

Environmental Stress Cracking of Polyethylene: Temperature Effect

P. L. SONI and P. H. GEIL, *Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106*

Synopsis

Polyethylene was drawn at temperatures ranging from 30° to 60°C in aggressive and nonaggressive environments. Fibrillation was found to occur in the aggressive environment, and this effect increased with temperature. The temperature effect was more prominent at lower strain rates. Thin films drawn in aggressive environments deformed inhomogeneously. Again, this effect was found to increase with increasing temperatures. Single crystal deformation was also found to be inhomogeneous, and "solvation" of the amorphous surface layer occurred in the presence of the aggressive environment. Infrared measurements of sorption under different loads indicated that there is an increase in the amount of sorbed materials with increasing load. Dynamic mechanical studies revealed the intracrystalline regions to be affected preferentially.

INTRODUCTION

Failure of polymers in the presence of aggressive environments is commonly referred to as environmental stress cracking. The aggressive environments can be broadly classified into two categories, namely, solvents and nonsolvents. The former class of liquids actually solvate the polymer and induce cracking under appropriate circumstances. The nonsolvents, however, do not attack the polymer chemically, solvate it, or produce any recognizable effect other than to bring about failure which would not occur in a reasonable period of time under the same stress conditions and the absence of the environment. When no stresses are present, these agents do not have any readily discernible effect on the polymer. The present work deals with this latter category of stress cracking agents.

Numerous variables in relation to environmental stress cracking have been studied in the past. The major ones are molecular weight^{1,2} and its distribution,³ branching, crystallinity,¹ and crosslinking.⁴ Other variables, such as thermal history, biaxial stress conditions, constant strain and load conditions, and effect of surface tension of the liquid have also been studied. In general, however, inconsistent results have been obtained which have been a major deterrent to the emergence of a general mechanism of stress cracking. For example, in the ASTM D-1693-70 bent strip test, the strain applied to the sample is complex, ranging from tension at the top surface to compression at the bottom surface of the sample. The strain, in turn, is sensitive to thermal history, thickness of sample, etc.⁵ In addition, once the crack starts to propagate, the stress distribution in its vicinity will change, and this will have an effect on the rate of crack growth and hence on the time to break.

To overcome these problems, we have approached the phenomenon of environmental stress cracking from a different angle. The morphology of samples

deformed in the presence of cracking agents has been studied in detail, and this is compared with the results of deformation in the absence of the environment. Preliminary work done in this laboratory⁶ previously has indicated that the fracture is not truly brittle in nature. It was suggested that the ESC agent weakens cohesion between fibers, which accounts for the fibrillar nature of the fracture surface. In the present work, the study on deformation of bulk samples and their films has been extended to higher temperatures. Diffusion of the agent into the polymer in the presence and absence of stress has been characterized. The effect of the stress cracking agent on the relaxation processes in the polymer is also reported.

EXPERIMENTAL

Resins

The low-density polyethylene (LDPE) used in this research was du Pont Alathon 2020, with a melt index of 1.1 and a density of 0.92 g/cc. The high-density polyethylene (HDPE) used was Dow HB resin, with a melt index of 1.2 and a density of 0.965 g/cc.

Stress-Strain Measurements

Films 1 mm thick were prepared by melting the polymer between Teflon-coated aluminum foils under pressure and subsequently quenching the sandwich in ice water. Dogbone samples were cut out of this sheet by means of a suitably shaped cutter. A stress riser was introduced in the form of semicircular holes on the two edges in the center of the gauge length of the sample. This was accomplished by using a special jig to ensure proper positioning.

The samples were then tested at strain rates of 0.05 cm/min and 5 cm/min on a gauge length of 3.5 cm, at temperatures ranging from 30° to 60°C. Methyl alcohol was used as the aggressive environment and water as the nonaggressive environment. An average of three to five samples were tested at each temperature and strain rate.

Because of the presence of the stress riser, deformation was localized in this region. The strain was calculated by using the size of the notch (2.375 mm) as initial length.

Scanning Electron Microscopy

The fracture surface of samples from the stress-strain measurements were examined with a Cambridge scanning electron microscope (SEM) S4-10. A layer of ~ 100 Å of Au-Pd was deposited on the surface to avoid charging under the beam. Fracture surfaces of samples from constant-strain measurements were also examined by this technique.

Transmission Electron Microscopy

Thin films (~ 1000 Å) of polyethylene were formed by dropping a hot solution, in xylene, of 0.4% concentration on a carbon-coated Mylar substrate mounted in a stretcher. The substrate was then heated to 130°–150°C in a vacuum oven

and cooled slowly to form a melt-crystallized film. The resulting films were stretched in air and alcohol environments for TEM study. Equilibrium was achieved in the latter by presoaking at the desired temperature for at least 12 hr. The air sample was maintained at the same temperature for the same length of time.

Single crystals studied by TEM were made by self-seeding as follows: A 0.01% solution of polyethylene in xylene was first quenched to room temperature. The crystals were redissolved at 103°C and recrystallized at 96°C. The single crystals were deposited on a Mylar substrate mounted in a stretcher, gold decorated vertically, and then stretched in air and alcohol environments, adopting the same procedure as for the thin films.

Subsequent to stretching, both single crystals and thin films were shadowed at 25° with Pt-C and vertically with C. Poly(acrylic acid) was used to peel the sample from the substrate.

Infrared Spectroscopy

Fourier transform infrared spectroscopy was used to study the time-dependent diffusion of the cracking agent out of the polymer and the effect of load on the same. Rectangular polyethylene samples ca. 8 microns thick were prepared by compression molding as previously described. The specimen were then presoaked in the aggressive environment (methyl alcohol) at the desired temperature for 12 hr to achieve equilibrium. Before mounting the sample in the spectroscope, it was taken out of the environment and the surface wiped clean with a tissue paper. Spectra were recorded at intervals of 1 min. The effect of load was studied by using the same procedure with the sample mounted in a stretcher and pulled to an overall strain of 10% prior to soaking.

Dynamic Mechanical Measurements

Quenched samples of LDPE were prepared as described earlier. Tests were conducted on a torsion pendulum at a frequency of ca. 1 Hz. Measurements in the presence of the environment were carried out by presoaking the sample to equilibrium and subsequently maintaining a saturated vapor environment in the column of the pendulum.

RESULTS AND DISCUSSION

A summary of the stress-strain measurements is presented in Tables I and II. It is clear that the strain at break is always lower in the presence of methanol and that the difference increases with increasing temperature. Furthermore, the difference is more pronounced at the lower strain rate. Fracture surfaces of samples tested at the lower strain rate and alcohol environment were found to be fibrillated, as reported earlier.⁶ The degree of fibrillation was found to increase with increasing temperature. Figures 1 to 3 show fracture surfaces of samples deformed to failure; the intense fibrillation in the methanol-drawn samples is obvious. It is this fibrillation that led to the suggestion of a lack of cohesion between fibrils in the presence of the stress cracking agent.⁶

The rough nature of the surface of the fibrils formed during deformation⁷ makes the interfibrillar region easily accessible to the stress cracking agent, which

TABLE I
Strain at Break for HDPE

Strain rate, cm/min	Temp., °C	Strain at break, %	
		Water	Methanol
0.05	30	1450	1253
	40	400	1076
	50	1276	763
	60	1183	600
5.0	30	522	504
	40	520	500
	50	494	460
	60	478	450

TABLE II
Strain at Break for LDPE

Strain rate, cm/min	Temp., °C	Strain at break, %	
		Water	Methanol
0.05	30	425	350
	40	500	326
	50	602	298
	60	687	170
5.0	30	285	220
	40	312	214
	50	350	200
	60	360	195

diffuses to these sites and reduces the cohesion between the fibrils. Higher temperatures cause a reduction in viscosity and surface tension of the agent, and these factors, we suggest, are responsible for the increased fibrillation at higher temperatures. At the higher strain rates, however, weakening of the polymer by the cracking agent is not complete, which accounts for the coherent failure surface.

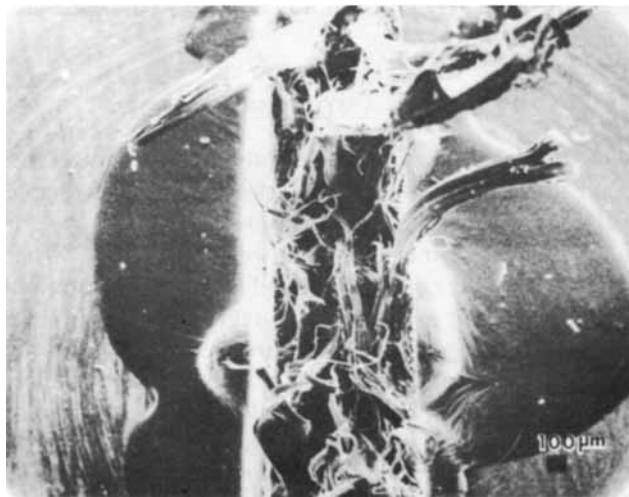


Fig. 1. Fracture surface of HDPE samples drawn in methanol at 60°C.



Fig. 2. Fracture surface of LDPE sample drawn in methanol at 60°C.

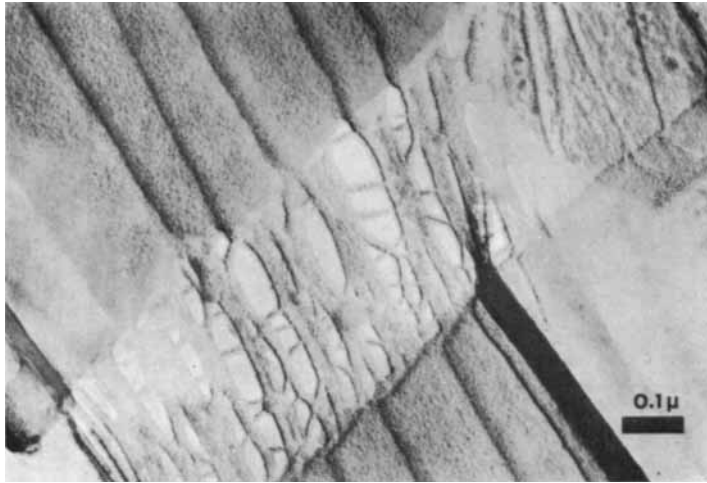


Fig. 3. Fracture surface of LDPE sample drawn in water at 60°C.

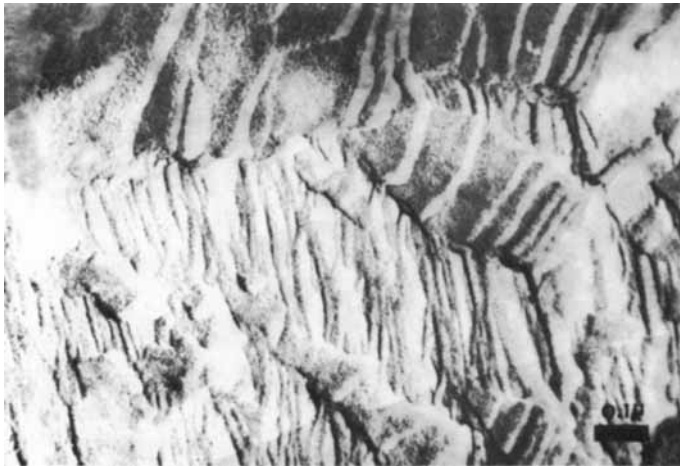
Thin-Film Observations

In the presence of a stress cracking agent, it was found that undeformed crystalline units were pulled along with the fibers, as reported earlier.⁶ At higher temperatures this effect becomes more pronounced. Figures 4 and 5 show samples of HDPE and LDPE deformed in water and alcohol (at 60°C). Undeformed blocks of lamellae are seen to be pulled along with the fibers. This, we suggest, is caused by the weakening at defect sites in the crystal, an effect which will be alluded to later in the section on dynamic mechanical measurements. Distinct blocks of lamellae do not appear in the LDPE sample drawn at 60°C in methanol because the drawing temperature is greater than the α -transition temperature in LDPE, the temperature at which motion in the crystal core is significant.

Also obvious from Figures 4 and 5 is the fact that in the alcohol-drawn samples



(a)



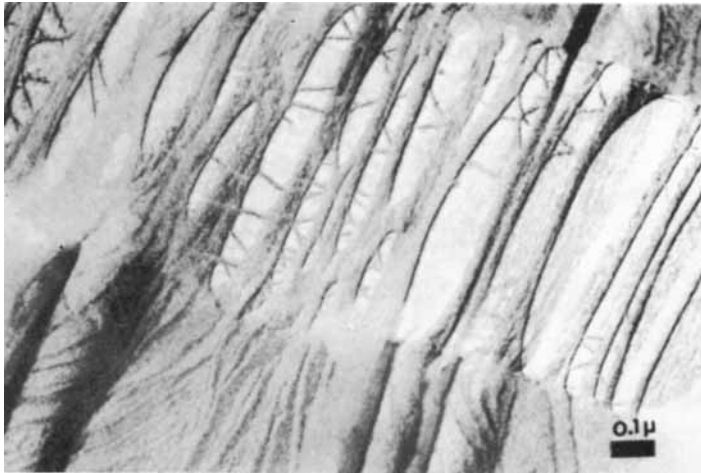
(b)

Fig. 4. (a) HDPE thin film drawn in water at 60°C. (b) HDPE thin film drawn in methanol at 60°C.

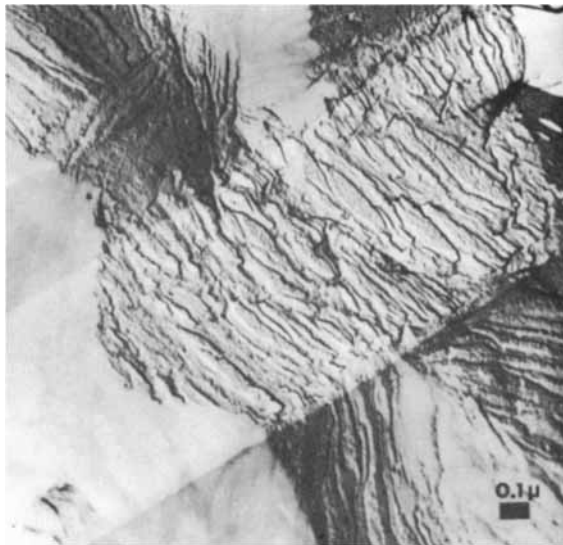
the fibers have not coalesced together. This agrees with the suggestion that the cohesion between fibrils is reduced in the presence of the stress cracking agent.

Single-Crystal Observation

As in the prior work from this laboratory,⁶ observation of HDPE single crystals drawn on Mylar in methanol shows the presence of numerous cracks spanned by fibrils. Of particular interest, however, was the presence of regions, on gold-decorated samples, containing numerous small cracks and a redistribution of the gold particles (Fig. 6). (Note that the fibrils spanning the cracks are difficult to observe, tending to merge with the drawn Mylar.) The small cracks may be forming at statistically distributed defects in the crystal, whereas the redis-



(a)



(b)

Fig. 5. (a) LDPE thin film drawn in water at 60°C. (b) LDPE thin film drawn in methanol at 60°C.

tribution of the gold particles is a result of the solvation of the amorphous surface layers of the crystal by the methanol.

Figure 7 shows gold-decorated crystals of HDPE that were kept in methanol for 12 hr. The gold in certain regions has been mobilized, causing an uneven distribution of the particles. Keller and Sadler⁹ have shown that flooding of single crystals with xylene causes mobilization of certain regions on surface. It was suggested that this is caused by solvation of long cilia to a major degree and, only to a lesser extent, large loops on the surface. Similar observations (Figs. 6 and 7) lead us to suggest that the methanol is solvating the amorphous surface material in an identical manner.

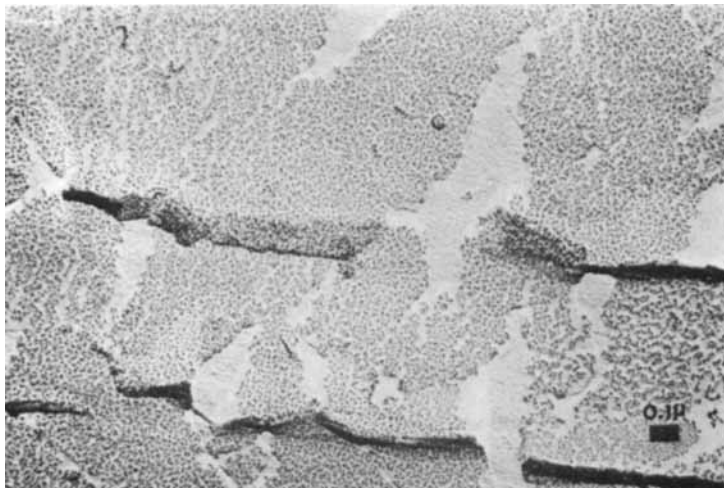


Fig. 6. Gold-decorated HDPE single crystal drawn in methanol.

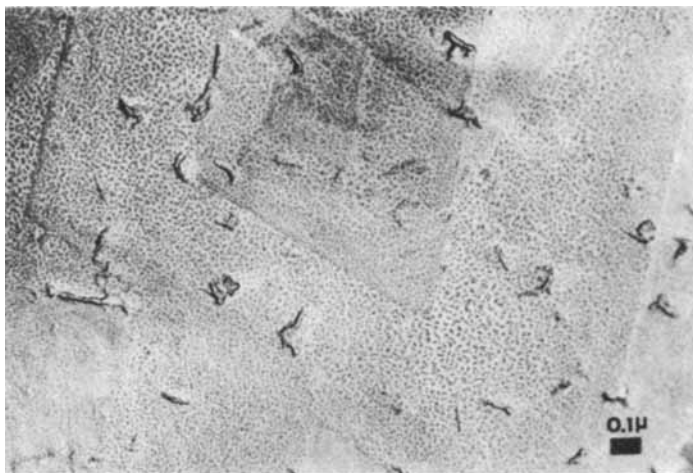


Fig. 7. Gold-decorated single crystal of HDPE flooded with methanol.

IR Spectroscopic Studies

Desorption of alcohol from samples of HDPE was examined by employing the IR procedure outlined in the experimental section. Figure 8 shows IR spectra of a HDPE film in the region between 900 and 1330 cm^{-1} . The peak at 1025 cm^{-1} is due to methanol.¹⁰ This was used to follow the desorption of methanol from the polyethylene film as a function of time. In order to ensure that the effect was not occurring only at the surface, IR spectra of samples of various thicknesses were measured under identical conditions. Figure 9 shows a plot of the height of the 1025 cm^{-1} peak versus sample thickness calculated from the 1303 cm^{-1} band (which was found to vary linearly with thickness). Since the same area was exposed to the IR beam at all thickness levels, it is clear that a purely surface adsorption would result in a more or less horizontal line, indicating a constant adsorbed quantity. The ascending nature of the plot does indeed indicate that the peak at 1025 cm^{-1} is due to absorption in the entire thickness of the sample and not just at the surface.

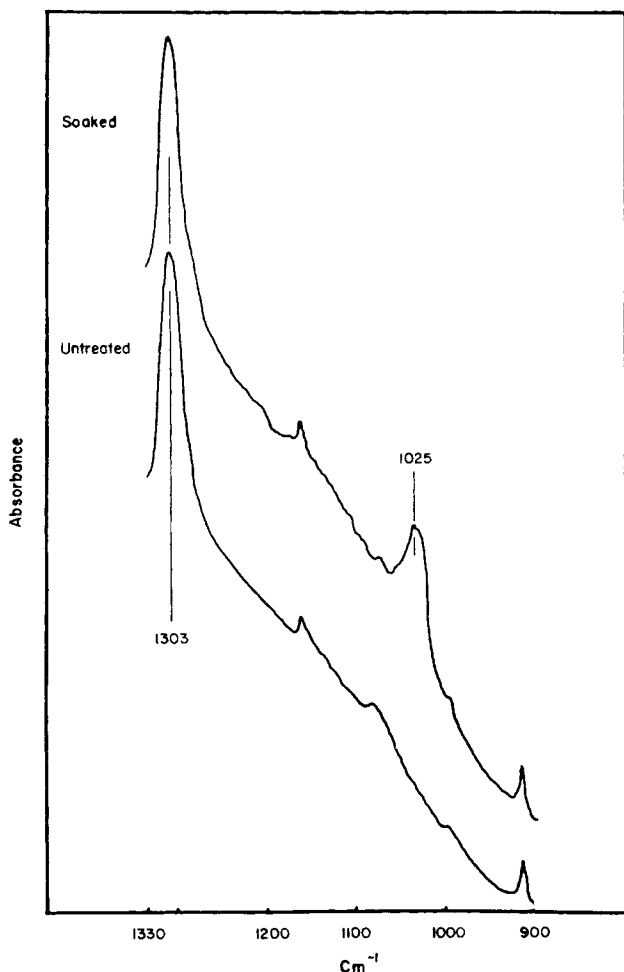


Fig. 8. Infrared spectra of HDPE samples with and without soaking in methanol.

The extinction coefficient for the band at 1025 cm^{-1} was obtained by running various concentrations of alcohol in water in the region of $950\text{--}1200\text{ cm}^{-1}$. It should be noted that this extinction coefficient is different from that in the presence of a pure hydrocarbon (like polyethylene) as a diluent because of the polar interactions between water and alcohol molecules. However, although the values of concentration obtained are not exactly representative, the relative values can be used with confidence.

Figure 10 shows the desorption of alcohol from the same polyethylene sample, with and without load. It is evident that under load the sample had taken up a larger amount of alcohol. A possible explanation for this is that it is caused by the change in free volume associated with stress. An increase in free volume would result from the application of tensile stress and would reduce the polymers resistance to the diffusing molecules.

The single-crystal results presented earlier indicate that solvation of the amorphous component occurs in the presence of methanol. The increased sorption of ESC agents under load, we suggest, results in higher solvation in the amorphous regions, reducing the strength of the polymer. McCammond and

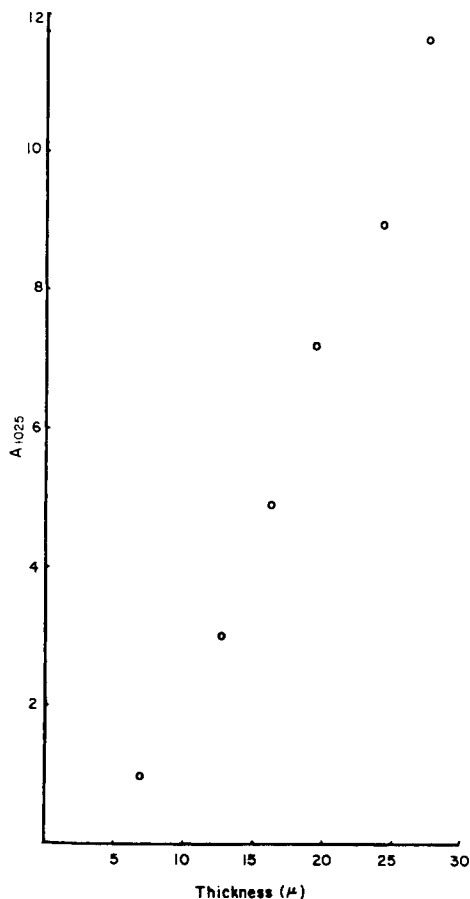
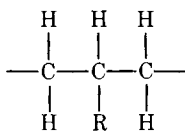


Fig. 9. Absorbance at 1025 cm^{-1} vs thickness for similarly treated HDPE samples.

Ward¹¹ have observed that the strength of PVC and ABS is reduced when immersed in isopropanol under tensile stress. No such effects were seen during torsion tests, indicating that the increase in free volume in the tensile test is responsible for the higher absorption and greater reduction in strength.

Dynamic Mechanical Observations

Figure 11 shows dynamic mechanical spectra of quenched LDPE in air and alcohol environments. It is seen that in the presence of alcohol the relaxation peak is somewhat broader and that a shoulder appears at 287°K . The β peak is surprisingly prominent in the quenched samples, with little or no indications of peaks at higher temperatures in the α regions. The β relaxation has generally been attributed to molecular motions in the amorphous regions.⁸ For instance, Boyer¹² has suggested that it is due to the motion of the main chain in the region of branch points, namely, regions such as



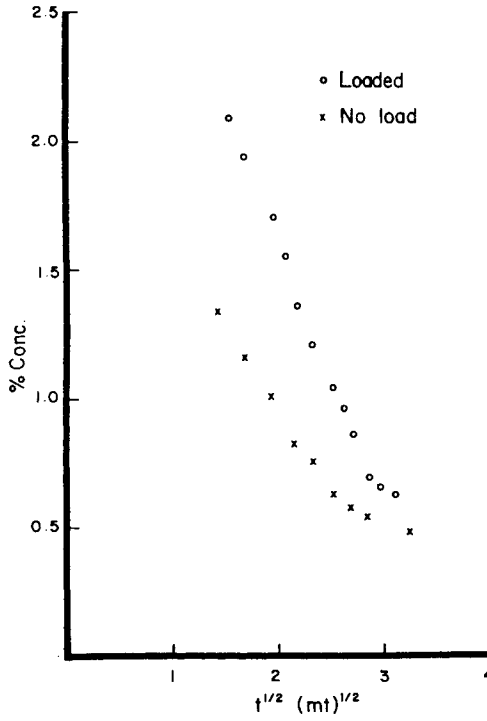


Fig. 10. Percent alcohol concentration vs $(time)^{1/2}$ with and without load for HDPE samples.

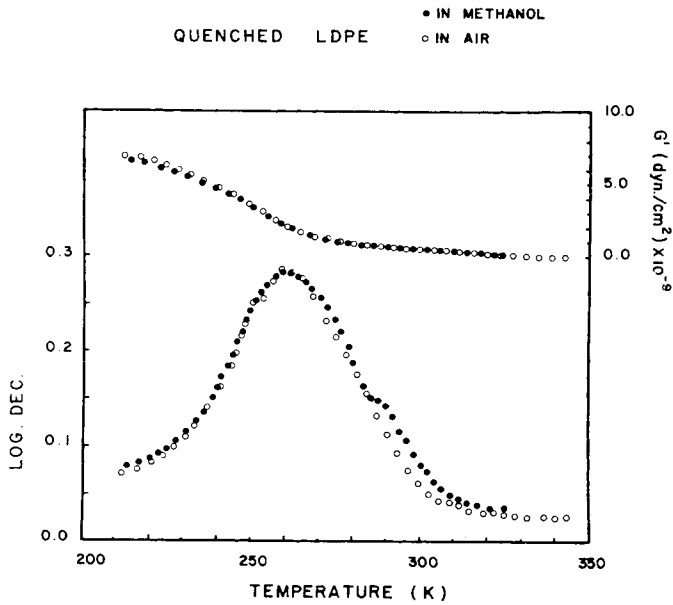


Fig. 11. Dynamic mechanical spectra of LDPE in the presence and absence of alcohol.

The broadening of the β peak indicates that some of these molecular motions are enhanced in the presence of the environment.

Takayanagi¹³ has reported the presence of two or more peaks in the α -relaxation region; the lower-temperature peak of these he attributed to motion in

mosaic block boundaries. On the other hand, Harrison et al.¹⁴ have suggested that electron-microscopic evidence for mosaic blocks can be interpreted as arising from other effects. These blocks, if present, are proposed to be smaller in diameter than the blocks we observe in the drawn samples. Thus, although at present the evidence for mosaic blocks is not compelling, we propose that the appearance of a shoulder on the high-temperature side of the β peak can be interpreted as indicating that the presence of the environment has caused an increase in mobility in intracrystalline defect regions. This is in agreement with our observations on thin films and single crystals. The appearance of blocks in the thin films may have been caused by the defect regions in the films being essentially "plasticized" by the environment, thus favoring draw in such regions. Once drawing starts, the undeformed block between two deformed regions is carried along with very little further deformation. As the stress is increased further, yield occurs at another defect site and another block is pulled off. Thus, the presence of the environment would cause inhomogeneous deformation to occur, in accordance with earlier observations. When samples of LDPE are annealed, the α transition starts to appear and becomes stronger with increasing time of annealing. This peak was found to increase in intensity and broaden considerably in the presence of methanol, again suggesting a "plasticization" effect at the defect sites.

CONCLUSIONS

It has been shown by stress-strain measurements that the strain at break of LDPE is always lower in the presence of stress cracking agents as compared to that in their absence and that this effect becomes more pronounced with increasing temperature. Fracture surface of samples drawn in stress cracking agents were found to be fibrillated. The fibrillation was found to increase with increasing temperature and decreasing strain rate.

Thin-film deformation studies indicate that deformation is localized and inhomogeneous in the presence of stress cracking agents. Again, this inhomogeneity was found to increase with temperature.

Deformation studies of single crystals in the presence of stress cracking agents show formation of a network of small cracks in some areas of the crystal, suggesting a weakening at the defect sites in the crystal. The amorphous surface layers of the crystals were found to be "solvated" by the cracking agent.

IR studies on the sorption/desorption of the agent from the polymer show an increase in the amount of sorption in the presence of a load. This effect, coupled with "solvation" of the amorphous regions and "plasticization" at the defect sites in the polymer in the presence of stress cracking agents, has been suggested to affect the deformation process.

Dynamic mechanical studies have shown that the defect sites are affected preferentially. This is in agreement with the observations made on thin-film and single-crystal deformation.

References

1. J. B. Howard, in *Crystalline Olefine Polymers*, Part II, R. A. V. Raff and K. W. Doak, Eds., Interscience, New York, 1965, Chap. 2.
2. R. McFedries, W. E. Brown, and F. J. McGarey, *SPE Trans.*, **2**, 170 (1962).
3. J. B. Howard, *SPE J.*, **15**, 397 (1959).
4. V. L. Lanza, *Mod. Plast.*, **34**(11), 129 (1957).
5. R. J. Roe and C. Gieniewski, *Polym. Eng. Sci.*, **15**(6), 421 (1975).
6. C. J. Singleton, E. Roche, and P. H. Geil, *J. Appl. Polym. Sci.*, **21**, 2319 (1977).
7. A. Peterlin, *J. Macromol. Sci., Phys.*, **B8**(1), 83 (1975).
8. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymers*, Wiley, New York, 1962.
9. A. Keller and D. M. Sadler, *J. Macromol. Sci., Phys.*, **B7**(2), 263 (1973).
10. The Sadtler Standard Spectra, Vol I, No. 1919, Sadtler Res. Labs., Philadelphia, Pa. (1962).
11. D. McCammond and C. W. Ward, *Polym. Eng. Sci.*, **14**(12), 831 (1974).
12. R. F. Boyer, *J. Polym. Sci., Symp. No. 50*, 189 (1975).
13. M. Takayanagi and T. Matsuo, *J. Macromol. Sci., Phys.*, **B1**(3), 407 (1967).
14. I. R. Harrison, A. Keller, D. M. Sadler, and E. L. Thomas, *Polymer*, **17**, 736 (1976).

Received October 13, 1977

Revised February 9, 1978