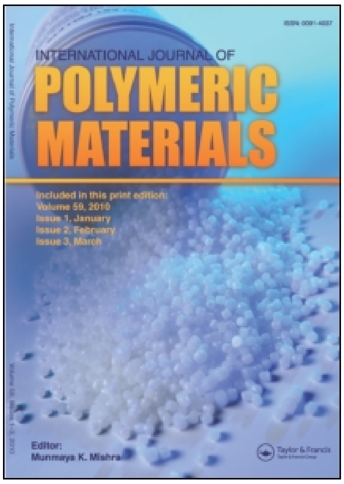

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Effects of Environmental Stress Cracking Agents on the Failure Mechanisms of Commercial Gas Pipe Resins

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Failure processes for two linear medium density polyethylene resins commonly used for producing piping for natural gas distribution systems have been compared in the absence and presence of environmental stress cracking (ESC) agents. A clear decrease in cohesion of the crazed, drawn material is seen in the presence of the ESC agents for both compact tension pieces and notched tensile bars. Creep experiments suggest the ESC agents only have an effect on polyethylene that has undergone micronecking.

KEY WORDS PE, stress cracking, environmental agents

INTRODUCTION

Since the introduction of PE pipe in the late sixties and early seventies for use in natural gas distribution, over one billion feet of various grades have been installed in North America.[1] A small number of unexpected field failures of the PE pipe have been reported.[2] Currently these pipes are expected to last more than 50 years; therefore PE resins used in this application can be considered an engineering thermoplastic. Due to the relatively new entry of PE material in the gas industry, only limited information on the failure behavior of PE pipe is currently available. Being able to rank various pipe resins as to their expected lifetime by use of a theoretically and experimentally sound accelerated test is of paramount importance; the research described in this paper was part of a project directed at that goal.[3]

Slow crack growth,[4,5] a brittle type failure, is the dominant mode of field failures for PE piping systems. Resistance to this type of failure thus dictates the service life of a given PE material. These failures generally occur under low loads after long periods of time in environments of relatively low and constant temperature, about 15°C. Environmental stress cracking (ESC) is a common failure mechanism

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for PE when loaded under stress in the presence of detergents or alcohols.[6] It displays many similarities to the slow crack growth observed in PE piping materials, such as temperature dependence and fracture surfaces, but with significantly increased crack growth rates which can be studied on a laboratory time frame. It is possible that a common molecular mechanism is responsible for both slow crack growth and ESC; therefore if the latter can be understood, better piping resins may be developed. Also, tests in the presence of an ESC agent might lead to the possibility of developing an accelerated test, allowing for the ranking of various PE resins with regards to expected service lifetime.

In a simplified schematic model of lamellae, it is the tie molecules that hold lamellae together and play a major role in the deformation process and slow crack growth. In slow crack growth it has been proposed[7] that as stress is applied normal to the faces of the lamellae the tie molecules would be straightened as the strain increases. After a certain point is reached, some of the tie molecules within the amorphous region can be pulled no further without breaking or destroying the lamellae. Under long-term, low level stress these tie molecules might slip out of the crystals, untangle and relax. Since the tie molecules can be expected to have undergone various amounts of strain, individual tie molecules would slip out of the crystalline region at different times as the lamellae separate further, by motions we suggest are related to the α relaxation,[8] until their number is depleted enough to cause failure. The proposed interlamellar failure does not occur exclusively during slow crack growth; depending on the resulting local stress concentration, lamellar disruption and microfibril formation may also occur. In the presence of an ESC agent the slow crack growth failure process is thought to be accelerated, as will be shown later, by reducing the cohesion between fibrils formed at yield in micronecked regions.

To characterize the effect of ESC agents three different types of experiments were conducted. First, compact tension samples were tested both with and without 10% by weight aqueous solutions of Igepal‡ CO-630 present in order to study its effect on crack growth. The second set of experiments were uniaxial creep tests conducted with and without the presence of the Igepal CO-630 solution to investigate the effects of an ESC agent on the creep process. In the third set of experiments notched tensile bars were drawn with and without isopropanol present to approximate the interactions of an ESC agent with a growing crack tip. This last set of experiments was conducted in isopropanol because alcohols are usually better ESC agents than Igepal CO-630; recent literature results have suggested that it is residual nonyl phenol, an alcohol which is present in Igepal CO-630, that may be acting as the actual ESC agent.[9]

EXPERIMENTAL

Materials

Two commercial gas pipe PE resins were used, Marlex HHM TR400 and Marlex 8600, both manufactured by Phillips Petroleum Company (Marlex HHM TR400

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‡ Trademark of GAF Chemical Corporation.

hereafter will be referred to as simply Marlex 400). These resins were available in both pellet and pipe form. Marlex 400 is a natural, medium density (0.950 gm/cc) commercial piping resin containing butyl branches. This resin has been chosen by the Gas Research Institute (GRI) as a standard resin for a number of related projects at various universities. It has been characterized by the National Bureau of Standards,[10] from which it is available in several forms, i.e. pellets, pipes of various diameters, elbows, piping tees and caps. Marlex 8600 was chosen to complement our studies of Marlex 400 because preliminary results from another GRI project[11] showed crack growth to be easier to initiate in Marlex 8600 than in the Marlex 400. Marlex 8600 is a black, medium density (0.957 gm/cc) pipe resin also containing butyl branches. Physical properties of these two resins are listed in Table I.[12] The Marlex 8600 pipe samples used were supplied by Phillips Driscopipe, Inc. and had an outside diameter of 11.4 cm and a wall thickness of 1.1 cm.

In addition to these commercial natural gas pipe resins, Marlex 6050 and Alathon 4275 were studied as necessary for comparison purposes. Marlex 6050 is a linear PE made by Phillips. Alathon 4275 is a free radical polymerized LDPE made by DuPont. Physical properties of these two resins are listed in Table II.[13]

Compact tension test

Compact tension (CT) samples identical to those discussed in the previous paper[8] were used to study the effect of ESC agents on craze/crack growth. Samples to

TABLE I

Physical properties of marlex gas pipe resins

Properties	Marlex 400	Marlex 8600
Comonomer	1-Hexene	1-Hexene
Density, g/cc	0.950	0.957
Melt Index, g/10 min	0.25	1.5
ESCR, F_{50}, hrs.	>1000	>5000
Yield Strength at 2"/min, psi	2800	3500
Ultimate Elongation at 2"/min, %	500	500
Modulus of Elasticity, psi	100,000	110,000

TABLE II

Description of polyethylene materials

Material	Type	Density gm/cc	MI gm/10 min	Comonomer	ESCR F_{50}, hrs.
Marlex 6050	LPE	.96	5.0	none	1
Marlex 4275	LDPE	.92	3.7	none	<0.1

test the effect of the ESC agent were tested, as per ASTM 1693, in a 10 percent aqueous solution of Igepal CO-630. Distilled water was used in order to prevent clumping of the soap solution which occurred after several days if tap water was used. Samples tested without the ESC agent present were drawn in air. All samples were tested at room temperature.

Tensile bar test

Tensile bars 3 mm thick with a gauge section of 12 mm by 5 mm were cut out of slabs of the various resins which had been compression molded from pellets. The molding pellets were heated in the press for 15 minutes under heat only at 165°C and then enough pressure was applied to adequately close the entire assembly which was heated another 15 minutes, after which the press was water quenched. A 0.5 mm inch deep razor slit was made across the middle of each bar, transverse to the draw direction, to act as a stress riser. Sample bars of each resin were immersed in isopropanol and drawn at a rate of either 5 cm/min or 0.5 cm/min. The failure surfaces of these samples were then compared to samples of the same resins drawn in air. Observations of the failure surfaces were made by scanning electron microscopy (SEM).

Scanning electron microscopy

Samples were observed on an ISI 130 SEM at an accelerating voltage of 15 kV after being coated with Au-Pd. SEM was chosen because of its large depth of field which is about 200 to 300 times greater than optical microscopy at the magnification required. The sample was not tilted, as is often done in SEM, in order to preserve proper perspective. In order to allow observation of the interior regions of a CT sample, they were sectioned and etched as discussed in the previous paper.[8]

Uniaxial creep test

Cylindrical tensile bars 5 mm in diameter, prepared from Marlex 8600 pipes were used in all creep tests. The specimens were made by cutting the pipe stock with a wall thickness of 1.1 cm into three equally sized sections. Each section was placed between two polished steel plates with straight bars 1.1 cm thick on each side of the pipe section. The entire assembly was placed for 10 minutes in a hot press heated to 165°C before adequate pressure was applied to bring the plates together and flatten the pipe section. The pressure was maintained for 10 more minutes after which the press was water cooled to 20°C in approximately 10 minutes. The sample preparation technique was chosen to insure that the pipe section was only reshaped, not melted and remolded. After each plaque was made, it was sectioned parallel to the machine direction and turned on a lathe until a gauge length of 2.5 cm with a 5 mm cross-section was attained. The radius of curvature at the end of the gauge length was 2.5 cm. In order to determine creep strain, parallel marks of aluminum were sputtered under high vacuum on the surface of each sample in the middle of the gauge length approximately 6.5 mm apart. The distance between marks was monitored as a function of time under load by a Nikon binocular microscope equipped with a set of cross-hairs and mounted on a 2-axis machinist track with five ten thousandth of an inch resolution. The resulting magnification was 30X.

Data at the higher temperatures and/or stress levels was collected with a 35 mm camera equipped with an autowinder because the creep strain rate was too fast to measure with the microscope. A 135 mm lens was mounted on the end of an extension bellows which resulted in an image-to-negative ratio of almost 1:1. The negatives were later mounted in 35 mm slide holders and enlarged onto a flat surface with a slide projector in order to make the measurements.

In order to allow the samples to be tested in a liquid environment, a creep tank measuring 77 cm wide, 49 cm tall and 14 cm deep with a transparent Lexan front was constructed. It contained three loading frames allowing three specimens to be tested simultaneously. The temperature was controlled by an immersion heater, therefore all tests had to be run with the tank filled. For tests that did not require an ESC agent the tank was filled with distilled water.

RESULTS AND DISCUSSION

Compact tension samples

Figures 1 and 2 are micrographs of a Marlex 400 sample with an initial crack length (ICL) of 8.2 mm drawn in air to a crack opening displacement (COD) of 2.5 mm. Figure 1 is the etched interior surface (described in Reference 8) after sectioning. No crack growth is seen on the exterior surface.[8] Three craze/cracks are seen in the interior in the direction of crack growth, one primary central craze/crack and two others, one on each side of the central one diverging at a slight angle. The origin of the dark regions surrounding each craze/crack is discussed in Reference 8. As seen in Figure 2 the drawn material within a crazed region forms a coherent

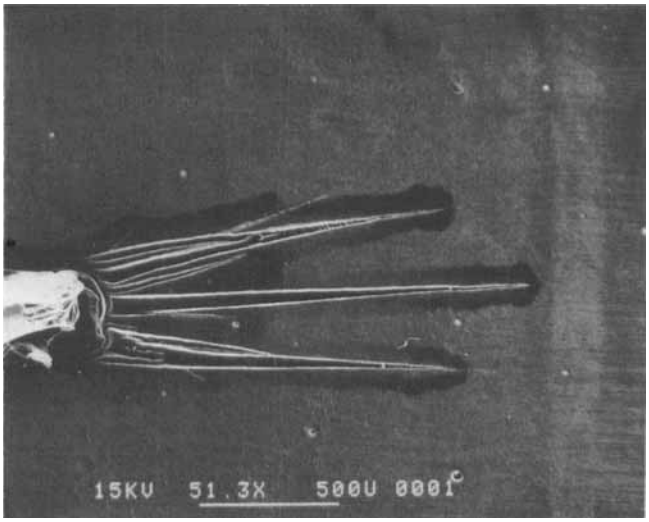

FIGURE 1 The interior surface of Marlex 400 drawn in air. ICL = 8.2 mm, COD = 2.5 mm.

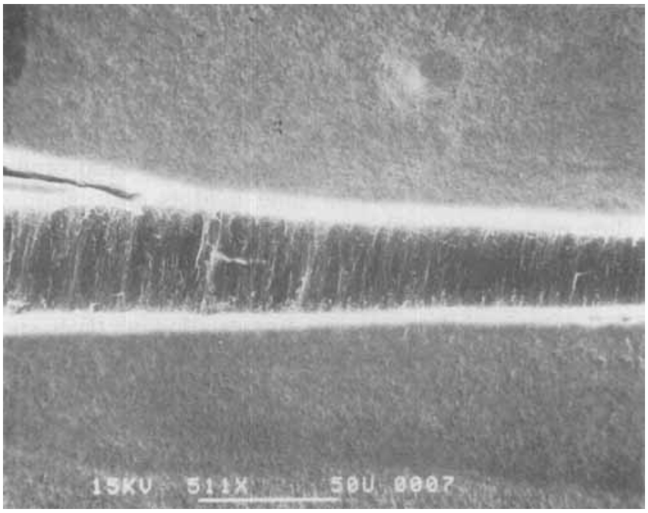

FIGURE 2 Marlex 400 drawn in air, near base of crack, ICL = 8.2 mm, COD = 2.5 mm.

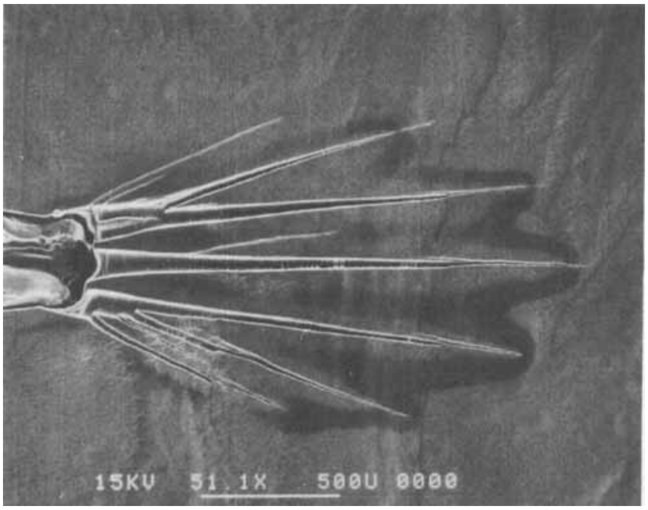

FIGURE 3 Interior surface of Marlex 400 drawn in an aqueous solution of Igepal.* ICL = 7.5 mm, COD = 2.5 mm.

structure that extends back to the base of the crack. A number of the fibrils in the figure appear to be broken; it is not known if this occurred during deformation or if some or all of the fibril breakage occurred during the etching or SEM observation. Figures 3–5 are similar micrographs of Marlex 400 drawn in Igepal solution at room temperature. As indicated in Figure 3, each side craze/crack has initiated several secondary ones not seen in samples drawn in air. This sample had an initial crack length of 7.5 mm and was drawn until a COD of 2.5 mm was reached. Figure 4 is a high magnification picture of the region within the central craze/crack; nu-

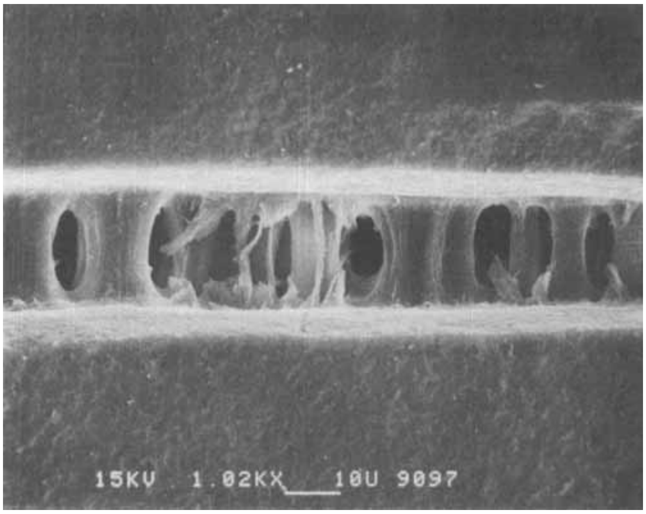

FIGURE 4 Marlex 400 drawn in an aqueous solution of Igepal (central crack), ICL = 7.5 mm, COD = 2.5 mm.

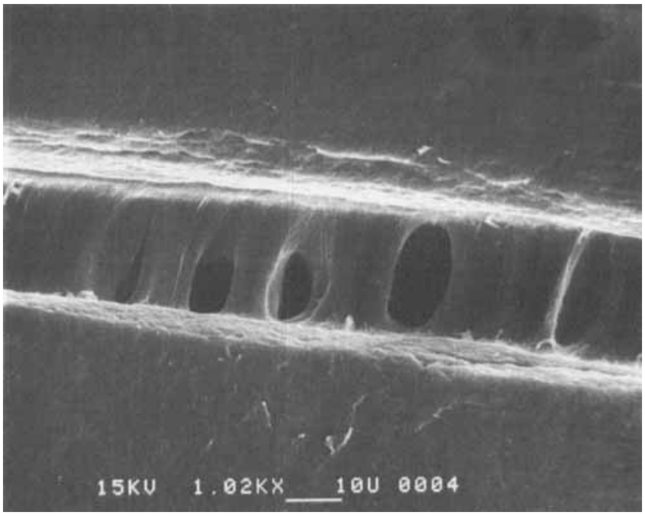

FIGURE 5 Marlex 400 drawn in an aqueous solution of Igepal (side crack), ICL = 7.5 mm, COD = 2.5 mm.

merous large voids are seen, presumably caused by the Igepal. The extent of deformation has been sufficient to cause some of the drawn material to fail. Figure 5 shows the lower, side craze/crack; again voids are seen to have formed but the material has not been drawn enough to cause failure. The presence of the ESC agent, Igepal, has caused additional craze/crack arms to form which were not seen in samples drawn in air; however the overall length of the craze/crack region has not changed. The additional craze/cracks and voids, we suggest, are caused by reduced cohesion of the drawn material in the presence of the Igepal.

SEM studies to examine the fracture process of Marlex 8600 were conducted with and without Igepal present, similar to those used to observe Marlex 400. Samples drawn in air (Figure 6, ICL = 7.8 mm, COD = 2.5 mm) showed symmetric craze/crack growth when sectioned in half and etched. In this material each side craze/crack has initiated an additional smaller one. The material within the craze/crack is uniformly drawn, very coherent in appearance, as shown in Figure 7, and totally absent of voids. Figure 8 is a SEM picture of a sample with an ICL of 7.4 mm

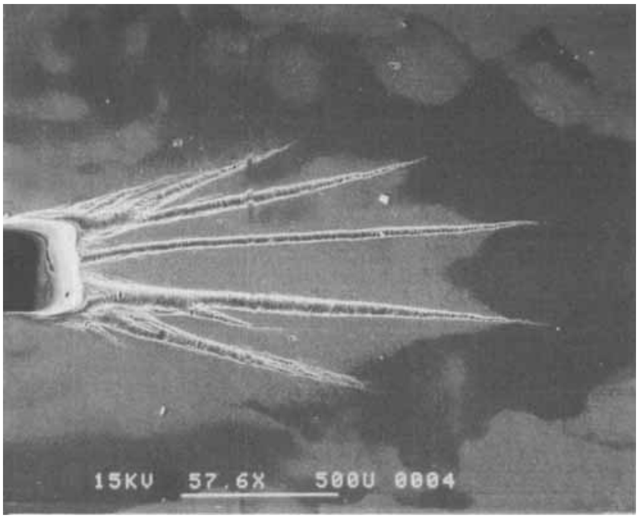

FIGURE 6 Interior surface of Marlex 8600 drawn in air, ICL = 7.8 mm, COD = 2.5 mm.

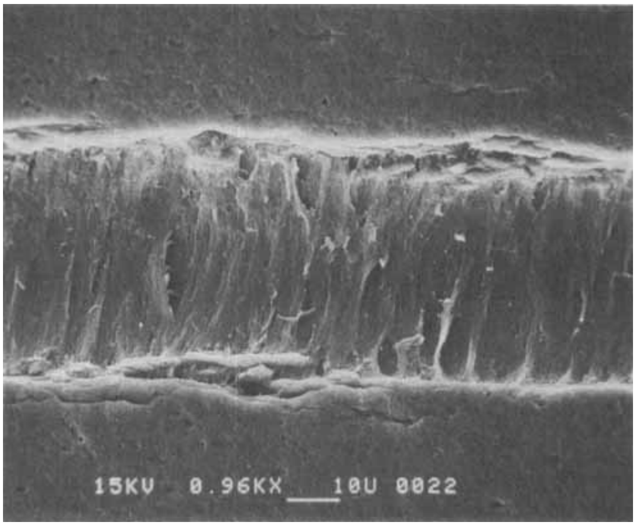

FIGURE 7 Marlex 8600 drawn in air, near base of crack, ICL = 7.8 mm, COD = 2.5 mm.

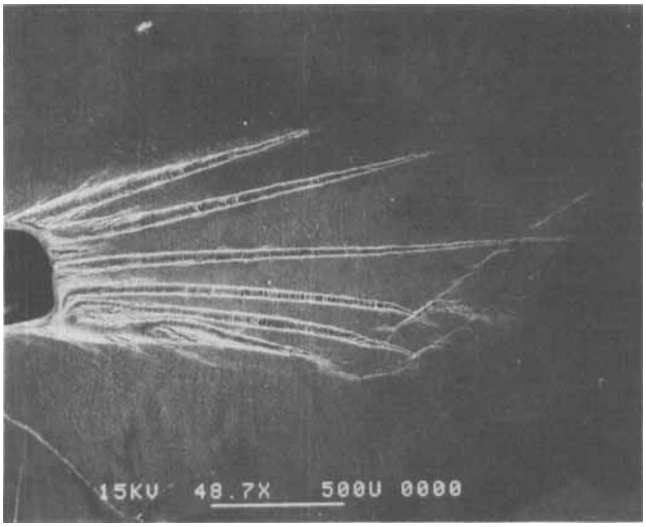

FIGURE 8 Interior surface of Marlex 8600 drawn in an aqueous solution of Igepal, ICL = 7.4 mm. COD = 2.5 mm.

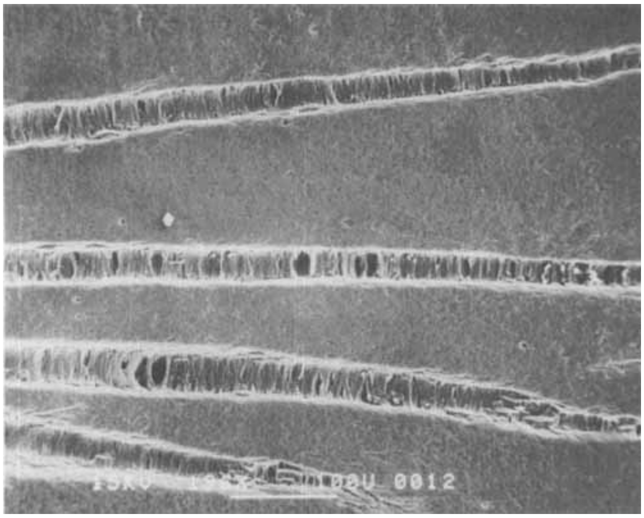

FIGURE 9 Marlex 8600 drawn in an aqueous Igepal solution, ICL = 7.4 mm, COD = 2.5 mm.

pulled in the aqueous Igepal solution until a COD of 2.5 mm was reached. After sectioning and etching, multiple, relatively symmetric crazes/cracks are seen in the sample. Figure 9, a higher magnification picture of the same piece, clearly shows several voids opening up in the crazes, as seen in Marlex 400 samples under similar circumstances. A good example of decreased cohesion caused by the presence of the Igepal solution is shown in Figure 10, a high magnification picture of one of the voids, where broken, retracted, drawn fiber ends are also visible.

Compact tension samples of Marlex 6050 were also tested; however, due to its

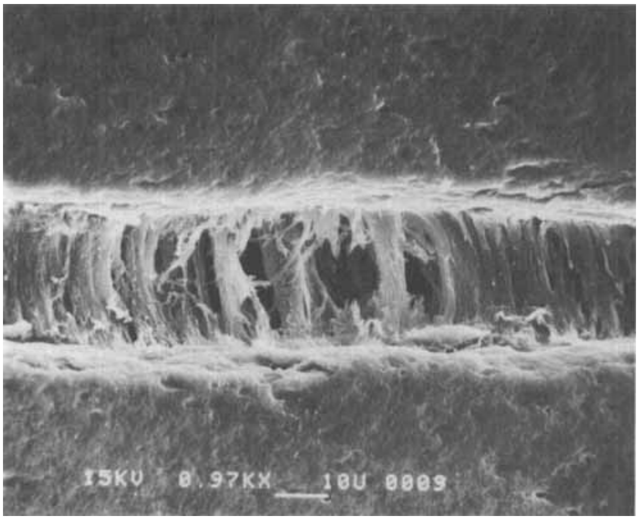

FIGURE 10 Voids formed in a Marlex 8600 sample pulled in an aqueous Igepal solution, ICL = 7.4 mm, COD = 2.5 mm.

low toughness, the specimens cracked in half under very low strain, making observation impossible.

In summary, even though on the surface no crack growth is seen with either Marlex 400 or 8600, internally the initial crack has advanced significantly through crazing and cracking. When crack growth is attempted in the presence of the ESC agent, Igepal CO-630, the material within the crazes is less coherent with voids and large broken fiber ends visible. This is in contrast to the same experiments conducted in air where neither voids nor large broken fibrils were seen. The voids and additional craze/crack arms formed in the presence of the Igepal solution are due to a reduction in cohesion of the drawn material caused by the ESC agent. This conclusion is supported by previous work in this laboratory[13,14] which suggests that under load ESC agents diffuse into and plasticize mainly the amorphous regions, reducing the cohesion between fibrils formed at yield in micronecked regions. The degree of diffusion and plasticization depends on the viscosity and surface tension of the ESC agent[15] since these parameters strongly affect the rate at which the ESC agent flows through the crack/craze.

Tensile bar test

In order to aid the characterization of the deformation process within the crazed regions, the effect of an ESC agent on the morphology of the resulting failure surface of notched tensile bars was studied. This notched tensile bar geometry was chosen in order to approximate the interaction of the ESC agent and the growing crack tip.

Figure 11 shows Marlex 400 drawn at 5.0 cm/min at room temperature in isopropanol. Before pulling, each notched bar was immersed in the isopropanol for several minutes to assure wetting of the samples. The sample's entire cross-section

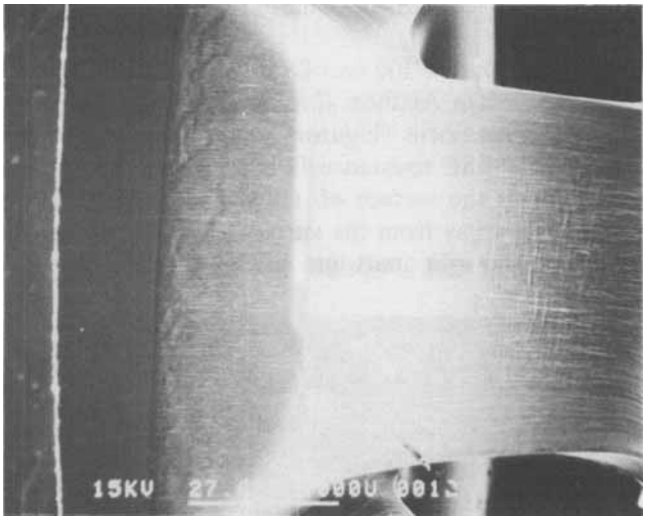

FIGURE 11 Failure surface of Marlex 400 drawn in isopropanol at 5 cm/min. The original razor notch is to the left.

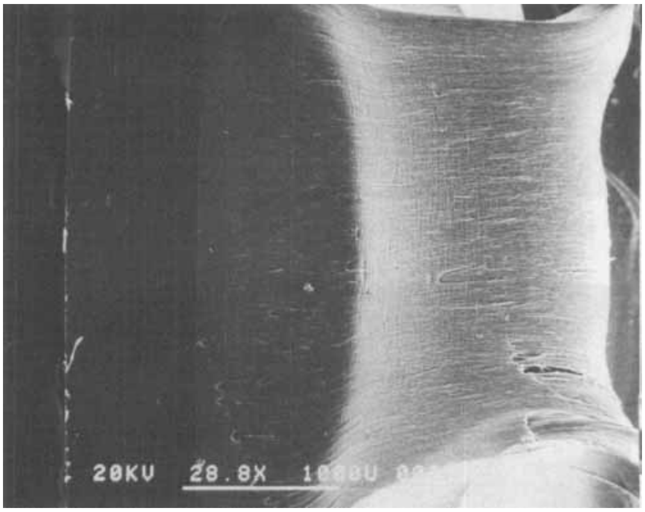

FIGURE 12 Failure surface of Marlex 8600 drawn in isopropanol at 5 cm/min.

(initial razor notch is to the left) is shown in Figure 11. The sample failed in a very ductile manner, as can be seen by the extremely long ligament drawn out of the surface. Failure surfaces of Marlex 400 samples drawn in air at 5.0 cm/min were identical to those for samples drawn in isopropanol.

Marlex 8600 tested in the same way shows nearly the same type of fracture surfaces. Figure 12 shows Marlex 8600 drawn at 5.0 cm/min in isopropanol after being soaked for several minutes. The failure surface of the entire sample shows that failure was again by a very coherent and ductile drawing process. Samples of

Marlex 8600 drawn in air showed the same failure process as did samples drawn in isopropanol.

When comparing the Marlex 400 and 8600 to Alathon 4275 several significant differences were seen. When Alathon 4275 was pulled in the presence of isopropanol at 5.0 cm/min, huge fibrils (Figure 13) are drawn out of the surface. This material has a very poor ESC resistance as is evidenced by examining the failure surface. Figure 14 shows the surface of one of these fibers, in which numerous smaller fibers have split away from the surface. The tip of one of the pulled out fibrils (Figure 15) has also split apart into several fine fibers at its end. This sep-

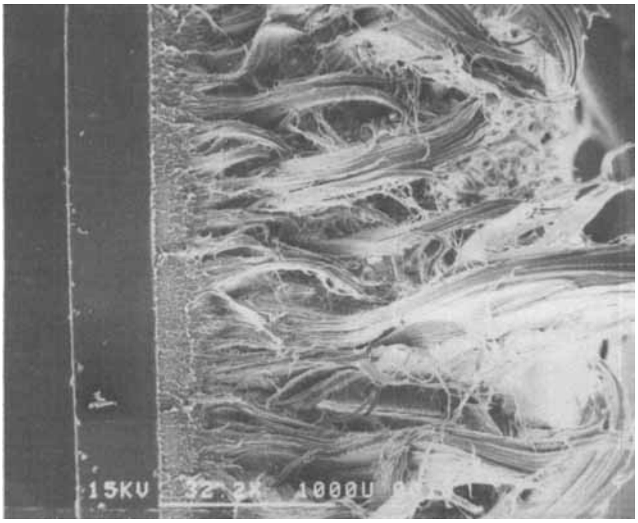

FIGURE 13 Failure surface of Alathon 4275 drawn in isopropanol at 5 cm/min.

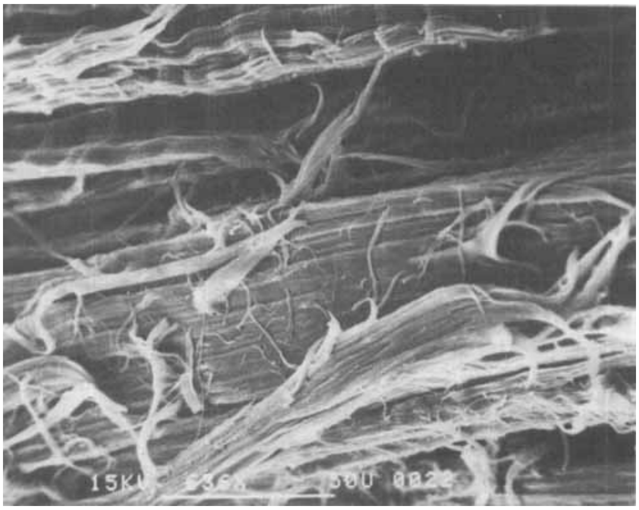

FIGURE 14 SEM micrograph of Alathon 4275 fiber formed during failure in isopropanol at 5 cm/min.

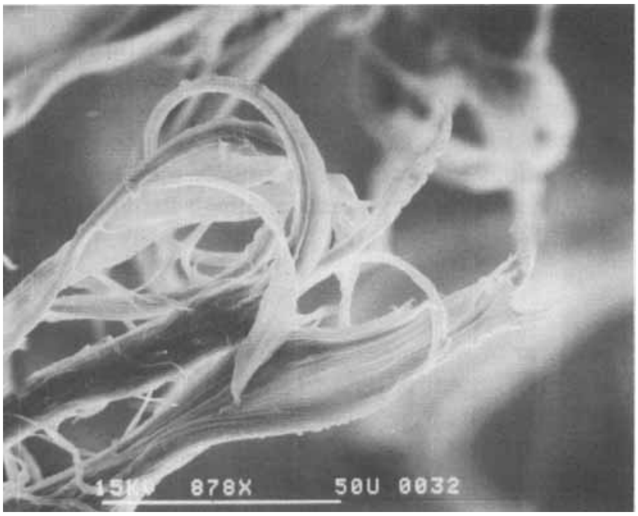

FIGURE 15 SEM micrograph of Alathon 4275 fiber end formed during failure in isopropanol at 5 cm/min.

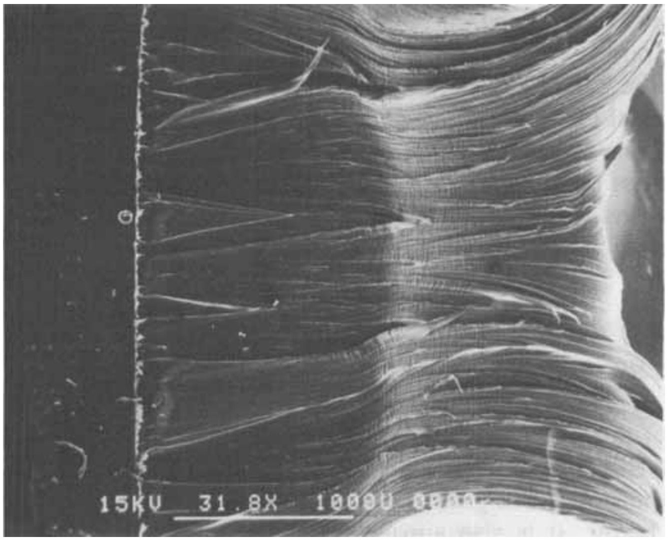

FIGURE 16 Failure surface of Alathon 4275 drawn in air at 5 cm/min.

aration is again attributed to the ESC agent weakening the drawn material's cohesion. Figure 16 is a SEM micrograph of Alathon 4275 pulled at 5.0 cm/min in air; the sample failed in a ductile manner as can be seen by the continuous long ligament drawn out of the surface; there is no fiber pull out or splitting. Samples of all materials (Marlex 400, 8600 and Alathon 4275) tested at 0.5 cm/min at room temperature showed identical results as those tested at 5.0 cm/min.

The results of this study suggest that the "resistance" of the medium density gas pipe resins to the ESC agent used in this study, isopropanol, is much better than that of LDPE. Also, it is clear that the ESC agent's effect is to reduce the cohesion of the drawn material resulting in a highly fibrous fracture surface which is not typical of samples drawn in air. These results also give an indication as to how quickly the ESC agent (in this case isopropanol) can penetrate and affect the deformation process. Although alcohols appear to be more effective as an ESC agent than Igepal solutions, they are not commonly used because of experimental limitations such as their low boiling points and high flammability.

Uniaxial creep

Uniaxial creep behavior of specimens prepared from Marlex 8600 pipe was tested with and without an ESC agent present to study the effects of ESC agents on the creep process. Measurements were taken at three temperatures 30, 40, and 50°C, and three stress levels 1160, 1450, and 1700 psi. The tests were run in either distilled water or a 10 percent by weight solution of Igepal CO-630 in distilled water. An aqueous solution of Igepal was used as the ESC agent in this test, because of the elevated temperatures. Precautions such as having the same machinist turn all the samples and using the same loading weights at each temperature were taken in order to keep the test conditions as identical as possible.

At the lowest stress level, at 30 and 40°, the curves were essentially linear; at the higher stress level and all values for 50°C, the curves rapidly become nonlinear, with the samples undergoing necking and subsequent large scale deformation. Uniaxial creep data collected with and without the presence of the ESC agents during the test yielded similar results within experimental error. Thus this tends to confirm our suggestion that the effect of the ESC agent is primarily on material that has already undergone yield and micronecking, as at the tip of a growing crack.

CONCLUSIONS

The results of this study suggest that the "resistance" of the medium density gas pipe resins to ESC agents is much better than that of LDPE. Therefore, one would also expect the slow crack growth resistance of commercial gas pipe resins to be significantly better. It is also apparent that the ESC agent does not affect the deformation process of PE until the yield stress of a localized region is exceeded. Examples include the crack tip of a compact tension sample and the notched region of a tensile bar. The additional crazes or pulled out fibrils seen in the presence of the ESC agent we suggest is caused by reduced cohesion of the drawn/micro yielded material. On the other hand, the presence of an ESC agent during uniaxial creep experiments had little effect on the creep process. The long term creep properties of the material were not affected by the ESC agent because the stress level was too low. As stated earlier, ESC agents are not expected to affect the deformation process until the sample is placed under a considerable localized stress, enough to cause micronecking and yielding, as would be the case at the tip of a growing craze.

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