Effect of Rubber on the Environmental Stress-Crack Resistance of Polyethylene

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Synopsis

The property of environmental stress cracking is a critical performance factor in the polyethylene product areas of rigid and flexible containers, wire and cable insulation and pipe or conduit. It has been known for quite some time that the addition of an elastomeric material to polyethylene can improve its resistance to environmental stress cracking. However, the information reported in the literature on the subject is rather limited and as far as can be determined no attempt has been made to determine the rubber variables affecting the environmental stress cracking performance of polyethylene. In studying the effect of rubber on the environmental stress crack resistance (ESCR) of low and high density polyethylene, the choice of base resin is important. With some resins the addition of rubber doubles the ESCR while with others a fiftyfold improvement can be effected. Of the elastomers investigated in this study, Enjay Butyl 007 a copolymer of isobutylene and isoprene gave the greatest stress-crack improvement in both low and high density polyethylene. Evaluation of a series of polyisobutylenes indicate that the higher its molecular weight the more effective its performance as a stress crack additive. The effect of rubber on other properties of the polyethylenes such as melt index, stiffness, permeability, chemical resistance, brittle point temperature, and impact strength is also discussed.

INTRODUCTION

The property of environmental stress cracking is a critical performance factor in the polyethylene product areas of rigid and flexible containers, wire and cable insulation, and pipe or conduit. It has been known for quite some time that the addition of an elastomeric material to polyethylene can improve its resistance to environmental stress cracking. However, the information reported in the literature on the subject is rather limited, and as far as can be determined no attempt has been made to determine the rubber variables affecting the environmental stress cracking performance of polyethylene.[1,2] Generally speaking, the term environmental stress cracking has been defined as the premature cracking of a polyethylene under stress in the presence of an active environment. Although great strides have taken place in the preparation of polyethylenes with superior stress-crack properties, relatively little is known about the mechanism by which polyethylene fails. In fact, there is still some question about the best test for measuring this property. The two commonest methods for measuring

the environmental stress-crack resistance (ESCR) of polyethylene are the Bell Bent Strip Test[3] and the Constant Load Test first described by Lander.[4]   The Bell test is essentially a constant strain test, while Lander's test measures sample specimens under constant stress.

A wide range of differing media can cause environmental stress cracking in polyethylene.[5]   The most active are usually polar in nature.   They may be hydrophilic like typical detergents or hydrophobic like the silicone oils. The mechanism appears to be basically a physical phenomenon involving adsorption rather than swelling or chemical attack.[6]   For example, alcohols which are nonsolvents for polyethylene accelerate stress cracking.   The potency of agents appears to be related to their ability to form a continuous stable film on the surface of the polymer and, furthermore, one which can penetrate into the microscopic flaws on the surface of the sample and contribute locally to the stresses which have to be supported.   Their effectiveness appears to depend upon on a combination of low surface tension, low viscosity, and their ability to adsorb a thin, extensible film on the polymer surface.

The objective of this study was to determine the extent to which the ESCR of high- and low-density polyethylene could be improved through the addition of elastomers.   In the course of this work, the effect of elastomer type, concentration, and molecular weight on ESCR was determined.

EXPERIMENTAL

The elastomer/polyethylene blends used in this study were prepared by Banbury mixing the components for 3 min at flux temperature.   Total mix cycles were generally 6 min and dump temperatures ranged from 310° to 330°F.

The preparation of the compression-molded ESC test samples was carried out using ASTM Method D-1928-68, procedure C.   A slight modification of procedure C was necessary due to equipment limitations.   The mold cooled at the rate of 25–30°C/min instead of the 15°C/min recommended by ASTM.   The specimens were then conditioned for a minimum of 40 hr at 23°C and 50% relative humidity as outlined in procedure A of ASTM D-618 and then tested for ESCR using the Bell Bent Strip Test (ASTM D-1693-70).

The slightly faster cooling rate used in this study should have the effect of increasing the F_{50} value (average time to break 50% of ten test specimens) by ~5%.   When the resin is cooled more rapidly from the melt, a a lower degree of crystallinity results and the product is less stiff.[6]   This would reduce stress in the specimen and therefore give improved stress cracking.

Test method ASTM D-1693-70 was used to determine the ESCR of the polyethylene compounds.   The test reagent used was Igepal CO-630, an alkyl phenoxy polyoxyethylene ethanol.

Most stress-crack testing on low-density polyethylene was carried out in 1% Igepal solutions. This concentration was chosen because it caused failure in the low-density polyethylene and LDPE/elastomer blends in time intervals that could be easily followed during the course of a working day. However, in some instances LDPE resins and LDPE/elastomer blends were tested over the entire range of Igepal solutions.

Condition B, with a 50% Igepal solution, was used for the evaluation of the ESCR of high-density polyethylene.

The phenomenon of environmental stress cracking, while dependent upon the environment to which the polyethylene is exposed, is also a function of the level of stress. The Environmental Stress Rupture Test developed by Lander provides a technique for determining the environmental stress and temperature, using Igepal as an environment. This test is now a standard ASTM method (ASTM D-2552-69) and was used in this study.

DISCUSSION

While the mechanism of environmental stress cracking of polyethylene is not fully understood, the phenomenon does have several distinguishing characteristics.[8] These include:

1. Surface initiation—cracking originates at a surface flaw.
2. Apparent brittle nature of the fracture.
3. Need for stress—often a combination of externally applied stress in conjunction with internal stresses arising from flow during molding.
4. Presence of an external sensitizing agent such as a detergent.

The average molecular weight as measured by melt index is generally recognized as a dominant factor affecting the ESCR of polyethylenes. In general, as the molecular weight of the polymer increases (melt index decreases), its ESCR increases. The molecular weight distribution of the polymer is also of prime importance. Narrowing the molecular weight distribution makes for improved ESCR while broadening it has the opposite effect. It is believed that elimination of the low molecular weight ends is responsible for the improvement shown by the narrower distributions.

Increased crystallinity (density) can have a marked effect on stress cracking, but whether it increases or decreases it depends on the conditions involved. Under constant load conditions the higher-density polyethylenes show superior stress-crack resistance. Under constant strain, the opposite effect can be realized.[8]

For this study several LDPE injection-molding grades were used as the base resins. A brief description of the materials is shown in Table I. The data in Table I which serves to characterize the polymer samples are somewhat incomplete, since neither the distribution of molecular weights nor the crystallinity of the resin is given by the manufacturer.

A brief description of the high density polyethylene resins used in this study is given in Table II.

TABLE I
Physical Properties of LDPE Used in this Research

Grade	LDPE A	LDPE B	LDPE C	LDPE D	LDPE E[a]	LDPE F
Melt Index	2.0	7.5	22	30	3.0	1.8
Density, g/cc	0.922	0.922	0.925	0.925	0.922	0.918
Tensile, psi	1600	1600	1700	1700	1400	—
Elongation, %	500	550	100	100	2000	—
Flex Stiff, psi	14,000	14,000	26,000	26,000	16,000	21,000

[a] Contains 3.4% vinyl acetate.

TABLE II
Physical Properties of HDPE Used in this Research

Grade	HDPE A	HDPE B	HDPE C
Melt index	0.7	0.3	8.7
Density, g/cc	0.962	0.950	0.950
Flexural modulus, psi	120,000	104,000	74,000

Effect of Rubber Type

Several investigators have previously reported that the crack resistance of polyethylene can be improved by blending it with polyisobutylene.[1,2] Compositions of this type have had extensive use in the wire and cable industry. Wilson[9] has described a submarine cable that is insulated with a compound consisting of 87.5% polyethylene and 12.5% polyiso-butylene.

In this study several elastomers were blended with LDPE B at the 10 wt. % level in an attempt to determine their effectiveness in preventing stress cracking. The elastomers used included polyisobutylene (PIB), butyl rubber (copolymer of isobutylene and isoprene), EPM (copolymer of ethylene and propylene), EPDM (terpolymer of ethylene, propylene and a nonconjugated diene). The results are shown in Table III.

TABLE III
Effect of Rubber on the ESCR of Low-Density Polyethylene

10% Rubber/90% LDPE	F_{50}, hr[a]	Flexural secant modulus, psi	Melt index, g/10 min
Butyl[b]/LDPE B	9.0	19,000	4.7
PIB[c]/LDPE B	5.8	19,000	4.2
EPDM A[d]/LDPE B	3.6	16,000	2.9
EPM[e]/LDPE B	1.2	19,000	4.5
EPDM B[f]/LDPE B	0.7	16,000	4.0
100% LDPE B	0.7	22,000	5.8

[a] 1% Igepal solution.
[b] ENJAY BUTYL 007, sold by Enjay Chemical Company.
[c] VISTANEX L-120, sold by Enjay Chemical Company.
[d] VISTALON 3708, sold by Enjay Chemical Company.
[e] VISTALON 404, sold by Enjay Chemical Company.
[f] VISTALON 2504, sold by Enjay Chemical Company.

Of the elastomers investigated, the butyl rubber imparted the greatest degree of stress-crack resistance. The F_{50} value increased from 0.7 hr to 9.0 hr. The butyl rubber used has a Mooney viscosity (ML) 1 + 8 min reading at 212°F of 65–75. It contains no stabilizer and has wide compliance with FDA regulations. The polyisobutylene also performed well; it increased the F_{50} value from 0.7 to 5.8 hr.

The improved crack resistance attained through the addition of rubber is probably related in part to the lower moduli of the blends and their greater tendency to relax under stress than the straight resin. However, lower blend moduli are not the complete answer since EPDM B, a low molecular weight polymer, produces a blend with the lowest flexural secant modulus, yet it is ineffective as a stress-crack additive.

The addition of rubber does cause some reduction in melt index. Melt index gives an indication of the processability of a resin. The higher the melt index, the better the flow properties of the compound.

The same group of elastomers were also blended with a 0.7 melt index high-density polyethylene. The results are shown in Table IV.

TABLE IV
Effect of Rubber on the ESCR of High-Density Polyethylene

10% Rubber/ 90% HDPE	F_{50}, hr[a]	Flexural modulus, psi	Melt index, g/10 min
Butyl/HDPE A	12.7	87,000	0.7
PIB/HDPE A	10.0	95,000	0.6
EPDM A/HDPE A	8.9	76,000	0.6
EPM/HDPE A	7.0	—	0.7
EPDM B/HDPE A	5.8	71,000	0.7
100% HDPE A	6.1	120,000	0.7

[a] 50% Igepal solution.

It is interesting to note that the order of effectiveness of the rubbers in imparting ESCR to the HDPE resin follows the same order found with LDPE. As expected, the rubber increases the flexibility of the HDPE resin, and this shows up as an appreciable decrease in flexural modulus.

In order to determine the effect of the elastomer's molecular weight on stress-crack performance, three polyisobutylenes with viscosity-average molecular weights ranging from 40,000 to 1,700,000 were blended with LDPE B at the 10% level. The results are shown in Table V.

TABLE V
ESCR of 90% LDPE/10% PIB Blends as a Function of MW of PIB

PIB Viscosity- ave. MW	F_{50}, hr	Melt index	Flex modulus, psi
40,000	1.5	8.4	19,000
900,000	3.8	4.5	18,000
1,700,000	5.8	4.2	17,000

As the viscosity-average molecular weight of the polyisobutylene increased, the ESCR increased. However, no direct correlation can be made between different classes of rubbers. For example, the butyl rubber which has proven to be so effective as a stress-crack additive has a viscosity-average molecular weight of 450,000.

Effect of Rubber Concentration

The effect of butyl rubber concentration on the ESCR of low- and high-density polyethylene was investigated. The butyl concentration was varied from 2 to 15 wt-%, and its effect on stress cracking is graphically shown in Figure 1. The addition of 25 and 40 wt-% butyl to the LDPE B resulted in a rubber-like compound which gave no indication of cracking even after 500 hr in a 1% Igepal solution. The 10% blends appear to give a good balance of properties providing adequate ESCR while maintaining the melt index and flexural modulus at a satisfactory level.

Effect of Polyethylene Grade

The stress-crack improvement that rubber imparts to polyethylene is greatly influenced by the choice of polyethylene grade. The results of blending 10 wt-% butyl with several low-density and high-density polyethylenes are shown in Table VI.

LDPE E contains 3.4% vinyl acetate and provides the best stress resistance of any of the low-density polyethylenes when blended with butyl rubber. As expected, the high melt index LDPEs exhibit the poorest stress-crack resistance. LDPE A is a general-purpose injection-molding resin with good stress-crack resistance. Its slightly better ESCR performance over the other three homopolymer LDPE can be explained in part due to its lower melt index. However, it is difficult to explain the dramatic increase in ESCR that the resin undergoes when butyl rubber is blended with it. At the 10% rubber level, the LDPE A blend has an F_{50} value that is more than 25 times better than the other homopolyethylenes.

TABLE VI
Effect of Butyl Rubber on ESCR of Polyethylene

PE Grade	100% Polyethylene		90% PE/10% Butyl	
	F_{50}, hr[a]	Melt index	F_{50}, hr[a]	Melt index
LDPE A	2.1	2.0	350	1.7
LDPE B	0.7	5.8	9.0	4.7
LDPE C	1.3	22.0	5.4	15.7
LDPE D	1.9	30.0	7.0	20.4
LDPE E	2.0	3.3	>500	3.1
HDPE A	6.5	0.3	500	0.3
HDPE B	6.1	0.7	12.7	0.7
HDPE C	0.5	8.7	2.0	6.8

[a] 1% Igepal solution used for LDPE testing and 50% Igepal solution used for HDPE testing.
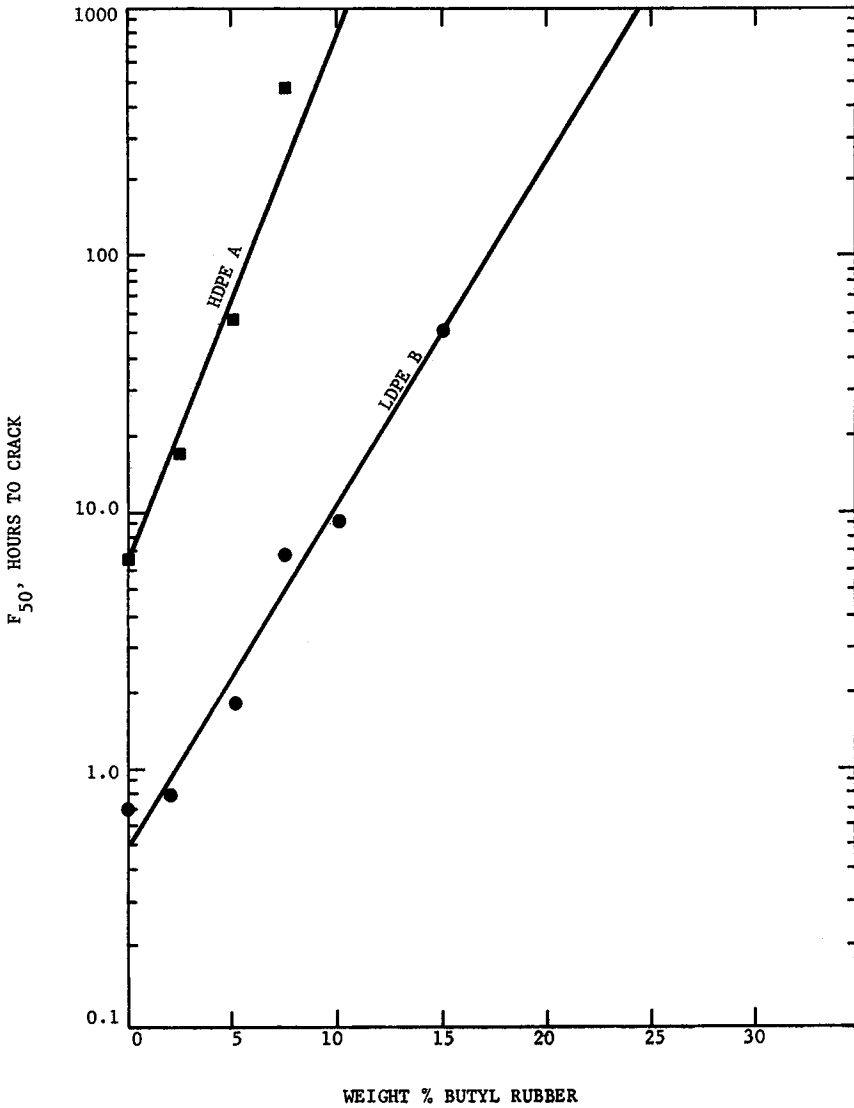
Fig. 1. Effect of butyl concentration on ESCR of polyethylene.

The ESCR of the high-density polyethylenes follows anticipated performance. HDPE A is a low-melt-index copolymer of 0.950 density and it displays the greatest degree of stress-crack resistance. HDPE B, a homopolymer with a 0.7 melt index, broad MWD, and a 0.962 density, displays a fair degree of ESCR. On the other hand, HDPE C, a high-melt-index copolymer of 0.95 density, has poor stress-crack resistance even after 10 wt-% butyl rubber is dispersed in it.

Effect of Fillers, Plasticizers, and Crosslinking Agents

For applications such as pipe and wire and cable insulation, carbon black is often added to polyethylene to improve its weatherability. Inorganic fillers are sometimes used to produce desired colors and properties, while plasticizers are occasionally added to enhance flow and gloss. Therefore, the effect of fillers and plasticizers on the ESCR of low-density polyethylene with and without rubber was investigated. In addition, the effect of crosslinking the polyethylene with a peroxide was studied. The results are shown in Table VII.

TABLE VII
Effect of Additives on the ESCR of Polyethylene

Additive	100% LDPE B		90% PE/10% Butyl	
	F_{50}, hr	Melt index	F_{50}, hr	Melt index
—	0.7	5.8	9.0	4.7
5% FEF Carbon black	0.3	6.9	1.9	5.6
5% Titanium dioxide	0.8	8.0	2.3	6.7
5% Primol 355 Oil	0.2	11.6	0.7	12.2
2.8% Dicumyl peroxide	>500	—	>500	—

The addition of fillers and plasticizer to polyethylene and the PE/rubber blend has the effect of increasing melt index while reducing the ESCR. One possible explanation may be that the addition of these additives has the effect of broadening and exaggerating the molecular weight distribution resulting in poor stress-crack resistance, particularly in the range of 5–10 melt index. On the other hand, crosslinking the polyethylene imparts outstanding ESCR since the effect is to increase the molecular weight of the polymer. The melt index of the polyethylene after crosslinking was so low that it could not be measured.

Effect of Igepal Concentration

There is conflicting data in the literature on the effect of Igepal concentration on stress cracking. Hittmair and Ullman[10] found stress cracking of polyethylene to be more rapid in the higher-concentration Igepal solutions. Howard,[8] on the other hand, found that the addition of water markedly enhances the rate of failure of a typical polyethylene in Igepal. Howard cites the case of a 0.25-melt-index low-density polyethylene where dilution of Igepal from 100% to 80% decreased the F_{50} value from 100 hr to 1 hr. This value then held constant down to 50% Igepal concentration. Further dilution down to 5% Igepal then increased the F_{50} value to 5 hr.

The data obtained in this study indicate that the effect of Igepal concentration on stress cracking is dependent on the particular polyethylene investigated. Figure 2 presents a semilogarithmic plot of Igepal concentration versus F_{50} value for a series of LDPE/butyl rubber blends. A
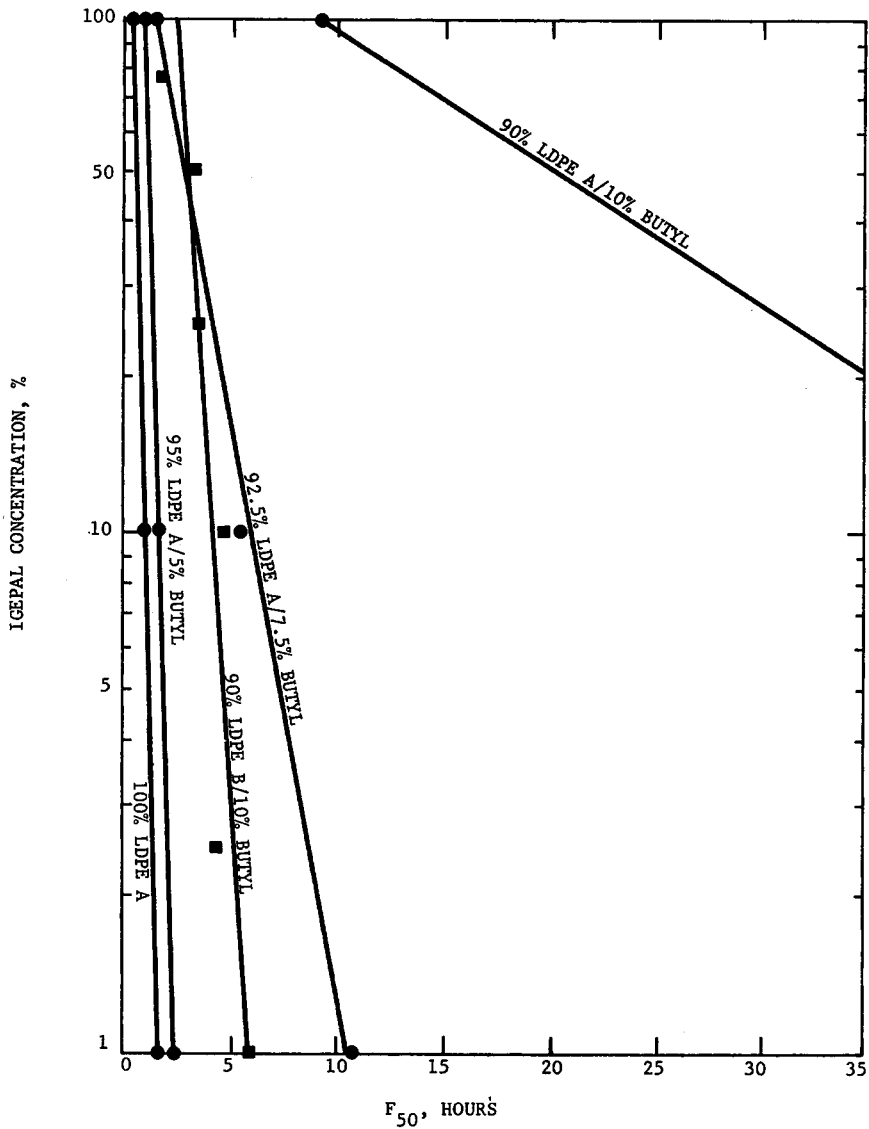
Fig. 2. ESCR as function of Igepal concentration and butyl concentration.

straight-line relationship was obtained, and stress cracking was found to increase as the Igepal concentration increased. On the other hand, LDPE F, a material noted for its excellent stress-crack resistance, gave results similar to those found by Howard (see Table VIII).

Effect of Chemicals and Foods

Igepal is generally chosen as a standard reagent for the ESCR test because it is an easily handled stable liquid producing rapid cracking. How-

TABLE VIII
Effect of Igepal Concentration on the ESCR of LDPE F

Igepal concn., %	F_{50}, hr
1	6.2
10	2.2
50	2.0
100	100

TABLE IX
Effect of Chemicals and Foods on ESCR

Material	LDPE A F_{50}, hr	90% LDPE A/10% Butyl F_{50}, hr
1% Igepal	1.8	>200
10% Tide soln.	5.7	>200
Lard	40	>200
Olive oil	32	>200
Safflower oil	27	>200
Oleomargarine	20	>200
Ethyl alcohol	0.2	>200
10% Sulfuric acid	>200	>200
10% Sodium hydroxide	110	>200

ever, polyethylene does come into contact with many other materials such as acid, bases, oils, and foods. The result of immersing bent strips of polyethylene and a polyethylene/butyl blend in a variety of chemicals is shown in Table IX.

As can be seen, the addition of 10% butyl rubber prevents stress cracking. This is the case even with ethyl alcohol which provides a very active cracking environment for polyethylene.

ESCR at Constant Stress

The phenomenon of environmental stress cracking, while dependent upon the environment to which the material is exposed, is also a function of the level of stress.[5,7,11] With the Bell Bent Strip Test, the stress level does not remain constant throughout the test due to the stress relaxation properties of these materials. This then raises the question as to whether the excellent ESCR performance that is obtained from the addition of rubber is due to reduced stiffness and increased stress relaxation. In order to answer this very pertinent question, Lander's Environmental Stress Rupture Test was employed (ASTM Test D 2552-69).

In the Environmental Stress Rupture Test, a specimen is subjected to a constant tensile load in the presence of 100% Igepal. Forty-mil-thick dumbbell-shaped specimens are cut from a compression-molded pad. The failure of polyethylenes under these conditions is a sudden and complete fracture.

TABLE X
Comparison of ESCR Results from Bent Strip and Stress Rupture Tests

Polymer blend	F_{50} (Bent Strip)	F_{50} (Stress Rupture)
100% LDPE A	0.3	0.7
97.5% LDPE A/2.5% Butyl	0.3	2.2
95% LDPE A/5% Butyl	0.4	4.9
92.5% LDPE A/7.5% Butyl	1.1	22
90% LDPE A/10% Butyl	9.0	150

In Table X a comparison of ESCR data taken by the Bell Bent Strip and the Lander Environmental Stress Rupture Test both in 100% Igepal at 50°C is shown. A constant stress of 600 psi was applied in the stress rupture test.

It is apparent that butyl rubber is an effective stress-crack additive even when measurements are carried out at constant stress. This would indicate that the beneficial effect of the rubber on stress cracking is not entirely due to the low stiffness or modulus it imparts to the polyethylene.

Effect of Rubber on Properties Other Than ESCR

The addition of butyl rubber does affect properties other than stress cracking. As the butyl rubber concentration is increased, some reduction in stiffness (flexural modulus), tensile, brittle point temperature, and tear strength can be expected. Other properties such as elongation, impact strength, and air and water permeability remain relatively constant. The data for a LDPE/butyl rubber blend varying in rubber from 0 to 15% are shown in Table XI.

TABLE XI
Effect of Butyl on Physical Properties of LDPE B

	0%[a]	5%	7.5%	10%	15%
Shore D	53	53	50	51	48
Tensile strength, psi	1630	1590	1540	1520	1410
Flex. modulus, psi	22,000	21,000	19,000	19,000	17,000
Elongation, %	145	145	145	145	145
Tear strength, ppi	525	485	490	460	420
T_b, °C	<−75	−72	−67	−62	−52
Dart impact @ 0°C	56	53	—	53	—
WVTR	0.036	0.035	—	—	0.035
Air Perm. × 10^{-3}	0.44	—	—	—	0.41

[a] % Butyl rubber.

CONCLUSIONS

1. The environmental stress-crack resistance of low- and high-density polyethylene can be markedly improved through the addition of rubber. The addition of ~10% rubber generally provides the best balance of properties of the elastomers evaluated in this study. Butyl rubber was found

to be the most effective elastomer, and the polyisobutylene rubbers were better than the EPDM and EPM rubbers.

2. ESCR was found to increase as the rubber concentration increased, while stiffness and melt index decreased. The addition of fillers and plasticizers have an adverse effect on ESCR, whereas crosslinking the polyethylene results in a material having outstanding ESCR.

3. Evaluation of a series of polyisobutylene rubber indicates that the higher its molecular weight, the more effective its performance as a stress-crack additive.

4. In studying the effect of rubber on the ESCR of polyethylene, the choice of base resin is important. With some resins the addition of rubber doubles the ESCR, while with others a hundredfold improvement can be effected.

5. Rubber is effective as a stress-crack additive even when measurements are carried out under constant stress.

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