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Retention: *Permanent*

Effects of Gamma Irradiation on EPDM Elastomers (Revision 1)

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EXECUTIVE SUMMARY

Two formulations of EPDM elastomer, one substituting a UV stabilizer for the normal antioxidant in this polymer, and the other the normal formulation, were synthesized and samples of each were exposed to gamma irradiation in initially pure deuterium gas to compare their radiation stability. Stainless steel containers having rupture disks were designed for this task. After 130 MRad dose of cobalt-60 radiation in the SRNL Gamma Irradiation Facility, a significant amount of gas was created by radiolysis; however the composition indicated by mass spectroscopy indicated an unexpected increase in the total amount deuterium in both formulations. The irradiated samples retained their ductility in a bend test. No change of sample weight, dimensions, or density was observed. No change of the glass transition temperature as measured by dynamic mechanical analysis was observed, and most of the other dynamic mechanical properties remained unchanged. There appeared to be an increase in the storage modulus of the irradiated samples containing the UV stabilizer above the glass transition, which may indicate hardening of the material by radiation damage.

Revision 1 adds a comparison with results of a study of tritium exposed EPDM. The amount of gas produced by the gamma irradiation was found to be equivalent to about 280 days exposure to initially pure tritium gas at one atmosphere. The glass transition temperature of the tritium exposed EPDM rose about 10 °C. over 280 days, while no glass transition temperature change was observed for gamma irradiated EPDM. This means that gamma irradiation in deuterium cannot be used as a surrogate for tritium exposure.

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ABBREVIATIONS

SRNL	Savannah River National Laboratory
SRS	Savannah River Site
EPDM	Ethylene propylene diene monomer
DMA	Dynamic Mechanical Analysis (Analyzer)

Introduction

Polymeric materials become damaged by exposure over time to ionizing radiation. Despite the limited lifetime, polymers have unique engineering material properties and polymers continue to be used in tritium handling systems. In tritium handling systems, polymers are employed mainly in joining applications such as valve sealing surfaces (eg. Stem tips, valve packing, and O-rings).

Because of the continued need to employ polymers in tritium systems, over the past several years, programs at the Savannah River National Laboratory have been studying the effect of tritium on various polymers of interest [1-5]. In these studies, samples of materials of interest to the SRS Tritium Facilities (ultra-high molecular weight polyethylene (UHMW-PE), polytetrafluoroethylene (PTFE, Teflon®), Vespel® polyimide, and the elastomer ethylene propylene diene monomer (EPDM)) have been exposed in closed containers to tritium gas initially at 1 atmosphere pressure. These studies have demonstrated the degradation of properties when exposed to tritium gas. Also, the radiolytic production of significant amounts of hydrogen has been observed for UHMW-PE [1, 3] and EPDM [2, 3].

The study documented in this report exposes two similar formulations of EPDM elastomer to gamma irradiation in a closed container backfilled with deuterium. Deuterium is chemically identical to protium and tritium, but allows the identification of protium that is radiolytically produced from the samples. The goal of this program is to compare and contrast the response of EPDM exposure to two different types of ionizing radiation in a similar chemical environment.

Experimental Materials and Methods

Material Synthesis

Two formulations of EPDM were compounded by the RD Rubber Technology Corporation (Table I), termed SRNL-KCP and SRNL-1 for this study.

Component	Parts by Weight
Royaline 580 HT	100
Zic-Stick 85	5
N-990 Carbon Black	40
N-539 Carbon Black	25
Dicup 40C	12
Flectol H Antioxidant	2
SR350 (TMP TMA)	10

Table I. Components and amount in parts by weight in SRNL-KCP. SRNL-1 is identical except Flectol H Antioxidant is replaced by Cyasorb UV5411 UV Stabilizer, same part by weight.

The two formulations were identical except SRNL-KCP had an antioxidant (Table I), and SRNL-1 replaced this component with a UV stabilizer. Each formulation was combined using a two roll mill, press cured using a moving die rheometer at 166 °C, followed by a post cure at 182 °C in a vacuum oven for 2-

4 hours. Sheets 5 ¾ ” by 5 ¾” by 1/16 ” were produced. Samples for exposure and testing were cut from these sheets.

Exposure Containers

Stainless steel containers were designed having a rupture disk to contain the samples and deuterium gas during exposure (Fig.1). Fabricated from a standard 2 ¾ ” CF type vacuum connection and a Nupro H series valve, the rupture disk burst pressure is 100 psig. This burst pressure was based on stress analysis and testing of the container using ASME pressure vessel design code. The design pressure is full vacuum to 100 psig and the design temperature is 100 °F. Samples are inserted and removed from the container by opening the main flange connection.

Sample preparation and preliminary measurements

Twelve samples, six of each formulation, were cut in rectangular shape (nominally 1 ¼” by 3/8”), and their actual dimensions (length, width, thickness) measured with calipers. The samples were weighed using a laboratory electronic balance. The six samples of each formulation were inserted into one of two containers. The two containers were closed, tightened, evacuated, and then backfilled with pure deuterium to 814 torr. Before loading with deuterium, the free volume in each container was measured using the loading manifold. The free volumes were 59.3 cc for the container with SRNL-1 samples, and 56.1 cc for the container with SRNL-KCP samples.

The two containers with samples and deuterium gas were placed in the Model 109 Irradiator in the SRNL Cobalt-60 Irradiation Facility. They were irradiated at ambient temperature for 459.66 hours. The irradiator dose rate at the beginning of the irradiation was 2.828×10^5 Rad/hour, so the total dose was about 130 MRad (not corrected for attenuation by the container).

After irradiation, the containers were attached separately to a gas manifold. The manifold had been volume calibrated, and the gas in the container was released into the evacuated manifold to allow the pressure to be measured by a pressure transducer. The final pressure in the containers at the end of irradiation was then calculated using the known system volumes of the manifold. In addition, “grab” samples of each containers gas was taken to a mass spectrometer to determine the isotopic composition of the gas after irradiation.

Dynamic Mechanical Analysis

Dynamic mechanical analysis measures the elastic and viscoelastic parameters related to small cyclic deformation of materials- storage modulus, loss modulus, and tan delta. The storage modulus is the constant relating the amount of elastic deformation to a given applied load. The loss modulus is a measure of the time-dependent deformation under a given load at the applied cycling frequency, and provides insight to the relative amount of molecular motion occurring at the specific applied cycling frequency. Tan delta is the ratio of the loss modulus to the storage modulus, and was the parameter used in old resonant-type DMA tests. Tan delta is also normally reported with storage and loss modulus as a way of comparing DMA data from resonant test with non-resonant tests.

A TA Instruments Model 2980 dynamic mechanical analyzer was used for this study. It is a forced oscillation, non-resonant, constant amplitude instrument. The single-cantilever-beam clamp, or sample holder, was used, being the clamp of choice for measuring the glass transition temperature of elastomers. The oscillation amplitude was chosen to be 40 microns for all samples. To determine the optimal amplitude for testing, a so-called “amplitude sweep” was performed in a previous study [2] of EPDM in which the amplitude was varied. The range of amplitudes that lead to equal DMA parameter (storage

modulus, loss modulus, tan delta) measurements reveal the region of "linear viscoelasticty" for the material.

Each DMA test involved stabilizing the temperature at the chosen lowest temperature (-70 °C for most of the tests), remaining at this temperature for 10 minutes to further stabilize the temperature around the sample, and then increasing the sample temperature at 1 °C per minute until the chosen highest temperature (-10 °C for most tests). The dynamic mechanical properties were continuously measured during the controlled temperature rise. The TA 2980 has both electrical resistance heating and cooling by evaporated cold nitrogen gas from a liquid nitrogen container called the Gas Cooling Accessory (GCA) which is a part of the DMA system. The control software enables optimized control of cooling and heating for a given temperature and heating rate. Data was taken using the DMA Multi-Frequency mode, at frequencies of 1, 3, and 10 Hz. The DMA continuously acquired data at each of the set frequencies in sequence during the increasing temperature scans. The sampling rate was set at 3.0 sec/point, which specifies the time over which data is acquired for each set frequency. The system was calibrated at least once a month during the testing program.

Results and Discussion

Sample Size, Mass, Density

The sample volume and mass for each of the six samples of a given formulation was added to calculate the relative change of volume and mass, and the density. The relative mass loss was 0.1% and the volume gain was 1.6% for SRNL-1 and 0.9% for SRNL-KCP. These numbers are insignificant and probably reflect the uncertainty in the measurements. The density was found to be about 1.13 g/cc, and did not change significantly with irradiation.

Bend Test

A small bench top vise (Fig. 2) was altered to perform bend tests per ASTM E 290 – 97a "Standard Test Methods for Bend Testing of Materials for Ductility". The specific test performed was a Semi-Guided test for thin material, Arrangement B. Three of the six exposed samples for each formulation were tested. No breaks were observed, and all samples could be fully bent (180°) and immediately straighten when released. No loss of ductility occurred during the exposure.

Gas Analysis

The final pressure in the SRNL-1 container was found to be 1973 torr, and in the SRNL-KCP container was 1996 torr. From the original deuterium pressure of 814 torr, this is a factor of about 2.4 increase in gas pressure caused by the irradiation. From the free volume of the container, the number of moles of gas can be calculated using the Ideal Gas Law- 0.00629 moles for SRNL-1 and 0.00602 moles for SRNL-KCP

A low Z mass spectrometer was used to determine the composition of the grab samples from each container. For SRNL-1, the gas was 16% H_2 and 84% D_2, and for SRNL-KCP the gas was 17% H_2 and 83% D_2. When these compositions are applied to the total moles of gas in the container, the amount of deuterium is seen to have increased (Fig. 3). This is a completely unexpected result- in previous studies of EPDM samples in tritium gas, the tritium in the gas was removed and absorbed in the samples. If all of the additional gas created was protium, as expected, the final mole fractions would have been 59% H_2 and 41% D_2. These results may have resulted from experimental error.

Dynamic Mechanical Analysis Results

The glass transition temperature, T_g, was determined for each sample using ASTM E 1640 "Standard Test Method for Assignment of the Glass Transition Temperature by Dynamic Mechanical Analysis". The intersection of two tangents of the storage modulus versus temperature curve- the tangent of data below T_g and the tangent at the inflection point of the sigmoidally changing storage modulus with temperature in the middle of the glass transition. The temperature of the tangents intersection is regarded as being T_g (Fig. 4). The standard requires an applied frequency of 1 Hz and a temperature increase rate of 1 °C/minute, which were used in this study. The glass transition temperature of all samples (both formulations and both unexposed and gamma irradiated samples) was -53° C., with a population standard deviation of 1.5° C.

An example of a full DMA scan shows the huge effect the glass transition has on the elastic and viscoelastic properties of the EPDM thorough the glass transition (Fig. 5). The temperature of the peaks in the Loss Modulus and Tan Delta curves increases when the excitation frequency increases; this means the glass transition occurs at higher temperatures for higher frequencies. This is expected and often observed in polymers. When these plots for other samples are compared, no significant change in viscoelastic properties is observed for either formulation. A convenient way to compare the storage moduli of different samples is to pick two temperatures- one significantly below T_g, -70 °C in this case, and one significantly above T_g, -15 °C, and compare the storage moduli (Fig. 6). There was no significant change of the storage modulus below T_g (Fig. 6 a.) the population standard deviation being 801 MPa. For the modulus at -15 °C, there appears to be a significant hardening of the storage modulus for the SRNL-1 gamma irradiated samples (Fig. 6 b.), the population standard deviation being 11 MPa. This could imply that SRNL-1 is less resistant to degradation by gamma irradiation than SRNL-KCP at temperatures above the glass transition, however more study is needed to confirm this hypothesis.

Summary and Conclusions

Two formulations of EPDM elastomer, one containing a UV stabilizer and the other an antioxidant normal for this type of elastomer, were synthesized and samples of each were exposed to gamma irradiation in initially pure deuterium gas to compare their radiation stability. A significant amount of gas was created by radiolysis; however the composition indicated by mass spectroscopy indicated an unexpected increase in the total amount deuterium. The irradiated samples retained their ductility in a bend test. No change of sample weight, dimensions, or density was observed for the irradiation dose tested. No change of the glass transition temperature was observed, and most of the other dynamic mechanical properties remained unchanged. Their appeared to be an increase in the storage modulus of the SRNL-1 gamma irradiated samples above the glass transition, which may indicate hardening by radiation damage.

A later comparison of gas production rates from tritium-exposed EPDM samples reveals that the gamma exposure discussed here produced about the same amount of gas that a 280 day exposure of EPDM samples would [Appendix]. The glass transition temperature of the 280-day tritium exposed EPDM would have risen by 10 °C., which is significantly greater than glass transition temperature change observed here. This means that gamma irradiation of EPDM samples in deuterium is not congruent with tritium exposure and so cannot be used as a surrogate for tritium exposure testing.

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2. "Tritium Effects on Dynamic Mechanical Properties of EPDM Elastomer", E.A. Clark, G.C. Staack, *Fusion Science and Technology*, **54 (2)**, pp. 576-579 (2008).
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5. "Investigation on the effects of beta and gamma irradiation on conducting polymers for sensor applications", Marie C. Kane, Robert J. Lascola, Elliot A. Clark. *Radiation Physics and Chemistry*, **79**, pp. 1189-1195 (2010).

Figure 1. Photograph of sample exposure container, with valve and rupture disk.

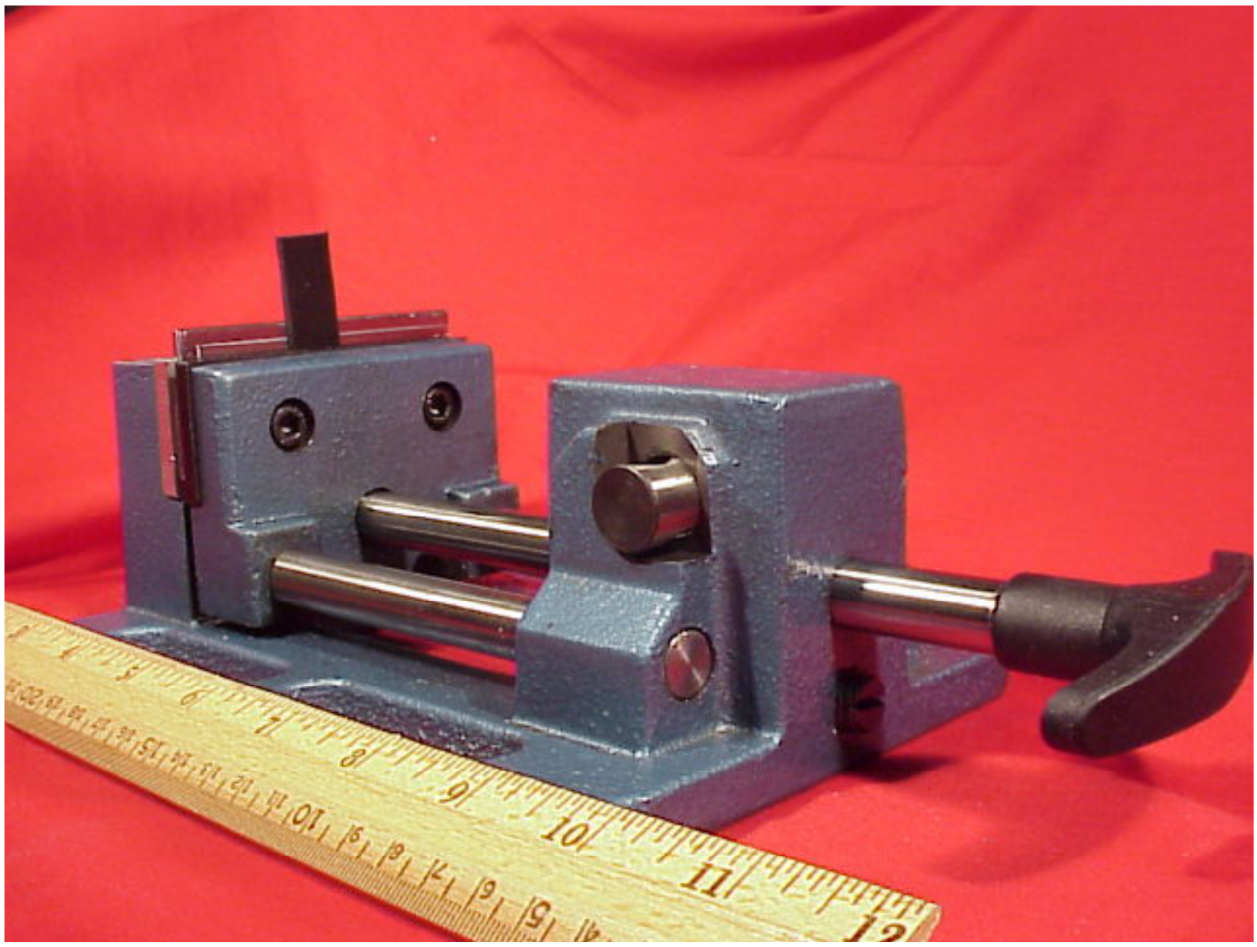
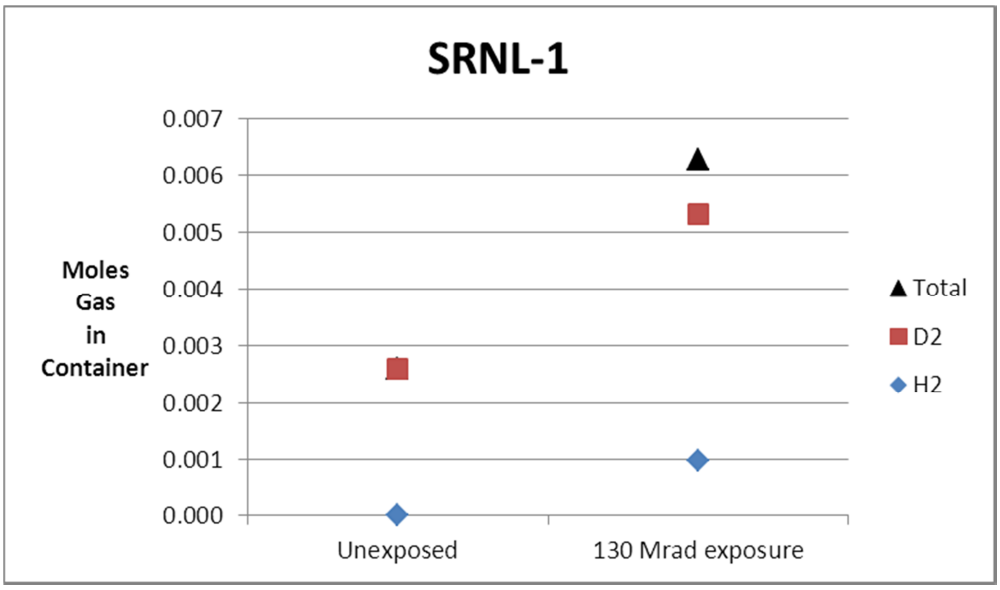
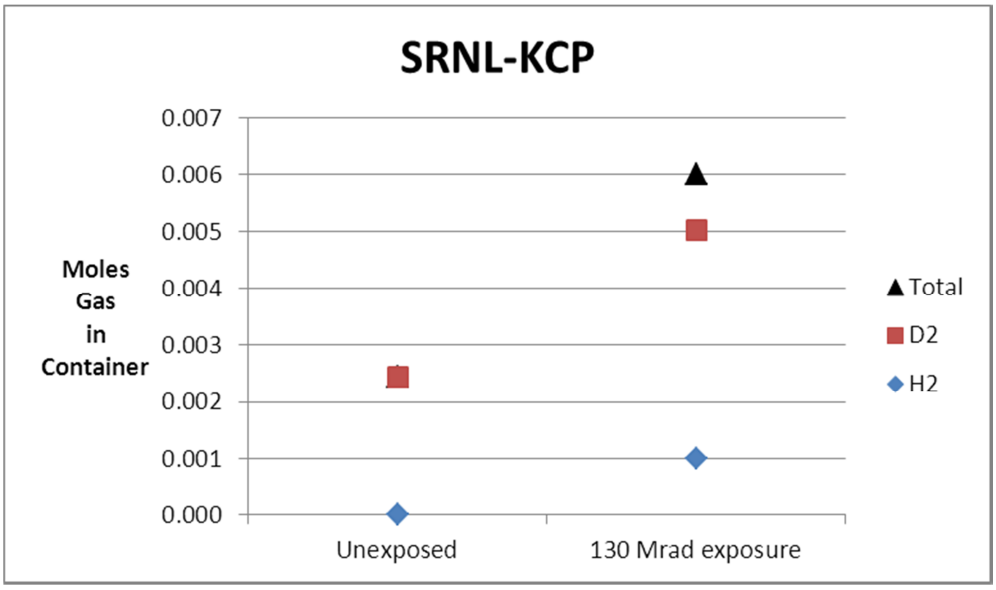


Figure 2. Photograph of small bench top vise altered for ASTM Bend Test. EPDM sample in vise is shown.



a.



b.

Figure 3. Moles gas in container, protium deuterium, and total, for formulations a. SRNL-1 and b. SRNL-KCP. Note unusual increase in deuterium after irradiation.

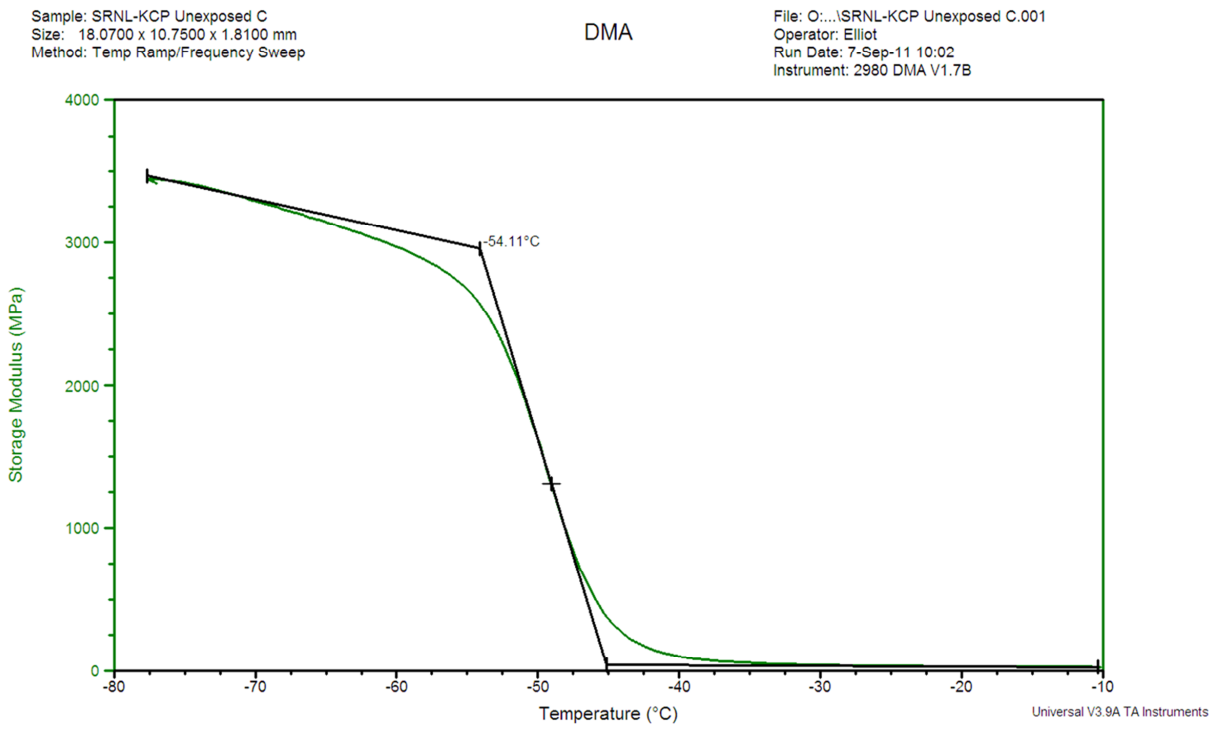


Figure 4. Storage modulus versus temperature for one sample tested, illustrating the tangent intersection method of ASTM E 1640 "Standard Test Method for Assignment of the Glass Transition Temperature by Dynamic Mechanical Analysis".

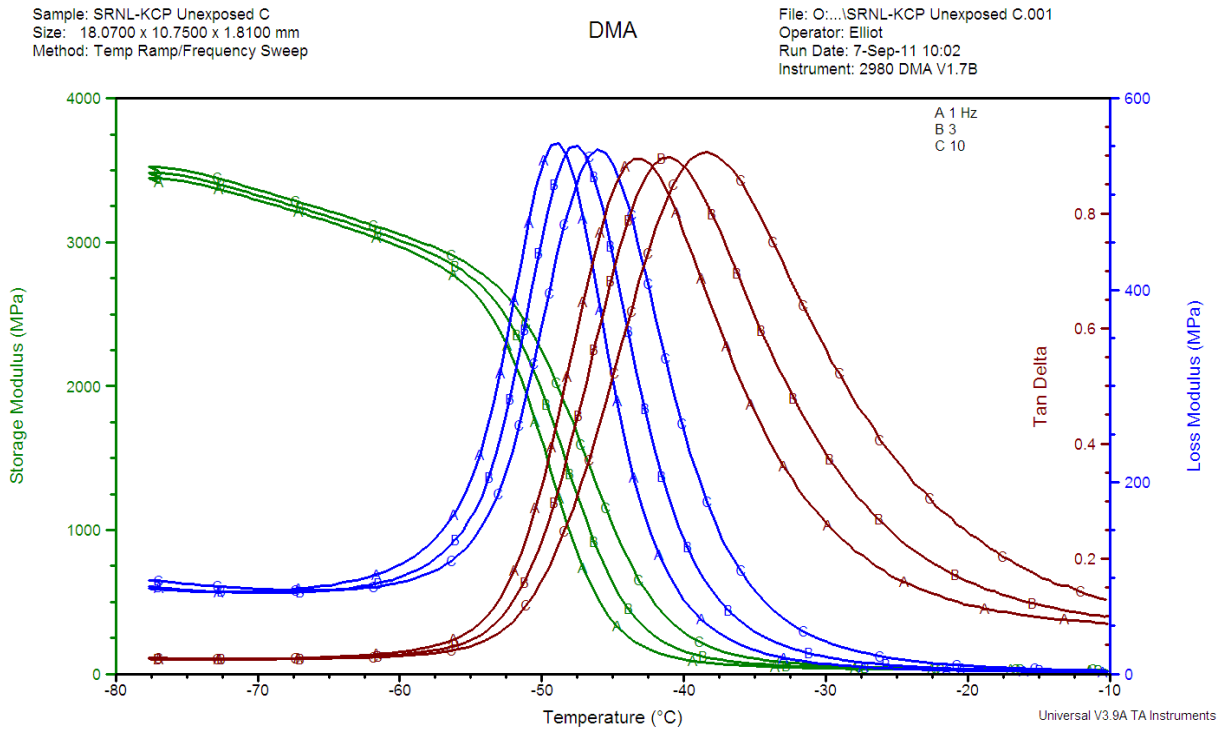
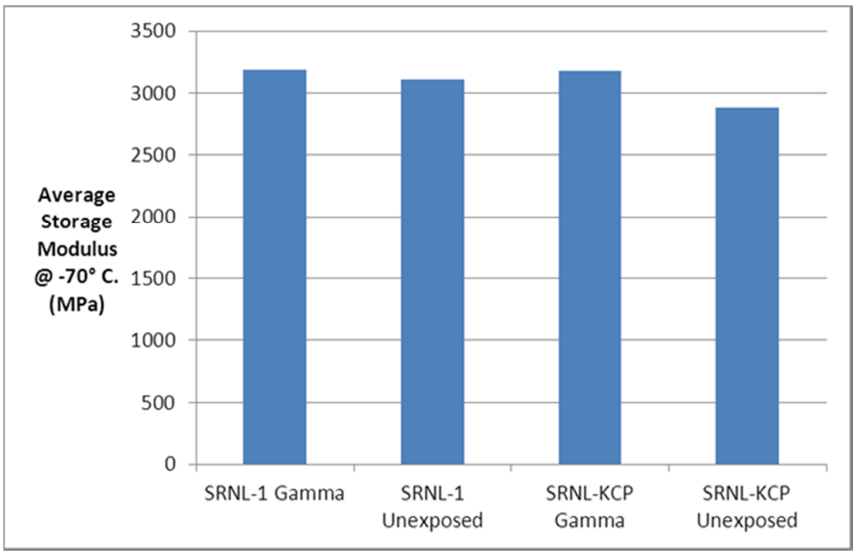
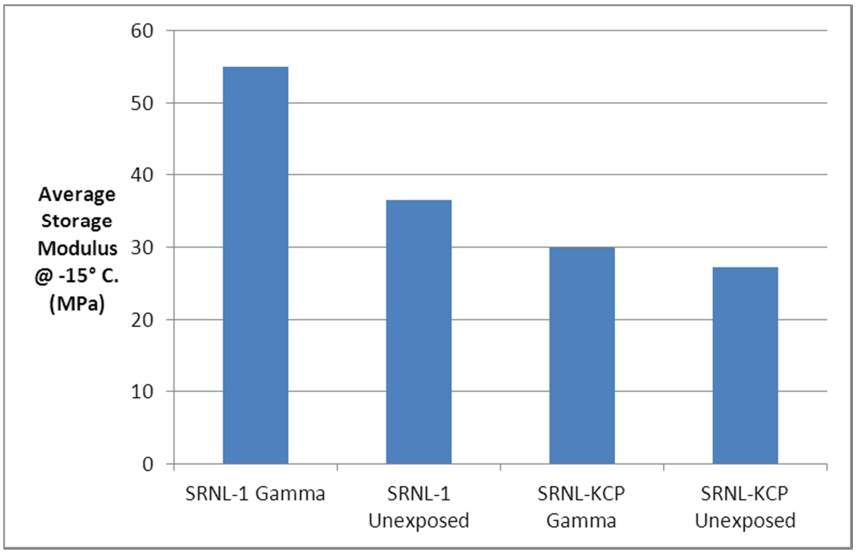


Figure 5. Storage Modulus, Loss Modulus, Tan Delta of unexposed SRNL-KCP sample C. Test run from -80 °C to -10 °C at 1 °C/minute. Excitation frequencies indicated by A- 1 Hz, B- 3 Hz, C- 10 Hz.



a.



b.

Figure 6. Average storage modulus for the formulations and gamma exposed/unexposed samples; a. at -70° C., b. at -15° C.

APPENDIX

Comparison of Tritium Exposure Studies with Gamma Ray Exposure Study of EPDM

A recent additional analysis of radiological gas generation data of polymers exposed to (initially) one atmosphere tritium gas in closed containers has resulted in estimation of gas generation rates. For carbon-black-filled EPDM, the rate is $1.04*10^{-3}$ mol gas produced/g polymer/year [A1]. This appendix compares the gas generation and glass transition temperature changes from the gamma irradiation study presented in this report to an earlier study of effects of tritium exposure on EPDM [A2]

For the case of samples "SRNL-KCP" exposed to 130 Mrad ^{60}Co gamma radiation for about 19.2 days at $2.8*10^{5}$ Rad/hour (not accounting for attenuation by the exposure container), 0.00356 moles of gas were created from samples having total mass 4.43 g. This amounts to 0.000804 mols created/g EPDM. The additional analysis found a gas creation rate of $1.04*10^{-3}$ mol gas/g EPDM/year for EPDM exposed to initially 1 atm tritium at ambient temperature [A1].

Dividing the moles created per gram EPDM by gamma irradiation by the molar gas creation rate per gram EPDM in tritium results in an equivalent tritium exposure of 0.77 year or about 280 days for the gamma irradiation material. This means that from the point of view of gas production, the gamma irradiation was equivalent to an exposure to initially 1 atm tritium for about 280 days.

The glass transition temperature of the filled EPDM exposed to tritium gas increased significantly, from -53 °C. to about -43 °C. over 280 days [A2]. The glass transition temperature of gamma-irradiated EPDM did not change within experimental error (discussed above in this report). Thus, it appears that for the doses and dose rates applied in these studies, the gas generation rate and glass transition temperature changes were not congruent for the two types of irradiation. This implies that tritium effects must continue to be studied by actual tritium exposure testing; gamma irradiation studies are not equivalent. This conclusion is also supported by previous studies comparing tritium and gamma ray exposures of Nafion® films [A3].

References for Appendix

[A1] E.A. Clark. "Radiolytic Gas Production Rates of Polymers Exposed to Tritium Gas", Report SRNL-STI-2013-00506 rev. 0, 31 August 2013.

[A2] E.A. Clark. "Effects of Tritium Gas Exposure on EPDM Elastomer", Report SRNL-STI-2009-00801 rev. 0, 11 December 2009.

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