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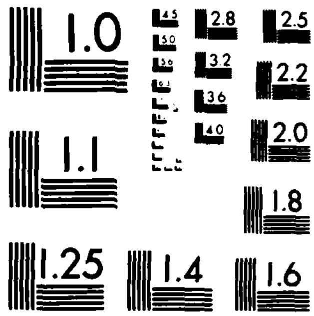


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FINAL REPORT

# Fabrication of Biaxially Oriented Films Via Poly(p-phenylene teraphthalamide)/$H_2SO_4$ Liquid Crystalline Dopes

by

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## ABSTRACT

The fundamental innovation arising from this research is that the state of spatial biaxial order in lyotropic Poly(p-phenylene terephthalamide) (PPTA)/$H_2SO_4$ liquid crystal solutions is strongly controlled by an externally imposed stress field. Also the orientation only relaxes slowly after the stresses are released. This enables processes to be devised that develop biaxial stress on a flowing liquid crystal to cause high levels of molecular orientation. Since the character of the stress, i.e., the magnitude and direction of the $\sigma_{ij}$ components, is set by the experimental conditions, then the orientation is also controllable. Thus a process has been developed which takes advantage of the rheological and phase behavior of PPTA/$H_2SO_4$ to create films ranging from uniaxial through unequal biaxial to equal biaxial orientation. This and other structural features have been documented by WAXS, pole figure analysis, microscopy and SAXS. Also mechanical property studies show that a range of strengths and moduli can be obtained including a film of equal biaxial orientation ($f_{zc}$ = 0.45, $f_{yc}$ = 0.50 using the White-Spruiell indices from 0.0 to 0.5 where 0.5 means perfect orientation). Property values for this film are modulus in the machine direction = 700,000 psi and transverse direction = 800,000 psi with tensile strengths in the machine direction = 25,000 psi and transverse direction = 30,000 psi.


## The Process

The development and evolution of the process is recorded in publications (4, 6 and 7). The basic understanding of the rheology and important features of the PPTA/$H_2SO_4$ liquid crystal system are reported in (1,2,3 and 5). The status of the process coincident with the close of this contract is described in the following paragraphs.

Films are produced by extrusion through an annular die using the apparatus of Figure 1. Oil is fed through a 1/4 horsepower Zenith gear pump into a cylindrical reservoir containing a piston below which is the solution of PPD-T/$H_2SO_4$. The oil pressure forces the piston downward, pushing the solution into an annular die of inside radius 49.45 mm and annular gap of 0.3 mm. The reservoir and annular die system are made from Type 304 stainless steel to resist corrosion by the $H_2SO_4$. The piston is made from stainless steel surrounded by a Teflon® seal.

The solution emerges from the die and flows into the bath directly or is drawn over a conical mandrel made from polyvinyl chloride. The mandrel is coated with an oil pumped from an overhead separatory funnel through the die. The purpose of the oil is to reduce friction and induce biaxial elongational flow in the PPD-T/$H_2SO_4$ solution. The mandrel used is 107 mm high, with a diameter of 33 mm at its top and 165 mm at its bottom.

The solution moves over the mandrel into the coagulation bath which contains 75% water, 25% methanol (MeOH) and is then allowed to stand at room temperature. This extracts the $H_2SO_4$ from the solution and coagulates the PPD-T into a solid film. The coagulation is an exothermic process. The density of the $H_2O$/MeOH coagulant is such that the oil settles to the bottom of the bath rather than rising to the top and interfering with the process.

It is possible to operate the apparatus over a wide range of concentrations and temperatures. It was, however, our intention to operate under conditions wherein the PPD-T/$H_2SO_4$ solutions are in a liquid crystalline form. The optimum conditions were found to be 70°C and a concentration of 17 weight percent. The mandrel was lubricated with a hydrocarbon mineral oil (viscosity = 170 centipoise).

## Film Characterization

The films produced via the above process have been characterized by WAXS pole figure analysis, SAXS, SALLS, SEM, mass density gradiant column techniques and tensile testing. A rather complete reporting and discussion of these results is given in (6 and 7).

Some representative results for orientation are given in Figures 2 - 5. Mechanical property data are shown in Figures 6 and 7.

## Conclusions

It is possible to create thin films of PPTA that range in strength, orientation and microporosity. The anisotropic character of the liquid crystalline PPTA/$H_2SO_4$ lends itself to the process developed in this research. A fundamental goal of polymer engineering is to create macroscopic structures of various dimensionalities that have useful properties that arise from and are controlled by the process used to fabricate them. A two dimensional structure with controlled anisotropic character and properties, notably the thin film resulting from this process, is a very successful achievement of this goal in polymer engineering.

Technical Reports and Journal Articles

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2. D. D. Harwood and J. F. Fellers, "The Imposed Polyelectrolyte Behavior of Poly(m-Phenylene Isophthalamide in LiCl/Dimethylacetamide)," Macromolecules, 12, 693 (1979).

3. Y. Onogi, J. L. White and J. F. Fellers, "Structural Investigations of Polymer Liquid Crystalline Solutions: Aromatic Polyamides, Hydroxypropyl Cellulose and Poly(-Benzyl-L-Glutamate)," J. Polym. Sci.: Polym. Phys. Ed., 18, 663 (1980).

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6. J. E. Flood, J. L. White and J. F. Fellers, "Process for the Formation of Biaxially Oriented Films of Poly(p-Phenylene Terephthalamide) From Liquid Crystalline Solutions," J. Appl. Polym. Sci., 27, 2965 (1982).

7. H. Bodaghi, T. Kitao, J. E. Flood, J. F. Fellers and J. L. White, "Characterization of Poly-p-Phenylene Terephthalamide Films Formed from Continuous Extrusion and Coagulation of Liquid Crystalline Sulphuric Acid Solutions: Void Structure," Polym. Eng. and Sci., 24, 242 (1984).

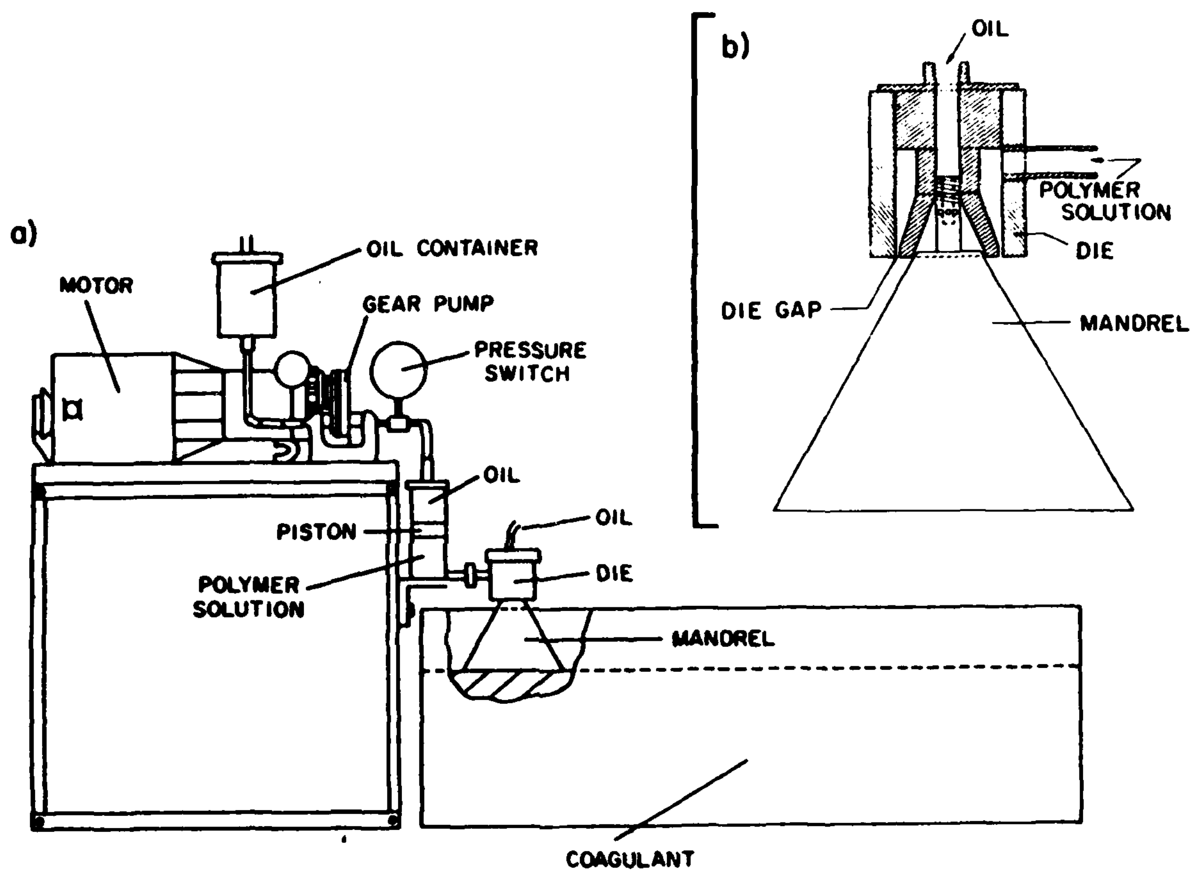


FIG. I Mandrel process for producing biaxially oriented PPD-T film.
a) Overview of the process
b) Cutaway view of the annular die and mandrel

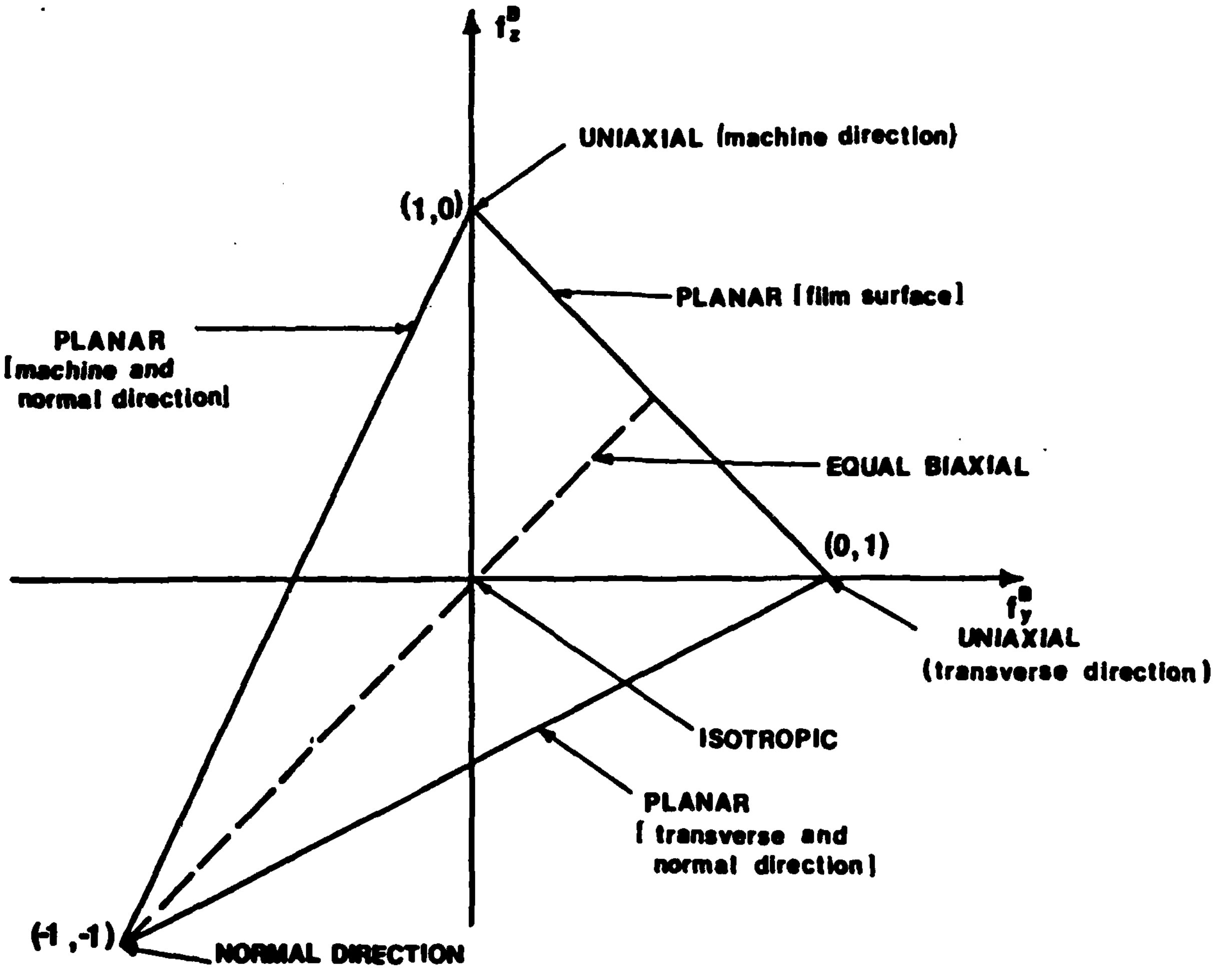


FIGURE 2. WHITE AND SPRUIELL'S ORIENTATION TRIANGLE.

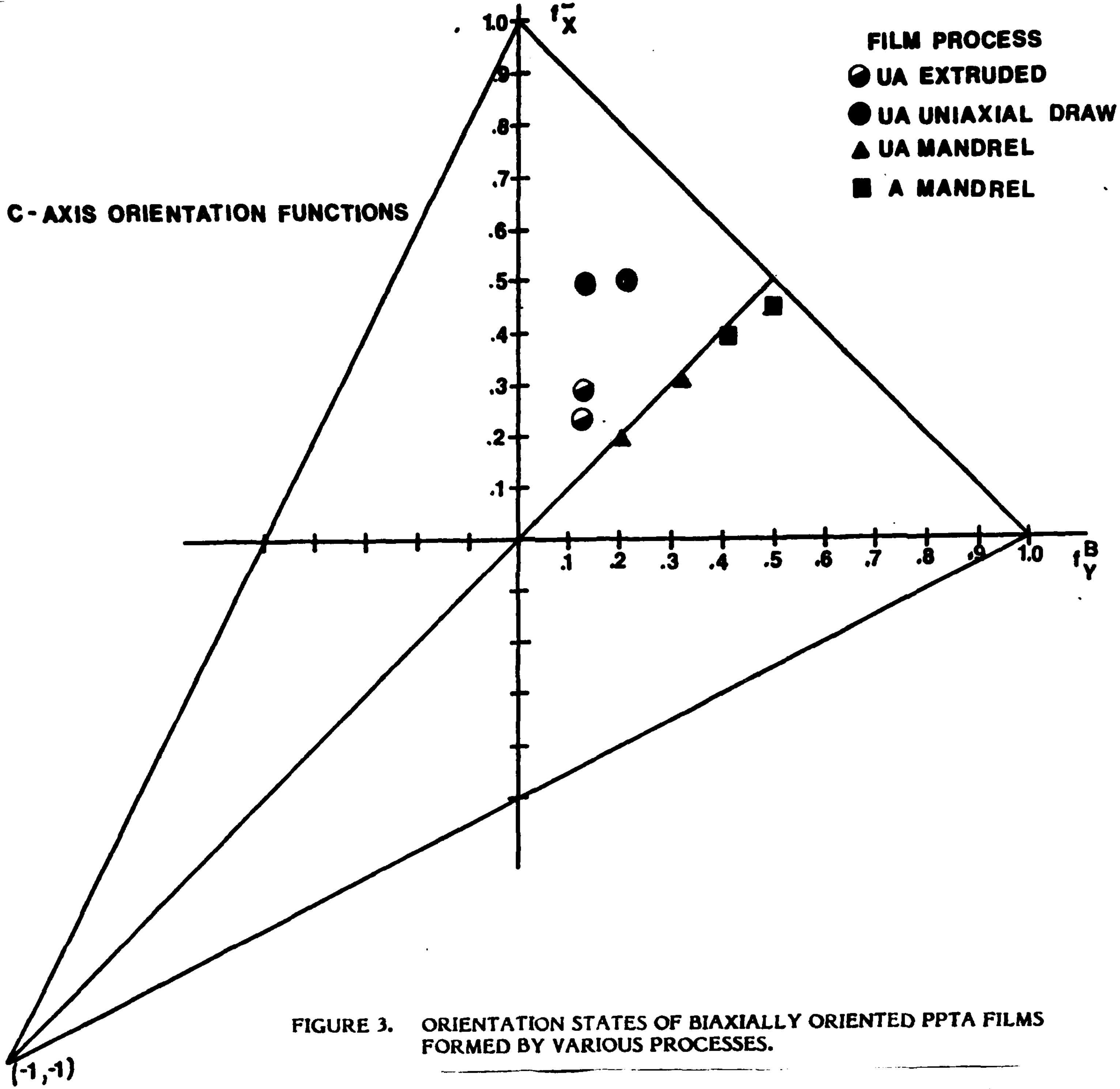


FIGURE 3. ORIENTATION STATES OF BIAXIALLY ORIENTED PPTA FILMS FORMED BY VARIOUS PROCESSES.

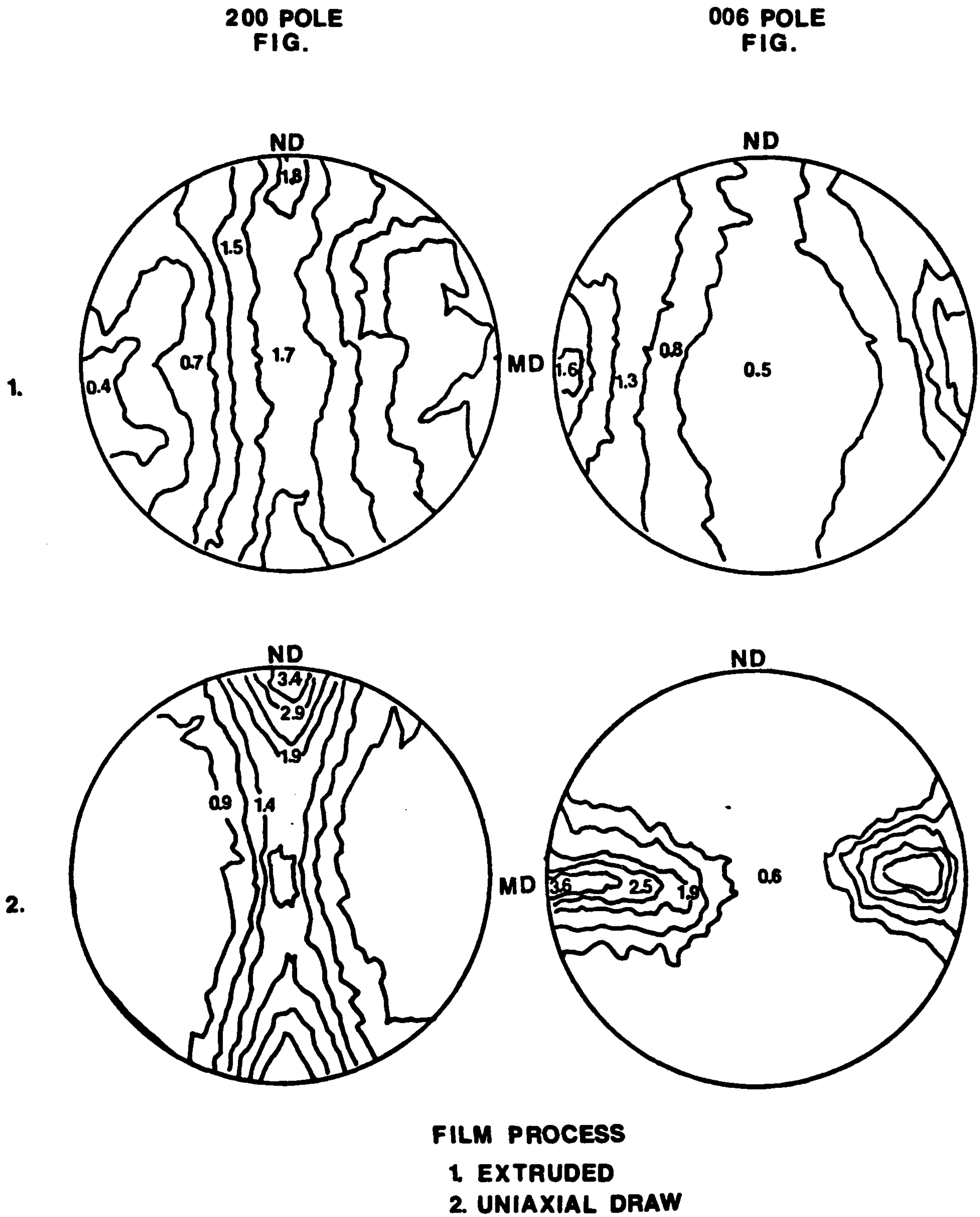


FIGURE 4. 200 and 006 Pole Figures for Extruded and Uniaxially Drawn Film

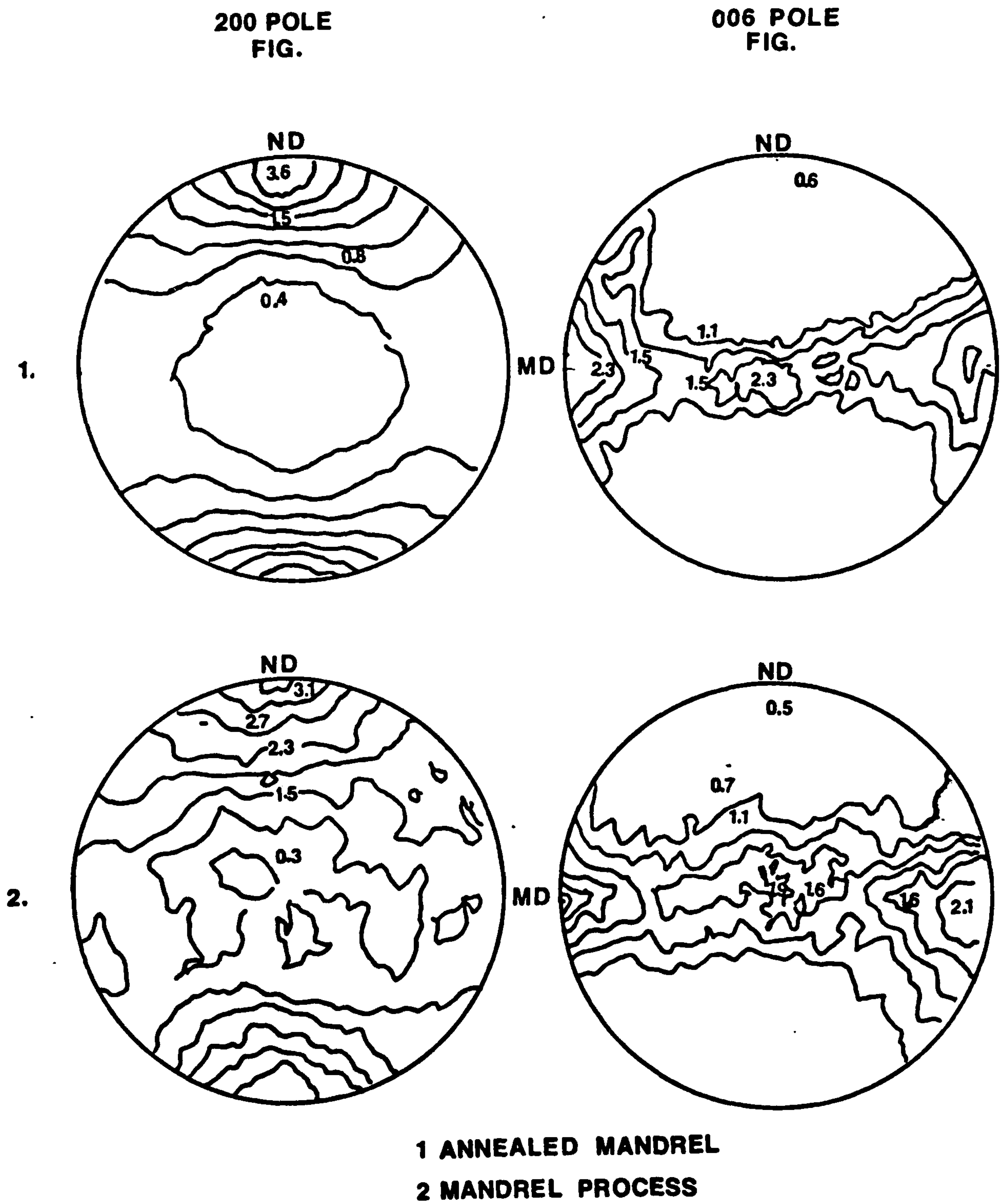


FIGURE 5. 200 and 006 Pole Figures for Mandrel Processed Films Annealed and Unannealed

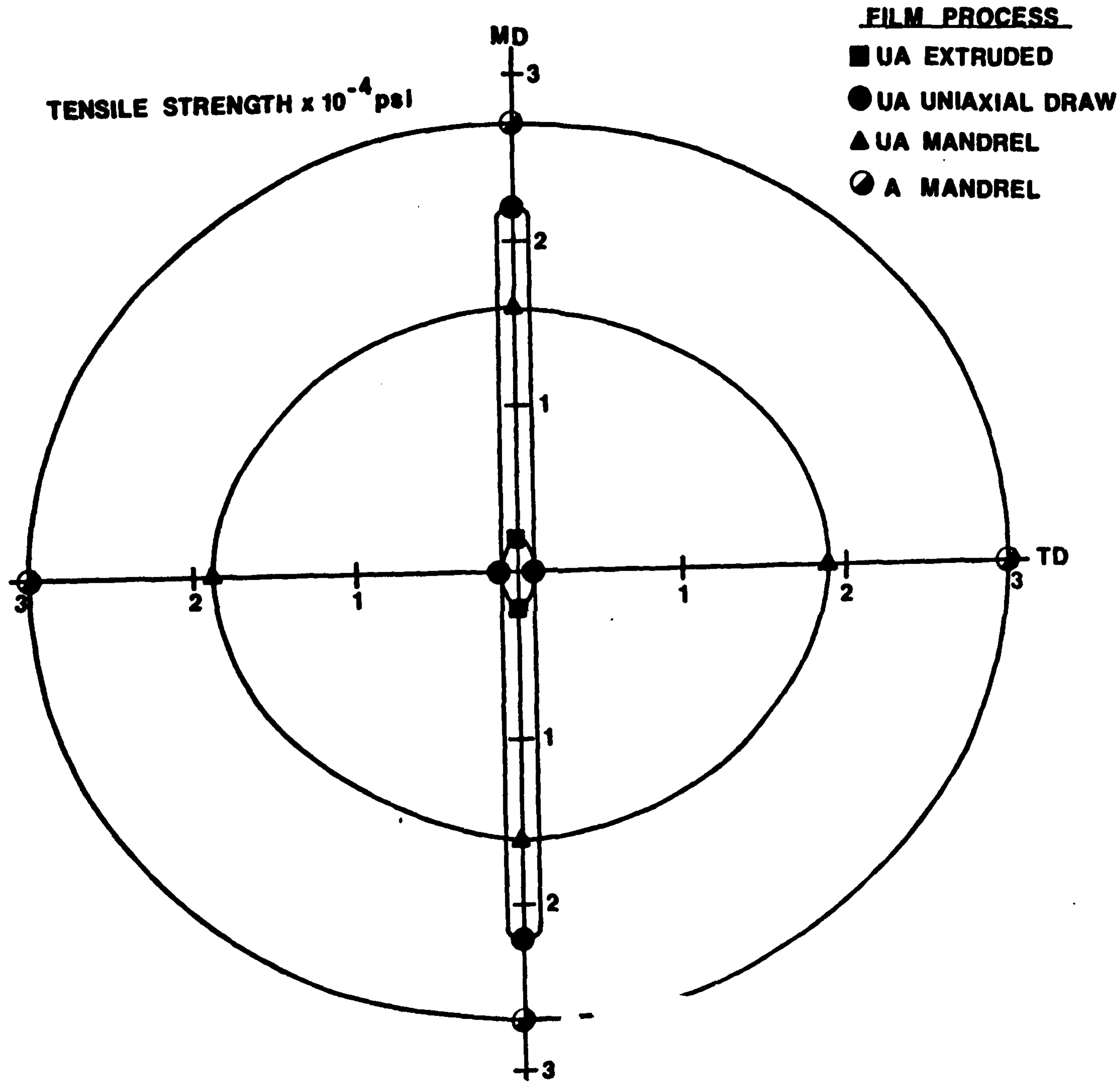


FIGURE 6. A PLOT OF TENSILE STRENGTH AS A FUNCTION OF FILM DIRECTION FOR EXTRUDED, UNIAXIALLY DRAWN AND MANDREL PROCESSED FILM.

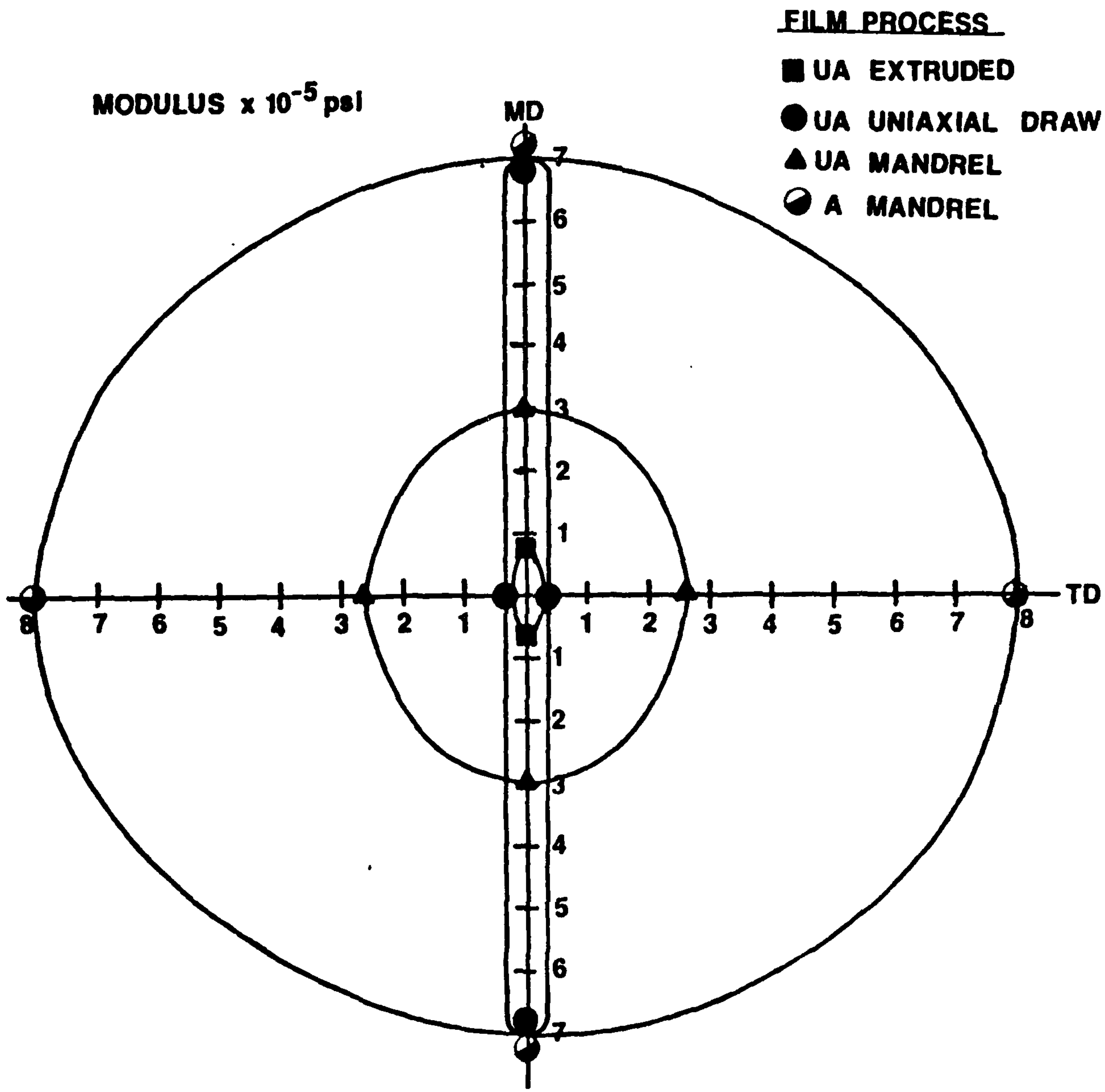


FIGURE 7. A PLOT OF INITIAL MODULUS AS A FUNCTION OF FILM DIRECTION FOR EXTRUDED, UNIAXIALLY DRAWN AND MANDREL PROCESSED FILM.

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