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Effect of Radiation of Polyethylene on Environmental Stress Cracking

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INTRODUCTION

In a previous note[1] some data were presented which showed that environmental stress cracking of polyethylene by surface-active agents was decreased by radiation but that the polymer deteriorated after standing in air for a week. The present work deals with a few experiments carried out to elucidate this phenomenon. We have found that environmental stress cracking may be substantially reduced or eliminated in polyethylene by an appropriate radiation treatment.

PROCEDURE

A high-density Ziegler-type polyethylene‡ was melted and cut into samples as described elsewhere.[2] The environmental stress cracking test used is a variation[2] of the Carey procedure,[3] the test pieces being strips $^1/_2$ in. in diameter and about 0.020 in. thick, in which a $^1/_{16}$ in. center hole was punched. A biaxial stress was achieved in the neighborhood of the hole by applying tension to the strip; the *nominal* tension at the edge of the hole at the equator was 2740 psi in all cases. This test is discussed in detail elsewhere.[2] All experiments were carried out at 50 ± 0.1°C. in Igepal Co-630.§ The stress cracking time $\bar{F}$ is given in minutes and is the average of the breaking times of 10 samples.

The samples were irradiated in a Co-60 source at the rate of 2.4×10^5 rad/hr.

Infrared spectra of a number of polymer samples were taken with the Infracord‖ spectrometer.

Samples were irradiated in air and in vacuum. When the samples were treated under vacuum, the system was flushed at least twice with nitrogen and the pressure reduced to about 10^{-5} mm. before sealing of the glass tube containing the specimens. Some of the irradiated materials were heated under vacuum before exposure to air. It was shown previously that stress cracking is a function of the thermal history of the polymer and, therefore, a series of unirradiated samples were heat-treated in the same way as these irradiated samples.

The unirradiated samples were used as controls in the stress cracking experiments. The melt index of a few samples was measured.* This is a technical viscosity measurement that describes the number of grams of polymer extruded through an orifice in a standard interval of time (3 min.). It is particularly sensitive to the high molecular weight portion of the material. The higher the melt index, the lower the viscosity.

RESULTS AND DISCUSSION

All the results on stress cracking are given in Table I. Briefly, irradiation of polyethylene will reduce or eliminate stress cracking if the sample is heated under vacuum before exposure to air. Apparently, the trapped radicals in the solid polymer combine with each other on heat treatment, while if the polymer is exposed to air they react with the oxygen. Materials of the latter type become brittle and crumble, and possess an infrared absorption at 1740 cm.$^{-1}$, indicating the presence of carbonyl groups on the polymer (Fig. 1). In Figure 1, B is the spectrum of sample 140 of Table I; A is a spectrum of unirradiated polymer. This absorption is not present in unirradiated polymer, or in irradiated polymer that has been heated for a long time (below the melting point) before exposure to air. The measurements of melt index in Table II

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‡ Super Dylan 6600, Koppers Co., Verona, Pa.

§ A polyalkyl-aryl glycol, General Aniline and Dyestuff Co., New York.

‖ Perkin-Elmer Corporation, Norwalk, Conn.

* Courtesy of Dr. F. P. Baldwin, Esso Research and Engineering Co., Linden, New Jersey.

TABLE I

Expt. no.	Irradiations (megarads) and conditions	$\bar{F}$, min.	Experimental conditions and observations after irradiation
Control	0	565	
Control	0	604	
144	0.72, vacuum	3196	4 days in dry ice under vacuum; samples opened to air and tested immediately.
150	" "	553	41 days in dry ice under vacuum; samples opened to air and tested immediately.
145	" "	448	25 days in dry ice, 1 week at 50°C. under vacuum; samples opened to air and tested immediately.
149	" "	433	24 days in dry ice under vacuum, 1 week in air, then tested.
151	" "	610	17 days in dry ice under vacuum, opened to air and tested immediately.
141	" "	611	28 days in dry ice under vacuum, 1 day in air, then tested.
136	1.4, vacuum	770	11 days in dry ice under vacuum, opened to air and tested immediately.
138	" "	640	10 days in dry ice under vacuum; opened to air and tested immediately.
146	" "	374	6 days in dry ice under vacuum, 1 month at room temp. in air
148	" "	549	25 days in dry ice under vacuum, 1 week at 50° in air and tested immediately.
147	" "	620	26 days in dry ice under vacuum, opened to air for 24 hr. and tested.
142	1.4, vacuum	416	38 days in dry ice under vacuum, opened to air for 24 hr. and tested.
139	5.8, vacuum	>10,000	10 days in dry ice under vacuum, 1 week at room temp., under vacuum, opened and tested immediately; 2 samples broke before 10,000 min.
137	" "	2658	25 days in dry ice under vacuum, opened to air for 24 hr. and tested.
140	5.8, in air	91 (samples very brittle)	Exposed to air from beginning of experiment, tested 33 days after irradiation.
143	5.8, vacuum	2927	38 days in dry ice under vacuum, opened to air and tested immediately.
153	" "	4755	3 days in dry ice under vacuum, opened to air and tested immediately.
152	" "	1100	38 days in dry ice under vacuum, opened to air and kept at room temp. for 1 week and tested.
154	None	604	Standard control.
155	"	648	Standard control.
156	5.8, in air	183	Tested 1 day later.
160	5.8, in air	90	Tested 1 week later.
162	" " "	50	Tested 50 days later.
159	" " "	30	Annealed for 24 hr. in air at 106°C., and tested immediately.
158	" " "	5	Annealed for 48 hr. in air at 106°C., and tested immediately.
166	5.8, vacuum	1104	Annealed 31 days later for 24 hr. at 106°C., tested 3 days after annealing.
167	" "	1205	Annealed 31 days later for 24 hr. at 106°C., tested 22 days after annealing.
168	" "	1558	Annealed 29 days later for 48 hr. at 106°C., tested 5 days after annealing.
169	" "	1107	Annealed 31 days later for 48 hr. at 106°C., tested 21 days after annealing.
170	" "	>10,000	No annealing; opened 36 days after radiation, melted and re-formed with only brief exposure to air; annealing cycle on cooling was the same as blanks 154, 155, 171, 172.

(continued)

TABLE I (*continued*)

Expt. no.	Irradiations (megarads) and conditions	$\bar{F}$, min.	Experimental conditions and observations after irradiation
171	None	410	Standard control.
172	"	450	" "
173	None	162	Similar to standard control except for postannealing in air for 24 hr.; very brittle.
174	"	44	Similar to standard control except for postannealing in air for 48 hr.; very brittle.
175	"	202	Similar to standard control except for postannealing under vacuum for 24 hr.; very brittle.
176	"	198	Similar to standard control except for postannealing in vacuum for 48 hr.; very brittle.
177	"	624	Standard control.
179	"	173	Standard control, except for postannealing in vacuum for 48 hr., very brittle.
180	"	194	Standard control, except for postannealing in vacuum for 48 hours, very brittle.
181	5.8, vacuum	>10,000	Irradiated pellets, annealed 48 hr. in vacuum, opened, melted and formed into sheets.
182	" "	>10,000	Irradiated pellets, annealed 24 hr. in vacuum, opened, melted and formed into sheets.

The numbers of the experiments were assigned chronologically. Changes in the control experiments apparently arise from small changes in sample preparation. Unless otherwise stated, samples were kept at room temperature.

show that irradiation under vacuum leads to a crosslinked polymer while irradiation at the same level in air does not.

TABLE II
Melt Index of Typical Samples

Exp. no.	Melt index
154	0.7
162	1.7
166	0.0
174	8.8
176	0.6
181	0.0

It should be noted that polyethylene resistant to stress cracking was not obtained in *all* experiments in which the irradiated polymer was crosslinked.

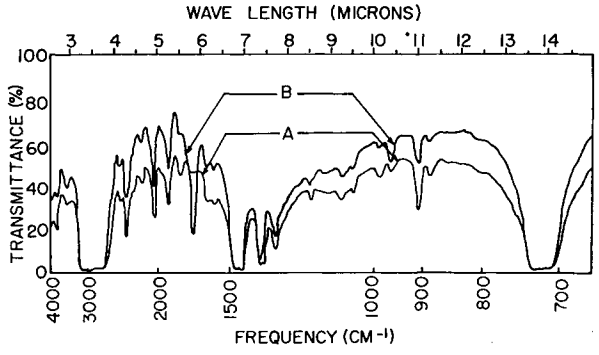

Figure 1

This arises, in our opinion, from one of two possible causes. First, the removal of oxygen from the system before irradiation may not have been complete in some cases. Second, heat treatment below the melting point may not have terminated all the free radicals. These subsequently could react with the oxygen of the air to degrade the polymer.

The stress cracking phenomenon in polyethylene is associated with the reduction in surface energy by the stress cracking agent at micro cracks in the sample. The crack is propagated in preferred crystallographic directions corresponding, perhaps, to faults or grain boundaries between the crystals, and certainly in directions in which a minimum number of primary chemical bonds are broken. Upon crosslinking, the primary crystal structure is broken down and, also, many new carbon-carbon bonds are formed, linking the entire sample in a single gigantic molecule. It appears that both the destruction of the crystallites and the formation of new chemical bonds inhibit stress cracking, although it is not clear which factor is most important. In this connection it should be pointed out that the irradiated and oxidized samples are no longer highly crystalline, nor are they strongly crosslinked. These break under stresses in the presence of Igepal more quickly than the unirradiated material. The data show quite clearly that unirradiated polyethylene samples embrittled by

heating at 106°C. either in air or under vacuum show increased susceptibility to environmental cracking.

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References

1. Hittmair, P., H. F. Mark, and R. Ullman, *J. Polymer Sci.*, **33**, 505 (1958).
2. Ullman, R., and P. Hittmair, *J. Appl. Polymer Sci.*, VI, 1 (1962).
3. Carey, R. H., *SPE Journal*, **10**, No. 3, 16–21, 41–42 (1954).

Synopsis

The influence of radiation on the environmental stress cracking of polyethylene is described. The polymer was irradiated by cobalt-60 γ-rays, and studied as a function of a variety of experimental conditions. The deleterious effects of oxygen were noted. To prevent oxidative deterioration, the free radicals created had to be terminated by a heat treatment in the absence of oxygen. Some procedures were developed in which polyethylene could be made resistant to environmental stress cracking.

Résumé

On décrit l'influence de radiations sur la fissuration sous contrainte du polyéthylène. Le polymère a été irradié au moyen des rayons-γ du CO^{60} et étudié dans des conditions expérimentales variées. On a remarqué l'effet néfaste de l'oxygène. Dans le but de prévenir la détérioration oxydante, les radicaux libres créés ont été détruits par chauffage en absence d'oxygène. Quelques procédés furent établis grace auxquels le polyéthylène a été rendu plus résistant à la fissuration sous contrainte.

Zusammenfassung

Es wird der Einfluss der Bestrahlung auf die milieubedingte Spannungsrissbildung von Polyäthylen beschrieben. Das Polymere wurde mit γ-Strahlen aus einer Cobalt-60-Quelle bestrahlt und unter verschiedenen experimentellen Bedingungen untersucht. Die schädigenden Einflusse von Sauerstoff wurden festgestellt. Zur Verhinderung einer oxydativen Schädigung mussten die gebildeten Radikale durch eine Hitzebehandlung unter Sauerstoffausschluss abgesättigt werden. Es wurden Verfahren entwickelt, um Polyäthylen gegen milieubedingte Spannungsrissbildung beständig zu machen.

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