Thermal Characterization
of Commercial Polyurethane
Elastomers Used in Petroleum
Containment Applications

by Dawn Crawford

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Thermal Characterization of Commercial Polyurethane Elastomers Used in Petroleum Containment Applications

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Abstract

Numerous commercial polyurethane elastomers were evaluated using Differential Scanning Calorimetry (DSC) after a variety of aging conditions including exposure to fuel and water for up to 42 days. The results indicated changes in the material as a result of aging conditions. These material or morphology changes were monitored by studying the thermal transitions detected by DSC. A general trend in thermal behavior of the conventional tank coatings was observed.
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1. BACKGROUND

The U.S. Army has used thermoplastic polyurethane elastomers (TPUs) as coatings on collapsible fuel and water tanks since the 1970s. The collapsible tanks are fabricated from woven nylon fabric that is coated on both sides with the TPU. This coated fabric is then heat-sealed together forming a pillow-shaped tank that, when empty, is easily transported. Collapsible tanks, which can be fabricated with holding capacities up to 200,000 gal, offer logistical advantages to ground and air missions by providing a mobile container for fuel and water.

Polyurethane coatings used in collapsible fuel and water tanks are conventionally made from polyester or polyether polyols. While the polyester based polyurethane has superior fuel resistance, it has a high susceptibility to hydrolysis. Polyether polyurethanes are therefore the preferred material for water storage. Improvements have been made in the hydrolytic stability of polyester polyurethane coatings, primarily by the incorporation of hydrolytic stabilizers. However, these polyurethanes continue to be less than satisfactory in humid tropic environments. Exposure of the polyester polyurethane coating to fuel has proven to leach hydrolytic stabilizers from the coating, accelerating deterioration by water (Feuer and Touchet 1990b).

Although previous work has been done to evaluate polyurethane coatings and coated fabrics in different environments using mechanical tests such as tensile properties and adhesion (Feuer and Touchet 1990; Gatza et al. 1992), limited work has been done on the thermal characterization of these materials after exposure to various aging conditions. Previous characterization using thermal techniques (Crawford et al. 1988) was conducted on materials that were not compounded for hydrolytic stability, pigmentation, or processing aids. Aging conditions were limited to exposure to humidity and water. Current work discussed herein includes exposure to fuel, water, and dry heat on a variety of materials, some of which are fully compounded and representative of actual tank coatings. Several of the materials are nonconventional experimental compounds. Therefore, the work discussed herein describes the thermal characterization of actual field materials as well as potential candidate materials, after exposure to a broad range of aging
conditions. The results serve as a database of commercially available thermoplastic elastomers for use as collapsible fuel tank and water tank coatings.

2. CHEMISTRY

Polyurethanes are made by step-growth polymerization, which was first described by Otto Bayer in 1937 (Grigat 1985). This polymerization involves the reaction of diols or diamines with di-isocyanates. Although the specific compositions of the compounds used in this work are proprietary and, therefore, not disclosed by the suppliers, TPU s typically comprise hydroxyl terminated polyester or polyether polyols and diphenylmethane di-isocyanate (MDI). The resulting properties of the polymer are highly dependent on the ratios of polyol and MDI used, the processing conditions, and additives such as hydrolytic stabilizers. The prepolymer sequence leading to polyurethane formation is shown in Figure 1 (Hepburn 1982).

![Prepolymer reaction sequence.](image)

Figure 1. Prepolymer reaction sequence.
Polyurethane elastomers are block polymers that have polymer chains composed of alternating, low-temperature glass transition "soft" segments and more rigid, higher melting-temperature, urethane "hard" segments. The soft segments typically comprise polyester or polyether polyols, and the hard segments are formed from the chain extension of a di-isocyanate with a low molecular weight diol. The hard and soft segments are joined end to end through covalent urethane bonds and, therefore, polyurethanes are classified as multiblock copolymers (Chau and Geil 1985).

The soft-segment domains are responsible for elastic behavior and are usually amorphous with a glass transition temperature ($T_g$) below room temperature. The hard-segment domain is often characterized as semicrystalline and provides stiffness to the material. These phases have distinct thermal transitions as shown in the DSC traces discussed later. It is believed that the physical properties of the polyurethane elastomers are enhanced as the degree of phase separation increases. It was the objective of the work discussed herein to investigate how numerous aging conditions affect the morphology of the materials as evidenced by changes in their thermal transitions.

3. APPROACH

Seven commercial polyurethane elastomers from four different suppliers were evaluated using Differential Scanning Calorimetry (DSC). The materials were characterized using DSC in their "as received" state and after various aging conditions including dry heat at 160°F, 180°F, and 190°F, immersion in deionized water at the same temperatures; immersion in fuel (JP-8 ST) at 160°F; and immersion in water at 160°F, 180°F, and 190°F after 7 days of exposure to fuel. In each of the aforementioned cases, the materials were evaluated after 7, 14, and 42 days of aging. Throughout the report, the materials are designated as A, B, C, D, E, F, and G. Confidentiality requires that the names of the suppliers be withheld. The specific aging conditions were performed in accordance with MIL-T-52983E.
DSC traces were obtained on a DuPont 9900 Thermal Analysis System using a dual sample cell. Each run was performed under a nitrogen purge of 50 cm$^3$/min. The method involved a heating rate of 20° C/min from -100° C to 250° C. Characteristic thermal transitions such as the $T_g$, endothermic melting, or exothermic degradation were investigated. The aged materials were allowed to come to ambient temperature (25° C ±2) before the DSC traces were obtained.

4. MATERIALS

Limited information regarding the composition of the polymers was provided by the suppliers due to the proprietary nature of the application. Each of the materials, however, was a thermoplastic elastomer that would enable thermal processing techniques necessary for the fabrication of the coated fabric. Some of the materials represented actual tank coatings while others were experimental polyurethane materials submitted as potential candidates for tank coating compounds. A brief description of the materials is given as follows:

A = polyester polyurethane,
B = polyether polyurethane,
C = polyester polyurethane,
D = polyether polyurethane,
E = experimental polyurethane,
F = experimental polyurethane,
and
G = experimental polyurethane.

5. RESULTS

5.1 General. Each of the materials exhibited three general thermal transitions. The DSC traces showed a low temperature (<0° C) $T_g$ and two broad endothermic transitions above 60° C shown in Figure 2. The $T_g$ was representative of the soft segment regions within the
polymer, allowing low-temperature flexibility similar to conventional crosslinked elastomers. The sharp endotherm at 5°C shown in Figure 2 was due to the test method and does not represent a thermal transition in the material. The broad endotherms at approximately 69°C and 160°C are related to the soft-segment reordering and hard segment dissociation, respectively (Seymour and Cooper 1971).

5.2 Polyester Polyurethanes. Compounds A and C both comprised polyester polyol. While polyester polyurethanes exhibit excellent resistance to fuel, they are prone to hydrolytic attack when exposed to water. Upon hydrolysis, the ester group is cleaved, reverting back to the carboxylic acid and alcohol. The resulting acid further catalyzes the ester hydrolysis leading to autocatalysis which has been shown to be associated with a significant reduction in average molar mass, and likewise, physical properties (Pegoretti, Penati, and Kolarik 1994). Polycarbodiimides, which act as acid scavengers, are usually added to polyester polyurethane elastomers to slow the hydrolysis of ester segments.
As shown in Figure 2, compound A has a $T_g$ of approximately $-49^\circ$ C. After aging in water for 7 days at 190° F, the $T_g$ was relatively unchanged, as can be seen in Figure 3. However, the onset and peak temperatures of the endothermic transitions shifted to higher temperatures. The enthalpy of the thermal transitions became smaller as a result of 7 days water aging at 190° F. Also, the transitions were sharper and more defined than the unaged material, indicating that this degree of aging did not significantly alter the degree of phase separation in the material.

Figure 4 shows the DSC trace of compound A after 14 days of water aging at 180° F. The $T_g$ was still relatively unaffected, shifting slightly upward to $-45^\circ$ C. The endothermic transitions appear broader and are shifted toward lower temperatures compared to the material aged for 7 days.

After 42 days water aging at 180° F, the DSC trace was drastically changed, as shown in Figure 5. The $T_g$ after this aging condition was shifted dramatically to $-15^\circ$ C. The sharp endotherm at 3° C was most likely due to the melting of frozen water that saturated the polymer. Most notable was the very large endotherm with an onset temperature of 31° C and an enthalpy of 68 J/g compared to the previous condition in which the enthalpy of transition ranged between 2 and 11 J/g. The higher temperature endotherm with an onset temperature of 156° C was very small (0.6 J/g). The large endothermic transition without the presence of the higher temperature endotherm is indicative of a loss of phase separation in the polymer. The large shift in $T_g$ ($-49^\circ$ C to $-15^\circ$ C) indicated embrittlement of the polymer after 42 days of aging in water. It is likely that hydrolytic attack of the ester linkage caused chain scission, disrupting the long-chain polyol soft segment. Disruption of the polymer backbone would likely affect the separation of the microphases as indicated by the presence of the large broad endotherm shown in Figure 5.

Compound A exhibited very different thermal behavior after heat aging for 7, 14, and 42 days at 160° F, 180° F, and 190° F. After 7 days of heat-aging, the $T_g$ was relatively unaffected, remaining at approximately $-45^\circ$ C. The two endotherms representing the two phases were distinct with higher onset temperatures than seen in the unaged material. After 14 and 42 days of dry air heat aging, the $T_g$ appeared to shift upward to $-20^\circ$ C and $-10^\circ$ C, respectively. This
Figure 3. DSC trace of compound A aged in deionized water for 7 days at 190°F.

Figure 4. DSC trace of compound A aged 14 days in deionized water at 180°F.
Figure 5. DSC trace of compound A aged 42 days in deionized water at 180°F.

would indicate phase-mixing in the polymer. It should be noted, however, that the $T_g$ of these materials is a weak transition, as shown using DSC and, therefore, it was difficult to detect reproducible changes in $T_g$. As the temperature of aging was increased from 160°F to 190°F, the onset temperature of the endothermic transition also increased (onset of endotherm 1: 91°C to 109°C; onset of endotherm 2: 132°C to 146°C). This implies that as the temperature is increased, the microphases are reordering, resulting in polymer melting occurring at higher temperatures.

Polyester polyurethanes are inherently resistant to fuel; however, only 7 days of fuel immersion at 180°F had a marked effect on the polymer morphology as indicated by DSC. The distinct endotherms seen in the unaged material became one large broad endotherm with an onset temperature of approximately 100°C. This endotherm had an enthalpy of approximately 67 J/g with two peaks, but the peaks were less separated than seen in the unaged material. This lower
degree of phase separation was observed after 7, 14, and 42 days of aging. This merging of the endothermic transitions may be due to a plasticization effect of the fuel on the polymer at the temperatures studied. Since the onset of this transition was relatively high (100° C) compared to water-aged specimens (31° C), the material aged in fuel should have better physical integrity than the polymer aged in water for the same conditions.

The final aging condition studied is termed “fuel extraction” and involves aging the polyurethanes in fuel for 7 days at 160° F, drying the specimens in a 120° F vacuum oven for 16 hr, and then reimmersing them in water for 7, 14, and 42 days at 160, 180, and 190° F. This is a vigorous aging condition in which the hydrolytic stabilizers are leached out by exposure to the fuel. The results are similar to, but more extreme than, the water-aging condition. This would be expected because in the water aging tests, the hydrolytic stabilizers are intact. The DSC trace after fuel extraction and water immersion for 7 days at 180° F is shown in Figure 6. This DSC trace is very similar to Figure 5 in which the material was aged in water for 42 days. Thus, the morphology change in the polymer after fuel extraction is very similar to water aging, but the degradation occurs much sooner.

Compound C, which is also a polyester polyurethane, exhibited thermal transitions similar to compound A after the various aging conditions. Water aging before and after fuel exposure resulted in the most significant changes in the thermal transitions, generally indicating poor phase separation as the aging time was increased from 7 to 42 days. Heat-aging caused an increase in endothermic onset temperatures and $T_g$, indicating a stiffer material that may be the result of increased order of the microphases.

5.3 Polyether Polyurethanes. Compounds B and D are based on polyether polyols. Polyether is inherently stable when exposed to water. Polyethers can be hydrolyzed, but this occurs at a much slower rate than in polyesters. In the hydrolysis of polyether polyurethanes, chain scission occurs at the urethane linkage, leaving the soft segment of the polymer intact (Hepburn 1982).
Figure 6. DSC trace of compound A after fuel extraction and water-aging for 7 days at 180° F.

Compounds B and D exhibit the same general features in the unaged DSC traces as seen in the polyester compounds. However, some of the DSC traces of compounds B and D show a third, higher temperature endotherm whose onset temperature ranged between 140° C and 200° C. A notable difference between compounds B and D occurred after both water immersion and fuel extraction aging conditions. After 42 days of water aging, compound D showed a merging of endotherms, forming a large endotherm similar to the polyester polyurethanes. Compound B continued to show phase separation as indicated by the presence of three distinct endotherms through 42 days of water aging. The distinct differences in the endothermic transitions of compounds B and D after 42 days immersion in water are shown in Figures 7 and 8, respectively. Although the $T_g$ would be helpful in determining the effect that water has on the integrity of the soft segment and elasticity of the material, the value of $T_g$ is very difficult to determine from these DSC traces. Because the composition of these polymers was not disclosed by their suppliers, it is
Figure 7. DSC trace of compound B aged 42 days in deionized water at 190° F.

Figure 8. DSC trace of compound D aged 42 days in deionized water at 190° F.
not clear why the two polyether polyurethanes exhibit very different thermal behavior as a result of long-term exposure to water.

The polyether polyurethane compounds exhibited similar thermal transitions to the polyester polyurethane compounds after dry heat aging. Separation between the phases remained evident throughout the heat-aging experiments. As with compounds A and C, compounds B and D showed a general increase in $T_g$ and onset temperature of both endothermic transitions.

Compounds B and D exhibited very similar DSC traces after immersion in fuel. In general, the endothermic transitions remained distinct, indicating the presence of both hard and soft phases in the polymer. However, after 42 days immersion in fuel at 160° F, the peaks began to merge together, with the larger peak occurring at approximately 157° C.

5.4 Experimental Materials. Compounds, E, F, and G represent materials other than the conventional fuel and water tank polyurethanes. None of these materials has been used in collapsible tank applications, but they were submitted by their suppliers as potential future candidate materials for tank coatings. Basic information regarding the polymer or composition of these compounds is not known.

Experimental material E exhibited two distinct endotherms in the unaged materials with peak temperatures of approximately 146° C and 175° C. Both compounds E and G showed the presence of a large endotherm at approximately 85° C and 96° C, respectively, after 42 days of water immersion. This is similar to the thermal transitions seen in the polyester polyurethanes A and C. A notable difference in the DSC traces of compounds E and F was the presence of an additional very sharp endotherm at higher temperature (approximately 200° C). These materials exhibited poor physical integrity after 42 days of water immersion before and after fuel extraction, which is indicative of polyester polyurethanes that have not been compounded with hydrolytic stabilizers. The presence of the sharp endotherm in the vicinity of 200° C remained present throughout all of the aging conditions for compound G and was prominent after water aging and fuel extraction for compound E. The presence of this sharp peak was not prominent for
compound F. Compounds E, F, and G did not exhibit a strong trend in upward shift of endothermic peak temperature as a function of heat aging as seen in the conventional polyester and polyether polyurethanes. Compound F did have a distinct sharp endotherm in all of the DSC traces after heat aging, which occurred around 200° C. Compounds E and G did not exhibit this sharp high-temperature endotherm, the presence of which may be due to highly ordered or crystalline regions. Compound F also retained physical integrity after long-term water aging before and after fuel extraction, which may be related to morphological or compositional features represented by the sharp endothermic transition around 200° C. The thermal transitions of compounds E, F, and G did not show significant changes after fuel immersion at 160° F.

6. CONCLUSIONS

A variety of commercial thermoplastic elastomers were evaluated using DSC after numerous aging conditions. The composition of these materials was not disclosed by their suppliers, making it difficult to explain their thermal behavior as it relates specifically to compositional differences between the materials. The conventional polyester and polyether polyurethanes showed some general trends. Polyester polyurethanes showed larger changes in their thermal transitions after aging in water. This was exemplified by the merging of two characteristic endotherms related to the separate phases in the polymer, into one large broad endotherm. In some cases, this was also accompanied by an increase in Tg. These changes would indicate that the original 2-phase morphology of these polymers, which imparts good elastomeric behavior, is destroyed after long-term water exposure at temperatures at or above 160° F. This trend was also seen, surprisingly, in one of the polyether polyurethanes. Both polyester and polyether polyurethanes showed an upward shift in endothermic peak temperatures, retaining phase separation throughout all dry heat aging. The heat aging at the temperatures used in this study most likely had an annealing effect on the polymer morphology, allowing reordering within the domains and possibly formation of larger hard-segment domains. Several of the experimental materials showed trends similar to the conventional polyurethane elastomers.
The $T_g$ would be very informative in determining the effect that the aging conditions had on the soft segment of the polymer. However, $T_g$ was a poorly defined transition in the DSC traces shown herein. Future work will involve utilizing Dynamic Mechanical Analysis (DMA) as a complementary technique to DSC in thermal characterization of polyurethanes. DMA is a very sensitive tool to detect $T_g$. DMA will also provide valuable information regarding the material's stiffness and viscous loss properties. Together, DMA and DSC will allow thorough thermal characterization of polyurethanes and potentially relate chemical and morphological changes in the material due to aging with mechanical properties.

The data presented in this report represent a baseline for the thermal properties of commercial urethanes and provide insight into the morphological changes these polymers undergo when subjected to numerous aging studies typical for fuel containment applications.
7. REFERENCES


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**Subject Terms**
- polyurethane elastomer
- collapsible fuel and water tanks
- differential scanning calorimetry (DSC)
- hydrolysis
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