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EFFECT OF FILM PROCESSING ON CRYOGENIC PROPERTIES OF POLY(ETHYLENE TEREPHTHALATE)

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ABSTRACT

The effects of stretch temperature, heat-set temperature and heat-set time on the cryogenic mechanical properties of PET film were studied by using a two-level factorial experiment. Squares of amorphous PET sheet were given a simultaneous biaxial 3X stretch in a laboratory film stretcher at either 85 or 95° C. The levels of heat-set temperature and time investigated were 190 and 210° C, and 15 and 120 seconds, respectively.

Crystallinities of the films were determined by the density-gradient technique. Tensile properties were measured in liquid nitrogen (77° K) and in liquid hydrogen (20° K). Biaxial burst properties were obtained in liquid nitrogen.

It was found that processing variables significantly affect the stress-strain properties of PET film at cryogenic temperatures. These results and encouraging values of flexibility offer leads for possible use of specially processed PET films for cryogenic space applications.

INTRODUCTION

Filament wound glass reinforced plastics offer an attractive solution to the problem of providing light-weight, high-strength tanks for the storage of cryogenic propellants. Permeation, or leakage, of the cryogen through the tank walls is the major problem which has to be solved before the full potential of these reinforced plastics can be realized. The porosity problem is associated with both the filament reinforcement and the resin matrix.

An obvious solution to the porosity problem is to provide some type of liner within the tank to prevent permeation of the fluid. The liner material should be capable of being elastically strained from zero to at least 2.5 percent and back to zero again under biaxial loading conditions for a number of times (ref. 1). In this study both metallic and nonmetallic films have been investigated as possible liner materials. The use of polymeric films would be desirable because not only are they light-in-weight, but they might also serve as a means for expelling the fluid from the tank under zero gravity conditions. If used in this manner, the polymeric film must be flexible as well as reversibly extensible.

The results of an extensive screening program performed by Beech Aircraft (ref. 2) showed that although none of the currently available plastic film materials were suitable for use as liners or bladders, poly (ethylene terephthalate)(PET) film possesses some cryogenic flexibility.

There are a number of approaches to obtaining a satisfactory cryogenic polymeric film; e.g., continued screening of commercial materials, synthesis of new or modified polymers (ref. 3), and study of polymer processing variables. Heffelfinger and Schmidt (ref. 4) studied the effect of processing on room temperature properties. The objective of this investigation was to determine if variation of processing conditions offered leads to significant improvement of cryogenic properties. Comparison with commercial PET was incidental to establishing these leads.

The effects of stretch temperature, heat-set temperature, and heat-set time on a number of properties of PET film were studied by using a two-level factorial experiment. Crystallinity of the films was determined by density-gradient at room temperature. Tensile properties were measured at room temperature, 77° K (LN_2) and at 20° K (LH_2). Biaxial burst measurements were made at 77° K.

MATERIALS AND PROCEDURES

The extruded amorphous sheet used in this study was reported to possess no orientation and to have a number average molecular weight of 19,500. It had a nominal thickness of 6 mils.

Film processing. - The factors studied in this investigation were stretch temperature, heat-set temperature and heat-set time. Two levels of each were selected to limit the number of experimental conditions to eight and form a 2^3 factorial experiment. This design permits independent estimates of the effects of all factors and their interactions using a minimum number of film preparation conditions. The two levels of each factor were selected to be far enough apart to determine these effects in the presence of random experimental error. However, the levels should not be so far apart that their range includes the level of optimum or minimum response. If these factors affect the response and the levels are wisely selected, the results of a two-level factorial experiment will provide leads to further improvement of properties. Optimization of processing variables to attain specific design properties can follow.

Stretching temperatures of 85 and 95° C were chosen to be sufficiently above the glass transition temperature of 69° C (ref. 5) to stretch the amorphous PET without tearing. Heat-set temperatures of 190 and 210° C were selected to be in the region which gives the minimum half-time for crystallization (ref. 6). Preliminary work had shown the biaxially stretched film changed little in density after 120 seconds at 190° C. Some heat setting is desirable to stabilize the film. Heat-set times of 15 and 120 seconds were used. Fifteen seconds is near minimum time to reproducibly heat treat the film.

Films were also prepared at the center point of the design, i.e., stretched at 90° C and set at 200° C for 42 seconds (the geometric mean of the two levels of set time). The difference between the response at this center point and the average for all eight conditions offers evidence of curvature of the response surface (which is a function of three independent variables). However, data at other experimental conditions are required to assess which factor is responsible for curvature.

Squares of the amorphous sheet (4 in. x 4 in.) were stretched in a commercially available film stretcher. The sheet was manually inserted into the stretching chamber which was controlled at the selected temperature and then both axes were simultaneously stretched to 3X at a rate of 1000 percent per minute. The amorphous sheet was given a 15 second equilibration in the stretching chamber before and after stretching. The stretching machine was provided with a special device which quenched the film to room temperature and enabled the film to be easily removed free of wrinkles and/or folds. Heat setting was accomplished by clamping the film in a restraining frame and placing it in a circulating air oven for the time and temperature specified. It was then removed from the oven and cooled to ambient temperature. Other films were stretched but not heat-set.

Film density. - Density of the films was determined by the density-gradient technique (ref. 7). The liquid system chosen for the column used in this study was n-hexane and carbon tetrachloride. Glass floats of known density were used to calibrate the column. The column was maintained at a constant temperature of $23\pm0.1^\circ$ C. Two small pieces of each film were placed in the column and allowed to reach equilibrium. The position of the calibration floats and samples, relative to an arbitrary reference, was measured with a cathetometer.

Uniaxial tensile properties. - Tensile properties of the films were evaluated in a universal testing machine with 1 inch wide specimens cut with length perpendicular to the direction of extrusion of the amorphous film. Load and extent of grip separation were automatically recorded. An initial grip separation of 4 inches was used for all tests. The rate of grip separation was 2.0 inches per minute. Cryostats of the type described in reference 8 were employed for the LN_2 and LH_2 tests.

Biaxial diaphragm burst test. - Biaxial stress-strain properties of the films were measured at 77° K in an apparatus similar to that described in reference 9. The test specimen was bolted between a circular flat plate and an 8 inch inside diameter annulus. The bottom plate was provided with means for introduction of the helium gas used for pressurization.

All tests were performed with a constant gas flow rate to rupture. Vertical deflection of the film was measured with a linear potentiometer connected to a one inch diameter counterbalanced disc which rested on the film. The pressure underneath the film was recorded with a pressure transducer. The entire diaphragm clamping device was submerged in LN_2.

DISCUSSION OF RESULTS

This section is divided into parts describing the results obtained for each response measured on the PET films. Included are crystallinity; uniaxial tensile tests conducted in liquid nitrogen at 77° K and in liquid hydrogen at 20° K; and biaxial diaphragm burst tests in liquid nitrogen.

Using the data for each experimentally determined response, coefficients of the following regression model were calculated except that b_D and b_{ABC} were zero for the tests with LN_2 and additionally b_{AC} was missing for the tests with LH_2.

$$y = b_0 + b_A x_A + b_B x_B + b_C x_C + b_{AB} x_A x_B + b_{AC} x_A x_C + b_{BC} x_B x_C + b_{ABC} x_A x_B x_C + \frac{1}{3} b_D \left(X_A^2 + X_B^2 + X_C^2\right) \tag{1}$$

where y is any response,

x's are -1 for the low level and +1 for the high level of each of the three factors designated by subscripts A, B, and C, and

b's are the corresponding coefficients determined by regression analysis.

These coefficients were then tested at a significance level of $\alpha = 0.05$ unless otherwise noted. Results are shown on bar graphs representing only factors which have a significant effect. When a factor does not show a significant effect, results are averaged over the two levels of that factor. Thus, each bar on a graph is based upon the average of a number of determinations.

Crystallinity

In this report crystallinity of the films is considered as a response to the processing conditions. Ideally, morphological properties of the film, such as crystallinity and orientation, should serve as factors upon which the mechanical property type responses depend. However, it was first necessary to learn how to prepare films with a suitable range of crystallinity, and in this sense crystallinity is a response.

Crystallinity, C, can be estimated from the film specific gravity, ρ, a value of 1.33 was measured for the amorphous PET and the calculated value of 1.455 was used for the perfect crystal (ref. 10).

$$C = \frac{\rho - 1.33}{1.455 - 1.33} = 8.00(\rho - 1.33)$$

Increasing the stretching temperature, heat-setting temperature, and setting time all increase the crystallinity of the film (fig. 1). The effect of the heat-setting temperature is most pronounced causing films heat-set at 210° C to have 3.6 percent higher crystallinity than films heat-set at 190° C. The effect of each of the other factors is only about one-third as large. The range of crystallinity is from 41.9 percent for the low levels of all three factors to 48.1 percent for the high levels.

Films stretched at 85° and 95° C and not heat-set are 15.8 percent and 20.9 percent crystalline, respectively. In both cases, this is less than half the crystallinity of heat-set films regardless of the conditions. Stretching therefore orients the polymer molecules resulting in increased density. However, an increase in density of a larger magnitude occurs upon heat-setting at higher temperature. The molecules develop a more ordered and closely packed form when heated to 190° C or 210° C for short times and films become over 40 percent crystalline. Heffelfinger and Schmidt (ref. 4) describe changes in the crystalline and amorphous regions during the stretching and heat-setting processes, as observed by X-ray diffraction, infrared, density, and stress-strain measurements at room temperature. The gauche form is transformed into trans during the stretching. The trans isomer crystallizes due to alignment of adjacent molecules. Their evidence favors isomerzation of gauche to trans to promote crystal growth during heat-setting.

The results on the film produced at the center point were included in the analysis and indicate that curvature of the crystallinity response over the range of these factors studied is not significant.

Uniaxial Tensile Properties

Strain at the proportional limit. - This property is defined as the strain at which the stress-strain curve departs from linearity. It is of particular importance since a liner must expand with the tank as internal pressure is applied and then contract to its original dimension. The strain at the proportional limit is more readily measured than the recoverable strain limit and yet serves as a guide to the usefulness of the film for the liner application.

Stretch temperature and heat-setting time are the factors affecting strain at the proportional limit in liquid nitrogen. Films stretched at 95° C and set for 120 seconds averaged 2.1 percent strain compared to 1.57 percent for setting 15 seconds (fig. 2). For films stretched at 85° C the longer set time increases the strain by only 0.15 percent strain compared to the 0.62 percent for the higher temperature. Thus, there is a significant interaction between these two factors in the manner in which they affect strain at the proportional limit. This response does not depend upon the heat-set temperature.

Since in liquid hydrogen there are data on strain at the proportional limit for just three different films, the only significant factor that can be established is the temperature of the tensile test. The average strain is 2.1 percent which is 0.2 percent greater than for the corresponding values obtained in liquid nitrogen.

Stress at the proportional limit. - This property is the stress at the same point of the stress-strain curve defined in the previous section. Stress at the proportional limit decreases with increasing stretch temperature (fig. 3). The values are also higher when tested at the lower temperature of liquid hydrogen. When these results are combined with the previous strain values, in general, the modulus is higher for films stretched at 85° C than those stretched at 95° C. Heat-setting time affects the modulus determined in liquid nitrogen giving higher values for shorter times of setting as seen in Table I.

Strain at break. - The strain at which these PET films break is much greater than the proportional limit strain and also varies more with processing factors (fig. 4). In liquid nitrogen the stretching temperature and heat-setting temperature both have large effects; the greatest ultimate strain of 15.4 percent is attained with both processing temperatures at the low levels. With high processing temperatures only 5.0 percent strain is reached at break. These are roughly inversely related to the crystallinity. However, heat-setting time, which affects the crystallinity to a limited extent, does not significantly change the ultimate strain. Note also that the stretching temperature generally causes opposite effects on the proportional limit and strain at break values (figs. 2 and 4). The highest proportional limit strain was obtained by stretching at 95° C and heating for 120 seconds.

The strain at break in liquid hydrogen is lower than in liquid nitrogen. Stretching temperature also affects the strain at break; 7.3 percent strain is obtained for 85° C stretching and 5.0 percent for 95° C.

Stress at break. - The breaking stress is affected significantly only by the stretching temperature and this effect is shown in figure 5. In both cryogens higher stress is reached with film stretched at 85° C, the lower temperature. Values in liquid hydrogen are about 15 percent higher than those obtained in liquid nitrogen. These results show the same pattern as for stress at the proportional limit, but values of the stress at break are over twice as high. Again, heat-setting temperature and time did not significantly affect stress at break.

Biaxial Burst Properties in Liquid Nitrogen

The results on the various stress-strain properties reported below are based on single tests of each of the eight films prepared with the eight different processing treatments of the factorial experiment previously described. In the absence of a good estimate of the reproducibility of films in this test, the significance of main effects was judged statistically by comparison with higher order (interaction) effects. This interpretation is, of course, conservative in reporting significant effects. True effects of smaller size would not be declared significant and would be "missed" by this procedure. However, examination of the results indicated duplicate tests are not necessary since smaller effects than those found are not of practical value.

Calculating stress and strain. - The engineering stress is calculated from the pressure difference across the film diaphragm using the following equation:

$$\text{Stress} = \frac{\Delta PR}{2t} \tag{2}$$

where

ΔP pressure difference across the film

R radius of curvature of deflected diaphragm

t original film thickness

The engineering strain is defined as the increase in length of a diameter line drawn on the circular film specimen divided by the original diameter

$$\text{Strain} = \frac{R\theta - 2r}{2r} \tag{3}$$

where

θ central angle of diameter arc formed by the deflecting film

r original radius of free film diaphragm

Since

$$\sin\frac{\theta}{2} = \frac{r}{R}, \tag{4}$$

and

$$R = \frac{r^2 + h^2}{2h} \tag{5}$$

where h is the measured deflection perpendicular to the original plane of the film, strain is calculated from the measured values of r and h.

A biaxial stress-strain curve for PET is shown in figure 6.

Strain at the proportional limit. - This property is defined by the point of departure of the calculated stress-strain curve from the linear relation which occurs at low strain. The high heat-setting temperature of 210° C results in strains of 1.76 percent while setting at 190° C gives 1.44 percent strain at the proportional limit (fig. 7). The difference, about one-third of a percent strain, is approximately a 25 percent increase in the value of this property. This is the same increase over the commercial PET film strain of 1.45 percent. A heat-setting temperature of above 210° C might result in further increasing the amount of strain at the proportional limit.

Strain at break. - The strain of the experimental films at break in nitrogen are all far above the 17.4 percent value for the commercial PET (fig. 7). Both stretching temperature and heat-setting temperature affect this property. Films stretched at 95° C give higher strain values than those stretched at 85° C. This effect is more pronounced if heat-setting is done at the higher temperature of 210° C. Films stretched and set at the higher temperatures averaged 37.5 percent strain, over twice the corresponding strain for the commercial film. As previously described, higher film processing temperatures result in high crystallinity. Thus, the most crystalline films attain the highest strain at break.

Stress at the proportional limit. - This is the stress corresponding to the strain at the proportional limit. This stress is almost 4000 psi higher for films stretched at 85° C than for those stretched at 95° C (fig. 8). Other factors do not show significant effects on this property. The modulus of the film stretched at 85° C is also higher. These results are similar to those obtained in the uniaxial tensile test, but are numerically higher in both stress and modulus. The biaxial modulus for the film stretched at 85° C is 2.46×10^{6} psi. These stress values are higher than those of commercial PET film.

Stress at break. - The average stress at break for films stretched at the lower temperature is over 10,000 psi greater than for those stretched at the higher temperature and 16,000 psi greater than for commercial PET (fig. 8).

SUMMARY OF RESULTS

1. The crystallinity of the biaxially oriented PET film was found to be higher for films heat-set at 210° C than for films heat-set at

at 190° C. Crystallinity is also promoted by an increase in stretch temperature and set time, but to a lesser degree for the range of this study.

3. The uniaxial strain at the proportional limit in LN_2 of biaxially oriented PET film increases with an increasing set time but there is an interaction with stretch temperature. The average strain at the proportional limit in LH_2 is about 0.25 percent strain higher than the corresponding value determined in LN_2, but the strain at break is lower. The strain at break in LN_2 shows an increase with decreasing stretch temperature. A lower heat-set temperature increases the strain at break at LN_2 temperature.

3. The proportional limit and breaking stresses in both LN_2 and LH_2 are higher with the lower stretch temperature of 85° C.

4. Biaxial burst tests performed in liquid nitrogen showed that both proportional limit and strain at break increase with higher heat-set temperature. The breaking strain of the experimentally processed film of this investigation was almost twice that of the commercially available PET film.

5. Biaxial burst tests performed in liquid nitrogen showed that the proportional limit and stress at break decrease with increasing stretch temperature. These stresses measured on the film stretched at low temperature were about 40 percent higher than for the commercially available PET film.

ACKNOWLEDGEMENT

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TABLE I. - UNIAXIAL TENSILE TEST MODULUS

AVERAGED OVER SET-TEMPERATURES

Test medium	Stretch temperature, °C	Heat-set time(sec)	Modulus of elasticity, psi
LN_2	85	15	1.25×10^6
LN_2	85	120	1.15
LN_2	95	15	1.21
LN_2	95	120	0.87
LH_2	85	15 and 120	1.35
LH_2	95	15 and 120	1.00

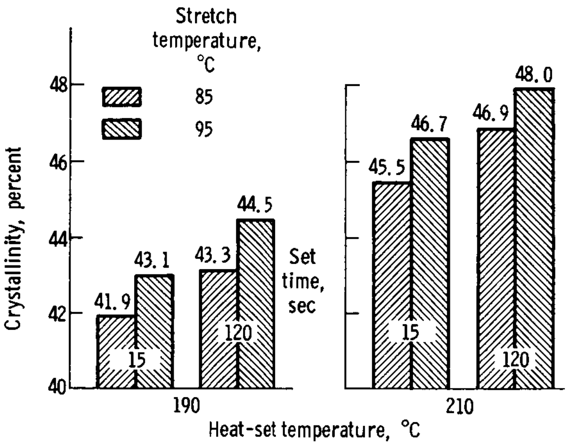

Figure 1. - Crystallinity of PET film as a function of the stretch temperature and the heat-set temperature and time.

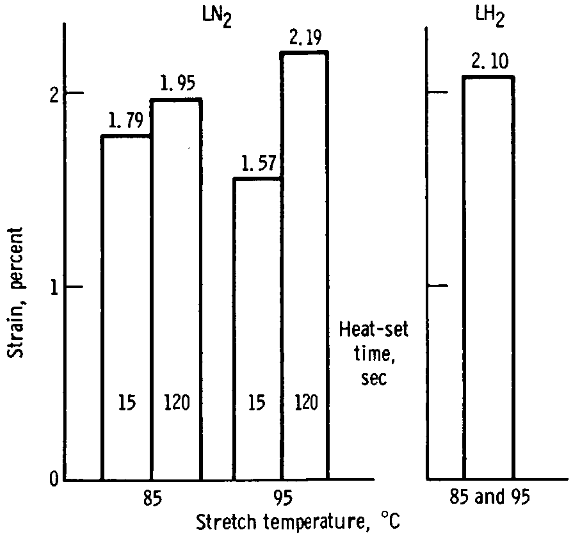

Figure 2. - Strain at the proportional limit determined from uniaxial tensile tests of PET film at cryogenic temperatures as a function of the stretch temperature and the heat-set time.

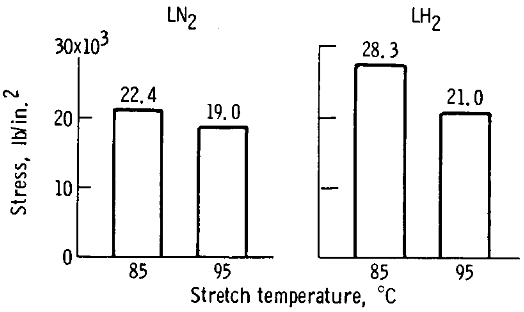

Figure 3. - Stress at the proportional limit determined from uniaxial tensile tests of PET film at cryogenic temperatures as a function of the stretch temperature.

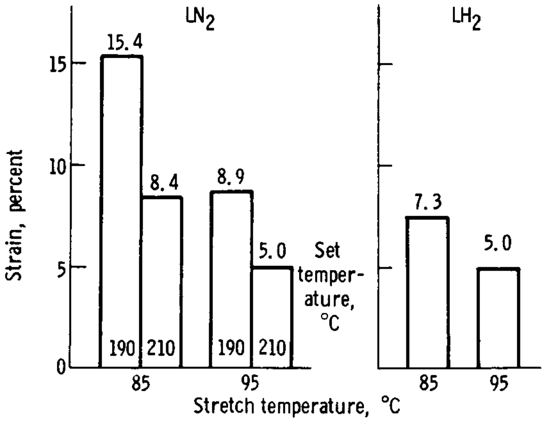

Figure 4. - Strain at break determined from uniaxial tensile tests of PET film at cryogenic temperatures as a function of stretch and heat-set temperatures.

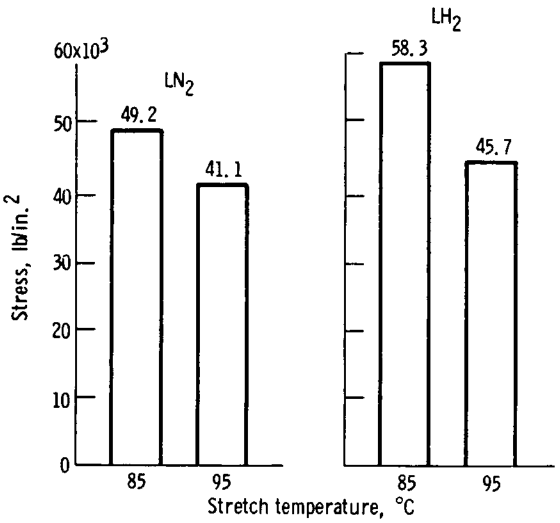

Figure 5. - Stress at break determined from uniaxial tensile tests of PET film at cryogenic temperatures as a function of stretch temperature.

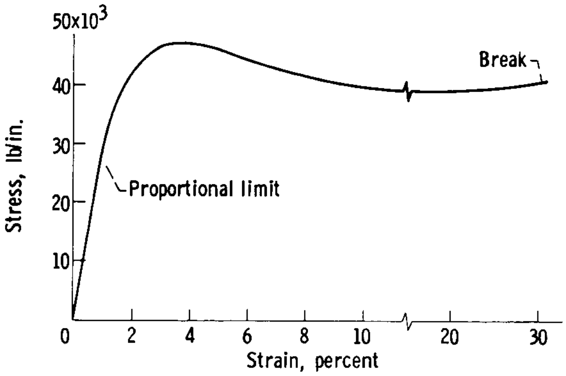

Figure 6. - Biaxial stress-strain curve for a PET film tested at 77° K.

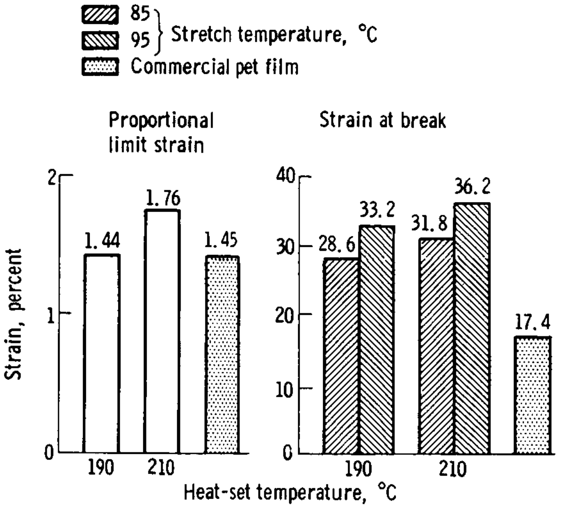

Figure 7. - Strain at the proportional limit and at break determined from biaxial burst tests of PET film in LN_2 as a function of stretch and heat-set temperatures.

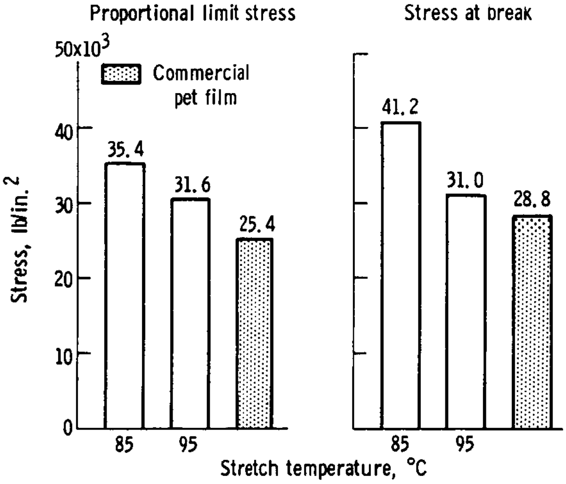

Figure 8. - Stress at the proportional limit and at break determined from biaxial burst tests of PET film in LN_2 as functions of stretch temperature.