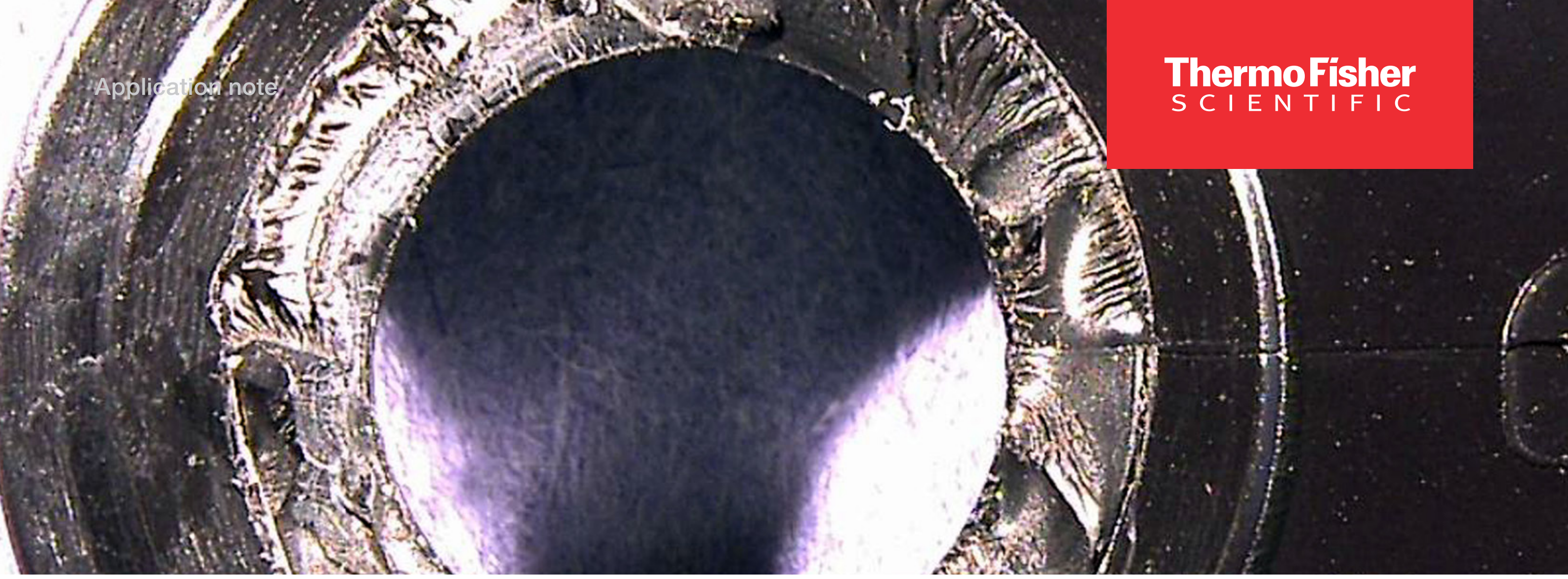

Identifying failures and ensuring quality of plastic materials

Authors

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Figure 1. Thermo Scientific™ Nicolet™ Summit™ X FTIR Spectrometer with Thermo Scientific™ Everest™ Diamond ATR Accessory.

Abstract

Appliance designers and manufacturers regularly utilize plastic parts as integral components. The production of high-quality appliance parts requires careful consideration of the functionality and environmental conditions of the final product. Owing to its ability to characterize the molecular makeup of polymers, infrared spectroscopy (IR) is an extremely useful analytical tool for scientists and engineers. It can be applied across all phases of the product lifecycle including design, manufacturing, and failure analysis during use. In this application note, we will demonstrate the utility of IR, by itself and in combination with other techniques, to assist in the design, manufacture, and support of products that use plastic components. Particular focus will be applied to IR analysis of failed parts; other analytical techniques that may have been used to help pinpoint the failure mode are also described.

Introduction

Those familiar with polymer chemistry undoubtedly understand the value of IR spectroscopy for the characterization of plastic materials. It can assess the largely organic make-up of polymer molecules, making IR an important tool for product development, quality control, and problem solving. Key areas where infrared analysis adds value include:

- Material identification and verification
- Copolymer and blend assessment
- Additive identification and quantification
- Contaminant identification, both in bulk and at surfaces
- Molecular degradation assessment

For unknown material identification, which is often used in failure analysis, the most common approach is to perform a quick IR analysis followed by a simple search comparing the sample spectrum to a spectral database of polymers, plasticizers, or other compounds. When used for quality control of incoming materials, comparisons are made against the spectra of known, high-quality materials.

Case studies

Incorrect material: plastic fastener cracking

Plastic fasteners, which are used to hold appliance assemblies together, need to be strong but not too brittle in order to achieve the desired behavior over the life of the product. In this case study, fasteners cracked over time while in service. The observed features of the failure indicated a slow crack growth (or creep rupture) under the load stress to which the parts were subjected. Upon further investigation it was determined that the failed parts appeared to be from a single production run.

The parts are injection molded from polypropylene copolymer resin. Known control parts from previous production runs were available for comparison. A quick infrared scan of the failed and control parts using the Everest Diamond ATR Accessory yielded the top two spectra in Figure 3. Comparison to the reference spectra of polypropylene and polyethylene confirms that both the failed and control parts are copolymers of these two materials.

However, closer examination of the expanded hydrocarbon stretching region of the failed and control parts tells a more complete story (Figure 4). The ratio of the polyethylene to polypropylene in the failed part is significantly higher than in the control part, resulting in a part that was not as stiff as intended, which made it more prone to deformation and cracking under long-term stress. This situation could have been prevented using quality control verification of the incoming polymer beads prior to molding. FTIR with the Everest Diamond ATR Accessory provides a quick and easy method for copolymer blend ratio analysis on polymer beads and plastic parts. The cost of the failure, in terms of resolution and potential product recalls, could easily offset the investment in running this routine QC test.

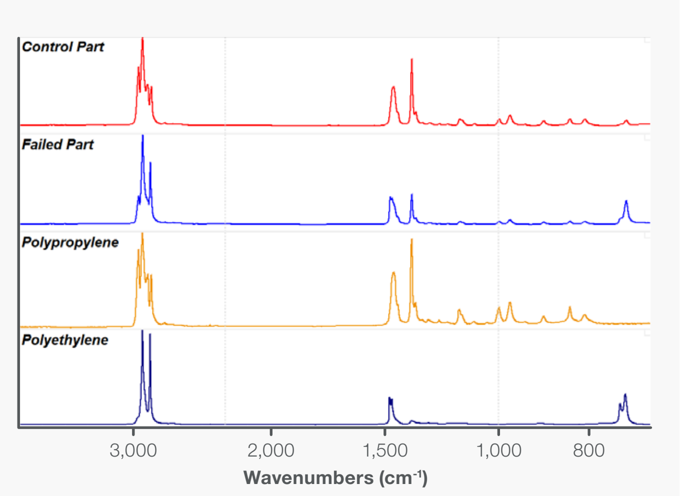

Figure 3. Spectra of a control and a failed plastic fastener, along with reference spectra of pure polyethylene and polypropylene.

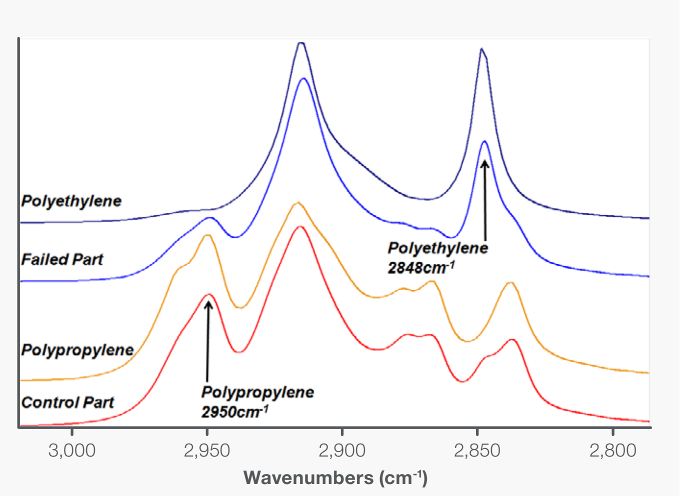

Figure 4. Expanded hydrocarbon stretching showing stronger polyethylene characteristics in the failed part.

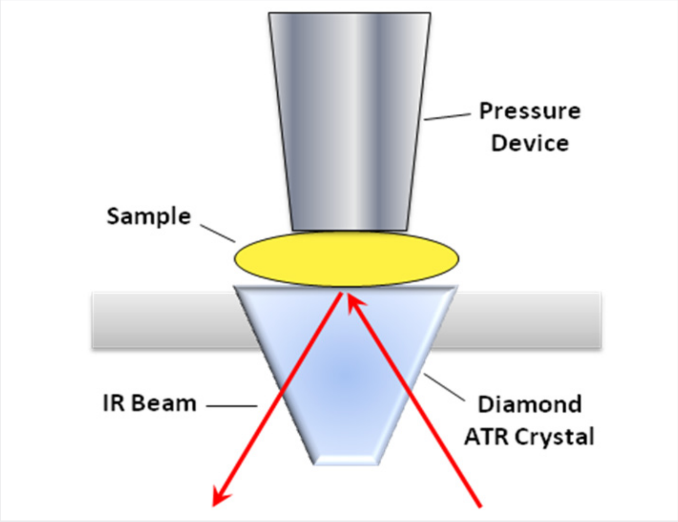

Figure 2. Schematic representation of a diamond ATR accessory.

Many sample analysis approaches can be applied to obtain useful information about a sample. The most popular and easy to use technique available in modern Fourier transform infrared (FTIR) spectrometers is attenuated total reflectance (ATR) using diamond crystals (Figure 1). The nature of the ATR technique ensures that spectral intensities remain within a linear range. Sample analysis is typically complete in less than a minute, making it a very rapid screening technique, and the diamond ATR crystal cannot be scratched. The sample is placed in close contact with the diamond crystal, so solid samples must be pressed into the crystal surface using a pressure device (Figure 2). It should be noted that ATR is a surface analysis technique, penetrating about 2–4 micrometers into the sample. Therefore, many times the sample surface must be cleaned or excised if identification of the bulk plastic is desired.

Inclusions: valve failure

A number of valves were evaluated, as they had failed during installation with their mating components. The failures occurred within the retention arm, which functions as a snap during installation of the valve assembly. The valves are produced from an unfilled, lubricated, injection-molding grade of poly(butylene terephthalate) (PBT).

Microscopic examination of the valve fracture surfaces showed generally similar features, characteristic of brittle fractures, across all of the failed parts. The failures exhibited crack initiation at an inclusion present within the molded retention arm, as illustrated in Figure 5.

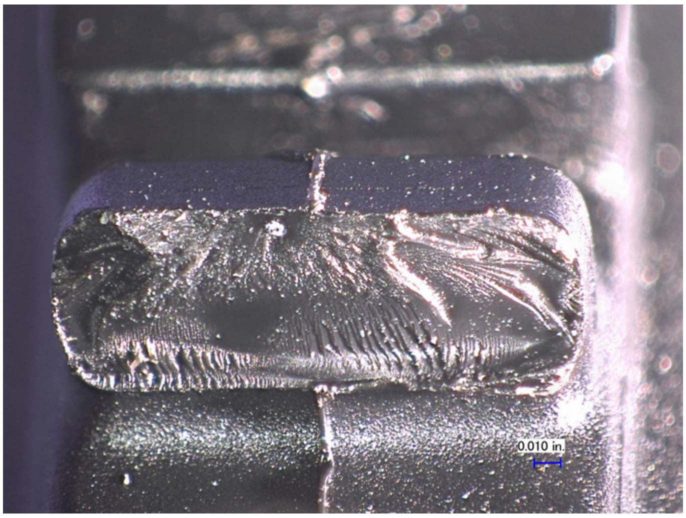

Figure 5. The fracture surface is shown with crack initiation at an inclusion.

The valves were initially analyzed using energy dispersive X-ray spectroscopy (EDS), and the results are presented in Table 1. Analysis of the base fracture surface showed exclusively carbon and oxygen, consistent with what is expected of an unfilled PBT resin. Analysis of the included particle, meanwhile, showed a significant amounts of sulfur and trace levels of chlorine, potassium, and sodium.

Element	Base material (relative weight %)	Inclusion (relative weight %)
Carbon	66.5	73.9
Oxygen	33.5	15.4
Nitrogen	---	4.8
Chlorine	---	0.2
Potassium	---	0.1
Sodium	---	0.1
Sulfur	---	5.5

Table 1. EDS analysis results.

The valve samples were directly analyzed using FTIR with the Everest ATR Accessory. Analysis of a base-material sample produced a spectrum characteristic of a thermoplastic polyester such as PBT. The fracture surface inclusion was excised and subsequently analyzed via FTIR. A direct comparison of the results with those obtained on the base material showed the presence of additional absorption bands (Figure 6). A spectral subtraction was performed removing the bands associated with the PBT base material. The resulting spectrum exhibited absorption bands characteristic of poly(phenylene sulfide) (PPS), as shown in Figure 7. PPS has a melting temperature of approximately 285°C, and as such, is consistent with its presence as a non-dispersed particle within the significantly lower melting PBT resin. The presence of the included contaminant acted as a point of severe stress concentration, focusing and multiplying the stress applied through the snap installation.

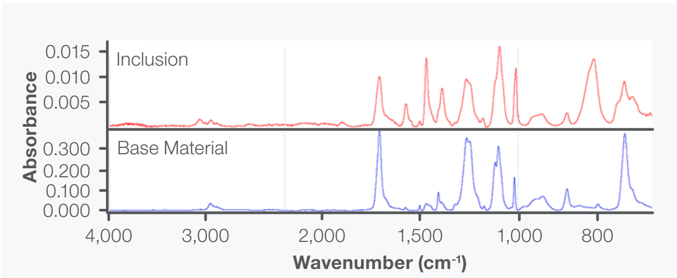

Figure 6. FTIR spectrum showing that the inclusion in the valve sample contained additional absorption bands in comparison with the base material.

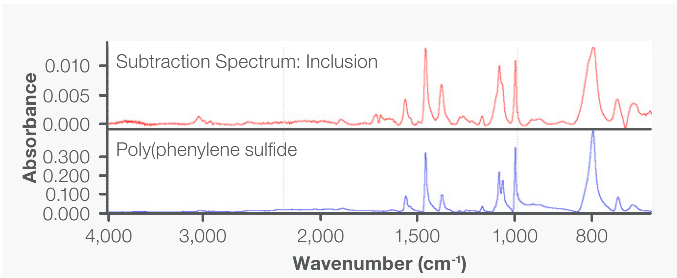

Figure 7. Spectral subtraction of the inclusion minus base material resulted in a spectrum characteristic of PPS.

Environmental stress cracking: brackets

A failure analysis was conducted on a set of brackets that had cracked while in service. Sporadic failures had been reported on these parts. The brackets are injection molded from a flame-retardant grade of polycarbonate + poly(acrylonitrile:butadiene:styrene) (PC+ABS).

The brackets were examined microscopically, identifying catastrophic transverse cracking at the base of the cylindrical boss, consistent with tensile or bending stresses. Inspection of the fracture surfaces presented the characteristics of a brittle fracture, with multiple apparent crack origins along the inner diameter of the boss wall (Figure 8). The observed features were indicative of a slow crack initiation and growth mechanism, transitioning into more rapid crack extension. Overall, the observed features were indicative of environmental stress cracking (ESC), a failure mechanism whereby a plastic material cracks due to contact with an incompatible chemical agent while under tensile stress. Several of the cracks exhibited a liquid residue emanating from the fractures.

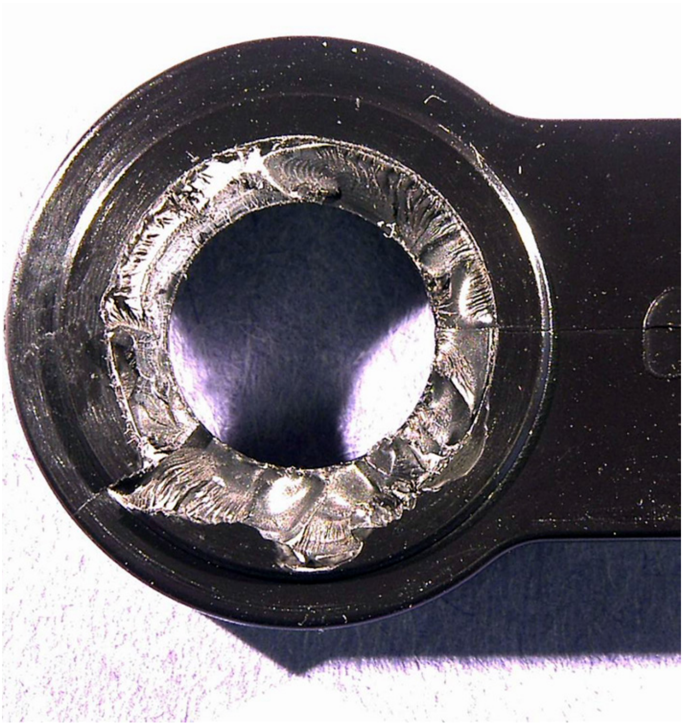

Figure 8. The failed bracket fracture surfaces exhibited features that are characteristic of environmental stress cracking (ESC).

Specimens representing the bracket material were analyzed using FTIR with the Everest ATR Accessory. Analysis of bracket core specimens showed absorption bands characteristic of a PC+ABS resin, as seen in Figure 9. Analysis of the residue removed from the fracture surfaces was indicative of organic esters, as shown in Figure 10, which are known to act as ESC agents in conjunction with PC+ABS resins.

Melt flow rate testing was also used, and determined that the part material had undergone substantial molecular degradation during the injection molding process. This degradation rendered the parts susceptible to premature failure and environmental stress cracking.

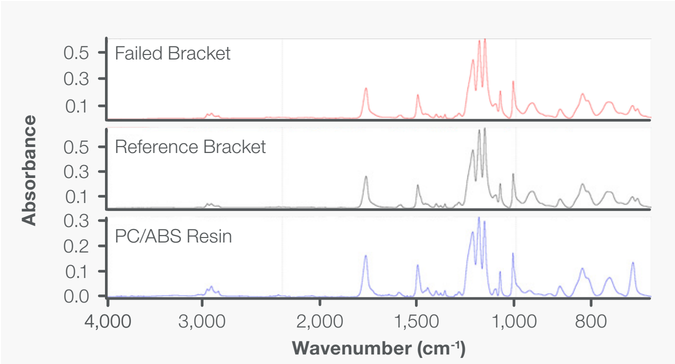

Figure 9. The FTIR spectra representing the failed and reference brackets contained absorption bands indicative of a PC+ABS resin.

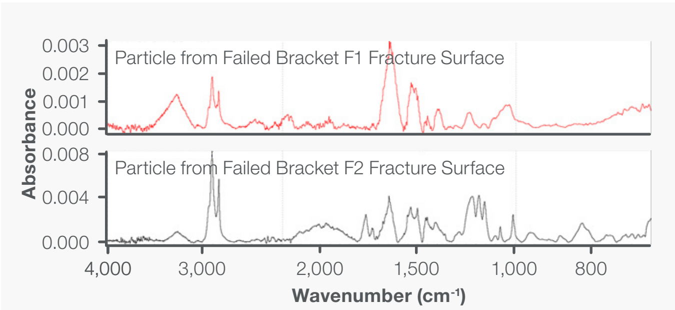

Figure 10. FTIR spectra obtained on the bracket fracture surfaces contained absorbances associated with organic esters.

Degradation: water tubing leakage

A section of plastic tubing was analyzed, as it had leaked while in use. The tubing was used to supply water to a refrigerator, and the leak resulted in significant property damage. This type of tubing is generally extruded from a grade of low-density polyethylene (LDPE).

The tubing was examined and found to exhibit a single through-crack and multiple partial cracks oriented transversely. The cracks, shown in Figure 11, exhibited features that are characteristic of brittle fracture, and indicated crack initiation along the inner diameter wall of the tubing. Some discoloration was also present, localized to the area of cracking. These observations indicated a slow crack growth mechanism associated with localized bending loads and the internal pressure within the system.

Figure 11. Broken tubing, showing a series of parallel transverse cracks with brittle fracture features.

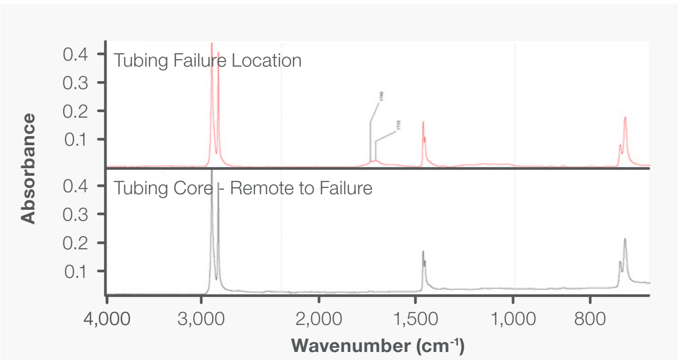

Figure 12. The FTIR spectrum of the failure location in the broken tubing exhibited carbonyl bands associated with the degradation of polyethylene resins.

A region of the tubing further away from the crack was analyzed using FTIR with the Everest ATR Accessory; the results were characteristic of a polyethylene resin. Analysis of the inner diameter surface adjacent to the primary through-crack also showed characteristics of polyethylene. However, additional absorption bands indicative of carbonyl functionality were also present. Specifically distinct bands at 1715 cm^{-1} and 1740 cm^{-1} were present, which are associated with carboxylic acids and esters (Figure 12). Such materials are commonly formed as by-products of the oxidation of polyolefin resins, such as polyethylene. Polyethylene can undergo oxidation through contact with chlorinated municipal water. The molecular degradation caused by the oxidation resulted in a marked reduction in the mechanical integrity of the tubing material. Together with the nominal internal pressure, this produced cracking within the tubing.

Conclusion

Infrared spectroscopy is a valuable polymer characterization tool which can be used effectively in product design, manufacturing, and, as demonstrated in this application note, failure analysis. Thermo Scientific FTIR Systems equipped with diamond ATR accessories can provide rapid analysis of samples with very little effort. Lessons learned from the included case studies can be used to inform decisions concerning product improvements and to determine the best control measures required to ensure quality.

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