A Future FOR THE Sport

BOWLING BALL FTIR RESEARCH REPORT

FEBRUARY 2024

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OVERVIEW

In our role as the National Governing Body for the sport and regulator of equipment specifications, USBC has always been interested in measuring the properties of the bowling ball. Each manufacturer knows the chemical composition of its products, but, understandably, those details are kept secret.

USBC has been conducting research to create a process that will allow for balls to be objectively measured and categorized. Specifically, USBC sought to categorize balls into one of four groups:

- Reactive
- Urethane
- Polyester
- Epoxy

To achieve this, USBC has used a Fourier Transform Infrared (FTIR) spectrometer to identify the chemical differences between the four major coverstocks. The USBC Equipment Specifications Department has developed a Standard Operating Procedure (SOP) for determining material type with the use of the instrument.

The key findings in this research study are:

- USBC has developed a process that can measure and distinguish between bowling ball coverstocks.
- USBC can categorize most balls clearly into one of these four categories using FTIR.
- An SOP for material identification has been developed.
- Using this SOP, USBC can objectively distinguish between a reactive and urethane ball after manufacturing.

Next steps:

- There is no specification change proposed as a result of this research.
- USBC is not publishing categorization results for individual ball models based on FTIR measurements.
- USBC will continue gathering data from bowling ball approval samples.
- USBC will continue to evaluate other areas where FTIR can be utilized.

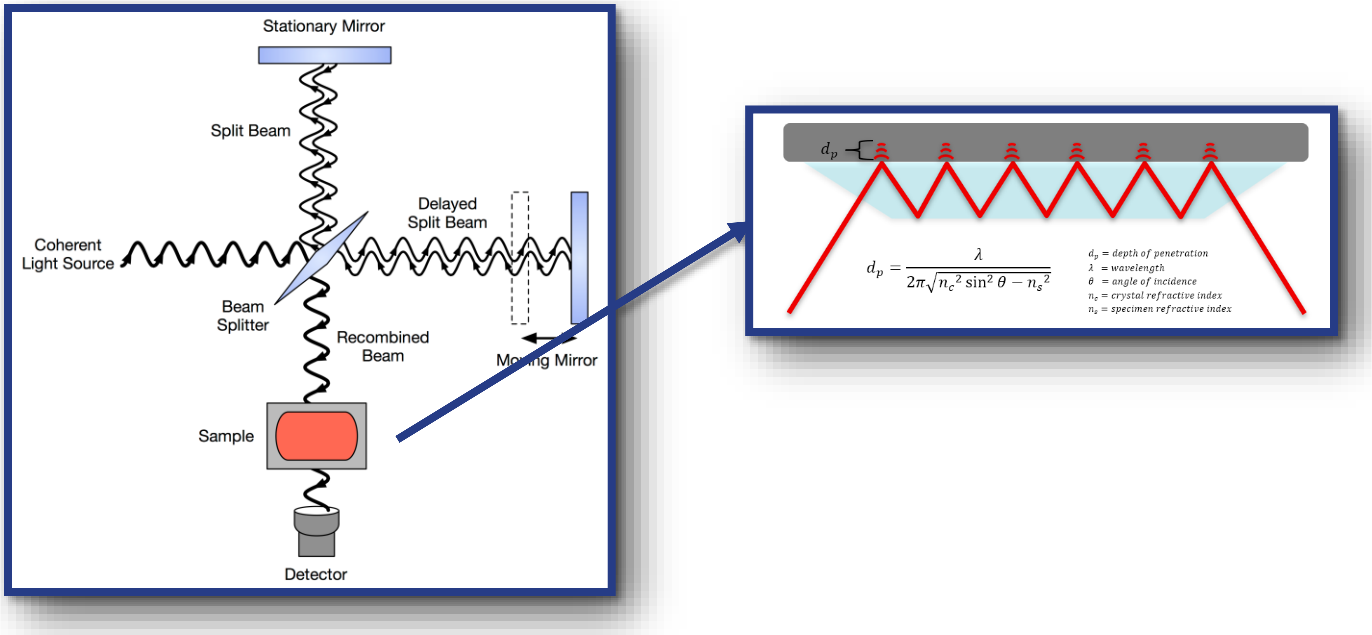
INTODUCTION TO FTIR

What is FTIR Spectroscopy?

FTIR Spectroscopy stands for Fourier Transform Infrared Spectroscopy. Infrared spectroscopy is the study of the behavior of infrared radiation with matter by absorption, emission, or reflection. A mathematical signal processing tool known as a Fourier Transform is applied to measure the results of the tool. Combining these aspects together results in a tool that can study the interactions of infrared radiation and matter at several wavelengths simultaneously.

How it works.

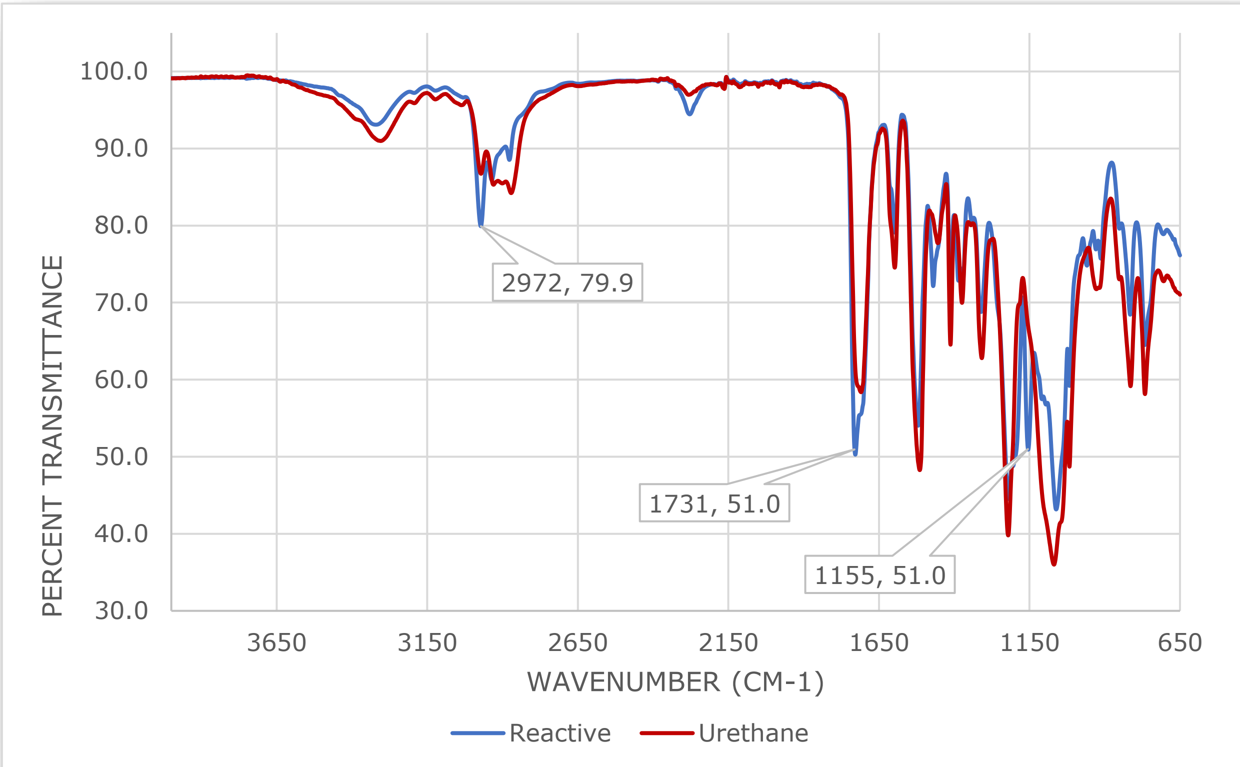
An FTIR spectrometer has a few main components, a laser light source, beam splitter, stationary mirror, moving mirror, a sample for testing, and a detector. Light is emitted from the infrared laser and travels toward the beam splitter. The beam splitter is a translucent material that allows some of the light through it and reflects the rest toward a stationary mirror. The light that travels directly through the beam splitter encounters a moving mirror. As the distance between the moving mirror and the beam splitter changes, the light from the stationary mirror and moving mirror combines back at the beam splitter. Based on the location of the moving mirror, these two lights will be in or



out of phase with each other. The light then travels to the sample. There are a few different sampling methods for FTIR analysis. We use the ATR method. ATR, or attenuated total reflection, is when the recombined beam is directed into a crystal where it reflects one or more times back and forth between the walls of the crystal. At each location where the beam encounters the interface between the crystal and the sample, some of the light is absorbed into the material based on the frequency of the combined light and the chemicals present in the material. Specifically, the materials FTIR interacts with are materials with molecules consisting of covalently bonded atoms with a dipole moment. The remaining light then exits the crystal toward the detector. The measured signal is known as an interferogram. A Fourier Transform on the interferogram separates the frequencies that interact with the sample, which results in the IR spectrum of the sample.

How does it relate to bowling?

When the infrared light interacts with bowling ball material, it generates a spectrum, which acts like a fingerprint for that material. When the frequency of the incident light interacts with the material, some frequencies are absorbed into the material, and others are transmitted back to the detector. By reviewing many different known materials, scientists have documented regions where certain molecule types absorb infrared light. The following figure represents the spectra graphs generated when the FTIR device is used on a known reactive sample and a known urethane sample.



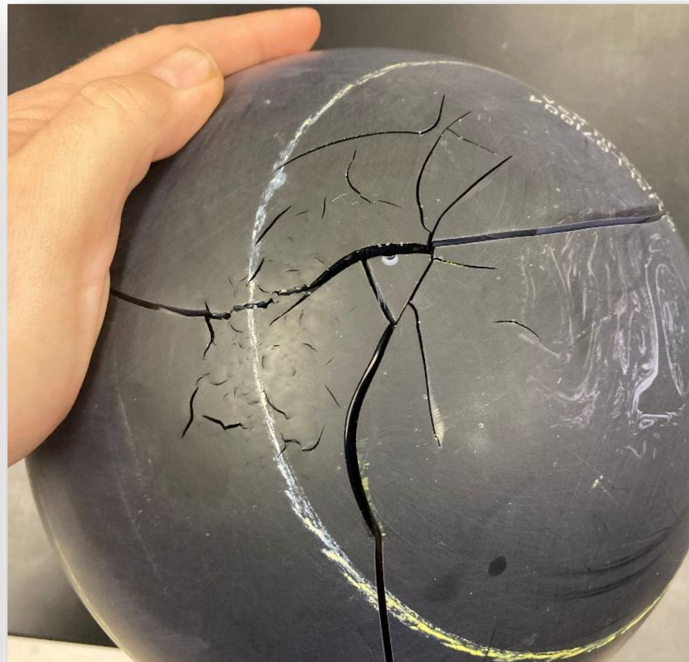
RESEARCH

These spectra for reactive and urethane balls are similar. After all, the urethane and reactive balls are both polyurethane chemistries. Polyurethane chemistries are known to exhibit the following properties on their FTIR spectrum:

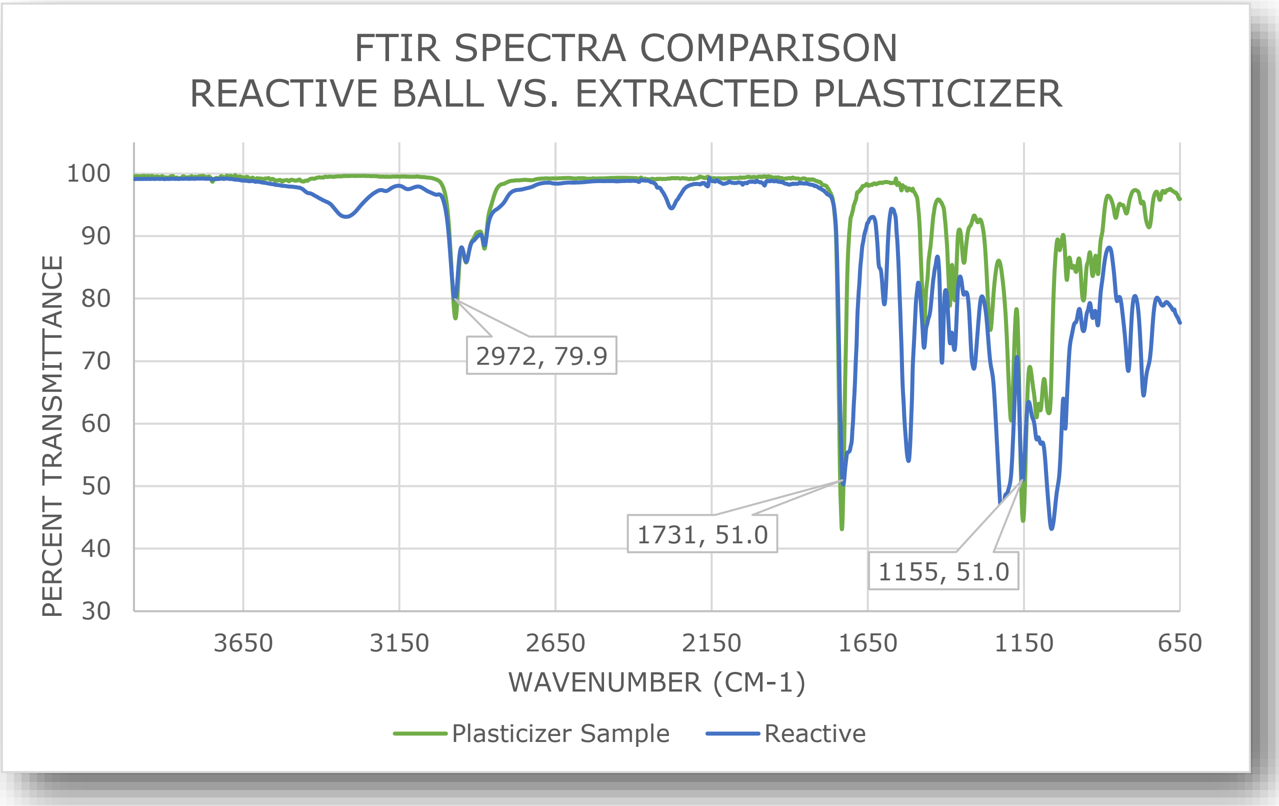
PEAK LOCATION WAVENUMBER (cm-1)	CHEMICAL STRUCTURE	MOTION
3420-3200	N-H	Stretching
3000-2800	CH_2 and CH_3	Stretching
2260	NCO	Stretching
1740	C=O	Non-bonded urethane stretching
1510	H-N-C=O amide II	Combined Motion

From Time-Based FTIR Analysis of Curing Polyurethanes [*https://tools.thermofisher.com/content/sfs/brochures/D10290~.pdf*](https://tools.thermofisher.com/content/sfs/brochures/D10290~.pdf)

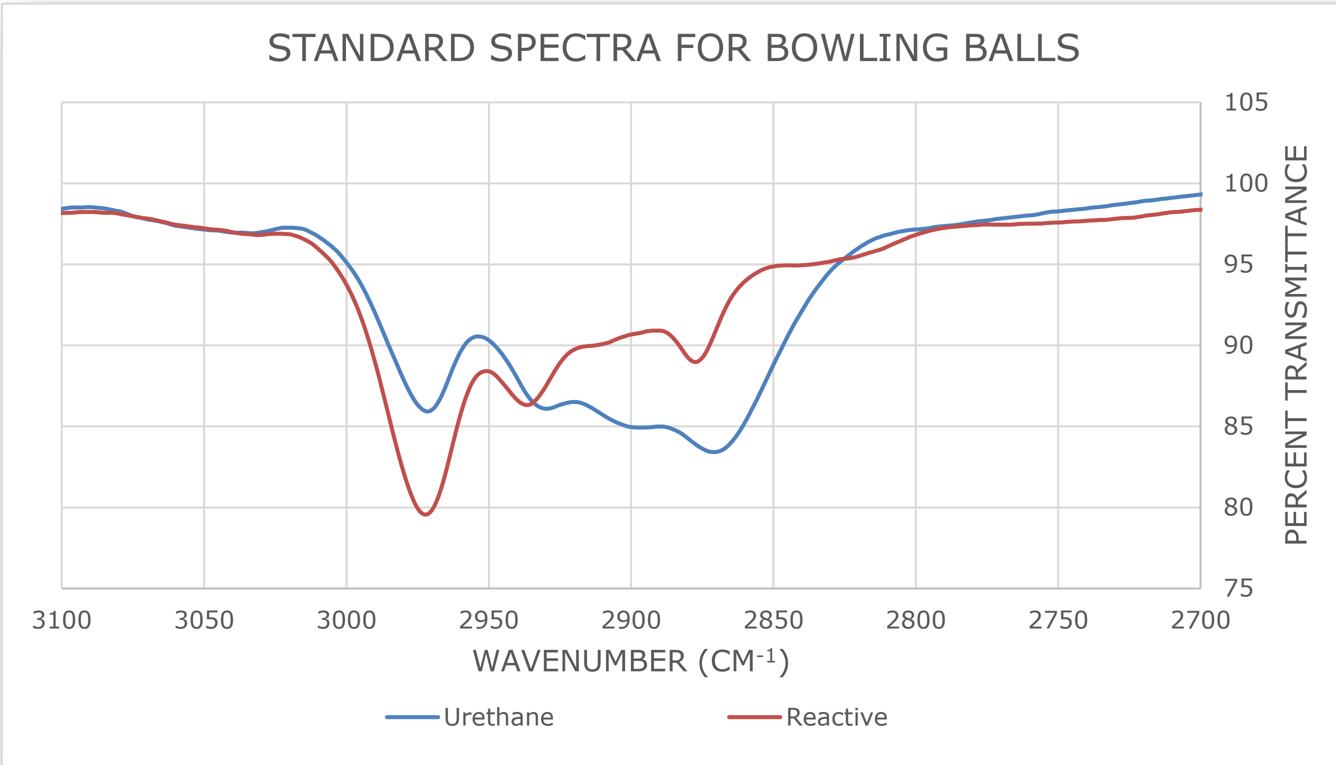
And we can see dips in the transmittance values at these known locations for both types. However, we also see some distinct differences at a few key locations. We see much sharper peaks in the reactive results at approximately 2970, 1730, and 1154. One of the key differences in the chemistry of reactive balls is the introduction of a plasticizer. Plasticizer does not chemically react in the formation of polyurethane. Polyurethanes consist of a polyol combined with an isocyanate. The plasticizer acts like a spacer getting trapped in areas within the coverstock where it prevents chemical bonds from forming. Plasticizer can be removed by heating up bowling balls. By subjecting a reactive ball to a heat lamp, we were able to extract plasticizer from the ball. A few hours later, the bowling ball exhibited severe cracking where the plasticizer was removed – please do not try this at home.



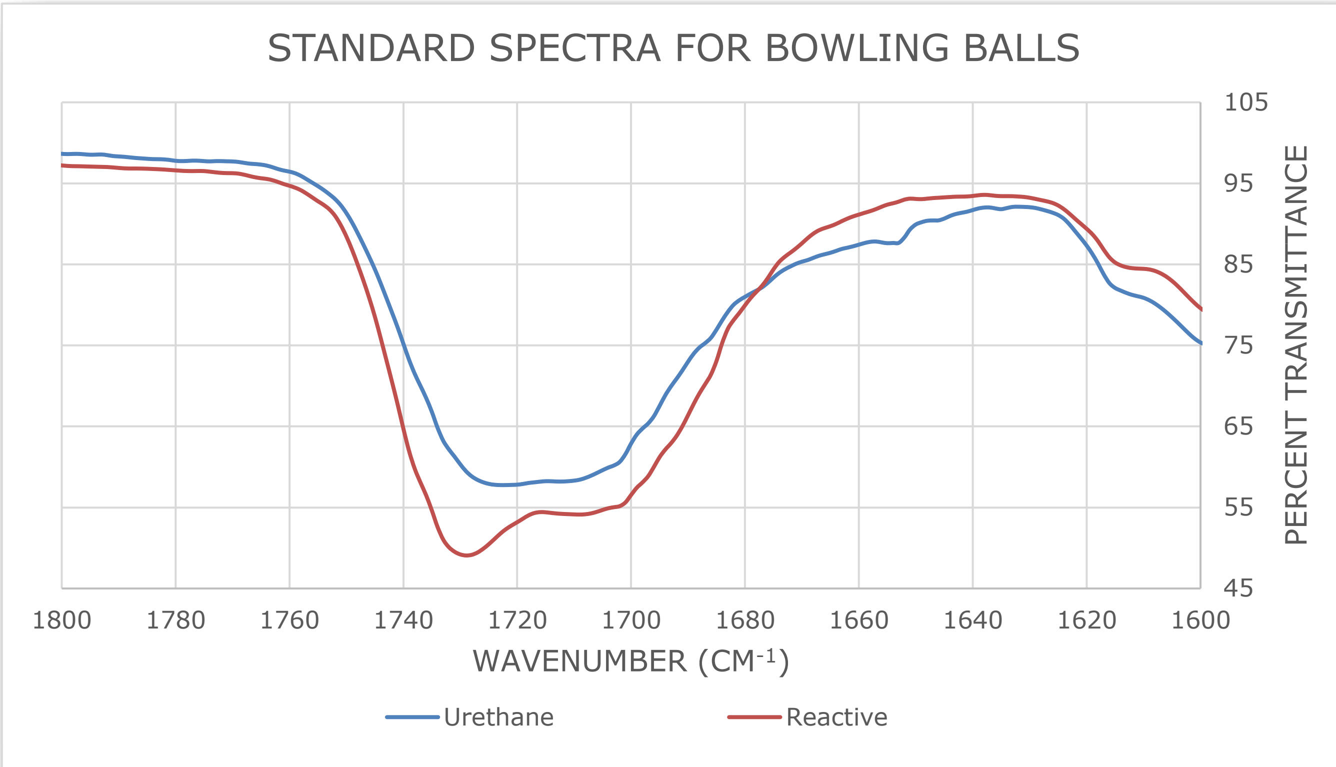
Performing an FTIR analysis on the extracted plasticizer confirmed that in the same areas where the reactive balls show peaks different than urethane balls, the extracted plasticizer has even more concentrated peaks.



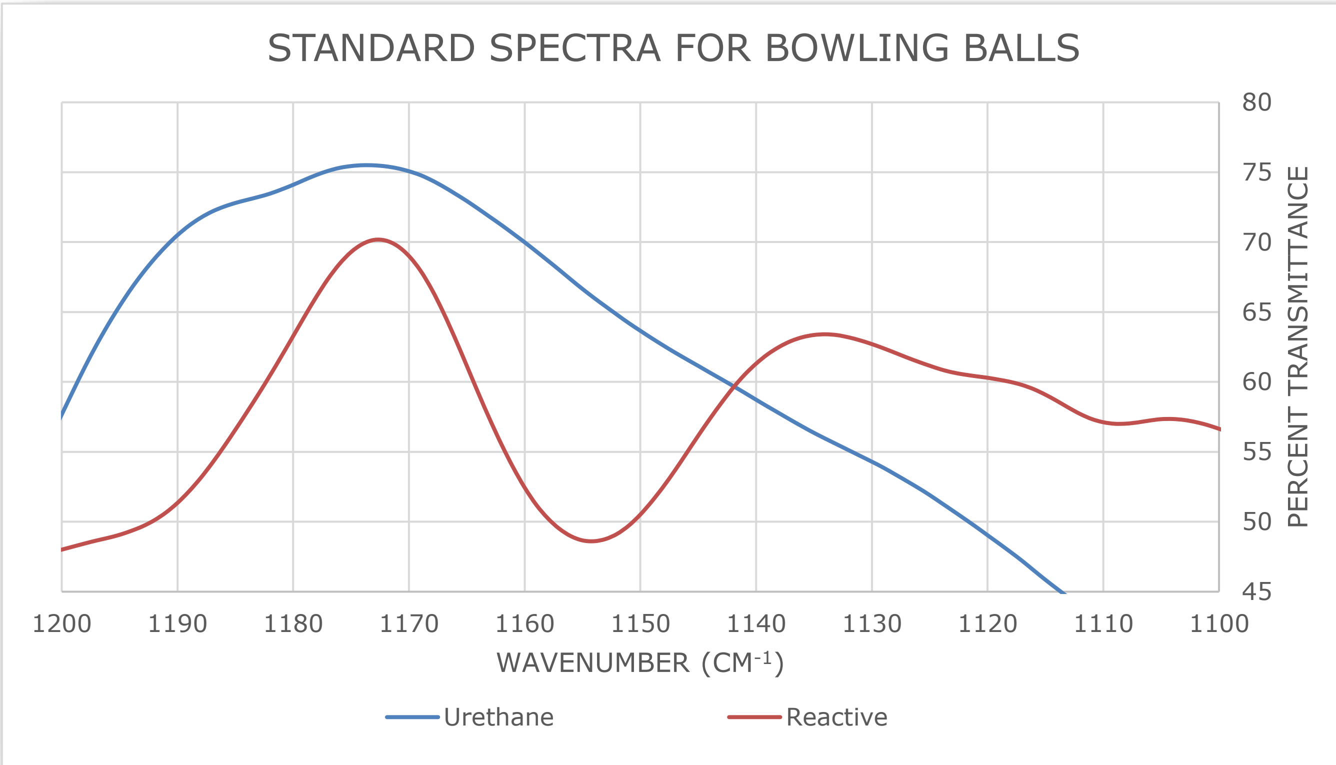
There are three key identifying locations where the plasticizer content appears in the results: 2970 cm^{-1}, 1730 cm^{-1}, and 1154 cm^{-1}. The following graphs zoom in on a comparison of our standard urethane and standard reactive spectra at those three locations.



At the 2970 cm-1 location, we see the reactive standard having a stronger peak than the urethane standard, but in both spectra in this region, we know from our research there is known CH_2 and CH_3 stretching occurring in polyurethanes, which makes it hard to fully determine the ball type on this region alone. We do see a difference where the strongest peak in the reactive spectrum is at the higher end of these wavenumbers, and the strongest peak in the urethane spectrum is on the lower end of this wavenumber range.



At the 1730 cm^{-1} location, we see that the plasticizer content adds an additional shoulder to the peak that exists here in the urethane standard. Our research showed that polyurethanes exhibit non-bonded urethane stretching at this location with the structure C=O. That is why we see the same overall behavior in both sample types. The additional peak on the reactive spectra does allow us another point for identifying between the two types.



At the 1154 cm-1 location, we see the clearest differentiator between the two types. Here, where urethane samples tend to have a steady decreasing trend, there is an additional peak in the reactive spectra that aligns with the sample of extracted plasticizer. This is our best location for trying to determine if plasticizer is present in the bowling ball sample.

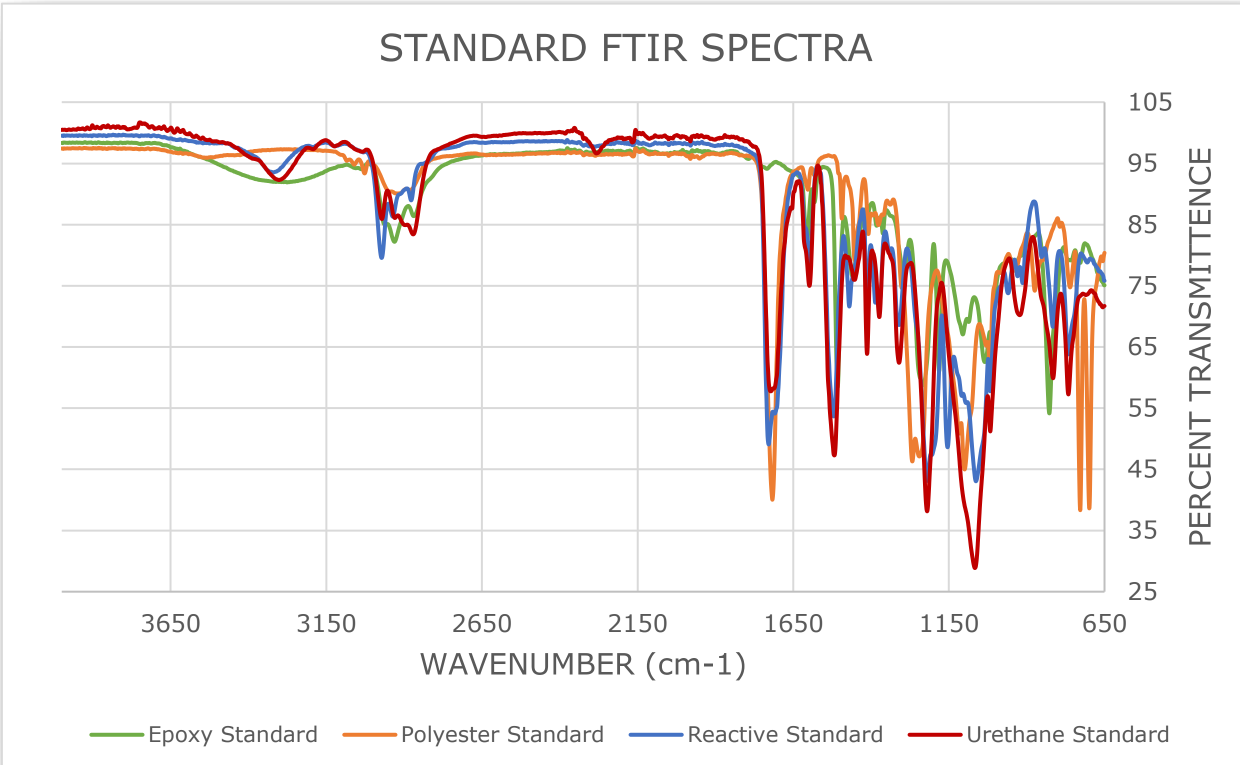
Additionally, our FTIR has built in spectra comparison features where we can compare exactly how similar two FTIR spectra are to one another. The Perkin Elmer COMPARE™ calculation iterates through each point in the spectra of a known standard and a measured spectra and outputs a correlation factor between 0.0 (completely different) and 1.0 (a perfect match).

We chose four standard bowling balls to be the baselines to which we compare everything else. The standard balls were chosen because we knew precisely what materials they were made of.

Compare Feature

The four standard bowling balls were chosen as a known reactive shell, a known urethane shell, a known polyester shell, and a known epoxy shell, the 4 most recently used materials for bowling ball coverstocks.

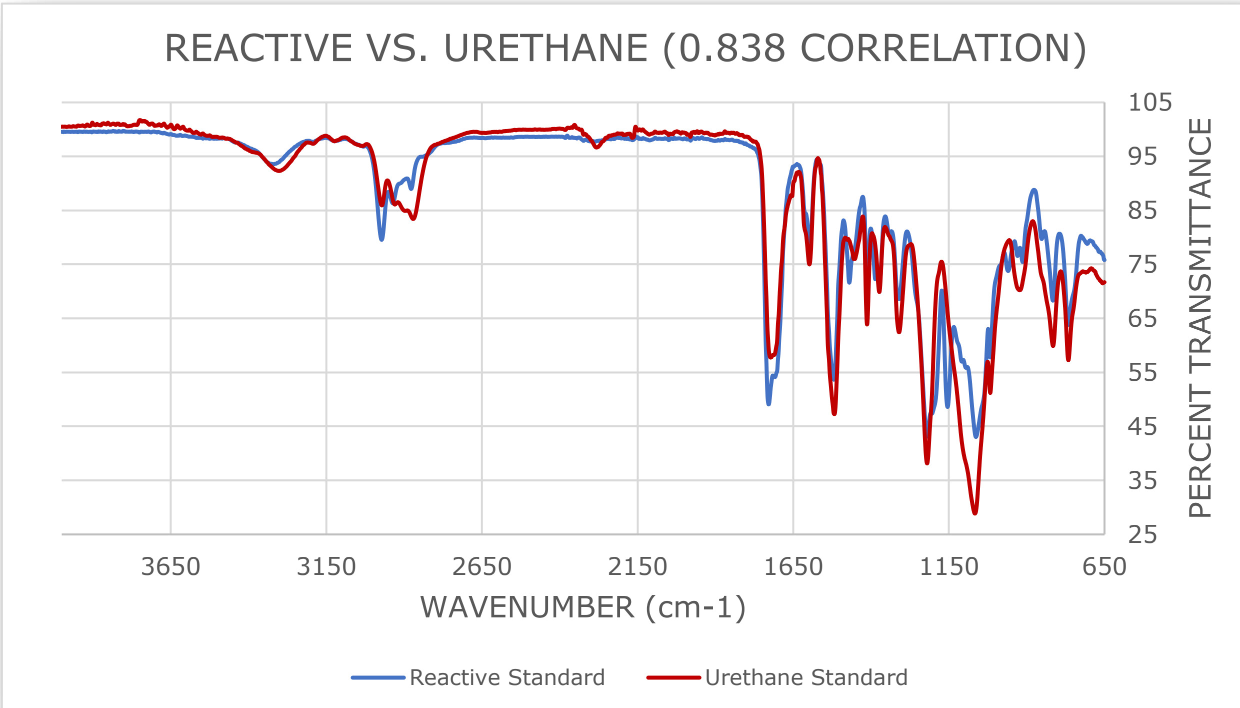
The following is a plot of the four standard spectrums:



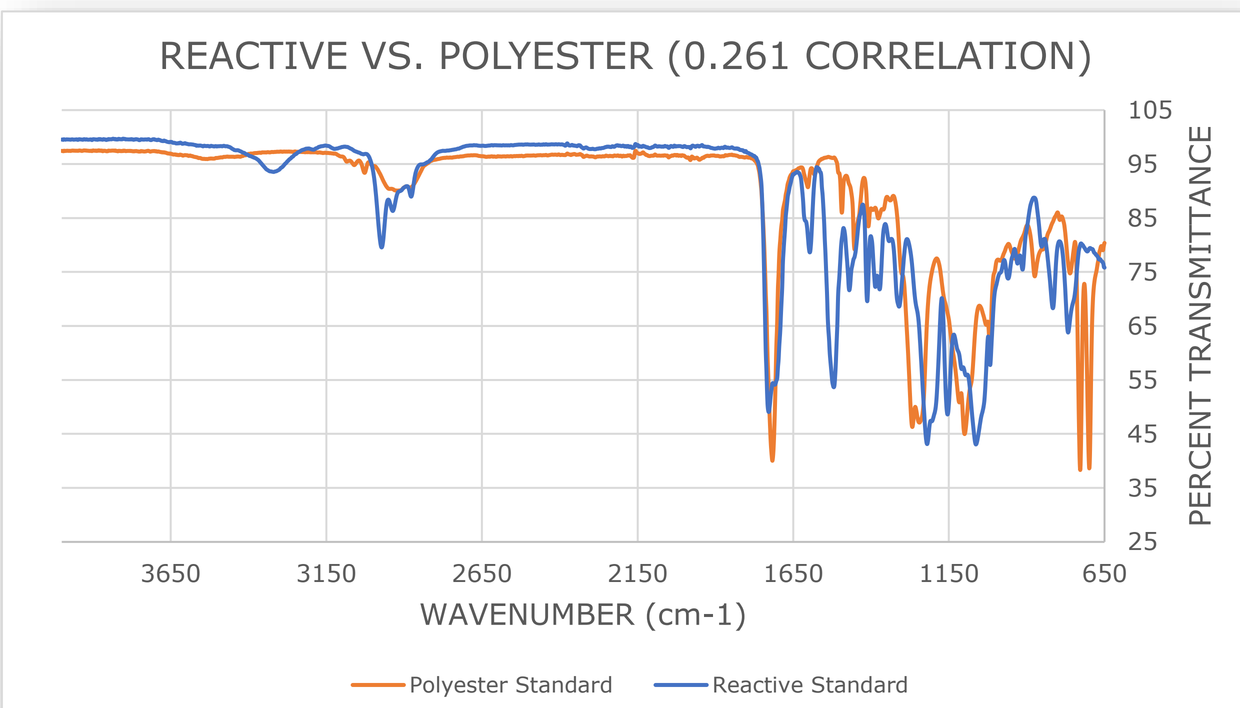
Here, we can see some extreme differences between the four coverstock types. If we tabulate the FTIR's compare feature comparing the standards of each back to the reactive standard and a modern reactive ball back to the reactive standard, we get the following results:

COMPARE SAMPLE 1	COMPARE SAMPLE 2	COMPARE Correlation
Reactive Standard	Reactive Standard	1.000
Reactive Standard	Urethane Standard	0.838
Reactive Standard	Polyester Standard	0.261
Reactive Standard	Epoxy Standard	0.088
Reactive Standard	Modern Reactive	0.990

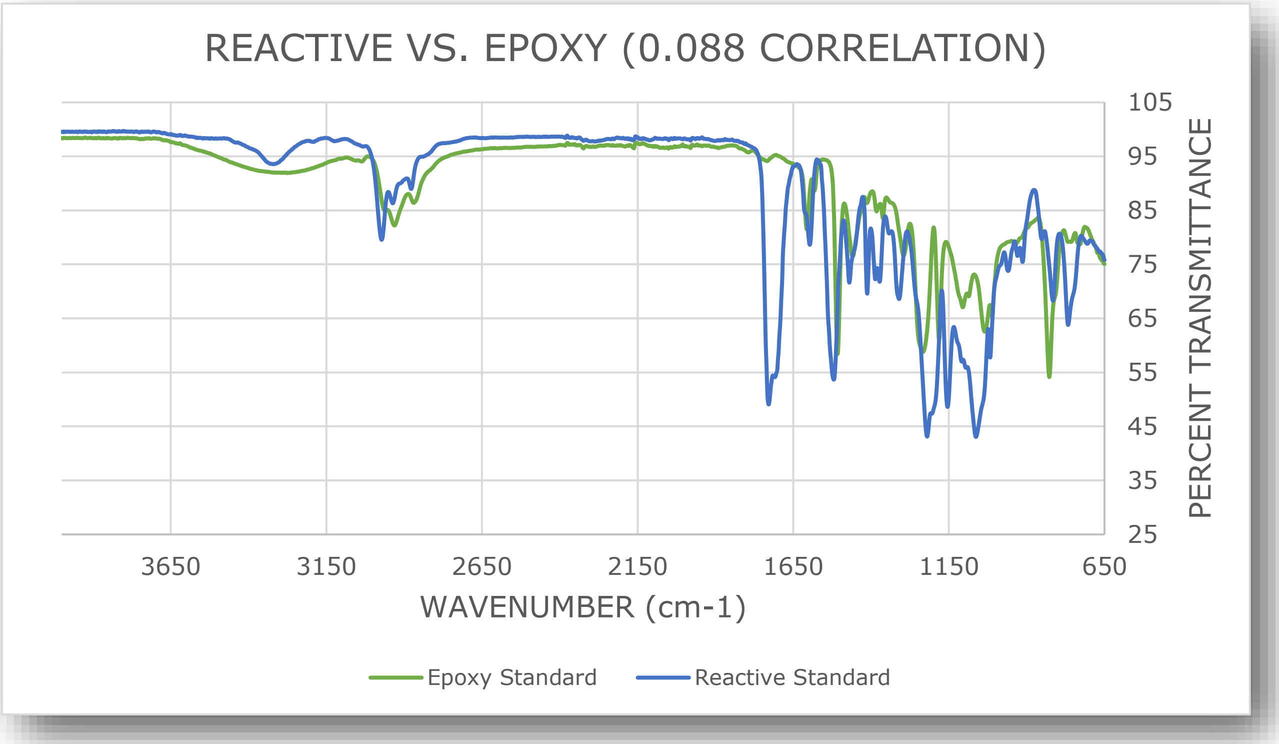
Anytime the same data is used as the data source and the comparison source, the outcome is always 1.000. For each of the remaining comparisons, the data from the reactive standard is compared to the data of each of the other spectra. Having these data points allows us to build some visuals to develop an understanding of what it means to have a 0.99 correlation versus a 0.838 correlation, versus a 0.261 correlation, etc. The following charts show a one-on-one visual comparison of each of the compared spectra.



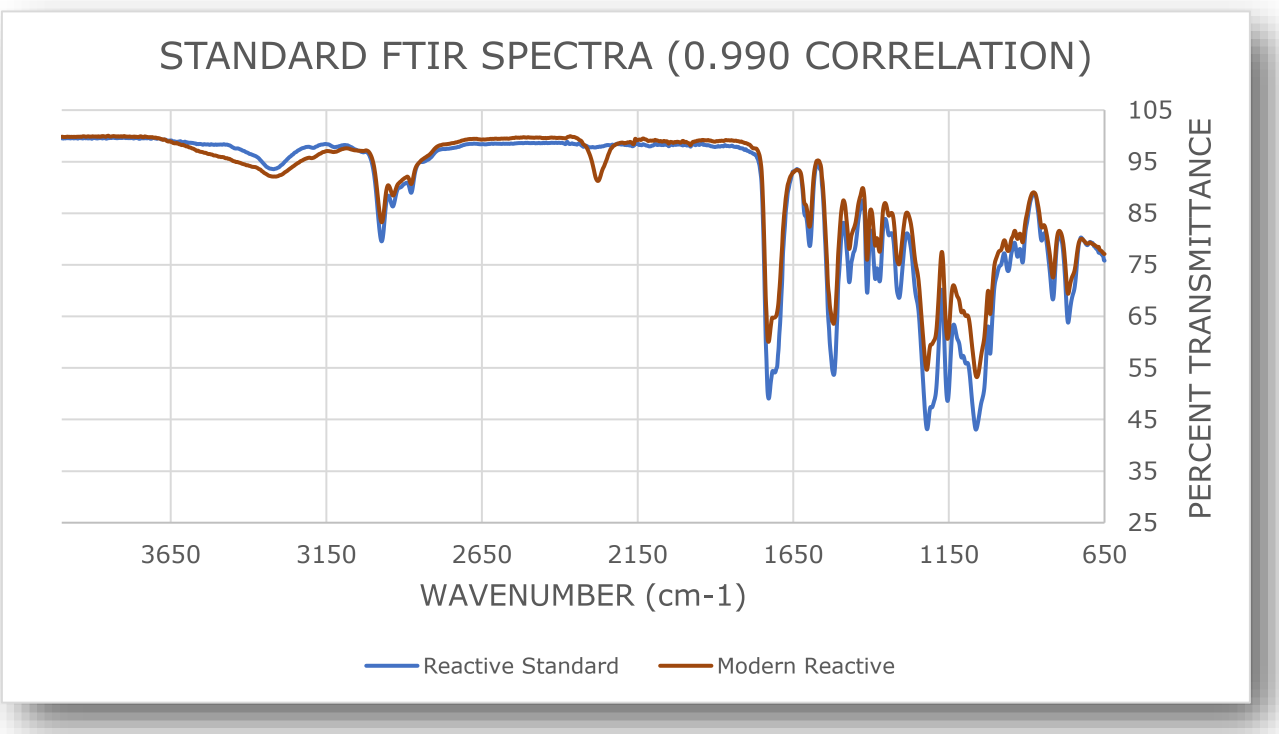
At a 0.838 correlation, we see a good amount of similarity in the spectra, but we can also see a handful of distinguishing peaks between the two.



At 0.261 correlation, we can identify several large peaks that are not in both data sets.



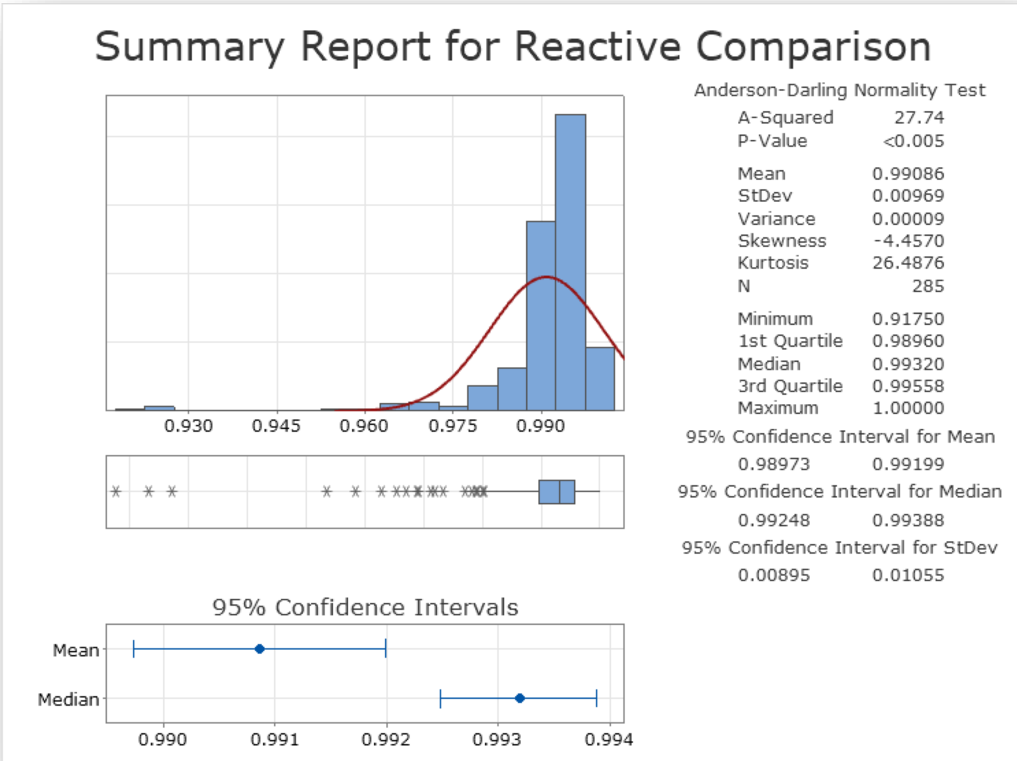
At 0.088 correlation, we see even more peaks that are present in one of the spectra are not present in the other.



At 0.990 correlation, we see that nearly all the peaks in both data sets occur at the same wavenumbers (x-axis locations). The magnitudes of the peaks at those locations are different between the data sets, and there is one peak (2260) that is not in both data sets.

Past research

When the FTIR was originally purchased by USBC, we were researching ways of differentiating between different reactive coverstocks. USBC investigated if we could categorize bowling ball material beyond simply what was submitted on the application forms.
USBC staff took readings on over 285 bowling ball samples between 2007 and 2009, and the results showed that reactive balls all measured similarly despite performing differently or having different particulates added to them.



The data had a 1st quartile of 0.9896 correlation to reactive. That means 75% of the measurements matched the reactive standard at approximately 0.990 or greater with the majority of reactive samples correlating to the standard well over 0.970.

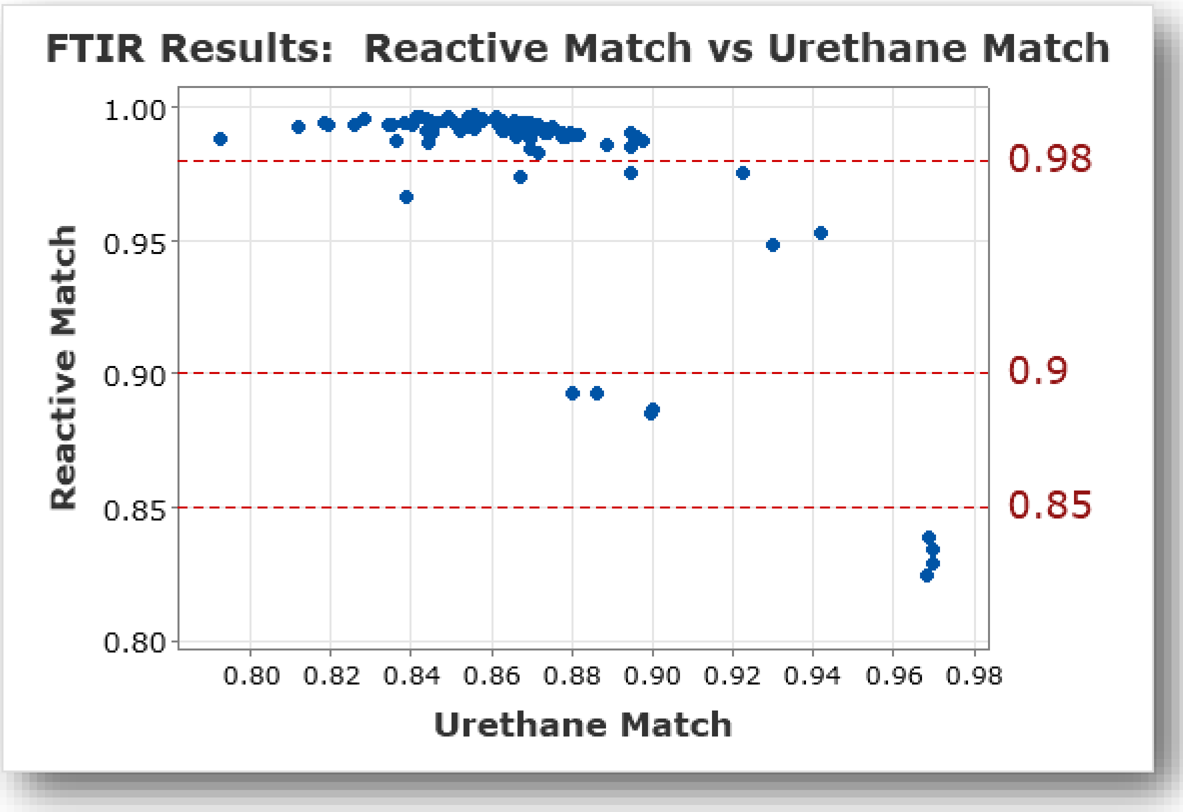
The team discontinued the use of the FTIR on bowling balls because it was deemed insufficient at distinguishing between different reactive samples. However, the tool continued to be used in the regulation of pin materials and the approval of ball cleaners.

New research

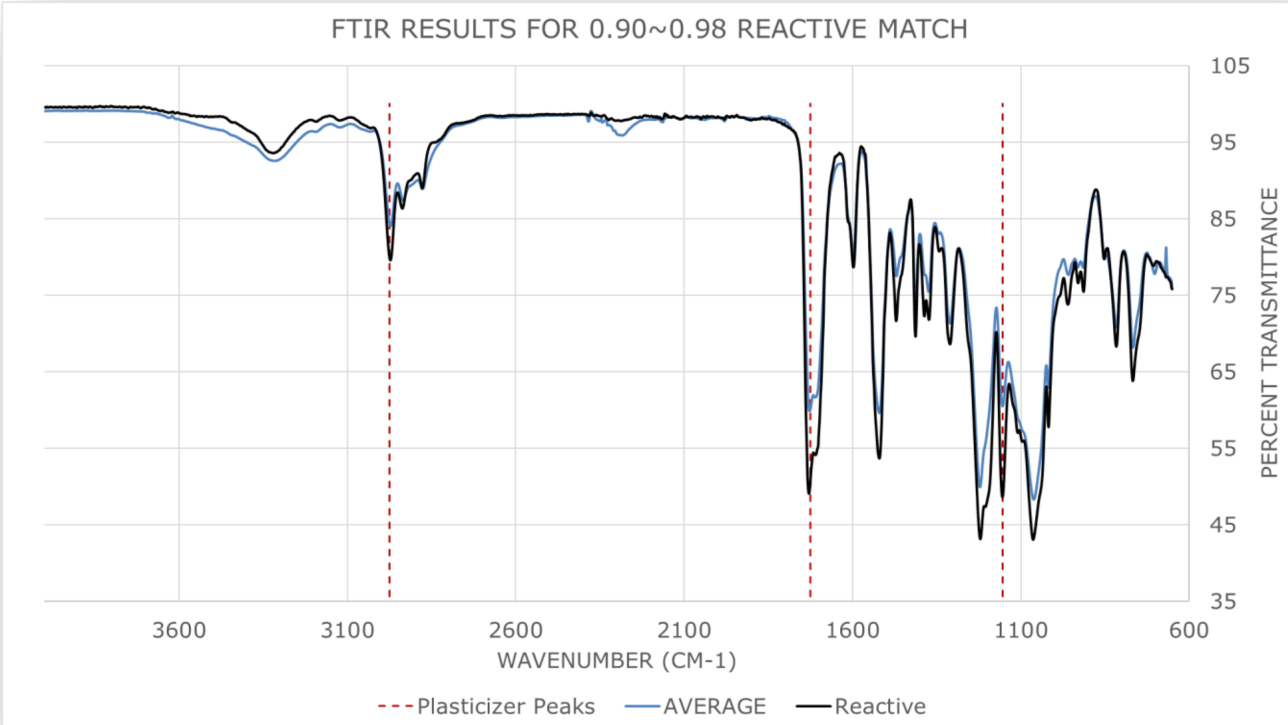
USBC has been revisiting the tool with the lens of using it to distinguish between reactive, urethane, and balls of other materials. Since April of 2023, USBC has been performing FTIR analysis on every ball that has been submitted for approval. Each ball was then compared to our standard reactive, urethane, polyester, and epoxy FTIR spectrum.

New findings

We have been studying the data and categorizing balls by how well they match the reactive and urethane standard samples. Below is a graph where each dot represents a bowling ball plotted by its reactive match on the vertical axis and its urethane match on the horizontal axis.



Now that we have scanned more than 110 bowling ball models, we see similar results to what we saw in the past. Most approval samples are reactive balls that match the reactive standard to over 0.980 correlation. There were six samples in the range of 90% to 98% match. When we review the average of these samples, the plasticizer peaks appear to be present but not as intense. This likely indicates that these models had a lower plasticizer content.



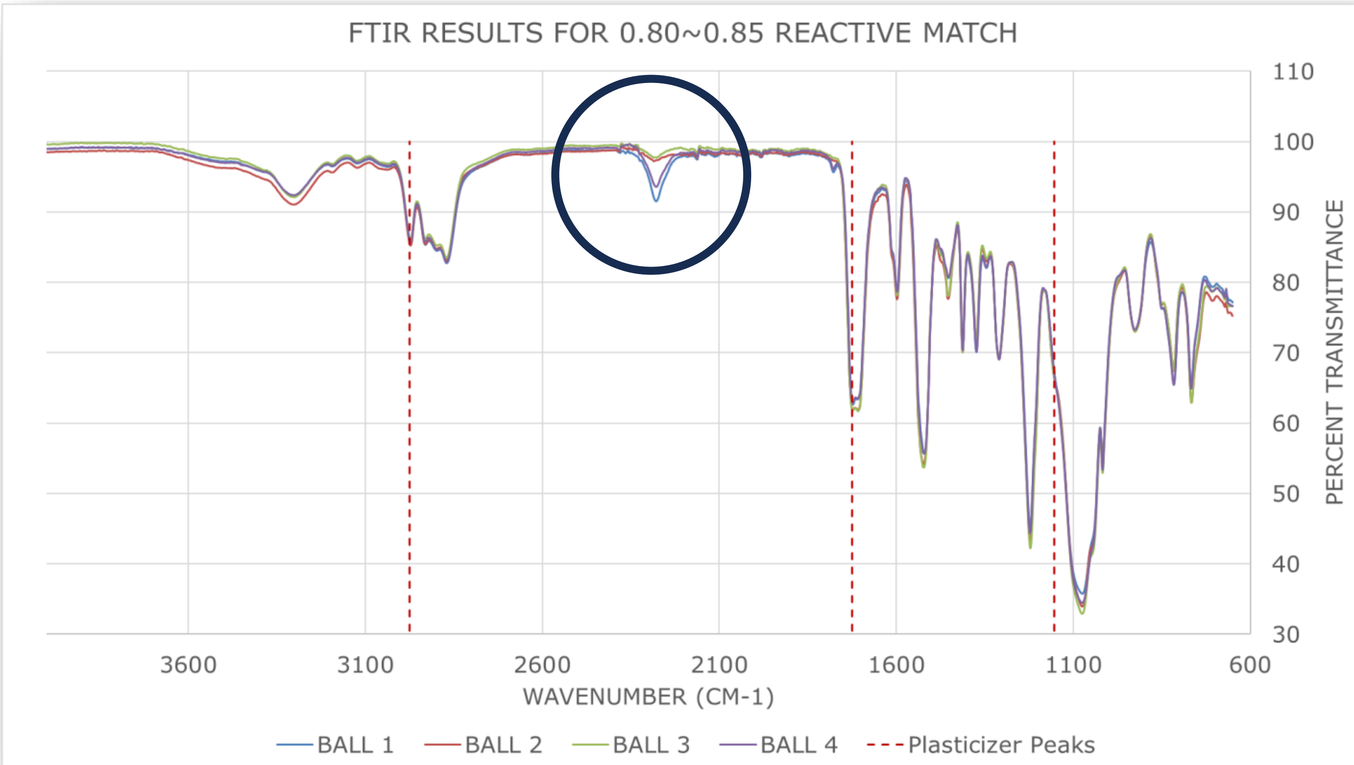
Four samples matched both the reactive standard and the urethane standard less than 90% to either. Reviewing these samples, they are reactive balls that are produced and sold overseas. The additional peaks in the FTIR spectrum suggest the presence of different chemicals. It could be the use of different polyols, isocyanates, or plasticizers.

The remaining four samples match the urethane standard over 96%, but the reactive standard less than 85%. These samples are our traditional urethane-type balls. If we review these samples compared to each other, we see that the only real demarcation between them is at a wavenumber of approximately 2260 cm^{-1}. From our research, we know that this is related to NCO stretching. How polyurethane reaction works is that the isocyanates have NCO groups that combine with the OH (hydroxyl) groups in the polyol to form urethane bonds. When balanced properly, each NCO group in the isocyanate will have a corresponding hydroxyl group in the polyol to bond with. The peak observed at 2260 cm^{-1} indicates a few possibilities:

A. The mix was poured isocyanate heavy, and there were not enough hydroxyl groups present for all the NCO to bond with.

B. Not enough time has elapsed since the reaction to allow all the NCO groups to bond with the hydroxyl groups.

C. Something could be interfering with the NCO groups from being able to reach an available hydroxyl group.


FTIR RESULTS FOR 0.80~0.85 REACTIVE MATCH
110
100
90
80
70
60
50
40
30
PERCENT TRANSMITTANCE
3600
3100
2600
2100
1600
1100
600
WAVENUMBER (CM-1)
BALL 1
BALL 2
BALL 3
BALL 4
Plasticizer Peaks

SUMMARY

The research shows us that FTIR is a suitable tool for determining chemical differences between bowling ball coverstocks. While the nuanced differences between many reactive bowling balls are too small to differentiate, differences between the macro coverstock types: reactive, urethane, polyester, and epoxy are readily apparent. Further research is starting to show observable differences that could be related to plasticizer content and use of different plasticizers. USBC will continue this research to better understand the chemical composition of bowling balls.

The key findings in this research study are as follows:

- USBC has developed a process that can measure and distinguish between bowling ball coverstocks.
- USBC can categorize most balls clearly into one of these four categories using FTIR.
- An SOP for material identification has been developed.
- Using this SOP, USBC can objectively distinguish between a reactive and urethane ball after manufacturing.

Next steps:

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