

INFLUENCE OF pH ON PROPERTIES OF MODIFIED WAXY CORN STARCH WITH ACRYLIC MONOMERS

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Abstract

In our research the influence of pH on the properties of crosslinked waxy corn starch modified with acrylic monomers has been studied. These systems are characterized with the ability to absorb and hold a large quantity of water and aqueous solutions. However, due to the presence of the starch granules in their structure they are easily biodegradable. In our study, a number of cross-linked hydrogels based on waxy maize starch and acrylic acid derivatives were synthesized. Acrylic acid used in reactions was partially neutralized with NaOH. N,N'-methylenebisacrylamide was used as the cross-linking agent. A series of polymers with different content of ionized carboxyl groups were obtained. These polymers were used for further study of their properties, in particular swelling properties and concentration of carboxyl and carboxylate groups. Presence of those hydrophilic groups is largely responsible for the high affinity of the polymer to water. A significant increase in the gelation time with increasing of sodium acrylate content was observed. As expected, the increase in content of carboxylate groups with an increase of neutralization degree of acrylic acid used in the synthesis of the polymer was observed, while content of unionized carboxyl groups decreased. A series of experiments were carried out to determine the effect of pH on the absorption of hydrogels. It should be noted that the amount of absorbed water is generally affected by the ionic strength of the solution, therefore, to compare the individual results of swelling in the range of pH 5.0-8.0 experiments were performed in buffers solution with the same ionic strength. High rate of absorption of aqueous solutions was observed. Approximately 60-70% of the maximum value is attained during the first 10 minutes. It was found that when pH of solution increases, amount of water absorbed per gram of hydrogel increases. Hydrogel composition also has a significant impact on the swelling properties of hydrogel. A minimum of water absorption was observed for polymers in which the ratio of acrylic acid to sodium acrylate was 1:1.

Keywords

hydrogels, maize starch, swelling properties

Introduction

Hydrogels are polymeric materials containing a hydrophilic groups which are able to hold large amount of water in their three-dimensional network [1]. Due to their characteristics, hydrogels has raised a considerable interests and researches. In the swollen state, they are soft and exhibit excellent water affinity, mechanical stability and biocompatibility [2]. Hydrogels are used extensively as superabsorbents, for this application high swelling capacity is the most important property. However, there is number of areas of use hydrogels as functional materials such as carries for controlled drug release [3], artificial organs [4], sensor devices [5–7]. They are also widely used in agriculture and food industry. Recently, the use of natural materials such as polysaccharides for hydrogel applications has attracted the attention of investigators due to their non-toxicity, low cost and biodegradability. Starch is renewable, biodegradable and low-cost polysaccharide which makes it attractive in modern materials. But the starch-based hydrogels also exhibit some disadvantages such as low mechanical strength. Grafting of hydrophilic polymer chains on starch granules is a way to combine advantages of acrylic hydrogels and starch [8–10].

Important property of hydrogels is their response to external stimuli such as temperature, pH, presence of solutes, electric and magnetic fields resulting in the absorption or release of water and solutes [3,11]. The objective of this study is to explore influence of degree of neutralization of acrylic acid on swelling behavior of starch-based acrylic hydrogels in aqueous solutions at different pH.

Methods

Commercial waxy corn starch was purchased from National Starch and was dried prior to use. Acrylic acid (AA), acrylamide (AAm) and N,N'-methylenebisacrylamide (MBA) as the crosslinking agent were purchased from Sigma-Aldrich and were used as received. Potassium persulfate, disodium hydrogen phosphate, boric acid, citric acid, hydrochloric acid and sodium hydroxide - POCh SA (Poland), were analytical grade and were used as received without further purification.

Hydrogel synthesis

Hydrogels based on waxy maize starch, acrylic acid and acrylamide were obtained by a one-step synthesis [12]. During synthesis simultaneous polymerization and crosslinking reaction of the polymer occurs.

10g of waxy maize starch was placed in a conical flask and 110 ml of distilled water was added. The mixture was heated on a water bath to 95°C and was mixed with a mechanical stirrer at a speed of 900 min⁻¹ until gelatinization of starch. In a separate vessel mixture of acrylic acid and sodium acrylate was prepared by adding to 10 g of acrylic acid, calculated amount of sodium hydroxide solution (Table 1) dissolved in 10 ml of distilled water. Additionally 10 g of acrylamide was dissolved in 12.5 ml of distilled water. Mixture of acrylic acid and sodium acrylate, then crosslinking agent (0.0066 g of N,N'-methylenebisacrylamide dissolved in 2 ml of distilled water) and acrylamide solutions were added to the gelatinized starch. To initiate polymerization reaction 0.0159 g of potassium persulfate, dissolved in 5.5 ml of distilled water, was added.

The mixture viscosity was increased during reaction to reach the gelation point where the stirrer rotation is stopped due to gelation. The time elapsed to reach the gelation point is referred to as gelation time. After reaction to the product 250 mL of MeOH was added. The product was scissored to small pieces and dried in an oven for 24h at 60°C to reach a constant weight. Dry products were ground with a hammer-type minigrinder.

Table 1. Amount of reactants used in polymerization reactions.

Starch [g]	AA [mol]	NaOH [mol]	AAm [mol]	MBA [mmol]	APS [mmol]	$\frac{[\text{NaAA}]}{[\text{NaAA}] + [\text{AA}]}$
10	0.139	0.0000	0.141	0.043	0.059	0.0
10	0.139	0.0278	0.141	0.043	0.059	0.2
10	0.139	0.0695	0.141	0.043	0.059	0.5
10	0.139	0.0834	0.141	0.043	0.059	0.6
10	0.139	0.1112	0.141	0.043	0.059	0.8
10	0.139	0.1390	0.141	0.043	0.059	1.0

*Calculated mole fraction of sodium acrylate in mixture of acrylic acid and sodium acrylate

Measurement of carboxylic group concentration

To determine concentration of carboxyl groups back titration method was used. Direct titration of carboxylic groups of starch-based hydrogels with bases or carboxylate groups with acids does not bring expected results, due to very long time to obtain acid-base equilibrium. Such phenomenon is caused by slow diffusion rate of ions into the structure of the crosslinked polymer. The content of-COOH groups in the starch-based hydrogels can be measured by neutralization of these groups with excess of NaOH, then back-titration of unreacted NaOH. A powdered hydrogel (0.2g) was immersed in 50 ml of distilled water for at least 24 h at ambient temperature to reach swelling equilibrium. After that an excess of 0.1 M NaOH was added to the sample and was mixed with a magnetic stirrer for 24 hours. Excess of NaOH was back-titrated with a 0.1 M HCl solution. The titration end point was judged by potentiometer.

Mole percent of carboxylic acid groups in the hydrogel was calculated by following equation:

$$C_{\text{COOH}} = \frac{C_{\text{NaOH}} \cdot V_{\text{NaOH}} - C_{\text{HCl}} \cdot V_{\text{HCl}}}{1000 \cdot m_d} \cdot 100\%$$

Measurement of carboxylate group concentration

In order to determine -COONa groups content at the beginning, all the COONa groups were transformed into -COOH group. Then determination of the sum of the carboxylic and carboxylate groups in the sample according to similar method to that used in the determination of the -COOH groups concentration [13].

About 3 g of dry hydrogel was added to 140 ml methanol and 60 ml of 0.5 M HCl solution and allowed to react for 24 h under magnetic stirring. After that the mixture was filtered and the precipitate was washed with 80% methanol. This process was repeated until pH=7 and to complete removal of chloride ions (no precipitation appears when the liquid was checked with AgNO₃).

Filtered hydrogel was dried at 60°C until constant weight and weighed as m_d . To the 50 mL of distilled water and 25 mL of 0.1 M NaOH in conical flask, 0.2 g of hydrogel was added. The

sample was shaken at ambient temperature for 24 hours. After that excess of NaOH was back-titrated with 0.1 M HCl in the presence of phenolphthalein.

Carboxylate group content in the sample was calculated using the formula below:

$$C_{COO^-} = \left(\frac{C'_{NaOH} \cdot V'_{NaOH} - C'_{HCl} \cdot V'_{HCl}}{1000 \cdot m_d} - C_{COOH} \right) \cdot 100\%$$

Swelling tests

Water absorption tests were performed at buffer solutions at given pH. Four buffer solutions at pH 5.0, 6.0, 7.0 and 8.0 were prepared by mixing, in suitable proportions, 0.1 M citric acid and 0.2 M sodium hydrogen phosphate solutions. Swelling ratio (SR) was determined by immersing dried and powdered hydrogel sample (0.2 g) 500 mL of appropriate buffer solution at ambient temperature. After defined period of time swollen hydrogel was taken out from solution and filtered through Büchner funnel. The weight of swollen hydrogel was recorded. The swelling ratio (SR) is defined as:

$$SR = \frac{m_t - m_d}{m_d}$$

where m_t is the weight of the swollen hydrogel at time t and m_d is the weight of the dried hydrogel.

Results and Discussion

Synthesis of starch-based hydrogels was carried out using the same amount of initiator (0.015 mol%) and the cross-linking agent (0.021 mol%) in relation to the sum of acrylic monomers. Hydrogel properties were investigated taking into account molar fraction of sodium acrylate in mixture with acrylic acid. Significant changes of gelation time during synthesis of different polymers were observed. Gelation time results in relation to molar fraction of NaAA in mixture with acrylic acid were presented in Fig. 1. There is observed more than two-fold increase in gelation time with an increase of $-COONa$ groups content. The shortest gelation time (20 min) is observed for hydrogels containing acrylic acid only, while for the mixture containing completely neutralized acrylic acid gelation time is increased to 60 min [14].

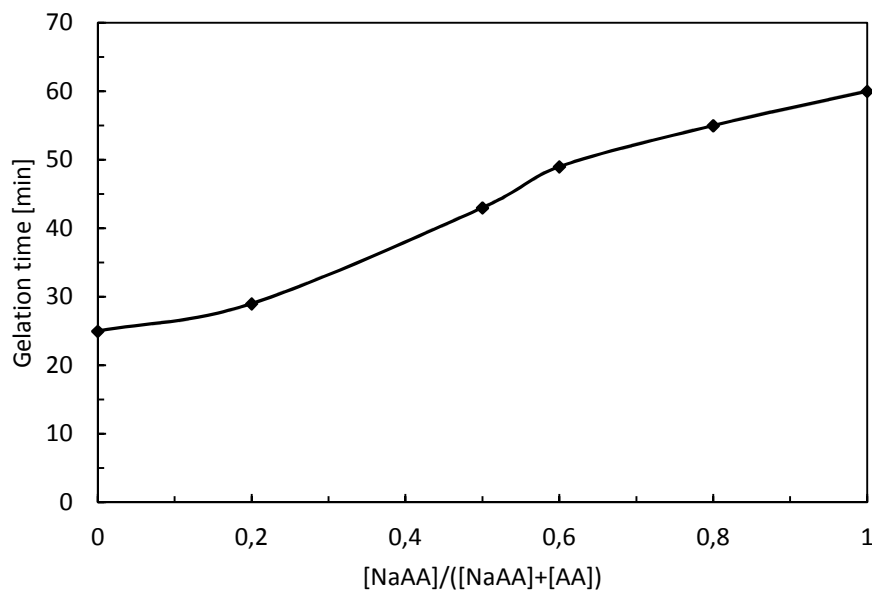


Fig. 1. Variation of gelation time with the mole fraction of NaOH to acrylic acid used in saponification reaction.

The relation between the amount of $-\text{COOH}$ and $-\text{COONa}$ group, calculated as mol of groups per gram of hydrogel sample, and the amount of NaOH taken in the saponification reaction is shown in Fig. 2. It can be found that amount of $-\text{COOH}$ group decreases and that of $-\text{COONa}$ group increases with the increase of the amount of NaOH in the saponification reaction.

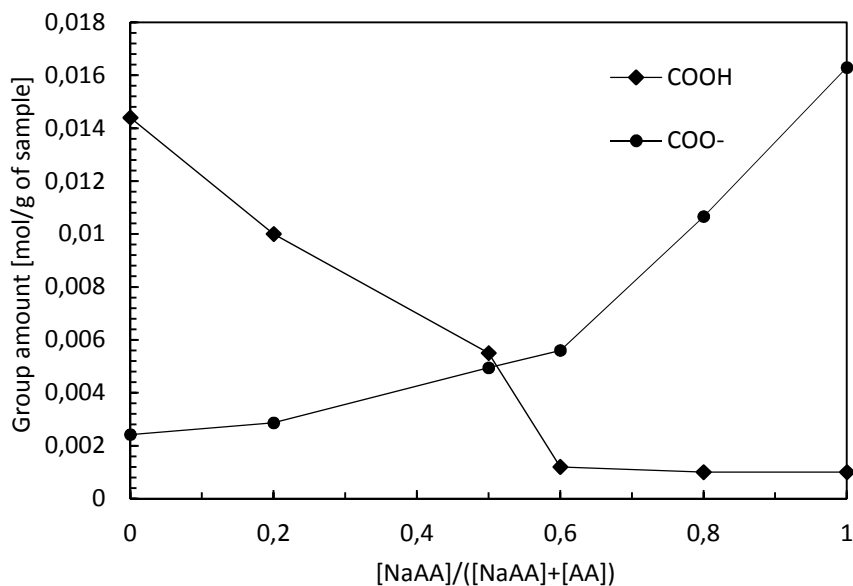


Fig. 2. Effect of the mole fraction of sodium acrylate to acrylic acid on the amount of hydrophilic groups in starch-based hydrogels.

The swelling capacity of the starch based hydrogels is very dependent on the pH and composition of absorbed liquid. To minimize this effect all used buffer solutions have got the same ionic

strength. The type as well as molar percentage of hydrophilic groups such as $-\text{COOH}$, $-\text{COONa}$ and $-\text{CONH}_2$ affects the ability of the polymer to absorb and swell in aqueous media. Taking into account data presented in Fig. 3, which represent the swelling capacity in buffers at different pH in range 5-8, for starch-based hydrogels with different ratio of sodium acrylate to acrylic acid, it could be observed that the highest swelling ratio has hydrogels in which only sodium acrylate was used as co-monomer. Such phenomenon is observed for all buffers. The relatively high swelling ratio is also observed for the hydrogels, in which only acrylic acid was used. For hydrogels, in which a mixture of acrylic acid and sodium acrylate, was used in polymerization reaction, the effect of deterioration of the water absorption properties could be observed. Minimum in swelling ratio in each buffer solution is observed when molar fraction of NaAA in mixture with AA is equal 0.5. It was found significant increase in swelling ratio from 36 g/g to 49 g/g, when the pH of buffer solution is increasing from 5 to 8.

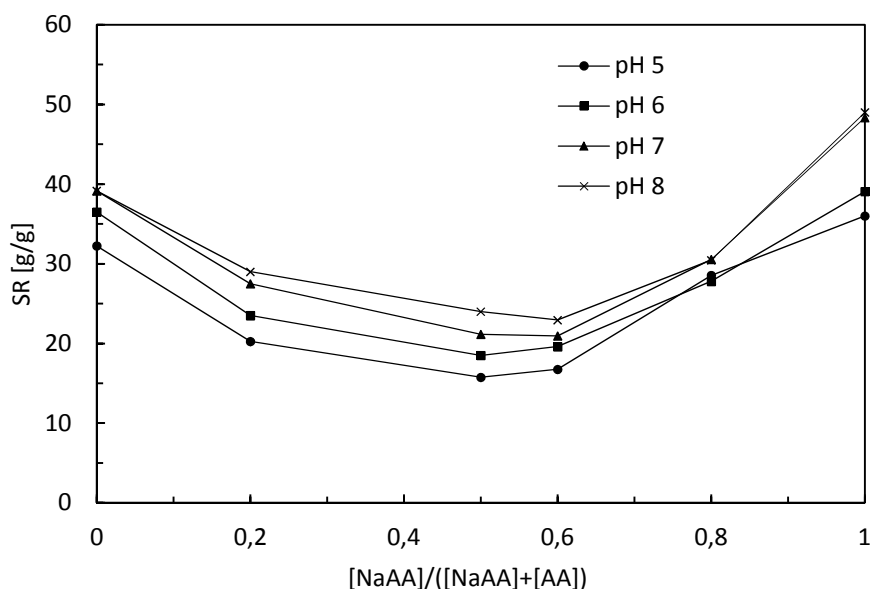


Fig. 3. Effect of the mole fraction of sodium acrylate to acrylic acid and pH of buffer solutions on swelling ratio of starch-based hydrogels.

Fig. 4 shows swelling kinetics in buffer solution at pH=8 for all starch-based hydrogels. At the initial stage of swelling, the swelling ratios of all hydrogel samples increases with the increasing in swelling time. When the swelling time was longer than 20 min, no significant changes were observed for SR value of each hydrogel sample, which indicates equilibrium in swelling process. The highest SR is observed within the first 10 minutes of the process. In that time over 70% of maximum SR is reached.

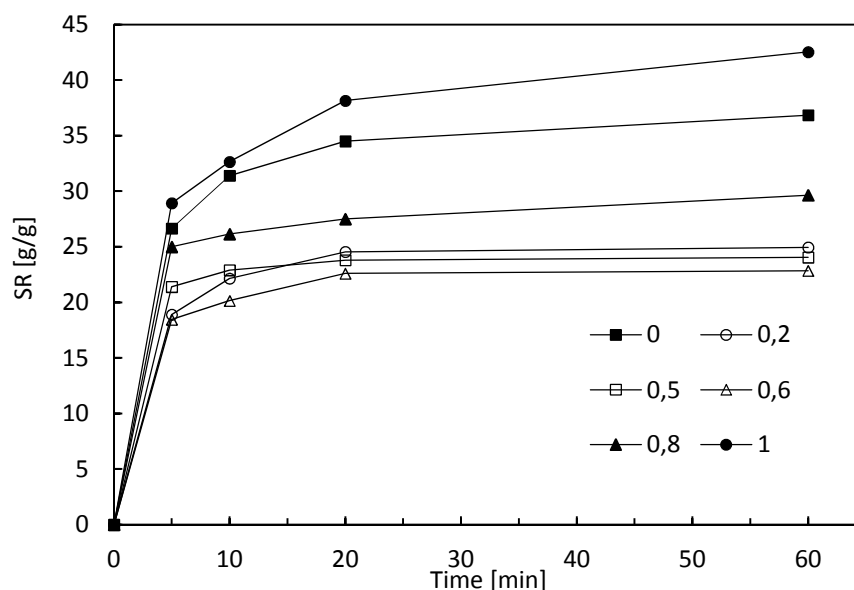


Fig. 4. Swelling kinetics of starch-based hydrogels with different mole fraction of sodium acrylate to acrylic acid (0 - 1) in buffer solution at pH=8.

Conclusions

Water-absorbing starch based copolymers of partially neutralized acrylic acid and acrylamide were synthesized by radical polymerization. Polymerization reaction was carried out in presence of crosslinking agent (N,N'-methylenebisacrylamide) and ammonium persulphate as an initiator. Highest swelling ratio is observed for hydrogels prepared with using of fully neutralized acrylic acid. It was observed for all buffer solutions. The water absorption ability is depending on the pH of the buffer solution. Swelling ratio is increasing when pH of buffer is increasing from 5.0 to 8.0.

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