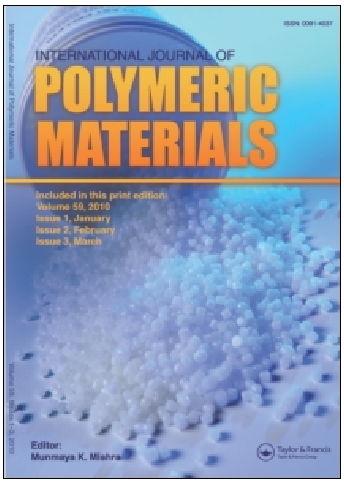

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A New Brittleness Criterion for Low Density Polyethylene Films†

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Since the existing methods of establishing brittleness criteria for low density polyethylene films were found to be unsatisfactory, the present study was undertaken to investigate the brittle–ductile transition and the factors that may influence it. By defining a brittle failure under uniaxial constant strain rate test conditions, a transition temperature from ductile to brittle failure was established at each strain rate. It was found that at low strain rates the transition temperature is almost independent of the strain rate. This temperature is suggested as the *cold brittleness temperature*.

This cold brittleness temperature is related to the energy dissipation ability of the material as found from dynamic mechanical tests. The correlation between the uniaxial constant strain rate test and the dynamic mechanical data was checked mathematically by using a viscoelastic model.

INTRODUCTION

As the use of plastics has expanded, it became obvious that for certain applications it is not sufficient to consider only the commonly used mechanical properties such as ultimate stress and strain or the elastic modulus. Additional aspects of the mechanical behavior must be considered to achieve satisfactory performance.

The work reported in this paper originated from a project to determine the

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causes of failure of high altitude balloons constructed of low density polyethylene films. The brittle rupture of these films may be one of the main causes of failure of high altitude balloons in the stratosphere. If the material can deform in a plastic manner there is the possibility that the stress can be relieved by deformation or a ductile rupture. A ductile rupture usually results in a local tear in the material. A brittle rupture causes a shattering of large areas resulting in an immediate loss of the balloon.

Balloon failures due to the brittleness of the film have accompanied balloon flights almost since polyethylene films were introduced as a balloon material. In the early fifties, M. M. Renfew and A. J. Freeman reported on the development of an inclined plane ball tester.[1] This tester was developed to evaluate balloon films for brittleness. However, the inclined plane ball test as well as the falling ball test, in which the ball is dropped directly on a suspended sample rather than rolled down an inclined plane, were found to be unsatisfactory. The results obtained did not correlate well with balloon flight experience and properties related to the surface of the ball were found to influence the test results.[2-5] A Round Robin testing program indicated little or no agreement among the results obtained at several different laboratories as was reported by Hauser.[6]

It has been suggested by Roth and Mahmoodi[7] that a study of tensile properties at progressively lower temperatures should yield information regarding the transition from ductile to brittle behavior. However, the difference between ductile and brittle rupture as is found in the ruptures induced by biaxial loading (Figures 1 and 2) is not observable in uniaxial testing. This necessitates the establishment of an independent criterion for ductile and brittle behavior. The criterion suggested by this paper is based on the observations of Amborski and Mecca.[8] They showed that at a constant temperature a curve of the ultimate strain vs. log of the strain rate yields a sudden transition from a large ultimate strain to a much smaller ultimate strain in a narrow range of strain rates, as can be seen in Figure 3. The strain rate at which this transition occurs is defined as the *Critical Strain Rate* (CSR) at the given temperature. Ductile behavior is therefore associated with large ultimate deformations while the brittle behavior is associated with much smaller ultimate deformations.

It can be expected that repeating these tests at various temperatures would yield a similar transition at each temperature with the CSR moving to higher strain rates as the temperature is increased. Plotting the same data as ultimate strain vs. temperature at a constant strain rate should yield a similar transition on the temperature axis as Amborski and Mecca observed on the strain rate axis. It is then possible to define a *Critical Temperature* (CT) equivalent to the CSR. Extrapolating these results to very low strain rates yields a new criterion for cold brittleness in the establishment of a *Cold Brittleness Temperature* (CBT).

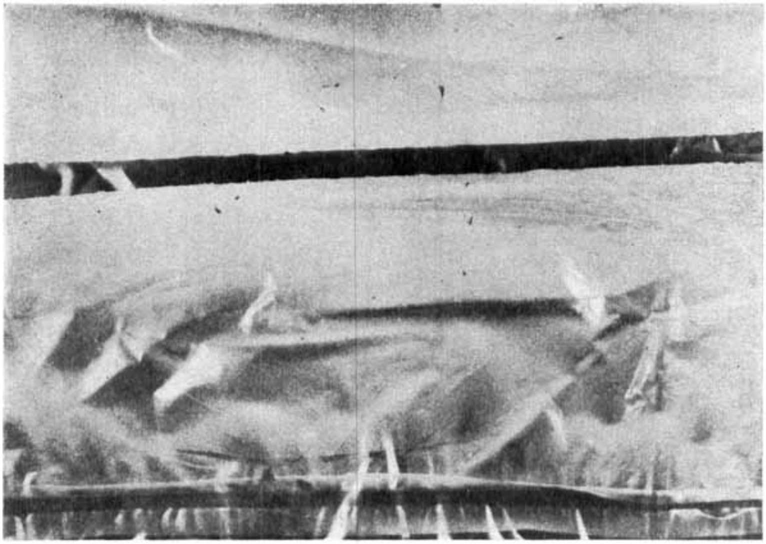


FIGURE 1 Ductile rupture.

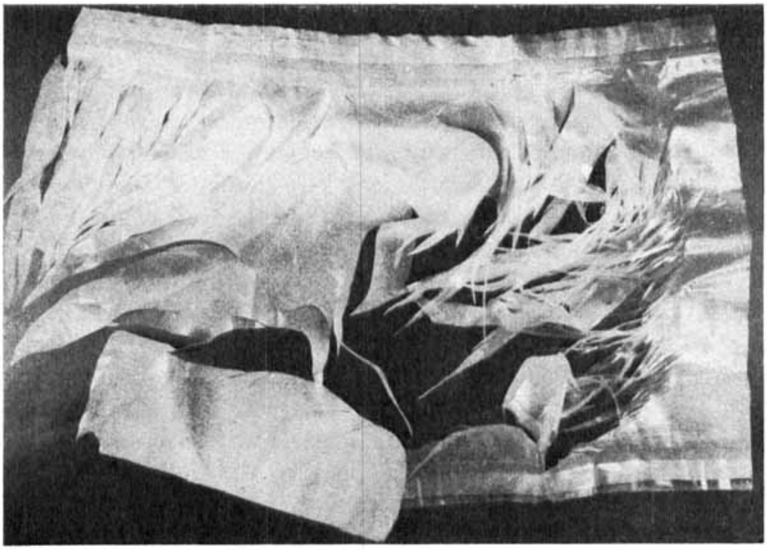


FIGURE 2 Brittle rupture.

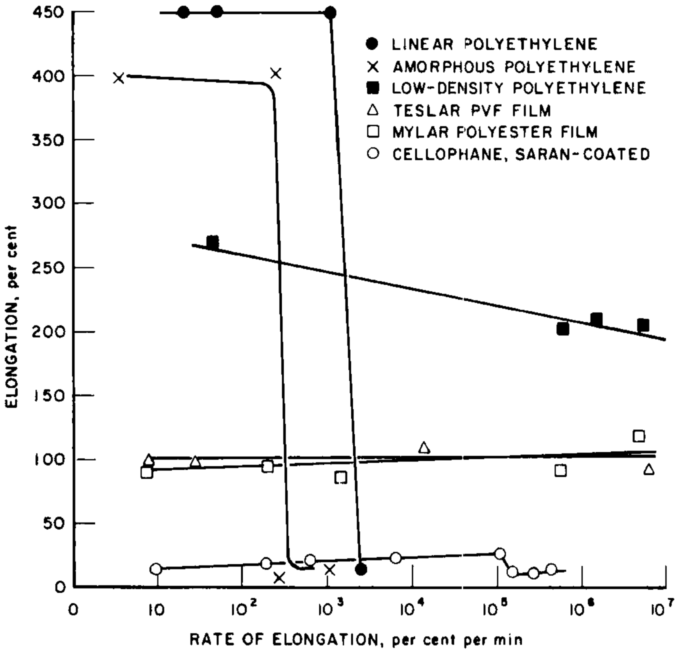


FIGURE 3 Critical strain rate determination at 23.5°C (from Amborski and Mecca[8]).

EXPERIMENTAL RESULTS

The experimental program leading to the establishment of the CBT consisted of constant strain rate uniaxial tests conducted on an Instron tensile tester. Tests were run at a number of strain rates between 50 and 5000% per minute at temperatures from room temperature to −75°C at intervals of 8–10 degrees on 1 inch gage length samples, ½ inch wide. Samples were cut in the machine and transverse directions from a single roll of 2.0 mil-thick film.

The film used in this test program was StratoFilm®-LDPE film manufactured by Winzen Research Corp. of Minneapolis, Minn. This film was developed to yield improved low temperature properties. Table I contains some physical and mechanical properties of this material. This film is produced by a blowing process after extrusion to give biaxial orientation. Relatively high blow ratios are used, which account in part for its superior strength when compared to commercial grade LDPE film.

The film is available in thicknesses from 0.35 mil to 3 mil. Although the same resin is used for producing all films, there is a difference between films of different thicknesses because the thin films are produced by additional drawing

TABLE I

Melt Index (MI) (ASTM Method D 1268-65T)	< 1.1[a]
Density	0.92[a]
$\bar{M}w$	~200.000[b]
Yield Stress (room temperature Instron tests at 100%/min)	~1500 psi

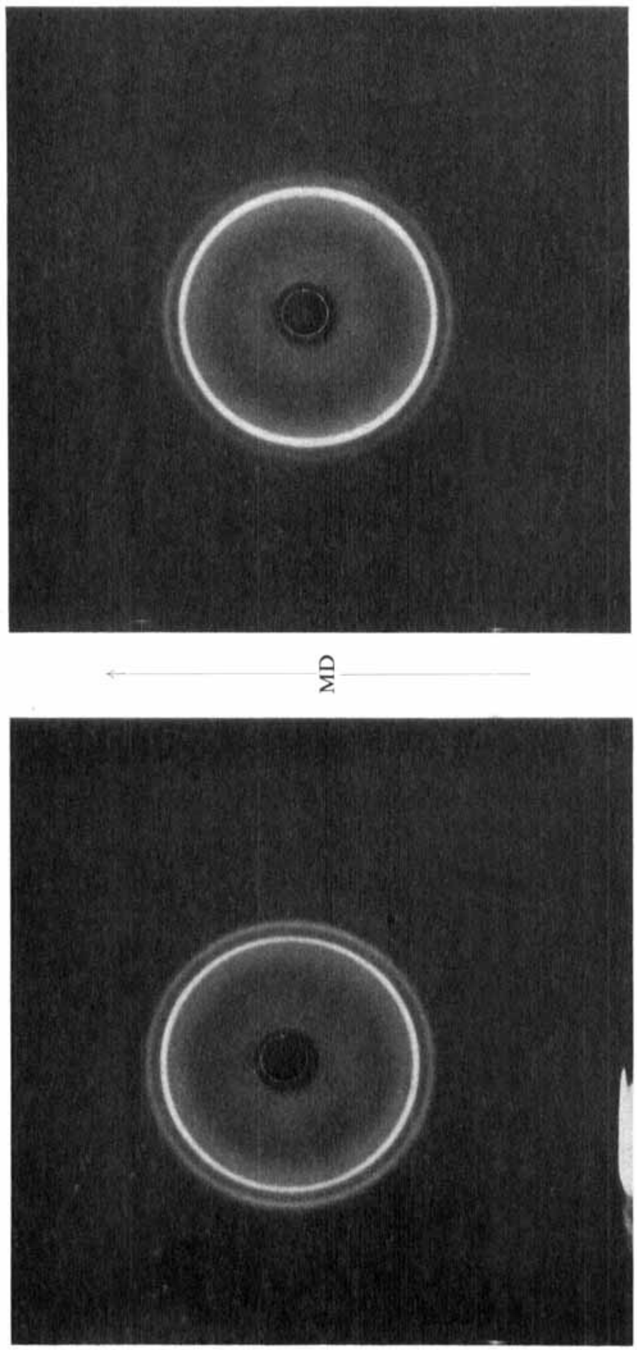
[a]Information courtesy of Winzen Research Inc.
[b]Values taken from GPC Analysis made by Waters Associates of Framingham, Mass.

of the film in the rolling direction during production resulting in additional preferred orientation in this direction. Figures 4a and 4b show X-ray diffraction patterns for 2.0 mil and 1.0 mil StratoFilm®. Only a little preferred orientation is visible in the heavier gage film; a larger amount is seen in the thinner films. This increased anisotropy of the thinner films was also observed by mechanical testing. The Infrared spectra of StratoFilm® (Figure 5) is typical of PE and shows no unusual features.

Typical Instron output is shown in Figure 6. It can be seen that at some temperature the ultimate strain starts to decrease. It should be noted that the curves do not show the "classical" brittle behavior (rupture without yield). In order to obtain this kind of behavior, much lower temperatures must be attained. At those temperatures the samples become highly sensitive to defects due to preparation or material imperfections.

It was first attempted to reproduce the characteristics of Amborski and Mecca's curve shown in Figure 3. Figure 7 shows that at −40°C, the CSR cannot be observed in the range of available strain rates, but at −52°C, it is clearly visible.

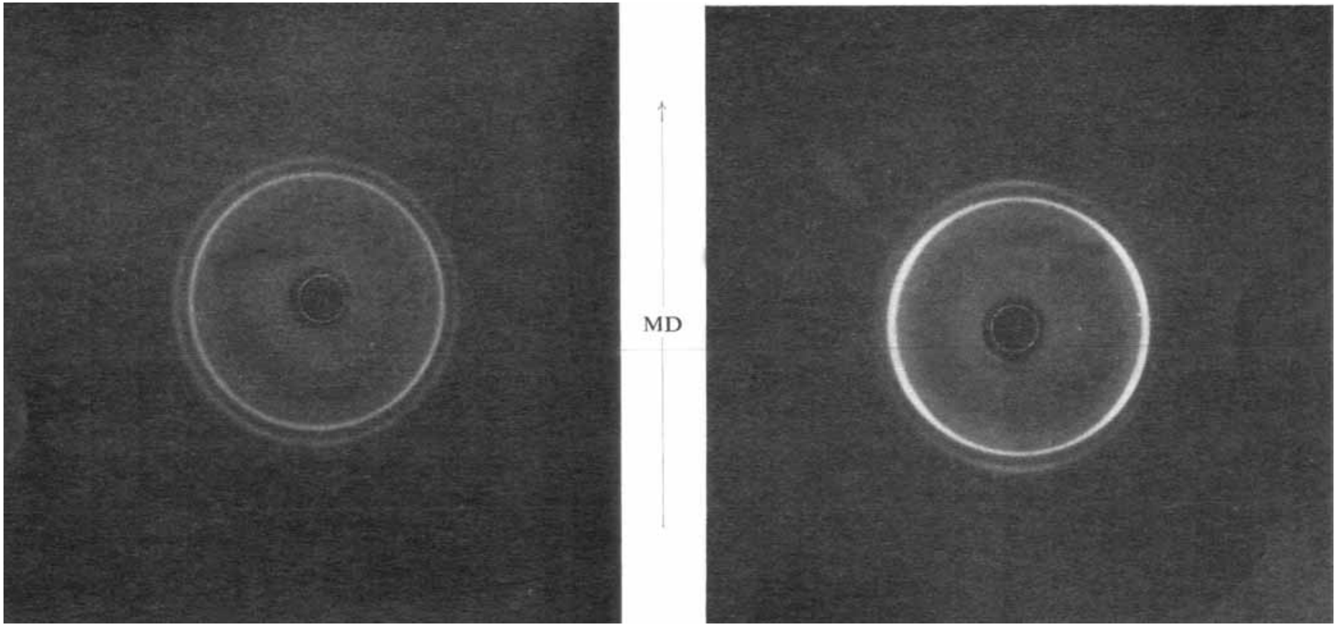
All of the data were then plotted as ultimate strain vs. temperature at a constant strain rate. Figure 8a contains the results for the machine direction and Figure 8b for the transverse direction. At each strain rate the critical temperature is defined. The maximum travel of the crosshead was restricted to 500% elongation to avoid excessive slippage from within the jaws. Combining the Critical Temperatures and their respective strain rates yields Figure 9. The points of this plot fall on a straight line divided into two sections, one for the lower strain rates (< 735% min) and the other for the higher strain rates (> 735% min). The approximation by straight lines on a plot of logarithm of rate vs. reciprocal absolute temperature is typical for viscoelastic materials in which the relaxation process can be described by an Arrhenius type rate equation. This is, therefore, frequently referred to as an Arrhenius plot and a straight line region indicates conformity to a single mechanism. Based on the Arrhenius equation the activation energy for the high



a. Through.

b. Edge.

FIGURE 4a X-ray diffraction pattern from two directions. StratoFilm®, 2.0 mil.



a. Through.

b. Edge.

FIGURE 4b X-ray diffraction pattern from two directions. StratoFilm®, 1.0 mil.

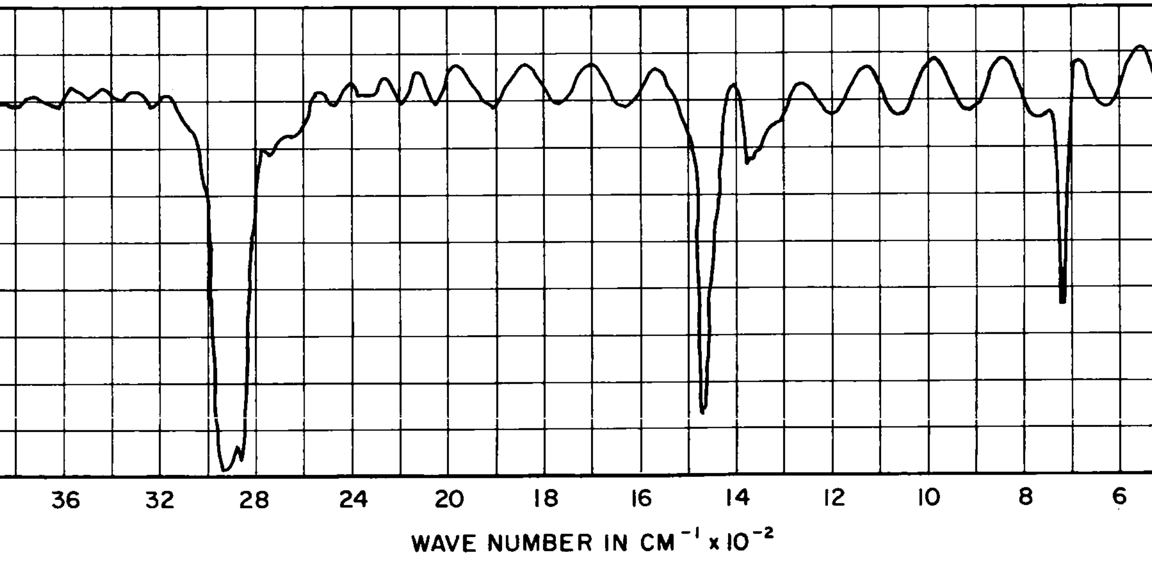


FIGURE 5 Infrared spectrum of StratoFilm® L.D. polyethylene film.

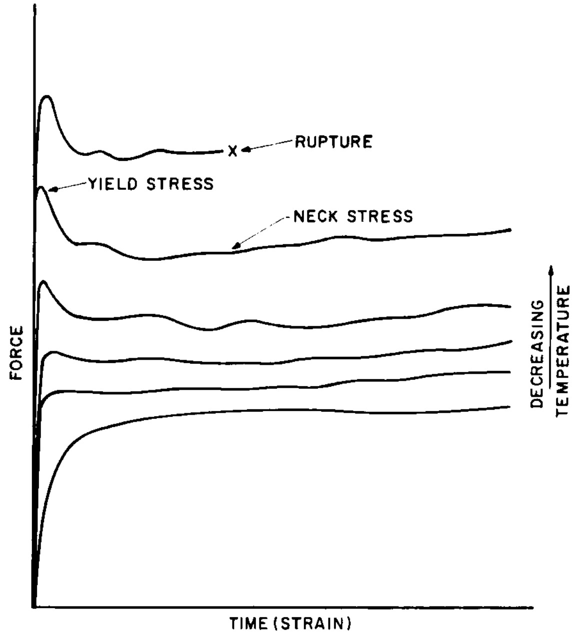


FIGURE 6 Typical constant strain rate data at different temperatures.

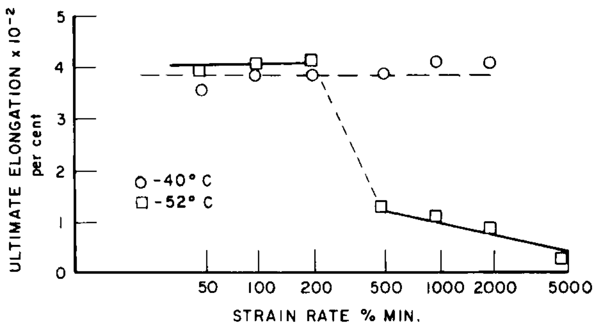


FIGURE 7 CSR determination for StratoFilm®.

strain rates region was found to be 10 Kcal/mole which is a typical value for a flow process.

The straight vertical line in the low strain rate region indicates that the response of the viscous part of the material becomes of secondary importance since this is the only part which is time or rate dependent. This suggests

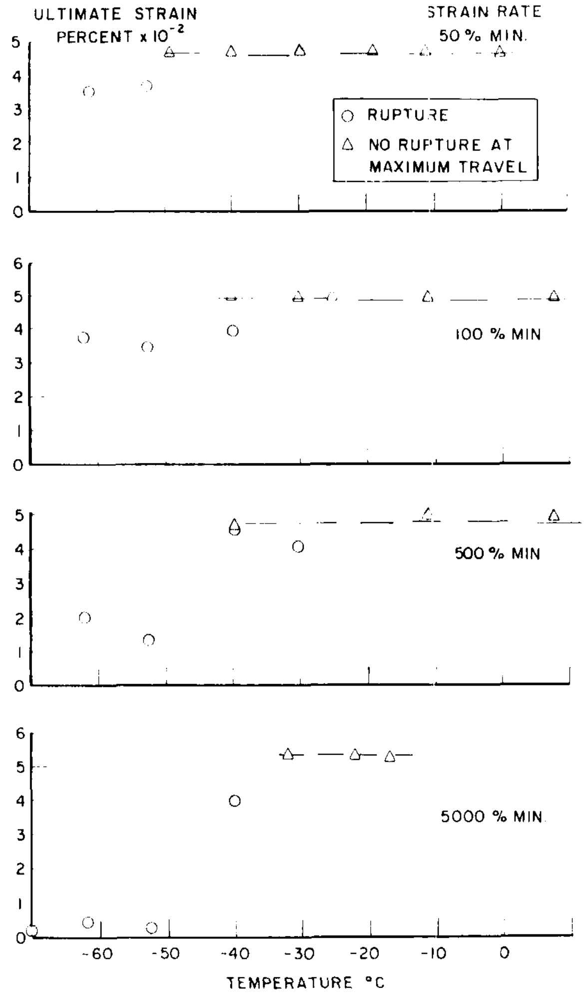


FIGURE 8a Evaluation of the critical temperature (CT). Machine direction.

that the brittle failure is associated with a lack of viscous response, or a lack of ability to dissipate strain energy. If the strain energy build-up rate is larger than the rate of energy dissipation, the result is rupture, i.e. the fastest energy release mechanism through the formation of new surfaces.

The temperature at which the viscous response became independent of rate (time) is suggested as the *Cold Brittleness Temperature* (CBT). For StratoFilm®

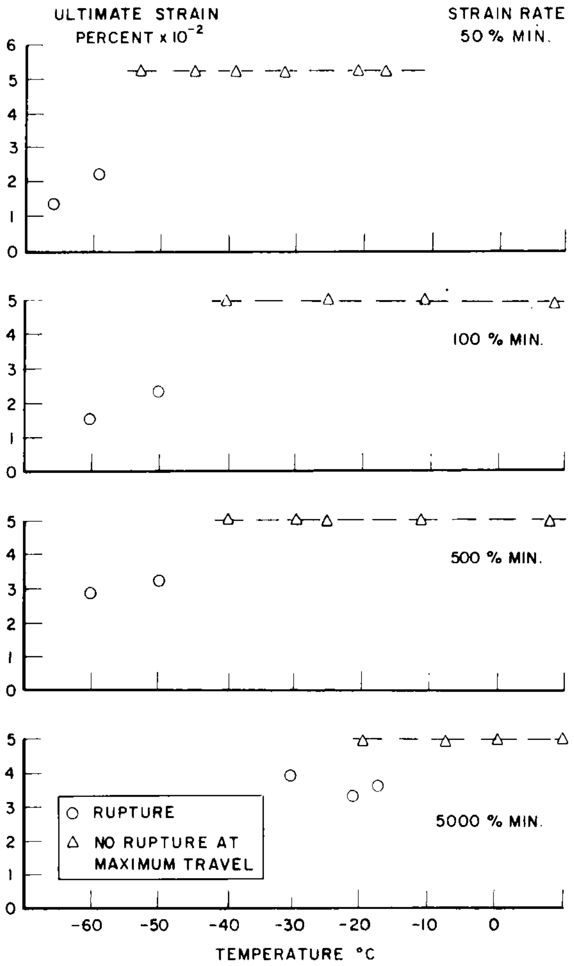


FIGURE 8b Evaluation of the critical temperature (CT). Transverse direction.

this temperature was found to be $-52°C$. Because of the way the CT was defined it was expected that the CBT would be somewhat higher than the usually obtained values, but a review of the literature showed the temperature of $-52°C$ to fall within the published data for polyethylene.[9,10] In addition to yielding the CBT, Figure 9 gives the relationship between strain rate and the temperature needed to cause brittle rupture at temperatures higher than the CBT.

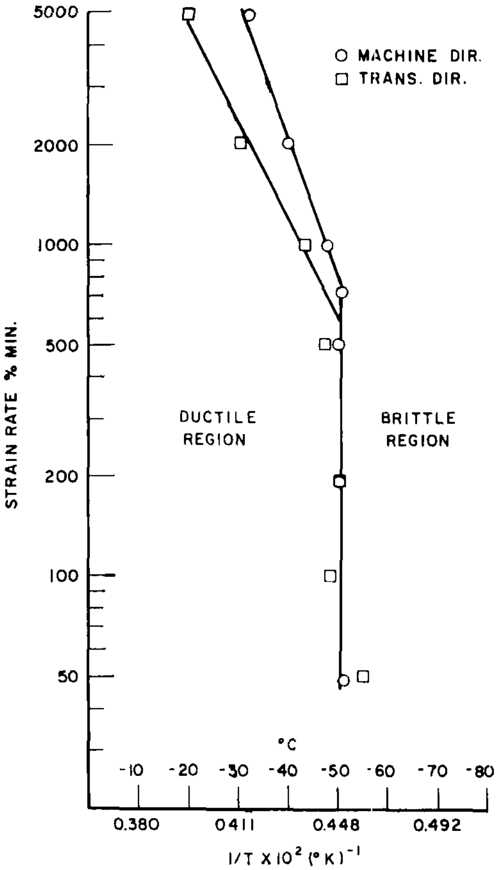


FIGURE 9 Critical temperature (CT) vs. strain rate.

DISCUSSION

The CBT as defined above is a function of orientation, film thickness and prior history of the sample, as well as the characteristics of the basic resin. Consequently, it is of value in determining which films might not be appropriate for balloon use. In fact, it can be of use in discriminating between "good" and "bad" films extruded from the same resin. The 2 mil StratoFilm® used in the above determination was an extremely successful balloon film. Another polyethylene film that was known to have been used in the fabrication of a number of balloons that failed was found to have a CBT 7°C higher than this StratoFilm.

As was shown in the previous section, the ductile behavior is due to the plastic deformation by which the material can relieve stored strain energy, while the brittle rupture occurs when the strain energy level is larger than the level that the material can sustain. It is relieved by forming new surfaces in the rupture process and releasing the remaining elastic energy.

The ability of a given material to dissipate energy is directly related to the damping properties as presented by the loss modulus E'' and the tan δ, the phase shift in a dynamic mechanical test. A series of dynamic mechanical tests were performed on a Rheovibron at a test frequency of 110 cps to evaluate E'' and tan δ curves for StratoFilm®. The resulting characteristics are given in Figures 10 and 11. It is clear that the CBT of −52°C falls in the area of a relative minimum of the E'' or the tan δ vs. temperature curves. The different peaks are indicative of the various relaxation mechanisms that appear at various temperatures at this test frequency. The low temperature, γ, transition peak is due to restricted local motion with the exact mechanism yet to be determined. At the β transition, in the temperature range of 0°C, large chain segments gain mobility needed for plastic flow. The dissipation of energy is due to flow of those chain segments.[11,12] The domination of the β relaxation mechanism starts at the minimum between the γ and the β transitions; in the region of the CBT. This may indicate that ductility is related to the type of behavior which is also responsible for the β transition.

To determine if any basic correlation could be established between the constant strain rate data used to define the Cold Brittleness Temperature and the dissipation spectra as given by tan δ and E'', it was decided to look for a theoretical correlation utilizing a model. Recognizing that the dynamic behavior is frequency as well as temperature dependent, qualitatively meaningful comparisons of cyclic and constant strain rate experiments can only be made in equivalent ranges of strain rate. Therefore, due to data limitations (a cyclic frequency of 110 cps) only high strain rate data can be compared with the dynamic mechanical results. The basic assumption underlying the analysis is that the material can sustain only a certain level of strain energy, V_{cr}. If the work done on the model exceeds this level, and the additional energy is not dissipated, rupture occurs.

Two requirements were established for a possible model: first, it should be a model of a viscoelastic solid, and second, it should be as simple as possible so that the contributions of the fundamental components of the response can be recognized. No attempt was made to quantitatively characterize the response to all loading histories of this biaxially oriented, partially crystalline film. A model that could do this would be much too complicated to provide any indication of the validity of the basic assumption concerning the storage of strain energy.

The simplest viscoelastic solid model is the Voiqt model. However, this model cannot be used here since the stored energy in the spring will always

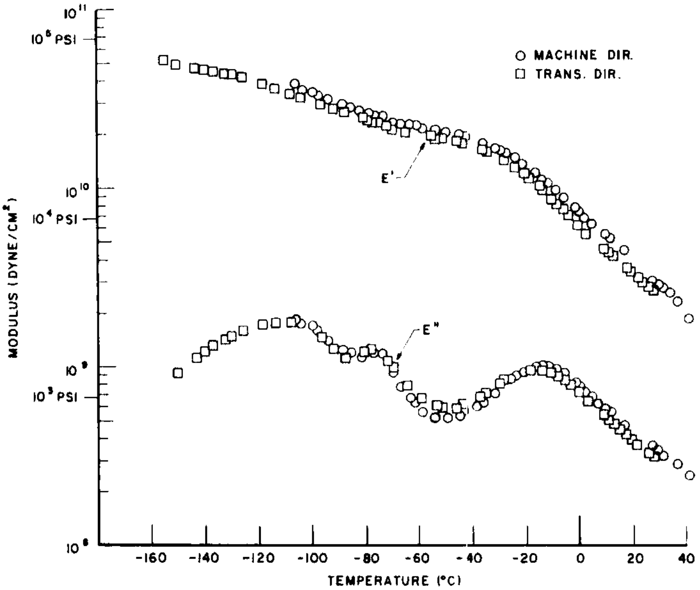


FIGURE 10 Storage and loss moduli vs. temperature.

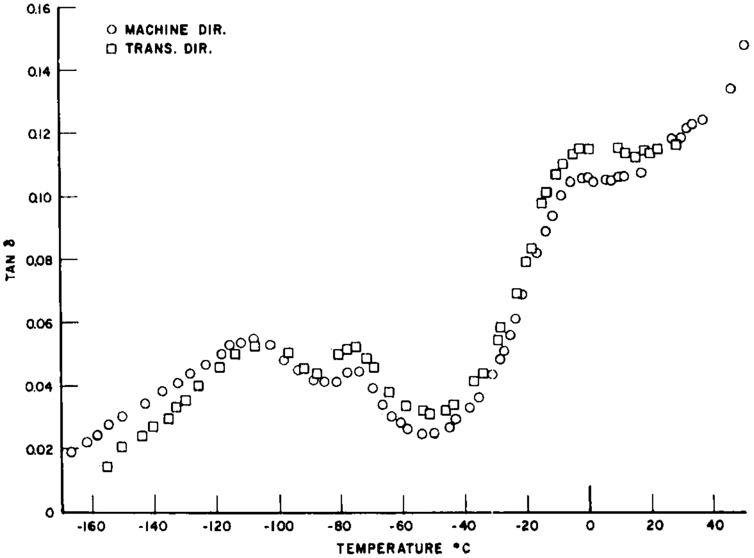


FIGURE 11 Tan δ vs. temperature.

reach the same value at the same elongation, yielding a constant elongation criterion for fracture. Consequently, the model used is a three-element model consisting of a Voiqt model in series with an additional elastic element, as is shown in Figure 12. It is recognized that this model does not adequately represent the creep characteristics of the material. However, an additional dashpot in series with the three-element model, which would improve the creep prediction, does not affect the prediction of the critical temperatures since in the constant ultimate strain region of temperatures this element is found to be essentially "frozen". The only marked effect on the results of an additional dashpot is to cause large ultimate strains when V_{cr} is reached at the higher temperatures. The parameters of the three-element model were evaluated as functions of temperature from the tan δ and E'' data available from the dynamic mechanical tests, as described in detail in the Appendix. Evaluation of the model parameters as functions of temperature results in acceptable behavior since the major interest is in the elastic response and when deviations from that response occur. After calculating the parameters E_1, E_2 and η, the model's response to constant rate stretching was determined analytically, solving for the ultimate strain at which the critical energy was reached.

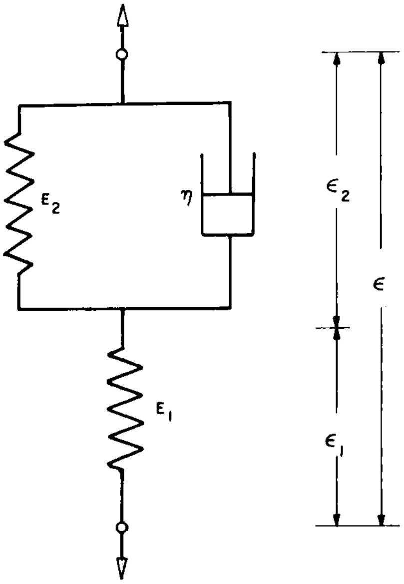


FIGURE 12 Three-element model.

A typical result of this analysis is given in Figure 13. One can see that the ultimate elongation is small and almost constant until a temperature is

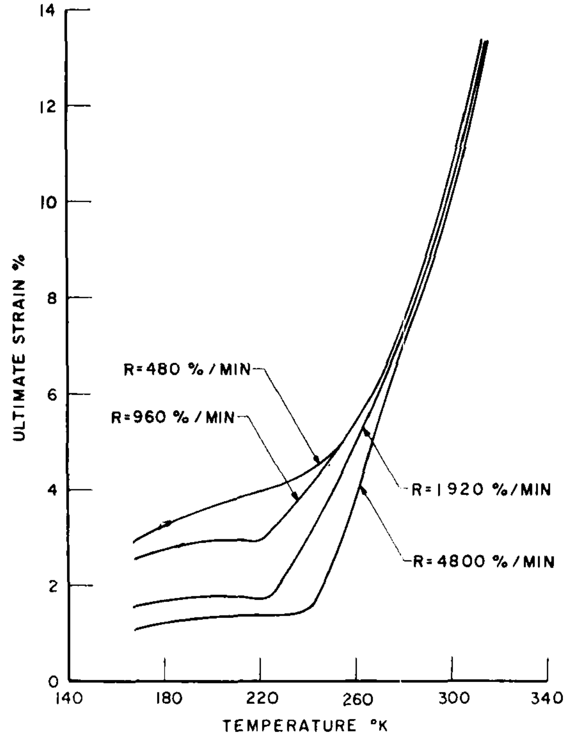


FIGURE 13 Ultimate strain for a three-element model using rheovibron data from Stratofilm®, machine direction. $E_2/E_1 = 0.100$ and $V_{CR} = 1.5 \times 10^6$ dynes/cm^2.

reached at which the elongation starts to increase due to the response of the viscous part and energy dissipation. At the lowest strain rate shown, 480%/min, there is no deflection point (where the elongation starts to increase). This is due to the non-validity of this low strain rate prediction using high frequency cyclic data. However, at the higher rates the deflection point is evident. It is found to shift to higher temperatures with increasing strain rate in the same temperature range as was found experimentally.

CONCLUSIONS

A systematic testing program was performed to determine the Cold Brittleness Temperature of a low density polyethylene film. This procedure yields, in addition to the Cold Brittleness Temperature, the relationship between the transition from ductile to brittle behavior and the strain rate and temperature.

It was shown that for low density polyethylene the ductile–brittle transition is related to the transition from the β relaxation mechanism to the γ relaxation mechanism, and the dissipation spectra of the material.

Theoretical model analysis indicated that there is a relationship between the E'' and tan δ vs. temperature curves and the ultimate elongation vs. temperature curves obtained by constant strain rate uniaxial testing. The behavior of the model indicates that it may be possible to use the stored strain energy as a failure criterion. However, even though additional research is necessary to prove if this is indeed the fundamental determinant of the Cold Brittleness Temperature, the analysis demonstrates that careful use of a rather simplistic model can yield useful information.

Acknowledgements

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Appendix

MODEL ANALYSIS GOVERNING EQUATIONS

The complex modulus obtained from dynamic test data on the three-element model of Figure 12 is given by:

$$E^* = E' + iE'' = \left(\frac{1}{E_2 + i\omega\eta} + \frac{1}{E_1}\right)^{-1}$$

where ω is the frequency of the test.[13] After some algebraic manipulation, this yields:

$$E' = \frac{E_1[E_2{}^2 + E_1E_2 + (\omega\eta)^2]}{(E_1 + E_2)^2 + (\omega\eta)^2}; \quad E'' = \frac{E_1{}^2\omega\eta}{(E_1 + E_2)^2 + (\omega\eta)^2}.$$

Introducing $\tan\delta = E''/E'$ and $A = E_2/E_1$, $E_1 = E_1(E'', \tan\delta, A)$ and $\eta = \eta\,(E'', \tan\delta, A)$ can be determined.

The constitutive equation for the model is

$$\dot{\sigma} + (E_1/\eta)\,[1 + A]\sigma = (AE_1{}^2\epsilon/\eta) + E_1\dot{\epsilon}$$

where σ is the applied stress, ϵ is the total strain and the ($\dot{}$) represents differentiation with respect to time.

The solution of this equation with initial conditions corresponding to a constant strain rate tensile test yields:

$$\sigma = C[1 - \exp(-\Omega t)] + Bt$$

where B, C and Ω are combined constants including E_1, A and η, and t is time. By substituting $t = \epsilon/R$ where R is the rate of elongation, and separating ϵ into ϵ_1 and ϵ_2 where ϵ_1 is the deformation of the single spring and ϵ_2 is the deformation of the Voiqt model, we can calculate the stored energy in the two springs. Equating this energy with the critical energy V_{cr} will yield the ultimate elongation (ϵ_u).

A computer program was written to calculate the behavior of the model as a function of temperature under the above assumptions.