FAILURE ANALYSIS OF AUTOMOTIVE AIR CONDITIONING CONNECTORS

Jeffrey A. Jansen, The Madison Group, Madison, Wisconsin

Abstract

Failures occurred within automotive air conditioning system connectors. The cracking was observed within connectors that had been installed in automobiles, which were part of a durability testing program. 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 connectors indicated that the failures occurred through a brittle fracture, slow crack initiation creep rupture mechanism of the material. However, the cause of the failure was severe molecular degradation as a result of the durability test program conditions. This paper will review 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 connectors were components of the air conditioning system within vehicles that were used as part of a durability assessment program. The failures ultimately resulted in leakage of the compressor fluid and system failure. The vehicles had been operated aggressively under conditions of high annualized mileage in a severe hot and humid weather climate. In the application, the air conditioning system, and specifically the connectors, are under elevated internal pressure and exposed to a combination of refrigerant and compressor fluid. The compressor fluid was described as a polyalkylene glycol (PAG) oil.

The connectors are injection molded from a 35% glass fiber reinforced nylon 6/6 molding resin. The material was further described as being specially formulated to be heat stabilized and hydrolysis resistant.

In addition to the failed components, control parts and molding resin were also evaluated for reference purposes. Unused glycol fluid samples were obtained from the failed installation site and from an air conditioning system that did not have failed connectors on a separate vehicle within the durability testing program.

Experimental

The failed and control parts were initially examined using a Keyence digital microscope at magnification between 5X and 200X.

Fracture surfaces of the cracked components were examined using an Amray scanning electron microscope (SEM). The specimens were cleaned ultrasonically in an aqueous solution of a mild detergent. Prior to the inspection, the surfaces were gold sputter coated to enhance the imaging.

Samples representing the failed assemblies were analyzed using Fourier transform infrared spectroscopy (FTIR) in the attenuated total reflectance (ATR) mode. A Nicolet iS5 spectrometer was used for the analysis.

Materials representing the parts were evaluated using differential scanning calorimetry (DSC). The testing was conducted using a TA Instruments Q200 DSC. The analysis involved heating the samples 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.

Sample materials from the failed and reference connectors were analyzed using thermogravimetric analysis (TGA). The testing was performed on a TA Instruments Q500 TGA system. The thermal program involved dynamic heating at 20 °C/min using sequential nitrogen and air purge atmospheres.

The molecular weights of the connector materials were evaluated through gel permeation chromatography (GPC). The samples were dissolved in hexafluoroisopropanol (HFIP) / 0.01M sodium trifluoroacetate with gentle agitation over a period of 24 hours. Refractive index chromatograms were obtained for each sample in order to produce cumulative weight fraction curves and molecular weight distribution curves. The samples were run in duplicate and the results were calibrated against reference standards of poly(methyl methacrylate) (PMMA).

The fluid samples were compositionally tested using gas chromatography - mass spectrometry (GC-MS). The samples were diluted in dichloromethane prior to the injection.

Tests and Results

Fractographic Examination

Examination of the connectors confirmed the presence of cracking within the parts. The cracking within the failed parts was oriented longitudinally, consistent with hoop stress within the connector. A likely source of the hoop stress was internal pressure associated with operation of the refrigeration system. The cracking was present within both legs of the connector Y geometry, positioned approximately 180 degrees around the part from the injection molding gate (Figure 1).

The cracking was present on the interior and exterior surfaces of the failed parts. However, the cracking appeared most prevalent on the interior surfaces. The appearance of the cracking was consistent with multiple individual cracks coalescing to form the unified, but irregular fracture pattern. No evidence was found to indicate significant macro ductility, as would be indicted by stress whitening and permanent deformation. Conversely,

the cracking exhibited features characteristic of brittle fracture. The cracking location likely represented a knit line, an area of union between the two resin flow fronts during the molding process.

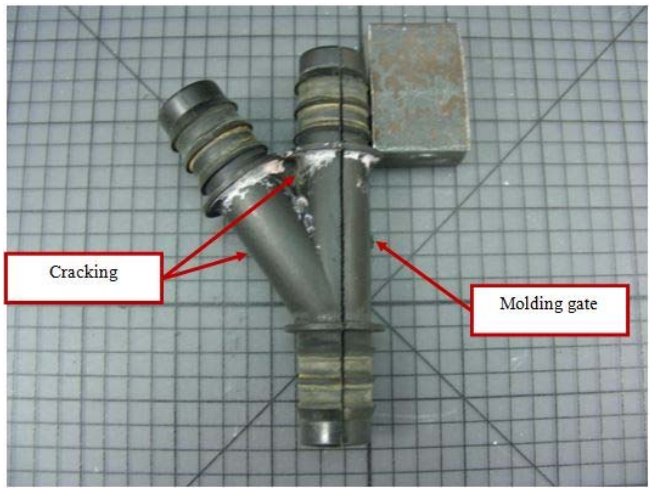

Figure 1. Close-up view showing one of the failed connectors in the as-received condition. The cracking was positioned approximately 180 degrees around the part from the injection molding gate.

The cracks within the connectors were completed in the laboratory to allow further inspection. The fracture surfaces of the various parts were very consistent, displaying similar features. The fracture surfaces showed no signs of macro ductility, and were indicative of a brittle fracture mechanism (Figures 2 and 3). The appearance of the fracture surfaces was consistent with crack initiation along the inner diameter walls of the connectors. During the examination, it was noted that the fracture surfaces showed the presence of glass reinforcing fibers oriented almost exclusively parallel to the cracking direction (Figure 3). This was likely the result of oriented flow of the resin into the molding tool within this location. Isolated areas on the fracture surface created during completion in the laboratory exhibited stress whitening. The presence of the stress whitening within the lab fracture zones was significant as it indicated that the material had some inherent ductility (Figure 2).

Microscopic examination of the interior surface of the connectors showed the presence of a network of micro cracks, commonly associated with molecular degradation (Figure 4). Additionally, during handling of the samples and subsequent sample preparation it was noted that the failed connector material cracked with very little applied stress or deformation, indicating that the connector material was in a compromised state.

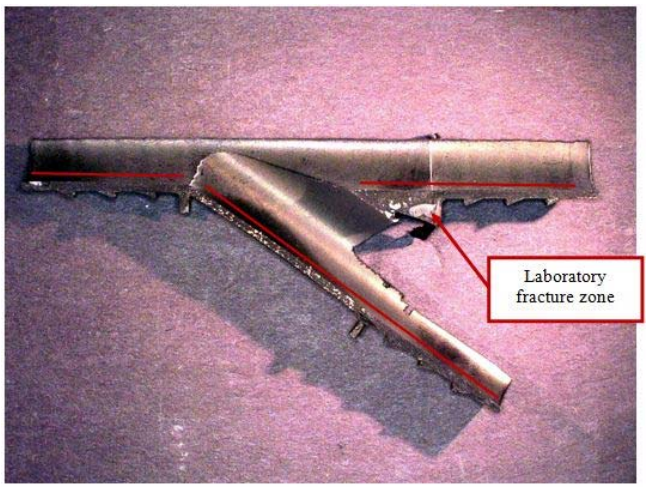

Figure 2. Photomicrograph showing the fracture surface after completion in the laboratory. The failure fracture surfaces are indicated by the red lines.

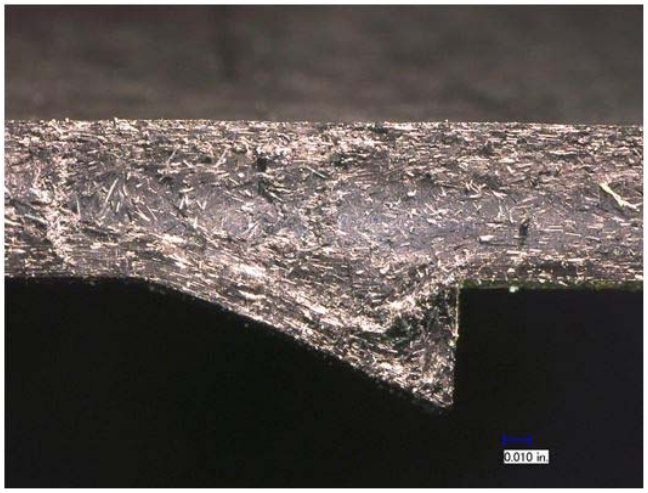

Figure 3. Photomicrograph showing a typical area on the failed connector fracture surface.

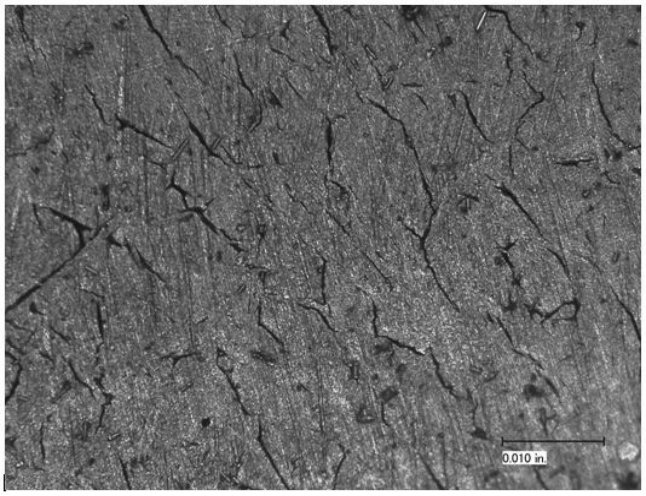

Figure 4. Photomicrograph showing a network of small micro cracks present on the inner diameter surface of the failed connector.

A cross-section was prepared through a supplied as-molded reference part at a location planar with the injection molding gate. Microscopic examination of the cross-section showed flow emanating from the injection molding gate. Inspection of the location corresponding to the cracking on the failed parts, approximately 180 degrees from the molding gate, did not show the presence of a poorly fused knit line. It was observed, however, that the glass fiber reinforcement within this area was oriented almost exclusively parallel to the crack direction (Figure 5). This glass fiber orientation was primarily longitudinal to the primary axis of the connector. Thus, the orientation of the glass fibers would not produce reinforcement against the hoop stress produced from internal pressurization.

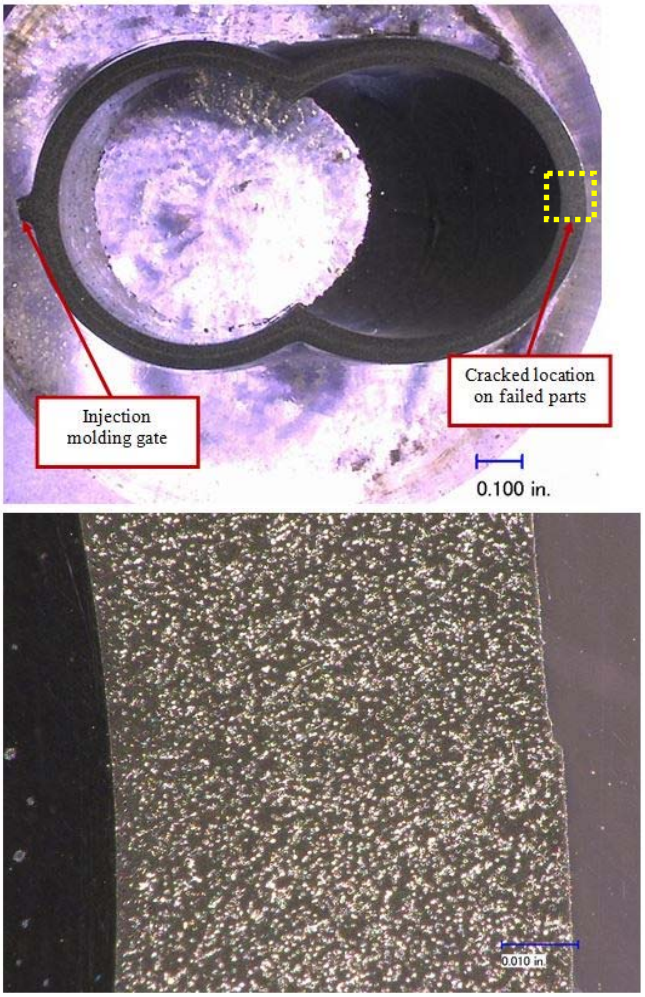

Figure 5. – Photomicrographs showing a cross-section prepared through an unused reference part. The area corresponding to the cracking within the submitted failed parts does not show fiber orientation to reinforce against hoop stresses. Clear markings indicating a poorly fused knit line are not evident.

The fracture surfaces of typical failed components were further examined via scanning electron microscopy (SEM) in order to characterize the mode of crack initiation and extension. Examination of the fracture surface showed features indicative of crack initiation along the inner diameter surface of the connector wall (Figures 6 and 7).

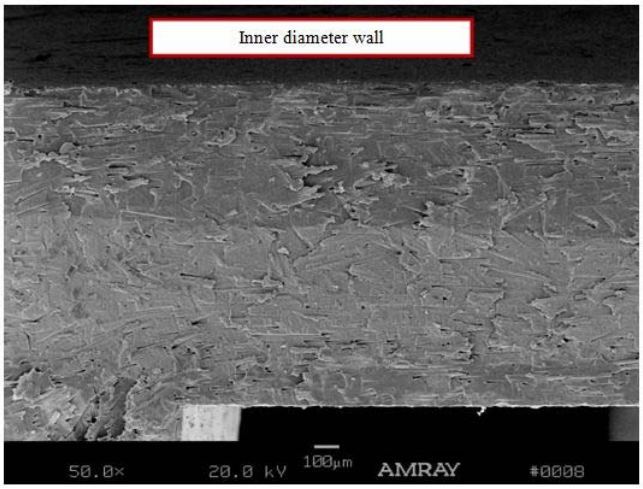

Figure 6. – Scanning electron micrograph showing a typical area on the failed connector fracture surface.

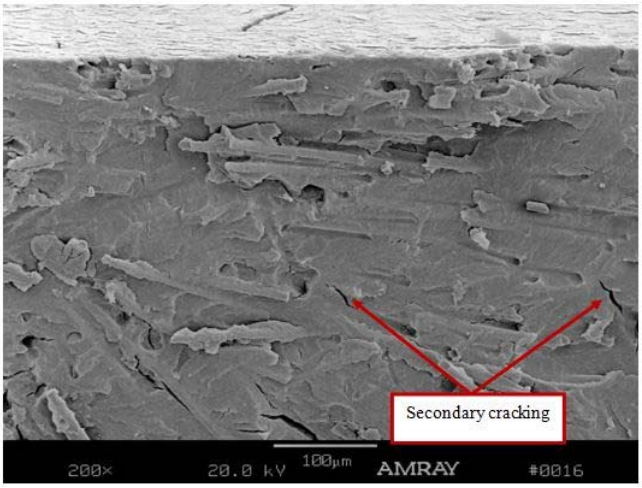

Figure 7. – Scanning electron micrograph showing a typical area on the surface adjacent to the inner diameter. Characteristics associated with crack initiation are present. Brittle fracture features are evident. The presence of secondary cracking is also apparent.

A distinct morphological difference was observed between the area adjacent to the wall inner diameter and mid-wall (Figure 8). The morphology along the inner diameter wall was relatively smooth and exhibited features characteristic of brittle fracture. No evidence was found of substantial micro ductility, as would be indicated by the presence of stretched fibril formation. An area within the mid-wall of the connector displayed a sharp contrast in features. The mid-wall locations showed the presence of fibril formation at high magnification.

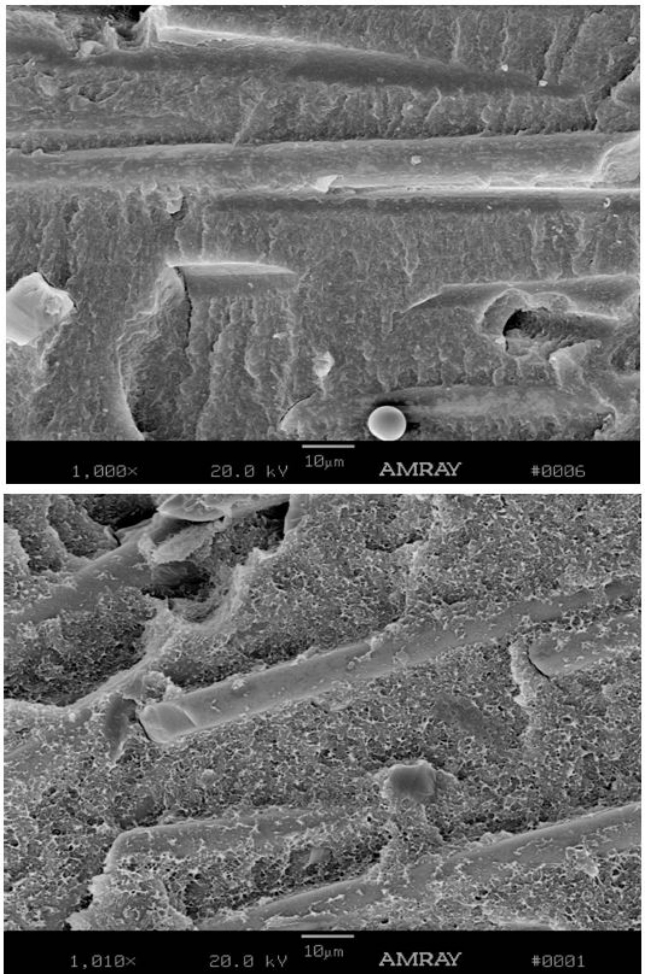

Figure 8. – Scanning electron micrographs showing the difference in morphology between locations adjacent to the inner diameter wall (upper) and the mid-wall (lower).

Examination of the laboratory fracture showed a high level of micro ductility, as indicated by the presence of stretched flaps and fibrils (Figure 9). This laboratory fracture zone was created through rapid mechanical overload, and the features were in sharp contrast to those present on the failure fracture surface. The SEM examination showed moderate bonding of the glass fibers to the surrounding polymer matrix.

The entirety of the visual, microscopic, and SEM examinations indicated that the connectors failed via a brittle fracture mechanism. While glass fiber reinforced resins are not noted for a high level of ductility, the features observed within the crack origin locations lacked stretching and fibril formation between the glass fibers, characteristic of brittle fracture. The cracking initiated along the inner diameter surface of the connectors at multiple individual locations. The cracking subsequently extended longitudinally and coalesced to form a continuous, but irregular fracture. Once the crack reached critical size mechanical overload took place, resulting in the rupture. The failure mechanism was creep rupture associated with the long-term exposure to relatively low internal pressure resulting in hoop stress. However, the principal factor in the failure was substantial molecular degradation, particularly of the material adjacent to the inner diameter surface. This degradation was indicated by the presence of a micro-crack network on the interior surface of the connector and the presence of secondary cracking on the fracture surface within the crack origin zone. This was supported by the relatively brittle nature of the part observed during handling and sample preparation. These features were consistent with degradation resulting from contact with chemicals within the connector associated with the refrigeration system.

While the failures occurred at the location of the union of mating flow fronts from the injection molding process, commonly known as a knit line, the appearance of the failed parts as well as the submitted reference part did not indicate a poorly fused knit line. A knit line will inherently be the weakest location on an injection molded part and the failure at this location in this case simply represents uniform stresses across the part.

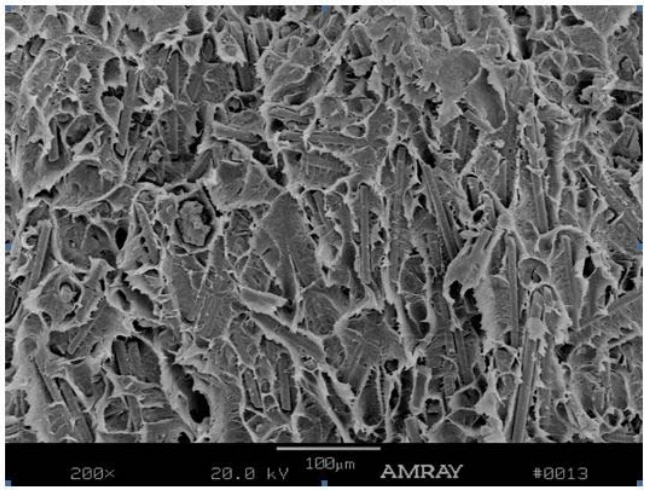

Figure 9. – Scanning electron micrograph showing stretched fibril formation indicative of a high level of micro-ductility.

Fourier Transform Infrared Spectroscopy

Compositional analysis of the sample materials was performed using Fourier transform infrared spectroscopy (FTIR). Analysis of specimens representing the exterior and interior surfaces of one of the failed connectors showed that the two results were generally consistent, but exhibited subtle yet distinct differences in the spectra. Specifically, the spectrum representing the interior surface exhibited additional absorption bands relative to the results obtained on the exterior surface. Subsequent interpretation of the results obtained on the exterior surface indicated that the spectrum contained absorption bands characteristic of a nylon resin. Spectral subtraction showed that the additional absorption bands present in the interior surface spectrum corresponded to the presence of a glycol-based chemical. These results indicated that the connector material had

absorbed a significant level of the glycol-based cooling agent (Figure 10).

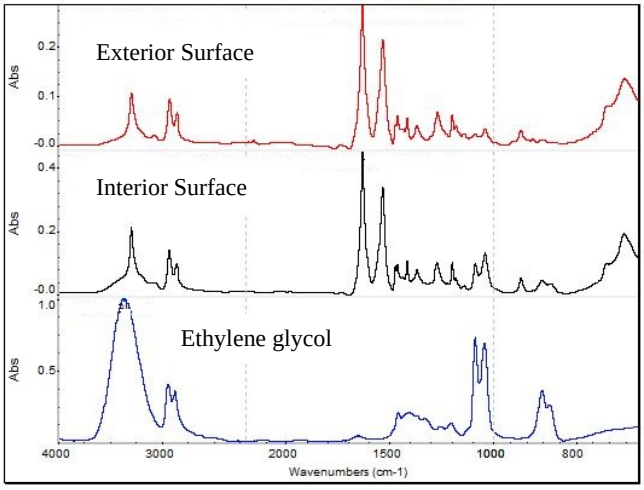

Figure 10. – The FTIR spectrum obtained on the interior surface of the failed connector exhibited absorption bands characteristic of a nylon resin, as well as the presence of a glycol-based chemical

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) of the failed connector material produced results that indicated that the connector material underwent a primary endothermic transition centered at 253 °C during the first heating run (Figure 11). These results were consistent with the melting point of the material. Generally, nylon 6/6 resins exhibit a melting point of approximately 263 °C. Correspondingly, the recrystallization of the polymer also occurred at a temperature somewhat lower than expected for a nylon 6/6 resin. A weaker endotherm was also evident in the first heating run results, centered at 172 °C. The relatively broad nature of the transition was indicative of evaporation or volatilization, not melting. Based upon the FTIR results and the determination of the presence of a glycol-based chemical, this transition was thought to represent the volatilization of the glycol-based coolant.

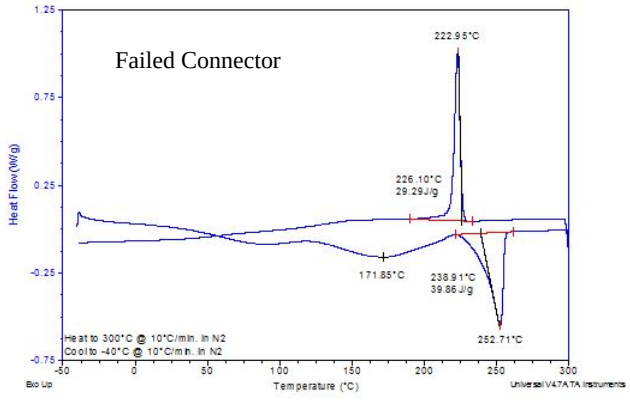

Figure 11. – The DSC thermogram obtained on the failed connector material.

The results obtained during the second heating run showed a bimodal endothermic transition with a primary maximum at 251 °C and a secondary maximum at 240 °C. The bimodal nature of the endotherm during the second heating run was in agreement with the expected results for a nylon 6/6 resin. The absence of the weaker endothermic transition observed during the first heating run was consistent with volatilization of the chemical from the plastic resin. The relatively low melting point determined during the first and second heating runs was indicative of significant molecular degradation of the nylon 6/6 resin.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of the resin and housing components was performed to further evaluate the compositions of the material. The thermogram representing the failed connector materials presented an initial weight loss of approximately 7.6% while heating under a dynamic nitrogen purge through 300 °C (Figure 12). This transition was associated with the presence of volatile materials, likely including water and the glycol-based coolant. Continued heating resulted in a weight loss of 55.2% centered at 376 °C, associated with the initial thermal decomposition of the nylon 6/6 polymer. The temperature of the weight loss was somewhat lower than expected, and was a further indication of degradation of the base polymer. Continued heating of the sample under an air atmosphere resulted in a weight loss of 2.4%, corresponding to carbonaceous char formed during the initial thermal decomposition of the polymer and carbon black pigment. Upon completion of the analysis a non-combusted residue content of 34.8% remained. Visual inspection of the residue revealed primarily short glass fibers. Both the amount and appearance of the residue were consistent with the stated description of the material as a nominal 35% glass fiber reinforced resin.

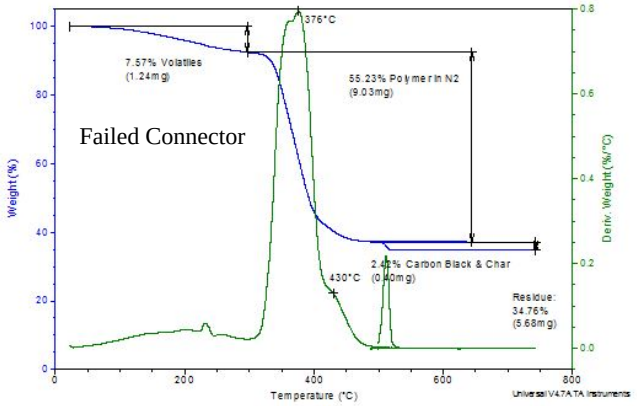

Figure 12. – The TGA thermogram obtained on the failed connector material.

Gel Permeation Chromatography

The molecular weight profiles of connector material samples representing the molding resin, the as-molded connector and the failed connector were evaluated using gel permeation chromatography (GPC). The testing identified the molecular weight distribution, as well as absolute molecular weight including the number average molecular weight (M_n), the weight average molecular weight (M_w), the peak maximum molecular weight (M_p), and the size average molecular weight (M_z). The results are presented in Table 1.

A review of the results showed two distinct molecular weight phenomena (Figure 13). A definite increase in the molecular weight was noted in the as-molded connector material relative to the molding resin. While it is possible that this difference in molecular weight resulted from materials with inherently different molecular weight profiles, the results were interpreted to indicate that a cross-linking mechanism takes place within the material during processing. All three tested molded connector samples exhibited a relative increase in the concentration of high molecular weight species compared with the molding resin. It is thought that a cross-linking reaction takes place, possibly through chain extension associated with the hydrolysis-resistant additive formulated into the resin. Such cross-linking could be expected to improve the mechanical and chemical resistance of the resin. The cross-linking was most evident upon direct comparison of the results obtained on the molding resin and the connector in the as-molded condition.

The results also indicated that the failed connectors had undergone significant molecular degradation, as indicated by a relative reduction in the molecular weight distribution of these samples. Such molecular degradation would be expected to reduce the mechanical integrity of the material and further reduce the chemical resistance. Given the overall results, the molecular degradation exhibited by the failed connectors occurred during field service, not the molding process.

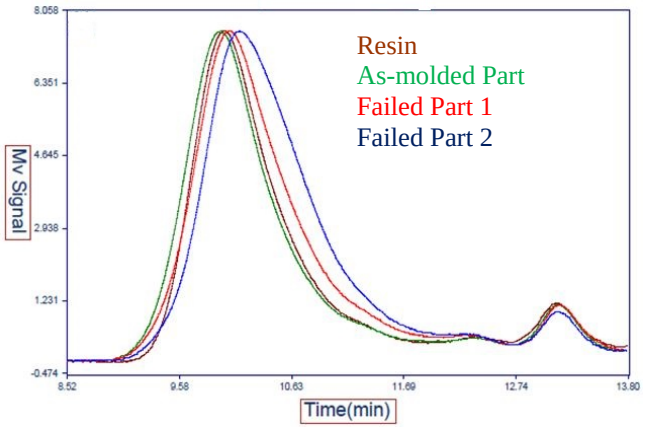

Figure 13. – The molecular weight profiles obtained on the connector materials.

Table 1
Gel Permeation Chromatography Results
(Average Molecular Weight)

Sample	Run	M_n		M_w		M_p		M_z		M_w/M_n	
Molding Resin	1	9,878	9,797	51,596	51,322	54,068	53,895	97,351	97,472	5.22	5.24
	2	9,715		51,048		53,722		97,593		5.25	
As-Molded	1	10,414	10,311	62,831	62,872	58,509	58,509	147,100	147,192	6.03	6.10
	2	10,208		62,914		58,509		147,284		6.16	
Failed 1	1	9,365	9,442	52,070	52,241	49,122	49,662	137,133	137,149	5.56	5.53
	2	9,519		52,412		50,201		137,164		5.51	
Failed 2	1	8,933	8,980	40,989	41,267	40,273	40,466	105,031	105,831	4.59	4.60
	2	9,028		41,545		40,661		106,630		4.60	

Gas Chromatography – Mass Spectroscopy

The received compressor oil samples were analyzed using gas chromatography - mass spectroscopy (GC-MS) to characterize their composition. The GC-MS analysis results, showed an important difference in the composition of the two different oil samples. Specifically, there was a component in the reference oil that was absent in the oil that was utilized in conjunction with the failed connectors. The reference oil contained 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate. This material, Chemical Abstract System Number 2386-87-0, is used commercially as a stabilizer serving as an acid scavenger in polymeric resins, such as the polyalkylene glycol (PAG) oil.

Conclusion

It was the conclusion of the investigation that the failures observed within the air conditioning connectors occurred via the brittle fracture, slow crack growth mechanism, creep rupture. The cracking was associated with hoop stresses from the internal pressurization of the air conditioning system. The applied stresses exceeded the long-term strength of the material, in a severely compromised condition. Cracking initiated along the inner diameter of the connector wall at multiple locations, extending longitudinally and subsequently laterally through the wall until rupture occurred.

The cracking within the connectors occurred at a knit line formed by the fusion of mating flow fronts during the injection molding process. The knit lines were present on the molded part at locations approximately 180 degrees around the part from the injection molding gate. Evaluation of the failed parts, as well as the supplied reference part did not show signs of poor fusion or an inherently weak knit line. Conversely, the knit line was simply the weakest location on the part and subsequently the first to exhibit through-cracking.

The failures within the connectors were the direct result of substantial molecular degradation of the molded material by the aqueous glycol solution used in the air conditioning system. Degradation of the connector material was indicated by the presence of a high concentration of micro cracking on the interior surface of the connectors, the presence of secondary cracking on the fracture surfaces, a substantial reduction in the melting point of the nylon 6/6

resin, the severe embrittlement of the material as indicated by the relatively low level of stress and deformation, which could produce cracking, and ultimately by the significant reduction in molecular weight indicated through gel permeation chromatography (GPC).

The failed connector material absorbed and became saturated by the glycol-based solution. This plasticization effect is normal, and nylon 6/6 resins can generally absorb approximately 9% of their weight in water and/or glycol-based chemicals. Over time, the nylon 6/6 underwent hydrolytic degradation through exposure to elevated temperatures while in contact with the refrigeration compressor fluid. Specifically, the chemical agent thought to be responsible for the degradation was carboxylic acid functionality created through degradation of the glycol-based coolant. Nylon resins are known to be incompatible with organic carboxylic acids. This resulted in a reduction in molecular weight of the polymer followed by a loss of mechanical properties. Ultimately, this rendered the part susceptible to failure at relatively low stresses under the service conditions.

The compressor oil used in the installation with the failed connectors was glycol-based. However, comparative analytical testing showed an important difference with other installations without failures. The coolant utilized in conjunction with the failed connectors was not formulated with an acid scavenger, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate. It is thought that without this acid scavenger, the glycol-based compressor oil broke down under conditions of exposure to elevated temperature during the durability testing, and generated carboxylic acid functionality.

The analysis of the submitted connector materials produced results consistent with a 35% glass fiber reinforced nylon 6/6 resin. No evidence was found to indicate contamination or other inherent material anomalies within the failed material.

Further Investigation

As a follow-up, it would be beneficial to further analyze the connector material. The resin used to produce the connectors is branded as being specially formulated to resist hydrolysis through contact with automotive coolants. Additional testing to verify the presence and determine the level of the hydrolysis-resistant additive in the resin, as-molded parts, and failed parts would be beneficial. Specifically, such testing would address some questions:

- Did the molding resin contain the additive at proper levels?
- Was the additive consumed during the injection molding process, as possibly suggested by the noted increase in molecular weight?
- Was the additive consumed as a result of the durability testing?

Keywords

failure analysis, molecular degradation, hydrolysis, nylon 6/6