

Polymer acrylic hydrogels with protein filler: Synthesis and characterization

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Abstract. The water-retention hydrogel composites were synthesized by the free-radical polymerization depending on the order of addition filler of the protein hydrolysate. As the filler was used protein hydrolysate, ‘Biostim’, obtained by processing cattle hides. The influence of gelation time on the synthesis parameters of hydrogel compositions was investigated. It is found that the gelation time of the sample without filler is 2–2.5 times longer than filled of hydrogel compositions. The structural characteristics of polymer composition by TGA, DSC and atomic force microscopy were determined. FTIR spectra found decrease in the intensity of vibrations of (-COO-) groups, indicating about additional ionic interactions. Decrease the beginning evaporation temperature of polymer composites with increase concentration of protein filler, indicating the destruction of the ordered structure of the polymer material revealed by thermogravimetric analysis (TGA). The influence of various media, such as distilled water, saline solution, and buffer solutions at different pH on the swelling behavior of hydrogels was also assessed. Maximum swelling capacity showed sample prepared with order of addition filler at the end of synthesis (Scheme I). The kinetics of the release protein hydrolysate from the polymer matrix was measurement by spectrophotometric method. The synthesized hydrogel composites with protein hydrolysate and improved physicochemical properties are of practical interest as water-retaining materials for increasing of crop the yield in agricultural.

Key words: hydrogel, radical polymerization, filler, protein hydrolysate.

INTRODUCTION

Maintaining a constant physical, chemical, metabolic and biological processes occurring in the soil environment, leads to the provision of high soil fertility and increased productivity of agricultural crops. The required conditions for this are: an increase in the moisture capacity of the soil, a decrease in denitrification, and the use of fertilizers (Olekhovich et al., 2016).

The development of hydrophilic moisture-retaining polymeric materials, which are called hydrogels, allows to solve the problem of not only improving the soil structure, but also storing soil moisture (Jhurry, 1997; Omidian et al., 2005; Mohanty et al., 2013). The content in the composition of such materials macroelements of nitrogen and potassium, contributes not only to increase crop yields, but also their resistance to

adverse environmental factors (Askari, 1993; Dessougi, 2002; Liu et al., 2006; Mahdavinia et al., 2009; Senna & Botaro, 2017).

The wide interest in creating water-holding materials are crosslinked polymers based on acrylic derivatives or their composites (Pereira et al., 2012; Olekhovich et al., 2015). Acrylamide hydrogels are most common, however, the question of their toxicity remains open.

Therefore, the search for other nitrogen sources when creating hydrogels for agriculture is quite important. In recent decades, much attention has been paid to the use of biologically active substances containing products of the hydrolysis of collagen-containing animal waste. (Maksimova, 2006). Treatment with such substance, having in its composition free amino acids, has a positive effect on crop yields (Kutsakova et al., 1997).

Therefore, the obtaining and study of the properties of hydrogels on the base of acrylic polymer containing as a filler protein hydrolyzate produced by processing secondary raw materials is important.

MATERIALS AND METHODS

Materials

Purified acrylic acid (AA) stored in the refrigerating chamber at a temperature of 3–5 °C. For neutralization of acrylic acid using potassium hydroxide (8 n KOH). Potassium hydroxide is a white, nearly transparent crystals, and stored in sealed standard containers. AA, ammonium persulfate (APS) analytical grade, potassium hydroxide, were purchased from Vekton (Russia).

N,N,N',N'-tetramethylethylenediamine catalyzer, N,N-methylenebisacrylamide cross-linking agent, were all of analytical grade, and purchased from Sigma-Aldrich (USA).

The filler used protein hydrolysate 'Biostim', derived from by-products in the processing of slaughter animals by chemical hydrolysis, the main raw material for the production of which is cattle hides beef. The molecular weight of peptides of the protein hydrolyzate is shown in Table 1. In addition to peptides, amino acids make up the bulk of the protein hydrolysate. Glycine is one third of the total number of amino acids.

Table 1. The molecular weight of peptides of the protein hydrolysate

Name of the peptide	Molecular weight (Da)
Dipeptide	215.0
Tripeptide	313.0
Tetrapeptide	412.1
Pentapeptide	510.6
Hexapeptide	609.2
Heptapeptide	707.7
Octapeptide	806.2
Nanopeptide	904.7
Decapeptide	1,003.3

Preparation hydrogel composite with filler 'Biostim'

Samples were prepared hydrogel composites based on acrylate potassium, with degree of filler 'Biostim' 5wt.%. The synthesis was carried out by free-radical copolymerization of the neutralized acrylic acid and crosslinking agent (MBA) with 0.1wt.%. As the initiator was used redox system: ammonium persulfate (PSA) –

N,N,N',N'-tetramethylethylenediamine (TEMED). The concentration of monomers in the initial aqueous solution was 30 wt.%.

First, the protein hydrolysate 'Biostim' was homogenized by stirring on a magnetic stirrer with the spin rate (1,200 rpm) for 45 minutes. The hydrogel compositions based on potassium polyacrylate and protein hydrolysate were synthesized by free radical polymerization in an aqueous medium, depending on the sequence of adding the filler. Then, AA was partially neutralized with potassium hydroxide (degree of neutralization of 0.9) and in the mixture was added redox system. After this, according to Scheme I, a cross-linking agent was first added and the filler added last (sampl No.1). According to Scheme II, a filler was first added, and then – a cross-linker MBA (sampl No.2). The obtained samples of acrylic hydrogel with and without filler were thermostated at the polymerization temperature 35 °C for 24 hours. Further, the structural differences in the samples obtained by Scheme I and Scheme II will be investigated by IR spectroscopy and thermal methods.

Characteristics of hydrogel compositions

Structural characteristics of acrylic hydrogels with protein filler 'Biostim' were recorded on the console FTIR (frustrated total internal reflection) with a ZnSe crystal at a resolution of 2 cm⁻¹, accumulating 32 scans on the spectrometer TENSOR37 'Bruker' and were measured between 500 and 4,000 cm⁻¹.

Photos of the microstructure of polymer samples were obtained on a measuring microscope STM6 Olympus.

Thermal analysis of the samples was performed on a differential scanning calorimeter DSC 204 F1 Phoenix 'Netzsch' in the range from 25 °C to 350 °C with a heating rate of 10 °C min⁻¹ in a nitrogen atmosphere.

Thermogravimetric analysis was performed on a TG 209 F1 Libra 'Netzsch' in the range from 25 °C to 900 °C with a heating rate of 10 °C min⁻¹ in a nitrogen atmosphere of 40 mL min⁻¹.

The start time of gelation and the sorption characteristics of acrylic hydrogel composites were determined according to the procedures described in (Uspenskaya, et al., 2006).

Studied sorption characteristics of acrylic composite materials in distilled water, salt solution and buffer solutions with pH = 4.1 and pH = 9.01 at a temperature of 25 °C.

DISCUSSION OF RESULTS

FTIR spectra analysis

In order to better understand the structural characteristics of the composite hydrogels obtained by the method of free-radical polymerization solution-casting method, the samples analyzed by ATR-FTIR (Fig. 1).

The broad peaks at 3,200–3,600 cm⁻¹ are attributed to the stretching vibrations of free and bound hydroxyl OH-groups. In addition, the overlapping double peaks at 3,343 cm⁻¹, and 3,280 cm⁻¹ indicating the presence of protein bands (or amino acid residues), in particular the valence vibrations of N-H groups take place due to the introduction of a protein filler in the polymer material.

The shift of peaks from $1,640\text{ cm}^{-1}$ to $1,650\text{ cm}^{-1}$ relative to the unfilled material, characteristic of the protein bands–amide I peptide group also occurs due to the presence of protein hydrolyzate in the composite. As you can see from Fig. 1 the intensity of the absorption band at $1,545\text{ cm}^{-1}$ shows the quantitative ratio of carboxylate and carboxyl groups in the hydrogel. Reducing the intensity of vibrations (- COO -) groups in the sample prepared by (Scheme II) because of additional cross-linking protein hydrolyzate with functional groups of the polymer matrix (Sitnikova et al., 2018).

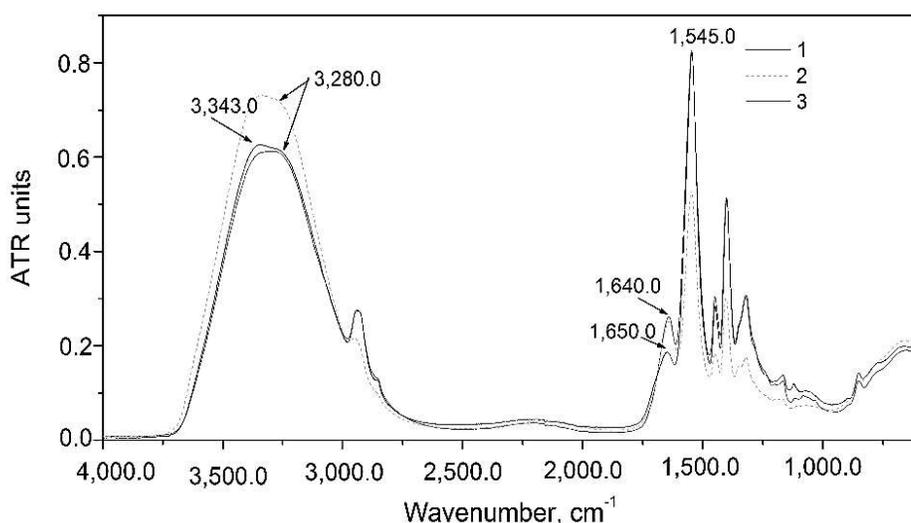


Figure 1. TR-FTIR spectra of the hydrogel samples filled with the protein hydrolysate prepared at different schemes: 1 – Scheme I; 2 – Scheme II; 3 – hydrogel without filler.

Thermal characterization

Thermal behavior of the hydrogel samples filled with protein hydrolysate and without filler were detected on DSC curves (Fig. 2).

As can be seen from Fig. 2, an intensive peak is observed on the DSC curves in the temperature range under study, which is characteristic of the evaporation of free and bound water. The maximum evaporation temperature for all samples is quite close. However, the evaporation temperature of the filled samples prepared according to different schemes differ. The sample prepared according to the Scheme II had a higher evaporation temperature of water ($148\text{ }^{\circ}\text{C}$) by obtaining a more cross-linked hydrogel sample (Kopp et al., 1989).

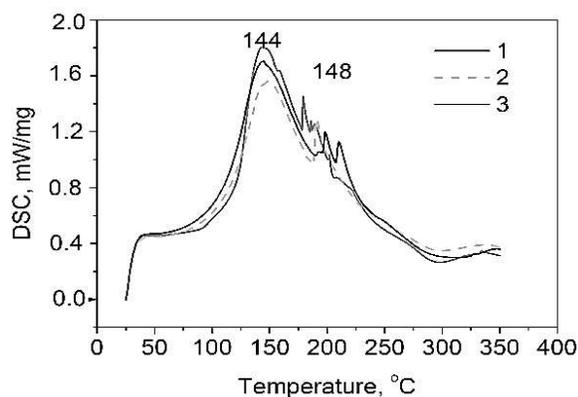


Figure 2. DSC curves of the hydrogel samples filled with the protein hydrolysate prepared at different schemes: 1 – Scheme I; 2 – Scheme II; 3 – hydrogel without filler.

The lowest value of the activation energy of I stage is possessed by hydrogel composites obtained according to Scheme I.

The thermal stability of hydrogel materials was studied by TGA and results were shown in Fig. 3 and Table 2. As shown in Fig. 3, the curves of composite hydrogels are characterized by three stages of mass loss corresponding to the evaporation of water, the destruction of the branches and functional groups of the protein filler and the polymer matrix, and the destruction of the main polymer chain of the hydrogel (Gharekhani et al., 2017).

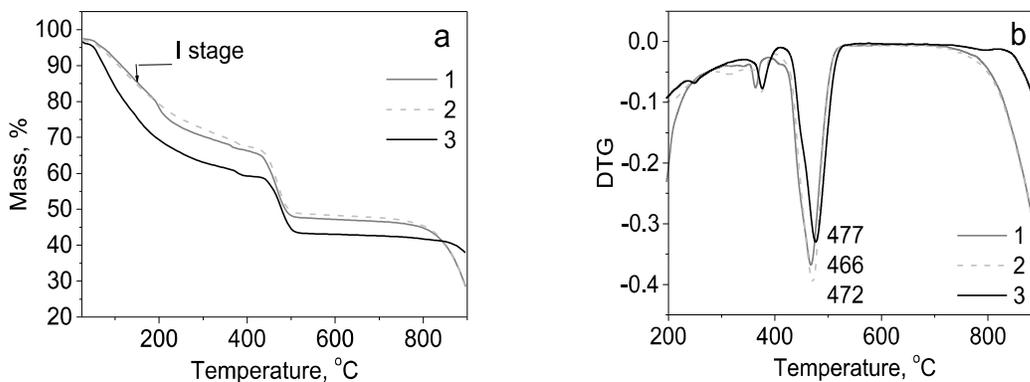


Figure 3. TGA (a), DTG (b) curves of the hydrogel samples filled with hydrogel prepared at different schemes: 1 – Scheme I; 2 – Scheme II; 3 – hydrogel without filler.

Table 2. Thermal characteristics of the hydrogel samples filled with the protein hydrolysate

No.	Moisture content, %	Temperature of evaporation, °C	Temperature degradation, °C	Activation energy of I stage, E_a , kJ
1	29.0	144.0	466.2	18
2	26.6	148.0	472.6	23
3	29.5	144.0	477.0	32

For a filled polymer hydrogel sample prepared according to Scheme I, the degradation temperature was 10 °C lower compared to the unfilled sample and was 466 °C. This phenomenon is primarily due to the formation of a more defective polymer network when embedding the peptide chains of the filler in the polymer matrix of an acrylic hydrogel. Thus the addition of the filler into hydrogel leads to a decrease in thermal stability and the formation of a more amorphous structure of the polymer matrix (Fathima et al., 2010).

This was also confirmed by photo of the surface of the obtained polymer samples shown in Fig. 4. The morphological investigation of the hydrogel composites with protein hydrolysate and without filler was conducted by optical microscope, as seen in Fig. 4. Hydrogel samples without filling have a less rough surface.

As can be seen from Fig. 4 (b, e) the synthesis of acrylic hydrogel composite according to Scheme I leads to a decrease in the size of protein agglomerates and the formation of a more homogeneous structure of the material compared with samples obtained according to Scheme II (Fig. 4, c, f) (Yang, et al., 2009).

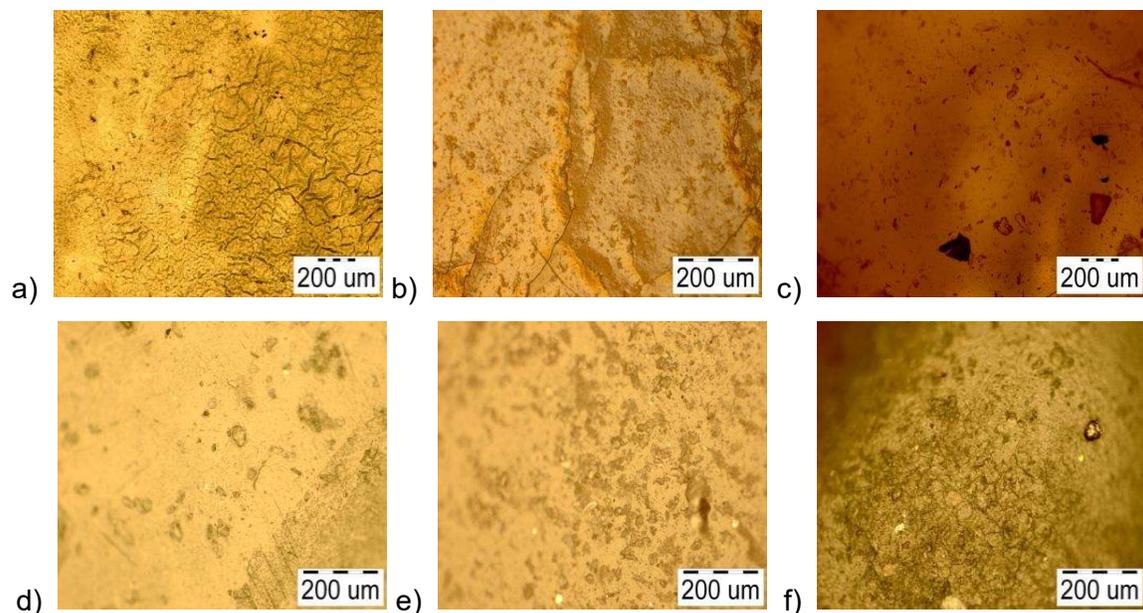


Figure 4. Photo of hydrogel samples in transmitted light and their surfaces: (a, d) without filler, (b, e) Scheme I, (c, f) Scheme II.

Swelling and Release

The sorption characteristics of hydrogels with protein hydrolysate and without filler in various aqueous media were studied in this work. The kinetic sorption curves for hydrogel samples of composites with and without filling in distilled water, physiological and buffer solutions are shown in Fig. 5.

It is well known that one of the basic properties of a guide is the equilibrium degree of swelling, which depends both on the characteristics of the reacting substances, which include: pK of the ionogenic group, degree of ionization, concentration and ratio of monomer units in the network, etc., and from external conditions of synthesis: pH, temperature, ionic strength of the environment, etc. (Kabakova, et al., 2003)

As can be seen from Fig. 5, the values of the equilibrium degree of swelling for filled hydrogel samples are 2.5–3 times larger than for unfilled ones. This may be due, on the one hand, to the formation of a looser structure, on the other hand, by an increase in the content of hydrophilic functional groups, due to the presence of a filler (Ottenbrite, 2010).

The presence of amino groups of the protein hydrolyzate in the composition of the hydrogel composite contributes to the absorption of more distilled water than the polymer matrix, consisting only of acrylic acid units (Zhao et al., 2013).

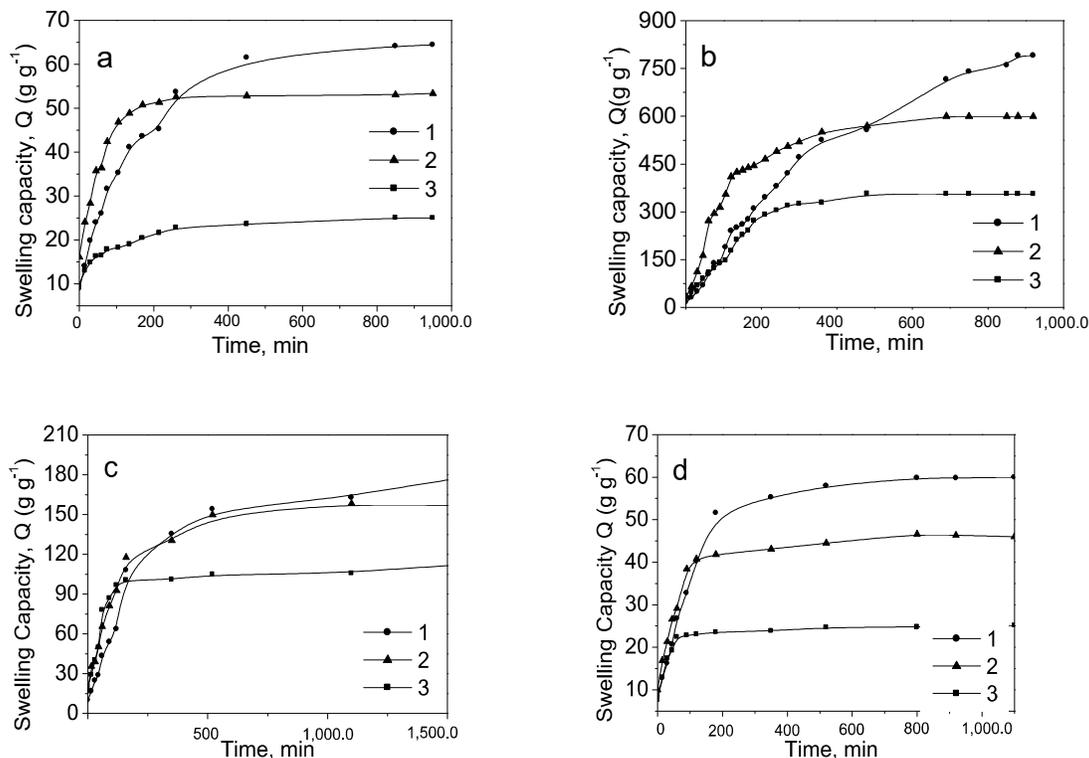


Figure 5. Kinetic sorption curves of composite hydrogels prepared at: 1 – Scheme I; 2 – Scheme II; 3 –without filler: (a) saline solution (b) distilled water (c) pH = 9.01 (d) pH = 4.1.

The values of the equilibrium degree of swelling of filled and unfilled hydrogel composites in various aqueous solutions were demonstrated in Table 3.

Table 3. Sorption characteristics of hydrogels filled with protein hydrolysate and without filling

No.	Moisture content (%)	Gelation time (m)	Maximum swelling degree, Q (g/g)			
			distilled water	saline solution	pH = 9.01	pH = 4.1
1	29.0	17	800.0	65.5	200.0	55.5
2	26.6	30	550.5	50.0	160.5	40.0
3	29.5	50	300.0	20.2	80.0	20.0

It is known (Omidian, et al., 2005) that acrylic anionic hydrogels are highly sensitive to changes in the pH of the external solution. The presence of acid groups in the polymer chain makes it possible to swell with acrylic hydrogels in an alkaline medium and collapse in an acidic medium.

As can be seen from Table 3 and Fig. 5 The swelling of filled and unfilled acrylic composites in a buffer solution pH = 9.01 varies between 80 and 200 g g⁻¹. In a buffer solution pH = 4.1, the maximum values of the degree of swelling are significantly lower and take the value of 55 g g⁻¹ for samples prepared according to Scheme I. For practical use of acrylic hydrogel composites in agriculture, it must be remembered that at pH < 5 the swelling is significantly reduced many times with the release of water structured in it from the hydrated gel.

From Table 3 it can be seen that with an increase in the onset time of gelation, the swelling capacity of hydrogels naturally decreased and the smallest value of the equilibrium degree of swelling, regardless of the nature of the external solvent under investigation, had an acrylic hydrogel without filler. The decrease in the degree of swelling of composite hydrogels prepared according to Scheme II is probably associated with the formation of more durable structures (Uspenskaya et al., 1998).

To determine the release of protein hydrolysate from the acrylic matrix, samples obtained according to Scheme I and Scheme II were measured using a UV-visible spectrophotometer UNICO.

Fig. 6 shows the release of protein hydrolysate at different time intervals in saline solution. The maximum degree of swelling reached the sample prepared according to the Scheme I. However the greatest release of protein hydrolysate from the polymer matrix was observed for the samples obtained according to Scheme II, and was 0.13 mg mL^{-1} after 72 hours.

On the basis of the achieved results, such as high adsorption properties and homogeneity of the structure for the hydrogel composite synthesized according to the Scheme I, it is necessary to conduct further studies of desorption properties in different pH media.

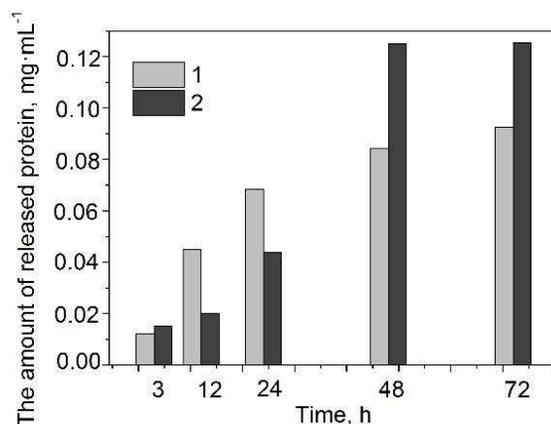


Figure 6. Release of protein filler from hydrogel composites prepared at different schemes: 1 – Scheme I; 2 – Scheme II at different times.

CONCLUSIONS

In the present work, acrylic composites filled with ‘Biostim’ protein hydrolysate were obtained and studied by radical polymerization in an aqueous medium, depending on the sequence of addition of the filler. Protein filler ‘Biostim’, having in its composition a set of amino acids and peptides, was obtained by processing secondary animal waste. The best sorption characteristics in various aqueous media were demonstrated by an acrylic polymer sample obtained according to Scheme 1. It was shown that the thermal stability of the filled materials naturally decreased due to the introduction of protein particles into the polymer matrix. The study of the laws governing the isolation of protein hydrolysate from the polymer matrix demonstrated the promise of using the obtained materials as soil conditioners and plant growth regulators in agriculture and horticulture.

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