig. 4a). Exposing a fibrillar structure by peeling can be criticized in that the structure may simply result from deformation during the peeling process. Electron microscopic observation of fibrils in deformed single crystals and thin films provides some of the strongest supporting evidence for the microfibrillar theories of oriented polymer structure and it is therefore important to demonstrate their existence in commercially important samples, such as oriented textile filaments. Preferential etching of interfibrillar material is therefore required, leaving the fibril unit largely untouched. Neither plasma etching nor conventional chromic acid etching seems entirely satisfactory for this purpose, although the chromic acid technique is at least partially successful in exposing a coarse fibrillar texture in polypropylene filaments. The problem of the very slow rate of etching inherent in the chromic acid technique may be overcome by the prior use of plasma etching which, although it causes restructuring of the surface, provides a rapid and convenient means of stripping the sample. The restructured material can then be rapidly removed by the chromic acid thus exposing the filament core to microscopic examination.

The formation of similar large scale corrugations in etched carbon fibres has been attributed by Goodhew [16] to the presence of irregularities in the original unetched material which are then magnified by the etching. The work of Warner et al. [7], involving initially chromic acid etching the surface of a carbon fibre to smoothness and then plasma etching (again producing the corrugated structure) seems, however, to contradict this. The introduction of very small scale corrugations (50 to 200 Å) into oriented semicrystalline polymers (corresponding to the long period as determined by SAXS) by very low degrees of plasma etching has, however, been convincingly demonstrated by several authors [3–6]. It is not inconceivable that these small scale corrugations could be magnified by further etching to lead to the gross structures an order of magnitude larger, although restructuring of the degraded surface seems a more plausible explanation from a comparison with the surface restructuring observed during the weathering of polypropylene surfaces [17].

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