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DEVELOPMENT OF ULTRA THIN GAUGE POLYMERIC FILMS

by Dale W. Cox, Jr.

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SEA-SPACE, INC.

NASA CR-72051

FINAL REPORT

DEVELOPMENT OF ULTRA THIN GAUGE POLYMERIC FILMS

by Dale W. Cox, Jr.

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

September 1966

Technical Management
NASA Lewis Research Center
Cleveland, Ohio
Chemical Rocket Division
R. F. Lark

SEA-SPACE SYSTEMS, INC.
Torrance, California

FOREWORD

This investigation, which was prepared by Sea-Space Systems, Inc., Torrance, California, under NASA Contract NAS 7-274, was initiated by NASA Headquarters to study the fabrication parameters of ultra-thin gauge polymeric films for space applications. The final portion of this work was managed technically by the Lewis Research Center with Mr. R. F. Lark acting as the technical manager. This report covers work conducted from April 16, 1965 to August 10, 1966 and is submitted in fulfillment of the subject contract.

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DEVELOPMENT OF ULTRA THIN GAUGE POLYMERIC FILMS

FINAL REPORT

Contract No. NAS 7-7274

SUMMARY

Continued experience in extruding crystalline olefin polymers in very thin gauges was achieved during this program. Polyethylene film was extruded consistently in gauges less than 1/10 mil and polypropylene film in gauges less than 1/5 mil.

Flexibility and tensile tests of thin films in cryogenic liquids indicated that thin-film polyethylene can be used at temperatures down to -423° F. These results contradict generally accepted cold brittle temperature data for polyethylene from previous researchers, who had based their investigations on heavier gauge films.

Successful performance of the double orifice die to extrude ultra thin gauge films in gauges below 1/15 mil was not achieved. Although six (6) extruder operations were conducted, problems due to blocking of the films and a very slight movement of the side-fed die barrel under load prevented film gauges less than 0.082 mil from being achieved. Continued attempts to adjust for this "loading" movement and to inject a suitable anti-block material between film layers were not successful.

Changes in physical properties of ultra-thin gauge polyethylene films with time was experienced and investigated. An analysis of these results is presented.

INTRODUCTION

Previous work (1) under this contract had resulted in the production of ultra-thin gauge (UTG) polyethylene films. Gauges of 1/16.3 mil (1.55 μ; 15,500 Å) had been achieved during one extruder operation. Samples of this film were furnished to NASA.

The extrusion techniques developed and the equipment modifications required were extensions of previous Sea-Space Systems technology in this area. Detailed discussions of both theoretical limitations, practical problems involved and equipment requirements were discussed in reference 1.

Extruding extremely thin gauge polymeric films is a time-consuming, laborious art. Frequent die blowouts, many times for which no reasonable explanation can be derived, are the general rule using existing commercial equipment. This is caused by using commercial equipment not designed for the application. The thinnest gauge polyethylene films produced by industry are generally 0.38 to 0.40 mil. Seldom is film produced less than 1/3 mil, particularly in polyethylene. The cost of any polymeric film rises rapidly with a decrease in gauge, sometimes by a factor of 3 or 4.

The contract extension of this previous work was made to (1) evaluate the double orifice die; (2) extrude polypropylene film in thin gauges; (3) evaluate new NASA supplied polyimides and polyesters; (4) fabricate test specimens for space applications; (5) test the UTG film extruded; and (6) provide composite film samples for NASA.

A total of ten (10) extruder operations were conducted in order to improve on the ultra thin gauge (UTG) films previously attained on the first program. Each run is discussed separately in the analysis of results described below.

Equipment description, extruder set up procedures and film production are discussed in detail in reference 1. Basic polymer technology pertinent to phases of this work is discussed in references 2 and 3. Testing procedures and methods are covered in reference 4.

In addition to extruder operations, film test data for physical properties were obtained using modified ASTM D-882 procedures (4). Also, UTG film was evaluated in a flexibility testing apparatus in liquid nitrogen and hydrogen.

TECHNICAL DISCUSSION

Problems continually arose in attempting to produce UTG film with the double orifice die. Consequently, a major portion of the contractual effort was expended in attempting to overcome these technical problems, and this, of necessity, shifted scheduled man hours and costs in the program. The following chronology presents highlights of this contract.

CHRONOLOGY OF PROGRAM

Amendment No. 5 dated April 20, 1965 for period through March 31, 1966
Interim Technical Report submitted May 1965

Extruder operation No. 1	May 22, 1965	Double orifice die/GEC $2\frac{1}{2}$"
Extruder operation No. 2	July 17, 1965	Double orifice die/GEC $2\frac{1}{2}$"
Extruder operation No. 3	Sept. 17, 1965	6" Variable orifice die/ Johnson $2\frac{1}{2}$"
Extruder operation No. 4	Nov. 19, 1965	6" Variable orifice die/MPM $2\frac{1}{2}$"
Extruder operation No. 5	Nov. 29, 1965	6" Variable orifice die/MPM $2\frac{1}{2}$"
Extruder operation No. 6	Jan. 3, 1966	Double orifice die/MPM $2\frac{1}{2}$"
Extruder operation No. 7	Jan. 4, 1966	Double orifice die/MPM $2\frac{1}{2}$"
Extruder operation No. 8	Jan. 18, 1966	Double orifice die/MPM $2\frac{1}{2}$"
Extruder operation No. 9	Jan. 19, 1966	Double orifice die/MPM $2\frac{1}{2}$"
Extruder operation No. 10	July 1, 1966	Faeco 9"/Prodex $2\frac{1}{2}$"

Final Report submitted July 29, 1966

After each extruder operation, samples of all film produced were tested for gauge, tensile strength, and elongation (at ambient temperature). In addition, some samples were tested in a cold brittleness tester to qualitatively determine film cold brittleness characteristics and in a leak detector unit to determine gas permeability.

Polyethylene Thin Films: Double Orifice Die

Extruder Operation No. 1

The double orifice die was operated for the first time on May 22, 1965 as shown on figures 1 and 2. A Gloucester Engineering Company $2\frac{1}{2}''$ extruder was used. Considerable experience and information was gained in producing double layer concentric blown film. Seven of the eight runs resulted in double layer film. The double layers were clearly visible between the die and the mating line; the latter varied during the runs between 4 to 8 inches above the die.

The approximate blow-up ratio for the two films were:

$$BP_{inner} = \frac{2 \times LF}{\pi D} = \frac{2 \times 21}{\pi 4} = 3.35$$

$$BR_{outer} = \frac{2 \times 21}{\pi 6} = 2.22$$

The approximate draw down ratio for the two films were:

$$DR_{inner} = \frac{\text{die gap}}{\text{film gauge} \times BR} = \frac{0.030}{0.0003 \times 3.35} = 29.85$$

$$DR_{outer} = \frac{0.010}{0.0001 \times 2.22} = 45.06$$

Two die gaps were used during the first operation. The first settings were 0.030" inner and 0.010" outer; the second set-up settings were 0.026" inner and 0.012" outer.

SSS Standard resin (polyethylene) was used. The resin had a melt index of 5.8 and a density of 0.9218. The following film was extruded:

Run number	Film gauge, mils			Lay flat width, in.
	Double layer	Approx. inner gauge	Approx. outer gauge	
1	0.70	*	*	20
2	.38	0.3	0.1	21
3	.28	*	*	21
4	1.0	.8	.2	21
5	.70	*	*	*
6	.70	.6	.1	24

*Not determined.

During the six successful runs, the height of the inner air ring, that is, the height at which the two film layers mated, was controlled and varied. In the most interesting run, No. 4, the film was stabilized at three conditions, minimum inner ring air, moderate inner ring air, and maximum inner ring air. All three conditions remained stabilized for extended periods. Also of note, the maximum inner ring air condition caused "bubbles" or air pockets to form between the two film layers.

Various techniques were attempted to deblock the concentric layers of film. However, because of the difficulty of inserting the proper amount and/or kind of anti-block agents between the two films, the film layers bonded to each other and became difficult, if not impossible, to separate. The method of metering anti-block agents between the film layers is one of the problem areas and requires refinement of the method of controlling both the amounts of blocking agent inserted and the volume of concentric air supply.

The die gas settings were selected to avoid the combined difficulties of starting a bubble, "puddling" and film cooling. The problem of cooling the inner film was critical and caused the extrudate to "puddle" at the die, even after satisfactory film had been drawn down for some time. The puddling most often would cause a "blow-out," although not always. Decreasing the gauge of the inner film correspondingly decreased the amount of heat to be dissipated, but still maintained adequate "gauge" to prevent "bubble oscillation." Of course, temperatures of the extruder and die were decreased at the start to obviate this problem; in fact, very low extrusion temperatures were used. This "puddling" problem was thus directly associated with the twin problems of die gap ratio and inner film cooling and, indirectly, with the frost line distance of the inner film. At no time were there any problems with the outer film, or with the inner film until a completely formed, concentric outer film surrounded the inner film. This caused an abrupt change in the rate of cooling of the inner film, which could result in puddling.

The double orifice die double layer film, extruded on this operation was tested using standard laboratory techniques. ASTM D-882 Test Procedures used were modified to provide constant-rate-of-grip loading instead of constant-rate-of-grip separation. Data is presented in the following list. For comparison, the standard mechanical properties of film extruded from this resin are:

	Machine direction	Transverse direction
Uniaxial tensile strength	2, 600 psi	2, 000 psi
Uniaxial elongation, ultimate	275%	400%

When the feed rates of the anti-block agents were not controlled during the double orifice die runs, the resultant films consisted of essentially bonded-double ply composite, bi-layer films. Each ply of the bi-layer film was oriented to a different degree.

Table 1 shows the principal results of these tests. This data shows that the double orifice die film had considerably less elongation in both directions than commercial films of the same resin. With one exception, run No. 4, the MD (machine direction) elongation was equal to normal film, but TD (transverse direction) elongation was again considerably less. MD strength was generally stronger and TD strength generally

TABLE 1. - TABLE OF MECHANICAL FILM PROPERTIES

Run number	Die gap (10^{-3} in.)		Gauge, mil			Tensile strength, psi (+70° F)		Elongation, %		Characteristics
	Inner	Outer	Both	Inner	Outer	MD	TD	MD	TD	
1	30	10	0.35	----	----	3140	1380	100	20	Good film; 21 in. LF; puddling problem
2	26	12.5	.32	0.20	0.10	3740	1465	110	20	Changed gap ratios
3	26	12.5	.30	----	----	2900	1345	100	33	Minimum air between ring
			.30	----	----	3100	1470	100	33	
			.26	----	----	3525	1450	100	33	Maximum air between ring
4	26	12.5	.77	----	----	2180	1320	260	50	Minimum air between ring
			.76	.50	.20	2340	1400	300	50	
			.70	----	----	2430	1690	300	60	Maximum air between ring
5	26	12.5	.75	----	----	2570	1325	85	30	Maximum air; H_2O anti-block
6	26	12.5	.66	.50	.10	2730	1395	100	50	Anti-block (H_2O)

less than regular films. The effect of increasing air between the concentric layers of film was to increase the strength of the film.

The results of the first double orifice die run and the subsequent physical tests indicate that desired useful (double layer) film properties can be generated through proper control and application of the double orifice die principal and the associated extruder techniques.

Polyethylene Thin Films: Double Orifice Die

Extruder Operation No. 2

A double-orifice die/extruder operation was conducted using the Gloucester $2\frac{1}{2}''$ extruder. The double orifice die had been set up to give a 0.005 inch inner and a 0.012 inch outer gap setting. Approximately 15 chemical agents were screened as candidates for an anti-block material that would be injected between the double film layers. Of these, six appeared promising - toluene, silicone oil, isobutyl alcohol, paraffin, glycerine, and amyl acetone (dilute).

Test procedure was to force the anti-block agent into the die cavity between the two layers of film under slight pressure. The anti-block material was brought to an elevated temperature under low pressure in a "boiler" and forced as a vapor through a connecting line into the die block and thence through passages between the two layers of film. It should be noted that the die itself was at 390° F, which raised the temperatures of the anti-block agents and thereby increased the difficulty of controlling their feed rates.

Figure 3 illustrates the film separation modes in the double orifice die On start-up the two layers of film form a small cavity and are quite stable. As the film take-up is increased and more air inserted between the layers, the mating line rises to about 6 to 8 inches above the die. This appears to be a nominal, easily developed operating point. More anti-block agent, either air or a chemical type, raises the mating line considerably but also results in unstable operation. This position is normally above the frost line for the outer film.

Test results were as follows:

Glycerine was used at three film mating line positions, low, medium, and high. The films did separate satisfactorily in the areas where the glycerine was forced; however, the equipment set-up used was not capable of deblocking completely around the circumference of the tube of film; also a slight deposit of glycerine residue remained on the deblocked film. The ratio between inner and outer film gauge was 3:1; (no attempt was made to extrude very thin film during the anti-block tests).

Amyl acetone (dilute) and toluene both provided separation of the film when injected in sufficient amounts. However, control of these materials was more difficult. Consequently, results tended to be erratic, and the film separated into "pockets" of anti-block instead of providing consistent and completely separated layers of film.

Isobutyl alochol and silicone oil yielded similar results as anti-block agents and provided adequate separation when injected properly. However, these materials were very difficult to control.

The principal conclusions to the anti-block tests are that the approach appears feasible, but in practical operation it was difficult to achieve consistent results. The use of air between the two film layers together with cooling techniques still appears the best method. However, using air requires better control of both the air injection and the extruder settings, as well as requiring the development of new cooling techniques.

Following the investigation of anti-block materials, extruder blow-up ratios (BR), and draw-down ratios (DR) were investigated. The following chart shows the maximum and minimum ratios used during this portion of the run.

Layflat, in.	Diameter, in.	BR	Gap, in.	Gauge, mil	DR
18	4	2.9	-----	----	----
30	4	4.8	0.005	0.25	4.2
18	6	1.9	.005	.25	10.5
30	6	3.2	-----	----	----
30	4	4.8	.012	.25	10.0
18	6	1.9	.012	.25	25.3

A blow-up ratio of 4.8 is higher than normal, 2.0 being a common value and 3.0 being the upper limit at which the majority of extruders are operated. A draw-down ratio of 4.2 is low and 25.3 is conventional. If thinner gauges were achieved the DR would have increased substantially.

It appeared that improved film characteristics would be available from film extruded on a double orifice die, since double orientation is potentially capable of being achieved in the composite double-layer film. This was checked by determining the principal physical properties of the films extruded above in the BR tests. Testing methods were similar to ASTM procedures, but were modified to accommodate the peculiar idiosyncracies of very thin films (edge effects are a major problem not properly solved by conventional ASTM test procedures and were alleviated by rolling a test specimen into a cylinder for test; see note 2 on table 2 for procedures.

Figure 4 shows ultimate tensile strength (psi) and ultimate elongation (%) as a function of blow-up ratio. All film properties improve as the blow-up ratio increases beyond 4.5. Standard film (1 mil thickness) for similar resin, by way of comparison, has an ultimate tensile strength in the machine direction of 2600 psi and 2000 psi in the transverse direction. Of course, percent elongation decreases as the layers of molecules in the thin film become oriented. Still the elongation achieved is superior to many other films, if elongation were an improtant property for a specific application. Actually, the tradeoff in film properties can be controlled to produce a desired set of characteristics. Thus, the double orifice die could potentially yield UTG polyethylene film of improved properties not attainable with any conventional die or extruding method.

Polypropylene Thin Films: Extruder Operation No. 3

Polypropylene (PP) film was extruded using a Johnson 6" Variable Orifice Die/$2\frac{1}{2}$" Extruder combination. The thinnest gauge film extruded was 0.19 mil.

Resin

Five companies were contacted to obtain a recommended polypropylene resin for this special application, viz., Union Carbide, DuPont, Grace, Avisun, and Hercules. None of the companies recommended extruding their resins below 1 mil. The Union Carbide personnel, who have cooperated consistently in this Contractor's efforts to extrude thin gauge films, recommended a competitor's resin for this run (the competitor failed to provide timely technical information). Although Hercules had slot extruded 1/3 mil PP film at one time, production was terminated because of poor film quality. The thinnest gauge PP film currently available is 1/2 mil thick.

The resin selected was Union Carbide Bakelite PP resin JMD-4503 Natural. This resin/film has the following characteristics:

Melt flow at 230° C/44 psi	4 dg/min	ASTM D1238
Specific gravity	0.905	ASTM D792
Tensile yield strength	5,000 psi	ASTM D638
Ultimate tensile strength	5,500 psi	ASTM D638
% Elongation	~9%	ASTM D638

Because polypropylene tends to crystallize, higher extruder temperatures were used, approximately 20° to 50° above polyethylene settings. (If too low a temperature is used, the extruder head bolts can be sheared, or the thrust bearing overloaded due to excessive pressures.) Screw cooling was not used, although this is a recommended procedure in certain cases.

The following successful runs were made:

Run numbers	Gauge, mil	Comment
2	0.50	Some gels and fisheyes
3	.40	BR 2.1; $19\frac{1}{2}''$ LF
4	.40	BR 2.2; $19\frac{1}{2}''$ LF (new screen pack)
6	.30	BR 2.6; 24" LF
8, 9	.25	BR 2.6; 24" LF
11	.20	BR 2.6; 24" LF
14	.19	Blowout; burned particles

Since the principal objective on the first run was to produce very thin gauge film, other extrusion variations were not attempted. Blow-up ratio was increased moderately from 2.1 to 2.6. Some bubble oscillation occurred which might become a problem at 1/10 mil, similar to polyethylene thin films. However, because of the higher strength of PP film, this is not expected to be a limiting factor. Fast film quench, which is very helpful in achieving superior mechanical properties, was not attempted.

The data shown below presents preliminary test results of the mechanical properties of thin gauge polypropylene film.

Test number	Direction	Ultimate tensile strength, psi	Elongation, %	Gauge, mil
1	Machine	6,000	11	0.192
2	Machine	5,850	12	.192
3	Machine	5,450	13	.196
4	Machine	6,000	11	.196
5	Transverse	3,450	3	.192
6	Transverse	3,535	3	.192
7	Transverse	3,375	3.5	.196
8	Transverse	2,570	4.5	.196

The film had very poor tear resistance in the transverse direction. This deficiency could be corrected by increasing the blow-up ratio and/or film quenching.

Composite Films

In addition to the above extrusion operations, fabrication of composite films and tests of the extruded films were being accomplished.

To support the Work Statement for the second phase of NAS7-274, ultra thin gauge film (produced during the first phase) was to be used for laminated and bonded film samples, as well as fabrication of composite film samples with reinforcing fibers. Since several rolls of film had tensile strengths in excess of 6,000 psi, the work statement specified 6,000 psi UTG film for this work.

Samples of composite films were fabricated using this high strength material in an attempt to fulfill contract requirements. However, the mechanical property tests made on these fabricated samples produced results substantially less than expected. This led to the assumption that in some way a mistake had been made and incorrect rolls of film used. Additional samples were made with careful attention that the proper UTG rolls were used. Again ultimate tensile strength and percent elongation data of the laminated, biaxially oriented film indicated values in the area of 2,500 psi and 100% elongation, values considerably different from the results from the series of tests made in early 1965.

In one of these early tests of single ply biaxially oriented, cross laminated UTG film, an ultimate tensile strength of 10,700 psi and 50% elongation had been obtained in both directions. The exact sample roll from which the above high values of tensile strength were obtained was retested in November 1965. These new results as shown in table 2 were very moderate, compared to the earlier results. It is theorized that the loss in tensile strength may be explained as indicated below.

It is generally agreed that plastic film, once extruded past the "frost-line," retains its physical properties almost permanently. Longtime weathering and aging of film is normally attributed to loss of plasticizers

TABLE 2. - ULTRA THIN GAUGE POLYETHYLENE FILM MECHANICAL PROPERTY TEST DATA

	DEX 8028 Resin				DEX 8026 Resin		DEX 8025 Resin		SSS Std Resin			
	Jan. 1965	Nov. 1965	Jan. 1965	Nov. 1965	Jan. 1965	Nov. 1965	Jan. 1965	Nov. 1965	Jan. 1965	Nov. 1965	Jan. 1965	Nov. 1965
Ultimate tensile strength, psi												
MD	9370 av	2365 av	7550	3830	Data not avail.	2640	5650	3370	5300	3060	5060	3410
TD	9370 av	2365 av	3380	1310		2640	2720	1440	2200	1020	2820	1140
Elongation, %												
MD	42 av	77 av	90	65		111	68	112	55	87	130	50
TD	42 av	77 av	150	300		111	120	16	87	29	115	91
Total gauge, mil	0.32	0.32	0.061	0.061		0.24	0.067	0.067		0.092		0.10
Number of layers	4	4	1	1		4	1	1	1	1	1	1
Number of samples tested	3	2	2	3		2	2	2	1	2	1	1

Note 1. Results of identical samples tested in January 1965 and November 1965.

Note 2. ASTM D-882 Test procedures were used in the above tests, modified to provide constant rate-of-grip loading vice constant rate-of-grip separation.

or additives, such as anti-block, slip, etc. The loss of physicals is usually on the order of 10 to 15%, unless extreme brittleness occurs as with plasticizer evaporation.

As a result, several theories are advanced to explain this change. The first theory assumes the film rolls did not receive external "conditioning." Thus, it is believed that highly oriented polyethylene films "relax" with time and lose their orientation. Conference with others knowledgeable in polymer chemistry did not produce any previous verification of this phenomenon or disagreement with this explanation.

A review of several technical works (refs. 2 and 3) show only the comments that for cold drawn film, "extension is irreversible at room temperature" (3). However, the gauges used in that investigation were presumably much thicker than the UTG film and were not necessarily applicable to blown tubular film.

The fact that normal film in gauges in excess of 1/2 mil apparently achieves much of its strength from moderate orientation of the outer molecular layers would mean that "molecular relaxation" would not occur in regular films. The much greater orientation of all molecular layers of UTG films, which is responsible for the high ultimate tensile strengths, appears to be reversible with time.

A second consideration that has not been ruled out is that the film became "annealed." The rolls of UTG film were maintained at room temperature. This temperature might have raised to 100° - 110° F during the summer and might have annealed the film somewhat, relaxing the highly oriented molecules in the films.

A third process which could partially explain the loss of mechanical properties is oxidation of the film, particularly at elevated temperatures. Although results of oxidation of polyethylene films have been reported in the literature, this work has primarily investigated the rise in power factor of the material and secondarily, in embrittlement. However, a combination of the above three processes is likely.

Polyethylene Films: Variable Orifice Die

Extruder Operations Nos. 4 and 5

Because of the change in physical properties of the UTG film with time, a determined effort was made to extrude more UTG film to investigate this phenomena further. Seven extruder runs were made, but gauges to only 0.087 mil could be obtained, as discussed below.

The 6" variable orifice die and the SSS MPM $2\frac{1}{2}$" extruder were used for two experimental extruder operations. The extruder had been modified by Sea-Space to improve the mixing and temperature control of the resin and to increase the back pressure in the extruder. These modifications, and other features discussed below, were all desirable in achieving maximum operational flexibility necessary in an experimental extruder installation, as well as to improve the quality of the extruded film.

Low density polyethylene is not normally extruded using cooling. Since the SSS experimental extruder has both a controlled screw and a barrel cooling system, cooling was used. These extruder features are provided to improve the effective rate of shear or mixing intensity, as well as the extrudability of the resin. While the flow behavior of thermoplastic materials in the channel of an extruder screw has been studied by a number of observers, simplifying assumptions have always been required. The problem is generally divided into two categories: one, of isothermal conditions of the molten material in the forward end of the machine and, the other, of "plug flow" of the solid, granular material in the feed and compression sections of the screw. Mechanisms occurring in the transition from solid to melt have usually been recognized as extremely complex, tending to defy treatment on a theoretical or mathematical basis.

Normally, the higher temperatures used by SSS for UTG films have bypassed some of these problems. However, the screw design itself is a major uncertainty in any extrusion process, which is not based on well founded theory, but rather on many educated opinions and empirical data.

The SSS extruder screw was designed specifically for low density polyethylene, but, since the extruder was built as a research unit, the feature of screw control was provided in case other resins, such as vinyl or polyurethane, were to be extruded. Since this feature of screw control was available, it was used for the first time and did, in fact, appear to help. However, other changes made at the same time, such as changing screen packs, re-leveling the die, adjusting the die gap, smoothing out the take-up, etc., could have also been influential in enabling thinner gauges to have been produced in the second run.

The following results were achieved using DEX 8025, DEX 8026, and SSS standard resins:

Extruder operation - November 19, 1965

Run number	Film gauge, mil	Layflat, in.	Comment
2	0.19	24	Neutral screw on all runs
3	.14	22	
4	.15	24	
6	.12	21	Changed screen packs; re-leveled die; decreased die gap to 0.014 inch
7	.11	22	
9	.11	21	

As a result of this run, which was the first attempt to achieve UTG film on the new SSS equipment, several modifications to the set-up were indicated. These were made and another run scheduled.

Extruder operation - November 29, 1965

Run number	Film gauge, mil	Layflat, in.	Comment
1	0.097	21	Neutral screw
2	.102	21	
3	.110	22	
4	.105	22.5	New screw packs
5	.089	22	Controlled screw
7	.095	21	
8	.087	21	

Although this operation was better than the first run, the results were not considered satisfactory for the goal of producing 0.05 mil film.

Polyethylene Films: Double Orifice Die Extruder

Operations Nos. 6, 7, 8, and 9

Following the above attempts with the 6" variable orifice die to produce UTG film, it was decided to return to the double orifice die and close off the outer die, using only the inner 4" diameter die. Four extruder operations were conducted using the SSS MPM $2\frac{1}{2}''$ extruder.

<table>
<tr><th colspan="4">Extruder operation - January 3, 1966</th></tr>
<tr><th>Run number</th><th>Film gauge, mil</th><th>Layflat, in</th><th>Comment</th></tr>
<tr><td>1</td><td>0.164</td><td>21</td><td>Note 1</td></tr>
<tr><td>2</td><td>.124</td><td>21</td><td>Note 1</td></tr>
<tr><td>3</td><td>-----</td><td>--</td><td>Note 1</td></tr>
<tr><td>4</td><td>.109</td><td>21</td><td></td></tr>
<tr><td>5</td><td>.110</td><td>22</td><td></td></tr>
<tr><td>6</td><td>.097</td><td>20</td><td>Note 2</td></tr>
<tr><td>7</td><td>.101</td><td>21</td><td></td></tr>
<tr><td>8</td><td>.098</td><td>20</td><td></td></tr>
<tr><th colspan="4">Extruder operation - January 4, 1966</th></tr>
<tr><td>1</td><td>0.13</td><td>22</td><td>Note 1</td></tr>
<tr><td>2</td><td>.099</td><td>21</td><td></td></tr>
<tr><td>3</td><td>.101</td><td>21</td><td>Note 2</td></tr>
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<tr><td>5</td><td>.098</td><td>20</td><td>Note 3</td></tr>
<tr><td>6</td><td>.095</td><td>20</td><td>Note 2</td></tr>
<tr><td>7</td><td>.101</td><td>21</td><td>Note 2</td></tr>
<tr><th colspan="4">Extruder operation - January 18, 1966</th></tr>
<tr><td>2</td><td>0.092</td><td>18</td><td>All neutral screw</td></tr>
<tr><td>3</td><td>.1285</td><td>22</td><td>Note 1</td></tr>
<tr><td>4</td><td>.096</td><td>21</td><td></td></tr>
<tr><td>5</td><td>.0867</td><td>21</td><td>Note 2</td></tr>
<tr><td>6</td><td>.082</td><td>21</td><td></td></tr>
<tr><td>7</td><td>.10</td><td>20</td><td>Note 1</td></tr>
<tr><td>8</td><td>.11</td><td>21</td><td></td></tr>
</table>

Note 1. Blow-out due to gel or fisheye.

Note 2. Blow-out due to burned resin.

Note 3. Discontinuity in circumferential gauge.

Extruder operation - January 19, 1966

Run number	Film gauge, mil	Layflat, in.	Comment
3	0.096	21	
4	.085	18	Note 1
5	.082	16	
6	.098	20	

Note 1. Blow-out due to gel or fisheye.

The above effort was moderately successful in that 0.082 mil film was extruded, although the goal was 0.05 mil. Physical property tests at room temperature were disappointing:

$$\sigma_M = 3600 \text{ psi} \qquad \sigma_T = 1350 \text{ psi}$$

$$\% \text{ elong (M)} = 45\% \qquad \% \text{ elong (T)} = 75\%$$

Although there is always a sampling spread, the ultimate tensile values for this gauge film would have been interesting if they had been $\sigma_M = 5000$ psi and $\sigma_T = 2000$ psi. It is believed extrusion conditions are responsible for these lower values.

One aspect of the very successful UTG film produced in December 1964 was that the run lasted well into the evening in a quite cold, open air building. More rapid cooling of the bubble, particularly before passing through the nip rollers appears to be one variable that was not controlled in the above runs and might be another reason for more successful results.

Also, the central mandrel in the double orifice die was found to move very slightly under the load of the extrudate. As the gauge being extruded is of the same dimensional order as the die movement, it was very difficult to eliminate this variable in the side fed double orifice die.

Polyethylene Films: Fixed Orifice Die

Extruder Operation No. 10

Because of the lack of success in extruding film less than 0.08 mil on the Sea-Space DOD/MPM $2\frac{1}{2}''$ equipment, it was decided to conduct one additional extruder run on a new 24:1 L/D Prodex $2\frac{1}{2}''$ extruder. This operation was conducted on July 1, 1966. Approximately 250 pounds of SSS standard resin was used attempting to draw down below 1/10 mil film. The thinnest gauge achieved was 0.09 mil. Several reasons for the lack of success in extruding UTG polyethylene films with this equipment are postulated, that is, the fixed die gap setting on the Faeco die, restriction of the screen packs, and the relatively high ambient temperatures.

The above operation was conducted after all contract funds had been expended and was funded as part of the SSS research program. Only one gap setting was possible on the Faeco die, 0.025 inch. This fixed die gap installation is contrary to the SSS Variable Orifice Die equipment used previously; the VOD die gap was normally set between 0.017 to 0.020 inch, although 0.012 inch had also been used. The draw down ratio with the Faeco die was 158 which is well within the range of values previously experienced in extruding UTG film. The blow up ratio was 1.76 due to the larger die diameter, and, although low, is satisfactory.

The Prodex extruder had a screen pack cavity only large enough for a single pack. The Gloucester equipment on which the 1/16.3 mil UTG film was extruded had a large screen pack cavity. Finally, the ambient temperature during the initial extrusion run (first phase) was cool compared to the relatively high temperature experienced during the second extrusion run (second phase). Accordingly the film cooling of the material entering the nip rollers was not as great as that in the first phase although the tower height (26 ft) is considered adequate.

Cryogenic Tests

Ultra thin gauge polyethylene film from this program was tested in cryogenic liquids to determine (a) the number of "flexing" cycles the film could withstand without rupture; (b) the ultimate tensile strength; and (c) the elongation. Liquid nitrogen and liquid hydrogen were the cryogens. Figure 5 shows the test set-up for determining stress versus strain, ultimate tensile strength and percent elongation at failure.

The flexibility tester is a device that subjects polymeric films to severe flexure loads in a controlled, repeated manner while immersed in a cryogenic liquid. The flexing action is a combination of a pure "up-down" motion and a pure "twist" motion.

The cylindrical test samples were 6 by $1\frac{1}{4}$-in. diameter. Although the tester was relatively crude compared to more sophisticated powered twist-test units, the qualitative results are equivalent. The UTG film did not rupture in 50 cycles of the "up-down/180° twist" flexing action of the tester. Fifty cycles were the greatest number of cycles attempted with a 0.09 mil gauge polyethylene film. Concurrent tests with this equipment using 1/4 mil Mylar film yielded results similar to that reported by the Beech Aircraft Corp. using more sophisticated equipment, that is, no apparent failure (visually) of Mylar film after 100 SSS flexing cycles in liquid hydrogen.

The samples of UTG film tested showed no sign of deterioration or change in physical properties after 50 cycles at -423° F. However, samples of thicker films of the same or similar polymers tested by the procedures of ASTM D-746 and ASTM D-1790 do show definite failure in flexure at specific cold temperatures. In fact, the general term "cold brittleness temperature" results from these and similar tests with film gauges of the order of 10 mils, and is defined as that temperature below which 50% of the samples fail in flexure. Consequently, the data from UTG film tests suggests that (a) the gauge must be identified with any "cold brittleness temperature" and (b) that UTG films have a cold brittleness temperature less than -423° F.

The attached stress-strain curve shown on figure 6 is a plot from the data of the tests in LN_2. For comparison a similar curve at room temperature is shown on figure 7.

From this data it is apparent that polyethylene can be used (in application where flexibility is required) at temperatures down to -423° F in thin gauges. Also, a cold brittleness temperature is only meaningful for a material when the test conditions and test sample are carefully defined, and does not apply for the polymer in general.

Gas Permeability Testing

Gas permeability data for various films was determined using helium. The test set up used a considerably larger film sample (113.09 in.^{2}) than used in the ASTM D-1434 Test Method. This is believed necessary for thin gauge films below 1/2 mil in order to obtain repeatable data. For example, a recent NASA report (NASA CR-54, 433) presented permeability data for identical samples of Mylar that differed by a factor of 1125. It is assumed this could be due to the small size of film sample used in the test as well as differences in the characteristics of the extruded film.

The SSS Permeability Test System, developed for balloon film testing is applicable to any gas. The film is held in the center chamber of an aluminum test unit. The bottom chamber has three outlets, one of which is connected to a helium source, another to a manometer and the third is a spare. The upper chamber has two ports, one for the thermal conductivity Leak Detector (TCLD) probe and the second is a spare. A plexiglas cover enables the sample to be inspected optically while under test. A consolidated Electrodynamics Thermal Conductivity Leak Detector - Type 24-301 is used to measure the leakage concentration. Detector sensitivity to helium is 1×10^{-5} atm/cc/sec/meter division. A change in helium concentration of 700 ppm causes 100% deflection of the leak rate meter on its most sensitive scale. Detector sensitivity to other gases is: H_2 - 7×10^{-6}; O_2 - 1.1×10^{-3}; CO_2 - 4.5×10^{-3}; Freon - 8×10^{-5}; atm/cc/sec/meter division.

When a suitably large area of film is used as the test specimen, this detector gives satisfactory, repeatable results. The set-up has been used for a variety of materials and film combinations.

The SSS permeability film tester has been qualified against a Consolidated Electrodynamics Mass Spectrometer Type 24-120B. Identical samples of Mylar were tested using both detectors. Results were comparable, although as expected, in all cases the mass spectrometer yielded lower permeability values, that is, was more sensitive to gas leakage.

The following permeability data as shown on table 3 was generated testing UTG/PE, polypropylene (PP) and poly(ethylene terepthalate) (PET) films using the SSS Permeability Test System.

TABLE 3. - GAS PERMEABILITY VALUES

Film	Gauge, in.	Permeability constant, ft^3 mil/ft^2 sec psi
PE/UTG	6.5×10^{-5}	1.9×10^{-6}
PP	1.9×10^{-4}	5.5×10^{-6}
PE(SSS Std)	1.4×10^{-4}	1.6×10^{-6}
PET	1.5×10^{-4}	2.4×10^{-7}

CONCLUSIONS

1. Ultra thin gauge polyethylene films can be extruded using the tubular blown film process in film gauges as thin as 0.061 mil (first phase).

2. Extruding conditions were not duplicated during this phase of effort to repeat the UTG success of the first phase of effort.

3. The thinnest gauge polyethylene film produced during the second phase effort was 0.082 mil; film less than 0.1 mil was produced routinely.

4. The thinnest gauge polypropylene film produced was 0.19 mil.

5. Use of the double orifice die in extruding thin films did not produce UTG film less than 0.082 mil due to (a) film blocking problems and (b) die barrel movement under extrudate pressure.

6. UTG films do not exhibit a cold brittleness temperature down to -423° F when testing in a flexibility tester; this is in contradiction to results using ASSM D-746 and D-1790 test procedures for heavier gauge films of the same basic polymer.

RECOMMENDATIONS

It is recommended that research in extruding UTG polymers be continued, specifically as follows:

1. Extrusion of UTG polyethylene to determine additional basic knowledge of ethylene molecular orientation.
2. Extrusion of other resins to produce UTG films.
3. Continue investigation of extruding polymers by use of the double orifice die.
4. Study of applications for UTG film for NASA programs.

REFERENCES

1. NASA CR-274 "Ultra Thin Gauge Polymeric Films for Space Applications" by D. W. Cox, Jr., dated August 1965.
2. Crystalline Olefin Polymers, Parts I and II, Edited by Raff and Doak.
3. "Polythene - The Technology and Uses of Ethylene Polymers," Edited by A. Renfrew and P. Morgan.
4. ASTM Standards, Part 27, Plastics - General Methods of Testing.

Fig. 1. - "Start up" of the double orifice die. Note: Mating line of two films is clearly visible (prior to opening air/anti-block valve).

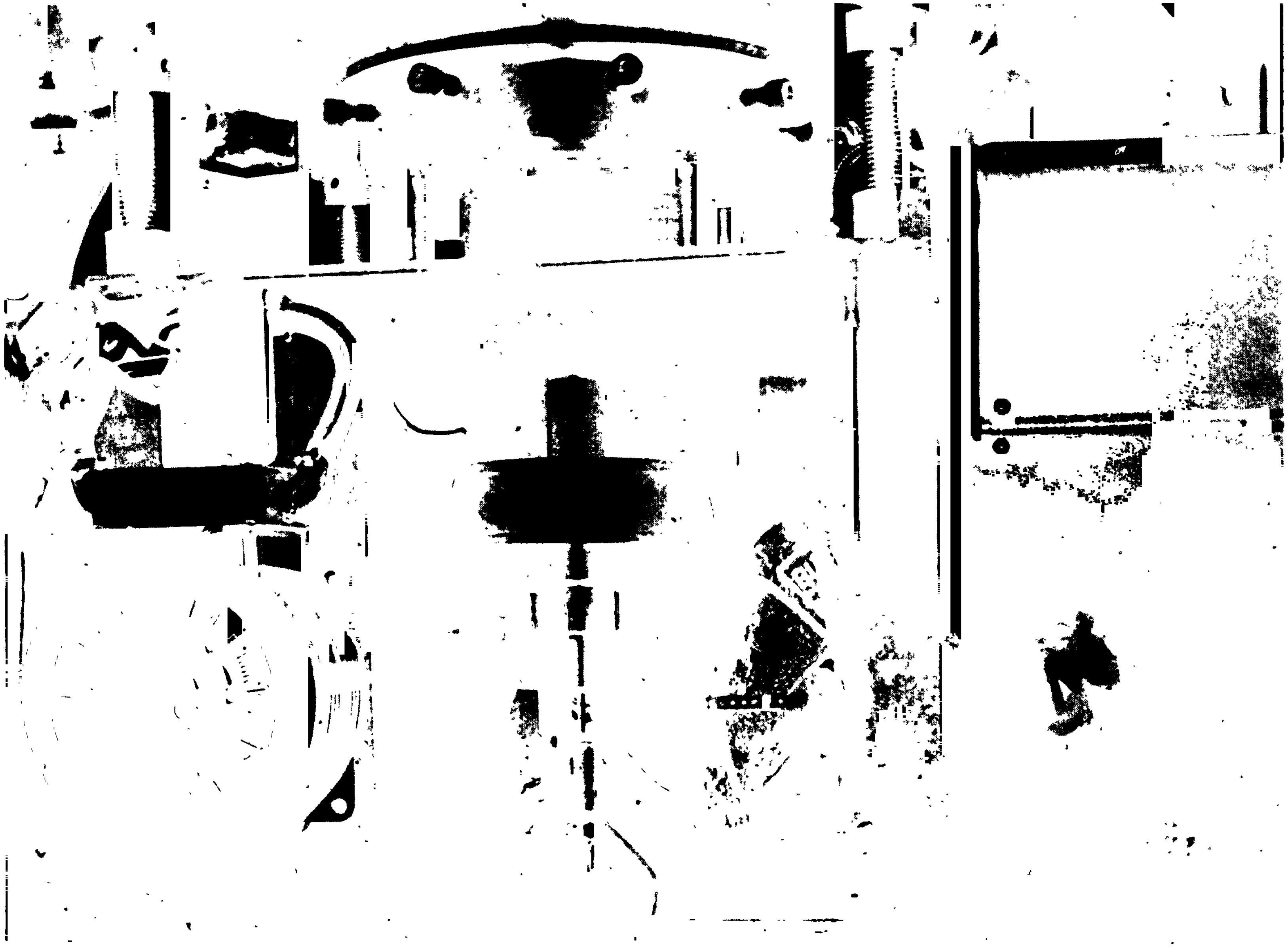

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Fig. 2. - Double orifice die in operation - May 22, 1965.

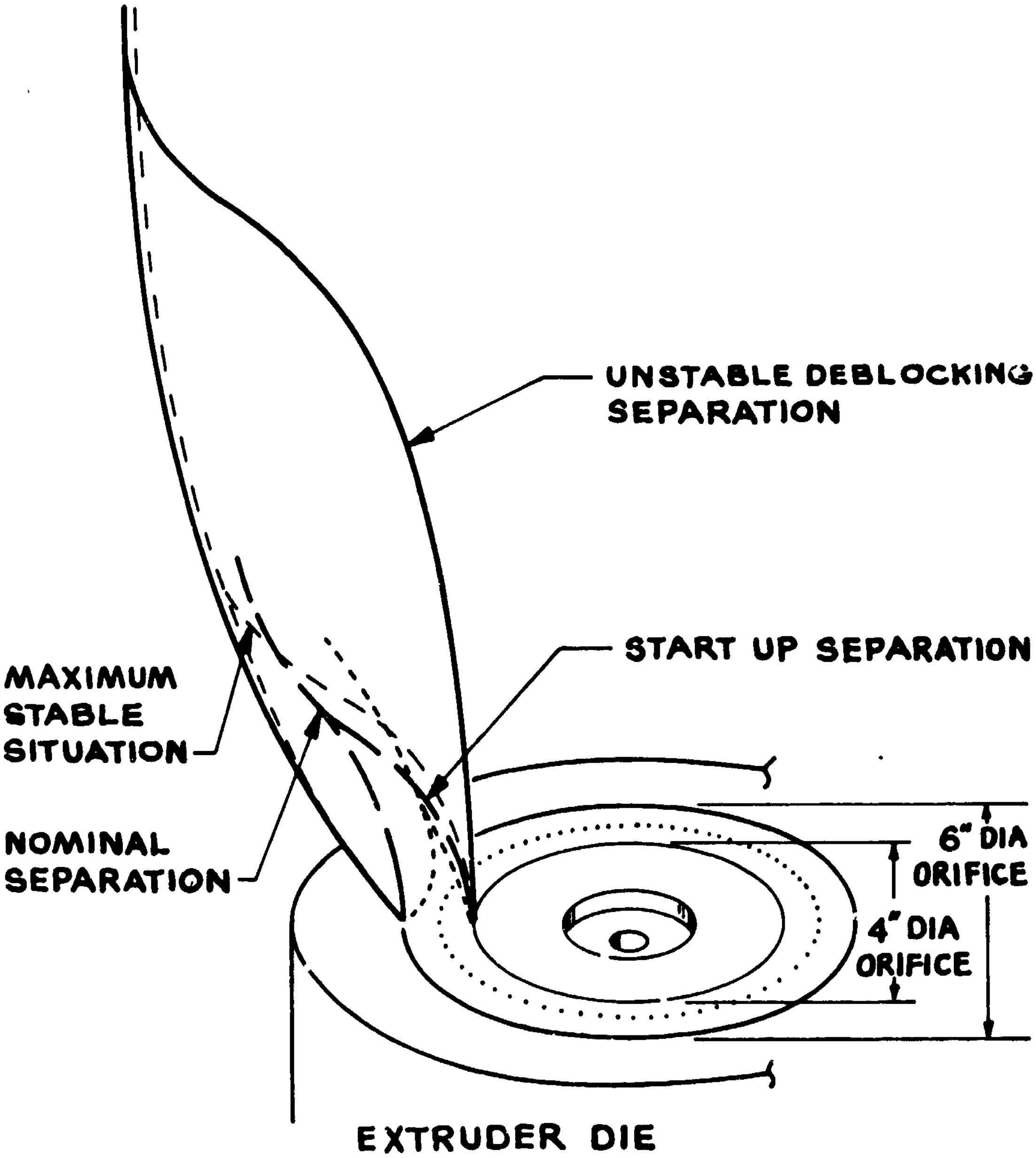
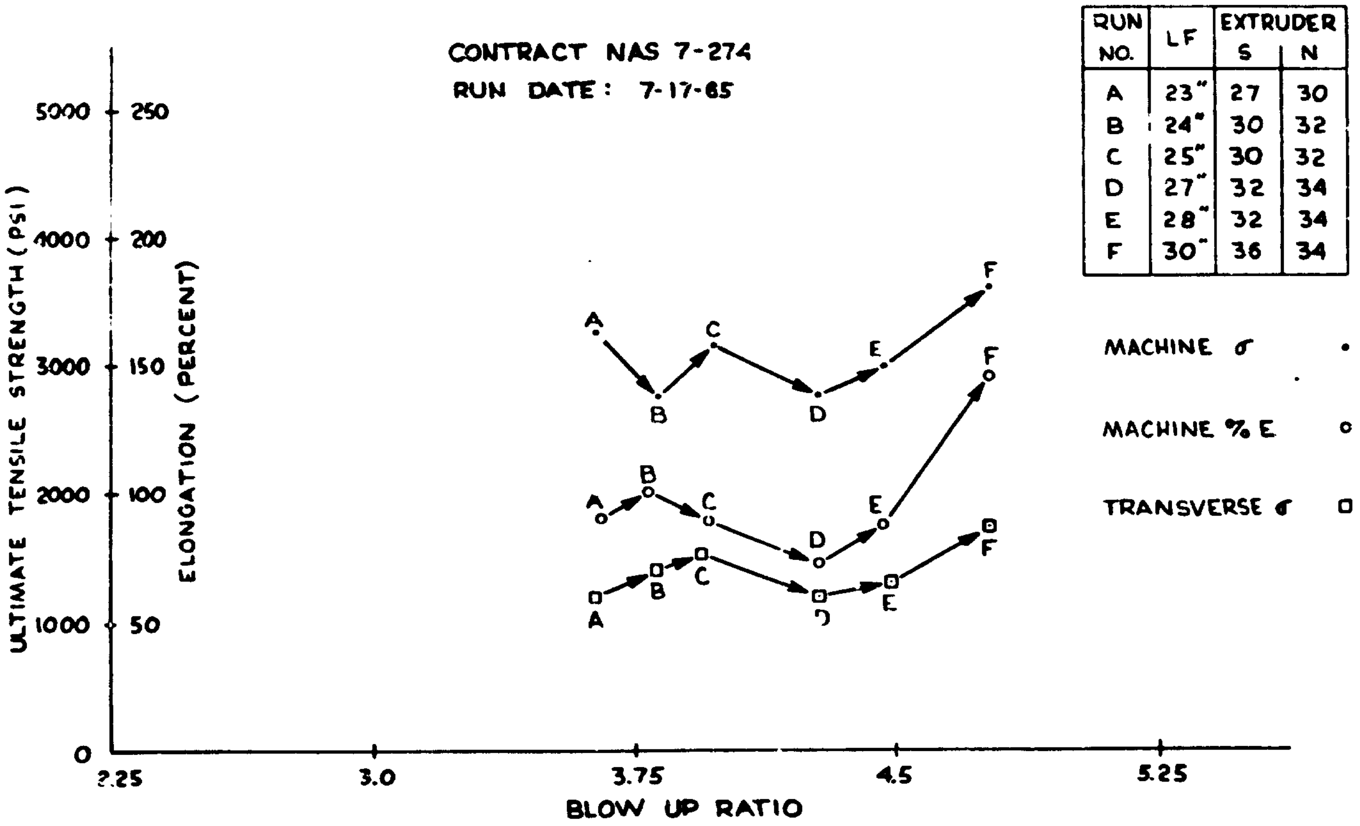


Fig. 3. - Film separation modes-double orifice die.



RUN NO.	LF	EXTRUDER S	EXTRUDER N
A	23"	27	30
B	24"	30	32
C	25"	30	32
D	27"	32	34
E	28"	32	34
F	30"	36	34

Fig. 4. - Variation of selected film properties with extruder blow-up ratios.

C-66-4219

Fig. 5. - Tensile testing of UTG films in liquid hydrogen.

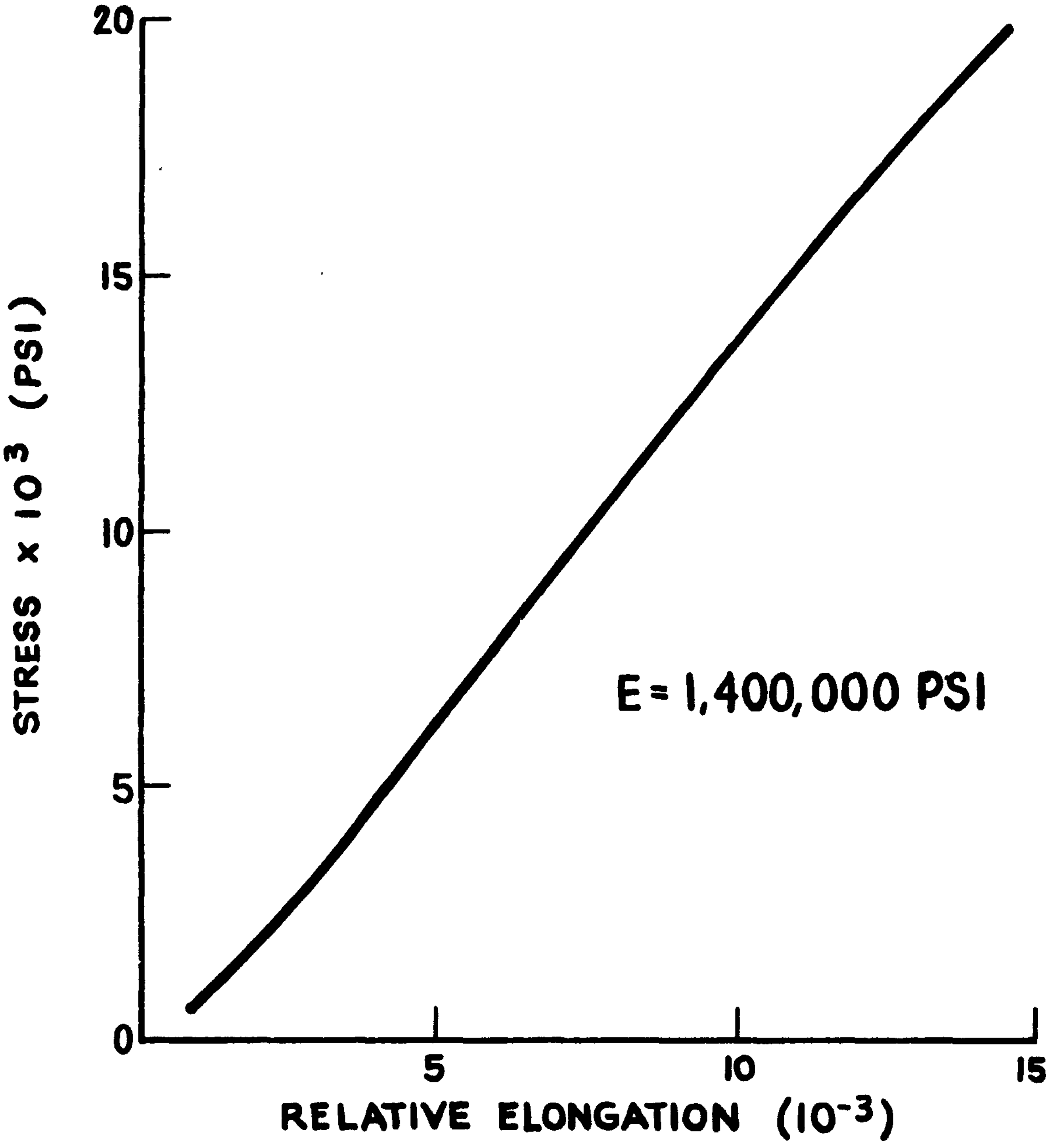


Fig. 6. - Stress versus strain for UTG film at -323° F.

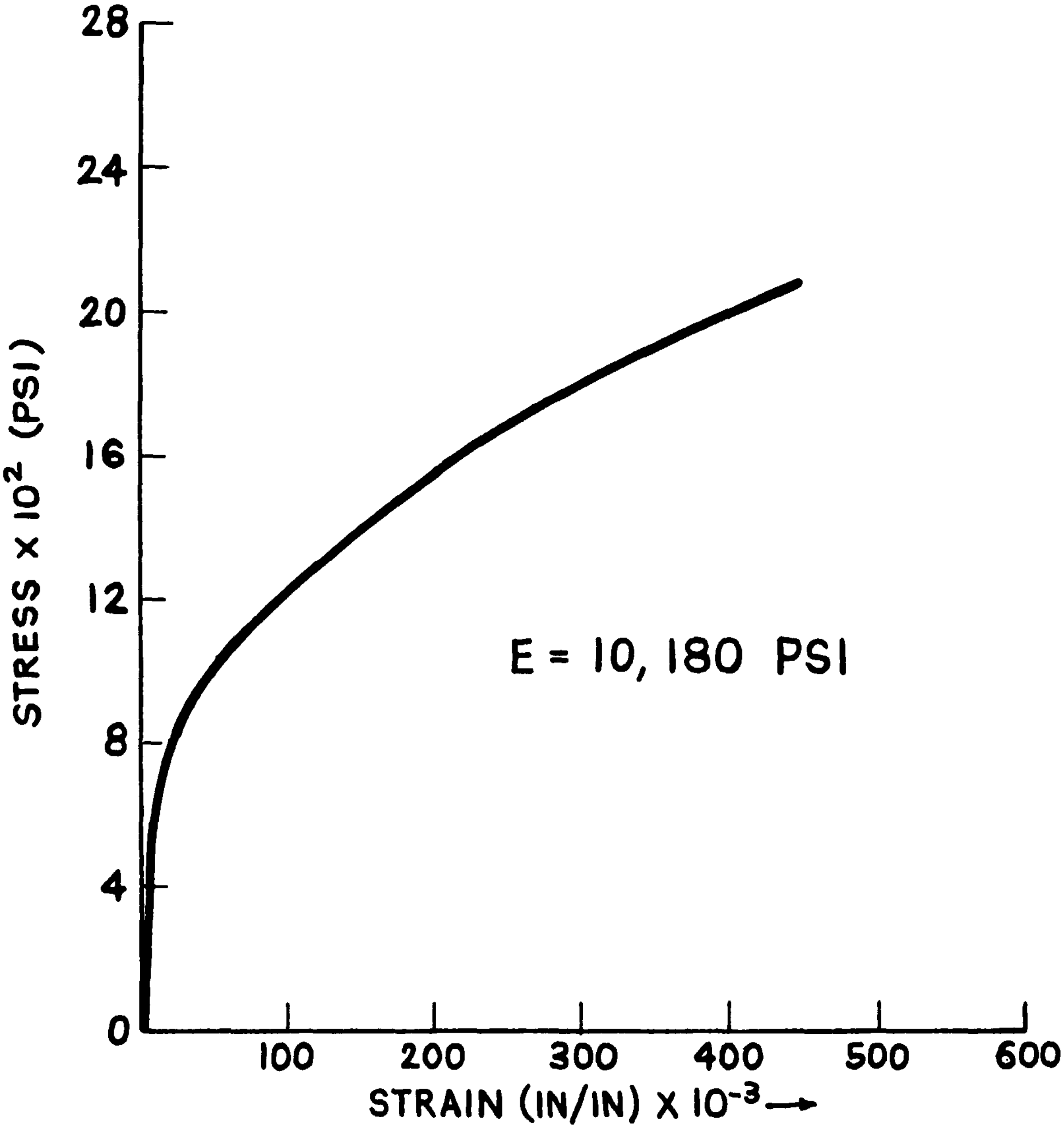


Fig. 7. - Stress versus strain for UTG film at +70° F.