FAILURE ANALYSIS OF GASOLINE STORAGE ASSEMBLIES

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Abstract

Failures occurred within tank assemblies used for the storage of gasoline. The cracking was observed in a significant number of assemblies that had been in service. The cracking was found within the injection molded spout in areas immediately adjacent to the surrounding blow molded tank body. The focus of this investigation was a determination of the nature and cause of the failures. The results obtained during the evaluation of the cracked components indicated that the failures occurred through slow crack initiation via a creep rupture mechanism. This paper will review some of the testing performed to characterize the failure mode and identify the cause of the cracking, while demonstrating the analytical procedures used in the investigation.

Background

The storage assemblies were used to hold gasoline, and catastrophic cracking occurred after an undetermined time in use. The spouts were comprised of an injection molded polyethylene spout integrated with a blow molded tank body. A separate mating cap is screwed onto the spout, such that the cap does not bottom out on the tank surface. The spouts are specified to be injection molded from Alathon® M 5370, a high density polyethylene resin from Equistar. In addition to the two failed tank sections, a spout, which had not been molded into a gasoline tank, was also evaluated for reference purposes.

Experimental

Fracture surfaces of the cracked spouts were examined using a Hitachi S-3500N scanning electron microscope (SEM). The specimens were cleaned ultrasonically in a mixture of isopropanol and deionized water. Prior to the inspection the surfaces were gold sputter coated to enhance the imaging.

Samples representing the storage assemblies were analyzed using micro-Fourier transform infrared spectroscopy (FTIR) in the attenuated total reflectance (ATR) mode. A Nicolet Magna 550 spectrometer interfaced with a Nic-Plan® IR microscope was used for the analysis.

Sample materials from the failed and reference assemblies were analyzed using thermogravimetric analysis (TGA). The testing was performed on a TA Instruments 2950 TGA system. The thermal program involved dynamic heating at 20 °C/min using sequential nitrogen and air purge atmospheres.

Materials representing the storage assemblies were evaluated using differential scanning calorimetry (DSC). The testing was conducted using a TA Instruments Q100 DSC. The analysis involved heating the samples at 10 °C/min to a temperature above the melt transition, followed by controlled cooling through recrystallization. The same sample was then reheated at the same 10 °C/min rate, through the melting point.

The specific gravity of the spout materials was determined in accordance with ASTM D 792. This testing was conducted at ambient laboratory conditions, 23 °C and 29% relative humidity.

The molecular weights of the assembly materials were evaluated indirectly by melt flow rate. The melt flow rate testing was conducted in accordance with ASTM D 1238 – Procedure B, using a temperature of 190 °C and a constant load of 2.16 kg.

Tests and Results

Visual Examination

Examination of the two storage tank sections confirmed the presence of catastrophic cracking within the corresponding spouts. One of samples exhibited cracking that extended around the entire spout circumference, while the second part exhibited cracking approximately 350° around the spout circumference. The form and location of the cracking was consistent across the two parts. The crack was located immediately above the formed corner in the spout, as illustrated in Figure 1. This area would be immediately outside of the natural reinforcement of the spout wall created through bonding with the mating tank. The visual examination did not show signs of apparent macroductility, as would be indicated by the presence of stress whitening or permanent deformation. Conversely, the parts displayed features associated with brittle fracture. No signs of apparent mechanical damage or abuse were noted during the visual examination. However, adhesive caulk was evident where repairs were attempted on the cracks.

The two failed parts were further examined with the aid of an optical stereomicroscope at magnifications up to 50X. The microscopic examination revealed similar features across the two failed spouts. Both parts exhibited multiple apparent crack origins along the outer diameter of the spout wall. The cracking primarily extended inward toward the inner diameter of the spout wall, where river markings were observed indicating that the orientation of the applied stress had changed. The fracture surfaces showed crack unions

where the individual cracks had coalesced. A typical fracture surface is presented in Figure 2. Very little evidence of circumferential cracking was noted, with the predominant fracture orientation being through the part wall. Importantly, no signs of bending were noted within the fractures, indicating essentially tensile loading, basically pulling the upper section of the spout from the lower section. Consistent with the observations made during the visual examination, no signs of macroductility were apparent during the microscopic inspection.

Scanning Electron Microscopy

The storage assembly fracture surfaces were further examined via scanning electron microscopy (SEM). Examination of the fracture surface confirmed the presence of multiple individual crack origins along the outer diameter of the spout wall. The crack origin locations exhibited a relatively smooth morphology, indicative of slow crack initiation, as shown in Figure 3. No signs of microductility were noted within the crack origin zone. The observed features indicated that the cracking had initiated along the outer diameter and progressed in a transverse orientation through the spout wall. Examination of areas adjacent to the inner diameter of the spout wall showed an increased level of microductility, as indicated by the presence of stretched fibrils. This is illustrated in Figure 4. This increase in ductility is representative of variation in the stress dynamics responsible for cracking at these locations. Throughout the SEM evaluation, no evidence was found to suggest molecular degradation of the spout material, such as direct chemical attack or thermal deterioration. Additionally, no signs of molding defects, such as voids or inclusions, were apparent.

Fourier Transform Infrared Spectroscopy

Core specimens representing the failed and reference parts were analyzed and a direct comparison of the results yielded an excellent match, without apparent differences. Subsequent library searching and interpretation indicated that the spectra exhibited absorption bands characteristic of a polyethylene resin. The results of the FTIR testing did not show evidence to suggest contamination or degradation of the failed or reference spout materials.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) analysis of the reference part produced results indicating that the material underwent a single endothermic transition centered at 130 °C and 132 °C during the initial and second heating runs, respectively. This transition was associated with the melting point of the material, and was consistent with that expected for a high density polyethylene resin. During the cooling portion of the analysis, the material underwent recrystallization centered at 117 °C. A comparison of the heats of fusion obtained during the initial and second heating runs showed generally good agreement, indicating that the material had been molded in such a way as to achieve an adequate state of crystallinity. The heat of fusion obtained during the second heating run, 209 J/g, was indicative of a relatively highly crystalline material.

Analysis of the failed spout produced results showing a single endothermic transition centered at 130 °C and 131 °C during the initial and second heating runs, respectively. The material underwent recrystallization centered at 116 °C during cooling. A comparison of the heats of fusion showed good agreement, indicating that the failed part material achieved proper crystallinity during molding. The obtained DSC results are presented in Figures 6 and 7. Overall, the results obtained on the failed spout were comparable to those obtained on the reference part, with both materials producing results as expected given the description of the material, Alathon® M 5370.

Thermogravimetric Analysis

The spout materials were analyzed via thermogravimetric analysis (TGA), and the results obtained on the reference spout indicated that the material underwent a relatively simple weight loss profile. While heating under a dynamic nitrogen purge, the sample underwent the primary weight loss of 99.0%. This weight loss was centered at 484 °C and corresponded to the thermal decomposition of the base polymer. Upon conversion to a dynamic air purge, the sample underwent a weight loss of 0.4%, corresponding to the combustion of carbon black pigment. This level of pigment would be sufficient to cause black coloration, but would not impart inherent ultraviolet (UV) stability to the molded article. Upon completion of the evaluation, a non-combusted residue content of 1.2% was obtained, indicating that the material was essentially unfilled. Overall, the results obtained on the reference part were consistent with a carbon black pigmented, unfilled polyethylene resin.

Analysis of the failed spout produced results that were generally similar to those obtained on the reference part, with a single notable difference. The results obtained on the failed spout material showed a weight loss of 1.4% while heating to moderate temperatures under the nitrogen purge. This weight loss corresponded to the evaporation of volatiles, such as gasoline, absorbed into the spout material. The remainder of the obtained results, including the polymer weight loss, the carbon black weight loss, and the non-combusted residue content were consistent with the results obtained on the reference part. The TGA thermogram obtained on the failed spout is included in Figure 8. The presence of absorbed gasoline is in agreement with the stated description of the material as a gasoline tank spout. At equilibrium, polyethylene resins can absorb between 10% and 15% of their weight in gasoline.

Specific Gravity

The specific gravity testing showed very good agreement between the reference and failed samples. The reference

part material produced an average specific gravity of 0.954, with the failed part material yielding a value of 0.953. These results matched the density indicated on the Alathon® M 5370 Data Sheet, 0.953 g/ml. The determined specific gravity values were consistent with the results obtained during the DSC results, indicating that this material has a relatively high degree of crystallinity.

Melt Flow Rate

The melt flow rate of the spout materials revealed a minor difference between the two samples. The reference part material produced an average melt flow rate of 6.11 g/10 min This was in excellent agreement with the nominal value indicated on the Alathon® M 5370 Data Sheet, 6.9 g/10 min The results obtained on the failed part material showed a slightly higher melt flow rate, 8.65 g/10 min This difference, while statistically significant, was relatively minor, and was likely the result of two factors. Such variation can be attributed to lot-to-lot differences within molding resin. Additionally, the presence of the gasoline, as indicated through the TGA analysis, will have a plasticizing effect on the polyethylene resin. This plasticization will result in increased flow and a higher melt flow rate result. As such, the results obtained on the failed and control spout materials did not indicate significant molecular degradation of either material.

Conclusion

It was the conclusion of the evaluation that the two submitted gasoline storage tank spouts failed via slow crack initiation through a creep rupture mechanism. Creep is the application of static, or near static, stresses to a component over an extended period of time. The exertion of stresses below the yield point of the material results in disentanglement of the polymer chains without substantial permanent deformation. The time required to produce cracking is a complex function of the applied load, temperature, and the condition of the material.

The visual, microscopic, and SEM examinations of the failed parts showed multiple individual crack origins located around the outer diameter of the spout wall. The presence of multiple individual origins along the entirety of the outer diameter of the cap indicated that the stresses were principally tensile in nature with minimal bending. The cracking progressed principally through the part wall, with very little circumferential progression. The entirety of the part displayed brittle fracture features, without evidence of substantial macroductility. High magnification inspection of the crack origin locations showed a relatively smooth morphology, characteristic of slow crack growth. An increased level of microductility was observed remote to the crack origins, as indicated by the presence of stretched fibrils. This change in morphology indicated that the fracture initiated via a slow crack growth mechanism, which transitioned into a ductile rapid overload mechanism once the cracking had extended sufficiently through the part wall. The location of the cracking was consistent across the two parts, immediately above the designed corner, just outside of the area of natural reinforcement associated with the bonding to the mating gasoline tank. It was noted that the cap does not bottom out onto the tank, and as such, the nature of the stresses responsible for the creep failure were not identified. Further information and evaluation of a complete tank/cap system would be required to more comprehensively assess the source of the stress.

Analysis of the spout samples produced consistent results across the failed and reference parts. The materials produced results characteristic of a carbon black pigmented, unfilled high density polyethylene resin. Analysis of the reference part material indicated a specific gravity of approximately 0.953, and a melt flow rate of 6.11 for the control sample. These values correlated well with those indicated on the Alathon® M 5370 Data Sheet. The results obtained on the failed part showed a specific gravity matching that of the control part. However, a slightly higher melt flow rate was obtained likely associated with the presence of gasoline absorbed into the spout material. The presence of gasoline was indicated through the TGA evaluation at a level of approximately 1.4%. It is likely that at the time of failure the gasoline was absorbed into the spout material at a considerably higher level and that subsequent evaporation occurred. Based upon previous testing, it has been demonstrated that high density polyethylene resins can absorb between 10% and 15% of their weight in gasoline at equilibrium.

The presence of gasoline within polyethylene resins results in a substantial loss of mechanical properties. The gasoline acts as a plasticizer, and as such, dramatically reduces the modulus, tensile strength, and creep resistance of the material. Thus, the presence of the gasoline is thought to have been a substantial factor in the failure. The gasoline acted as a plasticizer being absorbed into the bulk of the spout material. This is distinct from environmental stress cracking (ESC), which causes cracking localized on the chemical contact surface. The distinction in this case is subtle, yet important. The gasoline modified the bulk properties of the spout precipitating the creep rupture.

A second significant factor in the failure may be the selection of the plastic resin. The Alathon® M 5370 material has a stated density of 0.953 g/ml. This value, together with the results obtained during the DSC testing, indicated that the material is a relatively highly crystalline grade of polyethylene. In general, the higher the level of crystallinity, the more prone to creep the material will be. Thus, a polyethylene resin with a specific gravity of 0.945 would produce a spout that would be much more resistant to creep relative to the current material. Additionally, a resin with a higher average molecular weight corresponding to a lower melt flow rate would also improve the mechanical properties of the molded spout.

Ongoing Investigation

Pursuant to the failure investigation, two additional studies are being performed. The inherent stress of screwing the cap onto the spout is being is being investigated through strain gauging. Additionally, a comparative creep study between the current material and a proposed replacement is being completed.

Keywords

failure analysis, creep, polyethylene, gasoline

Fig. 1 - Cracking was evident within the spout of the storage assembly.

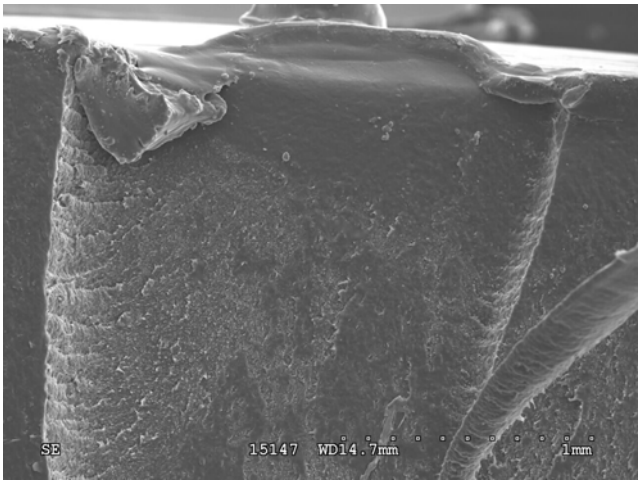

Fig. 3 - Scanning electron image showing a crack origin area. This region displayed a smooth morphology and distinct crack unions.

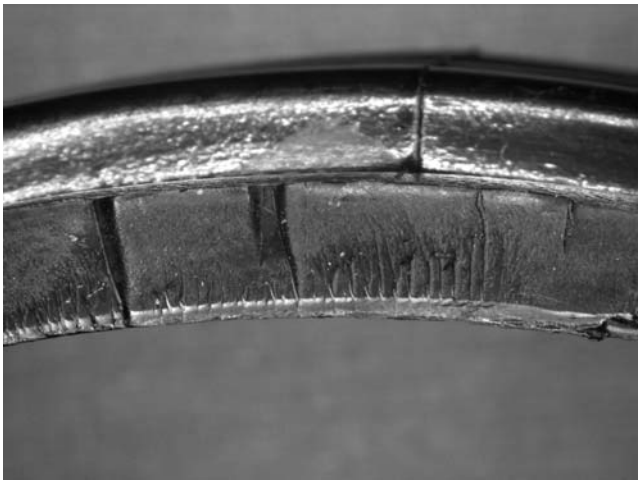

Fig. 2 - The fracture surface of the failed part showed cracking initiation along the outer diameter and no evidence of macroductility.

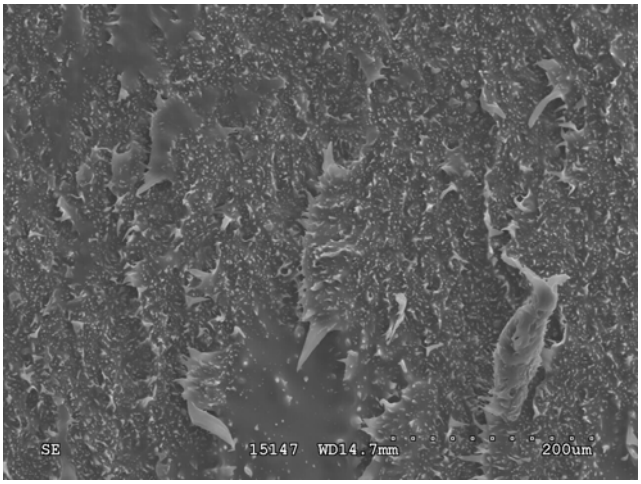

Fig. 4 - Higher magnification view of the central portion of Figure 3 showing limited microductility.

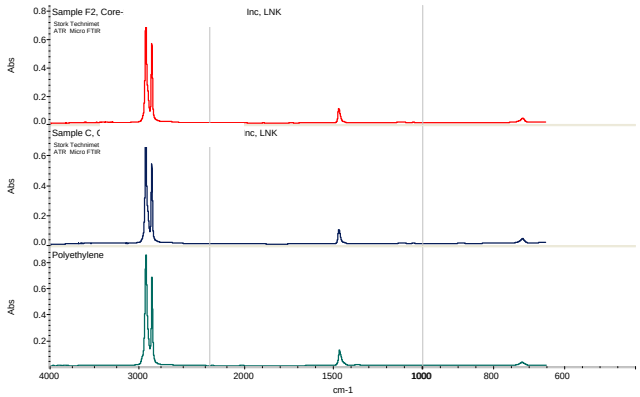

Fig. 5 - FTIR spectral comparison showing good agreement between the results obtained on the failed and reference materials.

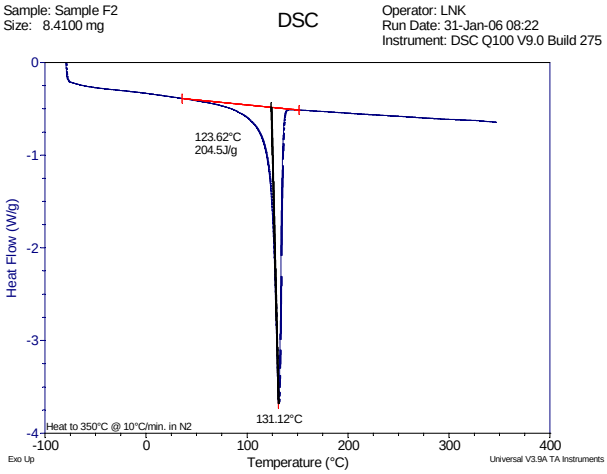

Fig. 7 - Second heating DSC thermogram obtained on the failed part material.

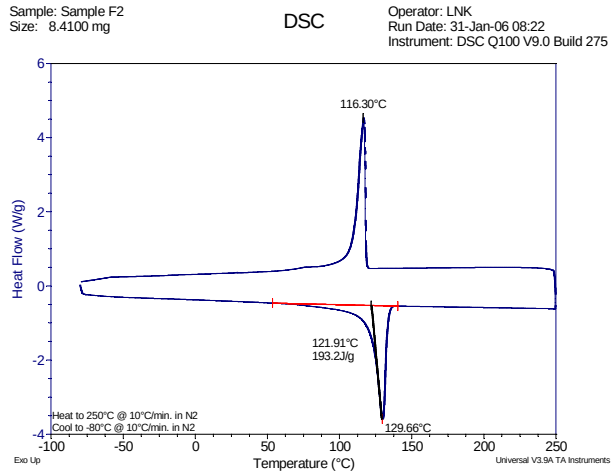

Fig. 6 - Initial heating DSC thermogram obtained on the failed part material.

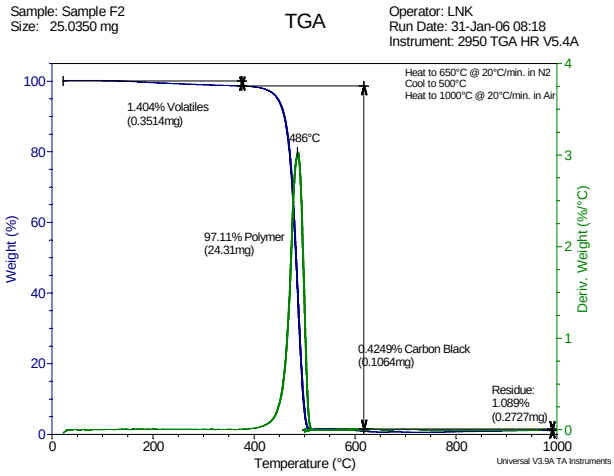

Fig. 8 - TGA thermogram obtained on the failed part material.