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Physicochemical properties of temperature/pH-sensitive hydrogel materials†

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Abstract: This paper presents the synthesis of fluorescein-modified hydrogel materials. The obtained materials were characterized by FT-IR spectroscopy. Then their sorption capacity in distilled water and Ringer's liquid was determined. Using digital microscopy, the morphology of the obtained systems was characterized.

Keywords: hydrogels; cross-linking; temperature/pH-sensitive materials

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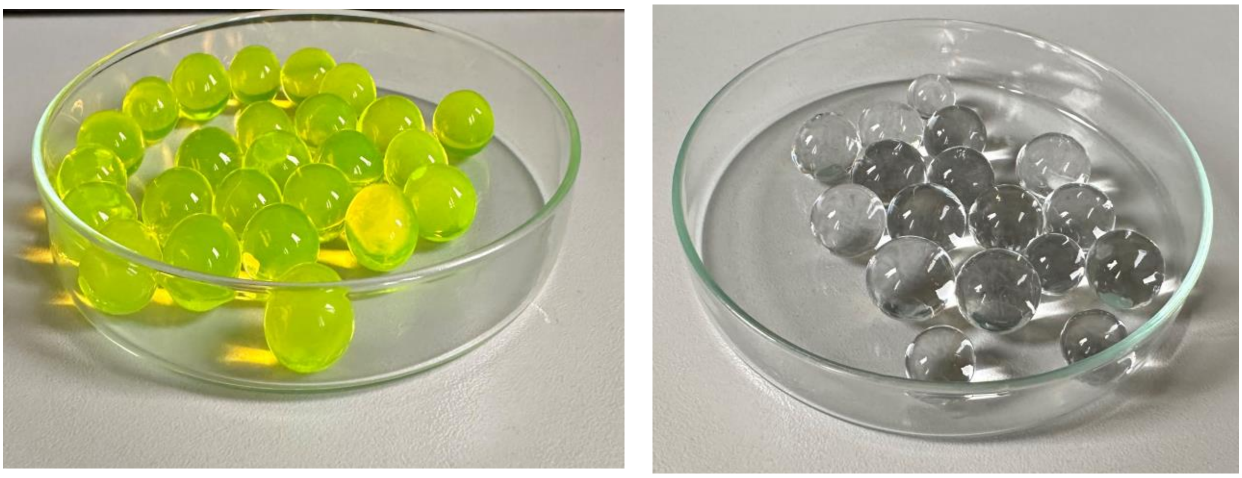
1. Introduction

Hydrogels, owing to their distinctive physical and chemical properties, have found extensive applications across diverse industrial domains. The hydrogel properties of materials depend on the degree and nature of cross-linking and the degree of crystallinity of the polymer [1,2]. Notably, hydrogels exhibit pronounced potential for biomedical applications, such as tissue engineering and drug delivery, attributable to their hydrophilicity, superabsorbent capacity, biodegradability, and biocompatibility. Despite their hydrophilic nature, these materials are non-soluble in aqueous media. Of significance, hydrogels display non-toxicity, absence of tissue damage, and an absence of inflammatory responses or thrombogenicity [3]. Hydrogel materials are commonly composed of natural polymers like collagen, gelatin, or cellulose, forming three-dimensional networks of hydrophilic polymer chains capable of absorbing substantial fluids water or bodily fluids. The structure and properties of hydrogel materials can be tailored through the selection of appropriate biomaterials, cross-linking methodologies, and fabrication techniques [4–6].

Hydrogels, constituted by intelligent polymers, exhibit sensitivity to alterations in their external environment. These smart hydrogels contain functional groups that are formed as a result of non-covalent interactions, such as hydrogen bonds, hydrophobic interactions or electrostatic interactions. The most common stimuli for hydrogel responsiveness encompass light, temperature, electromagnetic fields, ultrasound, chemical factors e.g., pH, as well as biological triggers like antigens or DNA [7,8]. Physical and chemical stimuli are harnessed to elicit various structural reactions from intelligent polymers. One or more of these stimuli can induce modifications in diverse properties, including phase transitions, shape alterations, optical, mechanical, and molecular attributes, surface energy, reaction rates, and permeability of the polymer system. A notable characteristic of temperature-sensitive polymers involves the presence of hydrophobic groups such as propyl, ethyl, and methyl groups [9,10]. When temperature-sensitive polymers reach the lower critical solution temperature (LCST), a phase transition is observed within the polymer structure. pH-responsive polymers represent another pivotal group of intelligent polymers. These polymers consist of polymer chains with ionic groups that can donate or accept protons as a result of changes in the pH of the environment. When these materials are exposed to these factors, properties such as porosity and hydrophilicity of hydrogels can regulate the loading and release of drugs in a controlled manner, thereby finding utility in drug delivery systems [11,12]. In this work, fluorescein-modified hydrogel materials were obtained, which can be used as various types of sensors in many industries. An example of unmodified and dye-containing materials is presented in Figure 1.



a) b)

Figure 1. Fluorescein-modified hydrogels (a) and unmodified hydrogels (b).

2. Materials and Methods

2.1. Materials

The primary reagents employed in this study encompassed poly(vinyl alcohol) (PVA, in crystalline powder form, hydrolyzed to a degree of 87–89%, with a molecular weight range of 13,000–23,000), poly(ethylene glycol) (PEG, in powder form, possessing an average molecular weight of 6,000), diacrylate poly(ethylene glycol) (PEGDA, a crosslinking agent, with an average molecular weight Mn = 700 g/mol), and 2-hydroxy-2-methylpropiophenone (a photoinitiator with a purity of 97%, density d = 1.077 g/mL). Additionally, fluorescein (in the form of the free acid) was procured from Sigma Aldrich (Saint Louis, MO, USA). All acquired reagents were of analytical grade purity.

2.2. Synthesis of hydrogel materials

Hydrogel materials were obtained in the photopolymerization process. First, specified amounts of PVP and PVA were mixed. Fluorescein was then added with various amounts of crosslinking agent. After thorough mixing, a photoinitiator was introduced into the reaction mixture, which was then placed in a mold for polymerization. The entire process was carried out at ambient temperature using a 180 W EMITA VP-60 UV lamp with a wavelength of λ=320 nm. The duration of polymerization for each material was set at 5 minutes. After synthesis, the materials were subjected to complex drying until they reached a solid state. The synthesized materials were then subjected to physicochemical characterization including infrared spectroscopy and sorption analysis. In addition, their surface morphology were evaluated. The composition of the hydrogel compositions is presented in Table 1.

Table 1. Composition of the hydrogel materials.

10 % PEG, mL	10 % PVA, mL	Photoinitiator, mL	Fluorescein, mL	PEGDA, mL	Sample no.
1.0	9.0	0.05	1	3	1
3.0	7.0				2
5.0	5.0				3
7.0	3.0				4
9.0	1.0				5

2.3. FT-IR infrared spectroscopy analysis

The investigation involving Fourier Transform Infrared (FT-IR) spectroscopy was executed utilizing the Thermo Scientific Nicolet iS5 spectrophotometer equipped with an ATR attachment. Spectra were recorded in the range 3600-500 cm^{-1} (32 scans, resolution 4.0 cm^{-1}). The measurement was carried out at room temperature.

2.4. Analysis of soprtion capacity

The sorption capacity for the polymeric materials was realized through the determination of the swelling coefficient. For each distinct material specimen, a circular sample measuring 1 cm in diameter was meticulously prepared and its initial mass was ascertained. Subsequently, these samples were introduced into separate volumes of distilled water and Ringer solution (each maintained atin 50 mL of the corresponding liquid). Post a designated incubation period of 24 hours and 48 hours, the samples were once again weighed, thereby facilitating the computation of the swelling coefficient using the subsequent formula (Equation 1).

$$\alpha = (m_t - m_0)/m_0 \quad (1)$$

where:
α—swelling ratio, g/g;
m_t—mass of swollen sample after time “t”, g;
m_0—mass of dry sample (before the study), g.

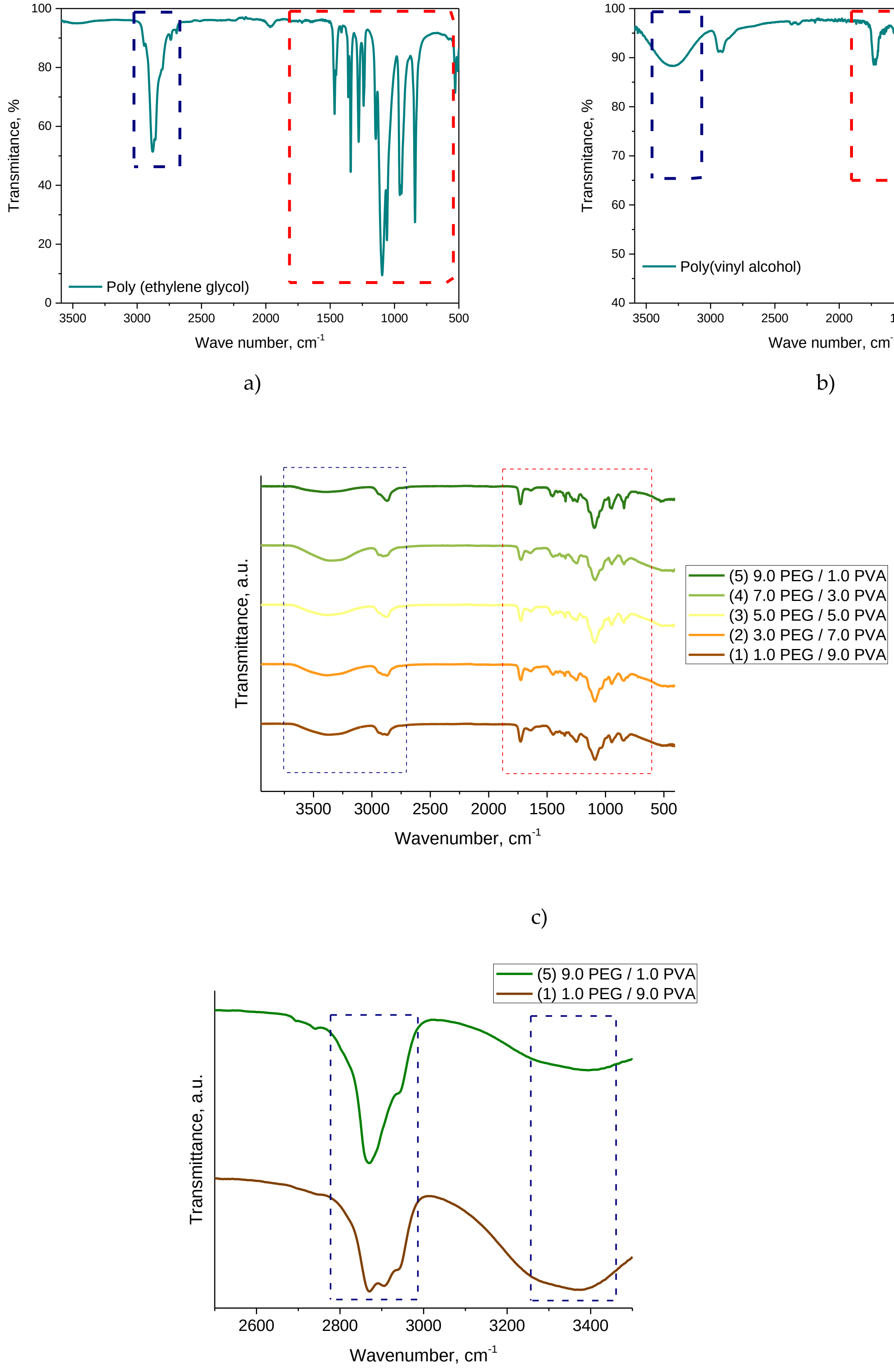
2.5. Microscopic observations and roughness profile

Then the surface morphology of the obtained materials were determined using advanced VKX-7000 Keyence digital microscope. Observations were conducted for all received materials at room temperature.

3. Result and discussion

3.1. FT-IR infrared spectroscopy analysis

Spectroscopic analysis was performed to determine the chemical structure of the resulting hydrogels. Spectroscopic spectra are presented in Figure 2. All hydrogel materials were analyzed. In addition, pure polymeric components such as PVA and PEG were tested as reference samples.



a) b)

c)

d)

Figure 2. FTIR spectra of hydrogel materials and reference samples: PEG (a); PVA (b); hydrogels samples (c); comparison of two samples (d).

Based on the analysis, the occurrence of absorption bands characteristic of the polymeric components included in the developed hydrogel systems was confirmed. No significant differences were noted. All spectroscopic spectra were similar to each other. They differed slightly in the intensity of the selected bands depending on the base solution used (the ratio of PEG to PVA). It was difficult to identify significant differences in the wavenumber range around 2000 cm^{-1} to 600 cm^{-1} because most of the absorption bands overlap in this range for both polymers. This is indicated by the red box in Figure 2. However, we can also indicate the difference between the starting materials as presented in Figure 2a and 2b. In the case of polyethylene glycol, we can distinguish an absorption band with a maximum around 2870 cm^{-1} corresponding to C-H stretching vibrations of the -CH$_2$ group. In the case of polyvinyl alcohol, on the other hand, a characteristic vibration of the -OH group was noted with a maximum of about 3300 cm^{-1}. These bands were compared for samples containing extreme values of both these components (sample 1 and 5). This is shown in Figure 2d. Accordingly, for sample 1 containing a higher proportion of PVA, we observe a high intensity of the band at 3300 cm^{-1}. While for sample 5, the intensity of this band decreases. In contrast, the band characteristic of polyethylene glycol stands out.

3.2. *Analysis of soprtion capacity*

The results of the sorption capacity analysis are presented in Figure 3.

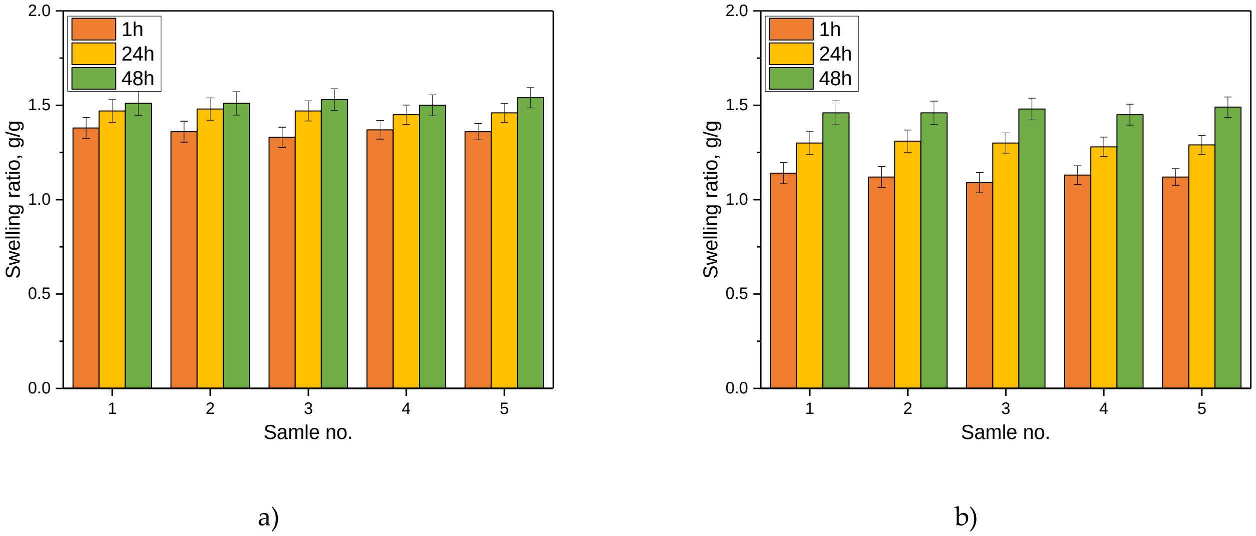
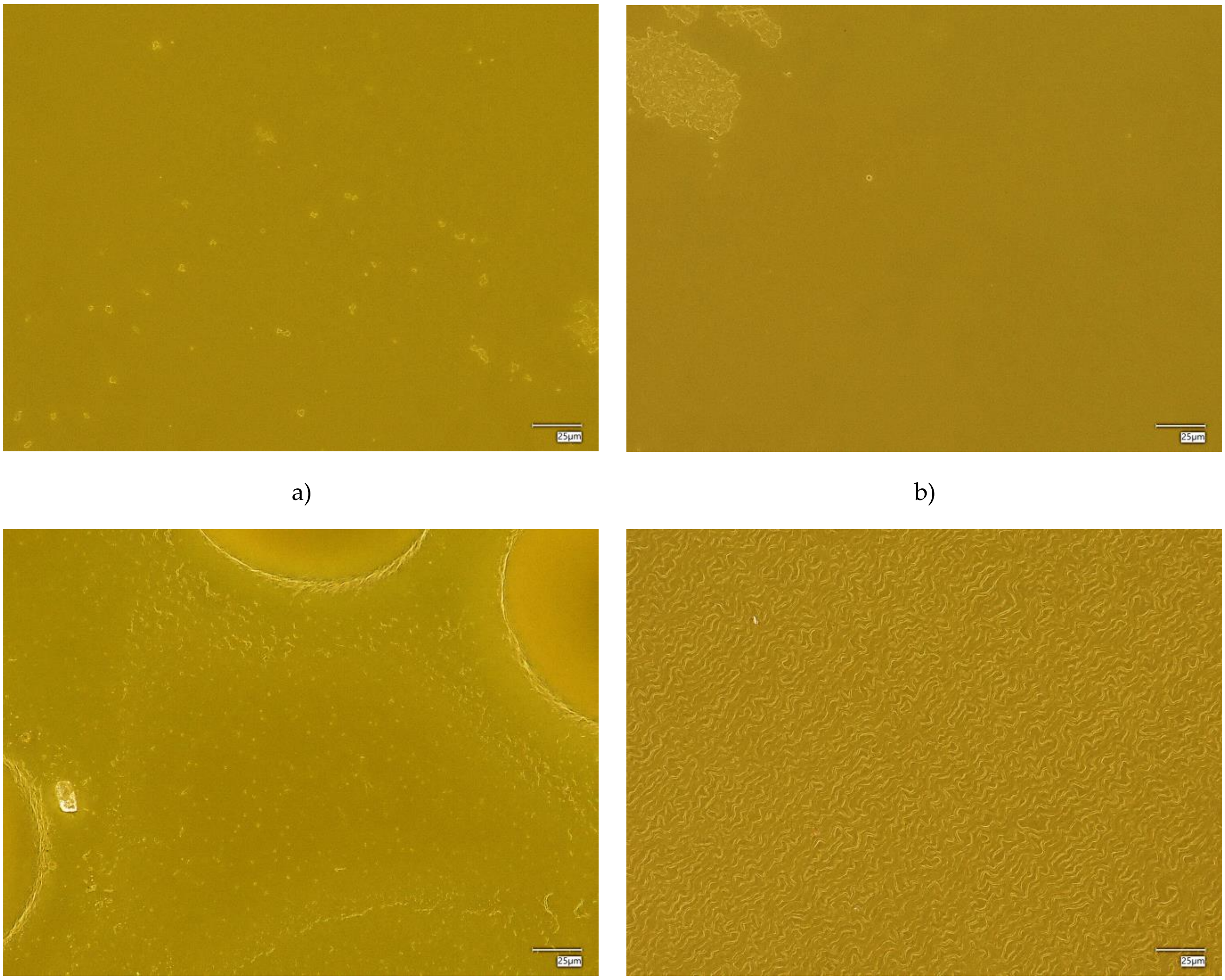


Figure 3. Results of sorption capacity analysis in distilled water (a) and Ringer solution (b) n – number of repetitions, n = 3).

Analysis of sorption capacity was carried out to determine whether the obtained polymeric materials are capable of absorbing water or aqueous solutions. Depending on their application, hydrogel materials should be characterized by an appropriate degree of swelling. For example, in biomedical applications when we care about absorbing wound exudate for materials that are innovative dressings, sorptive capacity is extremely important. Other properties, on the other hand, will be required of materials for pharmaceutical or cosmetic applications. For engineered materials containing dye as a marker, the properties mentioned are equally important. During swelling of the hydrogel material, the polymer network is loosened and the encapsulated substances can penetrate the polymer network respectively acting as a tracer. For the materials obtained, all of them showed sorption capacities of about 1.5 g/g in distilled water and 1.3 in Ringer's liquid. The highest weight gain was observed in the first hour of analysis. In contact with the liquid, the hydrogel material swelled, and with the passage of time there was a filling of all free spaces between the polymer chains, and the swelling coefficients changed only slightly. The swelling kinetics indicate that the first hour of contact between the material and the aqueous solution is the most significant. Then, with the passage of time, some stabilization occurs and the hydrogel material accepts only insignificant batches of solution. For all analyzed materials, smaller values of swelling coefficients were recorded for Ringer's fluid than for distilled water. It is likely that the ions present in this fluid may cause the occurrence of additional interactions in the polymer network limiting the penetration of larger amounts of fluid, which is not the case with distilled water. These ions may create additional interactions between the polymer chains. When this happens, the polymer network increases its cross-linked density and the penetrating liquid that penetrates the system has limited free spaces between the chains. This results in lower swelling coefficients. However, despite this phenomenon, hydrogel materials placed in Ringer's liquid also showed satisfactory values of swelling coefficients testifying to their sorption capacity.

3.3. Microscopic observations

The surface morphology of hydrgel materials is presented in Figure 4.



a) b)

c) d)

e)

Figure 4. Digital microscope images and roughness profile of hydrogel materials: 1.0 PEG/9.0 PVA (a); 3.0 PEG/7.0 PVA (b); 5.0 PEG/5.0 PVA (c); 7.0 PEG/3.0 PVA (d); 9.0 PEG/1.0 PVA (e).

The obtained materials are characterized by a rough surface structure, which is associated with the use of a selected amount of crosslinking agent. During polymerization a polymer network of a specific packing density is formed, depending on the composition of the polymer matrix, mainly the crosslinking agent and the photolinitiator. In the case of all the materials held, a homogeneous surface without discontinuities was found, which shows the correct polymerization of these systems.

Some differences were also noted between materials containing different amounts of selected polymers. It was found that with increasing ratio of PEG to PVA the roughness and corrugation of the surface increases. Poly(vinyl alcohol) is a polymer with excellent film-forming properties, so in the case of samples containing a higher amount of it, a smoothing of the surface of the hydrogel material is observed. While decreasing its amount in favor of PEG the smoothing disappears and the material becomes rougher. This is valuable information from the application point of view of these materials. Depending on the specific application, more or less surface roughness may be desired, which can be controlled and modified accordingly by changing the ratio of PEG to PVA, the base polymers.

4. Summary

- The selected photopolymerization technique enables the production of hydrogel materials that have been modified with a fluorescent dye.
- The obtained systems were characterized by their sorption capacities.
- Spectroscopic characterization showed no significant deviations between the materials studied.
- All materials were characterized by a continuous and homogeneous po-surface structure with an average degree of roughness.

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