

Fourier Transform Infrared Spectroscopy: Low Density Polyethylene,  
High Density Polyethylene, Polypropylene and Polystyrene

Eman Mousa Alhajji

North Carolina State University

Department of Materials Science and Engineering

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Patrick Snyder

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Abstract

The objectives of this experiment are to analyze the vibrational properties and Fourier Transform Infrared Spectroscopy (FTIR) measurements of four polymers assigned to unknown spectra, examine how different bonds and functional groups give rise to different FTIR signatures and estimate % crystallinity in LDPE and HDPE as semi-crystalline polymers. FTIR spectrum of sample A was identified to relate to PP molecular structure with two functional groups: methyl and methylene. The FTIR spectrum of sample A was identified to relate to PS molecular structure with two functional groups, methylene and Phenyl. The FTIR spectra of sample C and sample D were identified to relate to PE molecular structure with a functional group of methylene. With difference in the areas under peaks, sample C was determined to be LDPE and sample D was determined to be HDPE. The percent crystallinities of LDPE and HDPE were estimated correctly to be 52.787 % and 76.30% respectively. The implication of this experiment is that different functional groups and percent crystallinity are two major factors making each IR spectrum of the four samples a unique one by which chemical structural analysis can be achieved.

## Introduction

Fourier transform infrared spectroscopy (FTIR) is a method used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high spectral resolution data over a wide spectral range.<sup>1</sup> Figure 1 shows the typical arrangement of FTIR. The five main components of FTIR are radiation source, interferometer, sample, detector and mono IR beam.

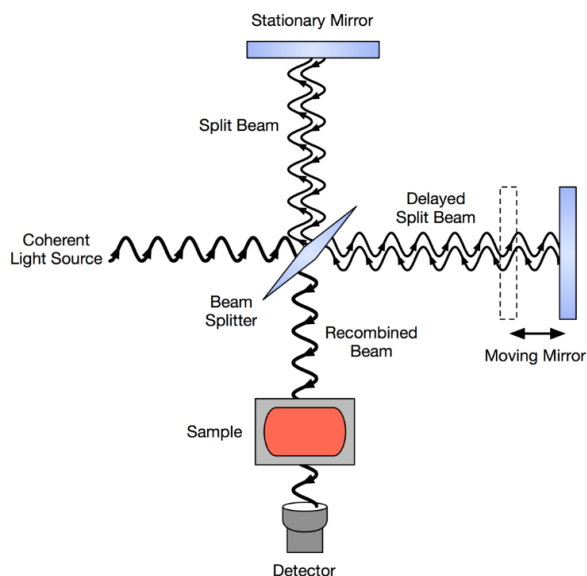


Figure 1. The typical arrangements of FTIR.<sup>1</sup>

The radiation source used in FTIR is polychromatic Xe lamp. An interferometer consists minimally of two mirrors and a beam splitter. It works by first dividing the beam coming from the lamp, which gives rise an optical path difference, then recombining them at a beamsplitter after being reflected off stationary and moving mirrors. The detector measures interference signal as a function of optical path difference. The beams undergo constructive interference and can be considered in phase with a maximum detector response if the split beams have a difference of  $\lambda$ . The beams undergo destructive interference and  $180^\circ$  out of phase if the optical paths differ by  $\lambda/2$ .

The amplitude of the wave is reduced by an amount proportional to sample in beam. Finally, the detected intensity as a function of moving mirror position converted to the final IR spectrum, A or T vs  $\nu$  (cm<sup>-1</sup>), by a Fourier transform.<sup>2</sup>

The principles of this technique rely on absorption or emission of the sample at a particular frequency in relation to its vibrational motion of molecules. Molecular vibration, the coupled motion of atoms within molecules, has the following modes: stretching, bending and rocking, each of which corresponds to an energy level. IR spectra contains peaks at frequencies where it represent transitions between quantized vibrational energy states, which corresponds to a particular functional group. Energy difference for transitions between the ground state and first excited state of most vibrational modes occurs in the mid-IR range, which is between 4000-400 wavenumber (cm<sup>-1</sup>). IR spectra is used in both chemical and structural analyses. A substance can be chemically identified by matching observed IR spectrum with known database. Also, structures can be determined as functional groups give rise to characteristic bands. FTIR is faster, more reliable and more powerful comparing to a classic dispersive IR spectrometer. In FTIR spectrometer, more energy reaches the sample and a wavelength range of IR does not have to be continuous when scanned.

The objective of this experiment is to analyze the vibrational properties of four polymers by measuring and observing the FTIR spectra Using Varian 640-IR, FT-IR Spectrometer. In addition, different bonds in relation to their functional groups giving rise to different FTIR signatures are examined. Finally, % crystallinity in semi-crystalline polymers are calculated. The specimens being examined are low density polyethylene, high density polyethylene, polypropylene and polystyrene.

## Experimental Procedure

The instrument used in this experiment was Varian 640-IR, FT-IR Spectrometer. The specimens being examined were low density polyethylene (LDPE), high density polyethylene(HDPE), polypropylene(PP) and polystyrene (PS). LDPE sample was taken from a milk container, HDPE sample was taken from 6 pack ring holder, PP sample was taken from CD case and PS sample was taken from coil installation. The hardware components were a Duraglow mid-IR source, KBr beamsplitter, and a Peltier-cooled DLaTGS detector; a HeNe laser, which was used for calibrating distance of the moving mirror. The software used with the FTIR spectrometer was Resolutions Pro. The experiment was operated at room temperature and an absolute pressure of 1 atm.

The method used was attenuated total reflection (ATR) attachment. An ATR attachment operates by measuring the changes that occur in a totally internally reflected infrared beam when the beam comes into contact with a sample. This internal reflectance creates an evanescent wave that extends beyond the surface of the crystal into the sample held in contact with the crystal. ATR is beneficial in the way it increases the signal ratio by contacting the sample at multiple points. The crystal material used for ATR was Zinc Selenide (ZnSe), known for its high reflective index. ZnSe scratched easily and care was taken when cleaning the crystal. The crystal was cleaned by using a lens paper and alcohol. The parameters were as following: 32 scans arrange with each other, 8 sensitivity, 4000-600 range of waves, and a resolution of 4 cm<sup>-1</sup>. Cautions were taken into consideration. Hand gloves were used in order to avoid oil contamination from fingers. Dry air was used to avoid lens exposure to air which could change the microstructure of the lenses and IPA was used to clean ZnSe.

Each sample one at a time was mounted, and pressed down right on the crystal. Then the FTIR spectrometer was turned on and the measurement was collected. As with all FT-IR measurements, an infrared background was collected as shown in Figure 2, from the clean ATR crystal to avoid positions of disturbing bands.

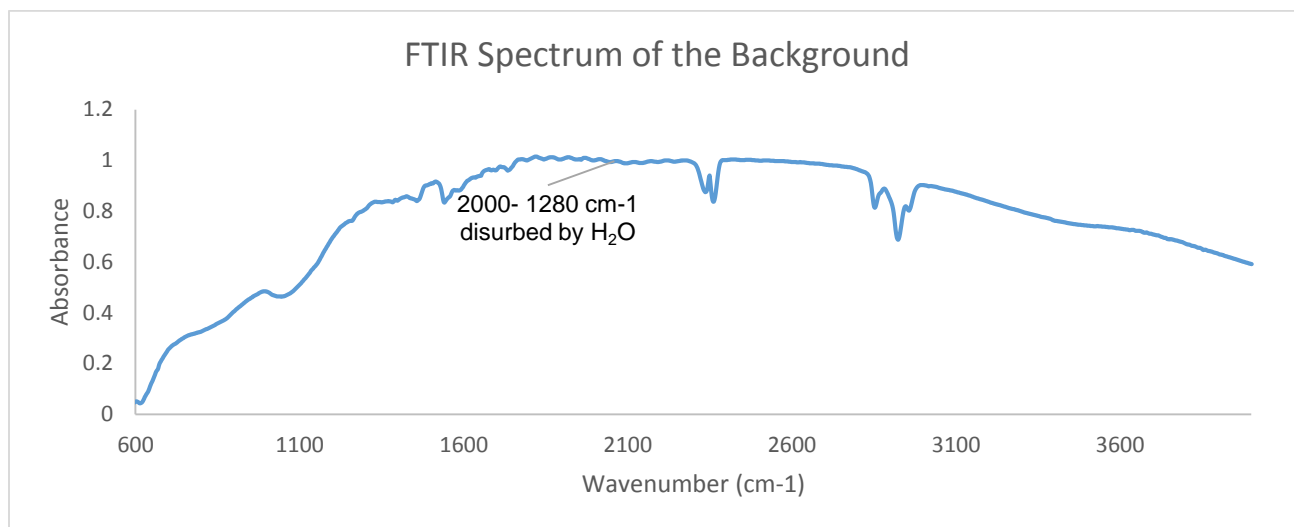


Figure 2. The FTIR spectrum of the background.

The repeat units, as shown in Figure 3, for the polymers being examined were used in order to relate the FTIR signatures to the polymer structures. The % crystallinities of the LDPE and HDPE samples were calculated using  $(1 - \text{Equation 1}) \times 100$ .

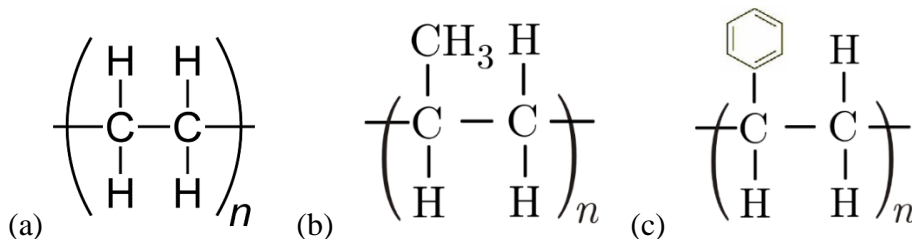


Figure 3. Repeat units for (a) polyethylene, (b) polypropylene, and (c) polystyrene.<sup>1</sup>

$$x = \frac{1 - \left(\frac{Ia}{Ib}\right)}{1.233 + \left(\frac{Ia}{Ib}\right)} \quad (1)$$

where x is the amorphous content, the value 1.233 is the intensity ratio of the two bands in a spectrum of a 100% crystalline PE sample, Ia is the intensity of crystallinity methylene rocking peak and Ib is the intensity of amorphous methylene rocking peak.

## Results

The FTIR spectra were calculated and given without the samples' names. Sample A indicates 10 major peaks, as labeled in Figure 3. It represents two active functional groups: methylene and methyl. Table 1 shows the frequencies with its corresponding vibrational modes and functional groups. Sample A shows peak splitting.

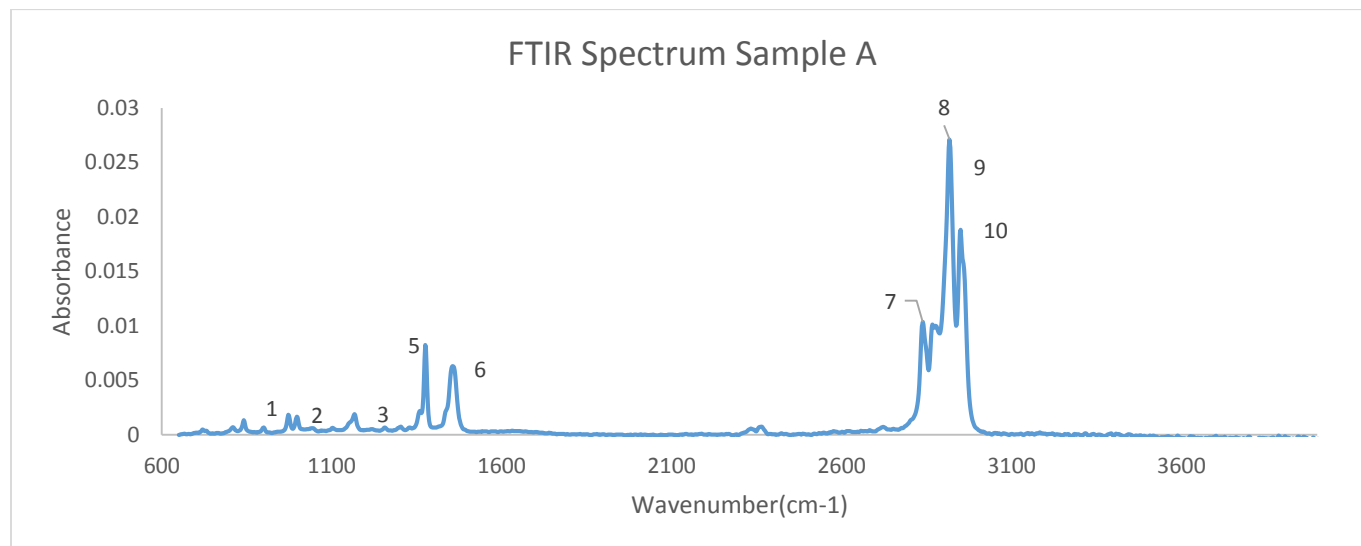


Figure 4: Sample A IR Spectrum.

Sample B indicates 12 major peaks, as labeled in Figure 3. It represents two active functional groups: groups: methylene and Table 2 shows the frequencies with its corresponding vibrational modes and functional groups. Sample B shows no or few peak splitting.

Table 1: Peaks corresponding to vibrational moods and functional groups of sample A.

<b>Peak Number</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
<b>Frequency (cm-1)</b>	845	910	1155	1370	1445.9
<b>Vibrational mood &amp; Functional Group</b>	Amorphous Rock Methylene(C-H2)	Crystalline Rock Methylene(C-H2)	Amorphous Bending Methylene(C-H2)	Crystalline Bending Methylene(C-H2)	C-H Bending Methylene(C-H2)
<b>Peak Number</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>	<b>10</b>
<b>Frequency (cm-1)</b>	1461.2	2849.12	2876.98	2910.34	2971.9
<b>Vibrational mood &amp; Functional Group</b>	Amorphous Bending C-H Bending Methylene(C-H2)	C-H asym/sym Stretching Methylene(C-H2)	C-H asym/sym Stretching Methyl (-CH3)	C-H asym/sym Stretching Methyl (-CH3)	asym/sym Stretching Methyl (C-H)

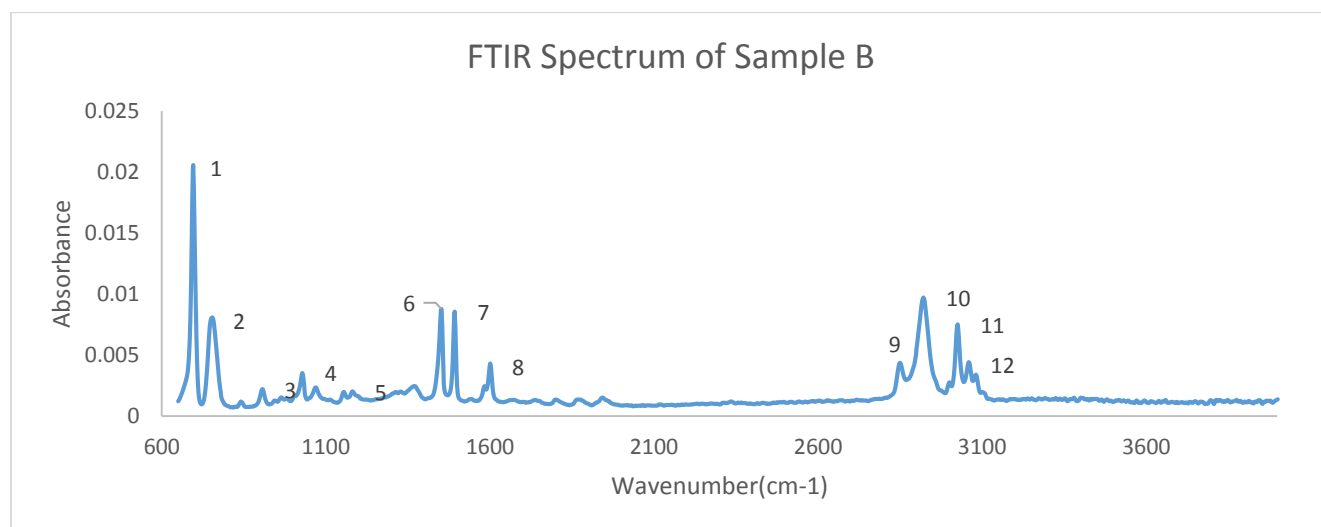


Figure 5: Sample B IR Spectrum.

Table 2: Peaks corresponding to vibrational moods and functional groups of sample B.

<b>Peak Number</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
<b>Frequency (cm-1)</b>	694.1	752.1	966.4	1025.7	1357.6	1448.8

<b>Vibrational mood &amp; Functional Group</b>	Monosubstitution (phenyl)	Rock Methylene(C-H2)	Amorphous Bending Methylene(C-H2)	Bending C-H	Bending C-H bonds	Bending C-H bonds Methylene(C-H2)
<b>Peak Number</b>	<b>7</b>	<b>8</b>	<b>9</b>	<b>10</b>	<b>11</b>	<b>12</b>
<b>Frequency (cm-1)</b>	1491.0	1599.3	2849.9	2920.1	3024.9	3059.9
<b>Vibrational mood &amp; Functional Group</b>	Bending C-H bonds Methylene(C-H2)	Atomic ring stretching (Phenyl)	Stretching C-H bonds Methylene(C-H2)	Stretching C-H bonds Methylene(C-H2)	C-H Stretching in aromatic ring (Phenyl)	C-H Stretching in aromatic ring (Phenyl)

C and D Samples have very similar FTIR spectra. They both indicate 6 major peaks, as labeled in Figure 6 and Figure 7. They represent one active functional groups: methylene. Table 3 shows the frequencies with its corresponding vibrational modes and functional groups. The FTIR spectra of C and D samples show some peak splitting. The only noticeable difference between the two spectra is that the peaks in the FTIR spectrum of sample C is narrower than those in sample D.

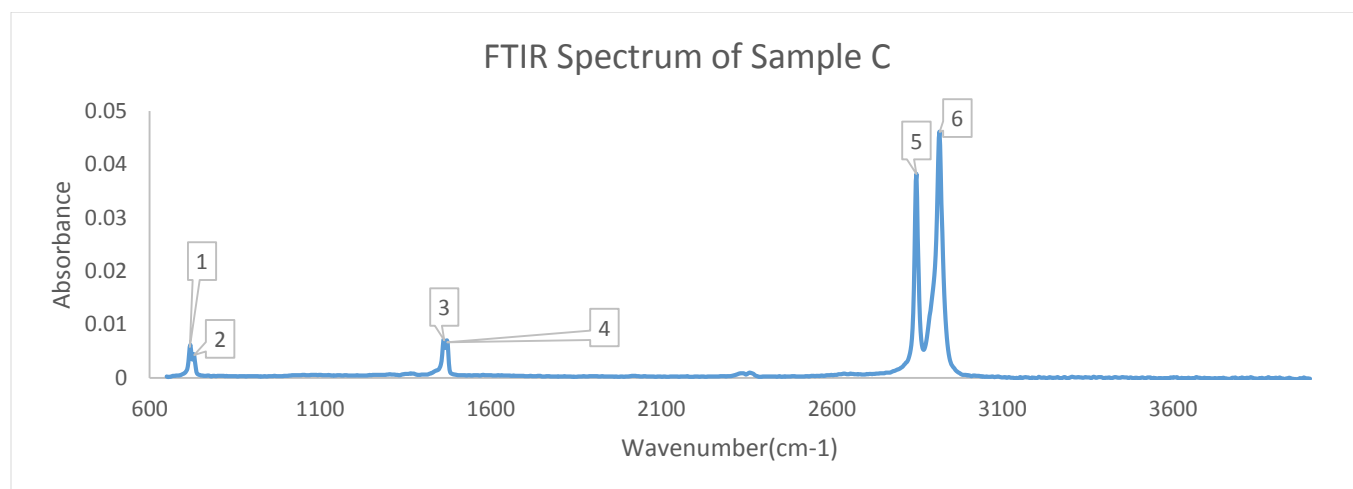


Figure 6: Sample C IR Spectrum.



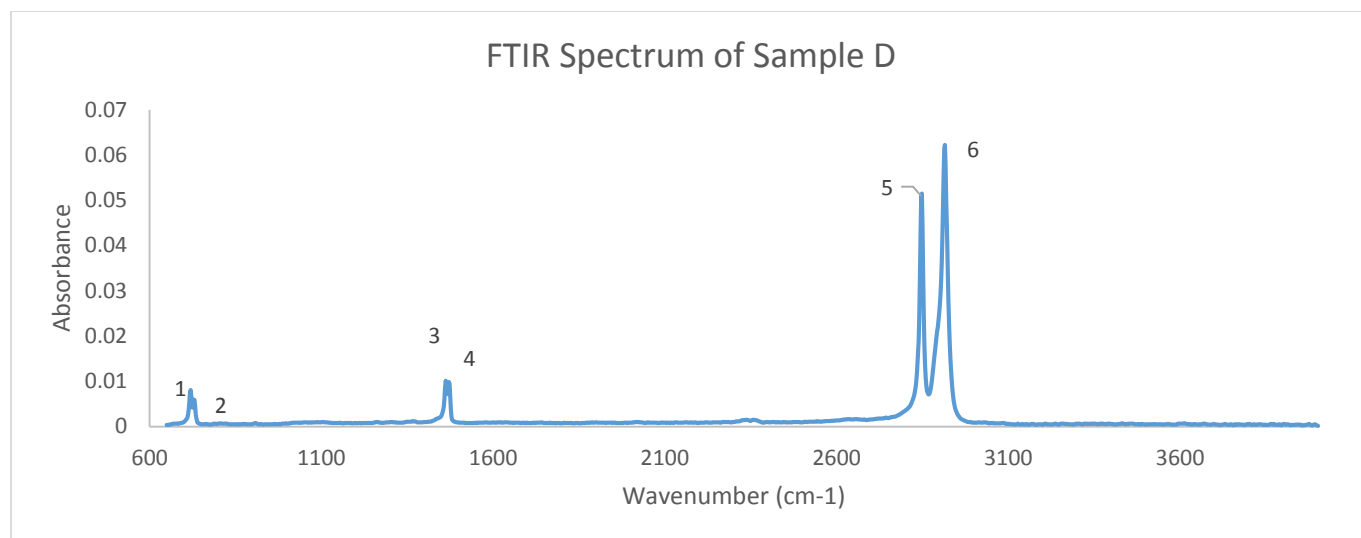


Figure 7: Sample D IR Spectrum.

Table 3: Peaks corresponding to vibrational moods and functional groups of sample C and sample D.

Peak Number	1	2	3	4	5	6
Frequency (cm-1)	719.32	730.89	1461.79	1473.36	2848.3	2915.87
Vibrational mood & Functional Group	Amorphous Rock Methylene(C-H2)	Crystalline Rock Methylene(C-H2)	Amorphous Bending Methylene(C-H2)	Crystalline Bending Methylene(C-H2)	Stretching Methylene(C-H2)	Stretching Methylene(C-H2)

In order to calculate the % crystallinity of LDPE and HDPE, the intensity were first determined by fitting each peak in the 700  $\text{cm}^{-1}$  and taking its area. Using Equation 1, the % crystallinity of LDPE was found to be 52.787 %. The % crystallinity of HDPE was found to be 76.30%.

## Discussion

After analyzing The FTIR signatures of the four samples, the unknown samples were identified. The FTIR spectrum of Sample A was found to be polypropylene. The peaks in FTIR spectrum of Sample A were found to split as shown in Figure 1, which indicates that this polymer molecule has to be semi-crystalline.<sup>1</sup> Moreover, the cluster of peaks around 2970  $\text{cm}^{-1}$  down to

around 2850  $\text{cm}^{-1}$  indicates that sample A has methyl as one functional group and the cluster of peaks around 1600  $\text{cm}^{-1}$  down to around 700  $\text{cm}^{-1}$  indicates that sample A has methylene as another functional group. Given the functional group, it can be concluded that the structure of this polymer has to be polyethylene. The peaks in FTIR spectrum of Sample B were found to have one phase as shown in Figure 1, which indicates that this polymer molecule has to be amorphous. Sample B was determined to be polystyrene. Similarly, Sample B has cluster of peaks around 1600  $\text{cm}^{-1}$  down to around 700  $\text{cm}^{-1}$ , which indicates that sample B has methylene as a functional group. The cluster of peaks around 1600  $\text{cm}^{-1}$  down to around 700  $\text{cm}^{-1}$  indicates that sample A has methylene as another functional group. The peaks around 3024 to 3059  $\text{cm}^{-1}$  indicates and the peak with frequency of 694.1  $\text{cm}^{-1}$  indicates that that this polymer has phenyl as a functional group. Sample C and D exhibit very similar FTIR signatures. The splitting of peaks around 700  $\text{cm}^{-1}$  and around 1400  $\text{cm}^{-1}$ , as shown in Figure 6 and Figure 7, implies that sample C and sample D are semi-crystalline polymers. From the FTIR signatures and its corresponding functional group as shown in Table 3, sample C and sample D were found to be polyethylene polymers. However, the peaks in the FTIR spectrum of sample C were observed to be narrower than those in the FTIR spectrum of sample D, which suggests that sample C has to be LDPE and sample D is HDPE.<sup>3</sup>

The FTIR signatures of PE, PP and PS have common peaks around 1400  $\text{cm}^{-1}$  that represent methylene as functional group. The difference in structures of PE, PP, and PS, is replacing one hydrogen atom in PE with a functional group,  $\text{CH}_3$  in PP and  $\text{C}_6\text{H}_6$  in PS.<sup>1</sup> These replacements influence % crystallinity of polymers. Percent crystallinity is also influenced by the density of a polymer.<sup>2</sup>

The percent crystallinities of LDPE and HDPE were estimated on basis of data obtained from their FTIR spectra to be 52.787 % and 76.30% respectively. The estimated % crystallinities

of HDPE and LDPE agree with the literature. HDPE is the most crystalline of the major categories of PE (70-90% crystalline). HDPE typically has molecular weight  $\sim 35$  kg/mol, and contains relatively few branches, which themselves are of relatively small molecular weight. The increased crystallinity also results in increased stiffness and higher density, with density  $\sim 0.935 - 0.960$  g/cm<sup>3</sup>. LDPE is a much higher molecular weight class of PE which contains many branches of high molecular weight. Its ability to crystallize is greatly impeded by the presence of branching, which limits degree of crystallinity to about 40%. LDPE has much better flexibility, impact toughness, and resistance to environmental stress cracking. The density of LDPE is lower due to the higher amount of amorphous content,  $\sim 0.910 - 0.925$  g/cm<sup>3</sup>.<sup>3</sup> From the IR spectra of the two PP samples, the lower the degree of crystallinity was, the more intensity of peaks were reported. Changes in intensity definitely signifies some changes related to the phase or crystallinity. Going from the FTIR spectra of PE to PP, lower stretching frequencies and lower energy peaks were deducted due to the change in functional group. It was also observed in the FTIR spectra of PP and PS with decreasing order of crystallinity that absorption bands shifted to lower frequencies and caused minimal peaks splitting. Disturbing bands were found to alter the intensity and positions of some peaks.<sup>1</sup> In sample B, the position of C-H bending was shifted to a higher frequency of  $1490\text{ cm}^{-1}$ .

## **Conclusions**

FTIR spectroscopy is a powerful tool for the determination of molecular structures because functional groups give rise to characteristic bands both in terms of intensity and frequency. Using Varian 640-IR, FT-IR spectrometer, four polymers were identified and related to their FTIR spectra: low density polyethylene, high density polyethylene, polypropylene and

polystyrene. The vibrational properties of LDPE, HDPE, PP, and PS were calculated. The findings of frequencies of the absorption bands confirmed with the samples structures. Percent crystallinity in LDPE and HDPE were estimated. Overall, the experiment succeeded in showing the identity of the unknown sample. The FTIR spectrum of sample A was identified to relate to PP molecular structure. The FTIR spectrum of sample A was identified to relate to PS molecular structure. The FTIR spectra of sample C and sample D were identified to relate to PE molecular structure. With difference in the areas under peaks, sample C was determined to be LDPE and sample D was determined to be HDPE. The experiment also succeed in showing that the percent crystallinities of LDPE and HDPE were estimated correctly to be 52.787 % and 76.30% respectively. It was concluded that different functional groups and percent crystallinity are two major factors making each IR spectrum of the four samples a unique one by which chemical structural analysis can be achieved.

## References

<sup>1</sup>L. Reynolds, Fourier Transform Infrared Spectroscopy, MSE 255 course locker, 2016.

<sup>2</sup>B. Stuart, Infrared Spectroscopy: Fundamentals and Applications (Wiley, West Sussex, 2004).

<sup>3</sup>W.D. Callister Jr., Materials Science and Engineering: An Introduction, Seventh Edition (Wiley, New York, 2007).