Analyses of structure and thermal properties of synthesized crosslinked poly(1-vinyl-2-pyrrolidone-*co*-vinyl acetate) hydrogels

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ABSTRACT

This paper describes the process for the synthesis of chemically crosslinked copolymer hydrogels based on monomer 1-vinyl-2-pyrrolidone and comonomer vinyl acetate, using the varied content of ethylene glycol dimethacrylate as a crosslinker, by the free radical polymerization method with thermal initiation. The content of unreacted reactants after poly(1-vinyl-2-pyrrolidone-co-vinyl-acetate), p(VP-VA), hydrogels synthesis was examined using high-pressure liquid chromatography (HPLC) method. Structure characterization of the obtained p(VP-VA) hydrogels was performed using the Fourier transform infrared spectroscopy (FTIR). In this study, the influences of crosslinker content and temperature on the swelling behaviour of p(VP-VA) were studied. Quantities of unreacted comonomers and crosslinker, calculated in relation to the initial amount present in the reaction mixture, confirmed their successful conversion into p(VP-VA) hydrogels. These unreacted values of 1-vinyl-2-pyrrolidone (in range of 0.605-1.609%), vinyl acetate (in range of 2.486-4.798%), and ethylene glycol dimethacrylate (in range of 0.889-3.240%) were within acceptable limits, and they were removed from the final products. FTIR spectra were verified that the copolymerization process was performed, and chemically crosslinking of polymer chains occurred by breaking double bonds from the reactants. Obtained crosslinked copolymers could be classified in the class of negative-thermosensitive hydrogels because they can swell and pass through a phase transition when heated from the swollen state at 25ºC to contracted state at 80ºC.

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Introduction

The monomer 1-vinyl-2-pyrrolidone, VP, has widely applied polymer for the production of homopolymer poly(1-vinyl-2-pyrrolidone) (p(VP)), heteropolymers and copolymers with acrylic acid, acrylates, vinyl acetate, and also with other monomers (Teodorescu and Bercea, 2015). It has unique, remarkable physical and chemical properties, such as chemical stability, good solubility in water and many organic solvents, affinity to complex both hydrophobic and hydrophilic substances, biocompatibility, nontoxicity. Thanks to these properties it is suitable as a biomaterial in various significant pharmaceutical and medical applications and many non-medical applications (*i.e.*, environmental, optical, electrical). Crosslinked polymers based on VP can be obtained by a series of processes as: a) slightly crosslinked (by γ-radiation) (Henglein, 1959) or by treatment with persulphate (Anderson et al., 1979) or with hydrazine and hydrogen peroxide (Schildknecht, 1953), b) more densely crosslinked (by copolymerization with crosslinkers) (Atkins et al., 1972); c) highly crosslinked products, obtained by popcorn or proliferous polymerization (Haaf et al., 1985).

Vinyl acetate, VA, is used as a monomer to synthesize poly(vinyl acetate), p(VA), and many copolymers. It is used as wood glue, known as "white glue", as paper glue, and yellow "carpentry glue", thanks to strong, flexible bonds and non-acidic nature. Also, it is used in paper coatings, paints, and other industrial coatings, as a binder in the nonwoven fabric in glass fibers, filter paper, and textile finishing.

Poly(1-vinyl-2-pyrrolidone-vinyl acetate), p(VP-VA), as a well-known copolymer, was usually produced as a white or yellowish-white powder, or colorless or yellowish transparent liquid (Ashland, 2022). The pharmaceutical industry has used it for decades, *i.e.*, as a processing aid in the production of granules and tablets, as a binder in direct compression, in film coatings on tablets, as a protective layer, and subcoat for tablet cores. Due to the fact that there is no irritation for skin and eyes, it has been mainly used for hair care products as a finalizing agent, film-forming agent, and viscosity regulator. Two commercial products of the p(VP-VA) copolymer are available in the market having the pharmaceutical quality required by the Pharmacopoeias (the European

Pharmacopeia (Ph. Eur. 10), the USP-NF monograph "Copovidone", Japanese Pharmaceutical Excipients) (Bühler, 2005).

Water-soluble p(VP-VA) copolymer contains the two components, VP and VA, in different ratios (60:40, 50:50, 70:30, 30:70, 35:65) and a wide range of molecular weights (Ashland, 2022). According to EP 0104042 (Eugene and James, 1982), VP and VA comonomers were polymerized using free radical initiator *tert*-butylperoxypivalate in a solvent consisting of water, isopropyl alcohol, secondary butyl alcohol, or mixtures thereof. Also, p(VP-VA) copolymer was produced by free radical polymerization method in 2-propanol with an organic peroxide as an initiator (Bühler, 2005). This copolymer is slightly more hydrophobic compared to homopolymer p(VP) because its VA comonomer is not soluble in water.

The powder p(VP-VA) copolymer is a spray-dried product in the form of deformed or partly broken hollow spherical particles. This irregular structure is one of the important reasons for the excellent dry binding properties of powder p(VP-VA) copolymer in the direct compression technology of tablets (Bühler, 2005).

Based on scientific opinion on the safety, the p(VP-VA) copolymer is safe for application in FDA approved food supplements, as a food additive, *e.g.*, in tablet form as a binding/coating agent in an amount of up to 10% of weight per tablet weight of 1000 mg (D'Amelia et al., 2019). The p(VP-VA) copolymers have found great application in the cosmetic industry, primarily in personal care products, in the manufacture of hair care products (Personal Care Products Council, 2017; Rothe et al., 2011).

The resins p(VP-VA) were produced as linear, random copolymers by the free-radical polymerization of the varying monomers ratios from 70/30 to 30/70 vinyl acetate to vinylpyrrolidone as 50% w/w ethanolic solutions (Browne et al., 2020). The commonly used p(VP-VA) polymer in amorphous solid dispersion systems has a VP:VA ratio 6:4, but it would be interesting to examine the effect of different ratios (*i.e.*, 4:6 and 5:5) for improvement the commercially used polymers.

Risk Assessment is important for VP to all environmental compartments for production, processing, and use of VP and release of VP during use of polymers which contain residual VP monomer, according to European Union Report (European Commision, 2003).

The term "hydrogel" is used to describe two- or multicomponent systems consisting of a three-dimensional network of polymer chains and water or fluid that fills the space between

macromolecules. Hydrogel networks can absorb different amounts of water or fluids within their structure, usually swell to equilibrium, but without dissolution (Gulrez et al., 2011). Hydrogels that show changes in swelling under the action of external stimuli from the environment, such as pH, temperature, light intensity, belong to the group of stimuli sensitive hydrogels, or "intelligent" materials (Ilić-Stojanović et al., 2017).

This work aims to synthesize chemically crosslinked copolymer hydrogels of 1-vinyl-2-pyrrolidone with 10 mol% of vinyl acetate by the free radical polymerization method with thermal initiation and their structure characterization, as well as the swelling behavior in relation to the temperature changes.

Experimental

Reagents

1-Vinyl-2-pyrrolidone, VP, ≥99.0% (Merck KGaA, Darmstadt, Germany), vinyl acetate, VA, ≥99.0% (Merck KGaA, Darmstadt, Germany), ethylene glycol dimethacrylate, EGDM, 97.0% (Fluka Chemical Corp, CH), 2,2'-azobis(2-methylpropionitrile), 98.0% (Acros Organics, New Jersey, USA), methanol, 99.5% (Merck KGaA), and methanol HPLC grade, 99.9% (Chromasolv, Sigma-Aldrich Chemie GmbH, DE). All chemicals were used as received.

Hydrogel synthesis

Polymerization of 1-vinyl-2-pyrrolidone monomers and vinyl acetate comonomers (10 mol%, relative to the amount of 1-vinyl-2-pyrrolidone monomer) was performed using the free radical polymerization method. Various amounts of ethylene glycol dimethacrylate (1.0; 1.5; 2.0; 2.5 and 3.0 mol% relative to the total amount of monomer) were used for crosslinking of long-chain polymer chains. The reactants were dissolved in methanol, and the 2,2'-azobis(2-methylpropionitrile) as initiator was added in the reaction mixtures (2.7 mol%). After homogenization and dissolution of the reactants, the reaction mixtures were injected into glass ampoules, which were closed after that. The polymerization process for all samples was thermally initiated, according to the following temperature regime: 30 min at 70°C, 120 min at 80°C, and 90 min at 85°C. After cooling, the obtained copolymer hydrogels poly(1-vinyl-2-pyrrolidone-*co*-vinyl acetate) were separated from glass ampoules in the form of long cylinders and cut into smaller cylinders.

Extraction of unreacted compounds

The hydrogels p(VP-VA) were then immersed in methanol (60 cm^3 of methanol per 1.0 g of hydrogel) and stirred for 48 h at room temperature to extract all unreacted compounds and any impurities. After treatment with methanol, the p(VP-VA) hydrogels were successively immersed in fresh methanol/distilled water solutions: 80/20%, 60/40%, 40/60%, 20/80%, and 0/100%, v/v, for 24 h, to gradually washed the methanol from obtained products. Purified hydrogels p(VP-VA) were dried in an oven at 40°C to constant masses, after which they were subjected to further characterization.

Characterization of synthesized hydrogels

Analysis of unreacted contents of comonomers and crosslinker

Analyses of the qualitative and quantitative composition of unreacted comonomers of VP and VA and EGDM crosslinker, from methanolic extracts decanted after synthesis of p(VP-VA) hydrogels, were performed by using high-pressure liquid chromatography (HPLC) method. For these analyses, the construction of calibration curves is necessary using standard substances. Firstly, three series of standard solutions substances (VP, VA, and EGDM) with known concentrations (0.005-1.000 $mg \cdot cm^{-3}$) were prepared in methanol as solvent. All samples for HPLC analysis were filtered through a cellulose membrane filter with a pore diameter of 0.45 μm and analyzed using defined conditions. The HPLC Agilent 1100 Series is equipped with a DAD 1200 detector with adjustable absorption wavelength and automatic sampling of the adjusted injected volume. The detector was set to wavelengths of 205 nm and 209 nm. The ZORBAX Eclipse XDB-C18 column, 4.6 × 250 mm, 5 μm, was applied. The mobile phase (eluent) was: (A) methanol HPLC purity, 80% and (B) redistilled water, 20%. The column was thermostated at 30°C, the flow rate of the mobile phase was 1 $cm^3 \cdot min^{-1}$, and the analysis time was 10 min. The injected volumes of the analyzed samples were 10 μl each. The obtained data for standard solutions and methanolic extracts decanted after p(VP-VA) synthesis were processed using Agilent ChemStation software.

Fourier transform infrared spectrophotometry (FTIR)

The FTIR spectra of liquid VP and VA comonomers were measured using the capillary film method between two polished CaF_2 plates. FTIR spectra of a synthesized sample of p(VP-

VA) xerogels with 10 mol% of the VA comonomer and 3.0 mol% of EGDM were ground to powder state in an amalgamator (WIG-L-BVG, 31210-3A, USA) and then recorded by the thin transparent pellets technique with potassium bromide of spectroscopic purity, after vacuuming and pressing under a pressure of about 200 MPa. All samples were recorded on an FTIR spectrophotometer Bomem Hartmann & Braun MB-series (Baptiste, Canada) in the wavenumbers range from 4000 to 400 cm^{-1}. Win-Bomem Easy software was used to process the recorded FTIR spectra of the reactants and the resulting products.

Thermosensitivity analysis

The temperature sensitivity of the synthesized p(VP-VA) hydrogels was examined by monitoring the change of the equilibrium swelling degree with increasing temperature in the range from 25ºC to 80ºC in a distilled water, which pH value was 6.0, measured using pH meter (HI9318-HI9219, Hanna, Portugal). The swelling process of p(VP-VA) samples was monitored gravimetrically. Firstly, the samples of dried hydrogels (xerogels) p(VP-VA) with 10 mol% VA and 1.0; 1.5; 2.0; 2.5 and 3.0 mol% of EGDM as a crosslinker, were immersed into the fluid at a temperature of 25ºC. The masses of the swollen samples were measured at a specific time until equilibrium was reached at a defined temperature. Changes in the swelling degree, α, and the equilibrium swelling degree, α_e, were calculated using equations (1) and (2), respectively, as the ratio of the mass of absorbed fluid and the xerogels mass:

$$\alpha = \frac{m_t - m_0}{m_0} \quad (1)$$

$$\alpha_e = \frac{m_e - m_0}{m_0} \quad (1)$$

m_o is the xerogel mass, m_t is the mass of the swollen hydrogel at the time *t*, and m_e is the mass of the hydrogel swollen at equilibrium state.

Results and Discussion

Synthesis of copolymer hydrogels p(VP-VA)

Free radical polymerization, as the most probable mechanism, was applied for the synthesis of a series of poly(1-vinyl-2-pyrrolidone-*co*-vinyl acetate) copolymer hydrogels with 10 mol%

vinyl acetate as comonomer and 1.0; 1.5; 2.0; 2.5 and 3.0 mol% EGDM as crosslinker. The reaction of free radical polymerization was initiated by the homolytic decomposition of the initiator 2,2`-azobis(2-methylpropionitrile) at a temperature higher than 70ºC. Produced primary radicals were transferred by adding the primary active center of the initiator most probable to the unsaturated vinyl groups of the 1-vinyl-2-pyrrolidone and the vinyl acetate molecules. Linear chains were probably crosslinked from two vinyl groups from the ethylene glycol dimethacrylate molecule during the propagation phase. The crosslinking between the linear chains was possibly performed thanks to two vinyl groups in the EGDM molecule. After the termination phase of the polymerization process, synthesized p(VP-VA) copolymer hydrogels were formed, with a possible structure presented at Figure 1(a). All copolymer hydrogels p(VP-VA) samples were of stable shape and soft consistency. The appearance of samples of synthesized copolymer hydrogels p(VP-VA) with 1.0 and 2.5 mol% of EGDM crosslinker was presented in Figures 1(b) and 1(c). Synthesized p(VP-VA) hydrogels were characterized in terms of chemical structure by the FTIR method, the amount of unreacted reactants during synthesis was calculated, and the swelling degree was examined depending on the surrounding temperature.

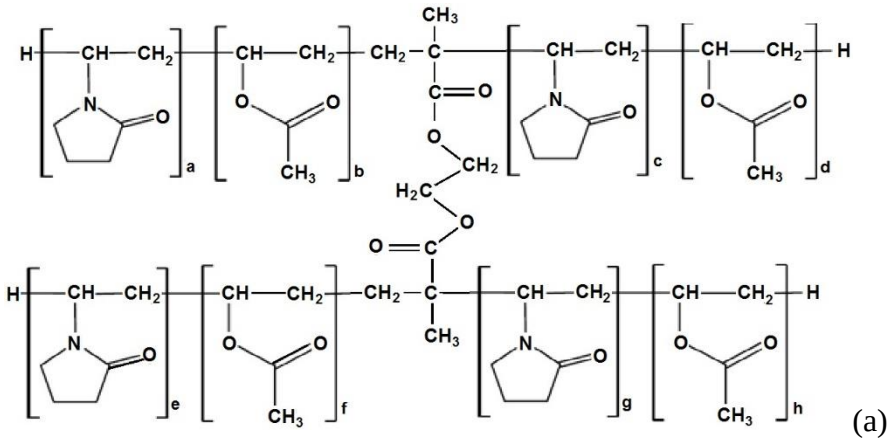
Analysis of unreacted contents of comonomers and crosslinker

The series of standards solutions with known amounts of VP, VA, and EGDM were prepared for the calibration curve construction and analyzed by the HPLC method. The quantification of the amount of the released VP and EGDM as a function of time was performed using the previously published method (Ilić-Stojanović and Eraković, 2019).

Calibration curve for 1-vinyl-2-pyrrolidone

The HPLC chromatogram of the VP standard solution had a retention time of R_t=3.191 min, and the maximum wavelength of UV absorption at λ_{max}=209 nm. The constructed calibration curve for VP was linear for peak areas in the range of 0.007-0.804 mg·cm^{-3}, *i.e.*, for peak areas in the range of 126-12200 mAU·s (Figure 2(a)); for this linearity equation (2) applies (Ilić-Stojanović and Eraković, 2019):

$$A_{209nm} = 124{,}20 + 16708{,}57 \cdot c_{VP} \qquad (2)$$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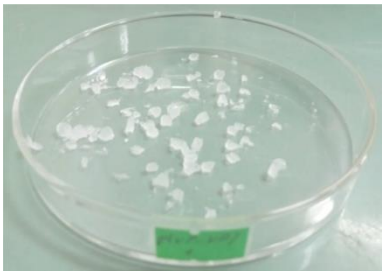
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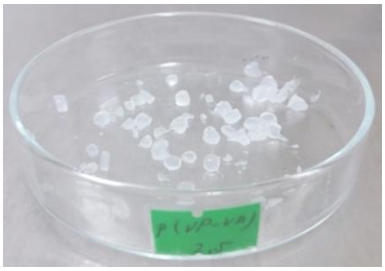

(c)

Figure 1. (a) Potential structural formula of crosslinked poly(1-vinyl-2-pyrrolidone-co-vinyl acetate) hydrogel. The appearance of synthesized hydrogels with 10 mol% vinyl acetate comonomer with (b) 1.0 mol% of EGDM as a crosslinker, and (c) 2.5 mol% of EGDM.

A_{209nm} is the peak area at λ_{max}=209 nm in mAU·s, c_{VP} is the concentration of VP in mg·cm^{-3}, the linear correlation coefficient is R^2=0.999, and the standard deviation of the blank is σ=106,408. The limit of detection, LoD, as the smallest amount or concentration of the analyte in the test sample that can be reliably distinguished from zero, was 0.0191 mg·cm^{-3}. The limit of quantitation (LoQ), as the lowest concentration of the analyte that can be determined with an acceptable repeatability and trueness, was 0.0637 mg·cm^{-3}.

Calibration curve for ethylene glycol dimethacrylate

The HPLC chromatogram of the EGDM standard solution under given conditions has a retention time R_t=6.125 min, and the UV spectrum shows the maximum absorption at λ_{max}=205 nm. The dependence of the peak area on the EGDM concentration is linear in the range of 0.005-0.3 mg·cm^{-3}, *i.e.*, for peak areas in the range of 300-18000 mAU·s. Equation (3) applies to the linear part of the constructed calibration curve for EGDM (Figure 2(b)) (Ilić-Stojanović and Eraković, 2019):

$$A_{205nm} = -19{,}34 + 76188{,}09 \cdot c_{EGDM} \quad (3)$$

where A_{205nm} is the peak area (mAU·s) at λ_{max}=205 nm, c_{EGDM} is the content of EGDM (mg·cm^{-3}), the linear correlation coefficient is R^2=0.999, σ=25.176, LoD=9.91·10^{-4}mg·cm^{-3}, and LoQ=0.0033 mg·cm^{-3}.

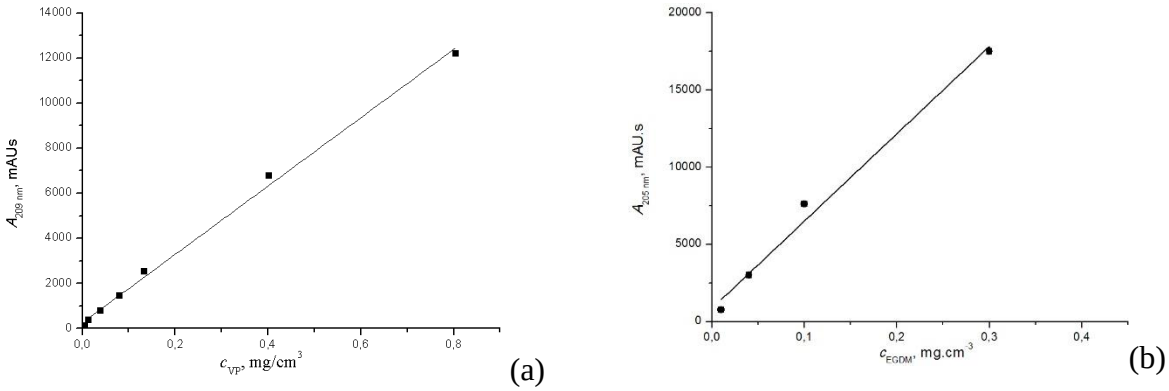


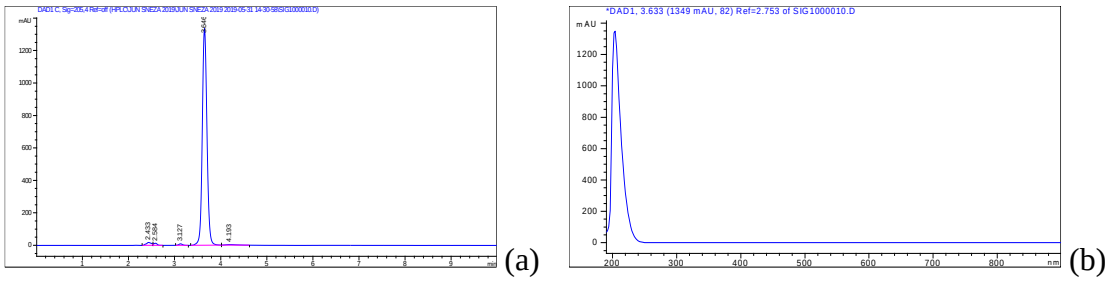
Figure 2. Calibration curve for: (a) 1-vinyl-2-pyrrolidone, (b) ethylene glycol dimethacrylate

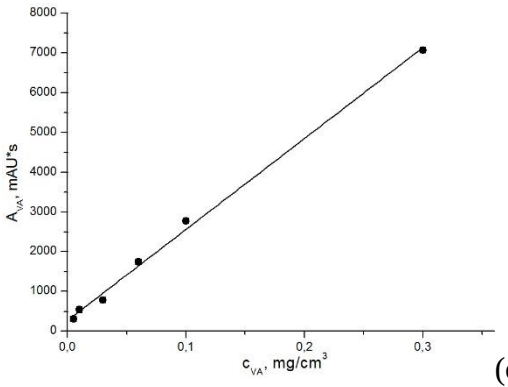
Calibration curve for vinyl acetate

On the HPLC chromatogram of the standard solutions, vinyl acetate has a retention time R_t=3.666 min (Figure 3(a)). The wavelength at which the maximum absorption in the UV region for VA occurs is λ_{max}=205 nm. The UV spectrum of the VA standard is shown in Figure 3(b). For the constructed calibration curve of the comonomer VA (Figure 3(c)) in the linear range (for peak areas in the range of 300-7100 mAU·s, *i.e.*, in the range of 0.005-0.300 mg·cm^{-3}), the equation (4) applies:

$$A_{205nm} = 276{,}88 + 22856{,}46 \cdot c_{VA} \quad (4)$$

A_{205nm} is the peak area (mAU s) at λ_{max}= 205 nm, c_{VA} is the content of VA comonomer in mg·cm^{-3}, where the linear correlation coefficient was R^2=0.997, σ=155.299, LoD=0.0204 mg·cm^{-3}, and LoQ=0.0679 mg·cm^{-3}.





(c)

Figure 3. Vinyl acetate: (a) HPLC chromatogram, R_t=3.666 min, (b) UV spectrum, λ_{max}=205 nm, (c) calibration curve.

Unreacted amounts of comonomers and crosslinker after p(VP-VA) synthesis

Methanol extracts from polymerized p(VP-VA) copolymer hydrogels were analyzed using the HPLC method to determine the unreacted amount of monomer, comonomer, and crosslinker during polymerization. Data from the peaks integration of the analyzed methanol extracts and the obtained values of peaks area were in the range of the calibration curve. The unknown contents of VP, EGDM, and VA in the decanted methanol extracts were calculated based on the constructed calibration curves using equations (2), (3), and (4), respectively. The peaks of all reactants in the tested samples are sharp and symmetrical, and the chromatographic conditions were determined to allow clear separation and detection. The HPLC method for the determination of VP and VA in copovidone according to the Ph. Eur. monograph "Povidone" (Impurity A), comprising mobile phase water/acetonitrile 92/8 (%w/w), column temperature 40 °C, retention time: 9–11 min (vinyl acetate) and 12-14 min (vinylpyrrolidone) (Bühler, 2005). The fast methods using gel permeation chromatography (GPC) and reverse-phase high-pressure liquid chromatography (RP HPLC) techniques were used to separate and quantify residual VP monomer present in homopolymer p(VP) and a copolymer of VP and vinyl caprolactam (Senak et al., 2008). Fast GPC and RP HPLC analyses were quantitatively compared to industrial and European Pharmacopeia methodologies. The presented method was different from the published method in Eur Ph 5 and provided faster analysis at lower temperature (Bühler, 2005). The results of the unreacted quantities of VP, VA, and EGDM during p(VP-VA) synthesis were calculated in relation to their amount present in the reaction mixture at the beginning of reaction compared to the total xerogel mass (in $mg \cdot g^{-1}$), and

to the initial amount present in the reaction mixture (in %), were shown in Tables 1 and 2, respectively.

Table 1. Unreacted amounts of 1-vinyl-2-pyrrolidone, vinyl acetate, and ethylene glycol dimethacrylate, calculated in relation to the total mass of p(VP-VA) xerogels ($mg \cdot g^{-1}$), the peaks area values of the methanol extract samples and masses of xerogels samples.

p(VP-VA) sample	sample mass, g	unreacted reactants compared to the total xerogel mass, $mg \cdot g^{-1}$					
		A_{VP}, mAU·s	VP	A_{VA}, mAU·s	VA	A_{EGDM}, mAU·s	EGDM
10/1.0	0.524	4409.1	14.682	978.2	1.757	486	0.379
10/1.5	0.529	2093.3	6.683	1370.7	2.714	523	0.404
10/2.0	0.531	2887.3	9.343	1104.2	2.045	1430	1.075
10/2.5	0.538	2617.8	8.322	1632.5	3.307	1391	1.032
10/3.0	0.541	1734.4	5.344	1221.2	2.291	578.9	0.435

Table 2. Unreacted amounts of 1-vinyl-2-pyrrolidone, vinyl acetate, and ethylene glycol dimethacrylate, compared to the initial amount present in the reaction mixture, %.

p(VP-VA) sample	unreacted reactants compared to the initial amount, %		
	VP	VA	EGDM
10/1.0	1.609	2.486	2.251
10/1.5	0.739	3.872	1.609
10/2.0	1.041	2.942	3.240
10/2.5	0.935	4.798	2.510
10/3.0	0.605	3.351	0.889

The obtained values of unreacted reactants compared to the total p(VP-VA) xerogel mass were in the range of 5.344-14.682 $mg \cdot g^{-1}$ for VP, 1.757-3.307 $mg \cdot g^{-1}$ for VA, and 0.379-1.075 $mg \cdot g^{-1}$ for EGDM (Table 1). The unreacted amounts in relation to the initial amount present in the reaction mixture were in the range of 0.605-1.609% for VP and 2.486-4.798% for VA, while for the EGDM in the range of 0.889-3.240% (Table 2). Although the presented results indicated that the free radical polymerization process did not lead to the complete conversion of the reactants, it was satisfactory for the presented study. Also, it is very important to perform removal of unreacted comonomers and crosslinker from the obtained hydrogels after polymerization, because of their

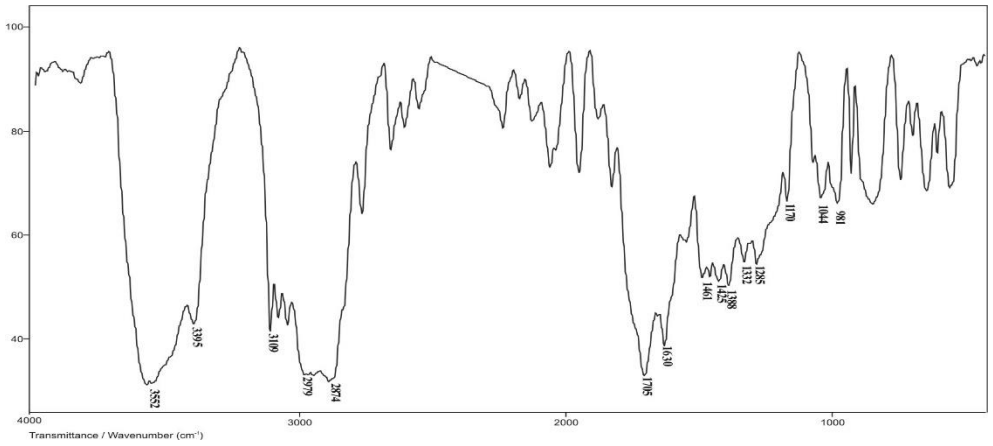
toxicity, as the next phase of the production process. In this way, all the unreacted reactants are removed, so hydrogels can be safe for further application. Unreacted monomers contents generally calculated below 10% were found in various dental composite resins (Kwon et al., 2015). For an example, the maximum amount of residual monomer in polyvinyl pyrrolidone for pharmaceutical applications has been reported to be as high as 1% (IARC, 1979), which is in accordance with obtained results presented in Table 2 (0.605-1.609% for VP, 2.486-4.798% for VA, and 0.889-3.240% for EGDM). Also, it has been assumed that 1-vinyl-2-pyrrolidone is readily biodegradable (Bühler, 2005). According to the standard ISO 1567:1999, the maximal allowed amount of residual methyl methacrylate for heat-polymerized acrylates is 2.2%. In contrast, for cold-polymerized acrylates, it amounts to 4.5%, and the amounts of residual monomers in this study were in similar limits. Water-bath post-polymerization may be an efficient way to diminish potential acrylate toxicity by diffusing unpolymerized monomer in water, additional polymerization at places with active radicals, or hydrolysis to methacrylic acid (Jorge et al., 2006; Koda et al., 1990).

Structural characterization of p(VP-VA) hydrogels

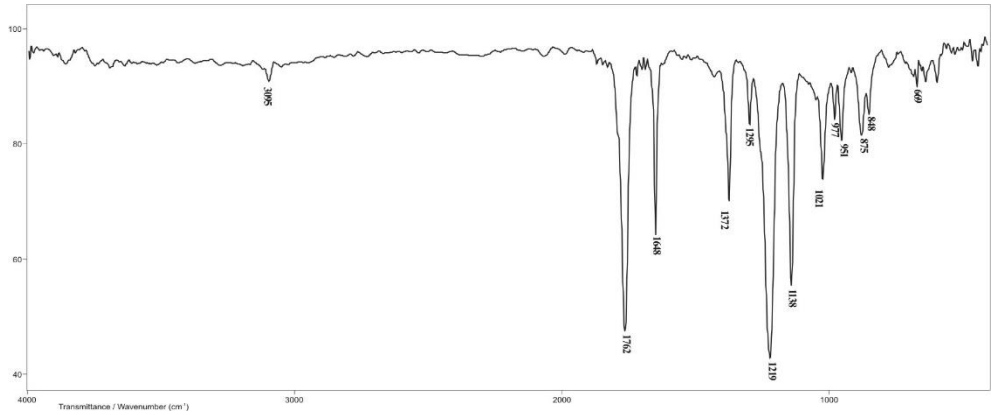
In the FTIR spectrum of VP monomer molecule, the presence of a characteristic strong band with maximum absorption at 1705 cm^{-1} confirms the structure of a five-membered ring of cyclic amide, γ-lactam (Figure 4a). The presence of the vinyl group is confirmed by absorption bands with maxima at 3109 cm^{-1} and 1332 cm^{-1} of stretching vibrations asymmetric ν_{as}(=C-H) and symmetric ν_s(=C-H) of the vinyl group. Additional confirmation of the vinyl group presence is given by the bending vibrations in the plane, δ(=C-H), and out of the plane, γ(=C-H), at 1425 cm^{-1} and 981 cm^{-1}, respectively. Confirmation of the CH_2 group presence is given by the absorption bands at 2979 cm^{-1}, 2874 cm^{-1} and 1461 cm^{-1} originating from the stretching asymmetric, ν_{as}(CH), symmetric, $\nu_s(CH_2)$, and bending vibrations of the CH group, δ(CH), respectively. The principal characteristic of VP monomer is the presence of a lower intensity absorption band with a maximum at 1630 cm^{-1}, attributed to the stretching vibrations of the double C=C bond, ν(C=C) (D'Amelia et al., 2019). This FTIR spectrum was similar to previously published (Ilić-Stojanović and Eraković, 2019).

In the FTIR spectrum of vinyl acetate comonomer (Figure 3), a strong key band with a maximum at 1762 cm^{-1} is present and originates from the stretching ν(C=O) vibrations. The medium intensity absorption band with a maximum at 1648 cm^{-1} results from stretching vibrations

of the double C=C bond, ν(C=C). The low-intensity absorption band with a maximum of 3095 cm^{-1} originates from asymmetric stretching vibrations of the vinyl group, ν_{as}(=CH), whose presence is also confirmed by the band from bending vibrations in the plane, δ(=CH), with a maximum at 1372 cm^{-1}. A characteristic, very strong band with an absorption maximum at 1219 cm^{-1} is attributed to the stretching ν_{as}(C-O) vibrations (D'Amelia et al., 2019).



(a)



(b)

Figure 4. FTIR spectra of comonomers: (a) 1-vinyl-2-pyrrolidone, and (b) vinyl acetate.

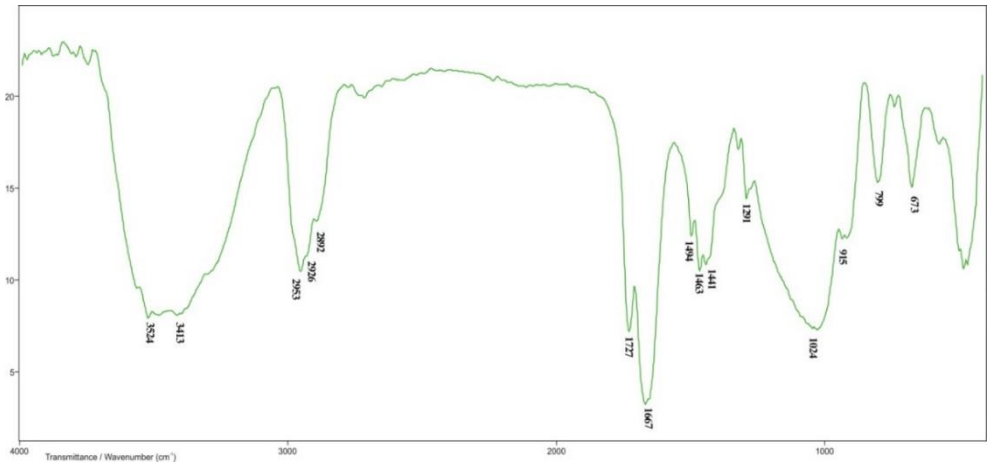


Figure 5. FTIR spectrum of p(VP-VA) hydrogel with 10 mol% of vinyl acetate comonomer.

The FTIR spectrum of the synthesized p(VP-VA) hydrogel with 10 mol% VA comonomer and 1.0 mol% of EGDM is shown in Figure 5. On the FTIR spectrum of the p(VP-VA) hydrogel, the absence of certain characteristic absorption bands present in the FTIR spectra of comonomers (VP and VA) and EGDM as crosslinker is observed which indicates that the structure of the new molecule was formed. There are no absorption bands from the stretching vibrations of the vinyl group (-CH=CH_2), ν(=CH), and bending vibrations in the plane, δ(=CH), and out of the plane, γ(=C-H), present in the spectra of comonomers and crosslinker (Figures 4 and 5). The absence of bands in the range of 1620-1640 cm^{-1} characteristic for stretching vibrations of the double C=C bond from VP and VA and EGDM, confirms that the copolymer structure was formed by double C=C bonds cleavage. Asymmetric stretching vibrations from the CH_3 and CH_2 groups, ν_{as}(C-H), give absorption band maxima at 2953, 2926, and 2892 cm^{-1}, respectively. Bending C-H vibrations in the plane, δ(C-H), from CH_3 and CH_2 groups show the maximum absorption at 1494 cm^{-1}. The sharp, intense band at 1727 cm^{-1} is a major characteristic of the p(VP-VA) hydrogel. It originates from the stretching vibrations of the C=O group, ν_{as}(C=O), from the remains of VP and VA molecules (D'Amelia et al., 2019). The maximum absorption of the characteristic band at 1291 cm^{-1} is attributed to the stretching vibrations of the C-O bond, ν_{as}(C-O) (D'Amelia et al., 2019; Ilić-Stojanović and Eraković, 2019).

The FTIR spectra of xerogel poly(1-vinyl-2-pyrrolidone-*co*-vinyl acetate) with 10 mol% vinyl acetate and 1.5, 2.0, 2.5 and 3.0 mol% of EGDM crosslinker show similarity. Structural analysis of the FTIR spectra of VP and VA comonomers, crosslinkers, and p(VP-VA) copolymers are in

agreement with data from the literature (D'Amelia et al., 2019; Ilić-Stojanović and Eraković, 2019; Milosavljević, 2020; Sa'adun et al., 2014).

Thermosensitivity analysis

The sensitivity of the synthesized p(VP-VA) hydrogels with 10 mol% of VA and 1.0, 1.5, 2.0, 2.5 and 3.0 mol% of EGDM to changes in external temperature was examined by monitoring the change in the equilibrium swelling degree, α_e, with increasing fluid temperature from 25ºC to 80ºC in a fluid with pH value 6.0. Hydrogels were swollen to equilibrium at a temperature of 25ºC, the massess were measured, and the process of changing the hydrogels masess with increasing temperature was monitored. The temperature dependence of the swelling degree, α, on p(VP-VA) hydrogels was shown in Figure 6, and equilibrium swelling degrees, α_e, achieved at 25ºC and 80ºC, was presented in Table 3.

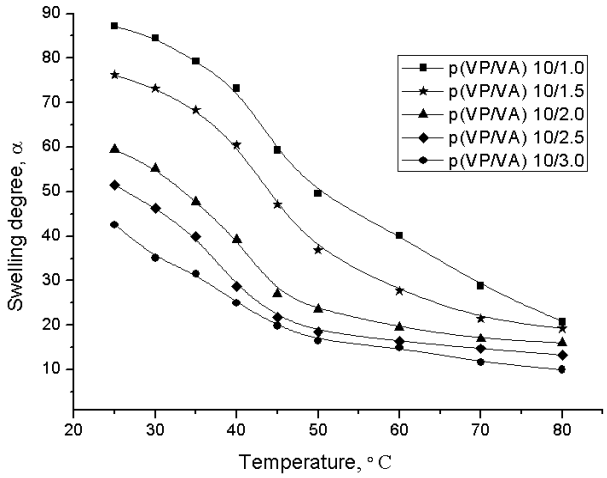


Figure 6. Temperature dependences of the swelling degree, α, p(VP-VA) hydrogels with 1.0, 1.5, 2.0, 2.5 and 3.0 mol% EGDM as crosslinker in fluid with pH value 6.0.

Table 3. Equilibrium swelling degree, α_e, of p(VP-VA) hydrogels at 25ºC and 80ºC.

p(VP-VA)	10/1.0	10/1.5	10/2.0	10/2.5	10/3.0
25°C	87.23	76.26	59.45	51.45	42.56
80°C	20.74	19.24	16.04	13.34	10.02

The swelling process of hydrogels p(VP-VA) was favored at a lower temperature (25°C) when the sample with 1.0 mol% EGDM was reached the highest swelling degree (1 g of a sample absorbed 87.23 g of water). Retention capacity continuously decreases with an increasing amount of EGDM in the hydrogel sample (1 g of a sample with 3 mol% absorbed 42.56 g of water). As the temperature increases, the swelling degree decreases for all samples of synthesized copolymers, and the achieved the most intense volume contraction in the temperature range from 40°C to 45°C (Figure 7). At the 80°C, the hydrogels dehydrated with the release of water from the polymer network, so that 1 g of the same sample with 1 mol% EGDM retained only 20.74 g of water. After hydrogel contraction, the swelling degree was asymptotically approached a constant value of approximately which was about 4 times lesser than at 25^0 C (Table 3). A proportional decrease in swelling capacity was noticed with an increase in crosslinking degree because these are polymer networks of higher density with less space between the network nodes. All synthesized hydrogels p(VP-VA) exhibit volume phase transition temperature (VPTT) in the range of 40–45 °C, which classifies them as negative thermo-sensitive (LCST). The sample with 3 mol% EGDM showed the smallest change in the swelling degree and in phase transition (from α_e=42.56 at 25ºC to α_e=10.02 at 80ºC). In the swollen state at lower temperatures, intermolecular hydrogen bonds between the free side keto groups of hydrogels (C=O) and ester C-O groups with -OH groups from water molecules are rewarded. When temperature increases above the LCST, the intermolecular hydrogen bonds break because long polymer C-C chains tend to reduce their surface area and lead to hydrogels dehydration (Ilić-Stojanović et al., 2017). Analyzed hydrogels show a thermosensitive reaction which is reflected in a significant decrease in the swelling with increasing external temperature. Based on the obtained results of sensitivity testing to changes in fluid temperature, crosslinked p(VP-VA) hydrogels with 10 mol% of VA and with 1.0, 1.5, 2.0, 2.5 and 3.0 mol% of EGDM can be classified as negative thermosensitive hydrogels having a lower critical solution temperature (LCST).

Conclusion

A series of poly(1-vinyl-2-pyrrolidone-co-vinyl acetate) copolymer hydrogels were successfully synthesized by the method of radical polymerization with thermal initiation in the presence of 2,2`-azobis(2-methylpropionitrile) as initiator. Analysis of FTIR spectra of xerogels p(VP-VA) showed that there are no bands of stretching and bending vibrations of the vinyl group,

nor bands of stretching C=C vibrations (present in comonomers and crosslinker molecules), which indicates that polymerization and crosslinking of polymer chains was carried out by breaking double bonds. Quantities of residual reactants after hydrogels synthesis were in the in acceptable values, confirmed the successful synthesis, and they were removed from final products. Crosslinked p(VP-VA) hydrogels with 10 mol% of VA show sensitivity to temperature changes, and they are negatively thermosensitive, *i.e.*, they swell at lower temperatures and contract at higher temperatures. They could be applied as potential absorbents or carriers for various molecules.

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Conflict-of-Interest Statement

No potential conflict of interest was reported by the authors.

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