

Quantitative Analysis of Polyvinyl Alcohol-Polyethylene (PVOH-PE) Copolymers and Polyvinyl Pyrrolidone-Polyvinyl Acetate (PVP-PVAc) Copolymers and Blends Using Fourier Transform Infrared Spectroscopy and Elemental Analysis

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Abstract Fourier transform infrared spectroscopy (FTIR) is a widespread instrumental technique used to determine the molecular structure of organic polymers. With the goal of increasing instrumental use in the undergraduate chemistry laboratory, we have devised a quantitative FTIR experiment to be used in instrumental analysis courses. The objective was to determine the % PVOH in copolymers with PE as well as to determine the % PVAc in copolymers and blends with PVP. We report on the methodology used to determine % PVOH and %PVP, as well as the results obtained via FTIR and elemental analysis. The literature regarding PVOH-PE copolymers refers to them as either EVOH copolymers or PVOH-PE copolymers, though EVOH is more common and thus these copolymers will be referred to as EVOH. The EVOH copolymers ranged from 73 to 56 mole% PVOH and the copolymers and blends of PVP-PVAc ranged from 70 to 30 mole% PVP.

Keywords: quantitative analysis, elemental analysis, Fourier Transform Infrared Spectroscopy, undergraduate laboratory experiment, hand-on learning, Ethylene-vinyl alcohol copolymer, n-vinyl pyrrolidone - vinyl acetate copolymer and blends

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1. Introduction

Infrared spectroscopy (IR) is a routine technique taught in many undergraduate organic, analytical, and instrumental analysis courses. It is used consistently for both qualitative and quantitative analyses [1-9]. In order to increase the signal to noise ratio of the IR signal, Fourier transform infrared spectroscopy (FTIR) was developed and has become a critical tool of chemists of all kinds in determining chemical structures. The utility of this technique has been well documented for determining the composition of copolymers in general [10-15] as well as for EVOH copolymers in particular [15-18]. Mieth and coworkers, for example, utilized FTIR to determine the presence of EVOH in multilayer films used in food contact materials [19]. Quality control has also been done with FTIR, Cobranchi, Rintoul, and Tani [16] utilized FTIR to design a high throughput method of quality

control of plastic products. Due to the omnipresence of instrumental work in the field of chemistry, our goal was to develop an undergraduate chemistry laboratory experiment designed to highlight both the qualitative and quantitative aspects of FTIR analysis. FTIR's functionality is based on the premise that within any polymer the atoms or groups of atoms vibrate with unique, sharply defined frequencies characteristic of the compound. These frequencies lie in the infrared region of the electromagnetic spectrum. When the sample is placed in the IR beam it absorbs energy at specific frequencies characteristic of the molecule and transmits all other frequencies. The resulting pattern is known as a molecular infrared vibrational absorption spectrum. The intensity of the absorption is a reproducible function of the amount present. The objective of our experiment is to determine the % composition of polyvinyl alcohol (PVOH) in copolymers with polyethylene (PE) as well as to find the % composition of Poly n-vinyl pyrrolidone (PVP) in copolymers and blends with Polyvinyl acetate (PVAc). The EVOH and PVP-PVAc

copolymers were selected because they are all commercial copolymers and are used in many everyday products. For example, ethylene-vinyl alcohol (EVOH) copolymers have many varied uses, in the food packing industry it is used as an oxygen barrier since it is superior to other plastics at keeping air out and flavors in. EVOH copolymers also have applications in the medical field as a critical component of Onyx, an FDA approved method for treating saccular aneurisms. Copolymers of *n*-vinyl pyrrolidone and vinyl acetate monomers are of critical importance in the pharmaceutical and cosmetic industries. Applications include hair styling, skin care, membranes for medical devices, water treatment, and as adhesives. The ratio of PVP to PVAc and PVOH to PE can significantly affect the physical properties of the final products, thus, there is a need for a quick method of quantifying the composition of these copolymers.

1.1. Learning Objectives

1. To record and analyze FTIR data on commercially available EVOH and PVP-PVAc copolymers of various compositions.
2. To prepare calibration curves plotting the absorbance ratio of specific peaks corresponding to unique moieties found in the substituent polymers in EVOH and PVP-PVAc copolymers versus % composition determined via elemental analysis.
3. To prepare and contrast calibration curves of PVP-PVAc copolymers and blends plotting absorbance ratios of carbonyl and acetate peaks versus experimental weight % composition.

2. Experimental Section

This experiment has three parts and each part can be done by a group of 2-3 students.

The first part is the analysis of EVOH copolymers with the objective of recording and analyzing FTIR data of EVOH random copolymers of differing compositions. Setting up a calibration curve by correctly identifying key peaks associated with the PVOH and PE components of the EVOH copolymers and plotting the ratio of those two quantities versus the PVOH content gained by elemental analysis.

Part 2 is similar to part 1 except PVP-PVAc copolymers will be studied in lieu of EVOH.

Part 3 is similar to part 2 except PVP-PVAc blends prepared by the instructor will be analyzed in lieu of copolymers.

2.1. Materials

The instrument used in this study was a Bruker Alpha-P®FT-IR spectrometer with a Platinum® attenuated total internal reflectance (ATR) quick snap module with a diamond crystal. The Alpha-P unit has a Michelson Interferometer with a SiC globar as the IR source, the time dependence of the IR intensity is measured with a pyroelectric DTGS detector. The data analysis was done using the Bruker OPUS® software version 7.0.122. The spectra were displayed as absorbance vs frequency in

wavenumbers ranging from 500 to 4000 cm^{-1} since absorbance is proportional to concentration according to Beer's Law. All of the EVOH copolymers were obtained as solids in the form of pellets from Scientific Polymer Products (SP²), Inc., Ontario, N.Y. The EVOH copolymers were randomized copolymers ranging from 73 to 56 mol% PVOH. The PVP-PVAc copolymers were also obtained from SP². These copolymers ranged from 30 to 70 mol% PVP. The 30, 50, and 70% copolymers were obtained as 50 w/w% solutions in isopropanol. Blends of PVP and PVAc were prepared by dissolving PVP homopolymers having a M_w of 40K Daltons with homopolymers of PVAc having a M_w of 39K Daltons in methanol. These solutions were evaporated in a vacuum oven at 50°C at 20 mm of Hg leaving solid blends of homopolymers ranging from 20 to 80% PVAc.

2.2. Methods

The EVOH copolymer pellets were made into thin films manually to increase surface area for FTIR spectroscopic analysis. The PVP-PVAc samples were analyzed with no sample preparation other than being pressed between the anvil and the diamond crystal of the ATR unit in solid phase. The samples were measured using 16 scans at a resolution of 4 cm^{-1} . Establishing the PVAc content was done using the ratio of absorbance of the carbonyl or C-O peak from the acetate of PVAc to the carbonyl peak from the PVP. The PVOH content was determined by the ratio of absorbance of the alcohol oxygen or OH peak of PVOH and the C-H peak of PE. Elemental Analysis (EA) of the EVOH and PVP-PVAc copolymers were performed by the Galbraith Laboratories, Knoxville, TN. The %C & %H were obtained for the EVOH copolymers whereas the %C, %H, %N were obtained for the PVP-PVAc copolymers.

2.3. Hazards

There are no safety hazards in this experiment; all samples are commercially available materials used in everyday products in solid form. Safety glasses are mandatory and the use of hoods is advisable. All waste materials were collected for waste disposal according to EPA as well as local guidelines.

2.4. Statistical Analysis

Each sample was analyzed eight times. The data reported is the average of the integrated peak areas obtained by FTIR. The standard deviations ranged from 0.259 to 0.0068. The elemental analysis of the %C, %H, and %N were reported as averages from duplicate analyses.

3. Results and Discussion

Figure 1 through 5 are FTIR spectra of PE, PVAc, PVP, EVOH, and PVP-PVAc copolymers respectively. Figure 1 shows the FTIR spectrum of 100% PE, there are characteristic peaks at 1470 cm^{-1} and 715 cm^{-1} with the 1470 cm^{-1} (C-H bending) peak being used to

quantify the presence of PE in EVOH copolymers due to higher resolution than the 715 cm^{-1} peak. Figure 2 shows the FTIR of PVAc which exhibits an intense ester peak at 1230 cm^{-1} (C-O stretch), this would be the peak used to quantify the presence of PVAc in the PVP-PVAc copolymers due to the fact that PVP does not exhibit a strong peak at 1230 cm^{-1} . Figure 3 includes the FTIR spectrum of PVP which has a characteristic peak at 1650 cm^{-1} (C=O stretch). Figure 4 showcases an

EVOH copolymer with 68 mole % PVOH with characteristic peaks at around 3300 cm^{-1} (O-H stretch) owing to the OH functionality of PVOH as well as a peak at 1430 cm^{-1} coming from the PE aspect of the EVOH copolymer. Figure 5 shows a 50 mole %PVP - PVP-PVAc copolymer with characteristic peaks at 1670 cm^{-1} due to the carbonyl functionality of PVP as well as a peak at 1230 cm^{-1} from the acetate moiety of PVAc.

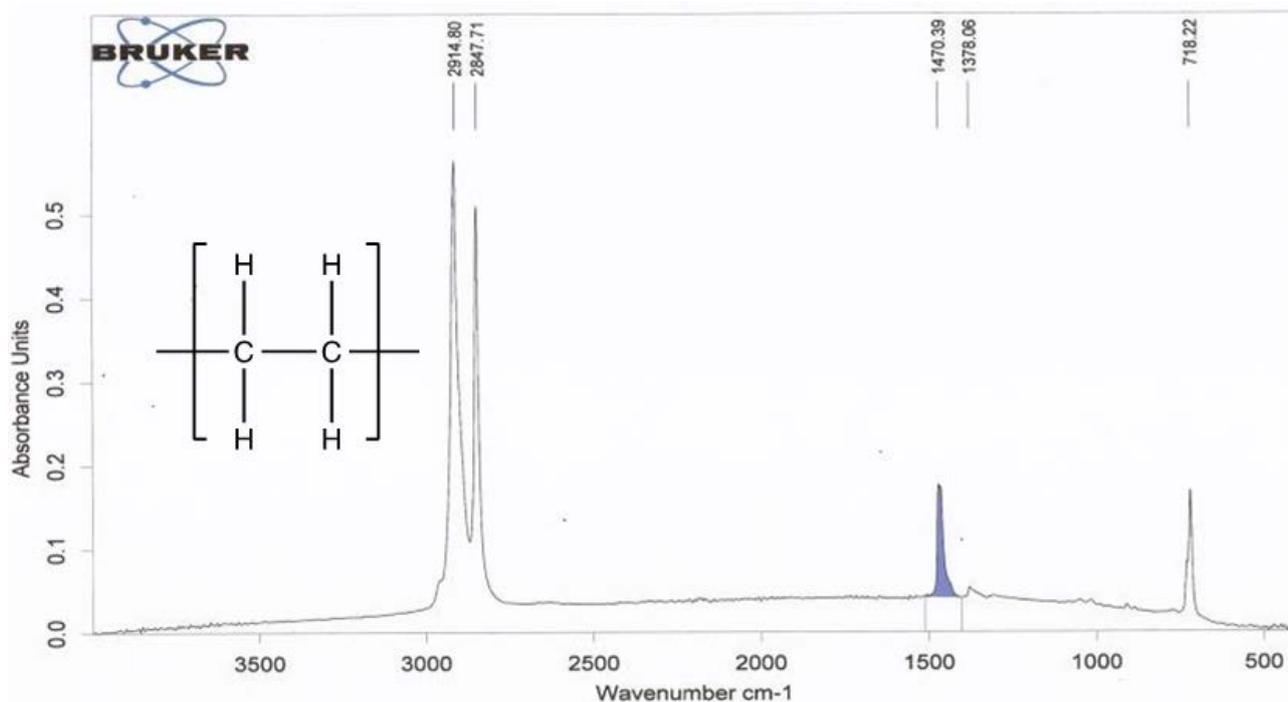


Figure 1. FTIR spectrum of PE. The characteristic PE absorbance bands are located at 2914 cm^{-1} , 2847 cm^{-1} , 1470 cm^{-1} , and 718 cm^{-1}

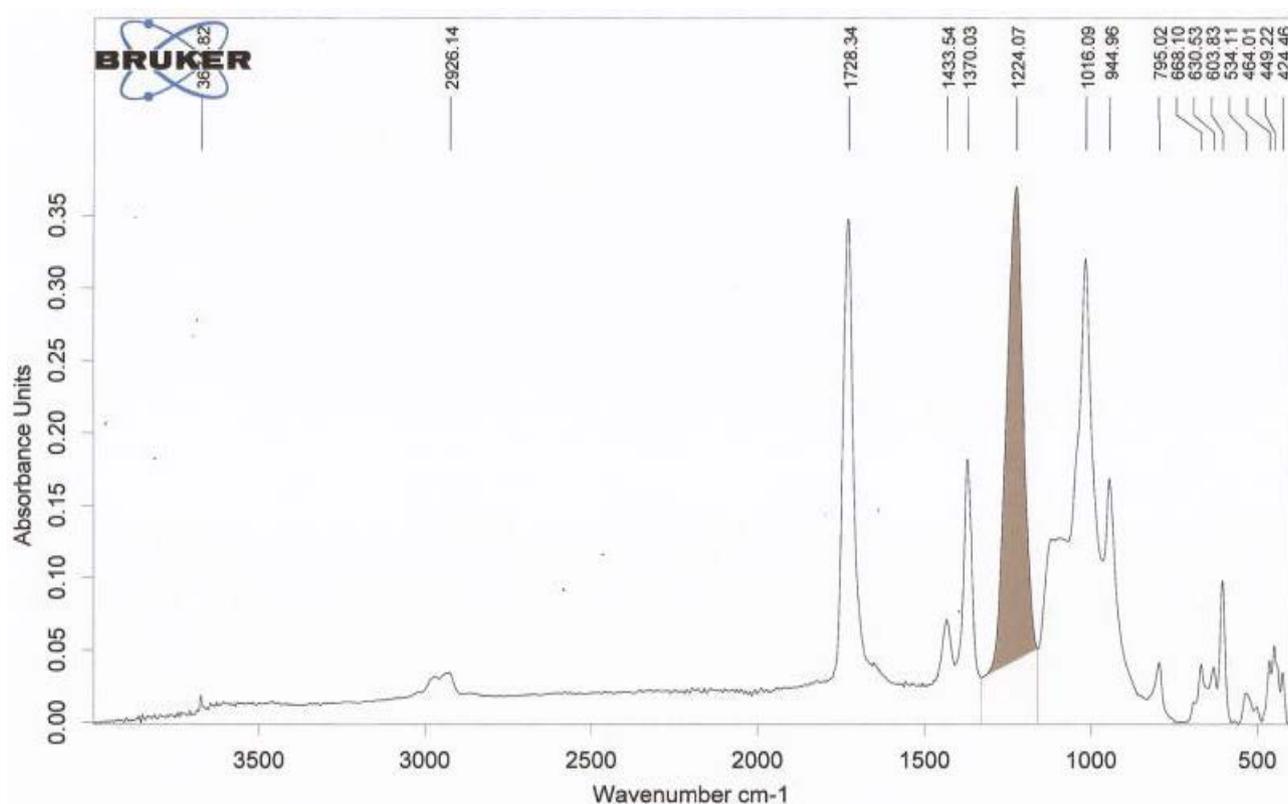


Figure 2. The FTIR spectrum of PVAc key bands are at 1728 cm^{-1} , 1433 cm^{-1} , 1370 cm^{-1} , 1224 cm^{-1} , and 1016 cm^{-1}

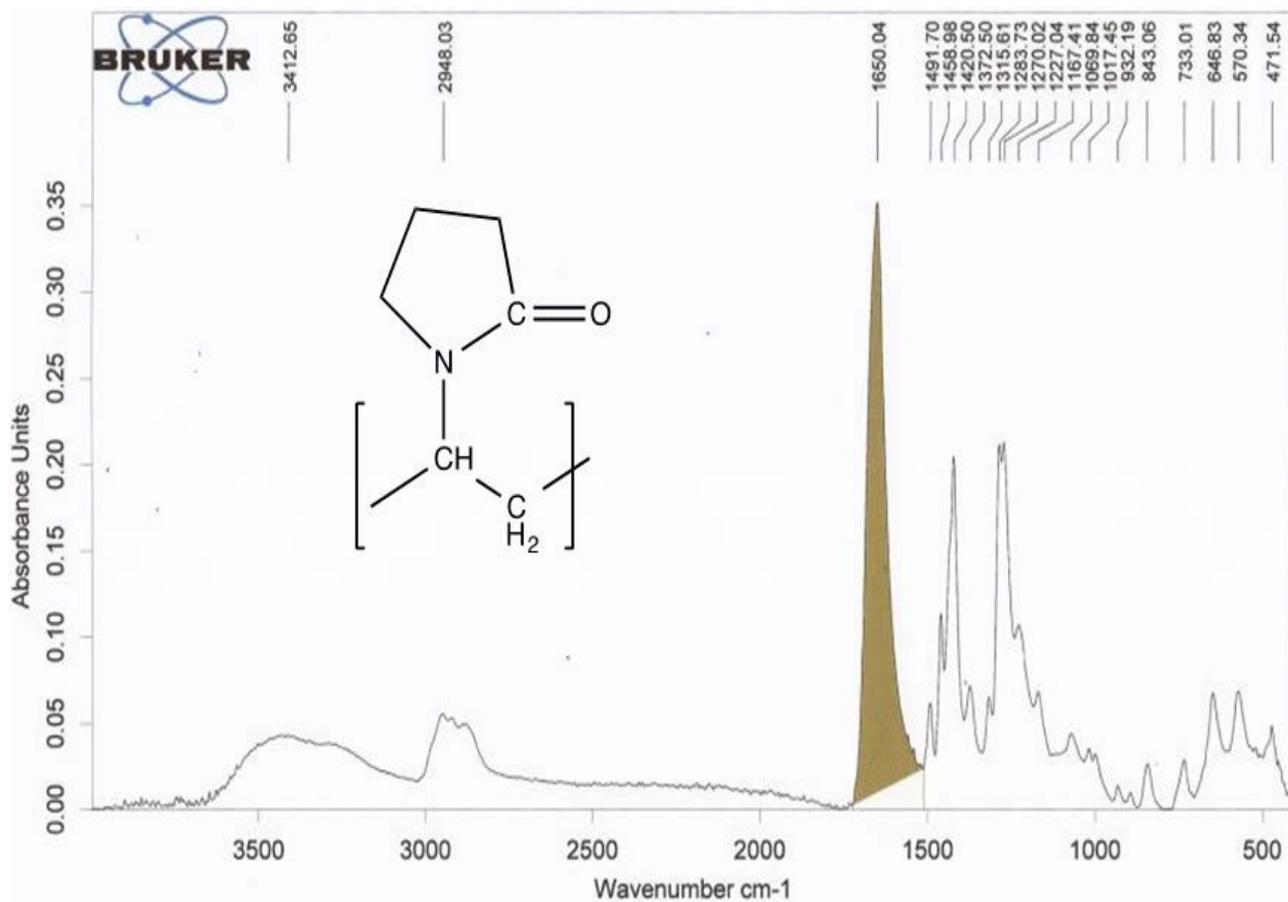


Figure 3. FTIR spectrum of PVP. The major characteristic PVP Absorbance band was located at 1650 cm^{-1}

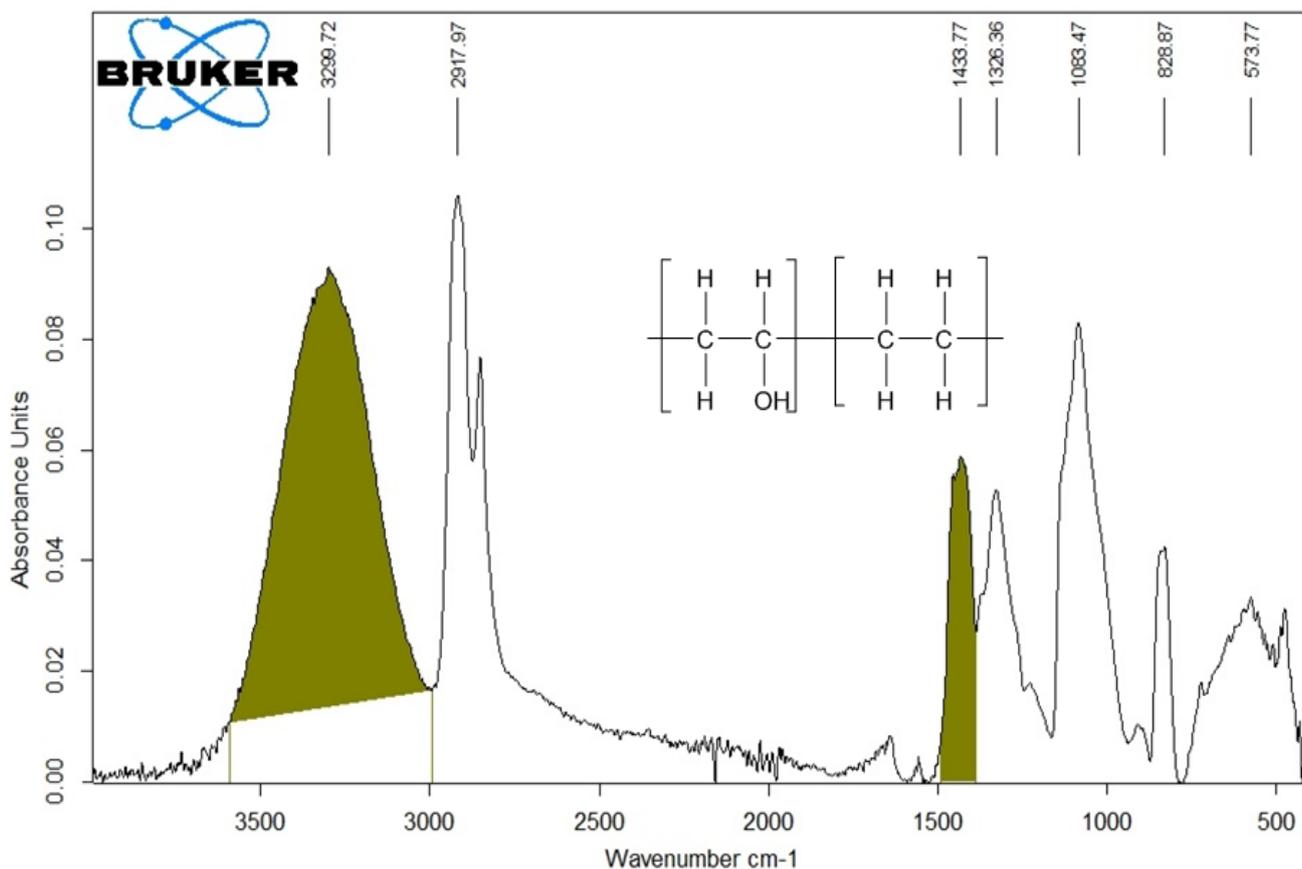


Figure 4. FTIR spectrum of 68 mole % PVOH in the EVOH copolymer. The characteristic PVOH absorbance band was located at 3300 cm^{-1} and PE absorbance band at 1430 cm^{-1}

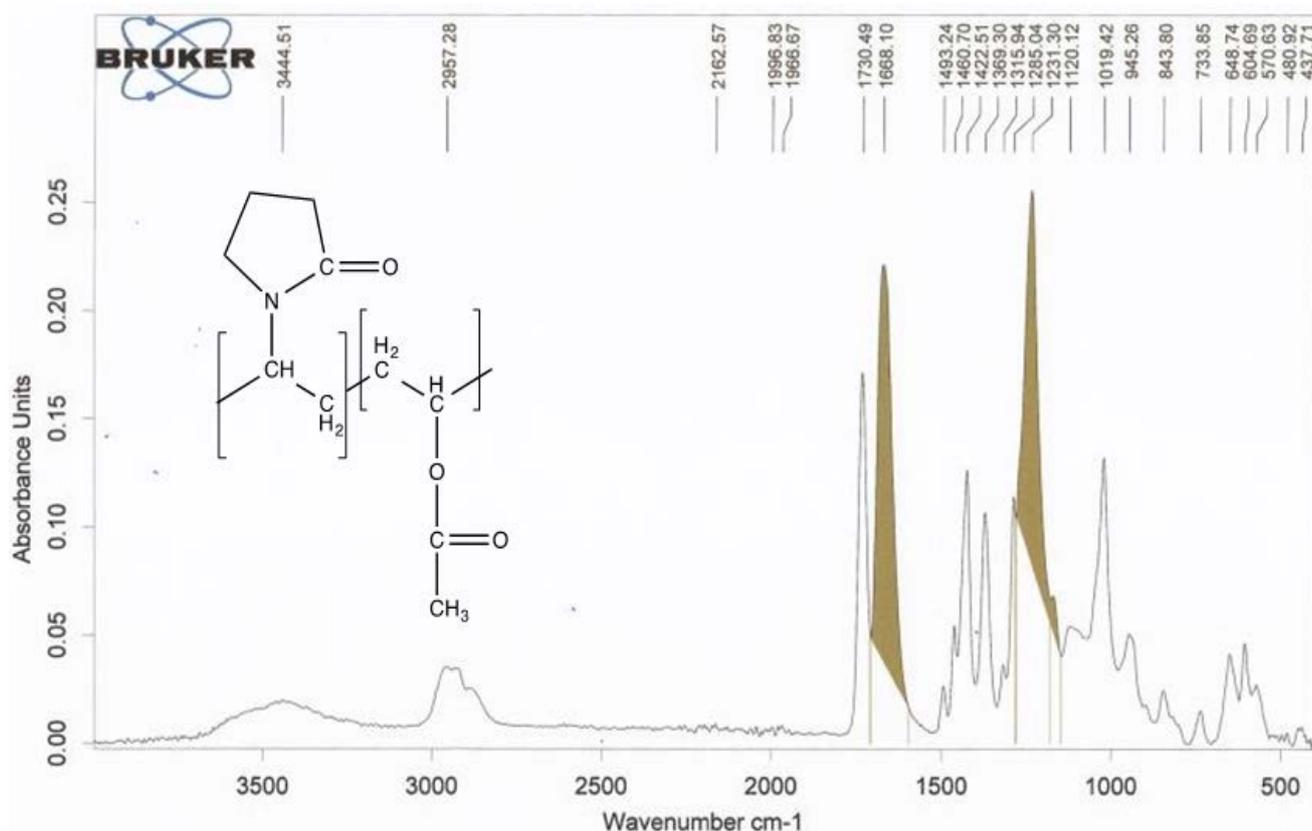


Figure 5. FTIR spectrum of 50% PVP, PVP-PVAc copolymer. The characteristic PVP band is located at 1670 cm^{-1} and the PVAc band is located at 1230 cm^{-1}

3.1. PART 1: Study of EVOH Copolymers

3.1.1. Results and Discussion

Table 1 displays the data obtained via elemental analysis of the various EVOH copolymers analyzed which ranged from 73% to 56% PVOH, included is the % C, % H, and % O as well as the calculated % PVOH. The % PVOH was calculated using the following equation:

$$\text{Exp\%PVOH} = [\text{Exp\%Oxygen} \div 36.4] \times 100. \quad (1)$$

Figure 6 shows the experimental % PVOH plotted versus the nominal % of PVOH indicated by SP² displaying a straight line relation with R² value of .9647 indicating that the experimental amount of PVOH present

and that provided by SP² correspond very closely.

Table 2 is a summary of the FTIR peak area ratios from the 3300 cm^{-1} band associated with the PVOH substituent and the 1430 cm^{-1} band associated with the PE constituent polymer. All values are presented in association with their corresponding nominal mole% PVOH constitution. As expected, the ratio increases as PVOH content increases. Figure 7, Figure 8, and Figure 9 depict the strong linear relationship between % PVOH content and the PVOH:PE peak area ratio. All show remarkable linearity, with the strongest correlation coefficient of .9998 belonging to Figure 7 which plots nominal mole % PVOH versus the integration ratios. All applicable figures include error bars which represent one standard deviation from the mean with $n = 8$.

Table 1. Summary of Elemental Analysis Results of the EVOH Copolymers

| Weight %PVOH in EVOH copolymers (Nominal) | Mole %PVOH in EVOH | %Carbon | %Hydrogen | %Oxygen by difference | %PVOH experimental |
|---|--------------------|---------|-----------|-----------------------|--------------------|
| 80.93 | 73 | 60.29 | 10.6 | 29.11 | 79.97 |
| 76.96 | 68 | 60.38 | 10.82 | 28.8 | 79.12 |
| 71.94 | 62 | 61.68 | 11.32 | 27.0 | 74.18 |
| 66.69 | 56 | 63.52 | 10.92 | 25.56 | 70.25 |

Table 2. Summary of FTIR Integration Ratios for EVOH Copolymers

| Weight % PVOH in EVOH copolymers (Nominal) | Weight % PVOH in EVOH copolymers (Experimental) | Mole % PVOH in EVOH copolymers (Nominal) | PVOH (3300 cm^{-1}):PE (1430 cm^{-1}) area ratio |
|--|---|--|--|
| 80.93 | 79.97 | 73 | 5.53 |
| 76.96 | 79.12 | 68 | 4.45 |
| 71.94 | 74.18 | 62 | 3.06 |
| 66.69 | 70.25 | 56 | 1.66 |

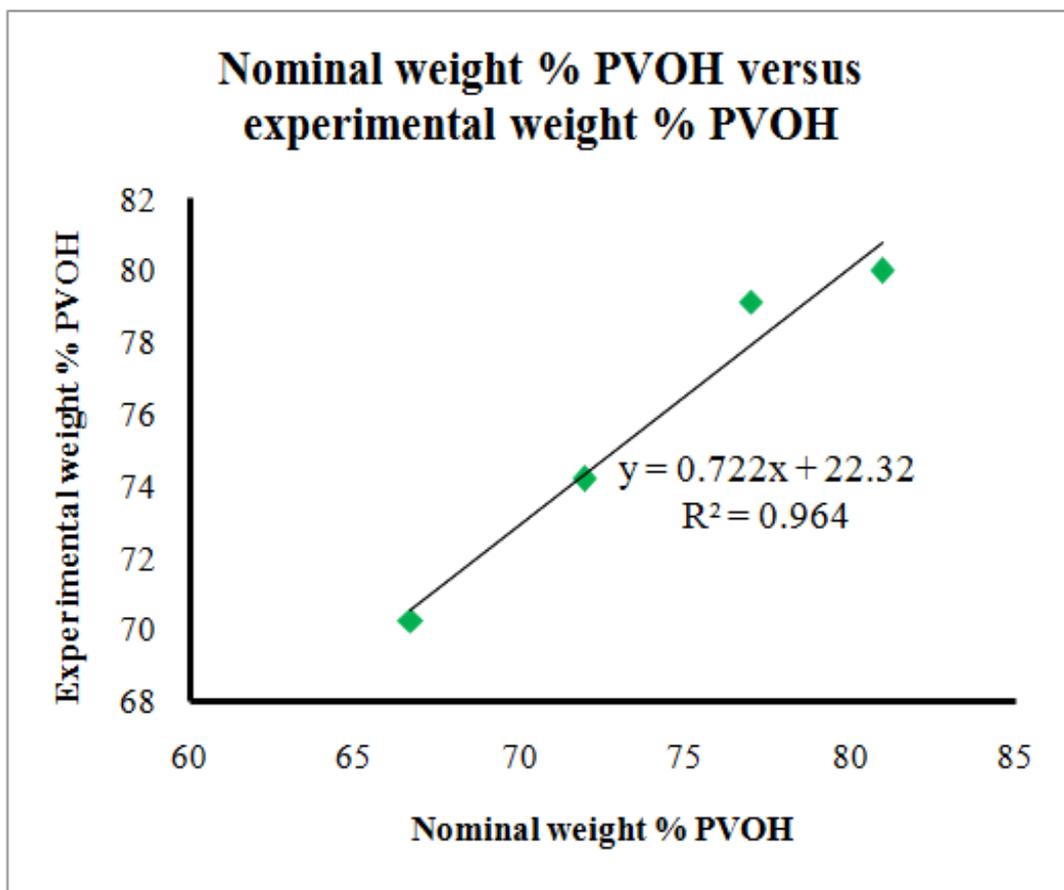


Figure 6. Nominal weight % PVOH plotted versus experimental weight % PVOH

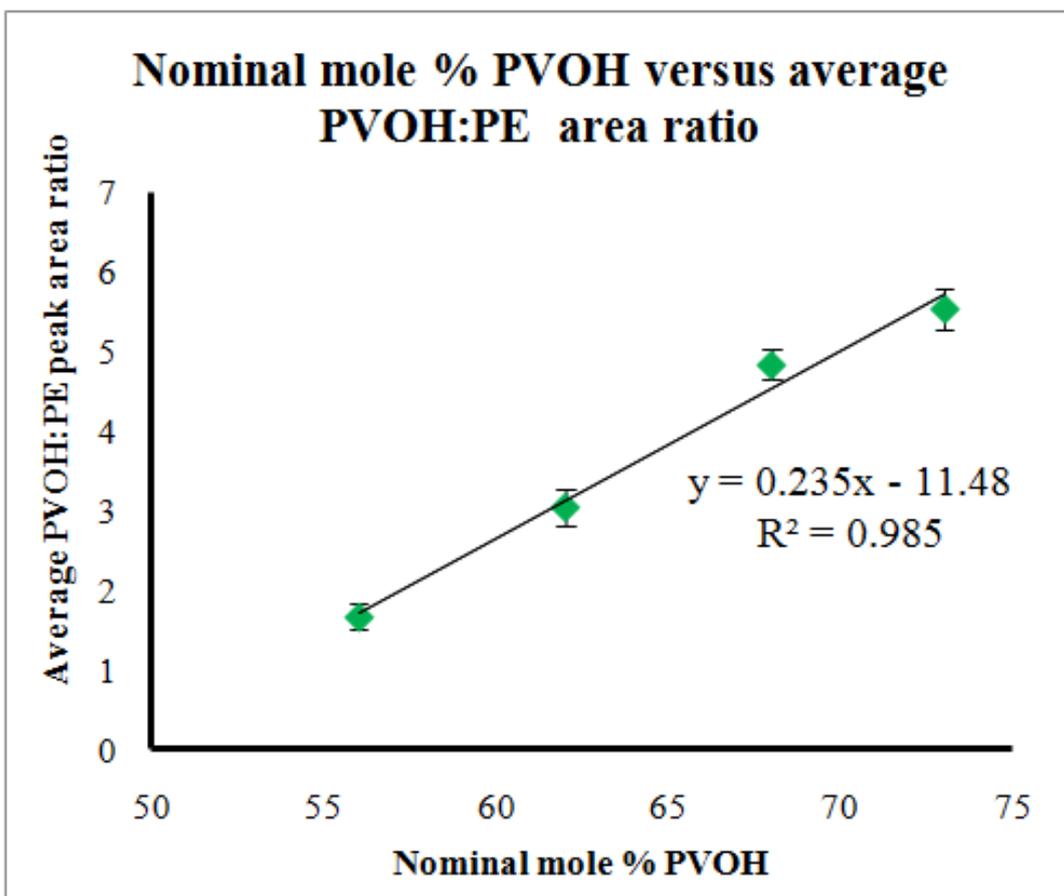


Figure 7. Nominal mole % PVOH plotted versus average PVOH:PE area ratio

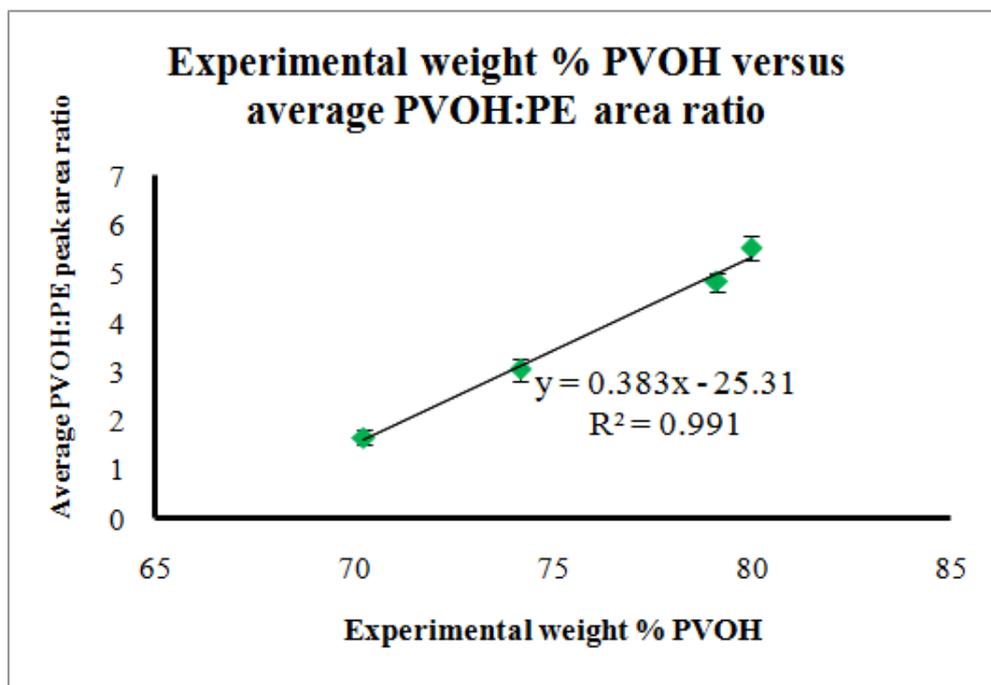


Figure 8. Experimental weight % PVOH plotted versus average PVOH:PE area ratio

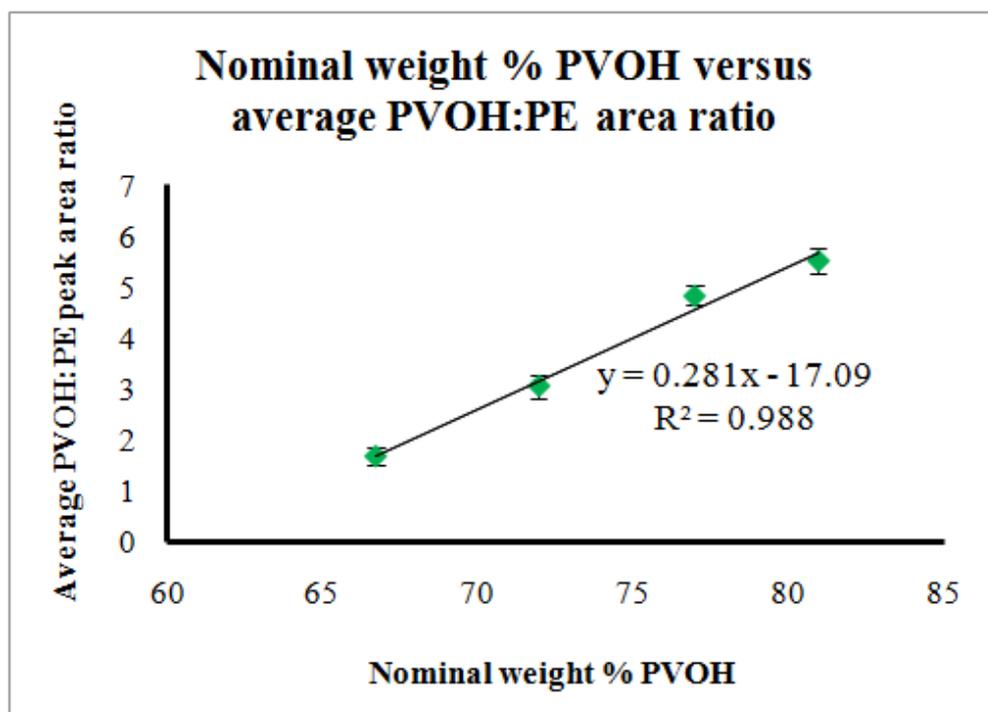


Figure 9. Nominal weight % PVOH plotted versus average PVOH:PE area ratio

3.2. PART 2: PVP-PVAc Copolymers

3.2.1. Results and Discussion

Table 3 shows the elemental analysis data for the PVP-PVAc copolymers which includes % Carbon, % Hydrogen, % Nitrogen, and % Oxygen obtained by difference. These copolymers ranged from 30-70 mol% PVP, based on the data from the elemental analysis, the experimental % PVP was determined using the following equation:

$$\text{Exp\%PVP} = [\text{Exp\% Nitrogen} \div 12.61] \times 100\%. \quad (2)$$

The experimental Wt% PVP was plotted versus the nominal Wt% PVP and is shown in Figure 10, a linear relationship is shown having a correlation coefficient of .9642 indicating that the experimental weight % PVP corresponds well with the nominal weight % PVP reported by SP².

Table 4 displays the FTIR integration ratio of the PVP peak (1670 cm⁻¹): PVAc peak (1224 cm⁻¹) data alongside the nominal mole % PVP, nominal weight % PVP, and experimental weight % PVP data. In all cases as the % PVP increases the ratio of the 1670/1230 cm⁻¹ peak also increased. Figure 11 – Figure 13 graph the data shown

in Table 4, all graphs show a strong linear relationship between the integration ratio and % PVP with the highest R^2 value being .9933 belonging to Figure 11 which plots

nominal mole % PVP versus average PVP: PVAc peak area ratios. All applicable figures have error bars that represent one standard deviation from the mean with $n = 8$.

Table 3. Summary of Elemental Analysis Results for PVP-PVAc Copolymers

| Nominal weight % PVP | Nominal mole % PVP | %Carbon | %Hydrogen | %Nitrogen | %Oxygen | Experimental Wt % PVP |
|----------------------|--------------------|---------|-----------|-----------|---------|-----------------------|
| 60.74 | 70 | 60.37 | 8.083 | 7.659 | 23.89 | 60.09 |
| 55.19 | 60 | 58.5 | 7.67 | 6.959 | 26.87 | 49.85 |
| 49.85 | 50 | 59.05 | 7.743 | 6.239 | 26.97 | 47.30 |
| 34.73 | 30 | 58.31 | 7.45 | 4.379 | 29.86 | 33.65 |

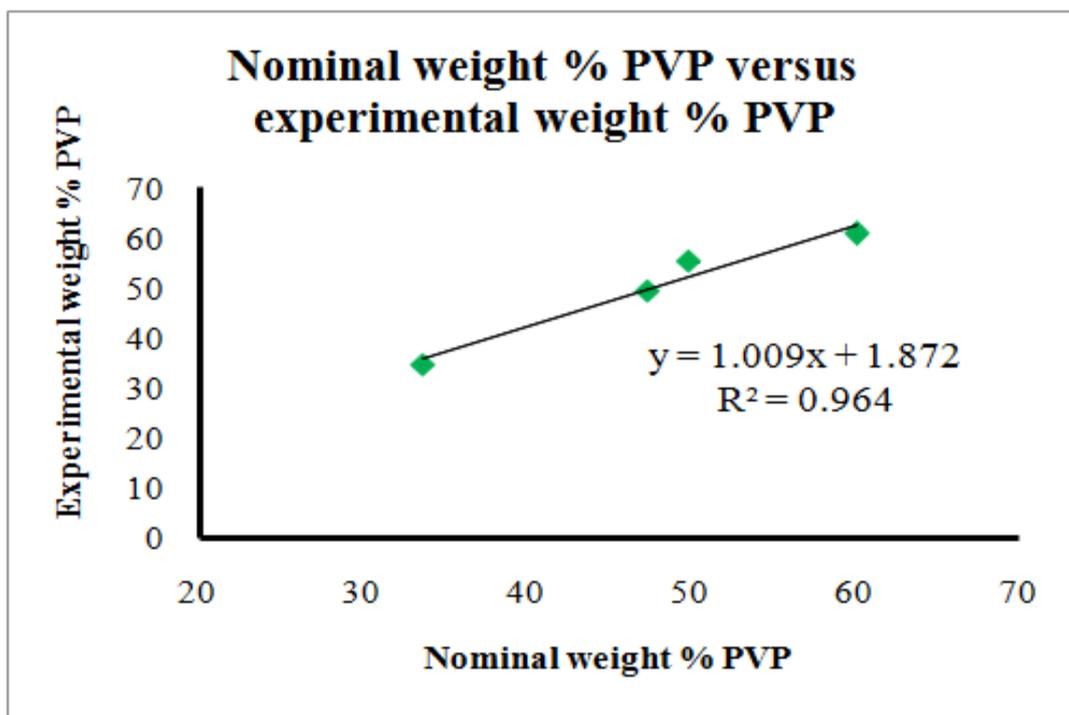


Figure 10. Nominal weight % PVP plotted versus experimental weight % PVP

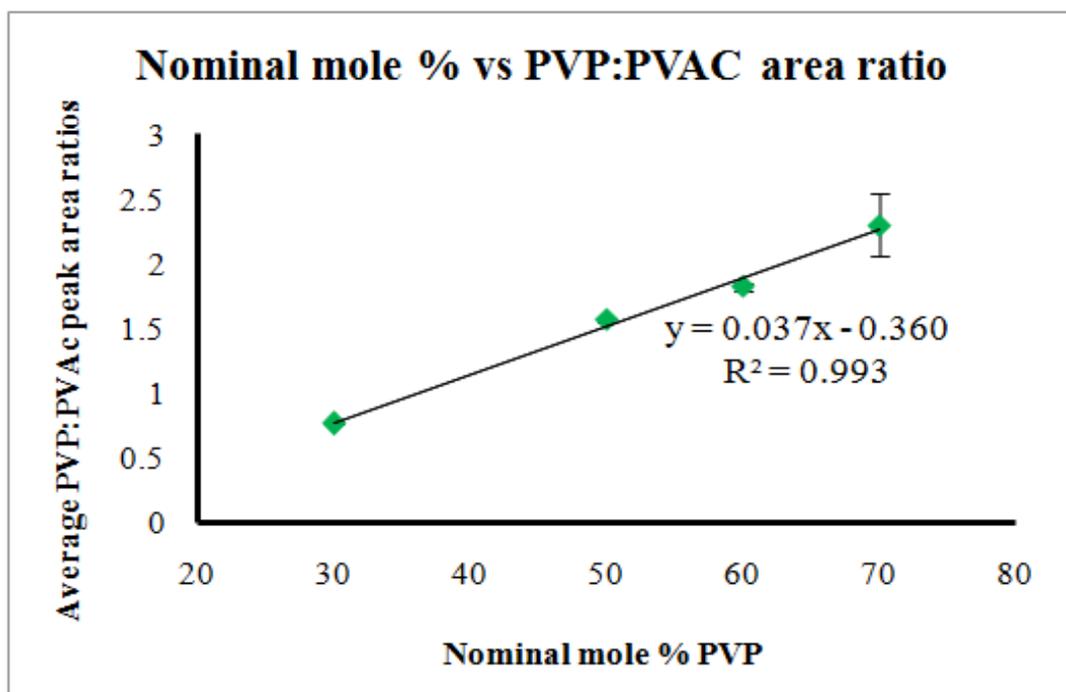
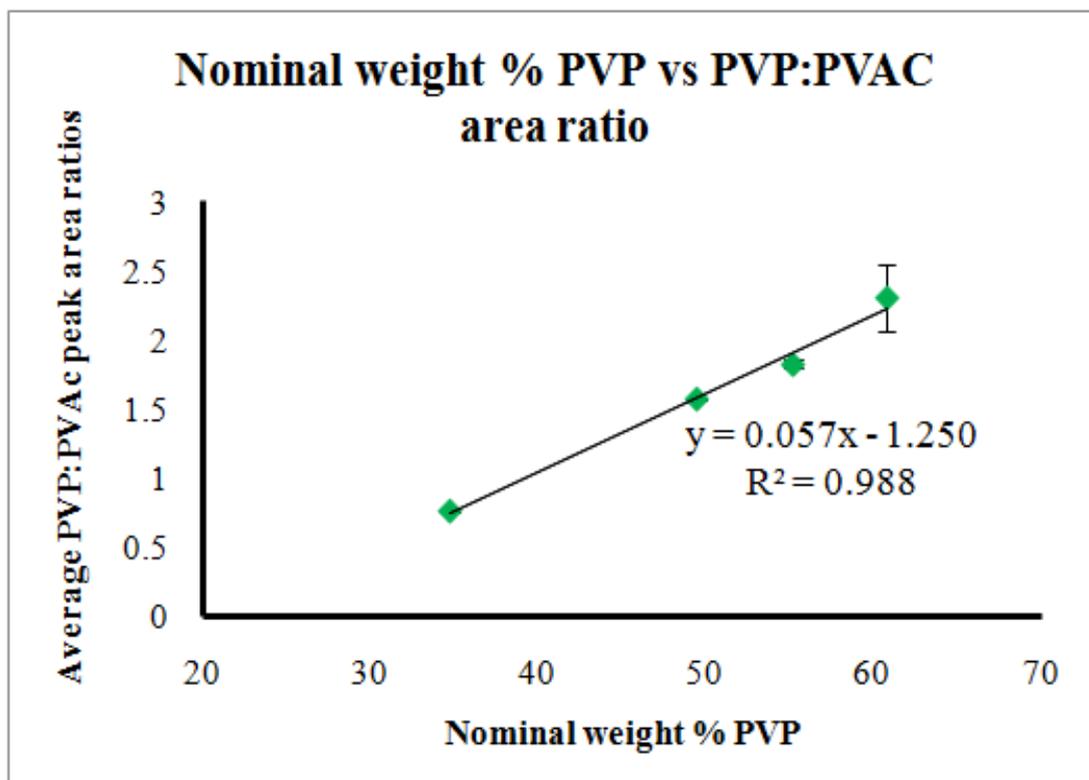
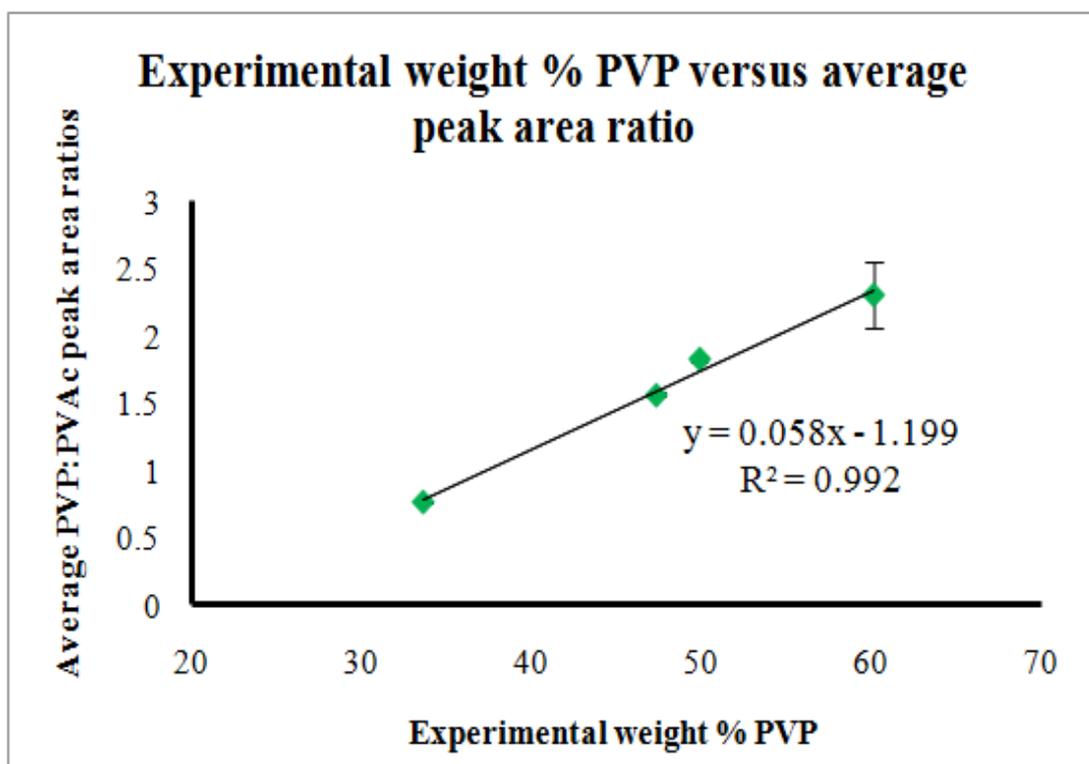


Figure 11. Nominal mole % PVP plotted versus average PVP:PVAc peak area ratios.

Table 4. Summary of FTIR Integration Ratios for Copolymers of PVP-PVAc

| Weight % PVP (Nominal) | Weight % PVP (Experimental) | Mole % PVP (Nominal) | PVP(1670cm ⁻¹):PVAc(1230cm ⁻¹) peak area ratio |
|------------------------|-----------------------------|----------------------|--|
| 60.74 | 60.09 | 70 | 2.30 |
| 55.19 | 49.85 | 60 | 1.82 |
| 49.48 | 47.30 | 50 | 1.57 |
| 34.73 | 33.65 | 30 | 0.76 |

**Figure 12.** Nominal weight % PVP plotted versus average PVP:PVAc peak area ratios**Figure 13.** Experimental weight % PVP plotted versus average PVP:PVAc peak area ratios

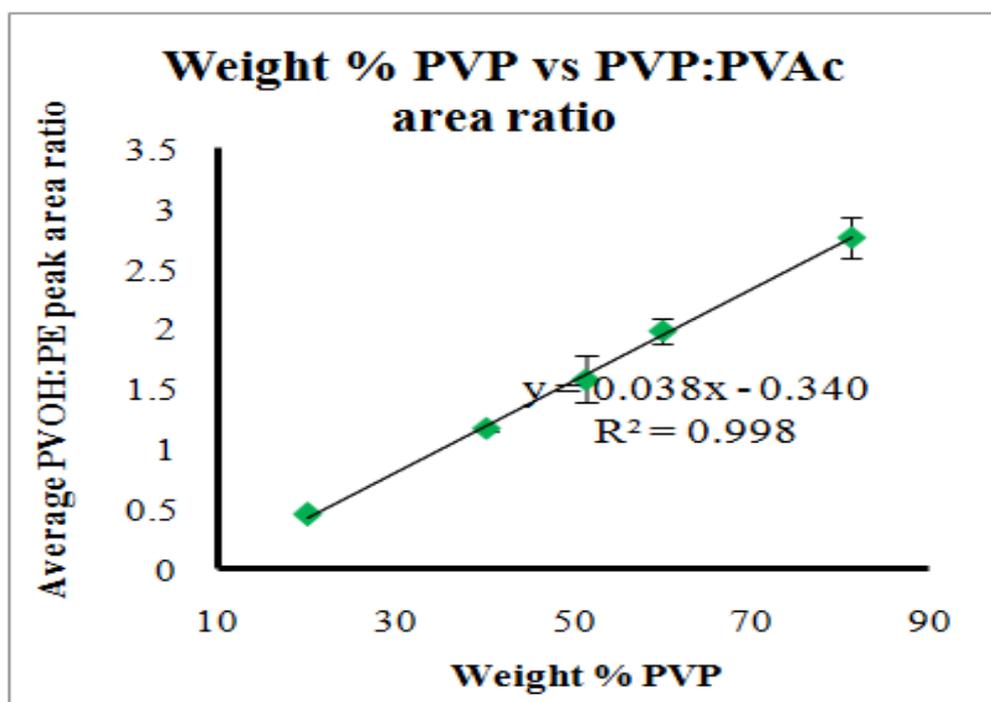


Figure 14. Experimental weight % PVP plotted versus average PVP:PVAc peak area ratios.

3.3. PART 3: PVP-PVAc Blends

3.3.1. Results and Discussion

Table 5 summarizes the FTIR integration ratios of the PVP-PVAc blends. As in the case with the copolymers, the ratio strictly increased as the weight % of PVP increased, a strong linear relationship was observed with an R^2 value of .9987, this is showcased by Figure 14 which plots the data summarized in Table 5. Figure 14 has error bars that represent one standard deviation from the mean with $n = 8$.

Table 5. Summary of FTIR Integration Ratios for Blends of PVP-PVAc

| Weight % PVP | PVP:PVAc peak area ratio |
|--------------|--------------------------|
| 81.17 | 2.71 |
| 59.99 | 2.01 |
| 50.39 | 1.59 |
| 40.31 | 1.17 |
| 20.09 | 0.45 |

4. Conclusions

FTIR both alone and in tandem with elemental analysis can be used to quantify the composition of both PVP-PVAc and EVOH copolymers with very accurate results. FTIR can also be used to determine the composition of blends of PVP-PVAc by using peak area ratios, corroborating what was found in previous experiments [15]. The FTIR results align very closely with the results obtained via elemental analysis. The above analysis showcases the importance of integration ratios in quantitative analysis at large and supports the hypothesis that FTIR can be used quantitatively to determine the composition of binary polymer blends and copolymers.

The methodology used can be quickly adopted for use in an undergraduate instrumental analysis course due to the pervasiveness of FTIR within the academic community as well as the ease of use. This experiment also enhances students' knowledge of the FTIR methodology, giving them hands-on experiences in analyzing functional group characteristics of the copolymers studied and applying them to create calibration curves.

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Statement of Competing Interests

The Authors have no competing interests.

List of Abbreviations

PVP – Polyvinyl pyrrolidone
 PVAc – Polyvinyl acetate
 PVOH – Polyvinyl alcohol
 PE – Polyethylene
 EVOH – Ethylene Vinyl alcohol, same as PVOH-PE

References

- [1] Gebel, M.E., Kaleuati, M. A., Finlayson-Pitts, B. J.. "Measurement of the Organics using Three FTIR Techniques: Absorption, Attenuated Total Reflectance, and Diffuse Reflectance", *J. Chem. Ed.*, 80 (6), 672-675, June 2003.
- [2] Conklin Jr., A., Goldcamp, M.J., and Barrett, J.. "Determination of Ethanol in Gasoline by FTIR Spectroscopy", *J. Chem. Ed.*, 91 (6), 889-891, April 2014.

- [3] Veening, H.. "Quantitative Infrared Analysis of Xylene Mixtures: Internal Standard Method", J. Chem. Ed., 46 (6), 319-320, June 1966.
- [4] Bellamy, M.K.. "Using FTIR-ATR Spectroscopy to Teach the Internal Standard Method", J. Chem. Educ., 87 (12), 1399-1401, December 2010.
- [5] Robinson J.W., Frame E.M.S., Frame II G.M.. Undergraduate Instrumental Analysis, 7th edition, CRC Press –Taylor Francis, Boca Raton, Florida., chapter 4, July 2014.
- [6] Silverstein,R.M., Webster F.X.. Spectrometer Identification of Organic Compounds, 7th edition, Wiley & Sons, New Jersey, December 2011.
- [7] Lambert J.B., Gronert S., Shurvell H.F., Lightner D.. Organic Structural Spectroscopy, 2nd, edition, , Prentice Hall, New jersey, October 2010.
- [8] Schuttlefield, J.D.; Grassian, V.H.. "ATR-FTIR Spectroscopy in the Undergraduate Chemistry Laboratory", J. Chem. Educ., 85 (2), 279-281, February 2008.
- [9] Smith iv, R.E., McKee, J.R., Zanger, M.. "The Electrophilic Bromination of Toluene: Determination of the Ortho, Meta, Para, ratios by Quantitative FTIR Spectroscopy", J. Chem. Ed., 79 (2), 227-229, February 2002.
- [10] Keefe, J.F.O.. "Identification of Polymers by IR Spectroscopy", Rubber World, 37, 27-32, 2004.
- [11] Ekpenyong, K.I., Okonkwo, R.O.. "Determination of Acrylonitrile/Methylmethacrylate Copolymer Composition by Infrared Spectroscopy", J.Chem. Ed. 60 (5), 929-030, May 1983.
- [12] Chakraborty, S., Bandyopadhyay, S., Ametra, R., Makhopadhyay, R., Deyri, A.S.. "Application of FTIR in Characterization of Acrylonitrile – Butadiene Rubber (Nitrile Rubber)", Polymer Testing, 26, 38-41, August 2007.
- [13] Schonherr, R.. "Application of TGA-IR Coupling for the Determination of EVA rubber with Variable VAc content" Kauts. Gummi Kunstst., 50, 564-568, 1997.
- [14] Tambe, S.P., Singh, S.H., Patri, M., Kumar, D.. "Ethylene Vinyl Acetate and Ethylene Vinyl Alcohol Copolymer for Thermal Spray Coating Application" Progress in Organic Coating, 62, 382-386, February 2008.
- [15] D'Amelia, R., Gentile, S., Niode, W., Huang, L.. "Quantitative Analysis of Copolymers and Blends of Polyvinyl Acetate (PVAc) Using Fourier Transform Infrared Spectroscopy (FTIR) and Elemental Analysis (EA)." World Journal of Chemical Education, vol. 4, no. 2 (2016): 25-31.
- [16] Cobranchi, S; Tani, N; Rintoul, S.. "Infrared Analysis of Single and Multilayer Films in the Production Area" Tappi, 1-18, 2001
- [17] G.S. Popova et al.. "Analysis of polymerized plastics", Khimiya, 1988, p.106.
- [18] Dupuy, N; Gaston,F; Marque, S; Barbaroux, M; Dorey, S. "FTIR study of ageing of gamma-irradiated biopharmaceutical EVA based film. Polymer Degradation and Stability", Elsevier, 2016, 129, pp.19-25.
- [19] Mieth, A; Hoekstra, E; Simoneau, C. "Guidance for the identification of polymers in multilayer films used in food contact materials: User guide of selected practices to determine the nature of layers", EUR 27816 EN.



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