Polyimide Fibers: Structure and Morphology

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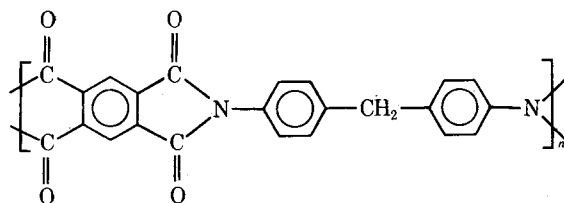
Synopsis

Polyimide fibers were prepared by wet spinning of poly(*p,p'*-diaminodiphenylmethanepyromellitamic acid). Density measurements and x-ray diffraction studies were carried out to study the structure of the resultant polyimide fibers. Polyamic acid as well as undrawn polyimide fibers were essentially amorphous with two amorphous haloes. Hot drawing of the fibers at 300°C resulted in increase in crystallinity, and a simultaneous decrease in density also took place. X-ray data revealed that meridional reflections correspond to the repeat unit length in the fiber. Scanning electron micrography studies indicated that polyamic acid fibers prepared by a wet-spinning technique developed voids during spinning which increased on cyclodehydration to the polyimide state. Hot drawing of fibers resulted in enlargement of these voids. However, a highly fibrillated structure was developed during drawing which could account for the strength of the fibers.

INTRODUCTION

Aromatic polyimides have excellent thermal and chemical stability and have been fabricated into films and fibers. Their mechanical properties depend not only on the backbone but also on intermolecular interaction, conformation, and existence of ordered structures. The crystalline structure of some polyimides have been discussed in the literature.[1-5]

In this paper we report studies of the crystalline structure and morphology of fibers having the structural formula

poly(*p,p'*-diaminodiphenylmethanepyromellitimide)

The fibers were prepared by chemical cyclodehydration of polyamic acid fibers, and the details of the spinning conditions have been discussed elsewhere.[6] Density measurements and x-ray diffraction studies were carried out to study the structure of the polyimide fibers. The morphology of the fibers was investigated by scanning electron microscopy.

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EXPERIMENTAL

Density of Fibers

Density of the fibers was measured by a Davenport density gradient column using xylene and carbon tetrachloride.

X-Ray Diffraction Of Fibers

Wide-angle x-ray diffraction patterns were recorded using nickel-filtered Cu $K\alpha$ radiation. The generator (Norelco Type 170-112-02 of Philips Electronic Instruments) was operated at 30-kV voltage and 30-mA current. A bundle of parallel filaments was wound on the specimen holder of a flat plate camera (mounted perpendicular to the path of the x-ray beam) and exposed for 5 hr with a film distance of 4 cm, after which the film was processed under standardized conditions.

Moisture Regain of Fibers

Fibers were dried in a vacuum oven at 100°C for 24 hr, weighed, and kept in a room maintained at 65% R.H., 20°C for 3 days. After repeated weighing the moisture regain was calculated.

Scanning Electron Microscopy of Fibers

Surface Topography

Small lengths of fibers were mounted on a specimen holder by applying adhesive (Quickfix) at the ends of the fibers.

Internal Structure

Peeling of Fibers. With the aid of a stereo light microscope, a cut was made on a fiber surface, mounted as above, using a razor blade, so that one edge of the cut could be held with a pair of tweezers and peeled along the longitudinal axis of the fiber.

Cross Sections of the Fibers. The fibers were embedded either in poly-(methyl methacrylate) (PMMA) or wax for cross section studies. Small length of fibers (1 cm) were tied on a thin card frame and then kept vertical in a capsule filled with monomer, having 0.2% initiator (benzoyl peroxide) and 100% plasticizer (dioctyl phthalate). After being kept under vacuum for some time to remove small air bubbles adhering to the surface of the fibers, polymerization was carried out in an air oven maintained at 60°C for 24 hr. Thick sections (0.5 mm) were subsequently cut with a sharp razor blade before examination. Alternatively, fibers were embedded by adding molten wax to a capsule, sections being cut after solidification.

Fracturing of Fibers. Fibers were dipped in liquid air and, after conditioning at that temperature for 10 min, were taken out and fractured immediately (in a tensile mode). Fractured ends were mounted on the specimen holder with

the help of adhesive tape. All the samples prepared by the above methods were coated with a thin film of evaporated silver, in an Edwards' coating unit, to make the samples electrically conducting, thereby overcoming the problem of local "charging."

RESULTS AND DISCUSSION

The density and mechanical properties[6] of the polyamic acid and polyimide fibers at various stages of fabrication are given in Table I. On cyclodehydration of polyamic acid fibers (sample A) to the polyimide state (sample B), the density increased from 1.2705 to 1.3750 g/cm^3, which suggests that the imide state has a better packing of chains. During imidization, cyclic structures are introduced thus increasing the rigidity of the backbone. A decrease in density was observed when polyimide fibers were hot drawn at 300°C (samples C and D) (Table I). A further decrease in density was observed on annealing the hot-drawn fibers at 300°C in silicone oil (sample E). The decrease in density may arise either due to a variation in crystalline structure of the fibers or development of voids during hot drawing. This aspect was studied by x-ray analysis and SEM.

Wide-angle x-ray diffraction patterns of fibers from polyamic acid (A), undrawn polyimide (B), hot-drawn polyimide (draw ratio 3.5) (D), and hot-drawn and annealed polyimide (E) were recorded and are given in Figures 1(a) to 1(d), respectively. The diffraction pattern of hot-drawn fiber prepared from a different batch under similar conditions of spinning was also recorded, Figure 1(e). The x-ray diffraction patterns of polyamic acid and undrawn polyimide fibers are characterized by the presence of two amorphous haloes, which suggest that the fibers have essentially amorphous structures. Increase in crystallinity on imidization of polyamic acid fibers has been reported by Koton.[5] However, our work indicates that undrawn polyimide fibers are essentially amorphous. The maximum in the haloes of undrawn polyimide correspond to d-spacings of 14–15 and 4–5 Å. In the x-ray diffraction patterns of chemically imidized poly(p-phenylenepyromellitimide) films, two haloes, signifying amorphous material (d = 12–16 and 3–5 Å), have been reported by Baklagina et al.[1]

The diffraction patterns of hot-drawn polyimides indicate considerable orientation and crystallization of molecules. On the meridional axis of Figures

TABLE I
Density and Mechanical Properties of Fibers at Various Stages of Spinning[a]

Sample[b]	Draw ratio	Denier	Tenacity	% Elongation	Initial modulus, mN/tex	Density, g/cm^3
A	0.0	167	53	119	1410	1.2705
B	0.0	143	80	182	2560	1.3750
C	2.5	64	212	12	3620	1.3320
D	3.5	38	380	10	4060	1.2245
E	3.5	39	273	8	5650	1.2050

[a] $[\eta]$ of polyamic acid = 140 cm^3/g; dope concentration = 20%; coagulation bath composition (water:DMF) = 60:40; jet stretch = 4; temperature of drawing = 300°C.

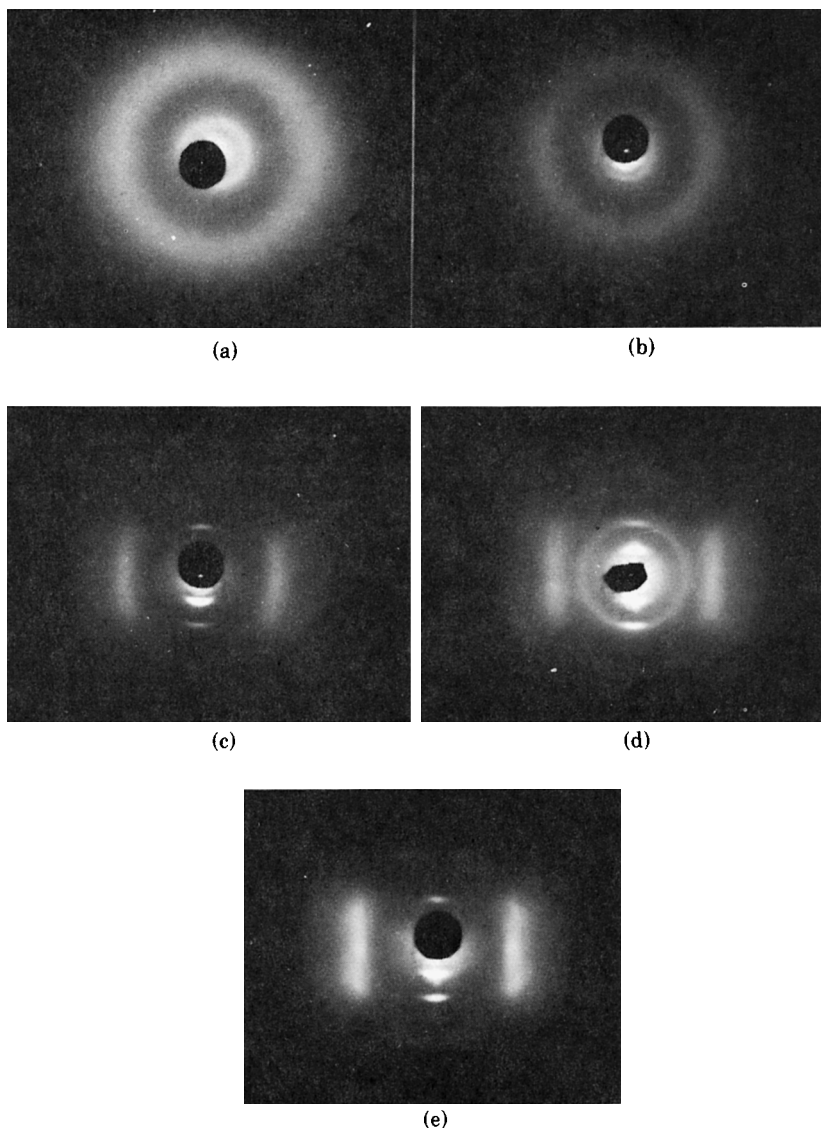[b] A, Polyamic acid fibers; B to E, polyimide fiber; (E = fiber annealed in silicone oil at 300°C under tension).

Fig. 1. X-Ray diffraction patterns of fibers (polyamic acid and polyimide) at various stages of fabrication: (a) polyamic acid (sample A); (b) polyimide (sample B); (c) polyimide (sample D); (d) polyimide (sample E); (e) polyimide (similar to sample D, but prepared in a different batch).

1(c) and 1(e), there are two strong reflections and three weak reflections. They seem to correspond to the 1st, 2nd, 3rd, 4th, and 6th order of reflection from the planes having d-spacing of 14.1 Å. Similar types of meridional reflections have been ordered by Baklagina et al.[1] They have reported the development of axial planar texture on heating films and fibers. They indexed the reflections observed in the x-ray diffraction pattern by assuming the equatorial lattice as rectangular. The period along the axis was calculated from meridional reflections for poly(p-phenylenepyromellitimide) and was found to be equal to 12.3 Å. The polyimide under investigation differs from these polymers by the presence of an additional phenylene group and —CH_2— groups. The length of monomeric

links was therefore calculated by taking this value for p-phenylenepyromelliti-mide along with 4.3 Å for the phenylene group[7] and considering the tetrahedral bond angle for the —CH_2— group. The calculated value comes to 14.7 Å, which is very near to the 14.1 Å d-spacing value of the first meridional reflection.

The first reflection on the equatorial axis had a d-spacing value of 4.7 Å. There is a concentration of amorphous halo around the equatorial axis. This may arise due to some orientation in the amorphous regions. PET is also found to exist in an oriented amorphous state. Comparing Figures 1(c) and 1(d), it is observed that on annealing in silicone oil at 300°C for 2 hr the x-ray reflections become sharper. Some disorientation of crystalline regions has also occurred during annealing. The crystallinity of hot-drawn polyimide was calculated[8] from
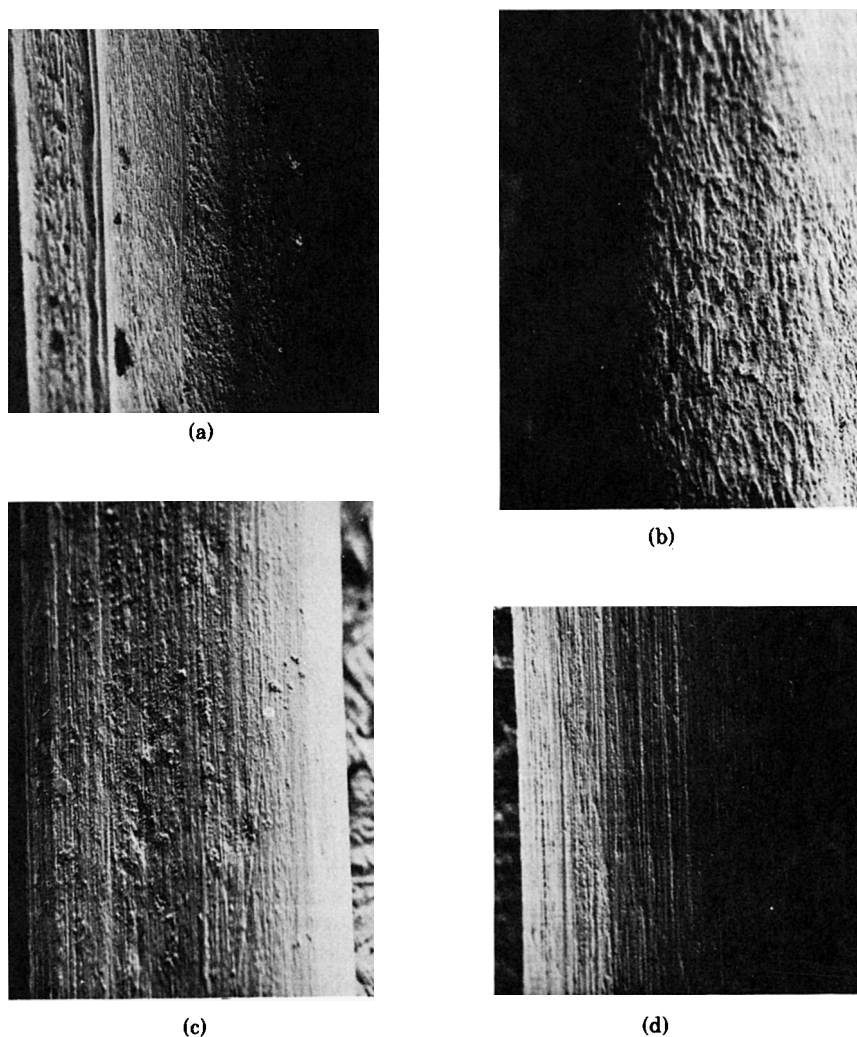

(a)

(b)

(c)

(d)

Fig. 2. Scanning electron micrographs of different fibers: (a) sample A (×590); (b) sample B (×730); (c) sample D (×720); (d) sample E (×730).

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(a)

(b)

(c)
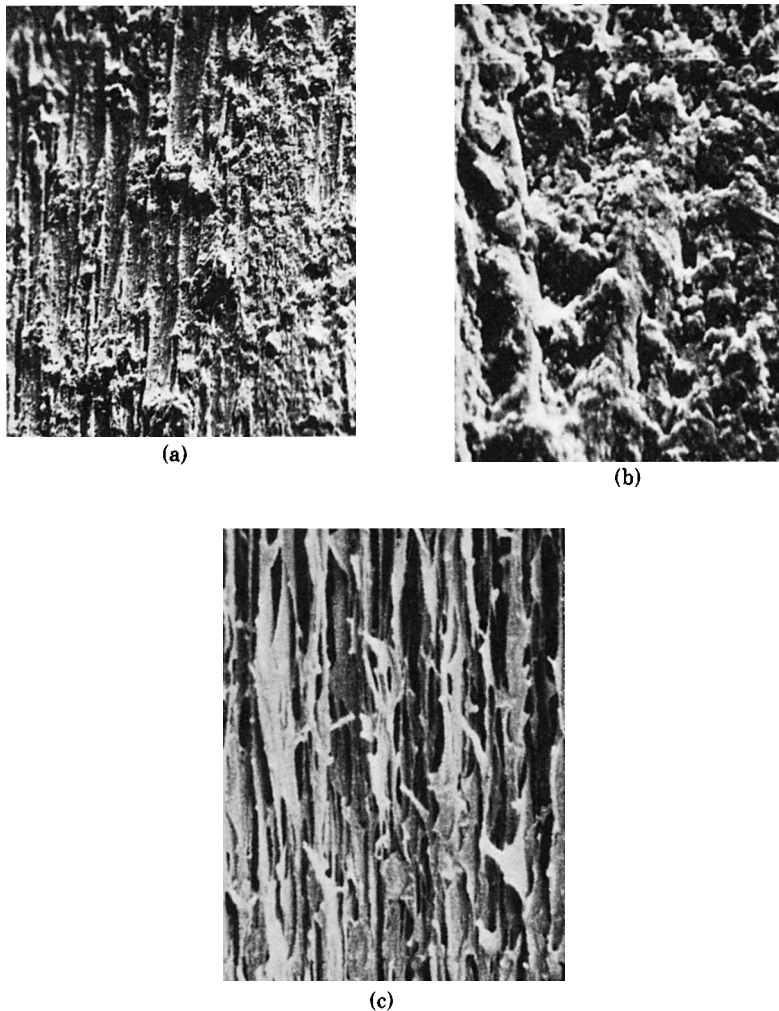
Fig. 3. Scanning electron micrographs of peeled surfaces of various fibers: (a) sample A (×2950); (b) sample B (×7250); (c) sample D (×6500).

powder x-ray diffraction patterns with the help of an amorphous standard and is approximately 20%. In these calculations the scattering due to oriented amorphous regions of the sample is considered as amorphous.

This increase in orientation and crystallization of hot-drawn polyimide fibers is further supported by moisture regain data. Thus, the moisture regain of undrawn polyimide fibers was found to be 3.6%, whereas that of hot-drawn polyimide fibers was only 1.8%. The crystalline regions of the fibers become inaccessible to the water molecules thus decrease the moisture regain of hot-drawn polyimide fibers.

The possibility of voids in the fiber structure was studied by taking fiber samples from each stage of fabrication and examining them by various techniques of scanning electron microscopy. After completing examination of surface topography, new surfaces were formed by "peeling" and investigated for the presence of voids. Cross sections and fractured surfaces (fracturing done at liquid air temperatures) were also examined.

The surface characteristics of the various fibers A, B, D, and E can be seen in Figures, 2(a) to 2(d), respectively, from which it is obvious that there are variations in the structure of respective surfaces.   The undrawn polyimide surface possesses a random structure, and, as may be expected, the surface of the drawn fibers shows considerable orientation of molecules along the longitudinal axis of the fibers.   The annealed fibers also show a similar texture, although it appears that the number of surface defects has been reduced, resulting in a smoother surface.   But after examination of these surfaces, it is difficult to comment upon any void formation.

The longitudinal structure of the core of these fibers was subsequently studied by peeling, see Figures 3(a) to 3(c).   In undrawn polyimide fiber (sample B, Fig. 3(b)), the peeled surface has a highly irregular structure, but voids are not visible. However, the polyamic acid peeled surface, Figure 3(a), shows some remains of
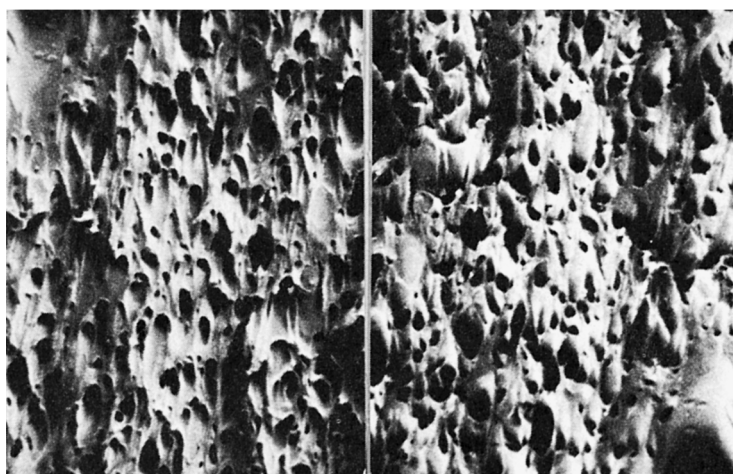

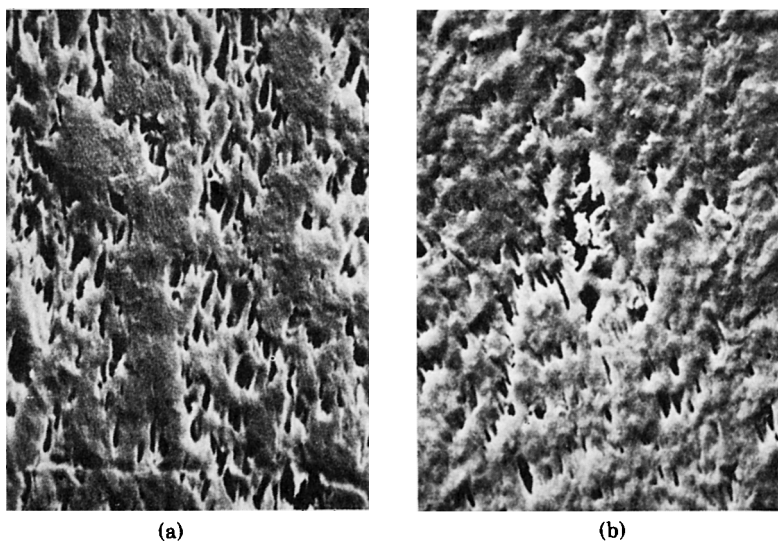Fig. 4. Stereo pairs of peeled surface of polyimide fiber, sample C (×6600).

(a)   (b)

Fig. 5. Scanning electron micrographs of the cut surfaces of the fibers: (a) sample A (×6500); (b) sample B (×7200).

(a)   (b)

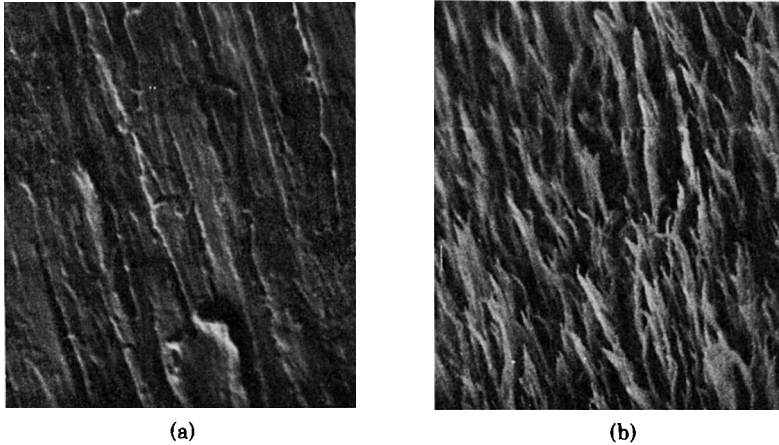Fig. 6. Scanning electron micrograph of cold-drawn polyimide fibers: (a) surface of fiber (×7000). (b) peeled surface of fiber (×6900).

voids and capillaries which run along the length of the fiber. Similarly, the peeled surfaces of hot-drawn fibers (sample C) also show the development of voids (see the stereo pair, Fig. 4, prepared by tilting through 10° toward the collector between the successive exposures), which in this case are present uniformly throughout the structure. With increase in draw ratio(draw ratio 3.5, sample D) these voids elongate and take the form of capillaries, and the structure becomes highly fibrillated, Figure 3(c).

It was interesting to observe some longitudinal sections of the fiber surfaces which were cut with the blade during the process of peeling. Polyamic acid fibers Figure 5(a), possessed a large number of holes in the section, whereas in the case of polyimide fibers, Figure 5(b), the number of holes is smaller, a reduction which may be due to formation of rigid and compact imide structure.

Fig. 7. Scanning electron micrographs of peeled surface of fiber E (×5700) (peeling was done very near to the fiber surface).
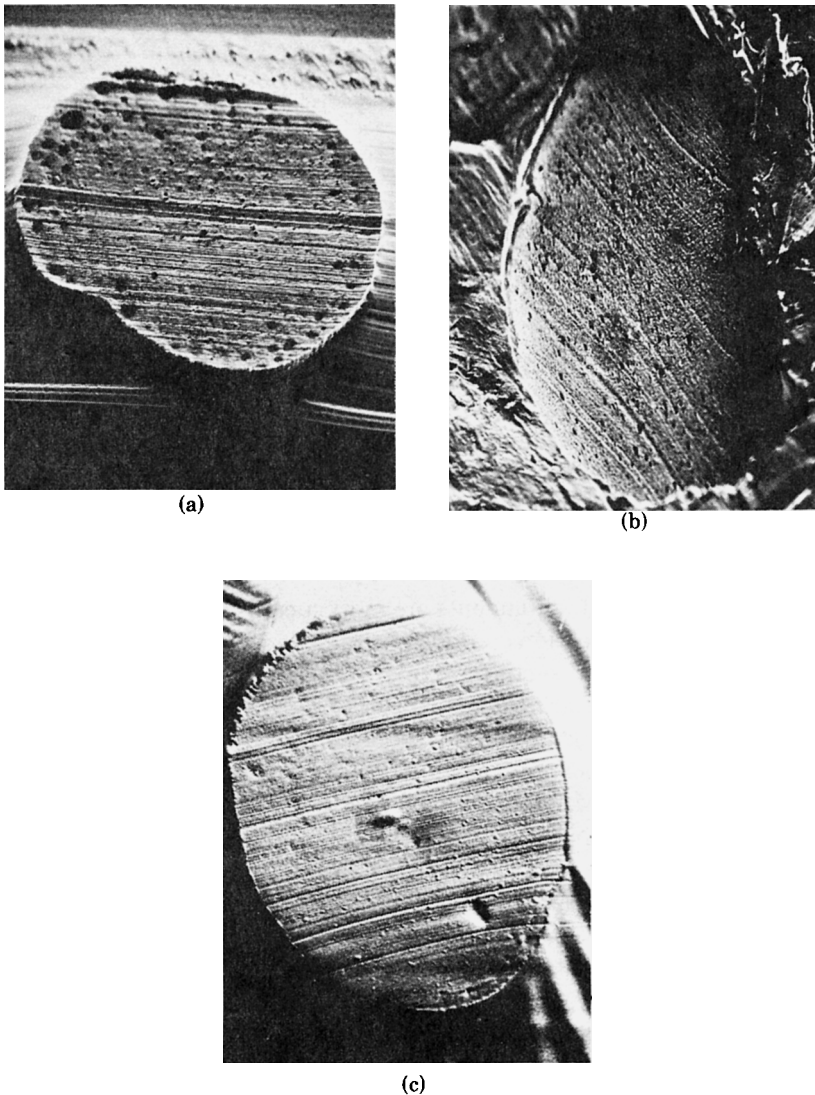
Fig. 8. Transverse sections of polyimide fibers as seen with SEM: (a) sample B (×450); (b) sample D (×450); (c) sample D (×450) embedded in PMMA.

The peeled structures of the cold-drawn fibers (to a maximum draw ratio 1.5) were also observed, Figure 6(a), and the micrograph clearly shows a highly fibrillated structure. The surface of the cold-drawn fiber has developed cracks, Figure 6(b), and a layer type of structure seems apparent. Because of the relatively rigid nature of the molecules, their mobility is highly restricted at room temperature, and therefore the application of stress may initiate fracture and the development of the above cracks.

In some of the peeled surfaces of the annealed samples (sample E), specifically when the peeling was done very near to the surface, voids were not visible even at high magnifications (Fig. 7), which probably suggests that the fiber has a relatively less porous outer surface which surrounds a soft and porous core.
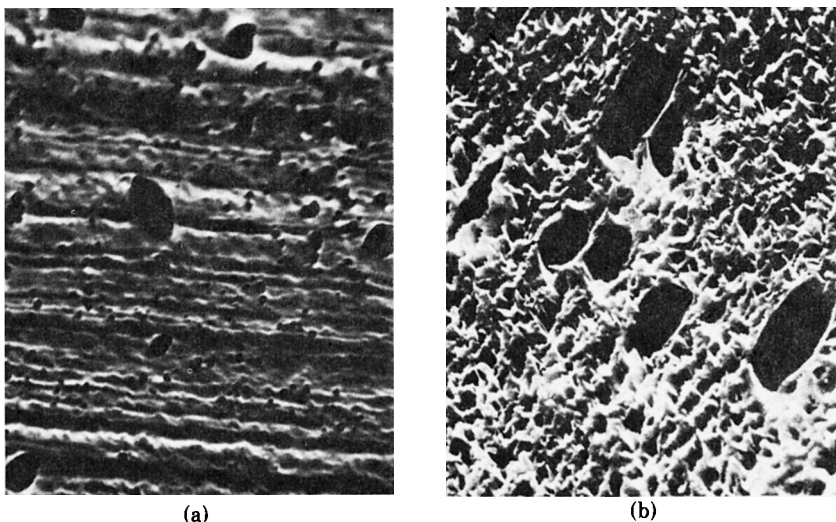
(a)   (b)

Fig. 9. Transverse sections of polyimide fibers at higher magnifications: (a) sample B (×7500); (b) sample D (×6000).

Any voids present in the filaments are most successfully studied by observing their transverse cross sections. Consequently, the fibers were embedded, initially, in PMMA prior to section cutting (in this case with a fresh, clean razor blade). However, contrary to our expectations, the PMMA-embedded cross sections of hot-drawn fiber (sample D) showed the absence of voids, Figure 8(c), whereas in undrawn fiber cross sections voids were clearly visible, Figure 8(a). It was thought that MMA might have penetrated the porous structure of hot-drawn fiber and then polymerized, thus filling the voids. Therefore, a second batch of sections were prepared by embedding in wax. The subsequent micrographs, Figure 8(b), clearly demonstrated the presence of voids, thus confirming the original hypothesis. Observation of the micrographs suggest that on hot drawing the fibers tend to become more elliptical. The undrawn fiber cross sections has a number of voids near the periphery, i.e., just below the surface of the fiber, and their size is relatively larger than those present in the core of the fiber. In the case of the drawn fiber, voids have mainly two different sizes, the smaller being densely distributed throughout the structure of the fiber. The larger voids occur at a much less frequency but are also randomly distributed. The micrographs at higher magnification are given in Figures 9(a) and 9(b).

The above studies show that the void content of the fiber has markedly increased and the structure has become considerably porous upon hot drawing. The pyromellitimide and phenylene groups constitute the rigid backbone of these polymers, whereas the methylene groups are responsible for the flexibility. When the fibers pass over the hot plate, the applied stress results into the flattening of the fiber. Polyimides generally have some solvents associated with them,[9,10] which during hot drawing will evaporate. The incomplete cyclodehydration of polyamic acid may be another cause of evolution of volatile products. If, in the polymer chains, some such uncyclized structures are left, during hot drawing they might cyclodehydrate and release water. This release of water and solvent from the core of the fiber due to increase in temperature may cause swelling of chains which are mobile enough due to higher temperature.
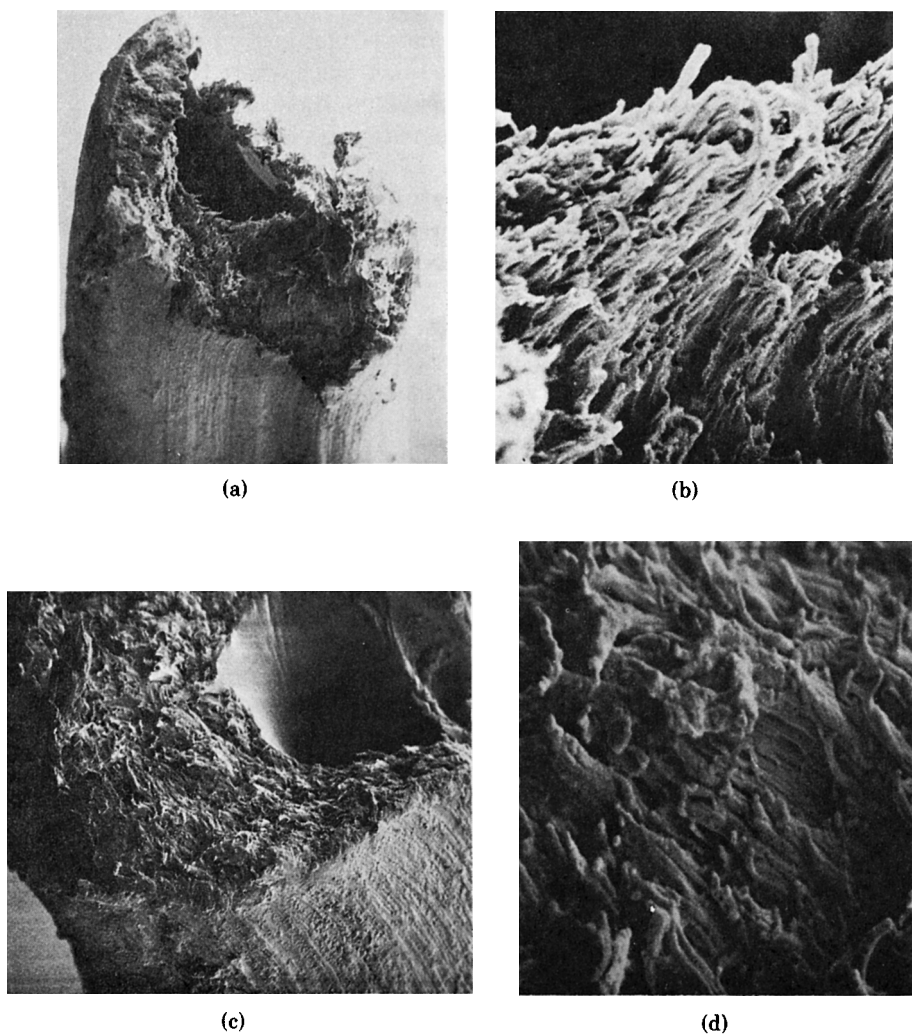
(a)

(b)

(c)

(d)

Fig. 10. Fractured sections of polyimide fibers: (a) sample D (×530); (b) sample D (×4800); (c) sample B (×1650); (d) sample B (×6700).

In this process the voids which are already present in the undrawn fiber expand; and, further, the axial stress acting on the fiber tends to elongate the voids in the direction of stress. The resultant effect of the two forces is a net increase in the dimensions of the voids present in the structure of the fiber.

Fracturing of Fibers

An alternative method of examining the structure of the core of the fibers was also investigated, i.e., fracturing at liquid air temperatures. Figures 10(a) and 10(b) show the fractured cross section of fibers D indicating a well-defined fibrillar structure and the presence of voids between. It appears that the break occurs as a result of the splitting of convoluted fibrils. Fractured cross sections of undrawn polyimide fibers are shown in Figures 10(c) and 10(d). Here also, the fractured cross sections are fibrillated although to a lesser degree. However,

even at liquid air temperatures, the tensile fracture is accompanied by drawing which might have caused the fibrillation of chains. One fact, which appears quite obvious from these results, is that fracture takes place where large voids occur in the cross section, i.e., at obviously weakened points.

From the above work the following conclusions can be drawn:

1. The polyamic acid fibers prepared by wet spinning developed some voids during spinning. These voids further increased on cyclodehydration to polyimide fibers. In this process water is evolved, and this may increase the void size.

2. The polyamic acid as well as undrawn polyimide fibers were essentially amorphous with two amorphous haloes.

3. The hot drawing of polyimide fibers results in an increase in crystallinity, and a fibrillated structure was formed. However, the small voids which were present in the undrawn fibers enlarged. Thus, the fibers become extremely porous and even the outer surface had developed pores.

4. A decrease in density was observed on hot drawing of polyimide fibers, which indicates that void content outweighs the increased crystallinity of fibers.

5. The weaker points in the fiber correspond to the locations of large voids.

One obvious question which arises here is, "To what may be attributed the fiber strength, especially in the presence of a large number of voids?" This can be reasonably explained by visualizing the fiber consisting of longitudinal continuous fibrils with some interconnecting links.

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