**STUDIES ON ELECTRICAL CABLE INSULATION
FOR NUCLEAR APPLICATIONS**

**B.S. LEE
P. BLACKBURN*
P. SOO
D.R. MACKENZIE**

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**BROOKHAVEN NATIONAL LABORATORY
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***Science Teacher at Beloit Jr.-Sr. High School, Beloit, KS.**

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ABSTRACT

Two new polyethylene cable insulations have been formulated for nuclear applications, and have been tested under gamma radiation. Both insulations are based on low density polyethylene, one with PbO and the other with Sb₂O₃ as additives. The test results show that the concept of using inorganic anti-oxidants to retard radiation initiated oxidation is viable, and PbO is more effective than Sb₂O₃ in slowing down radiation initiated oxidation (RIO). Also, radiation degradation data for polyethylene and polyvinyl chloride at 60°C have been generated, which will be used to understand radiation initiated oxidation process on these materials combined with the 25°C data that will be generated in the future.

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1. INTRODUCTION

The first comprehensive study of gamma radiation damage to insulation and jackets for electrical cables in nuclear reactor systems was conducted by Blodgett [Blodgett, 1969] two decades ago. In this study, thirteen different kinds of polymer were evaluated up to a total dose of 5×10^7 rads at a dose rate of 5×10^5 rads/h. It was estimated that the total radiation dose absorbed by a cable within the containment area may approach 5×10^7 rads during an assumed reactor lifetime of 40 years if there were no abnormal bursts of energy. One of the conclusions drawn from this study was that CSPE (chlorosulfonated polyethylene) or CPE (chlorinated polyethylene) jacketed insulation based on nonfilled CLPE (cross-linked polyethylene) or carbon filled CLPE should last at least 40 years when exposed to a total radiation dose up to 5×10^7 rads and would still be serviceable after exposure up to 10^8 rads.

However, in November 1976 an inspection of a pump suction valve in the Savannah River K-reactor at Aiken, South Carolina, revealed badly embrittled polyethylene (PE) insulation on the power control wiring. The maximum dose experienced by the cable materials was only 2.5×10^6 rads during the 12 years of operating life. The subsequent check of other cables in the C- and P-reactors disclosed more embrittled cables [Clough, 1982]. It was surprising to find this faster-than-expected degradation of the cables, so Clough and Gillen [Clough, 1982] conducted an extensive investigation of cable degradation by radiation.

The most important finding from the study of Clough and Gillen was that when oxygen exists in the environment, dose rate is another important parameter to consider in addition to total dose in the polymer degradation processes. It was also shown that strong synergisms of radiation and elevated temperature, as well as dose rate, led to unexpectedly rapid degradation of the Savannah River reactor cables.

These findings can be explained by the effects of diffusion of oxygen into the cable materials during service (see next section for detailed discussion). Thus, the degradation process for the cable insulation and jacket under radiation can be termed radiation initiated oxidation (RIO).

More studies have since been conducted to understand the mechanisms for RIO and to find means to control the degradation processes. Still, current knowledge on this subject is not enough to accurately predict the service lifetime for the cables for a given environment.

The objectives of the current study are to:

1. develop a polymer insulation material with prolonged service lifetime,
2. develop lifetime prediction procedures for the cables, by studying mechanisms for RIO.

To accomplish the above objectives, this study was conducted in two parts, which are described below:

PART 1. RIO Study on Polyethylene and Polyvinylchloride at Elevated Temperatures

To help understand RIO process on polyethylene (PE) and polyvinylchloride (PVC), samples were irradiated at a moderate dose rate (6.2×10^5 rad/h) at 60°C. This work is a joint study between BNL and Ontario Hydro of Canada; Ontario Hydro is responsible for experiments at 25°C. The results from the two studies will be combined and compared, and a better understanding of RIO processes on PE and PVC is expected as a result of this study.

PART 2. Development of Radiation Resistant Cable Insulation

In this study, new polymer insulations will be formulated and tested. The data and experience from this study will be used for future cable insulation development.

2. CURRENT UNDERSTANDING OF RIO

The two most important reactions induced by high energy radiation are main chain scission and crosslinking, which are schematically described below:

Main chain scission [Schnabel, 1981]

Crosslinking [Schnabel, 1981]

Polymers typically undergo simultaneous scission and crosslinking, but in most cases with one or the other clearly predominating [Clough, 1988]. Polyethylene and polyvinylchloride predominantly undergo crosslinking when irradiated in the absence of oxygen as shown in Table 2.1 [Clough, 1988]. It is believed that crosslinking is also the major degradation process after the dissolved oxygen in the polymer is used up in the case of high dose rate radiation. For many polymers, radiation induced oxidation strongly favors chain scission. Very frequently, materials, which predominantly crosslink when irradiated under inert conditions, undergo predominantly scission under oxidizing conditions. Also, for many materials, the presence of oxygen strongly enhances the extent of degradation; this can apply when oxygen is present during irradiation, and also when materials are exposed to oxygen following irradiation [Clough, 1988]. Clough summarized the current knowledge on radiation induced oxidation mechanisms, and the following is quoted from his work [Clough, 1988].

Table 2.1

Classification of Polymers
According to Their Predominant Degradation Mode
When Irradiated Under Inert Atmosphere Conditions
[Clough, 1988]

<u>Polymers Which Undergo Primarily Chain Scission</u>	<u>Polymers Which Undergo Primarily Crosslinking</u>
Polyisobutylene	Polyethylene
Poly- α -methylstyrene	Polypropylene
Polyvinylidenechloride	Polystyrene
Polyvinylfluoride	Poly(vinylchloride)
Polychlorotrifluoroethylene	Poly(vinyl alcohol)
Polytetrafluoroethylene	Poly(vinyl acetate)
Polyacrylonitrile	Poly(vinylmethylether)
Polyvinylformal	Polybutadiene
Polyvinylbutyral	Polychloroprene
Polymethylmethacrylate	Poly(styrene-co-acrylonitrile)
Polymethacrylamide	Poly(styrene-co-butadiene)
Polymethacrylonitrile	Poly(butadiene-co-acrylonitrile)
Polyoxymethylene	Natural Rubber
Poly(propylene sulfide)	Chlorinated polyethylene
Poly(ethylene sulfide)	Chlorosulfinated polyethylene
Cellulose	Polyamides
Polyalanine	Polyesters
Polylysine	Polyurethanes
DNA	Polysulfones
	Polyacrylates
	Polyacrylamides
	Polydimethylsiloxane
	Polymethylphenyl siloxane
	Phenol-formaldehyde
	Urea-formaldehyde
	Melamine-formaldehyde

"RIO Mechanisms

Oxygen, when present, will react with the free radicals generated upon irradiation of polymers. The degradation mechanisms which occur are largely comprised of oxidative reactions that are basically similar to those that apply to the oxidation of organic materials under the influence of other environments (i.e., elevated temperature, ultraviolet light, mechanical stress, chemical initiation involving radicals, etc.). The equations below outline the important reactions in RIO.

Because of its high diffusional mobility and its high reactivity toward radicals, oxygen serves to trap radicals in a very efficient manner, greatly impeding the radical reaction pathways which occur in the absence of O_2 , and channelling the course of the reactions into predominantly oxidative routes. Chemical reaction products include oxidized structures within the polymer, such as ketone, carboxylic acid, and alcohol functionalities, as well as peroxidic species. Gaseous products generally include those arising under inert atmosphere irradiation, together with significant amounts of CO_2 , CO , and H_2O . The oxidation chemistry which occurs can lead to entirely different molecular changes compared with those resulting under inert atmosphere. Oxidative reactions frequently favor chain scission.

A particularly important feature of the radiation-oxidation mechanism above, as compared with the radiation mechanism for inert atmosphere conditions is the occurrence of chain branching steps. The breakdown of peroxides (eq. 4) generates further radicals which enter into chemical reactions just as do radicals generated directly by the action of the radiation. This has two important implications. First, since numerous peroxides can potentially be formed from each radicals via repetitive propagation steps (eqs. 2 and 3), and

since each peroxide can decompose to yield two new radicals (eq. 4), this mechanistic feature can potentially give rise to an enormous enhancement of the total number of free radicals generated in the system, compared with the inert atmosphere situation. This type of chemical reaction has the potential for a greatly enhanced extent of degradation per equivalent dose. Secondly, peroxide decomposition (eq. 4) is a thermally-induced process having a moderately low activation energy, which introduces a time-temperature dependence into the degradation process. This in turn, can give rise to major dose-rate, temperature and post-irradiation effects."

3. GAMMA IRRADIATION FACILITY AT BNL

The gamma pool facility contains more than 100,000 curies of cobalt-60. The pool is 8 ft. by 10 ft. by 13 ft. deep. The water depth provides shielding from the Cobalt-60 gamma sources located at the bottom of the pool. The pool liner is a stainless steel tank, 3/8 in. thick at the sides and 1/2 in. thick at the bottom. A water chiller maintains the pool temperature at 10°C to prevent algae growth. The filter system contains two on-line fiber filters in the recirculation system, and a standby set of ion-exchange beds that can be valved into the system.

The cobalt is in the form of "pencil," "tabs," or "flat" sources encapsulated in stainless steel tubes or sleeves. The tubes are held in arrays in stainless steel source racks at the bottom of the pool in an upright, cylindrical orientation, arranged around the circumference parallel to the axis. The tubes form a cylinder about 6 in. diameter and 12 in. high. Most of the source arrays are inside open-topped lead casks. (The purpose of the casks was to provide shielding to prevent the arrays from interacting. Thus, dose rates at one source array were essentially entirely due to the cobalt contained in the array.)

There are 23 source arrays; the weakest sources contain less than 50 curies, the strongest has about 16,000 curies. Stainless steel air tubes 16 ft. long x 4 in. od x 16 gauge wall thickness are inserted vertically into the centers of the source arrays and rest on the bottom of the pool. One inch lead jackets around the air tube above the water level counterweigh the tube buoyancy, as well as providing shielding to personnel. The dose rates for the sources (at the bottom of the air tubes) range from kilorads per hour to megarads per hour.

4. RIO STUDY ON PE AND PVC AT ELEVATED TEMPERATURES

As discussed in the previous section, the diffusion rate of oxygen through a polymer is one of the major parameters in the RIO process. For a given specimen, the diffusion rate is determined by boundary conditions such as the oxygen concentration in the atmosphere and by temperature. In this task, which is a joint effort with Ontario Hydro, BNL will study the effect of temperature while Ontario Hydro will study RIO using oxygen concentration as an experimental parameter.

4.1 Experimental

4.1.1 Sample Preparation

Samples of polyvinylchloride (PVC) and crosslinked polyethylene (CLPE) were prepared by Ontario Hydro in a dogbone shape whose dimensions are shown in Figure 4.1.

4.1.2 Description of the Heater

Heating tape was wound around an alumina tube (o.d.: 5 cm, i.d. : 3.9 cm, length: 34 cm). The tape was surrounded by glass wool insulation and aluminum foil. The assembly was inserted into a steel basket (i.d: 9 cm, depth: 35 cm). Two thermocouples were used, one connected to the temperature controller and the other to the recorder. After the first run in the gamma pool, it was found that the jackets of the thermocouple wires were severely damaged. Thus, alumina thermocouple jackets were used for the latter experiments.

A time proportioning type temperature controller (Model 22) from Omega Engineering Inc. was used to control the sample temperature. Cold junction compensation is built into the controller. For the temperature recorder an Electronic Ice point (model MCJ) from Omega Engineering Inc. was used for cold junction compensation.

4.1.3 Irradiation

A dose rate of 6.2×10^5 rad/hour was used, and the sample temperature was kept at $60 \pm 0.5^\circ\text{C}$.

4.1.4 Mechanical Testing

An Instron tensile testing machine was used to measure elongation and tensile strength. At first, wedge type grips were used, but later were switched to a pneumatic type which performed better. The wedge type grips sometimes caused premature failures at the grip sites due to the high stresses in that area.

A displacement rate of 5 cm/minute was used. A one inch gauge was marked at the center of the sample, and the distance between the gauge marks was followed until the sample failed.

Figure 4.1 Samples used for RIO study at 60°C.
Left: CLPE, Right: PVC

4.2 Results and Discussion

The results from the mechanical tests for PE and PVC samples are shown in Figures 4.2. For the range of doses used, PE outperformed PVC, which may be partly due to the higher ductilities of the unirradiated PE samples than those of PVC. The generally accepted criterion for nuclear cable insulation is that the elongation should be higher than 50 % at a total dose of 10^8 , and both PE and PVC samples showed elongations higher than 50 % at a total dose of 10^8 rads. However, it should be noted that the dose rate used, 6.2×10^5 rad/hour is much higher than that expected in service.

4.3 Summary and Recommendations

For the dose rate and the temperatures used, PE performed much better than PVC. Unfortunately, the room temperature data from Ontario Hydro are not yet available. The following future studies are recommended.

1. It is recommended that room temperature elongation data be generated by BNL. In this way, two sets of tests run at different temperatures will be generated under the same radiation conditions, which will make the comparisons more meaningful.
2. If time and resources permit, it is desirable that this study be expanded to include one more polymeric material and to study dose rate effects and temperature effects on polymer degradation.

Figure 4.2 Elongation for CLPE and PVC as a function of total dose.

5. DEVELOPMENT OF A RADIATION RESISTANT POLYMER INSULATION

5.1 Development Strategy

Some of the early ideas to use inorganic additives to enhance radiation resistant polymer insulation have been documented previously [Mackenzie, 1989]. A copy of MacKenzie's memorandum is attached as an Appendix.

In attempting to reduce radiation initiated oxidation, one could consider adding chemicals to the polymer so that oxygen or radicals are consumed by reacting with the additives rather than with the polymeric structure itself.

Adding conventional antioxidants might be a useful approach, but this is not at all clear. Antioxidants are of four main types, all organic -- phenolics, amines, phosphites, and thioesters [Juran, 1988]. They have been developed to protect plastics against oxygen reactions initiated by heat and UV, but not gamma radiation. Thus, while they would presumably be of some help because of their chain terminating reactions, they themselves could form radicals and initiate oxidation under radiation, since they are also organic.

As an alternative to organic antioxidants, one could consider inorganic reducing agents. These would include, besides certain elements such as carbon, salts with cations in the reduced state, salts with reducing anions, or salts with both. Also, salts of certain organic acids might be appropriate, such as sodium gluconate, or sodium oxalate. Some of the cations and anions of interest include:

- Low valence states of the transition elements, e.g., Fe^{2+} , Mn^{2+} , Cr^{2+} , Co^{2+} . They might be used as oxides or as salts such as sulfate, phosphate, or possibly chloride.
- Multivalent cations in nitrogen family such as As^{3+} , Sb^{3+} and Bi^{3+} . Arsenic would probably not be welcomed by the user community.
- Multivalent cations in carbon family such as Pb^{3+} .
- Reducing anions which might be useful are sulfite, selenite, and phosphite.
- The reduced form of a cation could possibly be used as a salt with a reducing anion.

5.2 Choice of Polymer

Currently, PVC and low density polyethylene (LDPE) are widely used for cable insulation due to their good extrudability combined with good insulation properties. These materials also show acceptable radiation resistance, and a fair amount of data on radiation effects on these is available. High density polyethylene (HDPE) is less radiation resistant than LDPE at both high and low dose rates [Clough, 1988]. PVC is more sensitive to dose rate effects than LDPE (see Table 5.1), and cable makers generally prefer LDPE. Thus, LDPE was chosen as the base polymer for this study.

Table 5.1

Comparison of the Dose Required to Reduce the Elongation
at Break to 50% of Original, Under Low Dose Rate Condition
in Air vs. High Dose Rate (or Inert Atm.) Conditions
[Clough, 1988]

Polymer Type	Dose (in Gy) Req'd at 5-50 Gy/h in Air	Dose (in Gy) Req'd at Very High Dose Rate, and/or Inert Atmosphere
Phenol-formaldehyde (55% asbestos fiber, 9% sawdust)	3×10^6	5×10^7
Phenol-formaldehyde (47% sawdust)	2×10^6	6×10^6
Polyester (15% glassfiber, 56% inorganic filler)	2×10^6	5×10^7
Polystyrene	5×10^5	2×10^7
Chlorosulfonated Polyethylene	5×10^5	8×10^5
Polystyrene-butadiene (blend)	4×10^5	2×10^6
Poly(ethylene-co- vinylacetate)	4×10^5	2×10^6
Poly(ethyleneterephthalate)	3×10^5	3×10^6
Ethylene-propylene rubber	3×10^5	7×10^5
Polychloroprene	3×10^5	5×10^5
Silicone rubber	2×10^5	3×10^5
Poly(vinylchloride) (plasticized)	10^5	2×10^6
Low-density polyethylene	10^5	9×10^5
Poly(ethylene-co- tetrafluoroethylene)	8×10^4	6×10^5
Natural rubber	7×10^4	1.5×10^6
Polyamide (aliphatic)	2×10^4	4×10^5

5.3 Choice of Additives

As discussed earlier, several additives could be tried for this study. However, due to the limitation on time and resources, only two additives were selected, Sb_2O_3 and PbO , after discussions between the principal researchers at BNL and Rockbestos Cable Company in Connecticut. This company agreed to assist us in our work primarily by preparing the new polymer formulations.

5.4 Experimental

5.4.1 Sample Preparation

As shown in Table 5.2, LDPE samples with seven different compositions were molded into sheets of 15 x 15 x 0.17 cm by Rockbestos. The seven compositions are a LDPE control without additives, and LDPE with two different additives at three different concentrations.

Dogbone shaped samples shown in Figure 5.1 were stamped from the sheets using a hydraulic press and an ASTM recommended die. Sample ID's were indented on both ends of the samples. A batch of 14 samples (two for each composition) were stacked together with spacers between samples. The samples were degreased with alcohol before irradiation.

5.4.2 Mechanical Testing

An Instron tensile testing machine was used to measure elongation and tensile strength. At first, wedge type clamp was used, but later was switched to pneumatic type clamp which performed better. The wedge type grips sometimes caused premature failures at the grip sites due to the high stresses in that area.

A displacement rate of 5 cm/minute was used. A one inch gauge was marked at the center of the sample, and the distance between the gauge marks was followed until the sample broke.

5.5 Results

The results from the elongation measurements as a function of total dose are shown in Figures 5.2 - 5.19. The effects of different concentrations of PbO and Sb_2O_3 on the elongation are shown in Figures 5.20 - 5.22 and Figures 5.23 - 5.25, respectively. Figures 5.26 - 5.32 show the effects of dose rates on the elongation properties of the samples with seven different compositions irradiated up to 5.4×10^8 rads.

The elongations of six samples with different compositions, A - F, irradiated at three different dose rates are compared with those of control samples Z (no additives) in Figures 5.2 - 5.19. At the highest dose rate used, 1.1×10^6 rad/h, samples A - D behaved very similarly to the control sample. Samples E and F seem to have a little higher elongations compared to the control samples up to the total dose of 5×10^7 rads, but the differences might not be significant.

Table 5.2
Compositions of Test Samples

Sample ID	Composition (weight %)
A	LDPE homopolymer + 1% PbO
B	" + 1% Sb ₂ O ₃
C	" + 3% PbO
D	" + 3% Sb ₂ O ₃
E	" + 10% PbO
F	" + 10% Sb ₂ O ₃
Z (Control)	"

At a dose rate of 6.26×10^5 rad/h, all six samples showed improvements in elongation over control samples up to a total dose of 3×10^7 rads, with the PbO containing samples, A, C and E outperforming the Sb₂O₃ added samples, B, D and F. At total doses higher than 5×10^7 rads, all six samples behaved similarly to the control samples. Among the samples with the same kind of additive, the higher the concentration, the more distinct the improvement.

At a dose rate of 3.31×10^5 rad/h, for the PbO containing samples, only sample E (10 % PbO) showed better performance compared with the control sample up to the total dose of 1.6×10^7 . It seems that all three Sb₂O₃ containing samples, B, D and F showed slight improvements in elongation over the control samples up to a dose of 1.6×10^7 rads.

5.6 Discussion

5.6.1 The Effects of Additives

Figures 5.20 - 5.22 show the effects of the added PbO at three different dose rates. As mentioned earlier, at a dose rate of 1.1×10^6 rad/h, all three samples (A, C and E) behaved similarly to the control samples. However, at 6.26×10^5 rad/h and for the total dose of 3×10^7 , the beneficial effects of the added PbO are clearly shown. The elongations are in order of the amount of the added PbO. For the dose rate of 3.31×10^5 rad/h, only sample E that has 10 % PbO showed clear improvements up to the total dose of 1.6×10^7 rads.

Figure 5.1 Standard sample used for radiation resistant polymer insulation development study.

Figure 5.2 Elongation as a function of total dose for samples A and Z. Dose rate: 1.1×10^6 rad/hour.

Figure 5.3 Elongation as a function of total dose for samples B and Z. Dose rate: 1.1×10^6 rad/hour.

Figure 5.4 Elongation as a function of total dose for samples C and Z. Dose rate: 1.1×10^6 rad/hour.

Figure 5.5 Elongation as a function of total dose for samples D and Z. Dose rate: 1.1×10^6 rad/hour.

Figure 5.6 Elongation as a function of total dose for samples E and Z. Dose rate: 1.1×10^6 rad/hour.

Figure 5.7 Elongation as a function of total dose for samples F and Z. Dose rate: 1.1×10^6 rad/hour.

Figure 5.8 Elongation as a function of total dose for samples A and Z. Dose rate: 6.26×10^5 rad/hour.

Figure 5.9 Elongation as a function of total dose for samples B and Z. Dose rate: 6.26×10^5 rad/hour.

Figure 5.10 Elongation as a function of total dose for samples C and Z. Dose rate: 6.26×10^5 rad/hour.

Figure 5.11 Elongation as a function of total dose for samples D and Z. Dose rate: 6.26×10^5 rad/hour.

Figure 5.12 Elongation as a function of total dose for samples E and Z. Dose rate: 6.26×10^5 rad/hour.

Figure 5.13 Elongation as a function of total dose for samples F and Z. Dose rate: 6.26×10^5 rad/hour.

Figure 5.14 Elongation as a function of total dose for samples A and Z. Dose rate: 3.31×10^5 rad/hour.

Figure 5.15 Elongation as a function of total dose for samples B and Z. Dose rate: 3.31×10^5 rad/hour.

Figure 5.16 Elongation as a function of total dose for samples C and Z. Dose rate: 3.31×10^5 rad/hour.

Figure 5.17 Elongation as a function of total dose for samples D and Z. Dose rate: 3.31×10^5 rad/hour.

Figure 5.18 Elongation as a function of total dose for samples E and Z. Dose rate: 3.31×10^5 rad/hour.

Figure 5.19 Elongation as a function of total dose for samples F and Z. Dose rate: 3.31×10^5 rad/hour.

Figure 5.20 Effects of PbO concentration on elongation.
Dose rate: 1.1×10^6 rad/hour.

Figure 5.21 Effects PbO concentration on elongation.
Dose rate: 6.26×10^5 rad/hour.

Figure 5.22 Effects of PbO concentration on elongation.
Dose rate: 3.31×10^5 rad/hour.

Figure 5.23 Effects of Sb_2O_3 concentration on elongation.
Dose rate: 1.1×10^6 rad/hour.

Figure 5.24 Effects of Sb_2O_3 concentration on elongation.
 Dose rate: 6.26×10^5 rad/hour.

Figure 5.25 Effects of Sb_2O_3 concentration on elongation.
Dose rate: 3.31×10^5 rad/hour.

Figure 5.26 Elongation for unirradiated samples with different additive concentrations.

Figure 5.27 Normalized elongation for samples Z, A, C, and E irradiated at a dose rate of 1.1×10^6 rad/hour.

Figure 5.28 Normalized elongation for samples Z, A, C, and E irradiated at a dose rate of 6.26×10^5 rad/hour.

Figure 5.29 Normalized elongation for samples Z, A, C, and E irradiated at a dose rate of 3.31×10^5 rad/hour.

Figure 5.30 Normalized elongation for samples Z, B, D, and F irradiated at a dose rate of 1.1×10^6 rad/hour.

Figure 5.31 Normalized elongation for samples Z, B, D, and F irradiated at a dose rate of 6.26×10^5 rad/hour.

Figure 5.32 Normalized elongation for samples Z, B, D, and F irradiated at a dose rate of 3.31×10^5 rad/hour.

Based on these results, it is believed that PbO works effectively as an antioxidant until the total dose reaches a certain level which is determined by the dose rate used and the amount of additive. For instance, at 6.26×10^5 rad/h, for total doses higher than 3×10^7 rads, the addition of PbO did not make much difference. For a dose rate of 3.31×10^5 rad/h, the added PbO for the samples A (1%) and C (3%) does not seem to be effective in slowing down RIO after the total dose of 8×10^6 rads was reached, and only the sample E showed improved elongations up to a dose of 1.6×10^7 rads.

Figures 5.23 - 5.25 show the effects of Sb_2O_3 on the elongation. As can be seen in these figures, Sb_2O_3 seems to improve the elongation slightly, which can be said for all the three dose rates used. However, the degree of improvement is not as much as that for PbO.

It should be mentioned that the addition of PbO to PE reduces the ductilities, i.e., elongations of the unirradiated samples decrease significantly as shown in Figure 26. Thus, the real effects of the additives as antioxidants may be shown better if the elongation data are normalized to the elongations of the unirradiated samples. In Figures 27 -32 the elongation values were averaged, and normalized to those of unirradiated samples. The same trends as discussed earlier can be seen in these plots except that the rankings of performance are switched in some cases. Again, more data are needed to draw firmer conclusions regarding the optimum composition.

5.6.2 Dose Rate Effects

Another way of checking the effectiveness of the additives as antioxidants is by studying the dose rate effect on each sample. When samples are irradiated in an inert environment at different dose rates, the results should not make any difference, i.e., no dose rate effect is expected. By the same reasoning, when the antioxidants work, dose rate effects should be decreased.

Figure 5.33 shows the dose rate effect on the control sample that has no antioxidant. The dose rate effects are noticeable for most of the doses at which data were taken. For the PbO containing samples, A, C and E, there is a trend that the total dose at which dose effects begin to be noticeable increases as the amount of PbO added increases (see Figures 5.34, 5.36 and 5.38). The same trend can be seen in the samples containing Sb_2O_3 (see Figures 5.35, 5.37 and 5.39).

The fact that dose rate effects are negligible for the samples with additives until the total doses reach certain levels while dose rate effects are noticeable for the control samples at most of the total doses used can be interpreted that the additives function as antioxidants. Thus, the information from this dose rate effects analysis also support the conclusions obtained from the effects of the additives analysis.

5.7 Conclusions and Recommendations

The following conclusions may be drawn from this study:

1. The concept of using inorganic antioxidants to retard radiation initiated oxidation is viable.
2. PbO is more effective than Sb₂O₃ in slowing down radiation initiated oxidation.

The following future studies are recommended:

1. Add different inorganic antioxidants, including carbon black, to a study so that the radiation initiated oxidation mechanism may be studied in detail.
2. Longer term experiments at lower dose rates should be conducted to test the ability to predict the cable lifetime under realistic conditions.

Figure 5.33 Effects of different dose rates on elongation of sample Z.

Figure 5.34 Effects of different dose rates on elongation of sample A.

Figure 5.35 Effects of different dose rates on elongation of sample B.

Figure 5.36 Effects of different dose rates on elongation of sample C.

Figure 5.37 Effects of different dose rates on elongation of sample D.

Figure 5.38 Effects of different dose rates on elongation of sample E.

Figure 5.39 Effects of different dose rates on elongation of sample F.

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APPENDIX

BROOKHAVEN NATIONAL LABORATORY

MEMORANDUM

DATE: March 1, 1989

TO: File #90 *DFM*

FROM: D. R. MacKenzie

SUBJECT: Radiation Studies on Plastics Used for Insulation and Sheathing of Electric Cables in Reactor Containment and Other Relatively High Radiation Areas.

In the past dozen years, many studies have been carried out on the effects of radiation on polymeric materials used for electrical insulation, sheathing, gasketing and other applications in the relatively high radiation fields inside nuclear reactor containment buildings and around high-energy particle accelerators [1-7]. Much of this work was initiated when it became apparent that polymeric materials in service had become seriously degraded at radiation doses much lower than it had been thought would be damaging -- i.e., their service lives were much shorter than predicted on the basis of the previously standard radiation tests performed on them. The principal differences between service conditions and test conditions were in the dose rates and temperatures -- dose rates in service were several orders of magnitude lower, and temperatures were often modestly, though significantly, higher. Thus, the important work in this area has concentrated on dose rate effects and synergy between dose rate and temperature (see particularly references 1 and 2).

Although the exact reasons for and precise mechanisms of the radiation and thermal effects are not known in detail, a general idea of the chemical processes involved has begun to emerge. As an indication of the types of effects observed in the field, the following items are reproduced from R. L. Clough's chapter in the recently published, "Encyclopedia of Polymer Science and Engineering" [8].

"Dose-rate effects can have dramatic practical consequences. Several illustrative examples are given below. When pre-irradiated pipes constructed of low density polyethylene were subsequently pressurized to 4 N/mm², and the time to rupture measured, the following observation was made. For pipes pre-irradiated at high dose rate (10⁴ Gy/h), material properties improved: rupture time was increased from the initial (unirradiated) value of 100 hr up to 10⁴ hr at doses of 2 x 10⁵ Gy or higher. For pipes irradiated at low dose rate (4 Gy/h), material properties decreased: rupture times dropped to less than one minute at doses above 7 x 10⁴ Gy. For power cables

exposed to long-term irradiation at low dose rate (.25 Gy/h) in the containment room of a nuclear reactor, the polyethylene insulation was completely embrittled after a dose of 2.5×10^4 Gy. In short-term, high-dose-rate laboratory experiments (10^4 Gy/h), there was no detectable change in mechanical properties of this same material (within experimental error) after the same dose; embrittlement of the material required $>10^6$ Gy. When a Viton gasket material was irradiated at 6×10^3 Gy/h, the material became progressively harder as it degraded, eventually becoming embrittled. In contrast, when samples of the same Viton material were irradiated at 10^2 Gy/h, the material became progressively softer, weaker, and more easily stretched as it degraded."

The effects of high-dose-rate or inert atmosphere irradiation had been studied for many years before the low-dose-rate effects were realized. The former were determined to be largely due to polymer chain breakage or cross-linking between chains or a combination of the two. These reactions can be presented, for hydrocarbon chains, as:

At low dose rate in an atmosphere containing oxygen (e.g., air) the primary radicals formed from interaction of radiation with the polymer molecules undergo rapid reaction with molecular oxygen.

the oxygenated radical being represented simply by the formula $RO_2\cdot$. The $RO_2\cdot$ radicals then undergo various types of reactions, including chain propagation and chain branching. This generally leads to much higher G-values for polymer degradation than in the absence of oxygen, depending, of course, on the chemical nature of the particular polymer (e.g., it does not apply to silicones, but does apply to sheathing materials such as PE and PVC).

Approach to be taken by BNL

As stated earlier, there has recently been a great deal of work on the effects of dose rate and temperature on the radiation stability of polymers, particularly those used in radiation fields around nuclear reactors and particle accelerators. This work has encompassed property-oriented studies designed to understand what changes in properties occur under different conditions, as an aid to materials development as well as to gain some insight into what chemical reactions may be occurring, and also fundamental studies to try to determine reaction mechanisms. Changes in such properties as hardness, brittleness (measured, for example, by bend strength), tensile strength and elongation at break have been quite thoroughly studied, and it does not seem to be fruitful to try to extend such studies for the program proposed by the NWM division. Also, fundamental mechanistic studies, while they would certainly be useful, would be inappropriate in view of the need to obtain specialized equipment and manpower before they could be started. Rather it seems more relevant and appropriate to engage in a study to develop materials which would undergo relatively little damage under real life conditions of low dose rate and somewhat elevated temperature. In particular, the need for in-depth studies on the role of various additives in radiation-degradation behavior has been pointed out by Clough et al. [3], and it is felt that this is the direction which BNL should pursue.

Statement of the Problem

In high-dose-rate ($10^5 - 10^6$ rad/h) irradiation of organic polymeric materials of reasonable thickness (e.g., >1 mm), the oxygen gas present in the organic matrix is rapidly consumed in the initial stages of the irradiation. Deleterious reactions of the oxygen throughout the material are insignificant -- dissolved oxygen is consumed after $\sim 10^5$ rad total dose [9]. Subsequent reactions involving oxygen gas occur essentially only at the surface since the oxygen will react with radicals there before it can diffuse into the body of the material. Thus, relatively high total doses can be delivered to the material with oxygen reactions occurring only near the surface, and the radiation damage to the bulk material will be the same as that which occurs under inert atmosphere conditions for the same total dose.

On the other hand, at low dose rates (on the order of 10^2 rad/h) oxygen gas will diffuse into the bulk material of most plastics rapidly enough that a steady state will be maintained in which the dissolved oxygen content is the same as in unirradiated material. [It is estimated by Maier and Stolarz [7] that samples irradiated at CERN were oxygen saturated when the dose rate was as high as approximately 10^4 rad/h (30mGy/s)]. Thus, any deleterious oxygen reactions which can occur with a given plastic, will occur throughout the bulk material. In practice, with many plastics these oxygen reactions lead to a very large increase in polymer damage for a given total dose, due to the chain reactions which they initiate [10].

Approaches to Solving the Problem

In attempting to prevent this greatly increased damage, one can consider adding chemicals to the plastic which are designed to react with oxygen or its initial reaction products before they cause significant damage. Reaction with oxygen itself (before the O_2 can react with polymer radicals) does not seem to

be practical, since an additive which reacted with oxygen would, by definition, be unstable in air and thus not of much help as a long-term protective material. The other option, however, should be feasible. That is, it should be possible to find additives which can react with the primary oxygen products, $RO_2\cdot$ and $HO_2\cdot$ radicals, to compete with, and hopefully prevent (depending on relative reaction rates), the chain propagation reactions of $RO_2\cdot$ and $HO_2\cdot$ with polymer molecules. To the extent that this can be accomplished, the oxygen-related damage occurring at low dose rates would be mitigated or prevented. The radiation damage effects which occur in inert atmosphere presumably would not be reduced.

Adding conventional antioxidants might be a useful approach, but this is not at all clear. Antioxidants are of four main types, all organic -- phenolics, amines, phosphites, and thioesters [11]. They have been developed to protect plastics against oxygen reactions initiated by heat and UV, not gamma radiation. Thus, while they would presumably be of some help in irradiated plastics because of their chain terminating reactions, they could also be "part of the problem" so to speak, since, being organic, they would form radicals in a gamma field which could pick up O_2 to form the RO_2 (peroxy) radicals which lead to the accelerated damage characteristic of low-dose-rate irradiation.

As an alternative to the organic antioxidants, one could consider inorganic reducing agents. These would include, besides certain elements such as carbon, salts with cations in the reduced state, salts with reducing anions, or salts with both. Also salts of certain organic acids might be appropriate, such as sodium gluconate, or sodium oxalate. Some of the cations and anions of interest will now be mentioned.

- Low valence states of the transition elements, e.g., Fe^{2+} , Mn^{2+} , Cr^{2+} , Co^{2+} . They might be used as oxides or as salts such as sulfate phosphate, or possibly chloride.
- Certain other multivalent cations such as As^{3+} , Sb^{3+} and Bi^{3+} . Arsenic would probably not be welcomed by the user community.
- Reducing anions which might be useful are sulfite, selenite, and phosphite.
- The reduced form of a cation could possibly be used as a salt with a reducing anion, providing twice the bang for the buck, so to speak.

Reactivity of Inorganic Ions with $RO_2\cdot$

We must be concerned with both the ability of the reducing ions to react with $RO_2\cdot$ and the rates relative to those for reaction of $RO_2\cdot$ with polymer molecules. That is, for this approach to be useful, the proposed reactions must be thermodynamically feasible, and they must be fast enough to compete with the radical reactions which degrade the polymer. There seems no reason to think that the reaction with reducing ions will not occur in a polymer

matrix. Reactions of $O_2^{\cdot-}$ and $HO_2^{\cdot}$ with reduced metal ions have been studied in aprotic solvents [12,13], which should be a reasonable stand-in for the organic polymer matrix, the main difference being that of phase (solid vs. liquid) and the consequent very large difference in mobility of large molecules and radicals.

It is not known how mobile inorganic ions and elemental carbon are in solid polymer matrices, and thus how well they could interfere with the reactions of reactive (albeit large) radicals with polymer molecules. One way of aiding their effectiveness would be to make their concentration high enough that the probability of a reducing ion being "within range" of the active oxygen site of the $RO_2^{\cdot}$ radical was relatively high. A simplistic picture can be imagined where an additive thoroughly mixed into a polymer would have a molecule of additive in a cube of 125 carbon atoms (i.e., CH_2 groups, $CHOH$ groups, etc.) which was 5 carbons to a side, when the additive concentration was one molecule to 125 carbon atoms. That would mean, for a uniform distribution of additives, that the additive would always be within 2-3 carbon atoms of any radical that formed and would have a reasonably high probability of being able to react with it. Such a concentration is well within the range used for antioxidants, and well below that often used for fillers. In practice, of course, it would presumably not be feasible during formulation to achieve the sort of uniform distribution just described. However, reasonable effectiveness should still be attained.

Suggestions for Experimental Program

The scope of the initial BNL program must obviously be quite limited. Rather than attempting to develop one or more products to a "ready for market" stage, its object should be to obtain a proof of principle for the general approach being advocated, namely use of inorganic additives to inhibit oxidative polymer degradation at low dose rates. The various steps in carrying out such a program are discussed below:

1. Choice of Polymer

Ideally, several polymers which are or could be used as cable sheathing should be tested in parallel. However, there is probably not sufficient effort available to test more than one at this stage. Using as a criterion for radiation degradation the dose required to reduce elongation at break to 50% of original, PVC (plasticized) is 20 times more sensitive at low dose rate than at high (or under inert atmosphere) while LDPE is roughly 10 times more sensitive [14]. The PVC tested was somewhat more stable than the LDPE at high dose rate. Thus, either polymer should be a suitable choice for our purposes, and both are standard materials for cable sheathing. HDPE is a few times less stable than LDPE at high dose rate, and some 40 times more sensitive at low dose rate than at high. It presents the sharpest contrast between results at high and low dose rates, but probably should not be considered as the sole material to be used in this study since its radiation resistance at high dose rate is not at all impressive. If only one material is to be used, one might well opt for LDPE, since it appears that some ready-made samples of LDPE containing carbon black may be available from a vendor.

2. Choice of Additives

Carbon black has been considered an anti-oxidant (see p. 351 of Ref. 2), and should be tried in this program, especially if manufacturer's samples are available. It is not clear to the author that salts would be preferable to oxides as a source of reduced cations from a chemical standpoint. If one wishes to use a reducing anion, a salt is obviously required. Choices may have to be made on the basis of availability of a finely divided form of the desired materials, since suitable mixing during formulation will presumably require a very small particle size. Reduced Fe, Cr and Mn compounds should be considered for cations, and sulfites, phosphites, selenites and possibly cyanides and iodides for anions. Reduced cations combined with reducing anions represents a useful approach. Complex inorganic anions such as ferrocyanide, and organic anions such as gluconate, phosphinate, and oxalate may be more appropriate than simple inorganic anions.

3. Effect of Additives

The additives chosen for testing must not change the properties of the polymers to which they are added so as to appreciably decrease their effectiveness as insulating and sheathing materials. At the level of a few per cent, which is suggested for this program, it is felt that there should be no large effect to either insulating or other required properties such as flexibility.

4. Sample Preparation

The size and shape of samples will depend on the particular tests to be performed. If material containing additives can be obtained from vendors in sheets of suitable thickness, it can be cut into the geometry required for the chosen tests. If it cannot be obtained from a supplier, it will have to be formulated at BNL. In this case, flake or granular polymer (available from suppliers) can be melted, additive stirred in until thoroughly mixed, and the melt poured into molds of the geometry required for samples. It would be preferable to have the additive dispersed as a colloid -- ideally particle size would be near molecular dimensions, but it may not be feasible to achieve this. Although it might save time if polymer having the additive in it could be obtained from a supplier, an advantage of preparing material here is that BNL would have control over exactly what was put into the polymer and at what concentrations.

5. Experimental Parameters

(a) Specific Tests to be Performed on Irradiated Samples

Changes in a polymer due to irradiation can be followed by measurement of a number of different properties, including spectroscopic. Probably the most appropriate properties to monitor are those which affect the material's use in its actual application, i.e., mechanical strength and flexibility, as determined by measurement of tensile strength, bending strength, elongation at break, etc. It is thus appropriate, for this program, to measure at least one of these properties. Elongation at break has been used by Clough [8] as a means of ranking polymers in terms of resistance to radiation at low versus high dose rates, and should be the property measured if only one must be chosen. [Presumably tensile strength could be measured at the same time, and the results would constitute a useful addition to the data base.]

(b) Irradiation Conditions

The biggest problem with any study of the effect of low dose rate is to reach reasonable total doses within the time frame of the study period. For instance, one might like to irradiate material at 100 rad/h to a total dose of 10^6 rad, a rather modest total dose for real-life situations. This would require a little more than a year, which could only be fitted into a study period of about 1 1/2 years, when one considers that several months are required to prepare samples before they can be irradiated and to test them afterward. In order to fit a meaningful experimental program into a period of a year or less, some sort of accelerated testing will be required.

Design and use of accelerated testing as an aid in predicting the extent of radiation degradation in organic polymers are described in Reference 3. There are two principal ways to carry out accelerated tests in the proposed BNL program. One involves irradiating at several different dose rates, from the low rate desired up to one a factor of perhaps 100 higher but still in the dose-rate range in which oxygenation reactions are deleterious. Careful interpretation of trends in test results should indicate how the material being tested will be expected to perform at the low dose rates for higher total doses than can be achieved in the available time. The other way to accelerate testing is to use increased temperature. This is a standard way of carrying out accelerated tests of any kind, but is particularly useful here because of the synergism between the thermal and radiation effects in these deleterious reactions involving oxygen and $RO_2\cdot$ radicals. It is recommended that several different elevated temperatures be used in the BNL experiments, since in practice in reactor containment use the polymers used for cable insulation are maintained at elevated temperatures most of the time.

Thus, for the BNL experiments, both dose-rate and temperature should be varied. Varying dose rate will, of course, permit a range of total doses to be covered. It is suggested that dose rates from 100 rad/h to $\approx 10^4$ rad/h be used, and temperatures from ambient up to perhaps 60 or 70°C. In addition, a set of samples containing the chosen additives and no additive (as control) should be irradiated at high dose rate (10^5 to 10^6 rad/h) at ambient temperature. The number of different sets of conditions chosen will determine the level of effort needed, and the number of samples which will have to be prepared, as discussed below.

6. Number of Samples

The number of samples which can be used in the test program will be limited by the capabilities of the irradiation facility, e.g., the number of samples which can be simultaneously irradiated at the same dose rate. Let us assume that the properties to be measured are tensile strength and elongation at break and that they can both be measured on the same sample. Ideally several samples should be tested to obtain a "precise" average strength value for each particular set of irradiation conditions for each polymer and additive. It will probably not be feasible to irradiate enough samples simultaneously to have more than two for each additive plus two for the control (which will be the polymer without additive) for each temperature used. If, as seems likely, a choice will have to be made between the number of replicate samples to be used and the number of additives (and/or polymers) to be investigated, it is recommended that duplicate samples be tested (rather than a larger number giving higher precision), and several additives and temperatures be used. While it would be useful to investigate more than one polymer, this initial program need not try to cover so much ground, bearing in mind that we are trying merely to establish a "proof of principle" not carrying out a definitive research study.

cc: P. Soo

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