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PAA/PVA MATRIX FOR BIOMEDICAL APPLICATION

MATRYCE PAA/PVA DO ZASTOSOWAŃ BIOMEDYCZNYCH

Abstract

Acrylic acid modified with poly(vinyl alcohol) was used in preparation of polymer matrix. The synthesis of hydrogels in aqueous solution was carried out under microwave irradiation. The effect of polymerization conditions on swelling capacity was investigated. Results showed that the swelling capacity was affected by various doses of poly(vinyl alcohol). These polymers were characterized by swelling in distilled water and 0.9% NaCl solution, as well as by in vitro investigations in Ringer's solution.

Keywords: hydrogels, poly(vinyl alcohol), poly(acrylic acid)

Streszczenie

Kwas akrylowy modyfikowany poli(alkoholem winylowym) został użyty do otrzymania matrycy polimerowej. Synteza hydrożeli została przeprowadzona w wodnym roztworze w polu promieniowania mikrofalowego. Zbadano wpływ warunków polimeryzacji na zdolność pęcznienia. Wyniki pokazały, że różna zawartość poli(alkoholu winylowego) wpływa na zdolność pęcznienia. Polimery scharakteryzowano na podstawie pęcznienia w wodzie destylowanej oraz 0,9% roztworze NaCl, jak również poprzez badania in vitro w roztworze Ringera.

Słowa kluczowe: hydrożele, poli(alcohol winylowy), poli(kwas akrylowy)

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1. Introduction

Hydrophilic gels called hydrogels are cross-linked materials absorbing large quantities of water without dissolving. Softness, smartness, and the capacity to store water make hydrogels unique materials. The ability of hydrogels to absorb water arises from hydrophilic functional groups attached to the polymer backbone while their resistance to dissolution arises from cross-links between network chains. Water inside the hydrogel allows free diffusion of some solute molecules, while the polymer serves as a matrix to hold water together. Another aspect of hydrogels is that the gel is a single polymer molecule, that is, the network chains in the gel are connected to each other to form one huge molecule on macroscopic scale. It is natural to expect that the conformational transitions of the elastically active network chains become visible on the macroscopic scale of hydrogel samples. The gel is a state that is neither completely liquid nor completely solid [1–4].

Polymeric hydrogel networks may be formed by various techniques, however the most common synthetic route is the free-radical cross-linking copolymerization of a hydrophilic non-ionic monomer such as acrylamide (AAm) with a small amount of a cross-linker, e.g. N,N'-methylenebis(acrylamide) (MBAAm) [1, 5].

The equilibrium swelling degree and the elastic modulus of hydrogels depend on the cross-link and charge densities of the polymer network as well as on the cross-linked polymer concentration after the gel preparation [6].

In the application areas of polymer hydrogels, precise information on their molecular constitution as well as their elastic properties is required. Several interesting molecular features control the elastic properties of the hydrogels [7, 8].

Hydrogel structure and, therefore, the hydrogel properties are closely related to the conditions under which they are formed, i.e. the cross-linker concentration, the initial degree of dilution of the monomers and the chemistry of the units building the network structure. The understanding of the formation mechanism of hydrogels under various experimental conditions is one of great interest to predict their physical properties [5–8].

2. Experimental

2.1. Materials

Acrylic acid (AA), ammonium persulphate (APS), potassium hydroxide (KOH) and poly(vinyl alcohol) (PVA) were obtained from POCh Gliwice, Poland. Polyethylene glycol diacrylate (PEGDA) M_w = 256 was purchased from Sigma Aldrich. All chemicals were of analytical grade and were used without further purification.

2.2. Preparation of PAA/PVA hydrogel

The synthesis of PAA/PVA hydrogel was performed as follows: an appropriate amount of monomer acrylic acid (AA) was added to the solution containing KOH. The degree of AA neutralization was maintained at ca. 70%. PVA was added into the hot mixture of PAA

and KOH. In the next step the mixture was cooled slowly until the temperature dropped to 30°C, then an initiator (APS) and a crosslinker (PEGDA) were added. The synthesis of hydrogel was carried out under microwave irradiation at 600 W for 5 min. The application of microwave heating enabled a rapid growth of the three-dimensional PAA/PVA network structure.

2.3. Swelling measurements

A 1.0 g polymer sample was dispersed in 500 ml distilled water (or salt solution) for swelling equilibrium. After 1 h, the swollen sample was filtered. The water in the bag surface was removed, and then weighed. The swelling ratio (Q, g/g) was calculated as follows:

$$Q = \frac{w - w_0}{w_0}$$

where w was the weight of polymer after swelling, and w_0 was the weight of polymer before swelling [9–11].

2.4. Immersion in Ringer's solution

The physiological fluid was applied as an environment: Ringer's solution which simulated the natural human environment. The chemical stability and biological activity were evaluated on the basis of changes in the pH value. The in vitro research was done for 42 days at the temperature of 37°C using the multifunction device CPC-411 produced by the Elmetron company for pH analyses.

3. Results and Discussion

The swelling behaviour of the absorbent polymer depends on the composition of the polymer and the characteristic of the external solution. In the present work the PVA has varied in the feed mixtures in a concentration range of 5–15% and the effect of this variation on the swelling ratio of the hydrogel has been studied. The results are shownin figure 1 which reveals that the increasing concentration of PAV decreases the swelling ratio in distilled water, 0.9% NaCl solution or simulated body fluid. The presence of ions in the swelling medium has a profound effect on the swelling behaviour of the hydrogel. The underlying principle behind this ionic dependence of swelling is that it was the balance between the osmotic pressure of the swelling system and the elastic response of the polymeric material that controlled the extent of swelling. The osmotic pressure results from the difference between the mobile ion concentrations in the interior of the hydrogel network and the external immersion medium. Increasing the ionic concentration reduces the mobile ion concentration difference between the polymer gel and the external medium (osmotic swelling pressure) which, in turn, reduces the gel volume, i.e. the gel shrinks.

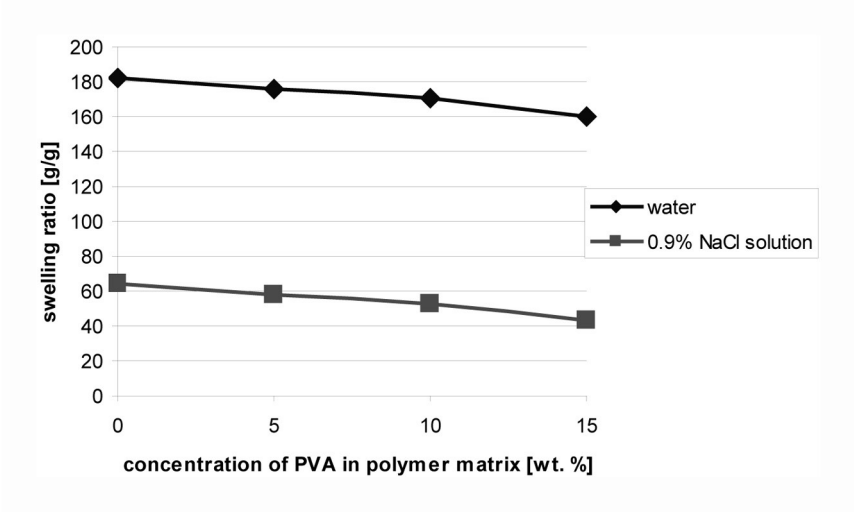

Fig. 1. Dependence of swelling ratio upon PVA concentration in dried hydrogels

Rys. 1. Zależność zdolności pęcznienia od zawartości PVA w suchych hydrożelach

For all the hydrogel samples a change in the pH value in the time of incubation in Ringer's solution was observed – figure 2. The pH value of pure Ringer's solution was 7.185. The samples containing PVA immersed in Ringer's solution had higher pH values than the pure PAA matrix because the PAA polymer was used which was anionic hydrogel. After 40 days the pH values of samples containing PVA were similar to the pH value of the simulated body fluid.

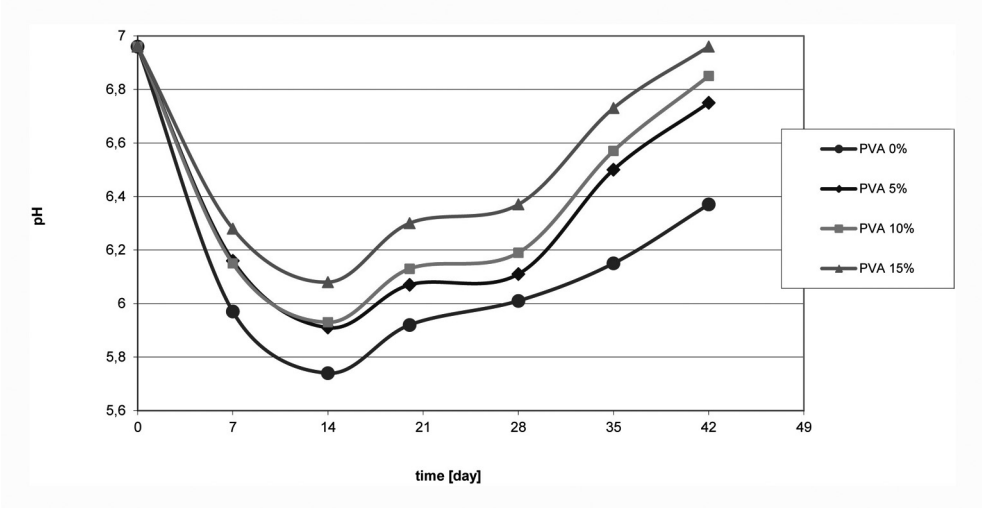

Fig. 2. Changes in pH value of Ringer's solution

Rys. 2. Zmiany wartości pH roztworu Ringera

4. Conclusions

In this work PAA/PVA hydrogels were synthesized under microwave irradiation in solutions. The swelling of polymers in distilled water and 0.9% NaCl solution was investigated. The increasing contraction of PVA in the polymeric matrix decreases the swelling ratio. The complex formation results from the formation of temporary physical crosslinks due to hydrogen bonding between the PVA and PAA pendant groups. This hydrogen-bonded complex causes the polymer network to be less hydrophilic because the carboxyl groups in the PAA graft chain participate in the complex formation. After incubation in Ringer's solution the samples containing PVA were characterized by the pH value similar to that of the simulated body fluid. These results indicated that the hydrogel matrix could be used as a potential biomaterial e.g. a wound dressing material.

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