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SPINNING OF FIVE SYNTHETIC POLYMERS INTO FIBERS

I. INTRODUCTION AND SUMMARY

This report summarizes the work carried out under Contract DAMD17-75-C-5026.

The U. S. Army Medical Bioengineering Research and Development Laboratories at Ft. Detrick have a program concerning the investigation of the performance and potential utility of sutures made from polycaprolactone, poly(DL-lactic acid), poly(L-lactic acid), poly(glycolic acid), and polypropiolactone. This program was undertaken to prepare both monofilament and braided sutures from samples of each of these polymers supplied to the Institute by the Medical Bioengineering Research and Development Laboratory.

Preliminary experiments were carried out to determine the feasibility of preparing filaments from each of the five polymers submitted. These preliminary experiments disclosed several unanticipated problems. Although polycaprolactone was easily melt spun into strong fibers, the fibers contained gel particles. The poly(glycolic acid) submitted was not satisfactory because of its low molecular weight. Because of these difficulties, the Institute investigated a commercially available polycaprolactone as an alternate to the samples supplied by the Army and also prepared a sample of poly(glycolic acid) for use in this program.

Both monofilament and braided sutures of poly(glycolic acid) and poly(L-lactic acid) were prepared and shipped to the U. S. Army Medical Bioengineering Research and Development Laboratory. The poly(glycolic acid) materials were made from polymers prepared by the Institute. The poly(L-lactic acid) materials were made from polymer supplied by the Army. The feasibility of preparing suture materials from commercially available polycaprolactone was demonstrated, but fibers were not made in sufficient quantity for the Army's purposes. The preliminary examination of poly(DL-lactic acid) indicated that satisfactory fibers could be made from the polymer but the quantity of fiber needed could not be made from the polymer as supplied. Since the polymer was a fluffy powder of low bulk density, only small amounts could be charged to the ram extruder. Although this polymer was converted into granules suitable for melt spinning, funds were exhausted before spinning was completed. Fibers of the polypropiolactone were too brittle to be collected. The molecular weight of this polymer was quite low.

Because of the unanticipated difficulties, the funds available did not allow for the preparation of all of the suture materials expected. However, a polycaprolactone suitable for spinning is commercially available, and an adequate quantity of poly(DL-lactic acid) for spinning has been prepared and is available. Only a limited effort would be required to convert these polymers into suture materials.

II. MATERIALS AND PROCEDURES

A. Materials

Five polymer samples were supplied by the U. S. Army Medical Bioengineering and Development Laboratories. A brief description of these samples together with the information supplied by the Army is given below. Information on two additional polymer samples (supplied by Union Carbide and SRI) is also included.

1. Polycaprolactone (Supplied by Army)

Approximately 500 g of this polymer was supplied. It was reported that this polymer had a molecular weight of 54,000, an inherent viscosity of 0.762 dl/g (in benzene), and a melting point of 52°C (DSC). This sample was assigned SRI Sample No. 7718-3-1.

2. Poly(L-Lactic Acid) (Supplied by Army)

Approximately 650 g of this polymer was supplied. It was reported to have a molecular weight of 220,000, an inherent viscosity of 1.15 dl/g, and a melting point of 60°C (DSC). This sample was assigned SRI Sample No. 7718-3-2.

3. Poly(DL-Lactic Acid) (Supplied by Army)

Approximately 360 g of this polymer was supplied. It was reported to have a molecular weight of 135,000, an inherent viscosity of 1.15 dl/g, and a melting point of 60°C (DSC). This sample was assigned SRI Sample No. 7718-3-3.

4. Poly(Glycolic Acid) (Supplied by Army)

Approximately 500 g of this polymer was supplied. No information regarding the properties of this polymer has been received. This sample was assigned SRI Sample No. 7718-47.

5. Polypropiolactone (Supplied by Army)

Approximately 460 g of this polymer was supplied. It was reported to have an inherent viscosity of 0.42 dl/g (in chloroform) and a molecular weight of 19,300. This sample was assigned SRI Sample No. 7718-43.

6. Polycaprolactone (Union Carbide)

Union Carbide Corporation, Chemicals and Plastics Division, supplied a sample of pelletized polycaprolactone identified as PCL-700, Code B-5283. This sample was assigned SRI Sample No. 7718-71.

7. Poly(Glycolic Acid) (Supplied by SRI)

The Institute prepared a sample of poly(glycolic acid) by the procedure described in Section III-B of this report. This sample was assigned SRI Sample No. 7718-46.

B. Equipment

1. Melt rheometer

The melt rheometer used in these experiments was a modified Slocomb melt indexer. The equipment was modified by attachment of a linear potentiometer to the piston and installation of simple circuitry to record piston travel as a function of time. This allowed calculation of polymer flow rate through the orifice. The effect of temperature on polymer melt viscosity was determined by measurements of polymer flow rates through the orifice at different temperatures. Indications of the thermal stability of polymers were obtained by observations of the effect of residence time in the melt on polymer flow rate. Decomposition of the polymer is indicated by an increase in polymer flow rate with increased residence time in the melt. In these experiments the rheometer was equipped with a single orifice having a diameter of 20 mils and a length of 80 mils.

2. Ram extruder

The ram extruder used in these experiments was designed and built at the Institute. The essential parts of this extruder are: a cylindrical electrically heated block about 4 inches in diameter, designed to accomodate metal inserts about 7 inches in length with either 1/2-inch- or 7/8-inch-diameter cylinders, a spinneret and screen pack assembly which fits into the block directly below the insert, a metal ram (either 1/2- or 7/8-inch-diameter) driven by

a variable-speed drive to force the polymer through the filter and spinneret, and a surface-driven winder located about 5 feet below the spinneret. In some experiments the tube holder of this winder was replaced with a pressure roll so that the winder mechanism served to draw the fibers away from the spinneret at a constant rate; the fibers were then packaged on a Leesona 959 winder.

Two different spinnerets were used in these experiments. One had a single orifice 20 mils in diameter with a 4:1 length-to-diameter (L/D) ratio, and the other 7 orifices 12 mils in diameter with a 2:1 L/D ratio.

The general operating procedure was as follows. The cylinder of the ram extruder was charged with polymer and the ram was inserted. After about 10 minutes for the polymer to melt and reach equilibrium temperature, the ram drive was activated and the molten polymer was forced through the spinneret. The force applied to the ram during extrusion was measured with a force gauge. The fibers extruded from the spinneret were quenched in air and packaged.

3. Pilot-scale melt spinning

A schematic of the pilot-scale melt spinning equipment used in this program is shown in Figure 1. The essential components of this equipment are a 3/4-inch screw extruder, a spinning head, a quench chamber, a take-up stand, and a winder. The screw extruder is a 3/4-inch extruder with a 20:1 L/D ratio having individually controlled electrical heaters on the feed zone and on the metering zone. The spinning head is an electrically heated cylindrical block containing a metering pump, a combination sand and screen pack, and a spinneret. In the quench chamber located below the spinning head, extruded filaments are quenched by a controlled air flow across the filament line. The take-up stand is a twin-godet type and is equipped with a spin-finish applicator which allows the application of spin finish at a metered rate. The winder is a Leesona 959 constant-tension winder.

4. Fiber orienting equipment

A draw winder was used to orient the fibers. This equipment consisted of two godets with a heated platen located between them. The yarn was fed onto the feed godet, and it passed over the heated platen onto the take-up godet. The yarn was stretched by operating the take-up godet at a higher surface speed than the feed godet.

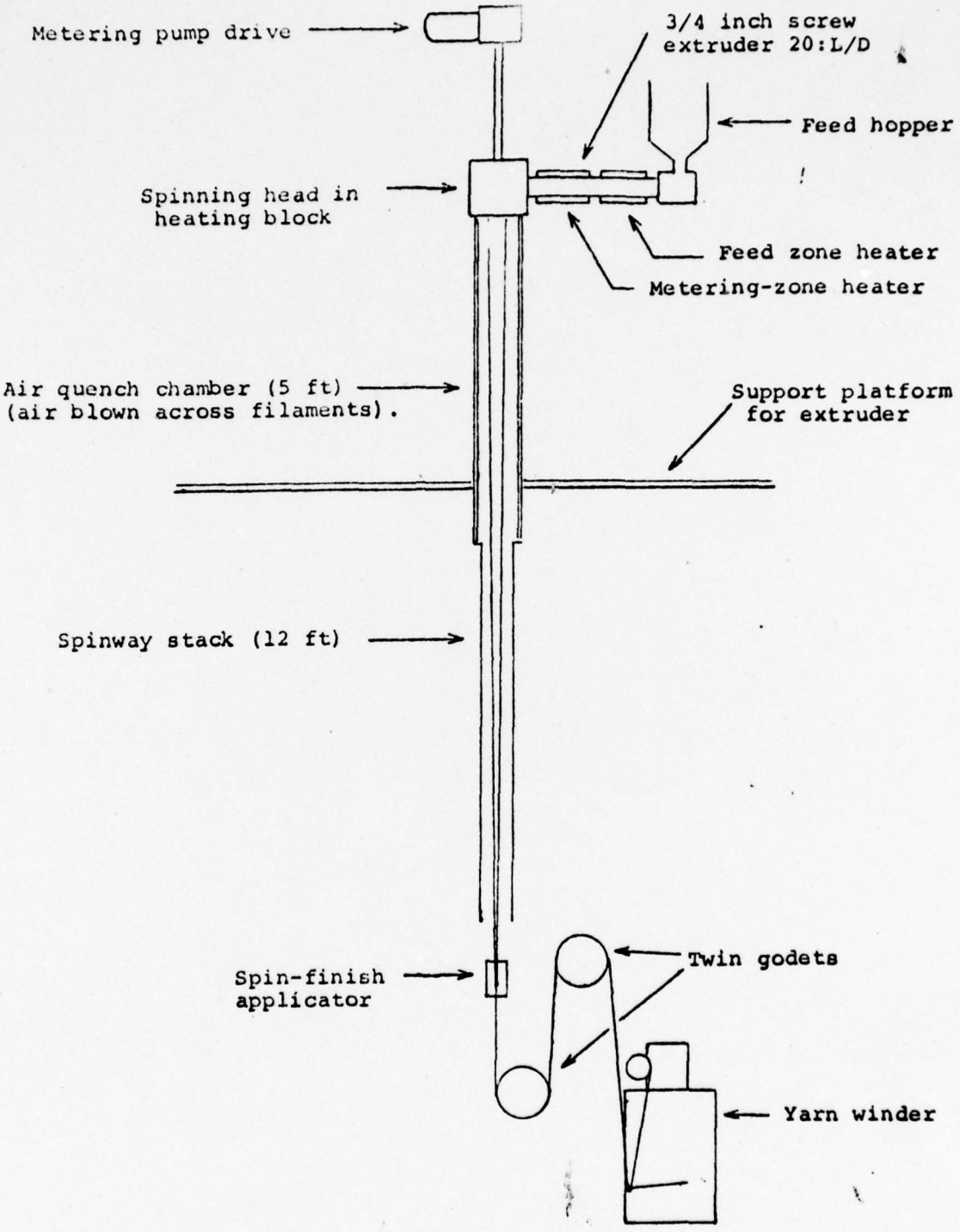

Figure 1. Schematic of Melt Spinning Equipment

III. EXPERIMENTAL AND DISCUSSION

A. Preliminary Experiments

Polycaprolactone - Sample No. 7718-3-1

The polymer sample was dried for about 18 hours at 30-40°C under vacuum (about 1 mm).

Melt rheometer studies were carried out to determine the effect of melt temperature on melt viscosity and to determine the heat stability of the polymer. The melt flow rate of the polymer was determined at three temperatures with the modified Slocomb melt indexer described in Section II-B.1. The polymer was charged to the melt indexer, and after a 4-minute heat-up time, the polymer was extruded under a load of 7,089 g on the piston. The flow rates at the three temperatures are given in Table I below.

Table I. Melt Flow Rate of Polycaprolactone at Various Temperatures

Temperature, °C	Melt flow rate, cm^3/min
115	0.026
123	0.031
143	0.059

Over a time interval of about 15 minutes, there was no evidence of a change in polymer flow with residence time. The polymer had good thermal stability.

These melt rheometer studies showed that the polycaprolactone could be melt spun. Melt spinning trials were carried out with the ram extruder. In an initial experiment an effort was made to melt spin a monofilament with the ram extruder fitted with the 7/8-inch-diameter cylinder. The monofilament was extruded without difficulty, but with the piston drive available, the minimum extrusion rate was too high to obtain adequate quenching of the monofilament before it reached the winder roll.

Additional spinning trials were then made with the ram extruder fitted with the 1/2-inch-diameter cylinder in order to reduce the extrusion rate. In the first experiment the block temperature was 112°C, the polymer extrusion rate was 0.23 cm^3/min, and the filament take-up rate at the winder was 21 ft/min. No

operational difficulties were experienced. Occasional enlarged sections along the length of the monofilament were observed. The appearance of these enlarged sections indicated that the polymer might contain gel particles.

Multifilament yarns were then melt spun with the ram extruder fitted with a spinneret having 7 orifices 12 mils in diameter with an L/D ratio of 2:1. Spinning trials were made with block temperatures of 92°C, 100°C, 125°C, and 140°C at a fixed polymer flow rate of 0.23 cm^3/min and a yarn take-up speed of 14 ft/min. No operational difficulties were experienced in any of these experiments. All of the filaments had occasional short lengths of enlarged diameters. A microscopic examination of the filaments did not disclose foreign material. The polymer probably contained gel particles. The nonuniformity in diameter of the filaments is not severe, and the yarns are probably of satisfactory quality for use in preliminary suture evaluation studies.

Portions of the monofilaments and the multifilament yarns melt spun with a block temperature of 100°C were oriented on the draw winder. Drawing conditions and the properties of the oriented filaments are given in Table II.

Monofilament Samples 7718-13-1 and -2 were oriented at 9:1 draw ratio over a heated platen at 25°C and at 50°C, respectively. No significant difference in the tensile properties of the monofilaments indicated that over the range of 25-50°C, variation in platen temperature has no effect. Monofilament Samples 7718-13-1 -2 and -3 were drawn over the platen at 50°C at draw ratio of 9:1 and 10:1, respectively. Increasing the draw ratio from 9:1 to 10:1 increased the tenacity from about 3.0 to 4.7 g/d. Monofilament Sample 7718-13-2-1 was prepared by orienting a monofilament that had received more draw down during spinning than the previous monofilaments. That the high draw down had no effect on the tenacity of the oriented monofilament showed that the polycaprolactone will tolerate a high draw down during spinning. Monofilament 7718-13-1 -4 was oriented by a two-stage draw. In the first stage the monofilament was drawn 6:1 and was then drawn again at 2:1 draw ratio for a total 12:1 draw. This oriented monofilament had a tenacity of 5.5 g/d. Sample 7718-29-4-3 was prepared by orienting the multifilament yarn at a 9.5:1 draw ratio over a platen heated to 40°C. The tenacity of this oriented yarn was 4.7 g/d.

The fiber-forming properties of the polycaprolactone were judged to be excellent. The polymer was melt spun without difficulty. Its melt flow properties were good, and it will tolerate a high draw down between the spinneret and the take-up. The melt spun yarns, both monofilament and multifilament, were oriented

Table II. Properties of Oriented Polycaprolactone Fibers

Sample 7718-	Draw ratio	Platen temp, °C	Denier/fil	Tenacity, g/d	Elongation at break, %	Filament diameter, mils	Tensile factor
13-1-1	9.0	25	60/1	3.9	169	3.0	51
-2	9.0	50	65/1	3.8	149	3.1	46
-3	10.0	50	55/1	4.7	55	2.7	35
2-1	10.3	50	17/1	4.5	48	1.7	31
1-4	6.0 2.0	50	35/1	5.5	27	3.0	28
29-4-3	9.5	40	62/7	4.7	53	1.2	34

without difficulty, and the tensile properties of the oriented fibers were good. There was more than normal variation in the tensile property data due to the diameter nonuniformity of the filaments. These nonuniformities would tend to make the measured denier of the fibers greater than the effective denier in the tensile test, and this in turn will tend to make the determined tenacity lower than the true value. Certainly with further effort, improvements in fiber quality can be attained.

Poly(L-Lactic Acid) - Sample No. 7718-3-2

The sample was dried for about 18 hours at a temperature of 30-40°C under vacuum (about 1 mm).

Melt rheometer studies were carried out to determine the effect of melt temperature on melt flow rate and to determine the thermal stability of the polymer. The data obtained are given in Table III below.

Table III. Melt Flow Rate of Poly(L-Lactic Acid) at Various Temperatures

Temperature, °C	Melt flow rate, cm^3/min
190	0.074
196	0.074
205	0.176

The constancy of melt flow rate over a residence time of about 15 minutes indicated that the polymer had good thermal stability.

Both monofilaments and multifilament yarns were melt spun with the ram extruder operating at a block temperature of 197°C. The monofilament was spun through a spinneret having a single orifice 20 mils in diameter with a 4:1 L/D ratio. The polymer flow rate was 0.23 cm^3/min. The monofilament was collected at a take-up speed of 30 ft/min. The multifilament yarn was spun through a spinneret having 7 orifices 12 mils in diameter with a 2:1 L/D ratio. The polymer flow rate was 0.80 cm^3/min, and the yarn take-up speed was 25 ft/min.

Both the monofilaments and the multifilament yarns were extruded without difficulty, but they were difficult to take up on the winder because they developed a high static charge. This

problem was controlled to some extent by placing an electric discharge static eliminator behind the thread line and by applying a mineral oil spin finish.

The monofilaments and the multifilament yarn were oriented with the draw winder. A platen temperature of 70°C was found to be suitable for orienting these fibers. The melt spun fibers were brittle and were difficult to handle in the drawing equipment. The properties of the oriented monofilament and the multifilament yarn are given in Table IV.

The tenacity and the tensile factor of the oriented fibers are comparatively low. We do not expect to be able to make hihg-strength fibers of this polymer. Since the reported molecular weight of this polymer is high, we doubt that further increases in molecular weight would result in substantial improvement in fiber strength, although this possibility cannot be ruled out.

Poly(DL-Lactic Acid) - Sample No. 7718-3-3

The polymer as received was dried for about 18 hours at a temperature of 35-40°C under vacuum (about 1 mm).

Melt rheometer studies were carried out at temperatures of 205°C and at 215°C. The polymer flow rate at 205°C was 0.11 cm^3/min and at 215°C the flow rate was 0.20 cm^3/min. A slight increase in polymer flow rate over a residence of 15 minutes indicated some thermal decomposition, but the change in flow rate with time was so small that the decomposition was not considered to be detrimental. The polymer was judged to have adequate stability for melt spinning trials.

The poly(DL-lactic acid) was melt spun in the ram extruder under conditions identical to those used for the poly(L-lactic acid). Both monofilament and multifilament yarns were melt spun at a block temperature of 197°C. The monofilaments were melt spun through a spinneret having an orifice 20 mils in diameter with a 4:1 L/D ratio. The polymer flow rate was 0.23 cm^3/min. One monofilament was collected at a take-up speed of 28 ft/min and another at 48 ft/min. The multifilament yarn was melt spun through a spinneret having 7 orifices 12 mils in diameter with a 2:1 L/D ratio. The polymer flow rate was 0.97 cm^3/min, and the take-up rate was 32 ft/min.

The extrusion characteristics of the polymer were good. The filaments were difficult to take up because they developed a high static charge. A static eliminator was used to reduce the static charge, and a mineral oil spin finish was applied to the multifilament yarn to help bind the filaments together.

Table IV. Properties of Oriented Poly(L-Lactic Acid) Fibers

Sample 7718-	Draw ratio	Platen temp, °C	Denier/fil	Tenacity, g/d	Elongation at break, %	Filament diameter, mils	Tensile factor
17-3-1	4.6	70	58/1	2.3	39	5.0	14
-2	5.2	80	49/1	3.1	33	-	18
21-1-1	5.4	80	125/7	1.8	54	1.5	13

Both the monofilaments and the multifilament yarn were oriented with the draw winder with a platen temperature of 70°C. The brittleness of the melt spun yarns made it necessary to devise a special feed system for the draw winder to avoid breakage. The properties of the oriented monofilaments and the multifilament yarn are given in Table V.

The tenacity and the tensile factor of the fiber of this polymer are rather low, being comparable to those of the fibers of poly(L-lactic acid). We do not expect to be able to make high-strength fibers of this polymer.

Poly(Glycolic Acid) - Sample No. 7718-47

The polymer as received was dried for 48 hours at 135°C under vacuum (about 1 mm). The inherent viscosity of the dried polymer was 0.54 dl/g, with hexafluoroacetone sesquahydrate as the solvent and at a polymer concentration of 0.5 g/dl. The Institute's experience with poly(glycolic acid) indicated that the inherent viscosity of this polymer was too low for fiber spinning. A monofilament of this polymer was extruded with the melt index equipment at a block temperature of 242°C. The extruded monofilament was quite brittle as anticipated.

Polypropiolactone - Sample No. 7718-43

The sample as received was dried overnight at 35°C under vacuum (about 1 mm).

Attempts to melt spin fibers of this polymer in the ram extruder were not successful. Spinning trials were made with both a monofilament and a multifilament (7 orifice) spinneret, with block temperatures ranging from 80°C to 100°C. The filaments made in all trials were brittle. The low molecular weight of the polymer may account for the brittleness.

B. Preparation of Poly(Glycolic Acid)

A sample of poly(glycolic acid) was prepared essentially by the procedure described in Example 1 of U. S. Patent 2,668,162 (Charles E. Lowe, to Du Pont, February 2, 1954). Minor modifications of the procedure are described below.

The glycolide was supplied by an industrial sponsor and purified by the method described in the Lowe patent.

Table V. Properties of Oriented Poly(DL-Lactic Acid) Fibers

Sample 7718-	Draw ratio	Platen temp, °C	Denier/fil	Tenacity, g/d	Elongation at break, %	Filament diameter, mils	Tensile factor
13-3C-,	5.0	70	28/1	2.3	44	1.9	15
17-1-1	5.0	70	18/1	2.0	28	1.5	11
25-1	5.0	70	120/7	1.6	59	1.5	12

The polymerization process is a slight modification of that described by Lowe. In the Lowe process, the glycolide is polymerized without a chain stopper, but this procedure gives polymers having a molecular weight higher than desirable for melt spinning. In British Patent 1,043,518 (September 1, 1966, to American Cyanamid), methoxyacetic acid is used as a chain stopper for control of molecular weight, and Santonox R is used as an antioxidant. The procedures of the two patents were combined.

The specific procedure used is as follows. A stainless steel resin kettle having a glass top was charged with 1500 g of glycolide, 0.45 g of antimony trifluoride, 0.30 g of methoxyacetic acid, and 0.45 g of Santonox R. The resin kettle was equipped with a horseshoe-type stirrer having a diameter about a half inch less than that of the kettle. The kettle was loaded in a dry box to protect the glycolide from moisture. In loading the kettle, the stirrer was set in place, half of the glycolide was charged, the catalyst, chain stopper, and antioxidant were then added, and the remainder of the glycolide was charged. The kettle top, fitted with an O-ring-sealed stirrer bearing, a thermocouple well, and a gas inlet tube, was then clamped onto the pot. The assembled kettle was positioned above an oil bath preheated to 195°C, and a slow stream of nitrogen was passed into the kettle. The oil bath was raised to submerge the kettle in the oil to a level about an inch below the top of the stainless-steel pot. The temperature of the oil bath dropped to about 185°C when the kettle was immersed, but the temperature rose to the set temperature of 195°C in about 30 min. After the glycolide melted, the stirrer was started and run at 20 RPM. At intervals, the stirrer was stopped, and the thermocouple well was lowered into the melt to measure the melt temperature. When the temperature reached 188°C, timing of the polymerization was started. After about 50 minutes, the viscosity of the polymer was so high that the stirrer labored excessively. The stirrer was then raised above the polymer. The kettle remained in the oil bath for a total of 4-1/2 hours polymerization time, and then the oil bath was lowered. The polymer was allowed to cool to room temperature under a nitrogen blanket. The top was then removed from the pot, and the block of resin was emptied onto a clean surface and immediately packaged in a polyethylene bag under nitrogen.

The block of polymer was crushed in a breaking box in a hydraulic press. The breaking box consisted of two stainless steel trays, one slightly smaller than the other. The larger tray was set on the lower platen of a press, the block was placed in this tray, the smaller tray was then set on top of

the block, and the press was closed. In this way the block was fragmented with the fragments being confined in the box. An effort was made to keep the polymer under a nitrogen blanket during this operation.

The polymer chips from the breaking box were ground in a No. 1 Wiley Mill fitted with a 1/4-inch screen. An effort was made to blanket the polymer with nitrogen during grinding. The ground polymer was dried for 48 hours at a temperature of 135°C under a vacuum of about 1 mm. Some unreacted monomer and possibly some low-molecular-weight polymer was liberated during drying. It was necessary to fit the vacuum oven with a 3/4-inch exhaust port to avoid line plugging.

The dried polymer was transferred while hot into a filter flask. The flask was evacuated and flushed with dry nitrogen three times. A dry nitrogen pressure of about 5 psig was maintained on the flask.

C. Preparation of Suture Materials

1. Poly(Glycolic Acid) (Supplied by the Institute)

The poly(glycolic acid) prepared as described in Section III-B above was melt spun in the pilot scale melt spinning equipment described in Section II-B.3. The melt spinning head was fitted with a spinneret having 8 orifices, having a diameter of 20 mils and length-to-diameter (L/D) ratio of 8 to 1. The temperatures in the melt spinning equipment were: extruder feed zone 299°C, extruder metering zone 250°C, and spinning head 224°C. The polymer extrusion rate was 2.5 lbs/hr. Four of the eight filaments were collected together as a yarn, and the remaining four were aspirated to waste.

This melt spun yarn was oriented with the draw winder. The temperature of the feed roll, the platen, and the take-up roll was 60°C. The yarn feed rate was 35 ft/min and the draw ratio was 5.8 X. A portion of this yarn was braided with an eight position braider. Samples of yarn and braid were packaged in a sealed metal can containing a packet of silica gel.

2. Poly(Glycolic Acid) (Supplied by the Army)

Although the preliminary experiments described in Section III-A above indicated that the poly(glycolic acid) supplied by the Army was not suitable for fiber formation, an effort was made to melt spin fibers of this polymer in the pilot scale melt spinning equipment. The process conditions selected were identical to those used to melt spin the poly(glycolic acid) prepared by the

Institute, but the polymer supplied by the Army would not form fibers under these conditions. The viscosity of the extruded polymer melt was too low.

3. Polycaprolactone (Supplied by the Army)

This polymer was melt spun with the ram extruder with the 7/8-inch-diameter cylinder. The extruder was fitted with a spinneret having four orifices of 2-mil diameter and 4-to-1 length-to-diameter ratio. The block temperature of the ram extruder was 100°C.

In initial experiments the polymer as received (fluffy flakes) was dried under vacuum at 40°C and then charged to the ram extruder. After 30 minutes to allow the polymer to melt and reach equilibrium, extrusion was started. The extruded filaments were not uniform in diameter primarily because of what appeared to be gel particles in the polymer and secondarily because of air entrapped in the polymer. Apparently even the long heat up time was not sufficient to cause all of the air entrapped in the fluffy polymer to escape.

A portion of the polymer was melted under vacuum in order to obtain an air-free sample. We found that the solid polycaprolactone could not be crushed in a press or ground in a Wiley Mill even when cooled in dry ice. Consequently, the polymer was melted into cylinders that would fit into the ram extruder cylinder. Test tubes of about 13/16-inch ID were filled with the flakes of polymer, and the tubes were evacuated and immersed in an oil bath at 100°C for 4 hours. The polymer melted down into cylinders about an inch long. The polymer was cooled under vacuum, and the tubes containing the polymer were placed in dry ice. The glass broke cleanly away from the polymer. About 200 g of the polymer as received was converted into solid cylinders of polymer in this manner.

Two spinning trials were made with the solid polymer blocks using a charge of about 50 g of polymer in each trial. In the first trial, a screen pack of two 250-mesh screens was used above the spinneret. The extruded filaments contained gel particles which caused enlarged sections along the length of the filaments. In the second trial, a sintered metal filter with 2-micron pore size was placed above the spinneret instead of the usual screen pack. This filter reduced the frequency of gel particles in the extrudate initially but became ineffective after a few minutes extrusion.

A portion of the melt spun filaments were oriented with the draw winder. The sections of the filaments that were free of gel particles were quite strong. We were not able to braid these filaments because they broke in passing through the fiber guides. The break invariably occurred adjacent to a gel particle.

4. Polycaprolactone (Supplied by Union Carbide)

One melt spinning trial was made with the polycaprolactone supplied by Union Carbide. The pelletized polymer was dried under vacuum at 40°C, and about 40 g of the dried polymer was charged to the ram extruder preheated to 98°C. The polymer was allowed to preheat under a pressure of about 5 psi for 30 minutes and then extrusion was started. The polymer was extruded through a spinneret having 4 orifices 20 mils in diameter with a 4-to-1 length-to-diameter ratio. No problems were encountered in melt spinning this polymer.

A portion of the melt spun yarn was oriented with the draw winder. No problems were experienced in orienting this yarn. The filaments in the yarn were uniform in size, and the yarn could probably have been braided without difficulty.

The polycaprolactone supplied by Union Carbide was melt spun under essentially the conditions as those used to melt spin the polymer supplied by the Army. At equal extrusion rates, the force applied to the ram of the extruder was identical for both polymers. There was no significant difference in the melt viscosity of the two polymers.

On the basis of the limited work with the polycaprolactone supplied by Union Carbide, good quality fibers and braids could probably be made from this polymer.

5. Poly(L-Lactic Acid) (Supplied by the Army)

The polymer as received was dried under vacuum at about 50°C. The bulk density of the fluffy dried polymer was too low to provide a satisfactory charge to the ram extruder. Therefore, the polymer was melted under vacuum to obtain a product of higher bulk density than the polymer as received. A 500-ml flask was filled with the fluffy polymer, and was then evacuated and immersed in an oil bath at 200°C for an hour. The polymer was then cooled to room temperature under vacuum. The flask was placed in dry ice, and the glass broke cleanly away from the polymer. The block of polymer was then crushed in a hydraulic press. About 190 g of polymer chips were prepared in this manner. The chips were dried under vacuum at 50°C, and the dried chips were used as charge for the ram extruder.

The poly(L-Lactic acid) was melt spun in the ram extruder (7/8-inch-diameter cylinder) fitted with a spinneret having 7 orifices 12 mils in diameter with a 2-to-1 length-to-diameter raio. About 50 g of the polymer chips was charged to the ram extruder preheated to 190°C. The polymer was held under a pressure of about 5 psi for 30 minutes to melt the polymer and

attain temperature equilibrium in the melt. The molten polymer was then extruded at the rate of 0.23 cm^3/min, and the yarn was taken up at the rate of 35 ft/min. A spin finish consisting of a 25% solution of Dracol 35 (Penzoil Company) in xylene was applied to the yarn to control static. Dracol 35 is a refined white oil.

The melt spun yarn was oriented by drawing with the draw winder. The yarn was drawn 5.3 X over the platen heated to 80°C at a feed rate of 13 ft/min. No difficulties were experienced in orienting this yarn under the process conditions used. Because the melt spun yarn was rather brittle, it was necessary to orient at low speed and exercise care in feeding the yarn into the draw winder.

A portion of the oriented yarn was braided with an eight-feed braider. No difficulties were encountered in the braiding operation.

6. Poly(DL-Lactic Acid) (Supplied by the Army)

The poly(DL-Lactic Acid) as received was a fluffy flake material having an even lower bulk density than the poly(L-Lactic Acid), and it was necessary to melt this polymer and cement it into chips.

In the first attempt to cement the polymer as received into a solid block, a 500-ml flask was filled with the flakes of polymer, and the flask was evacuated and then immersed in an oil bath at 200°C for an hour. The yield of solid polymer was only 15 g. A device was constructed to compact the flaky material before charging it to the flask. This device consisted of a 3/4-inch-diameter tube eight inches long fitted with a removable plug and a piston. One end of the tube was plugged, the tube was filled with polymer flakes, and the piston was inserted in the tube and driven downward with repeated blows of a hammer. The compacted pellets of the flaky polymer (about 1/2-inch long) were charged into a 500-ml flask. The flask was evacuated and then immersed in an oil bath at room temperature, and the temperature of the bath was raised to 200°C over a period of about an hour. The polymer was held at 200°C for an hour and then cooled at room temperature under vacuum. The flask containing the solid polymer was placed in dry ice, and the glass broke away from the polymer. The block of polymer was crushed in a hydraulic press and then ground in a Wiley Mill. The polymer chips were dried under vacuum at about 50°C.

A spinning trial was made with a small charge (about 20 g), and no problems were encountered.

The polymer chips will be retained so that they will be available for possible future work on fibers of this polymer.

D. Samples Supplied to Army

The following samples were shipped to Dr. Clarence W. R. Wade, Chief, Biomaterials and Evaluation Division, U. S. Army Medical Engineering and Development Laboratory, Fort Detrick, Frederick, Maryland.

SRI Designation	Description
7718-51-1	Fibers of Poly(Glycolic Acid) (60 g). The average filament diameter was 1.87 mils. The tenacity was 5.8 g/d and the elongation at break 25%.
7718-51-2	Braid of Poly(Glycolic Acid) yarns (60 g). The diameter of the braid was 14.5 mils and the breaking strength of the braid was 5.0 pounds.
7718-91-1	Fibers of Poly(L-Lactic Acid) (30 g). The average diameter of the filaments was 1.9 mils and the average breaking load was 3.41 g. The elongation at break was 34%.
7718-91-2	Braid of Poly(L-Lactic Acid) yarns (25 g). The diameter of the braid was 14.5 mils and the breaking load was 4.5 pounds.

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