



# Freeze-dried crosslinked anionic hydrogels composed of poly(vinyl pyrrolidone) and poly(vinyl alcohol): synthesis, characterization and degradability performance

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*Purpose:* Poly(vinyl pyrrolidone) (PVP) and poly(vinyl alcohol) (PVA) has enticed significant research interest and are acknowledged among the principal volume of synthetic polymers that have been fabricated globally for nearly one century. This is as a result of their excellent attributes which dictated its wide-ranging usage in a range of applications, chiefly in medical field. The investigation is aimed at preparing PVP/PVA hydrogels using freeze drying technique for its characterization and accessing the biodegradability of the prepared hydrogel. *Methods:* Scanning electron microscopy and Fourier transform infrared spectroscopy were employed for the description of the morphology and chemical composition of the prepared hydrogels. More characterization studies were implemented by measurement of apparent density, porosity, swelling ratio and crystallinity of the fabricated hydrogel with the use of X-ray diffractometer (XRD). The biodegradability of the prepared hydrogel was also carried out *in vitro* in phosphate buffered saline. *Results:* As the PVP content increased the percentage of porosities from  $45.00 \pm 1.00\%$  to  $81.80 \pm 0.20\%$ , which was also accompanied by an increase in density. The prepared hydrogel showed increase in swelling ratio as the PVP content increased, the highest swelling ratio was found in PP4 with 95.58% with the least swelling time of 4 minutes. *Conclusions:* To sum it up, PVP plays a role as network and performance regulator in this sort of anisotropic hydrogels. This investigation offers a fascinating means of regulating morphology and general characteristics of the PVA-based anisotropic hydrogels.

*Key words:* hydrogel, porosity, poly(vinyl alcohol), poly(vinyl pyrrolidone), swelling

## 1. Introduction

Hydrogels are three-dimensional macromolecular systems with the capability to captivate huge quantities of water or biological liquids, yet, with great strength in physiological circumstances [5], [10], [30]. Several cross-linking methods may be employed in the preparation of stable hydrogels, including physical, chemical, and radiation, or a mixture of diverse techniques [30]. Although cross-linking using chemical method (using

a chemical agent) is the most common system in hydrogel synthesis, in this day and age, physical cross-linking technique has attracted specific attention as they are much non-toxic for biomedical applications [30], [3]. Currently, there is a continual interest in developing polymer hydrogels owing to their outstanding penetrability, hydrophobicity and viscoelasticity, which elevate people's high outlooks for hydrogels with great performances [2], [18]. Hydrogels have been useful in pharmaceutical, biological and daily-care applications, such as vehicles for drug delivery, immunoassay, implantable

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artificial muscles, eye contact lenses and wound dressings, etc [6], [15], [21], [27], [30], [33].

Poly(vinyl alcohol) (PVA) is a hydrogel biomaterial with an extensive and efficacious history of use in humans. It is used in the production of embolic bodies, enzymes immobilization and cells for biomass transformation. Implants for avoidance of postoperative tissue collapse among others are the examples of its successful use over time [17]. PVA is a form of non-toxic, good biocompatible and non-carcinogenic water-soluble polymer [38]. Owing to its hydrophilic functional groups in every single molecular entity, PVA has the ability to chemically and physically form into a cross-linked hydrogel [14]. Typically at the expense of its strength and mechanical attributes, PVA can be effortlessly contrived into PVA hydrogel by absorbing sufficient water [13]. It is a synthetic polymer that has a biodegradability property in the natural environment [42]. Additionally, PVA is a remarkable polymer for drug delivery due to its good thermal and chemical stability, non-toxicity, lasting pH and temperature steadiness, outstanding film forming capability, and high biocompatibility with biological tissues. Nevertheless, wholesome PVA hydrogels are acknowledged to be quite naturally fragile. For instance, Kuiper et al. [20] confirmed that the PVA hydrogels do not entirely mimic the non-linear behaviour of the temporomandibular joint disc. Their results recommend that transversely-aligned tensile fortification may be vital to increase the compressive stiffness of PVA hydrogel materials at high strains in order to mimic the compressive behaviour of the temporomandibular joint disc. Thus, they have been successfully incorporated into an interpenetrating polymeric network (IPN) hydrogel when blended with another polymer to overcome their limitation of fragility via chemical and physical methods among others. PVA has been incorporated with a range of polymers to produce an extensive collection of hydrogels, and poly(vinyl pyrrolidone) (PVP) is one of such polymers, which fits so well in this category. PVP is an acceptable material owing to its hydrophilicity, biodegradability, low chemical toxicity, biocompatibility, realistic dissolvability in water and majority of the organic solvents, and elimination through both renal and hepatic routes [8], [36]. Hence, it has a varied array of industrial and biomedical uses including beverages, pharmaceutical, cosmetics, detergents, adhesives, paints, bioengineering and electronic materials [7], [36]. PVP furthermore absorbs up to 40% of its weight in water, thereby making it a perfect medium for the solid dispersal of inadequately soluble drugs [36],

[24]. As a decent proton-receptor, poly(vinylpyrrolidone) (PVP) retains sufficient carbonyl groups that can establish hydrogen bond with hydroxyl groups of PVA chain and the characteristics of this sort of two-constituent hydrogels are tunable [39], [40]. Hydroxyapatite reinforced with PVP/PVA offered an excellent *in vitro* biocompatibility response towards Human Mesenchymal stem cells(hMSC) making the blend to be one of the most promising alternatives for artificial cartilage substitutes [16]. Also, Malka et al. [23] used PVA/PVP matrix for the controlled release of pesticide for agricultural application. In their work, low-to-zero phytotoxicity was observed for hydrogen peroxide release. Thus, the strength of hydrogels could be well-controlled by adjusting PVP concentrations [29], [32].

For example, Mastrangelo et al. [26] assembled two-cog systems in the PVA/PVP hydrogels through freeze-thawing technique and observed that PVP intensely influenced the crystallization of PVA [40]. Furthermore, Kanca et al. [19] showed that increasing the content of PVP in PVA/PVP blend generally improved the tribological properties of the blend against articular cartilage.

Freeze-drying is an efficient method of obtaining permeable materials with exceptional morphology [4]. The key standard of the process of freeze-drying encompasses that a sample is iced up and desiccated under lessened force, thereby obliging the water contained by the sample to be transformed nonstop into the gas phase. This technique has been extensively utilized in biological examination, food production, biofoams, aerogels, unstructured materials, core-shell structures, and other nanoscale materials [4], [34]. By rapidly icing the sample, the creation of bulky freeze crystals can be prohibited, and permeable materials can be anticipated after eliminating the insignificant ice quartzes, which are the templates [25]. The freeze-drying technique is hence a pleasant choice to produce porous hydrogel blends from their respective consistent solutions [4], [34].

The aim of this study was to develop a cross-linked anionic hydrogels composed of PVP and PVA by freeze-drying method with different ratio. The effect of different ratio on the chemical and structural properties of all blends was investigated using XRD, FTIR and SEM, respectively. A freeze-drying technique was used in order to synthesize the hydrogel because freeze-drying is relatively cost-effective and an easy technique for hydrogel fabrication. Secondly, the swelling performance test and degradation stability evaluation of the hydrogel were carried out to check whether it was suitable for biomedical applications.

## 2. Materials and methods

### 2.1. Materials

Poly(vinyl alcohol) (PVA) (Product #: 341684, CAS: 9012-79-5, MW: 89,000 to 97,000 mol wt, hydrolysis of 97–99%), poly(vinylpyrrolidone) (PVP) (Product #: 341684, CAS: 9012-79-5, MW: 58,000 mol wt, hydrolysis of 97–99%) (K-30) were procured from Sigma Aldrich. Both polymers were utilized in the experiments with no additional purification. Sulfuric acid (98% purity), distilled water and other reagents were obtained from the Chemistry Laboratory of Cyprus international University.

### 2.2. Cross-linking of PVA/PVP hydrogel

5 g of PVA was solved in 95 ml sanitized water with magnetic stirring at 90 °C for 1 h in order to achieve 5 wt. % PVA solution. Afterward, a predetermined quantity of PVP was added into PVA solution of to form different percentage (0:100, 50:50, 80:20, etc.) (Table 1), agitated to acquire homogeneous PVA/PVP mixture solution. The diluted sulfuric acid ( $w = 10$  wt. %) was added dropwise into the acquired solution (1 vol. %), agitated at 95 °C for 10 min, then was allowed to cool down to room temperature.

Table 1. PVA and PVP content in each sample

Sample	%PVA	%PVP
PVA	100	0
PP1	50	50
PP2	40	60
PP3	25	75
PP4	20	80

### 2.3. Hydrogel freeze-drying

The freeze-drying procedure was implemented in the vacuum freeze-drying machine (LG-1.0, Shenyang Aerospace Xinyang Frozen Equipment Manufacturing Co., Ltd., China). The beaker containing the polymer was quickly moved into a freezer which was set to a low temperature (−70 °C) to solidify the polymer. After the samples has been solidified, they were kept for the minimum of 24 h in a freezer at −80 °C. Afterward, the samples were vacuum-dried in a research

laboratory freeze-dryer for about 48 h. At the commencement of the freeze-drying procedure, the sill was ventilated in liquid nitrogen to prevent a fractional unfreezing of the sample prior to sublimation. Subsequently, the sill temperature was not regulated any longer. The pressure of the dehydrating cavity was set to 0.04 mbar at a condenser temperature of −50 °C. The samples produced were stockpiled in a vacuum desiccator at room temperature for storage and for additional elimination of any lingering solvent prior to characterization.

### 2.4. FTIR spectroscopy

The chemical arrangements of the freeze-dried hydrogel were examined by using FTIR spectroscopy. Slab samples were arranged with the cross-linked PVP/PVA samples spread in KBr. The spectra of samples were taken at 400–4000  $\text{cm}^{-1}$  wavelength with Fourier-transform infrared spectrometer (Shimadzu-IRPRESTIGE – 21) in the frequency range of 400–4000  $\text{cm}^{-1}$  and with a general ATR sampling fitment to discover functional groups.

### 2.5. Scanning electronic microscopy measurements

The morphology of the hydrogels were observed by scanning electron microscopy (SEM, T-330A; JEOL, Tokyo, Japan). The samples were submerged into de-ionized water for 24 h before the process of freeze-drying. The freeze-dried samples were then cut along with the ranged direction to uncover their inside and then smeared with gold–palladium layer before testing.

### 2.6. Measurements of XRD

To measure XRD, a sample was arranged with the use of a glass-slide with a furrow to hold the sample. The specimen was positioned sideway the glass slide in an X-ray diffractometer of PHILIPS PW-1710 to determine the X-ray diffraction configuration from its compressed surface. The diffraction figures were documented employing a filtered homochromatic of  $\text{CoK}\alpha$  or  $\text{CuK}\alpha$  of wavelength  $\lambda = 179$  or 154 nm via a Ni filter. The data were obtained with a computer, interfaced via the diffractometer, at a scanning speed of 0.05  $\text{s}^{-1}$ , except otherwise stated, particularly in the instance of high resolution X-ray diffractograms in

designated measurements. The range of the diffraction angle  $2\theta$  was varied from 10 to  $110^\circ$ .

## 2.7. Determination of the density and porosity

We used the solvent displacement method for the measurement of density. Prepared freeze dried hydrogels, were used for density measurements, which essentially indicates the apparent densities of the hydrogels. Pieces of hydrogels were cut out and weighed for the determination of mass of each piece. A hydrophobic solvent such as hexane that is not absorbable by the hydrogels was used for this experiment. By the use of forceps, a piece of the hydrogel was submerged in a known volume of hexane in a measuring cylinder, and the increase in the hexane volume was valued as the volume of the hydrogel. The density was calculated using Eq. (1).

$$\text{Density} = \frac{M_{\text{scaffold}}}{V_{\text{scaffold}}}, \quad (1)$$

where  $M_{\text{scaffold}}$  is the mass of hydrogel and  $V_{\text{scaffold}}$  is the volume of hydrogel.

For the measurement of porosity, dried hydrogels were dipped in hexane overnight and evaluated when left-over solvent on the surface was blotted. The porosity was expressed mathematically using Eq. (2).

$$\text{Porosity} = V_p / V_T, \quad (2)$$

where  $V_T$  is the hydrogel total volume and  $V_p$  is the pore volume of the hydrogel. Hydrogel total volume could be determined from its dimensions (circular in shape). Pore volume could be determined by subtracting the hydrogel from  $V_T$ .

$$\text{Porosity} = \left[ \frac{V - V_p}{V} \right] \times 100\%. \quad (3)$$

The calculated density and porosity values were conveyed as means  $\pm$  standard deviation.

## 2.8. Swelling test

Samples from each prepared hydrogel (PVA, PP1, PP2, PP3 and PP4) were cut into pieces to approximately 300 mg and permitted to hydrate in surplus double distilled water (DDW, pH: 7.0) at  $38^\circ\text{C}$  so as to examine the swelling potentials. Samples were withdrawn from the DDW and the excess water was removed by blotting with filter paper. The mass of hy-

drated hydrogel was calculated for designated time interludes. Swelling percentage were determined mathematically by using Eq. (4).

$$\text{swelling ratio} = \left( \frac{W - W_0}{W_0} \right) \times 100\%, \quad (4)$$

where  $W_0$  represents the dry weight and  $W$  represents wet weight of each hydrogel.

## 2.9. Degradation performance of PVP/PVA hydrogel

The biodegradation of hydrogels (PVA, PP1, PP2, PP3 and PP4) was done employing the soil burial test. The trial was carried out in a tray (indoor) at relative humidity (36–92%) and room temperature ( $24\text{--}33^\circ\text{C}$ ), while the period of incubation was 30 days. Soil from the farm area of Cyprus International University was utilized. It was dampened with water and made to stand for 18 h to achieve even moisture. To obtain constant weight, polymeric hydrogel of PVA, PP1, PP2, PP3 and PP4 were dried under vacuum. Each of the samples was cut into quite a few pieces with a precise measurement ( $3 \times 3 \text{ cm}^2$ ) and concealed in the wet soil. After 30 days, the test samples were brought out, cleaned with water to get rid of the soil on the surface of the sample and dried at  $45^\circ\text{C}$  under a vacuum to arrive at constant weight. Degradation of each hydrogel was further performed in PBS at  $37^\circ\text{C}$ . The percentage of hydrogel weight loss was evaluated every week after lyophilization. The polymer degradation in both experiments was then determined using Eq. (5).

$$W_L(\%) = [(W_0 - W_n) / W_0] \times 100, \quad (5)$$

where  $W_0$  represents the original weight, and  $W_n$  represents the weight at the  $n$ th day of incubation.

## 3. Results

In the PVP/PVA sample, the signals of  $-\text{OH}$  groups resulting from hydrogen bonding are ascribed to  $3285 \text{ cm}^{-1}$ . A band around  $2900 \text{ cm}^{-1}$  characterising alkyl C–H stretching, was observed while a C–C broadening mode is noticed at  $946 \text{ cm}^{-1}$ . There was a variety of hydrogen bonding among hydroxyls of PVA chain and between hydroxyls of PVA chain and carbonyls of PVP chain, which was obviously demonstrated by the FTIR spectra shown in Fig. 1.

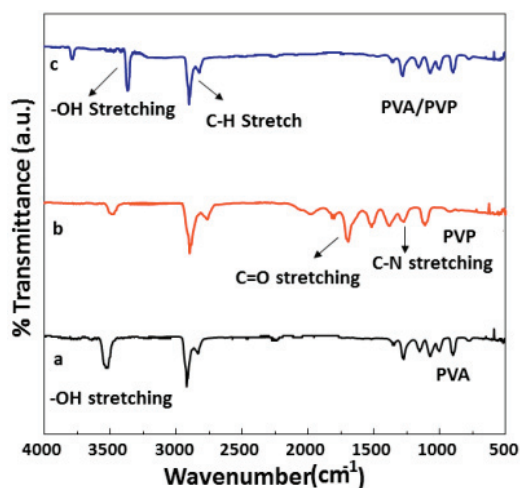


Fig. 1. FTIR spectra comparing of PVA, PVP and PVP/PVA freeze dried hydrogels

The SEM images of the unique microstructures of the PVA/PVP anisotropic hydrogels fabricated in this research were presented in Fig. 2. At microscale, slop-

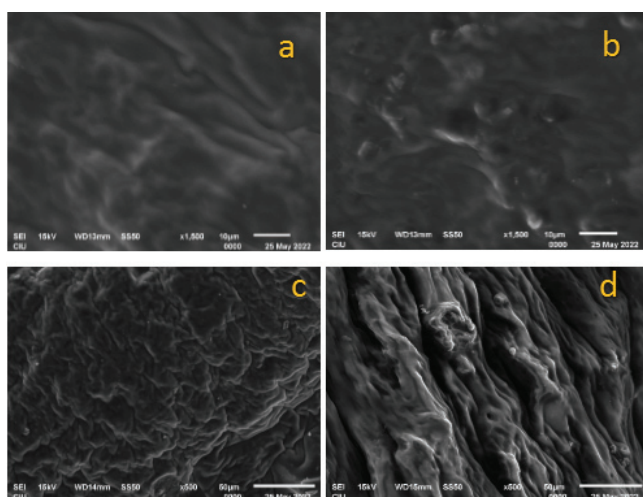


Fig. 2. SEM images of cross section of (a and b) PVP/PVA 50:50 (c) PVP/PVA 60:40 and (d) PVP/PVA 80:20 hydrogels in orthorhombic direction (scale bar 10  $\mu\text{m}$ )

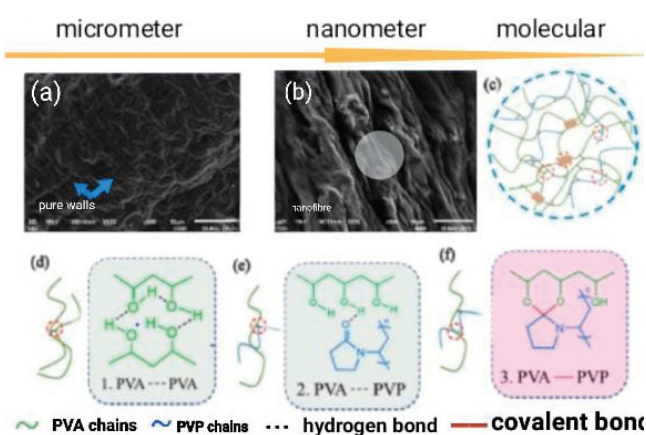


Fig. 3. Hierarchical structures of anisotropic hydrogels

ing networks resembling a fiber substructure between adjacent pore walls were shaped during the freeze drying-process (Figs. 2a, 3a). At molecular level, there was a range of hydrogen bonding, comprising the intramolecular and intermolecular several hydrogen bonds among hydroxyls of PVA chain (Fig. 2d), and between hydroxyls of PVA chain and carbonyls of PVP chain (Fig. 2d) [39], [40]. Several authors report that attributes projected for computer-generated PVA/PVP blend materials (Fig. 4) were constant with the investigational discoveries for analogous polymeric complexes prepared in the laboratory [41]. Furthermore, ketalization reaction between PVA chains and PVP chains resulted in a covalent cross-linking, under acid catalysis, there was a electrophilic reorganization between the carbonyl groups of PVP chain and the hydroxyl side-groups of PVA chain forming 1,3-dioxane between two polymers, which prompted the chemical cross-linking socket and resulted in a creation of molecularly cross-linked PVA/PVP networks (Fig. 2).

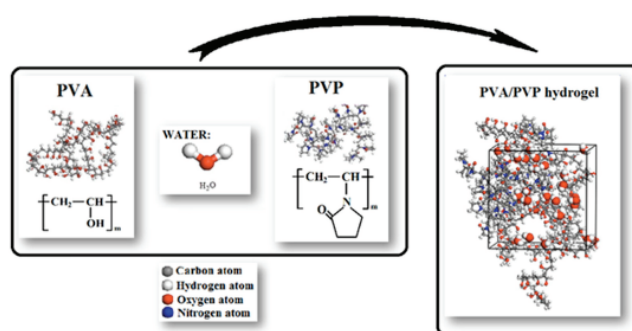


Fig. 4. Computer-generated microstructure of PVA/PVP hydrogel constructed by employing molecular dynamics model software Materials Studio (modified from Wei et al. [41])

Apparent densities and porosities of the hydrogels prepared are shown in Table 2. The prepared hydrogels showed increase in density from  $0.67 \pm 0.02$  g/cc to  $0.95 \pm 0.02$  g/cc, showing that the higher the amount of PVP in the blend, the higher the porosity. Hydrogels showed porosities in the range of  $45.00 \pm 1.00\%$  to  $81.80 \pm 0.20\%$ , indicating the increase in porosity with increase in PVP content, in this context, “porosity” designates the void volume between microspheres. This observation may be as a result of increase in cross-link density. The increase in porosity of the hydrogel is observed as a result of the formation of non covalent hydrogen bonding, which tends to increase the size of interlocking pores and the passageway structure. The images collected using SEM analysis support the formation of interconnected pore and capillary channels. A higher amount of PVP yields a bigger rate of hydrogel chains branching and creates a supplementary net-

work. By this means, with the higher PVP content, the hydrogen bonding density rises. Consequently, the network space gets increased.

XRD configurations of wholesome PVA hydrogel show distinctive diffraction peaks  $2\theta$  located at around  $19\text{--}21^\circ$  (Fig. 6). The pattern of this XRD is in agreement with those of Morariu [28] and Teodorescu [35]. These strong peaks resemble the (101) reflection, which indicate the presence of crystalline collections of PVA. The (101) diversion can be described by the consequence of intrusion between PVA macromolecules in the route of intermolecular H bonds [12], [35].

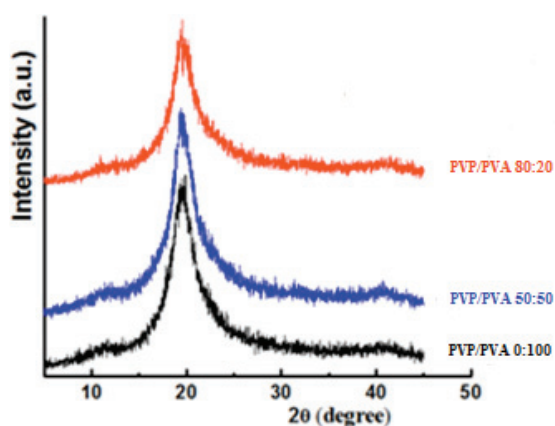


Fig. 5. XRD configurations of pure PVA and PVA/PVP hydrogels

XRD profiles of PVP/PVA blends also exhibit a core crystal peak concentrated at about  $20^\circ$  Bragg reflection as a result of PVA crystallinity, a number of minor signals at about  $2\theta \approx 12\text{--}13^\circ$ , and a wider unstructured peak of the mixed PVP/PVA, displaying semi-crystalline attribute of the blend having crystals dispersed in the formless structure [9], [12], [28].

Table 2. The physical properties of PVA and PVA/PVP hydrogel

Samples	Density	Porosity	Swelling ratio [%]	Swelling time
PVA	$0.67 \pm 0.02$	$45.00 \pm 1.00$	$3.93 \pm 0.34$	22
PP1	$0.70 \pm 0.02$	$55.70 \pm 0.10$	$10.43 \pm 0.22$	22
PP2	$0.74 \pm 0.00$	$65.00 \pm 0.50$	$36.58 \pm 0.22$	14
PP3	$0.84 \pm 0.01$	$75.10 \pm 0.10$	$83.50 \pm 0.29$	6
PP4	$0.90 \pm 0.02$	$81.80 \pm 0.20$	$95.58 \pm 0.35$	4

+ – means standard error.

The swelling behaviour of the freeze-dried hydrogels synthesized is shown in Table 2 at equilibrium time. The samples were subjected to swelling behaviour test for 24 hours in DDW. It was observed that the swelling ratio reached equilibrium time faster with increase in PVP content. The hydrogel generally exhibited increase in swelling capacity with increase in PVP content. This

observation is due to the fact that water molecule are taken up into hydrogel mainly by capillary forces in PVA hydrogel and the samples containing lesser amount of PVP, whereas as the content of PVP increases in the samples, water molecule is taken up by both diffusion process and capillary forces. PP3 and PP4 swollen in DDW showed relatively shorter swelling time as compared with PVA, PP1 and PP2 (Fig. 6). Overall the, decrease in PVP content tends to deprive swelling performance in the swelling media.

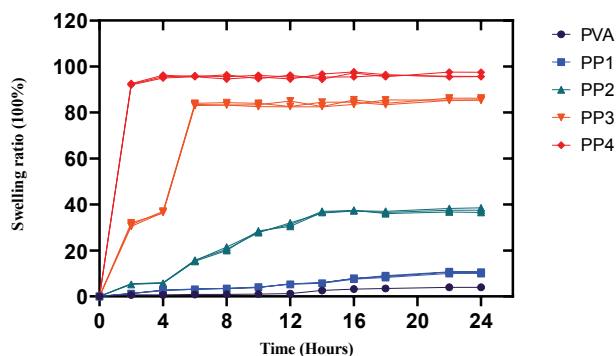
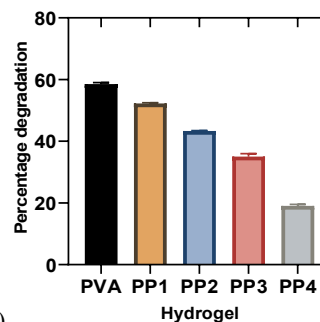
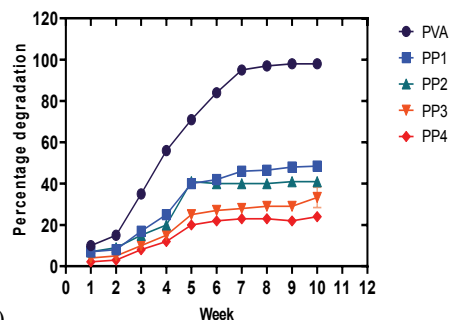


Fig. 6. Swelling behaviors of PVA/PVP hydrogels



(a)



(b)

Fig. 7. Percentage degradation in (a) soil and (b) PBS solution

The biodegradability property of any polymer considered a biomaterial is of utmost importance. The biodegradability of the prepared freeze-dried hydrogels was examined by employing the burial technique. The results indicated that wholesome PVA was the most decomposable, furthermore, the resistance to biodegradation augmented with the increment in PVP contents in the blended

hydrogel (Figs. 7). This observation is attributed to the increasing ratio of the cyclic compound PVP comprising pyridine cycles, providing the hydrogel more physical resistance compared to the pure aliphatic compound PVA. It was also noted that the sample with the highest PVP content is the most resistant to biodegradation.

## 4. Discussion

This study aimed to prepare PVP/PVA hydrogels using freeze drying technique for its characterization and to assess the biodegradability of the prepared hydrogel. FTIR was employed to ascertain the representative peak of the functional groups present in the prepared hydrogel. All peaks were validated using FTIR spectrum described by Pavia [31]. The FTIR ranges for the PVA, PVP and PVP/PVA freeze-dried hydrogels are displayed in Fig. 1. A characteristic peak of the O–H stretch vibration in PVA can be noticed at  $3400\text{--}3300\text{ cm}^{-1}$ ; between  $1150$  and  $1050\text{ cm}^{-1}$ , a signal that tallies to the C–O link can be seen, and around  $2900\text{ cm}^{-1}$ , a peak typical to alkyl C–H stretching is obvious. The PVP sample presented a wide peak at  $3447\text{ cm}^{-1}$  conforming to an overtone of C–O groups in the polymeric chains, another at  $2958\text{ cm}^{-1}$  attributed to alkyl C–H stretching signal, and a robust band seen around  $1660\text{ cm}^{-1}$  defined the stretching vibration of C=O ascribed to PVP. Stretching at  $1423\text{ cm}^{-1}$  is the C–H bending vibrations, and the signal at  $1285\text{ cm}^{-1}$  is related to the C–N vibration.

Hence, the linkage structures in the fabricated hydrogels were multi-scaled. It is observed that the hydrogel made of pure PVA without PVP did not possess the fibre-like arrangement [40]. The anisotropic hydrogels made with the use of a single-constituent aqueous polymer structures, such as PVA solution, usually had spotless honeycomb-like pore structure, void of the establishment of diverged structures. For the PVA/PVP blend system, the higher the PVP contents, the higher the viscidness of precursor by about one order of scale, which limited the polymer's chains diffusion in the course of freezing. Consequently, the evolution of the associated ice quatzes was restricted and some chains of polymer were entangled within the dendrites of ice crystal, resulting in the creation of channels between adjacent walls [40]. Thus, anisotropic PVA/PVP blend evidently exhibited dendritic structure among the pore walls, as shown in Fig. 2a. Furthermore, the SEM images obtained from this study is analogous to microstructures of natural cartilage dried under gamma-ray irradiation [31].

X-ray diffraction (XRD) examination offers vital facts concerning polymers crystallinity, thus it has been used for the characterization of PVA well as the mixture of PVA and PVP in this study.

In our study, the hydrogel was prepared by freeze-drying method, and it is observed that the addition of PVP have an influence on the crystallinity of the resulted samples [28], [35]. Thus, as the amount of PVP increased in the blends, a reduction in crystallinity was observed (e.g., 33.73% crystallinity degree for PVA/PVP hydrogels with 1% PVP, in contrast to 25.29% crystallinity grade for PVA/PVP hydrogels with 10% PVP, as reported by Morariu [28]). Therefore, the integration of some amounts of PVP contributes constructively in network steadiness of a polymer. Hence, crystallinity reduced as a result of nebulous nature of PVP, activated by the lesser capability of macromolecules to pack owing to pyrrolidone rings [35]. Some studies have shown that the existence of some quantities of PVP results in improved mechanical features (in shear conditions and compression) and more plane and less dishevelled hydrogel structure [28], [43]. PVP further decreases the measurement of friction owing to its greasing impact consequently reducing wear [11], [22], [28], [29]. Since natural tissues incorporate huge quantity of water, wholesome PVA-based materials have been indicted of a too condensed system with too insignificant permeability which does not permit them to adequately contain or appropriately swell fluids. Nevertheless, the usage of PVP as a pore forming booster for the PVA matrix results in biomaterials with a greater water content which is explained by the increased swelling ratio demonstrated with increasing amount of PVP in this investigation.

The documented percentage of biodegradation cannot be considered remarkable for plausible degradation of contaminants existing in PVP, which could have stayed there in the course of its fabrication [37]. This pattern may be as a result of the sorption of PVP to soil particles. The likely formation of complexes with PVP and soil constituents or with microbial enzymes which could result in the logged inhibition cannot also be totally excluded. The likelihood of the primary disintegration of PVP that could result in the formation of metabolites deterring soil microorganisms cannot be omitted [37]. Degradation tests of the prepared hydrogels (PVA, PP1, PP2, PP3 and PP4) were also conducted *in vitro*, where we submerged the hydrogels in PBS. Samples were placed under  $37\text{ }^{\circ}\text{C}$  and weighed at consistent intervals. At the same time, the results of the degradation test in PBS followed the same pattern as with that of soil degradation test. The higher the content of PVA in the hydrogel mix, the faster the hydrogel degraded.

The results of the degradation performance is similar to that of Abd El-Mohdy and Ghanem [1].

## 5. Conclusions

Concluding, PVP/PVA-based multi-constituent anisotropic hydrogels were synthesized through an easy technique of freeze-drying. This type of hydrogels, in contrast to single-component hydrogels has a better-off essential hierarchy and greater attributes a typical hydrogel for diverse applications ought to possess. It could be established that PVA-based hydrogel offers many inadequacies that can limit their suitability or performance. To conquer these restrictions, we have presented that blending PVA with PVP can improve vital properties of hydrogels such as porosity, swelling rate and crystallinity. Thus, the PVP/PVPA anisotropic hydrogels fabricated in this investigation have encouraging uses as useful or essential materials in diverse fields comprising robotics, artificial muscles, etc.

## Conflict of interest

Authors state no conflict of interest.

## References

- [1] ABD EL-MOHDY H.L., GHANEM S., *Biodegradability, antimicrobial activity and properties of PVA/PVP hydrogels prepared by  $\gamma$ -irradiation*, J. Polym. Res., 2008, 16 (1), 1–10, DOI: 10.1007/s10965-008-9196-0.
- [2] ALFURAYDI R., ALMINDEREF F., MOHAMED N., *Evaluation of Antimicrobial and Anti-Biofilm Formation Activities of Novel Poly(vinyl alcohol) Hydrogels Reinforced with Crosslinked Chitosan and Silver Nano-Particles*, Polymers, 2022, 14 (8), 1619, DOI: 10.3390/polym14081619.
- [3] BRANCO A.C., OLIVEIRA A.S., MONTEIRO I., NOLASCO P., SILVA D.C., FIGUEIREDO-PINA C.G. et al., *PVA-based Hydrogels Loaded with Diclofenac for Cartilage Replacement*, 2022, 8 (3), 143, DOI: 10.3390/gels8030143.
- [4] CHEN C., KANG Y., HUO Z., ZHU Z., HUANG W., XIN H.L., SNYDER J.D., LI D., HERRON J.A., MAVRIKAKIS M., CHI M., MORE K.L., LI Y., MARKOVIC N.M., SOMORJAI G.A., YANG P., STAMENKOVIC V.R., *Highly Crystalline Multimetallic Nano-frames with Three-Dim*, DOI: 10.1126/science.1249061.
- [5] CHOPRA H., BIBI S., KUMAR S., KHAN M.S., KUMAR P., SINGH I., *Preparation and Evaluation of Chitosan/PVA Based Hydrogel Films Loaded with Honey for Wound Healing Application*, 2022, 8 (2), 111, DOI: 10.3390/gels8020111.
- [6] CHU Z., XUE C., SHAO K., XIANG L., ZHAO X., CHEN C., PAN J., LIN D., *Photonic crystal-embedded molecularly imprinted contact lenses for controlled drug release*, ACS Appl. Bio Mater., 2021, 5 (1), 243–251, DOI: 10.1021/acsabm.1c01045.
- [7] CHUANGCHOTE S., SAGAWA T., YOSHIKAWA S., *Electrospinning of poly(vinyl pyrrolidone): Effects of solvents on electrospinnability for the fabrication of poly(p-phenylene vinylene) and TiO<sub>2</sub> nanofibers*, J. Appl. Polym. Sci., 2009, 114 (5), 2777–2791, DOI: 10.1002/app.30637.
- [8] DAS S., SUBUDDHI U., *Controlled delivery of ibuprofen from poly(vinyl alcohol)–poly(ethylene glycol) interpenetrating polymeric network hydrogels*, JPA. 2019, 9 (2), 108–116, DOI: 10.1016/j.jpha.2018.11.007.
- [9] ELASHMAWI I., ABDEL BAIETH H., *Spectroscopic studies of hydroxyapatite in PVP/PVA polymeric matrix as biomaterial*, Curr. Appl. Phys., 2012, 12 (1), 141–146, DOI: 10.1016/j.cap.2011.05.011.
- [10] FATIMI A., OKORO O.V., PODSTAWCZYK D., SIMIŃSKA-STANNY J., SHAVANDI A., *Natural Hydrogel-based Bio-Inks for 3D Bioprinting in Tissue Engineering: A Review*, 2022, 8 (3), 179, DOI: 10.3390/gels8030179.
- [11] GUO Y., HAO Z., WAN C., *Tribological characteristics of polyvinylpyrrolidone (PVP) as a lubrication additive for artificial knee joint*, Tribology International, 2016, 93, 214–219, DOI: 10.1016/j.triboint.2015.08.043.
- [12] GUPTA S., WEBSTER T.J., SINHA A., *Evolution of PVA gels prepared without crosslinking agents as a cell adhesive surface*, J. Mater. Sci. Mater. Med., 2011, 22 (7), 1763–1772, DOI: 10.1007/s10856-011-4343-2.
- [13] HOLLOWAY J.L., LOWMAN A.M., PALMESE G.R., *The role of crystallization and phase separation in the formation of physically cross-linked PVA hydrogels*, Soft Matter, 2013, 9 (3), 826–833, DOI: 10.1039/c2sm26763b.
- [14] HU X., TAN H., HAO L., *Functional hydrogel contact lens for drug delivery in the application of ophthalmology therapy*, J. Mech. Behav. Biomed. Mater., 2016, 64, 43–52, DOI: 10.1016/j.jmbbm.2016.07.005.
- [15] HUANG M., HOU Y., LI Y., WANG D., ZHANG L., *High performances of dual network PVA hydrogel modified by PVP using borax as the structure-forming accelerator*, Des. Monomers Polym., 2017, 20 (1), 505–513, DOI: 10.1080/15685551.2017.1382433.
- [16] JALAGERI M.B., MOHAN KUMAR G.C., *Hydroxyapatite Reinforced Polyvinyl Alcohol/Polyvinyl Pyrrolidone Based Hydrogel for Cartilage Replacement*, Gels, 2022, 8, 555, DOI: 10.3390/gels8090555.
- [17] JENSEN B.E., EDLUND K., ZELIKIN A.N., *Micro-structured, spontaneously eroding hydrogels accelerate endothelialization through presentation of conjugated growth factors*, Biomaterials, 2015, 49, 113–124, DOI: 10.1016/j.biomaterials.2015.01.036.
- [18] JIANG H., YANG Y., LIN Z., ZHAO B., WANG J., XIE J., ZHANG A., *Preparation of a novel bio-adsorbent of sodium alginate grafted polyacrylamide/graphene oxide hydrogel for the adsorption of heavy metal ion*, Sci. Total Environ., 2020, 744, 140653, DOI: 10.1016/j.scitotenv.2020.140653.
- [19] KANCA Y., MILNER P., DINI D., AMIS A.A., *Tribological properties of PVA/PVP blend hydrogels against articular cartilage*, J. Mech. Behav. Biomed. Mater., 2018, 1 (78), 36–45, DOI: 10.1016/j.jmbbm.2017.10.027.
- [20] KUIPER J.P., PUTTLITZ C.M., RAWLINSON J.E., DOBBS R., LABUS K.M., *A mechanical evaluation of polyvinyl alcohol hydrogels for temporomandibular joint disc replacement*, Front. Phys., 2022, 10, 928579, DOI: 10.3389/fphy.2022.928579.
- [21] LI P., JIANG S., YU Y., YANG J., YANG Z., *Biomaterial characteristics and application of silicone rubber and PVA hydrogels mimicked in organ groups for prostate brachytherapy*,



- J. Mech. Behav. Biomed. Mater, 2015, 49, 220–234, DOI: 10.1016/j.jmbbm.2015.05.012.
- [22] MA R., XIONG D., MIAO F., ZHANG J., PENG Y., *Friction properties of novel PVP/PVA blend hydrogels as artificial cartilage*, J. Biomed. Mater Part A, 2009, 9999, DOI: 10.1002/jbm.a.32552.
- [23] MALKA E., DOMBROVSKY A., MARGEL S., *Preparation and Characterization of a Novel PVA/PVP Hydrogel Containing Entrapped Hydrogen Peroxide for Agricultural Applications*, ACS Agric. Sci. Technol., 2022, 2 (3), 430–436, DOI: 10.1021/acscagritech.2c00003.
- [24] MARANI D., SUDIREDDY B.R., NIELSEN L., NDONI S., KIEBACH R., *Poly(vinylpyrrolidone) as dispersing agent for cerium-gadolinium oxide (CGO) suspensions*, J. Mater. Sci., 2015, 51 (2), 1098–1106, DOI: 10.1007/s10853-015-9439-5.
- [25] MARUI Y., KIDA T., AKASHI M., *Facile Morphological Control of Cyclodextrin Nano- and Microstructures and Their Unique Organogelation Ability*, Chem. Mater, 2009, 22 (2), 282–284, DOI: 10.1021/cm903407e.
- [26] MASTRANGELO R., CHELAZZI D., POGGI G., FRATINI E., PENSABENE BUEMI L., PETRUZZELLIS M.L., BAGLIONI P., *Twin-chain polymer hydrogels based on poly(vinyl alcohol) as new advanced tool for the cleaning of modern and contemporary art.*, Proc. Natl. Acad. Sci., 2020, 117 (13), 7011–7020, DOI: 10.1073/pnas.1911811117.
- [27] MAULVI F.A., LAKDAWALA D.H., SHAIKH A.A., DESAI A.R., CHOKSI H.H., VAIDYA R.J., RANCH K.M., KOLI A.R., VYAS B.A., SHAH D.O., *In vitro and in vivo evaluation of novel implantation technology in hydrogel contact lenses for controlled drug delivery*, JCR. 2016, 226, 47–56, DOI: 10.1016/j.jconrel.2016.02.012.
- [28] MORARIU S., BERCEA M., TEODORESCU M., AVADANEI M., *Tailoring the properties of poly(vinyl alcohol)/poly(vinylpyrrolidone) hydrogels for biomedical applications*, Eur. Polym. J., 2016, 84, 313–325, DOI: 10.1016/j.eurpolymj.2016.09.033.
- [29] NKHWA S., LAURIAGA K.F., KEMAL E., DEB S., *Poly(vinyl alcohol): Physical Approaches to Designing Biomaterials for Biomedical Applications*, Conference Papers in Science, 2014, 1–7, DOI: 10.1155/2014/403472.
- [30] OUSTADI F., HAGHBIN NAZARPAK M., MANSOURI M., KETABAT F., *Preparation, characterization, and drug release study of ibuprofen-loaded poly (vinyl alcohol)/poly (vinyl pyrrolidone) bilayer antibacterial membrane*, Int. J. Polym. Mater, 2020, 71 (1), 14–23, DOI: 10.1080/00914037.2020.1798437.
- [31] PAVIA D.L., LAMPMAN G.M., VYVYAN J.R., *Introduction to Spectroscopy.*, 2015.
- [32] SHI Y., XIONG D., ZHANG J., *Effect of irradiation dose on mechanical and biotribological properties of PVA/PVP hydrogels as articular cartilage*, Tribol. Int., 2014, 78, 60–67, DOI: 10.1016/j.triboint.2014.05.001.
- [33] SONG H.S., KWON O.S., KIM J.H., CONDE J., ARTZI N., *3D hydrogel scaffold doped with 2D graphene materials for biosensors and bioelectronics*, Biosens. Bioelectron., 2017, 89, 187–200, DOI: 10.1016/j.bios.2016.03.045.
- [34] TAVAKOLI M., ALHAIS LOPES P., HAJALILOU A., SILVA A.F., REIS CARNEIRO M., CARVALHEIRO J., MARQUES PEREIRA J., DE ALMEIDA A.T., *3R Electronics: Scalable Fabrication of Resilient, Repairable, and Recyclable Soft-Matter Electronics*, Adv. Mater. 2022, 34 (31), 2203266, DOI: 10.1002/adma.202203266.
- [35] TEODORESCU M., BERCEA M., MORARIU S., *Biomaterials of PVA and PVP in medical and pharmaceutical applications: Perspectives and challenges*, Biotechnol. Adv., 2019, 37 (1), 109–131, DOI: 10.1016/j.biotechadv.2018.11.008.
- [36] TORRES-MARTÍNEZ E.J., VERA-GRAZIANO R., CERVANTES-UC J.M., BOGDANCHIKOVA N., OLIVAS-SARABIA A., VALDEZ-CASTRO R., SERRANO-MEDINA A., IGLESIAS A.L., PÉREZ-GONZÁLEZ G.L., CORNEJO-BRAVO J.M., VILLARREAL-GÓMEZ L.J., *Preparation and characterization of electrospun fibrous scaffolds of either PVA or PVP for fast release of sildenafil citrate*, e-Polymers, 2020, 20 (1), 746–758, DOI: 10.1515/epoly-2020-0070.
- [37] VANHAROVA L., JULINOVA M., SLAVIK R., *PVP-based Materials: Biodegradation in Different Environments*, Ecol. Chem. Eng. S S, 2017, 24 (2), 299–309, DOI: 10.1515/eces-2017-0021.
- [38] WANG M., BAI J., SHAO K., TANG W., ZHAO X., LIN D., HUANG S., CHEN C., DING Z., YE J., *Poly (vinyl alcohol) hydrogels: The old and new functional materials*, Int. J. Polym. Sci., 2021, 30 (2021), 1–6, DOI: 10.1155/2021/2225426.
- [39] WANG N., LIU Z., YANG J., SONG Y., YANG J., *Investigation of antibacterial activity of one-dimensional electrospun Walnut green husk extract-PVP nanofibers*, Iran. Polym. J., 2022, 31 (6), 779–785, DOI :10.1007/s13726-022-01037-9.
- [40] WANG Y., LI J., MUHAMMAD N., WANG Z., WU D., *Hierarchical networks of anisotropic hydrogels based on cross-linked Poly(vinyl alcohol)/Poly(vinylpyrrolidone)*, Polymer, 2022, 251, 124920, DOI: 10.1016/j.polymer.2022.124920.
- [41] WEI Q., ZHANG Y., WANG Y., CHAI W., YANG M., *Measurement and modeling of the effect of composition ratios on the properties of poly(vinyl alcohol)/poly(vinyl pyrrolidone) membranes*, Mater. Des., 2016, 103, 249–258, DOI: 10.1016/j.matdes.2016.04.087.
- [42] YURONG G., DAPENG L., *Preparation and characterization of corn starch/PVA/glycerol composite films incorporated with  $\epsilon$ -polylysine as a novel antimicrobial packaging material*, e-Polymers, 2020, 20 (1), 154–161, DOI: 10.1515/epoly-2020-0019.
- [43] ZHENG Y., HUANG X., WANG Y., XI T., CHEN X., XU H., *The surface lubricative properties of PVA/PVP hydrogels treated with radiation used as artificial cartilage*, Appl. Surf. Sci., 2008, 255 (2), 568–570, DOI: 10.1016/j.apsusc.2008.06.144.