Application Note: 50829

Carbon Black Analysis Comparison with Diamond ATR and Germanium Crystals

Michael Bradley, Thermo Electron Corporation, Madison, WI, USA

Key Words

- Absorbance & Reflectivity
- ATR Crystals
- Depth of Penetration
- FT-IR
- Ge Crystals
- High Carbon Black Rubbers (CB-rubbers)
- Polymers & Additives

Introduction

Attenuated Total Reflection (ATR) is increasingly the method of choice for sampling many materials using Fourier Transform infrared (FT-IR) spectroscopy. There are many publications on basic ATR theory, and a huge array of accessories available commercially. A brief description of ATR follows; more details are available in many texts.

Radiation (light) passing between two materials with different indices of refraction change direction according to Snell's Law – this is how lenses work, and how magnifying glasses focus the sun's rays. Most of the time, the light is thought of as passing completely through, such as in eyeglasses or a window. However, the light can be "totally internally reflected" if two conditions are met: the light passes from a high index material into a lower index material (like glass to air), and the angle of incidence is greater than the "critical angle" (usually a shallow or grazing angle).

A common manifestation of total internal reflection (TIR) is the appearance of the side window in a fish aquarium. The viewer is looking in at a steep angle, which is greater than the critical angle, so TIR occurs and the viewer sees the glass as though it is a mirror. A finger pressed lightly against this side window reveals another property of internal reflection: the ridges of the finger are visible, but not the valleys between. The light exits the glass slightly, and interacts with the skin in intimate contact with the surface, but not with skin a few microns away. This propagation of the light out of the window is called the "evanescent wave."

The fact that the ridges are seen but not the valleys indicates this wave is traveling only a short distance out of the window, which is termed the depth of penetration. The appearance of the ridges indicates that the light is being absorbed by the ridges (otherwise, you would not see them) – this is the phenomenon of ATR. The light leaving the window is partially absorbed – attenuated – by the interaction with the finger tip.

ATR works extremely well with IR accessories. Samples are brought into intimate contact with the ATR element, which is a crystal made of an IR transparent material. The evanescent wave interacts with the sample, and passes back into the ATR crystal carrying information about the interaction (attenuation due to absorption). The key aspects of an ATR accessory are the available spectral range, the chemical and physical properties of the crystal, and the depth of penetration of the evanescent wave. Details about all of these parameters can be found in the Help files of Thermo's OMNIC™ software for the common ATR crystal types.

Choice of the crystal material has a profound effect on the ATR experiment. For instance, diamond is considered to be a "universal ATR material." The hardness, chemical inertness and spectral range are indeed impressive, and in many applications diamond is ideal. However, there are cases where other materials are better suited.

Many black rubber materials, such as seen in Figure 1, are used in heavy duty applications. Automobile tires and the gaskets used in door sweeps or flexible insulation are examples. These materials are difficult to analyze using IR, because the blackening is due to the presence of carbon black. This absorbs and scatters IR radiation severely, making these materials opaque to IR radiation even in thin sections. The analysis of these materials is critical, however, especially in failure analysis. There is much interest in additives in high carbon-black rubbers (20-30% or more), for which IR could be a useful probe. Also, wear patterns or sudden performance changes due to formulation need to be analyzed without destruction of the part.

The depth of penetration of an ATR crystal is determined by the formula

$$DP = \lambda / (2 \pi N_C (\sin^2\theta - (N_S/N_C))^{1/2})$$

Figure 1: Examples of black rubber materials used in heavy duty applications, such as automobile tires and door sweep gaskets

N_C and N_S are the indices of refraction for the crystal and the sample, respectively, θ is the angle of incidence of the light, and λ is the wavelength of the light. For diamond at 1000 cm^{-1}, this leads to a depth of penetration near 2 microns. For germanium, the higher index yields a depth closer to 0.67 microns.

Thermo ELECTRON CORPORATION

Experimental

Samples of high carbon black rubbers (CB-rubber) were analyzed using a Smart Orbit™ accessory mounted in a Nicolet™ 380 spectrometer, as seen in Figure 2. The Smart Orbit permits rapid exchange of top plates containing different materials, like diamond, Si or Ge (the unit can also use specular reflection plates). The spectrometer and accessory were purged with dry air. Spectra were obtained using 32 scans at 4 cm^{-1} resolution using OMNIC software; no post-processing was performed. Spectra using both diamond and Ge plates are shown in the figures.

Figure 2: Nicolet 380 FT-IR spectrometer with Smart Orbit accessory

Results

For this analysis, the key difference between the two top plates, diamond and Ge, lies in the different depths of penetration. The pressure used for Ge is lower than for diamond, but this material makes excellent contact without high pressure, so this is not a limitation. From the discussion above, the beam penetrates about 3 times further in the case of diamond than with Ge.

The 20% CB-rubber spectra in Figure 3 show considerable differences in the spectra. Spectra taken using diamond ATR show extreme absorption, with the peaks either not being visible or appearing as derivative bands. The same material on Ge, however, shows a much cleaner spectrum. Similar spectra of a 30% CB-rubber are shown in Figure 4.

Search results are strongly influenced by this phenomenon. The highest CB-rubber tested was 40%. The search against Thermo Electron Polymer and Additives Libraries shows a low match value with the diamond spectrum, while the Ge spectrum (Figure 5) searches accurately to the correct polymer class.

Conclusion

The flexibility of the Smart Orbit accessory allows the use of multiple crystals for analyzing different materials. While the diamond is an excellent choice for many materials, the Ge crystal does allow for the analysis of high CB-rubbers. The coupling of the accessory with spectrometer systems and libraries from Thermo provide an excellent solution for the analysis of polymers and other difficult to analyze materials. The all-reflective design of the Smart Orbit offers a wide spectral range when using a diamond crystal (at least down to 100 cm^{-1} in the far-IR region), but even when using a Ge crystal, the crystal designs allows you to collect data down to 500 cm^{-1}.

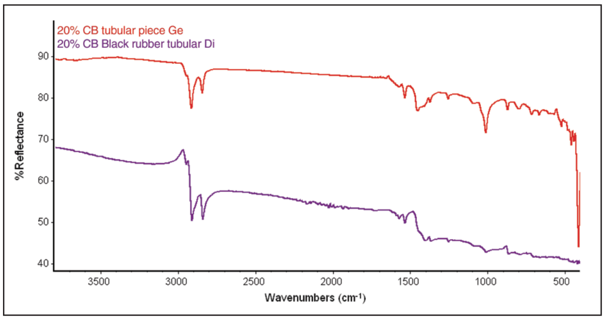

Figure 3: Comparison of Diamond and Ge ATR spectra for a 20% CB-rubber

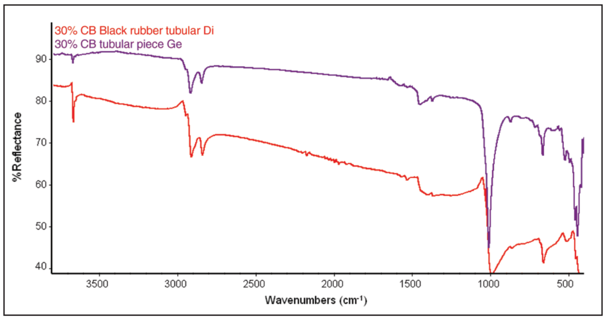

Figure 4: Comparison of Diamond and Ge ATR spectra for a 30% CB-rubber

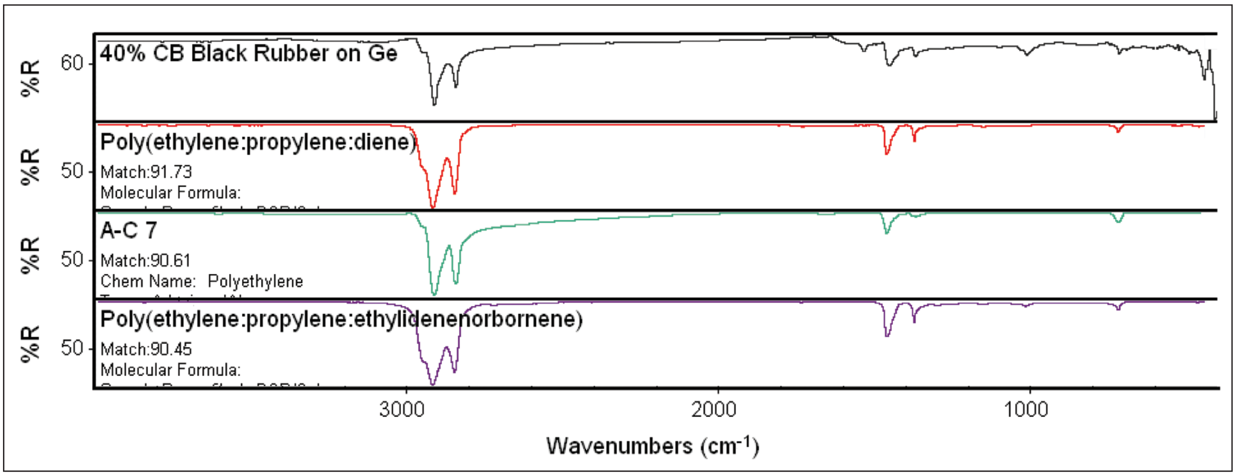

Figure 5: Ge spectra search results against polymer libraries from Thermo produced accurate class identification for a 40% CB-rubber

In addition to these offices, Thermo Electron Corporation maintains a network of representative organizations throughout the world.

Australia
+61 2 9898 1244
Austria
+43 1 333 50340
Belgium
+32 2 482 30 30
Canada
+1 800 532 4752
China
+86 10 5850 3588
France
+33 1 60 92 48 00
Germany
+49 6103 4080
India
+91 22 2778 1101
Italy
+39 02 950 591
Japan
+81 45 453 9100
Netherlands
+31 76 587 98 88
Nordic
+46 8 556 468 00
South Africa
+27 11 570 1840
Spain
+34 91 657 4930
Switzerland
+41 61 48784 00
UK
+44 1442 233555
USA
+1 800 532 4752

www.thermo.com

AN50829_E 01/05M

Thermo
ELECTRON CORPORATION