

Investigating why a plastic part failed

Key words

ATR, diffuse transmission, failure analysis, FTIR, FT-Raman, polymer testing, spectroscopy

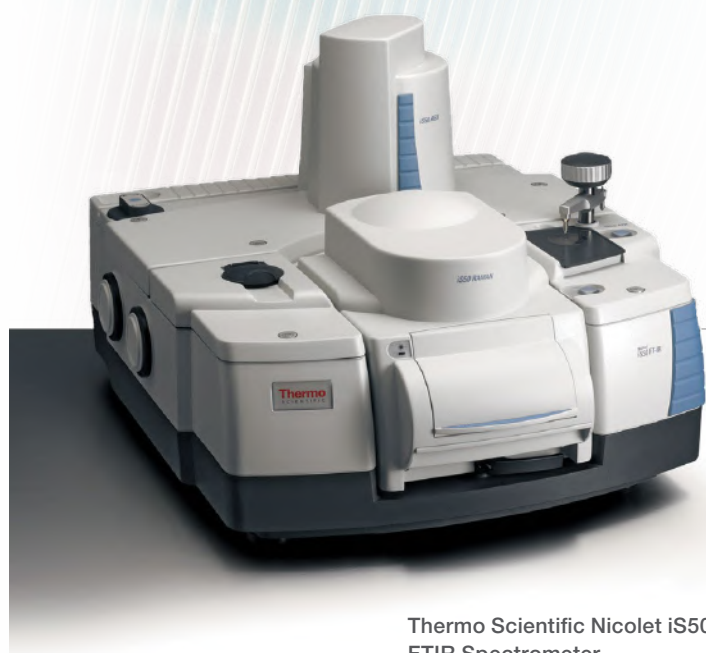
Abstract

Manufacturers employing plastic parts routinely face the challenge of analyzing failed parts to determine the root cause and corrective actions. The tools used to perform this analysis often include infrared and Raman spectroscopy for chemical composition, UV-Visible spectroscopy for color and optical transmissivity, and thermal analysis for determination of physical properties. This paper describes a study utilizing all of these tools to determine why a plastic part failed.

Introduction

A manufacturer of precision optical equipment designed a plastic cover for a device with specifications for chemical composition, surface texture, color and optical transmission. Briefly, the cover was to be made from a polycarbonate – acrylonitrile butadiene styrene (PC-ABS) blend with sufficient titanium dioxide to provide a slightly off-white color and optical transmissivity less than 0.01% T over a wide spectral range – from the UV into the near-infrared. The opacity was required to prevent ambient (room) light from entering the optical device and interfering with low light level measurements. Initially, all parts supplied met the specifications and the product provided satisfactory performance.

A re-engineering project was subsequently initiated to reduce costs and make the product more competitive. Alternate suppliers for various parts, including the cover, were asked for quotations. A new supplier underbid the original cover supplier, and the test parts met all the requirements for opacity. Production was shifted to incorporate this new supplier.



Thermo Scientific Nicolet iS50
FTIR Spectrometer

Shortly thereafter, the product began to fail critical performance tests. The failures were immediately traced to ambient light causing elevated backgrounds, strongly affecting low level optical measurements. Visual inspection of the covers did not reveal apparent differences from the original, but various control experiments led to tracing of the failure to the new cover. A root cause analysis using many techniques was undertaken to quickly identify and contain the issue.

Experimental results

UV-Visible spectroscopy

Diffuse transmission measurements of the original cover and failed cover were performed using a Thermo Scientific™ Evolution™ 220 UV-Visible Spectrophotometer and integrating sphere, displayed in Figure 1.



Figure 1: Evolution 220 UV-Visible Spectrophotometer (left), and sample compartment integrating sphere accessory (right)

The cover by design contained significant quantities of particulates, which would efficiently scatter any transmitted light. For this reason, transmittance was measured with an integrating sphere. Pieces of covers from both good and failing devices were placed at the transmittance port of the sphere and spectra were collected from 220 to 800 nm, resulting in the spectra shown in Figure 2.

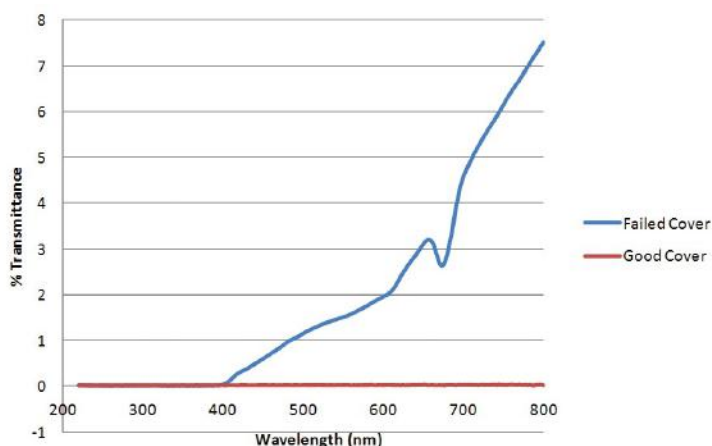


Figure 2: Diffuse Transmittance UV-Visible spectra of the failed cover (blue) and good cover (red), collected with an Evolution 220 UV-Visible Spectrophotometer and integrating sphere accessory

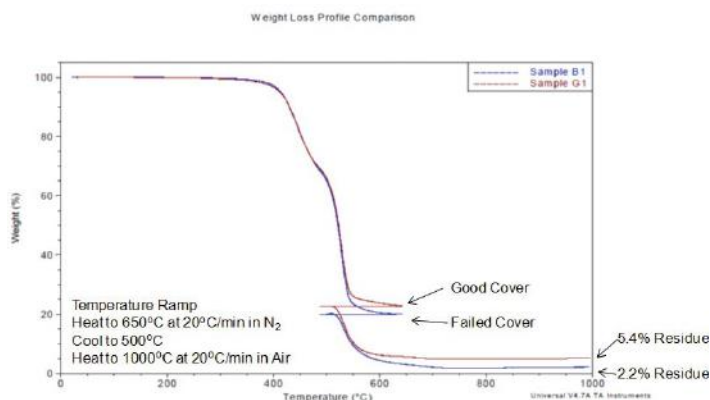


Figure 3: Thermogravimetric analysis weight loss curves for the good cover (red) and failed cover (blue), showing that the good cover has significantly higher inorganic content than the failed cover

Essentially no transmittance was measurable through the good cover. In contrast, a significant transmittance through the visible part of the spectrum, greater than 7% T, was measured from the failing cover. This clearly explained the poor performance – the light leak – of the device under ambient conditions, but did not identify the root cause.

Thermogravimetric analysis (TGA)

Small pieces of the two covers were then measured with a TA Instruments™ thermogravimetric analyzer to determine bulk composition, with results shown in Figure 3.¹ The samples were heated from ambient to 650 °C at 20 °C/min under N₂ purge, then cooled to 550 °C, and heated again to 1000 °C at 20 °C/min with air purge.

The initial heating ramp under nitrogen pyrolyzes the organic component of the covers, and the final temperature ramp in air burns the remaining organic components leaving only oxides of the inorganic content.

The organic decomposition profiles of the two covers were nearly identical, indicating that both had the same plastic composition. However, the good cover had residual inorganic component representing 5.4% by weight, while the failed cover had an inorganic component of only 2.2% by weight. This indicated a significant difference in the inorganic filler amounts between the covers and provided a strong clue as to the source of the light leak.

Infrared analysis

Infrared spectra of small pieces of the two covers were collected using the integrated diamond iS50 ATR on a Thermo Scientific™ Nicolet™ iS50 FTIR Spectrometer, as shown in Figure 4. The built-in iS50 ATR on the Nicolet iS50 has a dedicated detector which permits the collection of combined mid- and far-IR ATR spectra down to 100 cm⁻¹. The ability of the iS50 ATR to collect spectra in the far-IR allows easy measurement and identification of inorganic fillers in plastic parts.



Figure 4: Nicolet iS50 FT-IR spectrometer with built-in diamond iS50 ATR, iS50 ABX Automated Beamsplitter exchanger, and sample compartment iS50 Raman accessory

When combined with the iS50 ABX Automated Beamsplitter exchanger on the Nicolet iS50 Spectrometer, mid and far-IR spectra can be automatically collected and stitched together using a Thermo Scientific™ OMNIC™ Macros\Pro™ Visual Basic Program to provide a single spectrum of a sample from 4000 to 100 cm^{-1} .²

The ATR spectra of the plastic parts, shown in Figure 5, were corrected using the advanced ATR correction algorithm³ in Thermo Scientific OMNIC Software. The advanced ATR correction algorithm accounts for both relative intensity changes caused by sample penetration depth as a function of wavelength and also for peak shifts in the infrared spectra due to index of refraction differences between the ATR crystal and sample. Inspection of the infrared spectra of the two plastic pieces shows the polymer composition to be similar, but the original plastic part has an elevated baseline below 800 cm^{-1} , and a sharp peak at 360 cm^{-1} , as shown in Figure 6, that are absent or very weak in the spectrum of the replacement part. The peak at 360 cm^{-1} is below the range of a typical mid-IR spectrometer equipped with a KBr beamsplitter. The iS50 ABX with a solid substrate far-IR beamsplitter makes the far-IR range accessible in this analysis, while maintaining no compromise high performance across the entire range.

There are additional differences between the spectra which are emphasized through a spectral subtraction. The difference spectrum (Figure 5, bottom) shows small peak shifts in the polymer bands, indicating a small polymer composition difference between the two parts, typical when comparing plastic parts made by different suppliers, but a significant spectral difference is also observed below 800 cm^{-1} .

A library search of the difference spectrum against a forensic library of automobile paint pigments and fillers,⁴ shown in Figure 7, matches rutile, one of the crystalline forms of titanium dioxide, indicating a formulation difference between the two covers.

FT-Raman analysis

To confirm the conclusions drawn from the infrared analysis, the two samples were also analyzed using the iS50 Raman sample compartment FT-Raman accessory on the Nicolet iS50 Spectrometer (shown in Figure 4). The iS50 Raman accessory snaps into the sample compartment of the Nicolet iS50 FTIR Spectrometer, not requiring an external module typical of other FTIR spectrometer systems. The iS50 Raman accessory permits easy collection of Raman spectra with a near-infrared beamsplitter and InGaAs detector mounted inside the spectrometer.

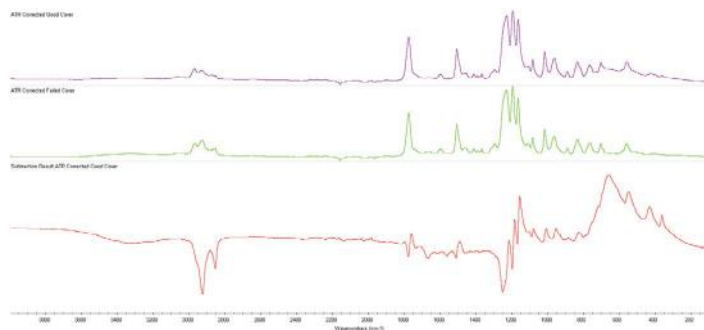


Figure 5: Advance ATR corrected infrared ATR spectra of the good plastic cover (top), failed plastic cover (middle) and difference spectra between the two (bottom)

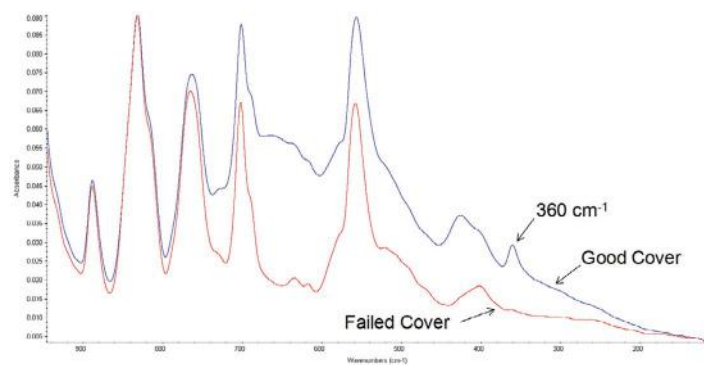


Figure 6: Overlay of the advanced ATR corrected spectra of the good cover (blue) and failed cover (red), over the spectral region from 940 to 100 cm^{-1} . Note the elevated baseline and the absorbance band at 360 cm^{-1} in the spectrum of the good cover that are absent or highly reduced in the spectrum of the failed cover.

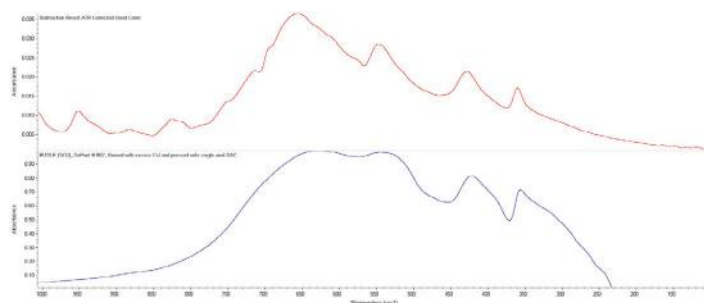


Figure 7: FT-Raman difference spectrum between the good and failed covers (blue), and top match from a library search against a forensic automobile paint pigment and fillers library (red), identifying a higher concentration of rutile (titanium dioxide) in the good cover.

FT-Raman spectra of the good and failed covers, along with the spectral difference spectrum between them, are displayed in Figure 8. FT-Raman spectroscopy allows collection of spectra into the far-IR region, complementing the capability of the Nicolet iS50 FTIR Spectrometer with the built-in iS50 ATR and ABX gaining access to this region. Again, the two spectra are very similar, demonstrating similar polymer composition, with small differences in the spectra observable below 800 cm^{-1} , clearly seen in the difference spectrum.

A library search of the difference spectrum against a minerals Raman library⁵ is displayed in Figure 9, identifying the difference between the two plastic parts as rutile, confirming the identification from infrared analysis.

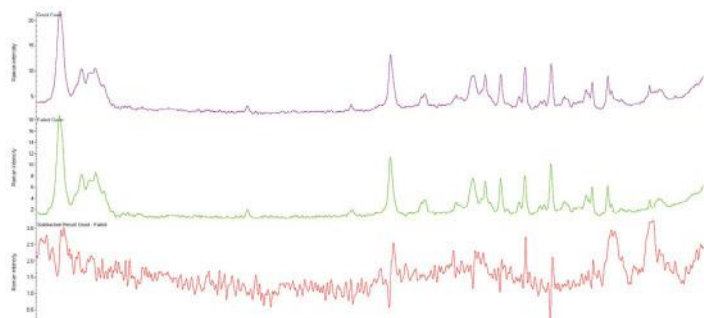


Figure 8: FT-Raman spectra of the good cover (top), failed cover (middle), and subtraction result between the two (bottom)

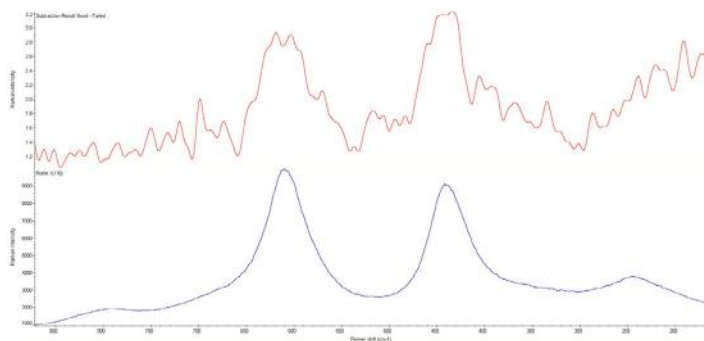


Figure 10: FT-Raman difference spectrum between the good and failed covers (top), and top library search result against a minerals Raman library (bottom), identifying a higher concentration of rutile (titanium dioxide) in the good cover

Summary and Conclusion

Ambient light leaking into the device caused erroneous measurements for low light level measurements. Diffuse transmission measurement of the parts by UV-Visible spectroscopy confirmed that the failed cover did not meet the specification for maximum transmittance. Thermogravimetric analysis demonstrated that the composition of the original cover contained approximately 3% more, by weight, of an inorganic filler compared to the replacement cover. Infrared ATR analysis over the mid and far-IR spectral regions showed that the original cover had significantly higher rutile (titanium dioxide) content than the replacement cover. The infrared results were confirmed by FT-Raman spectroscopy.

This study clearly shows the importance of having several tools available for root cause analysis. Many of the tools used can be found on the Nicolet iS50 FTIR Spectrometer. The Nicolet iS50 is able to collect multi-range spectra without compromise using the built-in iS50 ATR and iS50 Raman accessories. The analyses provided by the Thermo Scientific UV-Vis and FTIR instruments, along with thermogravimetric analysis, were decisive in determining the root cause failure of the plastic cover.

References

1. Thermogravimetric results provided by Jeff Jansen, The Madison Group, 2615 Research Park Drive, Madison, WI, 53711.
2. Mid-Far ATR iS50 collection program available upon request. Requires Nicolet iS50 FTIR Spectrometer configured with built-in diamond iS50 ATR, and ABX Automated Beamsplitter exchanger with KBr and solid substrate beamsplitter.
3. Thermo Scientific Application Note 50581, Advanced ATR Correction Algorithm.
4. An Infrared Spectral Library of Automobile Paint Pigments ($4000\text{--}250\text{ cm}^{-1}$), developed by Dr. Edward H. Suzuki at the Washington State Police Crime Laboratory, downloadable from the SWGMAT.org website
5. Downs R T (2006) The RRUFF Project: an integrated study of the chemistry, crystallography, Raman and infrared spectroscopy of minerals. Program and Abstracts of the 19th General Meeting of the International Mineralogical Association in Kobe, Japan. 003-13 Minerals 514 Raman Library.

Find out more at thermofisher.com/spectroscopy

ThermoFisher
SCIENTIFIC