POLYMER SOLUTIONS
INDEPENDENT TESTING LAB

CASE STUDY

Failure Analysis of a Thermoplastic Elastomer;

Melt Flow Index (MFI) Method Provided Critical Data Sets

Background

For companies that manufacture rubber and plastic parts, processing issues are a serious contributor to reduced profit and increased waste. Rapid evaluations that can pin-point the root cause of a process issue are vital to maintain productivity. In addition, third-party materials evaluations often serve to swiftly identify raw material compliance issues. Based on scientific data, the business issues caused by the raw material can be properly addressed and the production process can get back on track.

As is typically the case, Polymer Solutions Incorporated received a pair of samples that were described as “good” and “bad.” It was critical to our client and the rapid resumption of their manufacturing process that an objective science-based determination be made as to whether or not there were variations in the raw material. Comparative testing of the two samples was performed. From a root cause analysis perspective, three analytical methods were proposed and implemented. This was considered to be a technically appropriate, robust, and cost-effective first step. The three analytical methods included:

- ✓ Thermogravimetric Analysis (TGA) to Determine Inorganic Filler Content
- ✓ Differential Scanning Calorimetry (DSC) to Document Thermal Transitions
- ✓ Melt Flow Index (MFI) Tests to Compare Melt Flow Characteristics

Melt Flow Index (MFI)

Small portions of Good and Bad extrudates were cut using scissors and a razor blade. These specimens were then dried at 120°C in a convection oven. Preliminary melt flow index (MFI) tests were performed. Two critical observation resulted.

First, after initial drying for three hours, the samples exhibited significant bubbling when MFI testing was carried out. Therefore, the specimens were dried for 24 hours at 120°C. Second, it was noted that at the initial standard MFI conditions of 224°C and 1.2 kg (435°F and 2.65 lb), the resin flowed so quickly that highly accurate determinations of melt flow were difficult. Therefore, the test temperature was lowered to 199°C (390°F) and the modified protocol, agreed to by the client, was included as part of the formal report.

A significant difference was noted between the two samples in terms of their measured MFI values. It is clear that a noteworthy difference in MFI values is present between the two samples as shown in the inset table of data. The Bad sample shows a much higher MFI than the Good sample. This finding indicates that the Bad sample has a much lower molecular weight compared to the Good specimen. The actual molecular weight distributions can be further documented by using gel permeation chromatography (GPC) or size exclusion chromatography (SEC) to evaluate the molecular weight parameters (molecular weight averages and polydispersity, for example).

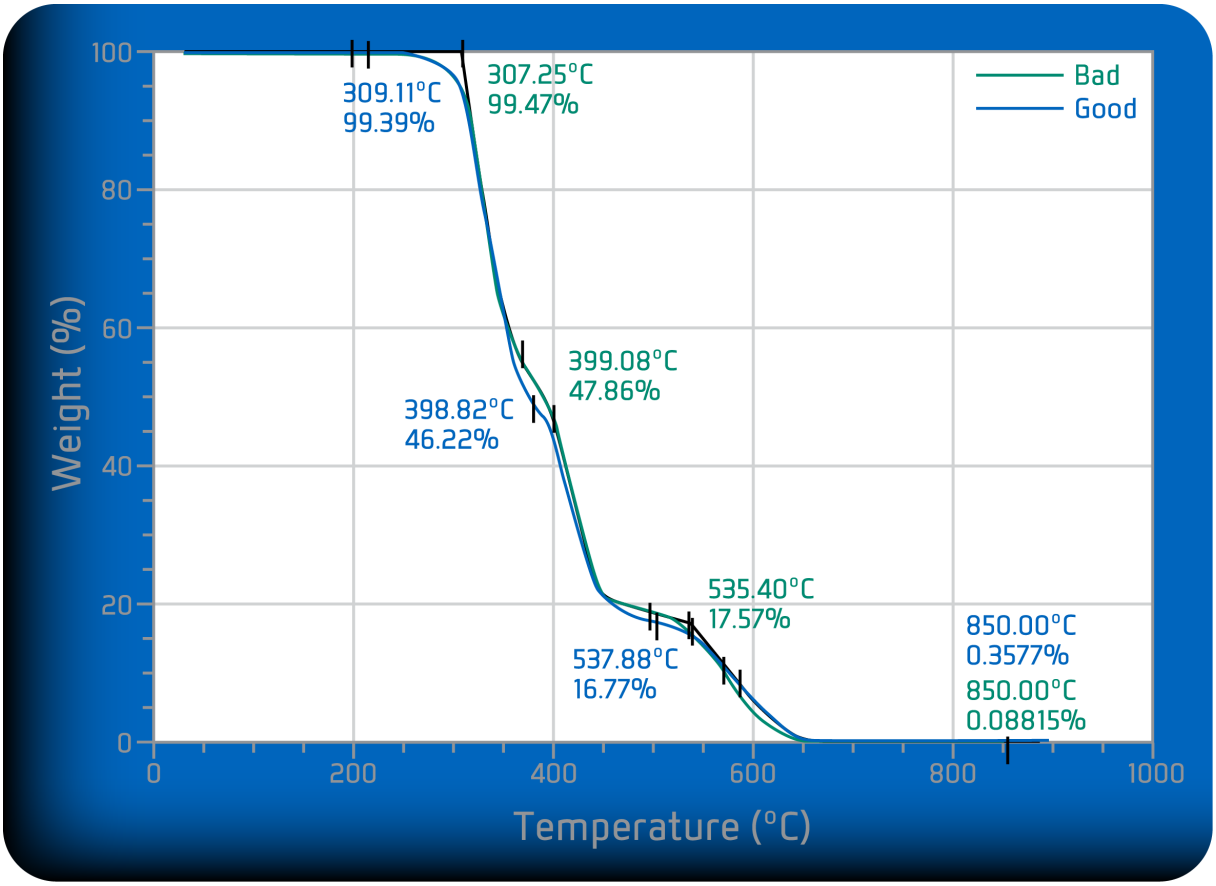
Sample	MFI, g/10 minutes	Avg.	St. Dev.
Good	16.68	16.97	0.50
	17.54		
	16.67		
Bad	34.77	34.14	3.65
	30.21		
	37.44		

Thermogravimetric Analysis (TGA)
In order to compare the degradation profile of the two samples, thermogravimetric analysis (TGA) was carried out using a TA Instruments Q500 instrument. Approximately 15 mg of sample was placed in a tared platinum TGA pan and heated from 30°C to 900°C at 10°C per minute in an atmosphere of air. The inset Figure shows the TGA curves that were recorded for this pair of samples.

The degradation profiles and the amount of inorganic residue were compared between the two samples. No significant differences were noted between the two samples.

A different thermal degradation profile would have indicated a substantially different polymer or additive package. If a different degradation profile had been observed, chemical identification of the base polymer followed by an analysis of the stabilizer package would have been performed. Analytical methods employed would include Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy.

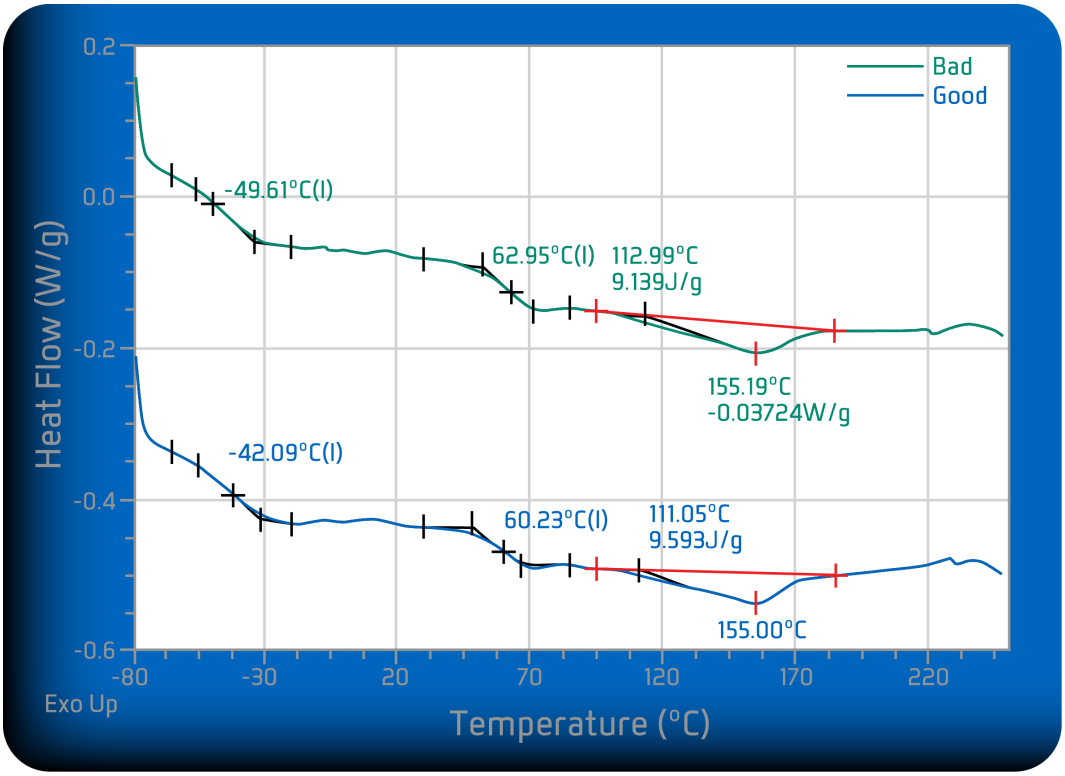
A difference in inorganic residue content would have indicated a difference in the amount or type of filler that was compounded into the thermoplastic elastomer resin. If a significant difference in inorganic residue content had been observed then the chemical composition, concentration, and the physical characteristics of the filler would have been documented. Scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS) provides this additional data, together with digital optical microscopy (OM).



Differential Scanning Calorimetry (DSC)

DSC was performed using a TA Instruments Q200. Approximately 7 mg of sample was encapsulated in an aluminum pan and heated from -80°C to 250°C at a heating rate of 10°C per minute. The samples were then cooled to -80°C and subsequently heated a second time to 250°C at a heating rate of 10°C per minute. The inset Figure shows the DSC curves that were recorded for this pair of samples.

Both samples show two glass transitions on the first heating scan that vary slightly. Both thermoplastic polyurethanes also demonstrate a melting point at 155°C. In addition to having the same melting peak characteristics (peak onset, peak minimum, peak termination) the level of crystallinity, as determined by the area of the melting peak (heat of fusion, ΔH_f), is equivalent for the two samples.



Conclusions

Melt flow index, thermogravimetric analysis, and differential scanning calorimetry were used to determine the root cause of substantial process variation with an extruded thermoplastic polyurethane. TGA testing revealed no significant differences between Good and Bad samples in terms of the thermal degradation profile or inorganic residue contents. No significant difference in either of the two glass transition temperatures or in the detailed characteristics of the melting endotherm were noted either. The most marked dissimilarity between the two samples was in the melt flow index (MFI) value. The melt flow rate was about twice as high for the Bad sample relative to the Good sample. These significantly different melt flow rate values indicate a large variation in the molecular weight distributions for these two thermoplastic polyurethane samples.