

Figure 1: Thermo Scientific Nicolet iS 5 FT-IR Spectrometer with Diamond ATR accessory. Source: Thermo Fisher



Identifying Failures and Ensuring Quality of Plastic Materials

Increasing the confidence in the plastic parts designers and manufacturers depend on.

by **jeff jansen**
and **mike garry**

Jeff Jansen is senior managing engineer, and partner, at The Madison Group, Madison, WI, with 20-plus years of experience as a polymer chemist and is an SPE member and contributing author. Mike Garry is senior product manager, FT-IR Products, at Thermo Fisher Scientific, Madison, WI, with 20-plus years of experience with FT-IR applications.

Making high quality products with polymeric materials requires careful consideration of the functionality and environmental conditions. Owing to its ability to characterize the molecular makeup of polymers, infrared spectroscopy is an extremely useful analytical tool for scientists and engineers. It can be applied across all phases of the product lifecycle including design, manufacture and failure analysis during a product's use. This article demonstrates the usefulness of infrared spectroscopy, by itself and in combination with other techniques, to assist scientists and engineers in the design, manufacture, and support of products using plastic components. Particular focus will be applied to its use in the analysis of failed parts.

Introduction

Those familiar with polymer chemistry undoubtedly understand the value infrared spectroscopy offers in the characterization of plastic materials. Its value comes from the technique's ability to assess the largely

organic make-up of polymer molecules. This makes it an important tool for product development, quality control, and problem solving. Key areas where infrared analysis adds value include:

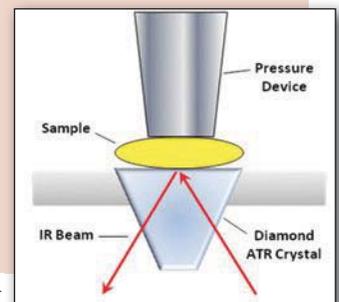
- ▶ Material identification and verification
- ▶ Copolymer and blend assessment
- ▶ Additive identification and quantification
- ▶ Contaminant identification - bulk & surface
- ▶ Molecular degradation assessment

For unknown material identification, such as in failure analysis, the most common approach is to perform a quick infrared analysis followed by a simple search comparing the sample spectrum to a spectral database of polymers, plasticizers or other compounds. When using the technique for quality control of incoming material, comparisons are made against spectra of known good materials to verify they are the same.

This article presents a series of case studies for failure analysis of plastics materials used in appliances where infrared analysis

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 (FT-IR) spectrometers is ATR, or Attenuated Total Reflectance, 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.

Figure 2: Schematic representation of diamond ATR accessory. Source: Thermo Fisher



FAILURE ANALYSIS

played a key part in the root cause analysis. Other analytical techniques which may have been used to help pinpoint the failure mode are also described.

Case Studies

Incorrect Material - Plastic Fastener Cracking

Plastic fasteners used to hold appliance assemblies together need to be strong but not too brittle 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 good control parts from previous production runs were available for comparison. A quick infrared scan of the failed and control parts using the diamond ATR yielded the top two spectra in **Figure 3**. Observation of these spectra compared to the reference spectra of polypropylene and polyethylene at the bottom of the figure 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 as shown in **Figure 4**. The spectra reveal that the ratio of the polyethylene to polypropylene in the failed part is significantly higher than in the control part. The higher relative amount of polyethylene created a part that was not as stiff as intended, making it more prone to deformation and cracking under long-term stress. This situation could have been prevented using a quality control verification of the incoming polymer beads prior to molding. FT-IR

using a diamond ATR provides a rapid and simple method for performing 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.

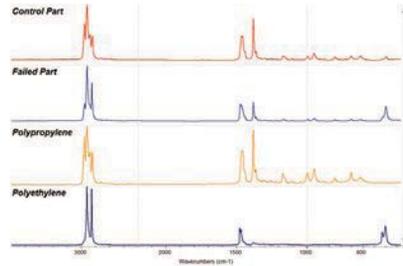


Figure 3: Spectra of control and failed parts along with reference spectra of pure polyethylene and polypropylene. Source: Thermo Fisher

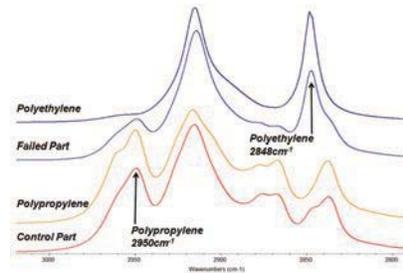


Figure 4: Expanded hydrocarbon stretching showing stronger polyethylene characteristics in the failed part. Source: Thermo Fisher

Inclusions - Valve Failure

A number of valves were evaluated as the parts had failed during installation with the 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 fracture, 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**.

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 the expected results based upon the description of the material as an unfilled PBT resin. Analysis of the included particle showed a significant amount of sulfur and trace levels of chlorine, potassium, and sodium.

The valve samples were directly analyzed using FT-IR with a diamond ATR. Analysis of a sample of the base material produced a spectrum characteristic of 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, as illustrated in **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 approximately 285 °C, and as such, 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 5: The fracture surface is shown with crack initiation at an inclusion. Source: Thermo Fisher

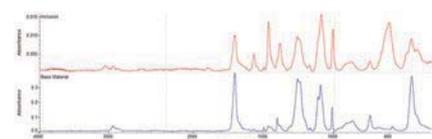


Figure 6: FT-IR spectrum representing the inclusion contained additional absorption bands in comparison with the base material. Source: Thermo Fisher

ELEMENT	BASE MATERIAL	INCLUSION
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 (Relative Weight Percent)

FAILURE ANALYSIS

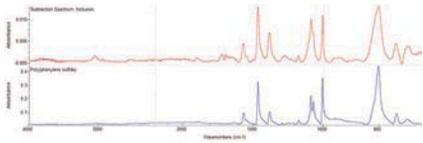


Figure 7: Spectral subtraction of inclusion minus base material resulted in a spectrum characteristic of PPS. Source: Thermo Fisher

Environmental Stress Cracking - Brackets

A failure analysis was conducted on a set of brackets which 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 characteristics of brittle fracture, with multiple apparent crack origins along the inner diameter of the boss wall, as illustrated in **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 the contact with an incompatible chemical agent while under tensile stress. Several of the cracks exhibited a liquid residue emanating from the fractures.

Specimens representing the bracket material were analyzed using FT-IR with a diamond ATR. 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 produced results indicative of the present of organic esters as shown in **Figure 10**. Organic esters are known to act as ESC agents in conjunction with PC+ABS resins.

Melt flow rate testing was used in the investigation to determine that the part material had undergone substantial molecular degradation associated with the injection molding process. This degradation rendered the parts susceptible to premature failure and environmental stress cracking.



Figure 8: The failed bracket fracture surfaces exhibited features characteristic of environmental stress cracking (ESC). Source: Thermo Fisher

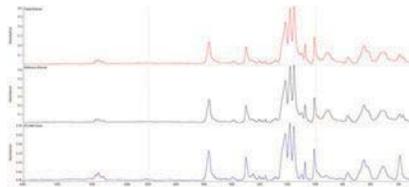


Figure 9: The FT-IR spectra representing the failed and reference brackets contained absorption bands indicative of a PC-ABS resin. Source: Thermo Fisher

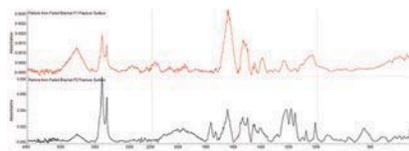


Figure 10: FT-IR spectra obtained on the bracket fracture surfaces contained absorbances associated with organic esters. Source: Thermo Fisher

Degradation - Water Tubing Leakage

A section of plastic tubing was examined and analyzed as the tubing 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 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. The observed features were indicative of a slow crack growth mechanism associated with localized bending loads and the internal pressure within the system.

The core remote to the cracking tubing material was analyzed using FT-IR with a diamond ATR, and the obtained results

were characteristic of a polyethylene resin. Analysis of the inner diameter surface adjacent to the primary through-crack also produced results characteristic 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 associated with carboxylic acids and esters. These results are presented in **Figure 12**. Such materials are commonly formed as by-products of 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 mechanical integrity of the tubing material, and together with the nominal internal pressure, produced cracking within the tubing.



Figure 11: The tubing showed a series of parallel transverse cracks with brittle fracture features. Source: Thermo Fisher

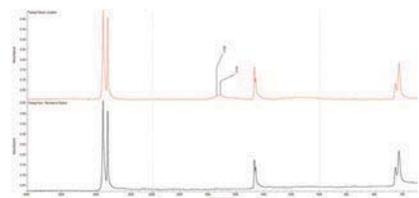


Figure 12: The FT-IR spectrum representing the failure location exhibited carbonyl bands associated with degradation of the polyethylene resin. Source: Thermo Fisher

Conclusion

Infrared spectroscopy is a valuable polymer characterization tool which can be used effectively in product design, manufacture, and as demonstrated in this article, failure analysis. In any of these applications areas modern FT-IR systems with diamond ATR sampling 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 determine the best control measures required to ensure quality. ■