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EFFECTS OF TRITIUM ON UHMW-PE, PTFE, AND VESPEL® POLYIMIDE

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Samples of ultrahigh molecular weight polyethylene (UHMW-PE), polytetrafluoroethylene (PTFE), and the polyimide Vespel® were exposed to tritium gas in closed containers initially at 101 kPa (1 atmosphere) pressure and ambient temperature for various times up to 2.3 years. Tritium exposure effects on the samples were characterized by dynamic mechanical analysis (DMA) and radiolysis products were characterized by measuring the total final pressure and composition in the exposure containers at the end of exposure period.

I. INTRODUCTION

Despite the well-known degradation of polymers when exposed to ionizing radiation, there are applications in which polymers are exposed to ionizing radiation for which they are uniquely suited and so are employed despite their limited service life. For example, in tritium gas handling systems polymers are used for valve stem tips, valve stem packing, and for other sealing functions. At the Savannah River Site, tritium processing uses ultra-high molecular weight polyethylene (UHMW-PE) for valve stem tips, glass-filled polytetrafluoroethylene (PTFE, one trade name is Teflon®) for the sealing part of valve packing, and the polyimide Vespel® for valve stem tips. The performance of these materials in tritium processing is monitored by regular leak checking, and components are replaced when they fail to meet various performance criteria (such as excessive leak rate through a valve).

The study described here was undertaken to investigate the effects of tritium gas exposure on these three polymers. Samples were exposed in closed containers to pure tritium gas initially at 1 atm. pressure. At the end of the allotted exposure time, radiolysis products were characterized by measuring the gas pressure and composition (determined by mass spectroscopy). The effects of tritium exposure on the samples were characterized by Dynamic Mechanical Analysis (DMA).

II. SAMPLE EXPOSURE TO TRITIUM GAS

Samples of UHMW-PE, "virgin" PTFE (unfilled), and Vespel® SP-1 were machined from nominally 0.16 cm (1/16") sheet to rectangles of 3.18 cm (11/4") long by 0.95 cm (3/8") wide. Five samples of a given polymer were inserted in Type 316L stainless steel exposure containers, which were about 25.4 cm (10") long and had an internal diameter of about 1.27 cm (1/2"). The containers were sealed by two metal bellows valves in series of a type normally employed in tritium service. Each container had only one type of polymer within, and each set of samples was removed from the container and characterized only once.

Initially, all exposure containers (containing samples) were evacuated and filled with 100% tritium gas to a pressure of 101 kPa (1 atmosphere) using a laboratory tritium manifold located in a once-through air glovebox. The container valves were then closed and the containers were stored at ambient (tritium glovebox) temperature for intervals between three months and 2.3 years. At the end of the exposure time for a given set of samples, their container was re-connected to the tritium manifold, and the total pressure at the end of the exposure was measured using the manifold- the container gas was expanded through calibrated volumes to a pressure transducer, and the final pressure in the container was calculated using the Ideal Gas Law. A sample of the gas at the end of exposure was taken to a mass spectroscopy facility for gas compositional analysis. The container was then fully evacuated overnight, and then opened the next day. The samples were transferred to a tritium hood for post-exposure characterization by DMA.

Dynamic Mechanical Analysis consists of applying a known force at one or more frequencies to the sample under study and the displacement of the sample at the location of the force is detected. The DMA calculates the elastic and viscoelastic parameters from the force, displacement, and the geometrical properties of the sample (width, thickness, gage length). The properties measured for this study were the storage modulus (instantaneous elastic constant), the loss modulus (measure of time-dependent visco-elastic deformation), and the quantity tan delta, which is defined as the ratio

of the loss modulus to the storage modulus. The phase angle delta is the phase angle between the applied force and the observed displacement.

A TA Instruments Model 2980 DMA was altered to separate the mechanical and electronic parts of the analyzer to allow the DMA to be located in a tritium hood, enabling analysis of the polymer samples. The three-point bend "clamp", or sample holder, was used for all experiments. Preliminary experiments on unexposed samples were performed to allow DMA parameters such as oscillation amplitude, static force, and auto-amplitude to be determined for each polymer. DMA characterization began at -60°C., and the temperature increased at 1°C./minute, until either the material became too soft to continue or until 270°C. for Vespel®.

III. RESULTS and DISCUSSION

III.A. Gas Analysis after Exposure

Analysis of the gas at the end of exposure reveals a significant production of protium ($^1H_2$) for UHMW-PE (Figs. 1, 2). There was little change in the total pressure in the Vespel® containers, however about half the gas was protium (Figs. 1, 2). The PTFE containers showed a net total pressure decrease, and no protium (excepting one container that is considered to be an anomaly) (Figs. 1, 2).

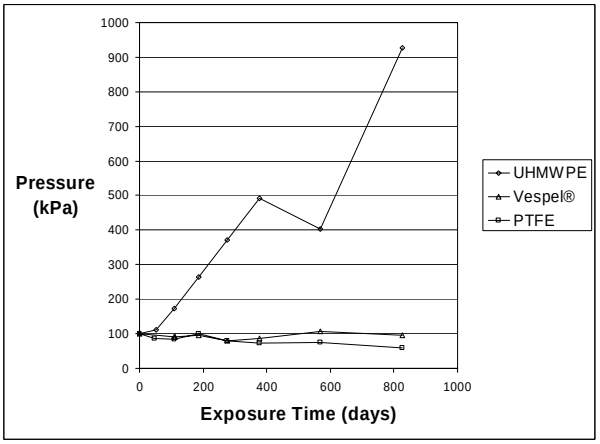

Fig. 1. Total pressure in exposure container at end of exposure, as function of exposure time. UHMW-PE, Vespel®, PTFE as marked.

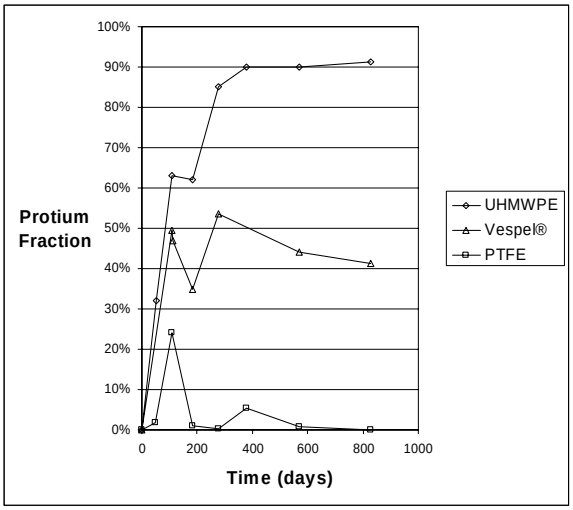

Fig. 2. Fraction of gas detected as protium, as function of exposure time. UHMW-PE, Vespel®, PTFE as marked.

The large production of protium during tritium exposure is consistent with observations of protium production during gamma ray irradiation of polyethylene[1]. Using a typical G value for protium production 3.1 molecule/eV for polyethylene[1] and the average beta decay energy of 5.7 KeV/decay, a calculation indicates that the protium partial pressure at 2.3 years (826 days Fig. 1) results from release of about 4% of the protium from the UHMW-PE samples.

The drop in pressure with tritium exposure of PTFE could result from the formation of ^{3}HF, which if chemically like HF tends form linear molecular aggregates and be adsorbed onto the surface of the container[2], and so would result in a net pressure decrease. The observed pressure decrease over 2.3 years can be estimated to result when 0.8% of the repeat units of the PTFE formed ^{3}HF.

It is noteworthy that the exposure gas exposed to Vespel® became about half protium after about six months exposure (Fig. 2). Vespel® is normally considered to be more resistant to ionizing radiation than many polymers, because of its aromatic molecular structure. The results of this study show that Vespel® is not immune to radiation effects, and shows that isotope exchange does occur when Vespel® contacts tritium.

III.B. Dynamic Mechanical Analysis

III.B.1.UHMW-PE

Tritium exposure dramatically reduced both the loss modulus peak at +50°C. and the large increase in tan delta above ambient temperature in UHMW-PE (compare Figs. 3 and 4).

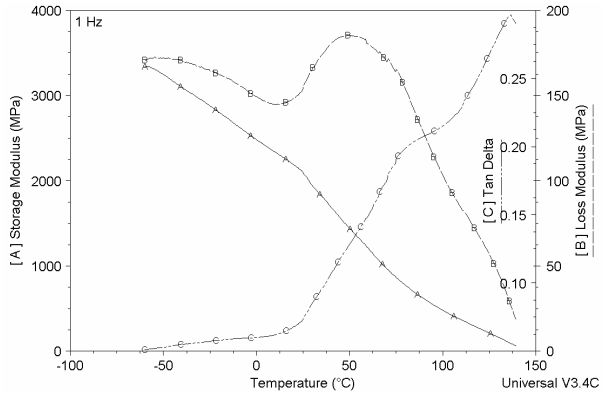

Fig. 3. Storage modulus, loss modulus, tan delta at 1 Hz of unexposed UHMW-PE as a function of temperature. Temperature increased 1°C/minute during test.

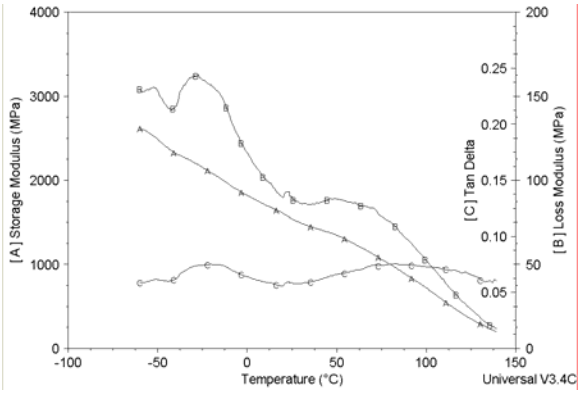

Fig. 4. Storage modulus, loss modulus, tan delta at 1 Hz of UHMW-PE after exposure to tritium for 2.3 years as a function of temperature. Temperature increased 1°C per minute during test.

During tritium exposure, the storage modulus of UHMW-PE first increased and then decreased (Fig. 5). This behavior fits the general paradigm of cross-linking during initial irradiation followed by a net degradation of properties at higher doses[3]. The storage modulus decreased after about one year at both -50° and +100°C.

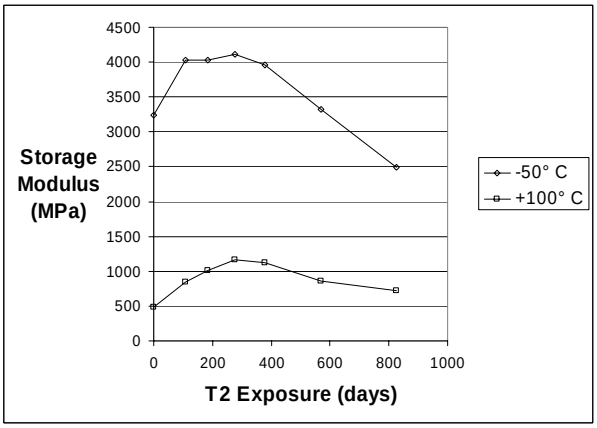

Fig. 5. Storage modulus measured at 1 Hz of UHMW-PE at -50°C. and at +100°C. as a function of tritium exposure time.

There is a strong frequency dependence of the storage modulus of unexposed UHMW-PE at elevated temperature, and this dramatically decreased with tritium exposure (Fig. 6). The reduction of the frequency dependence reflects the cross-linking that reduces the various molecular chain motions that causes the storage modulus to change with frequency.

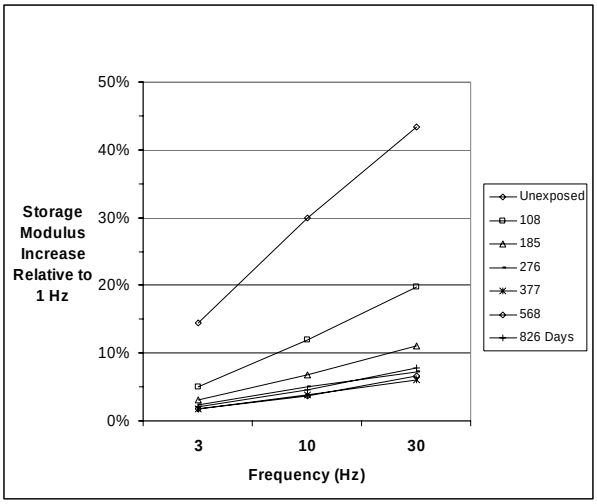

Fig. 6. Percent increase of storage modulus at 3, 10, and 30 Hz relative to 1 Hz of UHMW-PE at +100°C. as a function of tritium exposure time.

III.B.2.PTFE

DMA of unexposed PTFE (Fig. 7) reveals a discontinuity in the storage modulus and peaks in the loss moduli and tan delta at about 25-30°C. that reflect transitions in the crystallographic part of the polymer[4]. These features were not significantly changed by tritium exposure.

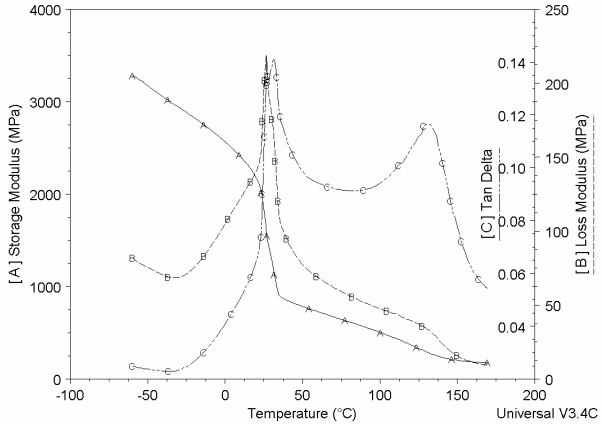

Fig. 7. Storage modulus, loss modulus, tan delta at 1 Hz of unexposed PTFE as a function of temperature. Temperature increased 1°C/minute during test.

The most important observation for PTFE was that after 9 months tritium exposure, the samples were too weak to handle and test by DMA. Up to 9 months, the moduli behaved qualitatively similarly to UHMW-PE- the storage modulus initially increased (Fig. 8), and the frequency dependence decreased with tritium exposure (Fig. 9).

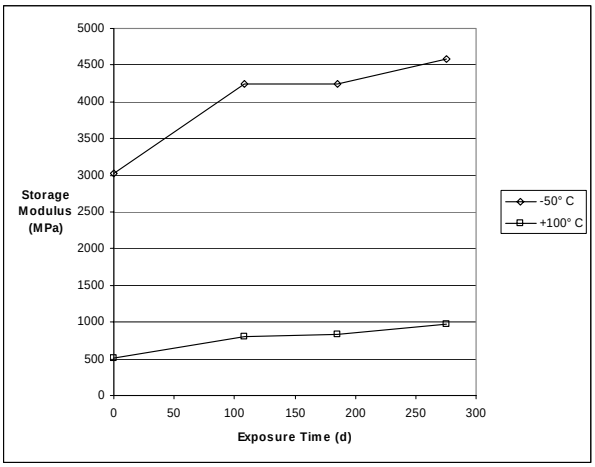

Fig. 8. Storage modulus measured at 1 Hz of PTFE at -50°C. and at +100°C.as a function of tritium exposure time.

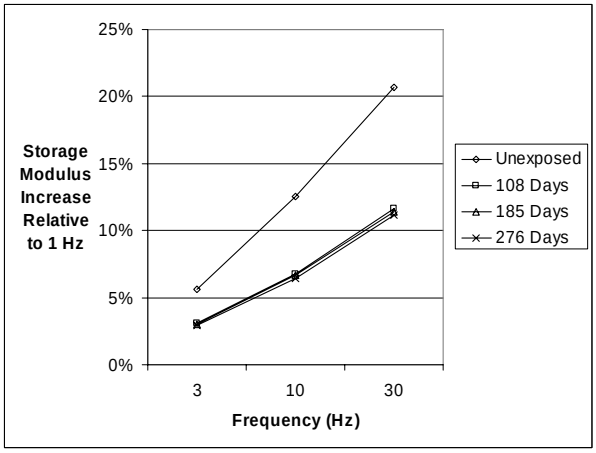

Fig. 9. Percent increase of storage modulus at 3, 10, and 30 Hz relative to 1 Hz of PTFE at +100°C. as a function of tritium exposure time.

Tan delta of tritium exposed PTFE decreased significantly above 50°C (Fig 10), again similarly to UHMW-PE (compare curve "C" in Figs. 3 and 4 with Fig. 10)

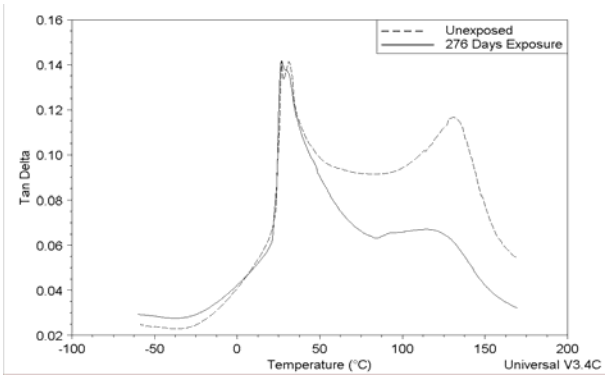

Fig. 10. Tan delta of PTFE at 1 Hz- unexposed and 276 days exposure as indicated. Temperature increased 1°C/minute during test.

III.B.3. Vespel®

There was no significant change in the dynamic moduli for Vespel® exposed to tritium (Figs. 11, 12). No effect of load frequency was found on the storage modulus at any temperature, and no effect of tritium was observed.

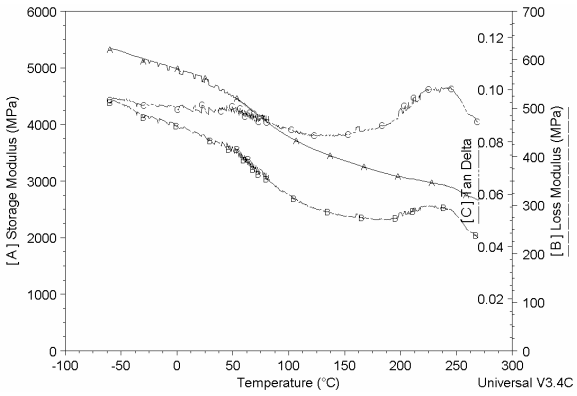

Fig. 11. Storage modulus, loss modulus, tan delta at 1 Hz of unexposed Vespel® as a function of temperature. Temperature increased 1°C/minute during test.

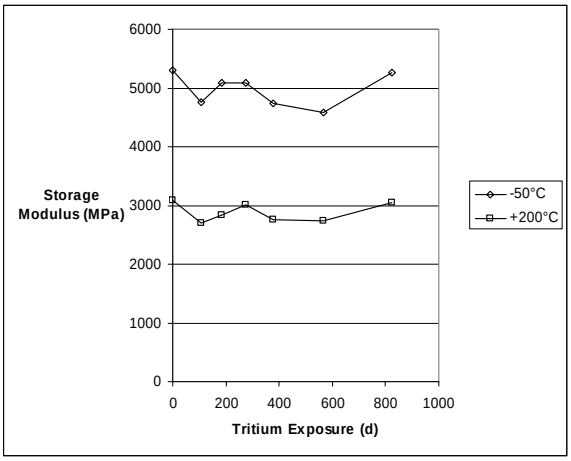

Fig. 12. Storage modulus measured at 1 Hz of Vespel® at -50°C. and at +200°C. as a function of tritium exposure time.

IV. SUMMARY

Samples of ultrahigh molecular weight polyethylene (UHMW-PE), polytetrafluoroethylene (PTFE), and Vespel® SP-1 polyimide were exposed to tritium gas initially at one atmosphere pressure in closed containers at ambient temperature for varying times up to 2.3 years. The gas in the containers was characterized by total pressure and mass spectroscopy, and the samples were characterized by dynamic mechanical analysis. The main observations of this study were:

- UHMW-PE samples generated protium ($^1H_2$), and the storage modulus initially increased and then degraded after longer than one year exposure. The frequency dependence of dynamical properties were drastically reduced by tritium exposure, as was the loss modulus and tan delta. These observations are consistent with the behavior of gamma irradiated UHMW-PE- initial cross-linking followed by overall degradation, and hydrogen (protium) production.
- PTFE became too weak to handle after 9 months exposure. Up to that point, the modulus increased similarly to UHMW-PE, and the frequency dependence and loss modulus decreased, also similar to UHMW-PE. The total pressure lowered with tritium exposure, possibly due to ^{3}HF formation.
- Vespel® exhibited no significant dynamic modulus changes with tritium exposure. The gas in the container remained at the starting pressure, but became 50% protium, revealing that tritium does interact with Vespel®.

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