

Oxidation Induction Time Correlations with Radiation Dose and Antioxidant Concentration in EPR and XLPE Polymers

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SYNOPSIS

Oxidation induction time (OIT), as measured by differential scanning calorimetry, is useful in assessing the extent of degradation in polymeric materials. Values of OIT for typical EPR and XLPE polymer insulation materials used for electric cable insulation in nuclear power plants were measured as a function of both radiation dose and antioxidant concentration after accelerated aging. Irradiations were performed at the University of Virginia Cobalt Irradiation Facility. OIT was found to decrease exponentially with increasing radiation dose and with decreasing antioxidant concentration for both ethylene-propylene rubber (EPR) and cross-linked polyethylene (XLPE) insulations. It was determined experimentally that, when polymers are subjected to a constant radiation dose rate, antioxidant concentration decreases linearly with time, and it was shown that this variation is consistent with theoretical autoxidation kinetics. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Normal environmental stresses are encountered by electric cables in a nuclear reactor containment include radiation, thermal exposure, mechanical stress, and electrical stress. Cables for use in nuclear power plants are qualified to withstand radiation absorbed doses (doses) during both normal operation and postulated accidents.^{1,2} Doses frequently used for qualification testing are 0.5 MGy (50 Mrad) to simulate normal operation and about 1.5 MGy (150 Mrad) more to account for an accident. Although thermal stresses are also included in nuclear-use cable qualifications, the present research is limited to gamma-radiation effects.

The amount of degradation in a polymer can be studied through the measurement of oxidation induction time (OIT). OIT is related to the amount of antioxidant in a polymer; hence, OIT, like antioxidant concentration, decreases with aging. OIT is measured with a differential scanning calorimeter (DSC) used in its isothermal mode. A reference pan and a sample pan are both heated to a predetermined

temperature in an inert nitrogen atmosphere and then immersed in a stream of pure oxygen at that temperature. The OIT is determined from the DSC thermogram as the time from oxygen introduction until the onset of rapid exothermic oxidation of the polymer sample, which occurs after the antioxidant in the sample has been consumed. This technique of aging assessment addresses chemical properties rather than the mechanical property of elongation to rupture that is commonly used for life assessment of cables.

In this investigation, correlations have been experimentally obtained between OIT and both radiation dose and antioxidant concentration at room temperature and constant dose rate for ethylene-propylene rubber (EPR) and cross-linked polyethylene (XLPE).³ Previous work on OIT as a life-assessment technique for nuclear-use cable products appears in Refs. 4 and 5.

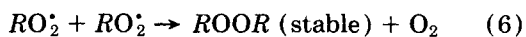
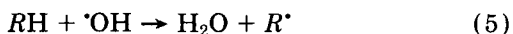
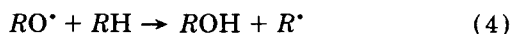
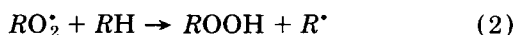
AUTOXIDATION KINETICS

A simplified analysis of autoxidation kinetics provides a useful framework for this study and leads to a relationship between antioxidant concentration and dose rate that was experimentally confirmed in

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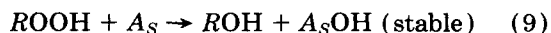
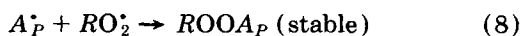
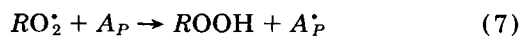
this investigation. Cable insulations are composite materials consisting of a polymer matrix, antioxidants for stabilization against degradation due to autoxidation, and other additives. These polymers degrade by a series of oxidation reactions initiated by thermal, radiative, chemical, electrical, and mechanical stresses. Radiation stress only is addressed here.

Conventional models for autoxidation include *initiation*, *propagation*, and *termination* phases. Radiation and thermal stresses cause the generation of polymer radicals, designated by R^* . A typical propagation and termination sequence without the presence of antioxidants is the following:



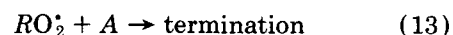
The decomposition of hydroperoxide [eq. (3)], occurs at a significantly lower rate than the preceding reactions; this rate is a function of temperature and becomes an important factor in thermal aging studies. The *termination* phase shown in eq. (6) is the most probable of several possible termination reactions.

Measures to safeguard against rapid oxidation include the introduction of primary and secondary antioxidants into the polymer composition that retard the aging process. Primary antioxidants, A_P , are proton donors known as *peroxy scavengers*, which interrupt the propagation stage by reacting with peroxy radicals. These are sometimes used in conjunction with secondary antioxidants, A_S , called *hydroperoxide decomposers*, which counter the production of free radicals by reacting with $ROOH$. Typical antioxidant reactions are shown below in eqs. (7-9):



The antioxidants in the polymer systems analyzed here are primary antioxidants, which will be referred to as A for the duration of this article. Agerite MA is a phenol and Aminox is a secondary amine.

Chemical formulae for these antioxidants and ZMTI are given in Ref. 6. Intuitively, one would expect that the rate of antioxidant consumption should be directly proportional to the radiation dose rate, D_R . Equations (10)–(13) represent a simplified autoxidation scheme initiated by gamma radiation at room temperature, which Gillen suggested to illustrate that such a relationship between antioxidant concentration and dose rate is theoretically reasonable⁷:



Reaction rate constants, k_i , are assigned to eqs. (11)–(13). The generation rate for R^* in the initiation reaction [eq. (10)] is proportional to the dose rate, D_R ; thus, this rate is CD_R , where C is a constant. The time-varying concentrations of R^* , RO_2^* , and A , where brackets indicate concentration, are

$$d[R^*]/dt = CD_R + k_2[RH][RO_2^*] - k_1[R^*][O_2] \quad (14)$$

$$d[RO_2^*]/dt = k_1[R^*][O_2] - k_2[RH][RO_2^*] - k_3[RO_2^*][A] \quad (15)$$

$$d[A]/dt = -k_3[A][RO_2^*] \quad (16)$$

Assuming steady state for eqs. (14) and (15), these two expressions can be set equal to zero, and by subtraction,

$$CD_R = k_3[RO_2^*][A] \quad (17)$$

Substituting this result into eq. (16) gives the simplified relationship between antioxidant concentration and dose rate:

$$d[A]/dt = -CD_R \quad (18)$$

MATERIALS TESTED

OIT was measured for both EPR and XLPE in cable and plaque forms. Each of the cable products tested had been qualified for nuclear plant use. The EPR cable materials were labeled EPM1, EPDM1, EPDM2, EPDM4, and EPDM5. EPM1, EPDM4, and EPDM5 are proprietary products for which the antioxidants are not publicly known. EPDM1 and

EPDM2 were known to be manufactured using A. Schulman, Inc.'s Superohm 4474 compound, which contains antioxidants ZMTI and Aminox. The composition of Superohm 4474 is given in Ref. 6. The XLPE cable materials were labeled XLPE1R, XLPE1W, XLPE2, XLPE3, XLPE4, XLPE5W, and XLPE7. The final letter identifies the color of the insulation, with *R* referring to red and *W* to white. XLPE1R and XLPE1W were from the same multiconductor cable, the only difference between them being color. XLPE3, XLPE4, XLPE5W, and XLPE7 all carried the same brand name, although they were manufactured at different times.

The EPDM plaque materials were made by A. Schulman, Inc. They were designated E2, E3, and E6, with E3 being the standard product marketed. The XLPE plaque materials, labeled X4, X5, X6, and X7, were made by Union Carbide. The only differences among the three EPDM plaque materials and, similarly, among the first three XLPE plaque materials were the amounts of antioxidant. The plaque materials X4, X5, and X6 are the same compounds as Union Carbide's EVA XLPE copolymer, HFDA-6522, except for the antioxidant concentrations; the concentration in Union Carbide's commercial product is proprietary, although the antioxidant used is publicly known to be Agerite MA. X7 is a different material from the first three XLPE plaques; it is General Electric Vulkene homopolymer, now manufactured by Union Carbide as HFDA-1440. Both the identity and concentration of its antioxidant are proprietary. Antioxidant concentrations, in parts per hundred (phr) of the base resin, for the plaque materials are summarized in Table I.

EXPERIMENTAL

Samples were irradiated at room temperature in the University of Virginia Cobalt Irradiation Facility

Table I EPR and XLPE Plaque Antioxidant Systems

Material Designator	Antioxidant Concentration/Type
E2	1 phr ZMTI, 0.5 phr Aminox
E3	2 phr ZMTI, 1.0 phr Aminox
E6	3 phr ZMTI, 1.5 phr Aminox
X4	1 phr Agerite MA
X5	2 phr Agerite MA
X6	3 phr Agerite MA
X7	Proprietary

(CIF), which consists of an array of Co-60 source pins underwater, as described in Ref. 8. Dose rates used were varied from 670 Gy/h for EPR to 65 Gy/h for XLPE to insure homogeneous aging, as dictated by previous results with the CIF and polymer cables.⁸

OIT measurements were performed with a Perkin-Elmer DSC-7. Several types of samples were compared, including slivers, wafers, and ground particles. Despite the possibility that grinding may lead to some chain scissioning and oxidation, consistency, reproducibility, and ease of thermogram interpretation prompted the use of ground particles for this investigation.^{9,10} ASTM standard for testing cable insulation was used as a guide, except for grinding of the samples.¹¹

The OIT data were obtained at a DSC temperature of 215°C with 8.0 mg samples of material ground with a Wiley Mill to a size less than 20 mesh using a U.S. Standard Sieve Series #20, which adheres to ASTM specifications.¹² Each sample was encapsulated in an aluminum pan with a stainless-steel screen top mechanically crimped in place. Samples were immersed in a steady flow of nitrogen gas while being heated to the OIT test temperature. Soon after the test temperature was reached, nitrogen was replaced by oxygen.

The OIT is determined graphically from a DSC thermogram. The thermal analyzing system used for this research is Perkin-Elmer TAS-7. Figure 1 illustrates a typical thermogram for use as reference. The *y*-axis is the differential heat flow needed to keep the reference and sample at the isothermal temperature of 215°C. The exotherm deviates from the horizontal base line when the antioxidant is consumed and the reaction becomes exothermic. The OIT is then defined as the time between the introduction of the oxygen into the pan assemblies and the intersection of the base-line extension and the exotherm slope.

Two sources of uncertainty were identified for the values of OIT reported here. The first is reproducibility, which varied from $\pm 2\%$ for OITs above 100 min to about $\pm 10\%$ for OITs below 10 min. The second source exists in the determination of slopes for nonideal exotherms and establishment of the base line for short OITs. The two errors were assumed to be random.

OIT and Radiation Dose

EPR and XLPE polymer cables were aged in the CIF to doses up to 0.5 MGy (50 Mrad). OIT measurements were then performed on unaged material,

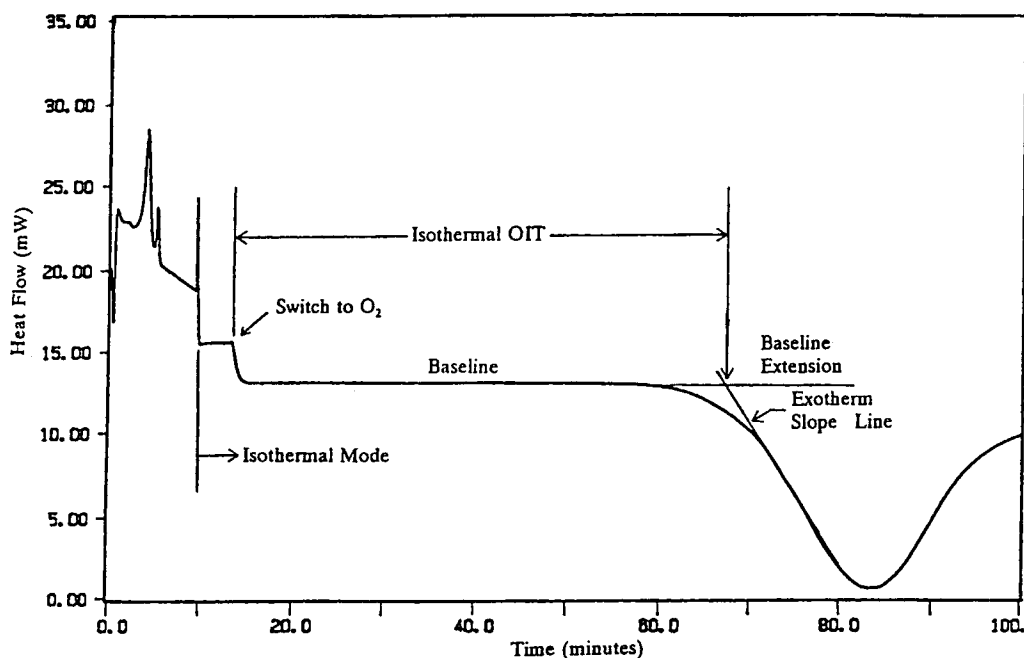


Figure 1 Example of DSC thermogram used to determine the OIT.

OIT₀, and as a function of dose, OIT(*D*). The results are given in Tables II and III for EPR and XLPE, respectively, and are plotted in Figures 2 and 3 for EPR and Figures 4 and 5 for XLPE. Normalized OITs for cables are OIT(*D*)/OIT₀. The following correlation between OIT and dose was found:

$$\text{OIT}(D) = \text{OIT}_0 e^{-\beta D} \quad (19)$$

where β is the material-dependent slope of the semi-log plot and is termed the *radiation aging constant*.

Values of the unaged OIT and radiation aging constants for each polymeric material tested are

Table II OIT as a Function of Dose in EPR

Dose (MGy)	OIT (Min)			
	0.0	0.1	0.2	0.3
EPM1	98 ± 2	44 ± 4	29 ± 2	18 ± 2
EPDM1	82 ± 3	28 ± 3	11 ± 1	3 ± 2
EPDM2	99 ± 4	48 ± 4	20 ± 3	11 ± 2
EPDM4	36 ± 3	16 ± 2	10 ± 1	6 ± 1
EPDM5	114 ± 2	77 ± 3	43 ± 3	31 ± 2
E2	38 ± 3	19 ± 3	14 ± 2	7 ± 1
E3	102 ± 2	63 ± 3	35 ± 3	18 ± 2
E6	203 ± 4	112 ± 4	81 ± 3	38 ± 3

presented in Table IV. It is noted that, except for EPDM1, the range of β for the EPR group is fairly narrow (3.8–7.5). For the XLPE group, with the exception of XLPE1, the range is also fairly narrow (2.2–5.3). The aging process proceeds at a greater rate for larger values of β .

Equation (19) can be solved for the dose, *D*, as function of OIT:

$$D = \beta^{-1} \ln[\text{OIT}_0/\text{OIT}(D)] \quad (20)$$

thus providing a means for the estimation of dose absorbed by a field-aged polymeric material for which OIT₀ and β have been determined.

OIT and the Antioxidant Concentration

The antioxidant concentrations are known for both the EPDM series of plaques (E2, E3, and E6) and the XLPE plaques (X4, X5, and X6), as given in Table I. Therefore, with these plaques, it was possible to measure the variation of OIT with antioxidant concentration.

The unaged OIT as a function of initial antioxidant concentration, *A*₀ (phr), for the two antioxidant systems is plotted in Figure 6. To the extent that three points can indicate a straight line, the data suggest another exponential correlation of the type:

Table III OIT as a Function of Dose in XLPE

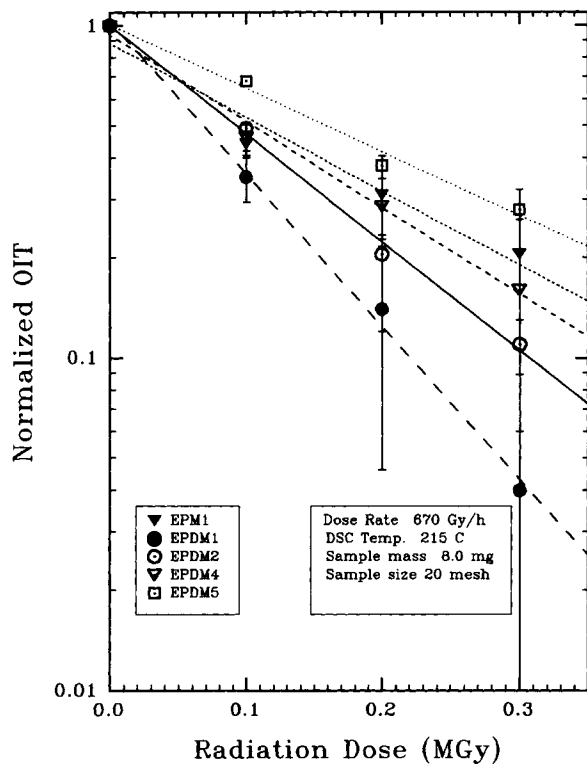
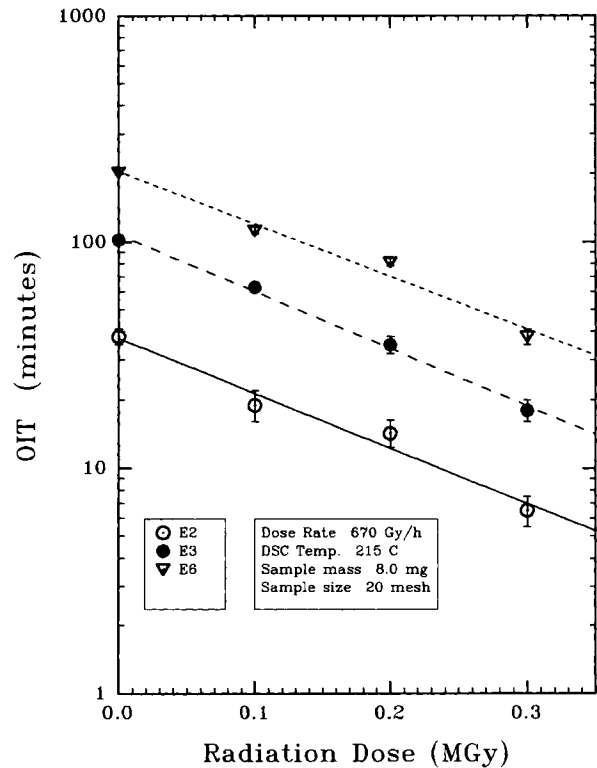
Dose (MGy)	OIT (Min)						
	0.0	0.1	0.2	0.3	0.4	0.5	
XLPE2	75 ± 3	59 ± 8	35 ± 2	29 ± 2	19 ± 2	12 ± 1	
XLPE5W	118 ± 4	45 ± 4	36 ± 4	26 ± 4	14 ± 2	10 ± 2	
XLPE1W	87 ± 4	15 ± 1	2 ± 1	0.5 ± 1	—	—	
XLPE1R	73 ± 4	24 ± 3	1 ± 1	0.3 ± 1	—	—	
XLPE3	186 ± 5	56 ± 3	32 ± 2	38 ± 5	24 ± 4	19 ± 3	
XLPE4	186 ± 5	78 ± 3	50 ± 3	44 ± 9	21 ± 4	17 ± 3	
XLPE7	108 ± 2	78 ± 3	46 ± 3	41 ± 3	33 ± 2	20 ± 2	
X4	17 ± 2	15 ± 2	9 ± 1	8 ± 1	6 ± 2	5 ± 1	
X5	91 ± 2	68 ± 3	53 ± 3	36 ± 3	34 ± 3	29 ± 2	
X6	301 ± 6	237 ± 10	192 ± 6	154 ± 6	123 ± 7	101 ± 3	
X7	90 ± 2	65 ± 3	35 ± 2	22 ± 2	11 ± 1	6 ± 1	

$$\text{OIT}(A_0) = Ce^{\theta A_0} \quad (21)$$

where C is a material-dependent constant, and θ , the slope of the semilog plot with the unit, phr^{-1} . The constant, θ , is unique to each antioxidant system and is termed the *antioxidant concentration constant*. For EPR plaques, this constant is based on the total antioxidant concentration, as two antioxidants are

present. Table V lists the θ values for different antioxidant systems.

To demonstrate that the relationship in eq. (21) holds true for aged materials, the OIT was plotted at different doses for each system, as seen in Figure 7. The parallel orientation of these regression fits reveal that the slopes, or θ values, do not vary with aging. Thus, it appears that OIT for a given material,


Figure 2 Normalized OIT as a function of radiation dose for EPR cables.

Figure 3 OIT as a function of radiation dose for EPR plaques.

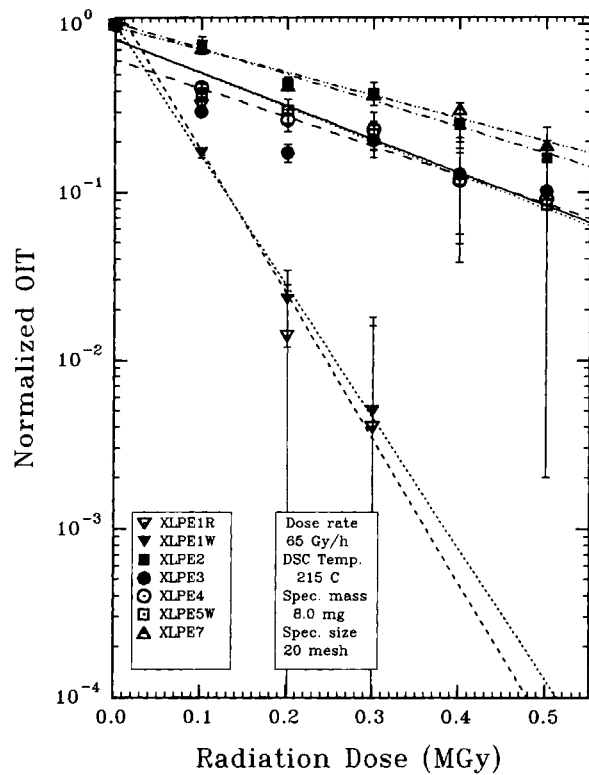


Figure 4 Normalized OIT as a function of radiation dose for XLPE cables.

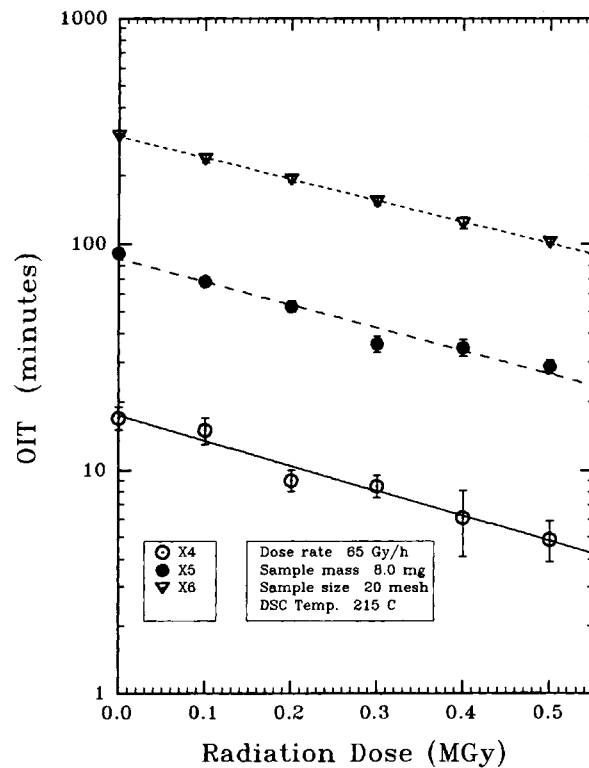


Figure 5 OIT as a function of radiation dose for XLPE plaques.

Table IV Radiation Aging Constants

XLPE		EPR	
Material Designation	Radiation Aging Constant: β (MGy ⁻¹)	Material Designation	Radiation Aging Constant: β (MGy ⁻¹)
XLPE2	3.5	EPM1	5.4
XLPE5W	5.0	EPDM1	10.5
XLPE1W	17.9	EPDM2	7.5
XLPE1R	19.7	EPDM4	6.0
XLPE3	4.5	EPDM5	3.8
XLPE4	4.8	E2	5.8
XLPE7	3.2	E3	5.8
X4	2.4	E6	5.8
X5	2.2		
X6	2.2		
X7	5.3		

both aged and unaged, depends only on the antioxidant concentration, throughout the aging process, so that

$$OIT(A) = Ce^{\theta A} \quad (22)$$

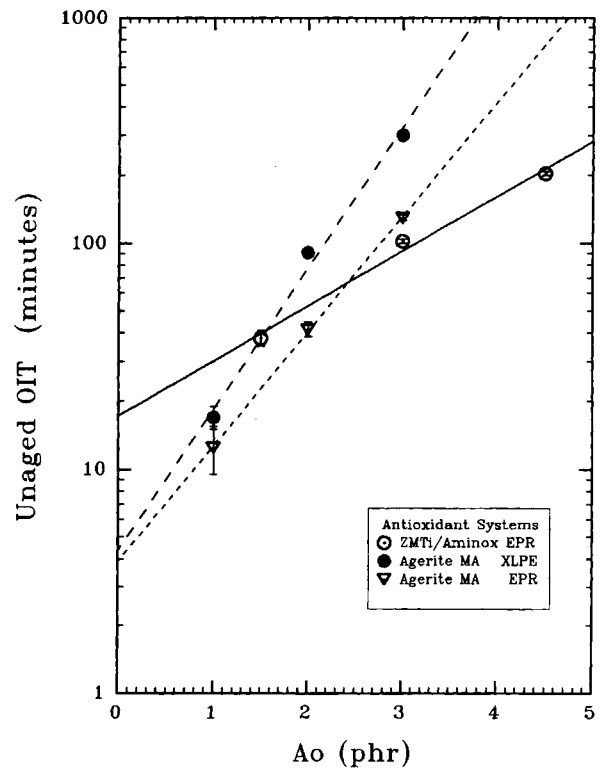


Figure 6 Unaged OIT₀ as a function of initial antioxidant concentration in EPR and XLPE plaque series.

Table V Antioxidant Concentration Constants in Plaque Materials

Antioxidant System	Plaque Materials	Antioxidant Concentration Constant, θ (phr ⁻¹)
ZMTi/Aminox	E2, E3, E6	0.59
Agerite MA	X4, X5, X6	1.44
Agerite MA	E9, E10, E11	1.17

for all A . Equations (21) and (22) can be combined to give

$$\text{OIT}(A) = \text{OIT}(A_0)e^{\theta(A-A_0)}, \quad (23)$$

which shows how the OIT is reduced as the antioxidant concentration is reduced.

Relationship between Radiation Dose and Antioxidant Concentration

The correlations from the two previous sections can now be used to derive an expression for the antioxidant behavior as a function of dose, $A(D)$. It may

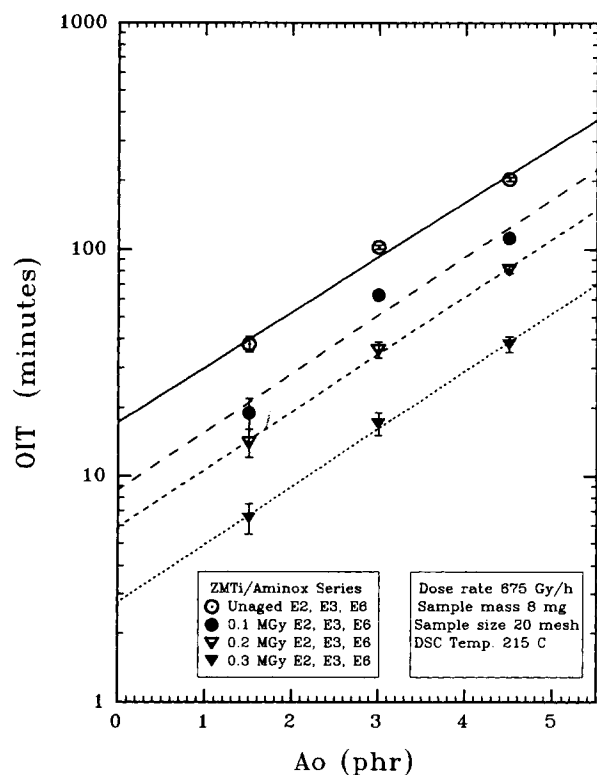


Figure 7 OIT as a function of initial antioxidant concentration in aged plaque series.

be useful to refer to Figure 8 when following this derivation. Figure 8, a modified version of Figure 3, shows OIT as a function of dose for the EPDM polymer plaque series (E2, E3, E6), where the initial antioxidant concentrations are ordered in the progression of $A_{E6} > A_{E3} > A_{E2}$. The horizontal dotted line delineates an equivalency between the OITs of an unaged sample of E2 and a sample of E3 aged to some dose, D . Using eq. (19), an expression of this equivalency is

$$\text{OIT}_0(A_{E2}) = \text{OIT}_0(A_{E3})\exp(-\beta D) \quad (24)$$

where $\text{OIT}_0(A_{E2})$ and $\text{OIT}_0(A_{E3})$ are the unaged OITs for plaques with different initial antioxidant concentrations. In general, one may express the unaged OIT of a material with an initial antioxidant concentration (A_{E2} in this case) in terms of a radiation-aged OIT of the same material formulation with a higher initial antioxidant concentration (e.g., A_{E3}). Utilizing eq. (23), a second expression for $\text{OIT}_0(A_{E2})$ is obtained as

$$\text{OIT}_0(A_{E2}) = \text{OIT}_0(A_{E3})\exp[\theta(A_{E3}^D - A_{E3})], \quad (25)$$

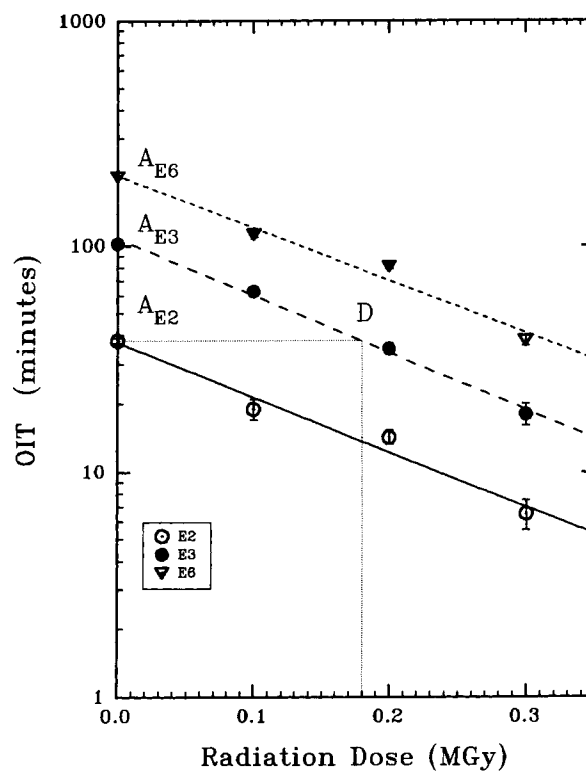


Figure 8 Reference plot relating OIT, antioxidant concentration, and radiation dose.

where A_{E3}^D is the antioxidant concentration in E3 after being aged to dose D and is equal to A_{E2} since the present analysis is predicated upon OIT being a unique function of antioxidant concentration. Equating the right-hand sides of eqs. (24) and (25) gives

$$A_{E3}^D = A_{E3} - (\beta/\theta)D \quad (26)$$

Since the above relationships are valid for any antioxidant concentration and dose, a more general relationship between antioxidant concentration and radiation dose can be written as

$$A(D) = A_0 - (\beta/\theta)D \quad (27)$$

where D is now any dose.

Taking the derivative of eq. (27) with respect to time gives

$$dA/dt = -(\beta/\theta)dD/dt \quad (28)$$

The derivative dD/dt is the dose rate D_R , so that

$$dA/dt = -(\beta/\theta)D_R. \quad (29)$$

It is noted that eq. (29) is consistent with the earlier theoretical result [eq. (18)] and that the constant, C , can now be identified as β/θ , the ratio of two material-dependent aging constants that can be determined experimentally.

CONCLUSIONS

Experimental correlations of oxidation induction time with both radiation dose and antioxidant concentration were obtained for EPR and XLPE materials. It was also demonstrated that the experimentally derived linear reduction of antioxidant concentration with time at constant dose rate is consistent with a simplified kinetics model for au-

toxidation. The previously unknown constant in the antioxidant reduction equation was identified as the ratio β/θ for the plaque materials tested.

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