APPLICATION NOTE

No. AN53141

Optimizing tire performance through proper chemical composition with FTIR

Key words
OMNIC Specta, additives, advanced ATR correction, ATR, carbon black rubber, infrared, multi-component search, polymers

Carbon black rubbers

Carbon black rubbers (CBRs) are most heavily used in automobile tires. The material adds reliancy and effectively conducts heat away from the tread, extending tire life. Ensuring CBRs have the proper chemical composition is an important aspect in optimizing the tire performance. CBRs have traditionally been difficult to analyze by FTIR, as they are opaque even when cut extremely thinly. Attenuated total reflectance (ATR) is a measurement technique that has been proven to effectively analyze these difficult samples.

Attenuated Total Reflection: diamond and germanium

ATR has become the method of choice for sampling materials using Fourier Transform Infrared Spectroscopy (FTIR). The simplicity of the sampling device and ease of cleaning are major benefits. However, ATR devices alter the appearance of the spectrum relative to what would be in transmission. A systematic understanding of the differences and the tools for addressing them will greatly enhance the utility of ATR in the laboratory.

Light passing between two different materials changes direction – this is how a magnifying glass works to focus the sun's rays. The change in direction is determined by the index of refraction of the two materials. In eyeglasses, high index of refraction materials like polycarbonate can be used to make thinner lenses than lower index materials like glass, because the polycarbonate redirects the light more effectively.

To understand ATR, consider a rectangular fish aquarium. Looking straight through, the far window is transparent. However, the side windows look like mirrors, an effect caused by internal reflection. When a finger is placed on the side glass, the ridges of the fingerprint are visible, but not the valleys between. Simply stated, at this angle,

Figure 1: Carbon black rubbers, such as this tire, represent a challenging sample for infrared analysis

the light exits the side window very slightly, and this "evanescent wave" interacts with the finger ridges allowing them to be visible to your eye. The depth of penetration – how far the light travels out of the glass is too shallow for the valleys of the fingerprint to be seen.

In infrared spectroscopy, the same basic ideas hold true. With proper alignment, IR light can be made to emerge slightly from an infrared transmissive crystal. This will interact with any sample in intimate contact with the crystal – like the fingerprint on the side of the aquarium. This is why most ATR accessories come with pressure towers, to press the sample against the crystal. The infrared light interacts with the sample at the crystal surface, which produces the spectrum.

The spectrum depends upon the depth of penetration d_p which, in turn, depends upon several factors. Mathematically, this is given by

$$d_p = \lambda / \{2 \pi n_C [\sin^2\theta - (n_S/n_C)]^{1/2}\}$$

where λ is the wavelength of the light, θ is the angle at which the light strikes the surface of the crystal, and n_S and n_C are the index of refractions of the sample and crystal, respectively. Thermo Scientific first developed a proprietary

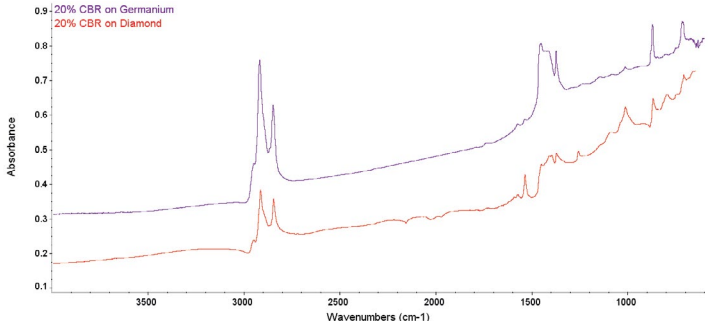


Figure 2: Comparative raw spectra from 20% CBR. The diamond ATR spectrum shows several problems, while the Ge ATR spectrum is clean.

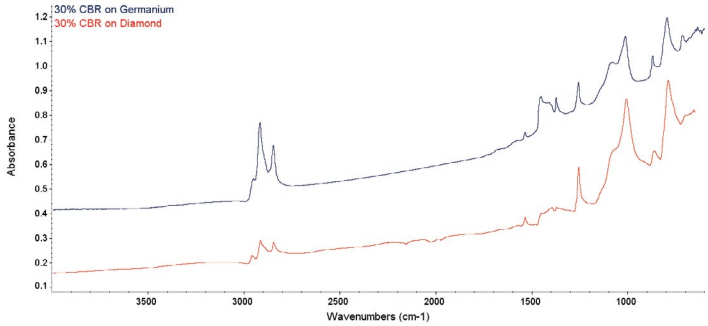


Figure 3: Comparative raw spectra from 30% CBR. Again, there are artifacts in the diamond ATR spectrum, but not in the Ge ATR.

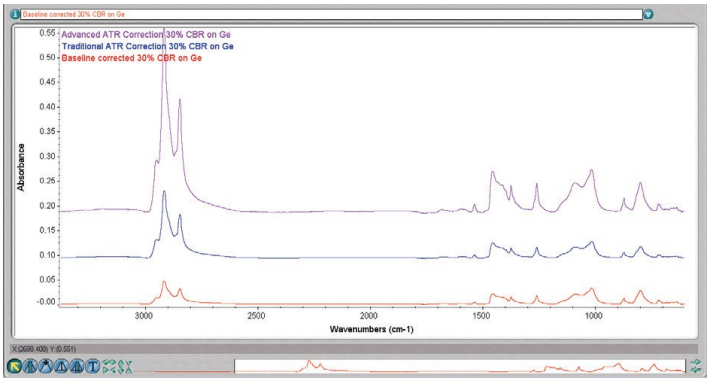


Figure 4: 30% CBR on Ge. Bottom spectrum is baseline corrected only, the middle has the traditional ATR correction applied, and the top has the Advanced ATR Correction applied. Common scaled, offset for clarity.

Two common ATR crystals are diamond and germanium (Ge). Diamond is highly robust, being both hard and chemically inert. For diamond, d_p is over 2 microns at 1000 cm^{-1}. Ge is also hard and inert, though less so than diamond. The key difference is the d_p, which is around 0.7 microns at 1000 cm^{-1}, due to the much higher index of refraction for Ge. It is this quality – the lower depth of penetration for Ge – that makes it ideal for carbon black rubbers. CBRs have a high index of refraction – close to that of diamond. In the equation above, if the sample index is too close to that of the crystal, the ratio of indices is almost 1, the square root term is negative and there is little to no ATR effect.

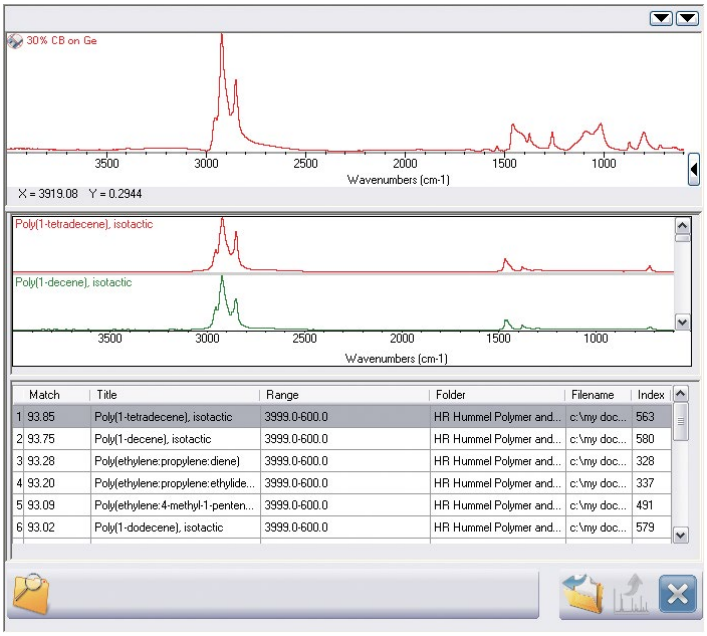
Advanced ATR Correction, which accounts for all the variables, permitting the use of transmission databases for comparison to ATR spectra for the first time.[1] The critical difference between the advanced correction and older ATR corrections is the recognition that the sample's index of refraction changes (increases) near an absorption peak. The effect of this is seen in Figures 2 and 3.

These spectra were obtained on an FTIR spectrometer like the Thermo Scientific™ Nicolet™ iS20 FTIR Spectrometer using a diamond and germanium ATR accessory. Near the strong absorption bands around 1400 cm^{-1}, the sample index is approaching or exceeding the index for the crystal, and there is a sudden change in d_p. This badly distorts the spectra and cannot easily be corrected. In contrast, the Ge spectra in the two figures show clean and well-defined peaks. This is the result of the much higher index of refraction for Ge and the shallow depth of penetration.

Furthermore, the strong diamond absorption bands in the center of the spectrum no longer ratio correctly. These diamond bands ratio out effectively when the light path through the crystal is the same in the background and the sample spectra. However, the close match of the index of refraction between the crystal and the CBR is causing the light path to change, and the diamond bands no longer ratio. The impact of this can be seen in the spectral artifacts present around 2000 cm^{-1} in the diamond spectra. Again, the Ge spectrum is totally clean.

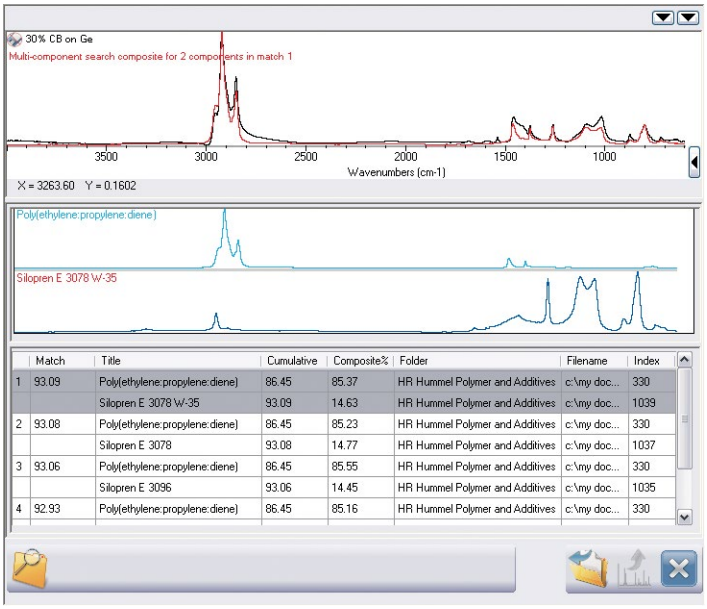
The complete analysis of the CBR is done using the powerful Thermo Scientific™ OMNIC™ Specta™ Software. First, the spectrum is baseline corrected and processed. Figure 4 shows the (baseline corrected) spectrum before ATR correction, with the ATR correction supplied by most vendors, and with Thermo Scientific™ Advanced ATR Correction. The change in the latter is more profound than just application of an intensity correction – the algorithm corrects the bands where strong absorbance alters the index of refraction. The corrected spectrum can now be searched against normal transmission libraries.

thermoscientific



	Match	Title	Range	Folder	Filename	Index
1	93.85	Poly(1-tetradecene), isotactic	3999.0-600.0	HR Hummel Polymer and...	c:\my doc...	563
2	93.75	Poly(1-decene), isotactic	3999.0-600.0	HR Hummel Polymer and...	c:\my doc...	580
3	93.28	Poly(ethylene:propylene:diene)	3999.0-600.0	HR Hummel Polymer and...	c:\my doc...	328
4	93.20	Poly(ethylene:propylene:ethylide...	3999.0-600.0	HR Hummel Polymer and...	c:\my doc...	337
5	93.09	Poly(ethylene:4-methyl-1-penten...	3999.0-600.0	HR Hummel Polymer and...	c:\my doc...	491
6	93.02	Poly(1-dodecene), isotactic	3999.0-600.0	HR Hummel Polymer and...	c:\my doc...	579

Figure 5: Simple search result for the top spectrum in Figure 4. The result is good, but there are extra peaks visible not in the result.



	Match	Title	Cumulative	Composite%	Folder	Filename	Index
1	93.09	Poly(ethylene:propylene:diene)	86.45	85.37	HR Hummel Polymer and Additives	c:\my doc...	330
		Silopren E 3078 W-35	93.09	14.63	HR Hummel Polymer and Additives	c:\my doc...	1039
2	93.08	Poly(ethylene:propylene:diene)	86.45	85.23	HR Hummel Polymer and Additives	c:\my doc...	330
		Silopren E 3078	93.08	14.77	HR Hummel Polymer and Additives	c:\my doc...	1037
3	93.06	Poly(ethylene:propylene:diene)	86.45	85.55	HR Hummel Polymer and Additives	c:\my doc...	330
		Silopren E 3096	93.06	14.45	HR Hummel Polymer and Additives	c:\my doc...	1035
4	92.93	Poly(ethylene:propylene:diene)	86.45	85.16	HR Hummel Polymer and Additives	c:\my doc...	330

Figure 6: Multi-component search result from OMNIC Specta. The search result is now complete and agrees remarkably well with the spectrum.

A simple search gives the results in Figure 5. The match is good, as the base polymer has been identified and a high match index is recorded. However, visual examination shows that several peaks around 1000 cm^{-1} are not present in the search result – a second component is present.

OMNIC Specta's unique multi-component search algorithm completes the analysis as shown in Figure 6. The powerful algorithm extracts two components from this CBR – the base polymer (notably, the same as the simple search) and the silane slip aid.[2] The sample, a car door insulation strip, uses a silane coating to prevent adhesion of the window to the insulation. The composite spectrum is visually remarkable – it represents an almost perfect agreement with the original spectrum.

Conclusion

Carbon black rubbers represent a challenging IR sample. Diamond is not a universal solution for CBRs, as the bands observed are distorted. Ge provides clean peaks. Thermo Scientific then provides all the tools required to complete the analysis, including Advanced ATR Correction and OMNIC Specta's multi-component search. The hardware and software combine into a powerful analysis tool.

References

1. Thermo Scientific Application Note AN01153
2. Thermo Scientific Technical Note TN51506

**Experiment can be conducted using the Thermo Scientific™ Nicolet™ iS5, iS10 or iS50 FTIR Spectrometer systems.*

Find out more at **thermofisher.com/is20** and **thermofisher.com/auto**

ThermoFisher SCIENTIFIC