

# The Study of Polyvinyl Pyrrolidone-Polyvinyl Alcohol Copolymers and Blends

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**Abstract** The synthesis of new biodegradable polymers is of critical importance for preserving the environment and finding new ways to process ubiquitously used polymers to enhance their biodegradability is crucial for minimizing waste and anthropogenic environmental degradation. Polyvinyl alcohol (PVOH) is known to be a biodegradable polymer and thus saponification of the pervasive Polyvinyl Pyrrolidone-Polyvinyl Acetate (PVP-PVAc) copolymer represents an unexplored opportunity for the production of a new biodegradable, water-soluble copolymer (PVP-PVOH). Herein we report on the facile saponification/hydrolysis of PVP-PVAc copolymers of various molecular weights and copolymer compositions and characterize the PVP-PVOH copolymer product via Nuclear Magnetic Resonance Spectroscopy (NMR), Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), differential refractive index increment measurements (DNDC), and Elemental Analysis (EA).

**Keywords:** water-soluble polymers, saponification, biodegradable, nuclear magnetic resonance spectroscopy, fourier transform infrared spectroscopy, differential refractive index increment, differential scanning calorimetry, polyvinyl alcohol, polyvinyl pyrrolidone, polyvinyl acetate, copolymers

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## 1. Introduction

Water-soluble polymers serve a wide variety of functions, being used in water treatment, food processing, cosmetics, as well as pharmaceutical products [1-5]. The synthesis of the novel water-soluble polymer described herein is only available through hydrolysis of PVP-PVAc due to rapid tautomerization of the vinyl alcohol monomer unit [6]. The PVP-PVAc copolymer is used ubiquitously in the cosmetics, hair-styling, and pharmaceutical industries and comprises over 40% of paste masks and mudpacks [7,8,9,10]. Unfortunately, personal care products are some of the most commonly detected compounds in surface water and their low biodegradability makes them enter the ocean largely unchanged [11,12]. The biodegradability of PVP-PVAc is hampered because PVAc must first be hydrolyzed in order to be degraded [13]. Polyvinyl alcohol has shown remarkable biodegradability in aqueous solution and is known to be more biodegradable than PVAc [13]. Industrial synthesis of PVOH homopolymer is done by the hydrolysis of PVAc dissolved in methanol in the presence of potassium hydroxide (KOH) [14]. It was therefore reasoned that PVP-PVAc copolymer could be hydrolyzed in the same fashion since the amide functional group of PVP is substantially more resistant to hydrolysis than PVAc [15]. The PVP-PVOH copolymer has not been extensively studied, however, PVP and PVOH blends

have been the subject of numerous investigations as films for nitric oxide release, formation of nano-spheres/ nano-rods, and biomaterials [16-24]. The large variety of applications of the PVP and PVOH blends suggest that PVP-PVOH copolymer may have unique applications in the same areas in addition to being substantially more water-soluble and biodegradable compared to PVP-PVAc copolymers. PVP-PVAc copolymers and blends have been studied in the past using FTIR and Proton Nuclear Magnetic Resonance Spectroscopy (pNMR). [25,26,27]. In this study, we report on the facile hydrolysis of PVP-PVAc copolymers of various molecular weights and copolymer compositions and the spectral, thermal, and physical characteristics thereof by NMR, FTIR, DSC, and DNDC. Copolymers of PVP-PVOH were synthesized with molecular weights ranging from 3 to 15 kDa and with nominal mole percent PVP ranging from 30 to 70%. Blends of PVP and PVOH were also analyzed via FTIR and NMR with weight percent PVP ranging from 20 to 80%. Yields of PVP-PVOH copolymer from hydrolysis of PVP-PVAc were consistently higher than 70%.

## 2. Materials and Methods

### 2.1. Materials

The PVP-PVAc copolymer starting materials were purchased from Scientific Polymer Products (SP2). The

30, 50, and 70% PVP copolymers were purchased as 50 w/w% solutions in isopropanol with average molecular weights ranging from 3 to 15 kDa. The 60% PVP-PVAc copolymer was purchased as a white powder from SP2 with GPC average molecular weights ranging from 3 to 5 kDa. Potassium Hydroxide (KOH) was purchased from Sigma Aldrich as 85% pure flakes. Methanol was purchased as reagent grade (>99% pure) from Sigma Aldrich. Deuterated dimethyl sulfoxide (>99% deuterated) was purchased from Sigma Aldrich in 0.5 mL ampules. Deuterated chloroform (>99% deuterated) was purchased from Sigma Aldrich in 50 mL vials. The PVP and PVOH homopolymers that were used to prepare the blends were obtained from SP2 with an average molecular weight of 35 kDa each. The PVP-PVAc copolymer samples were isolated in solid form by vacuum drying the respective isopropanol solutions at 50 degrees Celsius at 20 mm of Hg. All NMR spectra were obtained using a 400 MHz JEOL model ECS-400 NMR spectrometer. FTIR spectra were obtained using 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 DSC measurements were done using a Perkin Elmer Pyris 1 Differential Scanning Calorimeter. The differential refractive index increment measurements (DNDC) were done using a Wyatt Optilab DSP interferometric refractometer.

## 2.2. Methods

### 2.2.1. PVP-PVOH Copolymer Synthesis

An overview of the synthetic procedure for making PVP-PVOH from PVP-PVAc is shown in Figure 1. All PVP-PVAc copolymers were saponified by dissolving 10 grams of each PVP-PVAc in 25 mL of methanol in a three-neck round bottom flask (19/22) which was fitted with a water-cooled condenser, thermometer, and dropping funnel. The PVP-PVAc was allowed to dissolve under heat and medium stirring before adding 1g of KOH dissolved in 25 mL of methanol. This represented a slight excess of KOH, a 1: 1.1 mole ratio of PVP-PVAc: KOH. The addition of the KOH to the reaction media resulted in a sharp temperature decrease and the reaction was allowed to gently reflux for 3.5 hours at approximately 65 degrees Celsius (the boiling point of methanol). After the reaction went to completion, the resultant viscous solution was poured into a 150 mL beaker and neutralized with 3M HCl to a pH of 6-7. The neutralized solution was then covered with a watch glass and allowed to evaporate overnight in the vacuum oven at 50 degrees Celsius and 20 mm Hg. This yielded the crude PVP-PVOH product.

### 2.2.2. PVP-PVOH Copolymer Purification

To purify the PVP-PVOH, the solid was dissolved in minimal amount of water in a 400 mL beaker. To this aqueous solution, a sufficient amount of acetone was added until no more PVP-PVOH precipitated out of solution. This mixture was then decanted and the purified PVP-PVOH solid was allowed to dry in a vacuum oven

under the same conditions as before. The PVP-PVOH solid was a nearly transparent, brittle material that displayed remarkable water solubility as well as a tendency to pick up ambient moisture in the air. The PVP-PVOH samples were stored in a desiccator with CaCl<sub>2</sub> as the desiccant and were heated prior to analysis in order to liberate any residual water.

### 2.2.3. FTIR Analysis of PVP-PVOH Copolymers

ATR-FTIR analysis was done simply by pressing the purified PVP-PVOH samples against the anvil and diamond crystal. Each sample was scanned 16 times at a resolution of 4 cm<sup>-1</sup>. 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<sup>-1</sup>. Each PVP-PVOH sample was analyzed 5 times and integration values for the PVP and PVOH critical peaks (1650 cm<sup>-1</sup> and 3300 cm<sup>-1</sup> respectively) were obtained using the built-in integration function.

### 2.2.4. NMR Analysis of PVP-PVOH Copolymers

For NMR analysis all samples were dissolved in deuterated dimethyl sulfoxide (DDMSO) or deuterated chloroform (CDCl<sub>3</sub>) and ran as 64 scan single pulse <sup>1</sup>H NMR with a 0.25 Hz resolution and a relaxation delay of 5 sec. The JEOL Delta NMR control and process software version 5.0.2 (Windows) was used to analyze individual spectrum.

### 2.2.5. DSC Analysis of PVP-PVOH Copolymers

DSC analysis was done to obtain the glass transition temperatures of each copolymer synthesized. The DSC was calibrated using a 5 mg indium metal standard and each copolymer was analyzed in 5 mg portions in volatile aluminum pans. Nitrogen was used as the purge gas and was flowing at a rate of 20 mL/min. The temperature programming was the same for all PVP-PVOH samples analyzed and was the following: hold for 1 min at 65.00 C, heat from 65 – 165 degrees at 10 degrees per min, hold at 165 degrees for 0.5 min, cool down to 65 degrees, and repeat two additional times. All glass transition temperatures recorded were the onset temperatures.

### 2.2.6. DNDC Measurements of PVP-PVOH Copolymers

The Wyatt Optilab DSP interferometric refractometer was calibrated using aqueous NaCl solutions ranging in concentration from 0.1 mg/mL to 0.7 mg/mL. All DNDC measurements were made at 30 degrees Celsius, at 690 nm wavelength, and with water as the solvent system. Each sample was prepared by dissolving appropriate amounts of material in 50 mL volumetric flasks to make solutions of concentrations ranging from 0.1 mg/mL to 0.7 mg/mL. After each copolymer composition was analyzed, the instrument was flushed with 15 mL of double deionized water through both the reference and sample cells. The detector cell used in the Optilab DSP was a P10 cell. A syringe injection was used for each sample, injection rate was 6mL/hour and changes in refractive index were recorded after the signal stabilized for more than five seconds after each sample injection.

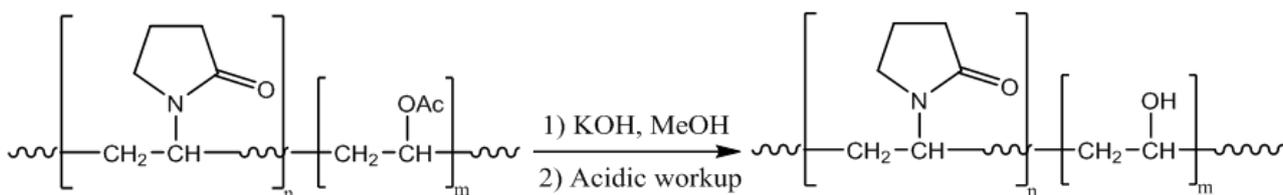


Figure 1. General Saponification Reaction Scheme for the Synthesis of PVP-PVOH

### 2.2.7. PVP-PVOH Elemental Analysis

PVP-PVOH copolymers of all compositions were sent to Galbraith Laboratories in Knoxville, Tennessee, a combustion analysis was done in order to obtain percent C, H, and N. The percent O was obtained by difference.

### 2.2.8. PVP-PVOH Blend Preparation and Analysis

PVP and PVOH blends were made by weighing out appropriate amounts of PVP and PVOH homopolymers having GPC average molecular weights of 35kDa and dissolving them in 50 mL of water. The aqueous mixture of PVP and PVOH was then stirred manually for several minutes before being placed into a vacuum oven at 50 degrees Celsius and 20 mm Hg. The blends were then allowed to evaporate yielding the solid blends. PVP and PVOH blends were analyzed through NMR and IR in the same ways as the PVP-PVOH copolymers were.

## 2.3. Hazards

KOH is a caustic chemical, which can cause skin burns and eye damage, use of KOH necessitates working with gloves, a lab coat, and a fume hood. HCl is a corrosive chemical and toxic vapor, acidic workups of concentrated HCl should be done exclusively in the fume hood to minimize inhalation of HCl. Methanol is a toxic and flammable liquid and should be worked with using proper PPE. Dimethyl sulfoxide is a flammable liquid and therefore care should be taken in order to avoid exposing it to heat sources and static discharge. Chloroform is a toxic chemical which should be used in the fume hood and wearing proper PPE.

## 2.4. Statistical Analysis

All data reported is the arithmetic average of the data collected. All error bars represent 95% confidence intervals. All copolymer compositions have statistically significant spectral and thermal property differences at the 95% confidence level.

## 3. Results and Discussion

### 3.1. FTIR Analysis of PVP-PVOH Copolymers

The PVP-PVOH copolymers were analyzed quantitatively through FTIR analysis using absorbance measurements.

An example absorbance spectrum of the PVP-PVAc starting material is presented in Figure 2 and an example absorbance spectrum of PVP-PVOH product is presented in Figure 3. Plotted in Figure 4 are the data representing the ratio of the PVP peak which represents the C=O stretching vibration at 1650  $\text{cm}^{-1}$  to the PVOH peak which is represented by the O-H stretching vibration at 3300  $\text{cm}^{-1}$  of the various copolymer ratios studied. The relationship is distinctly linear and all sample compositions have statistically significant differences in integration ratios. Figure 5 showcases the overlapping spectra of all the different copolymer compositions to demonstrate the effects copolymer composition has on IR spectral data. Table 1 characterizes the IR vibrational modes of the PVP-PVAc reactant and Table 2 summarizes the IR vibrations for the PVP-PVOH product with critical differences bold-faced. The product shows retention of the PVP amide peak at 1650  $\text{cm}^{-1}$ , but also shows loss of the ester functional group at 1730  $\text{cm}^{-1}$ . The IR data also shows that the PVP moiety was untouched, because hydrolysis of PVP would yield the carboxylic acid shown in Figure 6. Carboxylic acids are known to have strong C=O stretches at 1760  $\text{cm}^{-1}$ , therefore absence of this peak from all products suggests full retention of PVP and full hydrolysis of PVAc. The PVP-PVAc had a peak at 3440  $\text{cm}^{-1}$ , this is likely due to small residual isopropanol.

Table 1. Peak Analysis of PVP-PVAc Copolymer Starting Material

Wavenumber ( $\text{cm}^{-1}$ )	Functional Group	Type of Vibration
3440	Alcohol (from residual isopropanol)	O-H stretch
2949	CH aliphatic	C-H stretch
<b>1729</b>	<b>Ester</b>	<b>C=O stretch</b>
<b>1657</b>	<b>Amide</b>	<b>C=O stretch</b>
1422	CH aliphatic	C-H bend
1369	CH aliphatic	C-H bend
<b>1233</b>	<b>Ester</b>	<b>C-O stretch</b>

Table 2. Peak Analysis of PVP-PVOH Copolymer Product

Wavenumber ( $\text{cm}^{-1}$ )	Functional Group	Type of Vibration
<b>3339</b>	<b>Alcohol</b>	<b>O-H stretch</b>
2919	CH aliphatic	C-H stretch
<b>1642</b>	<b>Amide</b>	<b>C=O stretch</b>
1423	CH aliphatic	C-H bend
1288	Alcohol	O-H bending
<b>1089</b>	<b>Secondary Alcohol</b>	<b>C-O stretch</b>

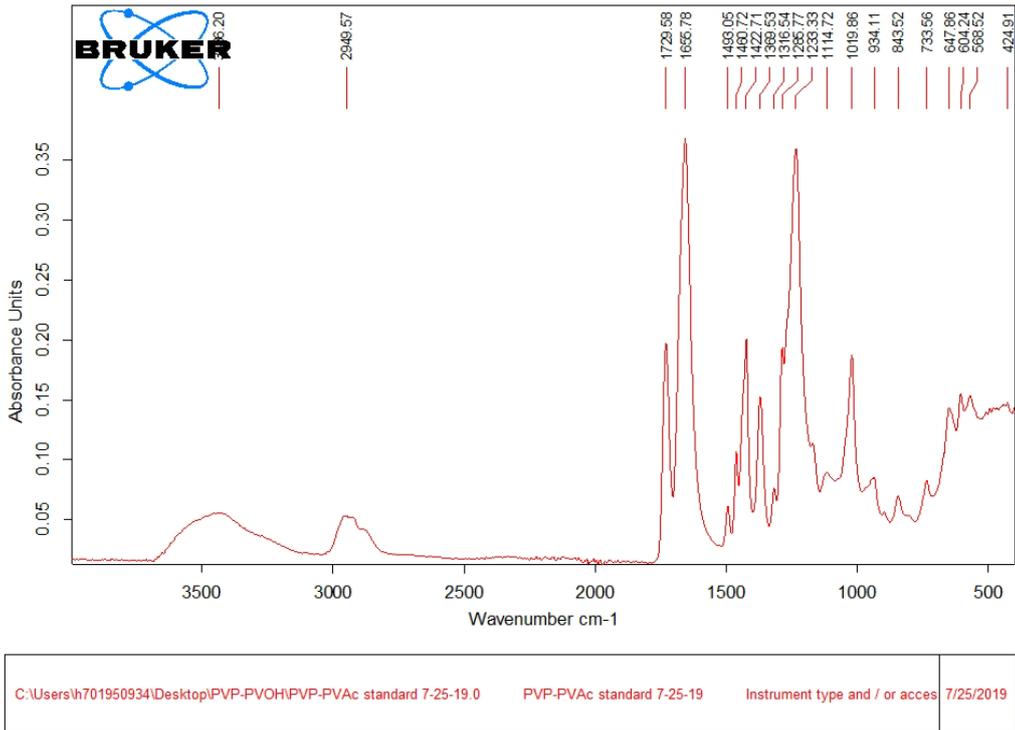


Figure 2. FTIR Spectrum of 50% PVP-PVAc

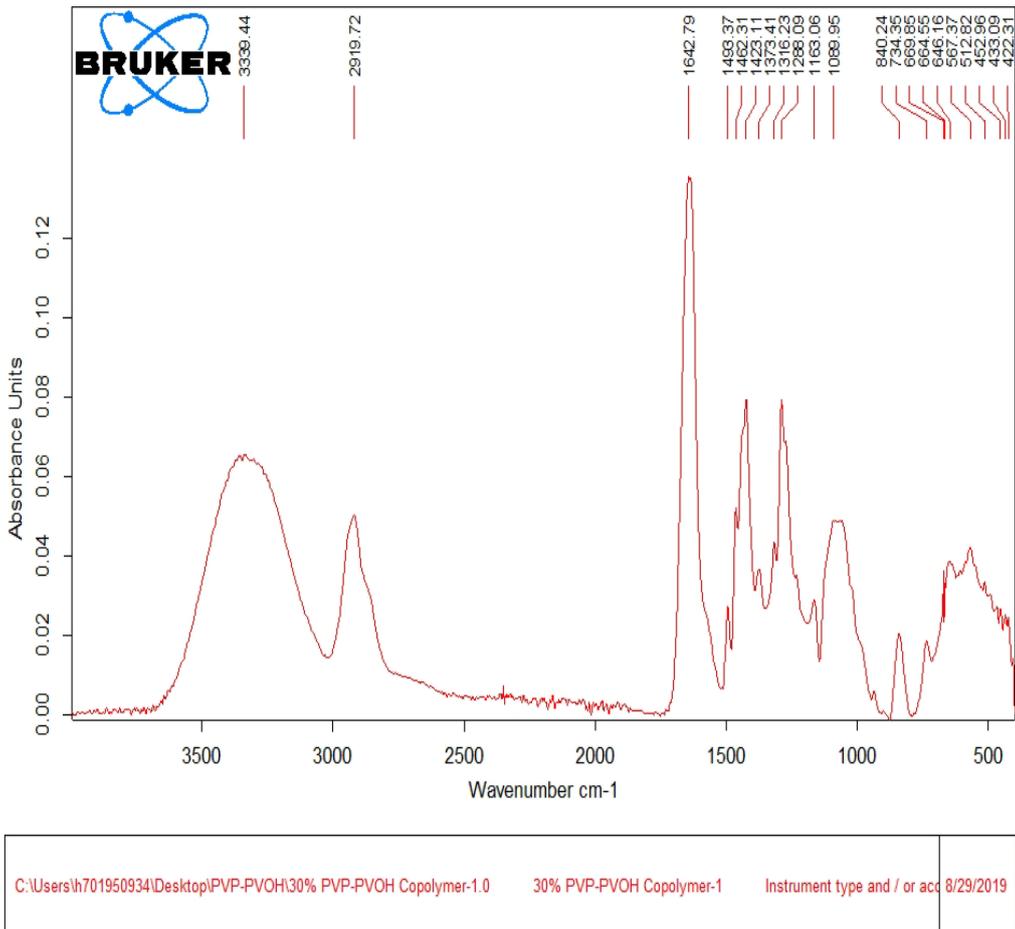


Figure 3. FTIR Spectrum of 30 % PVP-PVOH Copolymer

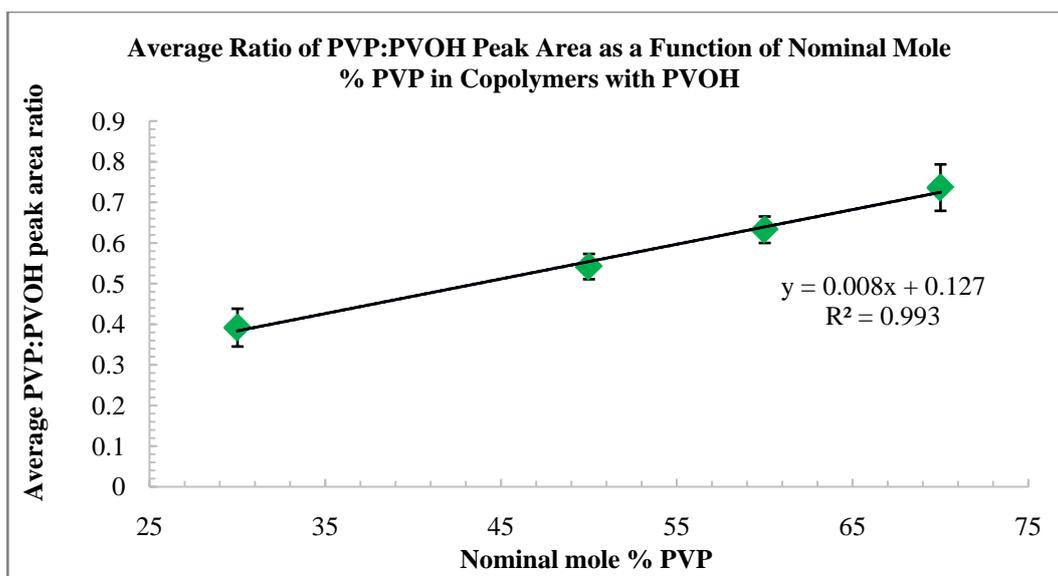
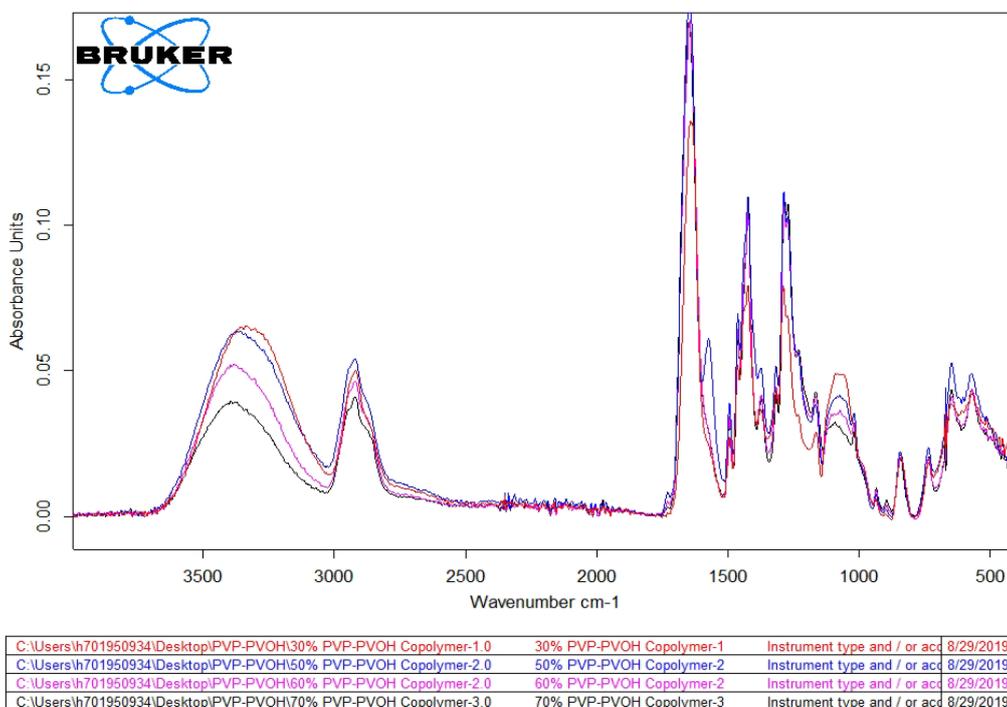


Figure 4. Nominal Mole Percent PVP Plotted Versus Average PVP( $1650\text{ cm}^{-1}$ ):PVOH( $3300\text{ cm}^{-1}$ ) Peak Area Ratios.



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Figure 5. Overlapped FTIR Spectra of the PVP-PVOH Copolymers of Various Nominal Mole Percent PVP Content

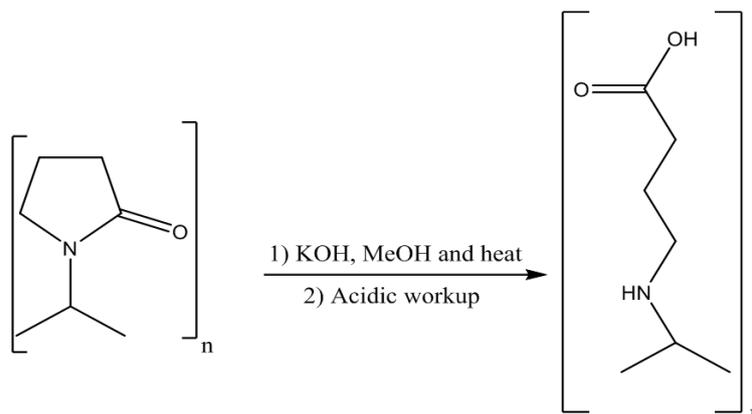


Figure 6. Theoretical Product of the Base-Promoted Hydrolysis of PVP

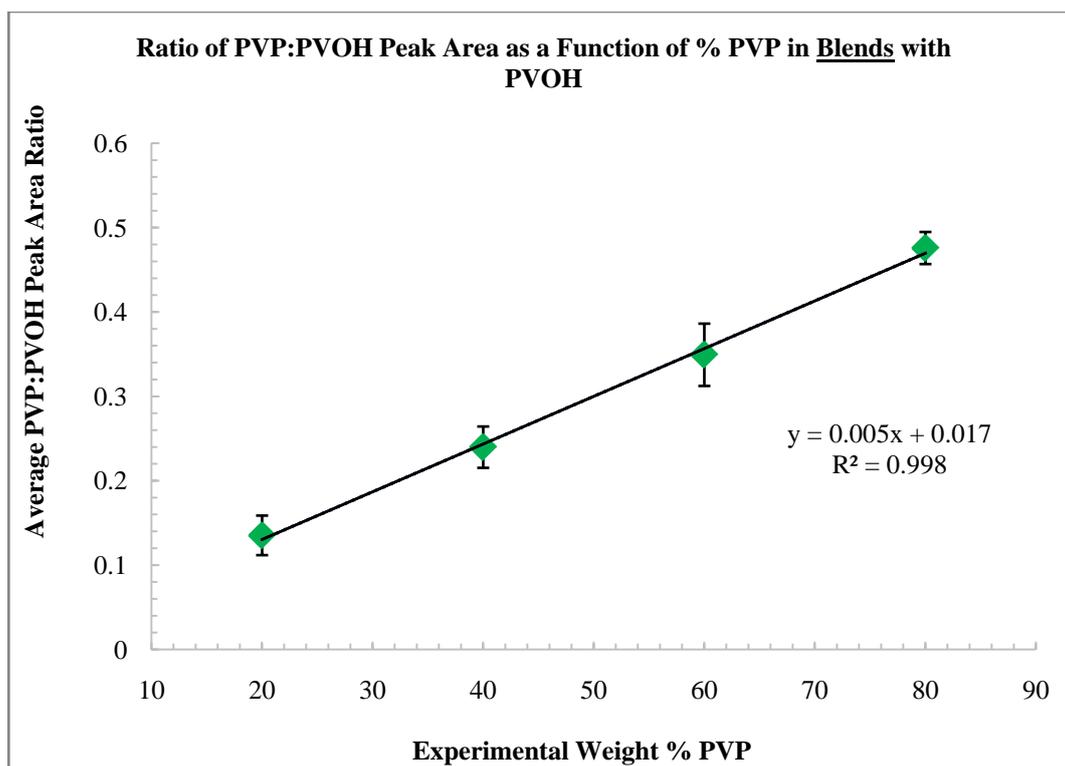


Figure 7. Average PVP:PVOH Peak Area Ratios as a Function of Weight Percent PVP in Blends with PVOH.

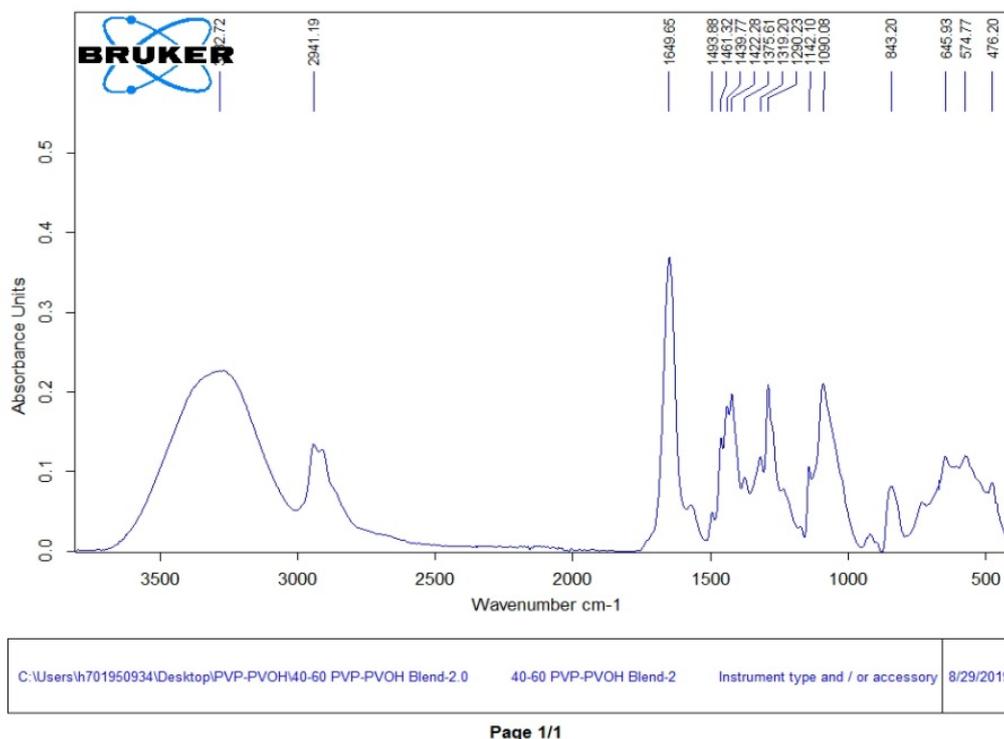


Figure 8. FTIR Spectrum of 40-60 PVP and PVOH Blend

### 3.2. FTIR Analysis of Blends of PVP and PVOH

The blends of PVP and PVOH showed a linear relationship between the corresponding IR peaks and all compositions tested had statistically significant differences in their integration ratios, suggesting that quantitative IR analysis of PVP and PVOH blends is highly sensitive to changes in percent PVP. These data are

plotted in Figure 7 and an example IR spectrum of a PVP and PVOH blend is shown in Figure 8.

### 3.3. NMR Analysis of PVP-PVOH Copolymers

Figure 9 and Figure 10 show the proton NMR of pure PVP in  $\text{CDCl}_3$  and PVOH in  $\text{DMSO}$  respectively. Figure 11 displays the proton NMR for the 60%

PVP-PVOH copolymer in DDMSO. Table 3 summarizes the peak assignments for each of the various peaks in the NMR spectrum for PVP and PVOH. Table 4 specifies the peaks found in the 60% PVP-PVOH copolymer. The peaks are slightly shifted compared to what was found in the PVP and PVOH homopolymers for several reasons, firstly the PVP and PVOH homopolymers analyzed via NMR had a higher molecular weight than the 60% PVP-PVOH copolymer, meaning that the end groups at the end of the polymer are less meaningful in determining chemical shifts. Secondly, the PVP-PVOH copolymer has the PVP and PVOH moieties located next to each other, which alters their chemical environment relative to the pure homopolymers, leading to differences in chemical shift. The peaks in each of the NMR's are much more diffuse than would be expected, this is likely because the polymers analyzed are not monodisperse; the sample analyzed represents a statistical mixture of different molecular weights, tacticities, etc. thus each signal represents the peaks for all the different arrangements of the different molecules in the mixture. The PVP spectrum shown was done in deuterated chloroform to better demonstrate the integration values for the peak at 2.359 ppm ( $C_1$ ). The most downfield proton in PVP is the proton on the carbon bonded to the nitrogen in the backbone ( $A_1$ ).

This proton is the most downfield because it is a methyne proton and the carbon to which it is bonded is closest to the electronegative nitrogen atom in the pyrrolidone ring. The second most downfield peak of PVP is the methylene protons on the carbon closest to the nitrogen in the pyrrolidone ring ( $B_1$ ), these protons experience the inductive electron-withdrawal of the nitrogen, but are not methyne protons. The next most deshielded proton of PVP are the methylene protons closest to the carbonyl group in the pyrrolidone ring ( $C_1$ ). The carbonyl is an electron-withdrawing group and thus these protons will be slightly deshielded. The two methylene protons far from the carbonyl and nitrogen atom are the two most shielded protons and thus have very similar chemical shifts. Because of a very similar chemical environment and the heterogeneity of the PVP homopolymer, these peaks ( $D_1$  and  $E_1$ ) overlap with each other [28]. The peak corresponding to the backbone methylene protons ( $E_1$ ) (1.694 to 1.406 ppm) likely has a wide range of chemical shifts and thus got absorbed by the larger peak at 1.912 ppm preventing the integration from being 2. This is corroborated by the fact that the sum of the integration for the  $D_1$  and  $E_1$  protons add up to 4 protons, which is what the molecular formula would suggest.

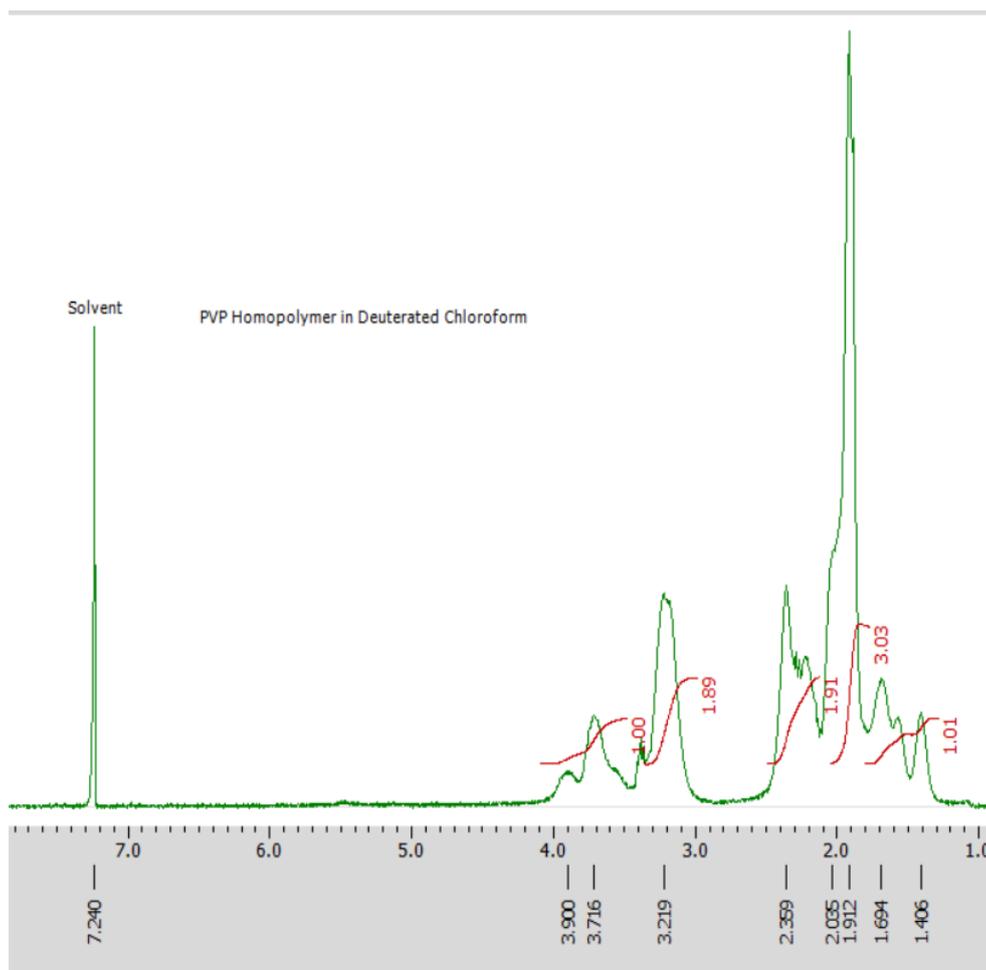


Figure 9. Proton NMR of PVP Homopolymer in CDCl<sub>3</sub>

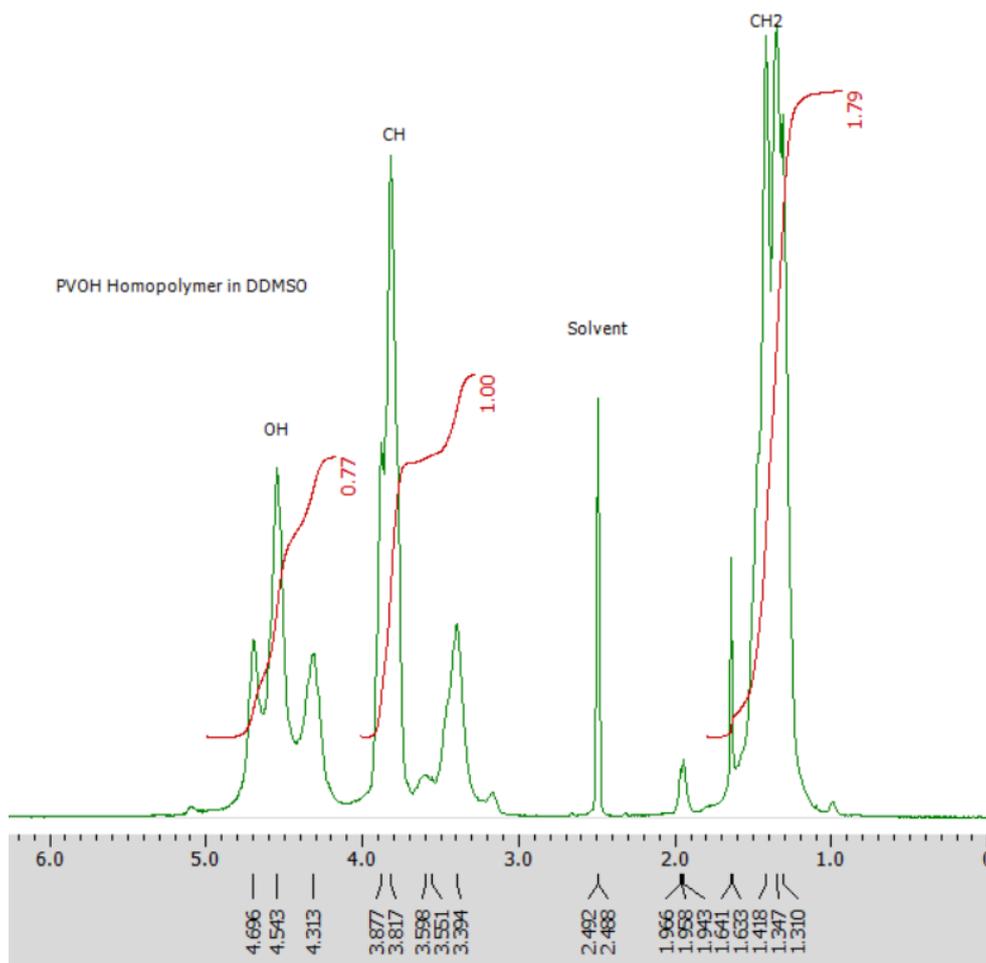


Figure 10. Proton NMR of PVOH Homopolymer in DDMSO

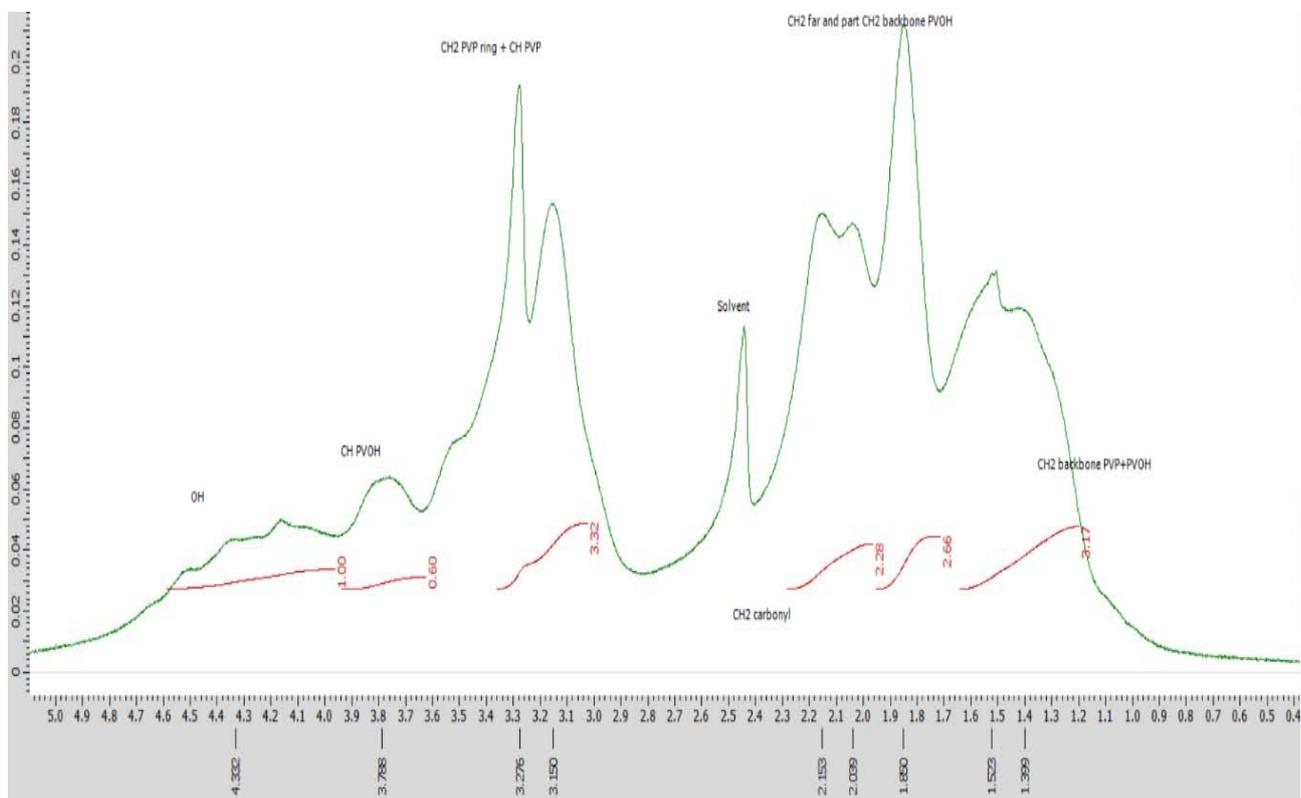


Figure 11. Proton NMR of the 60 % PVP-PVOH Copolymer in DDMSO

Table 3. Peak Assignments for PVP and PVOH Homopolymer

PVP			PVOH		
Protons	Chemical shift value (ppm)	Normalized Integration value	Protons	Chemical shift value (ppm)	Normalized Integration value
A <sub>1</sub>	3.7	1.00	A <sub>2</sub>	4.7-4.3	0.77
B <sub>1</sub>	3.2	1.89	B <sub>2</sub>	3.9	1.00
C <sub>1</sub>	2.4	1.91	C <sub>2</sub>	1.6-1.3	1.79
D <sub>1</sub> + E <sub>1</sub>	2.0 – 1.4	4.04			

Table 4. Peak Assignments for PVP-PVOH Copolymer

Proton	Chemical shift value (ppm)	Normalized Integration value
A	4.6 - 4.1	1.00
B	3.8	0.60
C	3.3	Part of 3.32 integration
D	3.2	Part of 3.32 integration
E	2.2	2.28
F	1.85	Part of 2.66 integration
G	1.52	Part of 2.66 and 3.17 integration
H	1.40	Part of 3.17 integration

The most downfield peak in the proton NMR of PVOH is from the proton associated with the hydroxyl moiety (A<sub>2</sub>). This is because oxygen is very electron withdrawing owing to its high electronegativity; in previous studies, the OH peak of PVOH has been associated with the three peaks from 4.6-4.3 [29]. The different peaks are associated with the various ways that the OH groups can be oriented when the vinyl acetate monomers combine during free radical polymerization (head-head, head-tail, and tail-tail). The next highest chemical shift is associated with the methyne in the backbone of PVOH (B<sub>2</sub>); this proton experiences the strong electron-withdrawing effects of the oxygen, causing the proton to be more deshielded. The lowest chemical shift in PVOH is associated with the methylene protons of PVOH (C<sub>2</sub>) because these protons are not directly connected to the electron-withdrawing oxygen and is located farthest away from it, thus the methylene protons are the most shielded (most upfield). The integration values for the OH peak of PVOH in the homopolymer is less than one because the

OH proton is acidic and can undergo hydrogen-deuterium exchange with the solvent, accounting for its lower than expected integration value. In the PVP-PVOH copolymer, the peaks of protons C and D, F and G, and G and H overlap due to their very similar chemical environments.

### 3.4. NMR Analysis of PVP and PVOH Blends

The PVP and PVOH blends were quantified using the integration values associated with the hydroxyl proton of PVOH and the methylene PVP protons adjacent to the nitrogen. Figure 12 shows a sample NMR spectrum of a 20-80 PVP and PVOH blend and Figure 13 shows the plot of the quantitative NMR (qNMR) percent PVP versus the gravimetric weight percent PVP in the blends. The qNMR percent PVP was determined using the following equation:

$$\% PVP = \frac{Protons_{PVP}}{Protons_{PVP} + Protons_{PVOH}} * 100\% \quad (1)$$

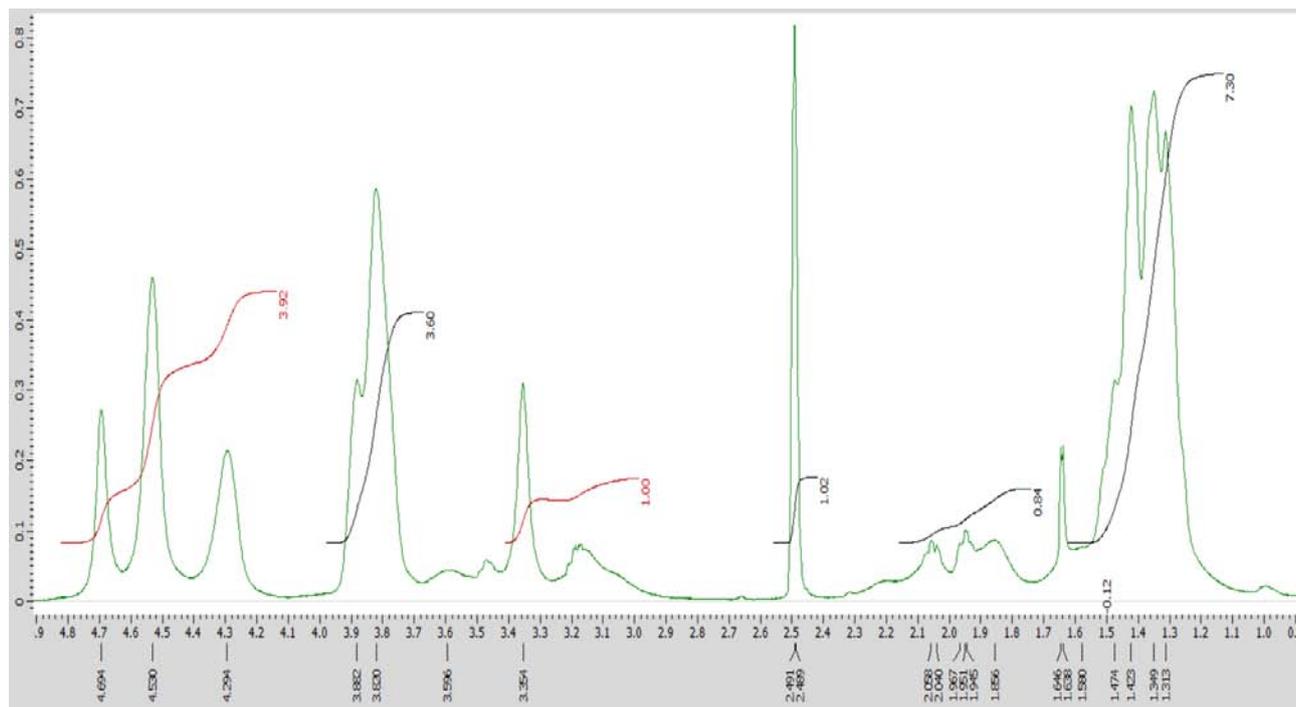


Figure 12. Proton NMR Spectrum of 20-80 PVP and PVOH Blend in DMSO

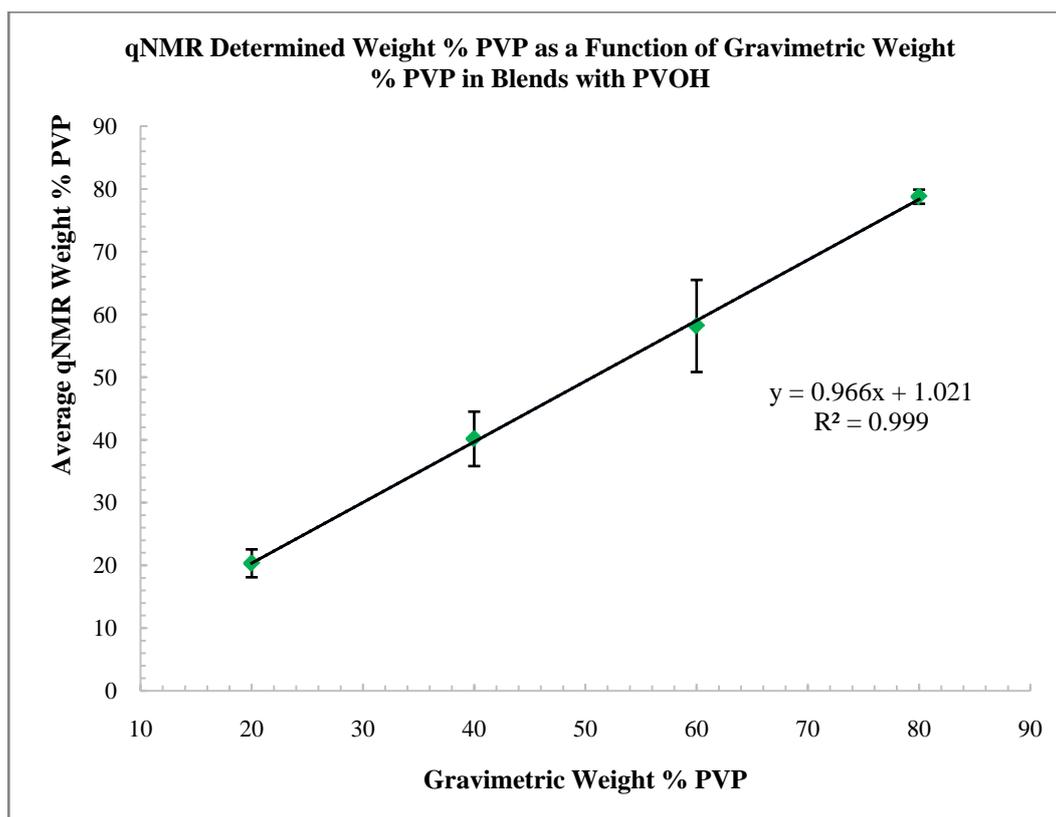


Figure 13. Percent PVP in Blends With PVOH Determined by NMR

### 3.5. DSC Analysis of PVP-PVOH Copolymers

The glass transition temperature for PVP is 170 degrees Celsius and the glass transition temperature for PVOH is 85 degrees Celsius [30,31]. Therefore, as the percent PVP content increases in the copolymers of PVP-PVOH, the observed glass transition temperature should increase. Figure 14 shows the linear relationship between percent PVP and the observed glass transition temperature, the

y-intercept, which should represent the glass transition temperature for pure PVOH is 84.2, which is extremely close to the known glass transition temperature for PVOH homopolymer and falls within error. Figure 15 shows an example DSC thermogram for the 70% PVP-PVOH copolymer, all glass transition temperatures recorded are the onset temperature. Frequently the glass transition temperature occurred concurrently or shortly before the melting of the copolymer occurred.

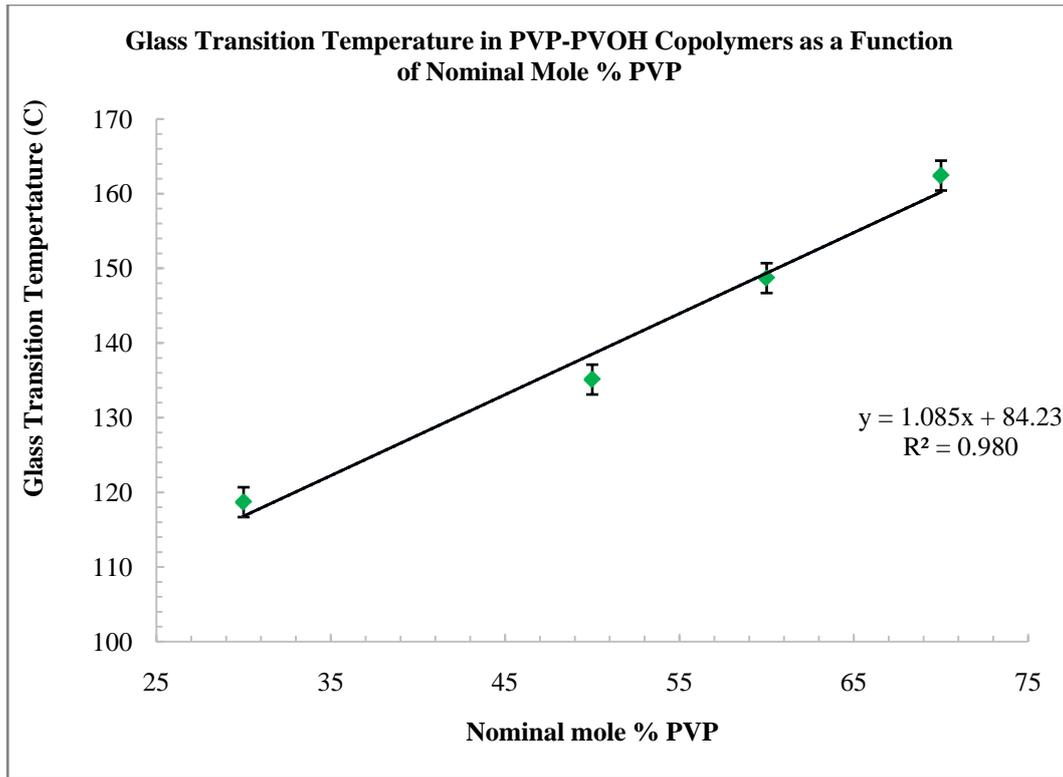


Figure 14. Glass Transition Temperature of PVP-PVOH Copolymers Plotted Against Nominal Mole Percent PVP

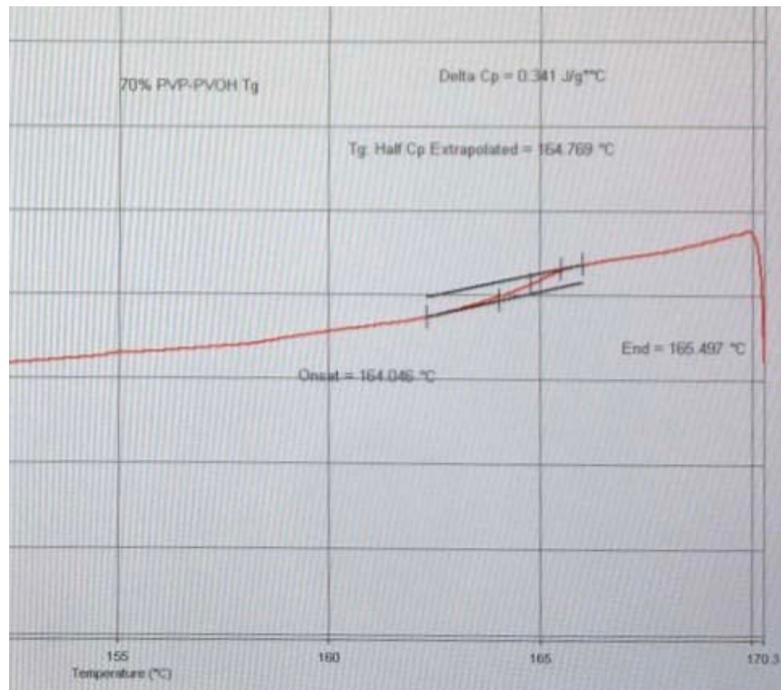


Figure 15. DSC Thermogram of 70% PVP-PVOH Copolymer

### 3.6. DNDC Analysis of PVP-PVOH Copolymers

The specific refractive index increment parameter of copolymers has been related to copolymer composition in previous studies by the following relationship:

$$v = w_A v_A + w_B v_B \quad (2)$$

where  $w$  represents the weight percent of each component of the copolymer and  $v$  represents the specific refractive

index increment for each component as a homopolymer [32]. The DNDC values for PVOH and PVP were determined to be 0.136 and 0.175 mL/g respectively. It was therefore expected that as the percent PVP increases, so too should the observed DNDC value. Figure 16 shows the linear relationship between copolymer composition and the observed DNDC value. Table 5 shows the percent errors between the expected DNDC values of the copolymers compared to the experimental DNDC values.

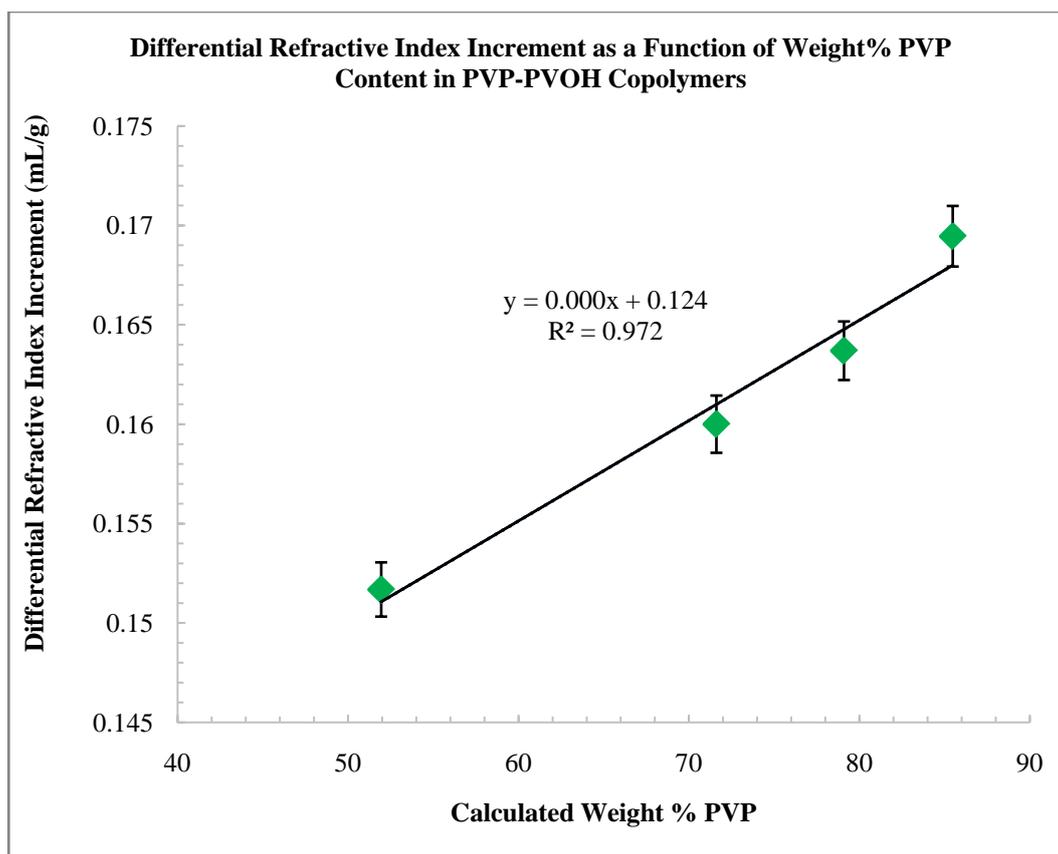


Figure 16. DNDC Values of PVP-PVOH Copolymers Plotted Against Nominal Weight Percent PVP

Table 5. Summary of DNDC Values for PVP-PVOH Copolymers

Weight Percent PVP	dn/dc experimental (mL/g)	dn/dc theoretical (mL/g)	Percent Error
51.95	0.152	0.156	2.92
71.61	0.160	0.164	2.40
79.10	0.164	0.167	1.89
85.48	0.169	0.169	0.08

### 3.7. Elemental Analysis of PVP-PVOH Copolymers

The elemental analysis results were used in order to obtain experimental weight percent PVP by using the following equation:

$$\%PVP = \frac{\%N}{12.11} * 100 \quad (3)$$

as PVP is the only source of N in the copolymer of interest. The calculated weight percent PVP was determined with equation 4 below:

$$\%PVP = \frac{n_{PVP} * MM_{VP}}{n_{PVOH} * MM_{VOH} + n_{PVP} * MM_{VP}} * 100 \quad (4)$$

Summarized in Table 6 is the elemental analysis data. The calculated weight percent PVP and experimental weight percent PVP are plotted in Figure 17.

Table 6. Summary of Elemental Analysis Results for PVP-PVOH Copolymers

Calculated Weight Percent PVP	Experimental Weight by EA Percent PVP	Percent Error
52.0	50.5	3
71.6	63.0	13
79.1	73.0	8
85.5	80.2	6

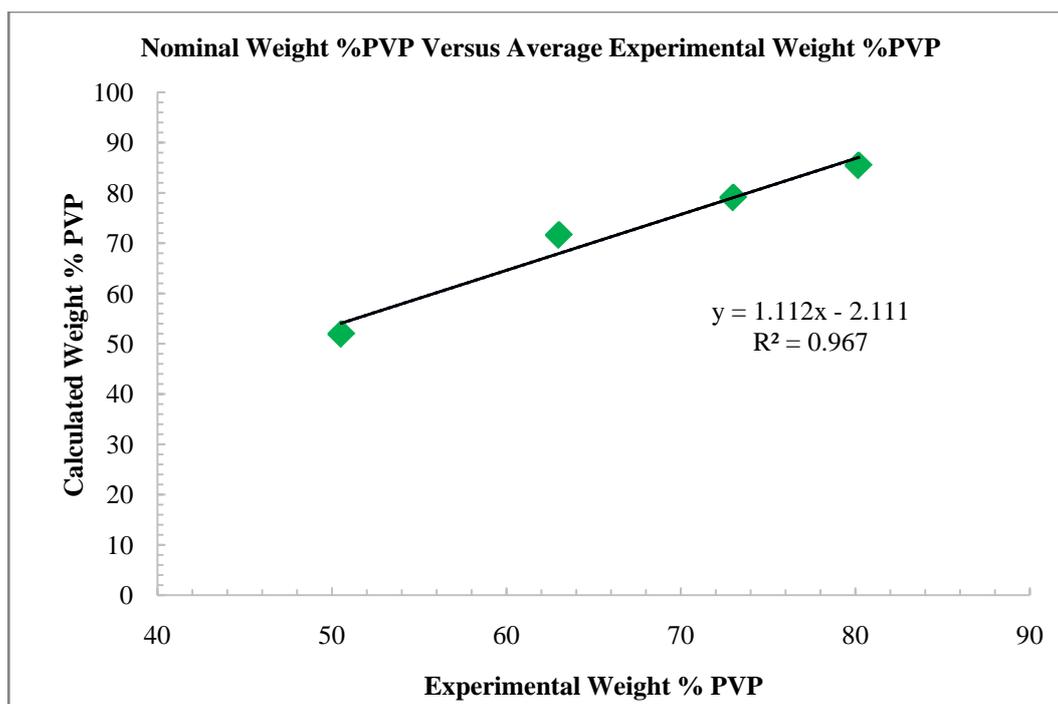


Figure 17. Calculated Weight % PVP Plotted Against Elemental Analysis Determined Weight % PVP

## 4. Conclusions

The commercially used PVP-PVAc copolymer can be effectively hydrolyzed to PVP-PVOH copolymer whose composition can be determined by FTIR, NMR, DSC, DNDC, and EA measurements. The PVP-PVOH product showed critical IR peaks at  $3300\text{ cm}^{-1}$  and  $1089\text{ cm}^{-1}$  indicating the formation of an alcohol functional group in the polymer and specifically a secondary alcohol respectively. The IR spectra of each PVP-PVOH copolymer also displayed loss of the ester C=O stretch peak at  $1730\text{ cm}^{-1}$  indicating complete hydrolysis of the PVAc moiety to PVOH. The PVP moiety was shown to be in tact both via NMR and by IR, the NMR of the copolymer showed retention of the peak at 3.2 ppm corresponding to the methylene ring protons adjacent to the nitrogen of the pyrrolidone ring. The peak associated with the methylene protons adjacent to the carbonyl carbon at 2.2 ppm was also retained. The IR showed no carboxylic acid C=O peak at  $1750\text{ cm}^{-1}$  suggesting that the PVP was not hydrolyzed. This was likely because the reflux temperature (65 degrees Celsius) was not high enough to allow the hydroxide to attack the PVP moiety; amides are resistant to hydrolysis due to their poor nitrogen-leaving group. The elemental analysis results are in good agreement with the expected weight percent N and give a good prediction of average percent PVP in the copolymers, further corroborating that the product is produced in a clean fashion, without contamination. PVP and PVOH blends can also be effectively quantified using FTIR and proton NMR. The facile and high yielding nature of this hydrolysis makes it suitable for industrial-scale processing of PVP-PVAc to PVP-PVOH. In addition to PVP-PVOH being useful by itself due to its water-soluble and biodegradable nature, it can be further modified through traditional synthetic organic techniques to yield new types of copolymers. One such chemical transformation that could be done to further enhance the biodegradability of

the PVP-PVOH copolymer is oxidation to the corresponding polyvinyl pyrrolidone- poly enol ketone (PVP-PEK). Previous literature regarding the oxidation of PVOH to PEK has been reported and PEK has been shown to coordinate metal ions, suggesting a role in water-treatment [33,34,35]. The oxidation of PVOH to PEK also cleaves the polymeric backbone, suggesting oxidation of PVP-PVOH would be an efficient means of processing this polymeric material into smaller molecules that can be further degraded [33,34,35]. Further tests evaluating the biodegradability of PVP-PVOH compared to PVP-PVAc should be done in order to verify its unique benefit as a novel biodegradable copolymer accessible from common commercial material. Further chemical modification of PVP-PVOH will be reported in due course.

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## Statement of Competing Interests

The Authors have no competing interests.

## List of Abbreviations

PVP – Polyvinyl Pyrrolidone  
 PVOH – Polyvinyl Alcohol  
 PEK – Poly Enol Ketone  
 PVAc – Polyvinyl Acetate  
 ATR – Attenuated Total Reflectance  
 FTIR – Fourier Transform Infrared Spectroscopy  
 NMR – Nuclear Magnetic Resonance Spectroscopy  
 DNDC – Differential Refractive Index Increment

DSC – Differential Scanning Calorimetry  
 EA – Elemental Analysis  
 qNMR – Quantitative NMR  
 GPC – Gel Permeation Chromatography  
 DDMSO – Deuterated Dimethyl Sulfoxide  
 CDCl<sub>3</sub> – Deuterated Chloroform  
 KOH – Potassium Hydroxide  
 MeOH – Methanol  
 HCl – Hydrochloric Acid  
 SP2 – Scientific Polymer Products  
 PPE – Personal Protective Equipment

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