A Sensitive Mechanical Test for Slow Crack Growth in Polyethylene

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Slow crack growth (SCG) in a wide variety of polyethylenes has been investigated by a constant tensile load test (the PENT test) for a single edge notched specimen. The PENT test is very sensitive to the changes in molecular structure and morphology of polyethylene. The resistance to SCG depends on the density of the tie molecules and the strength of the crystals.

INTRODUCTION

It has been well known for nearly 30 years that polyethylene (PE) gas pipes fail in a brittle manner by SCG. This failure mechanism occurs in pipe lines, liners for solid waste landfills, and storage containers. The routine tests in industry for controlling resin quality such as MI, density, and yield stress are not sensitive measures of the resistance to SCG. ESCR measures SCG, but it is crude and very slow. It is necessary to develop an accelerated test method for predicting the service lifetime and to develop a fundamental understanding of SCG process in PE. A constant tensile load test with single-edge notched specimen under plane strain condition was developed (1), and has become an ASTM standard test method, ASTM F 1473, also called the PENT test. Using the PENT test, the structure property relationship in terms of SCG as a function of stress, notch depth, and temperature (2, 3), molecular weight and distribution (4), branching (5), quenching and annealing (6), orientation (7), blending (8), irradiation and crosslinking (9), welding (10), and organic active agents (11), have been investigated in details for the past 15 years based on approximately 200 PE pipes and resins collected worldwide and manufactured since 1965. This presentation focuses on the SCG mechanism and the relationship between SCG and the molecular and morphological structure.

EXPERIMENTAL

SCG was carried out with a single edge notched tensile specimen under a constant load at plane strain conditions. The PENT specimen with a notch depth of about 35% of the thickness of the specimen has been designed to rapidly produce the same fracture that occurs in pipe lines. The specimen may be cut from either pipes or compression molded plaques in the slow cooled (SC) or quenched (Q) state. The notch was carefully controlled by inserting a fresh razor blade at a speed of 250 μm/min. The temperature of the tests ranged from room temperature to 80°C and was controlled within ±0.5°C. The scatter in duplicate tests is within ±15%.

RESULTS AND DISCUSSION

Improvement in SCG Resistance Over the Past 30 Years

Since the first PE gas pipe was installed in 1965, the SCG resistance of the gas pipe grade PE resins has been improved dramatically by modifying the polymerizing process and changing the molecular parameters by the resin manufacturers. *Figure 1* shows the time to failure versus the manufacturing year for ethylene-hexene copolymers with a density of about 0.94 g/cm^3 from the same producer. The test was carried out at 80°C and 2.4 MPa. The lifetime has been improved from about one day for resins manufactured in the 1970s to about several years for resins manufactured in 1988. The resins from 1970 to 1981 were polymerized by the same process. In 1982, the polymerizing process was modified and the lifetime increased significantly. In 1988 a further modification was made.

Lot-to-Lot Variations

Figure 1 shows that, in terms of the time to failure, the lot to lot variations are about a factor of 2 to 3 for the resins made from 1970 to 1981, and a factor of 2 to 10 for the resins manufactured from 1982 to 1986. Extensive testing shows that a factor of 2 to 3 on lot to lot variations is usual and occasionally a lot may vary by a factor of 10. Density, elastic modulus, yield stress, GPC, melt index, DSC, and NMR are insensitive to these lot-to-lot variations.

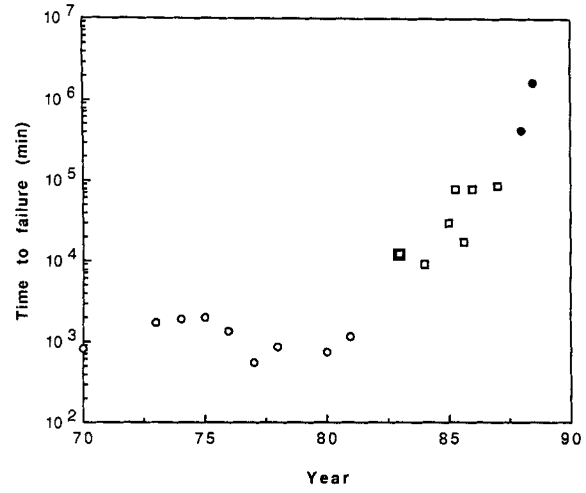

Fig. 1. Lifetime vs. manufacturing year for ethylene-hexene copolymers from the same producer.

Molecular Weight

Polyethylene homopolymers with a weight average molecular weight (MW) of 66.8K, 106K, 137K, and 158K, but with about the same *MWn* of 20K, were tested at 42°C and 10 MPa. The time to failure versus *Mw* is plotted in *Fig. 2*. The lifetime increases proportionally with *MW*. The extrapolation shows that when *MW* reduces to about 10^4, the material fractures immediately.

The Effect of Short Chain Branches (SCB)

Ethylene-hexene copolymers having short chain branches of 0, 0.8, 1.2, 2.0, 2.3, and 4.5 SCB/1000C were tested at 42°C and 3 MPa. The resins have about the same molecular weight. The time to failure vs. SCB density is shown in *Fig. 3*, where the lifetime increases from 100 min for the linear polymer to 2×10^6 min for the copolymer with 4.5 SCB/1000C. *Figures 2* and *3* show that the increase in SCB has more profound effect on the lifetime than the increase in molecular weight.

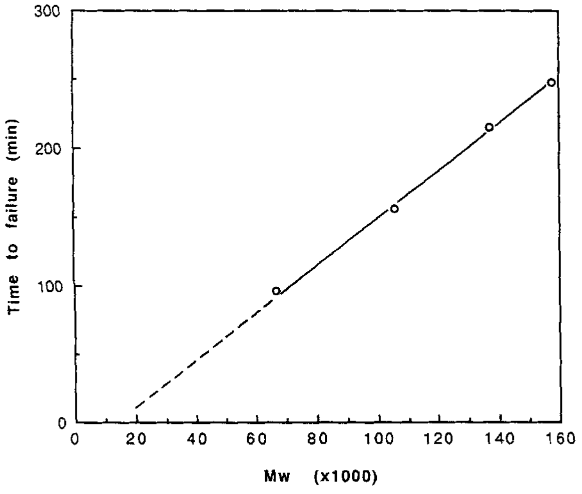

Fig. 2. Lifetime vs. molecular weight.

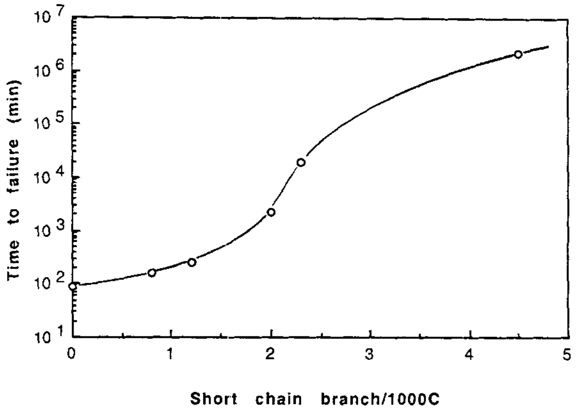

Fig. 3. Lifetime vs. branch density.

SCG for the Fractionated Resin

The effect of *MW* and SCB on SCG has been studied by fractionating an ethylene-hexene copolymer resin. The characterization of the five fractions is listed in *Table 1*. Each fraction consisted of about 0.2 g. It was necessary to devise a special technique for studying SCG behavior for such small amount of material. The technique involved welding a wafer of the resin between PE grips. *Table 1* also shows the SCG resistance for the five fractions and a comparison of those results against the original unfractionated resin. If *MW* is less than 1.5×10^5, the resistance to SCG is nearly 0, but above a *MW* of 1.5×10^5, the failure time increases by a factor of about 10^5. These data show the importance of the high *MW* tail in the distribution curve. The low *MW* fractions are necessary for extruding the pipe. The SCB are useless when placed on molecules with $MW < 1.5 \times 10^5$.

Morphology Effects

An ethylene-hexene copolymer was quenched at a cooling rate of 40°C/min and then annealed for 24 hr at a constant temperatures ranging from 86 to 127°C. The lifetime at 80°C and 2.4 MPa against the annealing temperature is shown in *Fig. 4*. The lifetime is a maximum for an annealing temperature in the neighborhood of 113°C and is a minimum for an annealing temperature of about 123°C.

Blending

A linear polyethylene was blended with an ethylene-hexene copolymer. The failure times at 42°C and 3 MPa against the fraction of the copolymer are shown in *Fig. 5*. The resistance to SCG increased monotonically with the amount of the copolymer and the rate of increase began to increase significantly when the copolymer fraction was above 50%.

Crosslinking

SC molded plaques of a linear PE were irradiated at room temperature by γ-ray at doses from 0.05 to 160 Mrd. SCG tests were carried out at 42°C and 3 MPa for these as-irradiated specimens and the specimens re-

Table 1. Characterization and Lifetime (min) by SCG Testing of Fractions and Whole Resin.

Sample	Yield (%)	Intrinsic Viscosity (dl/g)	SCB/1000c	Range of MW	t_f, 1.8 Mpa	t_f, 1 Mpa
F1	23.0	0.29	7.4	10^3 -3 × 10^4	0	0
F2	24.6	0.84	5.1	3 × 10^4 -8 × 10^4	6.1	735
F3	18.5	1.53	3.3	8 × 10^4 -1.5 × 10^5	7.0	5328
F4	20.4	2.70	1.9	1.5 × 10^5 -4 × 10^5	3.6 × 10^5	—
F5	12.3	5.81	1.4	4 × 10^5 -4 × 10^6	>5.2 × 10^5	—
Whole polymer		1.91	4.5	10^3 -4 × 10^6	2.5 × 10^5	—

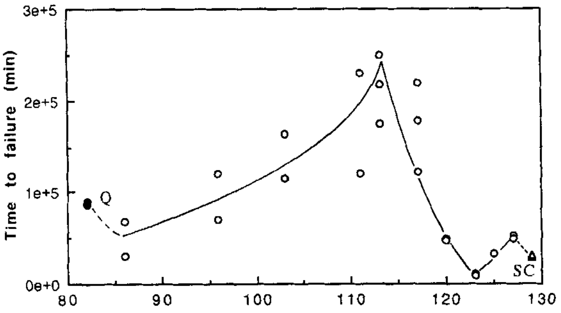

Fig. 4. Lifetime vs. annealing temperature.

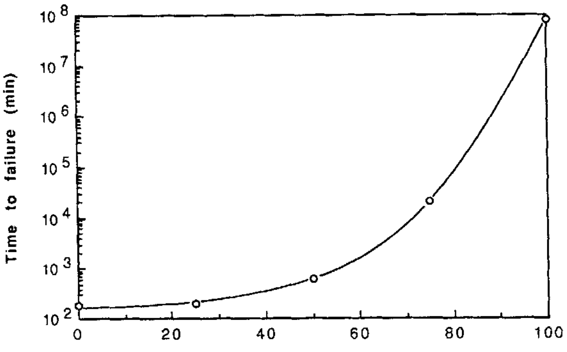

Fig. 5. Lifetime vs. composition in blend system.

molded from the as-irradiated state. The lifetimes against the irradiation doses are shown in *Fig. 6*. The resistance to SCG for the as-irradiated specimens initially decreased slightly to a minimum at a dose between 0.05 and 0.1 Mrd and then increased rapidly to a maximum value at a dose of 50 Mrd. For doses beyond 50 Mrd, the resin became very brittle and fractured during the loading of the specimen. The dependence of the resistance to SCG on irradiation doses for the remolded specimens is about the same as the as-irradiated specimens up to about 50 Mrd, and beyond 50 Mrd the remolded specimens show exceptionally longer lifetimes.

ESCR

The PENT test for ethylene-hexene copolymers was carried out in 10% solution of Igepal CO-630 (GAF Corp.) and in air respectively. The tests in Igepal were at 50°C and 4.2 Ma. The ratios of the lifetime in Igepal over the lifetime in air against the lifetime in air are shown in *Fig. 7*. The effectiveness of Igepal in reducing the lifetime increases as the resistance to SCG increases. It was observed that a concentration of about 50% Igepal reduces the lifetime more than does a 100% Igepal.

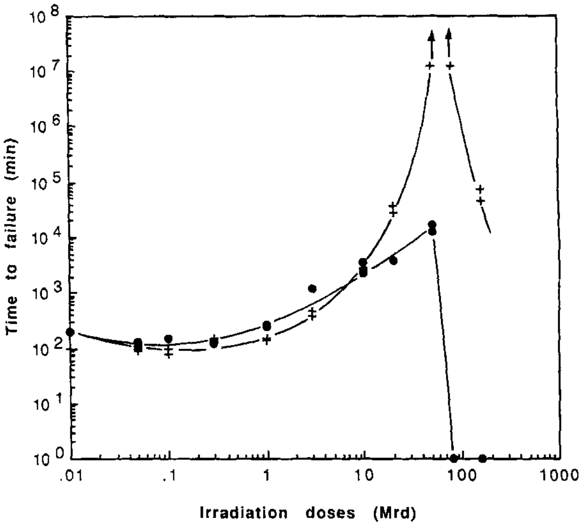

Fig. 6. Lifetime vs. irradiation doses: (●) as-irradiated; (+) remolded from the as-irradiated state.

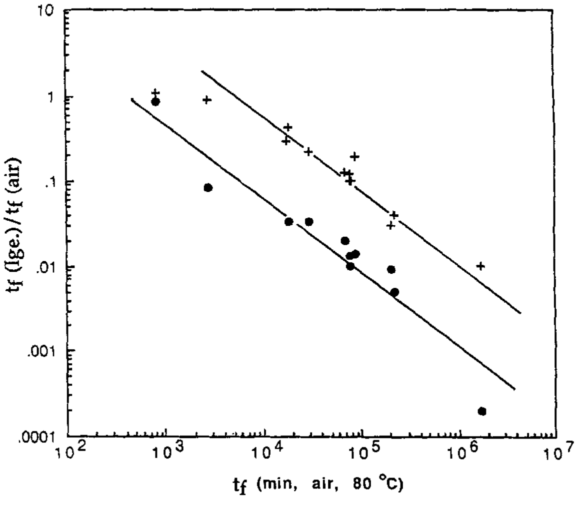

Fig. 7. t_f (Ige.)/t_f (air) vs. lifetime in air. (+) in air at 80°C and 2.4 MPa; (●) in air at 50°C and 4.2 MPa.

Mechanism of SCG

Extensive studies show that the SCG process includes the formation of a craze-like damage zone at the notch tip, fibril growth, crack initiation and crack growth. *Figure 8a* shows the fibrils viewed from within the notch. *Figure 8b* illustrates the damage zone from the side by slicing the specimen, and *Fig. 8c* shows the network structure of the fibril at a high magnification. PE is a semicrystalline polymer in which the lamella crystals are bounded by the tie molecules and entanglements that join the adjacent lamellae and pass through the amorphous region. It is the tie molecules and entanglements that transfer the stress to crystals. The importance of the tie molecules was initially emphasized by Lustiger and Markham (12). It is assumed that the fibrils fail by disentangling the tie molecules from the crystals if the stresses are low. The disentangling rate of the tie molecules depends on the density of the tie molecules since the average stress born by tie molecules is inversely proportional to their density. The disentangling rate also depends on the strength of the crystals. The stronger the crystal, the greater the resistance to the movement of the tie molecules.

The density of the tie molecules is dependent on *MW* and crystal size. Huang and Brown (4, 5) gave an equation to calculate the possibility, *P*, for a molecule in melt to form a tie molecule:

$$P = \frac{\int_{2L_c}^{\infty} + L_a^{r^2} \exp(-b^2\bar{r}^2)dr}{3\int_0^{\infty} r^2 \exp(-b^2\bar{r}^2)dr} \tag{1}$$

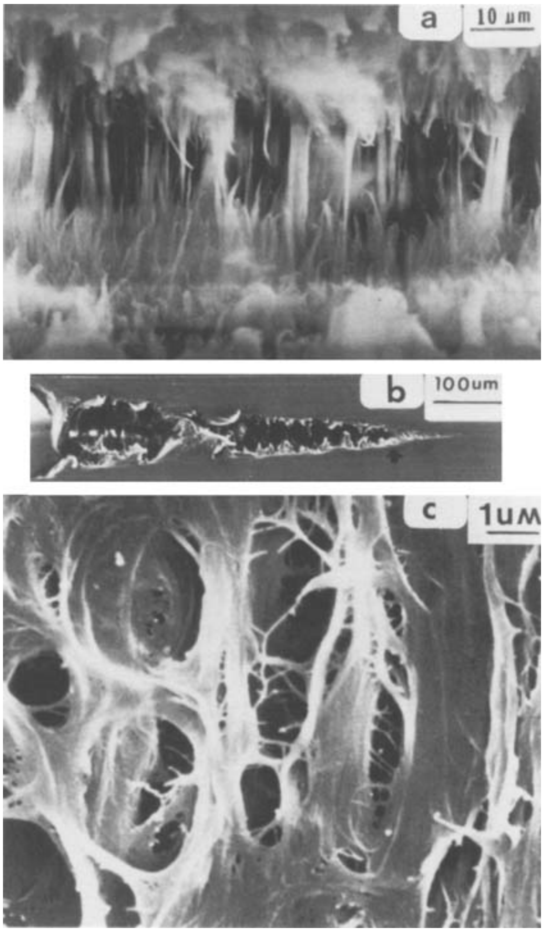

Fig. 8. a) Fibrils at the damage zone viewed along the notch; b) from the side; c) the detailed structure of the fibrils by SEM.

where r is the end-to-end distance of the molecule in melt, $b^2 = 3/2\bar{r}^2$ in which $\bar{r}$ is the root-mean-square value of the end to end distance of the random coil. $L_c + L_a$ is the long period in which L_c is lamella thickness and L_a is the thickness of the amorphous layer. If the random coil is greater than about twice the long period, tie molecules will be formed during crystallization. SCB not only acts as pins that retard the disentangling of the tie molecule, but they also limit the lamella thickness and thereby increase the density of the tie molecules. Both facts increase the lifetime, as shown in *Fig. 3*. To be effective the SCB need only be on the tie molecules. A better resin has been recently introduced (13) with a bimodal molecular weight distribution and with the SCB only on the high molecular weight molecules. This resin has excellent resistance to SCG and higher density compared with other resins with the same average density of SCB.

Annealing increases the crystal strength and the lifetime when the annealing temperature is below 113°C, below which most thick crystals are not melted on annealing. At higher annealing temperatures, the lifetime decreases because of a decrease in the tie molecules due to melting and recrystallizing of the crystals.

The resistance to SCG is most effective when the network of tie molecules and crystals is continuous. The tie molecule–crystal network becomes continuous as for the copolymer fraction above 50% in the blend system (see *Fig. 5*). The resistance to SCG increases greatly for doses of γ-irradiation beyond the gel point. Excessive crosslinking for doses above 50 Mrd can make PE very brittle. The irradiated and the then remelted state has a longer lifetime and is not brittle like the as-irradiated state because remelting results in more amorphous material.

Igepal reduces the friction during the disentangling of the tie molecules. Since the amount of Igepal that is absorbed increases with time, the Igepal shows a greater effect the longer the test lasts.

A slight difference in *MW* distribution and the distribution of SCB on the main chains can make a large difference in the resistance to SCG. These differences occur because there are practical limitations on the control of molecular structure during the large-scale polymerization process in industry. The differences in molecular structure are in the range of experimental error by most chemical, physical, and mechanical test methods in current use. However, the PENT test is very sensitive to the tie molecule–crystal network. Most important is the fact that the PENT failure time is directly related to the performance of the resin during its practical application.

CONCLUSION

PE structures fail by SCG. The SCG resistance of PE depends on the density of the tie molecules, the strength of the crystals, and the continuity of the tie molecule–crystal network. The PENT test is very sensitive to the change in the molecular structure and morphology of polyethylene.

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