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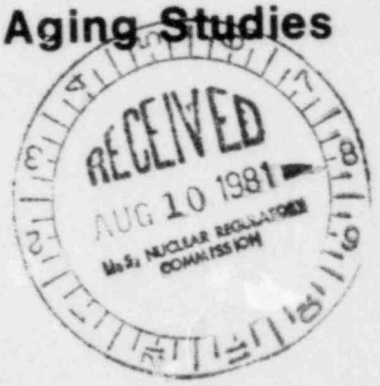
Occurrence and Implications of Radiation Dose-Rate Effects for Material Aging Studies



Kenneth T. Gillen, Roger L. Clough

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OCCURRENCE AND IMPLICATIONS OF RADIATION DOSE-RATE EFFECTS FOR MATERIAL AGING STUDIES

Kenneth T. Gillen and Roger L. Clough

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ABSTRACT

A number of commercial cable materials, including ethylene propylene rubber and crosslinked polyolefin insulations and chloroprene and chlorosulfonated polyethylene jackets have been radiation aged in air and nitrogen at radiation dose rates ranging from approximately 10^3 to 10^6 rad/hr. Material degradation was followed using ultimate tensile properties (elongation and tensile strength), swelling measurements and infrared spectroscopy. The tensile results indicate that in air environments radiation dose rate effects are important for all four materials, with more mechanical damage occurring as the dose rate is lowered. These results are interpreted as coming from a competition between crosslinking and oxidative scission in which scission becomes more important as the dose rate is lowered. The swelling results offer direct evidence in support of this interpretation. In addition the infrared results show increased carbonyl content at lower dose rates, also indicative of increased oxidation. The conclusions of this study have important implications for the qualification of elastomeric materials for nuclear applications, since they clearly indicate that the mechanism of degradation is quite different (and the amount usually more severe) under low dose rate exposures compared to the mechanism occurring under the high dose rate exposures normally utilized for simulating the natural aging.

KEYWORDS

Radiation effects; dose-rate effects; polymer degradation; aging of insulation; crosslinking; oxidative scission.

INTRODUCTION

In nuclear applications a variety of polymeric materials receive radiation exposure at relatively low dose rates (typically less than 10^3 rad/hr) for long periods of time (up to 40 years). In order to make estimates of the long-term degradation occurring in a material, it becomes necessary to carry out accelerated aging studies. These are normally accomplished by raising the radiation dose rate to the order of 10^6 rad/hr with the assumption that the amount of degradation will depend only on the integrated radiation dose. On this basis extensive studies have been carried out. Results from such studies are often summarized in compilations, (Schonbacher and Stolarz-Izycka, 1979; VandeVoorde and Restat, 1972) which indicate, for typical polymeric materials, the total allowable radiation dose before significant material damage occurs. On the other hand evidence exists (Makhlis, 1975; Schnabel, 1978) that in air environments, certain polymeric materials can show significant dose rate effects. Recently Kuriyama and co-workers (1979) studied the dose rate effect (for the range of 10^4 rad/hr to 5×10^5 rad/hr) on the mechanical and electrical properties of representative insulation and jacketing materials and found strong dose rate effects for a chemically crosslinked polyethylene, some evidence of a different type of

dose rate effect for an ethylene propylene rubber and little evidence for dose rate effects in a chloroprene rubber and a chlorosulfonated polyethylene.

We have been interested for some time in determining the importance of dose rate effects for polymeric materials used in nuclear applications. In particular we have been following the degradation of commercial cable insulation and jacketing materials in room temperature radiation environments using dose rates ranging over 3 orders of magnitude, from approximately 10^3 rad/hr to 10^6 rad/hr. The effect of humidity on the aging (dry air vs. 70% relative humidity air) is also being monitored. Preliminary results reported earlier (Gillen and Salazar, 1978) indicated that dose rate effects were present for a radiation crosslinked polyolefin insulation material and an ethylene propylene rubber insulation and that no effect of humidity on room temperature radiation aging was apparent. Sufficient data has now been accumulated from the low dose rate experiments to indicate that dose rate effects are present for every material which we have studied and must therefore be considered before extrapolating high dose rate accelerated simulations to low dose rate ambient conditions. Here we highlight some of the relevant data.

EXPERIMENTAL

Materials

The materials for this study were carefully stripped before aging from modern Class IE (qualified for nuclear power

plant safety applications) low-voltage electrical cables obtained from a number of manufacturers. Table 1 gives the material abbreviations used in this paper, a description of the materials, their nominal wall thickness and unaged tensile properties.

The two insulation materials were aged as tubes; rectangular samples approximately 5.5 mm wide by 150 mm long were cut from the jacket materials for use in the aging experiments.

TABLE 1 Material Characteristics

Abbreviation	Material	Nominal Wall Thickness, mm	Tensile Elongation %	Tensile Strength (MPa)
CLPO	Fire retardant radiation crosslinked polyolefin insulation	0.8	240	15
EPR	Ethylene propylene rubber insulation	1.0	420	8
CSPE	Chlorosulfonated polyethylene jacket	1.4	300	25
CP	Chloroprene rubber jacket	1.5	185	11

Radiation Exposures

The radiation aging was carried out 1) at the Naval Research Laboratories facility (Campbell, 1964), modified such that continuous air flow was supplied to the aging chambers and 2) at Sandia's dedicated radiation aging facility (Bonzon and co-workers, 1978). The latter facility has been upgraded such that dose rates up to 1 Mrad/hr are now available. Radiation dose rates at NRL were obtained from the extensive mapping data

generated by NRL personnel. Dose rates at the Sandia facility were obtained using a Victoreen Model 550 Radocon III Integration/Rate Electrometer and thermoluminescent CaF_2 wafers; agreement between the two methods was excellent.

Tensile Tests

Tensile testing was accomplished with an Instron Testing Machine Model 1020. Samples were gripped using pneumatic jaws with an air pressure of approximately 3×10^5 Pa. Initial jaw separation was 50 mm and samples were strained at 125 mm/min; the strain was monitored with an Instron electrical tape extensometer clamped to the sample.

Infrared Spectra

Spectra were obtained on KBr pellets made from polymer samples that had been ground at -196°C. A Nicolet Model 7199 FTIR spectrometer was employed.

Swelling Measurements

Samples of initial weight ranging from 0.3 - 1.0 g were extracted with THF at 50°C in a Soxhlet extractor for 24 hrs. After quickly removing excess solvent from the surface and capping the samples in a bottle to retard evaporation of solvent, the samples were weighed, yielding W_s; they were then dried in a vacuum oven and weighed again, yielding W_d. The weight swelling ratio (WSR) was then calculated as

$$WSR = \frac{W_s - W_d}{W_d}$$

RESULTS AND DISCUSSION

Figures 1-4 summarize the results to date of the extensive ambient temperature radiation aging experiments on the 4 materials described earlier. The tensile strength after aging divided by the tensile strength before aging (T/T_o) and the tensile elongation after aging divided by the tensile elongation before aging (e/e_o) are plotted against the total integrated radiation dose at the various indicated radiation dose rates. The crosses represent data for experiments run in a nitrogen environment; the remaining experiments were run in flowing air environments. Each data point represents an average of between 4 and 8 tensile tests.

It is apparent from Figs. 1-4 that dose rate effects exist for all 4 materials. In every case as the radiation dose rate in air is lowered, the tensile strength results shift to lower values for a constant value of the total radiation dose. The overall degradation mechanism for polymers in an oxygen-radiation environment is quite complex, but in general is pictured as a competition between crosslinking and scission processes (Makhlis, 1975; Schnabel, 1978). Since crosslinking usually increases tensile strength values and scission usually leads to a decrease in tensile strength, the tensile strength results from Figs. 1-4 can be interpreted as evidence that scission becomes more important relative to crosslinking as the radiation dose rate is lowered. The tensile strength results for moderate dose rate aging in a nitrogen atmosphere for CLPO and EPR shift to higher values compared to the high dose rate results in air. This implies that oxygen is implicated in the

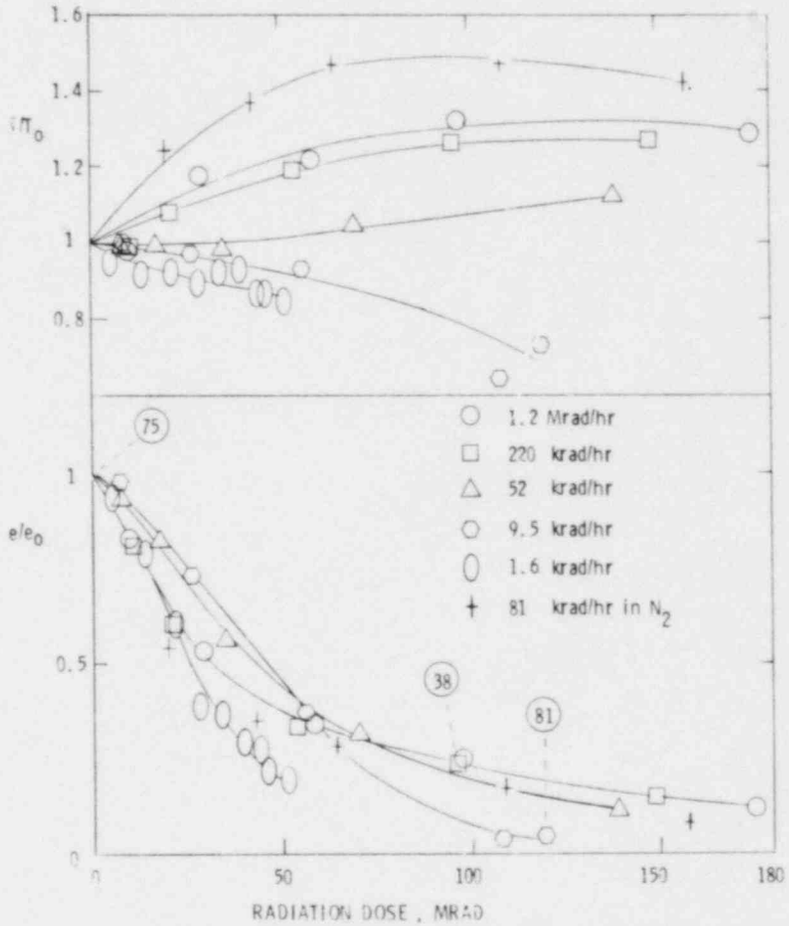

Fig. 1. Aging of crosslinked polyolefin insulation. The tensile strength after aging divided by the tensile strength before aging (T/T_o) and the tensile elongation after aging divided by the tensile elongation before aging (e/e_o) plotted against the total integrated radiation dose at the various indicated dose rates. The circled numbers refer to the weight swelling ratios corresponding to the indicated experimental conditions.

dose rate effects, and hence that the scission is associated with oxidation. Figure 5 shows the carbonyl region ($\lambda \sim 1710$ cm^{-1}) of the infrared spectra of 1) unaged EPR, 2) EPR aged in air at 1.2 Mrad/hr to a total dose of 95 Mrad, and 3) EPR aged

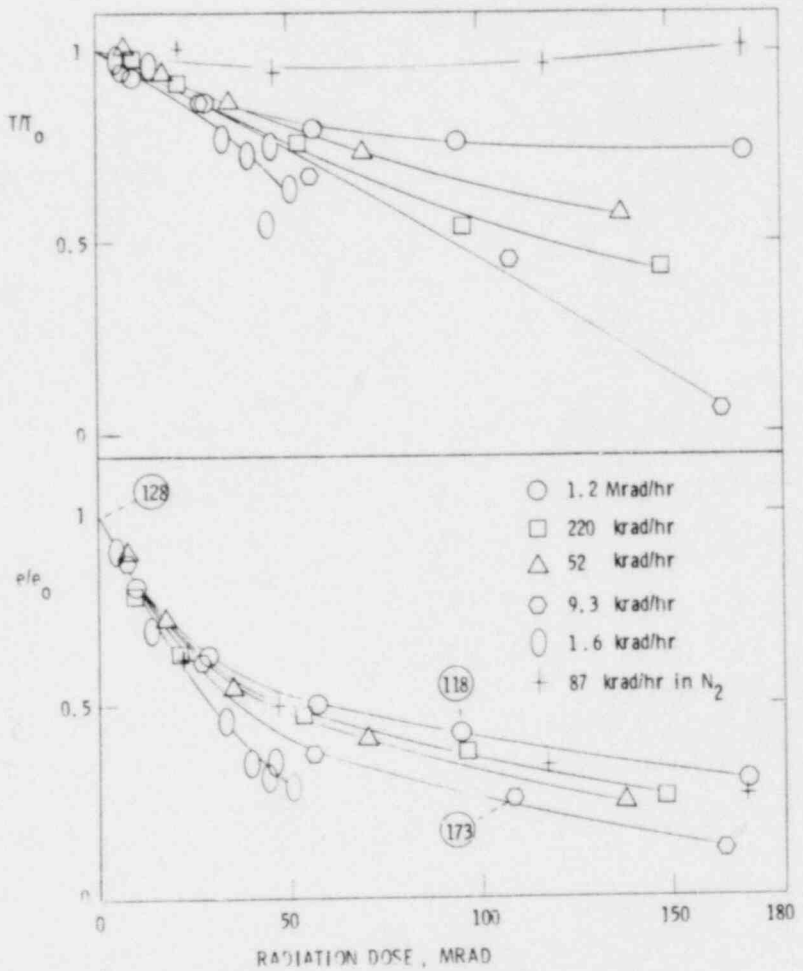

Fig. 2. Aging of ethylene propylene rubber insulation. Explanation of figure is identical to Fig. 1.

in air at 9 krad/hr to a total dose of 108 Mrad. The much larger carbonyl peak produced under low dose rate conditions is consistent with the expected increase in the extent of the oxidative reaction.

Although the elongation results for EPR (Fig. 2) imply dose rate effects for the whole dose rate range investigated, clear e/e_o dose rate effects for the other three materials become apparent only at the lowest dose rates. The relative

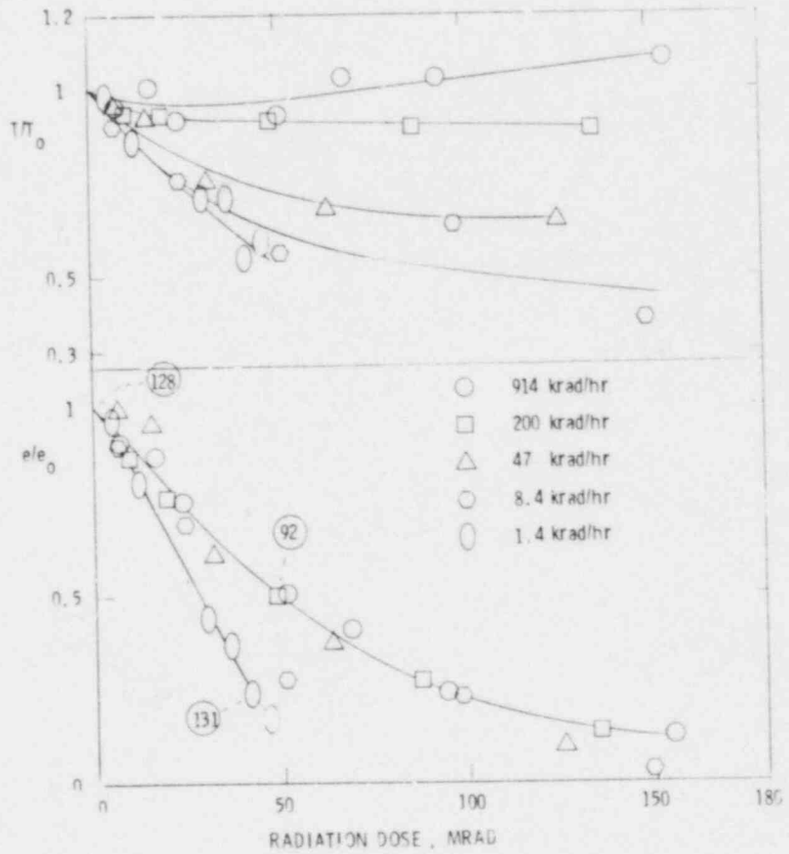

Fig. 3. Aging of chloroprene rubber jacket. Explanation of figure is identical to Fig. 1.

lack of sensitivity of elongation to the changing competition between crosslinking and scission is due to the fact that both phenomena tend to lower this parameter, leading in general to a rather complicated dependence on dose rate. In CLPO for example, degradation dominated by crosslinking appears to lead to a faster initial rate of decrease in the elongation only to be followed later in the degradation by a smaller rate of decrease. Eventually at dose rates where scission becomes sufficiently important, the rate of degradation reflected by the elongation begins to accelerate for all 4 materials.

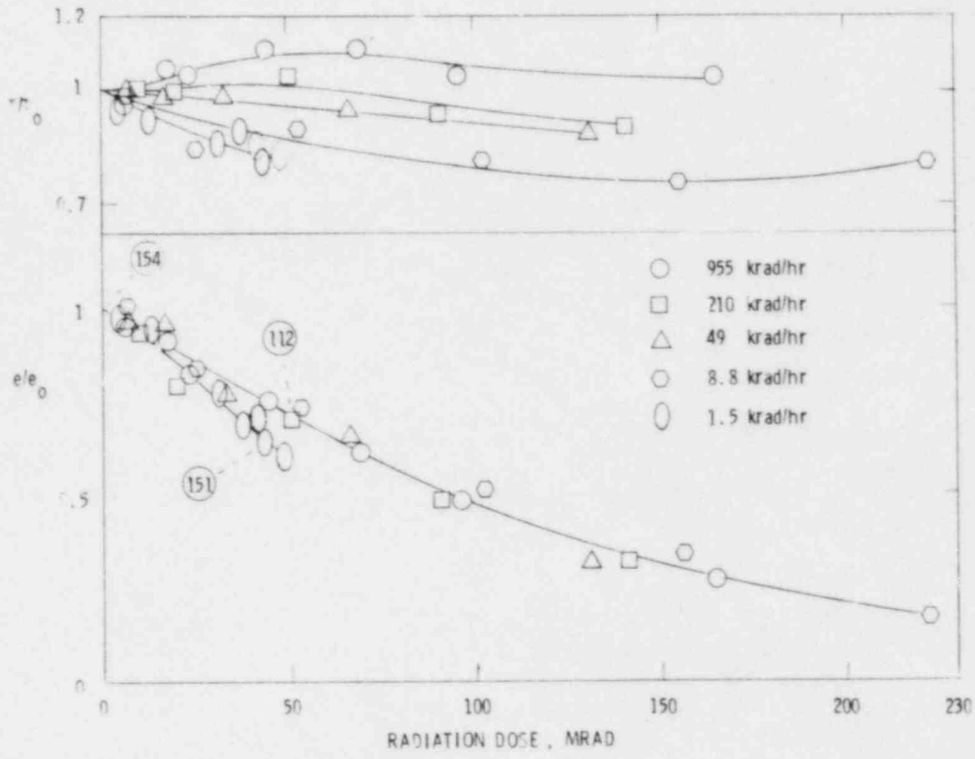

Fig. 4. Aging of chlorosulfonated polyethylene jacket. Explanation of figure is identical to Fig. 1.

Solubility determinations and swelling techniques are two other excellent methods of assessing the relative importance of crosslinking and scission. Since the 4 materials studied represent commercial formulations whose exact constituents and constituent proportions are unknown, the numbers obtained in our measurements represent the solubility and percentage swell of the commercial filled material rather than the polymeric component. Some representative results from the swelling experiments are shown in Figs. 1-4, where the circled numbers represent the weight swelling ratios corresponding to the indicated experimental conditions. For example in CLPO,

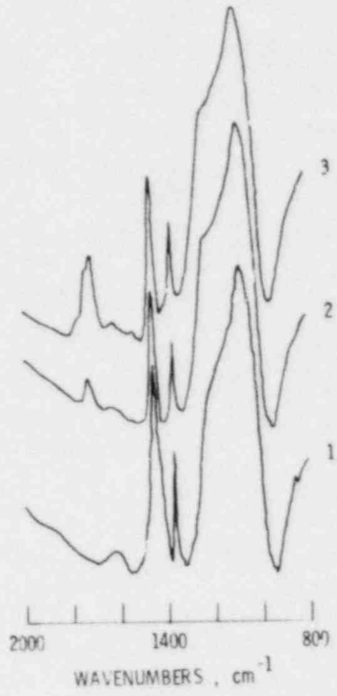

Fig. 5. Infrared spectra of ethylene propylene rubber insulation. Curve 1 - unaged material. Curve 2 - aged in air at 1.2 Mrad/hr. Curve 3 - aged in air at 9.3 krad/hr.

unaged material swells 75%, material aged in air at 220 krad/hr to a total dose of 96 Mrad swells 38% and material aged in air at 9 krad/hr to a total dose of 119 Mrad swells 81%. The swelling data shown in Figs. 1-4 is typical of the swelling (and solubility) data generated to date and again indicates that crosslinking dominates scission at high dose rates but scission becomes more important relative to crosslinking as the dose rate in air is lowered. The results from these techniques therefore offer confirmatory evidence for our interpretation that the changing competition between

crosslinking and scission leads to the observed dose rate effects for the 4 materials.

A number of possible explanations for the above dose rate effects exist. One possible mechanism involves oxidative degradation limited by the rate of breakdown of hydroperoxides; these can be relatively stable at room temperature, but will break down over long periods of time, yielding free radical precursors to oxidative degradation. Clough and Gillen (1981) found evidence that this mechanism contributes to substantial dose rate effects in polyvinyl chloride and low density polyethylene. One piece of evidence came from thermal treatments of samples which were previously irradiated at room temperature. The relatively rapid degradation which occurred during the thermal treatment and the fact that the degradation could be blocked by chemically removing the hydroperoxides implicated hydroperoxide breakdown as important to the observed dose rate effects. Similar sequential experiments run on the 4 present materials did not lead to rapid deterioration during the thermal portion of the exposure; we therefore conclude that hydroperoxide breakdown is not a major cause of the present dose rate effects.

A second plausible explanation involves oxidative degradation limited by the rate of oxygen diffusion into the polymer, a mechanism that has been invoked in the past to rationalize dose rate effects (Kuriyama and co-workers, 1979; Schnabel, 1978). We are currently carrying out experiments to assess the importance of diffusion effects for our materials.

The results of this study indicate that dose rate effects exist for CLPO, EPR, CSPE and CP, four commonly used cable insulation and jacketing materials. We also find evidence of important dose rate effects in polyvinyl chloride cable jacketing material and in low density polyethylene cable insulation material (Clough and Gillen, 1981). These results have important implications for the use of such materials for nuclear applications, since they clearly indicate that the mechanism of degradation is often quite different (and the amount usually more severe) under the low dose rate exposures characteristic of actual aging conditions compared to the mechanism occurring under the high dose rate exposures normally utilized for aging simulations. Material aging data generated at high dose rates (Schonbacher and Stolarz-Izycka, 1979; VandeVoorde and Restat, 1972) must therefore be treated cautiously if a low dose rate application is intended.

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