FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY FOR MATERIAL CHARACTERIZATION AT THE UNIVERSITY OF WASHINGTON BOTHELL

Luke B. Daanomah, Bryce Denis
Under the direction of John W. Bridge Ph.D, P.E.

ABSTRACT: Fourier Transform Infrared (FTIR) Spectroscopy is a powerful material analysis technique that can be used to help solve engineering problems. It can be used alone as a quick material characterization tool, as well as in complement with other techniques such as Differential Scanning Calorimetry (DSC), Gas Chromatography (GC), Nuclear Magnetic Resonance (NMR), or Raman Spectroscopy to gain the complete physical and chemical makeup of a material. The application of FTIR spectroscopy in undergraduate research at University of Washington Bothell (UW Bothell) has greatly aided in solving materials-related problems in a variety of real-world engineering problems. At the UW Bothell, FTIR techniques are being used to analyze synthetic granular composites used on horse racetracks, crumb rubber from artificial turf and rubber flooring material (RFM), and for comparative studies of polymers such as polyvinyl acetate (PVAc). Within the granular composite track surface, FTIR tests indicated oxidation degradation of the wax binder used to hold sand, polymer fiber, and rubber constituents together (Bridge, Weisshaupt, Fisher, Dempsey, & Peterson , 2016). In the RFM, the FTIR spectra exhibits the presence of strong C-H and C-C bonds at approximately 2850 cm-1 and 915 cm-1 respectively. Also, shown was the presence of calcium stearate at 1600 cm-1, calcite at 1400cm-1, and zinc oxide (ZnO) at 690 cm-1 that gives RFM its waterproofing, scratch hardness, and UV protection properties, which are especially important properties desired in the tire industry. Finally, in the comparative study of PVA, FTIR revealed that different amounts of acrylic contents in PVAc give it slightly different properties. The PVAc sample with higher acrylic content shows a peak in the FTIR spectra around 1173 cm-1 which is of the acrylate copolymer group. This gives PVAc "special properties"—a disruption in the crystal structure of the PVAc, making it more flexible at room temperature.

Introduction

There are many analytical tools available to the materials engineer to characterize polymeric materials in order to design the best material for an application or to solve problems with existing materials. Fourier Transform Infrared (FTIR) is arguably one of the best tools available for quick, efficient analysis of engineering polymers. FTIR is a spectroscopy technique, which involves passing an infrared light source through a sample to measure its reflectance, or absorbance in the infrared spectrum. This technique produces a spectrograph, which reveals compositional information on material structure to help identify or characterize a given material sample. Figure 1 shows a typical spectrograph of a poly vinyl acetate (PVAc) glue sample taken with the Thermo-Nicolet iS50 Spectrometer with an ATR (Attenuated Total Reflectance) diamond crystal; the specific peak wave numbers and absorption strengths indicate the type of material.

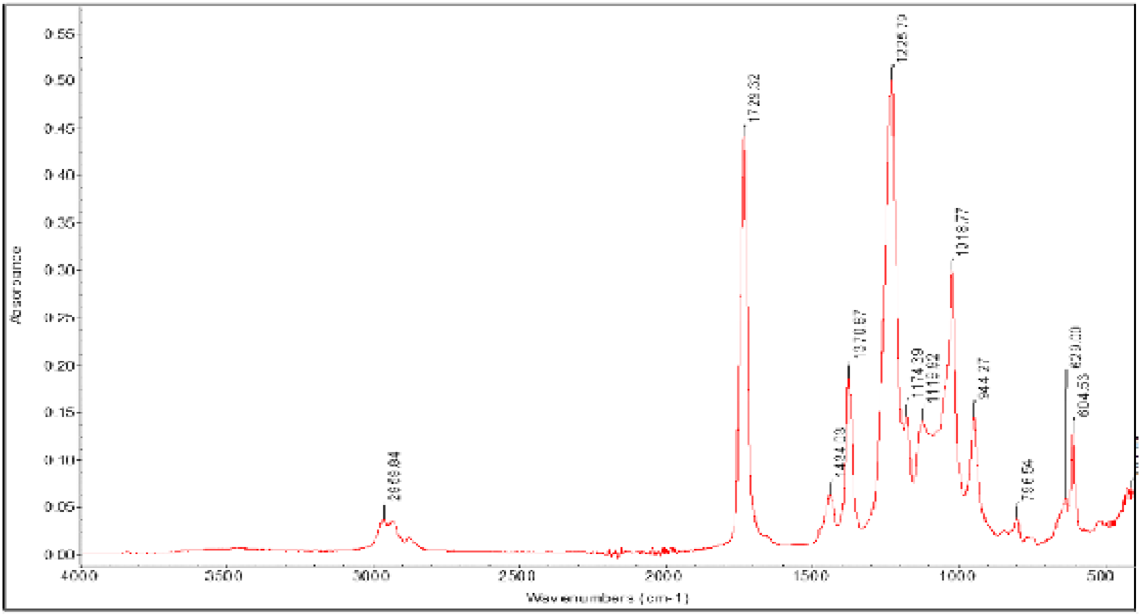

Figure 1: A spectrograph of poly vinyl-acetate (PVAc) Glue sample taken with the Thermo-Nicolet iS50 Spectrometer.

Figure 1 above is a typical FTIR spectrum of PVAc and water. It exhibits the prominent absorbance peaks, often occurring between 1800 and 500 wave numbers. Figure 2 below is a sample spectrum of a rubber flooring material obtained with the same FTIR machine but configured with a germanium crystal. The various peaks/depressions in an FTIR spectrum indicates the chemical and structural composition of a material (i.e. the material's bonding structure and chemical nature) that gives the material its physical, mechanical, chemical, and other properties.

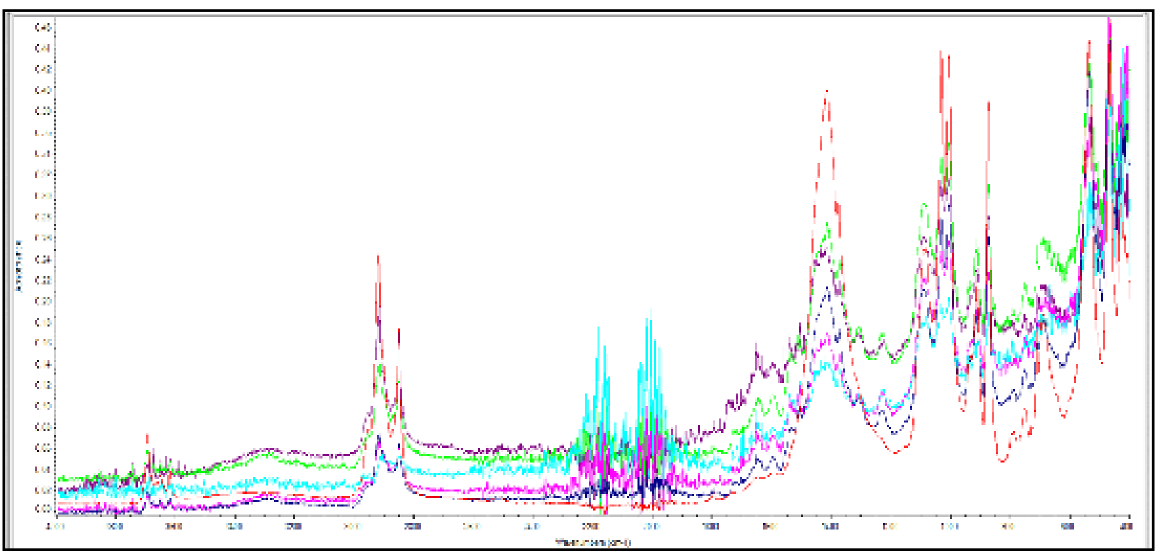

Figure 2: Sample FTIR Spectra (superimposed) of a rubber material showing various functional groups between the 400 cm-1 and 4000 cm-1 range.

Operation

In an FTIR instrument, an infrared (IR) beam is passed through the sample where part of the energy, or photons, are absorbed and part is transmitted. The transmitted IR reaches a detector, which records the intensity of the IR. The response of the detector yields information about the wavelengths being transmitted at once, which provides information about the signature of the composition of the given sample. The given signal is then digitized and processed via a computer. Finally, the various frequencies measured for the given material sample is translated into a spectrum by a Fourier transform algorithm. Every element has a distinct light wave signature and can be easily identified based on the output light pattern. The physical properties and characteristics of a molecule or substance is produced from the vibration spectra of the substance. An infrared spectrum of absorption or emission of a solid, liquid or gas is obtained in FTIR spectroscopy, and the infrared spectrum can be used as a fingerprint for identifying a substance by comparing it with the spectrum of previously recorded reference spectra (PerkinElmer, Inc., 2005). Most FTIR instruments are accompanied by software that has a spectral library or database which one can use to search for a quick match of the functional groups in a sample. However, the most useful factor in FTIR spectral interpretation is prior knowledge of the sample or experience analyzing spectra of the material under investigation. This is something one quickly finds to be an art and it is especially true for more complex materials such as polymers and composites. Additionally, a good knowledge of chemistry is very useful and makes spectral interpretations much easier.

Application

FTIR application cuts across all phases of a product's lifecycle, from design through manufacturing to failure analysis. There are several areas where the application of FTIR analysis have proven to be very useful including material identification and verification, copolymer and blend assessment, identification of additive and quantification, contaminant identification, molecular degradation assessment and so on (Coates, 2000). FTIR has proved effective for "the characterization of polymers used as protective and consolidant treatments" (Doménech-Carbó, 2008; Chércoles Asensio, San Andrés Moya, De la Roja & Gómez, 2009; Casadio &; Toniolo, 2004; Miliani et al., 2010). FTIR reflectance has also been used as a non-invasive technique for identifying pigments and organic binders in wall paintings and contemporary artworks (Rosi et al., 2009 & 2010; Vagnini et al., 2009). FTIR can be used on materials ranging from simple compounds

Figure 3: Thermo Scientific Nicolet 380 (Left) & Nicolet iS50 (Right) FTIR Spectrometers used at UW Bothell.

to complex compositions which requires careful analysis and efficient use of accompanying FTIR software libraries.

FTIR spectroscopy is used in undergraduate research and has greatly aided in solving materials-related problems in real-world engineering application and practice. This paper discusses three example projects in which FTIR techniques were utilized at the UW Bothell's Material Testing and Characterizing Lab (MTCL); 1) the oxidative analysis of the wax binder used in synthetic granular composite horse racetracks, 2) the characterization of rubber flooring material, and 3) comparative studies of three grades of Polyvinyl Acetate (PVAc).

Materials and Experimental Methods

The UW Bothell – MTCL has access to the Thermo-Nicolet 380 and iS50 FT-IR spectrometers (Figure 3) which run the OMNIC Specta software that has an elaborate spectral library, which is useful in gaining quick insights about a material sample. For all FTIR projects an approximate sample size of 2 – 5 ± 1.0 mg are placed on the spectrometer crystal and clamped down.

FTIR Method Applied

1. Turn on Spectrometer and allow to warm up for an hour.
2. Clean the surface of the crystal using a Q-tip dipped in Isopropyl alcohol.
3. Open OMNIC Specta software on computer
4. Run background test as a baseline against which the sample's spectra will be taken.
5. Place very small amount of the sample (2-5 ± 1.0 mg) on the surface of the crystal and clamp down.
6. Run test via the OMNIC Specta software.
7. Use analysis tool on the software and run spectral match by comparing sample's spectra with the spectral library of materials with known spectral signature.

All FTIR tests follow the same procedure with the only difference involving what type of sample is tested. For liquid samples the clamp is often not used. Additionally, the type of crystal selected for the given test depends on the material being tested. A diamond crystal (Figure 4) is commonly used due to its robustness and durability. Also, a germanium crystal can be used for high absorption materials such as carbon black filled rubber. The Nicolet 380 uses a diamond crystal and the Nicolet iS50 has both a diamond and a germanium crystal (Figure 5). The average test-run time for an FTIR is between 30 seconds and 1.5 minutes. The test results can be printed or emailed from the computer for further inspection.

Figure 4: Diamond crystal for the Thermo – Nicolet iS50 FTIR – ATR

Figure 5: Germanium crystal for the Thermo- Nicolet iS50 FTIR ATR

The Oxidative Analysis of the Wax Binder used in Synthetic Granular Composite Horse Racetracks

FTIR techniques were used to analyze a wax or polymer binder used to hold sand, polymer fiber, and rubber constituents together in horse racing synthetic surfaces (Figure 6). To study the degradation of these surfaces over time, the oil in the wax binder was extracted via Soxhlet extraction and analyzed using FTIR spectroscopy. The objective of this investigation was to analyze the wax binder to quantify and determine any oxidative degradation of this binder material that held the granular composites together. It is hypothesized that the degradation of the wax binder leads to loss in performance of the track surface over time. Several FTIR runs of the sample wax binder from the Thoroughbred horse racetrack over a period of seven-years were performed and compared. The test was performed using the diamond crystal of the Nicolet iS50 FTIR-ATR spectrometer.

Figure 6: Photo of fresh synthetic granular composite used on horse racetrack surfaces made up of silica sand particles mixed with binder (wax), polypropylene fibers and rubber (black) particles.

The Characterization of Rubber Flooring Material (RFM)

The next project involved the use of the Thermo-Nicolet iS50 FTIR spectrometer to help identify the functional groups in crumb rubber used on sports surfaces such as those in many football stadiums. Again, FTIR was hypothesized to be the most efficient and effective tool for this analysis. RFM is also used as a safe and comfortable alternative to wooden and tile flooring or carpets. They are often used in places like gymnasiums, stores, and office spaces as comfortable standing pads. Safety hazards have been brought up about different rubber particles in the past because many of these materials are made from recycled car tires and the different chemical components in them raise a lot of health and safety concerns for people who are exposed to them on a regular basis (for instance, athletes). Also, over time, exposure to the elements and other factors affect their mechanical and chemical structure and may cause them to lose their properties. FTIR was therefore used to gain a quick understanding of the structural and chemical makeup of this material. Several test runs were made using the diamond crystal (Figure 4) but the spectra generated from these tests had too much signal-to-noise-ratio (SNR)—the ratio of a signal (intensity of a peak) in a spectrum to noise (random fluctuations of baseline) in the spectrum. This was due to both the crystal used and the high carbon content of the rubber material. Hence, the diamond crystal was switched out for a germanium crystal (Figure 5) which has a better working pH range and much higher refractive index of all FTIR crystal materials available.

Comparative Studies of three grades of Polyvinyl Acetate (PVAc)

This last project involved the use of the Thermo-Nicolet 380 FTIR spectrometer to analyze the structural properties of polyvinyl acetate adhesives. Three separate PVAc grades were prepared (Figure 7) and an FTIR of each sample grade was performed to compare their properties and help determine the cause of cracks and fractures. The goal of this project was to quickly test and characterize a replacement product from different grades of PVAc and determine suitability. FTIR spectra were coupled with DSC testing to analyze this material by finding the thermal glass transition temperature (Tg) and comparing the FTIR spectra to known PVAc spectra. The spectra revealed composition information of the different grades of PVAc.

Figure 7: Oven Cured 7g Samples. Samples 1-3 are laid out from left to right. Sample 1 has been bent over to show ease of deformation. Samples 2 and 3 show cracking.

Results and Discussion

The Oxidative Analysis of the Wax Binder used in Synthetic Granular Composite Horse Racetracks

The resulting spectra from the FTIR analysis revealed an increase in oxidation peaks as the horse racetracks age to account for the deterioration in the performance of the tracks, due to the degradation of the wax binder (Bridge et al., 2016). The FTIR was extremely effective in identifying and quantifying oxidation activity. Below are the spectra from the FTIR analysis showing the spectra time series near 1700 cm-1 for both the wax binder and the extracted oil for the racetrack over the period of seven years. The peak around 1730 cm-1 is due to stretching of the C=O bond which results in the molecular vibration of this carbonyl group in the wax binder as shown in Figure 8 & 9.

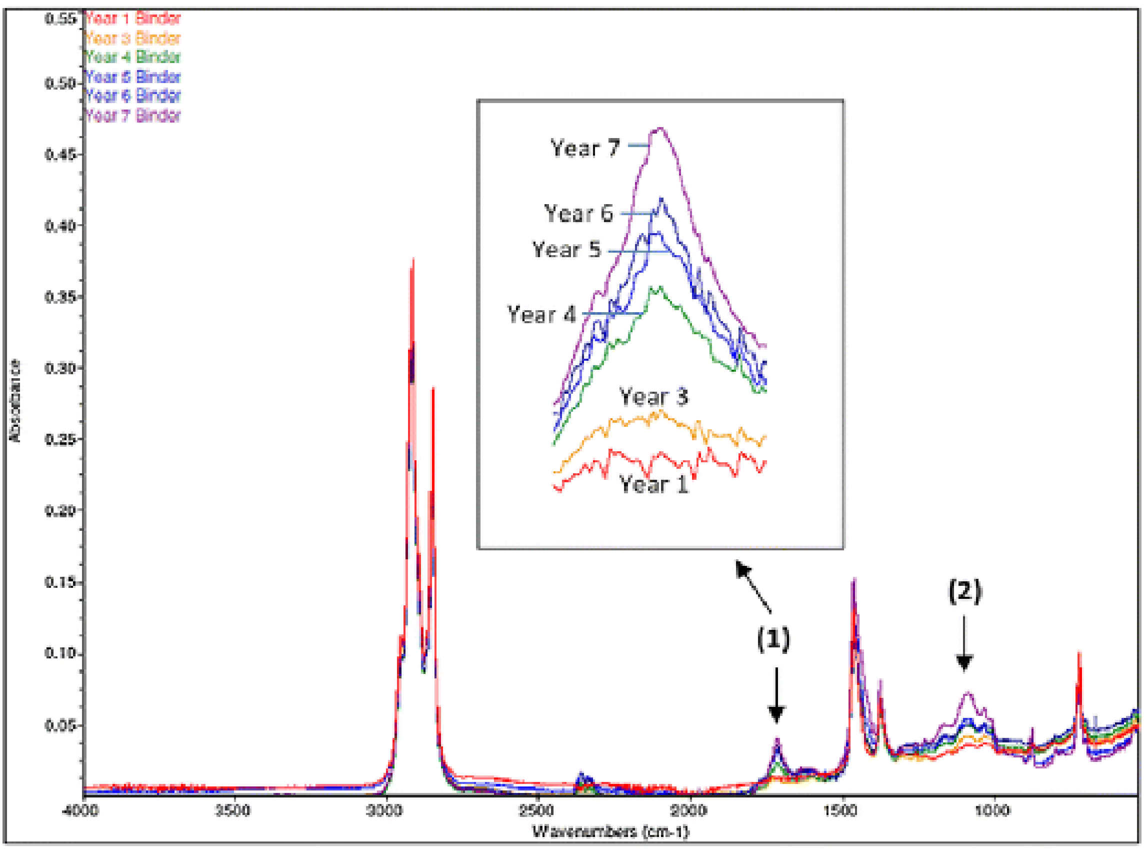

Figure 8: Binder FTIR Spectrum showing difference in spectra time series near 1700 cm^{-1}.

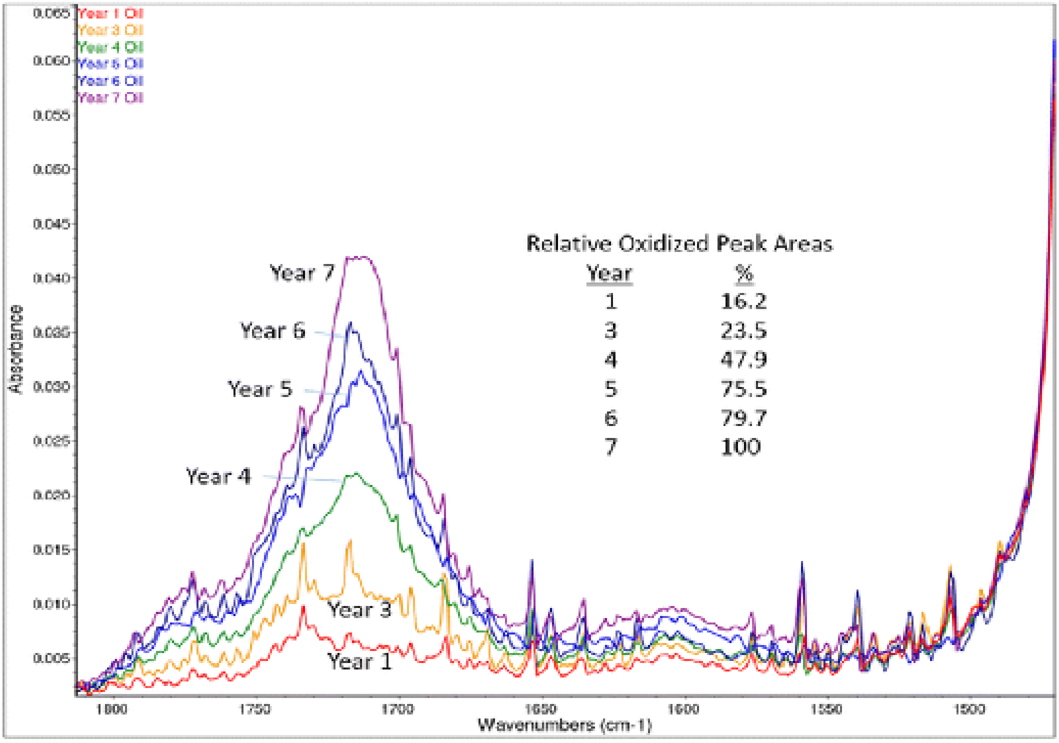

Figure 9: Expanded view of extracted oil FTIR spectrum comparing oxidative peaks in 1700 cm^{-1} region.

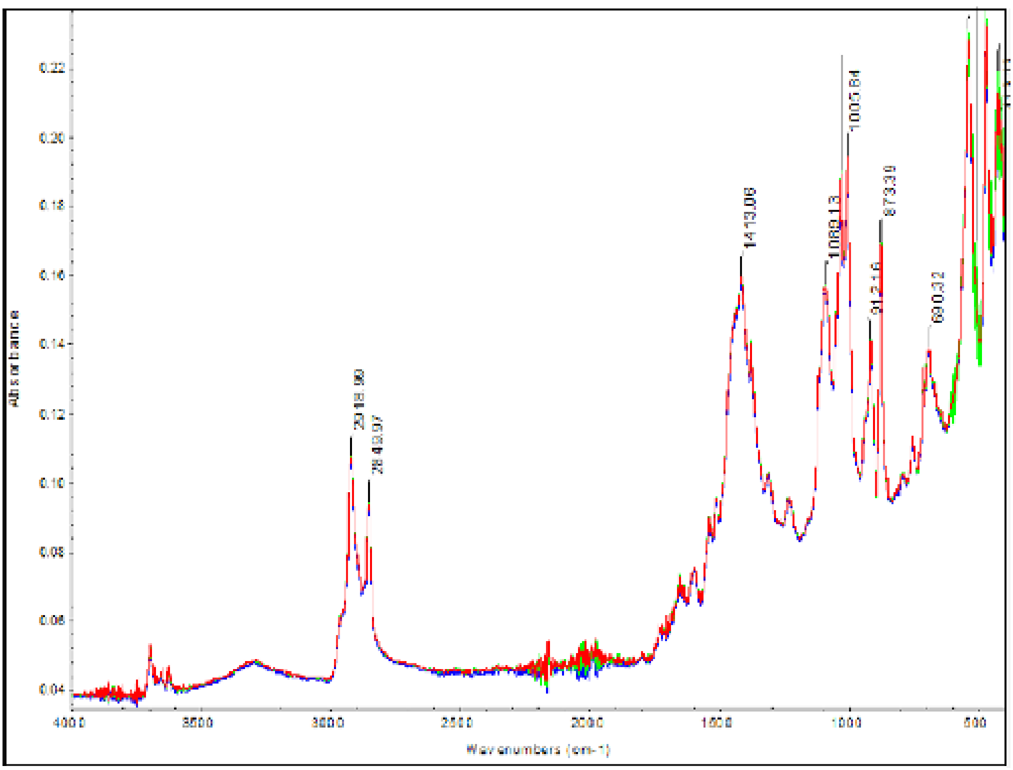

Figure 10: FTIR Spectrum of RFM taken using a germanium crystal. It shows the C-C, C-H & CH_3 bond peaks at 915 cm^{-1}, 2850 cm^{-1}, and 3000 cm^{-1} respectively.

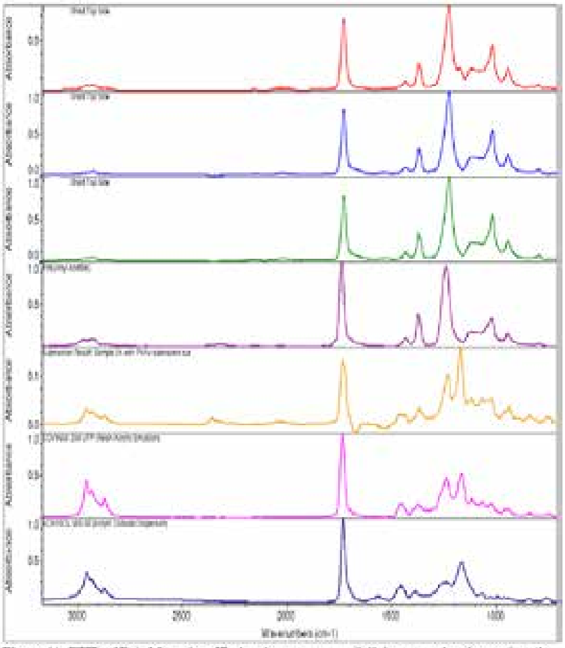

Figure 11: FTIR of Dried Samples. IR absorbance spectra of all three samples show primarily PVA. Sample 1 shows additional peak structure at 1173 cm^{-1} due to acrylic content.

Also, the performance of FTIR testing has been complemented with DSC testing to fully characterize the degradation of granular composite material. In addition to that, Raman spectroscopy has recently been employed and will hopefully shed more light on the degradation of the granular composite components.

Characterization of Rubber Flooring Material (RFM)

From the FTIR Spectrum of RFM (Figure 10), two peaks clearly indicate the presence of the C-H and C-C bonds at approximately 2850 cm-1 and 915 cm-1 respectively. These single-carbon, hydrogen and oxygen bonds are very strong and makes the material non-reactive as well as give this material good bond strength in its covalent bonds. The presence of the CH3 bond at 3000 cm-1, the calcium stearate at 1600 cm-1, and calcite at 1400cm-1, give RFM its waterproofing and scratch hardness properties, especially important properties in tires. Also, the identified zinc oxide (ZnO) found near 690 cm-1 is heavily used in the rubber industry for the vulcanization of rubber, and as a good UV protection in tires. This information is critical when comparing other RFM materials in conjunction with mechanical property tests. Below in Figure 10 is the FTIR spectra of RFM that was obtained using the germanium crystal.

Comparative Analysis of Polyvinyl Acetate (PVAc)

A comparison of the FTIR absorbance spectra after 48 hours of drying (Figure 11) reveals a peak in sample 1 around 1173 cm-1 which is not present in the infrared (IR) spectra of samples 2 and 3. Further analysis of this peak showed that

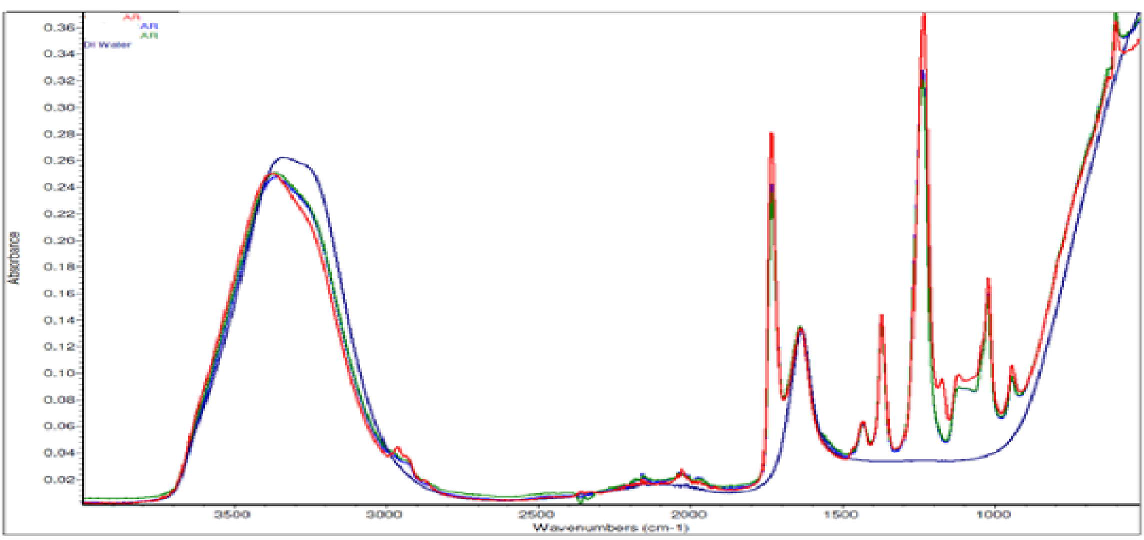

Figure 12: FTIR of as Received Samples. The wet samples show similar IR peak structure, primarily PVA and water. Sample 1 (red) shows slight differences due to acrylic content.

it is of the acrylate copolymer group. These two samples (2 & 3) show purely PVAc spectra as shown in Figure 11. Performing further examination on the three samples revealed that they are slightly viscous at room temperature (22-degree C). Sample 1 was found to be very pliable at room temperature, and can deform and stretch without breaking. Samples 2 and 3 were found to be comparatively brittle at room temperature and would crack if bent more than a few degrees (evident from image of the 3 samples in Figure 7 above). The glass transition temperature (Tg) values measured using DSC were consistent with these observations. The comparative analysis of these three samples therefore revealed that different amounts of acrylic contents in PVAc will give it slightly different properties.

Finally, the comparison of the FTIR absorbance spectra for the uncured samples prepared shows a slight difference due to acrylic contents in the samples as indicated in Figure 11 below. The different PVAc/Acrylic mixtures in the 1100 cm-1 region is due to slightly different bond energies of the C-O bonds in the ester groups of each polymer. This indicates that the addition of a small amount of acrylic to PVAc gives it “special properties.” That is, the small acrylic content in PVAc disrupts the crystal structure of the PVAc, making it more flexible at room temperature as seen with the image of sample 1 in Figure 7, and evidenced in its FTIR spectrum in Figure 12 compared with that of sample 2 & 3.

Conclusion

FTIR proved to be a powerful analytical technique that has been employed to solve commonly encountered engineering problems, particularly with polymeric materials. As exhibited in the three successful projects described at UW Bothell, the use of FTIR resulted in definitive chemical analyses that resulted in immediate engineering decisions or shed light on compositional changes that affect mechanical properties. In the degradation study of the wax binder used to hold sand, polymer fiber, and rubber constituents together in synthetic horse racetrack materials, substantial oxidation was discovered - this may be contributing to the deterioration in performance of these tracks over time. FTIR also successfully identified the functional groups in a rubber flooring material (AFM); thereby aiding in correlating composition to mechanical properties. Finally, FTIR was used in a comparative study of three (3) different grades of polyvinyl acetate (PVAc) - to determine which grades were better suited for use in a given application. FTIR spectroscopy can be used as a quick analytical tool for gaining insights on material composition, and complements other techniques such as DSC, NMR, and Raman Spectroscopy. FTIR spectroscopy has therefore proven to be a very effective and useful tool for material characterization and testing at the UW Bothell Materials Testing and Characterization lab. Its application in undergraduate research at the UW Bothell MTCL has indeed aided the development of useful solutions for real world engineering problems for industry clients and partners.

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References

Bridge, J. W., Weisshaupt, K. S., Fisher, R. M., Dempsey, K. M., & Peterson, M. L. (2016). Chemical degradation of a paraffin wax-based binder used in granular composite sport surfaces. *Sports Engineering*, 20(1), 41-51.

Casadio, F., & Toniolo, L. (2004). Polymer treatments for stone conservation: methods for evaluating penetration depth. *Journal of the American Institute for Conservation*, 43(1), 3.

Chércoles Asensio, R., San Andrés Moya, M., De la Roja, J. M., & Gómez, M. (2009). Analytical characterization of polymers used in conservation and restoration by ATR-FTIR spectroscopy. *Analytical and Bioanalytical Chemistry,* 395(7), 2081-2096.

Coates, J. (2006). Interpretation of infrared spectra, a practical approach. *Encyclopedia of Analytical Chemistry.*

Doménech-Carbó, M. T. (2008). Novel analytical methods for characterizing binding media and protective coatings in artworks. *Analytica Chimica Acta,* 621(2), 109-139.

Jansen, J., & Garry, M. (2016). Technical Note: Identifying Failures and Ensuring Quality of Plastic Materials (AR52594_E 05/14M). Retrieved from appliance DESIGN website: http://tools.thermofisher.com/content/sfs/brochures/AR52594-Identifying-Failures-Ensuring-Quality-Plastic-Materials.pdf

Miliani, C., Rosi, F., Brunetti, B. G., & Sgamellotti, A. (2010). In situ noninvasive study of artworks: The MOLAB multi-technique approach. *Accounts of Chemical Research*, 43(6), 728-738.

PerkinElmer, Inc. (2005). FT-IR Spectroscopy Attenuated Total Reflectance (ATR) [PDF Document]. Retrieved from http://www.utsc.utoronto.ca/~traceslab/ATR_FTIR.pdf

Rosi, F., Daveri, A., Miliani, C., Verri, G., Benedetti, P., Piqué, F., … Sgamellotti, A. (2009). Non-invasive identification of organic materials in wall paintings by fiber optic reflectance infrared spectroscopy: a statistical multivariate approach. *Analytical and Bioanalytical Chemistry,* 395(7), 2097-2106.

Rosi, F., Miliani, C., Clementi, C., Kahrim, K., Presciutti, F., Vagnini, M., … Sgamellotti, A. (2010). An integrated spectroscopic approach for the non-invasive study of modern art materials and techniques. *Applied Physics A*, 100(3),

Vagnini, M., Miliani, C., Cartechini, L., Rocchi, P., Brunetti, B. G., & Sgamellotti, A. (2009). FT-NIR spectroscopy for non-invasive identification of natural polymers and resins in easel paintings. *Analytical and Bioanalytical Chemistry,* 395(7), 2107-2118.