

PHASE SEPARATION SPINNING OF POROUS POLYPROPYLENE HOLLOW FIBERS

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I. INTRODUCTION

In 1967 Moshe M. Zwick reported on a novel fiber spinning technique called phase separation spinning. The idea was based upon the fact that polymer-solvent systems exist such that homogeneous solutions formed above a certain temperature will separate into two phases when cooled below this temperature. The two phases formed are a polymer phase consisting of either pure polymer or concentrated polymer gel, and a solvent phase consisting of pure solvent or solvent mixture⁽¹⁾. The purpose of the investigation was to test the feasibility of an alternate spinning method for polymers which cannot be melt spun without degradation or for which other spinning methods cause problems. This method also allows for high spinning speeds in the same range as those used for melt and gel extrusion spinning.

Zwick's main objective was to survey polymer-solvent systems to determine those that would spin under phase separation conditions. He did not correlate the properties of any one system over a wide range of spinning conditions. Subsequent studies by Williams⁽²⁾ and Andrade⁽⁴⁾ have concentrated on the properties of polypropylene fibers spun by the phase separation technique in which naphthalene was used as the solvent. In this system the polypropylene first separates from the liquid naphthalene upon spinning; the naphthalene then solidifies before reaching the windup unit. The naphthalene is subsequently extracted from the fiber by diethyl or petroleum ether.

In his discussion of results Williams suggested that the spun fibers had a fine porous structure after the naphthalene had been extracted. Andrade later partially confirmed this by calculating the void fraction of the fibers from denier and diameter data. This possibility opens a whole new area of potential for phase separation spinning. In recent years much work has been devoted to the development of hollow-fiber membrane technology. Several chemical companies have commercialized hollow fiber membrane separations units for different applications such as reverse-osmosis, dialysis, and ultrafiltration. Assuming that the phase separation technique can be used to spin hollow fibers and that the resulting hollow fibers are porous, two ideas come to mind that seem worth exploring:

- 1) The use of the resulting porous hollow fibers in separations units. If it is found that the pore size distribution can be controlled by adjusting the spinning conditions then it is conceivable that one polymer-solvent system could be used to design hollow fiber membrane separations units for varied specific applications and processes.
- 2) The use of the porous hollow fiber as a support for ultrathin semipermeable membranes. When solvents are used in the spinning solution that are solid at room temperature it may be possible to spin the hollow fiber, coat it with a thin semipermeable membrane, and then extract the

solid solvent with an agent that would act as a nonsolvent to the polymer and semipermeable membrane. This would eliminate the problem of the membrane solution flowing into the pores of the support during the coating process. This system also has the advantage of allowing porous supports and the membranes to be independently optimized and combined for specific applications.

This investigation is the beginning of a series of studies with the long term goal of exploring the feasibility and developing the idea of using phase separation spun hollow fibers in membrane separations applications. The immediate objective is to develop techniques for spinning and characterization of phase separation spun hollow fibers and to develop recommendations for future work.

II. LITERATURE REVIEW

The literature was reviewed with the aim not only of collecting information pertinent to the immediate goals of this study but also of collecting and evaluating information that could be helpful in the continuing effort of developing hollow fibers by separation spinning. Since review of the work and ideas of others in the field will be important to subsequent workers, the literature concerning manufacture, evaluation, testing, and applications of products similar to those expected from phase separation spun hollow fibers are cited and discussed.

Phase Separation Spinning

Phase separation spinning is a form of solution spinning as are dry and wet spinning. In phase separation spinning the polymer-solvent system is chosen so that between the temperature of the solution as it leaves the spinneret and its temperature at the wind-up the solution separates into two phases: a polymer or polymer gel phase and a solvent phase. Even though it could be argued that phase separation or precipitation occurs in wet spinning and possibly some examples of dry spinning, the difference is that in wet spinning and dry spinning the separation of the polymer phase is due to removal of the solvent either by evaporation or extraction. In phase separation spinning the solvents are either relatively nonvolatile liquids or solids whose freezing points lie between the phase separation temperature and ambient temperature. Therefore, the solvents

or cosolvents remain in the fiber after windup to be extracted later in the process. Zwick examined six polymers in polymer-solvent systems that included combinations of twenty-three solvents or solvent mixtures. The polymer-solvent system he used are listed in Table I. He divided these systems into eight subgroups according to the mechanism of phase separation. The six most important are:

A. Single solvent systems.

- 1) Separation occurs so near the freezing point of the solvent that simultaneous solidification of the polymer and the solvent phases results.
- 2) Separation occurs at a temperature that lies between the initial temperature of the spinning solution and the freezing point of the solvent. The solvent freezing point is above ambient temperature.
- 3) The solvent is a liquid at room temperature. Phase separation takes place at a temperature between that of the spinneret and that of the surroundings.

B. Systems in which there are two-component solvent mixtures, usually consisting of a good solvent and either a poorer solvent or a nonsolvent.

- 4) The two solvents are only partially miscible and their miscibility is strongly temperature dependent. Some of the poorer

TABLE I

Phase Separation Systems Studied by Zwick⁽¹⁾

Subgroup	Polymer	Solvent 1	Solvent 2
1	Poly (vinyl alcohol)	Benzene sulfonamide	---
	Poly (vinyl alcohol)	Toluene sulfonamide	---
	Poly (vinyl alcohol)	Caprolactam	---
	Poly (vinyl alcohol)	Trimethylol propane	---
	Polystyrene	Naphthalene	---
	Polypropylene	p-Dichlorobenzene	---
2	Polypropylene	Naphthalene	---
	Polypropylene	Stearic Acid	---
	Polypropylene	Paraffin Wax	---
	Polyethylene	Naphthalene	---
	Polyacrylonitrile	Caprolactam	---
4	Poly (vinyl alcohol)	Water	Urea
	Poly (vinyl alcohol)	Water	Thiourea
	Poly (vinyl alcohol)	Dimethylsulfoxide	Pentaerithritol
	Poly (vinyl chloride)	Cyclohexanone	Caprolactam
	Polyacrylonitrile	Dimethyl formamide	Dimethyl sulfone
5	Polypropylene	Naphthalene	Stearic Acid
	Polypropylene	Naphthalene	Paraffin wax
	Polyethylene	Naphthalene	Sulfur
	Polyethylene	Naphthalene	Stearic Acid
6	Polyacrylonitrile	Dimethyl sulfoxide	MgCl ₂ ·6H ₂ O
	Polyacrylonitrile	Dimethyl sulfoxide	Urea
	Polyacrylonitrile	Dimethyl formamide	Urea

solvent separates as a liquid or solid as the filament cools, concentrating the polymer in the remaining solvent mixture.

- 5) The polymer separates from the solvent mixture which later solidifies.
- 6) The polymer separates from the solvent mixture in the form of a swollen gel. The solvent mixture remains a liquid at ambient temperature.

Zwick speculated that each of these subgroups would impart specific properties to the resulting fiber as to fine structure, molecular orientation, percentage crystallinity, and surface texture.

Zwick limited his objectives to identifying polymer-solvent systems that would spin under phase separation conditions and to determining the conditions for what he considered to be optimum spinnability. His definition of optimum spinnability was the conditions by which a polymer-solvent system could be spun that allowed the highest winding speed without breaking the fiber during one minute of operation. The most significant variable was polymer concentration, which he limited to a range of between 10 to 25 weight percent for all systems. Some of the physical properties of the final fiber product were determined for selected systems spun at "optimum" conditions. However, no correlations of fiber properties versus spinning conditions were attempted.

In 1970 Williams and Fricke⁽²⁾ began a study aimed at investigating properties of fiber made from the polypropylene-naphthalene

system in more detail than Zwick. Fiber denier, tenacity, elongation at break, and modulus were correlated against spin draw ratio (the ratio of fiber windup velocity and the average velocity of the solution filament as it leaves the spinneret) using solution temperature and composition as parameters. The temperature and composition values chosen for the experiments were the four combinations of 145°C and 160°C; 15% and 22% polymer concentration.

One of William's conclusions was that it was highly probable that the fibers spun in his experiments had a fine porous structure. The main basis for this conclusion was the high rate by which the solid naphthalene could be extracted from the fiber with diethyl ether. It took less than one minute to extract essentially all the naphthalene. Other results that lead to this conclusion were rough surfaces of the fibers as observed through an optical microscope and the relative low deniers of the fiber samples.

Between 1971 and 1972 Andrade and Fricke⁽⁴⁾ explored more concentrated polypropylene-naphthalene spinning solutions (25-60 wt % polypropylene). They expanded the investigation to include fiber diameter and void fraction measurements as well as the tensile strength and denier measurements made by Williams. Also included were the relationship of polypropylene solubility temperature as a function of concentration in naphthalene, confirmation of the extremely fast naphthalene extraction rates reported by Williams, and void fraction as a function of spinning solution concentration and temperature. The spinning solution temperatures were varied

between 0 and 20°C above the minimum solubility temperature for each solution.

Figure 1 shows the general relationship of void fractions versus polymer concentration that Andrade found. He also concluded that void fraction was relatively independent of spinning draw ratio and that it decreased as spinning temperatures neared the solubility temperature of the spinning solution.

Based on the results he obtained from his void fraction and solvent extraction rate measurements Andrade joined Williams in concluding the fibers must have a fine porous structure. He suggested that the pore structure should be measured more directly and the effects of spinning conditions and fiber finishing treatments on porosity should be studied.

Several "phase separation" systems have been used in the spinning of regenerated cellulose or cellulose acetate hollow fiber membranes. In one process⁽⁶⁾ the spinning dope consists of between 10 and 40% cellulose acetate in triethylene glycol and methyl carbitol. At temperatures between 100 and 150°C the solution is a homogeneous melt but gels near 90°C. The spinning solution is extruded through an annular spinneret into a gelation bath. After the solvents have been extracted the water content of the fibers can be as high as 65-70%, indicating that the fiber possesses a highly porous structure. In an effort to develop hollow fiber reverse-osmosis membranes with optimum salt rejection and water flux qualities and ability to operate under higher pressures another cellulose

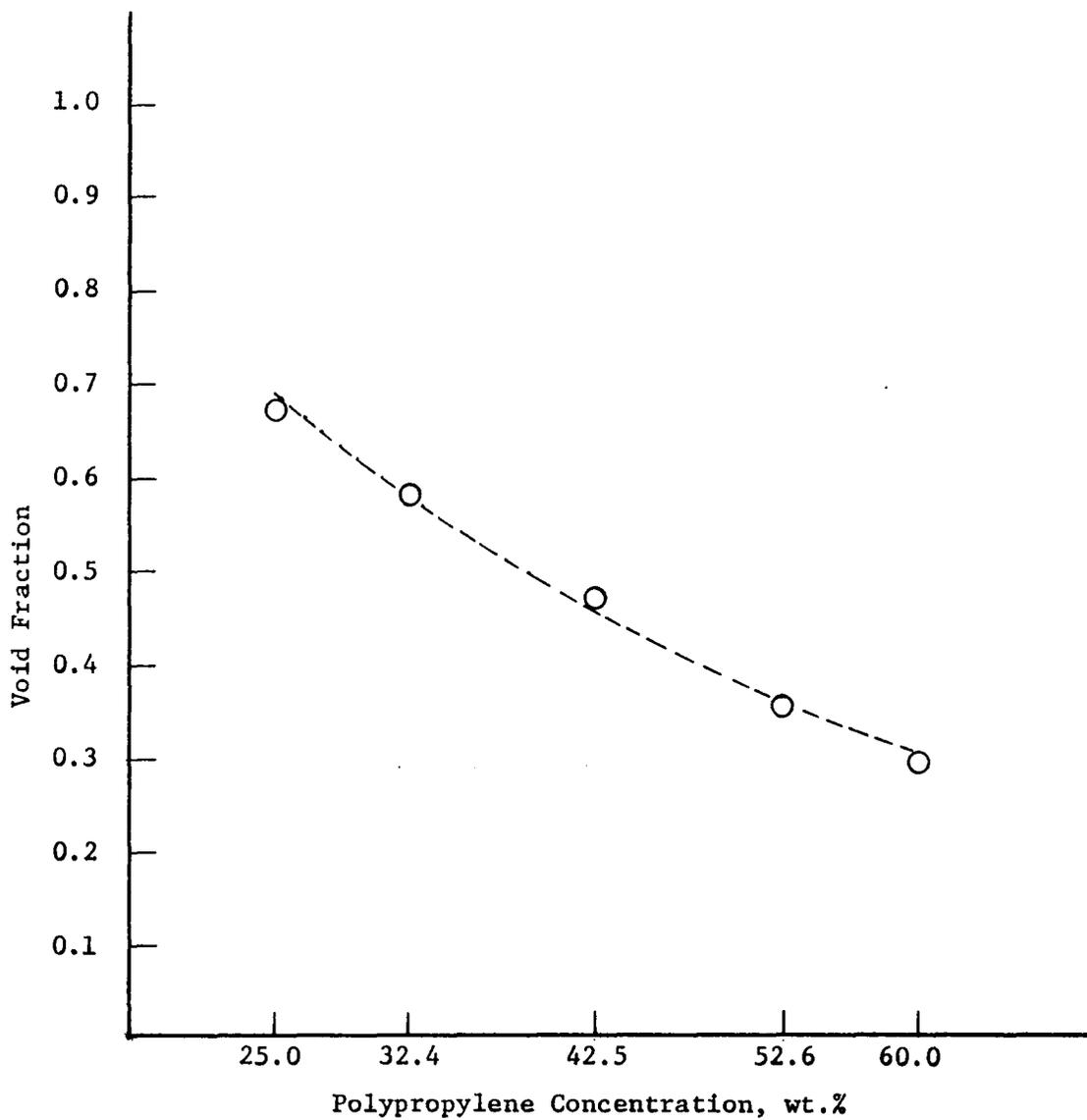


Figure 1. Effect of Concentration on Fiber Void Fraction Observed by Andrade⁽⁴⁾

acetate phase separation system was studied^(7,13). The solution consisted of 50-60% cellulose acetate, 20-30% dimethylphthalate, and 20% glycerol. In this system dimethylphthalate is a good solvent that acts as a plasticizer and glycerol, the poor solvent, causes the phase separation. It was found that the manner with which the solvents were extracted from the fibers had a significant effect on the water flux and rejection properties of the fibers during reverse osmosis tests. The best procedure was to extract the solvents in a dimethyl formamide-water solution and to keep the fiber wet until use. The fibers resulting from this spinning and finishing procedure had a water flux approximately ten times greater than fibers spun in a cellulose acetate-dimethylphthalate plasticized "gel extrusion" system, indicating a higher porosity due to the phase separation mechanism. It was also found that the dispersion of the two phases could be made finer by spinning the solution through a heated chimney (up to 300°C) and immediately into an organic quench bath held at room temperature.

Since the salt rejection performance of other polymer systems and fiber spinning techniques studied proved more promising, the work on phase separation spinning was discontinued. However the author concluded with the statement that "...it is worth pointing out that the techniques developed for inducing porosity could have application with other polymer systems".

Hollow Fiber Spinning and Membrane Systems

Several chemical companies have developed hollow fiber membrane systems and are trying to cultivate a profitable market for them. Dow Chemical Company has been marketing hollow fiber devices mainly for use in the laboratory for separations that could be accomplished by ultrafiltration, dialysis, gas permeation, etc^(14,15). The most important devices manufactured by Dow are hollow fiber hemodialysis units or "artificial kidneys". The Dow fibers are made from cellulose acetates and regenerated cellulose.

Of the commercially available hollow fiber devices du Pont's systems have been applied to the widest industrial use. A du Pont system containing polyester hollow fibers is used to remove hydrogen from process gas streams⁽¹⁶⁾. Also, du Pont's hollow fiber reverse-osmosis systems are finding wide use in municipal and industrial water treatment facilities⁽¹⁷⁾.

Much of the research dealing with reverse-osmosis membranes systems has been supported by the U.S. Department of Interior, Office of Saline Water. One of the major accomplishments realized under this program was the development of asymmetric hollow fibers analogous to the Loeb-type membrane⁽¹⁸⁾. Monsanto, under contract to the Office of Saline Water, was able to produce cellulose acetate hollow fibers whose outside surface contained a skin of dense polymer no more than several microns thick⁽⁸⁾. The rest of the fiber wall consisted of an integral microporous support structure. The fibers were spun from a solution of 30% cellulose acetate in a 60:40 acetone-

formamide mixed solvent. The method of spinning was called "dry jet-wet spinning" by the author. It entails extruding the spinning dope through an annular spinneret into a temperature controlled chimney that retards the evaporation of the acetone. There is a gap of one-half to three inches between the bottom of the chimney and the surface of the coagulation bath. Enough acetone evaporates when the fiber passes through this gap to form the dense outer skin. The coagulation bath was usually water at 0°C. The fast quenching and extraction that took place in the coagulation bath caused the formation of the microporous support structure.

Du Pont's hollow fiber reverse-osmosis membranes are also asymmetric, having a dense outer skin about 0.1 micron thick. However, the polymer used is an aromatic polyamide. It is spun by a technique similar to the dry jet-wet spinning procedure. The spinning solution consists of polymer and dimethyl acetamide. The quench bath is again water^(17,19).

Applying Semipermeable Membranes to Porous Supports

Since the development of the Loeb-Sourirajan membrane, attempts have been made to produce asymmetric composite membranes. The idea would increase the versatility of the asymmetric membrane concept by allowing the dense outer skin and porous support to consist of separate polymers.

Since resistance to mass transfer is almost entirely attributable to the dense skin layer, it is desirable to make this layer as

thin as possible. Two of the methods that have been most successful for the fabrication of thin dense membranes are: surface casting a solution (.5-25% polymer) on water^(17,19), and dip-coating smooth surfaces (usually glass) with a dilute polymer solution^(22,23). Membranes having thickness in the range of 1500-2500Å can be prepared by the former method by pouring, for example, a cellulose acetate-cyclohexane solution on the surface of a tank of water. The solution spontaneously spreads across the water due to surface effects. The solvent evaporates leaving the thin cellulose acetate membrane. By the latter technique (The Carnell-Cassidy method) membranes 300-1500Å were prepared by dipping clean glass slides into polymer solutions of concentrations in the range of one weight percent polymer. The slide was then withdrawn from the solutions at a controlled rate; the draining and solvent evaporation rates affecting final membrane thickness. The edges of the slide were scored and the slide was immersed in water where the membrane would separate from it. In both procedures the membranes could be transferred onto porous supports after formation.

Neither of the above methods is amenable to continuous production or to the geometry of a fiber surface. The most promising procedure for applying thin membranes to porous hollow fibers is that of Riley and Lonsdale⁽²⁴⁾. This method is similar to the Carnell-Cassidy technique, except that the intermediate step of removing the membrane from the glass plate and reattaching it to a porous support has been eliminated. Instead, the membrane solution

is cast directly onto the porous support. In their study they dip coated and surface cast Millipore VFWP filters in cellulose triacetate-chloroform solutions of polymer concentrations of 0.04 to 1.37 weight percent. One problem they encountered was the intrusion of the membrane dope into the pores of the filter, thereby increasing the effective thickness of the final membrane. This problem was solved by coating the surface of the support with water leachable polyacrylic acid, which is insoluble in chloroform. In subsequent work by the same authors cellulose triacetate membranes as thin as 400\AA were deposited on porous cellulose nitrate-cellulose acetate support membranes by the same dip-coating method as used with the Millipore filter supports⁽²⁵⁾.

This technique could easily be modified for coating porous hollow fibers. It may even be possible to devise a scheme by which the hollow fiber supports could be coated by the membrane material in a continuous operation integrated with the fiber spinning process. The thickness of the dense membrane skin could be controlled by adjustment of such process variables as fiber travel speed, fiber dwell time in the membrane solution tank, temperatures of the solution tank, and ambient conditions above the tank. In the context of the phase separation spinning technique emphasized in this study, it may be possible to send the fiber directly from spinning to the membrane coating tank. The non-volatile spinning solvent could then possibly be extracted with a solvent that would not affect either the membrane or the polypropylene support fiber.

With the high spinning solvent extraction rates reported by Williams and Andrade, it is worth exploring this supposition. If this proves impossible, then perhaps a substance analogous to the polyacrylic acid in the Riley-Lonsdale method could be used to fill the pores in the support fiber prior to coating in the membrane dope tank.

Fiber Characterization

Pore Size Distribution. One of the simplest methods of measuring pore size distribution of a material is by mercury intrusion porosimetry. The technique is based on the fact that a liquid that does not wet a solid's surface (i.e., a liquid that exhibits an angle of contact with a solid surface of greater than 90°), will not penetrate into the solid's pores unless pressure is applied. If it is assumed that the pores possess a cylindrical geometry, the force pulling the nonwetting liquid out of a pore is

$$-\pi d \sigma \cos \theta$$

where πd is the perimeter of the pore of diameter, d , σ is the surface tension of the liquid, and θ is the contact angle of the liquid with the solid surface. The liquid will remain in the pore only if an external pressure, P , is applied so that the force, $\frac{\pi d^2}{4} P$, is equal to or greater than the force tending to pull the liquid out. Therefore, the relationship of minimum applied pressure to cause a nonwetting liquid to penetrate into a pore of diameter, d ,

can be simplified to

$$P = - \frac{4\sigma\cos\theta}{d} . \quad (1)$$

The surface tension of mercury is 474 dynes per centimeters at 25°C. A value for the contact angle of mercury on polypropylene could not be found. However, a good approximation would be the contact angle of mercury on polyethylene, which is about 145°⁽²⁶⁾. Therefore, for mercury intruding into porous polypropylene equation (1) can be written empirically as

$$d \approx \frac{223}{P} \quad (2)$$

where d is the pore diameter in microns and P is the applied pressure in pounds per square inch, absolute.

A mercury intrusion porosimeter measures the change in volume of the system for given changes in applied pressure caused by mercury penetrating into a porous solid. Therefore, by increasing the pressure at discrete increments and measuring the corresponding volume of mercury that has penetrated into the pores, curves such as those in Figure 5 are obtained. It can be shown that

$$D(d) = \frac{2P}{d} \frac{dV}{dP} \quad (3)$$

where $D(d)$ is the pore size distribution function and dV/dP is the slope of the pressure-volume curve at any pressure, P . $D(d)$ indicates the relative volume contributions of the pores as a

function of diameter. $D(d)$ can be directly related to the numerical pore distribution by assuming a pore geometry. Therefore, $D(d)$ also serves as an indicator of the relative numerical contributions of the pores.) Therefore, the pore size distribution can be obtained by graphically differentiating the pressure-volume curve at selected values of P , and solving equation (3) for $D(d)$ (27,28).

Two sources of error should be mentioned in relation to measuring the pore size distribution of porous polypropylene hollow fibers. First, the pores are assumed to be cylindrical, which is probably far from the truth. However, the order of magnitude of the calculated effective diameters and the shape of the distribution curve should be a good indication of relative pore size contributions. The other source of error is the compressibility of a porous polymer. No simple way to compensate for the compression of a porous structure could be found. It is not only a function of the compressibility of the bulk polymer, but is also a function of the structure and distribution of the unpenetrated pores. Again, it will be assumed that calculated values will give good indications of relative pore sizes without compensating for compressibility.

Scanning Electron Microscopy. The most direct means of studying the structure of a hollow fiber is by observation under a microscope. The scanning electron microscope (SEM) offers certain advantages over the optical microscope. Its greater resolution

permits greater magnification and sharper images. Also, the much greater depth of field perception possible with a scanning electron microscope permits a more direct interpretation of the images.

There are also some disadvantages inherent in the use of the SEM, especially when observing polymeric materials. The SEM is analogous to a reflected light optical microscope and thus "sees" only the surface structure of a substance. The high energy of the image producing electron beam can fuse polymer materials if allowed to stay in one spot too long, altering the original surface of the specimen.

As with optical microscopy, there are some problems related with preparation of specimens for SEM observation. It is required that the surface of a specimen be electrically conductive. If a nonconductor such as polypropylene is not coated with a conductive material the surface will "charge", causing the image to be disturbed. There are various conductive materials, such as carbon or gold-palladium alloys, that can be used to coat the surface of a specimen by vapor phase deposition. In preparation of the polymer specimen, questions have to be answered as to which coating material or procedure will produce the most conductive surface with the least possibility of altering the specimen surface structure.

If the internal wall structure of a polymeric hollow fiber is to be observed then a method must be found for sectioning the fiber perpendicular to its axis while preserving the integrity of

the wall structure. For polymers that become brittle in liquid nitrogen the fiber sectioning could be carried out by immersing the fiber and breaking it. Another method involves embedding the fiber in epoxy resin blocks and sectioning the blocks with an ultramicrotome⁽⁹⁾. The embedding and sectioning procedure must be designed so that the original wall structure remains observable.

Interpretation of Stress-Strain Behavior. Reverse-osmosis operations occur at relatively high pressures. Therefore hollow fibers intended for use in reverse-osmosis applications must be able to resist mechanical failure. Physical properties of the hollow fiber derived from stress-strain behavior can be used to predict the pressure a fiber of given dimensions can stand before it collapses. If elastic collapse is assumed to be the mechanism of failure then the elastic modulus of the fiber is the significant property. If plastic failure or progressive yield is assumed, then the yield stress is important. Progressive yield or compaction usually begins to occur at pressures lower than those that would cause elastic or plastic collapse⁽¹⁰⁾.

Test Cell Design. The ultimate method of testing hollow fibers for permeability characteristics and pressure resistance is to install them in a cell and test them directly. A good design for a hollow fiber test cell for external pressure application is analogous to the design of a U-tube and shell type heat exchanger⁽¹¹⁾.

The major problem encountered in this design is the potting of the hollow fibers in an epoxy resin "tubesheet" so that the fiber capillaries are not blocked with resin, and that the adhesion of the epoxy to the fibers and the body of the test cell is strong enough to prevent leakage or blow-out.

III. EXPERIMENTAL

Plan of Experimentation

The original plan of this investigation was to study the feasibility of depositing thin membranes on the surface of unextracted polypropylene hollow fibers spun by the phase separation technique. It was assumed that spinning the hollow fibers would be relatively easy and only incidental to the overall objective. However, problems were encountered in the initial spinning attempts. It was therefore decided to devote the entire study to hollow fiber spinning. The final form of the plan of experimentation is presented below.

Literature Review. The literature reviewed in preparation for this investigation included the following subjects:

- 1) phase separation spinning
- 2) hollow fiber spinning
- 3) membrane technology
- 4) ultrathin membranes
- 5) hollow fiber membranes
- 6) polyolefin membranes
- 7) polypropylene
- 8) mercury intrusion porosimetry

Spinning Equipment. The spinning equipment used was designed by Williams⁽³⁾ and built by the Chemical Engineering shop of Virginia Polytechnic Institute and State University. It consists of a temperature controlled piston-type batch extruder mounted directly

above variable speed windup mechanisms (see Figure 2 for schematic drawing). Some slight modifications to the original design were made during this study. These changes will be discussed in the appendix.

A "tube-in-orifice" spinneret design was used. A schematic drawing of the spinneret is given in Figure 7 in the appendix.

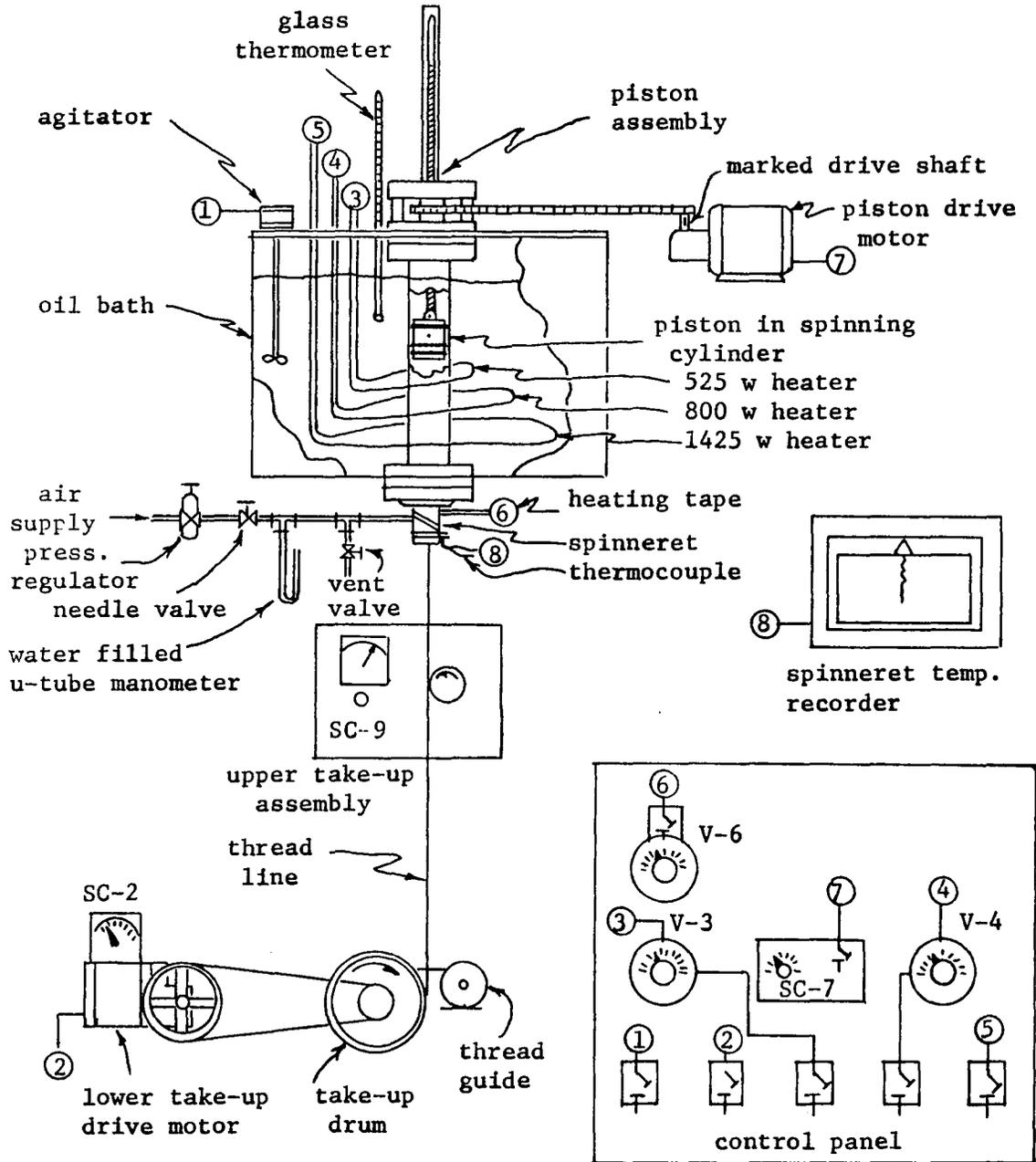
Polymer Systems. Two polymer-solvent systems were used in the spinning trials. The polymer in each system was polypropylene. Paraffin wax was used as the solvent in one system and naphthalene was used in the other. The majority of trials were made using the polypropylene-naphthalene system.

Spinning Conditions. The variables controlled during the spinning trials were:

- 1) spinning solution concentration
- 2) spinning solution temperature
- 3) spinneret temperature
- 4) pressure of air injected through the tube of the spinneret
- 5) draw ratio.

The polymer concentration was determined prior to each trial. After the solution had been prepared and transferred to the spinning cylinder a spinning trial was conducted and samples were collected for various settings of the other variables.

The variables were not changed according to any predetermined schedule but were varied during the spinning operation in such a way



KEY

SC - speed controls
 V - variable transformers
 Circled number represent electrical connections

Figure 2. Schematic Diagram of Spinning Apparatus

as to promote the formation of uniform hollow fibers.

Fiber Measurements. The outside and inside diameters of fiber samples were measured. Weight and length measurements were made for fiber samples containing continuous capillaries in order to determine denier, fiber density, and void fraction.

Examination of fiber samples were made using optical and electron scanning microscopes in an attempt to determine directly the structure and size ranges of the fiber pores. Pore size distribution were measured for selected samples using a mercury intrusion porosimeter.

Procedures

Polymer Solution Preparation. For most spinning trials, the apparatus used to melt and dissolve the polymer solution components consisted of a stainless steel or glass cylindrical, 1000 milliliter resin flask inserted into a heating mantle. A four-necked head was clamped to the flask. A heating tape and fiber-glass insulation tape were wrapped around the head. The heating mantle and heating tape were connected to variable transformers. A laboratory stirrer was installed in the flask and the stirrer motor supported by a ring stand. The stirrer was connected to a variable transformer for speed control.

The solvent was weighed (usually 500 grams) and poured into the resin flask. The heating mantle and tape were turned on to melt the solvent (the maximum voltage supplied to the heating mantle and

tape was 60 volts). After the solvent had become fluid the stirrer motor was started and adjusted to a slow speed. Once the heat was turned on the flask head was kept sealed with glass stoppers except during polymer addition. The powdered polypropylene was weighed and slowly added to the flask after the solvent had completely melted. As the polymer was added and the solution became more viscous, the temperature of the solution and the voltage supplied to the stirrer motor were slowly increased. The temperature was usually between 160 and 180°C when the polymer had become entirely dissolved. The solution was stirred for one-half to one hour at this temperature to assure homogeneity. Then the agitator was turned off and the solution was left for about an hour to allow air bubbles to escape.

Spinning Apparatus Preparation and Solution Charging. (Refer to Figure 2). While the polymer solution was being mixed, the spinning apparatus was also prepared for the trial. The spinneret assembly was wrapped with a silicone rubber heating tape in between two layers of asbestos insulation tape. The assembly was then bolted to the spinneret receiver flange beneath the oil bath and the air supply, thermocouple leads, and heating tape connected. All three oil bath heating elements and the agitator motor were turned on to bring the oil bath to operating temperature (usually between 140 and 170°C). Also, the spinneret heating tape was turned on and the spinneret heated to a temperature usually about five degrees below the oil bath operating temperature. The oil bath temperature was measured with a three inch immersion glass thermometer. The spinneret

temperature was measured with an iron-constantan thermocouple soldered to the side of the spinneret and connected to a calibrated temperature strip chart recorder. When the oil bath reached the desired temperature, the start-up heater was turned off, the 525 watt heater controlled by Variac V-3, was set at 100 volts, and the Variac to the 800 watt heater (V-4) was used to control the temperature. The spinneret temperature was controlled by adjustment of V-6.

Small strips of aluminum foil which had been rolled around a hypodermic needle the same size as the spinneret tube were used as plugs for the spinneret.

When the spinning solution and apparatus were ready for charging, the heaters and the agitator motor to the solution flask were turned off and disconnected. As quickly as possible the solution flask was carried to the spinning apparatus and the solution was poured directly into the spinning cylinder until it was completely full. A clean glass rod was partially immersed into the cylinder and withdrawn to remove enough solution to lower the level about one and a half inches. This was done because the solution level could not be seen during charging until it had reached the top of the spinning cylinder.

The electrical power to the spinning apparatus was disconnected during the piston installation for safety. The piston was inserted into the spinning cylinder and the piston assembly was lowered onto the bolts connected to the top of the spinning cylinder. If the piston assembly could not be lowered completely in place because of

too much solution in the cylinder, the aluminum foil plug was removed from the spinneret and force applied to the assembly to extrude the excess solution. Once the piston assembly was completely in place, it was bolted and the drive chain installed to the motor drive sprocket. A copper tubing brace was placed between the piston assembly and the apparatus framework to hold the assembly upright during operation. Once the installation procedure was completed, the electrical power was again turned on.

An aluminum foil plug was inserted into the spinneret orifice and the oil bath temperature was held constant for at least 45 minutes to allow the system to reach thermal equilibrium.

Spinning Procedure. The spinneret plug was removed, the piston drive motor was turned on, and set to drive the piston downward. A cardboard sheet was held under the spinneret to catch the exiting polymer solution. The air pressure regulator was cracked slightly open and the needle valve opened to allow air to be injected through the tube of the spinneret. By adjusting the air pressure with the needle valve to several inches of water and observing the polymer filament, it was possible to determine whether the air injection tube was blocked. If it was blocked the piston drive motor was turned off, the spinneret face wiped and a 0.008 inch diameter steel wire was reamed through the air tube. Once it was determined that the spinning dope and air were flowing uniformly, the piston drive motor was set at its operating speed. This was done by marking the piston motor drive shaft and timing one revolution of the shaft. The oper-

ating speed was usually set as near to 25 seconds per revolution as possible. A cardboard spindle was placed on the lower take-up drum and the drum drive motor was turned on. The filament was wound around the drum by hand until it began to take up. The filament was then inserted into the thread guide loop and the guide was turned on. The speed of the drum was measured with a hand tachometer and adjusted with the speed control SC-2. The drum was adjusted to the minimum take-up speed, i.e., the speed at which there was excessive slack in the thread line. The take-up speed was then increased slightly and the spinneret air supply line was vented to the atmosphere. The cardboard spindle was replaced by another by breaking the thread line, exchanging the spindles, and rewinding the filament around the drum. A sample of fiber was then taken for later polymer concentration measurements. Each time a sample was taken, the spindle was replaced with a new one. All samples were marked and placed in large polyethylene bags. The bags were sealed with tie wires. After a sample was taken with the air injection tube vented, the vent valve was closed and the needle valve adjusted to an air pressure of about 0.2 inches of water. Subsequent samples were taken at air pressure increments of about 0.2 inches of water. The maximum pressure was determined when the hollow filament began intermittent "ballooning" directly below the spinneret face. Once the maximum air pressure was reached, the air injection line was again vented and the take-up speed increased by an increment of 20 to 40 feet per minute, and samples were again taken at increments of increasing air pressure.

Before each sample was removed from the take-up drum the speed of the piston motor drive shaft was measured.

An upper take-up assembly was installed near the end of the experimentation. The assembly consists of a drive motor, speed indicator and control, and windup spool in one cabinet. The assembly was installed so that the spool would be eleven inches below the spinneret. This take-up unit was installed so fiber samples of larger dimensions could be obtained. Commercially fabricated cardboard spindles could be slipped over the take-up spool and removed for sample taking. The procedure when this unit was in use was essentially the same as that for the lower take-up except no thread guide was used.

Apparatus Shutdown. Once all the desired samples were taken, all electrical power was disconnected, the spinneret orifice was plugged and the oil bath was allowed to cool overnight. The following day the spinneret assembly was unbolted and removed. For some spinning trials a sample of solidified polymer solution was chipped out of the bottom of the spinning cylinder for concentration measurements. The oil bath heaters were then turned on and the oil bath temperature increased until the solid polymer solution plug began to melt near the wall of the spinning cylinder. The piston was then lowered to push out the plug. The piston was then raised to the top of the spinning cylinder, the electrical power disconnected, and the piston assembly removed. The hot spinning cylinder and piston were cleaned with tetralin. The spinneret was heated and cleaned

with tetralin.

Temperature Control. It was found that the oil bath temperature could easily be held constant during spinning by setting V-3 at 100 volts and making slight adjustments in V-4. If it was desired to raise the temperature, then the start-up heater was turned on until the oil bath temperature was one degree below that desired. It was then turned off, the oil bath temperature watched, and V-4 adjusted until constant temperature was again achieved. If a lower temperature was desired then all oil bath heaters were turned off until the thermometer read one degree above the desired temperature. The 525 and 800 watt heaters were then turned on and V-4 was adjusted until constant temperature was maintained.

The spinneret temperature was easily held constant by slight adjustments of V-6.

Fiber Polymer Concentration Determination. For most spinning trials, the first sample taken was used for determination of the polymer concentration of the spun fiber. Immediately after the completion of a spinning trial the cardboard spindle on which the sample was wound, was removed from the sealed plastic bag. Two cotton threads were tied tightly around the fiber band about one inch apart. Any excess thread left after the knots were tied was cut off. The fiber was cut between the threads, leaving a fiber bundle tied at both ends. This bundle was weighed immediately. The fiber bundle was then placed in an erlenmeyer flask containing

100 milliliters of diethyl ether to extract the solvent. The fibers were kept in the stoppered flask at least one-half hour with periodic agitation by hand. The fiber bundle was then removed from the flask and left to dry in room air on a paper towel for at least one-half hour. The fiber bundle was then reweighed.

Spinning Solution Concentration Determination. As explained in the description of spinning apparatus shutdown, samples of the solidified polymer-solvent mixture were chipped out of the spinning cylinder after the oil bath had cooled down. This was done to determine if any significant change in the polymer concentration resulted from the charging procedure due to the loss of solvent into the air. (This sample was only taken after certain spinning trials using a polypropylene-naphthalene system.) The sample was sifted through a screen to remove all particles more than one sixteenth of an inch in diameter. The remaining sample was weighed (usually about three grams) and placed into an erlenmeyer flask containing 100 milliliters of diethyl ether. The contents were stirred continuously using a magnetic stirrer for no less than two hours. The contents of the flask were then poured into a filtering funnel attached to a vacuum flask. After all the polymer particles were washed from the flask, the polymer was allowed to dry for at least one hour. The polymer particles were carefully scraped off the filter paper and reweighed.

Measurement of Fiber Dimensions. Short lengths of fibers were placed on a glass microscope slide. A drop of Permount* slide cement was placed on the slide and a glass slide cover was placed over it. As the slide cement soaked into the fiber, they would become transparent, allowing the fiber capillary to be seen. The slide was placed under an optical microscope with a scaled eyepiece lens by which the fiber dimensions could be measured.

Weight and Length Measurements. Fiber denier, density, and void fraction measurements were based on weights of known lengths of fiber. A piece of 1 1/2 inch masking tape was pressed over the fiber band on a spindle. The spindle was then cut in half through the middle of the masking tape so the fiber band remained attached to the cardboard. Two half-inch strips of masking tape were pressed over a small portion of the fiber band a measured length apart (usually ten centimeters). The fibers between the two strips of tape were then carefully counted and cut at the inside edges of the tape strips. The fibers were then washed in diethyl ether, dried, and weighed.

Microscopic Examination. Several fiber sectioning procedures were examined so that the fiber wall structure could be observed. The best procedure used is described as follows:

- 1) Soak a small fiber bundle, tied with a cotton thread, in propylene oxide for at least one hour.

*Product of Fisher Scientific Company.

2) Soak the bundle for three to four hours in a solution consisting of one part Epon 328* epoxy resin containing 30 percent U-curing agent* and two parts propylene oxide.

3) Suspend fiber bundle with cotton thread in oven at 40°C for 30 minutes.

4) Cut small hole (about one millimeter) in point of a Beem polyethylene capsule.

5) Place fiber bundle in the Beem capsule through the hole so that it is held straight and in the center of the capsule.

6) Pour mixture of Epon 828 epoxy resin and U-curing agent (30 percent) into capsule. Place capsule in upright position in a holder. When the epoxy resin has become hard enough that it has stopped draining through the capsule hole, refill the capsule with the resin mixture.

7) Allow the resin to harden at room temperature for at least 24 hours.

After the resin hardened the polyethylene capsule was cut away. The hardened "bullet" was placed in an ultramicrotome sectioning chuck, trimmed, and sliced to thicknesses of one micron or less. The sections were floated on a drop of water for ease of handling.

If the specimens were intended for examination with an optical microscope, the sections were picked up on a glass slide. The slide was placed on a warm heating plate; when the water evaporated the fiber sections would adhere to the slide. If SEM examination was

*Products of Shell Oil Company.

intended, the sections were picked up on an aluminum pedestal and dried. The pedestal was then coated with a gold-palladium alloy or carbon.

If it was desired to observe the longitudinal view of a fiber with the SEM, then a short length of fiber was glued to the surface of a pedestal with silver paint. The pedestal was then coated.

Pore Size Distribution Measurements. The procedure used to operate the Aminco porosimeter is found in the Aminco-Winslow-Porosimeter Instruction Manual No. 597⁽²⁹⁾. However, some special procedures had to be developed due to the nature of the samples being measured.

To weigh the fiber sample to be measured, a small bundle of fiber was cut and shaken to remove any loose fibers. The bundle of fibers was pushed into the penetrometer sample bulb. When it was removed, the fiber bundle retained the shape of the inside of the sample bulb. The bundle was shaken again and weighed. The bundle was returned to the sample bulb for measurement. This procedure prevented any loss of loose fibers when placing the sample into the penetrometer.

The penetrometer used had a greater volume than that mentioned in the instruction manual. Therefore, much more mercury was added during the filling procedure than that called for by the manual. Enough mercury was added to the filling device to bring the mercury level to the 0.050 cubic centimeter mark on the penetrometer capillary (the manual stated that the mercury level should be brought to the 0.028 cubic centimeter mark).

Between 38 and 41 data points were taken during each test. The increments between points were gradually increased as the pressure was increased. The increments were increased from two pounds per square inch at the lowest pressures to 400 pounds per square inch at the highest pressures.

Results

Twenty-eight spinning trials were conducted. A brief summary of the operational data and observations for each trial is presented in Tables II and III.

Two spinneret designs were tested during this investigation. The design consisting of a solid mandrel centered in the spinneret orifice proved not to be suited for hollow fiber spinning. The tube-in-orifice design, however, performed well.

Hollow fibers could not be produced using the polypropylene-paraffin system.

Continuous hollow fibers were obtained from two of the 18 trials conducted using the polypropylene-naphthalene system. Table V lists the dimensions of the samples from the successful trials as well as their denier, density, and void fraction.

The reasons for so few successful spinning trials will be reviewed in the discussion.

The pore structure of the fibers from samples 12-2, 12-3, and 12-4 were examined by optical and scanning electron microscopy. The SEM micrographs in Figure 4 show the pore structure observed.

The pore size distribution of the fibers from samples 12-2, 12-3, and 12-4 was also partially determined with the use of mercury intrusion porosimetry. The pressure-volume curves obtained for the samples are shown in Figure 5. The pore size distribution functions for the samples appear in Figure 6.

TABLE II

Operational Data on Polypropylene-Paraffin System Spinning Trials

Trial No.	Polymer Conc. (wt.%)	Spinneret Design	Oil Bath Temp. (°C)	Spinneret Temp. (°C)	Samples	Remarks
1	20	mandrel centered in orifice .250" orifice .156" mandrel	123	Not measured	None	Capillary breakup.
2	20	mandrel centered in orifice .250" orifice .156" mandrel	131-145	Not measured	None	Capillary breakup. Spinneret annulus too large.
3	20	.170" orifice .156" mandrel	140-150	Not measured	None	Soln. did not flow evenly over spinneret mandrel.
4	30	.261" orifice .250" mandrel	145	Not measured	None	Soln. leaked through spinneret flange. Soln. leaked through piston check valve.
5	30	.261" orifice .250" mandrel	145	Not measured	None	Soln. did not flow evenly over spinneret mandrel.
6	30	tube-in-orifice .035" orifice .025" tube O.D.	185-200	150-165	None	Intermittent spinneret blockage with gel. Capillary breakup 3 ft. below spinneret.
7	30	tube-in-orifice .035" orifice .025" tube O.D.	150-162	150-157	None	Intermittent spinneret blockage with gel. Capillary breakup.

TABLE II (continued)

Operational Data on Polypropylene-Paraffin System Spinning Trials

Trial No.	Polymer Conc. (wt.%)	Spinneret Design	Oil Bath Temp. (°C)	Spinneret Temp. (°C)	Samples	Remarks
8	30	tube-in-orifice .035" orifice .025" tube O.D.	145-155	133-150	None	Excess soln. from trial 7 remelted. Made continuous fiber at high take-up speeds. Solution leaked through piston check valve.
9	30	tube-in-orifice .035" orifice .025" tube O.D.			None	Excess soln. from trial 7 remelted. Trial canceled. Soln. left in spinning cylinder for trial 10.
10	30	tube-in-orifice .035" orifice .025" tube O.D.	146-159	126-135	None	Capillary breakup. Excess load on piston drive.

TABLE III

Operational Data on Polypropylene-Naphthalene System Spinning Trials

Trial No.	Polymer Conc. (wt.%)	Spinneret Design	Oil Bath Temp. (°C)	Spinneret Temp. (°C)	Samples	Remarks
11	30	tube-in-orifice .035" orifice .025" tube O.D.	154-156	137-140	One for conc. mea- surement	Hollow fiber spun with ease. Max. air press. before "ballooning" =4" H ₂ O. Excess load on piston drive.
12	30	tube-in-orifice .035" orifice .025" tube O.D.	161-162	150	12-1-12-4	Remaining soln. in spinning cylinder from trial 11 remelted. Max. air press. = 1" H ₂ O. Hollow fiber spun under wide range of conditions.
13-A	35	tube-in-orifice .035" orifice .025" tube O.D.	170	150	None	Soln. leaked through spinneret flange. Excess load on piston drive.
13-B	35	tube-in-orifice .035" orifice .025" tube O.D.	167-177	156-160	one for conc. mea- surement	Excess soln. from trial 13-A remelted. Excess load on piston drive.
14-A	35	tube-in-orifice .035" orifice .025" tube O.D.	157-161	146-152	None	Excess soln. from trial 13-A remelted. Can only spin fine denier <u>solid</u> fiber.
14-B	35	tube-in-orifice .035" orifice .025" tube O.D.	164	151	one for conc. mea- surement	Remaining soln. in spinning cylinder from trial 14-A left overnight at 150°C. Not able to spin continuous hollow fiber.

TABLE III (continued)

Operational Data on Polypropylene-Naphthalene System Spinning Trials

Trial No.	Polymer Conc. (wt.%)	Spinneret Design	Oil Bath Temp. (°C)	Spinneret Temp. (°C)	Samples	Remarks
15-A&B	25	tube-in-orifice .035" orifice .025" tube O.D.	155-156	144-147	15-B-1 - 15-B-7	Soln. mixed on Friday - remelted and charged Monday. Soln. tended to wet spinneret face when slack in filament. Filament pulsing-filament tension unsteady.
15-C	25	tube-in-orifice .035" orifice .025" tube O.D.	140-160	120-136	one for conc. mea- surement	Excess soln. from trial 15-A&B remelted. Air injection tube blocked intermittently. Filament tension unsteady.
16-A	30	tube-in-orifice .035" orifice .025" tube O.D.	155-160	145-150	16-A-1 - 16-A-6	Soln. mixed & charged - left overnight at 175°C - spun next day. Filament pulsing & unsteady tension.
17-A	30	tube-in-orifice .035" orifice .025" tube O.D.	156-165	145-155	one for conc. mea- surement	Soln. mixed & charged - left overnight at 180°C - spun next day. Soln. leaked through spinneret flange. Excess load on piston drive.
17-B	30	tube-in-orifice .035" orifice .025" tube O.D.	141-155	133-144	None	Soln. charged & left overnight at 175°C - spun next day. Soln. leaked through spinneret flange. Problems with piston drive. Soln. not spinnable.

TABLE III (continued)

Operational Data on Polypropylene-Naphthalene System Spinning Trials

Trial No.	Polymer Conc. (wt.%)	Spinneret Design	Oil Bath Temp. (°C)	Spinneret Temp. (°C)	Samples	Remarks
18-A	35	tube-in-orifice .035" orifice .025" tube O.D.	155	145	18-A-1 - 18-A-21	Soln. mixed as fast as possible - max. temp. allowed 165°C Cooled & stored overnight - remelted & spun next day. Pulses in filament. Melt fracturing. Spun fiber nonuniform.
18-B	35	tube-in-orifice .035" orifice .025" tube O.D.	145	136	None	Excess soln. from trial 18-A remelted. Soln. leaked from spinneret flange. Soln. not spinnable - soln. yellow before charging.
19	35	tube-in-orifice .035" orifice .025" tube O.D.				Added antioxidant to soln. Soln. clear when charged. Soln. not completely dissolved when charged. Trial canceled.
20	35	tube-in-orifice .035" orifice .025" tube O.D.	149-151	139-140	20-1 - 20-17	.24 grams antioxidant added to soln. Soln. mixed one day - remelted & charged next day. Melt fracturing - beads superimposed on filament. Large die swell.

TABLE III (continued)

Operational Data on Polypropylene-Naphthalene System Spinning Trials

Trial No.	Polymer Conc. (wt.%)	Spinneret Design	Oil Bath Temp. (°C)	Spinneret Temp. (°C)	Samples	Remarks
21	35	tube-in-orifice .035" orifice .025" tube O.D.				Soln. too badly degraded to spin. (Deep yellow-low viscosity).
22	35	tube-in-orifice .035" orifice .025" tube O.D.				Used S/S stirrer paddle. Soln. worse than that from trial 21.
23	35	tube-in-orifice .035" orifice .025" tube O.D.	147	140	23-1 - 23-4	Eliminated at metal from soln. mixing vessel. Soln. clear & viscous when charged. Three hours work trying to fix mechanical problems, then tried to spin. Melt fracturing.

IV. DISCUSSION

The questions to be answered in this study are mostly operational rather than theoretical. Therefore, more emphasis is placed on discussion of procedures and observations made during the spinning trials than on deriving relationships from experimental data.

Procedures and Equipment

Solution Preparation. There was much difficulty dissolving the spinning solutions with the equipment available. Upon dissolution of the polymer the solutions became so viscous that the stirrer motor was not able to turn and the stirrer shaft would have to be rotated by hand. The dissolution process was extremely slow, taking between 6 to 12 hours for the solution to become completely homogeneous.

Temperature control of the solution was also difficult. Fifteen to thirty minutes was required for the solution temperature to respond to any change in voltage input to the heating mantle.

Solution Charging. Because of the high viscosity, the spinning solutions flowed very slowly from the solution flask into the spinning cylinder. Between fifteen to thirty minutes was required to completely charge the spinning cylinder. If the temperature of the solution was not high enough the solution would begin to solidify in the flask before the spinning cylinder could be filled. However, it was found that when the solution temperature was above 160°C at

the start of the charging procedure the spinning cylinder could be filled before solidification would begin to occur.

Another problem encountered during the charging of a polypropylene-naphthalene solution was solvent fumes. There was no ventilation hood or other adequate means of reducing the concentration of naphthalene vapor during charging.

Spinning Procedure. Many mechanical problems were encountered during the spinning trials. The piston had been designed with a valve that allowed air to escape from the spinning cylinder when the piston assembly was being lowered in place during installation. During spinning operations the spinning solution would leak through the valve. In order to eliminate this problem the valve was silver soldered to the piston. However, this caused the piston assembly installation to be more difficult and also reduced the capacity of the spinning cylinder because of the trapped air pocket between the piston and the solution level.

During many of the spinning trials it was noticed that the tension in the piston drive chain would increase greatly indicating a malfunction in the piston assembly or a blockage in the spinneret causing an increased load on the piston drive. When this would happen a constant piston speed could not be maintained and in some instances the piston drive motor would stop due to the excessive load. Originally, it was thought that this problem was caused either by blockages in the spinneret orifice or possibly the piston catching on the side of the spinning cylinder due to misalignment of

the piston assembly. However, upon further examination it was decided that the problem was caused by compression of the thrust bearing between the two piston assembly flanges (see pages 63-65, William's thesis). Brass spacer sleeves had been used to hold the flanges the proper distance apart. However, after much use the spaces had compressed enough to cause pressure to be applied to the thrust bearing during the spinning operation.

Another problem was the leaking of spinning solution from between the spinneret support flange and the spinneret receiver flange. The receiver flange, which was bolted beneath the oil bath to the bottom of the spinning cylinder, had a 1/16" deep, 2" diameter recess in which the spinneret assembly fit. If this recess had been deeper, the leaking could have been prevented.

The pressure of the air injected into the spinneret tube was measured with a water filled manometer and controlled with a needle valve. The operating pressures were between zero to four inches of water above atmospheric pressure. The manometer had to be observed constantly and the needle valve carefully adjusted in order to maintain constant positive pressures long enough to obtain a sample of fiber.

A "jury-rigged" thread guide consisting of a fishing reel coupled to a variable speed motor was used on the lower take-up mechanism. It worked well, requiring no thread lubricant.

During even the most successful spinning trials nonuniformity in the spinning filament tension was noted. Also pulses of irregular-

ity were observed in the filament every one to two seconds. It was observed that during each revolution of the lower take-up drum the windup speed would oscillate from 20 to 40 feet per minute. This oscillation, particularly prominent at lower speeds, was possibly the cause of the filament pulsing. The inconsistency of the filament tension could probably be eliminated by using a take-up mechanism containing a tension control device.

Solvent Losses. By examining Table IV, it can be seen that considerable losses of naphthalene occurred during solution preparation, charging, and spinning. As the experimentation progressed, procedures improved and the loss of naphthalene was reduced. However, the fiber was spun into ambient air with no control of the temperature or flow of air. Therefore, no close control of the solvent content in the resulting fiber could be made. Since the rate of sublimation of the naphthalene during spinning would have an effect on the structure of the spun fiber, an effort should be made in future studies to maintain constant conditions in the spinning cabinet.

Spinneret Designs

Two spinneret designs were used in the course of this study. The first design used basically consisted of a solid mandrel centered in the orifice of the spinneret. The mandrel protruded from the spinneret a distance of between 0.5 to 1.5 inches. Several combinations of mandrel and orifice diameters were tested, however, none were successful. This type of annular spinneret is successful in

TABLE IV

Solvent Losses During Charging and Spinning

Trial No.	Original Polymer Conc. of Spinning Solution (wt.%)	Polymer Conc. of Sample From Spinning Cylinder (wt.%)	Polymer Conc. of Spun Fiber (wt.%)
11	30.0	---	48.4
12	30.0	---	48.5
13-B	35.0	47.0	56.5
14-B	35.0	38.9	48.2
15-B	25.0	27.4	34.0
15-C	25.0	---	29.2
16-A	30.0	---	36.9
17-A	30.0	30.8	36.1
18-A	35.0	---	42.5
20	35.0	---	43.2

certain tubular extrusion systems in which the polymer gels or freezes almost immediately after leaving the die. However, with the spinning system in use for this study, the polymer solution merely flowed unevenly over the mandrel and ran off the end.

Upon searching the literature a proper spinneret design for hollow fiber production was found⁽¹²⁾. This "tube-in-orifice" design (see Figure 7) worked well throughout the remainder of the study. How well the tube was centered in the orifice was an important factor since any eccentricity of the tube with respect to the orifice was exaggerated in the resulting fiber.

Polymer Systems

The first ten spinning trials of this study were carried out using the polypropylene-paraffin system. The solid-mandrel-in-orifice spinneret design was used for trials 1 through 5 and the tube-in-orifice design was used for all others. All the trials using this system were unsuccessful. In none of these ten trials could a hollow fiber be spun even momentarily. In only one case, trial 8, was it possible to take-up a continuous filament at all. This was accomplished only at the maximum windup speed possible with the take-up mechanism (about 600 m/min.). In all other trials the liquid threads would break up into droplets at distances from the spinneret of from two to five feet. This "capillary breakup"⁽³⁰⁾ of the filament indicated that the viscosity of the spinning dope is too low, that is, the solution temperature is too high or its polymer concentration

is too low. However, when the temperature of the solution was lowered gel formation, resulting in spinneret orifice blockage, would occur before the thread length could be increased enough to be taken up.

Zwick had reported successful phase separation spinning of solid fibers using the polypropylene-paraffin system. He reported the maximum polymer concentration for optimum spinnability to be 21 percent. However, his criterion for optimum spinnability was the maximum speed a fiber could be continuously taken up. The spinning conditions under which this criterion is met do not necessarily correspond to the conditions that would be conducive to the continuous production of uniform hollow fibers.

Even though the possibility of using the polypropylene-paraffin system for phase separation spinning of hollow fibers was not entirely rejected, it was decided to discontinue attempts to spin hollow fibers from polypropylene-paraffin solutions.

Spinning trials 11 through 23 were conducted using naphthalene as the solvent. Trials 11 and 12 were preliminary tests conducted to determine the relative difficulty and the range of conditions under which hollow fibers could be produced. The results obtained from these tests were encouraging. The 30 weight percent solution was easily spun into continuous fibers under widely varying conditions of solution temperature, solution velocity in the spinneret, and take-up speeds. Of the four fiber samples taken during trial 12, three contained continuous capillaries (see Table V). The varia-

TABLE V

Results Derived From Weight, Length, and Diameter Measurements

Sample No.	Spin Draw Ratio	Injection Air Press. (in. H ₂ O gauge)	Mean Outside Diameter (Standard Dev.) (μm)	Mean Inside Diameter (Standard Dev.) (μm)	Denier	Density (gm/cm ³)	Void Fraction
12-1	38.	0.0	92.0(22.)	---	*	*	*
12-2	36.	.8	75.0(9.6)	26.5(3.4)	26.1	.75	.17
12-3	31.	0.0	90.0(15.)	17.0(8.1)	45.0	.82	.089
12-4	31.	.9	119. (27.)	74.0(22.)	36.0	.59	.34
20-1	37.	0.0	88.0(14.)	---	*	*	*
20-2	36.	.2	109. (10.)	---	*	*	*
20-3	36.	.4	75.5(30.)	---	*	*	*
20-4	39.	.6	110. (32.)	44.5(23.)	26.9	.38	.58
20-5	41.	.8	124. (20.)	76.5(16.)	23.7	.35	.61
20-6	46.	0.0	60.3(13.)	---	*	*	*
20-7	43.	.2	92.7(29.)	24.7(16.)	23.3	.41	.54
20-8	45.	.4	72.8(21.)	15.7(12.)	19.9	.56	.38
20-9	44.	.6	89.5(45.)	41.5(31.)	20.6	.46	.49
20-10 ⁺	5.2	0.0	256. (31.)	32.2(21.)	150.	.33	.63
20-11 ⁺	5.7	.2	188. (22.)	25.3(11.)	132.	.54	.40
20-12 ⁺	5.1	.4	297. (110.)	78.9(47.)	158.	.27	.70
20-13 ⁺	4.9	.6	227. (39.)	88.5(26.)	149.	.48	.47
20-14 ⁺	7.3	0.0	190. (31.)	---	*	*	*
20-15 ⁺	7.3	.2	196. (54.)	71.7(29.)	102.	.44	.52
20-16 ⁺	7.0	.4	214. (31.)	84.8(22.)	93.5	.34	.62
20-17 ⁺	8.0	.6	198. (64.)	89.6(37.)	88.9	.40	.55

*Not measured.

⁺These samples were wound up on upper take-up apparatus.
Distance between spinneret and lower take-up = 5 ft.
Distance between spinneret and upper take-up = 11 in.

tion of dimensions in each sample were large. However, this was attributed to the relative crudeness of the spinning equipment used and was not considered to be indicative of any limitations to phase separation spinning of hollow fibers.

In all subsequent trials, however, serious difficulties arose. Many of the problems were mechanical in nature and have already been reviewed in the discussion of procedures and equipment. Others were related to the behavior of the polymer solution. These problems will be discussed in separate sections.

Melt Fracturing and Die Swell

During trials 11 and 12 little or no distortion or irregularity in the liquid jet was observed, even with large variations in solution velocity in the spinneret. In all subsequent trials, however, several forms of end effects were observed. Figure 3 is an attempt to graphically illustrate some of the observed effects. Several forms of melt fracturing were noted. The internal stresses causing the melt fracturing would partially relax by the time the filament began to solidify. The resulting fiber, when examined under an optical microscope, had the appearance of "frozen" turbulent flow. Die swell ratios as large as eight have been reported in the literature⁽³¹⁾. The die swell ratios observed in this study were sometimes greater than eight and in some instances had a tendency to form into large cohesive bulbs. It was impossible to obtain hollow fiber samples while these effects were occurring. The end effects did not necessarily occur throughout the entire spinning trial. At

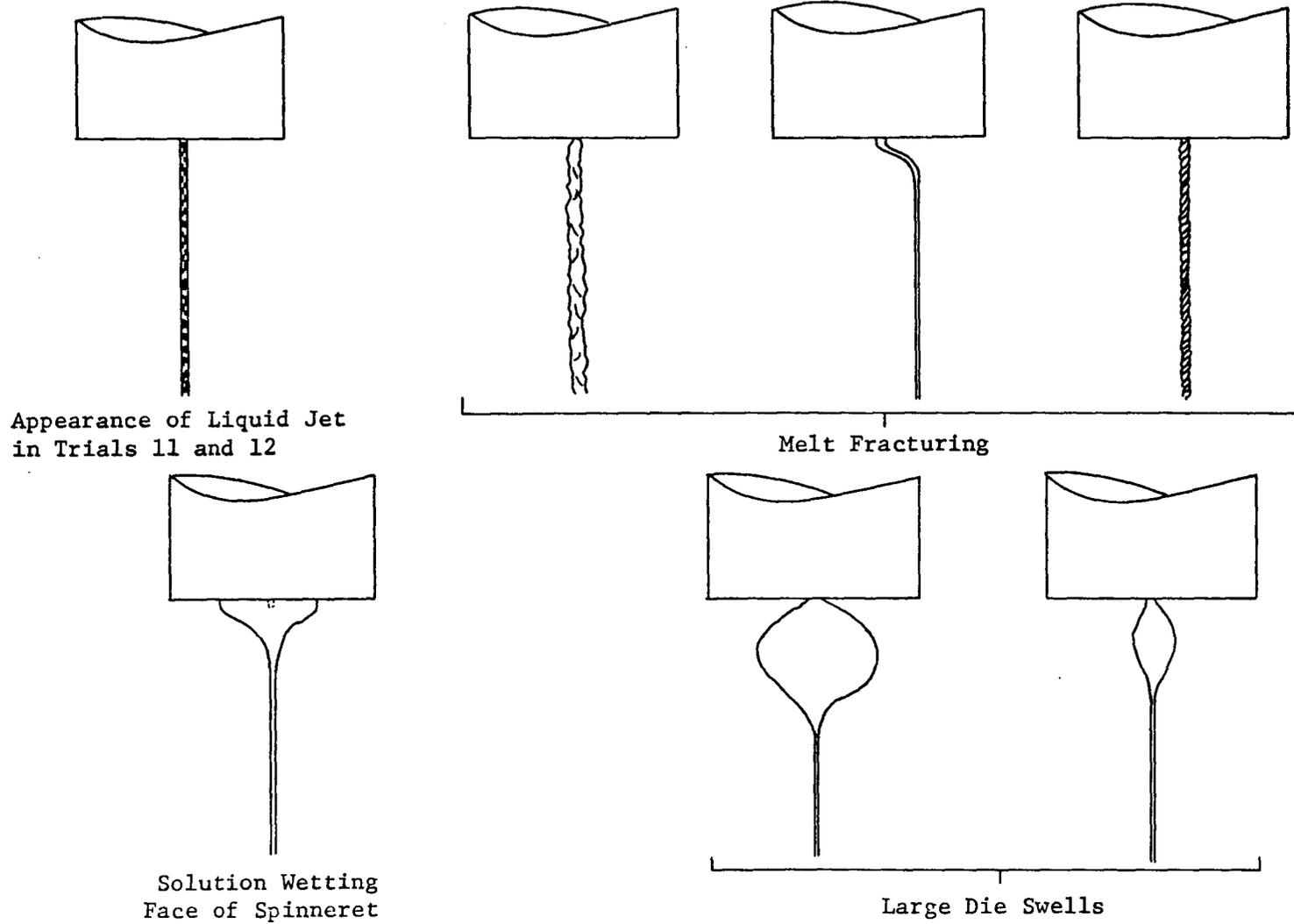


Figure 3. Irregularities in Liquid Jet Observed During Trials 13-A Through 23

times it was possible to obtain uniform jets similar to those observed in trials 11 and 12 long enough to obtain fiber samples. In the case of trial number 20 most of the fiber samples obtained contained continuous capillaries (see Table V).

Polymer Degradation

Melt fracturing and die swell are common occurrences in melt spinning of polyolefin fibers. Both effects increase with increasing shear rate in the spinneret channel and with fluid viscosity. Also, increasing ratios of length to diameter of the spinneret channel tend to decrease the effects. However, the widely varying, unpredictable flow behavior of the polymer solutions observed during the course of the study led to the speculation that the polymer was being altered chemically. After trial 17-B was conducted, a review of the procedures and observations from the previous trials was made in order to determine the procedural differences between trials 11 and 12, the successful trials, and the others. The color of the spinning solutions observed during the charging procedures for the trials following trial 12 varied in degrees of yellow, indicating degradation of the polymer. It was decided that the major difference in procedure between trials 11 and 12 and the others was the length of time at which the solution was held at elevated temperature. In trials 14B, 16-A, 17-A, and 17-B the spinning dopes had been left overnight in the spinning cylinder at temperatures from 150 to 180°C. In all trials following trial 17-B this practice was eliminated. In trial

18-A the solution was dissolved as fast as possible with the equipment available (four hours), and the maximum temperature was limited to 170°C. The behavior of the solution in trial 18-A appeared to be an improvement over previous trials. No large die swells were observed and melt fracturing did not appear to interfere with fiber formation. However, upon observation of the fiber samples under an optical microscope it was noted that none of them had continuous capillaries throughout the length of the fibers. The capillaries, where present, had extremely chaotic wall structures. Therefore, it was apparent that not all factors influencing the behavior of the polymer solution had been accounted for.

A thermal oxidation stabilizer, Ethyl "Antioxidant 330"*, was added to the spinning solution of trial 20. However, when the solution was ready for charging it had turned yellow. Also, the first attempts at spinning resulted in pronounced die swell and melt fracturing. After waiting an hour at constant oil bath temperature another attempt at spinning was made. This time the flow through the spinneret was more uniform and samples were taken. Most of the samples had continuous capillaries. However, the outside diameters of fibers had greater variations and the outside and inside walls appeared rougher than those of the samples taken from trial 12.

The solution preparation procedure for trial 21 was nearly the same as for trial 20. However, by the time all the polymer had been

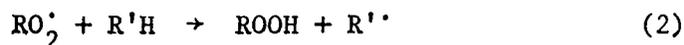
*1,3,5-trimethyl-2,4,6-tris [3,5-di-tert-butyl-4 hydroxybenzyl] benzene. A product of the Ethyl Corporation.

added to the resin flask the solution had turned dark brown and the viscosity had decreased drastically. The trial had to be canceled. Again procedures and the literature was reviewed in order to determine the problem.

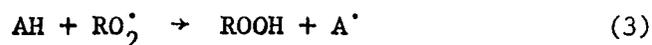
Oxidation is initiated when polymer molecules are converted to radicals by heat or ultraviolet light. In polypropylene this occurs by abstraction of the hydrogens adjacent to the tertiary carbons. Oxygen reacts with the radicals as follows:



The RO_2^\cdot radicals react with other polymer molecules to form hydroperoxides, transferring the chain reaction to the other molecule:



Antioxidants, such as hindered phenols, react with the RO_2^\cdot radicals as follows:

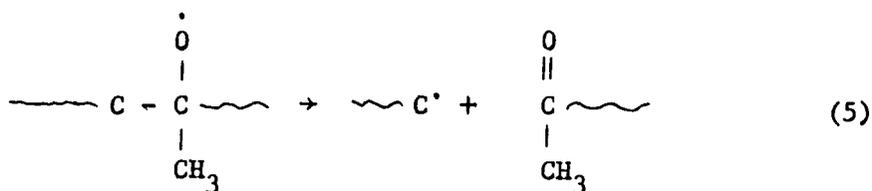


The A^\cdot radical is less likely to react with oxygen, so the overall oxidation rate is decreased. The hydroperoxides formed from reaction (2) and (3) can decompose as follows:



This reaction is catalyzed by copper or copper compounds and further accelerates the oxidation rate. Also, the RO^\cdot divides in such a

way to cause chain scission of the polypropylene:



The result would be a decrease in the molecular weight and thus the viscosity of the polymer⁽³²⁾.

In trial 11 the spinning solution had been mixed in a glass cylindrical resin flask using a 3" long Teflon stirrer paddle attached to a glass rod. During the mixing procedure much difficulty was encountered because the paddle was not rigid enough to stir the viscous solution. For this reason, a brass paddle and steel stirrer rod were made for solution preparation in subsequent trials. This brass and steel stirrer was used in trials 13-A through 21 (except for trial 19) without being aware of its significance, i.e., that the copper in the stirrer paddle caused chain scission of the polymer molecules.

The only significant difference in procedures or equipment between trial 20 and 21 was found to be that a greater amount of antioxidant was added to the polymer solution of trial 21 than that of trial 20 (see Table VI). Yet the spinning solution from trial 21 degraded drastically; while in trial 20 some evidence of nonuniformity was observed, but not enough to prevent hollow fibers from being spun. From the above discussion of degradative mechanisms it can be suggested that the antioxidant, when used in the presence of copper,

TABLE VI

Materials Which Had Influences on
Polymer Degradation

Trial No.	Stirrer Paddle Material	Resin Flask Material	Antioxidant Added (gram/100 gram polymer)
11,12	Teflon	glass	none
13-A,B, 14-A,B, 15-A,B,C, 16-A	brass	glass	none
17-A,B, 18-A,B	brass	S/S	none
19	Teflon	S/S	0.15
20	brass	S/S	0.15
21	brass	S/S	0.69
22	S/S	S/S	0.69
23	Teflon	glass	0.29

actually accelerated the chain scission of the polypropylene by increasing the concentration of hydroperoxides.

In trial 22 a stainless steel stirrer paddle was fabricated and used to mix the solution. The resulting polymer solution degraded more drastically than that of trial 21. This fact led to the conclusion that other metals, in addition to copper can promote chain scission in polypropylene.

In trial 23 all metal was eliminated from the mixing vessel. When the solution was charged into the spinning cylinder it appeared clear and viscous. The solution flowed evenly by gravity from the spinneret showing no irregular effects. However, a mechanical breakdown of the take-up apparatus caused a three hour delay before spinning could be attempted. When spinning was resumed the liquid jet displayed considerable melt fracturing, and hollow fibers could not be produced. Apparently, the stationary contact of the polymer solution with the metal walls of the iron spinning cylinder, coupled with the effect of the antioxidant, altered the polymer enough to impede hollow fiber formation.

It should be noted that only in trials 21 and 22 did the polymer solution viscosity decrease drastically. The irregularities that occurred in many of the other trials; the exaggerated die swells and the pronounced melt fracturing; were perhaps more indicative of crosslinking than chain scission. The polymer radicals produced by heat and light could crosslink as well as react with oxygen. Only in trials 21 and 22 was chain scission prominent. The effects

observed in the other trials were most likely caused by a combination of crosslinking and chain scission.

Time limitations prevented further trials from being conducted. However, enough was learned about operational problems to prevent their occurrence in future studies.

Results Derived From Weight, Length, and Diameter Measurements

The denier, density, void fraction, and diameters of the fiber samples containing continuous capillaries are presented in Table V. Because of the inconsistent behavior of the polymer solutions already discussed, no rigorous analysis of these results were made. However, some obvious conclusions can be discussed.

Fiber Dimensions. The spin draw ratio had an inverse effect on the outside and inside diameter of the fibers. For fibers which had had the same injection air pressure applied the effect of spin draw ratio was greater on the outside diameter than the inside diameter. Since relatively large fiber dimensions are desirable for membrane separations applications (100-300 μm O.D., 50-150 μm I.D.) low spin draw ratios must be used. However, the minimum spin draw is limited by the length of the filament from spinneret to take-up. The longer the filament, the higher the minimum spin draw ratio. The maximum average diameters possible from the lower take-up were 124 microns, outside diameter, and 76.5 microns, inside diameter. maximum average diameters possible on the upper take-up were 297

microns, O.D.; and 89.6 microns I.D.

Increasing injection air pressure had the effect of increasing outside and inside diameter. The thickness to outside diameter ratio of the fibers generally decreased with air pressure.

No clear correlation existed between thickness to diameter ratio and spin draw.

The variations in fiber dimensions were generally higher for samples from trial 20 than from trial 12. Consequently, the wall thickness of fiber samples from trial 20 also had greater variations. Because of this most of the samples in trial 20 had "weak spots" where the wall thickness was too small to have any mechanical strength.

Denier, Density and Void Fraction. Spin draw had the expected effect of decreasing denier, and was the dominant influence on denier.

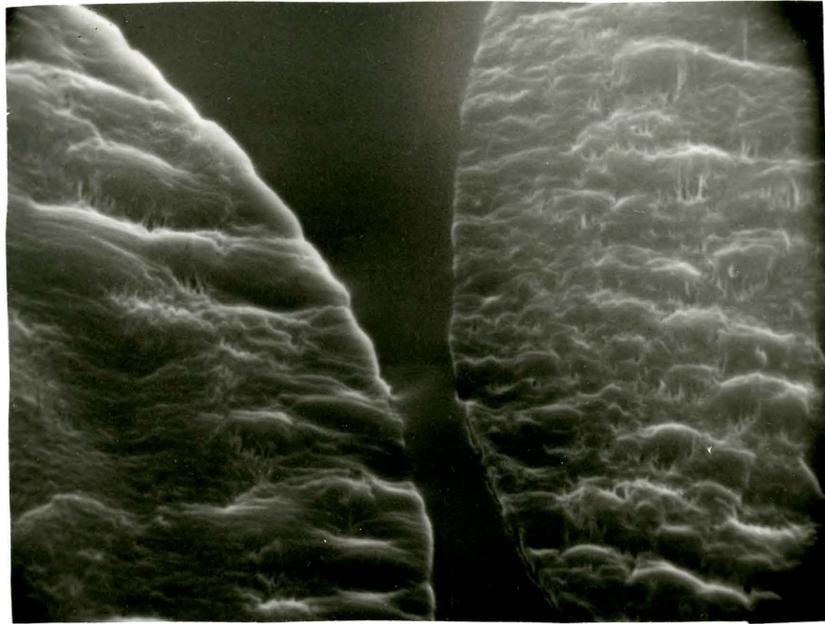
The prominent effect on density and void fraction was polymer concentration. The fiber densities observed in trial 12 were significantly higher than those reported for trial 20. From Table IV, it can be seen that the polymer concentration in the fiber samples of trial 12 were about 48 percent while the polymer concentration in trial 20 was about 43 percent.

Pore Structure and Pore Size Distribution. When the fibers were observed under an optical microscope they appeared opaque. However, when a drop of Permunt or toluene was placed on the slide the fiber would become transparent as the liquid permeated through the walls of the fiber. As this process of permeation took place, an

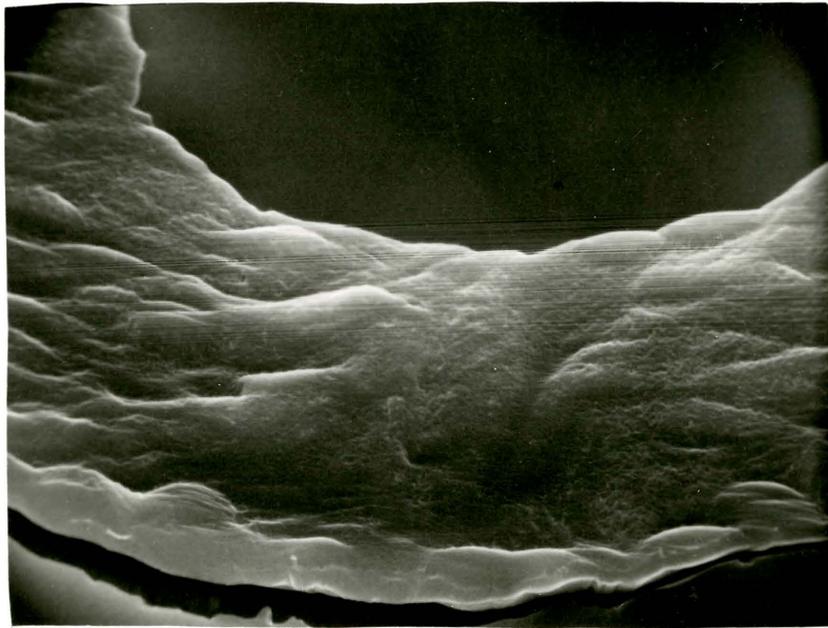
apparent pore structure could be discerned. The porous structure, when observed in this manner, appeared to be a "spongy" network of interconnecting voids. The maximum void diameter observed by this method appeared to be 2-3 microns.

Cross-sections of sample 12-2 were examined using a scanning electron microscope (see Figure 4). The maximum void diameter observed by this procedure was about 0.2 microns. The fiber structure appeared to consist of a fine network of microvoids.

The pore size distributions of samples 12-2, 12-3, and 12-4 were determined by mercury intrusion porosimetry. The pressure-volume curves are shown in Figure 5. The pore size distribution functions are shown in Figure 6. The distribution curves, particularly that of sample 12-4, are erratic at low values of pore diameter. This is because at high pressures, very small increases in penetrated volume correspond to large increases in the distribution function. Therefore, error in the distribution function at low pore diameters is high. Nevertheless, the trend of the curves should be revealing. The range of pore size in sample 12-4 appears to be slightly higher than those of samples 12-2 and 12-3. The significant population of pores in samples 12-2 and 12-3 appear to possess pore diameters smaller than one micron. The pressure limit for the porosimeter was 5000 pounds per square inch which corresponds to a pore diameter of approximately 0.045 microns. Therefore, no conclusions could be reached as to what percentage of the pore population have diameters smaller than this figure or what the minimum pore diameter would be.



→ | ← 5μm



→ | ← 5μm

Figure 4. Scanning Electron Micrographs of Cross-Sections of Fibers from Sample 12-2

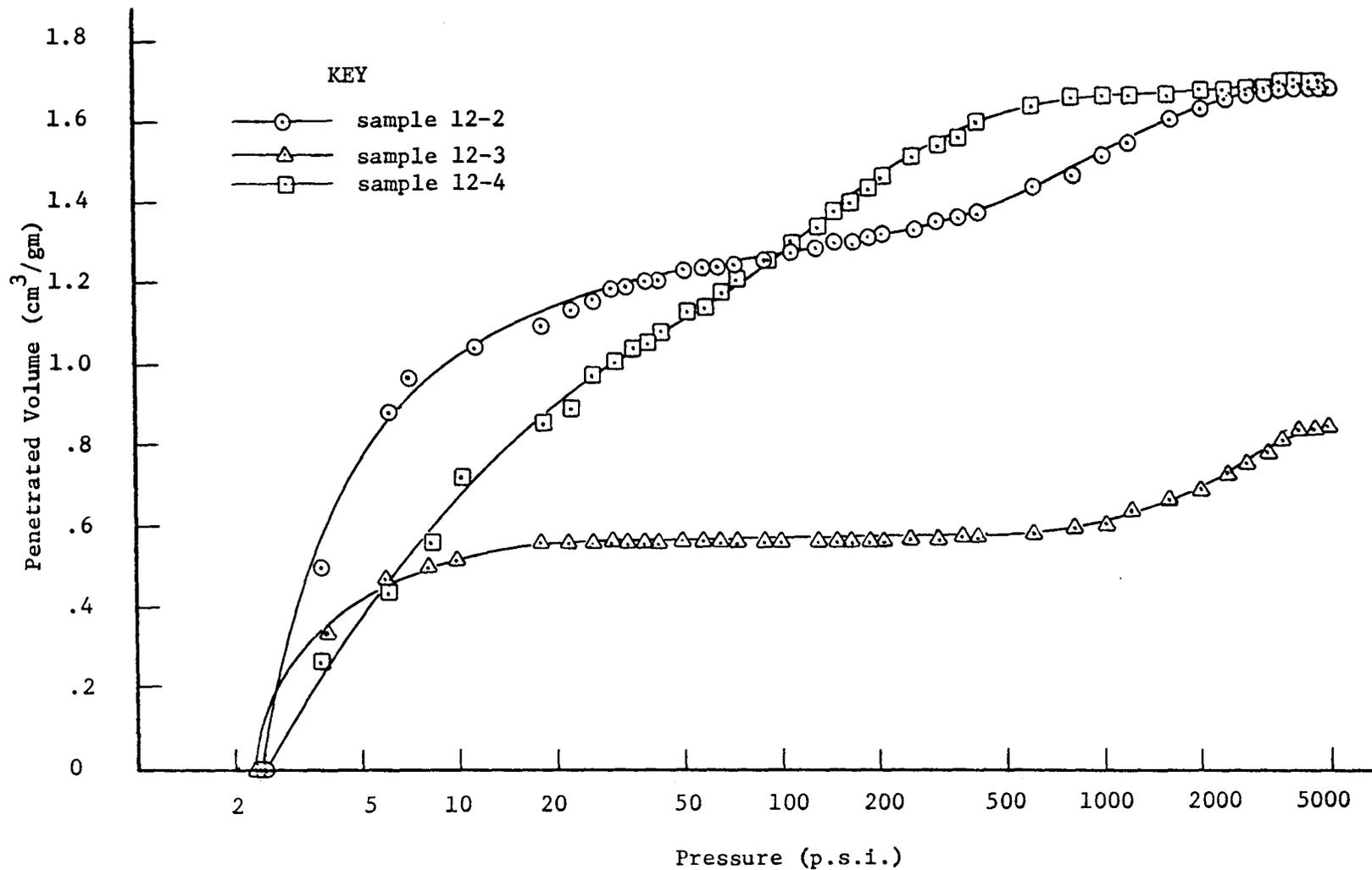


Figure 5. Mercury Intrusion Pressure-Volume Curves

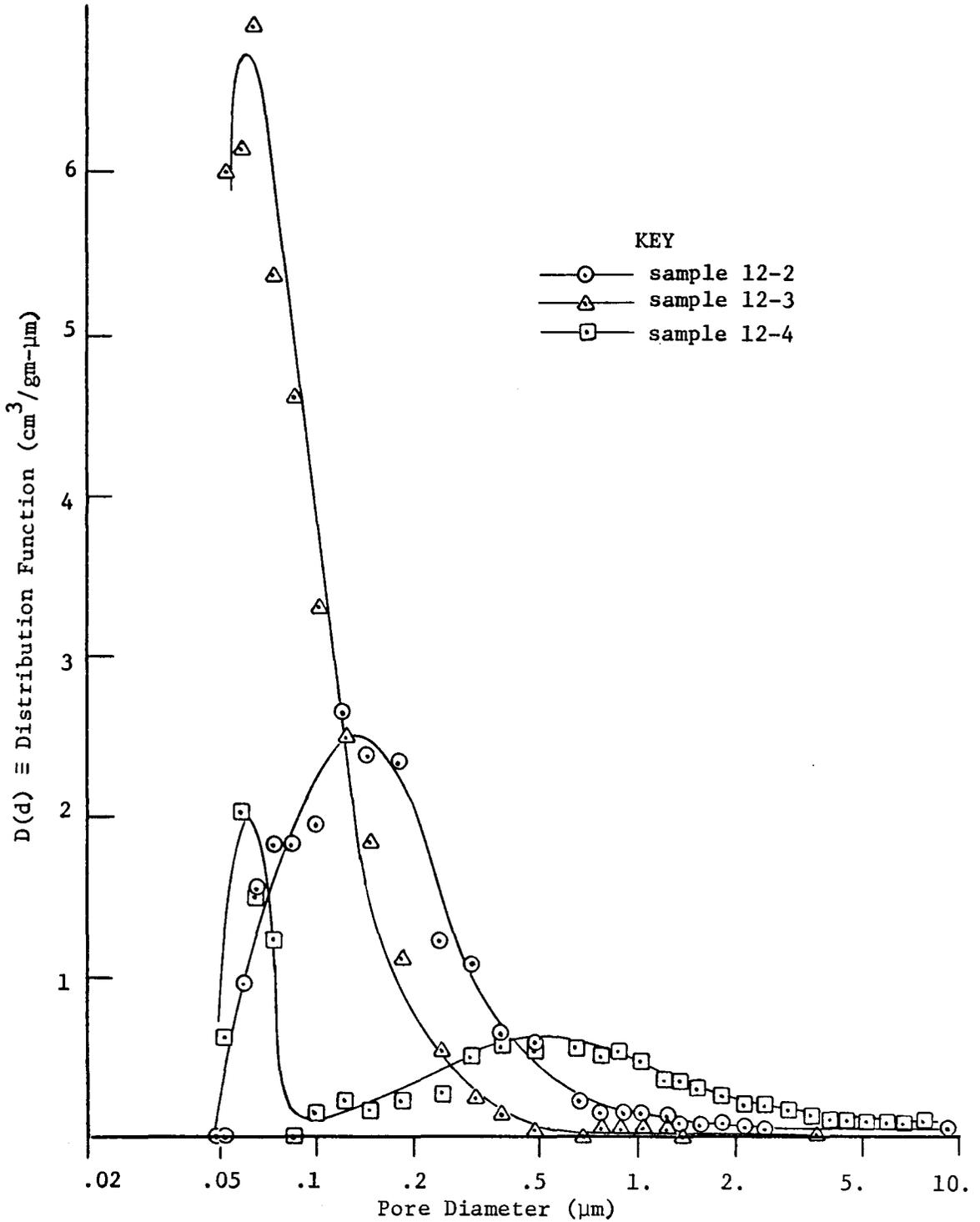


Figure 6. Pore Size Distribution of Fiber Samples

Recommendations

Further Studies. Despite the many mechanical and chemical problems encountered during the course of this study, it was shown that hollow fibers can be spun from polypropylene-naphthalene solutions and that the resulting fibers are porous. Also much was learned about how to eliminate the problems. It is recommended that the development of hollow fibers spun from polypropylene-naphthalene be continued, building upon what has been learned in this investigation. Later, much of the technology gained from the development of polypropylene-naphthalene hollow fibers could be applied to other polymer-solvent systems.

Among the specific areas relating to the further development of hollow fibers spun from polypropylene-naphthalene solutions that should be examined are:

- 1) A study should be conducted to determine what stabilizing agents would best alleviate the problem of chain scission caused by contact of the polymer with metals. It has already been concluded from this investigation that hindered phenolic antioxidants should not be used since they appear to accelerate the metal catalyzed decomposition of hyperoxides into active radicals. Instead, the spinning solution should be prepared in a nitrogen atmosphere. Two other classes of stabilizers should be examined. Certain disulfides and thiosulfonates decompose hyperoxides into inert products (33). Compounds that counteract the copper catalyzed decomposition of hyperoxides into active radicals are oxalic, succinic, and aminophthalic

acid dihydrazides^(34,35,36,37) .

2) A more thorough investigation should be made of the pore structure and effects of spinning conditions on pore size distribution. In future studies more dilute polymer solutions should be spun in order to produce fibers with higher void fractions.

3) A study should be made of whether improved porous polypropylene hollow fibers could be produced if the spinning process included a controlled temperature quench bath. Also, an effort should be made to control the conditions of the atmosphere surrounding the spinning filament.

4) Possible applications for polypropylene porous hollow fibers should be studied. Perhaps the most viable applications could be found in separations of components in organic process streams. A test cell should be built that could be used to test the permeability and rejection characteristics of the hollow fibers with various solutions.

Among the suggested areas of future study would include polymer-solvent systems other than the polypropylene-naphthalene system.

One of the original objectives of this study was to investigate the feasibility of coating phase separation spun hollow fibers with thin semipermeable membranes before extracting the solvent. This would possibly eliminate the problem of the membrane solution intruding into the pores during the coating process. Naphthalene served well in this study as a spinning solvent. However, polypropylene-naphthalene solution spun fibers would be difficult to store

for subsequent coating without losses of naphthalene to the atmosphere. Therefore, a search should be made for non-volatile compounds which are solid at room temperature, and would form phase separation systems with polypropylene. Among the candidates for such solid solvents should be included different types of waxes.

New Equipment. Before any further studies are conducted, better solution preparation and spinning equipment should be designed and built, or purchased. Specific suggestions for new equipment would include:

- 1) The polymer solution should not come in contact with any metal during solution preparation. A glass mixing vessel should be used along with a rigid, Teflon coated stirrer.

A heavy-duty, high torque motor should be purchased for mixing the solution. A system should be devised by which the power required for the motor to rotate at a constant speed could be measured and correlated to solution viscosity. Any degradation in the polymer could thereby be detected and spinning conditions could be more closely controlled and analyzed.

- 2) The manner in which the injection air pressure is controlled should be improved. A low pressure gas regulator connected by a length of small diameter tubing and a micrometer needle valve would possibly permit more precise control.

- 3) Another spinneret should be fabricated from stainless steel. Closer tolerances should be met in relation to centering the injection tube in the orifice.

4) There is a strong need for a more reliable spinning apparatus that could be more easily operated. Long distances between the spinneret and the windup mechanism are not required to produce hollow fibers of desirable dimensions. Therefore, a more compact bench scale spinning apparatus could be designed. The apparatus should be adaptable to changes in the spinning process.

Existing Equipment. If it is necessary to use the existing spinning apparatus in future studies, then the following modifications should be made:

1) A ventilation hood should be installed above the spinning apparatus to reduce the concentration of naphthalene or other solvent vapors during the solution charging procedure.

2) The brass spacer sleeves in the piston assembly should be replaced with hard steel. The length of the spacers should be designed to prevent any pressure from being applied to the thrust bearing by the assembly flanges.

3) A high temperature cut-off switch should be installed in the electrical circuit to the 1450 watt heating element for safety.

4) The recess in the spinneret receiver flange should be deepened to at least 1/4 inch in order to prevent leakage of the solution through the flange. The spinneret flange or the receiver flange will have to be modified so that the spinneret will fit tightly against the deepened recess in the receiver flange.

5) The length of the filament between the spinneret and the take-up is an important factor in determining the final dimensions of the fiber. A platform should be designed for the upper take-up mechanism so that the distance between the spinneret and the take-up roll could easily be changed by raising or lowering the platform.

The indirect drive mechanism of the lower take-up assembly has proven to be mechanically unreliable. The lower take-up is also subject to vibration and oscillations in rotational speed. It should be replaced with a more direct, balanced drive mechanism.

6) All the controls and indicators should be placed together for more efficient operation. A thermocouple should be installed in the oil bath to replace the glass immersion thermometer. The thermocouples from the oil bath and the spinneret should be connected by way of a three-way switch so that the recorder could be used for both measurements.

Mercury Intrusion Porosimetry. Since the pore size distribution function is sensitive to very small changes in penetrated volume at high pressures, the limits of error by which the volume is measured should be minimized. One way to do this is to use a penetrometer with a smaller scale range. In order that the total change in penetrated volume remains within the scale range of the penetrometer, a smaller sample size should be used. The penetrometer used in this study had a scale range of 0.20 cm^3 . The maximum total volume change measured during the tests was 0.18 cm^3 for a 0.1 gram sample. Therefore, if a penetrometer is used with a 0.10 cm^3 scale range, the

weight should be no more than 0.05 grams.

At pressures lower than atmospheric pressure much of the volume change observed during a test is attributable to filling the voids between the fibers in the fiber bundle. Since these low pressure readings are of little significance, the penetrometer filling procedure should be changed so that the mercury level reads zero at atmospheric pressure rather than 6.8 pounds per square inch as was the case in this study.

V. CONCLUSIONS

Techniques for spinning and characterizing phase separation spun hollow fibers were explored in this investigation. The results of the study led to the following conclusions:

1. Hollow fibers can be spun from polypropylene-naphthalene solutions using a tube-in-orifice spinneret.

2. Problems with degradation of the polymer can be overcome by using proper stabilizing agents, eliminating metal contact with the polymer during solution preparation, and preparing the solution in a nitrogen atmosphere.

3. The hollow fiber walls consisted of a fine network of interconnecting voids or pores. The significant majority of the population of pores in the fibers had diameters of less than one micron.

4. The development of phase-separation spun hollow fibers should be continued. After the polypropylene-naphthalene system has been thoroughly investigated other polymer-solvent systems should be studied.

5. A more adaptable and compact spinning apparatus should be designed for testing different processing methods of producing improved phase separation spun hollow fibers.

VI. SUMMARY

The results of two previous studies of phase separation spinning of polypropylene-naphthalene solutions suggested that the resulting fiber had a fine porous structure after extraction of the naphthalene. In recent years much research and development has been devoted to the production of porous hollow fiber membranes for use in separations unit operations. This study is the beginning of a long range program to investigate the possibilities of phase separation spun hollow fibers as membranes or membrane supports.

The objective of this study was to develop techniques for spinning and characterizing phase separation spun hollow fibers and to develop recommendations for future work.

Two phase separation polymer-solvent systems were studied: polypropylene-paraffin wax, and polypropylene-naphthalene. A spinneret design consisting of a hollow tube connected to an air supply and centered in the spinneret orifice was used.

All ten attempts to spin hollow fibers using the polypropylene-paraffin wax system failed.

Initial attempts to produce hollow fibers from polypropylene-naphthalene solutions resulted in fiber samples averaging 95 microns and 39 microns, outside and inside diameter, respectively. However, subsequent spinning trials resulted in unpredictable flow behavior of the solution through the spinneret or drastic degradation of the polymer. A review of spinning procedure and a search in the literature led to the conclusion that chain scission of the polymer mole-

cules was being catalyzed by contact of the polymer with metals during solution preparation. However, with the use of a non-metallic mixing vessel and stirrer, the use of a nitrogen atmosphere, and addition of proper stabilizers this problem should be prevented in future studies.

Diameter, denier, density, and void fraction measurements were made for the fifteen samples containing continuous capillaries.

From observations made by optical and scanning electron microscopes, and mercury intrusion pore size distribution measurements, it was concluded that the structure of the fibers consisted of fine networks of interconnecting voids or pores. The significant majority of the population of these pores had diameters of less than one micron.

Among the suggested areas of further study in the development of hollow fibers spun from polypropylene-naphthalene solutions are spinning condition effects on pore size distribution and the possibility of using a controlled temperature quench bath in the spinning process. It is also suggested that other phase separation polymer-solvent systems be studied. Before any further studies are conducted, however, a more compact, easier to operate, and more adaptable spinning apparatus should be designed and built.

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VIII. APPENDIX

This section contains information which would be needed in order to reproduce the results of this investigation. A listing of materials and apparatus used is included.

Data Tables

This section contains the data obtained during the course of this study. Table VII lists the conditions under which each sample was spun. Table VIII contains dimensional data for each fiber sample possessing a continuous capillary from which average outside and inside diameters were determined. Table IX lists the data from which denier, density, and void fraction determinations were made for the samples obtained from trials 12 and 20. Table X contains porosimetry data from tests conducted on samples 12-2, 12-3, and 12-4. Table XI contains data calibrating the windup speed of the upper take-up apparatus with the indicator meter reading.

Calibration of Upper Take-Up

The windup speeds of the lower take-up drum were measured directly in feet per minute using a hand held tachometer. The measurements were later converted to units of meters per minute using the multiplication factor 0.305. The speed indicator of the upper take-up assembly read directly in units of feet per minute. However, the spindles on which the samples were taken had different outside diameters than the wheel for which the indicator was calibrated. Therefore, the speed indicator had to be recalibrated for the average

TABLE VII

Spinning Conditions for Samples Collected

Sample No.	Oilbath Temp. (°C)	Spinneret Temp. (°C)	Motor Shaft Speed (sec/rev)	Take-Up Speed (ft/min)	Injection Air Pressure (in. H ₂ O gauge)
12-1	162	153	23	240	0.0
12-2	161	150	23	240	.8
12-3	161	150	23	180	0.0
12-4	161	150	23	180	.9
15-B-1	155	144	36	360	0.0
15-B-2	155	144	35	360	.3
15-B-3	155	144	37	390	0.0
15-B-4	155	144	38	390	.3
15-B-5	156	145	25	460	0.0
15-B-6	155	144	25	440	.3
15-B-7	150	140	30	350	0.0
15-B-8	150	140	32	350	.3
16-A-1	160	150	26	240	0.0
16-A-2	160	150	24	240	.3
16-A-3	155	145	28	190	0.0
16-A-4	155	145	27	190	.6
16-A-5	155	145	27	190	1.3
16-A-6	155	145	28	190	1.7

TABLE VII (continued)

Spinning Conditions for Samples Collected

Sample No.	Oilbath Temp. (°C)	Spinneret Temp. (°C)	Motor Shaft Speed (sec/rev)	Take-Up Speed (ft/min)	Injection Air Pressure (in. H ₂ O gauge)
18-A-1	155	146	27	230	0.0
18-A-2	155	146	26	230	.3
18-A-3	155	146	25	240	.5
18-A-4	155	145	25	265	0.0
18-A-5	155	145	25	260	.2
18-A-6	155	145	25	260	.4
18-A-7	155	145	24	260	.5
18-A-8	155	145	24	290	0.0
18-A-9	155	145	26	290	.2
18-A-10	155	145	29	290	.4
18-A-11	155	145	26	290	.5
18-A-12	155	145	32	40*	0.0
18-A-13	155	145	31	40*	.2
18-A-14	155	145	33	40*	.4
18-A-15	155	145	32	40*	.5
18-A-16	155	146	32	50*	0.0
18-A-17	155	145	33	50*	.2
18-A-18	155	145	34	50*	.4
18-A-19	155	145	32	60*	0.0
18-A-20	155	145	31	60*	.2
18-A-21	155	145	31	60*	.4

*These samples taken-up on upper windup unit. Speed indicator reads in ft/min. but must be recalibrated.

TABLE VII (continued)

Spinning Conditions for Samples Collected

Sample No.	Oilbath Temp. (°C)	Spinneret Temp. (°C)	Motor Shaft Speed (sec/rev)	Take-Up Speed (ft/min)	Injection Air Pressure (in. H ₂ O gauge)
20-1	149	140	25	220	0.0
20-2	149	140	25	220	.2
20-3	150	140	25	220	.4
20-4	151	140	27	220	.6
20-5	149	140	28	220	.8
20-6	149	140	28	260	0.0
20-7	149	140	25	260	.2
20-8	149	140	26	260	.4
20-9	149	140	25	260	.6
20-10	149	140	27	30*	0.0
20-11	149	140	29	30*	.2
20-12	149	140	26	30*	.4
20-13	149	140	26	30*	.6
20-14	151	139	24	45*	0.0
20-15	151	139	24	45*	.2
20-16	151	139	23	45*	.4
20-17	151	139	27	45*	.6
23-1	147	140	34	25*	0.0
23-2	147	140	34	25*	.4
23-3	147	140	34	25*	.6
23-4	147	140	34	25*	1.0

*These samples taken-up on upper windup unit. Speed indicator reads in ft/min. but must be recalibrated.

TABLE VIII

Data on Fiber Dimensions

Sample No. 12-2:

<u>N</u>	<u>O.D.</u> <u>(scale units)*</u>	<u>I.D.</u> <u>(scale units)</u>
1	15.0	5.0
2	17.5	6.0
3	14.0	5.0
4	19.0	7.0
5	13.0	5.0
6	13.0	5.0
7	14.5	5.5
8	13.5	4.5
9	16.5	5.0
10	15.0	6.0
11	14.5	5.0
12	16.0	5.0
13	17.0	6.0
14	13.0	4.5
15	13.0	5.0

Sample No. 12-3:

<u>N</u>	<u>O.D.</u> <u>(scale units)</u>	<u>I.D.</u> <u>(scale units)</u>
1	19.0	2.5
2	20.0	5.0
3	16.0	1.0
4	21.5	5.0
5	18.0	2.5
6	21.0	2.0
7	21.0	4.0
8	17.5	4.0
9	16.5	2.0
10	20.0	3.0
11	13.5	1.5
12	13.5	3.5
13	13.0	3.0
14	22.0	7.0
15	18.0	5.0

Sample No. 12-4:

<u>N</u>	<u>O.D.</u> <u>(scale units)</u>	<u>I.D.</u> <u>(scale units)</u>
1	21.0	12.0
2	35.5	25.0
3	22.0	13.0
4	19.5	14.0
5	27.0	17.5
6	15.0	8.5
7	16.0	8.5
8	24.0	15.5
9	20.5	11.0
10	27.5	18.0
11	30.5	19.5
12	20.0	13.0
13	25.5	15.5
14	28.0	18.0
15	24.0	13.0

*One scale unit = .005 mm

TABLE VIII (continued)

Data on Fiber Dimensions

Sample No. 20-4:

<u>N</u>	<u>O.D.</u> <u>(scale units)</u>	<u>I.D.</u> <u>(scale units)</u>
1	18.0	6.0
2	20.5	8.5
3	15.0	3.0
4	26.0	9.5
5	35.0	18.5
6	26.5	12.5
7	17.0	6.0
8	24.5	11.0
9	15.5	5.0
10	16.5	5.0
11	34.5	18.5
12	22.0	8.0
13	18.0	6.5
14	22.0	9.0
15	18.5	6.5

Sample No. 20-5:

<u>N</u>	<u>O.D.</u> <u>(scale units)</u>	<u>I.D.</u> <u>(scale units)</u>
1	24.5	15.5
2	31.0	21.5
3	19.5	11.0
4	25.5	15.0
5	21.5	12.5
6	26.5	18.0
7	20.5	11.5
8	25.5	14.0
9	33.0	23.0
10	20.0	11.0
11	25.0	15.5
12	20.0	12.0
13	25.5	17.0
14	28.0	17.5
15	25.0	14.5

Sample No. 20-7:

<u>N</u>	<u>O.D.</u> <u>(scale units)</u>	<u>I.D.</u> <u>(scale units)</u>
1	11.5	1.0
2	25.0	9.0
3	17.0	4.5
4	31.0	12.0
5	14.0	2.0
6	14.0	3.0
7	13.5	3.0
8	19.5	2.5
9	25.5	8.0
10	14.0	3.0
11	26.0	9.5
12	17.0	4.5
13	17.0	5.0
14	18.0	4.0
15	15.0	3.0

Sample No. 20-8:

<u>N</u>	<u>O.D.</u> <u>(scale units)</u>	<u>I.D.</u> <u>(scale units)</u>
1	14.5	2.5
2	13.0	2.0
3	14.5	5.0
4	12.0	1.0
5	12.0	2.0
6	12.5	1.0
7	13.5	3.0
8	12.0	3.0
9	15.0	2.5
10	22.5	8.0
11	12.0	2.5
12	13.5	1.0
13	12.0	1.0
14	26.5	9.0
15	13.0	3.5

TABLE VIII (continued)

Data on Fiber Dimensions

Sample No. 20-9:

<u>N</u>	<u>O.D.</u> <u>(scale units)</u>	<u>I.D.</u> <u>(scale units)</u>
1	22.0	11.0
2	20.0	8.0
3	14.5	7.0
4	13.5	5.5
5	13.0	4.5
6	16.0	7.0
7	41.0	23.0
8	14.5	6.5
9	36.0	22.0
10	11.5	4.0
11	12.0	5.0
12	18.0	7.5
13	9.5	2.5
14	14.5	6.0
15	12.5	5.0

Sample No. 20-10:

<u>N</u>	<u>O.D.</u> <u>(scale units)</u>	<u>I.D.</u> <u>(scale units)</u>
1	58.5	10.0
2	51.0	10.0
3	42.0	2.0
4	49.5	1.0
5	61.0	14.0
6	52.5	5.0
7	54.5	5.5
8	45.0	4.0
9	47.0	6.5

Sample No. 20-11:

<u>N</u>	<u>O.D.</u> <u>(scale units)</u>	<u>I.D.</u> <u>(scale units)</u>
1	42.0	7.5
2	35.0	5.0
3	32.5	3.0
4	38.0	2.5
5	40.0	5.0
6	33.0	4.5
7	35.0	4.0
8	45.0	9.0

Sample No. 20-12:

<u>N</u>	<u>O.D.</u> <u>(scale units)</u>	<u>I.D.</u> <u>(scale units)</u>
1	58.0	15.0
2	50.0	13.0
3	47.0	12.0
4	113.0	40.0
5	60.0	11.5
6	73.0	16.5
7	56.0	16.0
8	38.0	9.5
9	39.0	9.0

TABLE VIII (continued)

Data on Fiber Dimensions

Sample No. 20-13:

<u>N</u>	<u>O.D.</u> <u>(scale units)</u>	<u>I.D.</u> <u>(scale units)</u>
1	49.0	20.0
2	59.0	28.5
3	42.0	14.0
4	45.0	17.0
5	57.0	23.5
6	38.0	13.0
7	44.0	18.0
8	35.5	11.0
9	38.5	15.0
10	45.0	17.0

Sample No. 20-14:

<u>N</u>	<u>O.D.</u> <u>(scale units)</u>	<u>I.D.</u> <u>(scale units)</u>
1	44.0	15.0
2	31.0	9.0
3	37.5	12.0
4	37.0	15.0
5	37.5	16.0
6	39.0	11.0
7	45.0	16.0
8	42.0	17.5
9	54.5	24.5
10	42.0	16.0
11	40.0	13.0
12	16.0	4.0
13	62.0	26.0
14	26.5	6.0
15	35.0	14.0

Sample No. 20-16:

<u>N</u>	<u>O.D.</u> <u>(scale units)</u>	<u>I.D.</u> <u>(scale units)</u>
1	42.5	16.0
2	40.5	14.0
3	35.5	14.0
4	45.0	16.0
5	46.0	17.5
6	53.0	24.0
7	43.0	16.0
8	40.0	16.0
9	38.0	15.0
10	41.0	15.5
11	56.0	28.5
12	34.0	11.5
13	47.5	18.5
14	38.5	15.0

Sample No. 20-17:

<u>N</u>	<u>O.D.</u> <u>(scale units)</u>	<u>I.D.</u> <u>(scale units)</u>
1	61.0	31.0
2	30.5	12.5
3	39.0	19.0
4	25.0	9.0
5	46.0	19.0
6	37.5	15.5
7	31.0	11.0
8	29.5	11.5
9	23.0	13.0
10	43.0	21.0
11	47.0	21.0
12	61.5	31.5

TABLE IX

Data from Denier and Density Measurements

Sample No.	No. of Fibers	Length per Fiber	Weight of Sample (gm.)
12-2	10	10.0 cm.	.0029
12-3	10	10.0 cm.	.0050
12-4	10	5.0 cm.	.0020
20-4	37	20.0 in.	.0561
20-5	30	20.0 in.	.0401
20-7	39	20.0 in.	.0512
20-8	40	20.0 in.	.0450
20-9	41	20.0 in.	.0477
20-10	10	9.5 in.	.0403
20-11	10	10.0 in.	.0372
20-12	10	10.0 in.	.0446
20-13	5	10.0 in.	.0210
20-15	10	10.0 in.	.0289
20-16	10	10.0 in.	.0264
20-17	10	10.0 in.	.0251

TABLE X

Porosimetry Data

Sample 12-2:

Sample Weight = .0555 grams

N	Press. 1 (p.s.i.)	Press. 2 (p.s.i.)	Scale Reading (cm ³)	N	Press. 1 (p.s.i.)	Press. 2 (p.s.i.)	Scale Reading (cm ³)
1	7.0	---	.0000	22	14.2	180.	.0730
2	8.0	---	.0280	23	14.2	200.	.0735
3	10.1	---	.0490	24	14.2	250.	.0740
4	12.0	---	.0540	25	14.2	300.	.0750
5	14.0	---	.0575	26	14.2	350.	.0755
6	14.2	8.	.0610	27	14.2	400.	.0760
7	14.2	12.	.0630	28	14.2	600.	.0800
8	14.2	16.	.0645	29	14.2	800.	.0810
9	14.2	20.	.0655	30	14.2	1000.	.0840
10	14.2	24.	.0660	31	14.2	1200.	.0855
11	14.2	28.	.0670	32	14.2	1600.	.0890
12	14.2	32.	.0670	33	14.2	2000.	.0905
13	14.2	40.	.0685	34	14.2	2400.	.0915
14	14.2	48.	.0690	35	14.2	2800.	.0920
15	14.2	56.	.0690	36	14.2	3200.	.0925
16	14.2	64.	.0695	37	14.2	3600.	.0930
17	14.2	80.	.0700	38	14.2	4000.	.0930
18	14.2	100.	.0705	39	14.2	4400.	.0930
19	14.2	120.	.0715	40	14.2	4800.	.0930
20	14.2	140.	.0720	41	14.2	5000.	.0930
21	14.2	160.	.0720				

TABLE X (continued)

Porosimetry Data

Sample 12-3:

Sample Weight = .0882 grams

N	Press. 1 (p.s.i.)	Press. 2 (p.s.i.)	Scale Reading (cm ³)	N	Press. 1 (p.s.i.)	Press. 2 (p.s.i.)	Scale Reading (cm ³)
1	6.8	---	.0000	21	14.1	160.	.0490
2	8.0	---	.0300	22	14.1	180.	.0490
3	10.0	---	.0410	23	14.1	200.	.0495
4	12.0	---	.0440	24	14.1	250.	.0500
5	14.0	---	.0450	25	14.1	300.	.0500
6	14.1	8.	.0480	26	14.1	350.	.0500
7	14.1	12.	.0480	27	14.1	400.	.0500
8	14.1	16.	.0480	28	14.1	600.	.0510
9	14.1	20.	.0480	29	14.1	800.	.0520
10	14.1	24.	.0480	30	14.1	1000.	.0530
11	14.1	28.	.0480	31	14.1	1200.	.0550
12	14.1	32.	.0480	32	14.1	1600.	.0580
13	14.1	40.	.0490	33	14.1	2000.	.0610
14	14.1	48.	.0490	34	14.1	2400.	.0640
15	14.1	56.	.0490	35	14.1	2800.	.0660
16	14.1	64.	.0490	36	14.1	3200.	.0690
17	14.1	80.	.0490	37	14.1	3600.	.0710
18	14.1	100.	.0490	38	14.1	4000.	.0730
19	14.1	120.	.0490	39	14.1	4400.	.0740
20	14.1	140.	.0490	40	14.1	4800.	.0750

TABLE X (continued)

Porosimetry Data

Sample 12-4:

Sample Weight = .1064 grams

N	Press. 1 (p.s.i.)	Press. 2 (p.s.i.)	Scale Reading (cm ³)	N	Press. 1 (p.s.i.)	Press. 2 (p.s.i.)	Scale Reading (cm ³)
1	6.9	---	.0000	21	14.2	160.	.1490
2	8.0	---	.0275	22	14.2	180.	.1520
3	10.0	---	.0460	23	14.2	200.	.1550
4	12.0	---	.0600	24	14.2	250.	.1600
5	14.0	---	.0760	25	14.2	300.	.1640
6	14.2	8.	.0900	26	14.2	350.	.1660
7	14.2	12.	.0940	27	14.2	400.	.1690
8	14.2	16.	.1030	28	14.2	600.	.1735
9	14.2	20.	.1070	29	14.2	800.	.1750
10	14.2	24.	.1100	30	14.2	1000.	.1760
11	14.2	28.	.1120	31	14.2	1200.	.1760
12	14.2	32.	.1150	32	14.2	1600.	.1765
13	14.2	40.	.1200	33	14.2	2000.	.1770
14	14.2	48.	.1215	34	14.2	2400.	.1770
15	14.2	56.	.1250	35	14.2	2800.	.1770
16	14.2	64.	.1290	36	14.2	3200.	.1770
17	14.2	80.	.1340	37	14.2	3600.	.1790
18	14.2	100.	.1380	38	14.2	4000.	.1790
19	14.2	120.	.1420	39	14.2	4400.	.1790
20	14.2	140.	.1470	40	14.2	4800.	.1795

TABLE XI

Calibration Data for Upper Take-Up
Speed Indicator

Meter Reading	10x Period of Take-Up Wheel (sec/10 rev)
25	21.1
30	17.6
35	15.0
40	13.2
45	11.3
50	10.1
55	9.0
60	8.2
70	7.4

diameter of the sample spindles. Table XI shows the times required for the windup spool to make ten revolutions for various settings of the speed control. The range of speeds possible were slow enough to allow measurement by visual observation of a mark on the windup spool. The average diameter of the sample spindles was determined to be 0.0836 meters. From this information the windup speed of fiber on the upper take-up assembly could be calculated. For example, the speed indicator was set at 30 during the collection of sample 20-10. From Table XI it can be seen that a meter reading of 30 corresponds to 17.6 seconds per ten revolutions. The take-up speed was calculated as follows:

$$\text{Take-up speed} = \left(\frac{10}{17.6}\right)(60)\pi(0.0836) = 8.95 \text{ m/min}$$

Sample Calculations

The following are examples of calculations made during this investigation.

Average Spinning Solution Velocity in the Spinneret. The piston drive motor shaft speed for sample 20-10 was 27 sec/rev (see Table VII). The sprocket on the piston drive shaft had nine teeth; the sprocket in the piston assembly had 25. The piston drive rod had 20 threads per inch, thus the piston would travel 1/20 inch per revolution of the piston assembly sprocket. Therefore,

$$\begin{aligned} \text{Piston travel rate} &= \left(\frac{1}{27}\right)\left(\frac{9}{25}\right)\left(\frac{1}{20}\right) = 0.000667 \text{ in/sec} \\ &= 0.00102 \text{ m/min} \end{aligned}$$

The inside diameter of the spinning cylinder is 0.998 inches. The outside and inside diameters of the annular spinneret channel are 0.035 and 0.025 inches, respectively. Therefore, the average velocity of the solution through the spinneret annulus for sample 20-10 was

$$\text{Average velocity} = \frac{(0.998)^2}{(0.035)^2 - (0.025)^2} (0.00102) = 1.71 \text{ m/min}$$

Spin Draw Ratio. The spin draw ratio is the take-up speed divided by the average velocity of the polymer solution in the spinneret. For sample 20-10 this would be

$$\text{Spin draw ratio} = \frac{8.95}{1.71} = 5.23$$

Average Fiber Dimensions. The dimensions of the fiber samples were measured using a scaled eyepiece lens (10X) on an optical microscope. With a 20X objective lens each scale unit represented 0.005 millimeters. The outside and inside diameters were measured at randomly selected, non-repeated locations in the fiber sample. From Table VIII it can be seen that measurements of fiber dimensions for sample 20-10, were taken at nine locations. The average of the outside diameter measurements for sample 20-10 was 51.2 scale units. Therefore,

$$\begin{aligned} \text{Average outside diameter} &= (51.2)(0.005) = 0.256 \text{ mm} = \\ &= 256 \text{ microns.} \end{aligned}$$

The average inside diameter was calculated in the same way.

Denier. Denier is the weight of 9000 meters of fiber. It may be calculated as follows:

$$\text{Denier} = \frac{900,000 (\text{weight of fibers, gm})}{(\text{length of each fiber, cm})(\text{number of fibers})}$$

From Table IX the weight of the fibers taken from sample 20-10 was 0.0403 grams. The length of each of the ten fibers was 9.50 inches or 24.2 centimeters. Therefore, the denier for sample 20-10 was

$$\text{Denier} = \frac{900,000(0.0403)}{(24.2)(10)} = 150$$

Density. The average outside and inside diameters for sample 20-10 were 256 and 32.2 microns, respectively (see Table V). Therefore, the average cross-sectional area of the fiber is

$$\begin{aligned} \text{Cross-sectional area} &= \frac{\pi}{4} [(256)^2 - (32.2)^2] = 5.06 \times 10^4 \mu\text{m}^2 \\ &= 5.06 \times 10^{-4} \text{ cm}^2 \end{aligned}$$

It can be seen from the above denier calculation that the weight of 242 centimeters of fiber from sample 20-10 was 0.0403 gram. Therefore the average fiber density of sample 20-10 is

$$\text{Density} = \frac{0.0403}{242(5.06 \times 10^{-4})} = 0.33 \text{ gm/cm}^3$$

Void Fraction. The void fractions of the fiber samples were calculated assuming a bulk density of polypropylene of 0.90 grams per cubic centimeter. Therefore, the average void fraction of sample 20-10 would be

$$\text{Void fraction} = 1 - \frac{0.33}{0.90} = 0.63$$

Pore Size Distribution

The porosimetry data for the mercury intrusion tests are shown in Table X. The applied pressure for each data point was calculated as follows:

$$\text{Applied pressure} = \text{Press. 1} + \text{Press. 2} - \text{Mercury head}$$

The mercury head was calculated from the empirical equation:

$$\text{Mercury head} = 4.53 - (13.6)(\text{scale reading})$$

The scale reading for each data point was divided by the sample weight in order to obtain the penetrated mercury volume in units of cubic centimeters per gram fiber. The applied pressure versus penetrated mercury volume curves are shown in Figure 5. The distribution function was calculated using the following equation:

$$D(d) = \frac{P^2}{112} \frac{dV}{dP}$$

The distribution function was "smoothed out" by calculating dV/dP as the average of the slopes between four adjacent points. The value for P used in the above equation was the average pressure of the four points. The pore diameter corresponding to each value of the distribution function was calculated as follows:

$$d \approx \frac{223}{P}$$

Again, the pressure used was the average of the four adjacent

points. The distribution function was plotted in Figure 6. All calculations were done by computer.

Materials

Antioxidant 330. (1,3,5-trimethyl-2,4,6-tris [3,5-di-tert-butyl-4 hydroxybenzyl] benzene). Manufactured by Ethyl Corporation, Baton Rouge, La. Used as a polymer antioxidant.

Diethyl Ether. Anhydrous. Reagent grade. Purchased from Fisher Scientific Co., Fairlawn, N.J. Used to extract naphthalene from fibers.

Epon 828 Epoxy Resin and U-Curing Agent. Product of the Shell Chemical Company, New York, N.Y. Used to embed fiber samples for sectioning.

Naphthalene. Crystals, certified. Lot 734228. Residue after ignition 0.0004%. Purchased from Fisher Scientific Co., Fairlawn, N.J. Used as a solvent in polymer solution.

Paraffin Wax (F-3505). Sample No. 72-1122. Donated by Humble Oil and Refining Co., Baton Rouge, La. Used as a solvent in polymer solution.

Permout. Manufactured by Fisher Scientific Co., Fairlawn, N.J. Used as a permanent slide mounting material for fiber samples.

Polypropylene. Dry powder, uninhibited. Specification 6501. Donated by Hercules Co. Used as polymer in fiber production.

Propylene Oxide. Lot No. G3B. Manufactured by Eastman Kodak Co., Rochester, N.Y. Used as solvent in fiber embedding procedure.

Stopcock Grease. Silicone lubricant. Manufactured by Dow Corning Corp., Midland, Mich. Used to seal resin kettle.

Tetrahydronaphthalene (Tetralin). Purified. Purchased from Fisher Scientific Co., Fairlawn, N.J. Used as a cleaning solvent for glassware and spinning apparatus.

Apparatus

The following is a list of apparatus used in this investigation.

Agitator Motor. Fultork Labmotor. 115 volts. Purchased from Fisher Scientific Co., Chicago, Ill. Used to stir solution in resin flask.

Balance. Type H15. Capacity 160 grams. No. 263987. Manufactured by Mettler Instrument Corp., Highstown, N.J. Purchased from Scientific Products, Evanston, Ill. Used to weigh fibers for denier, density, void fraction, and concentration measurements.

Balance. Single-beam type. Capacity 1100 grams. Manufactured by Eimer and Amend, New York, N.Y. Purchased from Fisher Scientific Co., Pittsburgh, Pa. Used to weigh components of polymer solution.

Heating Mantle. 115 volts. Series 0 Type. For 1000 ml. cylindrical flask. Serial No. 792820. Manufactured by Glas-Col Apparatus Co., Terre Haute, Ind. Purchased from Ace Glass, Inc., Vineland, N.J. Cat. No. 6478-10. Used for heating solution in resin flask.

Heating Tape. Flexible. 192 watts at 115 volts. 1/2" x 4 ft. Manufactured by Briscoe Manufacturing Co., Columbus, Ohio. Purchased from VWR Scientific, Baltimore, Md. Cat. No. 33735-046. Used to heat resin flask head during solution preparation.

Heating Tape. Glas-col. Double element. Silicone rubber coated. 150 watts at 45 volts. 1/2" x 4 ft. Manufactured by Glas-Col Apparatus Co., Terre Haute, Ind. Purchased from VWR Scientific, Baltimore, Md. Cat. No. 33729-021. Used for heating spinneret.

Mercury Intrusion Porosimeter. Aminco-Winslow. Cat. No. 5-7107. Manufactured by American Instrument Co., Inc., Silver Spring, Md. Property of the Metals and Ceramics Engineering Department, VPI&SU. Used to measure the pore size distribution of selected fiber samples.

Microscope. Optical camera microscope and metallograph. Model U-11. No. 552272. Manufactured by Unitron Instrument Co., Newton Highlands, Mass. Used to observe pore structure of fibers.

Resin Flask. Cylindrical. Pyrex glass. Capacity 1000 ml. Purchased from Ace Glass, Inc., Vineland, N. J. Cat. No. 6476-81. Used as solution preparation vessel in trials 1-12.

Resin Flask. Cylindrical. Stainless Steel. Capacity 1000 ml. Purchased from Ace Glass, Inc., Vineland, N. J. Used as solution preparation vessel for trials 13-18B, and 20.

Resin Flask Clamp. Purchased from Ace Glass, Inc., Vineland, N. J. Cat. No. 6496. Used to clamp resin flask head and bottom during solution preparation.

Resin Flask Head. Glass. 29/42 center joint, 24/40 side joints, 14/35 thermometer joint. Purchased from Ace Glass, Inc., Vineland, N. J. Cat. No. 6488-15. Used in solution preparation vessel.

Ring Stand. Purchased from Fisher Scientific Co., Chicago, Ill. Used to support resin flask and agitator.

Scanning Electron Microscope. AMR Model 900. Manufactured by Advanced Metals Research Corp., Burlington, Mass. Property of the Division of Forestry and Wildlife Sciences, VPI&SU. Used to observe pore structure of fibers.

Spinning Apparatus. The spinning apparatus consists of an 1 1/2 inch angle-iron framework supporting a jacketed oil bath tank surrounding a vertical extrusion tube (spinning cylinder). The removable extruder piston assembly is installed to the top of the spinning cylinder and attached by a drive chain to a variable speed piston drive motor. The spinneret assembly is bolted to the bottom flange of the spinning cylinder beneath the oil bath tank. Two variable speed take-up mechanisms are installed directly below the spinneret. The distance between the spinneret and the upper windup is eleven inches. The distance between the spinneret and the lower windup is five feet. The complete description of the spinning apparatus can be found in William's⁽³⁾ or Andrade's⁽⁵⁾ thesis. The modifications to the apparatus that have been made during this study are as follows:

The 1 1/2 inch wide, 1/4 inch thick steel bar used previously to hold the spinning cylinder in place during spinning was replaced with a 13 1/4 inch long, 3/4 inch copper tubing brace.

The 950 watt oil bath heating element was replaced with an 800 watt element.

A new piston was fabricated. The dimensions were the same as the previously used aluminum piston. However, it was made from steel. The valve placed in the bottom of the piston to allow air to escape during installation of the piston assembly was sealed shut with silver solder because of leakage of the solution through the piston during the spinning operation.

The four two inch long, 5/8 inch bolts welded to the bottom flange of the piston assembly were removed. Three 3 1/3 inch long, 5/8 inch bolts and one 3 1/2 inch long, 3/8 inch bolt were welded in the boltholes of the upper flange of the spinning cylinder so that they passed through the boltholes in both flanges of the piston assembly. This allowed the piston assembly to be installed much more easily.

Preliminary spinneret designs consisted of aluminum spinneret bodies with orifice diameters ranging from .170 to .261 inches. Solid three inch long steel mandrels .156 and .250 inches in diameter were centered in the orifice with a steel crosspiece.

The final spinneret design is shown in Figure 7.

The air injection port of the spinneret was connected to a 1/4" tubing air supply line. The supply line was connected to a

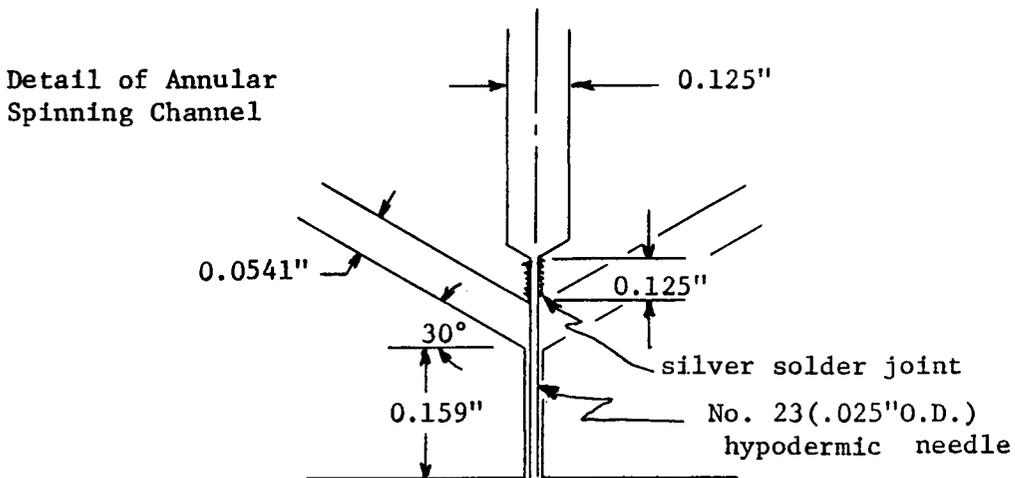
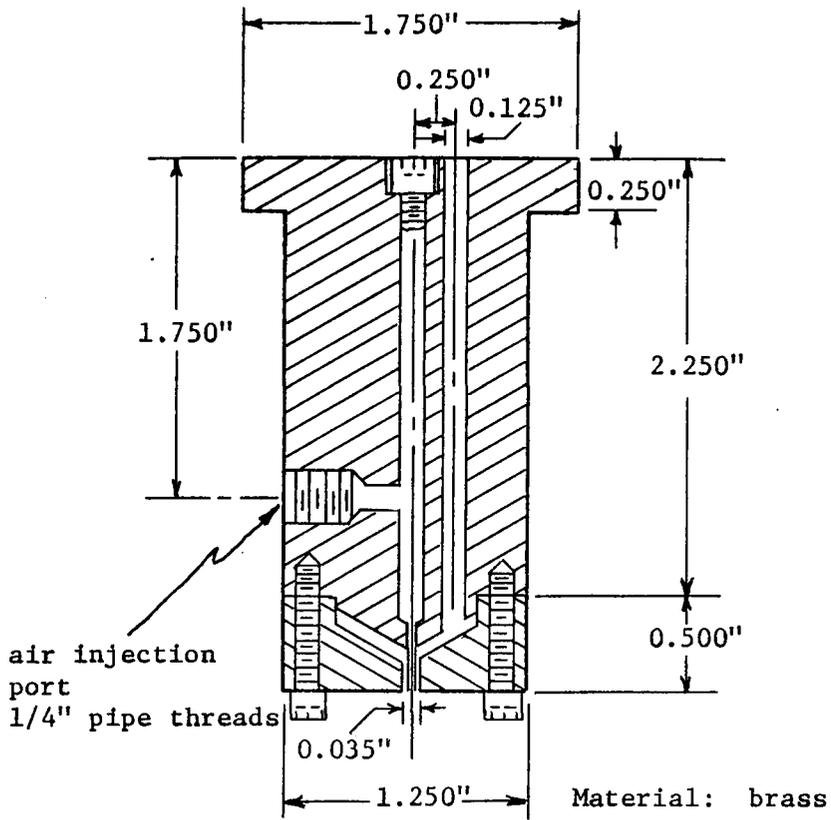


Figure 7. Tube-in-Orifice Spinneret Design
(Based on design in Office of Saline Water
Report No. 549(12))

vent valve, U-tube manometer, needle valve, and pressure regulator as shown in Figure 2. The spinneret also had an iron-constantan thermocouple soldered to its side about one inch from the bottom. The thermocouple was connected to a strip chart temperature recorder.

A second take-up mechanism was installed in the spinning cabinet so that the windup spool was eleven inches below the spinneret. The mechanism was mounted on a framework of one inch angle-iron which was, in turn, attached to the framework of the spinning apparatus. The take-up apparatus contained the drive motor, speed control, and windup spool in one cabinet.

A fishing reel was adapted for use as a thread guide by connecting it to a variable speed motor and mounting it adjacent to the lower take-up drum.

Some of the equipment used in these additions to the spinning apparatus are as follows:

1. Fishing Reel - True Temper. No. 945F. Manufactured by True Temper Corporation, Anderson, S.C. Used as a thread guide.
2. Manometer - 14 inch scale. Glass U-tube. Manufactured by Meriam Co., Cleveland, Ohio. Used to measure pressure of air supplied to spinneret injection port.
3. Motor - Model B-2420C-40L. One sixth horsepower, 73 inch pounds torque, 2.6-52 rpm. Manufactured by B&B Motor Control Corp., New York, N.J. Used to drive thread guide.
4. Temperature Recorder - Honeywell-Brown Potentiometer. Model No. 153R10RS-135W7-20, Serial No. 733555. Manufactured by Minneapolis-Honeywell Regulator Co., Philadelphia, Pa. Used to record spinneret temperature from thermocouple.

5. Thermocouple - Iron - Constantan. Glass on asbestos insulation. From spool No. 52620-12. Manufactured by Leeds and Northrup Co., North Wales, Pa. Used to measure spinneret temperature.
6. Variac - Powerstat voltage regulator, type 3PN116, 0-140 volts output. Manufactured by Superior Electric Co., Inc., Bristol, Conn. Purchased from Fisher Scientific Co., Chicago, Ill. Used to control voltage to spinneret heating tape.

Stirrer Paddles (3). 1) 1/8 inch thick, 1 1/2 inch wide blade, brass. 2) 1/8 inch thick, 3 inch wide blade, brass. 3) 1/8 inch thick, 3 inch wide blade, stainless steel. Made by the VPI&SU Chemical Engineering Department shop. Used to stir polymer solution.

Stirrer Paddle. Teflon, multi-paddle. 1 1/2" blades. Purchased from Ace Glass, Inc., Vineland, N. J. Cat. No. 8089-04. Used for stirring polymer solution.

Thermometers (2). Immersion type. Range -10 - 260°C. One °C divisions. Purchased from Ace Glass, Inc., Vineland, N. J. Cat. No. 8290-16. Used to measure temperature of solution during preparation and to measure temperature of the oil bath.

Variac (2). Powerstat voltage regulator, Type 3PN116, 0-140 volts output. Manufactured by Superior Electric Co., Inc., Bristol, Conn. Purchased from Fisher Scientific Co., Chicago, Ill. Used to control voltage to resin flask heating mantle and resin flask head heating tape during solution preparation.

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PHASE SEPARATION SPINNING OF POROUS POLYPROPYLENE HOLLOW FIBERS

by

Douglas E. Nelson

(ABSTRACT)

Two phase separation polymer-solvent systems were studied: polypropylene-paraffin wax, and polypropylene-naphthalene. A tube-in-orifice spinneret design was used.

All attempts to spin hollow fibers using the polypropylene-paraffin wax system failed. Initial attempts to produce hollow fibers from polypropylene-naphthalene solutions resulted in fiber samples with outside diameters ranging from 60 to 297 microns, and inside diameters ranging from 15 to 90 microns. However, subsequent spinning trials resulting in unpredictable solution flow behavior through the spinneret or drastic polymer degradation. A review of spinning procedures and pertinent literature led to the conclusion that chain scission of the polymer molecules was being catalyzed by contact of the polymer with certain metals (e.g. copper and iron) during solution preparation. However, with the use of a non-metallic mixing vessel and stirrer, the use of a nitrogen atmosphere, and the addition of proper stabilizers, this problem should be prevented in future studies.

From observations made by optical and scanning electron microscopes, and mercury intrusion pore size distribution measurements, it was concluded that the structure of the fibers consisted of fine

networks of interconnecting voids or pores. The significant majority of these pores had diameters of less than one micron.

Among the suggested areas for further study in the development of hollow fibers spun from polypropylene-naphthalene solutions were spinning condition effects on pore size distribution and the possibility of using a controlled temperature liquid quench bath in the spinning process.