

Oxidative Degradation of Poly(ethylene Sulfide)

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Synopsis

Poly(ethylene sulfide) which is a strong, stiff, solvent-resistant thermoplastic resin, upon preparation and molding, undergoes rapid degradation upon aging in air with significant loss in impact strength and other physical properties. This is attributed to surface crazing and shrinking caused by molecular breakdown and crystallization.

Infrared spectral studies show the rapid formation of sulfoxide, sulfone, and carbonyl moieties in the polymer and mass spectral analysis shows the principal gaseous degradation products to be acetaldehyde, carbon dioxide, sulfur dioxide, and water.

The addition of antioxidants, blending with other resins, and polymer modification give only minor improvement in oxidation resistance. This poor oxidation resistance has prohibited the development of poly(ethylene sulfide) as a commercial thermoplastic.

INTRODUCTION

Ethylene sulfide is readily polymerized to a high molecular weight polymer by various anionic or coordinate-anionic catalysts, e.g., by diethylzinc-water initiator (Furukawa catalyst),¹ seed initiator,² reactive zinc oxide,³ or amines.⁴ Ethylene sulfide has also been polymerized by simpler catalysts of the alkali thiolate types,⁵ by the Szwarc initiator sodium naphthalene,⁶ and by various other ionic systems.⁷ Poly(ethylene sulfide) is a high-melting (210°C) crystallizing thermoplastic material with exceptional dimensional stability. It belongs in the class of engineering thermoplastics with tensile strength 10,000 psi, tensile modulus 0.3×10^6 psi, and elongation at break of 15%. Because of its high crystallinity and high sulfur content, it is insoluble in most common organic fluids below its melting point and, hence, is most suitable for applications where high solvent resistance would be required, such as in gasoline tanks, etc.

However, two basic problems have been encountered with this polymer. These are rapid degradation upon molding at elevated temperature⁸ and loss of impact resistance and other physical properties on aging in air. The former problem has been adequately solved by incorporation of additives into the polymer so that the polymer experiences no significant degradation on processing.^{8,9} The latter problem of degradation on aging in air is the subject of this report.

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The sequence of events leading to the deterioration of molded poly(ethylene sulfide) products appears to involve oxidative attack of the surface, particularly in regions of high strain. The oxidation results in random scission and, in addition, apparent rearrangement of the surface molecules to a more orderly placement with concurrent increase of crystallinity and density. A direct effect of this chemically induced morphologic change appears to be shrinking and craze formations at right angles to the mold flow with the related loss in impact strength and other properties influenced by surface defects.

It is assumed that while the surface is changing rapidly under these elevated-temperature aging conditions, the bulk of the polymer is also undergoing a slow physical, rather than chemical, change to higher crystallinity due to greater mobility at the higher temperature. Hence, it is also possible to modify the overall properties of poly(ethylene sulfide) even in the absence of oxygen by this process of annealing.

To maintain initial physical properties, two approaches come to mind readily: (a) inhibition of further crystallization to larger spherulites and (b) prevention of oxidative attack with subsequent degradation at the surface. The techniques employed in the first approach were: nucleation by additives such as potassium thiocyanate and other salts, causing a more microcrystalline stable surface structure; copolymerization to prevent formation of a highly ordered lattice; and blending with suitable polymers. None of these methods was successful with poly(ethylene sulfide). Due to the inherent incompatibility of poly(ethylene sulfide) with other polymers, both nucleation and blending tend to adversely affect its good and even marginal properties. However, a proper selection of the nucleating agent or the second polymer or combinations might lead to the formation of an oxygen barrier at the surface, or at least function to inhibit crystallization and possibly flow into the surface crazes arising from poly(ethylene sulfide) degradation.

Ethylene sulfide is readily copolymerized with other episulfides such as propylene sulfide or allyloxymethylthiirane.¹⁰ No homopolymer of propylene sulfide or allyloxymethylthiirane could be extracted from the copolymer samples. The copolymer with only a low percentage of propylene sulfide exhibits a reduced melting point and loss in physical properties.

As for approach (b), suitable antioxidants are normally very effective in protecting most polymers from oxidative attack, and presumably compounds or combinations can be found to afford similar protection to poly(ethylene sulfide). However, the problems of selection are formidable when one considers that the candidates must first withstand high process temperatures in the presence of reactive thermal stabilizers: secondly, they must be capable of migrating readily through the polymer matrix to the locations where they will protect the surface; and thirdly, they must function by the most appropriate mechanism for that polymer. One cannot readily surmise an antioxidant that functions primarily as a peroxide decomposer to be particularly useful in poly(ethylene sulfide) protection.

An antioxidant for this polymer would need to act as an effective barrier to oxygen migration, healing polymer chains where oxidative scission has occurred, or, less desirably, act as a sacrificial point of attack which would ultimately lead to depletion of the protecting agent.

Two aspects of the study on degradation and stabilization of poly(ethylene sulfide) are reported here. These are the analytical characterization of the effects of oxidative aging on the polymer by mass-spectral, infrared, spectrophotometric, and density techniques, and the effect of aging and some stabilizing additives and blends on physical properties.

EXPERIMENTAL

Polymer Samples

Ethylene sulfide was shaken with an equivolume of aqueous solution containing 5% w/v lead oxide and 50% w/v sodium hydroxide to remove mercaptan impurities. Purified monomer was distilled under vacuum at room temperature.

Samples of purified ethylene sulfide were polymerized in benzene diluent with the following initiators: diethylzinc-water, heat-treated zinc carbonate, and triethylenediamine.

No effort was made to remove zinc-initiator residues, although alkaline residue was titrated with acetic acid and the polymer was waterwashed and vacuum dried. The polymers used in these experiments had molecular weight in the range of 200,000 to 500,000 as calculated from their melt viscosity (ASTM D-1238-57T). Since poly(ethylene sulfide) is a highly crystalline polymer, it cannot be dissolved without serious degradation in conventional solvents below its melting point (210°C).

The polymers of this study are coded as follows: PES I, poly(ethylene sulfide) polymerized with diethylzinc-water initiator; PES II, the same polymer as PES I, but stabilized to thermal degradation by the addition of 2 phr bis[*p*-(2,5-diazapentyl)phenyl]oxide plus 1 phr zinc hydroxychloride^{8,9}; PES III, poly(ethylene sulfide) polymerized with heat-treated zinc carbonate initiator; and PES IV, poly(ethylene sulfide) polymerized by triethylenediamine initiator.

The zinc carbonate initiator is Fisher technical-grade zinc carbonate heated at 250°C for 15 min.

Analytical Characterization

Infrared spectra were obtained on thin films of poly(ethylene sulfide) of 0.01 cm thickness which were prepared by pressing a powdered polymer at 210°C for 1 min under 1000 psi pressure. Absorption data were obtained on the Perkin-Elmer Model 521 infrared spectrophotometer and are reported as absorbance units/cm thickness. Infrared spectra of gaseous samples were obtained by transmission, in a 70-ml Perkin-Elmer gas cell.

Mass spectra of gaseous samples were obtained on the Consolidated Electrodynamic Corporation MS-21-103C instrument at Gulf Research Laboratory, Sheridan Park, Ontario.

Density of the test specimens was determined by the ASTM D-1505-63T method for density of plastics by the density-gradient technique. The density-gradient column was prepared by continuously filling with less dense solution of carbon tetrachloride-toluene and calibrated with glass floats from Scientific Glass Apparatus Co., Bloomfield, N.J.

Melting temperatures were determined using the Fisher-Johns apparatus.

RESULTS AND DISCUSSION

Products from Oxidative Degradation of Poly(ethylene Sulfide)

The gaseous compounds produced when a sample of poly(ethylene sulfide) is heated to 150°C in the presence of air, as identified by mass-spectral and infrared spectrophotometric analysis, are listed in Table I.

TABLE I
Composition of Gas Over PES-I After 10 Days at 150°C in Air^a

Compound	Concentration, mol-%
N ₂	80.0
O ₂	16.9
CO	trace
Argon	1.0
CO ₂	0.5
C ₂ H ₂	0.1
H ₂ O	0.3
CH ₃ CHO	0.8
$\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \diagdown \quad \diagup \\ \text{O} \end{array}$	trace
SO ₂	0.22
COS	0.09
H ₂ S	0.042
CH ₃ SH	0.008
C ₂ H ₆ SH	0.015
CS ₂ and/or CH ₃ SH	0.008
	100.

^a Poly(ethylene sulfide) PES-I, 5 g, was heated in a sealed air-filled 70-ml glass cell.

The principal decomposition products are acetaldehyde, carbon dioxide, sulfur dioxide, and water.

Infrared Spectral Studies on Poly(ethylene Sulfide) Films

Thin (0.01 cm) films of poly(ethylene sulfide) were aged in both nitrogen and air and their infrared adsorption spectrum measured by transmission. Thin films were chosen since their reaction with air would be similar to the

reaction of the surface of a bulk sample with air. The infrared spectra of PES-I as a film at room temperature, in the melt at 220°C and as a re-crystallized film, are shown in Table II.

The absorbance bands at 2960 cm^{-1} , 2815 cm^{-1} , 2700 cm^{-1} , 745 cm^{-1} , and 692 cm^{-1} are assigned to crystallinity since they disappear upon melting. The bands at 1255 cm^{-1} and 840 cm^{-1} due to methylene twisting and rocking modes increase in amplitude upon melting. Upon cooling the melts, the infrared spectrum exhibits a distorted shape (sharp peaks with broad shoulders), indicating a degree of crystallinity of lower homogeneity or the presence of other crystal structure.

TABLE II
Infrared Spectra of PES-I*

Film at room temp.	Liquid at 220°C	Film at room temp. after cooling from the melt
2960w	2930s	2960w
2910m		2920m
2835w	2840w	2840w
2815w		2805w
2700w		
	1715w	
	1575w	1575w
1420s	1420s	1420s
		1370w
1255m	1255s	1260m
1180s	1190s	1185s
1140s	1135s	1140s
		1050w
1015w	1010w	1015w
950w		960w
900w	900w	900w
840w	840m	840w
745w		745w
720s	715s	720s
692w		692w
670s	680w	670s

* IR absorbance bands at wavelength in cm^{-1} , s, m, and w, refer to strong, medium, and weak absorbance, respectively.

Films of PES-I were aged in both nitrogen and air atmosphere at 121°C. The data of Table III record the relative absorption for infrared bands at 1050 cm^{-1} due to sulfoxide groups, 1580 cm^{-1} due to vinylic unsaturation, and 1710 cm^{-1} due to carbonyl groups.

In air, only bands indicative of carbonyl and sulfoxide groups are observed. However, in nitrogen, bands indicative of unsaturation are also observed. No band at 1050 cm^{-1} for sulfoxide groups is observed for films aged in nitrogen. However, this may be due to the relatively low absorptivity coefficient of this band, and thus, for low concentrations, it is below the level of detection.

The concentration of the sulfoxide groups in the poly(ethylene sulfide) films increases rapidly with time on heat aging and then tends to level off at some steady concentration. This suggests that some sulfoxide groups are depleted with time. This is likely due to the further oxidation of sulfoxide to sulfone. Also, the sulfone group is readily split out of the polymer as sulfur dioxide with resulting chain scission of the polymer molecule. The concentration of carbonyl groups in poly(ethylene sulfide) tends to increase rapidly over the first 24 hr and then tends to increase more slowly thereafter. This decrease in rate of carbonyl formation is attributed to the

TABLE III
Increase in Infrared Absorbance Bands on Aging at 121°C of PES-I Films^a

Time, hr	In air		In nitrogen	
	=CO	=SO	=CO	—CH=CH ₂
	A at 1710 cm ⁻¹	A at 1050 cm ⁻¹	A at 1710 cm ⁻¹	A at 1580 cm ⁻¹
0.5	1.01	n.d.	—	—
1	1.00	n.d.	—	—
2	1.09	n.d.	0.70	0.47
3	1.00	n.d.	—	—
4	1.59	n.d.	0.94	—
8	3.03	n.d.	1.05	0.66
16	4.43	1.87	0.99	0.93
24	5.25	2.79	0.97	1.43
48	9.45	5.32	1.31	1.33
72	—	—	1.43	1.75
96	11.79	5.85	1.40	1.82
120	12.50	4.48	1.42	1.77
144	11.48	4.18	—	—
168	—	—	1.75	1.82
192	14.92	5.18	—	—
240	14.92	5.38	2.20	2.19
360	—	—	4.21	—
480	—	—	1.68	1.97
960	—	—	1.92	2.08

^a A = (Absorbance/cm thickness) × 10³.

the loss of the oxidized group as acetaldehyde and CO₂ for simultaneous chain scission. The formation of some carbonyl groups in the polymer films aged under high-purity nitrogen may be attributed to reaction with air trapped in the polymer.

The band at 1580 cm⁻¹ is assigned to vinylic unsaturation, which is confirmed by the presence of bands in the infrared spectrum in the 900 cm⁻¹ region. The 1580 cm⁻¹ band increases rapidly with time when the polymer films are aged in nitrogen. This increased unsaturation is likely the simple product of homolytic thermal scission of the polymer with concurrent formation of mercapto endgroups.

Density Changes in Poly(ethylene Sulfide) Films on Aging at 121°C

The curves relating density of poly(ethylene sulfide) of type PES-II to aging time at 121°C in both air and nitrogen are shown in Figure 1. The density of polyethylene sulfide as synthesized is 1.360. In general, the density increases rapidly with time. An increase in density is due to crystallization with its accompanying compaction. The rate of crystallization of polymers increases as the molecular weight decreases, probably owing to molecular mobility and ease of ordering into crystal spherulites. Therefore, upon thermal scission, the molecular weight decreases and density increases. The rate of density change is a function of recrystallization, of molecular weight decrease due to both thermal and oxidative scission, and of the retardation of these phenomena by antioxidant protection or stereochemical interference. Of interest is the observation that density increases slowly in air during the early hours of aging at 121°C (that is, ≤ 20 hr) and then accelerates with aging time after 20 hr. This inhibition of crystallization during the early aging hours is attributed to the formation of sulfoxide groups as evidenced in the infrared spectrum. These sulfoxide groups inhibit crystallization by interfering with the folding and packing of polymer molecules into the crystal spherulites. The increased rate of crystallization for aging in air after 20 hr is likely due to accelerated chain scission proceeding via an oxidative mechanism as evidenced by the greater rate of carbonyl formation. Presumably the carbonyl functionality is concentrated at aldehydic endgroups since crystallization is not inhibited.

The spherulites of poly(ethylene sulfide) have been observed by optical microscopy to grow in size with aging time.¹¹ The lower rate of crystallization of poly(ethylene sulfide) when aged in nitrogen over the first 100 hr may be attributed to simple thermal reordering and spherulite growth since the effect of trace oxygen is small.

The Effect of Aging on Physical Properties

Both PES-I and the thermally stabilized PES-II were tested for impact strength, tensile strength, tensile modulus, and elongation after several hours of aging with and without antioxidant protection.

Approximately 5-kg lots of the recipes shown in Table IV were mixed in a twin-shell dry blender (Patterson Kelley Co. Inc., E. Stroudsburg, Pa.) and injection-molded to form tensile, Izod, and tensile impact testpieces for testing according to ASTM D638-68.

Test data on impact strength, tensile strength, tensile modulus, and elongation as a function of aging are shown in Tables V, VI, VII, and VIII, respectively.

Poly(ethylene sulfide) samples as stabilized in compounds A and B undergo rapid loss of overall physical properties when exposed to air at 120°C and 200°C for short times. However, the latter compound exhibits somewhat better antioxidant properties in that it appears to offer adequate protection for at least one day at 120°C. Loss through evaporation or re-

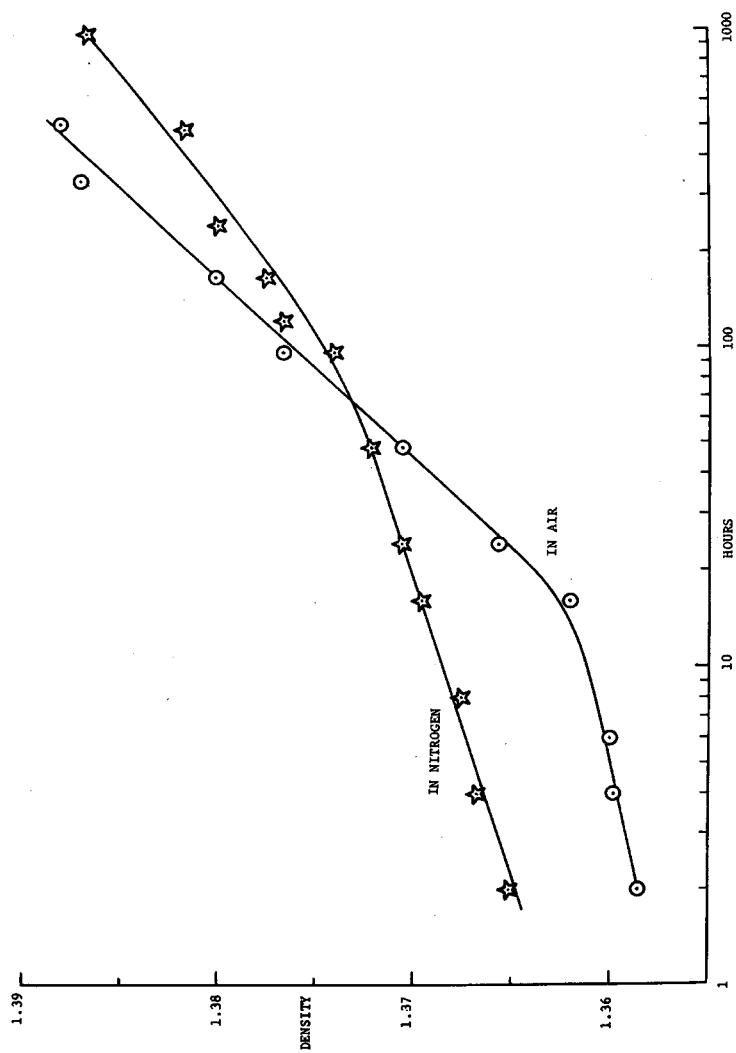


Fig. 1. Density of PES II with aging at 121°C.

TABLE IV
Recipes for Compounds A, B, C, and D

	A	B	C	D
PES-I	—	100	—	100
PES-II	100	—	100	—
ABS resin (Marbon 201) ^a	—	—	25	25
Triethylenetetramine (TETA)	—	1	—	1
Potassium thiocyanate	—	1	—	1
Zinc oxide	—	1	—	1
Zinc dibenzylthiocarbamate	—	1	—	1
Copper diethylthiocarbamate	—	0.1	—	0.1

^a Product of Borg-Warner Corp.

TABLE V
Izod Impact Strength^a

Aging conditions	Series A	Series B	Series C	Series D
Unaged	1.11	1.16	0.30	0.47
Recycled, unaged	1.07	1.12	0.49	0.47
1 day at 120°C	0.35	0.96	0.33	0.50
7 days at 120°C	0.20	0.33	0.36	0.47
21 days at 120°C	0.18	0.28	0.28	0.63
1 hr at 200°C	0.26	0.32	0.26	0.52

^a In units of ft-lb/in.

TABLE VI
Effect of Air Aging on Tensile Strength^a

Aging conditions	Series A	Series B	Series C	Series D
Unaged	9.6	9.9	8.5	8.6
Recycled, unaged	9.6	9.6	7.8	7.7
1 day at 120°C	6.3	9.5	7.7	8.6
7 days at 120°C	4.2	5.7	3.9	5.5
18 days at 120°C	4.0	5.0	4.0	4.9
1 hr at 200°C	7.9	8.8	7.6	7.7

^a In units of psi $\times 10^{-3}$.

action of the antioxidant at the surface is apparently irreversible and not supplanted by further migration from the interior of the test specimen.

Aging of PES-II results in surface discoloration due primarily to the amine (none or little discoloration occurs on aging unstabilized poly(ethylene sulfide)). In conjunction with this discoloration, crazing perpendicular to the direction of mold flow increases rapidly, apparently because of volume shrinkage. Part of the shrinkage may be attributed to weight loss, but it is most likely the result of chain scission due to oxidation attack resulting in an increase of crystallinity and density. Onset of crazing is considerably delayed in the case of formula B.

TABLE VII
Effect of Air Aging on Tensile Modulus^a

Aging conditions	Series A	Series B	Series C	Series D
Unaged	2.8	3.0	3.0	3.0
Recycled, unaged	3.2	2.8	3.0	3.4
1 day at 120°C	3.8	3.2	3.2	3.4
7 days at 120°C	3.6	3.2	3.4	3.4
21 days at 120°C	3.8	4.0	4.1	4.0
1 hr at 200°C	4.0	4.0	4.0	4.0

^a In units of psi $\times 10^{-5}$.

TABLE VIII
Effect of Air Aging on Elongation^a

Aging conditions	Series A	Series B	Series C	Series D
Unaged	13.8	15.0	13.0	15.7
Recycled, unaged	12.4	12.9	8.8	8.5
1 day at 120°C	4.3	9.7	7.7	8.8
7 days at 120°C	2.6	4.2	2.5	3.9
21 days at 120°C	2.8	3.5	2.5	3.6
1 hour at 200°C	6.9	10.9	8.3	8.1

^a In units of %.

Modulus (Table VII) tended to increase for all test pieces significantly with aging, possibly indicating an increase in crystallinity in the bulk of the test sample, due to an annealing process without any concurrent degradation, such as occurs at the surface which is directly in contact with oxygen.

The changes influencing Izod impact strength on aging are largely phenomena related to surface morphology. Bucknall has shown that the formation of a brittle layer on the sample surface markedly reduces impact strength.¹² The bulk of the polymer is not appreciably affected by aging as determined by the physical data on samples obtained from test pieces that were reground and extruded. Similarly, the impact data obtained on molded samples that were notched after aging gave values similar to those for nonaged samples.

Stabilizer Systems

Variations of the components in the TETA/KSCN/zinc oxide/zinc dibenzylthiocarbamate/copper diethylthiocarbamate system (compounds B and D) have been investigated with the hope of improving the antioxidant properties to an acceptable level and to determine more precisely the important chemical groups required for protection.

It has been shown that an amine⁸ is essential to impart adequate thermal or processing stability, however, no extensive correlation has been obtained relating base strength, structure, concentration, and stability to stabilizing ability. Structures containing aliphatic polyamine chains appear to be the most effective as shown by melt viscosity measurements in the presence

of triethylene tetramine and Dow Amine F (4,4-bis[N-(β -aminoethyl)-aminomethyl]diphenyl ether), with allowances made for molecular weight.

Zinc dibenzylthiocarbamate has proved to be one of the most successful dithiocarbamates as a major component in the stabilizer system. However, other sulfur-containing compounds are also effective. The extent of their effectiveness appears broadly related to their thermal stability and mole concentration within family groups.

Although quite adequate thermal stability is imparted without copper ion in the formulation, a significant improvement is noted when copper is introduced in very low quantities and in a readily dispersible form. Manganese is also effective, and it is anticipated that other metal compounds can be used with similar positive results.

Thiocyanates of the various alkali metals can be used interchangeably. The presence of zinc oxide in the formulation is necessary to obtain maximum thermal stability. Various other zinc salts and diphenyltin oxide are virtually useless as replacements. However, it is interesting to note, contrary to their behavior in the present formulation, zinc hydroxychloride and diphenyltin oxide are superior to zinc oxide when used with Dow Amine F.

Blending with Other Resins

Compounds C and D for which physical properties are reported in Tables V, VI, VII, and VIII are the same basic compound formulations as compounds A and B, respectively, with the addition of 25 phr of Marbon 201 ABS resin (Borg-Warner Corp.).

The blending of poly(ethylene sulfide) with Marbon 201 ABS resin results in improved extrusion and smoother surfaces. Although initial Izod impact values (Table V) are relatively low, they are slightly improved with aging, and no crazing is apparent at the surface even after two months aging. Loss of elongation was similar for both blended and unblended samples on aging (Table VIII).

A survey of other ABS modifying resins revealed that the low initial Izod impact values reported for blends with Marbon 201 could be improved somewhat. Unfortunately, the aged specimens failed to hold up and showed up actually inferior to the Marbon 201 blends under more severe conditions of aging. As previously, elongation and tensile strength were adversely affected in all blends while the modulus increased.

As might be expected, stress relaxation data obtained at 3% strain at room temperature indicated that considerable creep is introduced by blending, which negates one of the important properties of poly(ethylene sulfide). Aging decreases the stress relaxation appreciably, reflecting the increase in tensile modulus previously noted.

Comments on Mechanism of Oxidative Degradation

In the oxidative degradation of poly(ethylene sulfide), the attack of oxygen at both the sulfur atom and the α -carbon atom should be similar to

that proposed by Colclough et al.¹³ for degradation of monosulfidic cross-links in conventional elastomers.

The major gaseous product of oxidation is acetaldehyde. This compound could be generated from a two-step process involving the prior formation of aldehydic endgroup or from simultaneous oxidation of adjacent repeat units in the polymer chain. This latter might involve the formation of $\text{CH}_2=\text{CH}-\text{OH}$ as an intermediate with the formation of either a sulfide or sulfoxyl radical or their combination product. The presence of ethylene oxide in the products can be accounted for by rearrangement of some of the vinyl alcohol or direct oxidation of ethylene formed by thermal scission.

CONCLUSIONS

The studies on the oxidative aging of poly(ethylene sulfide) described in this paper illustrate the basic problems encountered with this plastic, i.e., loss of strength and toughness upon exposure to air. The system of additives and blends described, as well as others undisclosed, impart only a small measure of oxidative stability to poly(ethylene sulfide). Even the most promising additives exhibited some critical disadvantage, including expense and toxicity, so that the development of a commercial poly(ethylene sulfide) plastic has been suspended.

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