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THERMAL AGING OF POLYURETHANE FOAM FOR 9977 SHIPPING PACKAGE

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ABSTRACT
The 9977 shipping package is being evaluated for long-term storage of special nuclear materials at the Savannah River Site. Polyurethane foam serves as an impact absorber, thermal insulator, and fire protective material inside the package. The foam can degrade due to heat, moisture, and oxidation, which could lead to diminished performance. Aging studies have been conducted to evaluate the aging effects on the physical, mechanical, and thermal properties of polyurethane foam, and support the development of aging models and service life predictions. The foams were aged at temperatures ranging from 160 °F to 250 °F for up to four years. Several properties have shown a trend with aging time and temperature, including weight, dimensional stability and intumescence.

INTRODUCTION
The 9977 shipping package is approved for transporting and storing special nuclear materials in K-Area Complex (KAC) at the Savannah River Site (Figure 1). The package is currently being evaluated for long-term storage, and investigations are underway to verify the integrity and performance of age-sensitive materials. A literature review assessed materials of potential concern for degradation in the 9977 shipping package and recommended focusing on evaluating polyurethane foam [1]. Polyurethane foam serves as an impact absorber, thermal insulator, and fire protective material in the 9977 shipping package. FR-3716 is a rigid, closed-cell, intumescing polyurethane foam with a nominal density of 16 lb/ft^3 [2]. The foam is poured between the inner container and the outer shell of the 9977 package and foamed in place to fill the interstitial volume.

Polyurethane foam can degrade when exposed to elevated temperatures, moisture, and oxygen; all these conditions are present in the service environment for 9977 packages in KAC. The 9977 package can contain two 3013 containers and decay heat load of up to 38 watts. At 100 °F ambient storage conditions, the temperature of the polyurethane foam is estimated to be a maximum of 188 °F for 24 watt payload and 242 °F for 38 watt payload [1]. The 38 watt loading configuration approaches the upper limit of FR-3716 foam's service temperature range (250 °F) and glass transition temperature (270 °F). There is a lack of aging studies on rigid, intumescent polyurethane foam at elevated temperatures.

Polyurethane foam samples were aged at different temperatures (160 – 250 °F) and periodically removed from the ovens to test their physical and chemical properties. These tests include examining the foam's dimensions, mass, thermal conductivity, heat capacity, and intumescence. This report presents accelerated aging results of polyurethane foams after conditioning for up to four years.

EXPERIMENTAL

Representative samples were cut from FR-3716 and loaded into five conditioning furnaces, 160 °F, 160 °F with 50% relative humidity (RH), 185 °F, 215 °F, and 250 °F. The acceptance criteria [3] for the polyurethane foam in the 9977 transportation packaging were used as a guideline for acceptability in this aging evaluation.

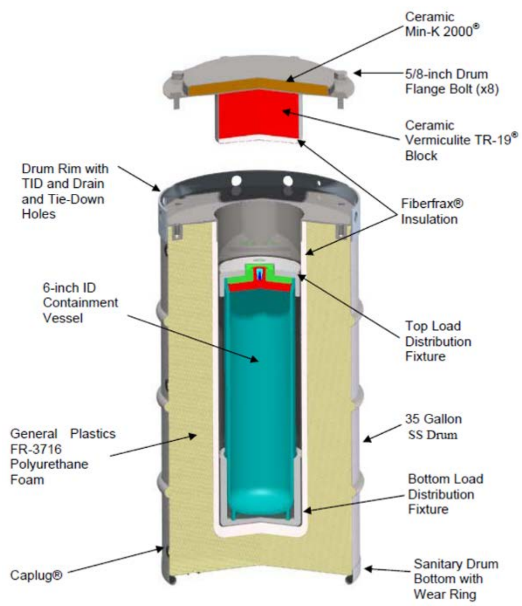

Figure 1. Cross-section schematic of 9977 package.

The thermal conductivity of polyurethane foam samples were tested using a LaserComp heat flow meter per ASTM method C518-10 with a 20 °C difference between plates. The results are presented as the average of the plates (i.e. at 25 °C, 55 °C and 85 °C). The foam aged at 250 °F only has results up to 255 days due to the physical deformation of the samples. The specific heat capacity of polyurethane foam samples were tested using a TA Q20 differential scanning calorimeter (DSC) per ASTM method E1269-11. The foam samples were heated to 150 °C at 20 °C/min and held at 150 °C for 10 min.

The compressive behavior of the polyurethane samples was tested using an Instron compression tester per ASTM method D1621-10. The integrated area under the stress-strain curve up to a strain of 25% provides a relative measure of the energy absorption capability of each sample. The 25% strain level is arbitrary but provides a consistent point of comparison.

Foam samples were sent to General Plastics Manufacturing Company for intumescence testing and to determine amount of leachable phosphorus. The sample was placed inside a furnace at 800 °C for 90 seconds and the overall sample thickness was measured [4]. The percent intumescence, I, of the sample was calculated by comparing the initial and final thicknesses, T_i and T_f, respectively, in the equation $I = (T_f - T_i)/T_i \times 100$. The presence of leachable phosphates was detected by spectrophotometer using method SM 4500-P E.

RESULTS

Rigid polyurethane foam samples were aged at elevated temperatures (160 - 250 °F) for over 4 years. Discoloration and changes in dimensions as a function of aging time and temperature have been reported for polyurethane foams [5-9]. Figure 2 shows foam samples demonstrated noticeable color change with increasing aging temperature and time. Samples conditioned at 160 °F, for over 48 months yellowed slightly, whereas foams aged at 250 °F rapidly discolored to dark brown and then black. Additionally, the faces of the foam samples aged at 250 °F depressed with aging time and cracks appeared on the sample.

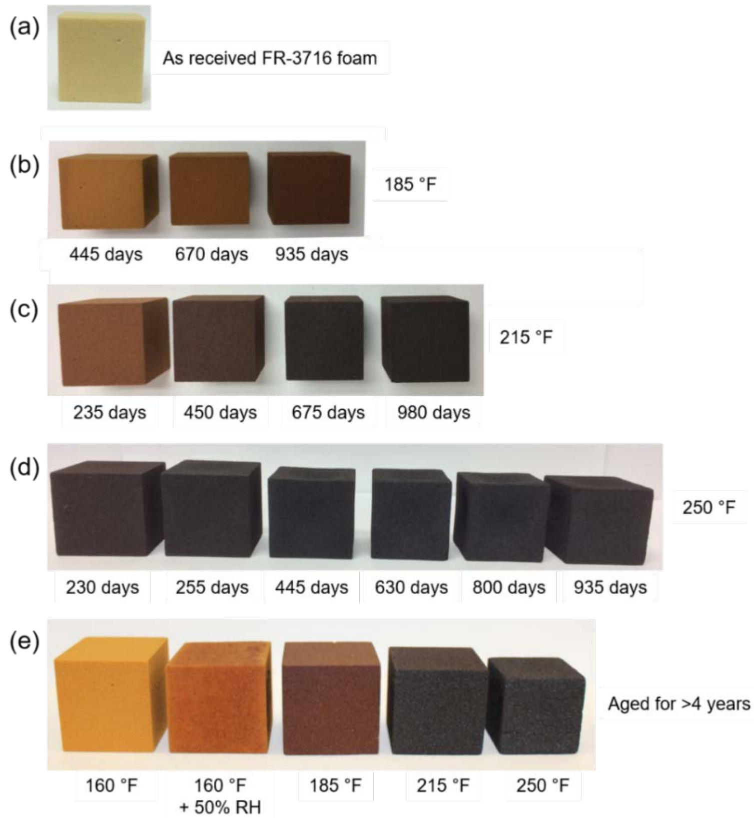

Figure 2. Pictures of polyurethane foams (a) as received, aged at (b) 185 °F, (c) 215 °F, (d) 250 °F, and (e) representative foam samples aged for >4 years.

Samples conditioned at 250 °F displayed the most dimensional instability. Figure 3 shows that the foam samples conditioned at 250 °F had the most significant decreases in weight and volume, and consequently, the highest change in density, during the 4 years of aging. Note that the volumes, and subsequently, the densities, of samples aged at 250 °F were approximated due to sample deformation. There is little change in the weight or volume for samples aged up to 185 °F; samples retained >97% of initial weight and >96% of initial volume after 4 years. Samples aged at 215 °F displayed a small change in their weights and volumes, retaining 92% of initial weight and 87% of initial volume after 4 years. After over 4 years of aging, the normalized weight and volume of samples aged at 250 °F is 79% and 60%, respectively. The rate of volume shrinkage is greater than weight loss which results in samples with densities greater than 16 lb/ft^3.

Thermal conductivity of polyurethane foam was measured at three different temperature points and the results are shown in Figure 4. The thermal conductivities of aged FR-3716 polyurethane foam samples are slightly higher than the initial values measured at 25 °C, 55 °C, and 85 °C. The increase in thermal conductivity is due to the diffusion of carbon dioxide out of the closed-cell foam over time while air (of higher conductivity) diffuses in [10-11]. In addition, samples aging in a humid environment have higher thermal conductivities compared to samples in low humidity conditions. The average thermal conductivity for the foams, ~0.372 Btu·in/hr·ft^2·°F, is within the limits of the acceptance criteria for the 9977 package (0.271-0.407 Btu·in/hr·ft^2·°F) at 25 °C [3]. The specific heat capacities of the foams were measured using DSC and the results are shown in Figure 5. The specific heat capacities of aged FR-3716 polyurethane foam samples are comparable to the initial values, and the average specific heat capacities for the aged foam are within ±20% of the initial values.

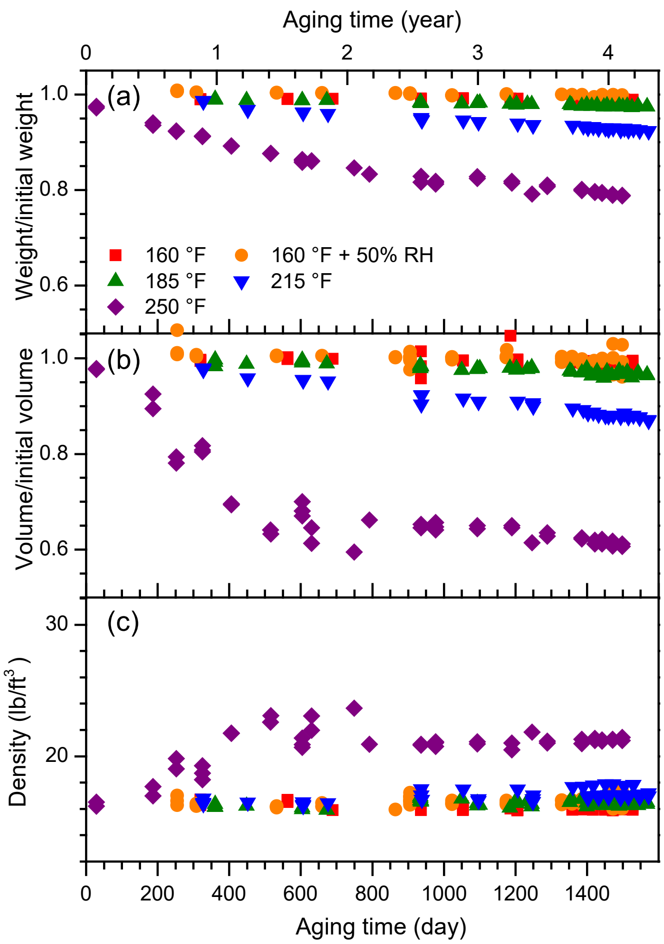

Figure 3. Dimensional analysis of FR-3716 foams aged at different temperatures, including (a) relative mass, (b) relative volume, and (c) density measurements over time.

The mechanical properties of the polyurethane foams were evaluated using compression testing and some representative stress-strain curves are shown in Figure 6. The compression stress-strain curve was used to determine absorbed energy of the polyurethane foam sample. Foam samples conditioned at 215 °F or below have comparable absorbed energies, while samples conditioned at 250 °F show substantial decrease in absorbed energy with aging time. During testing, the former samples are compressed into a compact board while the latter readily fractured and collapsed. These results demonstrate that aging at 250 °F has significant and detrimental effects on the compressive behavior of polyurethane foams.

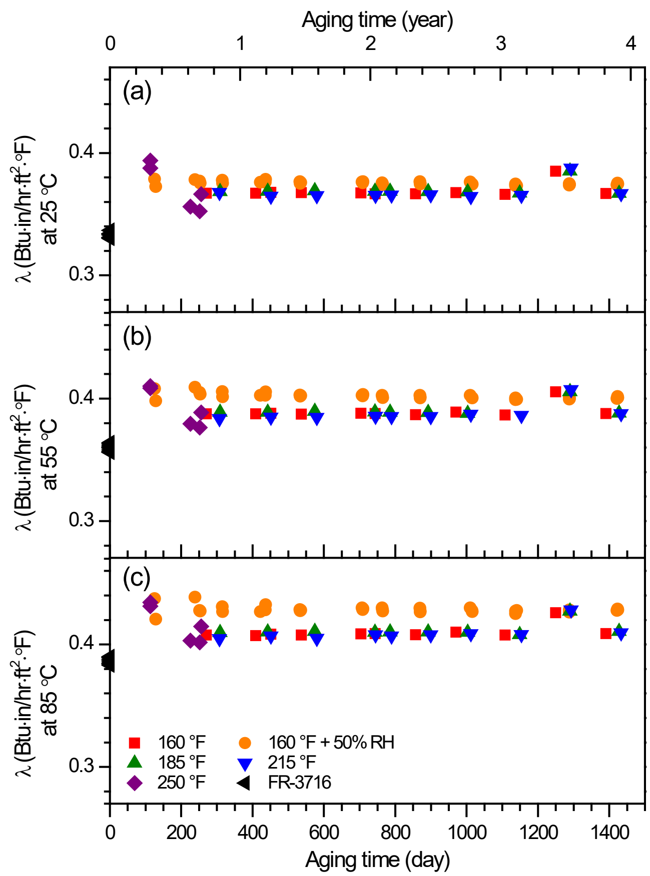

Figure 4. Thermal conductivity, λ, of aged FR-3716 foams measured at (a) 25 °C, (b) 55 °C, and (c) 85 °C.

The intumescence and amount of leachable phosphorus were measured over time and the results are shown in Figure 7. The intumescing polyurethane foam plays an important role in protecting the containment vessel against fire. The foam decomposes to form an intumescent char that expands to fill void spaces and acts as an insulating physical barrier when it is exposed to elevated temperatures (>532 °F) [12]. The initial value for intumescence is 229% and the acceptance criterion for the 9977 package requires a minimum of 50% intumescence. Foam samples aged at 250 °F did not intumesce (1% intumescence). Foam samples aged in non-humid conditions show a decreasing trend in intumescence with aging time, with more progressive decreases at higher aging temperatures. Initial leachable phosphorus content is under 1.0 mg/L and all aged samples had >5 mg/L leachable phosphorus. The leachable phosphorus content steadily increased for foams aged at 250 °F with a value of 26 mg/L after 32 months. The leachable phosphorus content of intumescing FR-3716 is likely due to phosphorus fire retardant additives and/or reactants.

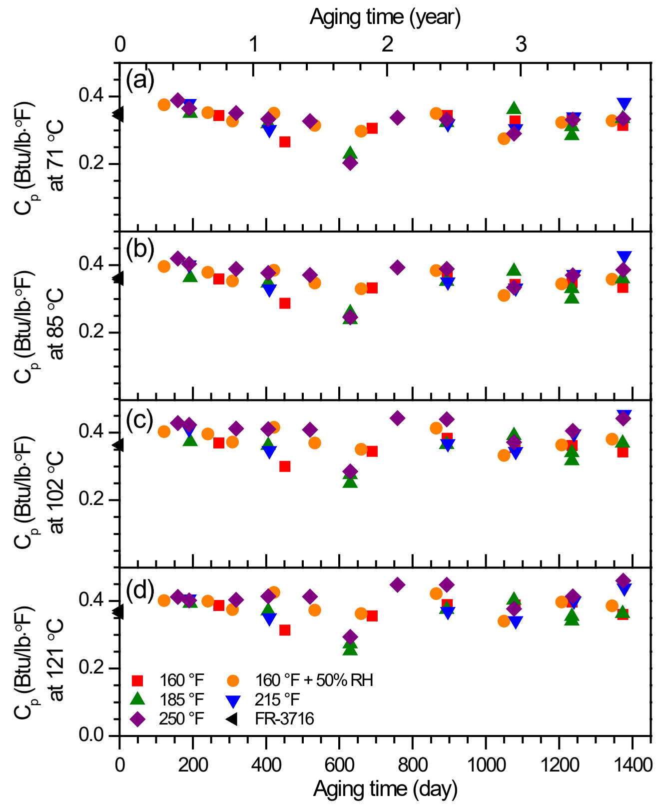

Figure 5. Specific heat capacity, C_p, of aged FR-3716 foams measured at (a) 71 °C, (b) 85 °C, (c) 102 °C, and (d) 121 °C.

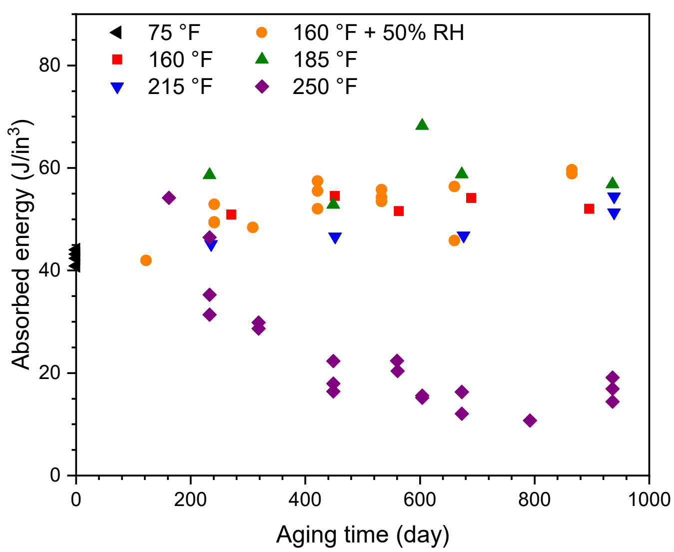

Figure 6. Compression tests results for absorbed energy for aged FR-3716 foams over time.

It is worth noting that General Plastics has tested a twenty-year old FR-3720 foam sample for compressive strength and char formation and found comparable results to nominal FR-3720 samples [13]. The foam sample was originally laminated to an aluminum sheet and no details were given for the sample's aging conditions. These results suggest that FR-3700 polyurethane foams can retain their properties for long-term applications.

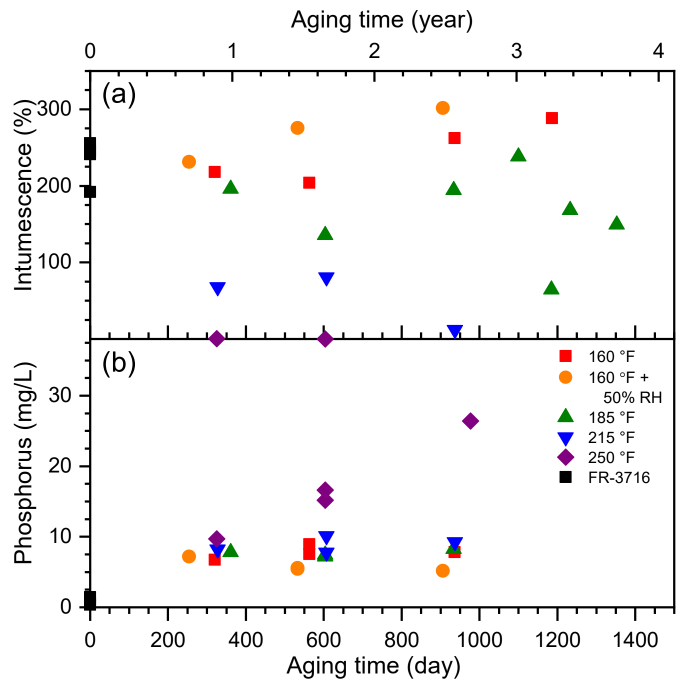

Figure 7. Physical characterization results for aged FR-3716 foams, including (a) intumescence, (b) amount of leachable phosphorus.

CONCLUSIONS

FR-3716 polyurethane foam samples have been aging in 160 °F, 160 °F + 50% RH, 185 °F, 215 °F and 250 °F furnaces for over 4 years. The effect of aging on FR-3716 was evaluated by monitoring the thermal conductivity, specific heat, weight, dimensions, compressive strength, amount of leachable phosphorus, and intumescence of polyurethane foam samples. The thermal conductivity and specific heat capacities for all aged foam samples were fairly stable and within the limits of the acceptance criteria or ±20% of the nominal values. Foams aged at 250 °F exhibited deteriorating physical and chemical properties with time and it is recommended to avoid prolonged exposure of FR-3716 polyurethane foams to ≥ 250 °F.

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