2019

Case Studies of Potential Reference Materials in Cultural Heritage Science

Heidi Kastenholz
Butler University

BUTLER UNIVERSITY HONORS PROGRAM

Honors Thesis Certification

Please type all information in this section:

Applicant   Heidi Kastenholz
                              (Name as it is to appear on diploma)

Thesis title   Case Studies of Potential Reference Materials in Cultural Heritage

               Science

Intended date of commencement   May 11, 2019

Read, approved, and signed by:

Thesis adviser(s) _____   5/8/19
                                                    Date

Reader(s) _____   5/8/19
                                                    Date

                                                    Date

Certified by   _____   _____
                    Director, Honors Program   Date

For Honors Program use:

Level of Honors conferred: University   _____

                            Departmental _____

                                         _____

                                         _____

Case Studies of Potential Reference Materials in Cultural Heritage Science

A Thesis

Presented to the Department of Chemistry and Biochemistry

College of Liberal Arts and Sciences

and

The Honors Program

of

Butler University

In Partial Fulfillment

of the Requirements for Graduation Honors

Heidi Violet Kastenholz

May 10, 2019

Abstract:

The study of cultural heritage objects requires reference materials for comparison in order to determine the identity of chemical compounds in historically/culturally significant artifacts. The reference materials available today can be inaccurately labeled, can contain inauthentic compounds, or can simply be formed differently than what the labeled material should be. Utilizing the laboratory at the Indianapolis Museum of Art at Newfields, three case studies were conducted over three different potential reference materials in order to properly identify each of the three materials being focused on here. Based on the analysis, the labels for these materials often do not match the actual material. This mislabeling should be addressed as incorrect properties can result in misinformed conservation efforts that have potential to go awry.

Table of Contents

Background:

At the intersection of science and art, there is cultural heritage chemistry. It is here that conservation scientists work to perform qualitative and quantitative analyses in their efforts to identify materials used in historical and cultural objects, by comparison to a reference material. In broad terms, a reference material is a standard compound that all in the field can agree has a known composition/purity. The need for references in conservation science comes from the need to identify what materials were used to create the artifact. Through non-destructive techniques, conservation scientists are able to compare information gained from the analysis of a material in the artifact to a library of reference information.[1]

However, in the field of heritage chemistry, materials used for reference today are not always similar to those used hundreds or thousands of years ago; the new materials may only share a name and nothing else with their historic counterpart, such as paints labeled as "Cadmium Red Hue." A hue means the color is similar but there is no cadmium present in the paint. Or new materials may be an industrial material where the composition does not matter (only the end product does), like in house paint made from earth pigments where the color of the paint needs to be within a range but the natural material doesn't always fall within such a range. This can result in compounds being added to the material to control for characteristics like color, like a synthetic pigment to house paint to make sure the color is correct, and texture, such as the commercial product Floetrol which reduces brush marks in acrylic and latex house paint.

My interest in cultural heritage research came from two experiences I've had through Butler University. The first was taking a study abroad course, Chemical Issues: Chemistry in Art (CH418). In this class, we learned about primarily the painter's materials from the ground to the varnish of a painting and how we can identify the materials used in the work with chemical

instrumentation. The second experience was conducting this kind of research through the Butler Summer Institute this summer in the Conservation Science Lab at the Indianapolis Museum of Art at Newfields. The issues I encountered through these experiences led me to become increasingly interested in helping address issues related to artists' materials. Many in the field of cultural heritage science are familiar with and study forgeries – a work that is purported to be by a particular artist, when in actuality it was created by another with the intent to pass it off as an original. Less often seen is a "fake" reference material – for example, a pigment which is labeled as genuine, pure Verona Green Earth but is actually a low-quality earth pigment mixed with a synthetic green to brighten the color to imitate the color of the high-quality Verona Green Earth. This idea of a fake reference material is relatively novel in its appearance in the literature.[2]

The field of cultural heritage science relies on the authenticity of reference materials for accurate identifications to be made. When references are accidentally or purposefully mislabeled, this makes the job of conserving a work that much more challenging. My thesis will describe efforts toward the authentication of reference materials and will the highlight the inaccuracies that are present in reference materials available for purchase today. Through completing my thesis, I will gain experience with a variety of analytical instruments, in-the-moment problem-solving, and finding pertinent information through literature reviews.

Experimental:

Raman Spectroscopy

The instrument used was a Bruker Senterra microspectrometer on a Z-axis gantry. The spectrometer utilized an Andor Peltier-cooled CCD detector and a 50 μm confocal pinhole. Excitation at 532 nm and below 5 mW power at the focal point of the laser was used for Raman scattering from an area of approximately 1 μm in diameter. A 50X ultra-long working distance objective was used to focus on the particles. The spectra were measured at 9-18 cm^{-1} spectral resolution with 5-10 second integrations and 5-30 coadditions. OPUS software allowed for automated cosmic spike removal, peak shape correction, and spectral calibration. To prepare pigments for Raman spectroscopy, the particles were placed on glass slides and flattened with a metal scoopula.

Fourier transform infrared (FTIR) spectroscopy

FTIR was performed on a Continuum microscope with an MCT A detector coupled to a Nicolet 6700 spectrometer purged with dry, CO_2-free air. Analysis was done in transmission mode. A square microscope aperture of approximately 100 μm was used to isolate the sample area under a 15X Schwarzschild objective. The spectra collected are the average of 32 scans at 4cm^{-1} spectral resolution. Samples were prepared by placing a few particles of the minerals on the diamond cell and then flattening them (Thermo Spectra Tech), removing the top diamond window, and analyzing the thin film of sample on the bottom diamond window. Analysis was also performed using a SpectraTech Smart Orbit diamond ATR attachment and a DTGS detector. In this instance, the spectra collected are the average of 64 scans. Samples for this technique did not require any preparation. Sample identification was aided by using the Infrared and Raman Users Group (IRUG) spectral reference library.

Imaging

Darkfield images were taken using a Zeiss AxioImager A1m compound microscope with a 20X
objective using a MRc5 digital photomicrography camera. Images were also taken when the
same area of a sample was being examined under UV irradiation. A DAPI filter cube was
utilized in order allow for UV-induced visible fluorescence microscopy.

X-ray Fluorescence

A Bruker Tracer III-V energy dispersive X-ray spectrometer system was utilized to collect X-ray
fluorescence spectra. The excitation source was a rhodium X-ray tube with a 3x5 mm oval
window operating at 40 keV and 6.5 μA current. The pigment particles were collected onto an
adhesive film that held the sample in place during data collection. The X-ray signals were
detected by a silicon pin diode detector. The samples were run under vacuum. Spectra were
collected over a sixty second live time. The pigment particles were collected onto an adhesive
film that held the sample in place during data collection.

Pyrolysis-Gas Chromatography-Mass Spectroscopy

PY-GC-MS was performed using a Frontier Lab Py-2020iD double-shot pyrolizer system with a
320 °C interface to a Thermo Trace GC Ultra and ISQ mass spectrometer. For the separation, a
Thermo TraceGold TG-5ms capillary column (30 m x 0.25 mm x 0.25 μm) was used with 1
mL/min of He as the carrier gas. The spilt injector was set to 275 °C with a spilt ratio of 100:1.
The GC oven temperature program was 40 °C for 2 minutes, ramped to 320 °C at 20 °C/min,
followed by an isothermal stage at 320 °C for 14 minutes. The MS transfer line was at 250 °C
and the source at 300°C. The mass spectrometer was scanned from 29-600 amu for the first 3
minutes and then scanned from 45-600 amu for the rest of the run with no solvent delay. Samples
were pyrolyzed, after being purged for five minutes in the pyrolysis chamber, using a single-shot

method at 600 °C for 0.20 minutes. A small scraping from the chips were collected and were placed into a 50 μL stainless steel Eco-cup for sample preparation. Sample identification was aided by searching the NIST14 MS library for comparisons to chromatograms of authentic samples. Additionally, samples' chromatogram were compared to spectra in Tsuge *et al.* as the final deciding factor for the samples' authenticity.[3]

Case Study 1: Calcium Carbonate Polymorphs

Background:

Calcium carbonate ($CaCO_3$) is a common mineral used in various industries. It occurs naturally all over the world from the shells of marine organisms to limestone rock. It has three different polymorphs that can form depending on the temperature: calcite, the most common, aragonite, and vaterite, the least common.
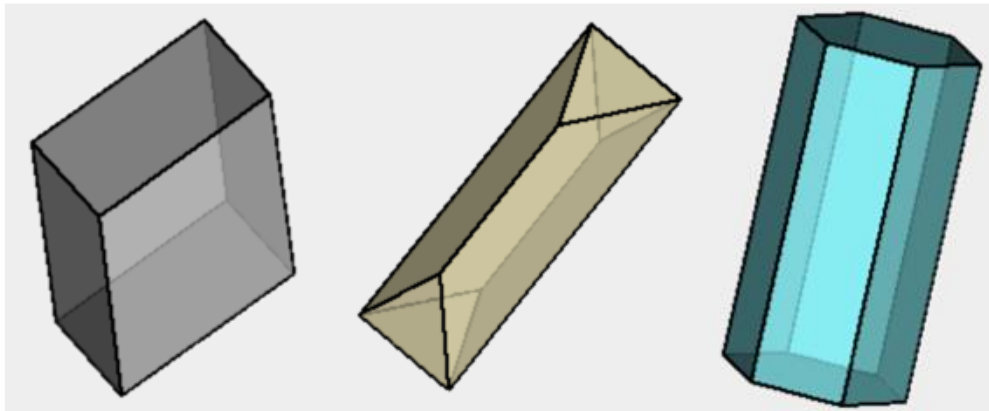
Image 1: Crystal Structure of Calcite (gray), Aragonite (tan), and Vaterite (blue). Images from: Minerals.net Glossary of Terms

Calcite has been used in various ways in works of art: it functions as a white pigment on its own, it has been added to pigments to act as an extender/ bulking agent, and it can be added to animal glues and be used as a ground for paintings.[4] Aragonite, being less common, is not used in works as art as frequently; when it is present, it is typically found as coral in jewelry. There are commercially available samples that are labeled as calcite and aragonite for use as reference materials in art conservation. After a Raman analysis of a piece of coral jewelry performed at the IMA produced two library matches, one for calcite and one for aragonite (even though only one of these should have matched), it was determined that further characterization of these minerals was required to prevent inaccurate reference library matches.

Materials:

The materials used in this case study consisted of Calcite and Aragonite from Kremer Pigmente and Calcite and Aragonite from a reference set of comminuted minerals, samples that have been finely ground to minute particles, from Cargille Labs.

Data:
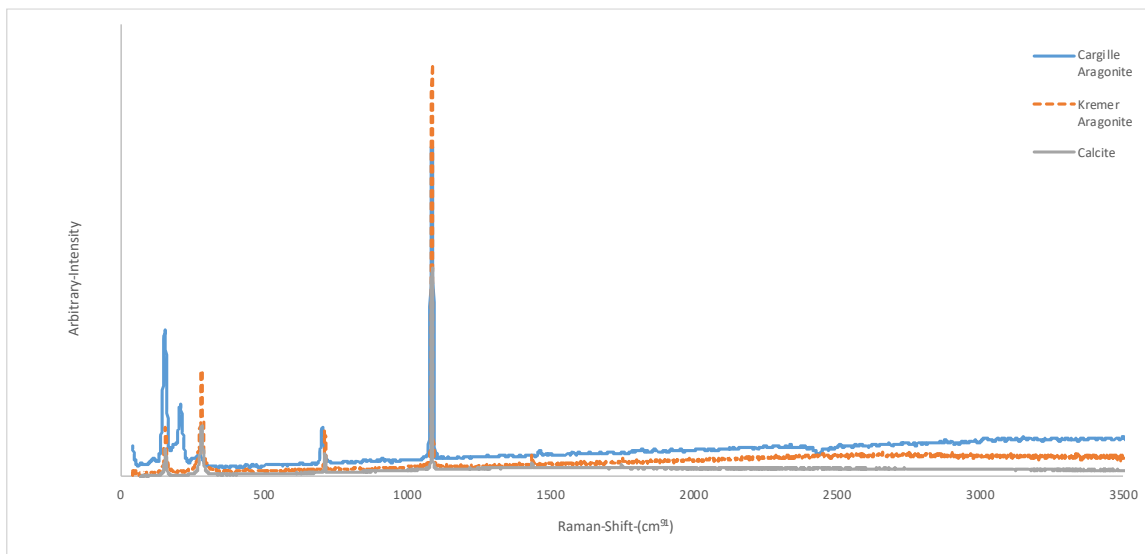
Spectrum 1: Raman Spectra of Cargille Aragonite sample (blue), Kremer Aragonite sample (orange), and Calcite sample (grey).

The data collected indicate that the sample of Kremer Aragonite has the same characteristic Raman shifts in the crystal lattice vibration region, 10-200 cm^{-1}, as the sample of Calcite. However, the sample of Cargille Aragonite had different characteristic Raman shifts in the crystal lattice vibration region as the sample of Calcite, Spectra 1. When the Kremer Aragonite was compared to the Cargille samples of Aragonite and Calcite using Infrared Spectroscopy, the IR data mirrors the Raman data in that the Kremer Aragonite spectrum is more similar to the Cargille Calcite than the Cargille Aragonite. Additional spectra for this case study can be found in Appendix 1, A: Raman spectra and B: FTIR spectra.

Discussion:

Based on the Raman and Infrared spectroscopy of the samples collected, the Kremer Aragonite can be identified correctly as actually being Calcite as the shifts in the spectra match those of a Calcite sample and not an Aragonite sample.

Conclusion:

As calcite and aragonite present as the same to the naked eye as ground white powder, it is no wonder that the Kremer supply of aragonite is more than likely not what it is purported to be. The problem may lie in that Cargille Labs is considered a scientific supplier of materials and Kremer Pigmente is not. Cargille Labs are more likely to test their products and verify their identification as they are more likely to be used for scientific analyses then the Kremer Pigmente products. A way to address this could be that Kremer does their own scientific verification or also that their products are not considered to be potential reference materials until they undergo scientific verification by individual labs. The way Kremer Pigmente buys and sells pigments also introduces the possibility that they are unaware of what the product is exactly. They buy in bulk and then repackage and sell smaller quantities to those fraction of individuals who need only 100 grams to 1 pound of a dry pigment. Perhaps Kremer's source for this product doesn't understand the relevant distinction between aragonite or calcite.

Case Study 2: Green Earth Pigments

Background:

Green earth pigments are composed of natural minerals that display varying shades of green due to the varying amounts of glauconite or celadonite that can be present in the sample. Both minerals can vary in color from light green to blackish green to blueish green. The chemical composition of the green earths vary greatly due to varying amounts of iron, chrome, and/or nickel, which provide the green color, present in the deposits. Much of the

2009.52
Madonna & Child, c. 1320
Master of Badia a Isola (Italian)
Tempera paint and wood panel

Image 2: Painting with Green Earth Pigment. Image from Indianapolis Museum of Art at Newfields.

composition is silicate with all combinations being naturally occurring.[4] It is also worth noting that the green earth pigments were named for the place from which they were dug. Regionally, there were enough deposits to prevent trading of these earth pigments.[6] The green earth pigments were most commonly used during the Renaissance. They would be used as an underpainting for the red lake pigments used for flesh tones to avoid the figures appearing as sunburnt. As the red

Image 3: Map indicating where Verona is in Italy. Image from Pickatrail.com.

lake pigments have faded, the figures in the paintings now have a greenish hue and that is seen in museums today.[7] Verona Green Earth, $(K,Na)(Fe_3,Al,Mg)_2(Si,Al)_4 O_{10}(OH)_2$, is one of the more popular green earth pigments. The best quality green earth from Verona is no longer available due to a landslide that occurred in 1922. The quality of the Verona Green Earth accessible today is estimated to be comparable to the medium to low quality pigment available historically.[6]

Aside from being used as an artists' pigment, today green earths are also used for house paints. As house paints are required to be within a standardized range of color to assure customer satisfaction, it is possible that synthetic pigments may be added to naturally occurring deposits when the color varies outside of the acceptable range. Samples of Green Earth today for conservation science can be ordered from pigment companies such as Kremer Pigmente or Blick Art Supplies. However, in order to know that the composition of the pigment is free from synthetic compounds for it to be a valid reference for historical works, the pigment or paint should be tested to ensure that they are free from adulteration. Adulteration is when a chemical is present in a compound even though it would not be present in any contents of the compound under normal circumstances. Adulteration in this case would be the presence of synthetic pigments, primarily the synthetic pigment phthalocyanine green, PG7.[8, 9] This case study revolved around determining if the synthetic pigment phthalocyanine green, PG7, is present in samples of green earth available in the Reference Library at the Indianapolis Museum of Art at Newfield (IMA) and in recently purchased samples.
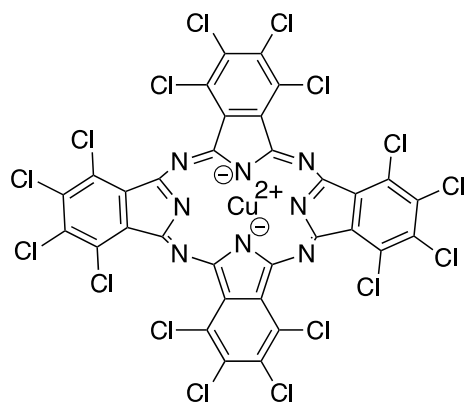
Image 4: Structure of Phthalo Green, PG7.

The purpose of this project is to distinguish adulterated samples of green earth from samples that do not have synthetic pigments present.

Materials:

Green earth pigments were tested from two suppliers: Kremer Pigmente and Williamsburg Oils, which is a trademark of Golden Artist Colors, Inc. Five dry pigment samples were analyzed from Kremer Pigmente: 11000 Verona Green Earth, 40810 Bohemian Green Earth, 40821 Green Earth from Verona genuine, pure, 40830 Green Earth from France, and

41700 Verona Green Earth enhanced with Viridian Green. Also, a pigment chart of the green pigments sold by Kremer Pigmente. The swatches tested were of pigments 40821, 40830, and 41700. There were two dry pigment samples analyzed from Williamsburg Oils: French Terre Verte and Italian Terre Verte.

Data:
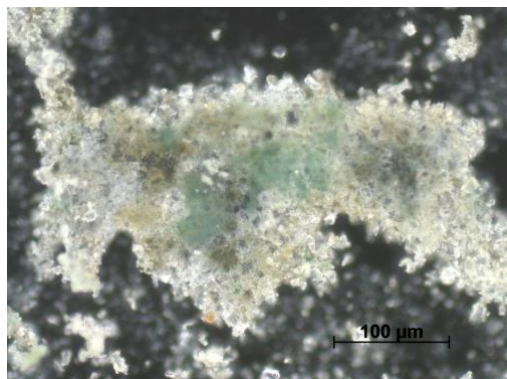
Image 5: Darkfield Image of Kremer 11000 Verona Green Earth
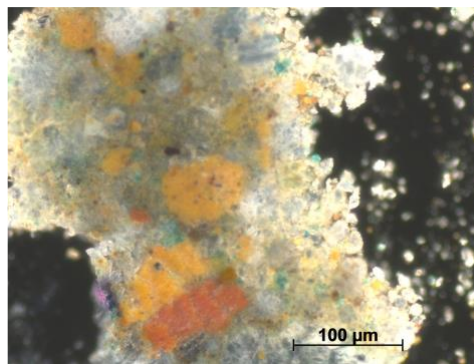
Image 6: Darkfield Image of Kremer 40821 Verona Green Earth genuine, pure

X-ray Fluorescence Data	
Sample	Elements Identified
11000, Kremer	**Fe**, Ca (Al, Si, Cl?, K, Ti, Mn, Ni, Cu, Sr)
40810, Kremer	**Fe**, K (Al, Cl?, Ti, Mn, Ni, Ca, Cr?, Cu?, Br?)
40821, Kremer	**Ca**, **Fe**, Mn, Ti (K, Al, Cl?, S, Cr?, Cu, Ni, Br?, Sr)
40830, Kremer	**Ca**, **Fe**, Ti (Al, Si, S, Cl?, K, Mn, Ni, Cu, Sr,)
41700, Kremer	**Ca**, **Fe**, Ti (Al, Si, Cl?, K, Mn, Ni, Cu, Br, Sr)
French Terre Verte, Williamsburg	**Ca**, **Fe**, **Ba**, **Co**, **Cr**, **Sr**, Mn, Zn, Sr (Al, Si, S, Cu)
Italian Terre Verte, Williamsburg	**Fe**, **Ca**, Ti, Mn, Sr (Al, Si, S, K, Ni, Cu, Br)

Table 1: X-Ray Fluorescence Data for Case Study 2: Green Earth Pigments

Imaging of select samples was done in order to analyze the size, color, and shape of the particles present in the dry pigments.

The first analysis done was an elemental technique, X-Ray Fluorescence, to determine if any elements were present that would suggest a synthetic pigment. The seven samples were each analyzed and the elemental peaks were divided into three groups: **major elements**, minor elements, and (trace elements), shown in Table 1. The second set of data collected, represented

in this section by Spectrum 2, was Raman Spectroscopy, which allowed for comparison of the

sample spectra to the spectrum of PG7. This was done in order to determine if the synthetic PG7,

specifically, was present. More data is available in Appendix 2.
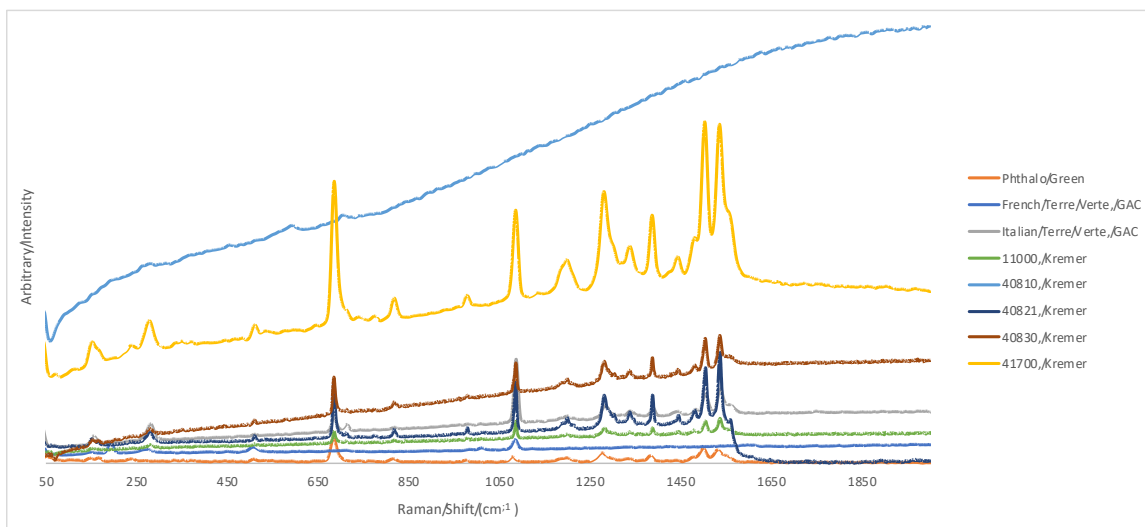
Spectrum 2: Raman Spectrum with all seven green earth samples and PG7. Legend key above.

Discussion:

Imaging showed that there are discrepancies between samples of Verona green earth. The

major elements detected in the XRF analyses correspond with what is expected of earth

pigments, Fe and Ca. However, the presence of Cu, Cl, and Br are not expected and suggest PG7

is present. However, it must be pointed out that the Rh peaks (due to the instrument containing a

Rh excitation tube) tends to interfere or mask the Cl K lines. Cr being present may suggest the

presence of Viridian ($Cr_2O_3 \cdot 2H_2O$) and Co can suggest the presence of Cobalt green (CoO ·

ZnO). Raman spectroscopy confirms PG7 is present by its characteristic peaks at 684, 1503,

1531 cm^{-1} being observed in five samples.

Conclusion:

Samples of green earth were obtained from Kremer Pigments and Williamsburg Oils and

have been found to contain PG7. There are many interesting things of note in these samples. The

first is the sample from Kremer labeled "40821 Green Earth from Verona genuine, pure". This label misleads the consumer to believing this particle pigment is natural pigment only. The second is another sample from Kremer, "41700 Verona Green Earth enhanced with Viridian Green". It should be noted that Cr was not qualitatively detected in this sample, suggesting that it lacks Viridian Green. The final issue of note is that the XRF data suggests that the Williamsburg French Terre Verte contains Cobalt Green, through detection of Co and Zn. As mentioned in the previous case study, Kremer Pigmente typically buys its product in bulk and repackages for distribution. In the case of the green earth pigments, Kremer Pigmente most likely purchases their supplier from distributors whose main focus is house paints. The color ranges for house paint must meet specific expectations. Because of this it is suspected that the distributors add synthetic pigments, such as PG7, to the natural earth pigments whose color can vary greatly. Since the issues of note were in contradiction with what was on the label, this leads us to believe that both suppliers are unaware of a synthetic pigment being present or, in the second case, being absent. The best way to address this issue would be for these art materials suppliers to test their pigments as done here and for conservators and conservation scientists to verify the materials they use as references.

Case Study 3: The ResinKit [TM]

Background:

As new industrial polymers were being developed in the 19th and 20th centuries, these materials would be used in pieces of art as well, such as Antoine Pevsner' *Head of a Woman*. The 1923 sculpture on display at the Hirshhorn Museum and Sculpture Garden of the Smithsonian Institution is made of cellulose nitrate and has deteriorated. Since these materials were so new, little was known about how they age and if and how they would react with other materials over time. As the use of plastics became more common, the processes of deterioration and degradation became better understood. When a polymer decomposes, the polymer chains break down to monomers, which are the smallest structural unit of a plastic material. Furthermore, plasticizers and other additives used to modify the properties of the plastic (e.g., to increase flexibility) can migrate to the surface of the material or be leached out of the material. As pieces of art would degrade, conservation scientists studied the materials in order to better understand how to care for the pieces of art. The need grew for samples of these polymers that were well-characterized in order to identify what exact plastic was used in a piece as many artists just use what would be available. The Plastics Group of America is one company that addresses the need for samples of various types of plastics with their product, The ResinKit[TM]. The kit includes fifty resin (polymer) chips. These chips represent both common materials, such as PVC (polyvinyl chloride) and less common materials, like polymethylpentene. This product is marketed as the "most comprehensive and cost-effective tool of its kind".[10] However, some of the
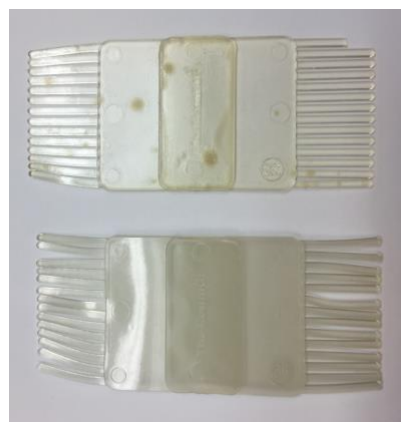
Image 7: Two chips from a ResinKit[TM] purchased in 2010.

sample chips have been identified (in personal communication to Dr. Gregory D. Smith of the IMA and in the literature as mislabeled or contaminated. [1, 11, 12] The purpose of this case study is to identify and categorize chips in a kit purchased in 2010 compare these results to a kit purchased in August of 2018.

Materials:

A complete ResinKit[TM] was purchased by the Conservation Science Lab at the Indianapolis Museum of Art at Newfields in 2010. Another complete ResinKit[TM] was purchased in the summer of 2018 through funds provided by the Butler Summer Institute program.

Data:
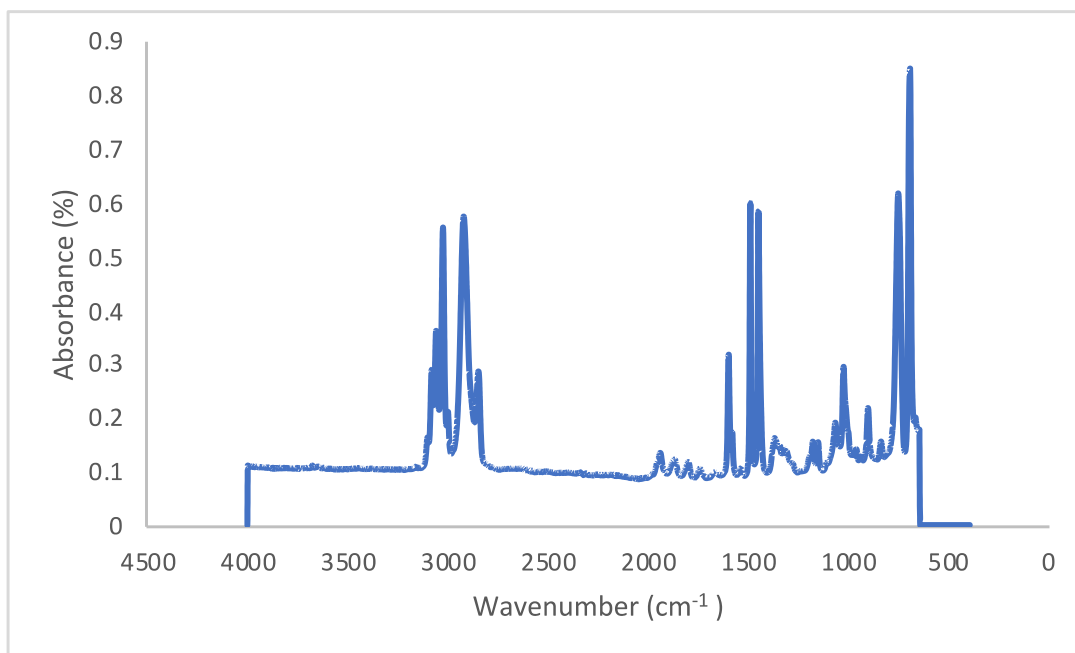
Spectrum 3: Infrared Spectrum of 2010 ResinKit No. 1 General Purpose Polystyrene

All 100 chips from the two ResinKit sets were analyzed using FTIR spectroscopy. The 99 other spectra are in Appendix 3A. 27 pairs of chips were also analyzed with PY-GC/MS: No. 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 22, 23, 26, 27, 31, 32, 41, and 42. The 53 other pyrograms can be seen in Appendix 3B.
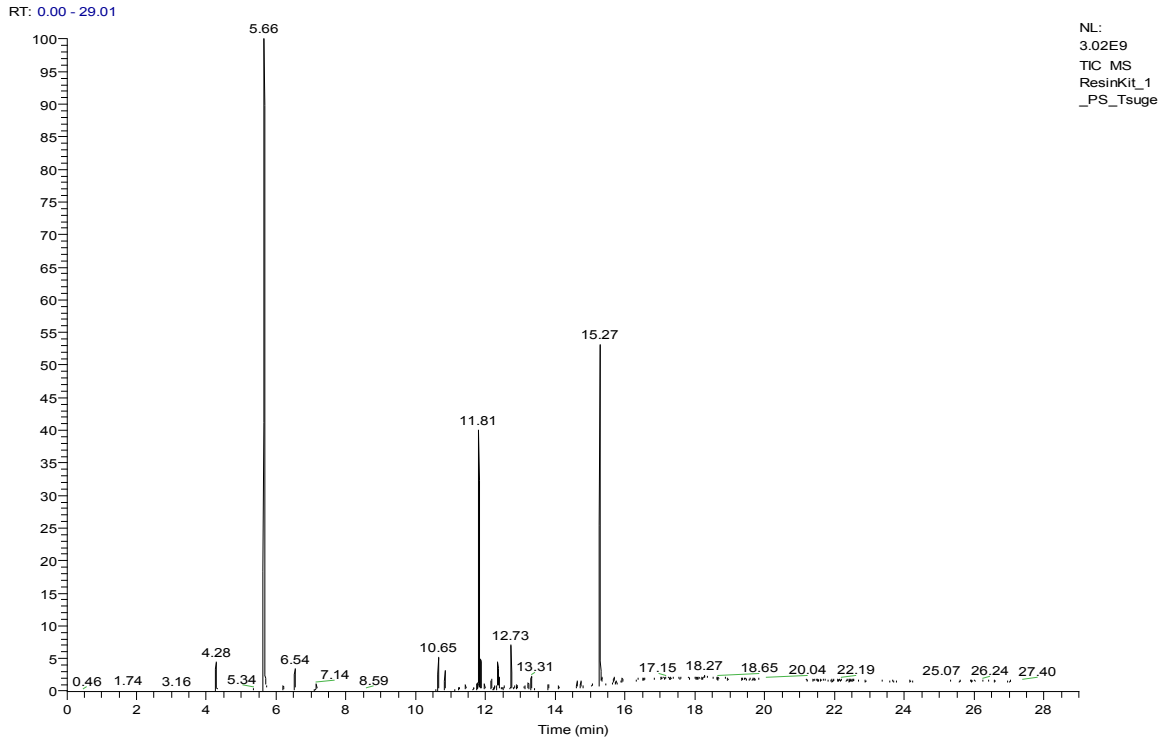
Spectrum 4: Pyrogram of 2010 ResinKit No. 1 General Purpose Polystyrene

Discussion:

FT Infrared Spectroscopy indicates that 37 pairs of corresponding chips in the 2010 and 2018 kits do not present with potential inaccuracies (No. 1, 2, 3, 4, 8, 9, 10, 14, 15, 16, 17, 20, 21, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 43, 44, 45, 46, 47, 48, and 50). There were 7 pairs of corresponding chips that did present with present with potential inaccuracies. In two pairs, No. 5 transparent ABS and No. 7 high impact ABS, butadiene is difficult to identify in the IR spectrum when conducting a spectral comparison. For another pair of chips, No. 13 CAP, acetate is difficult to identify in the IR spectrum when conducting a spectral comparison. The other four pairs presented with issues of a different polymer being present or completely absent. In two pairs, No. 18 PETG and No. 19 PPO, there are whole polymers present that are not assumed to be included based on the name. No. 18 presents as PET and PC instead of PETG; No. 19 presents as PS and PPO, not just PPO, based on spectral

comparison. The final two pairs, No. 41 Polyallomer and No. 42 Styrenic Terpolymer, both appear to be without entire compounds during spectral comparison. Polyallomer should be a copolymer, but identifies as only a single polymer, polypropylene. The label of Styrenic Terpolymer suggests a copolymer of three monomers, including styrene in this case. Spectral comparison identify the pair of No. 42 chips as being the copolymer SAN only. For five pairs of chips, No. 6, 11, 12, 22, and 49, only one of the chips presented with one of the previously mentioned issues. For, the 2018 chip of No. 6 Abs, the butadiene is difficult to identify in the IR spectrum when conducting a spectral comparison. For the 2010 chips of No. 11 CA and No. 12 CAB, both present as being CP or CAP instead of the polymers of their respective labels. For the 2010 chip of No. 22 PB, the chip presents in the FTIR spectrum as also having styrene present. The 2010 chip of No. 49 Medium Density PE presents as a PP/PE copolymer.

While FTIR spectra can be collected quickly, PY-GC/MS produces more comprehensive qualitative data. PY-GC/MS was conducted for 28 pairs of chips. 12 pair of chips had pyrograms that supported the accuracy of the labels: No. 1, 2, 3, 4, 6, 7, 15, 16, 17, 23, 26, and 27. For the 2010 chip No. 5 transparent ABS and the 2010 chip No. 8 SB block copolymer, while no 1,3-butadiene, a common compound found in polymers with butadiene, is identified in the pyrogram for either chip, both seem to match their respective Tsuge *et al*. pyrgorams. The 2018 chips for both No. 5 and 8 have identifiable 1,3-butadiene. For the 2010 chip No. 11 Cellulose Acetate and the 2010 chip No. 12 CAB, propanoic acid is present and indicates both chips are CAP and not what their respective labels say. The 2018 No. 11 and No. 12 chips are identifiable for what their respective label say. For the set of No. 13 chips, CAP, there is very little acetic acid present in the sample according to their respective pyrograms. Due to this, it is difficult to identify the polymer as being CAP, instead of CP. Both the 2010 and 2018 No. 18 PETG chips' pyrograms

appear to match both the Tsuge *et al.* pyrogram for both PET and PC. Tsuge *et al.* does not have a reference for PETG. Another sample of PETG from McMaster Carr was analyzed and does not completely match the two ResinKit™ samples. The pyrograms for both the 2010 and 2018 No. 19 PPO chips indicate that they are a copolymer of PPO and PS instead. For the 2010 No. 22 PB chip, Tsuge *et al.* SBS pyrogram matches the sample's. For the 2018 chip, however, there is no comparison in Tsuge *et al.* While the sample's pyrogram matches with what would be expected of PB, a sample of PB from another source needs to be obtained. For the sets of No. 31 Acetal Resin – Homopolymer chips and No. 32 Acetal Resin – Copolymer, both of the 2010 chips for are the homopolymer and both of the 2018 chips are the copolymer. Therefore, one in each set is incorrectly labeled. The label of Acrylic for No. 9 suggests that the polymer would be PMMA, however for 2010 chip the pyrogram indicates the chip is MMA-Higher methacrylate copolymer and for 2018 chip the pyrogram indicates the chip is MMA-ethyl acrylate copolymer. The No. 10 chip is labeled as Modified Acrylic but does not indicate in what way the polymer is modified. Both the 2010 and 2018 chips are identified as being an MMA-ABS copolymer based on spectra in Tsuge *et al.* Another label issue comes up with No. 14 transparent Nylon chips. Nylon is a generic term for multiple types of nylons, such as type 6 or type 66. There is no clear match for the No. 14 chips in Tsuge *et al.* and more spectral comparison to other samples will be required. Both No. 42 Styrenic Terpolymer chips can be identified to have at least two polymers, Styrene and Acrylonitrile. As the label suggests, these chips should have three polymers. The chips could also have butadiene, but as discussed earlier, it can be difficult to identify in the pyrogrom. The set of chips for No. 41 Polyallomer was difficult to identify based on comparison to Tsuge *et al.* spectra or peak identification. Further research needs to be done.

In 23 of the chips from both of the ResinKit™ the same plasticizer was found at the same time in the pyrogram, diisooctyl phthalate. The chips from the 2010 kit are No. 8, 9, 11, 12, 13, 14, 15, 19, 22, 27, 31, 32, and 41. The 2018 chips with the plasticizer are No. 11, 12, 13, 15, 16, 19, 31, 32, and 41. The peak for this compound can be seen at time of 15.58 minutes in the pyrogram.

Conclusion:

Based on the FTIR analysis, the chips in either ResinKit™ are mostly identified correctly. While the PY-GC/MS has not been done for all 100 chips yet. It too shows that many chips are labeled correctly. However, mostly and many are not enough to excuse the minority that are incorrect. The ResinKit™ is marketed as a way to correctly identify unknown polymers, but it cannot fulfill that purpose when roughly 20% of the kit is misidentified. It is important to note that the kits even have a disclaimer in the informative pages about the accuracy and the content of the kits. In order for this item to be functional as a reference, it must first be assessed on its own and only those chips that can be properly identified should be used as reference materials.

Overall Conclusion:

From these three case studies, the importance of verifying a potential reference that does not come with its own label of authenticity can be seen. The message here is not one ignorance, but of informed research. Even if a pigment or polymer is mislabeled, if that material can be properly identified, it can provide useful and important information to conservation scientists and conservators about the materials used in the creation of an object. The ease of mislabeling a material and the importance of material identification are made clear through the analyses done in each of the three case studies.

References:

1. Smith, G. D., Sr. Conservation Scientist at the Indianapolis Museum of Art at Newfields, personal communication.

2. Picollo, M.; Bartolozzi, G.; Cucci, C.; Galeotti, M.; Marchiafava, V.; Pizzo, B. Comparative Study of Fourier Transform Infrared Spectroscopy in Transmission, Attenuated Total Reflection, and Total Reflection Modes for the Analysis of Plastics in the Cultural Heritage Field. *Applied Spectroscopy* **2014,** *68* (4), 389-397.

3. Tsuge, S.; Ohtani, H.; Watanabe, C. *Pyrolysis - GC/MS Data Book of Synthetic Polymers*, Elsevier: New York, 2011.

4. Eastaugh, N.; Walsh, V.; Chaplin, T.; Siddall, R. *Pigment compendium: A dictionary and optical microscopy of historical pigments*. Routledge, Taylor et Francis Group: New York, 2013.

5. WebExhibits. http://www.webexhibits.org/pigments/indiv/overview/greenearth (accessed May 1, 2018). Pigments through the Ages. Green Earth. Technical Details.

6. Kremer Pigments. https://shop.kremerpigments.com/en/pigments/earth-pigments/ (accessed July 1, 2018) Green Earths. Details.

7. Coloulex. https://colourlex.com/project/green-earth/ (accessed May 1, 2018). Green Earth. History of Use.

8. Coccato, A,: Bersani, D.; Coudray, A.; Sanyova, J.; Moens, L.; Vandenabeele, P. Raman spectroscopy of green minerals and reaction products with an application in Cultural Heritage research. *J. Raman Spectrosc.* **2016**, 47 (12), 1429-1443.

9. Ospittali, F; Bersani, D.; Di Lonardo, G.; Lottici, P.P. 'Green Earths': vibrational and elemental characterization of glauconites, celadonites and historical pigments. *J. Raman Spectrosc.* **2008**, *39* (8), 1066-1073.

10. http://www.plasticsgroup.com/resinkit.php (accessed Dec 29, 2017), ResinKit™.

11. Picollo, M.; Bartolozzi, G.; Cucci, C.; Galeotti, M.; Marchiafava, V.; Pizzo, B. Comparative Study of Fourier Transform Infrared Spectroscopy in Transmission, Attenuated Total Reflection, and Total Reflection Modes for the Analysis of Plastics in the Cultural Heritage Field. *Applied Spectroscopy* **2014,** *68* (4), 389-397.

12. Schilling, M.; Bouchard, M.; Khanjian, H.; Learner, T.; Phenix, A.; Rivenc, R. Application of Chemical and Thermal Analysis Methods for Studying Cellulose Ester Plastics. *Accounts of Chemical Research* **2010,** *43* (6), 888-896.

Appendix 1: Additional Spectra for Case Study 1: Calcium Carbonate Polymorphs

1A: Raman Spectra
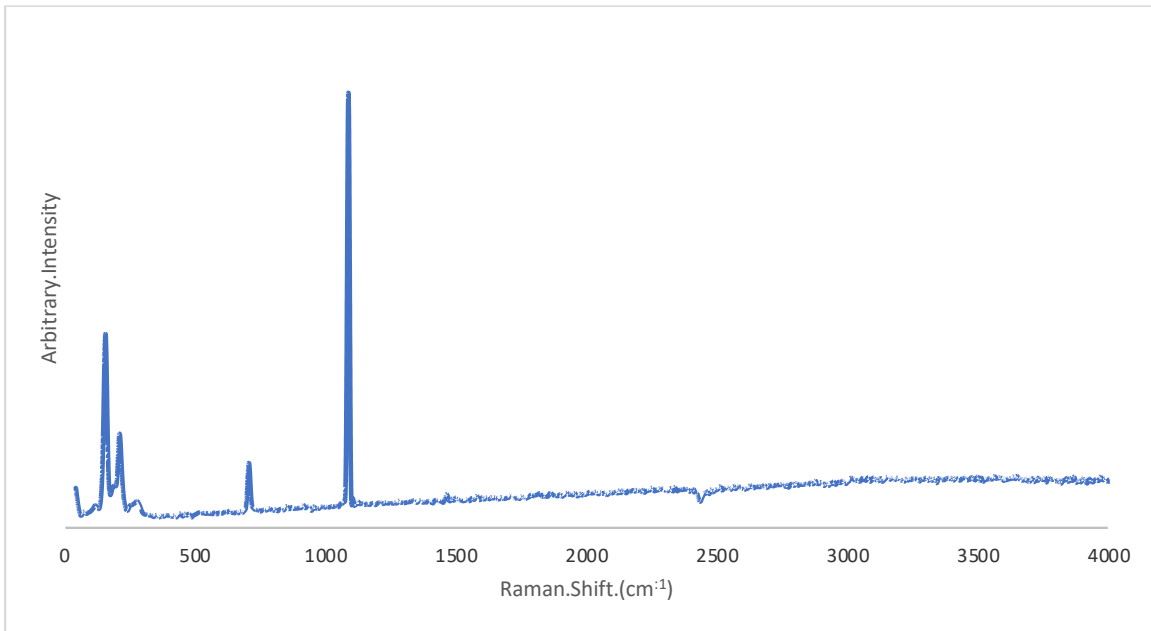
Cargille Aragonite, 532nm
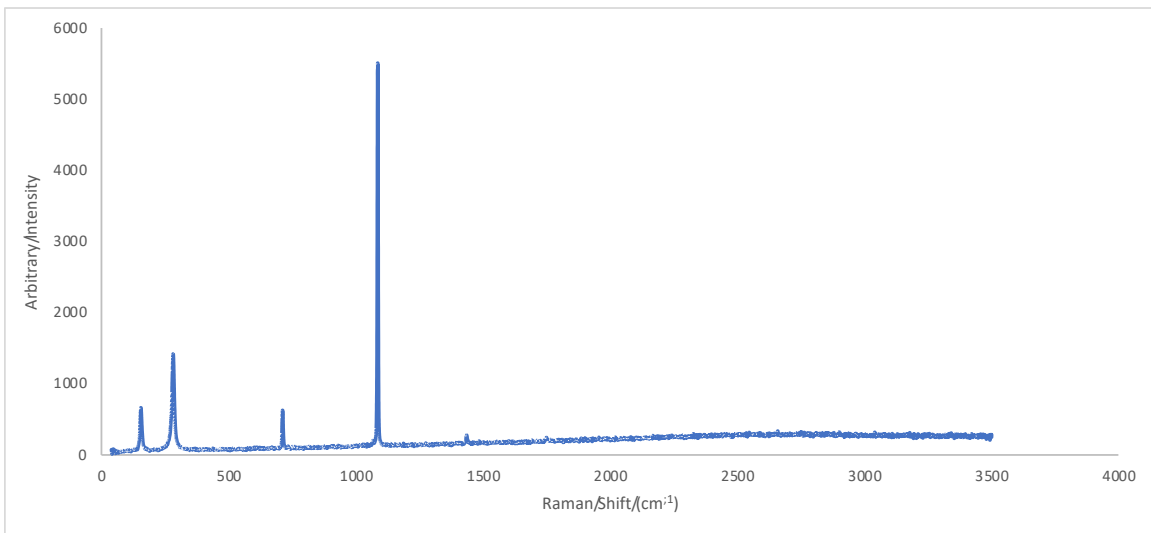
Kremer Aragonite, 532 nm
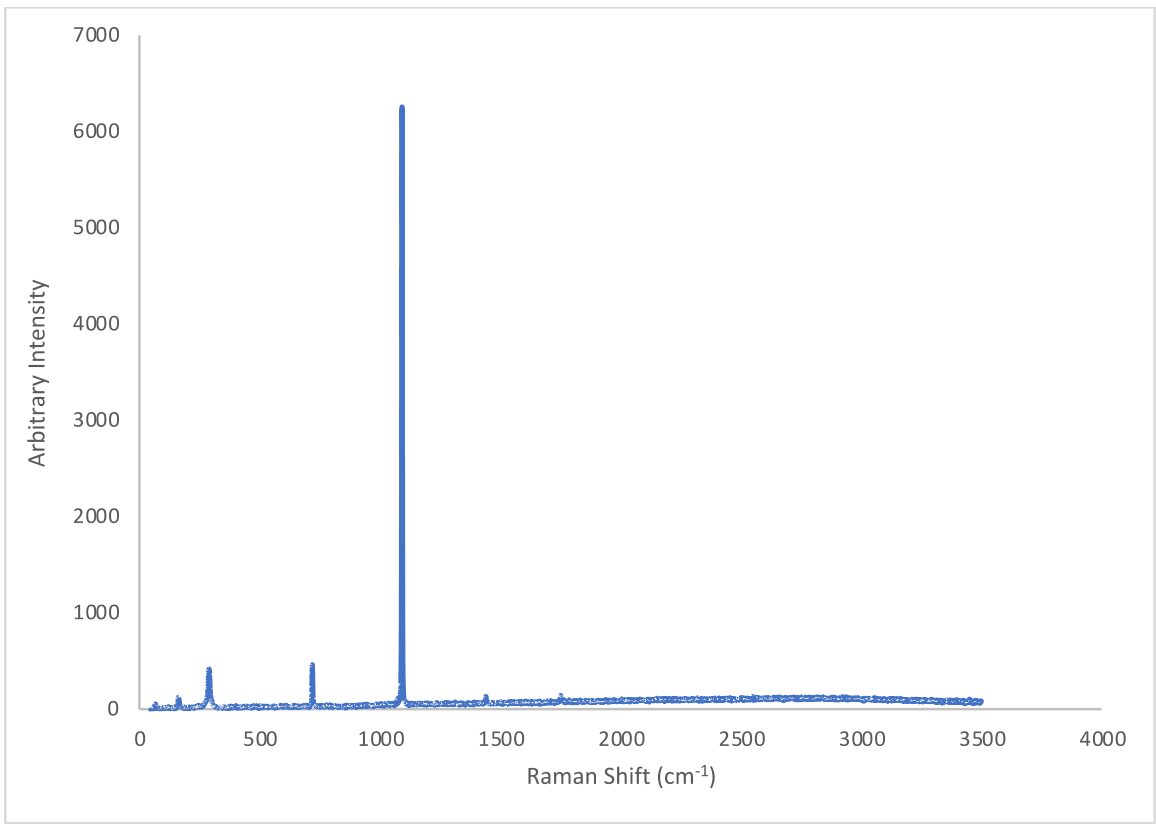
Cargille Calcite, 633nm
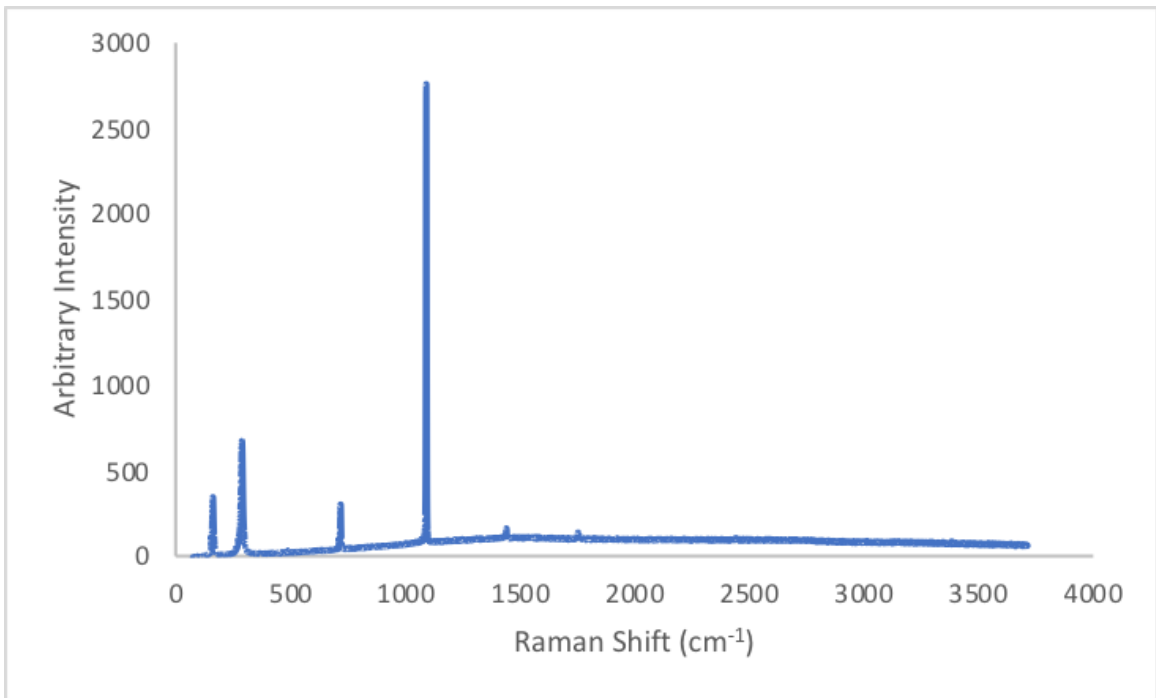
Kremer Calcite, 532 nm
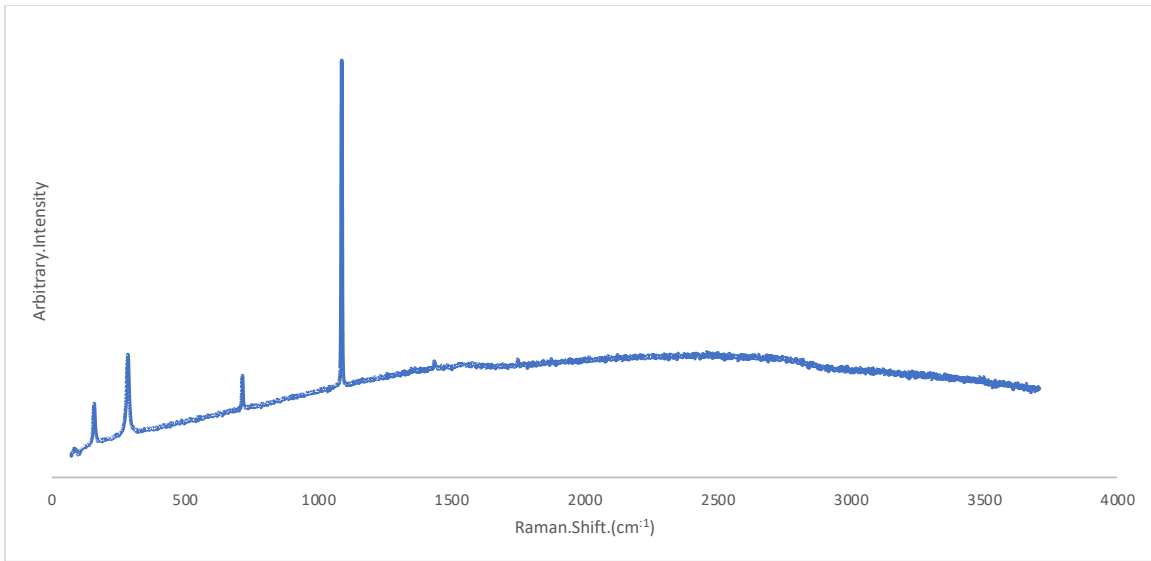
Reference Library Spectrum of Kremer Aragonite from 2010-2011, 532nm

1B: FTIR Spectra
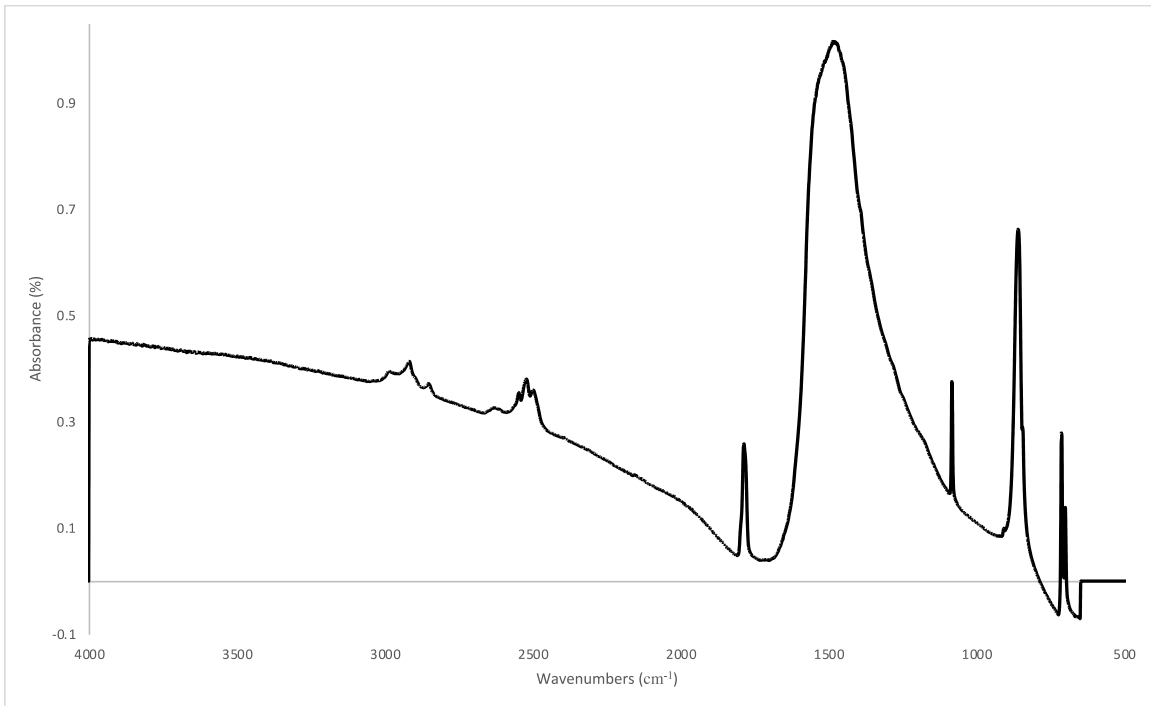
Cargille Aragonite
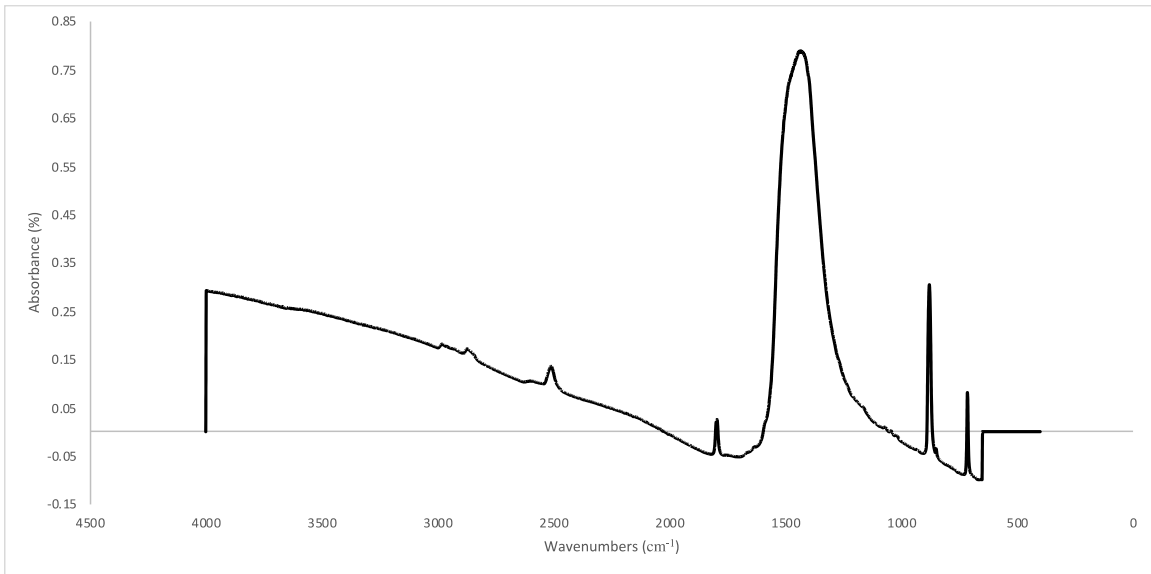
Kremer Aragonite
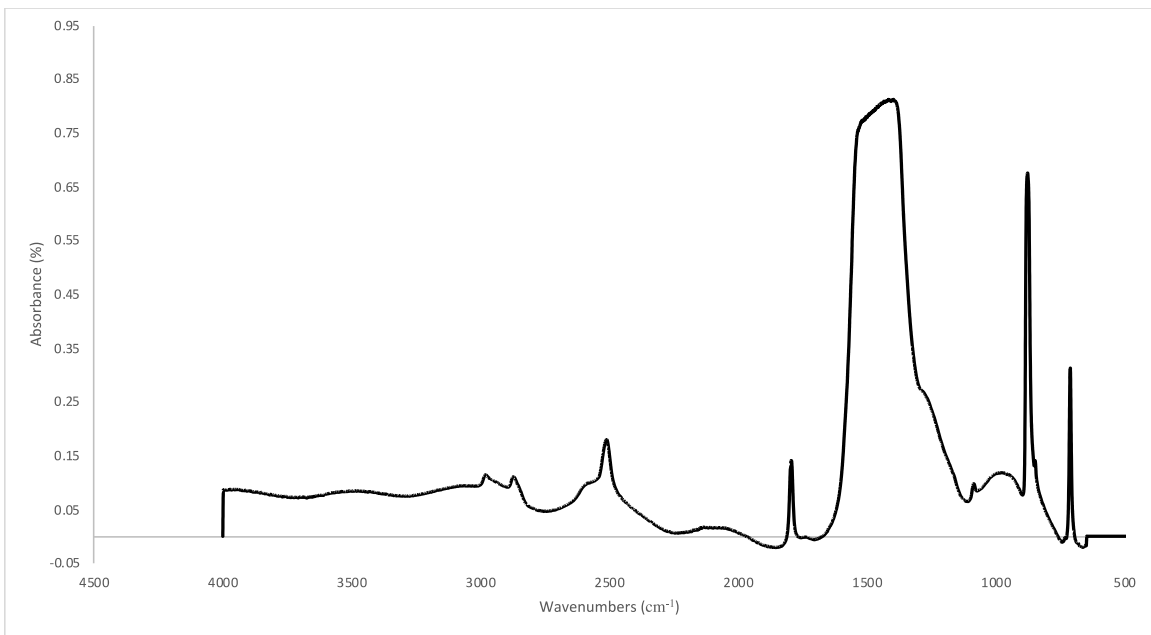
Cargille Calcite

Appendix 2: Additional Spectra for Case Study 2: Green Earth Pigments

Raman Spectra
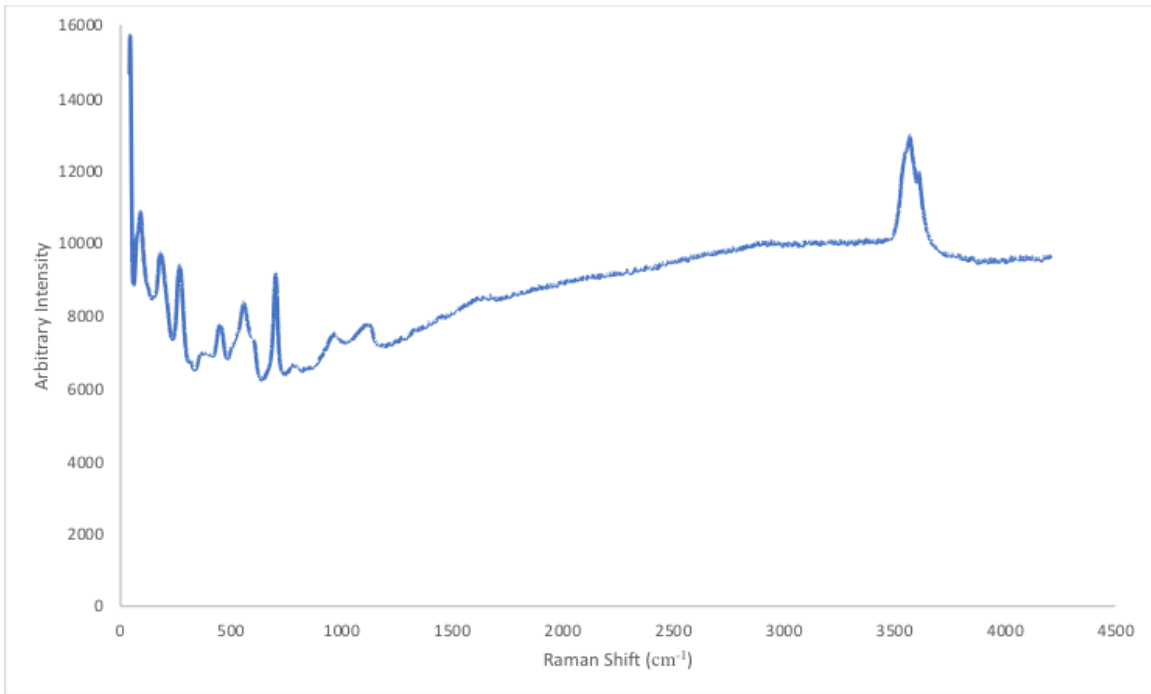
Celadonite, 532 nm
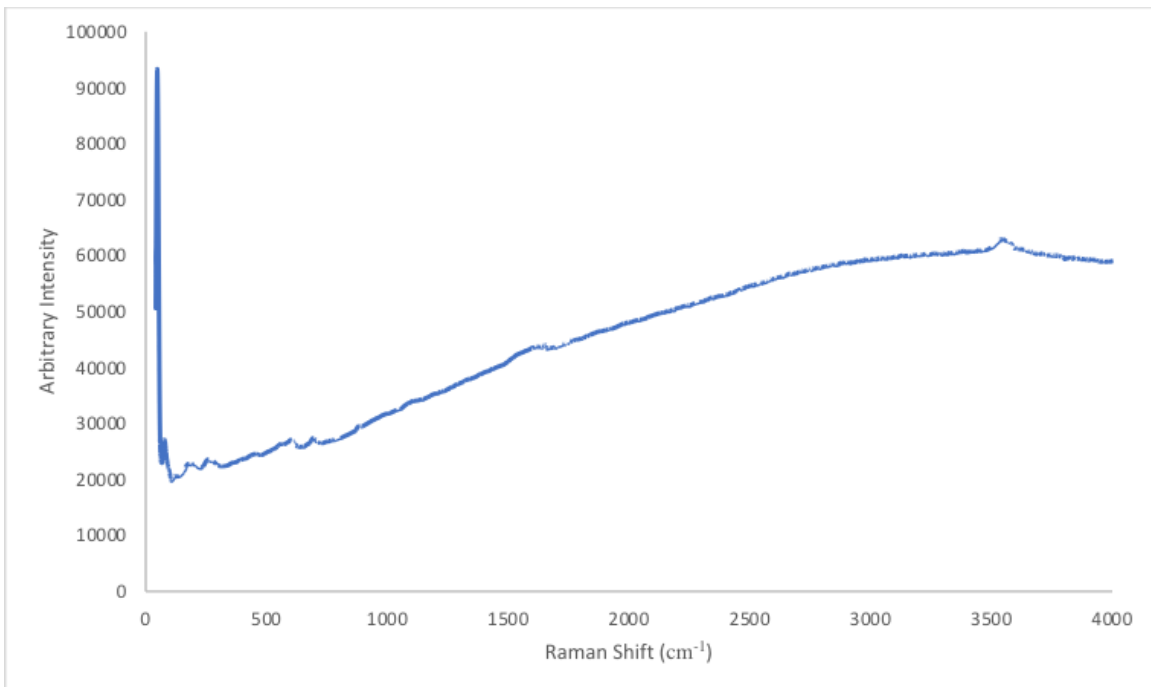
Glauconite, 532 nm
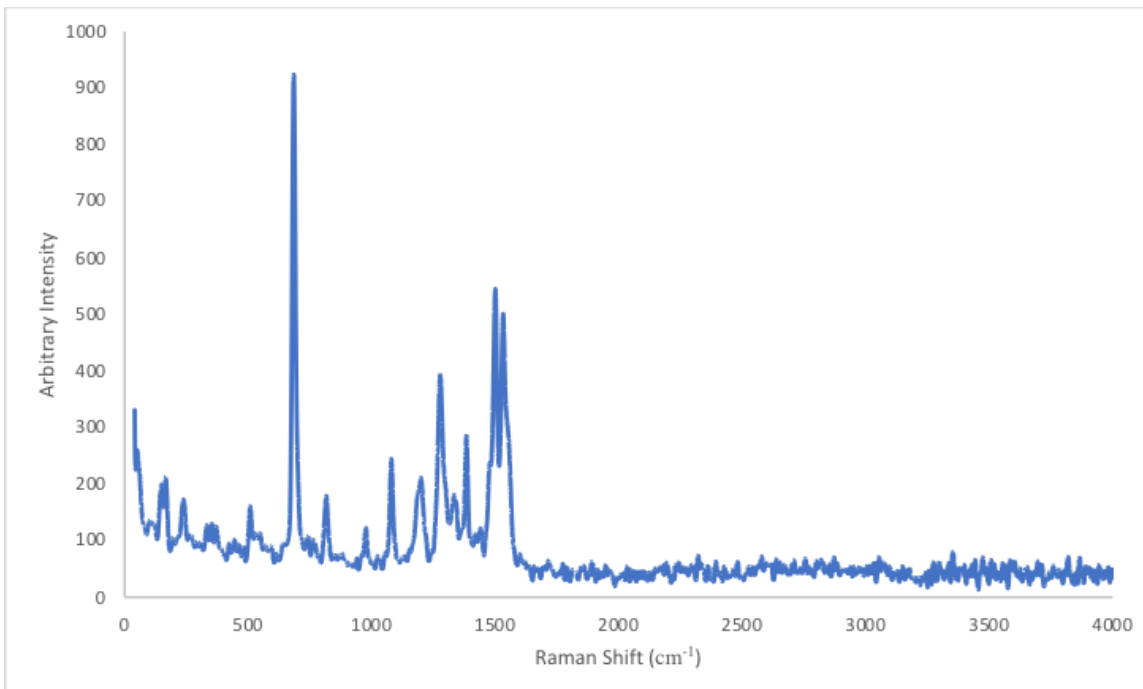
Pthalocyanine Green, PG7, 532nm
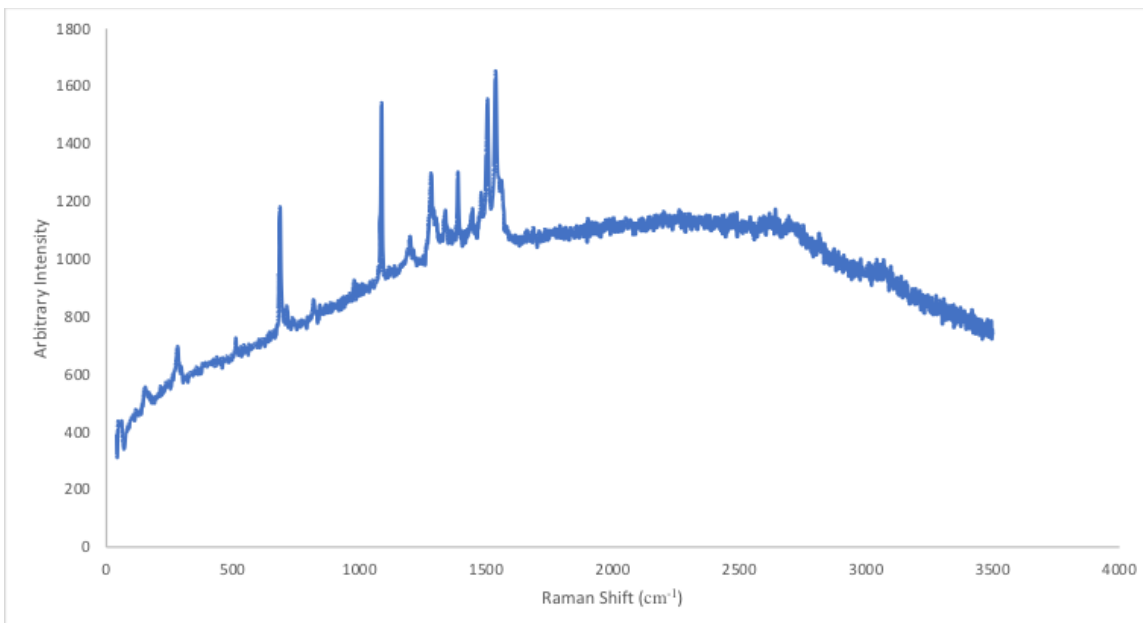
Kremer 11000 Verona Green Earth, 532 nm
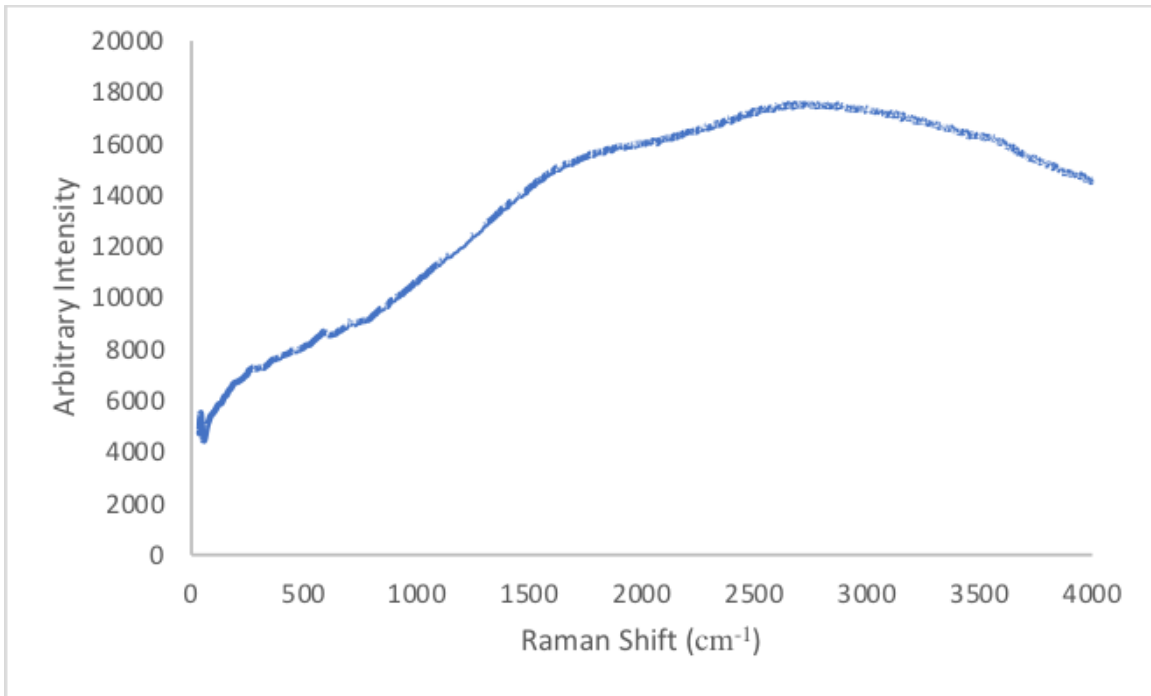
Kremer 40810 Bohemian Green Earth, 532 nm
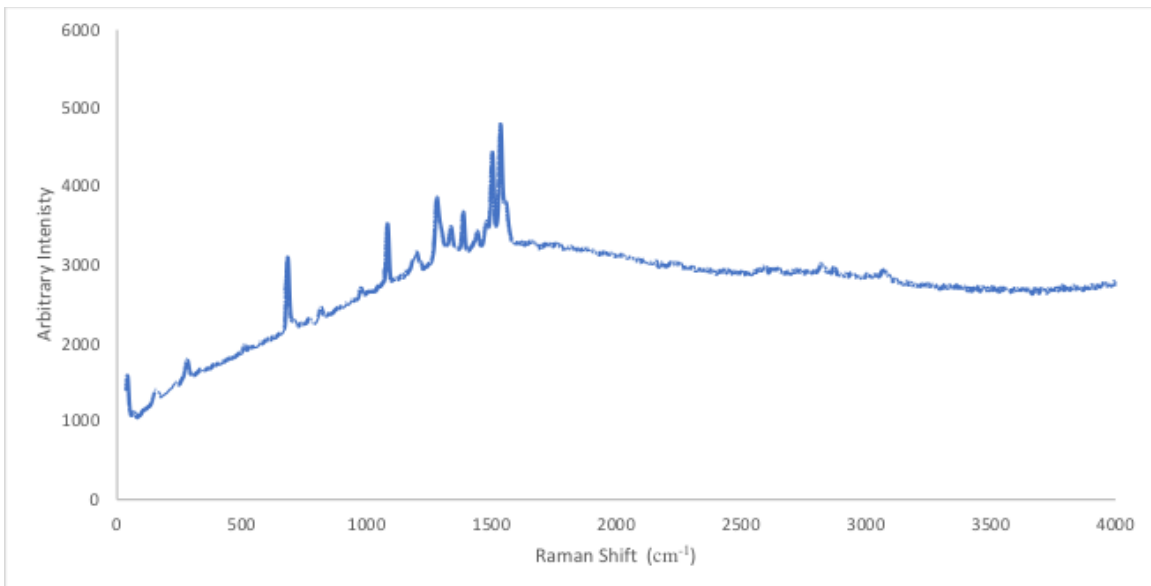
Kremer 40821 Green Earth from Verona Genuine, Pure, 532 nm
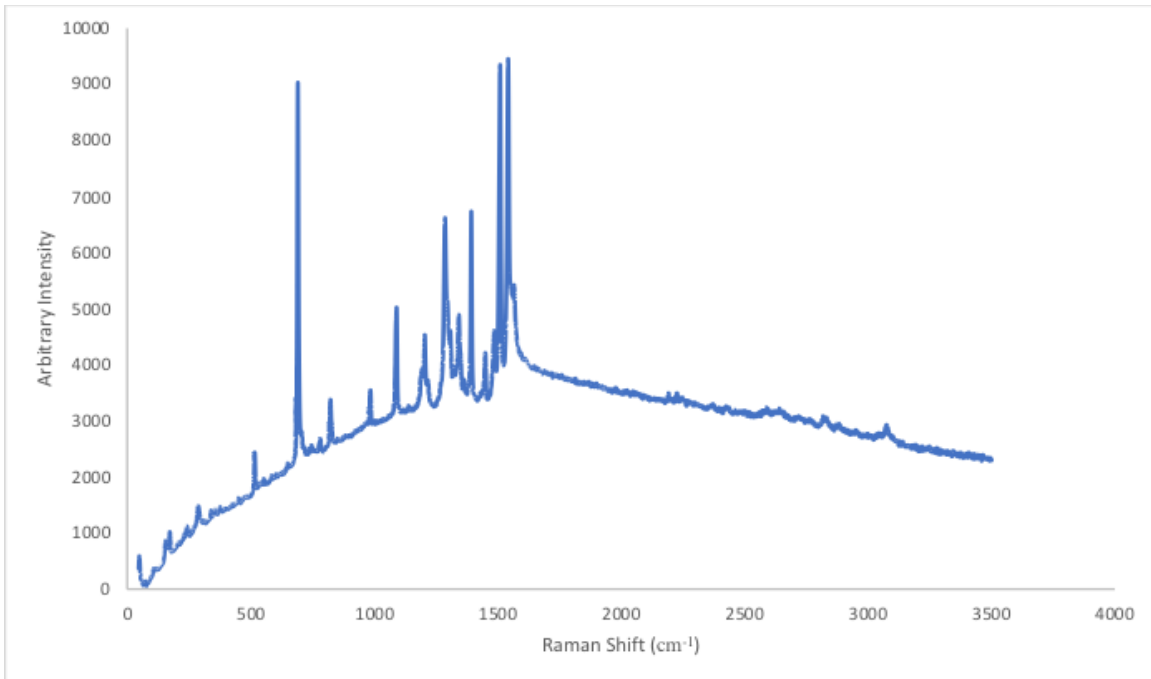
Kremer 40821 Green Earth from Verona Genuine, Pure from Pigment Chart, 532nm
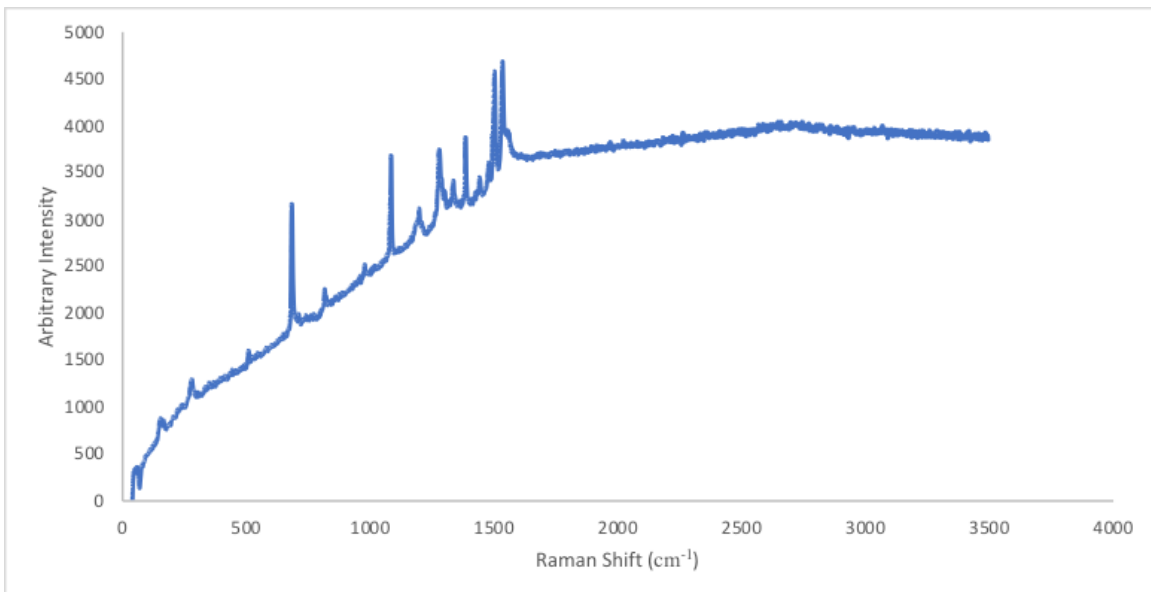
Kremer 40830 Green Earth from France, 532 nm
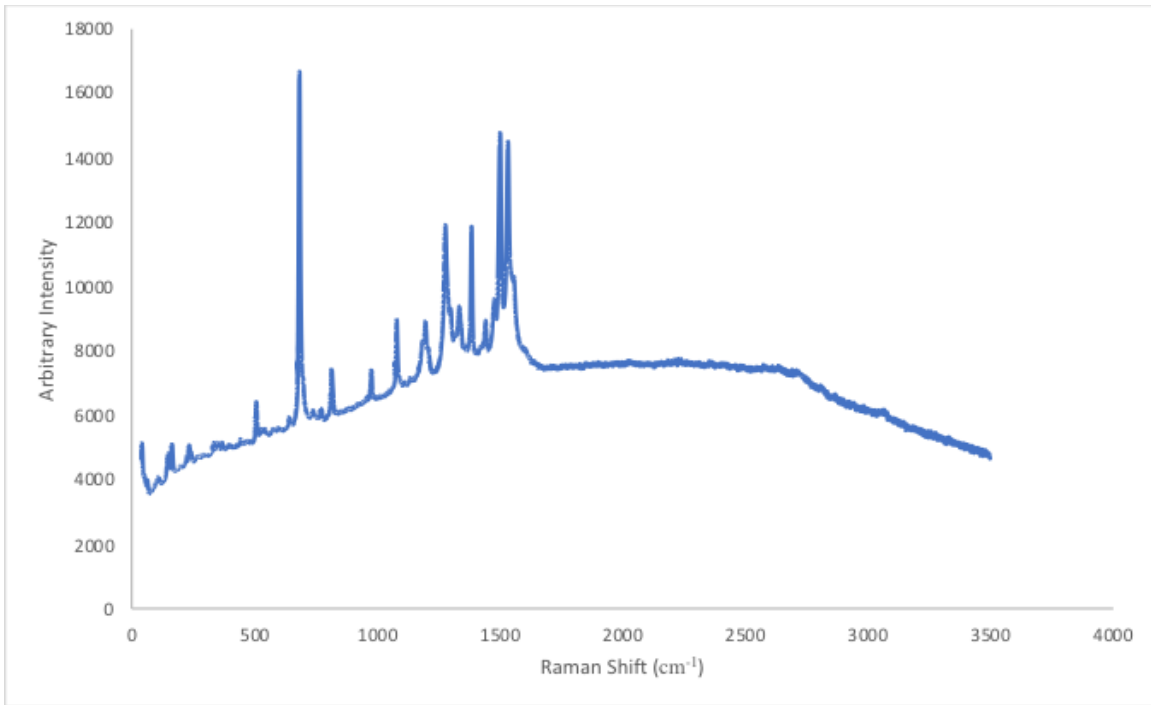
Kremer 40830 Green Earth from France from Pigment Chart, 532 nm
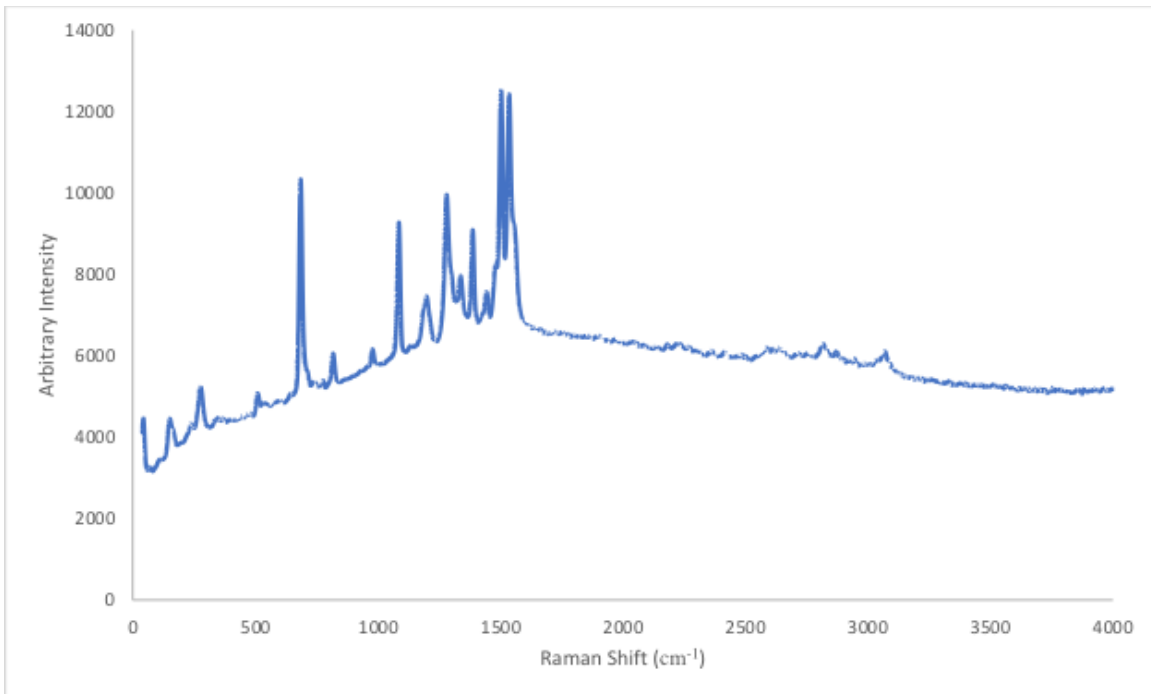
Kremer 41700 Verona Green Earth enhanced with Viridian, 532 nm
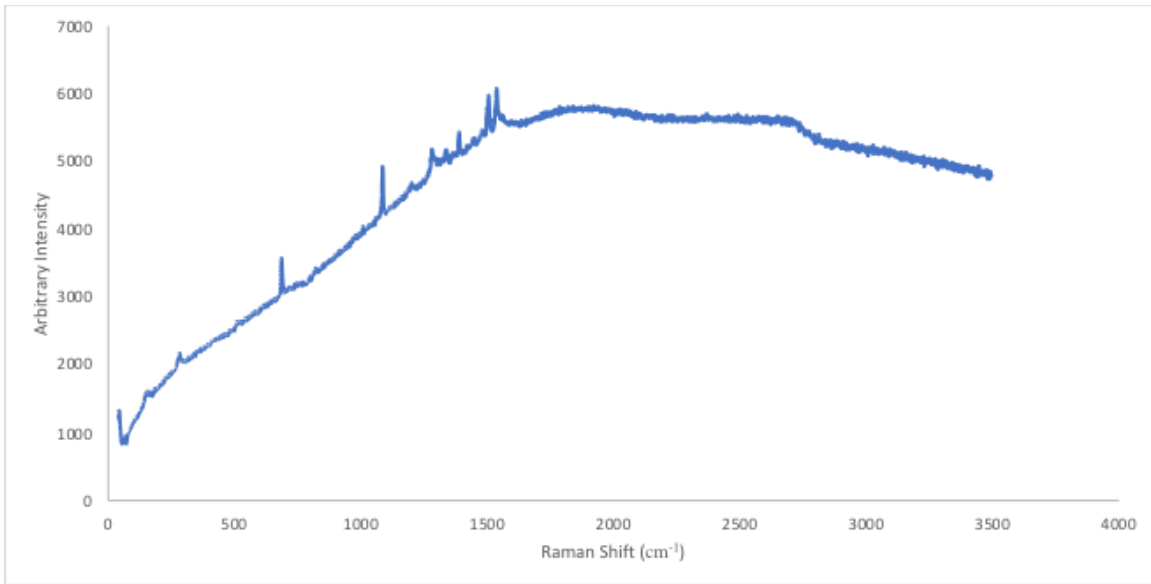
Kremer 41700 Verona Green Earth enhanced with Viridian from Pigment Chart, 532 nm
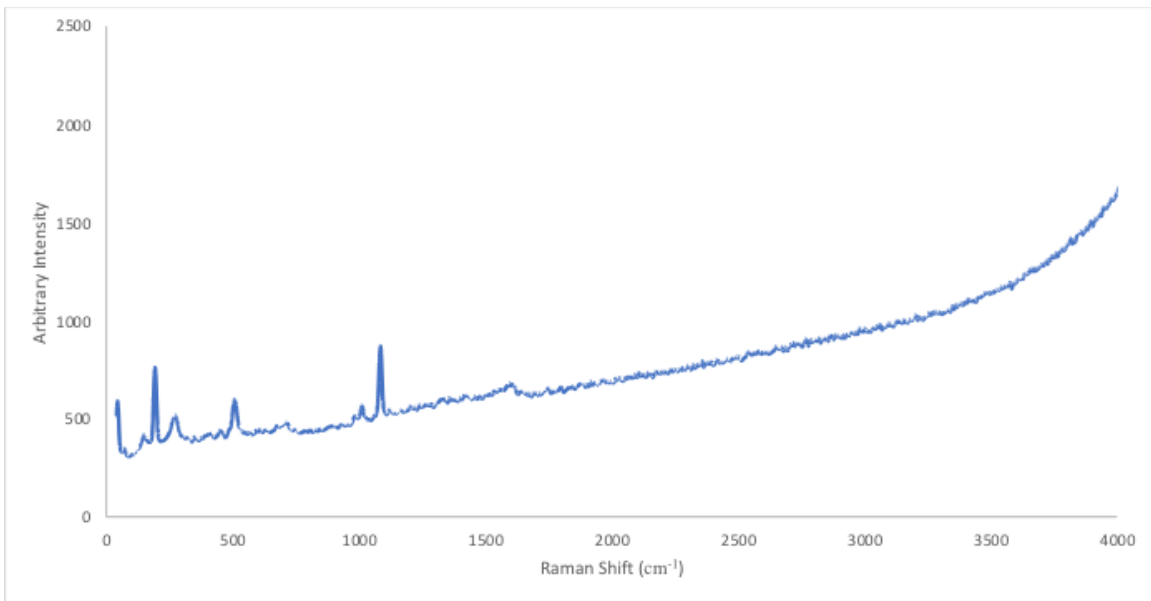
Williamsburg French Terre Verte, 532nm
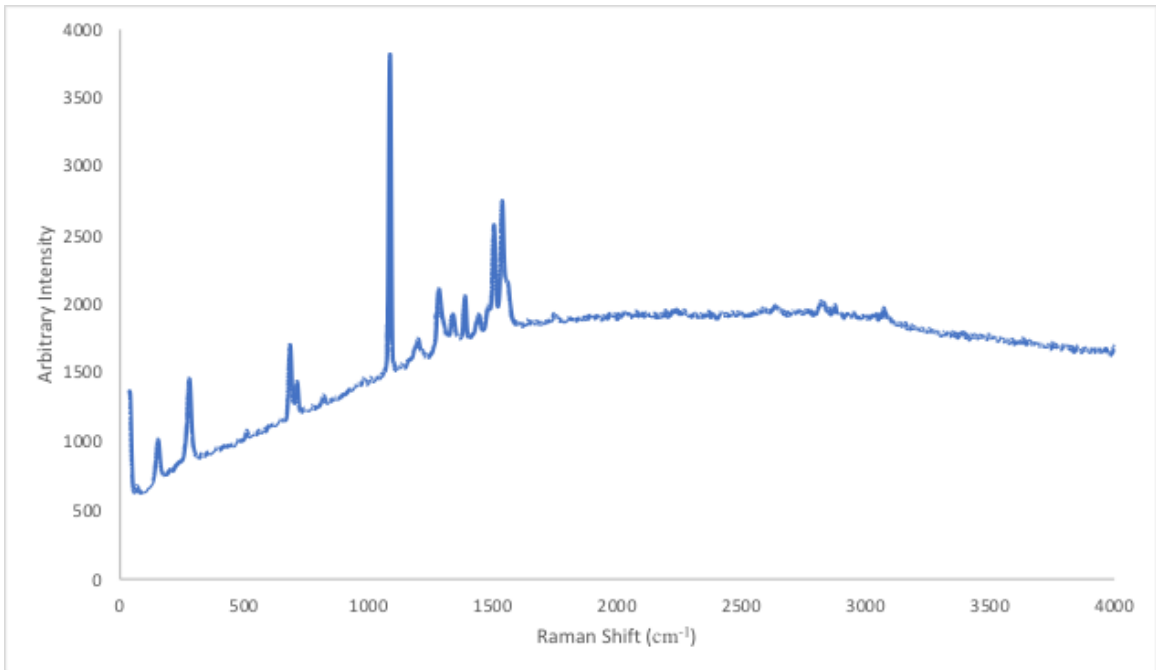
Williamsburg Italian Terre Verte, 532 nm

Appendix 3: Additional Spectra for Case Study 3: The ResinKit™

3A: FTIR Spectra

2018 ResinKit No. 1 General Purpose Polystyrene

2010 ResinKit No. 2 Medium Impact Polystyrene

2018 ResinKit No. 2 Medium Impact Polystyrene

2010 ResinKit No. 3 High Impact Polystyrene
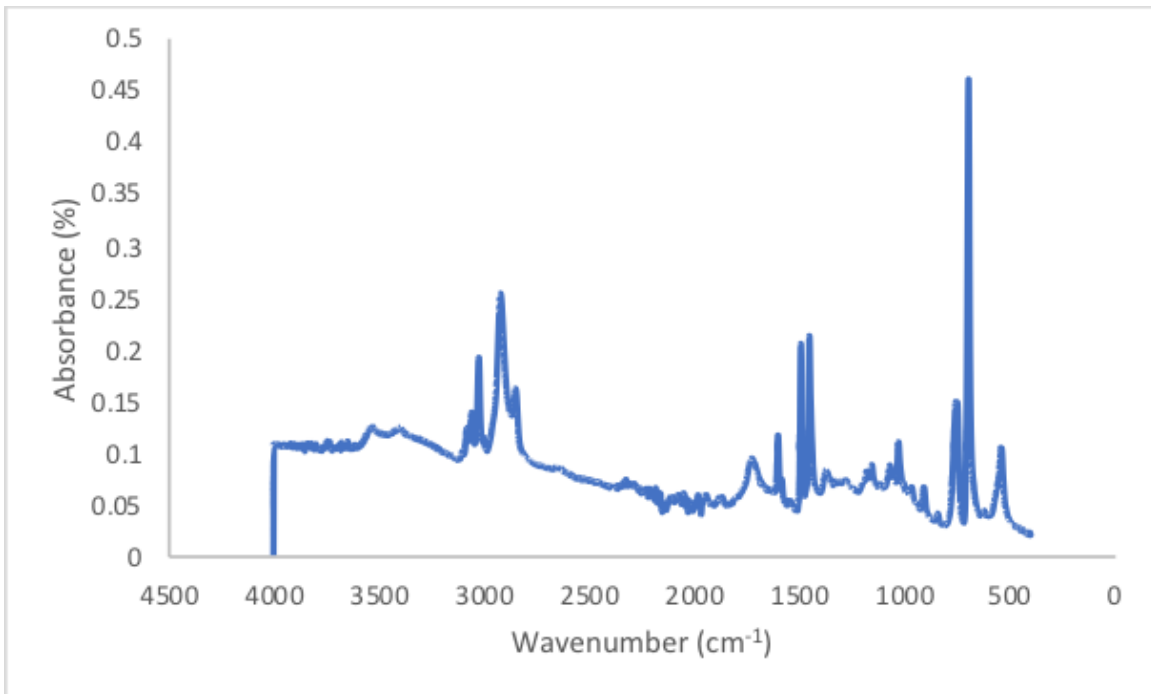
2018 ResinKit No. 3 High Impact Polystyrene
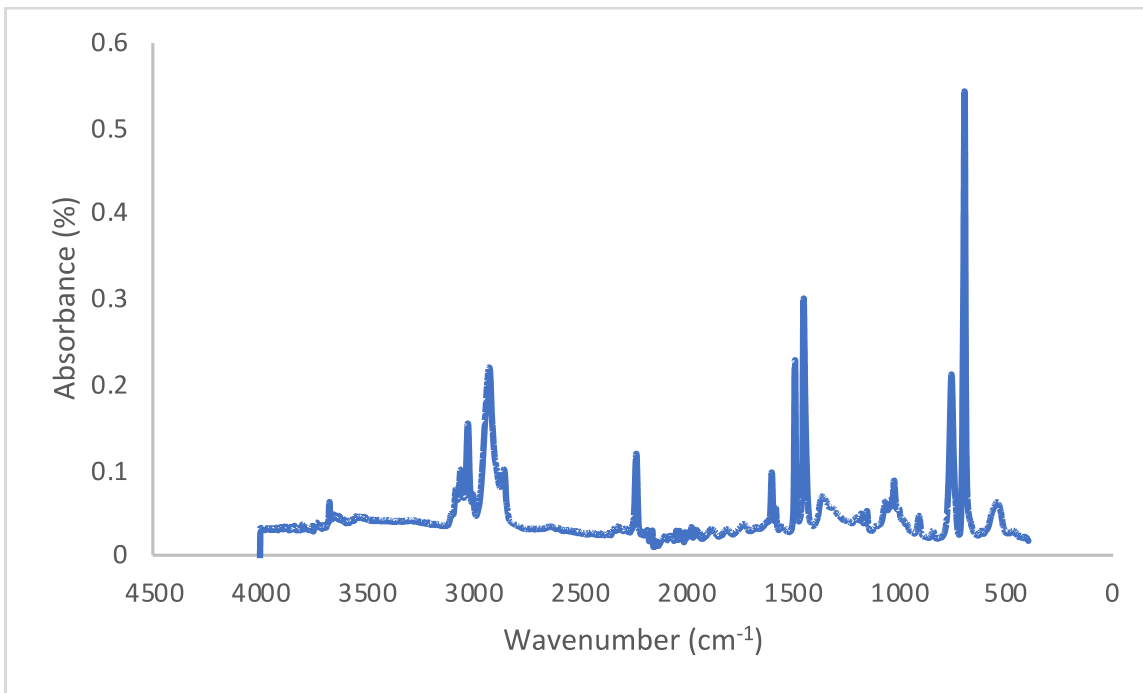
2010 ResinKit No. 4 Styrene Acrylonitrile
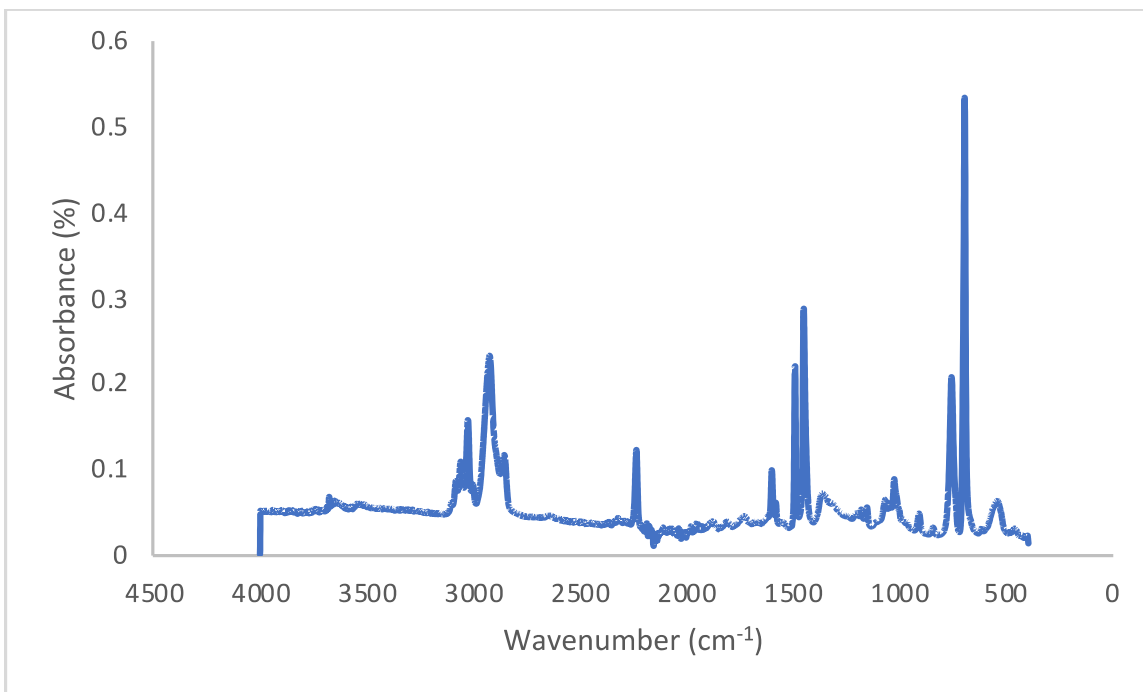
2018 ResinKit No. 4 Styrene Acrylonitrile
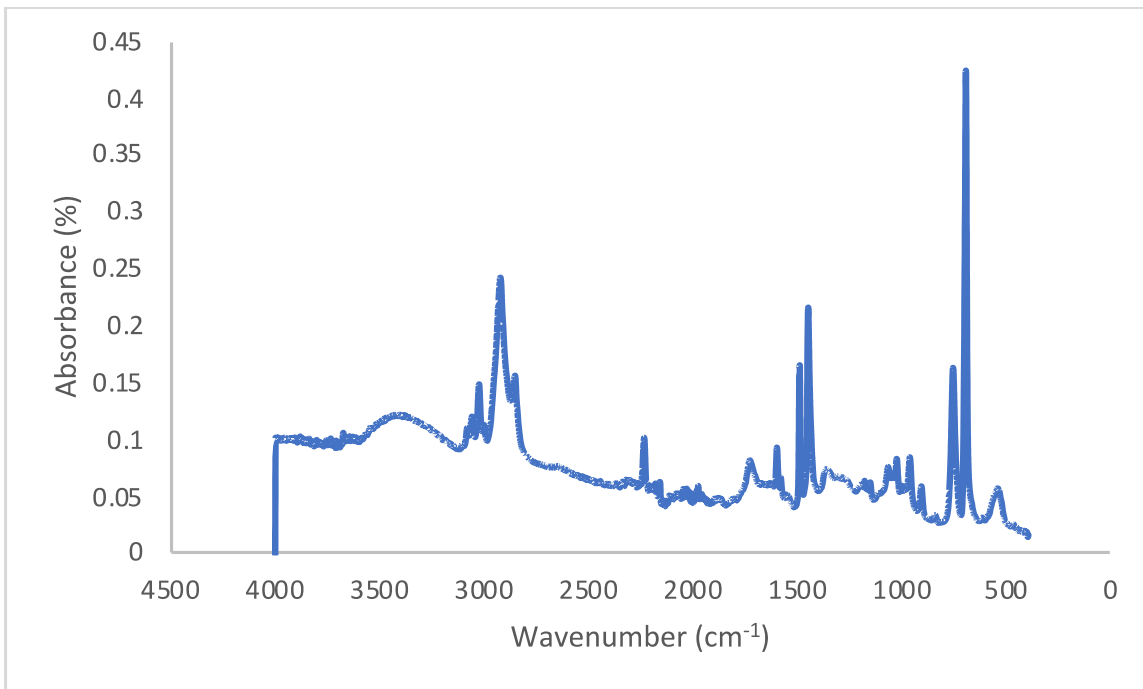
2010 ResinKit No. 5 Transparent Acrylonitrile-Butadiene-Styrene
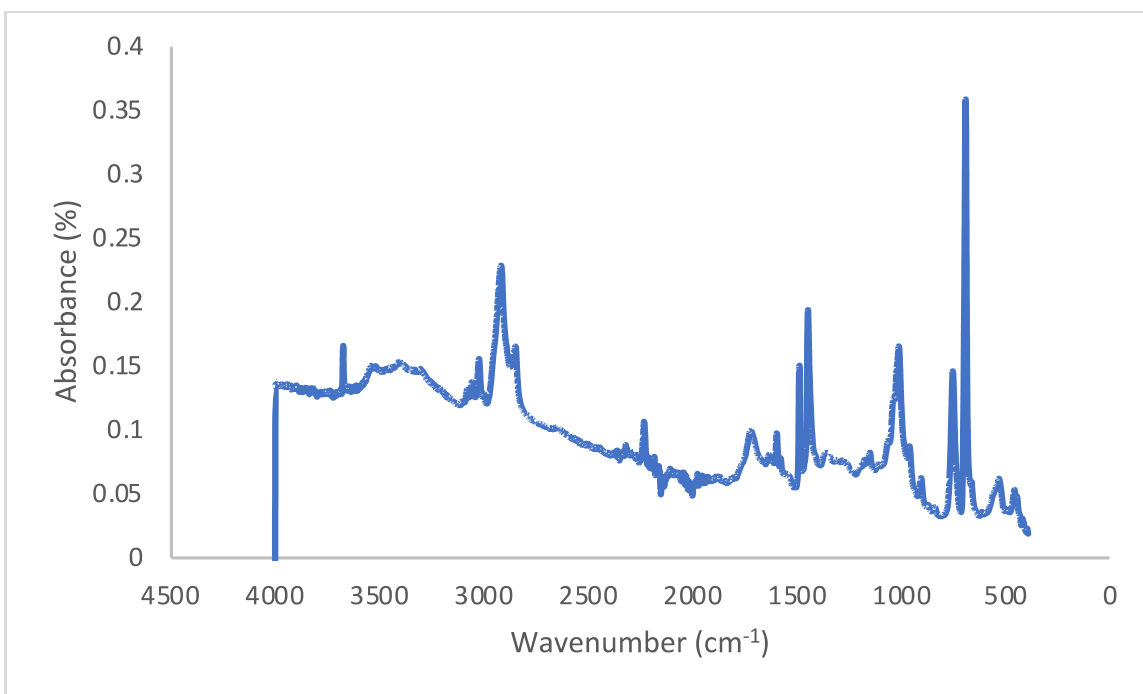
2018 ResinKit No. 5 Transparent Acrylonitrile-Butadiene-Styrene

2010 ResinKit No. 6 Medium Impact Acrylonitrile-Butadiene-Styrene
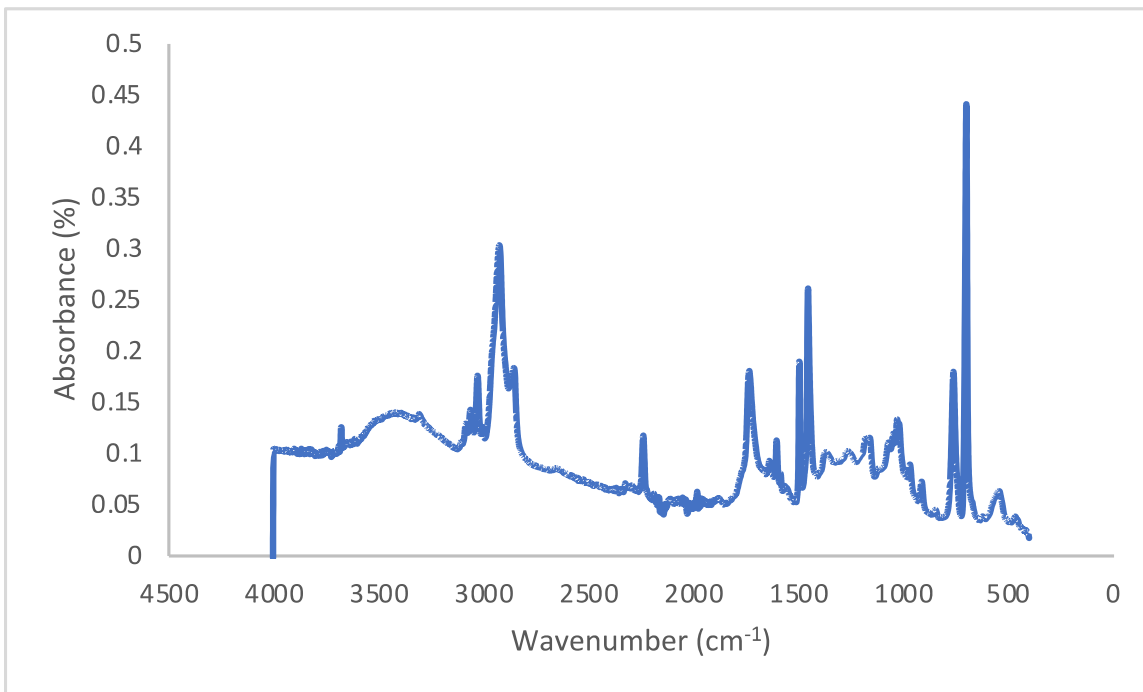
2018 ResinKit No. 6 Medium Impact Acrylonitrile-Butadiene-Styrene
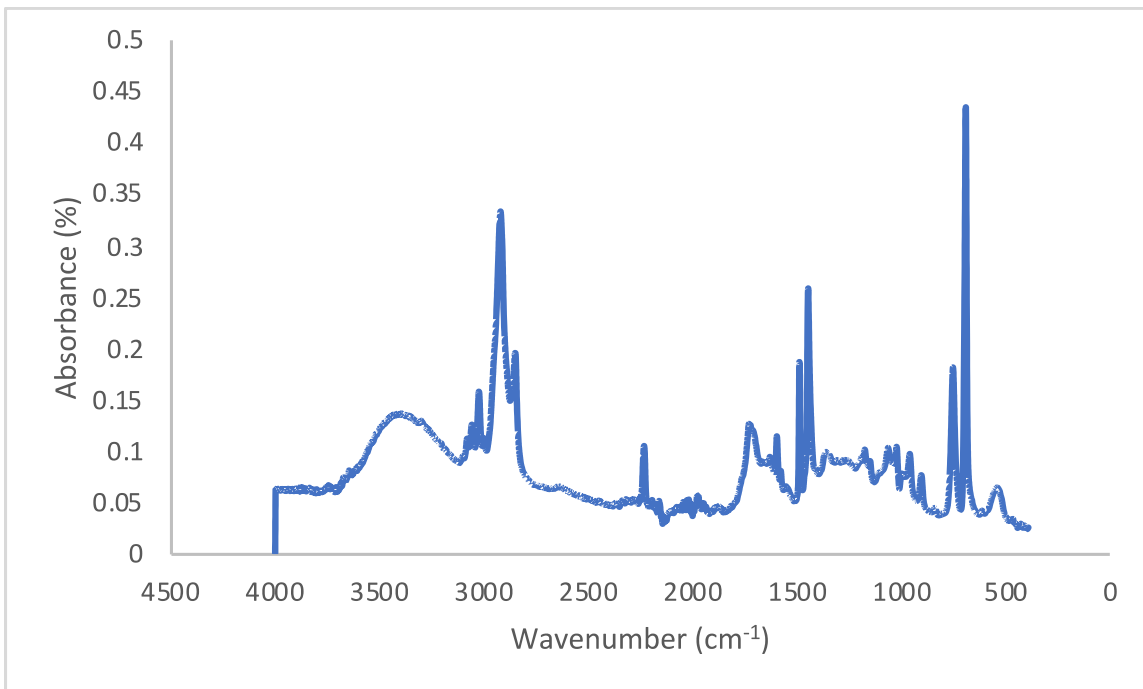
2010 ResinKit No. 7 High Impact Acrylonitrile-Butadiene-Styrene
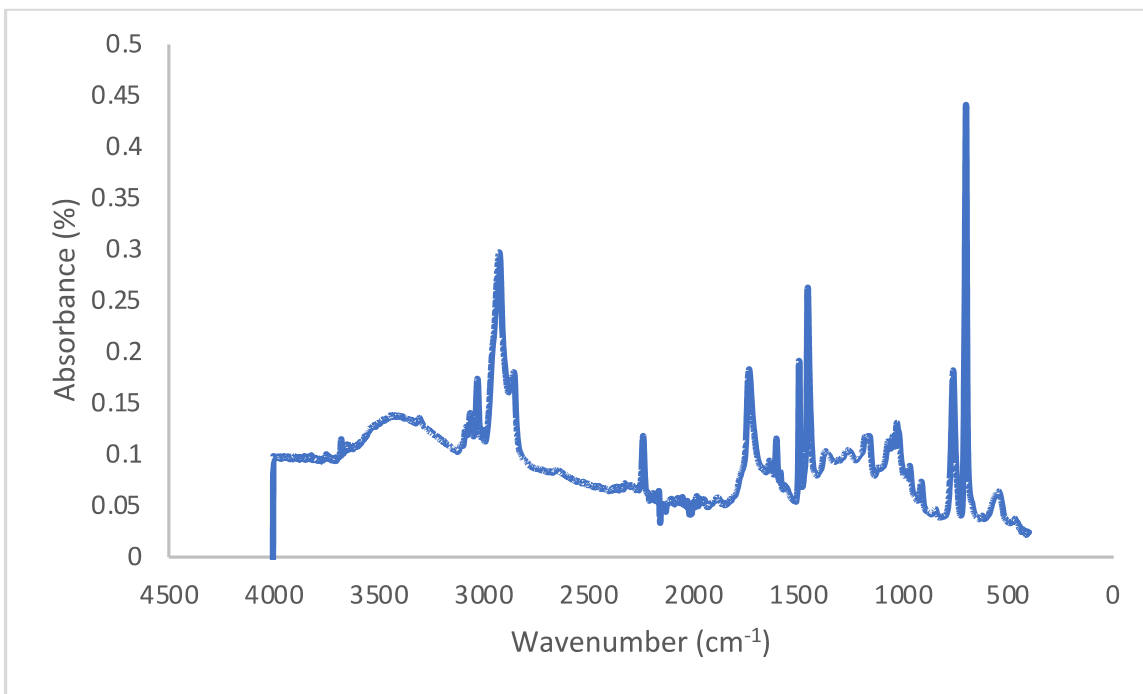
2018 ResinKit No. 7 High Impact Acrylonitrile-Butadiene-Styrene

2010 ResinKit No. 8 Styrene Butadiene

2018 ResinKit No. 8 Styrene Butadiene

2010 ResinKit No. 9 Acrylic

2018 ResinKit No. 9 Acrylic

2010 ResinKit No. 10 Modified Acrylic
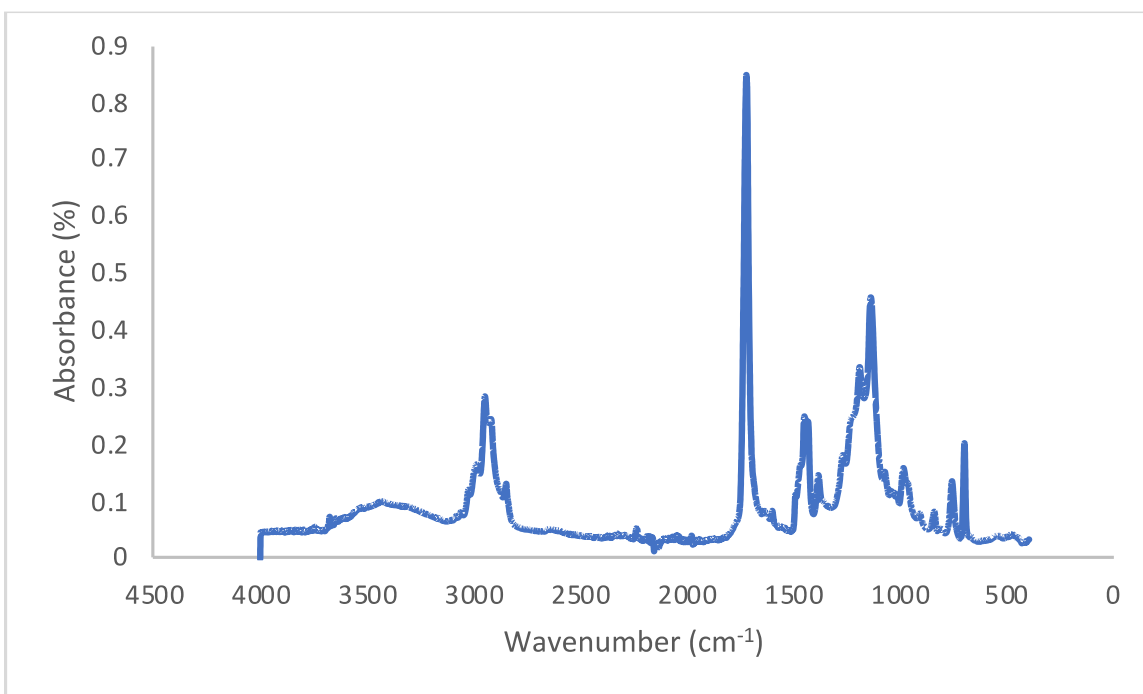
2018 ResinKit No. 10 Modified Acrylic
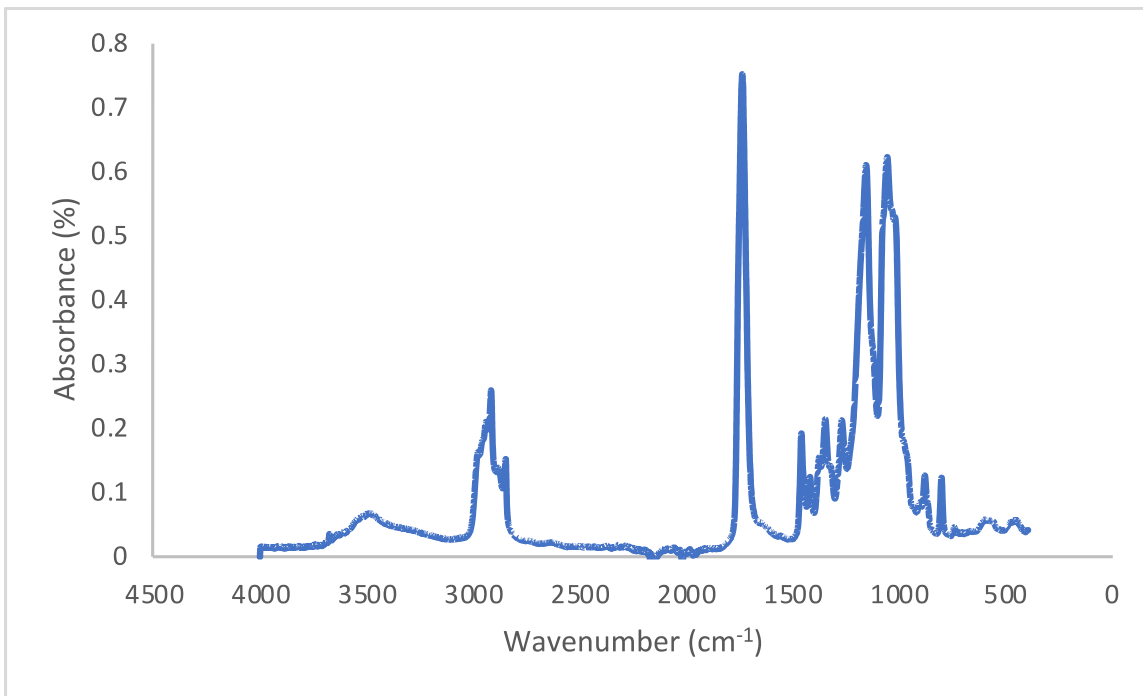
2010 ResinKit No. 11 Cellulose Acetate
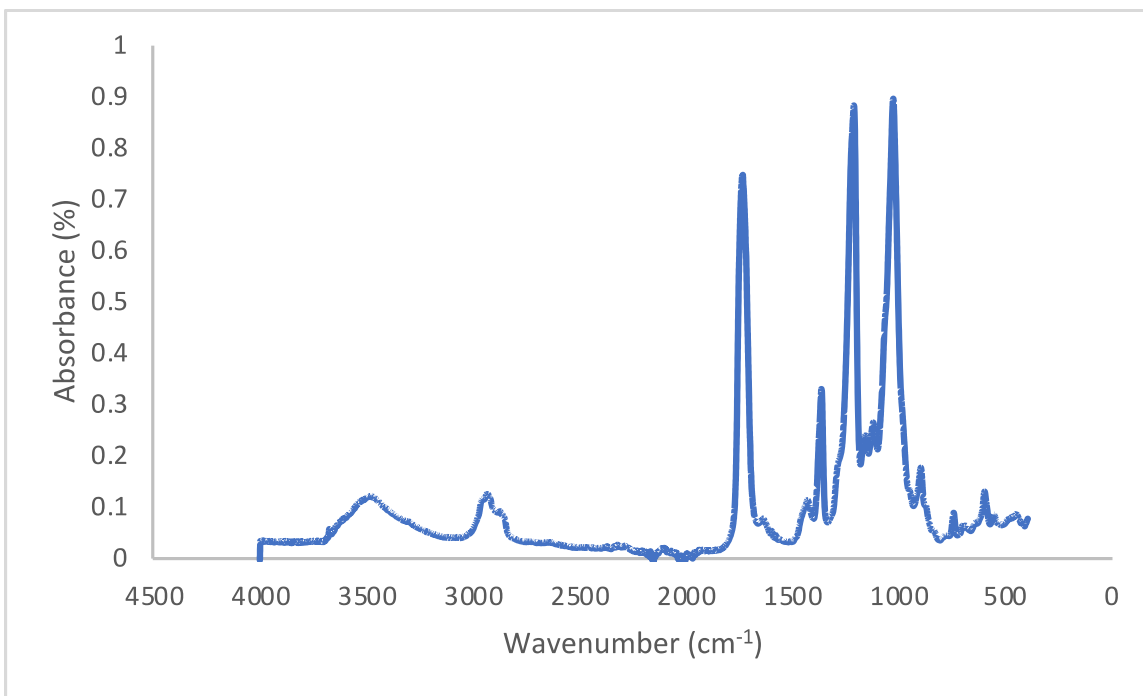
2018 ResinKit No. 11 Cellulose Acetate
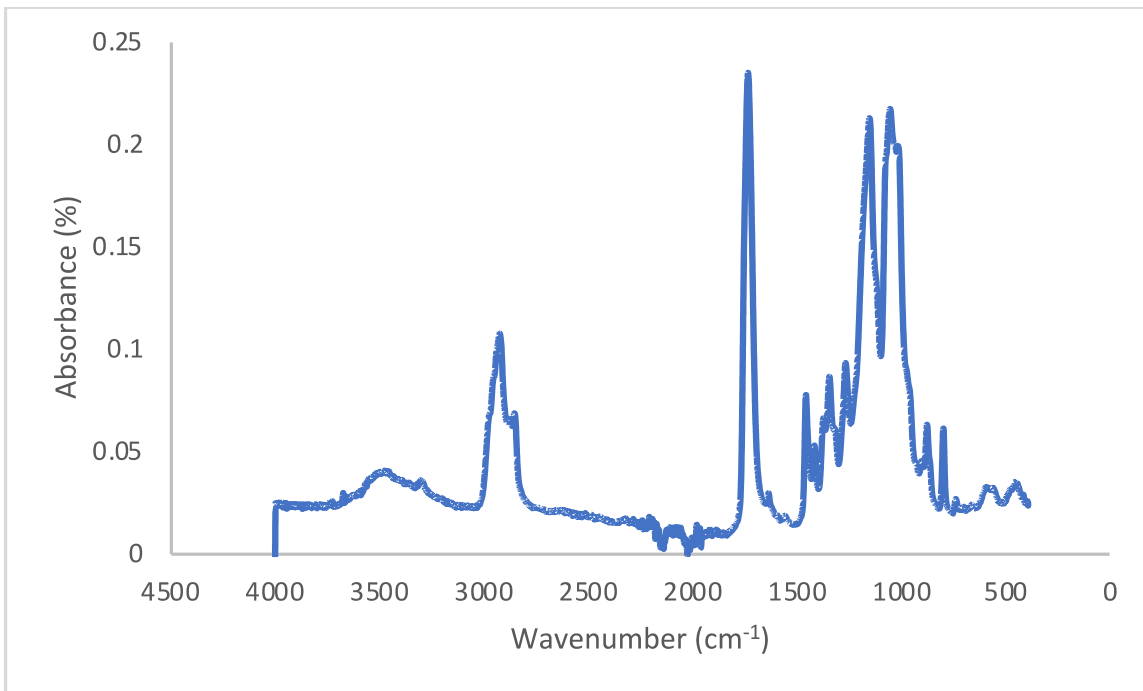
2010 ResinKit No. 12 Cellulose Acetate Butyrate
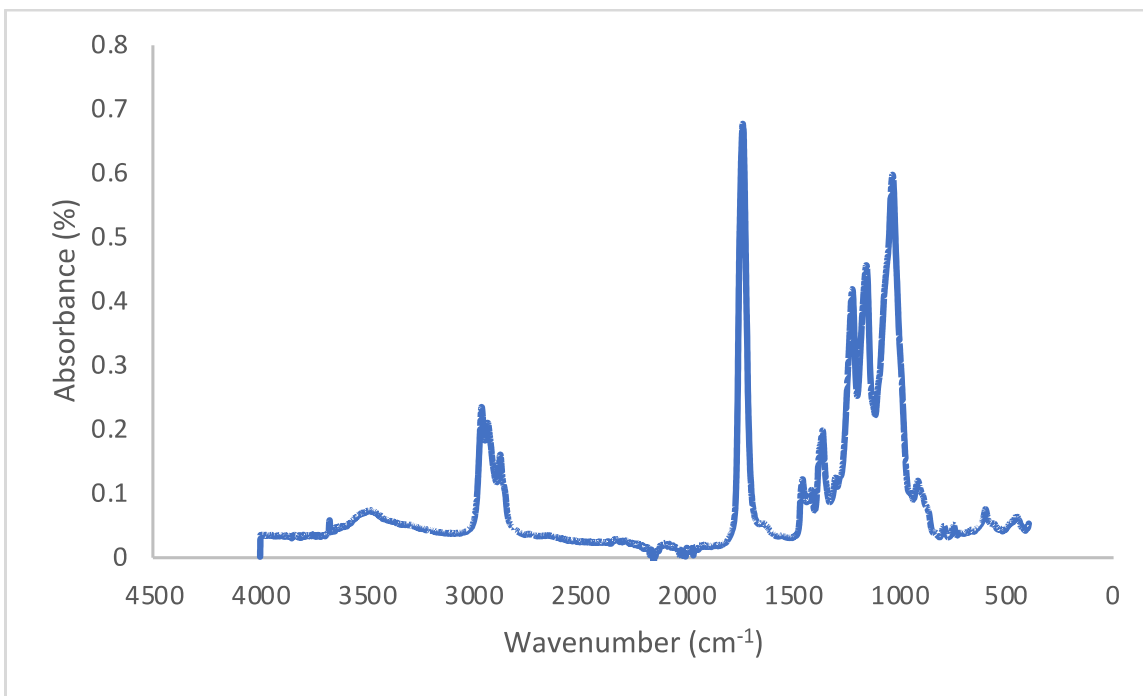
2018 ResinKit No. 12 Cellulose Acetate Butyrate
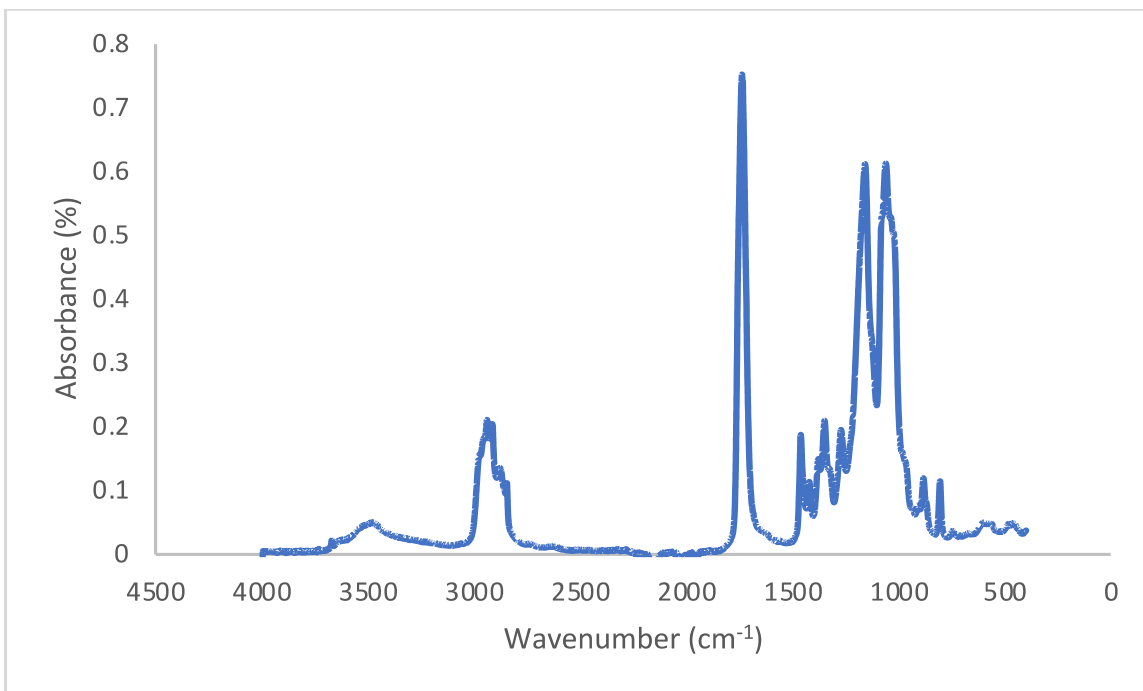
2010 ResinKit No. 13 Cellulose Acetate Propionate
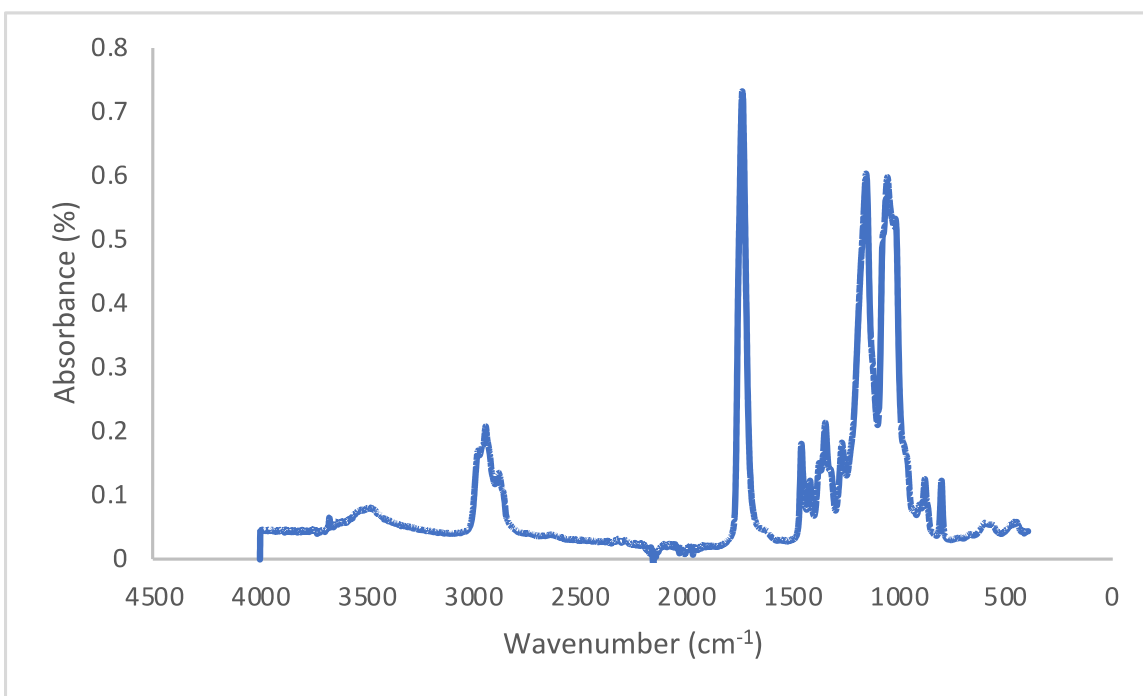
2018 ResinKit No. 13 Cellulose Acetate Propionate
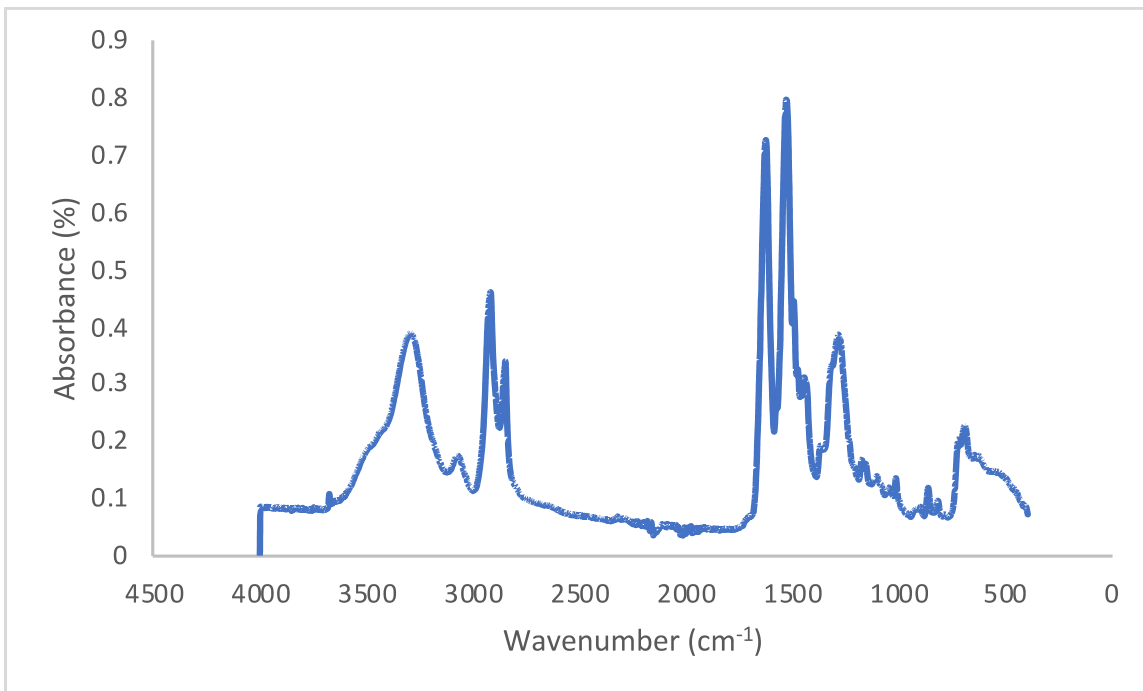
2010 ResinKit No. 14 Transparent Nylon
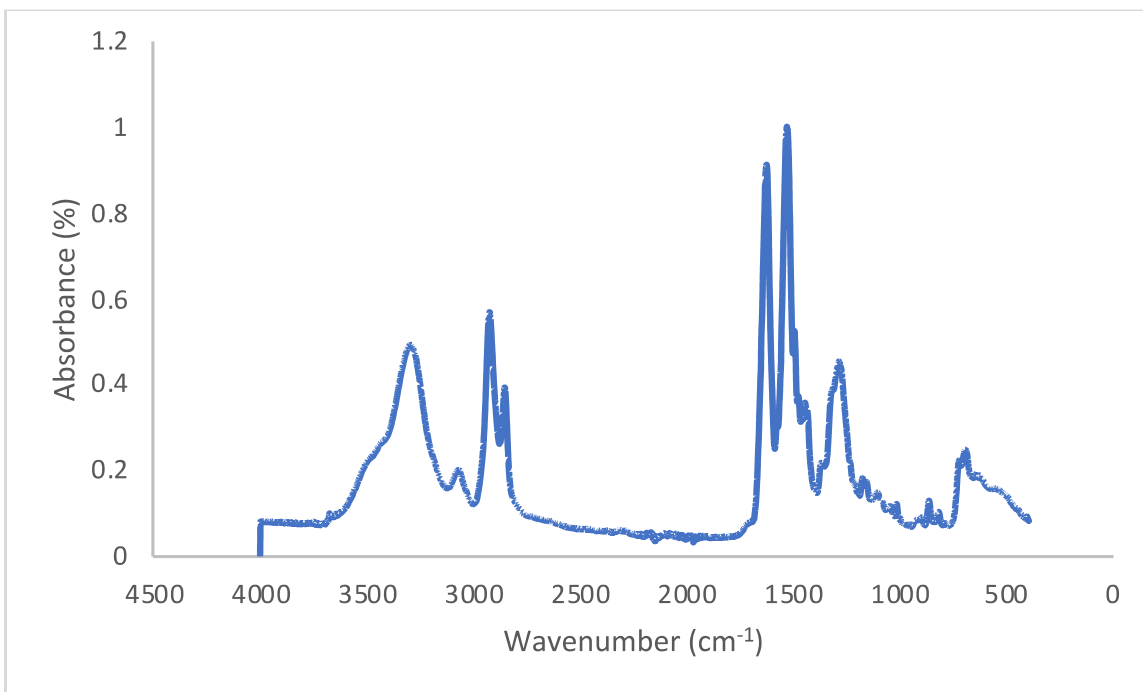
2018 ResinKit No. 14 Transparent Nylon
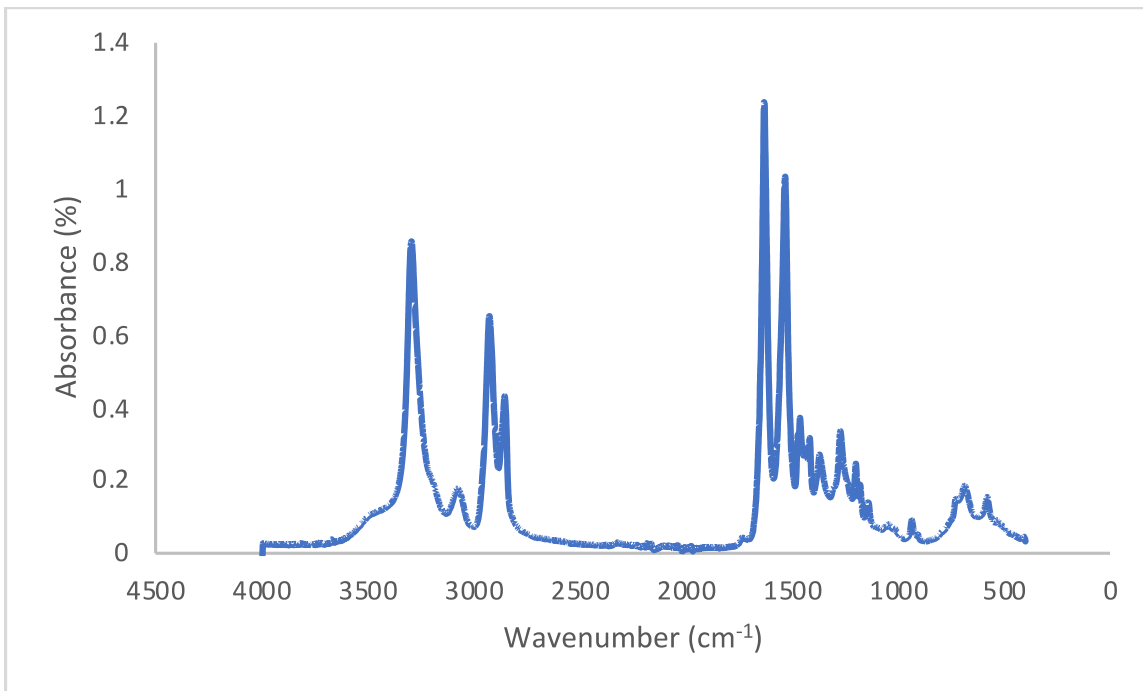
2010 ResinKit No. 15 Nylon Type 66
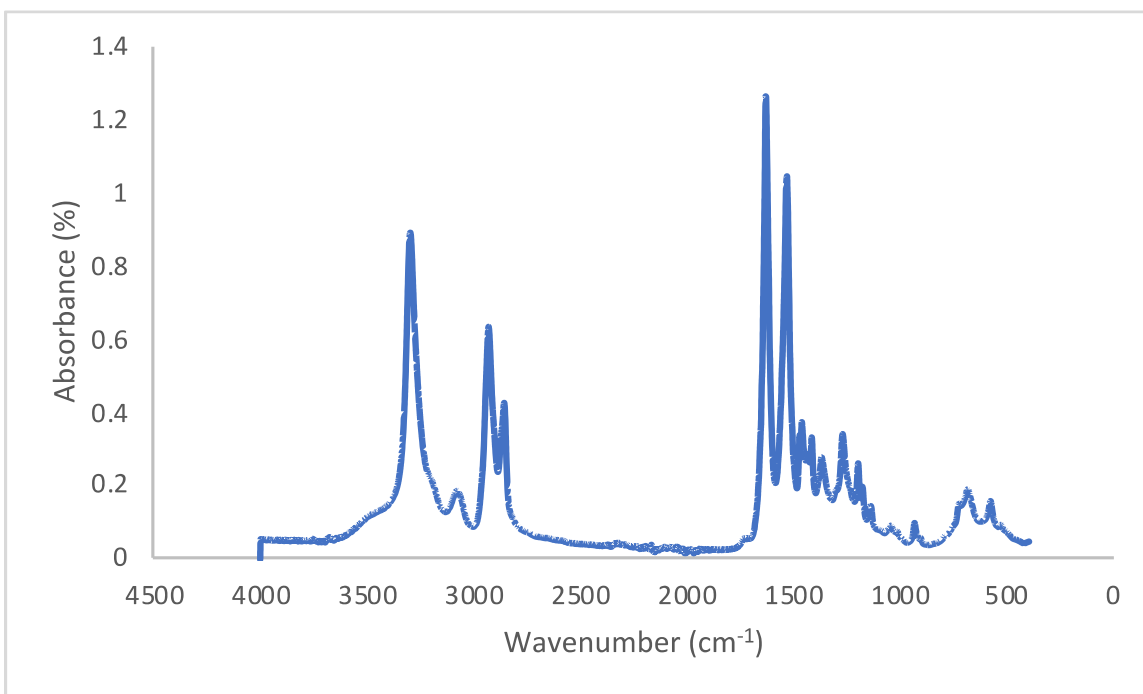
2018 ResinKit No. 15 Nylon Type 66
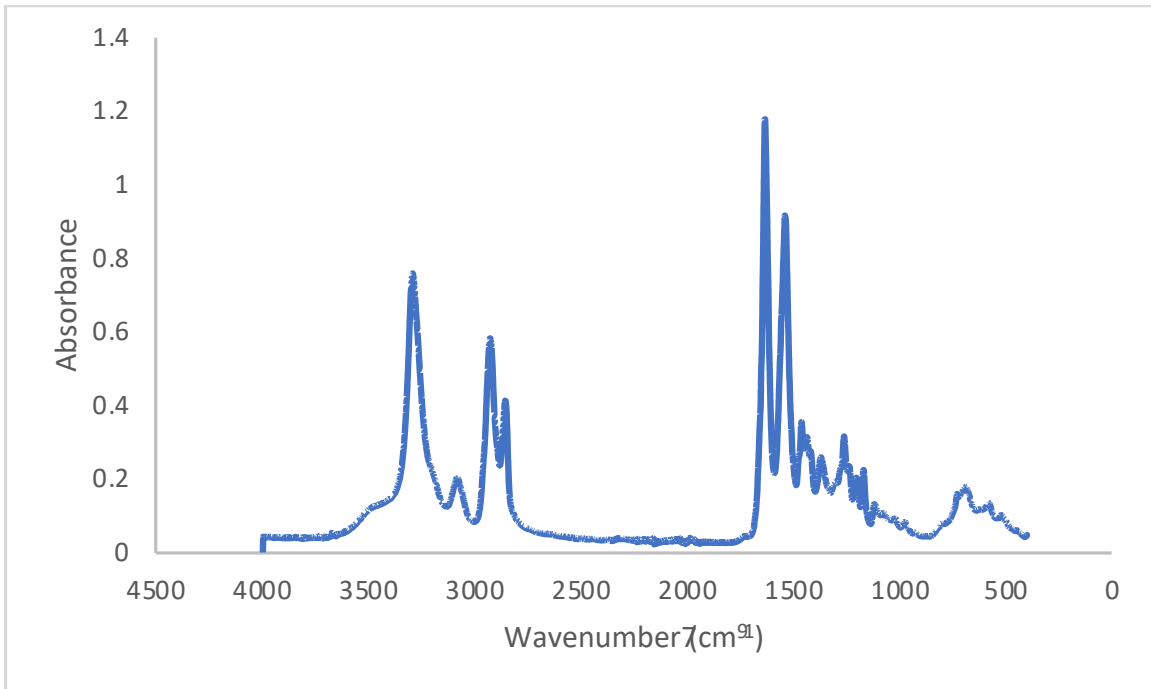
2010 ResinKit No. 16 Nylon Type 6
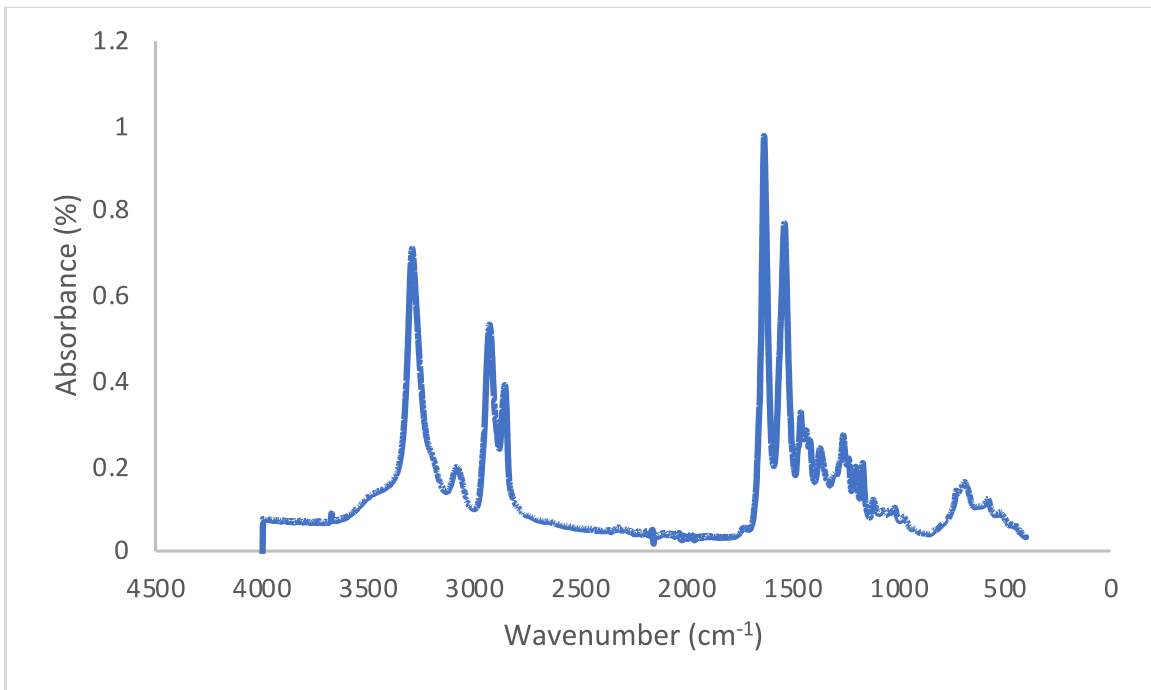
2018 ResinKit No. 16 Nylon Type 6
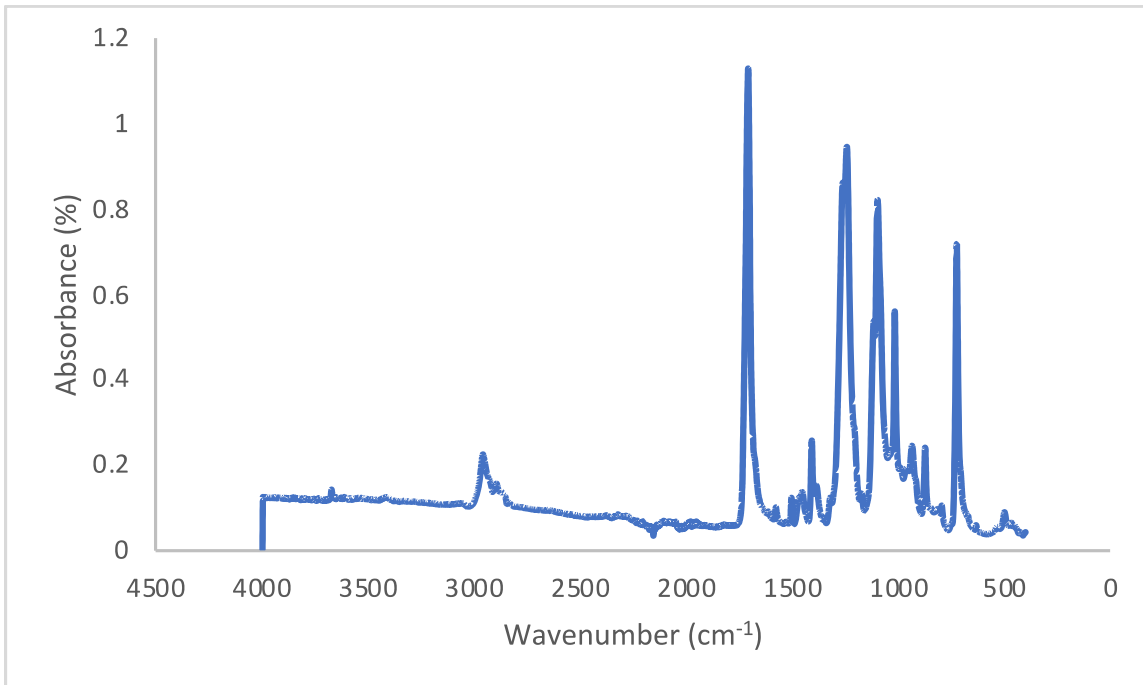
2010 ResinKit No. 17 Thermoplastic Polyester (Polybutylene terephthalate)
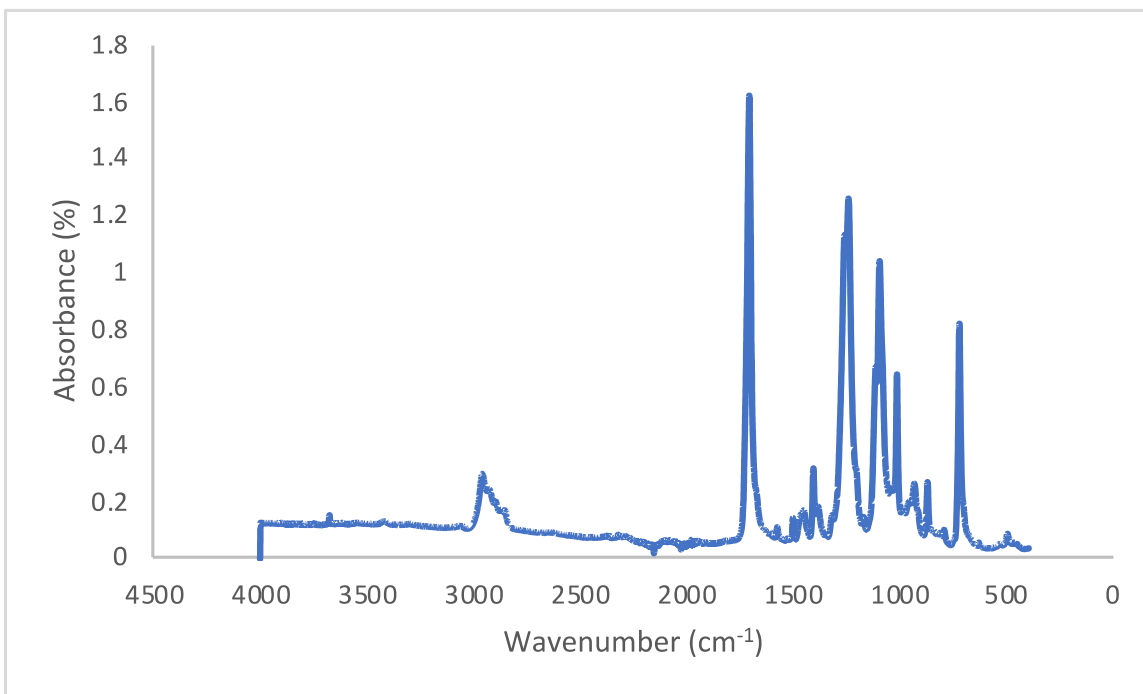
2018 ResinKit No. 17 Thermoplastic Polyester (Polybutylene terephthalate)
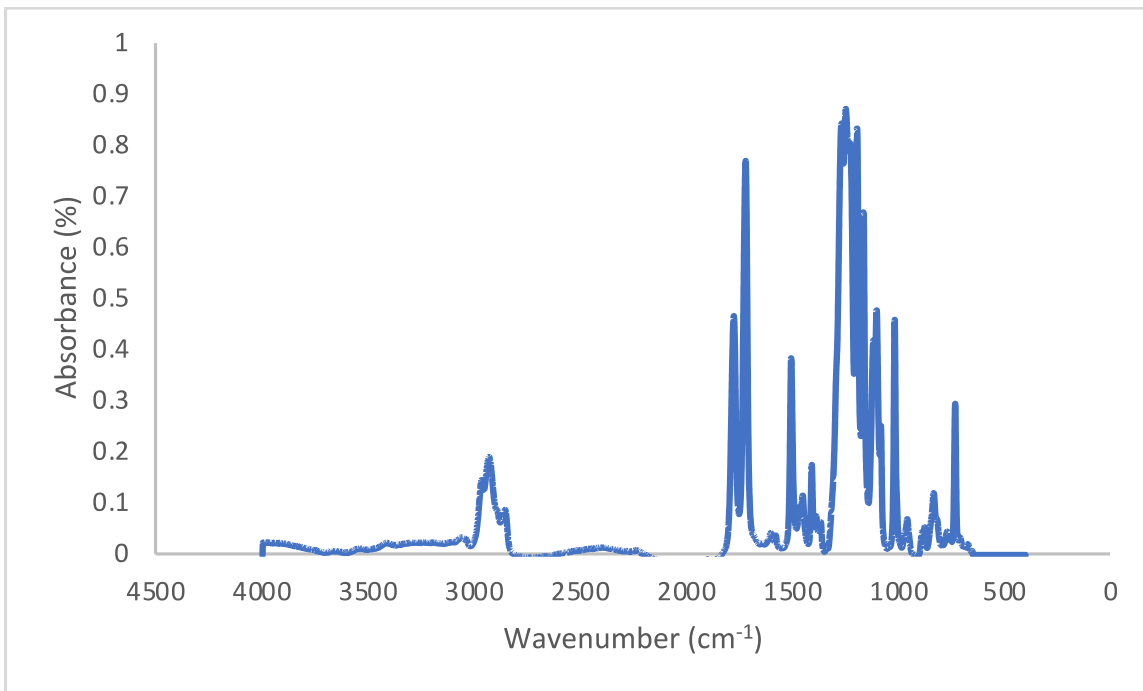
2010 ResinKit No. 18 Thermoplastic Polyester (Polyethylene terephthalate Glycol)
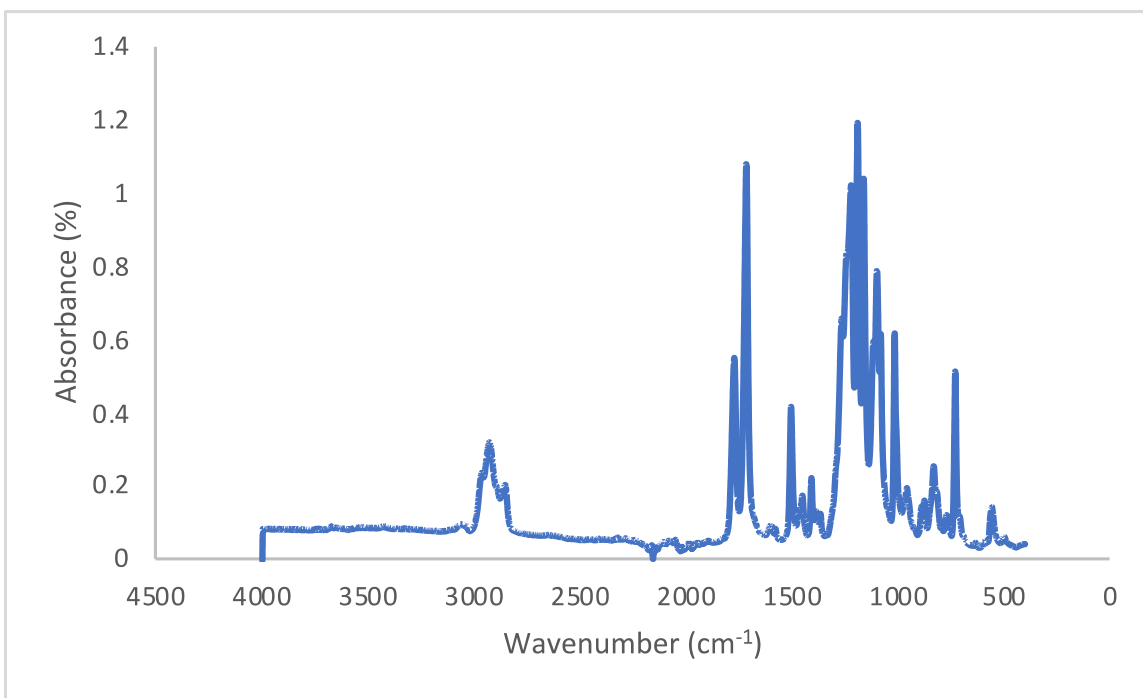
2018 ResinKit No. 18 Thermoplastic Polyester (Polyethylene terephthalate Glycol)
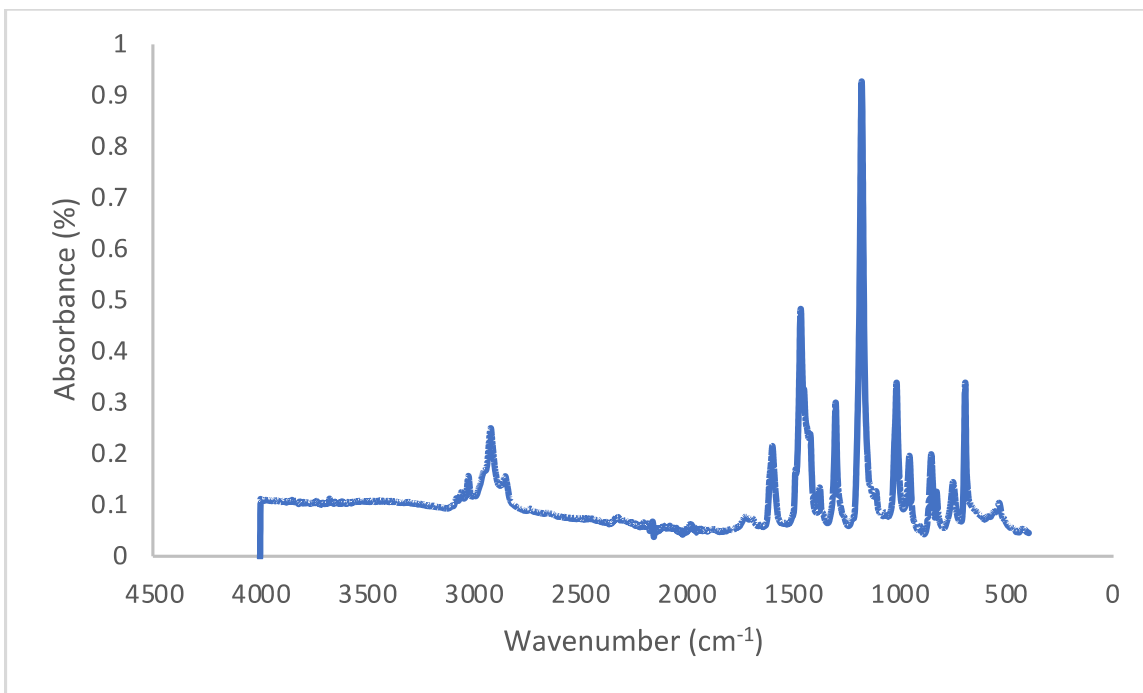
2010 ResinKit No. 19 Polyphenol Oxide
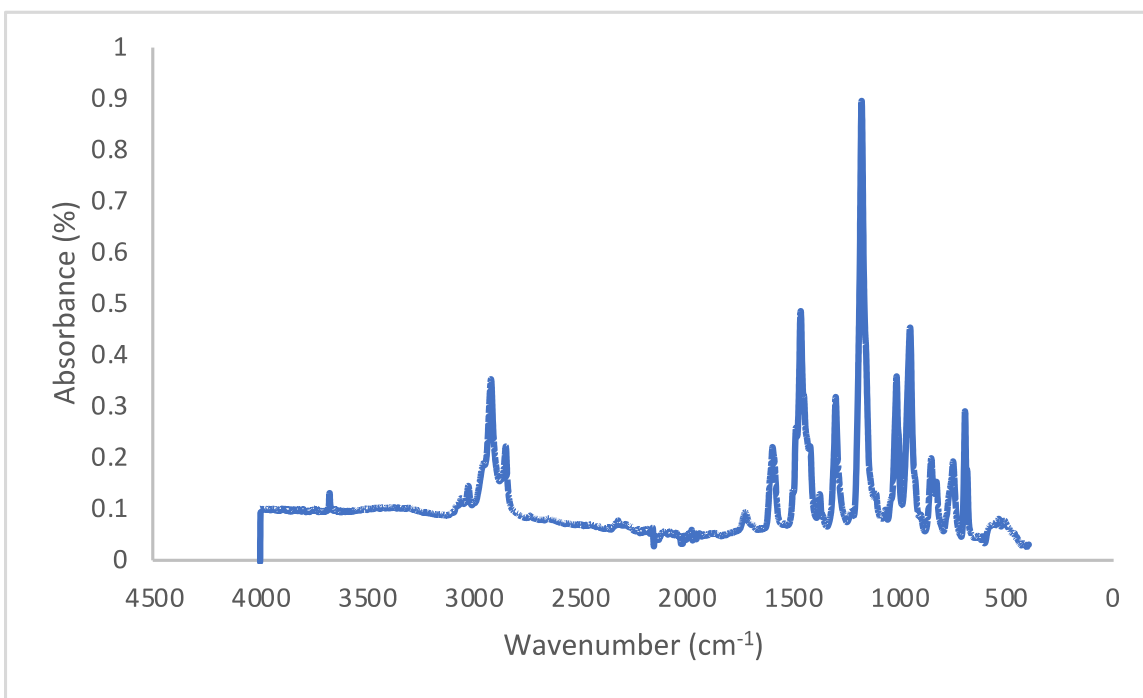
2018 ResinKit No. 19 Polyphenol Oxide
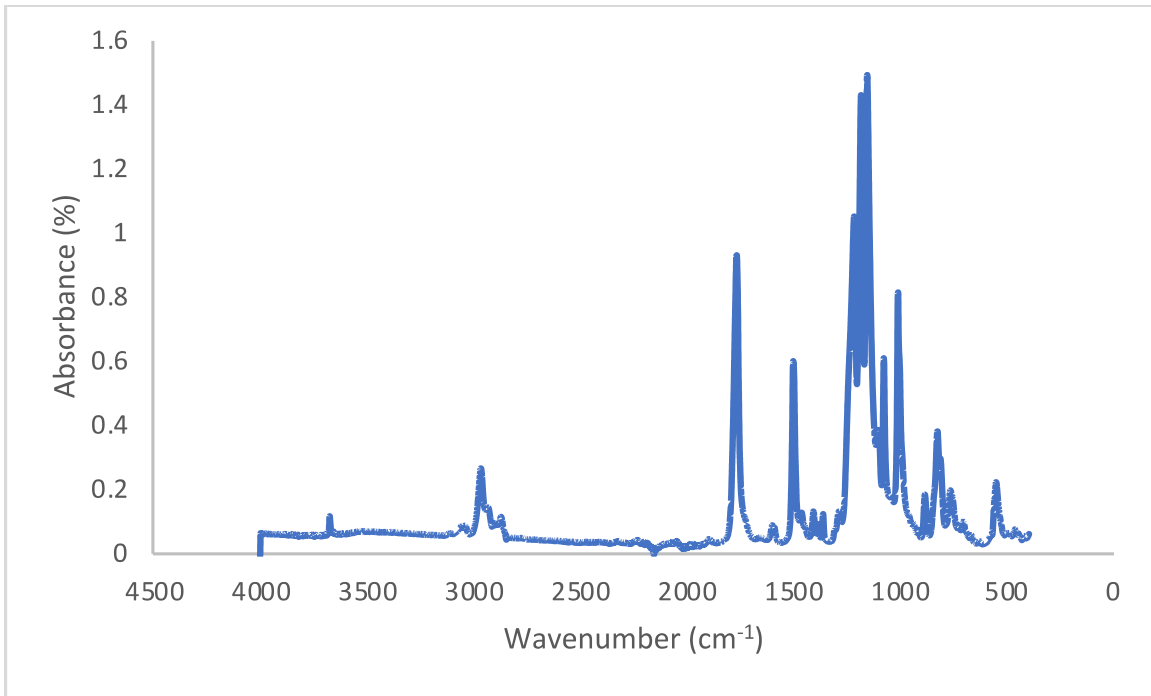
2010 ResinKit No. 20 Polycarbonate
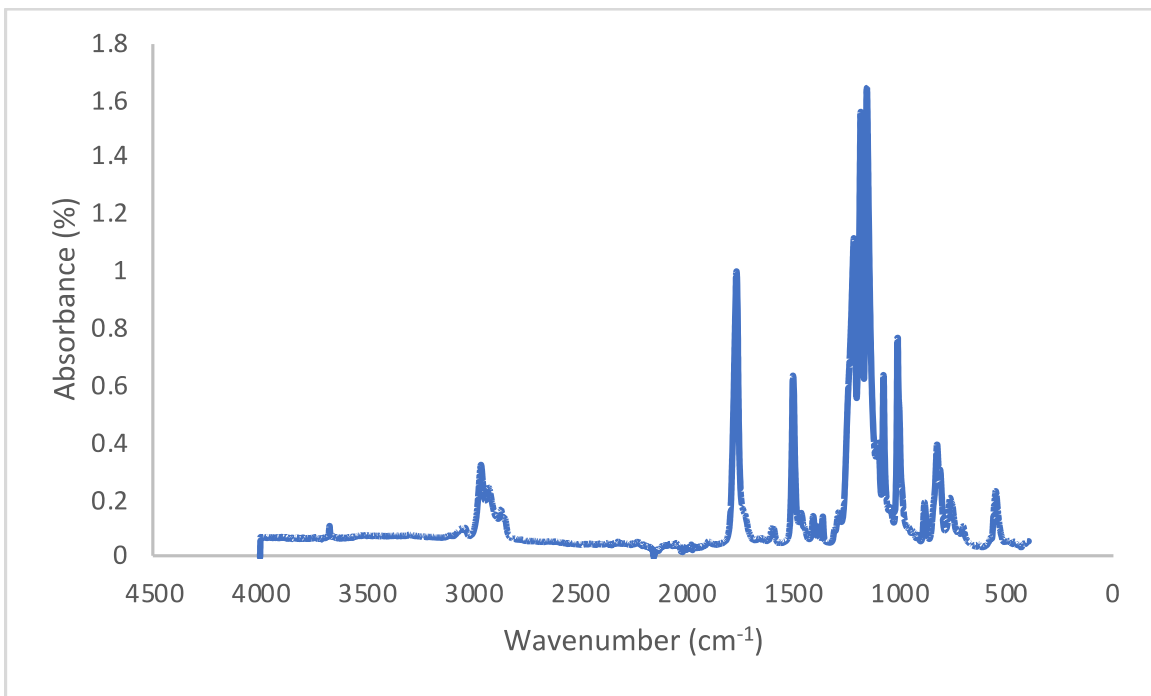
2018 ResinKit No. 20 Polycarbonate
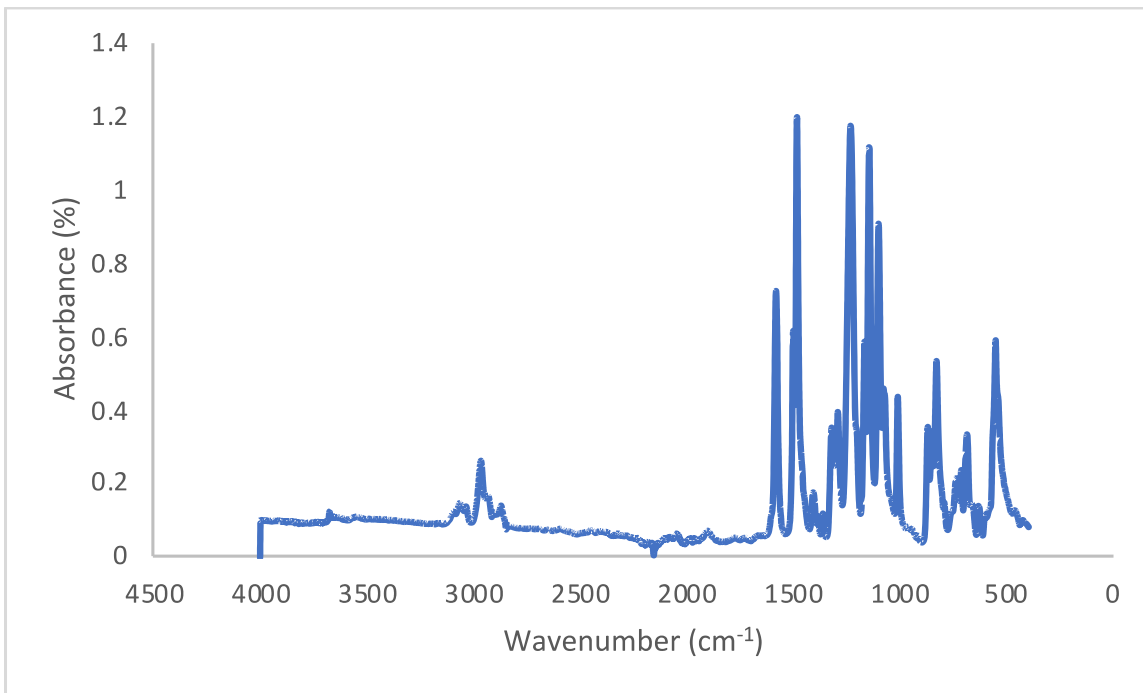
2010 ResinKit No. 21 Polysulfone
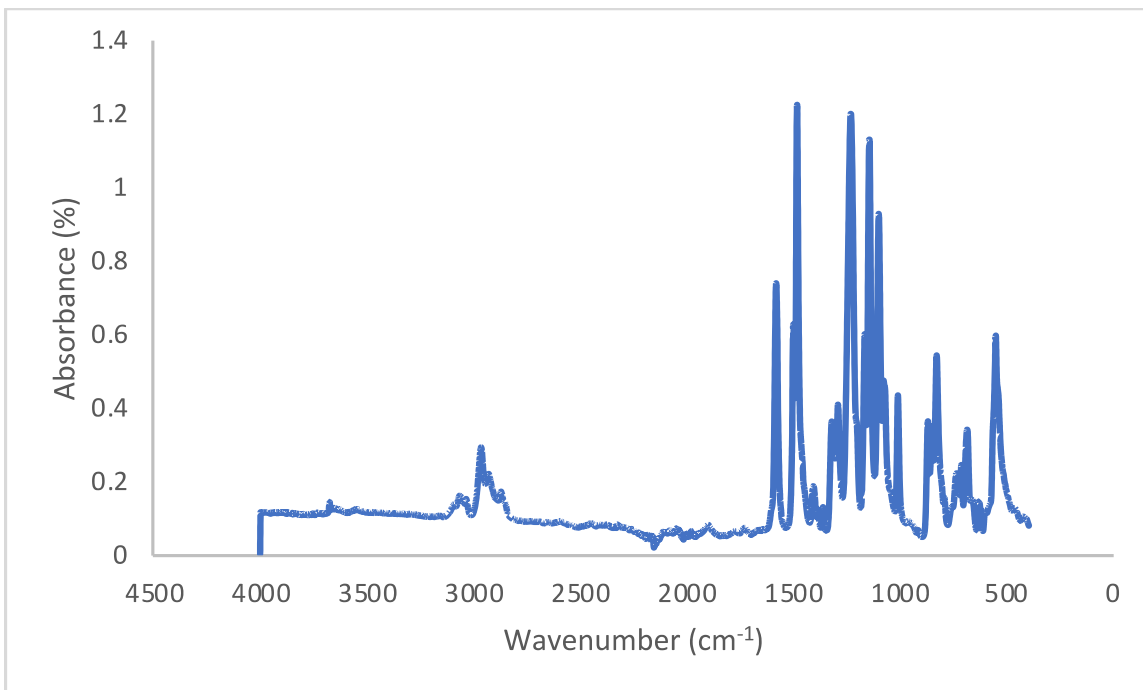
2018 ResinKit No. 21 Polysulfone
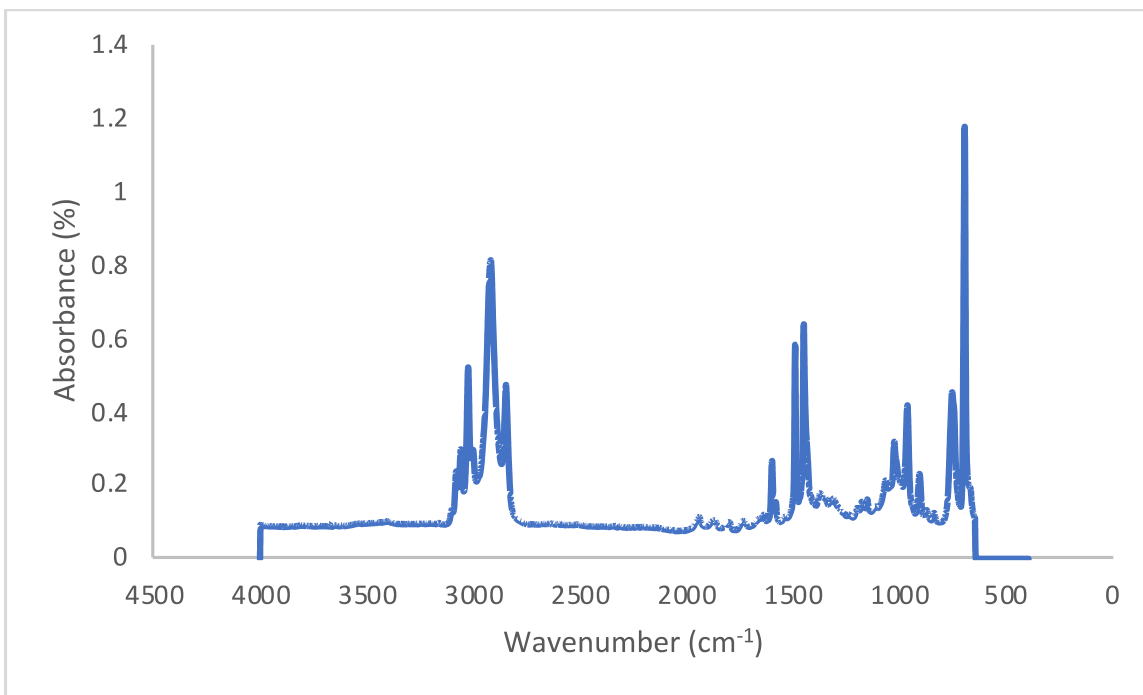
2010 ResinKit No. 22 Polybutylene
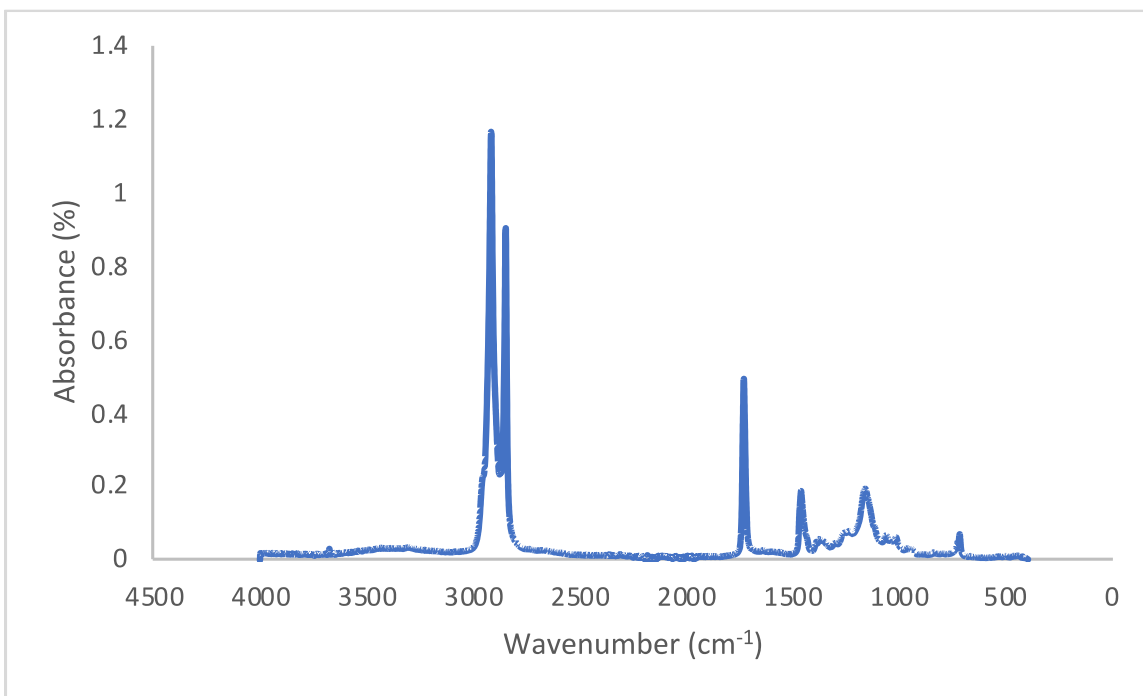
2018 ResinKit No. 22 Polybutylene
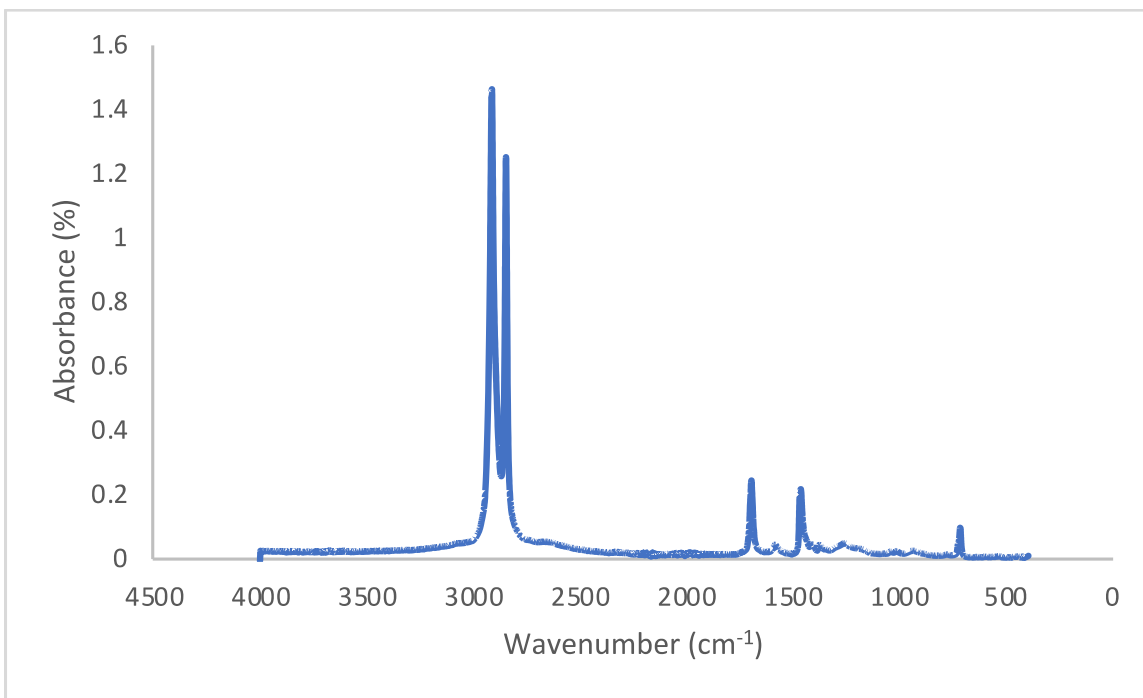
2010 ResinKit No. 23 Ionomer
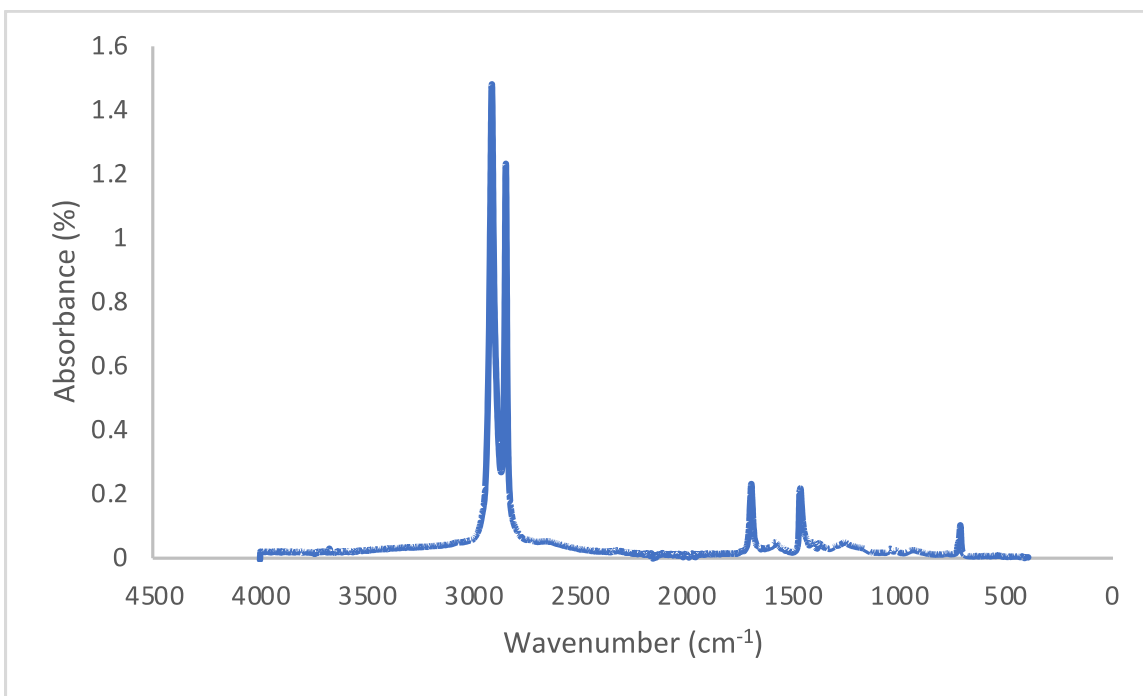
2018 ResinKit No. 23 Ionomer
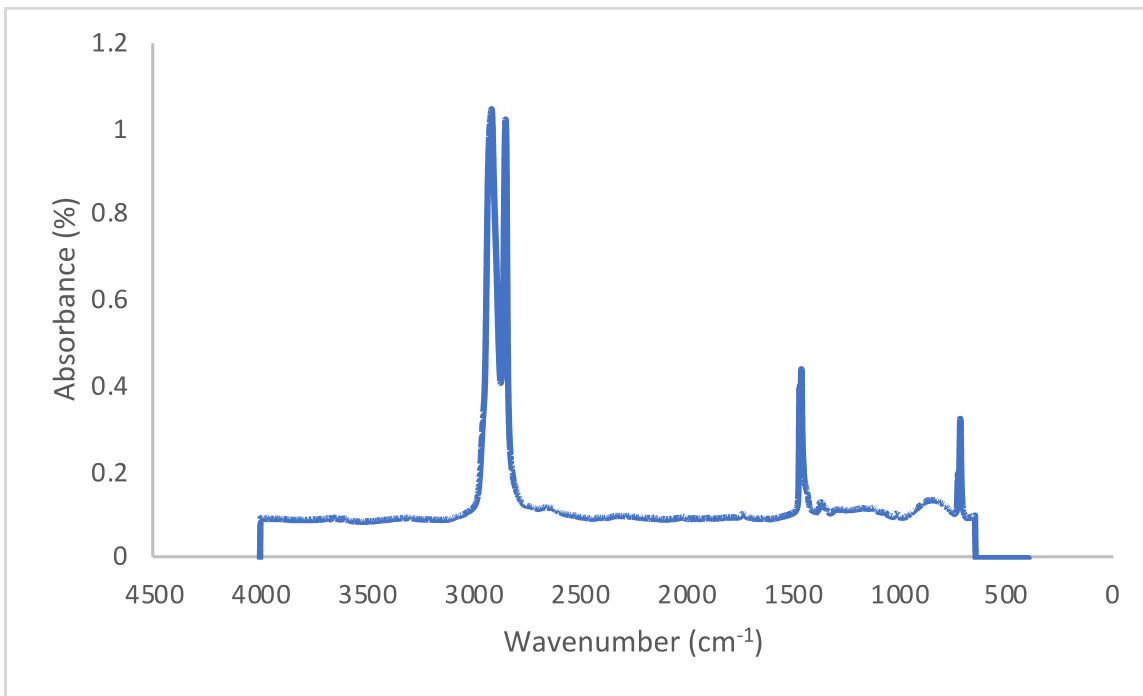
2010 ResinKit No. 24 Low Density Polyethylene
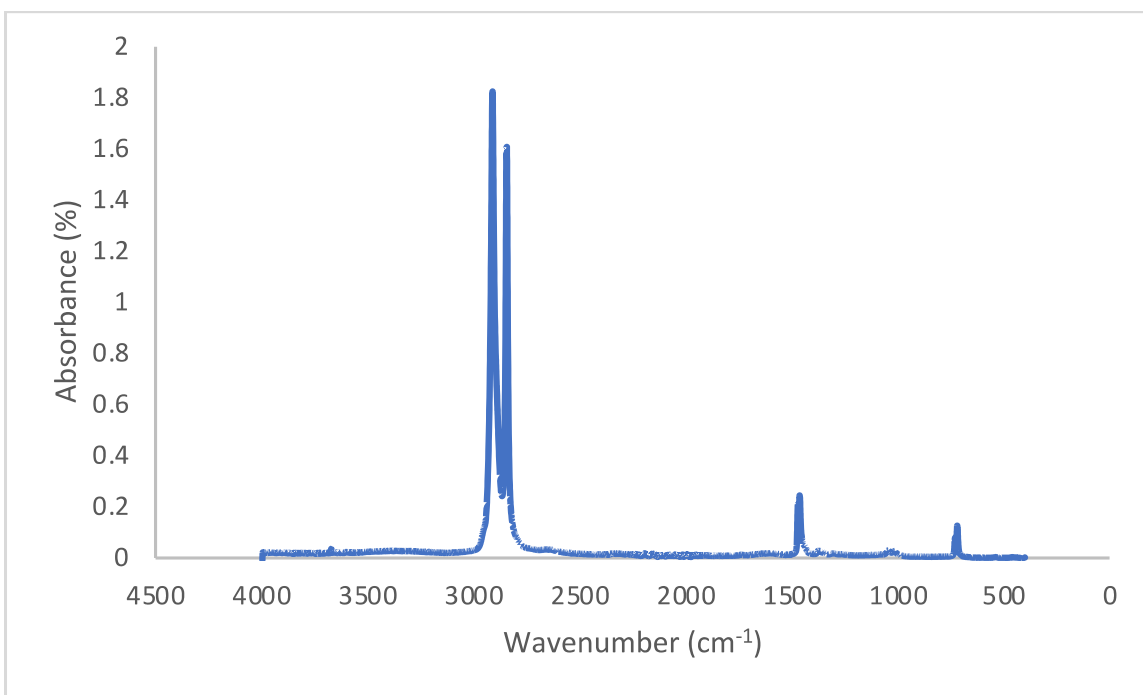
2018 ResinKit No. 24 Low Density Polyethylene
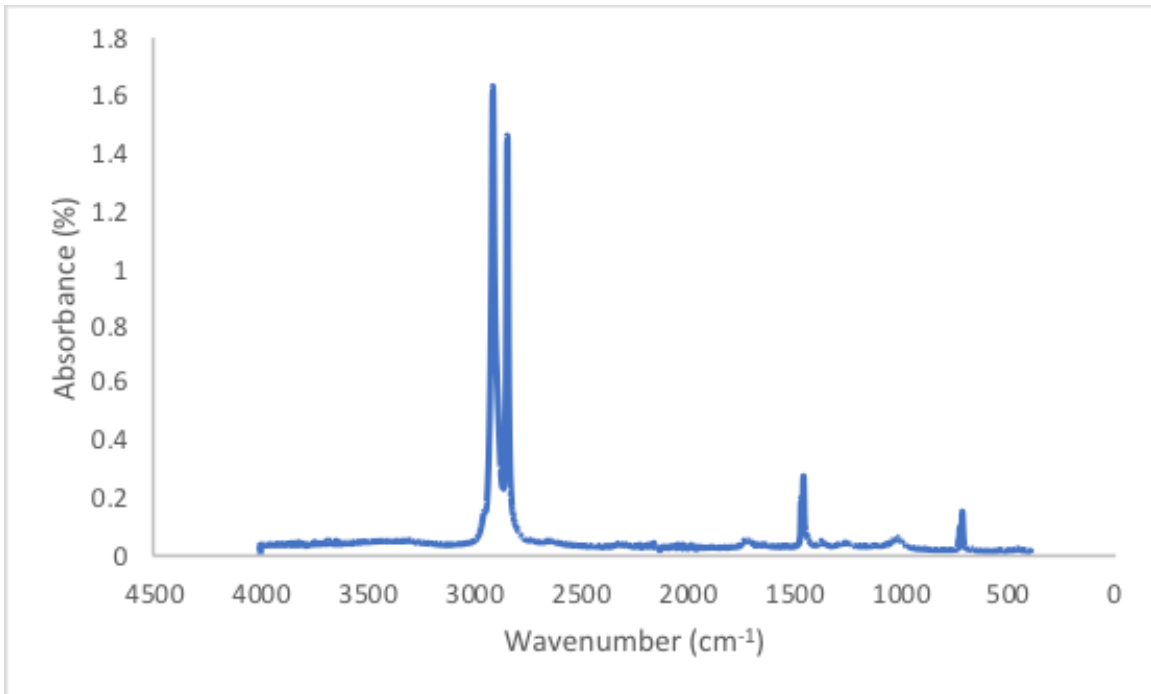
2010 ResinKit No. 25 High Density Polyethylene
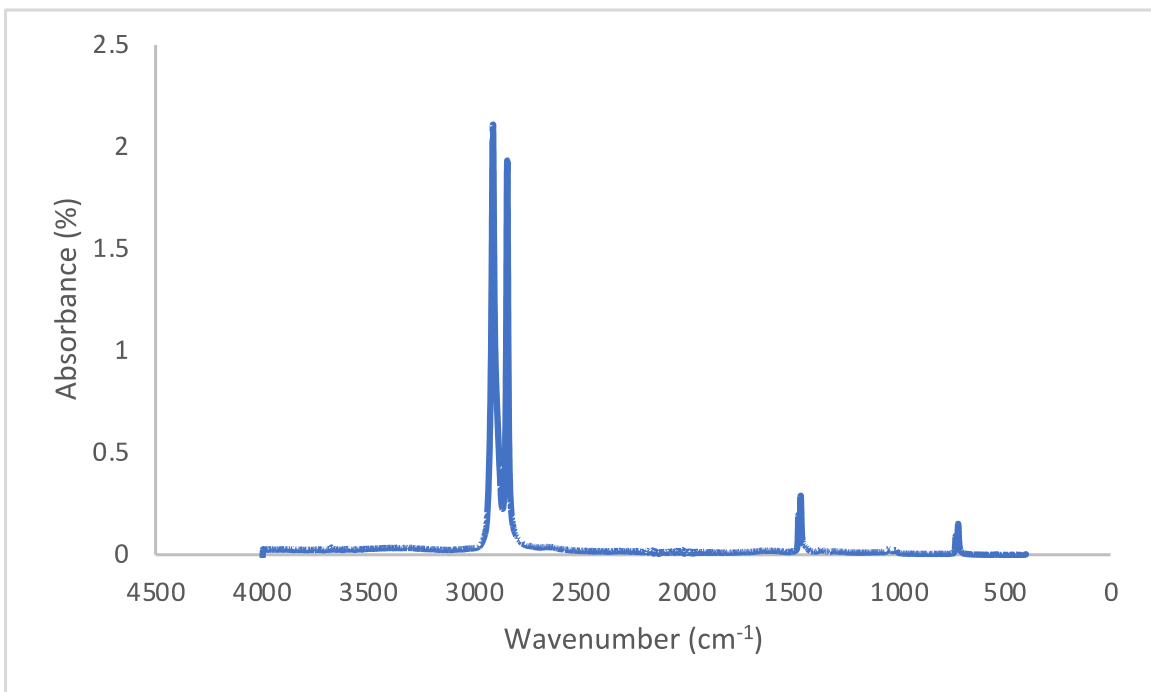
2018 ResinKit No. 25 High Density Polyethylene
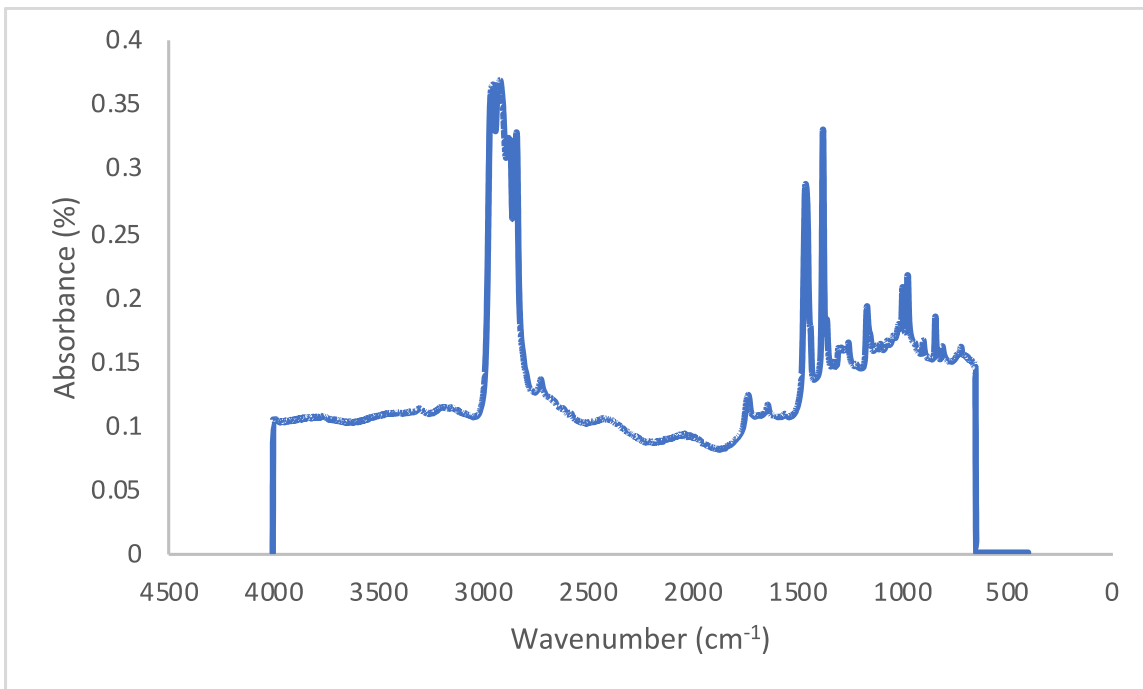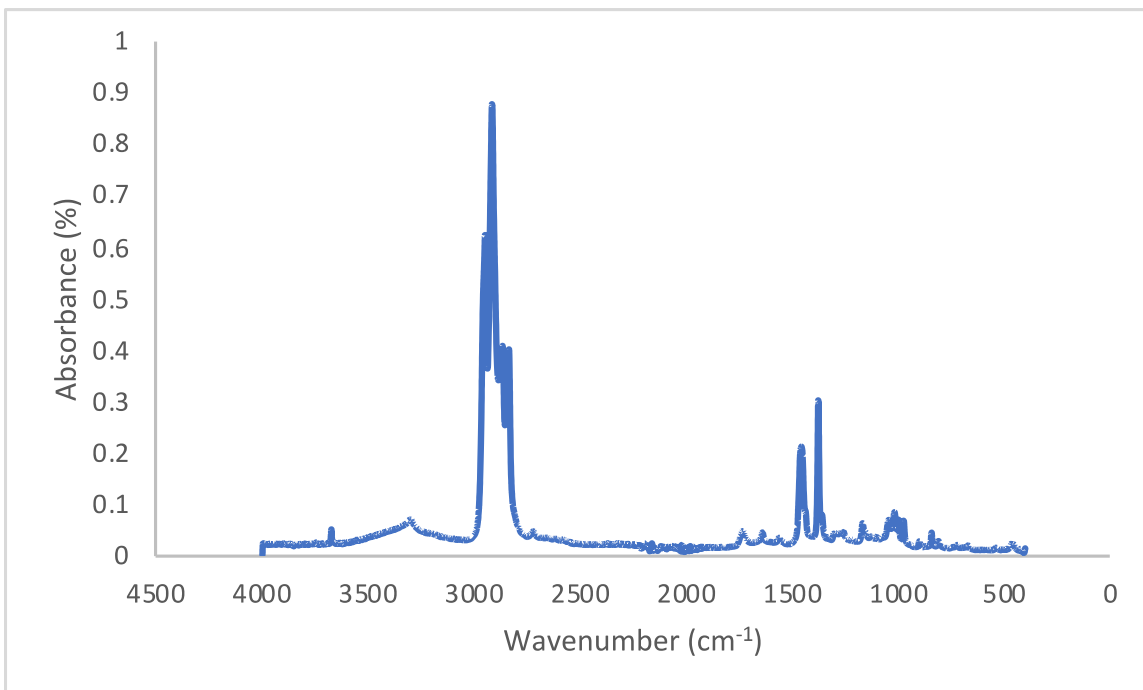
2010 ResinKit No. 26 Polypropylene Co-Polymer

2018 ResinKit No. 26 Polypropylene Co-Polymer
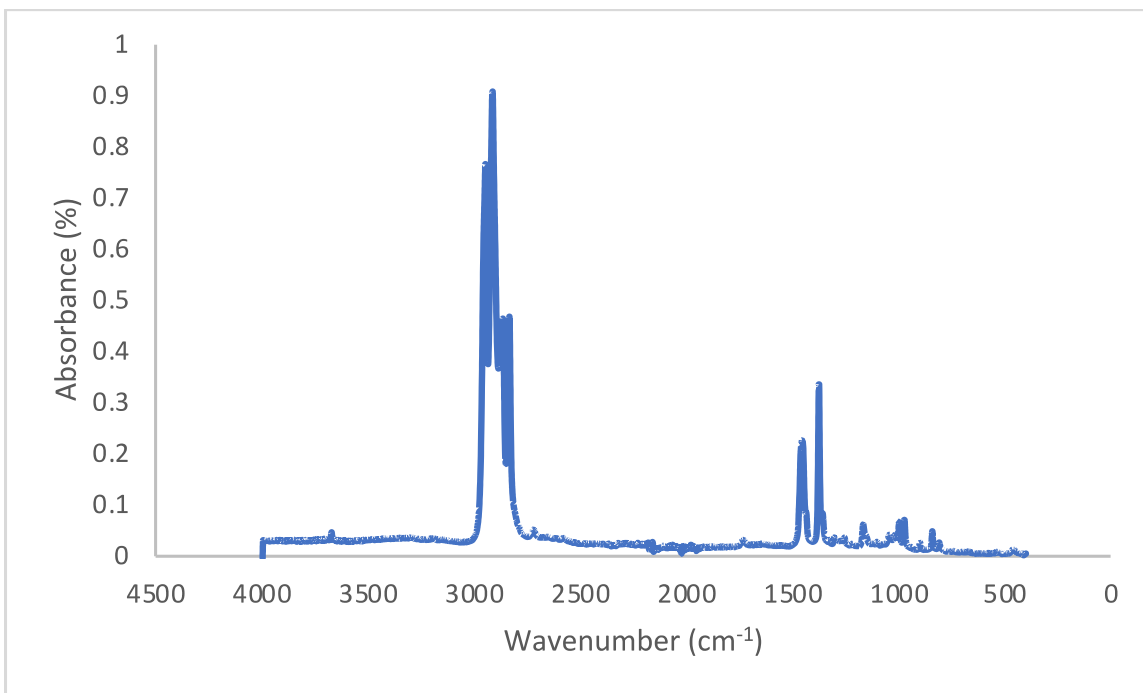
2010 ResinKit No. 27 Polypropylene Homo-Polymer
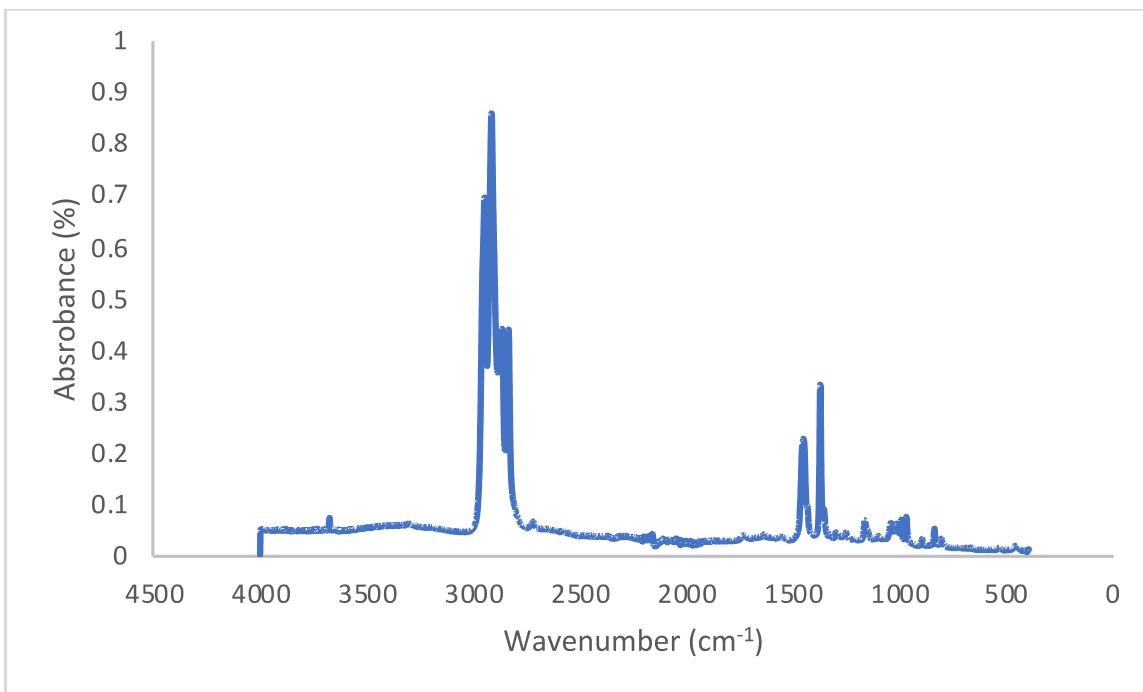
2018 ResinKit No. 27 Polypropylene Homo-Polymer
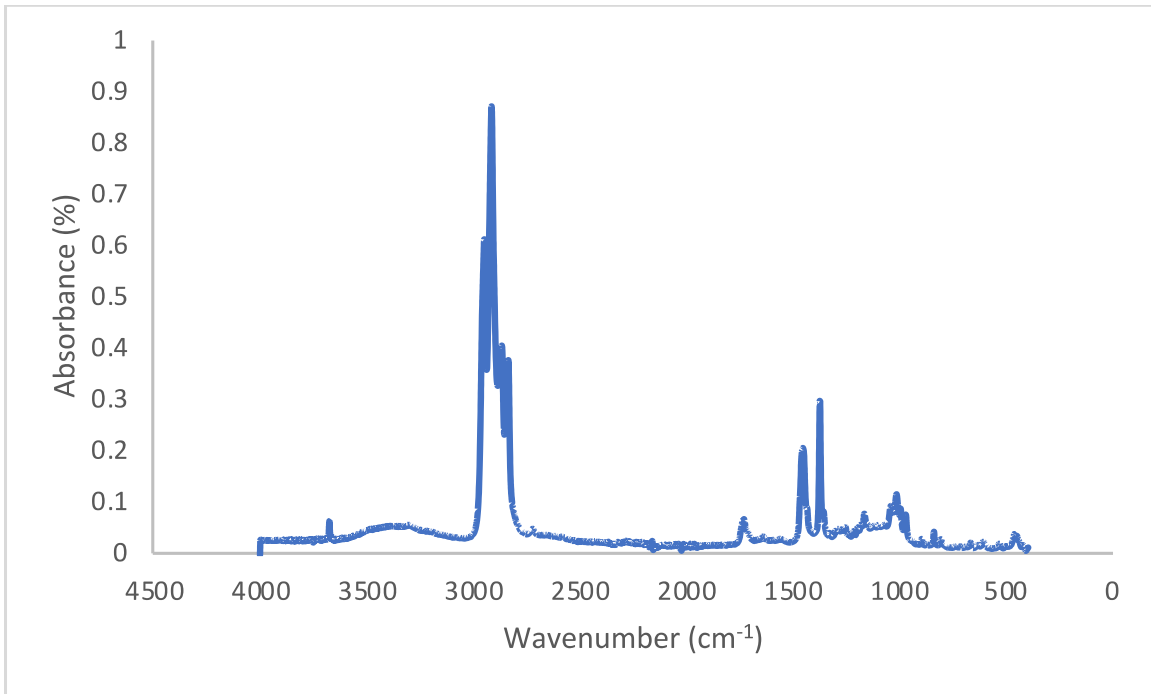
2010 ResinKit No. 28 Barium Sulfate Reinforced Polypropylene
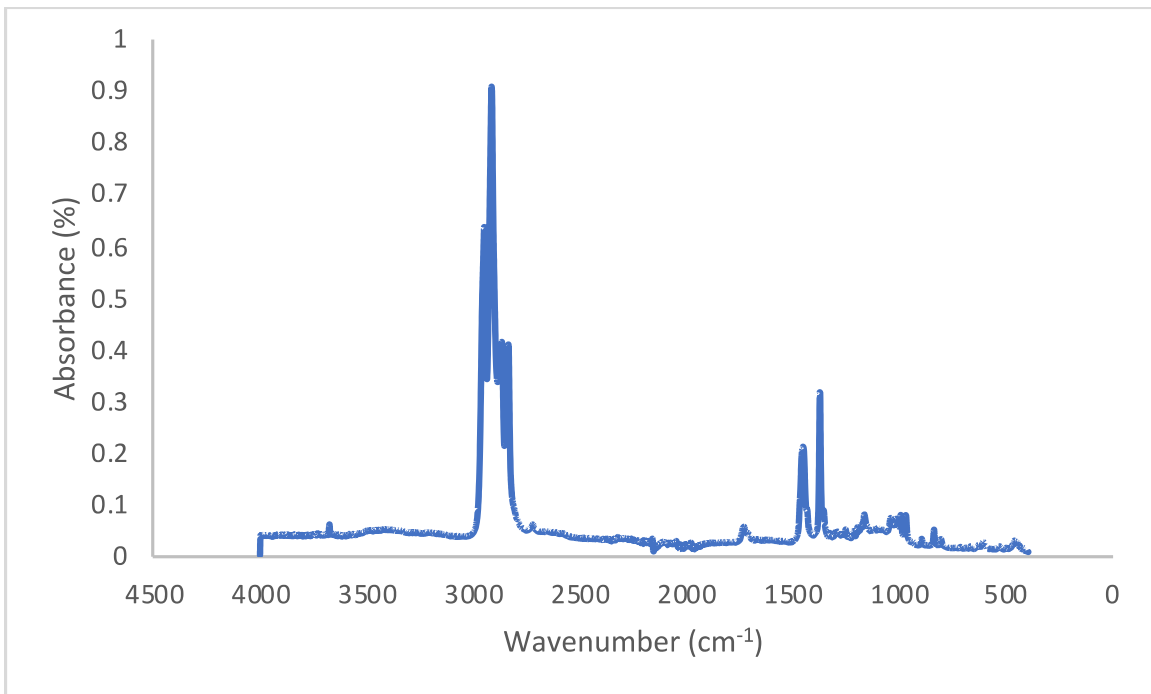
2018 ResinKit No. 28 Barium Sulfate Reinforced Polypropylene
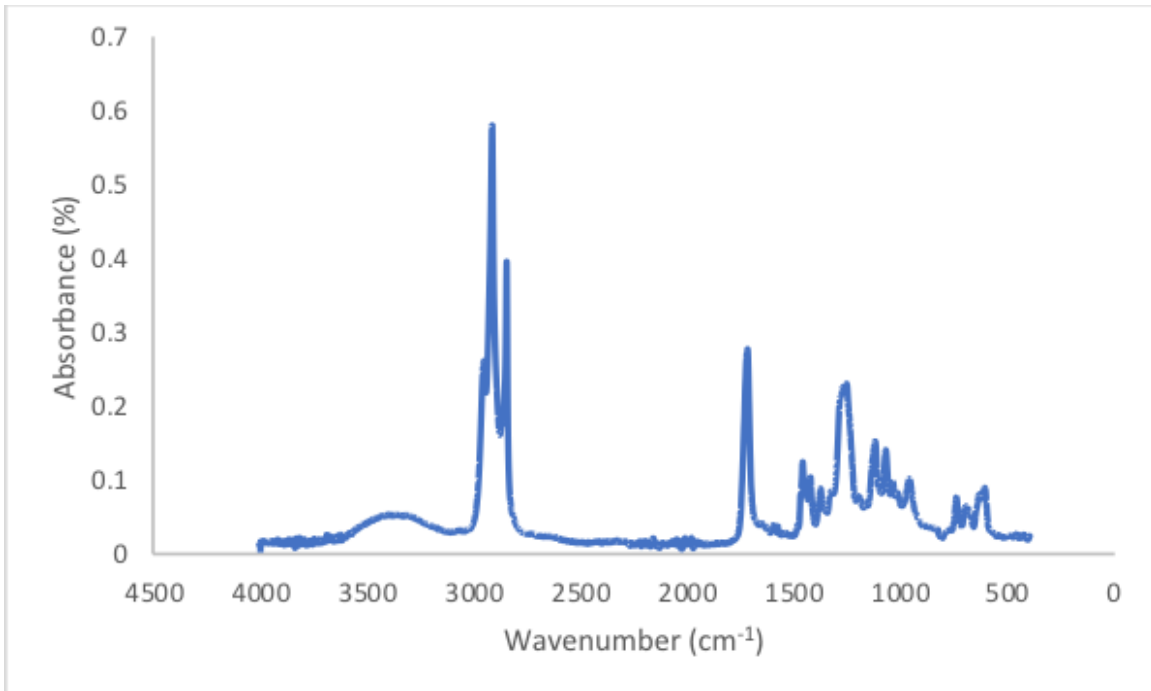
2010 ResinKit No. 29 Flexible Polyvinyl Chloride
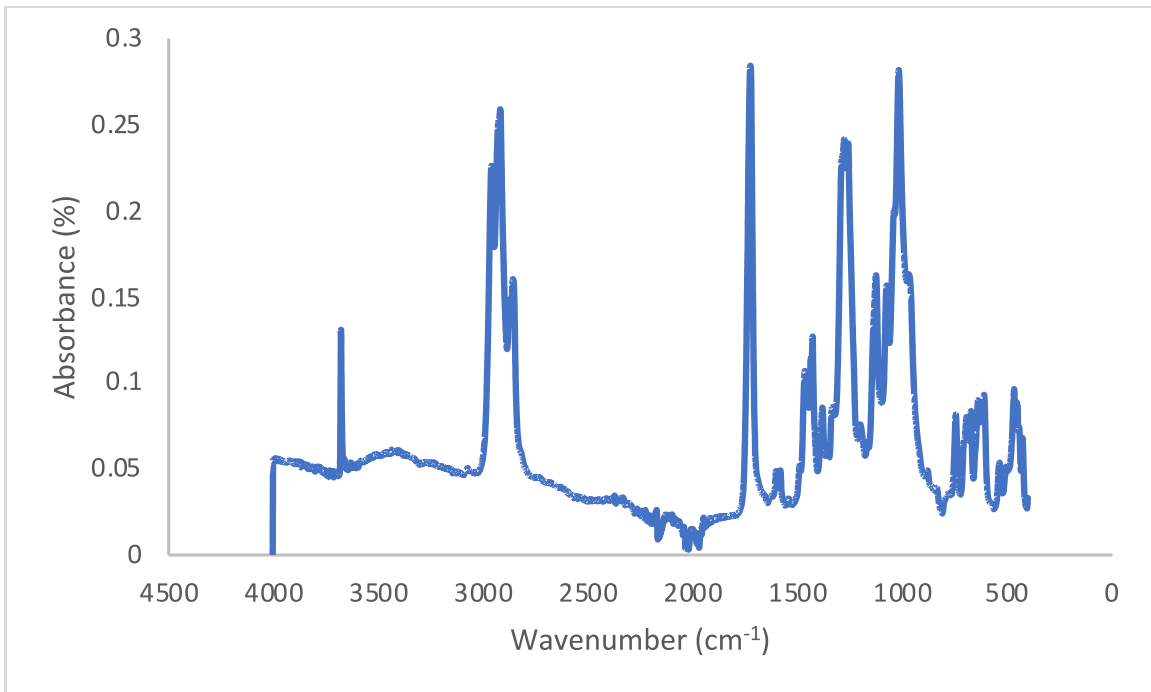
2018 ResinKit No. 29 Flexible Polyvinyl Chloride
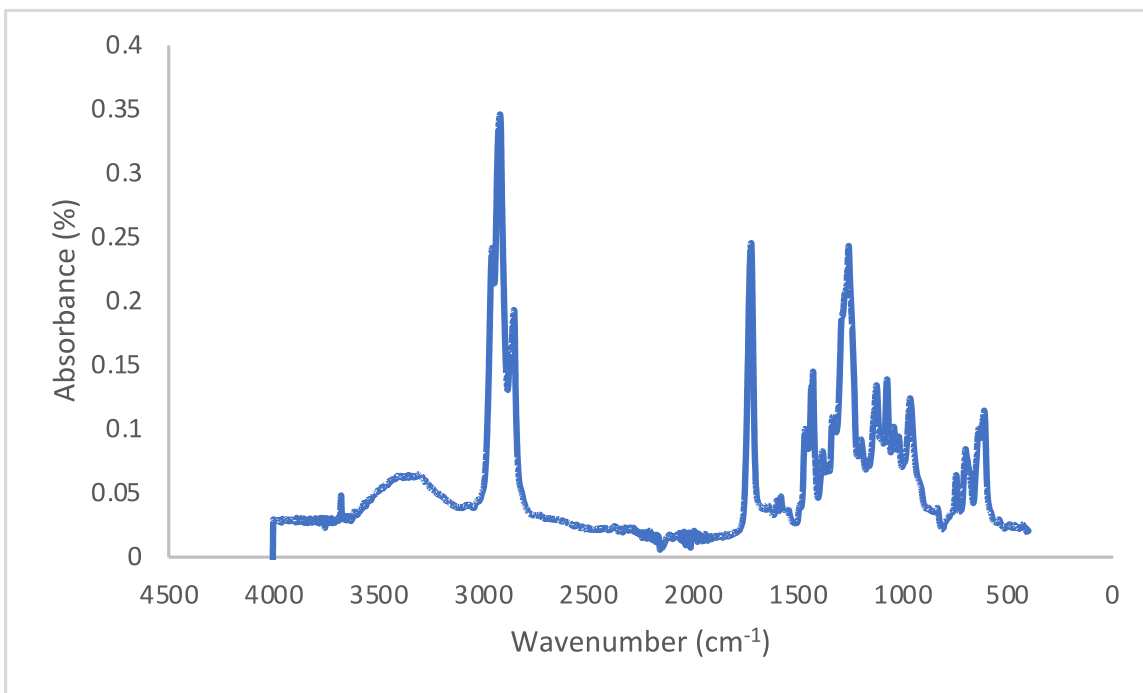
2010 ResinKit No. 30 Rigid Polyvinyl Chloride
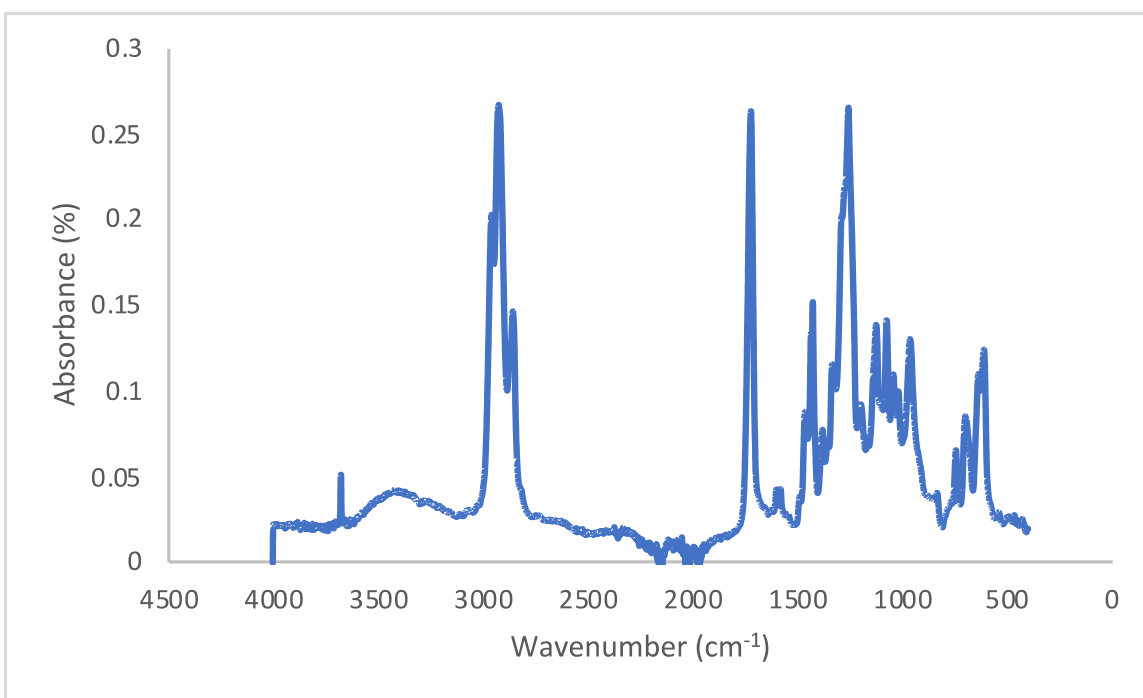
2018 ResinKit No. 30 Rigid Polyvinyl Chloride
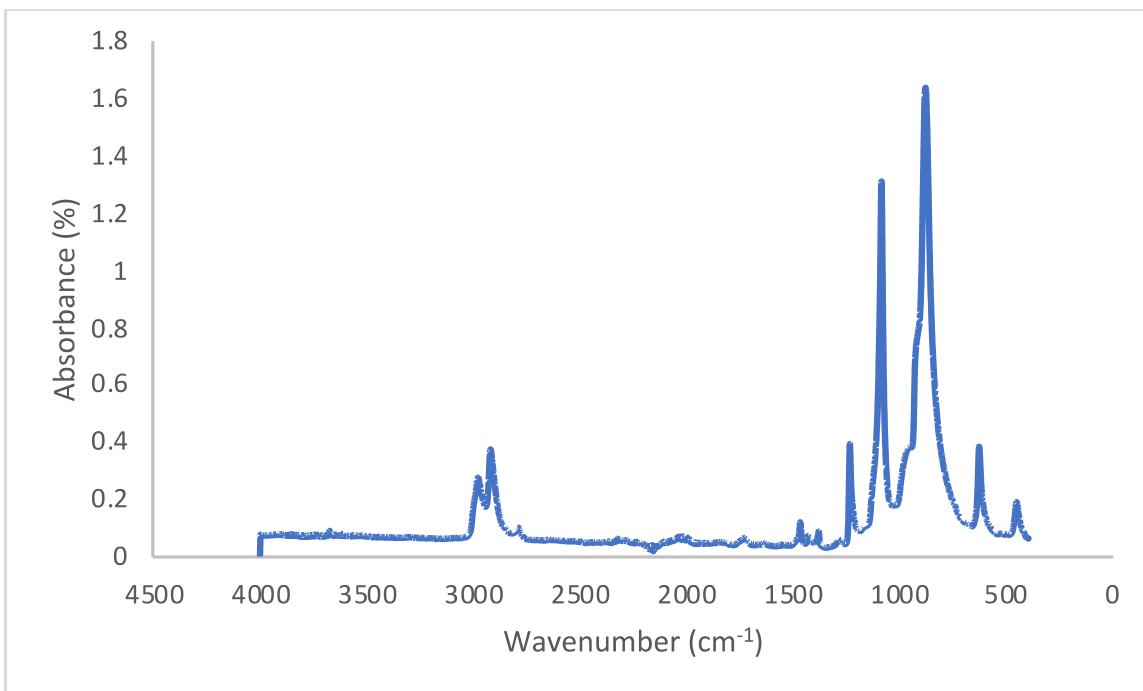
2010 ResinKit No. 31 Acetal Resin Homo-Polymer
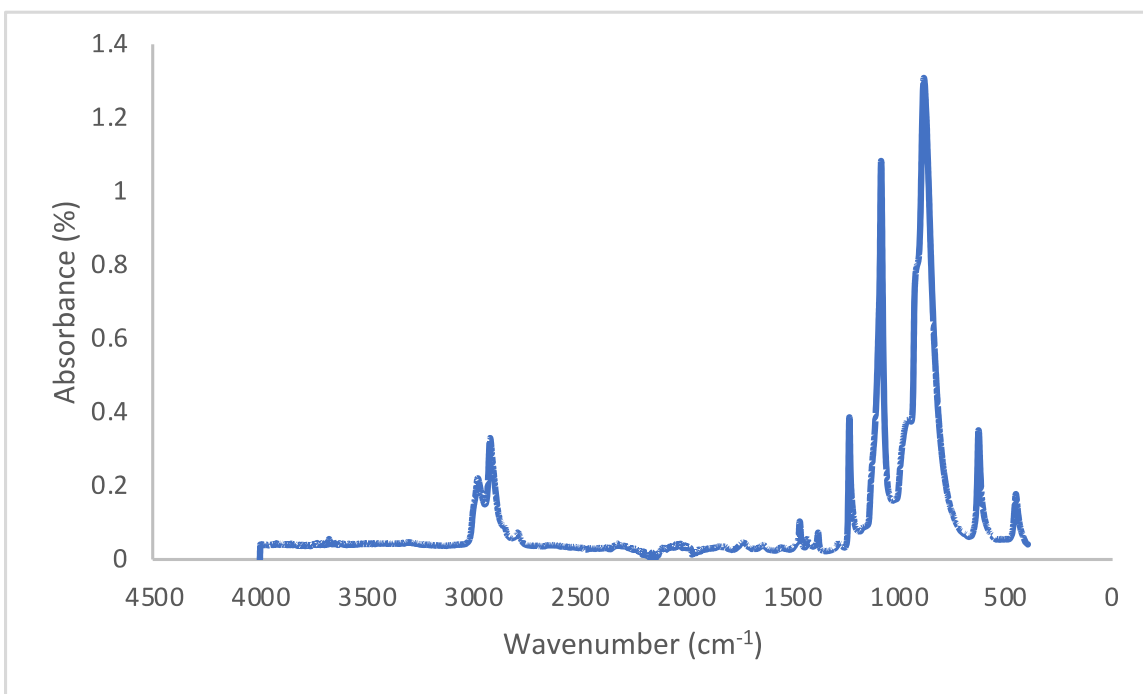
2018 ResinKit No. 31 Acetal Resin Homo-Polymer
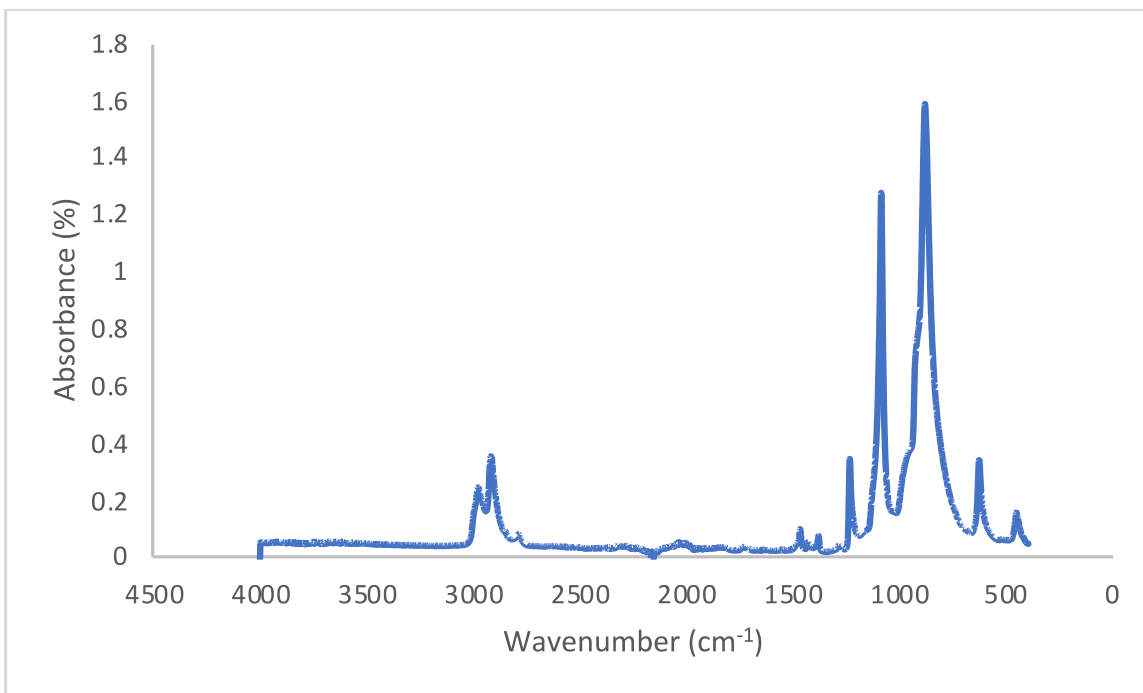
2010 ResinKit No. 32 Acetal Resin Co-Polymer
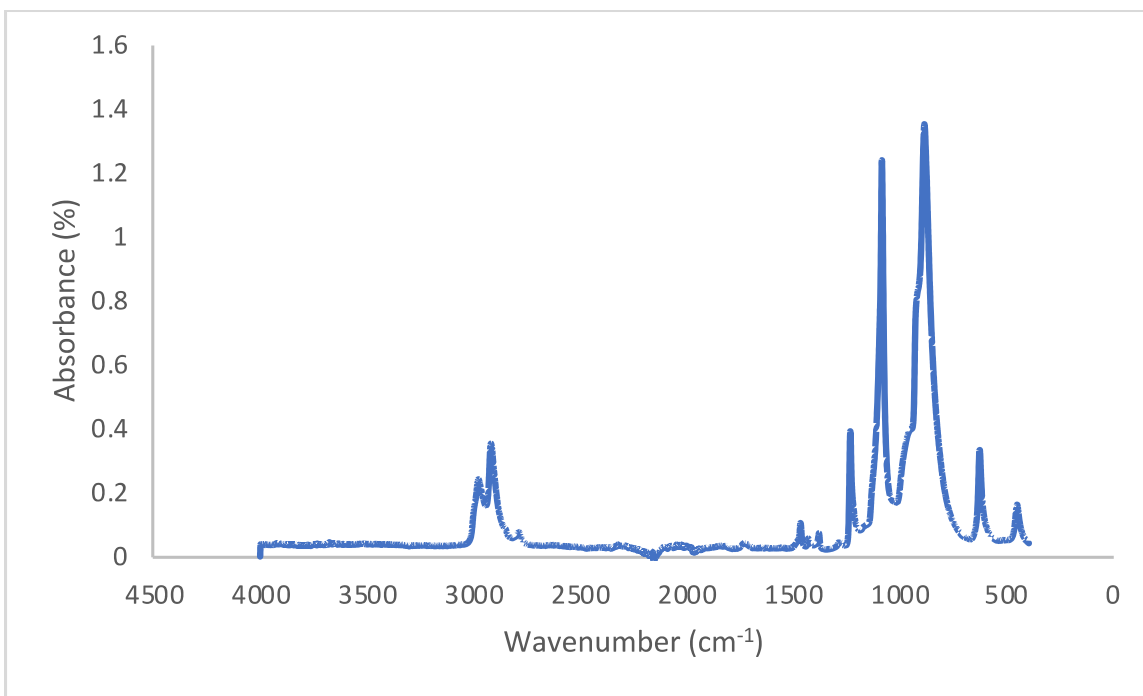
2018 ResinKit No. 32 Acetal Resin Co-Polymer
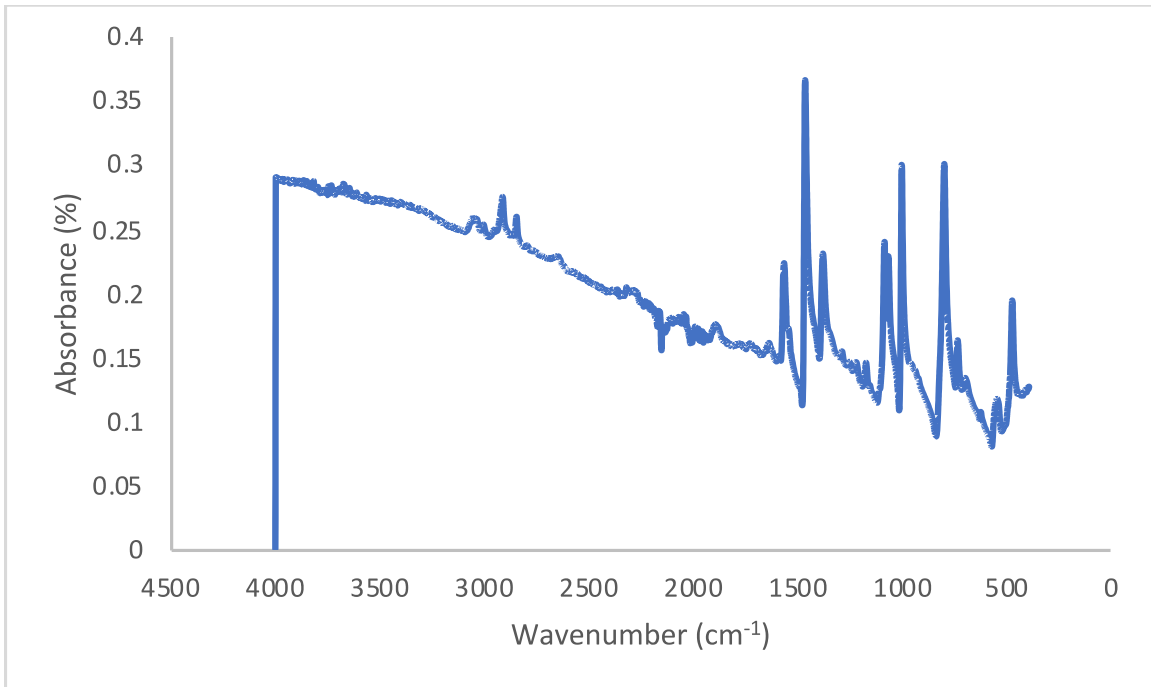
2010 ResinKit No. 33 Polyphenylene Sulfide
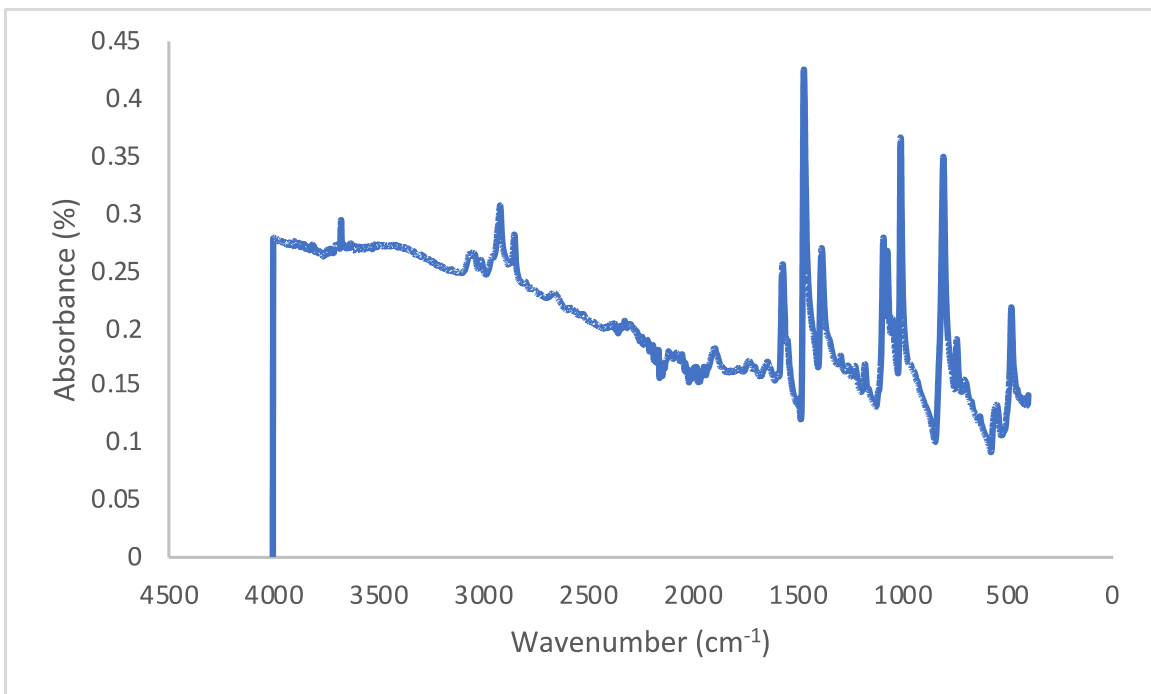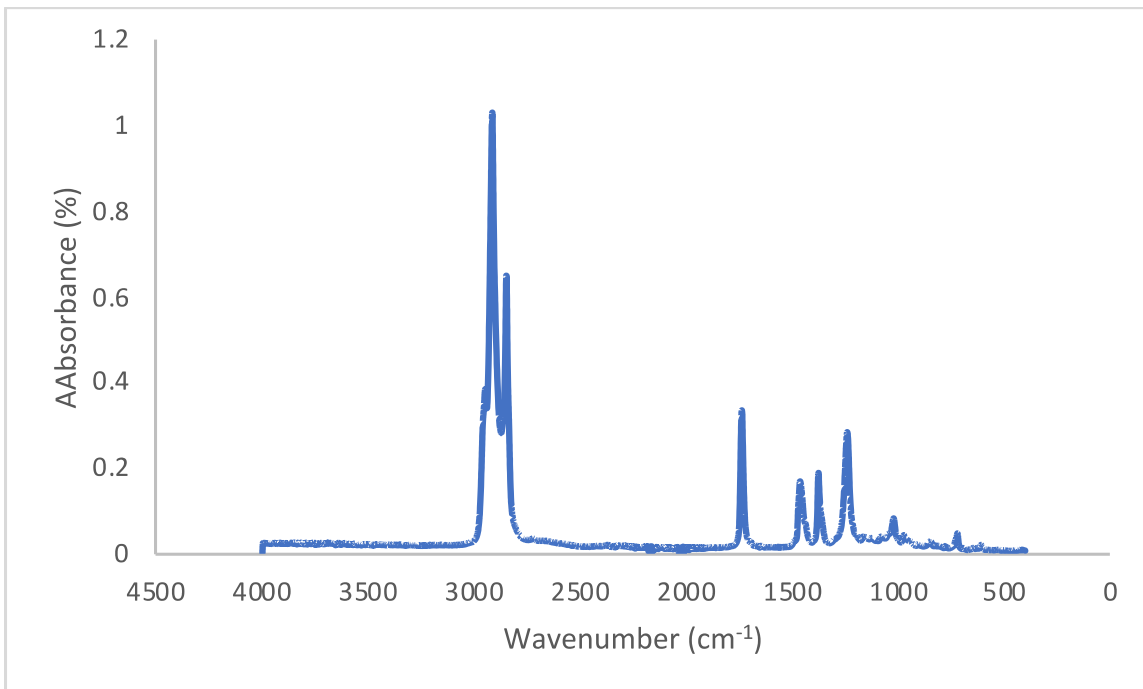
2010 ResinKit No. 34 Ethylene Vinyl Acetate Co-Polymer
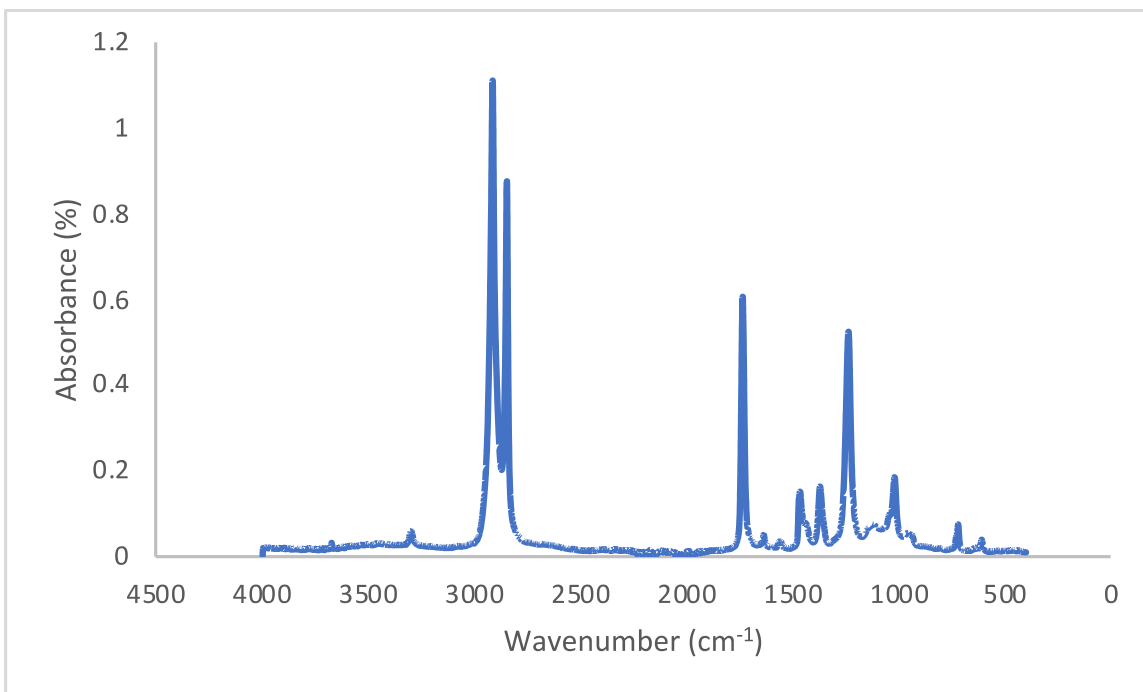
2018 ResinKit No. 34 Ethylene Vinyl Acetate Co-Polymer
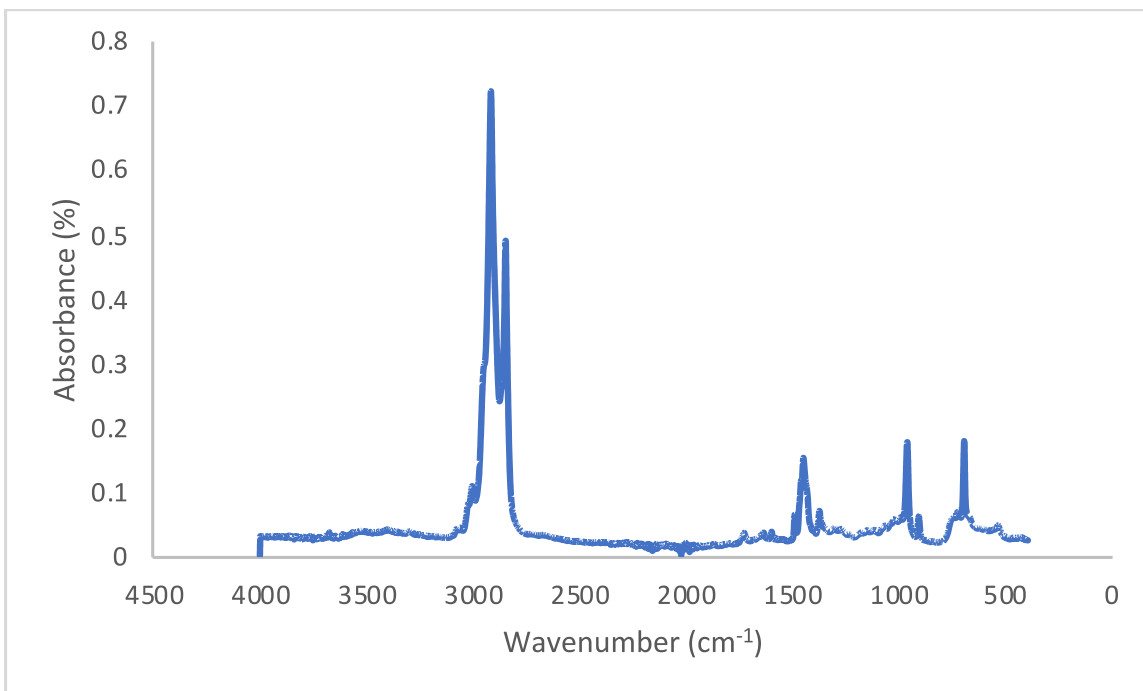
2010 ResinKit No. 35 Synthetic Elastomer Styrene-Block Co-Polymer
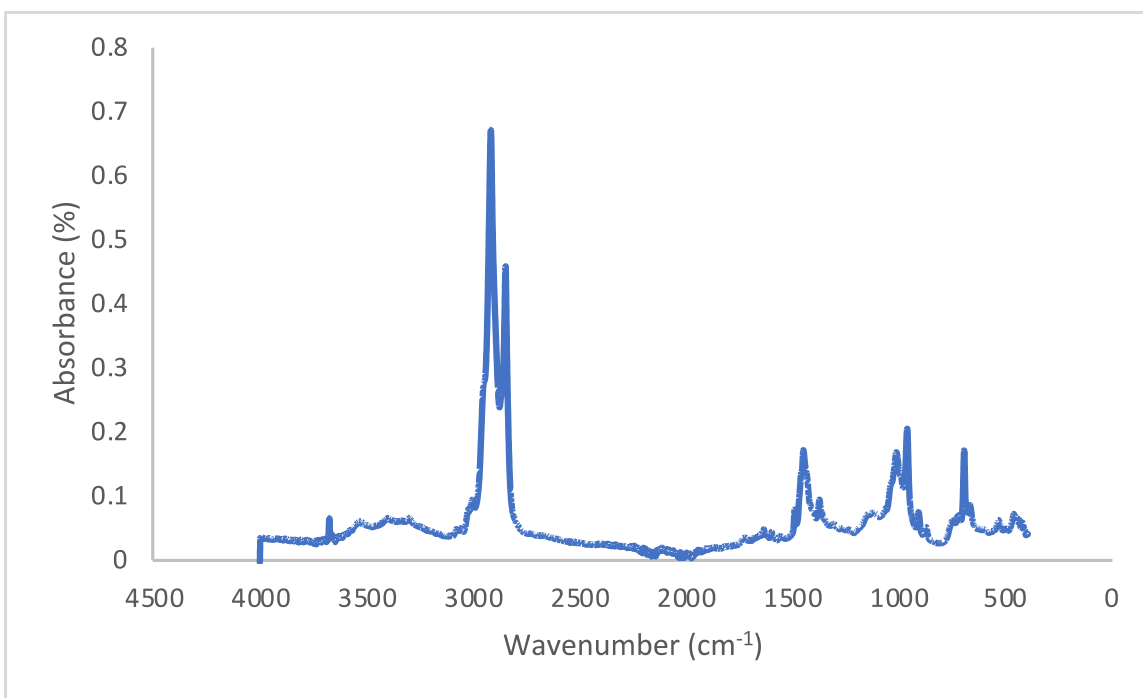
2018 ResinKit No. 35 Synthetic Elastomer Styrene-Block Co-Polymer
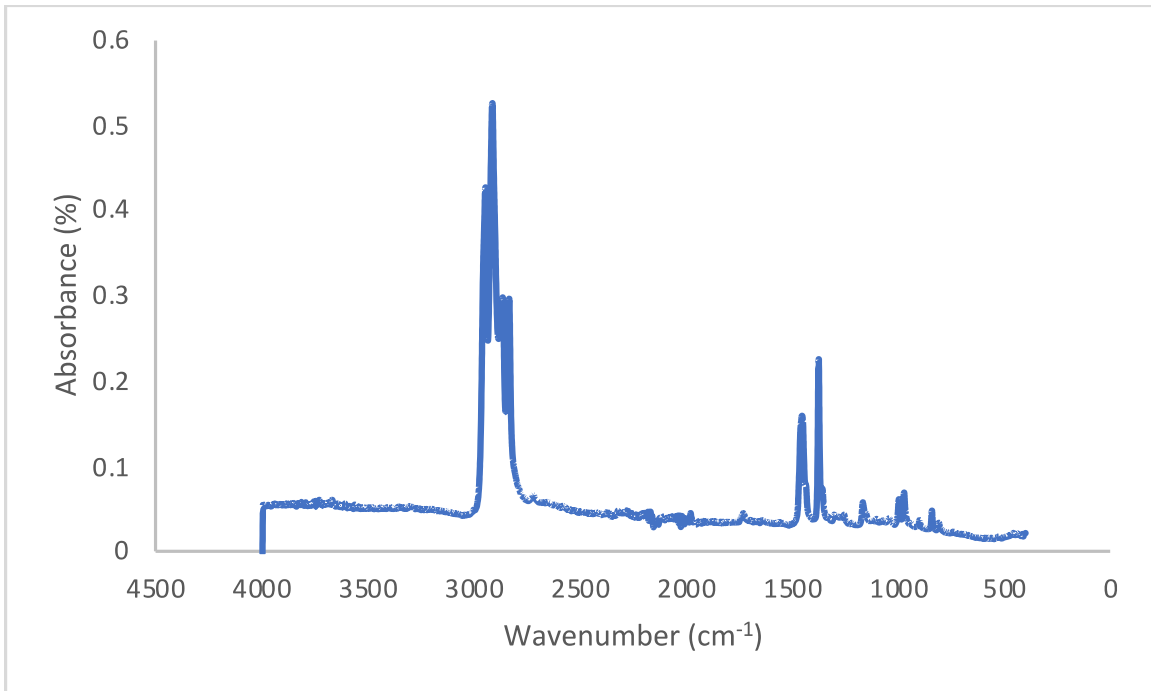
2010 ResinKit No. 36 Glass-Filled Polypropylene
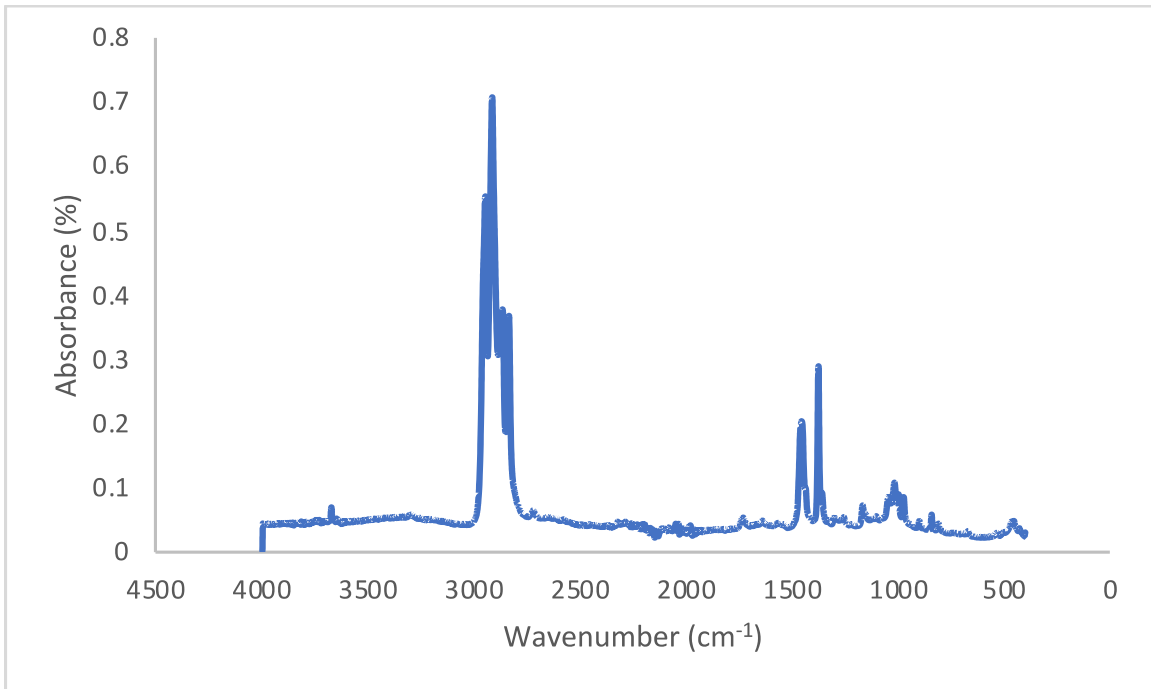
2018 ResinKit No. 36 Glass-Filled Polypropylene
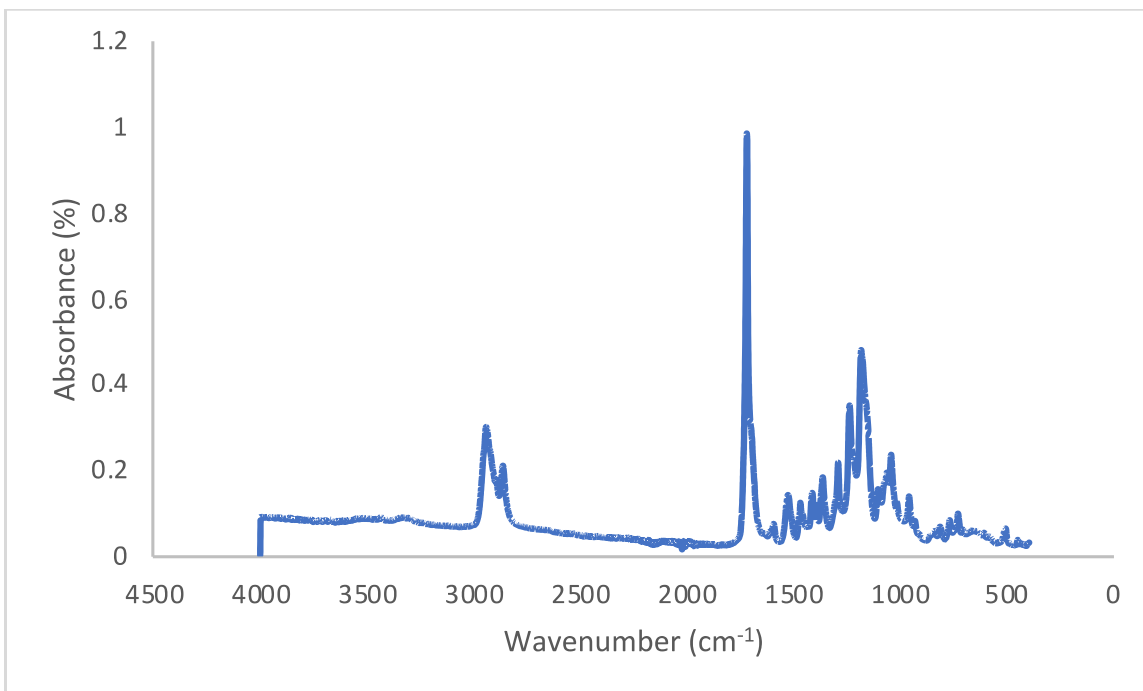
2010 ResinKit No. 37 Urethane Elastomer (Polyether)
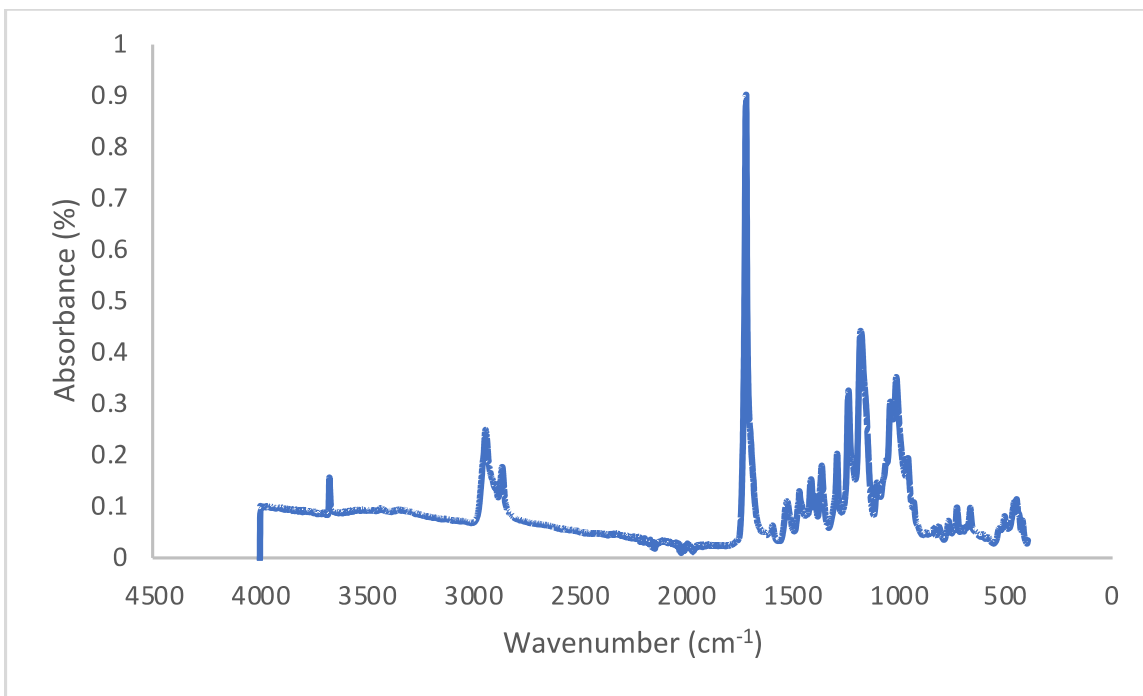
2018 ResinKit No. 37 Urethane Elastomer (Polyether)
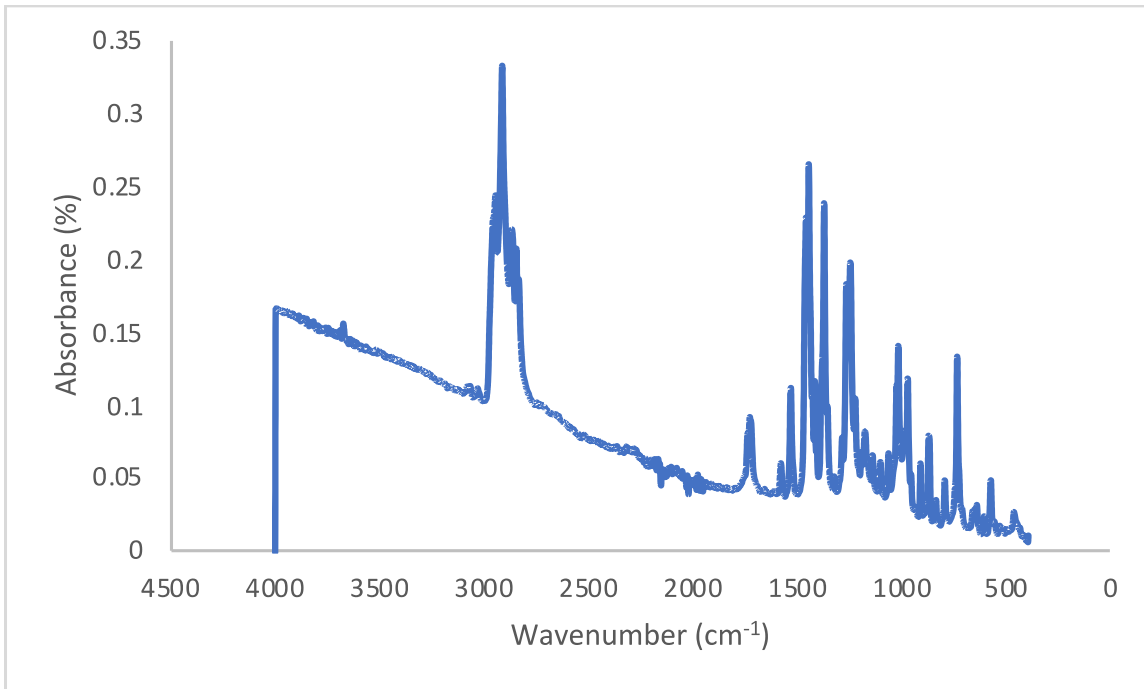
2010 ResinKit No. 38 Flame Retardant Polypropylene
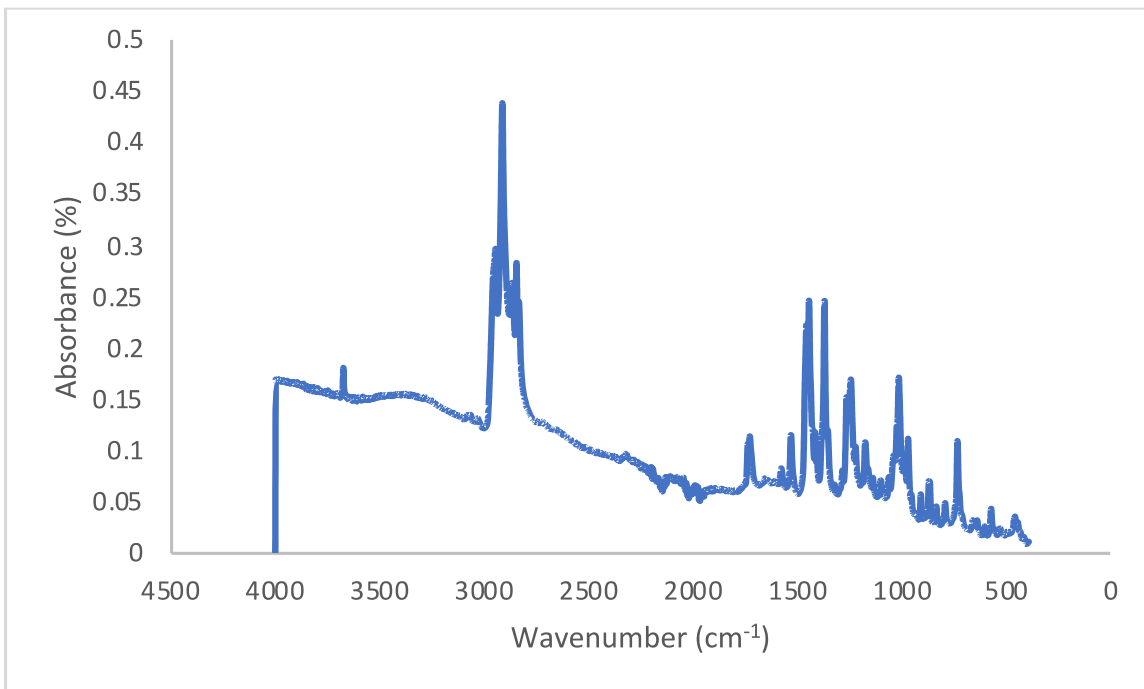
2018 ResinKit No. 38 Flame Retardant Polypropylene
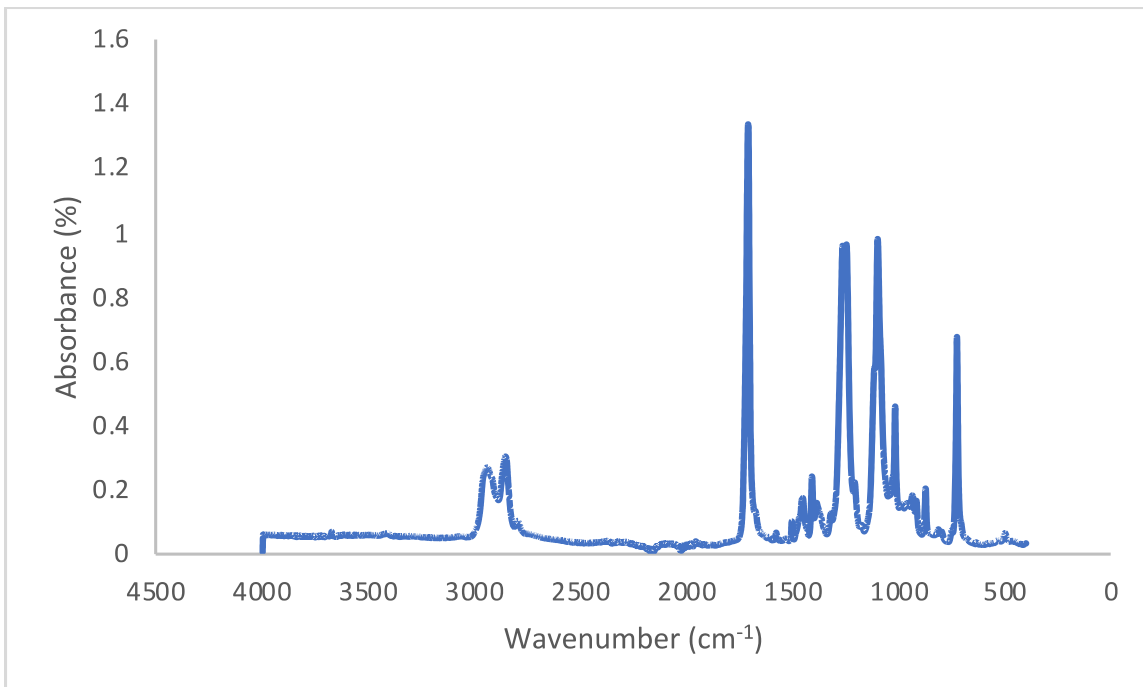
2010 ResinKit No. 39 Polyester Elastomer
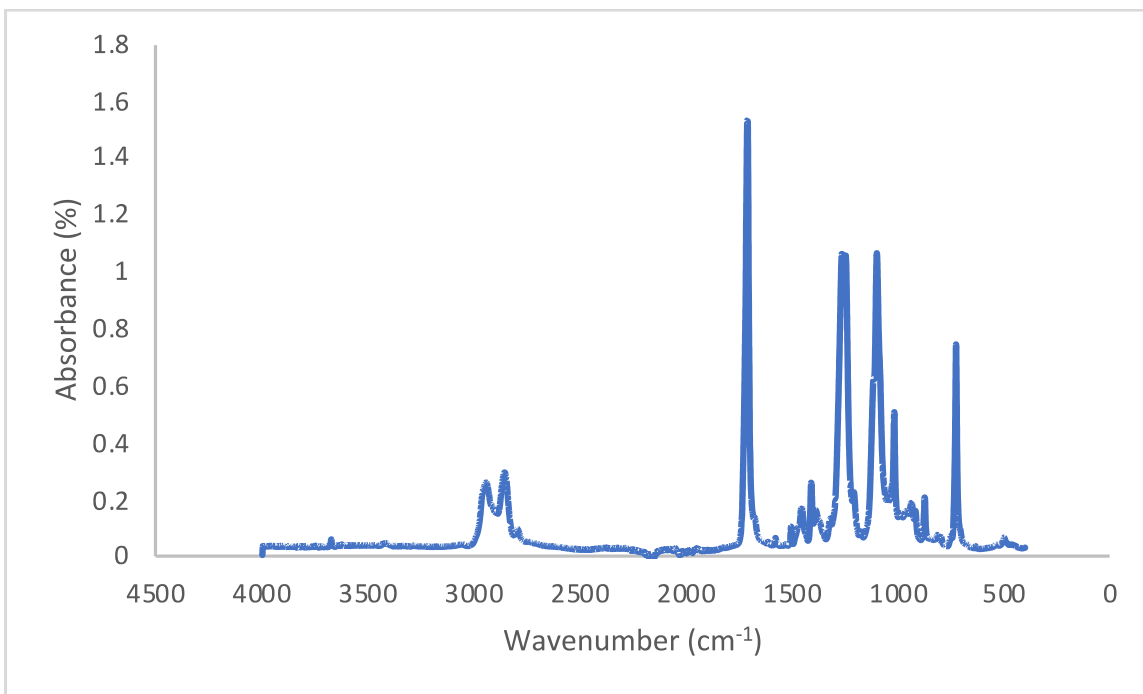
2018 ResinKit No. 39 Polyester Elastomer
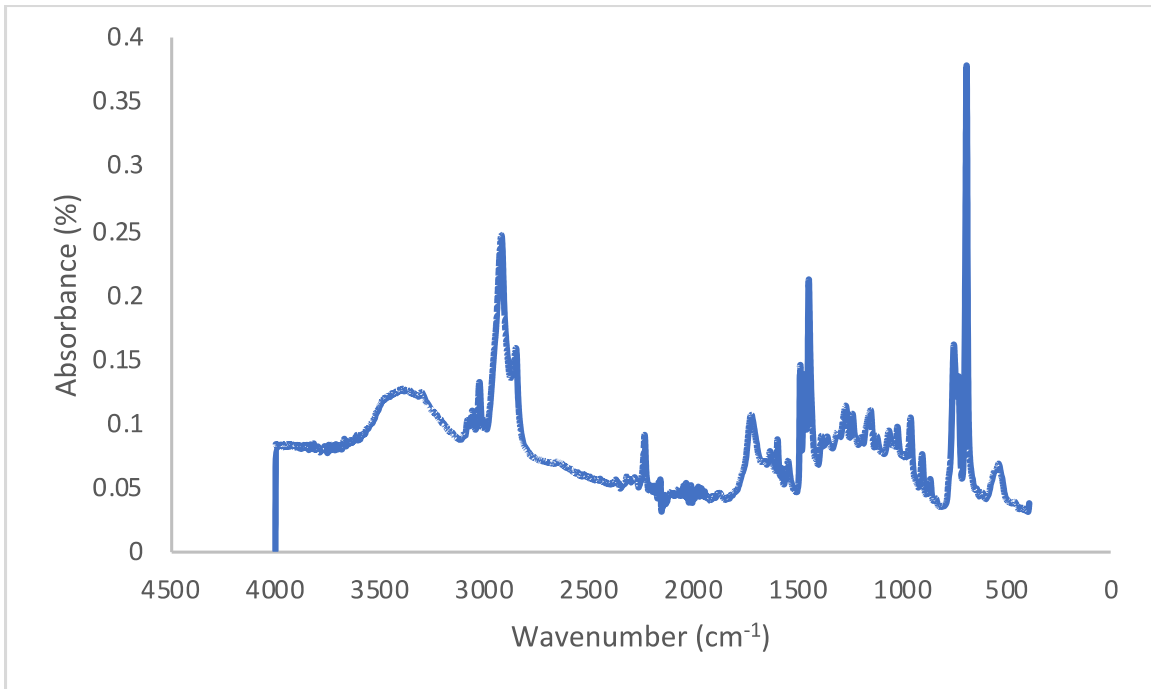
2010 ResinKit No. 40 Flame Retardant Acrylonitrile-Butadiene-Styrene
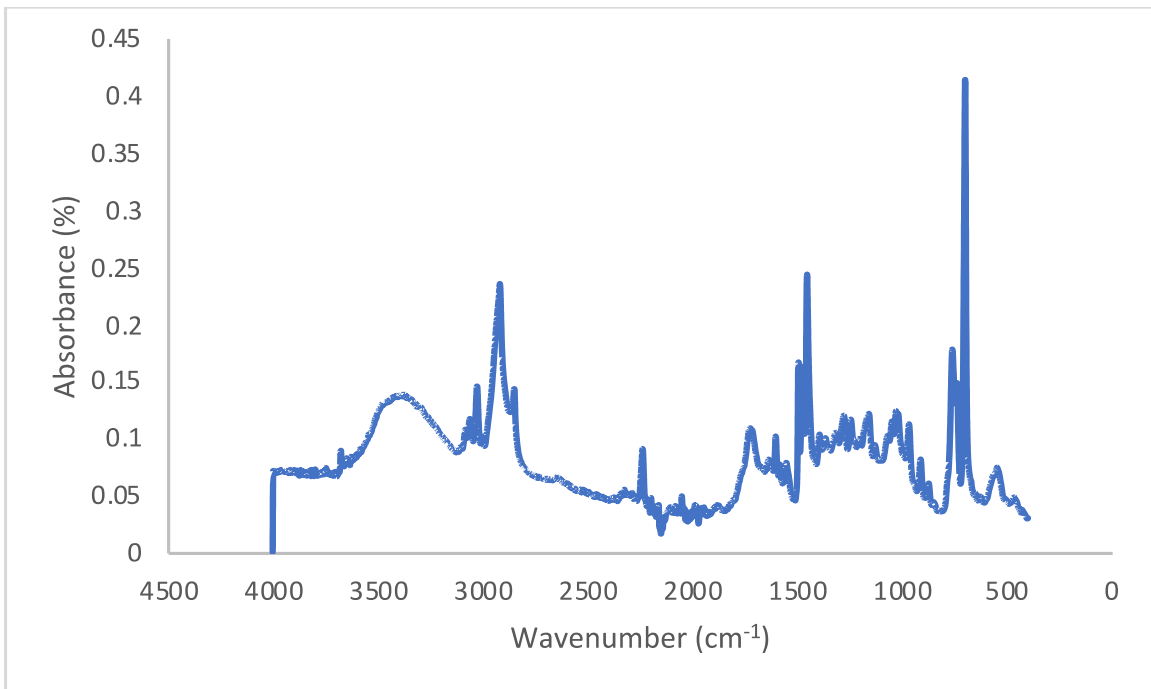
2018 ResinKit No. 40 Flame Retardant Acrylonitrile-Butadiene-Styrene
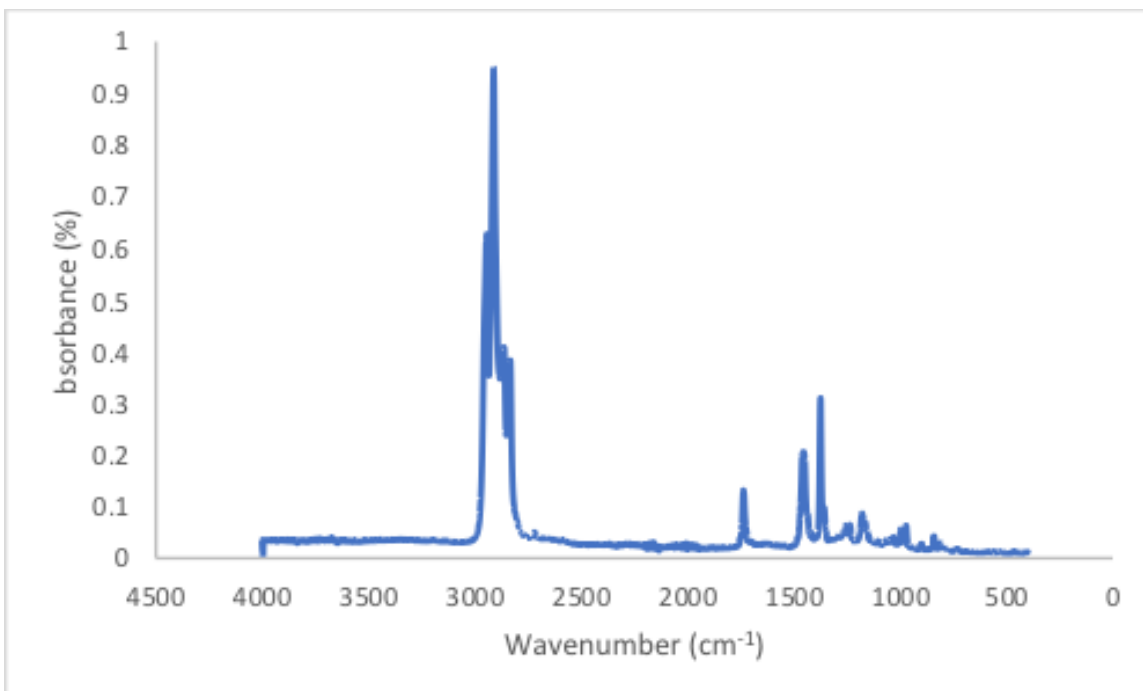
2010 ResinKit No. 41 Polyallomer
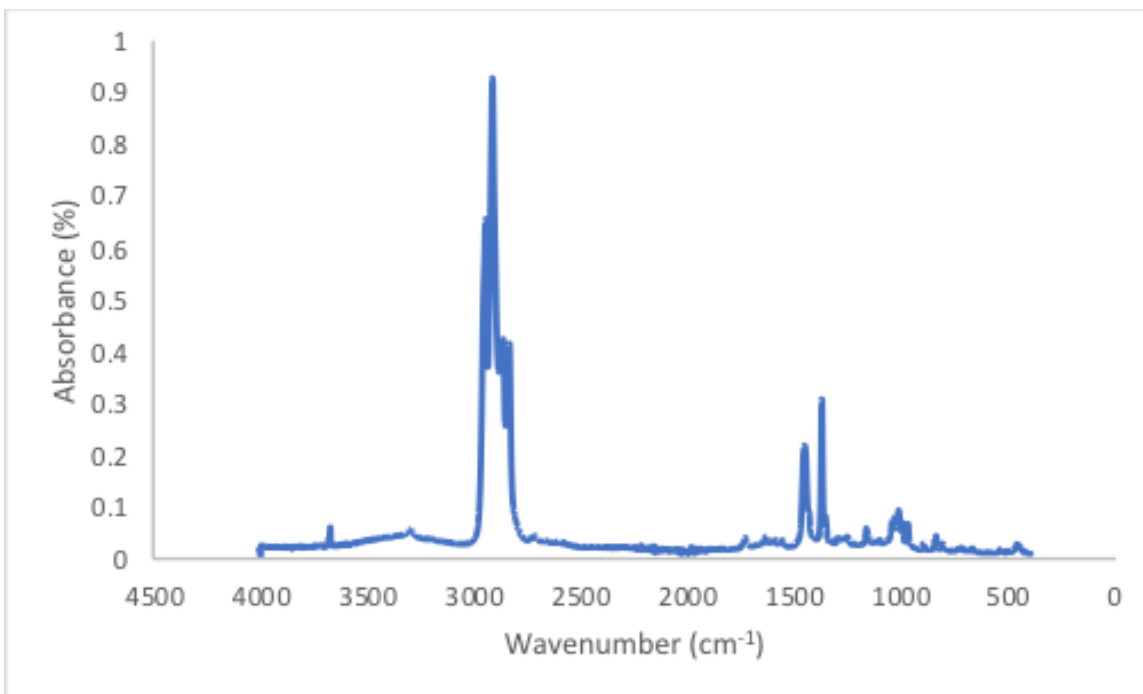
2018 ResinKit No. 41 Polyallomer
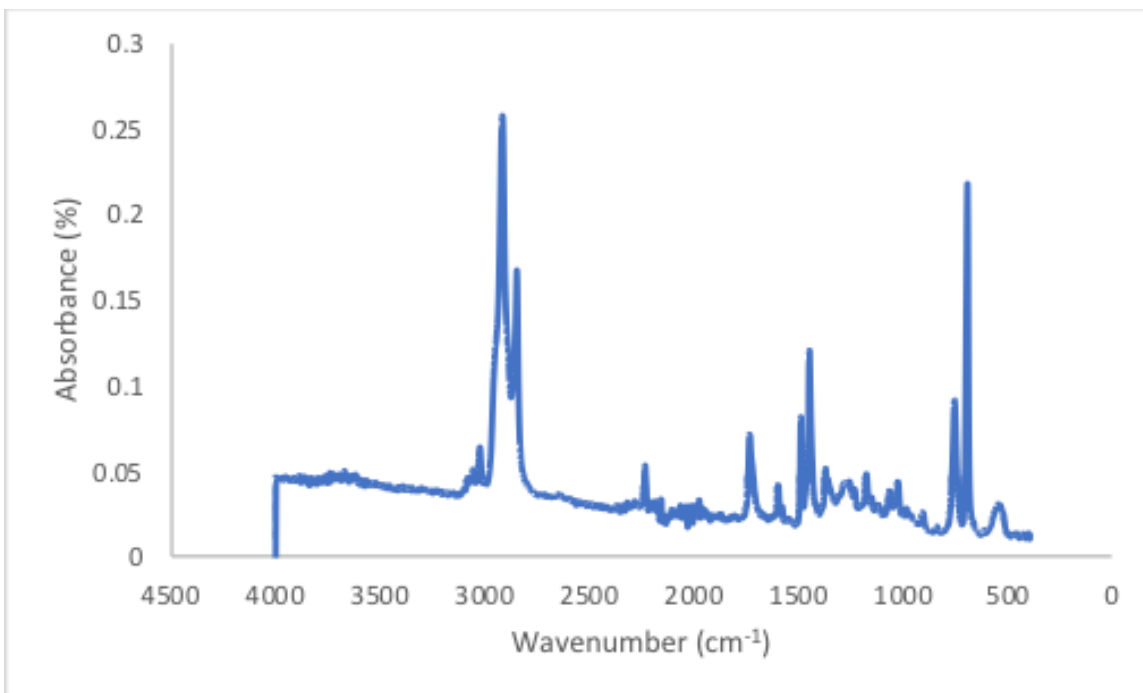
2010 ResinKit No. 42 Styrene Terpolymer
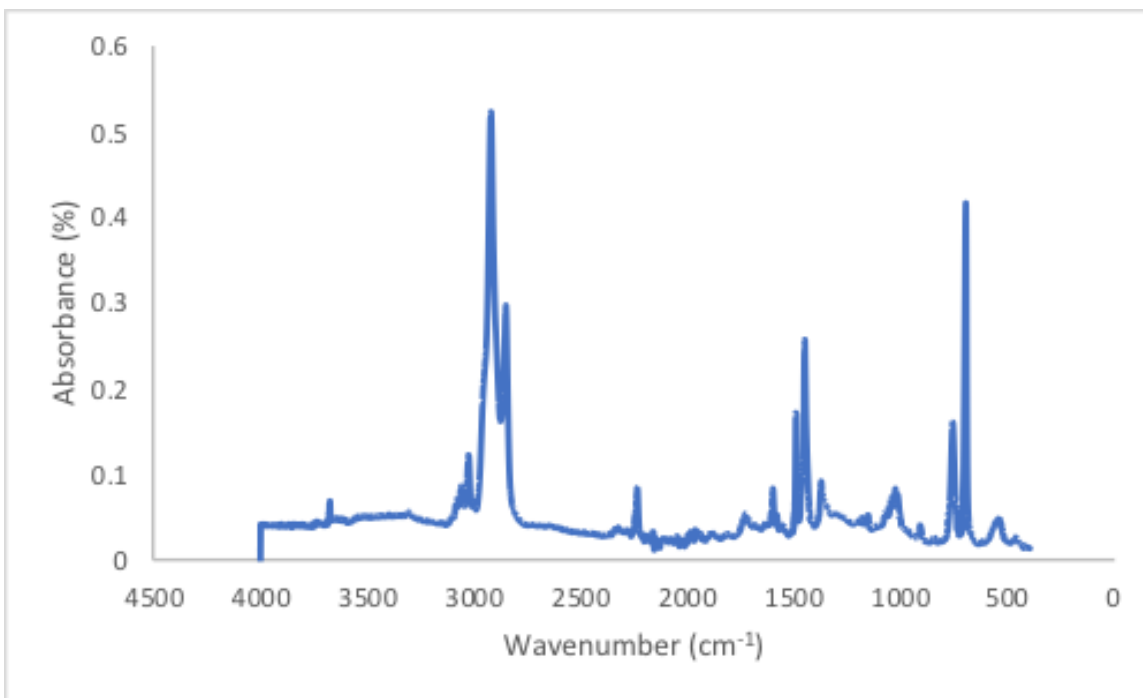
2018 ResinKit No. 42 Styrene Terpolymer
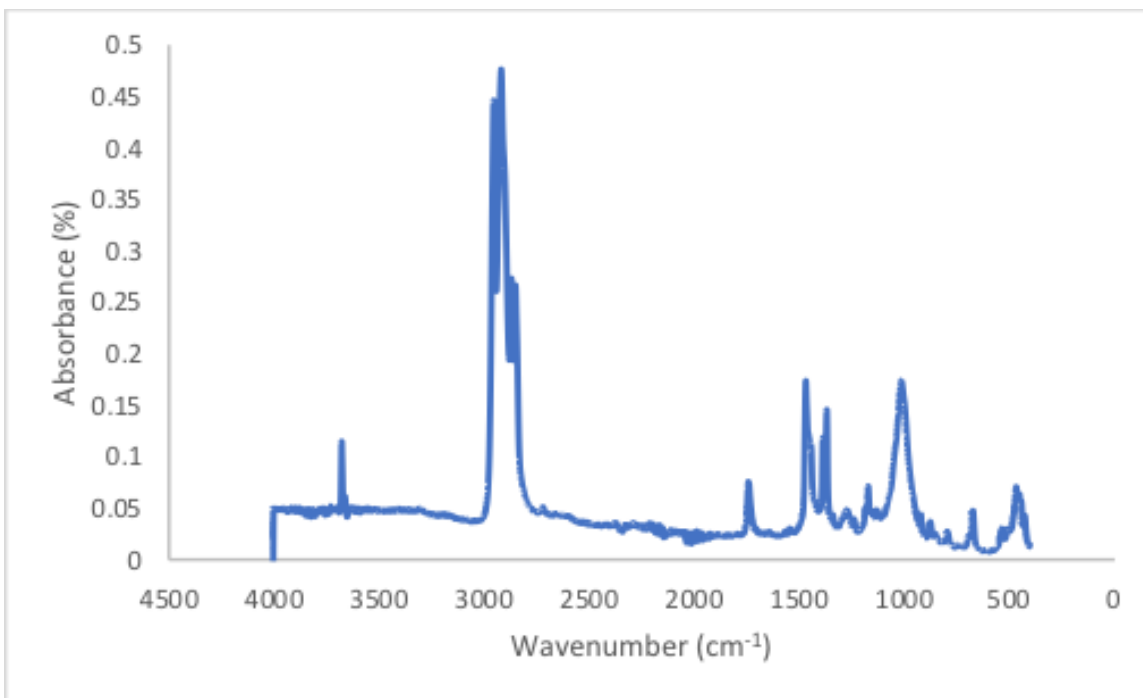
2010 ResinKit No. 43 Polymethylpentene
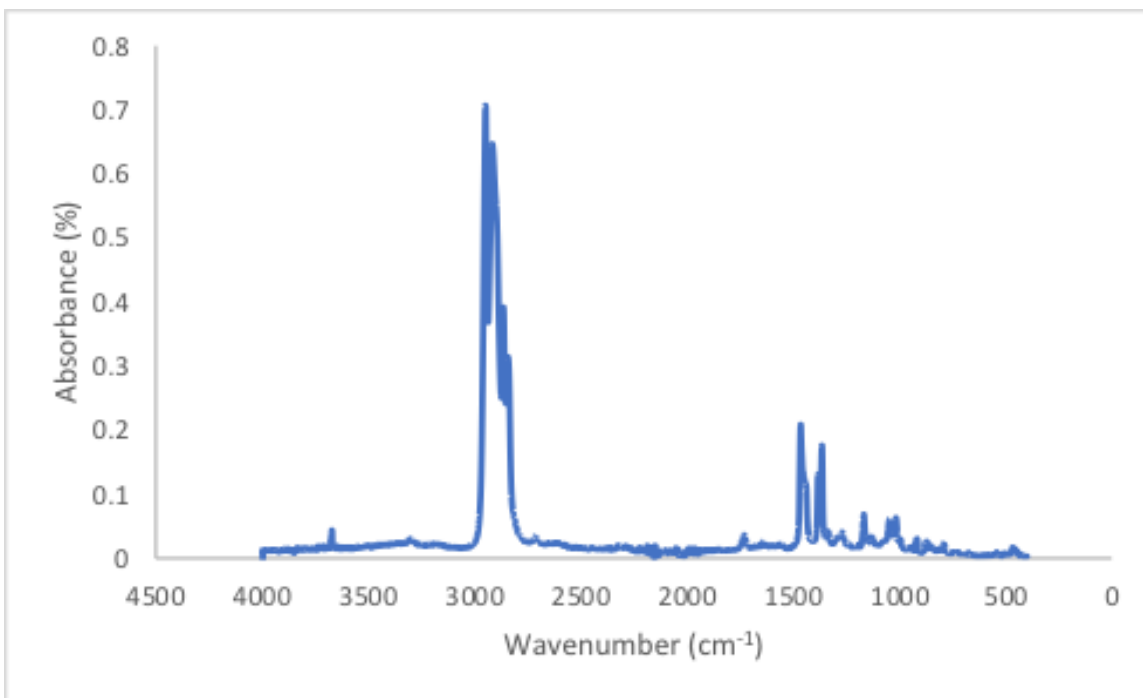
2018 ResinKit No. 43 Polymethylpentene
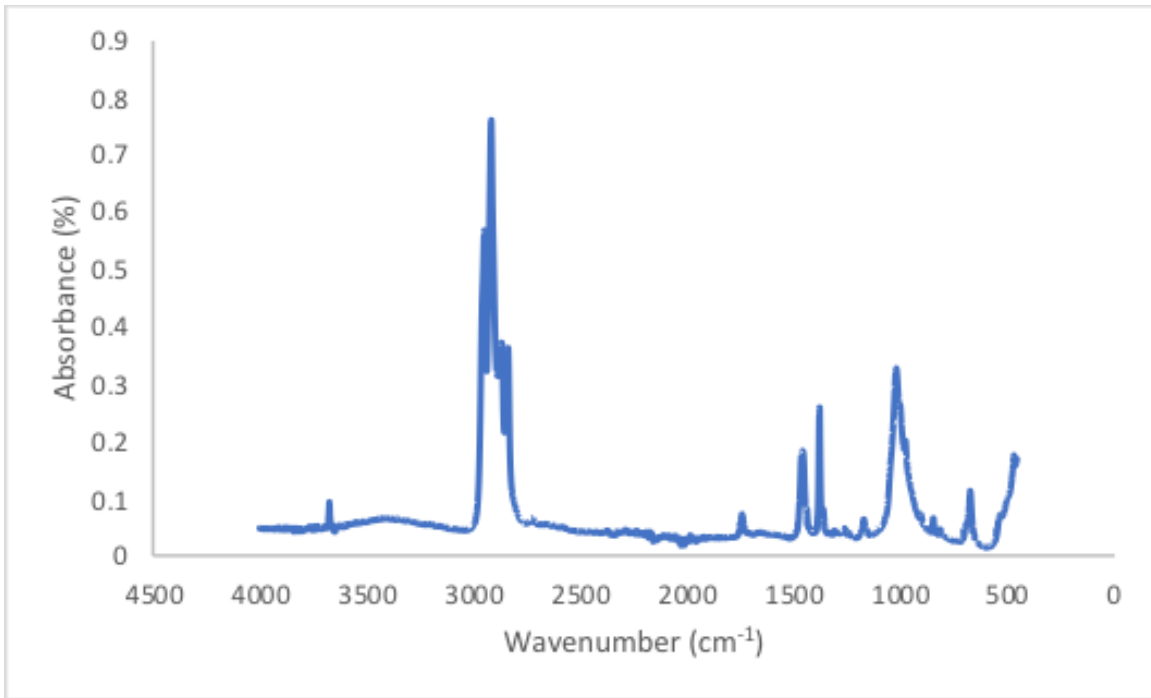
2010 ResinKit No. 44 Talc Reinforced Polypropylene
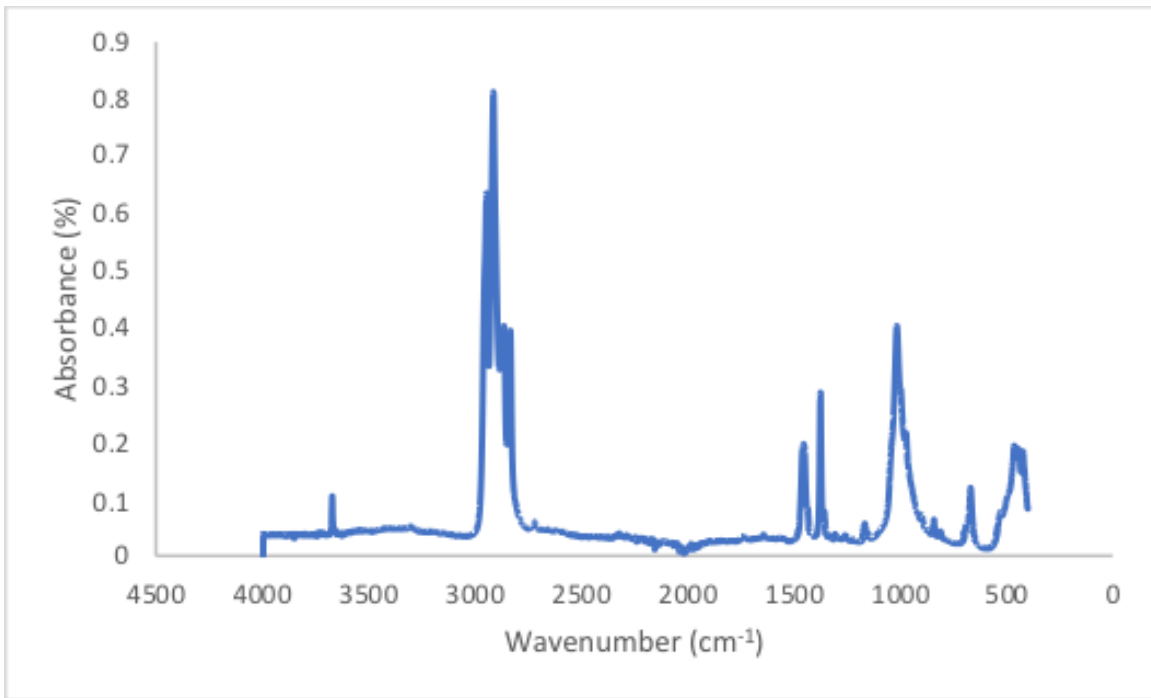
2018 ResinKit No. 44 Talc Reinforced Polypropylene
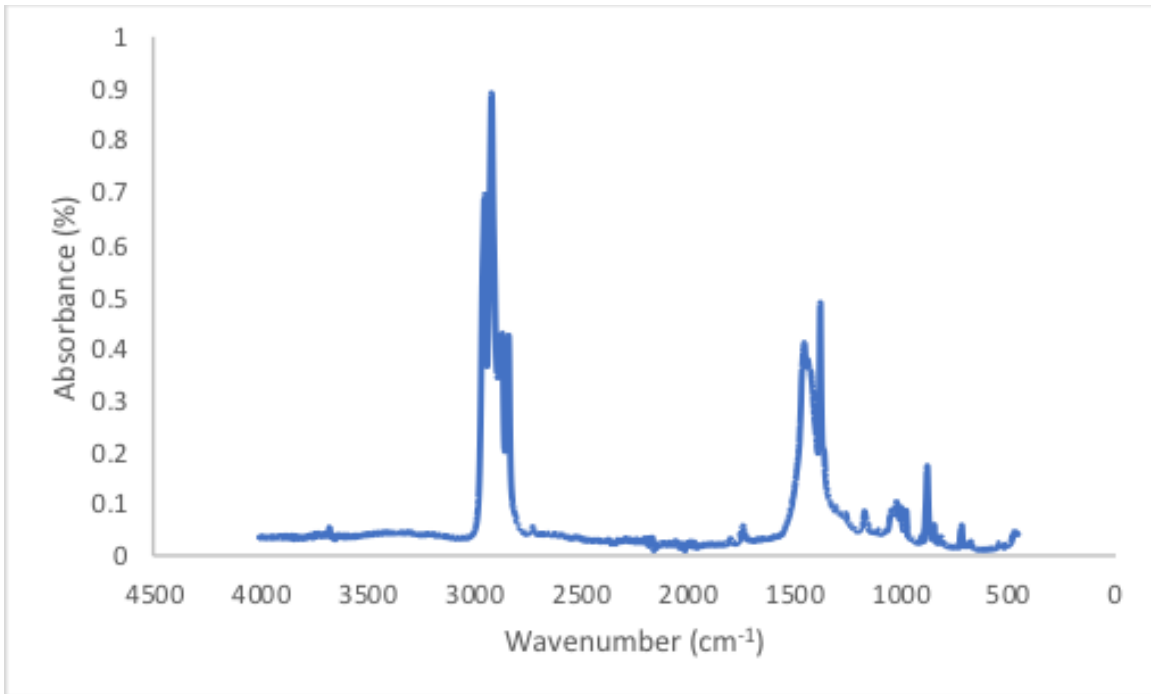
2010 ResinKit No. 45 Calcium Carbonate Reinforced Polypropylene
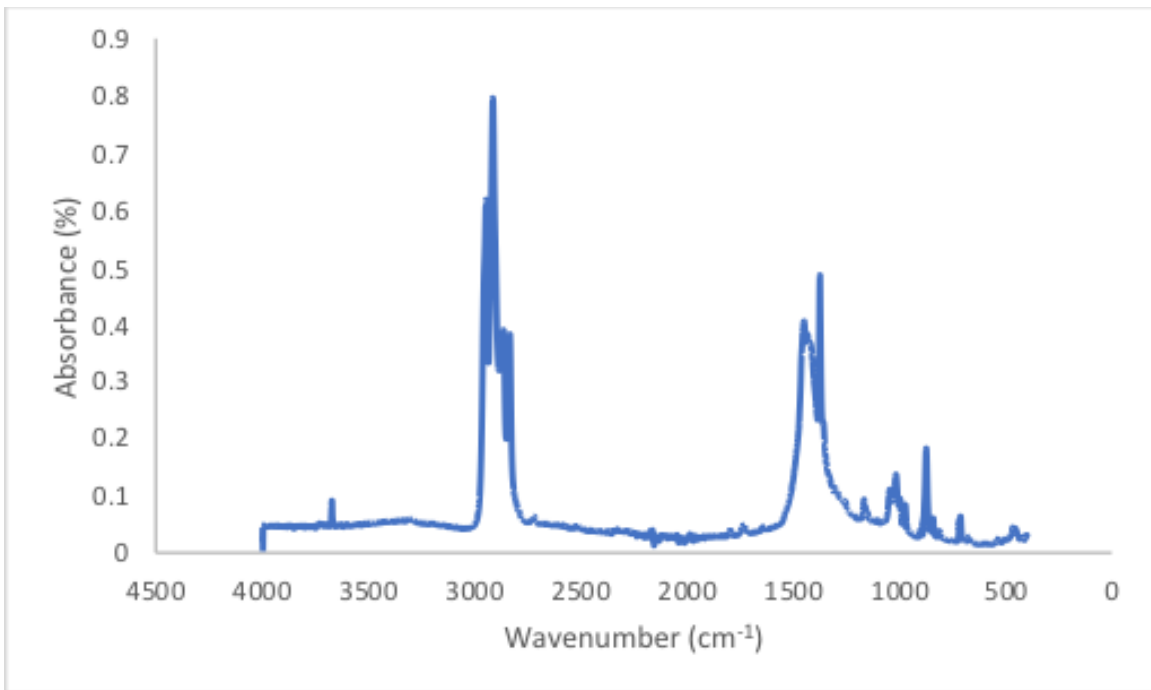
2018 ResinKit No. 45 Calcium Carbonate Reinforced Polypropylene
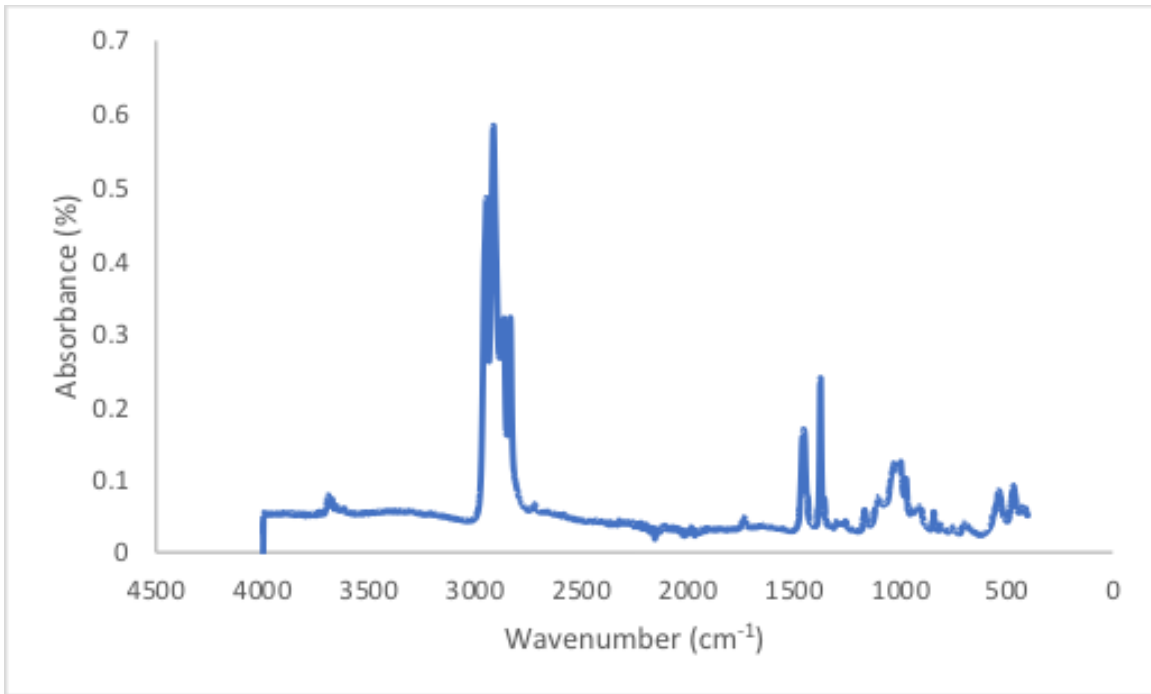
2010 ResinKit No. 46 Mica Reinforced Polypropylene
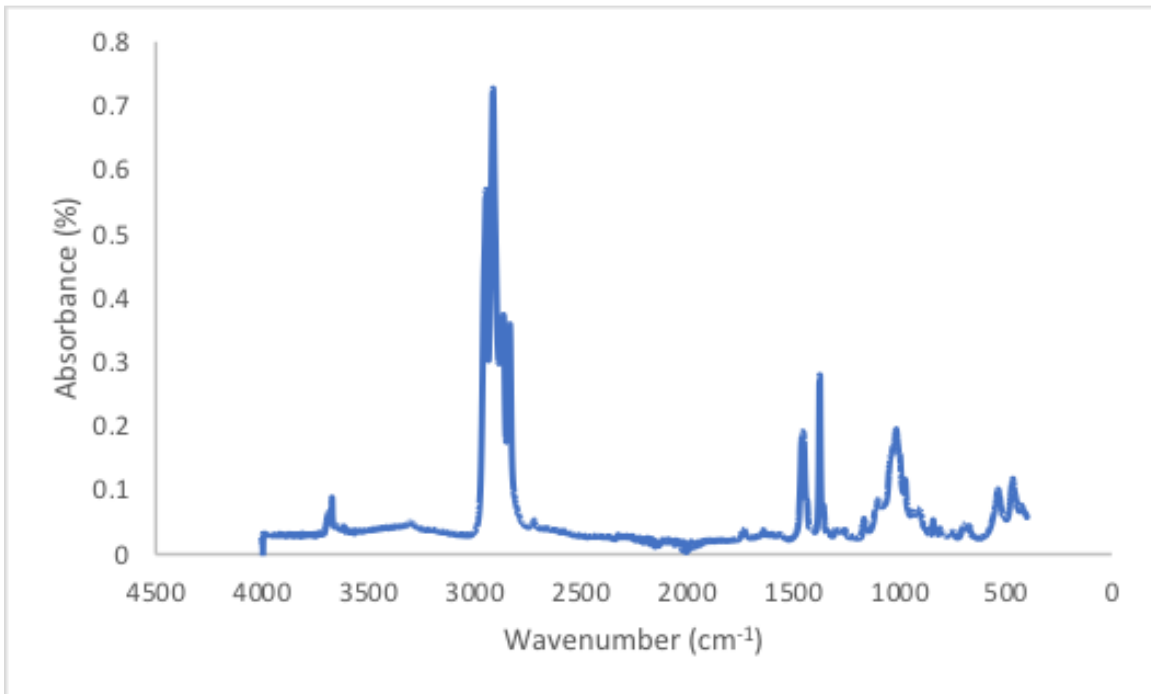
2018 ResinKit No. 46 Mica Reinforced Polypropylene
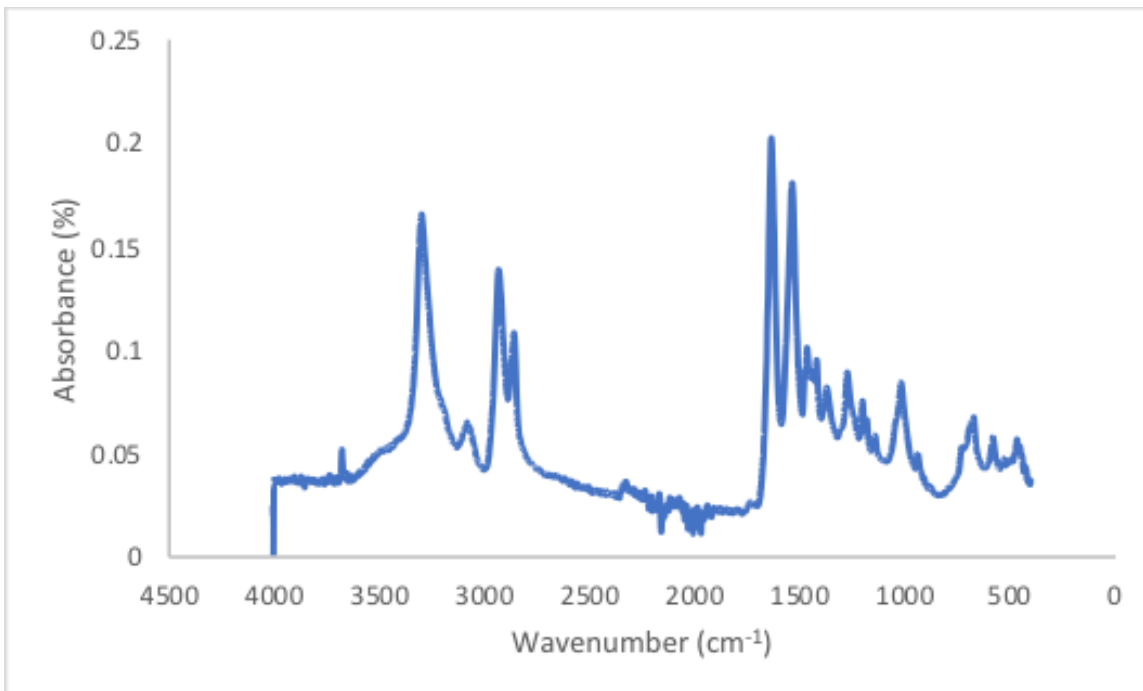
2010 ResinKit No. 47 Nylon Type 66 – 33% glass
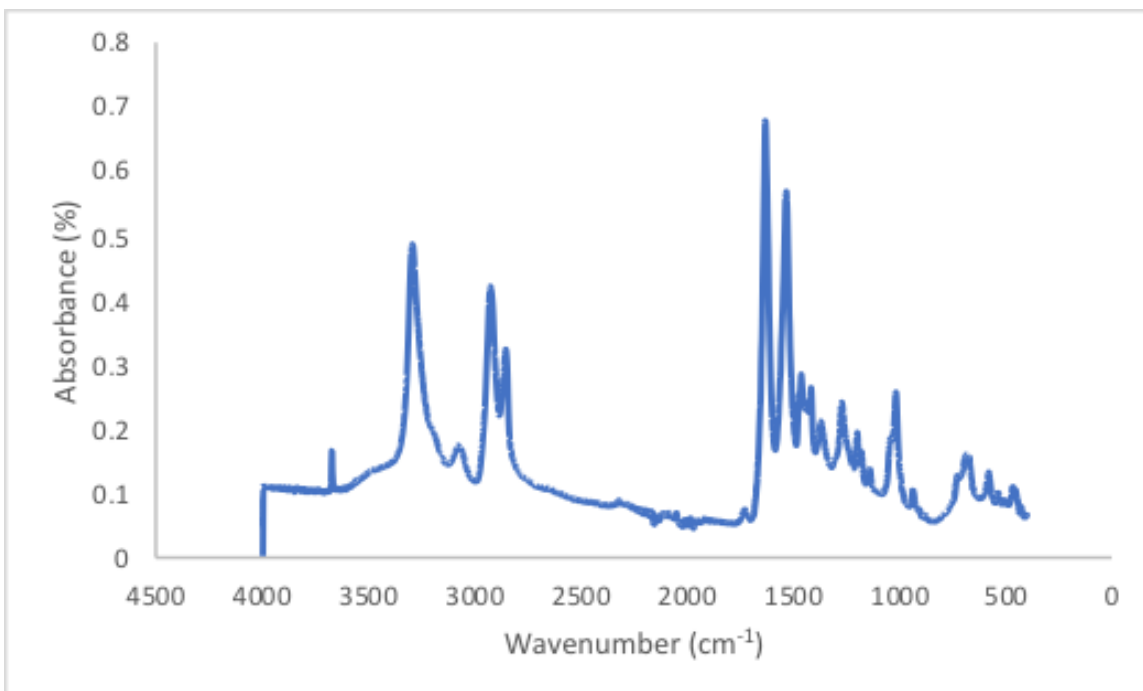
2018 ResinKit No. 47 Nylon Type 66 – 33% glass
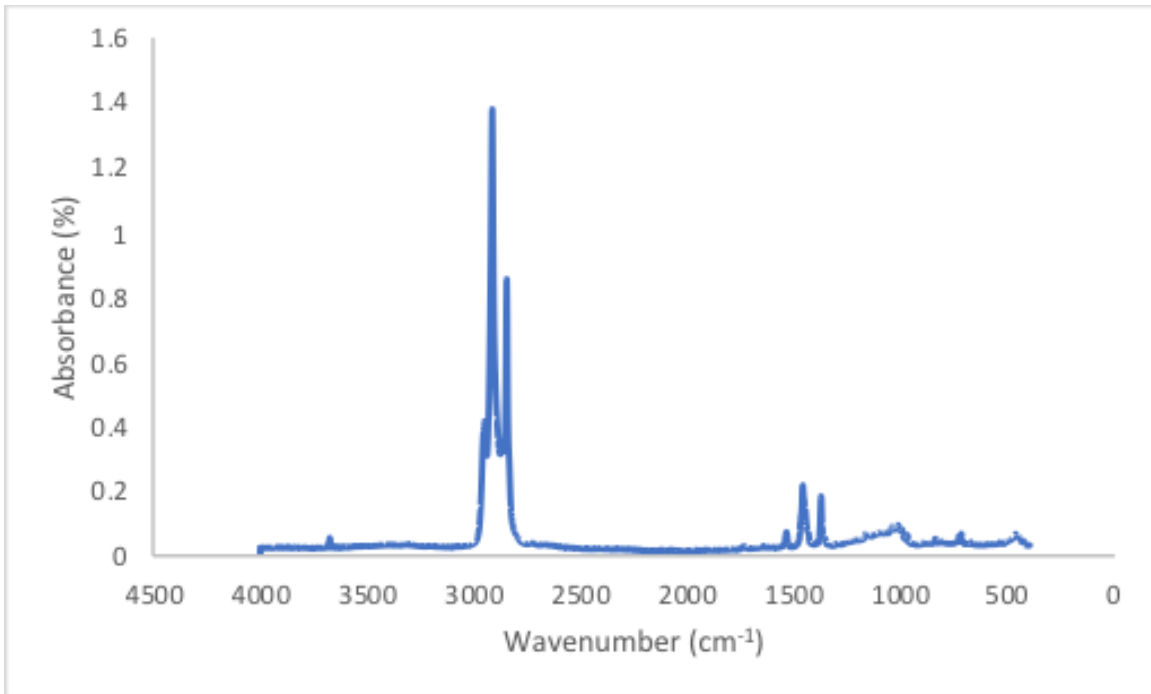
2010 ResinKit No. 48 Thermoplastic Rubber
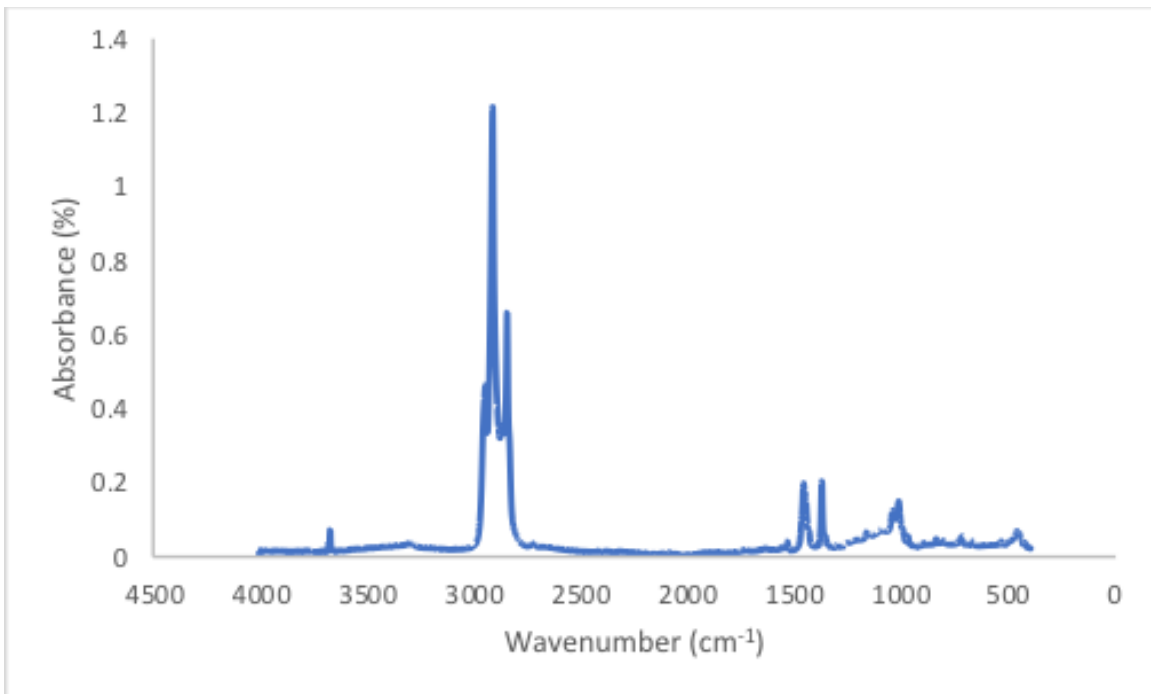
2018 ResinKit No. 48 Thermoplastic Rubber
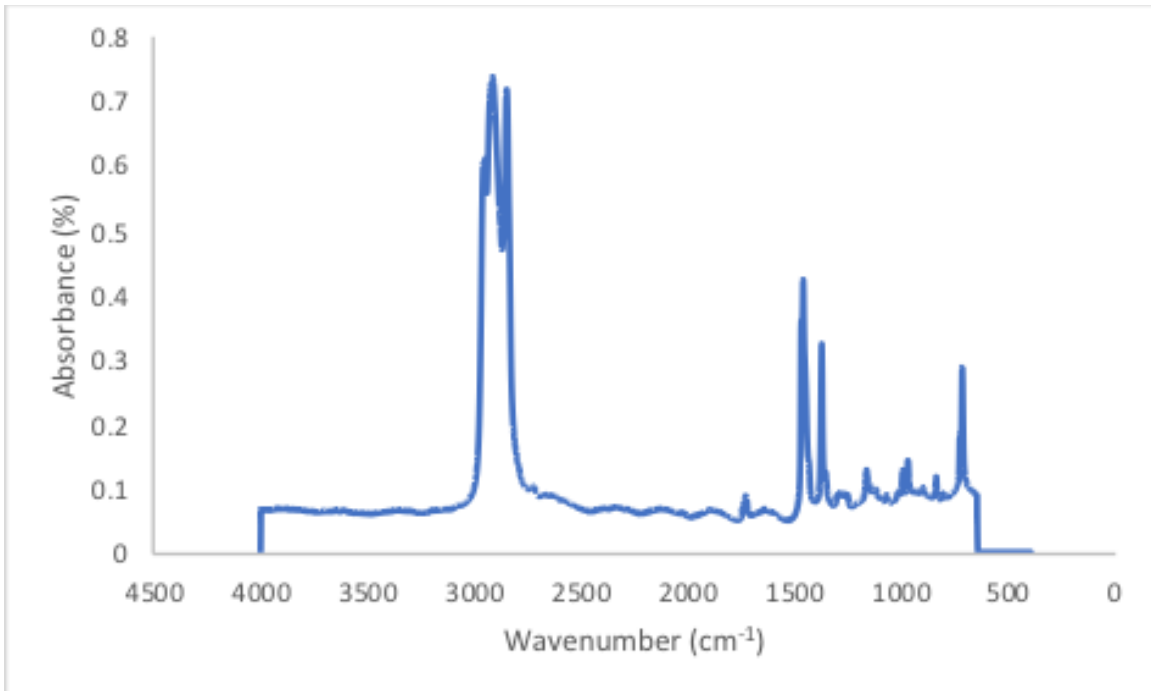
2010 ResinKit No. 49 Medium Density Polyethylene
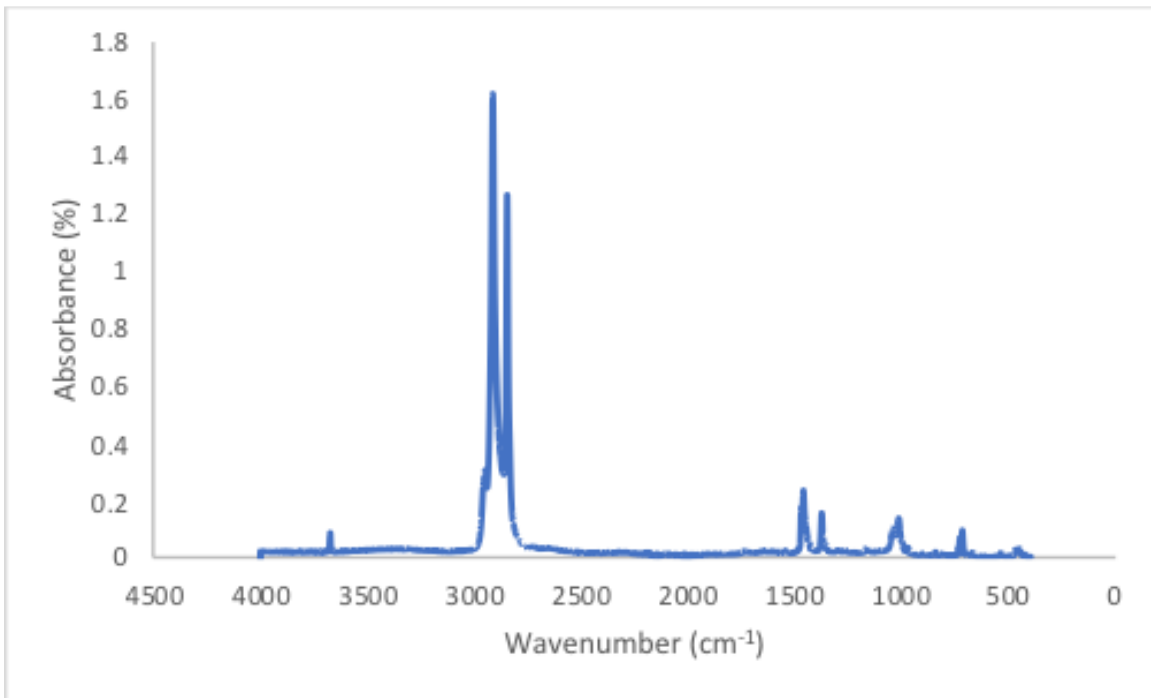
2018 ResinKit No. 49 Medium Density Polyethylene
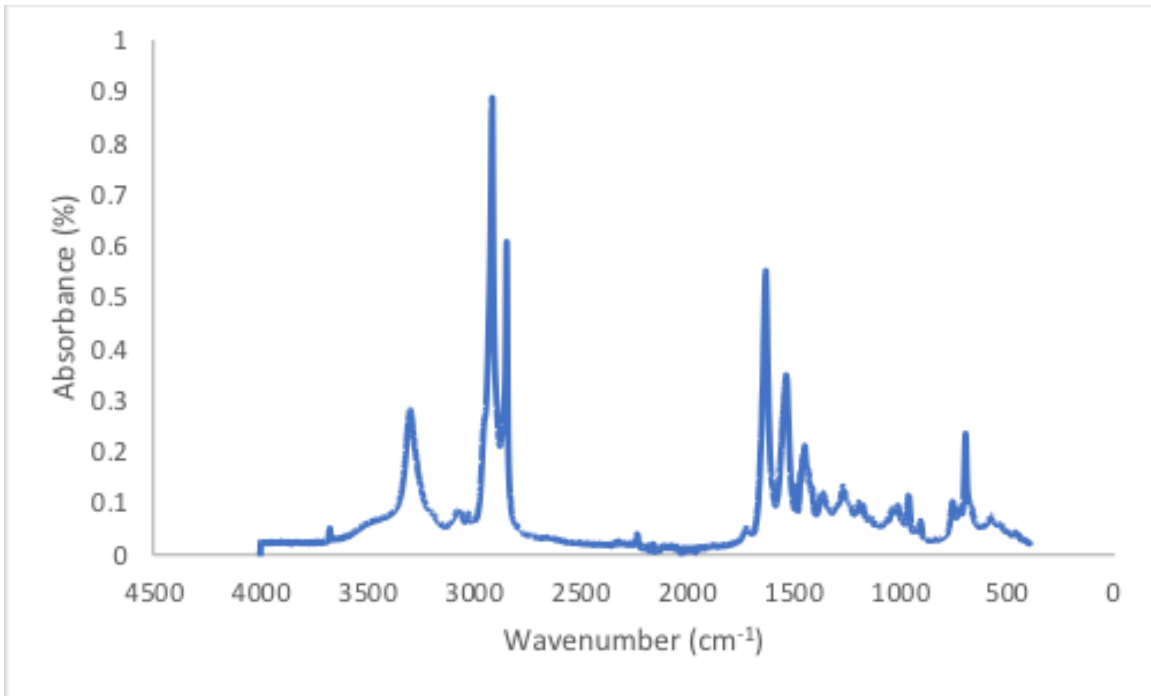
2010 ResinKit No. 50 Acrylonitrile-Butadiene-Styrene Nylon Alloy
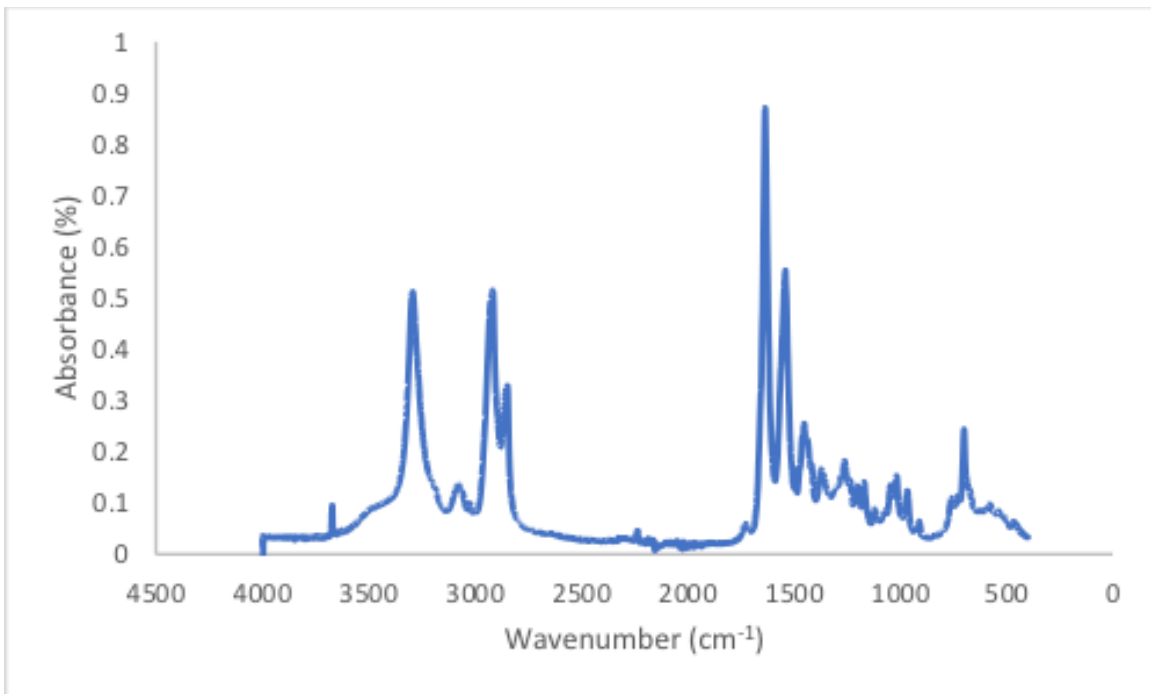
2018 ResinKit No. 50 Acrylonitrile-Butadiene-Styrene Nylon Alloy

3B: Pyrograms

2018 ResinKit No. 1 General Purpose Polystyrene

2010 ResinKit No. 2 Medium Impact Polystyrene

2018 ResinKit No. 2 Medium Impact Polystyrene

RT: 0.00 - 29.02

NL:
2.20E9
TIC MS
ResinKit_3
_PS-
H_Tsuge

2010 ResinKit No. 3 High Impact Polystyrene

RT: 0.00 - 29.00

NL:
1.20E9
TIC MS
ResinKit_3
_PS-
H_2018_Ts
uge

2018 ResinKit No. 3 High Impact Polystyrene

2010 ResinKit No. 4 Styrene Acrylonitrile

2018 ResinKit No. 4 Styrene Acrylonitrile

2010 ResinKit No. 5 Transparent Acrylonitrile-Butadiene-Styrene

2018 ResinKit No. 5 Transparent Acrylonitrile-Butadiene-Styrene

91

2010 ResinKit No. 6 Medium Impact Acrylonitrile-Butadiene-Styrene

2018 ResinKit No. 6 Medium Impact Acrylonitrile-Butadiene-Styrene

2010 ResinKit No. 7 High Impact Acrylonitrile-Butadiene-Styrene

2018 ResinKit No. 7 High Impact Acrylonitrile-Butadiene-Styrene

2010 ResinKit No. 8 Styrene Butadiene

2018 ResinKit No. 8 Styrene Butadiene

2010 ResinKit No. 9 Acrylic

2018 ResinKit No. 9 Acrylic

NL:
2.18E8
TIC MS
ResinKit_1
0_Mod_Acr
ylic_Tsuge

2010 ResinKit No. 10 Modified Acrylic

RT: 0.00 - 29.03

NL:
1.74E8
TIC MS
ResinKit_1
0_Mod_Acr
ylic_2018_
Tsuge

2018 ResinKit No. 10 Modified Acrylic

96

RT: 0.00 - 28.99

NL:
2.22E9
TIC MS
ResinKit_1
1_CA_Tsug
e

2010 ResinKit No. 11 Cellulose Acetate

RT: 0.00 - 29.02
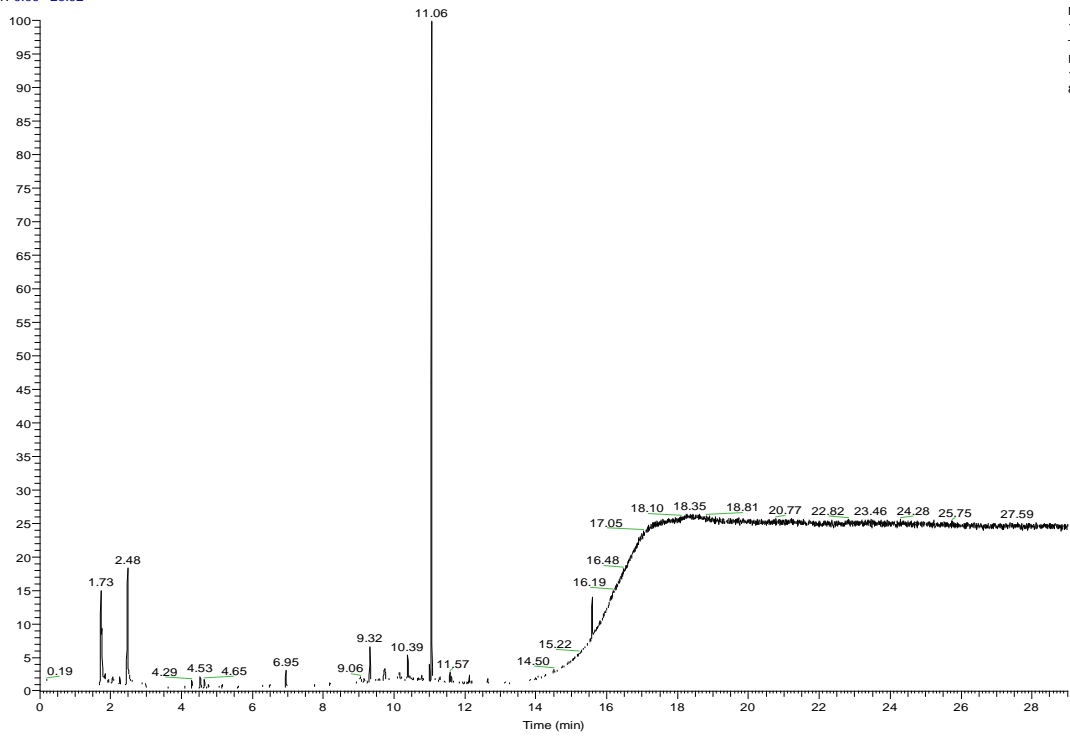
NL:
1.74E8
TIC MS
ResinKit_1
1_CA_201
8_Tsuge

2018 ResinKit No. 11 Cellulose Acetate
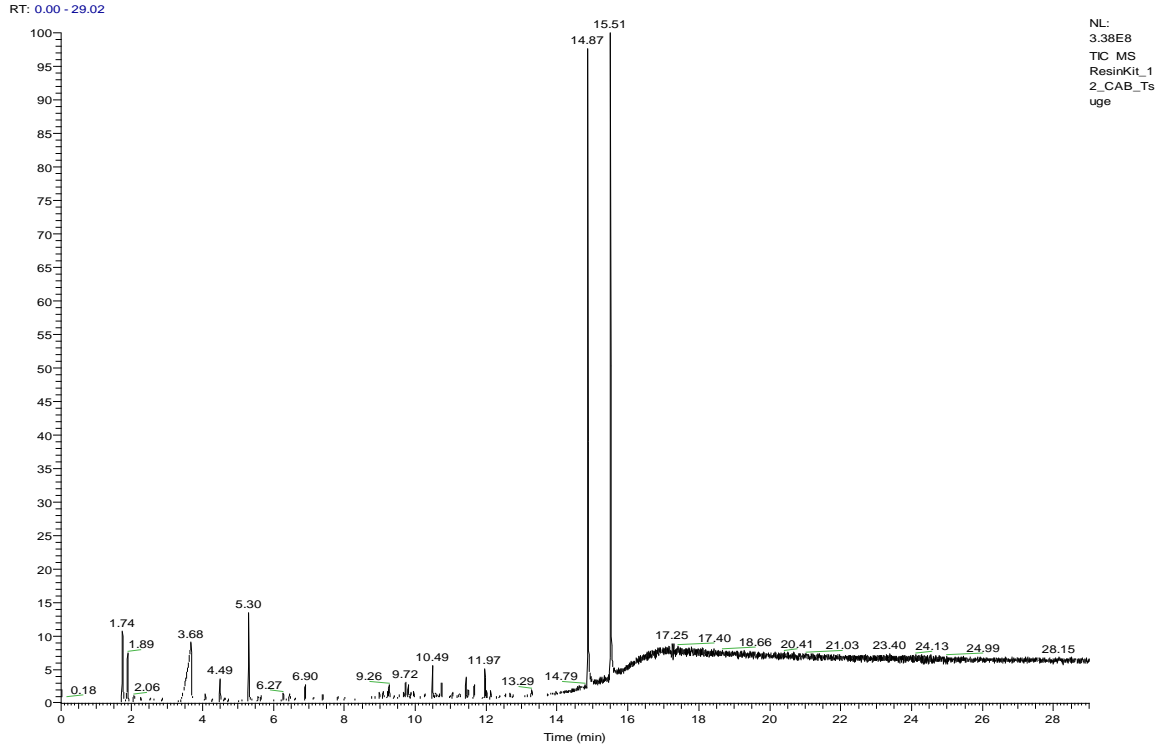
97

2010 ResinKit No. 12 Cellulose Acetate Butyrate

2018 ResinKit No. 12 Cellulose Acetate Butyrate

NL:
9.04E7
TIC MS
ResinKit_1
3_CAP_Ts
uge

2010 ResinKit No. 13 Cellulose Acetate Propionate

NL:
3.92E9
TIC MS
ResinKit_1
3_CAP_20
18_Tsuge

2018 ResinKit No. 13 Cellulose Acetate Propionate

2010 ResinKit No. 14 Transparent Nylon

2018 ResinKit No. 14 Transparent Nylon

100

RT: 0.00 - 29.02

NL:
5.94E8
TIC MS
ResinKit_1
5_Nylon66_
Tsuge

2010 ResinKit No. 15 Nylon Type 66

RT: 0.00 - 29.02

NL:
5.62E8
TIC MS
ResinKit_1
5_Nylon66_
2018_Tsug
e
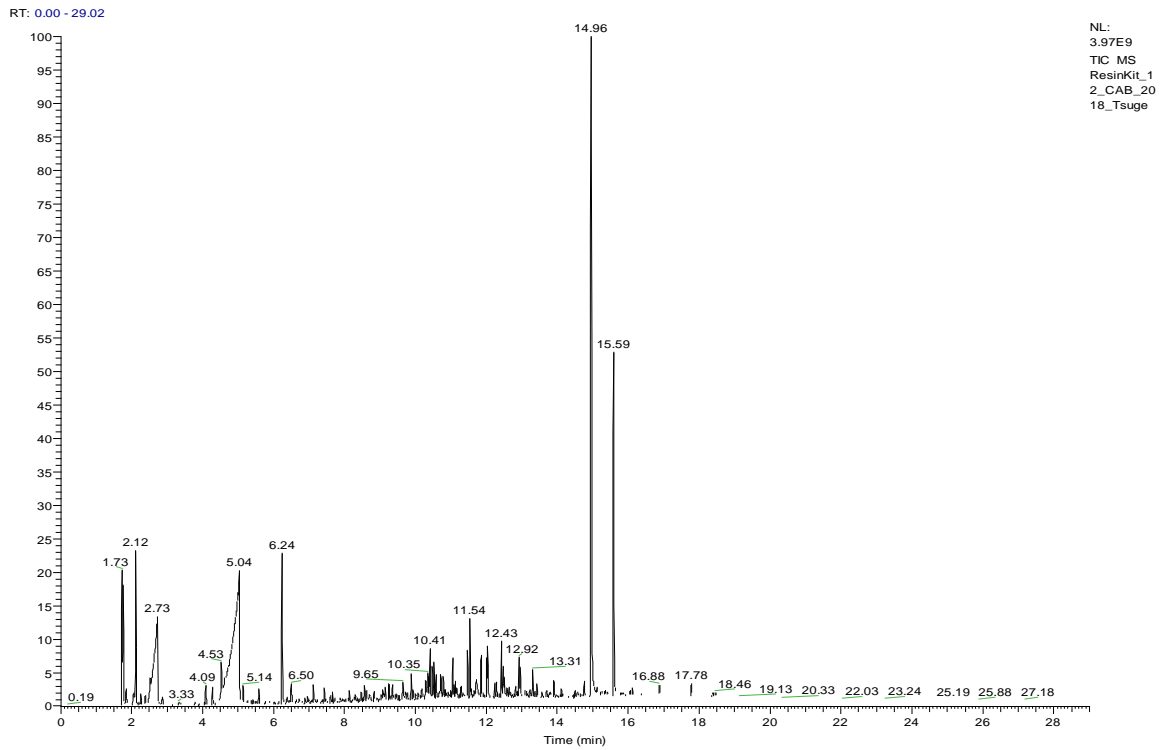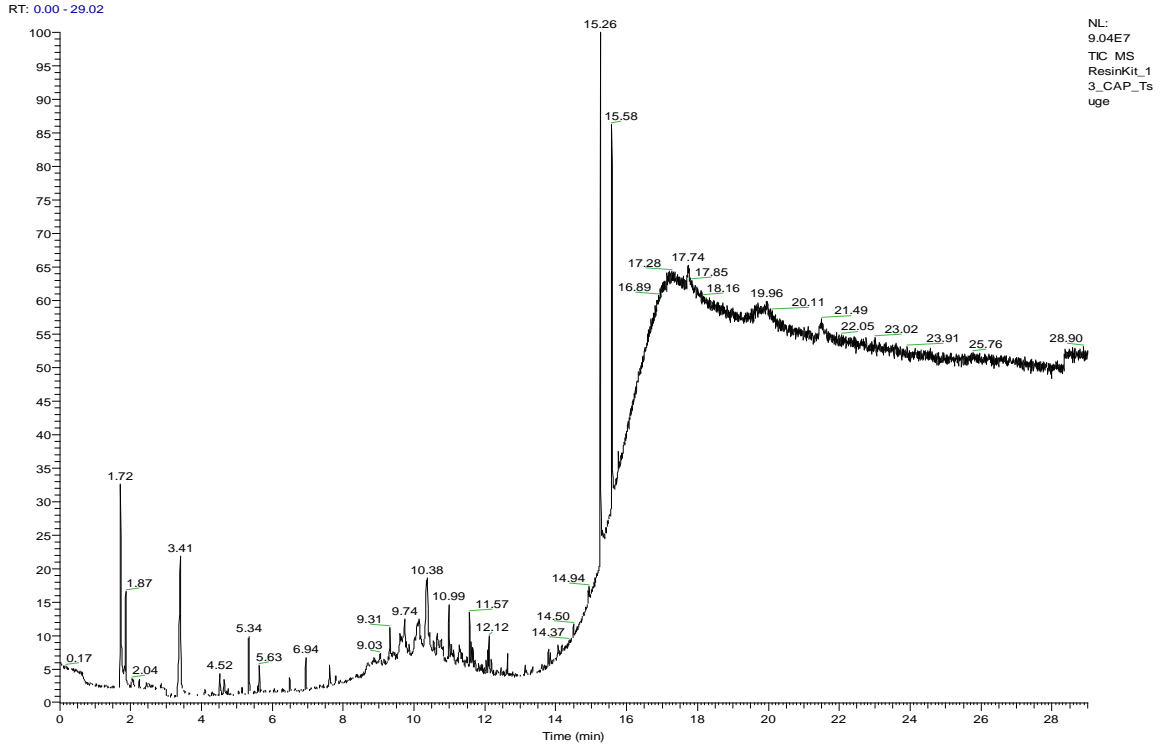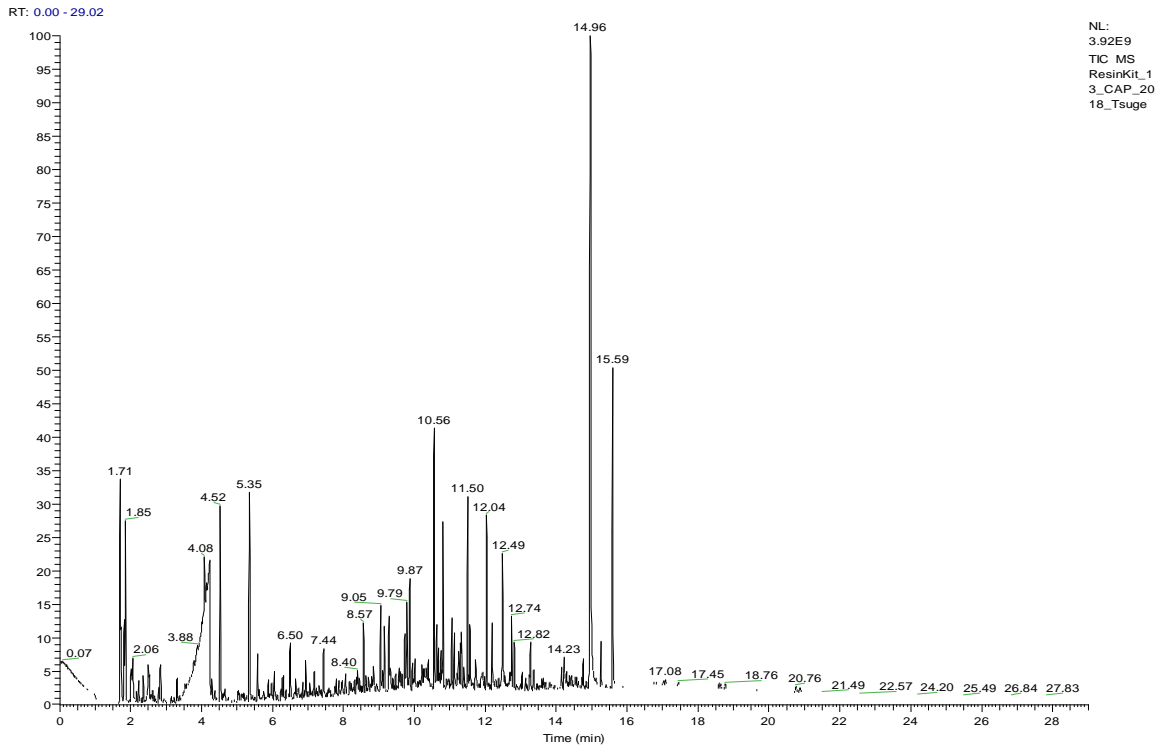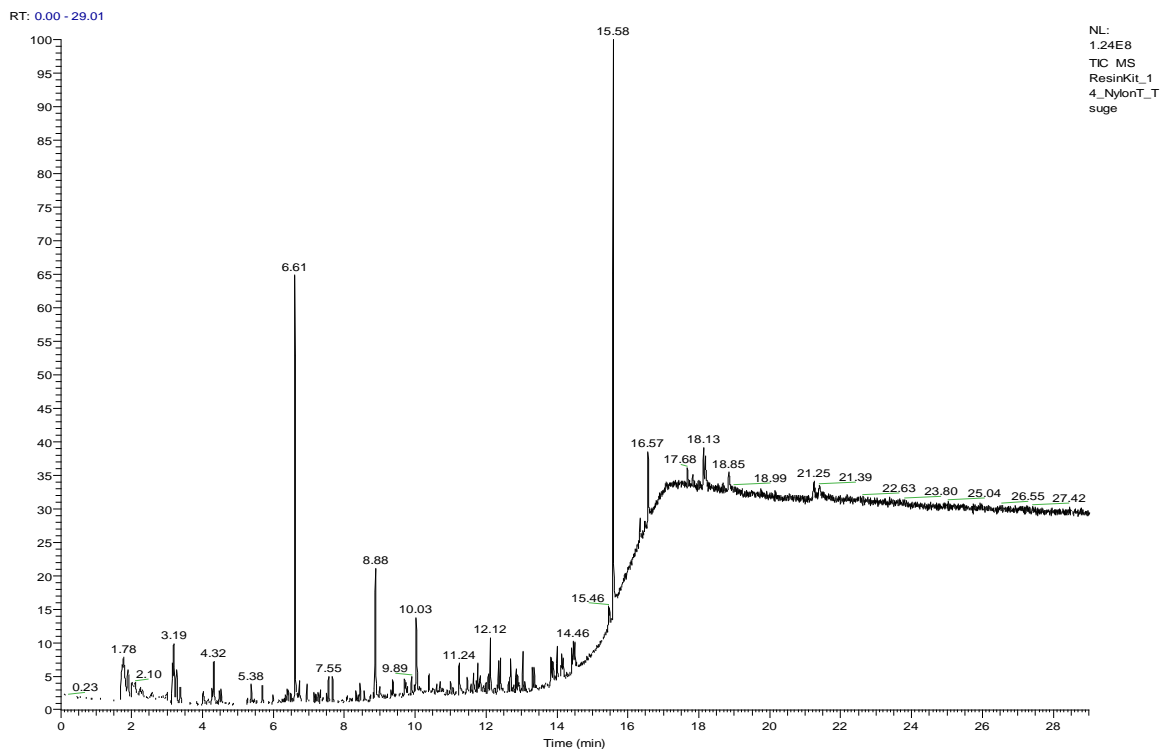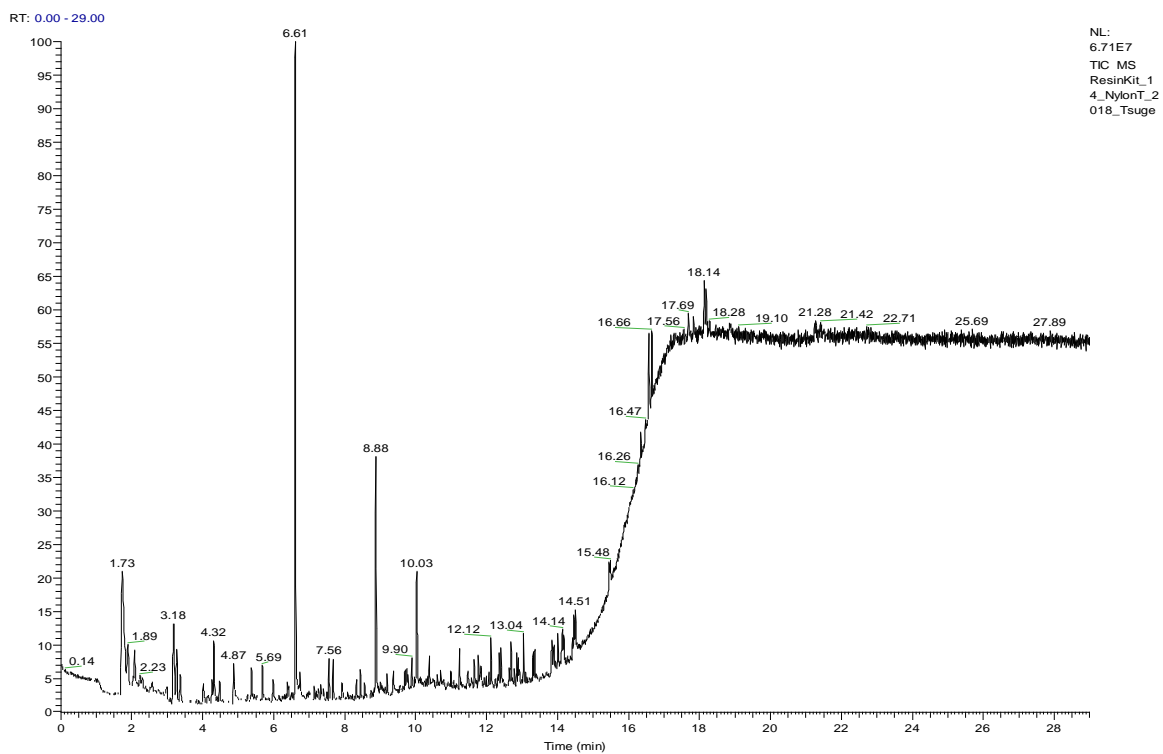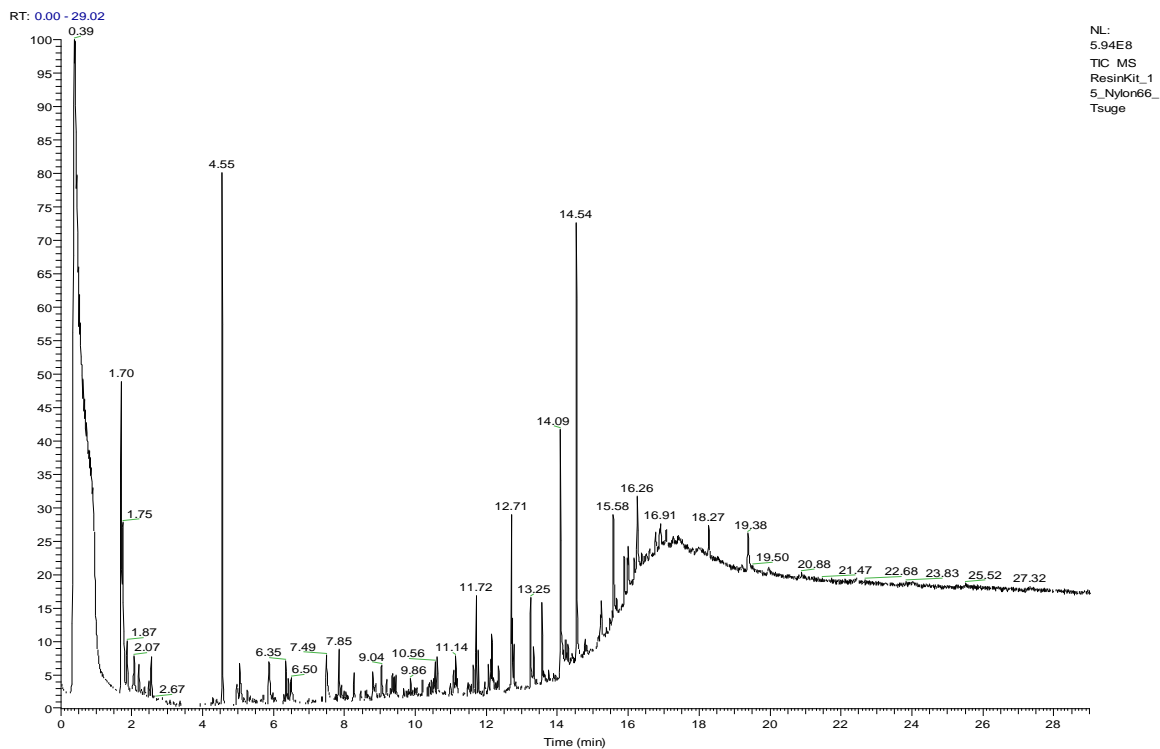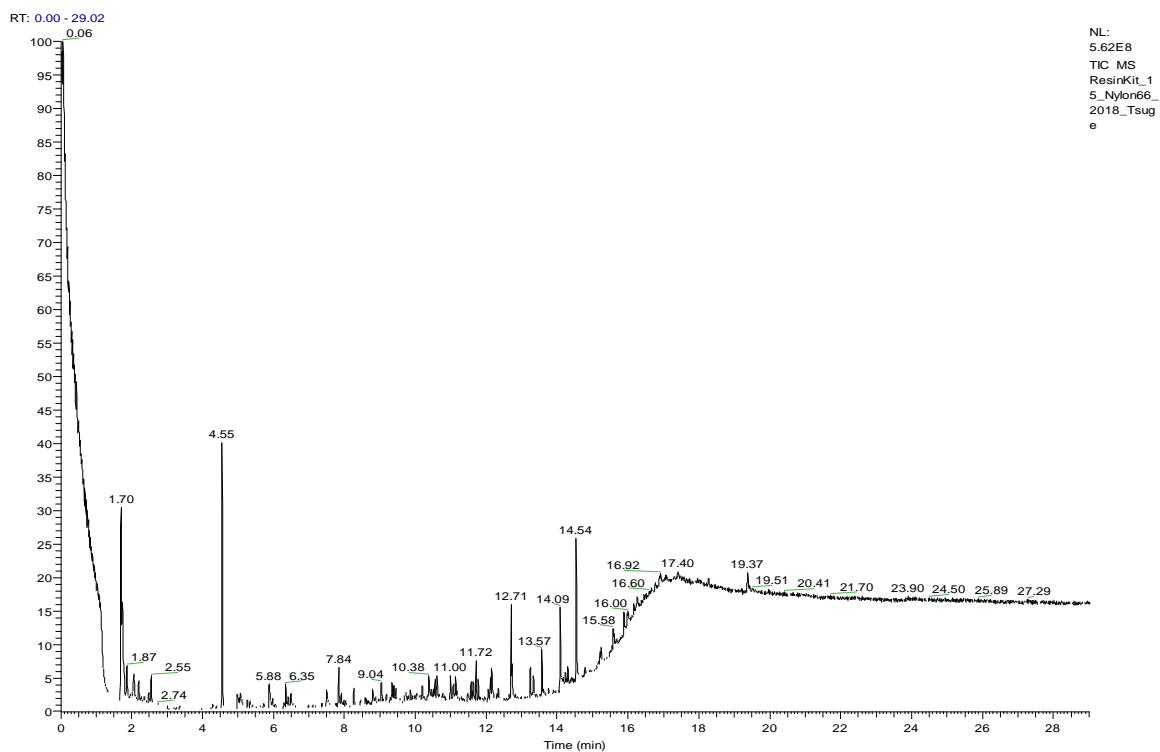
2018 ResinKit No. 15 Nylon Type 66
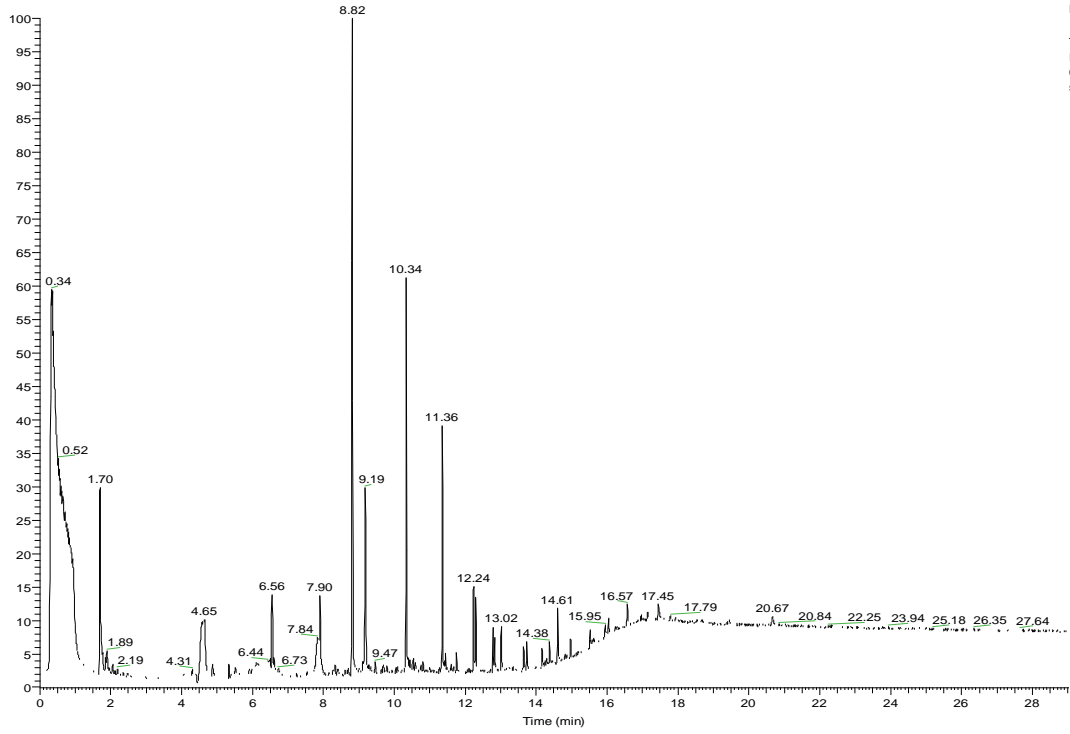
RT: 0.00 - 29.03

NL:
1.34E9
TIC MS
ResinKit_1
6_Nylon6_T
suge

2010 ResinKit No. 16 Nylon Type 6

RT: 0.00 - 29.03

NL:
1.98E9
TIC MS
ResinKit_1
6_Nylon6_2
018_Tsuge

2018 ResinKit No. 16 Nylon Type 6

NL:
2.68E9
TIC MS
ResinKit_1
7_PBT_Tsu
ge

2010 ResinKit No. 17 Thermoplastic Polyester (Polybutylene terephthalate)

NL:
1.55E9
TIC MS
ResinKit_1
7_PBT_20
18_Tsuge

2018 ResinKit No. 17 Thermoplastic Polyester (Polybutylene terephthalate)

2010 ResinKit No. 18 Thermoplastic Polyester (Polyethylene terephthalate Glycol)

2018 ResinKit No. 18 Thermoplastic Polyester (Polyethylene terephthalate Glycol)

NL:
5.64E8
TIC MS
ResinKit_1
9_PPO_Ts
uge

2010 ResinKit No. 19 Polyphenol Oxide

NL:
1.56E8
TIC MS
ResinKit_1
9_PPO_20
18_Tsuge

2018 ResinKit No. 19 Polyphenol Oxide

2010 ResinKit No. 22 Polybutylene

2018 ResinKit No. 22 Polybutylene

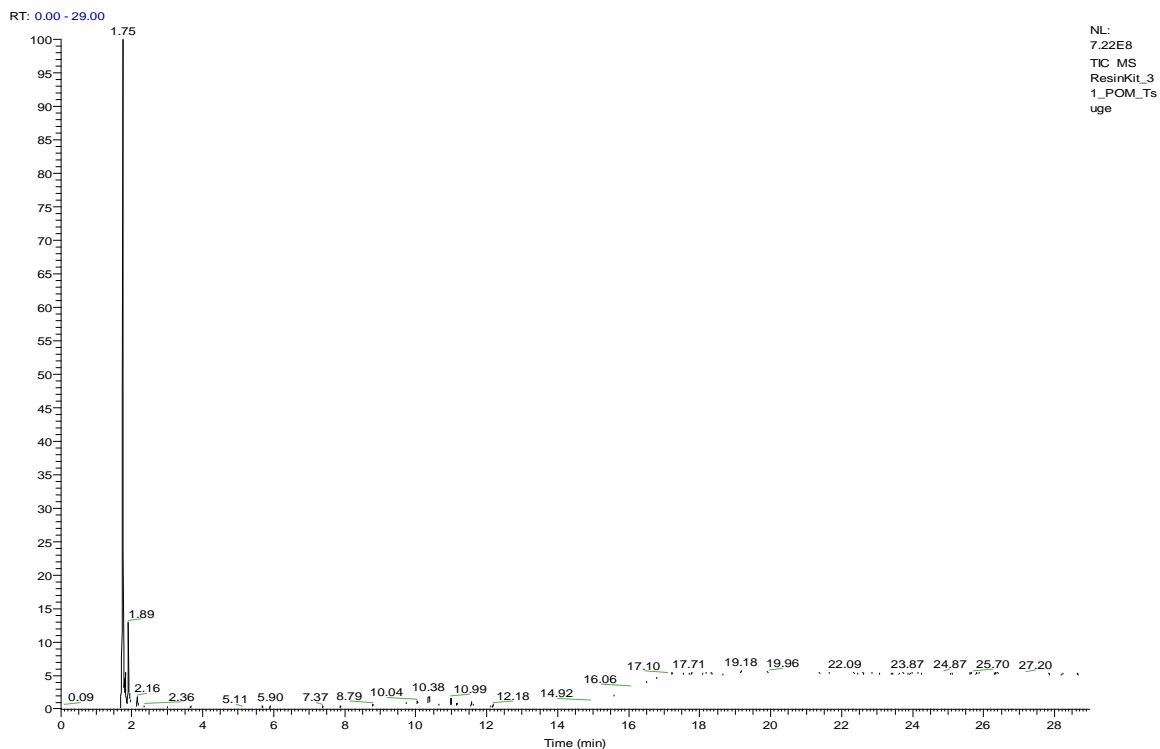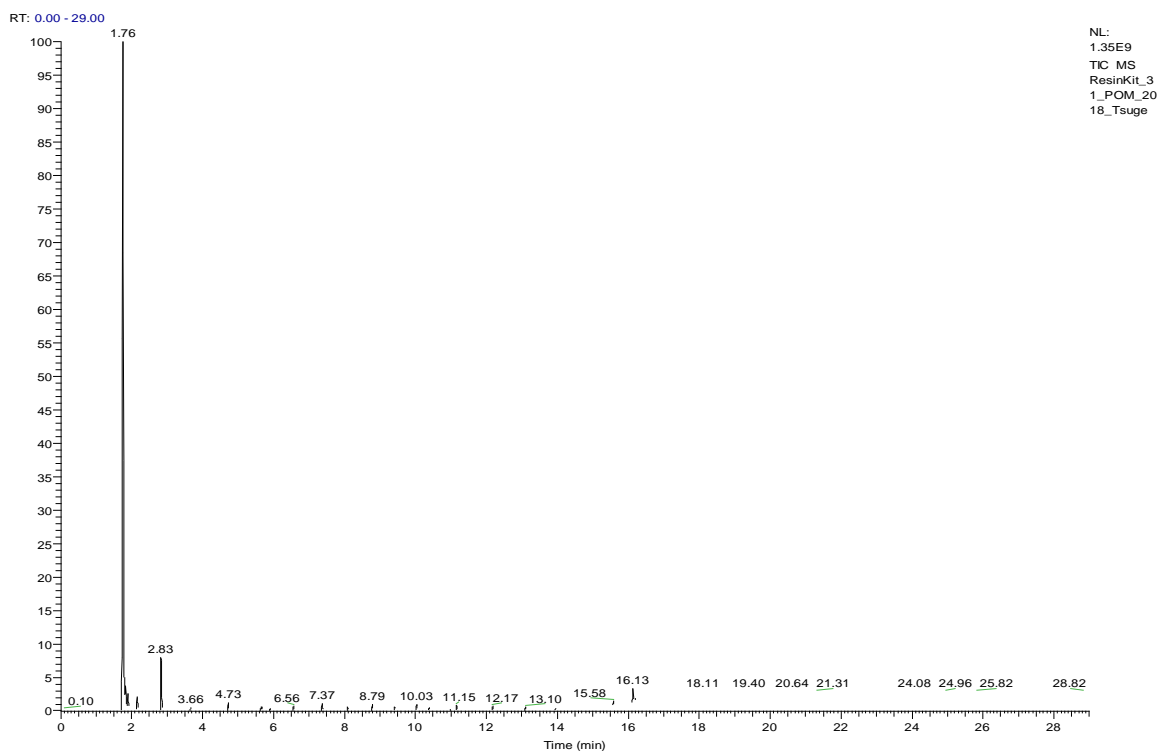2010 ResinKit No. 23 Ionomer

2018 ResinKit No. 23 Ionomer

107

2010 ResinKit No. 26 Polypropylene Co-Polymer

2018 ResinKit No. 26 Polypropylene Co-Polymer

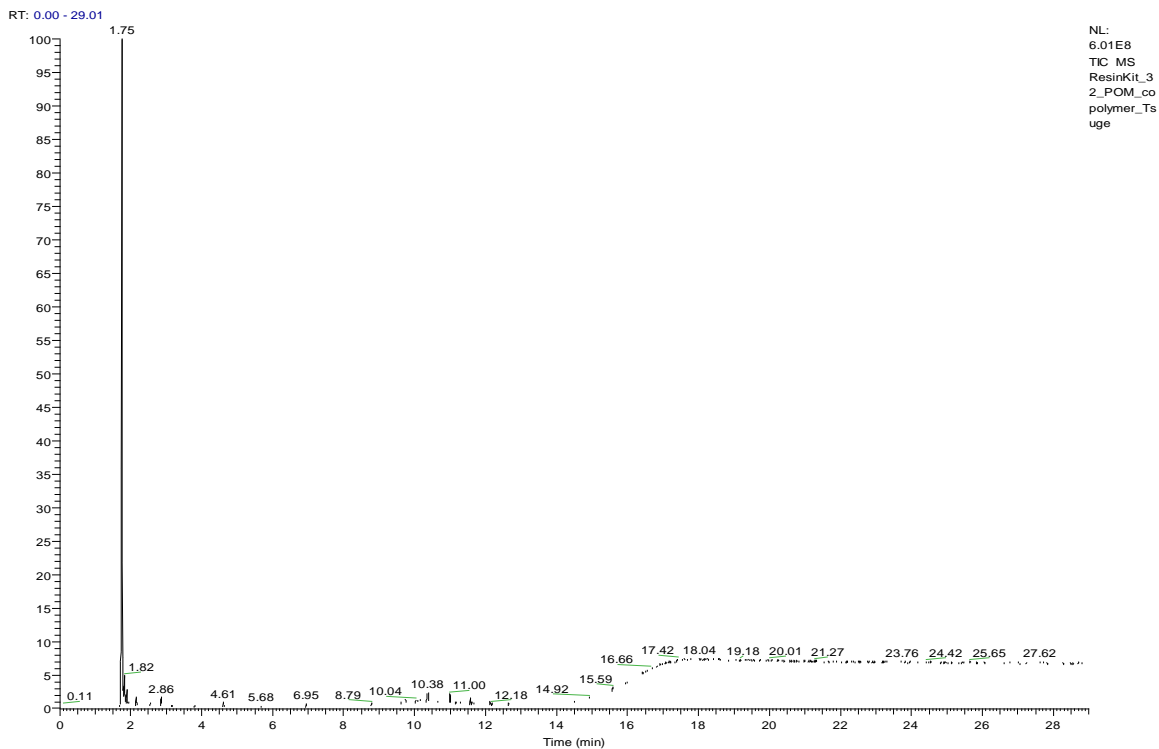2010 ResinKit No. 27 Polypropylene Homo-Polymer
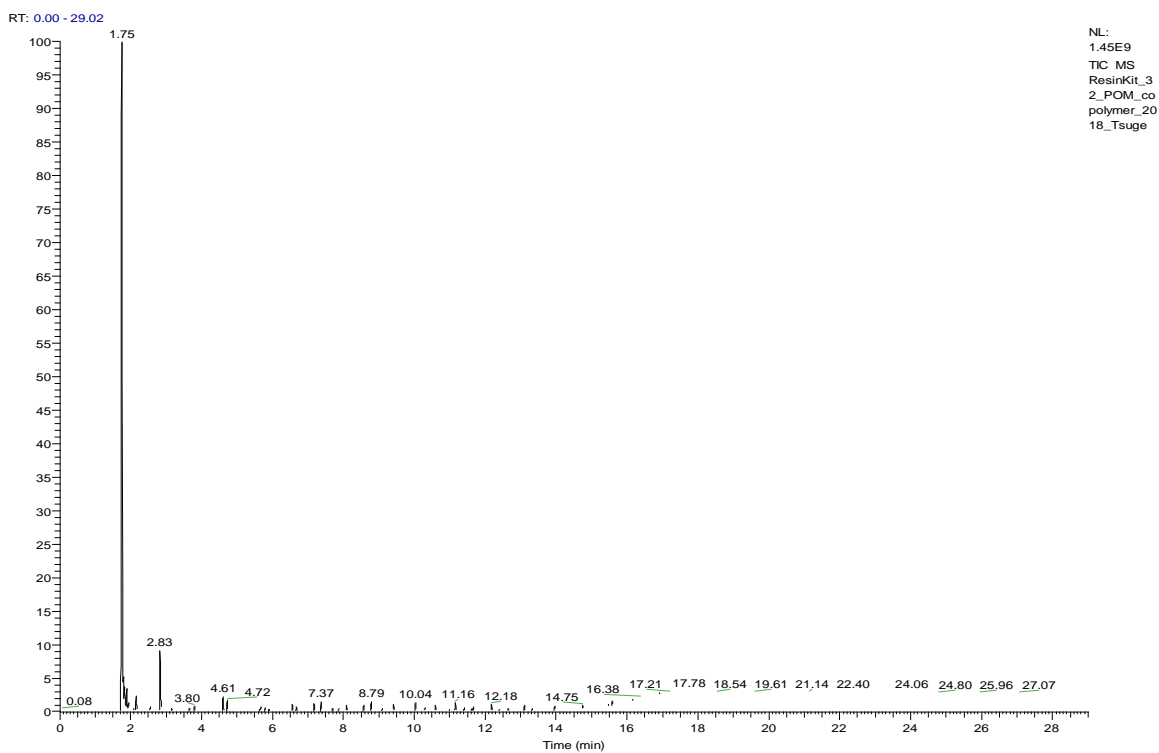

2018 ResinKit No. 27 Polypropylene Homo-Polymer
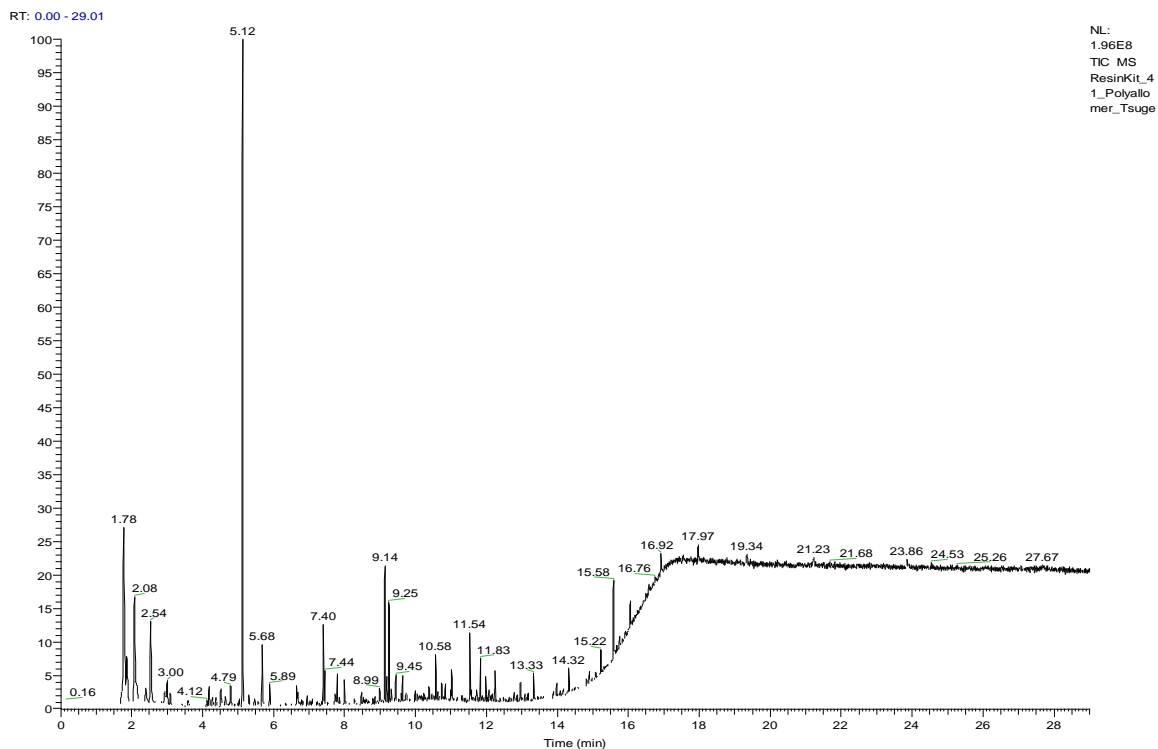
2010 ResinKit No. 31 Acetal Resin Homo-Polymer
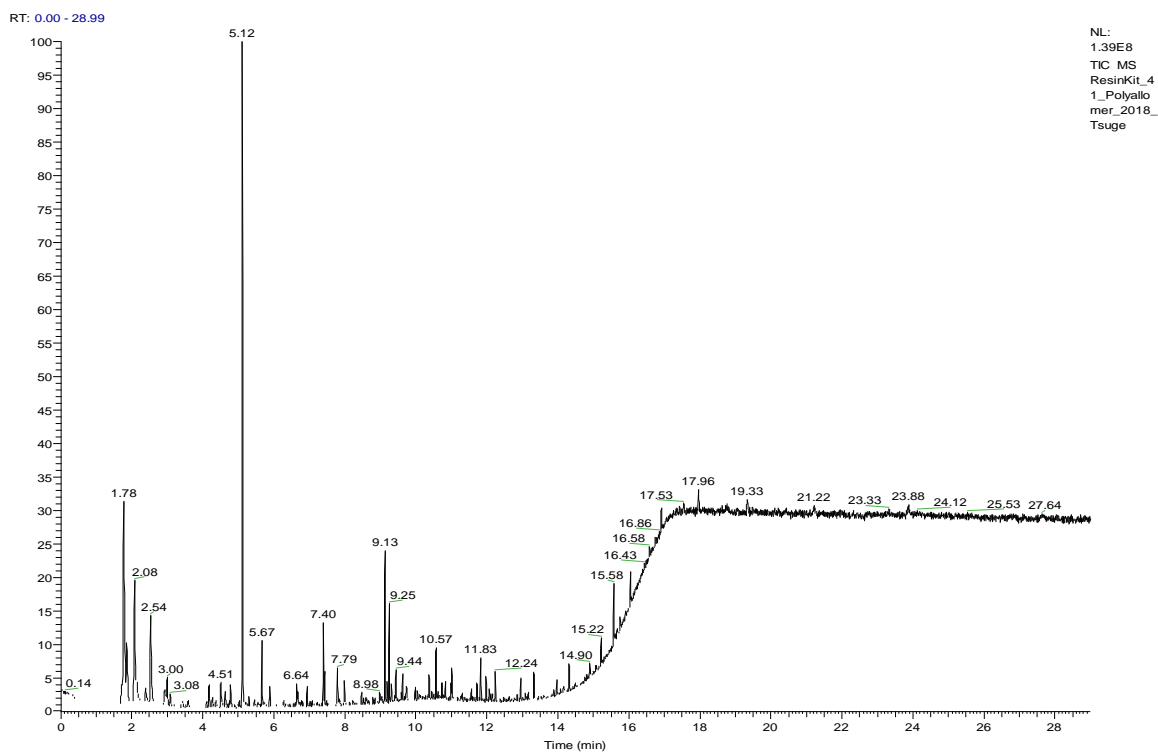

2018 ResinKit No. 31 Acetal Resin Homo-Polymer
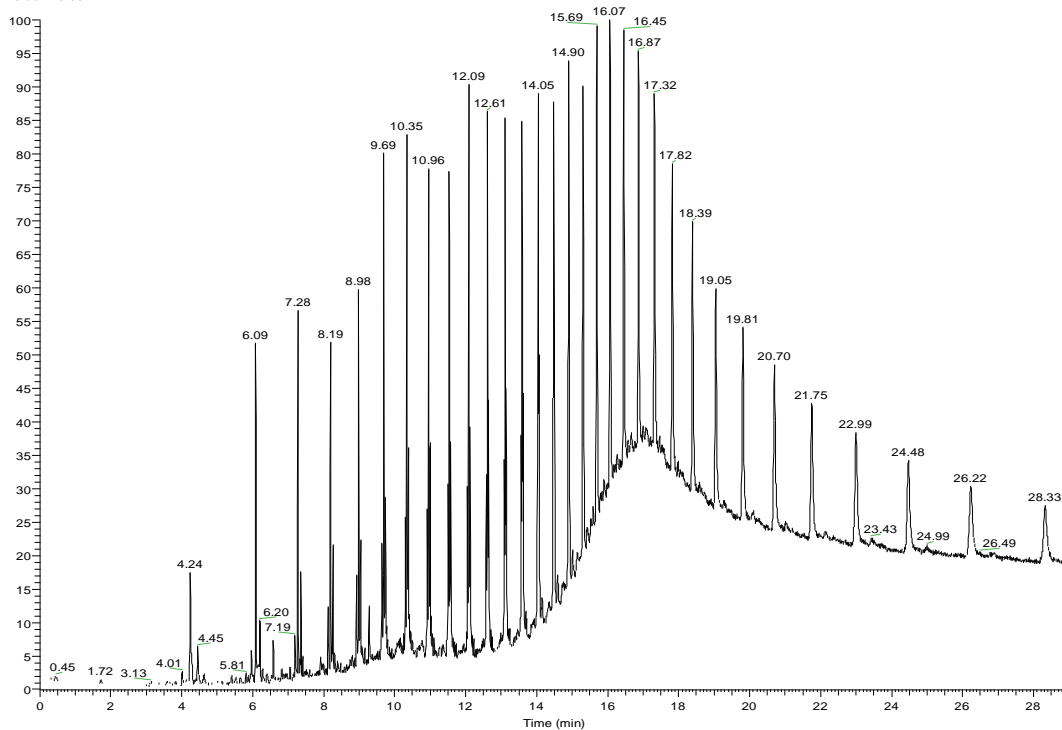
NL:
6.01E8
TIC MS
ResinKit_3
2_POM_co
polymer_Ts
uge

2010 ResinKit No. 32 Acetal Resin Co-Polymer

NL:
1.45E9
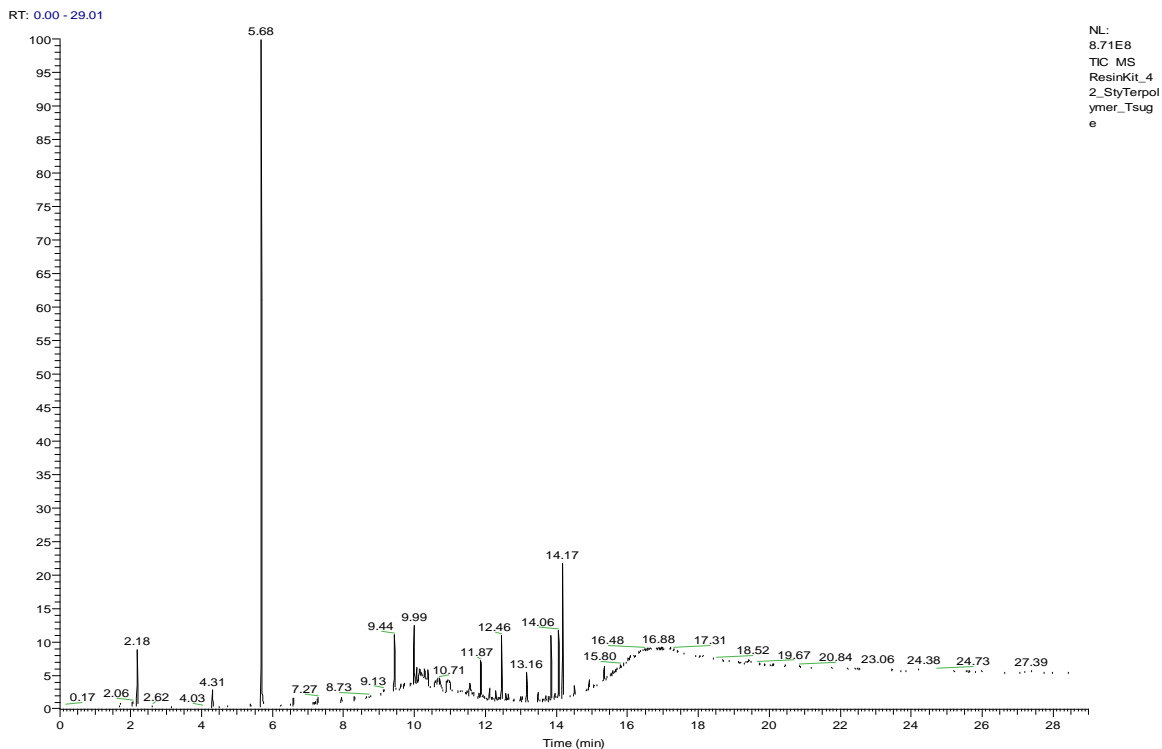TIC MS
ResinKit_3
2_POM_co
polymer_20
18_Tsuge

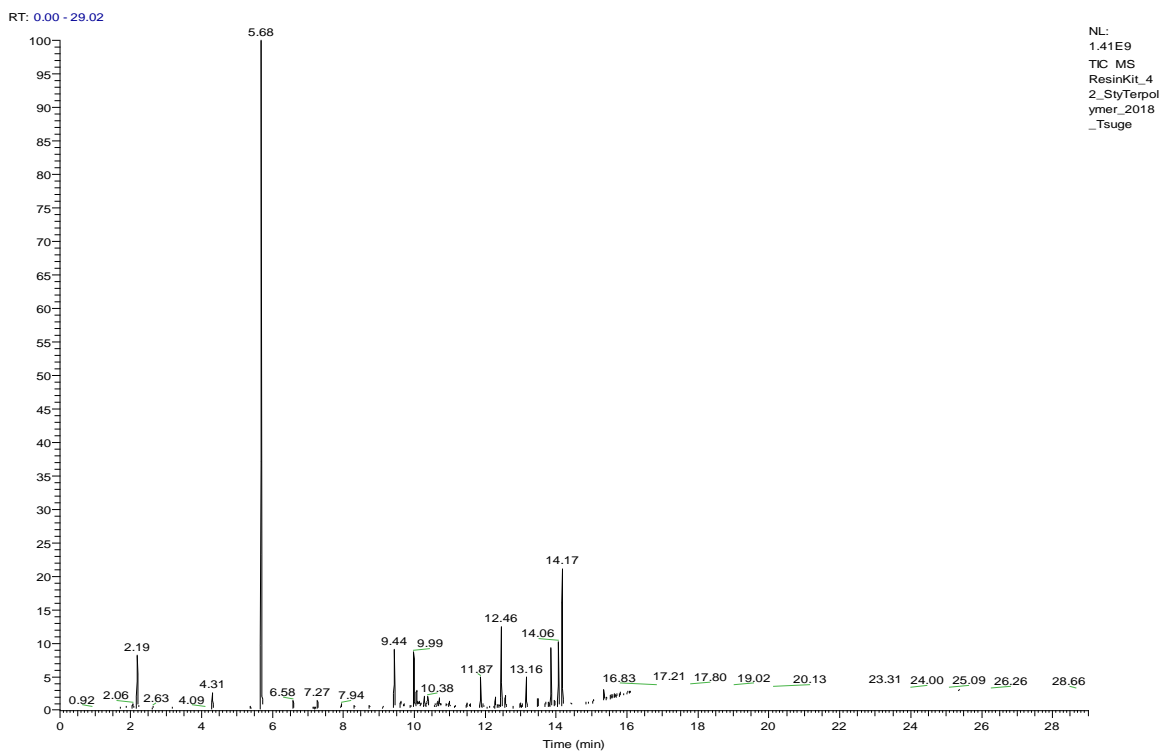2018 ResinKit No. 32 Acetal Resin Co-Polymer

2010 ResinKit No. 41 Polyallomer

2018 ResinKit No. 41 Polyallomer

2010 ResinKit No. 42 Styrene Terpolymer

2018 ResinKit No. 42 Styrene Terpolymer