Morphology of Man-Made Fibers

R. D. VAN VELD, G. MORRIS, and H. R. BILLICA, *Fiber Surface Research Section, Textile Fibers Department, E. I. du Pont de Nemours and Company, Inc., Kingston, North Carolina 28501*

Synopsis

Recent advances in electron microscopy of polymer systems have produced new structure theories (lamellar versus micellar) and considerable speculation on the nature of synthetic fiber structure. This paper illustrates what can be seen directly on the structure of nylon 66, polyester, and acrylic fibers with high-resolution and scanning electron microscopy and attempts to relate the structure seen in the complex fiber systems with simpler structure observed in bulk polymer and solution grown crystals. Instances of support for the lamellar and fibrillar theories of structure are noted.

INTRODUCTION

The nature and importance of fiber morphology has excited a good deal of interest in recent years, and publication[1] of papers presented at the October 1966 Fiber Society Symposium on supramolecular structure in fibers provides a good review of the scope of effort and current state of knowledge in the field.

These recent studies have resulted in the development of the lamellar folded-chain theory of crystalline structure in polymers to replace or supplement the older fringed micellar or fringed fibrillar theories of structure. Hearle[2] and Keller and Machin[3] in recent articles have summarized the present state of structural theory in polymeric systems. Experimentation supporting the theories has been carried out largely on crystals grown from solution and to some small extent on bulk polymer systems. The reported work has primarily dealt with polyethylene and polypropylene and little has been reported on studies of man-made fibers, as such, particularly the commercially important systems of nylon 66, polyacrylonitrile, and poly(ethylene terephthalate).

Of the several classical approaches to study of molecular structure, as reviewed, e.g., by Statton,[4,5] x-ray diffraction techniques have been most widely applied to study of the crystalline and amorphous nature of man-made polymeric fibers and considerable understanding of structure has derived from the data obtained. Over the past few years, several workers in the polymer morphology field have turned out some elegant electron micrographs of crystal structure in polymers and this work has strongly supported the lamellar folded-chain concept of structure. This work,

however, has again been done primarily with carefully grown crystals of polyethylene and polypropylene and, while this lamellar structure theory seems to explain well the structure of crystalline bulk polymer, there is still some doubt as to the precise nature of fine structure in oriented, manmade polymeric fibers. Perhaps some combination of structure theories, as suggested by Hearle[2] will prove to explain and satisfy all the requirements of these complex systems. The work reported in this paper has been primarily microscopy—optical, transmission electron, and scanning electron—to determine what could actually be seen and deduced with these tools concerning fiber morphology. While no firm conclusion can be made yet concerning supermolecular structure of synthetic fibers, additional perspective may be obtained from this work.

EXPERIMENTAL

Samples of nylon 66, acrylic, and polyester fibers obtained from several sources of commercial manufacture were used in these studies. Samples for study were replicated (for transmission electron microscopy in a Philips EM-100C) or shadowed (for scanning electron microscopy in a Stereoscan) with gold/palladium alloy (60/40). Procedures were all standard for these types of microscopy.

The three polymer systems were studied as (1) crystals grown from solution, (2) bulk polymer, (3) thin films, and (4) textile fibers. We hoped to relate the more complex polymer and fiber structures to the simple crystal systems and thus obtain a better understanding of the structure of our important man-made fibers.

Solution-Grown Crystal Structure

The objective of our work with solution-grown structures was to determine what could be observed by using the simplest possible preparation techniques. Such observations with the electron microscope might be useful, for example, in tracing the source of unusual crystallization behavior of production fibers. These tests were useful to us in that we could trace the evolution of crystalline structures from the simple forms at their inception to their mature, complex forms.

Nylon 66 crystals were grown by dissolving polymer flake in 90% formic acid at room temperature, drops of solution placed on carbon-coated Formvar electron microscope grids, and the solvent allowed to evaporate. Several sets of solution concentration (0.01–1.0%) and evaporation temperatures (20–50°C) were used. Poly(ethylene terephthalate) crystals were prepared by growth (at 25°C) from benzyl alcohol solutions (0.01%); polyacrylonitrile by growth (at 100°C) from dimethylformamide solution (0.01%).

Similar growth habits were observed for polyamide 66, poly(ethylene terephthalate), and polyacrylonitrile. Two growth habits, lamellar and fibrillar, were observed. The most striking observation appears at the
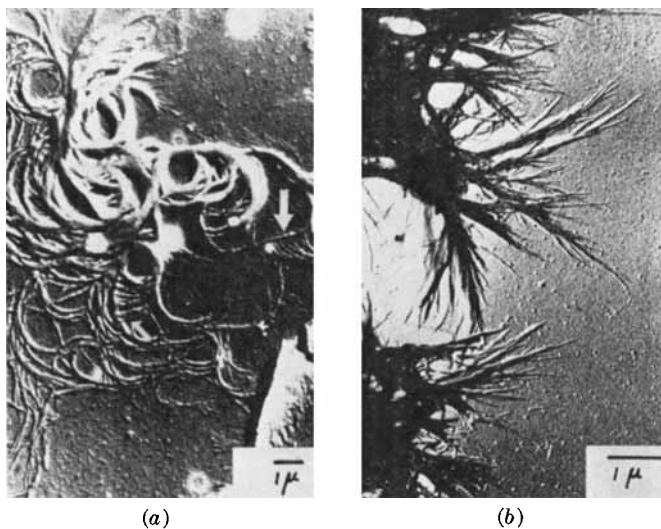
(a)   (b)

Fig. 1. Fibrillar growth of (a) polyamide 66 and (b) poly(ethylene terephthalate) from solution. Arrows in (a) point to areas where further growth of polyamide 66 fibrils was blocked by fibrils crossing the path.

growing tips of fibrils in polyamide 66 versus poly(ethylene terephthalate). Figure 1 shows fibrillar growth of these two polymers. In the polyamide, fibril ends appear blunt and growth is blocked by other fibrils, both indications that growth occurs by laydown of molecules across a growing tip rather than parallel to the fibril growth. With polyester, however, fibril tips are pointed and growth appears to occur by molecule laydown along the growing fibril. Thus, the polyamide structure illustrated here appears consistent with lamellar growth while the polyester appears to show fibrillar type growth.

Bulk Polymer and Film Structure

Spherulite growth and crystallization in bulk polymer systems have been well documented. Structures are observed which strikingly resemble what is seen in solution grown structures of polyamide, polyacrylonitrile, and polyester. Fracture of these materials occurs in definite lamellar planes; both bulk polymer and film show this phenomenon. Fracture of bulk poly(ethylene terephthalate) can occur as shown in Figure 2. Not only is fracture laminar, but a cobblestone-like structure can be seen on the surface of these planes similar to what Geil and Yeh[6] have called "ball" structure.

Fiber Structure

The surface character of man-made fibers is an important subject, although not much has been published on the work done in different industrial laboratories. It is generally known that changes in surface character
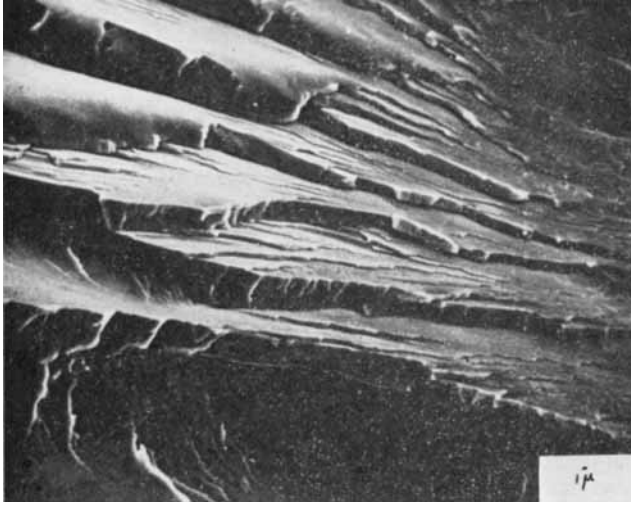
Fig. 2. Fracture of a block of poly(ethylene terephthalate) showing laminar structure and "ball" structure visible on some of the fracture planes.

can affect runnability and end-use aesthetics and that variability which may or may not be understood occurs from time to time. There is not much to indicate, however, that any significant attention has been directed at understanding how surface structure (a) may be different from internal structure (the so-called skin–core effect), (b) may be affected by internal structure, or (c) may give clues leading to understanding of the basic supermolecular structure of the fiber.

Commercial fibers do show significant surface structure differences. Of the three subject fibers, nylon 66, acrylic, and polyester, it is generally accepted that nylon and polyester as commercially produced have a smooth surface and that acrylics are generally rougher. Three polyacrylics from different manufacturers, have surfaces as shown in Figure 3. Not only will these process differently and show different aesthetics, but the surface
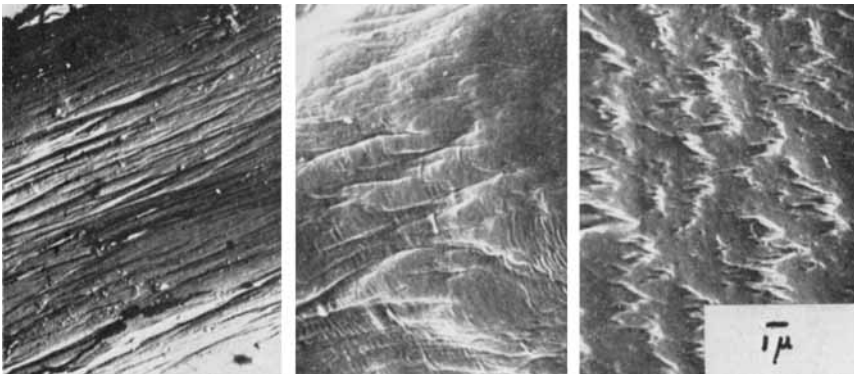

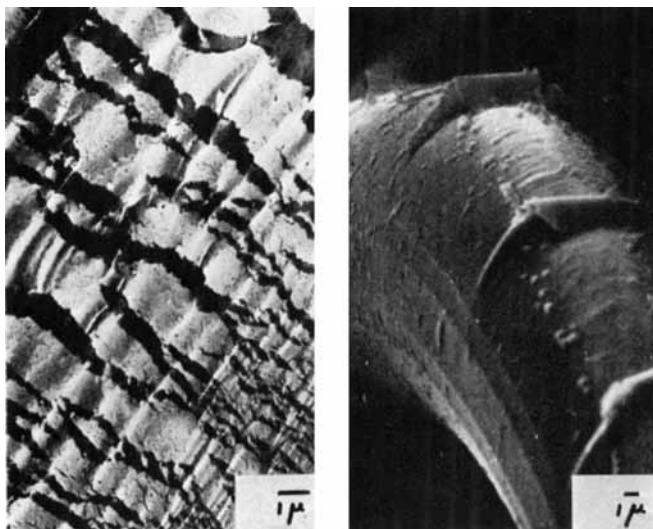Fig. 3. Surface structure of acrylic fibers from three different sources of manufacture.

Fig. 4. Surface skins or crusts on polyester fibers.

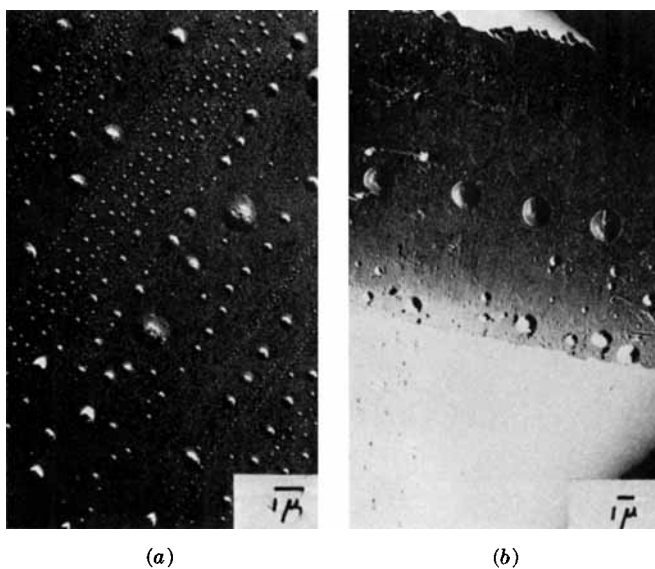(a)   (b)

Fig 5. Liquid exude on the surface of polyester: (a) film, (b) fiber.

character undoubtedly reflects differing basic supermolecular structure, particularly in light of the knowledge that such variables as molecular weight, draw ratio, processing temperatures, etc. can produce a definite change in the surface nature of these polyacrylic fibers.

A magnified look at the two "smooth" fibers, polyamide and polyester, shows a considerable amount of surface structure. Undrawn nylon 66 shows spherulite growth structures resembling closely what can be seen in
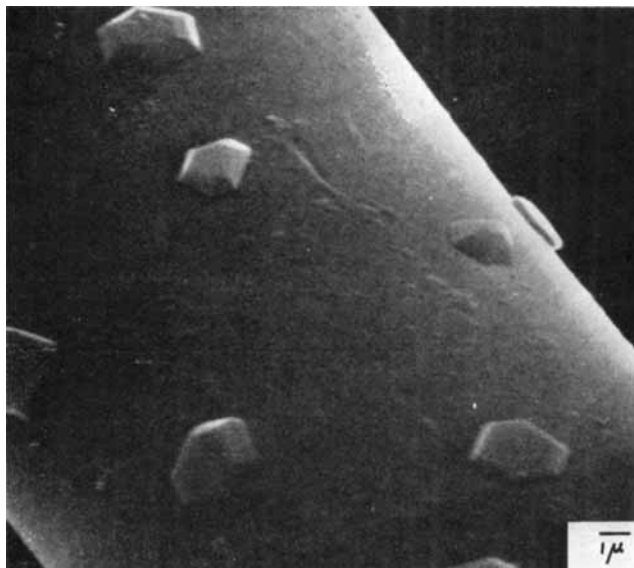
Fig. 6. Cyclic trimer sublimate on the surface of a polyester fiber.

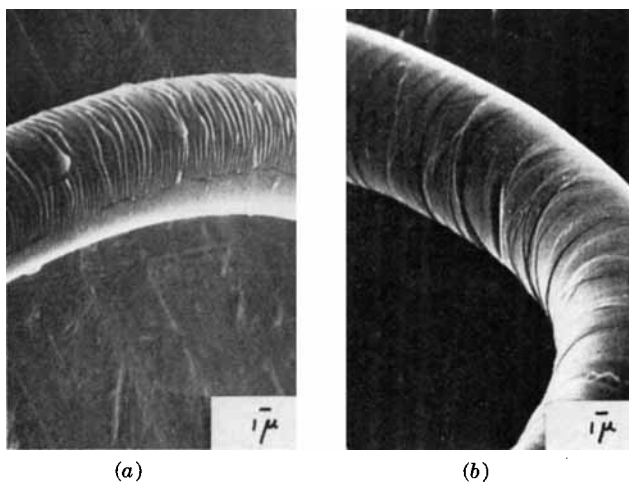(a)   (b)

Fig. 7. Structure on loops of polyester fibers: (a) undrawn, showing surface wrinkles and liquid exudate; (b) drawn, showing structure resembling Lüder's bands.

solution-grown crystals. Upon drawing, the spherulite structure disappears and small longitudinal striations are seen, probably associated with subsurface supermolecular structure, and only trace signs of spherulites.

Polyesters, for a "smooth" surface fiber, are perhaps the most complex system of all. A variety of different characteristics can be seen separately or combined. A surface skin or crust may be found (Fig. 4). A high-viscosity liquid exudate containing crystalline material may come to the surface as in Figure 5, Figure 5a showing a commercial film and Figure 5b

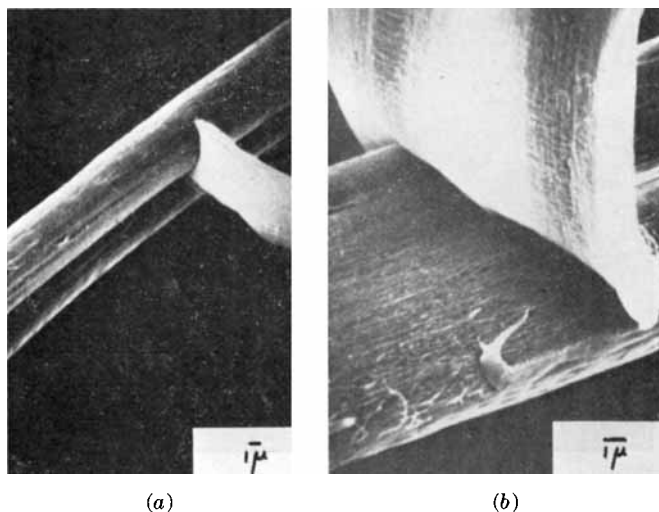(a)   (b)

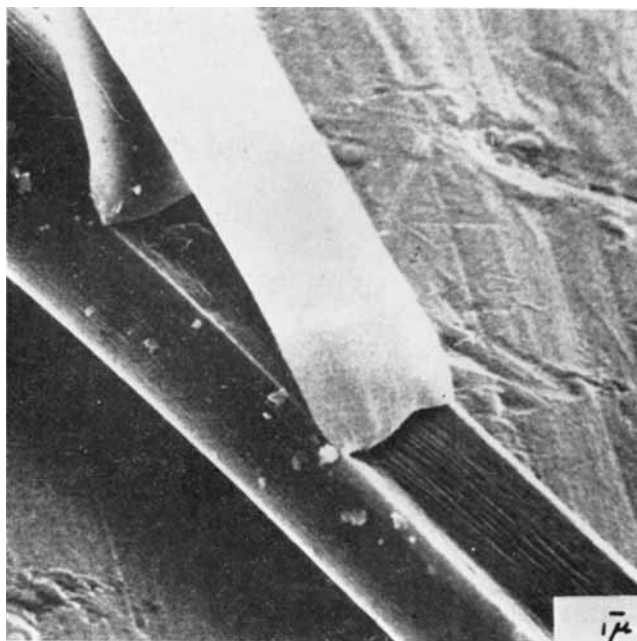Fig. 8. Peeling habit of acrylic fibers: (a) skin peeling, (b) chord peeling.

Fig. 9. Chord peeling habit of nylon 66.

a commercial fiber, each from a different manufacturer. Exposure of polyester to heat can also result in crystal deposits on the surface (Fig. 6), cyclic trimer sublimed from the interior. These last two phenomena are certainly strong indicators of an internal structure consisting of quite an inhomogeneous mixture of various sizes and species.
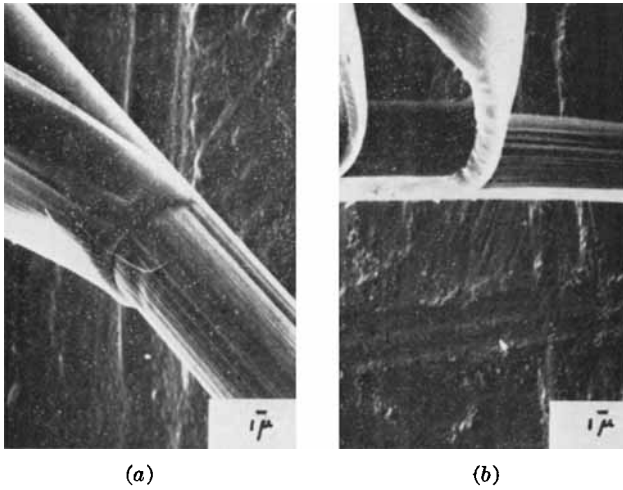
(a)   (b)

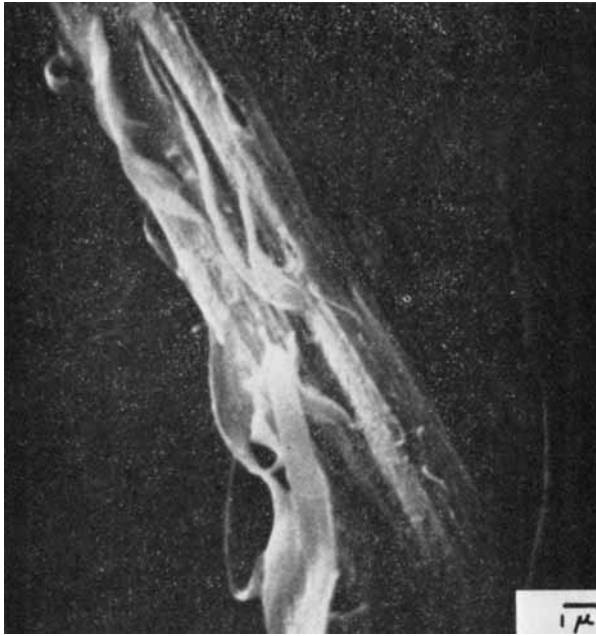Fig. 10. Peeling habit of polyester fibers: (a) skin peeling, (b) chord peeling.

Fig. 11. Fibrillar structure of acrylic fibers as revealed by peeling.

Figure 7 shows two simple loops of polyester fiber, undrawn and drawn. It is interesting that wrinkling of the undrawn fiber occurred on the outside of the loop.   Note the liquid exudate on the wrinkled area.   The drawn fiber shows an interesting, and reversible, phenomenon resembling what in metal has been called Lüder's bands.   Bosley has discussed both these phenomena in a recent publication.[7]   In metals, this effect has been shown to accompany slip planes generated in the crystal structure when strained.
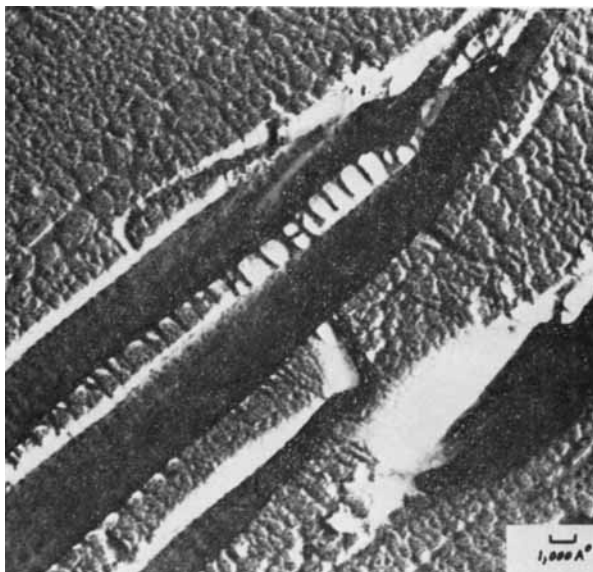
Fig. 12. Acrylic fiber structure at 77 000× showing cross ties between sheets of fibril.
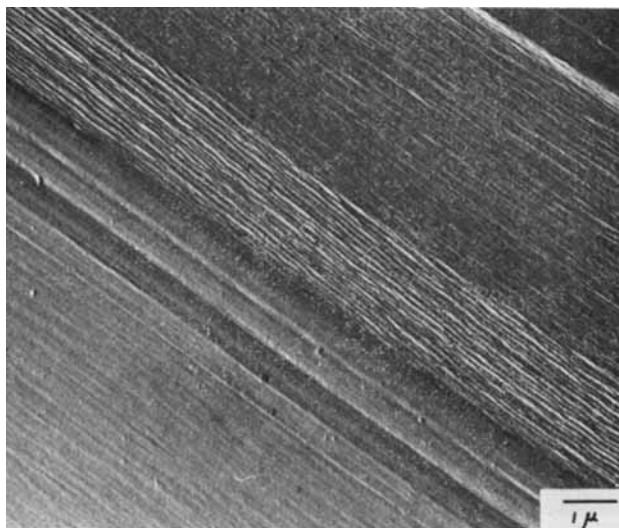

Fig. 13. Structure exposed by peeling nylon 66 showing original surface and two different size domain fibrillar structures in the peeled area.

Other phenomena also are associated with the surface and internal structure of fibers which give clues to the basic supermolecular structure. Fibrillar nature revealed by damage is one. Fracture study is another approach to revealing interesting character of fibers and fiber structure revealed in this manner will be the subject of a forthcoming paper.

Perhaps the most interesting and fruitful approach we have found in revealing internal structure of man-made fibers has been the use of "peel-
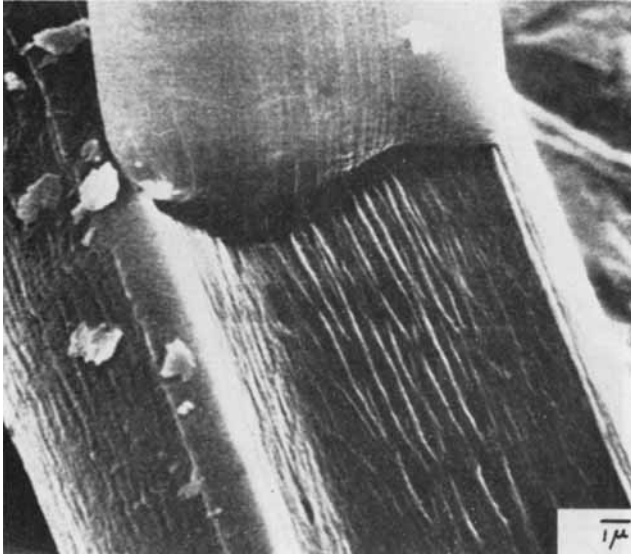
Fig. 14. Apparent intermittent elongated cell structure revealed by peeling nylon 66.
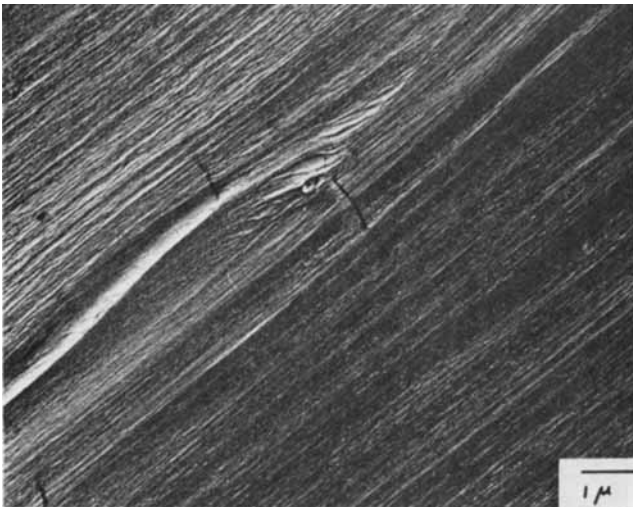

Fig. 15. Cell structure variation around an inclusion in nylon 66 as revealed by peeling.

ing." In this technique, the fiber is simply nicked with a razor blade, and the upper part of the fiber grasped and peeled back as first described by Scott.[8] Each type of fiber has a characteristic peeling behavior which can be affected by changes in fiber nature or production conditions. Acrylic fibers are usually difficult to peel but they can be peeled, generally as skin peeling (Fig. 8a) and occasionally as chords (Fig. 8b). Nylon 66 peels only as chords (Fig. 9). Polyesters will peel in skin layers like an onion (Fig. 10a) or as a chord peel (Fig. 10b).
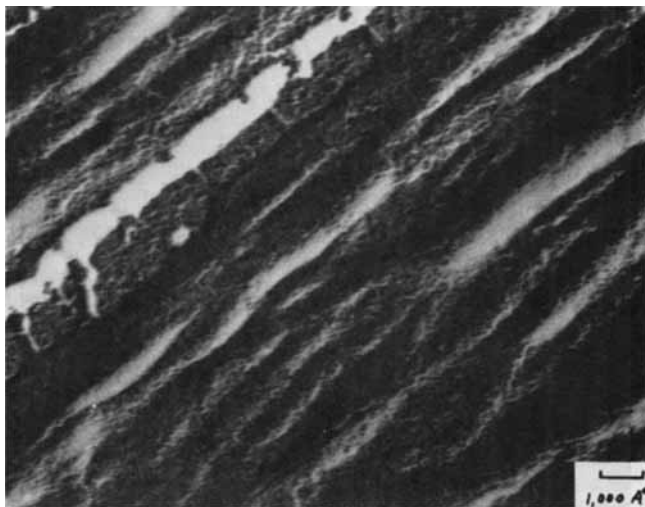
Fig. 16. Detail at 77 000× of the grosser structure seen in Fig. 13 showing cross ties between two adjacent fibrillar sheets.

Fig. 17. Detail of fine fibrillar structure in peeled nylon 66.   Fibrils are 100–150 Å wide and have a uniform nodular structure of approximately 150 Å.

Peeling of undrawn fibers before drawing has oriented the supermolecular structure, as might be expected, does not show much significant internal structure, even at magnifications of 75 000–100 000×. With drawn, oriented fibers, however, the story is different. Much of interest can be seen:

Polyacrylonitrile. Peeling of drawn acrylic fibers reveals a definite fibrillar structure 1 (Fig. 11) which seems to be a relatively loose bundle of long fibrils. This correlates well with x-ray studies[9] which showed polyacrylonitrile to be a relatively open structure. At higher magnification,
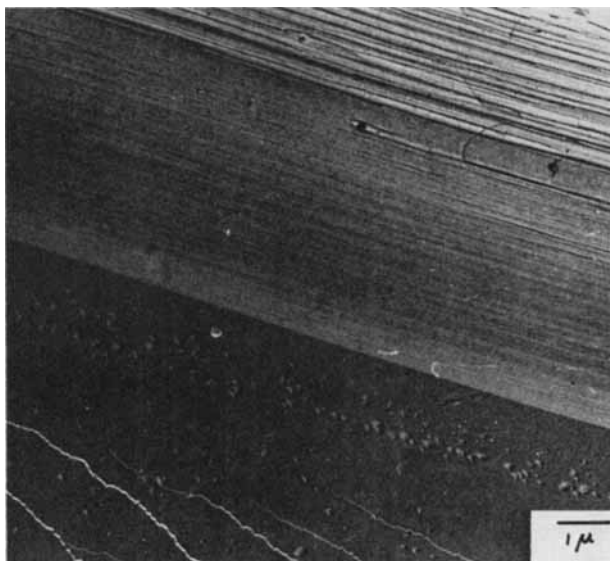
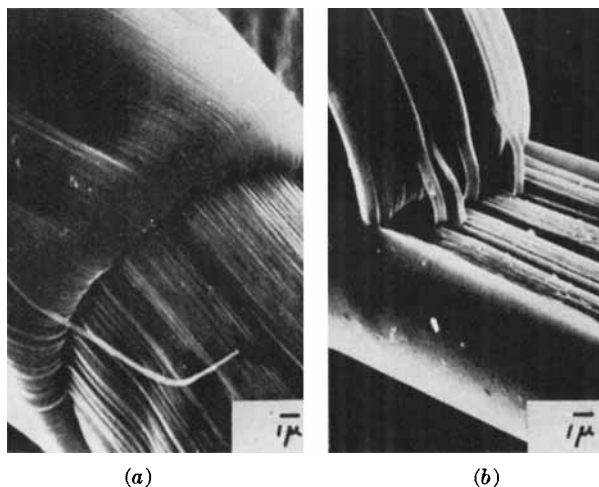Fig. 18. Peeled polyester fiber showing original surface and long continuous fibrillar interior structure.

(a)   (b)

Fig. 19. Relatively loosely bound nature of fibrils in a polyester fiber illustrated in (a) skin peeling and (b) chord peeling.

(77 000×), bundles of fibrils in sheet form are seen (Fig. 12) to have connecting "ties" between them similar to what we have observed and generally called "shish kabobs" in crystals grown from solution.

Polyamide. Figure 13 shows the surface exposed by peeling a strip from a drawn nylon 66 fiber. On both sides is a normal surface with the characteristic mild longitudinal striations resembling the character of the subsurface. The exposed longitudinal striations appear to be elongated
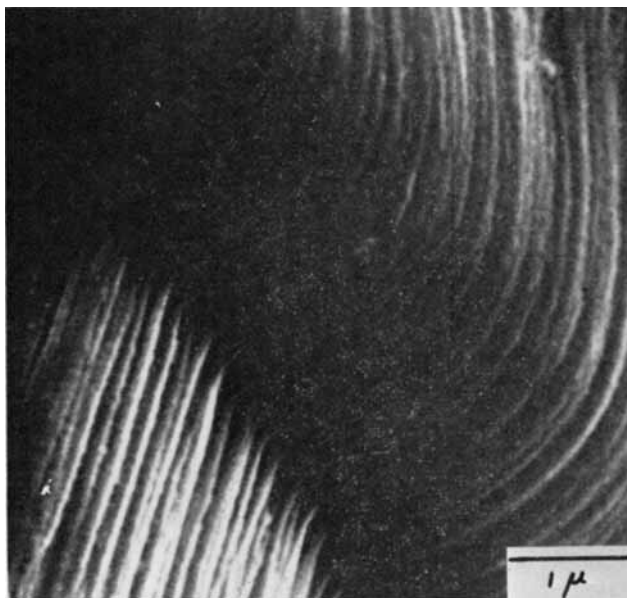
Fig. 20. Nodular structure along fibrils revealed by a skin peel of a polyester fiber. Magnification 34 000×.
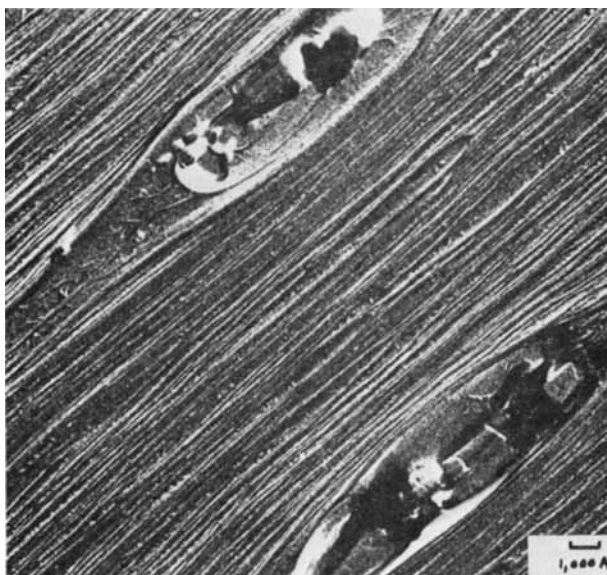

Fig. 21. Variation in structure around particulate inclusions in a polyester fiber.

cells, with two different size domains revealed in this figure.   The coarse striations measure 1000–1500 Å across; the finer are only 100–150 Å. The apparent intermittent cellular structure is quite evident in Figure 14.

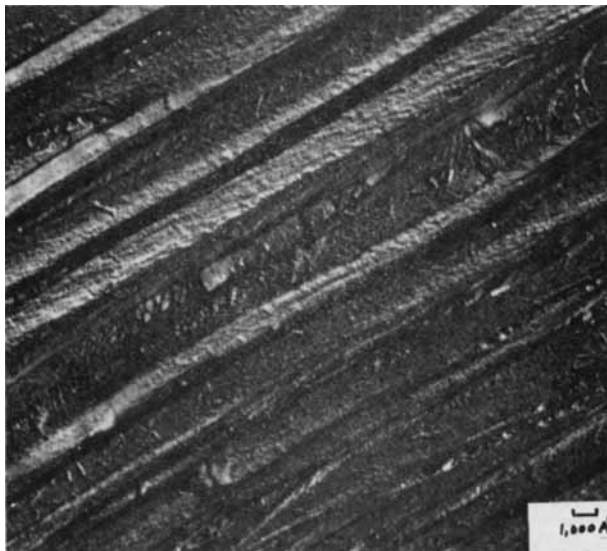   We were aware that demarcations seen in peeled fibers could derive from

Fig. 22. Apparent cross-tie growths between sheets of fibrils revealed by peeling of a polyester fiber.

stress concentrations during peeling. Evidence relating it to true structural differences is strong, one item being that nonuniformities are frequently observed, e.g., Figure 15 shows an area of conchoidal fracture and polymer flow around an inclusion. This resembles the knot area in a split log. In the area of the knot, cell structure is greatly enlarged, and the total area affected is much greater than would be expected from simple stress concentrations at the inclusion.

Looking at these structures under still higher magnification, additional features can be seen. In a detail of the grosser structure of Figure 13 at 77 000× (Fig. 16), one can again see what appears to be cross-tie growths between two adjacent fibrillar sheets. Figure 17 shows fine fibrillar structure with fibrils quite uniformly 100–150 Å wide and with a definite nodular structure. The nodular structure is quite uniform and is such as might be seen either from stacked lamellae or helical coils. Much of the nodular structure appears elliptical and is oriented on an angle other than perpendicular to the axis of the fibril.

Polyester. Peeling off the surface of a polyester filament reveals a structure resembling that of nylon 66 (Fig. 18), with the undisturbed surface at one side and two different subsurface structures. However, the intermittent cell structure of the nylon 66 is replaced by a long continuous striation structure. This fibrillar structure appears at times to be so loosely bound that individual fibrils can separate easily. This marked tendency of the polyester fibrillar structure to separate randomly is shown in Figures 19a and 19b. Note the tendency, particularly in chord peeling, for the torn fibrils to aggregate into flat ribbons. Thickness of these ribbons has been observed as thin as 100–150 Å, but generally thicker.

At higher magnification (Fig. 20) skin peeling begins to show a nodular structure, again somewhat resembling the "ball" structures Geil and Yeh described.   Figure 21 shows how structure varies around particulate inclusions such as TiO_2 added to deluster fibers.   Cross ties between fibrils
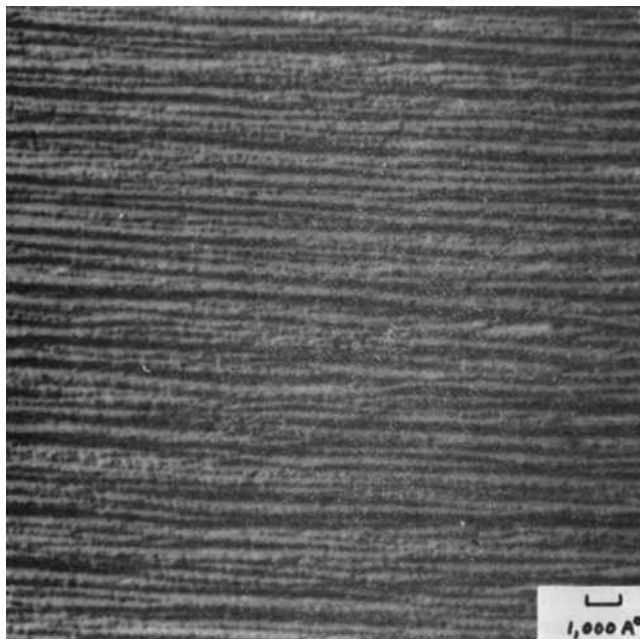

Fig. 23. Uniform fibrillar and nodular structure revealed by peeling a polyester fiber.   77 000×.
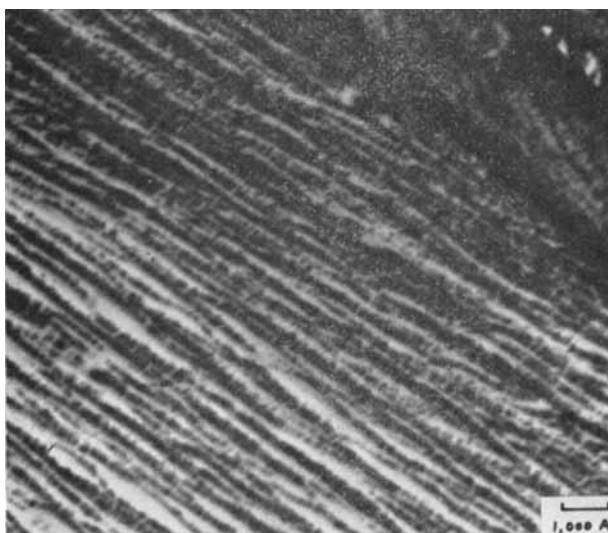

Fig. 24. Nodular structure of fibrils in a polyester fiber.   140 000×.

begin to appear again as do some randomly oriented fibril adjacent to the ends of the flow patterns around the inclusions. Cross ties between fibrils and sheets of fibrils appear distinctly in Figure 22.

Nodular structure is also quite evident at high magnification. Figure 23 at 77 000X shows an area with fibrils uniformly 150 Å wide and nodes with 150 Å spacing. Figure 24 at 140 000X gives an impression that the nodular structure could be associated with helically coiled fibrils, although resolution is not quite good enough to reach that conclusion with certainty. Low-angle x-ray measurements of basic cell size of the polymers shown in the last two figures was 140–170 Å, in good agreement with visual detail.

CONCLUSIONS

In tracing structure of man-made polymers from solution growth to bulk polymer to film to fibers, some striking similarities have been seen, no matter how simple or complex the material or conditions under which the structures were formed. This seems true within any single polymer system and the same general picture seems to prevail for man-made fibers regardless of polymer. Whether this structure derives from folded-chain lamellar growth or from fibrillar-fringed micelles with resulting helical coil fibrils cannot yet be resolved. Domain resolution with the electron microscope in this study was not sufficient to define ultimate structure accurately. It appears, however, that further work with the techniques described can give worthwhile information and may help lead to final resolution of the supermolecular structure of man-made fibers.

References

1. P. H. Lindenmeyer, Ed., *Supramolecular Structure in Fibers* (*J. Polym. Sci. C*, **20**), Interscience, New York, 1967.

2. J. W. S. Hearle and R. H. Peters, *Fiber Structure*, Butterworth, London, 1963.

3. P. Keller and M. J. Machin, *J. Macromol. Sci.*, **B1**, 41 (1967).

4. W. O. Statton, in *Supramolecular Structure in Fibers* (*J. Polym. Sci. C*, **20**), P. H. Lindenmeyer, Ed., Interscience, New York, 1967, p. 117.

5. W. O. Statton, in *The Meaning of Crystallinity in Polymers*, (*J. Polym. Sci. C*, **18**), F. P. Price, Ed., Interscience, New York, 1967, p. 33.

6. G. S. Y. Yeh and P. H. Geil, *J. Macromol. Sci.*, **B1**, 251 (1967).

7. D. E. Bosley, *Text. Res. J.*, **38**, 141 (1968).

8. R. G. Scott, *ASTM Bull.*, **No. 257**, 121 (1959).

9. W. O. Statton, unpublished work.