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Polymer Exposure and Testing Facilities at the Savannah River Site

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Tritium Focus Group

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Outline

- How we expose our materials
- Available characterization methods
- Previous and current work

Sample Exposure

- Design rating for 500 psig and 260°C
- Typically loaded with six samples or the same material - ½" * 2"
- Load with 1 atm T
- Partial pressures have also been loaded
- Gas composition confirmed by GC at loading
- Record pressure, temp., test cell volume.
- Allowed to sit at designated temp. for time needed

Tritium Gas Exposure Container

Materials Test Facility

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Materials Test Facility - Polymer Capabilities

Characterization of Tritiated Materials

Mission

- Characterization of materials in tritium service
- Support existing operations by suggesting alternative polymer formulations
- Help identify counterfeit materials
- Determine life of service for new materials

Examples of Current and Past Projects

- Demonstration that gamma and beta radiation damage to materials is not equivalent
- Demonstration of increased polymer stability by using carbon additives in EPDM rubbers
- Examination of stability of Nafion for tritium removal from water by electrolysis

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Materials for Tritium Service

The beta decay of tritium is ionizing radiation that significantly damages polymeric materials. Although selecting polymers for use in tritium handling systems is avoided where possible, there are always components in tritium systems that have no non-polymeric alternatives.

World Class Characterization Facilities – Science at Work

Researchers at the Savannah River National Laboratory have spent the past two decades building a fully functioning characterization facility that can provide both mechanical and chemical property information on polymers and other related materials that are used in tritium service. These facilities are capable of handling tritiated materials. An array of characterization techniques are available.

Mechanical

Dynamic Mechanical Analysis: DMA enables us to study the viscoelastic properties of materials. Changes in glass transition temperature (T_g) of materials can be identified, as well as changes in the storage modulus, or stored energy, versus temperature.

Bend Testing: Bond testing will tell you how brittle materials are relative to one another.

Chemical

Fourier Transform Infrared (FT-IR): Every polymer has a distinct chemical fingerprint. We can determine the identity of materials with this technique. In addition, as polymers are exposed to tritium, bonds may break or new bonds may form. With FT-IR we can watch the chemical transformations as they occur. This helps us determine time scales for acceptable service life as well as mechanisms for failure.

Time Domain Nuclear Magnetic Resonance (TD-NMR): This compact ^{1}H-NMR has a single sided magnet that can depth profile at 0, 3 and 5 mm. We can determine the crosslinking density of polymers, porosity, and moisture content. This aids in the failure prediction for materials.

Bruker Fourier Transform Infrared (FT-IR) ALPHA with Platinum ATR

Bruker Minispec ProFiler Time-Domain Nuclear Magnetic Resonance (TD-NMR)

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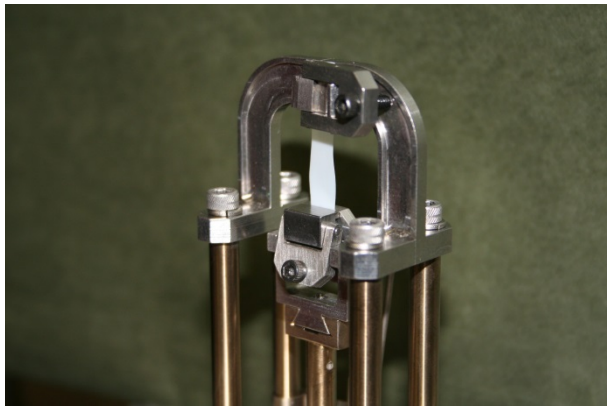
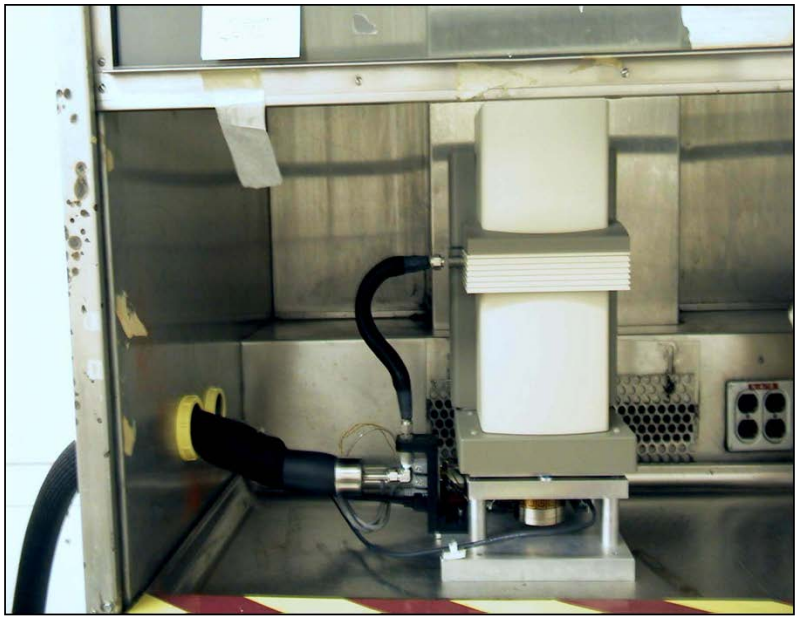
DMA

- TA Instruments 2980 DMA
- Studies the elastic and viscoelastic properties of materials
  - Tg
  - Storage modulus
- Applies small vibrational deformation
- Cryogenic capability

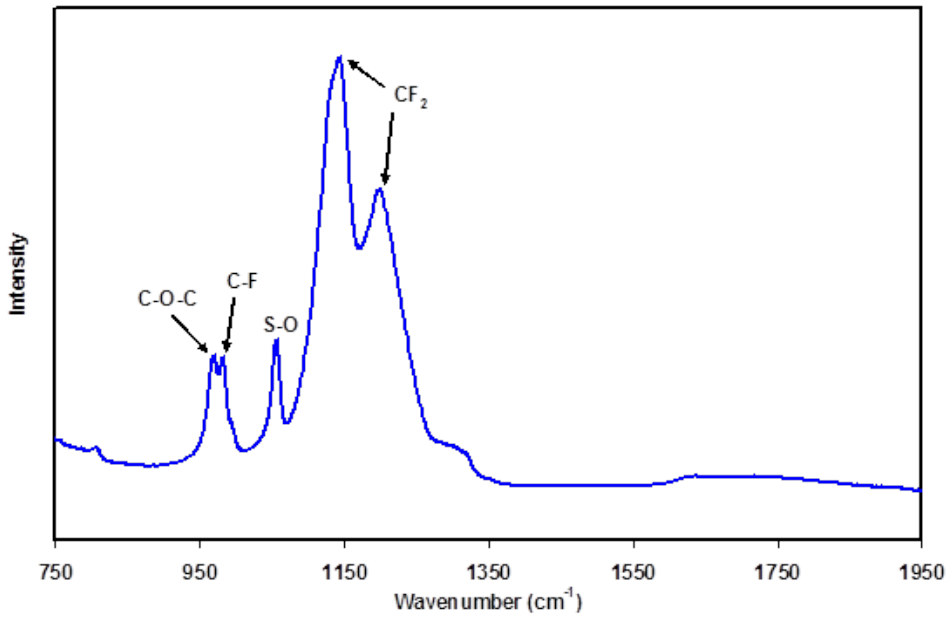




Dynamic mechanical analyzer in tritium hood

FT-IR

- Bruker ALPHA FT-IR with Platinum ATR
- Typically run between 4000-400 cm^{-1}
- Gives important chemical information
- In polymers can determine changes in cross-linking and bonding of atoms



TD-NMR

- Bruker MiniSpec Profiler
- Handheld unit to measure ^{1}H spin at 0mm, 3mm, and 5mm depths
- Can determine crosslinking, porosity, and moisture content
- Gives relative values for T_1 (spin-lattice) and T_2 (spin-spin) relaxation
- FID (free induction decay)
  - Different values for monomer, polymer, additives

Additional Testing and Characterization

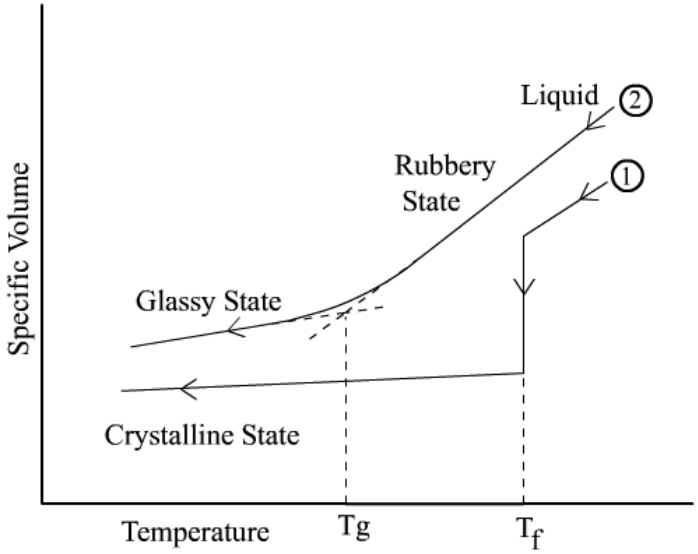
- Bend test
- Auger
- XRD
- Mass Spectrometry

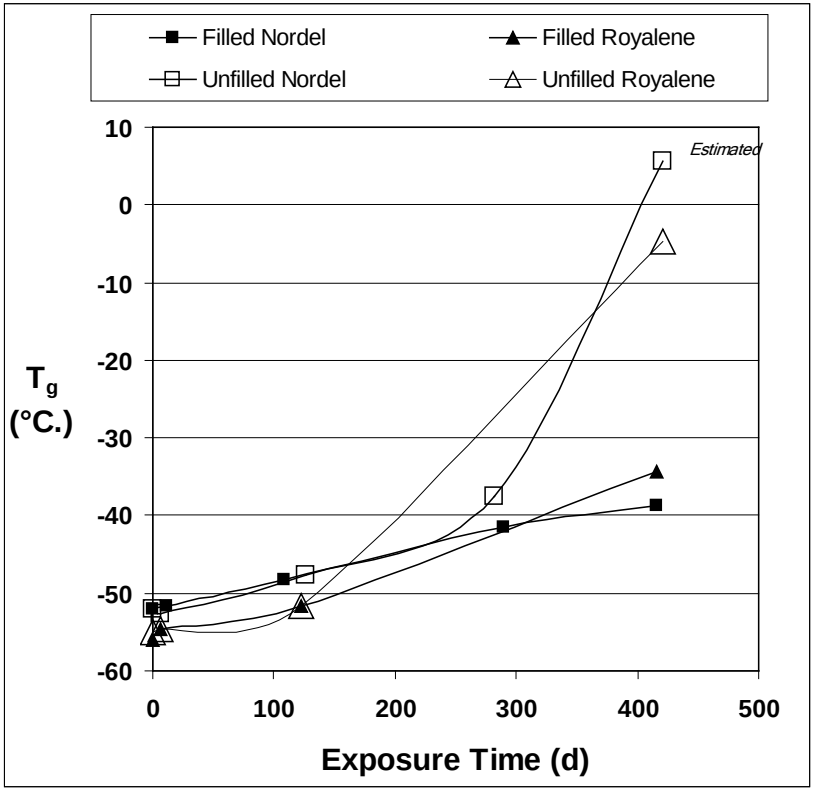
Previous and Current Work

- Validation testing of materials used in Tritium service
  - Teflon
  - UHMW-PE
  - EPDM
- Nafion characterization for PEME in isotope separation
  - Nafion®
- Normatex pump replacement
  - GraFOIL®
  - PEEK
  - Vespel® (polyimide)
- Next generation polymer development
  - Nanotube and graphene filled EPDM
- Polymer sensor materials
  - PANi
  - PEDOT-PSS

EPDM

- Examined filled (carbon black) versus unfilled for two commercial compositions
- Increase in Tg as exposure increases
- Filled polymers have greater resistance to damage at longer exposures, i.e. polymer becomes more brittle





Nafion

- Proton Exchange Membrane Electrolyzers (PEME) are of interest as a replacement of Mg beds to separate T from HTO.
- Currently used in ITER, but little known about stability of membranes
- Gamma irradiation of a saturated membrane was used as a surrogate for beta
- It was found that there were considerable differences in damage after the equivalent of 6 months PEME operation (11 Mrad, 1 w in T)

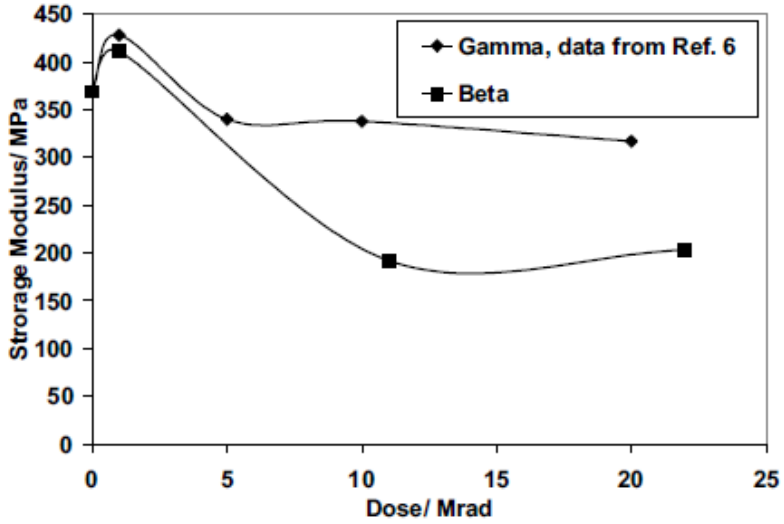
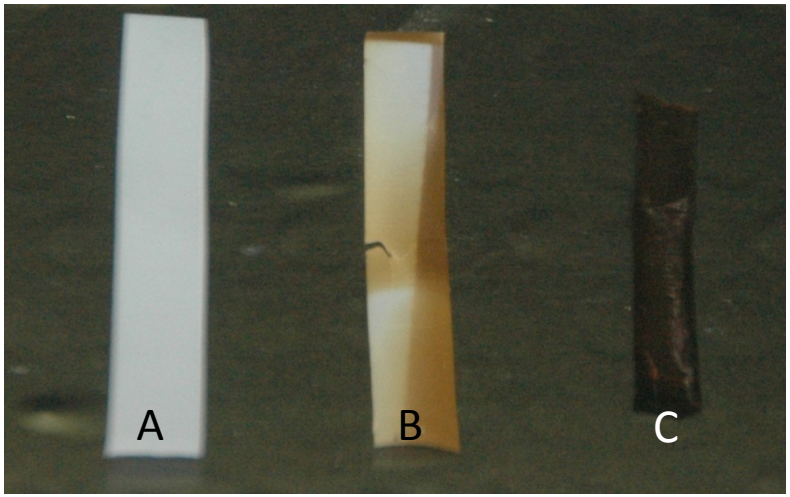


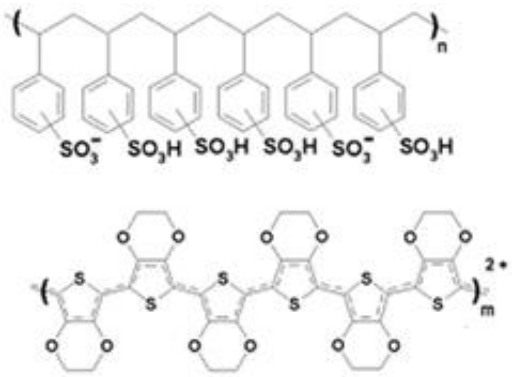
Fig. 3. Storage modulus of Nafion® at 60°C after exposure to both gamma irradiation by a ^{60}Co source and beta irradiation by 1 atmosphere of tritium gas.

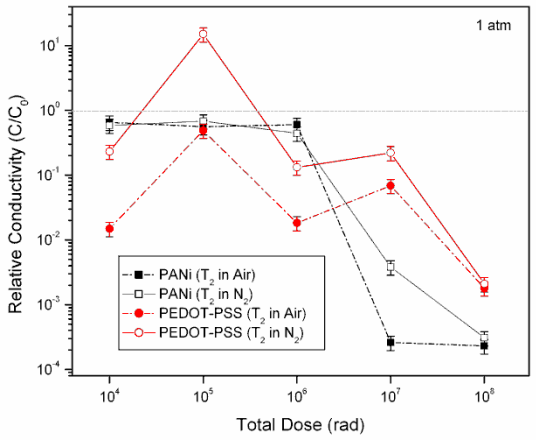


PTFE unexposed (A), PTFE exposed (B) and Nafion 117 (C) after 40 weeks of tritium exposure.

Polymers as sensors

- Electrically conducive polymers Polyaniline (PANi) and Poly(3,4-ethylenedioxythiophene) poly (styrenesulfonate) (PEDOT-PSS) were analyzed to determine if they could be used to detect the presence of T.
- sensitive to tritium gas, even after six minutes exposure time- both materials good candidates for sensor applications.
- Chain scission/free radical formation main degradation mechanism at higher total doses, and main degradation mechanism for PANi in general.
- Oxidation of PANi is quite extensive while PEDOT-PSS is less susceptible





Normatex Pump Replacement Materials

- Normatex Company is no longer making all metal pumps
- Alternatives are sought for the Teflon® seals that are used in most commercial pumps
- Five materials were exposed to tritium: PTFE, UHMW-PE, Vespel, PEEK, and GrafFOIL®
- Samples were to age for 6 months and 1 year
- Loaded in May 2013
- Funded not provided in Year 2 for the analysis of the samples

Carbon Nanotube and Graphene filled EPDM

- Goal to extend service life of existing polymers
- Electrically conducive materials exhibit less radiation damage
- Can use a lower wt% of nanomaterials that carbon black
- Currently:
  - Synthesizing materials
  - Exposed to T starting in May
  - Analyzing baseline properties

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