

Effect of Morphology on Biaxial Stress Rupture of Polyethylene

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Synopsis

The relationship between biaxial stress-rupture behavior and polymer morphology has been investigated for a series of compression-molded disks of linear polyethylene. Rupture data were obtained over a range of temperatures on polymers of several melt indices that had been solidified at two rates. Two failure mechanisms were observed: one at high stress levels, which was ductile; the other at low stress levels, which was brittle. The stress level at which the mechanism changed from ductile to brittle decreased as the measurement temperature increased, as the melt index of the polymer increased, and as the rate of solidification decreased. It was shown that initial pressurization of the disks causes the formation of microscopic surface fissures along spherulite boundaries as well as within individual spherulites. The extensive growth of these fissures at high stress levels sufficiently raises the stress on the sound portions of the polymer to cause large-scale macroscopic drawing of the spherulites. At low stress levels the initially formed fissures grow by a localized drawing process at their ends. A macroscopic crack forms by a chance coalescence of a number of individually growing fissures. This process is more rapid in disks of polymer that form large spherulites when cooled slowly from the melt. The spherulite size in disks of polymer of low melt index is much smaller under the same conditions of cooling and is less sensitive to the cooling rate than in disks of polymer of high melt index. Annealing of rapidly cooled disks whose microstructure contains relatively small spherulites reduces the stress at which the failure mechanism changes without appreciably altering the spherulite size. Oxidation of the polymer also reduces the transition stress.

INTRODUCTION

The physical properties of crystalline polymers have been shown by a number of investigations to depend on the morphology developed during fabrication.^{1,2} Properties such as impact strength, yield strength, and ultimate elongation have been correlated with the size of spherulites present in the test samples. Spherulite size has been shown to depend on the thermal history of the material both during and after fabrication.³ Bryant⁴ and, more recently, Keith and Padden⁵ and Yu and Ullman⁶ have studied the deformation behavior of spherulitic films of polyethylene subjected to tensile stresses, which give rise to large plastic flow. Little attention has been given, however, to the influence of morphology on time-dependent mechanical properties such as stress rupture under biaxial stresses.

The short-time biaxial stress-strain behavior of polyethylene is not

significantly different from its short-time uniaxial behavior in that, in both cases, several hundred per cent elongation is achieved prior to rupture.⁷ But Bragaw⁸ and Richard, et al.,⁹ using polyethylene pipe in studies of biaxial creep, have observed ruptures occurring at elongations of less than 10%. Similar ruptures of biaxially stressed polyethylene in the presence of surface-active agents is an important problem which may be a special case of this general phenomenon of stress rupture. In this paper, the relationship between thermal history, morphology, and biaxial creep rupture are reported.

EXPERIMENTAL

Four linear polyethylenes with melt indices of 0.2, 0.8, 1.8, and 3.6 were used in this study. The density of the four materials, in the form of molding shot, ranged from 0.953 to 0.957 g./cm.³. Rupture disks, 4.0 in. in diameter and 0.125 in. thick, of the materials were prepared by compression molding. The thermal history of the disks was varied by heating the disks in thin-walled brass molds above the melting point of the polymer (137°C.) in a vacuum oven operated at 10⁻² mm. Hg. A temperature of 175°C. for 30 min. was maintained to "erase" any prior thermal history, and then solidification was carried out by rapidly transferring the mold either to an oil bath at 125 ± 0.2°C. or to a Dry Ice-alcohol mixture at -77°C. The cooling rates as determined by measurement with embedded thermocouples, in the vicinity of the melting point achieved by the two procedures were 25°C./min. when the sample was placed in the hot oil bath and 125°C./min. when the sample was placed in the Dry ice-alcohol mixture. To achieve reproducible measurements of creep rupture with the samples cooled through the melting point at 25°C./min. the disks were allowed to remain in the oil bath for 6 hr. before being cooled with water over a period of 5 min. to ambient temperature.

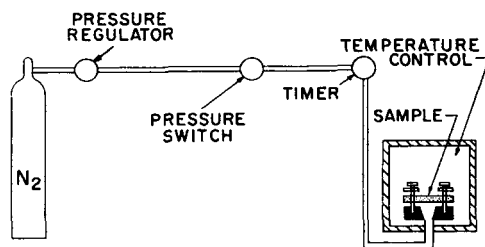


Fig. 1. Biaxial stress-rupture apparatus.

Stress-rupture data for the disks were obtained under conditions of equibiaxial (1:1) stress as shown schematically in Figure 1. Under pressure, a bubble formed in the disk so that the principal stresses could be calculated as

$$S = Pr/2t \quad (1)$$

where P is the pressure, r the radius of the bubble, and t is the sample thickness. The temperature of the sample was maintained constant to $\pm 2^\circ\text{C}$. in a circulating-air oven, which was also equipped with a cooling unit. The time required to rupture the disks at different stress levels was recorded automatically to 0.1 hr. by means of a pressure-actuated switch. The times reported in this paper are the averages for five samples.

The microstructure of thin microtomed sections of the materials was examined before and after rupture in bright-field and polarized light and recorded photographically. Before microtoming, the samples were embedded in a polyamide-epoxy resin in a weight ratio of 60:40. A sliding microtome was used to prepare sections $\frac{1}{2}$ in. long \times $\frac{1}{4}$ in. wide \times 20 μ thick. A comparison of serial sections taken with the microtome knife at different orientations with respect to the sample and with the sample at different temperatures showed that no gross distortion was introduced into the structure by the cutting process.

RESULTS AND DISCUSSION

Temperature Dependence of Stress Rupture

Figure 2 shows stress-rupture data at different temperatures for linear polyethylene of melt index 3.6 solidified at the slow rate of $25^\circ\text{C}/\text{min}$. The ruptures occurring to the left of the "knee" were accompanied by a reduction in sample thickness of several hundred per cent. To the right of the "knee," however, less than 10% thickness reduction took place. The transition time, defined by the intersection of tangents drawn to the curve above and below the "knee," was used to characterize the material. At the lower temperature, some difficulty was experienced in determining the transition time as the "knee" became less distinct. These general features are similar to the data obtained by Richards⁹ on extruded polyethylene pipes, so we may conclude that the extrusion process and the 2:1

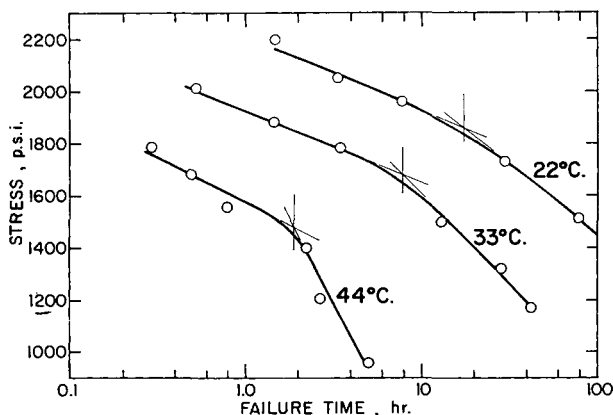


Fig. 2. Effect of temperature on biaxial stress-rupture of linear polyethylene.

biaxial stress system of the pipes are not solely responsible for the transition phenomenon.

The linearity of the data above and below the transition suggests that the theoretical treatment of Coleman¹⁰ or Bueche¹¹ may be applicable. In both treatments, the slope of the stress-rupture line is inversely proportional to the displacement volume generated by chain segments in moving to new equilibrium positions under the influence of the applied stress. The change in slope in the transition region is then attributable to a decrease in the displacement volume. The decrease could be brought about by a decrease in either the size of the segment or the distance between equilibrium positions or both. Similarly, the decrease of the slope with temperature in the brittle regions implies an increase in either the size of the segment or the distance, or both. This dependence of the molecular parameters on temperature appears to be unique to the biaxially stressed polymer as it is not found in the uniaxial stress-rupture measurements.

Transition time is an exponential function of temperature, indicating that the change in mechanism from ductile to brittle failure is an activation process. An activation energy of 7 kcal./mole is calculated for the process in the customary manner.

Influence of Melt Index and Solidification Rate

Figure 3 shows the stress-rupture data at 33°C. for disks prepared from linear polyethylene of melt index 1.8 which were solidified at different rates. The transition time is increased by a factor of three by the fivefold increase in solidification rate. The magnitude of the transition-time difference decreases as the temperature at which the stress-rupture measurements are made is increased. For example, at 40°C. the transition times differ only by a factor of 1.5. Diminution of the effects of cooling rate on mechanical properties at higher measurement temperatures appears to be a general phenomenon, as it was also found in the measurement of uniaxial properties.¹² The higher resistance to biaxial rupture at high stress of the more slowly cooled polymer is also in agreement with the observation that

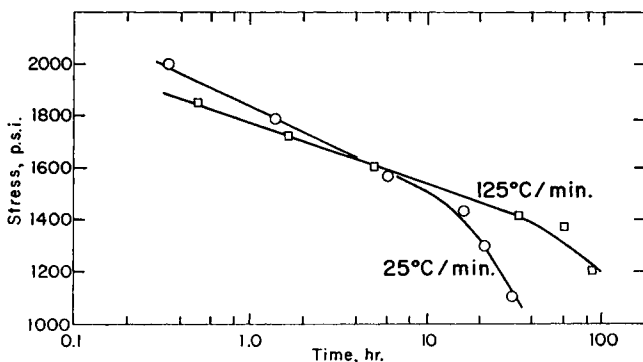


Fig. 3. Effect of solidification rate on stress-rupture behavior.

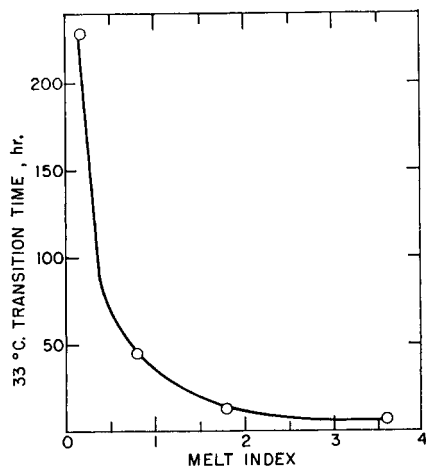


Fig. 4. Influence of melt index on transition time.

annealed samples have a higher yield strength. A decrease in the melt index of the polymer also diminishes the influence of the solidification rate. For example, the polymer of melt index 0.2 gave a difference in transition time of only 5% for the differently solidified samples.

Figure 4 shows the influence of melt index on transition time for disks cooled at the same rate. This parameter appears to have the most influence in determining the ease with which brittle failures can occur.

Morphology

Figures 5a and 5b compare the transverse microstructure obtained by the different cooling rates for polyethylene of melt index 1.8. The spherulitic structure is well defined in the quenched sample, the spherulites being, on the average, smaller and more compact than in the annealed sample. An accurate comparison of the spherulite size distribution is difficult because of a lack of definition of spherulite boundaries in the annealed sample. The surface structure (Fig. 5c) consists of a row of columnar grains. Figure 6 shows a microtomed section taken from the surface of the disks after being stressed but prior to rupture. The initial deformation opens fissures both at spherulite boundaries and also within spherulites. This behavior is common to both rapidly and slowly cooled samples. In some spherulites the nucleus appears to have disintegrated. After a prolonged period of low stress, a macroscopically visible fissure forms and runs completely through the sample. One of these is shown in Figure 7a. The fissure is created by a chance coalescence of several smaller fissures, most of which have a curved trajectory. In Figure 7b, two small fissures in proximity are shown just prior to joining. Even these smaller fissures appear to have a compound nature. The opposite edges of the fissures do not match, indicating that material may be lost when fine fissure networks

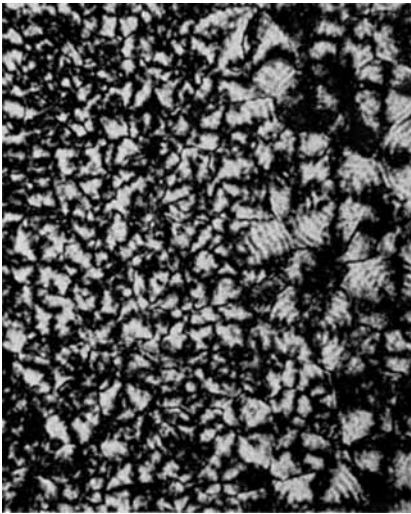
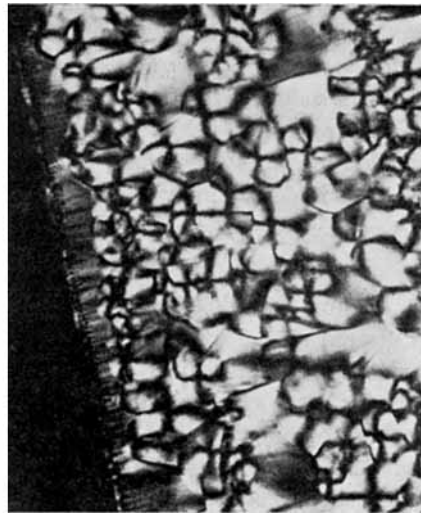
*a**b**c*

Fig. 5. Spherulitic texture of (a) rapidly solidified polyethylene (70 \times); (b) slowly solidified polyethylene (70 \times); (c) surface texture of slowly solidified polyethylene (140 \times).

meet. Figure 8 shows the advancing tip of another fissure. Here, the fissure appears to be growing by a localized drawing mechanism. This mechanism is more dominant in quenched samples and, in general, is observed in samples that rupture near the transition time. Propagation of the fissure through the thickness of the disk takes place by both the chance coalescence and the localized drawing mechanisms.

Ruptures at high stress are accompanied by gross alterations of the

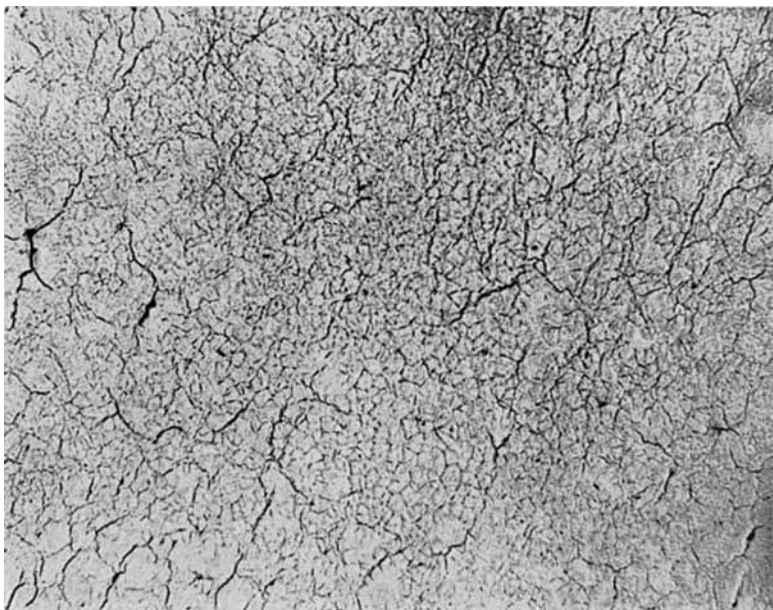
*a**b*

Fig. 6. Effect of pressurization on microstructure; (a) bright-field light (40 \times); (b) cross-polarized light (200 \times).

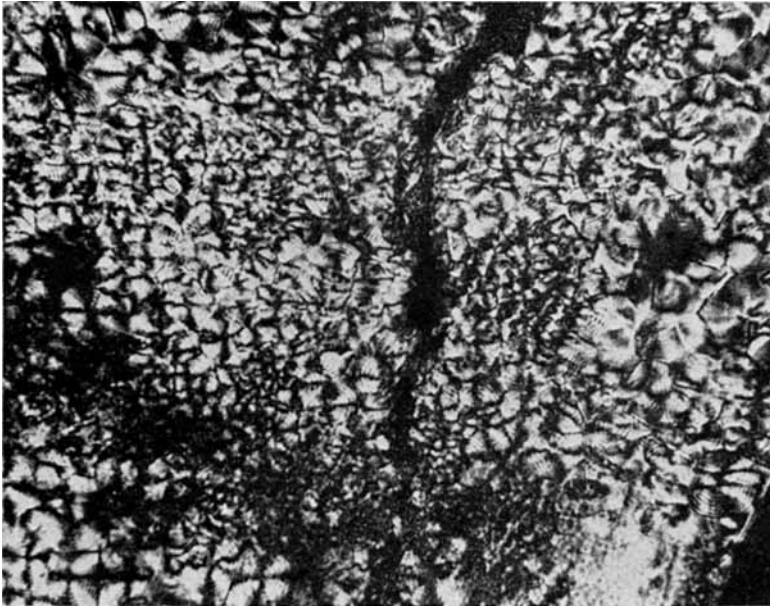
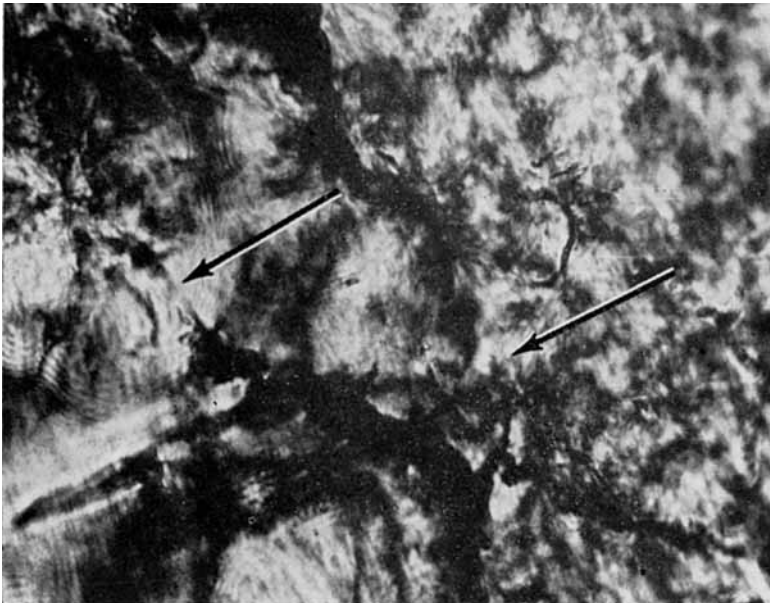
*a**b*

Fig. 7. Low stress failure (*a*) fissure formed by coalescence of smaller fissures ($100\times$); (*b*) fissures before joining ($400\times$).

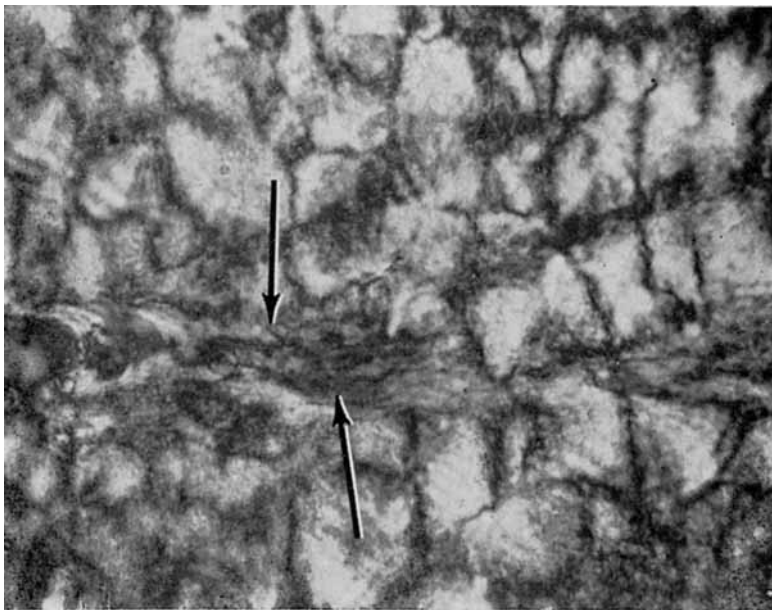


Fig 8. Low stress failure: fissure growth by localized drawing (400 \times).

microstructure, as can be seen in Figures 9a and 9b. The initially formed fissures have greatly increased in size, so that the stress on the remaining material increases, resulting in extensive drawing. The drawing process often causes the fissures to become highly elongated in the direction of the draw, which gives the rupture area a delaminated appearance. The drawn microstructure is similar to that observed by Keith and Padden⁵ in the neck region during uniaxial line drawing of polyethylene. However, in the deformation process observed here, the sample thickness decreases continuously from the base of the bubble to the tip of the rupture. Failure of the material to form a stable neck may be due to large voids in the drawn material, which greatly reduces the effective cross section carrying the stress. A further deterrent to the formation of a stable neck is the rapid rate of elongation just prior to rupture. At very high rates of elongation, the process becomes adiabatic, and the local temperature becomes high enough for melting to occur.

Figure 10 compares the microstructure of polymers of high and low melt index. The spherulite size is very much smaller in polymers of lower melt index, even though the materials were prepared under identical conditions. The microstructure of the polymer of lower melt index does not vary as significantly with cooling rate as does that of the polymer of higher melt index.

Brittle failures appear to occur more readily in large, well-developed spherulites that interleave well with their neighbors; such a structure results from the slow cooling of high melt index polymers. Size *per se*,

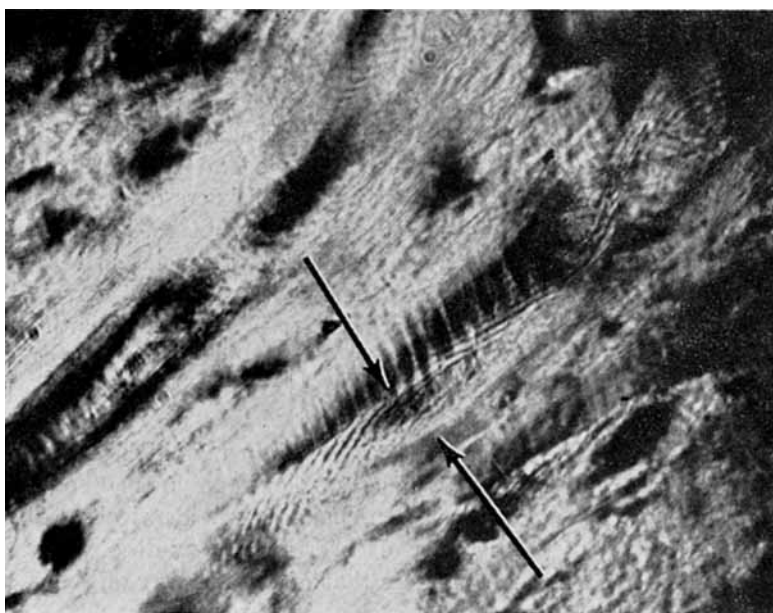
*a**b*

Fig. 9. High stress failure: (a) moderate elongation of spherulites and fissures (100 \times); (b) extensive elongation of spherulites (400 \times).

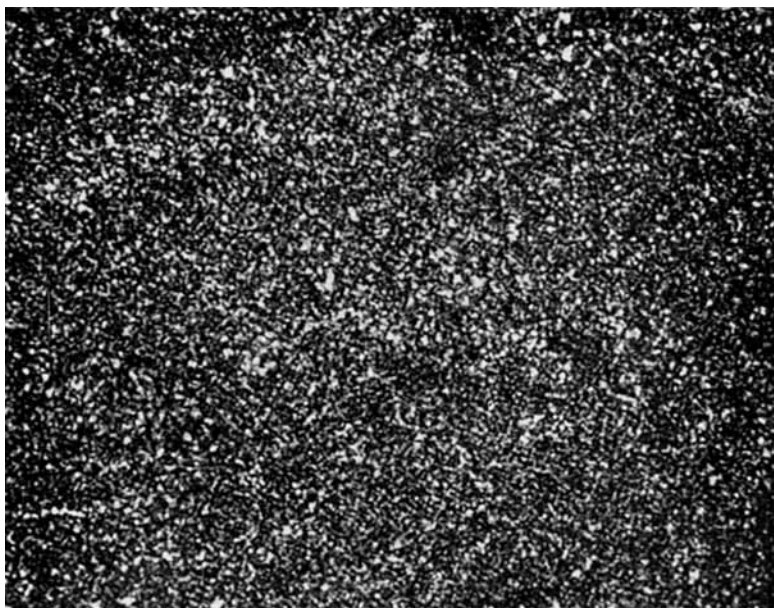
*a**b*

Fig. 10. Spherulitic texture of linear polyethylenes (*a*) of melt index 0.2 (200 \times); (*b*) of melt index 3.6 (200 \times).

however, does not completely control transition time, since annealing of quenched polymers at 128°C. for 15 hr. considerably reduced their transition times without producing microscopically visible changes in their microstructure. Changes in annealed structure, seen by electron-microscopic examination,¹³ have been reported to result from the refolding of polymer chains within the lamellar crystals comprising the spherulites. During such a process, it is possible that the numbers of chains incorporated in adjacent lamellae is decreased. This would make the initiation and propagation of fissures less difficult and hence shorten the transition times.

The change in the slope of the stress-rupture curve in the brittle-failure region as the temperature increases appears to be too large to be explained solely on the basis of recrystallization so far below the melting point. An additional explanation is possible based on the known influence of oxidation on polymer morphology. For example, van Schooten¹⁴ has shown that oxidation produces large numbers of cracks in the spherulites. Therefore, at the higher temperatures, the chance coalescence of fissures produced by biaxial stressing may be facilitated by the presence of oxidation cracks. Incorporation of antioxidants in the polymer shifted the transition time at 44°C. from 1.8 hr. to 7.0 hr. This change is not wholly brought about by the increased oxidation resistance, as the antioxidant also reduced the spherulite size.

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Résumé

On a étudié la relation qui existe entre le comportement à la rupture par étirage biaxial et la morphologie du polymère pour une série de disques comprimés de polyéthylène linéaire. Les résultats de rupture ont été obtenus sur toute une gamme de températures et sur des polymères d'indices de fusion variables, et qui ont été, en outre, solidifiés à deux vitesses différentes. Deux mécanismes de rupture ont été observés: un à des niveaux d'étirage élevés, correspondant à une rupture ductile, l'autre à des niveaux d'étirage faibles caractérisés par une rupture "cassante." Le taux d'étirage auquel le mécanisme change de caractère, décroît avec l'élévation de la température, avec l'augmentation de l'indice de fusion et avec l'abaissement de la vitesse de refroidissement de l'échantillon. On montre que la mise sous pression initiale des disques cause des fissures

microscopiques à la surface et à l'intérieur des sphérulites. La croissance rapide de ces fissures aux niveaux d'étirage élevés augmente suffisamment la tension sur les parties vierges du polymère pour produire un étirage macroscopique des sphérulites. Aux niveaux d'étirage plus modestes, les fissures initiales croissent par un processus d'étirage localisé à leurs extrémités. Une fissure macroscopique a une certaine probabilité de se former par la réunion d'un certain nombre de microfissures en croissance. Ce processus se produit plus rapidement dans les disques de polymère refroidis lentement qui contiennent des sphérulites plus volumineuses. A vitesse de refroidissement similaire, la taille des sphérulites dans les disques de polymères de faible indice de fusion est plus petite, et est moins sensible à la vitesse de refroidissement que dans les disques de polymère à indice de fusion élevé. Le recuit de disques trempés, contenant des sphérulites relativement petits, diminue le taux d'étirage auquel se produit le changement de mécanisme de rupture sans altérer pour autant la taille des cristallites. L'oxydation du polymère réduit également le niveau de tension à laquelle se produit le changement de mécanisme.

Zusammenfassung

Die Beziehung zwischen dem Bruchverhalten bei biaxialer Spannung und der Polymorphologie wurde an einer Reihe von gepressten Scheiben aus linearem Polyäthylen untersucht. Die Bruchdaten wurden an Polymeren mit verschiedenem Schmelzindex, die bei zwei Erstarrungsgeschwindigkeiten erhalten worden waren, in einem grösseren Temperaturbereich bestimmt. Zwei Bruchmechanismen wurden beobachtet—zäher Bruch bei hoher Spannung und spröder Bruch bei niedriger Spannung. Die kritische Spannung, bei welcher der zähe Bruch in den spröden überging, nahm mit steigender Messtemperatur, mit steigendem Schmelzindex des Polymeren und mit abnehmender Erstarrungsgeschwindigkeit zu. Es wurde gezeigt, dass die anfängliche Druckbelastung der Scheiben die Bildung mikroskopischer Oberflächenrisse entlang der Sphärolithgrenzen und innerhalb der Sphärolithe verursacht. Das grosse Wachstum dieser Risse bei hoher Spannung führt zu einer genügenden Erhöhung der Spannung am unverletzten Teil des Polymeren, um einen makroskopischen Zug an den Sphärolithen in grossem Massstab zu verursachen. Ein makroskopischer Sprung entsteht durch zufälliges Zusammentreffen einer Anzahl für sich wachsender Risse. Dieser Vorgang erfolgt rascher in Polymerscheiben mit grossen, bei langsamer Abkühlung der Schmelze gebildeten Sphärolithen. Die Sphärolithgrösse ist bei Polymeren mit niedrigem Schmelzindex unter gleichen Abkühlungsbedingungen bedeutend geringer und gegen die Abkühlungsgeschwindigkeit weniger empfindlich als bei Scheiben mit hohem Schmelzindex. Temperung rasch gekühlter Scheiben, deren Mikrostruktur verhältnismässig kleine Sphärolithe enthält, setzt die Spannung, bei der sich der Bruchmechanismus ändert, ohne wesentliche Änderung der Sphärolithgrösse herab. Auch eine Oxydation des Polymeren verringert die Umwandlungsspannung.

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