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**MASTER**

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## POLYIMIDE AND POLYAMIDE-IMIDE IN A TRITIUM ATMOSPHERE

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### ABSTRACT

Five different commercial polyamide-imide and polyimide specimens were kept in a tritium atmosphere (96.9 mol%, 101 kPa, initial fill conditions) for three months. Selected physical and mechanical properties of the five plastics were examined. Mass spectrometric data showed the growth of protium and HT impurity in the tritium gas.

### INTRODUCTION

Gasket, valve seating, and valve packing failures are undesirable events in a gas-handling system, and even more so when the gases are experimental isotopic mixtures of tritium and deuterium. For this reason, one is always seeking to increase the reliability of the system through the selection and use of better materials and techniques. E. I. du Pont de Nemours' Vespel SP-1 is one material with an excellent service record over the past seven years in hydrogen-helium atmospheres.

Vespel SP-1 is a heat-resistant organic engineering polymer. Major progress in the development of this class of polymers over the past decade has been made only with carbocyclic rings, heterocyclic rings, or a combination of these two in the chain's backbone. Both AMOCO Chemicals and Upjohn Company market competitive heat-resistant organic engineering polymers. The service record of Vespel SP-1 and the availability of competitive materials prompted a comparison of these plastics in a tritium atmosphere.

Only a few individuals have reported work with a polyimide in tritium gas, or a polyimide in an ionizing radiation field. References to line-engineering-type studies using or involving Vespel are contained in the Savannah River monthly reports. L. L. Akkrachkoya and his coworkers reported on the tensile strength and elongation at failure of polyimide film following electron bombardment.<sup>1</sup> In an unpublished paper, S. D. McLaughlin reported on compression set and hardness tests following 130 days' (133 kPa, seven millimoles, initial fill conditions) tritium gas exposure of Vespel, Viton, and Kalrez (all three are du Pont trade names).<sup>2</sup> For use as a gasket,

McLaughlin ranked these three du Pont products in the following order: Kalrez, Viton, and Vespel.

#### EXPERIMENTAL

Five different rod stock samples were purchased from the four fabricators listed in Table I. The reason for purchasing the extruded form of TORLON and ENVEX is that both are basic resins with a single filler. For example, TORLON 4203 consists of TORLON 4000T plus 3% titanium dioxide, compounded and pelletized. This grade of TORLON is used primarily for the extrusion of stock shapes. A similar comment can be made for ENVEX and its 2% Teflon filler. The primary purpose of this filler is to allow extrusion of the polymeric material, which increases the production rate with a consequent cost reduction. According to a Rogers Corporation representative, they intend to convert entirely to extruded ENVEX and discontinue the compression molding technique.

#### SURFACE EXAMINATIONS

Injection molding is employed to obtain valve stem tips, valve stem packings, and gaskets prepared from many polymeric materials. These shapes must be

machined from polyimide and polyamide-imide rod stock. Thus, the rod stock must possess surface features that are sufficiently free from hardness variations, visible porosity, and inclusions, to permit a gas seal.

#### 1. METALLOGRAPHIC TECHNIQUE

A metallographic examination of commercially available polyimide and polyamide-imide rod stock samples was conducted to ascertain whether hardness variations, visible porosity, and/or impurity inclusions existed on the polished surface. The importance of this examination is based on their potential use as a gasket, valve stem tip, or valve stem packing in a tritium gas handling system.

Point-to-point hardness variations are present in the different rod stock samples examined. These variations are detectable in the form of polish-relief, and are seen using either oblique illumination or Nomarski differential interference contrast. This polish-relief is observed in the as-polished condition and represents local differences in material removal during polishing. It is important

to note that abrasion hardness may be quite different from the usual indentation hardness (Shore or Rockwell), although the two will frequently correlate positively. Possible explanations for these differences in abrasion hardness include nonuniform prefabrication blending and nonuniform chain lengthening during the final thermal curing cycle.

One of the samples, extruded ENVEX 1000, has a significant amount of porosity, which is visible in the polished section, but no porosity is seen in any of the other samples. If these pores are interconnected, it could conceivably have an adverse effect on the material as a gas seal. In this case, however, it is believed that the porosity is not the interconnected type.

Other than the titanium dioxide particles (typically submicron) visible in the samples of TORLON 4203, the only other features of interest are various types of impurity inclusions. These inclusions ranged in appearance from metallic to nonmetallic, as judged from their reflectivities. Some of the former have the appearance of particles

abraded from handling equipment. The latter are probably stray mineral particles picked up as dirt during handling. In none of the samples did it appear that there are enough such inclusions to significantly abrade metal surfaces against which the polymeric material might slide.

## 2. SCANNING ELECTRON MICROSCOPE TECHNIQUE

Scanning electron microscope (SEM) examinations of the polyimide and polyamide-imide samples provided further information while substantiating the metallographic study as to surface hardness variations, visible porosity, and impurity inclusions. This examination included seeing both the as-polished and ion-etched surface of each sample. Sample etchings were performed by bombardment with 3 keV protons, for times ranging from 15 to 30 minutes, with a current densities of the order of 0.1 milliamperes per square centimeter. In some cases, surface structure was brought out, indicating variations of attack by the protons from one location to another. The titanium dioxide present in TORLON 4203 remained as unique globules, apparently unaffected by the proton attack.

Visible porosity appeared only in the extruded ENVEX 1000 as a multiple cell polymerization matrix; with one pore in each cell. The cell interfaces were outlined with aluminum, copper, potassium, and calcium. Other observed impurity inclusions were identified as being polishing compound constituents.

### 3. SECONDARY-ION MASS SPECTROMETRY

Secondary-ion mass spectrometry (SIMS) studies were conducted on five unirradiated polyimide and polyamide-imide specimens. These samples were bombarded at 298 K with a characterized argon ion beam generated in the ion source and focused on the sample. Surface contamination was removed by sputtering before measurements were made. The major signals observed during this examination were attributed to negative ions of H, C, CH, O, OH, F, C<sub>2</sub>, C<sub>2</sub>H, C<sub>2</sub>H<sub>2</sub>, and Cl.

### MECHANICAL, PHYSICAL, AND THERMAL PROPERTIES

Machined cylindrical samples were used in the tests listed in Table II and the compression studies shown in Figure 1. All samples were machined into cylindrical configurations 1.27 cm diameter by 2.54 cm long.



In the water absorption test, a completely dry sample was immersed in 100% relative humidity for 24 hours. The percentage changes in sample weights and sample dimensions were then determined. Both compression molded and extruded ENVEX 1000 exhibited an affinity for water rivaling that of nylon. These water absorption values indicated that any polyimide or polyamide-imide must be dried before it is exposed to a dry gas.

The softening temperatures and Shore hardness of irradiated specimens were the same as those reported in Table II for unirradiated specimens.

Stress relaxation studies (compression, 10% engineering strain, 299 K) performed on irradiated and unirradiated specimens are summarized in Figure 1. A polychlorotrifluoroethylene (PCTFE) specimen, Kel-F, was also exposed to the tritium atmosphere as a control. Stresses in this presentation are relative to the maximum stress, which was exhibited by the irradiated compression-polymerized ENVEX 1000 specimen. The polyamide-imide and polyimide specimens exhibited a nominal increase in strength following 90 days' exposure to tritium.

The extent of this increase in strength after irradiation and the initial strength upon attaining the 10% strain are related to specific material and vendor. Vespel SF-1 is the weakest of the polyimide and polyamide-imide specimens. The initial strength of Vespel SP-1 is approximately 55% that of compression-polymerized ENVEY 1000. Kel-F, the control, exhibited an initial strength that is approximately 45% less than Vespel SP-1. Irradiation weakened the Kel-F specimen. These stress relaxation studies illustrate that the strengths of various materials are related to the polymerization, fabrication, and curing.

#### MASS SPECTROMETRY

A mole analysis of the gas recovered from around each tritium-exposed polyimide and polyamide-imide specimen (Table III) showed an increase of protium in the form of  $H_2$  and HT molecules, and a decrease in the number of  $T_2$  molecules. The lack of methane coupled with an atom balance of this gas supports a tritium-protium exchange as being the dominant degradation mechanism in these polyamide-imide and polyimide specimens. Gas recovered from around

the tritium-exposed Kel-F specimen was rich in methane and depleted in  $T_2$ . The presence of methane in this gas is indicative of chain scission with the subsequent release of fluorine.

REFERENCES

1. L. L. Akrachkova, Yu. N. Timko, E. E. Findel, M. I. Bessonov, L. A. Laius, and T. E. Zhukova, "Aging of Polyimide Films in the Presence of Beta-Radiation," *Plasticheski Massey*, Number 4, Pages 34-35, 1977 (in Russian).
2. B. D. McLaughlin, "Gasket Material Evaluation for Tokamak," 1979 (unpublished Savannah River Laboratory data).

TABLE I

The five engineering polymeric materials examined.

TABLE II

Selected mechanical, physical, and thermal properties of unirradiated engineering polymeric materials.

TABLE III

Selected mass spectrometry results of gas recovered from around polyimide, polyamide-imide, and polychlorotrifluoroethylene specimens after 90 days' exposure to a tritium atmosphere (96.9 mol%, 101 kPa, initial fill conditions). (Each result is based on a mole balance of the gas surrounding the polymeric specimen. Negative signs are used to denote those molecular species lost from the gas, and positive signs denote those molecular species added to the gas.)

FIGURE 1

Stress relaxation studies (compression, 10% engineering strain, 299 + 3 K) performed on irradiated and unirradiated cylindrical polyimide, polyamide-imide, and polychlorotrifluoroethylene specimens. Compression polymerized ENVEX 1000, extruded ENVEX 1000, TORLON 4000T, TORLON 4203, Vespel SP-1, and Kel-F are represented by 1000S, 1000E, 4000T, 4203, and Kel-F, respectively. Specimens exposed to the 96.9 mol% (initial fill) tritium atmosphere (101 kPa) for 90 days are represented by the letter H. Unirradiated cylindrical specimens are represented by the letter C.

| TRADE NAME   | GENERIC NAME     | RESIN SUPPLIER  | ROD STOCK FABRICATOR | FABRICATION TECHNIQUE | FILLERS             |
|--------------|------------------|-----------------|----------------------|-----------------------|---------------------|
| VESPEL SP-1  | POLYIMIDE        | DU PONT         | DU PONT              | COMPRESSION MOLDED    | NONE                |
| TORLON 4000T | POLYAMIDE -IMIDE | AMOCO CHEMICALS | THERMECH ENGRG       | COMPRESSION MOLDED    | NONE                |
| TORLON 4203  | POLYAMIDE -IMIDE | AMOCO CHEMICALS | POLYMER CORP         | EXTRUDED              | 3% TITANIUM DIOXIDE |
| ENVEX 1000   | POLYIMIDE        | UPJOHN CO       | ROGERS CORP          | COMPRESSION MOLDED    | NONE                |
| ENVEX 1000   | POLYIMIDE        | UPJOHN CO       | ROGERS CORP          | EXTRUDED              | 2% TEFLON           |

| TRADE<br>NAME     | SPECIFIC<br>GRAVITY<br>(299 K) | WATER ABSORPTION<br>24 HRS AT 295 K |                          | SOFTENING<br>TEMP<br>(±5 K) | HARDNESS<br>(SHORE<br>D-2) |
|-------------------|--------------------------------|-------------------------------------|--------------------------|-----------------------------|----------------------------|
|                   |                                | % CHANGE IN<br>WEIGHT               | % CHANGE IN<br>DIMENSION |                             |                            |
| KEL-F             | 2.15                           | 0.01                                | 0.02                     | 531                         | 82                         |
| TEFLON            | 2.17                           | 0.01                                | 0.01                     | 523                         | 56                         |
| NYLON             | 1.13                           | 0.72                                | 1.28                     | 645                         | 83                         |
| VESPEL<br>SP-1    | 1.43                           | 0.26                                | 0.47                     | 633                         | 86                         |
| TORLON<br>4000T   | 1.37                           | 0.44                                | 0.79                     | 548                         | 91                         |
| TORLON<br>4203    | 1.40                           | 0.40                                | 0.71                     | 548                         | 92                         |
| ENVEX<br>1000 (S) | 1.34                           | 0.75                                | 1.33                     | 548                         | 92                         |
| ENVEX<br>1000 (E) | 1.34                           | 0.61                                | 1.08                     | 548                         | 90                         |

| TRADE NAME                 | VESPEL SP-1 (CM) | TORLON 4203 (E) | ENVEX 1000 (CM) | ENVEX 1000 (E) | KEL-F (E) |
|----------------------------|------------------|-----------------|-----------------|----------------|-----------|
| RESIN SUPPLIER             | DU PONT          | AMOCO           | UPJOHN          | UPJOHN         | 3-M       |
| COMPOSITION (MOLE PERCENT) |                  |                 |                 |                |           |
| HH                         | 13               | 21              | 21              | 21             | 2         |
| HD                         | 0                | 0               | 0               | 0              | 0         |
| HT                         | 36               | 28              | 26              | 27             | -1        |
| DD                         | 0                | 0               | 0               | 0              | 0         |
| DT                         | 0                | 0               | 0               | 0              | 0         |
| TT                         | -48              | -48             | -49             | -48            | -66       |
| METHANE                    | 0                | 0               | 0               | 0              | 27        |

CM: COMPRESSION MOLDED  
E: EXTRUDED

AFTER 90 DAYS EXPOSURE TO A TRITIUM  
ATMOSPHERE  
96.9 MOL%  
0.101 MPa

[INITIAL FILL  
CONDITIONS]



