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Failure Envelope Curves in Polyethylene Solids

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Summary: The present work demonstrates that the failure envelope analysis can be applied for characterizing the ultimate tensile properties of polyethylene solids in which the inhomogeneous necking process is avoided. As a result, the ultimate properties are essentially identical to those of vulcanized rubbers above the glass transition temperature, suggesting that tie molecules connecting the fragmented lamellar clusters transmit the external led to the fracture site in the same manner as cross-linked rubbers do. Consideration of this crystal-network model may provide information about the molecular processes that lead to rupture. Furthermore, the present analytical method can possibly be developed for predicting rupture times when different types of tests, such as constant drawn, constant stress and constant rate of stress, are conducted.

Keywords: failure envelope curve; polyethylene; ultimate strain; ultimate stress

Introduction

Polyethylene is one of the most widely used polymers because it is chemically simple and it has a wide applicability in practical use. However, polyethylene solids exhibit complicated tensile behavior accompanying inhomogeneous deformation, such as neck propagation and plastic flow, compared to rubber-like materials. Such complicated deformation processes make it difficult to accurately characterize the ultimate tensile properties as well as the deformation behavior. The inhomogeneous deformation due to the neck propagation often causes strong dependence of the ultimate parameters, such as the elongation at break or the time to break, on the shape and length of the test piece. This is because the neck gradually propagates through the sample with increasing time of draw, with the result that the elongation at break or the time to break increases with increasing length of the test piece, because a specimen is elongated at a constant elongation rate. In this work, by eliminating such overestimation of the ultimate elongation due to the neck propagation process, the ultimate properties of polyethylene solids can be adequately investigated.

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Experimental [1]

The polymers used in this work were metallocene-catalyzed polyethylenes: a high-density polyethylene (HDPE) and a linear low density polyethylene (LLDPE). Their molecular characteristics are listed in Table I. Polymer pellets were melted in a mould between flat metal plates in a hot press at 190 °C. A pressure of 10 MPa was applied to remove air bubbles and excess melt and then the samples quenched at 0 °C were prepared for the measurements.

Double edge-notched specimens with a gauge length of 2 mm, a ligament length of 2 mm, a width of 8 mm and overall length of 40 mm were used for the tensile tests. They were punched out from the compression-moulded sheets of 200 μm thickness. The shape of the tensile specimen was designed in such a way as to eliminate/avoid the plateau region or necking region in the stress-strain curves. In the specimen, the neck immediately reaches a whole portion of the gage length just after the neck is initiated, with the result in that uniform deformation can be realized throughout the tensile test.

The sample specimens were deformed using a small tensile tester designed and built in our laboratory. It was equipped with a temperature-controlled environmental chamber. The samples were elongated over a wide range of elongation rates and temperatures.

Table 1. Molecular characteristics of polyethylene samples

Sample	$Mw \times 10^{-4}$ g/mol	$Mn \times 10^{-4}$ g/mol	Mw / Mn	SCB mol% [1)]
HDPE	7.3	2.9	2.5	0
LLDPE	7.8	4.4	1.8	0.88

1) short chain branching

Results and Discussion

Figure 1 shows a series of stress-strain curves for HDPE measured over a wide range of temperatures from –40 ° to 100 °C at 5 mm/min, and a wide range of elongation rates from 0.125

to 5 mm/min at 25 °C. At below 0 °C, the results show a strong strain-hardening effect immediately after the yield peak. The strain-hardening effect is reduced as the test temperature increases. As seen in Figure 1, the ultimate stress increases with decreasing temperature whereas the ultimate strain has a maximum point. Comparison between these figures reveals that the ultimate behavior measured at elevated temperatures from 25 ° to 75 °C, as shown in the top figure, is congruent with the behavior measured at reduced elongation rates from 5 to 0.125 mm/min, as shown in the bottom figure. Thus, the decrease in elongation rate has a similar influence to an increase in temperature. This experimental fact will be explained on the basis of the time/temperature superposition principles later.

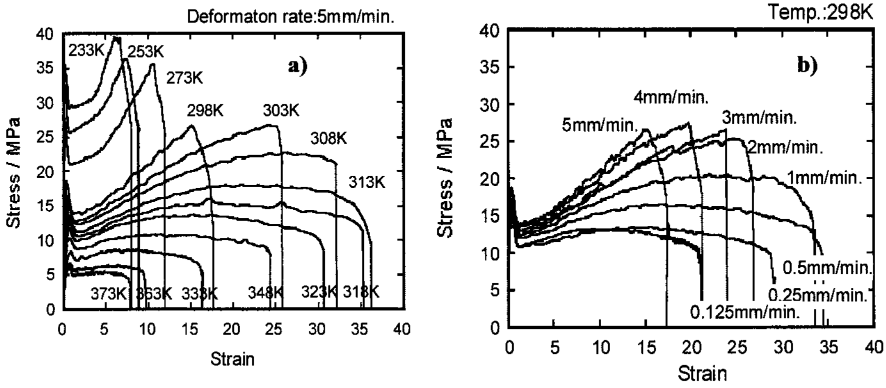

Figure 1. Temperature dependence of stress-strain curves for HDPE measured at the elongation rate of 5mm/min (a) and elongation rate dependence of stress-strain curves of HDPE measured at 25 °C (b)

Figure 2 shows the temperature and elongation rate dependences of stress-strain curves of LLDPE, respectively. As shown in these figures, the stress-strain behavior of LLDPE is greatly sensitive to the temperature compared to the deformation rate. Contrary to the case of HDPE the ultimate properties of LLDPE appear not to be based on the time/temperature superposition principles.

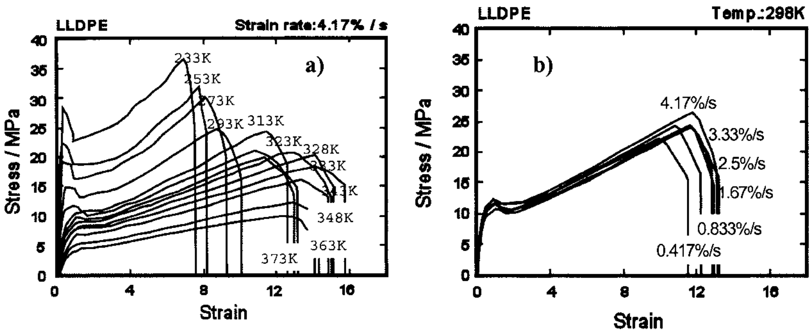

Figure 2. Temperature dependence of stress-strain curves for LLDPE measured at the elongation rate of 5 mm/min (a) and elongation rate dependence of stress-strain curves of LLDPE measured at 25 °C (b).

As is well known, elastomeric materials such as vulcanized rubber exhibit an extremely large strain to failure in uniaxial tension and they do not involve permanent plastic deformation. In the tensile deformation of these types of materials, an important experimental result has been found by Smith,[2-3] i.e. changing the deformation rate at a constant temperature has the equivalent effect on the failure strain as changing the temperature at a constant deformation rate. It is therefore very interesting to note that polyethylene solids and the elastomeric materials have the similar tendency despite the fact that they show plasticity rather than elasticity. In general, the fact that the observed values of the ultimate nominal stress σ_b and the ultimate nominal strain ε_b or the time to break t_b are interdependent is a reflection of the controlling influence exhibited by the viscoelastic response of the material. As a result of this situation a logarithmic plot of the reduced ultimate stress $\sigma_b(T_0/T)$, where T is the test temperature in Kelvin and T_0 is a reference temperature, against the strain at break ε_b, will also yield a master curve called the failure envelope. The values of σ_b are multiplied by the ratio T_0/T to correct for the temperature effect resulting from entropy elasticity. This procedure is in accordance with the kinetic theory of rubberlike elasticity, which predicts that the elastic retractive force in a specimen at a fixed extension ratio increases in direct proportion to the absolute temperature, even though the theory has no ability to treat rupture phenomena, plastic deformation nor time-dependent mechanical behavior. Here we applied this analytical procedure to the ultimate data of the present polyethylene samples, as it is.

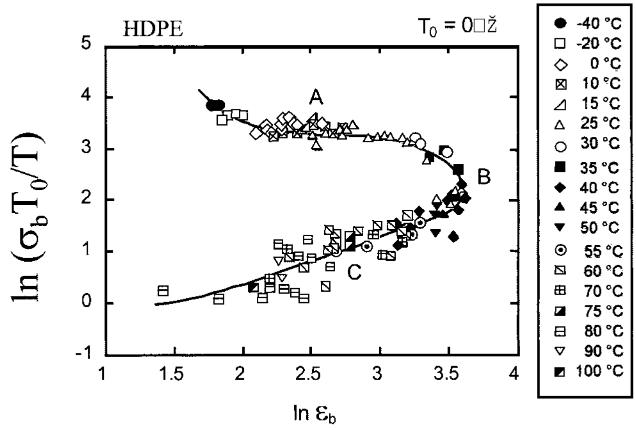

Figure 3. Failure envelope for HDPE. The data were obtained at various temperatures between -40 and 100 °C and rate of deformation at 0.5 to 5 mm/min at each temperature

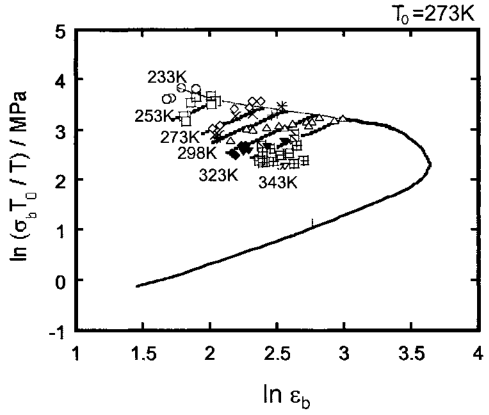

Figure 4. Failure envelope for LLDPE. The data were obtained at various temperatures between -40 and 100 °C and rate of deformation at 0.5 to 5 mm/min at each temperature

As shown in Figure 3, all the ultimate data surprisingly fall on a failure envelope curve within experimental errors for HDPE. The envelope is defined by experimental values of σ_b and ε_b, which were determined at various temperatures between –40 ° and 100 °C and at 0.5-5 mm/min elongation rates at each temperature. The reference temperature T_0 was taken to be 0 °C. It is also very interesting to note that the ultimate properties of typical plastics such as polyethylenes showing essentially energetic elasticity can be treated in the same method as those of rubber materials showing entropic elasticity.

It is likely that over an elevated temperature range above room temperature LLDPE crystals partially melt. As time-temperature superposition is normally not applicable to data obtained when partial-melting occurs, ultimate property data for LLDPE from tests under many conditions would not be expected to define a failure envelope. The ultimate data for LLDPE, which are obtained at various temperatures between –60 ° and 70 °C and at 0.5-5 mm/min elongation rates at each temperature, are shown in Figure 4. This figure indicates that those data appear to define the low-temperature segment of the failure envelope, in which the solid line of Figure 4 is the same with the line presented in Figure 3. The dotted lines show approximately the variation of the ultimate properties with strain rate over the experimental range of temperature. Along any of these lines, a point tends to move upward as the deformation rate is increased. It seems likely that if partial-melting did not occur, all data obtained between –60 ° and 70 °C would cover onto a line to provide a continuous failure envelope. The explanation for the progressive displacement of a dotted line with temperature is that each dotted line is recognized as a segment of the failure envelope of a different material, and for each material the ultimate properties are controlled by viscous effects.

The rupture point moves counterclockwise around the envelope, either as the elongation rate is increased or as the test temperature is decreased. Such a failure envelope, which is independent of time and temperature, must result, provided the well-known time-temperature superposition principle is applicable to ultimate property data determined at different temperatures and elongation rates. To determine specifically how elongation rate and temperature affect the ultimate properties, such data can be analyzed by applying the method of time-temperature superposition. The time dependence of the reduced ultimate strain at seven temperatures from 0 ° to 80 °C is exemplified in Figure 5.

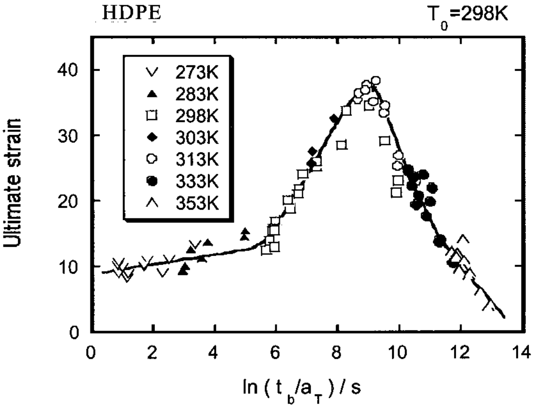

Figure 5. The time dependence of the reduced ultimate strain for HDPE

The curves, representing data at different temperatures, were shifted along the log *t* axis to superimpose. Let the shift distance required to superimpose data at temperature *T* with those at a selected reference temperature to be a_T. To test the applicability of the Williams-Landel-Ferry (WLF) equation,[4] a plot was made of $-(T-T_0)/\ln a_T$ vs $T-T_0$, where the reference temperature T_0 was taken to be 25 °C (Figure 6).

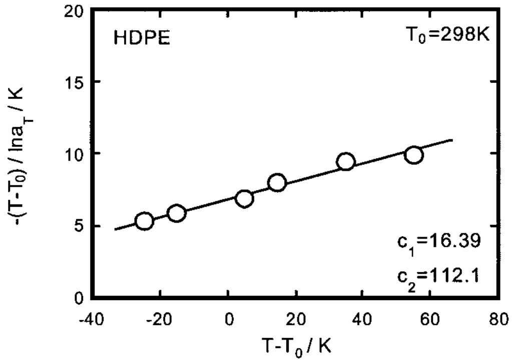

Figure 6. WLF analysis of ultimate parameters of HDPE

As shown in Figure 6, all data between 0 ° to 80 °C fall on the straight line, indicating that the WLF equation fits the temperature dependence of ln a_T. The slope and intersection of the straight line provided the following WLF equation when the reference temperature T_0 is 25 °C.

$$\ln a_T = -\frac{16.4(T-T_0)}{112.1+T-T_0} \tag{1}$$

In studying the linear viscoelastic properties of amorphous polymers above T_g, we have found the shift factor to be extremely useful for interconverting the effects of the temperature and experimental timescale. The conclusion drawn from the present results for PE materials was that the shift factor could also be used to interconvert the effects of the temperature and elongation rate on the ultimate properties in the same way as for rubbery elastomeric materials. This implies the importance of the noncrystalline regions in the fracture process. So far, it has been well established that crystalline polymers exhibit strong nonlinearity in their stress-strain behavior, even as small strains, with the result that not only Boltzmann superposition principles are not applicable at small strains. This agrees with the experimental fact that the stress-strain curves up to yield point, as shown in Figure 1, are very sensitive to the temperature in comparison with the deformation rate, and the time-temperature superposition cannot be applicable to the initial stress-strain regions.

Conclusion

The influence of elongation rate and temperature on the ultimate tensile properties of melt-crystallized linear PE solids was investigated using a double edge-notched specimen to avoid necking in which uniform deformation may be assumed throughout the experiment. The tensile tests were performed over a wide range of temperatures, from –40 ° to 100 °C, and of elongation rates from 0.125 to 5 mm/min. The data on ultimate properties such as tensile strength and elongation at break for different temperatures could be superimposed, by shifts along the elongation rate axis, to give a master curve as a function of the time to rupture. It was found that the ultimate stress decreases monotonously with reduced time to rupture whereas the ultimate strain has a maximum point. This behavior was the same as that of rubbery materials. The shift factors obtained from superposition of both tensile strength and ultimate strain took the form of the WLF equation, resulting in that rupture times can be predicted when the tensile tests are conducted at any experimental condition. Experimental results indicate that the ultimate properties of PE solids that show time-temperature dependence demand a physical process, which is viscoelastic in nature.

The ultimate data provided a failure envelope curve, which has the same shape as that for rubbery materials. The rupture point moves counterclockwise around the envelope either as the elongation rate is increased or the test temperature is decreased. It is very interesting to note that the ultimate properties of typical plastics such as PEs showing essentially energetic elasticity can be treated in the same method as those of rubber materials showing entropic elasticity.

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