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Effects of Irradiation on Thermal Properties of Polyurethane Foam

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Abstract:

Polyurethane foam is used as a thermal insulator, fire protective material, and impact absorber in the 9977 shipping package. The 9977 shipping package is used to transport special nuclear materials (SNM), and store SNM in the K-area complex at the Savannah River Site. The primary fire-retardant mechanism in the foam is that it produces intumescent char when exposed to high temperatures. Intumescence occurs in the direction of heat application and can allow the foam to "repair" cracks in the event of a mechanical impact, in addition to serving as a secondary thermal barrier with decreased heat conductivity. Because the foam is being used for long-term storage applications, it is vital that it retain its physical, thermal, and mechanical properties over the course of time and with the events of exposure of heat and irradiation. The goal of this project was to determine the effects of gamma irradiation on the thermal properties of polyurethane foam, both in terms of cumulative irradiation and rate of irradiation. At the dose rates and cumulative doses of irradiation measured, there was no correlation between higher cumulative irradiation and thermal stability, specific heat capacity, or chemical structure. Based on the results of the experiments, the fire protective properties in the 9977 shipping containers should be retained with the expected amount of radiation exposure.

Introduction:

Polyurethane foam is used as a thermal insulator, fire protective material, and impact absorber in the 9977 nuclear material shipping package. (Dowds) General Plastics, the manufacturer of the polyurethane foam, describes the foam FR-3700 as being a rigid thermoset plastic with a high strength-to-weight ratio due to its cellular structure and crosslinked resin features. It is also stable, inert, and resistant to both water and most chemicals. (General Plastics 2003) The primary fire-retardant mechanism in the foam is that it produces intumescent char when exposed to high temperatures. Intumescence occurs in the direction of heat application and can allow the foam to "repair" cracks in the event of a mechanical impact. The char can also provide a secondary thermal barrier that decomposes slowly at temperatures above 2000 °C. (Bourbigot 2004, 2019) The foam is used for long-term nuclear material storage applications, so it is critical that the physical, thermal, and mechanical properties are not affected by long-term exposure to heat and irradiation. (Olson)

A typical intumescent material contains three general components: an acid source, a char forming agent (often a polymer), and a blowing agent. Stages of intumescence and charring occur along specific temperature margins that are dependent on the specific additives in the material. The first stage of the process of intumescence begins when the char forming agent reacts with the acid species. The carbonaceous material formed from the intumescent additives has two main roles in preventing damage from fire. (Bourbigot 2019) The first is that this material contains free radical species that can react with the free radical products that form when the polymer degrades. As the polymer undergoes pyrolysis, these free radical species can play a role in the termination steps of the protective material's degradation. The second role that the

carbonaceous material plays is as support for the reaction of the acidic catalytic species and the oxidized products that occurs during this degradation process. When the intumescent material degrades, the blowing agent also decomposes to yield gaseous products, which get trapped in the phosphorocarbonaceous cellular material. This causes char swelling, and the typical "foamed" characteristic of an intumescent material. The char also has decreased heat conductivity, which results in additional enhanced insulation of the substrate. (Lams and Williamson)

High amounts of irradiation have been shown to have effects on the chemical structure of polymers, particularly in the formation of cross-linked bonds and the degradation of the main chain links of the polymers. A prior study looked at gamma radiation as a means of enhancing physical properties of polyurethane and exposed polyurethane to 50-150 cumulative Mrad at the rate of 2.05 Mrad an hour. It was found via SEM imaging that there were changes in the morphological microstructure of the polyurethane with increasing radiation, as well as color changes. The paper also determined that there was a higher degree of cross-linking in the irradiated samples, however, at a total dose of 150 Mrad, there was an increase in polyurethane degradation. (Ghobashy)

At SRNL, a previous study (Dowds) looked at the effects of 16.67 and 90.9 krad/hr on FR-3700 polyurethane foam samples and found that at a cumulative dose of 2 Mrad, which is approximately what a 9977 package would be expected to receive cumulatively in 100 years of storage, the visual effects of irradiation were 'minor.' intumescence was observed to a degree far smaller than that of the non-irradiated foam, which indicates that gamma radiation affects the other components of the foam responsible for the intumescence phenomenon. (Dowds)

The central objective of this project was to determine the effects of irradiation on the thermal properties of polyurethane foam, both in terms of cumulative irradiation and rate of irradiation. It was hypothesized that high doses of irradiation would cause a decrease in the thermal properties of the polyurethane foam. It was also predicted that a higher dose rate of irradiation would have more of an effect on the thermal properties than the cumulative dose of irradiation. The experiments and tests done in this project were selected to look at the thermal stability, chemical structure, heat capacity, and qualitative intumescence properties of the foams at a range of dose rate and cumulative doses of irradiation. It is critical that irradiation of the foam, particularly at the rates and cumulative doses that it would be expected to see in storage, does not impact the thermal properties.

Experimental:

A cobalt-60 gamma source was used to irradiate polyurethane foam samples cut into cubes of approximately 5 cm. x 5 cm. x 5 cm. dimernsions. The samples were placed at varying distances from the Co-60 source to expose them to different dose rates of radiation from 50 to 50,000 rad/hr. according to the table below:

Table 1: Dose rates and cumulative doses at said time point

Group Label	Dose Rate	Cumulative dose (total rad)-1	Cumulative dose (total rad)-2	Cumulative dose (total rad)-3	Cumulative dose (total rad)-4	Cumulative dose (total rad)-5	Cumulative dose (total rad)-6	Cumulative dose (total rad)-7	Cumulative dose (total rad)-8	Cumulative dose (total rad)-9	Cumulative dose (total rad)-10	Cumulative dose (total rad)-11	Cumulative dose (total rad)-12
Time (hr)	Rad/hr	8	24	48	72	96	168	200	336	384	504	720	800
A	50	400	1200	2400	3600	4800	8400	10,000	16,800	19,200	25,200	36,000	40,000
B	500	4000	12,000	24,000	36,000	48,000	84,000	100,000	168,000	192,000	252,000	360,000	400,000
C	5000	40,000	120,000	240,000	360,000	480,000	840,000	1,000,000	1,680,000	1,920,000	2,520,000	3,600,000	4,000,000
D	10,000	80,000	240,000	480,000	720,000	960,000	-	-	-	-	-	-	-
E	12,000	96,000	288,000	576,000	864,000	1,152,000	-	-	-	-	-	-	-
F	15,000	120,000	360,000	720,000	1,080,000	1,440,000	-	-	-	-	-	-	-
G	50,000	400,000	1,200,000	2,400,000	3,600,000	4,800,000	-	-	-	-	-	-	-
H	5000	8000	120,000	240,000	360,000	480,000	840,000	1,000,000	1,680,000	1,920,000	2,520,000	3,600,000	4,000,000
I	5000	8000	120,000	240,000	360,000	480,000	840,000	1,000,000	1,680,000	1,920,000	2,520,000	3,600,000	4,000,000

The highlighted samples were removed from the irradiator at various times corresponding to amounts of cumulative irradiation. Cumulative irradiation ranged from 4 to 4.8 Mrad. Samples were then analyzed for thermal stability using thermogravimetric analysis (TGA), specific heat capacity using differential scanning calorimetry (DSC), chemical structure using Fourier-transformed infrared spectroscopy (FTIR), and intumescence through caliper measurements and visual observation.

Thermogravimetric Analysis:

Small circular samples of approximately 10-15 mg were cut out of the polyurethane foam cubes. They were cut with a small razor blade to ensure that the sample fit inside the pan, and the bottom and top of the sample was flat. The aluminum pans selected were approximately 20 mg.

For the thermal stability measurements, the Shimadzu DTG-60 Simultaneous DTA-TG instrument started at room temperature and was ramped to 550 °C in 10 °C increments, then allowed to cool to room temperature. The TA60 analysis software was used to determine the onset, inflection, and end temperatures of the curve on the temperature versus mass graph. Values for total percent mass weight loss versus cumulative irradiation were also obtained from this instrument. In the interest of time, only oxygen gas was used to obtain these measurements.

For qualitative measurements of intumescence, a range of end point temperatures were tested to see where maximum expansion of the samples due to intumescence was found before the sample began charring. It was determined that 260 °C provided the best visual data. For these measurements, the instrument began at room temperature and was ramped to 260°C in 10 °C/min increments before being allowed to cool to room temperature. Calipers were used to measure the approximate height of the samples before and after heating. These measurements were taken at 3 points and averaged. There was a lot of variability even within one sample for height, although an effort was made to try to get the tops and bottoms of the samples as flat as possible. Photographs with a ruler reference were also taken before and after heating. These measurements were done under N_2 and O_2 ga.

Differential Scanning Calorimetry:

The TA DSC Q20 instrument was ramped from room temperature to 50 °C at the rate of 20 °C per minute, held at 50 °C for ten minutes, ramped to 150 °C at the rate of 20 °C per minute, and held at 150 °C for ten minutes before being allowed to cool to room temperature. The same aluminum sample pan and lid and reference pan and lid were used for all measurements. Cylindrical samples of 8-15 mg were cut from the foam and placed in the sample pan. Prior to running the samples, the empty sample pan and sapphire standard were run in order to be able to convert the heat flow data obtained from the TA Universal Analysis software into specific heat capacity measurements. Specific heat capacity was calculated via the ASTM E1269-11 Standard at 71 °C and 102 °C.

Fourier-transformed Infrared Spectroscopy:

The Jasco FT/IR-6300 Type A was used to analyze the polyurethane foam samples with a triglycine sulfate (TGS) detector. Prior to data collection, a small portion of the sample was purged in nitrogen gas for approximately 10-15 seconds. The resolution was 2.0 cm^{-1} with 8 scans being taken, measuring absorbance of the sample from 500 to 3600 cm^{-1} wavenumber.

Results and Discussion:

Thermogravimetric Analysis:

Figure 1: Sample TGA curve. The onset, inflection, and end temperatures on the curve are labeled for reference.

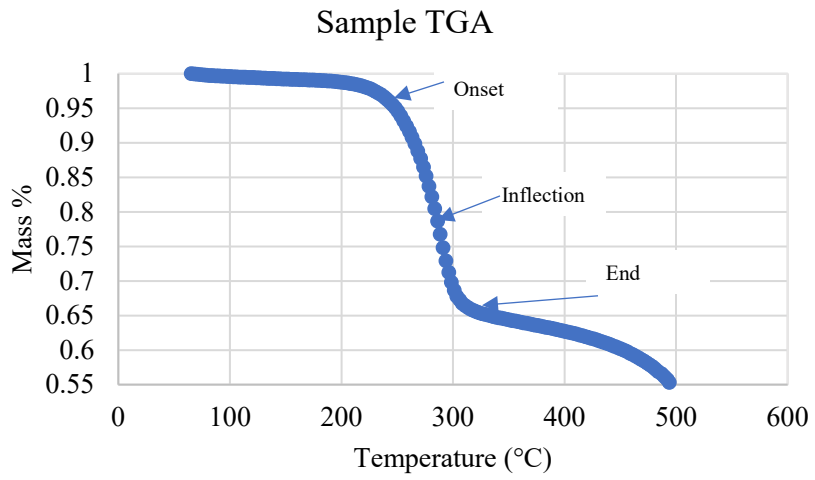


Figure 2- Onset (blue), inflection (orange), and end (grey) temperatures (°C) on the TGA curve vs. cumulative irradiation of foam samples (krad.)

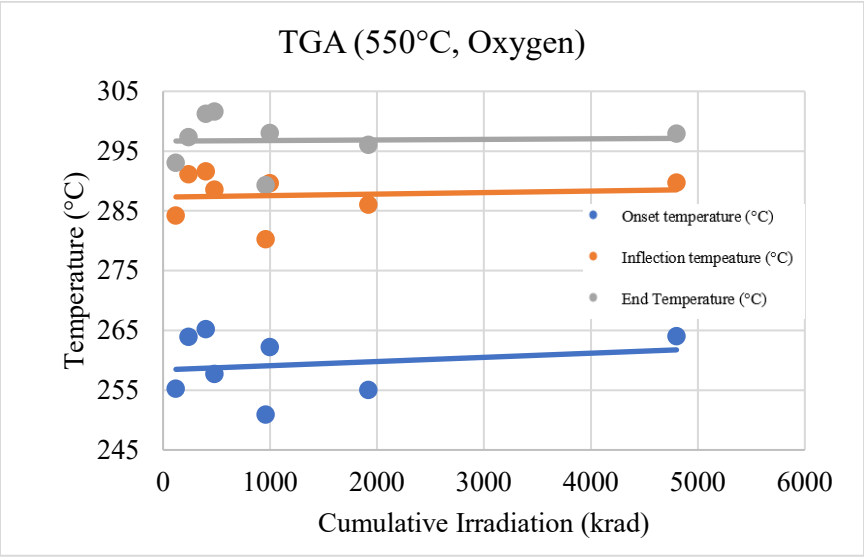
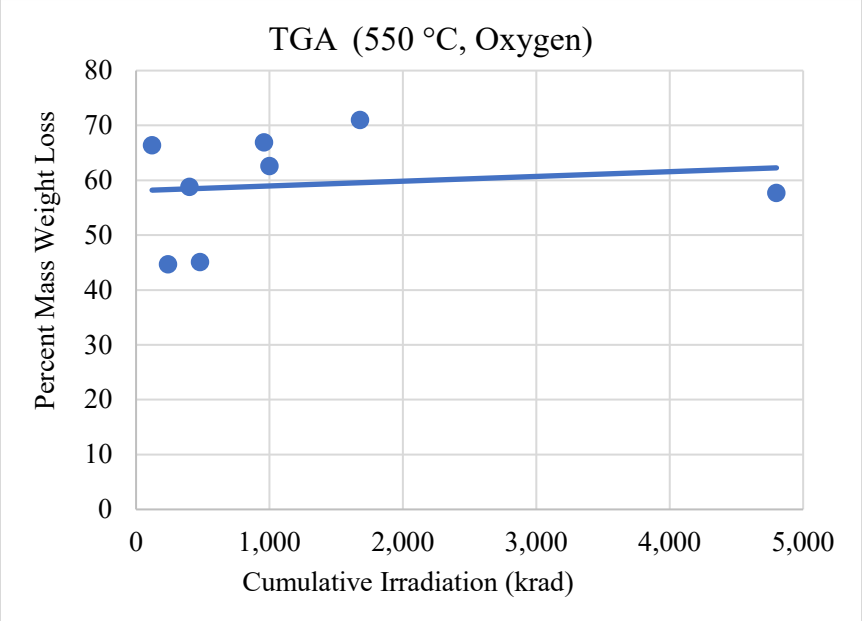


Figure 3.- Percent mass weight loss of foam samples versus cumulative irradiation (krad)

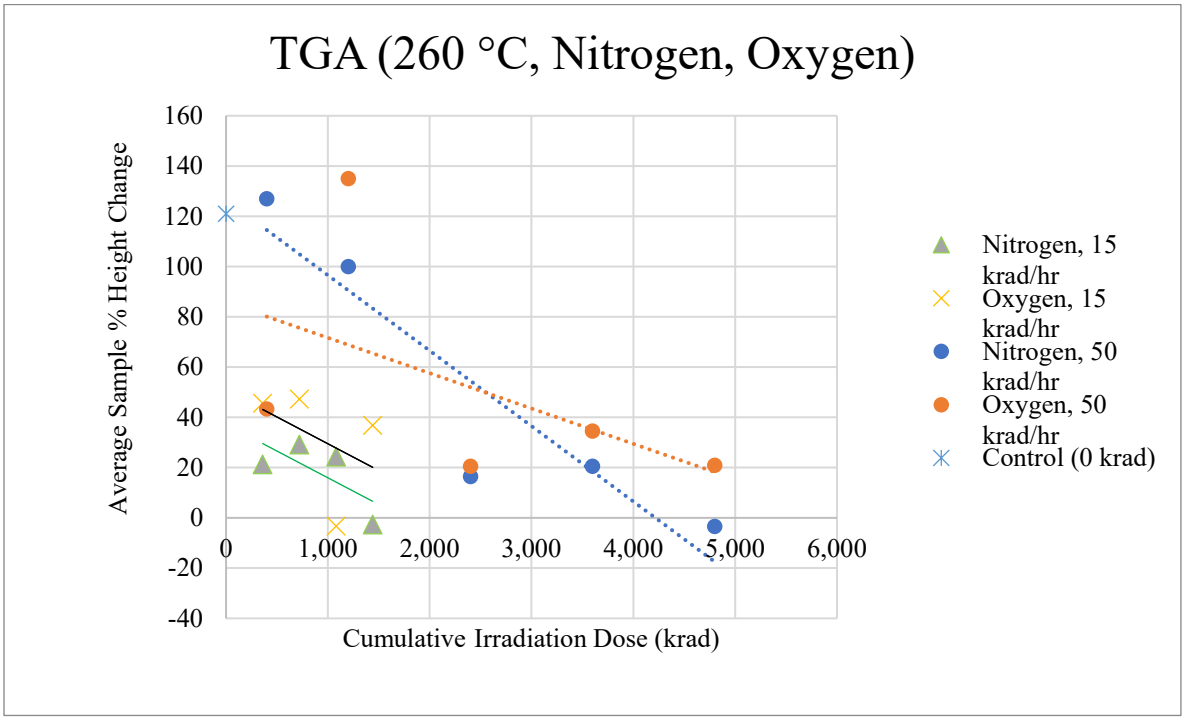


The onset temperature of the TGA graph is the point in the TGA curve where there is first a deflection from the established baseline. It is the point of intersection of the initial baseline and the tangent to the curve at the point of the steepest gradient. The inflection and end temperature points provide a more complete analysis of this gradient. Lower onset, inflection, and end temperatures on the TGA curve suggest less thermal stability because it indicates decomposition under the influence of a lower temperature. It is worth noting that the initial sample mass,

heating rate, and flow rate of the atmosphere affect these measurements significantly, therefore, it is important to standardize the samples and instrument parameters as much as possible to avoid uncertainty within the measurements. The total percent mass weight loss of a sample also indicates thermal stability: if a greater amount of a mass loss occurs at the same temperature parameters and starting mass in one sample than in another, it indicates that the former is less thermally stable.

Based on the onset, inflection, and end temperatures in Figure 2 compared to cumulative irradiation in Mrad, it can be seen that there is no correlation observed between the cumulative irradiation doses measured and thermal stability. The percent mass weight loss versus cumulative irradiation in Mrad was also analyzed. There was no correlation observed between these two variables either.

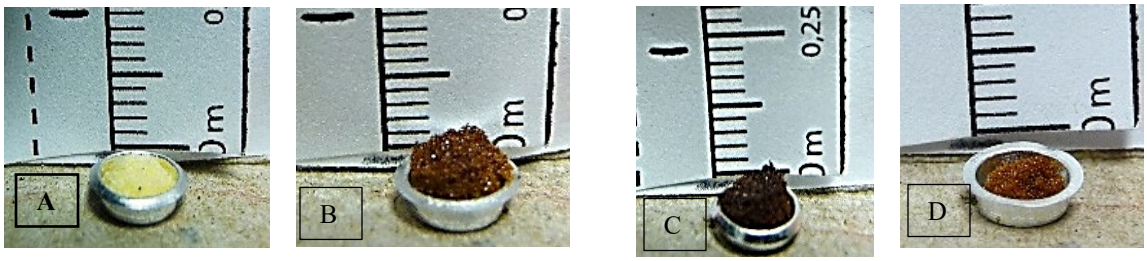
Figure 4: Average sample percent height change versus cumulative irradiation.



The TGA instrument was also used as a means of heating the foam samples to 260 ° for qualitative analysis of intumescence. This was done under both a nitrogen and oxygen atmosphere. The samples were measured in millimeters with calipers before and after. Many samples had between 100-200% height increase following heating, although it varied significantly even from points within the same sample cylinder. This variation in heights and how even the top and bottom of the samples were when initially cut made a significant difference in the measurements, and could be a possible reason as to why the 15 krad/hr group had smaller height increases than the 50 krad/hr. While most of the samples had little visual or measured differences in sample percent height change before and after heating as compared to a non-irradiated sample, there were some notable differences in qualitative intumescence for the two highest dose rates, 15 and 50 krad/hr. Less intumescence was observed with a higher cumulative

irradiation dose, and at higher doses, there was even a slight negative percent height change as the sample collapsed in on itself. These trends were observed with both nitrogen and oxygen. These changes can be seen visually in the photographs taken below:

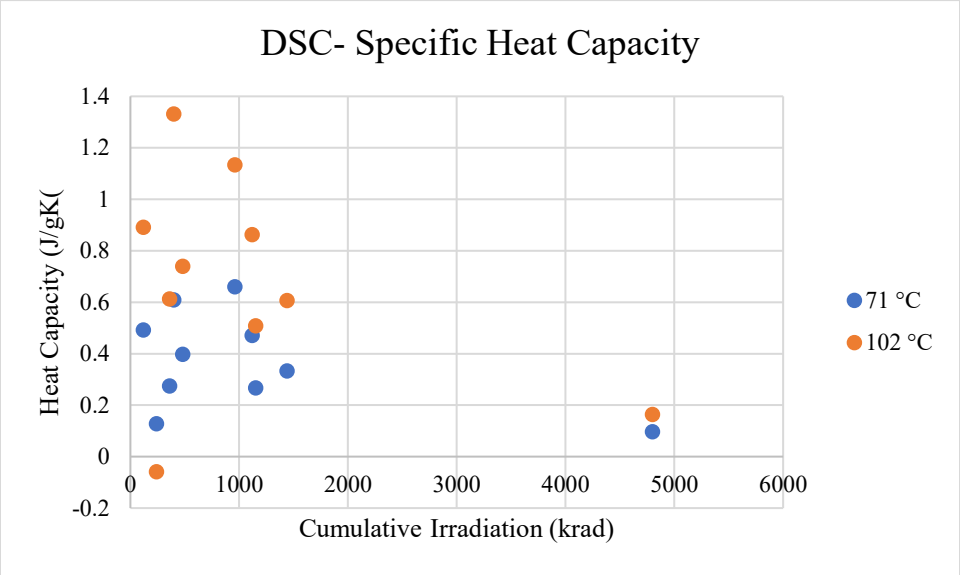
Figure 5: Images of polyurethane foam before and after TGA.



A. An irradiated sample prior to TGA. Most of the samples looked extremely similar visually. There was a very slight darkening of the foam at higher dose rates, but it wasn't very dramatic.
B. A sample exposed to a cumulative dose of 400 kRad, following TGA to 260 °C in nitrogen. This sample had approximately a 127% increase in height and looked nearly identical following TGA to the samples that had lower cumulative doses of irradiation, including the non-irradiated sample.
C. A sample exposed to a cumulative dose of 1.2 Mrad, following TGA to 260 °C in nitrogen. This sample had approximately a 100% increase in height, which indicates that intumescence still occurred. It was darker in color than samples that had lower cumulative doses of irradiation.
D. A sample exposed to a cumulative dose of 4.8 Mrad, following TGA to 260 °C in nitrogen. This sample actually had approximately a -3.4% decrease in height from prior to heating. It was also dark in color and crumbled easily.

Differential Scanning Calorimetry:

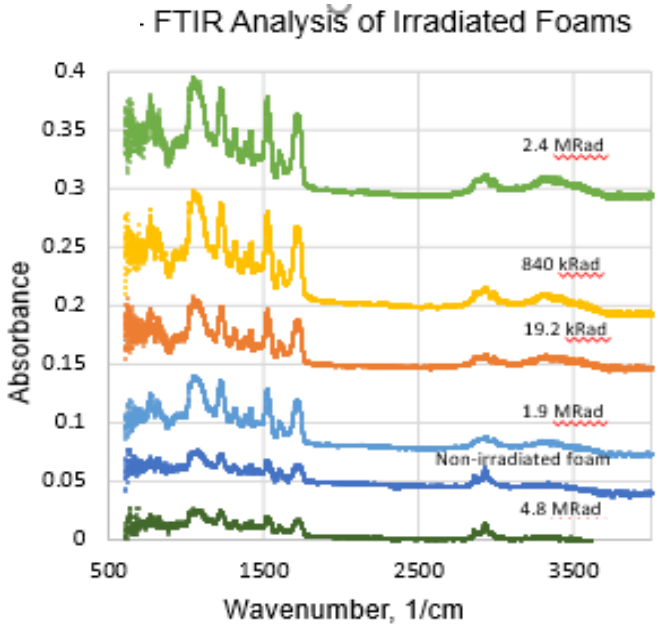
Figure 6: Heat capacity (J/gK) versus cumulative irradiation (krad) of polyurethane foam.



The heat flow data from the TA Universal Analysis software into specific heat capacity measurements as seen above. Specific heat capacity was calculated via the ASTM E1269-11 Standard at 71 °C and 102 °C. Lower specific heat capacity would have indicated a potential breakdown of foam chemical structure due to irradiation. However, based on this data, there was no correlation between cumulative irradiation in Mrad and heat capacity when analyzed at both 71 °C and 102 °C. This indicates that there was not significant chemical structure breakdown at the cumulative irradiation points measured.

FTIR:

Figure 7: FTIR Analysis of Irradiated Foams



Selected polyurethane samples at a range of cumulative doses of irradiation were analyzed via FTIR and shown in Figure 7. There was no significant difference in chemical structure as seen by FTIR peaks for any of the irradiated samples or the non-irradiated foam. Notable peaks in the FTIR spectrum include benzene at around 700 cm^{-1} , N-H at around 1580 cm^{-1}, C=O at around 1700 cm^{-1}, C-H at around 2800 cm^{-1}, and carboxylic acid at around 3200 cm^{-1}. Based on the chemical structure of polyurethane, these peaks are expected.

Conclusions:

Based on the analyses performed of the irradiated polyurethane foam samples, there was no correlation between higher cumulative irradiation and thermal stability, specific heat capacity, or chemical structure. Qualitative data suggested that at cumulative irradiation doses at greater than 4 Mrad in less than 96 hours, intumescence decreases. It is expected that the polyurethane foam used in the 9977 shipping container will be exposed to approximately 2 Mrad of cumulative irradiation or less after 50 years, far less than the doses used in these experiments, so the fire protective properties in the shipping containers should hold up with the expected amount of radiation exposure.

Future work:

While the experiments performed indicated a lack of correlation between irradiation at selected dose rates and the thermal properties of the polyurethane foam, there was not time to perform analysis on every sample at every time point. Instead, a range of cumulative doses was selected for analysis in order to provide a “broad picture” of trends. An original goal of the experiment was to compare different dose rates at the same cumulative doses, however, there was not

enough time to fully accomplish this task. A more complete analysis of all samples may yield different trends. In addition, the tests on the samples were run once. While an effort was made to keep samples for TGA and DSC analysis as close to the same weight and dimensions as possible, the nature of the material made this somewhat difficult. Since sample weight can induce an element of variability into TGA and DSC measurements, running multiple tests on the same sample could help to improve the statistical significance of the measurements.

As far as further directions for this project go, analyzing the effects of both foam aging at certain temperatures and relative humidity levels in conjunction with irradiation could provide a more complete set of data, as well as performing additional tests like compression testing to look at the mechanical strength of the foam. Quantitative testing for intumescence could also be useful.

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