STRUCTURAL AND SWELLING PROPERTIES OF HYDROGEL MEMBRANES BASED ON CHITOSAN CROSSLINKED WITH GLUTARALDEHYDE AND SODIUM TRIPOLYPHOSPHATE

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Abstract

Chemically and physically crosslinked chitosan hydrogel membranes were obtained by treatment of chitosan (Ch) with glutaraldehyde (GA) and with GA and subsequently with sodium tripolyphosphate (TPP). The formation of covalent and ionic crosslinks between Ch, GA and ionic TPP was confirmed by FTIR spectroscopy. The studies of dynamic swelling behaviour of synthesized membranes in buffer solutions of different pH (1.0, 7.4, 9.0) indicated that the swelling process obeyed a second-order kinetics. Values of an apparent swelling rate constant for Ch/GA and Ch/GA/TPP membranes were of the same order for acidic and neutral swelling media but they increased for alkaline solutions.

Key words: chitosan, membranes, crosslinking, swelling kinetics

1. Introduction

Hydrogels are hydrophilic polymeric materials arranged in three-dimensional network, that are capable of swelling in water or biological fluids and retaining a large amount of fluids in the swollen state. Three-dimensional networks are usually formed by chemical or physical crosslinking of hydrophilic polymer chains. In chemical gels polymer chains are connected by covalent bonds, but in physical gels they are held together by noncovalent bonds, such as van der Waals interactions, ionic interactions, hydrogen bonding, hydrophobic interactions, traces of crystallinity and multiple helices or by molecular entanglements [1, 2]. Different synthetic, natural and modified natural polymers, including chitosan, are used to form hydrogels.

Chitosan (Ch) is a cationic polysaccharide obtained by alkaline deacetylation of chitin. It is a linear copolymer of β-(1→4)-linked 2-acetamido-2-deoxy-β-D-glucopyranose and 2-amino-2-deoxy-β-D-glucopyranose [3] (Fig. 1). Due to such properties of chitosan as non-toxicity, biodegradability, biocompatibility, ability to easy modification, good film forming ability, etc., since many years it has been studied as membrane material [4-6]. Chitosan membranes have been extensively studied for different separation processes, including dehydration of alcohols and other solvents [5, 6]. However, chitosan is soluble in organic and inorganic acids. Therefore, various physical and chemical modifications have been developed to improve the chemical and mechanical stability of chitosan in acidic media.
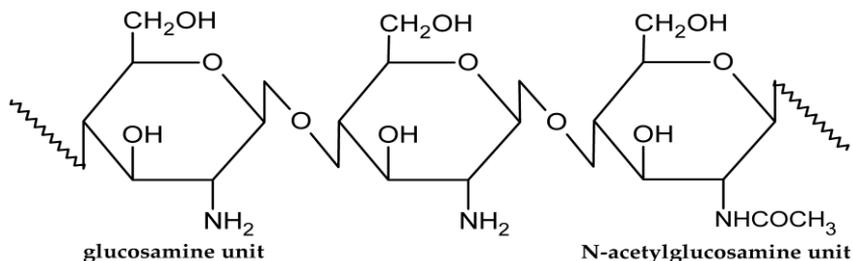
Figure 1. Chemical structure of chitosan.

The application of chitosan and another hydrogel membranes in different separation processes is highly influenced by their swelling properties. In this study chitosan membranes, based on Ch chemically crosslinked by glutaraldehyde (GA), Ch/GA, and Ch chemically crosslinked by glutaraldehyde and physically crosslinked by sodium tripolyphosphate (TPP), Ch/GA/TPP, were prepared and their swelling behaviour were analysed. Both equilibrium water content in Ch/GA and Ch/GA/TPP membranes as well as kinetics of swelling in swelling media of pH=1.2, 7.4 and 9.0 were analysed and compared to data obtained for non-crosslinked chitosan membranes.

2. Materials and Methods
2.1. Materials
Commercially available chitosan (molecular weight Mv = 720 kDa determined by viscometry [7, 8], degree of deacetylation DDA = 77.0% ± 2.3% determined by potentiometric titration method [7, 9]) from crab shells in the powder form was purchased from Sigma Aldrich (Germany). Crosslinking agents: glutaraldehyde (GA, 25 wt. % solution in water) and sodium tripolyphosphate (TPP) of analytical grade were purchased from Sigma-Aldrich (Germany) and POCh (Poland), respectively. Other reagents: acetic acid, hydrochloric acid, sodium hydroxide, sodium acetate, sodium chloride and TRIS buffer of analytical grade were purchased from POCh (Poland). Potassium bromide (KBr) for spectroscopy was purchased from Merck (Germany).

2.2. Membrane preparation
One–component chitosan membrane (non-crosslinked chitosan membrane, Ch) was obtained by casting of 1% (w/v) chitosan solution in 2% (w/v) acetic acid on a clean glass plate and evaporating to dryness at 37°C. Two-component chitosan membrane (chitosan membrane crosslinked with glutaraldehyde, Ch/GA) was obtained by mixing GA solution and chitosan solution and casting the obtained mixture on a clean glass plate and evaporating to dryness at 37 °C. The content of GA in casting solution was 1 wt.%. Ch and Ch/GA membranes after removing from the glass plate were immersed in 2M NaOH solution to remove the residual acid, thoroughly washed with water and dried at 37°C. Three-component chitosan membrane (chitosan membrane crosslinked with glutaraldehyde and sodium tripolyphosphate, Ch/GA/TPP) was prepared by immersing Ch/GA membrane in 1.3 % (w/v) TPP solution for 1h. The crosslinking conditions were as follows: T=4°C, pH=5.5. Ch/GA/TPP membrane before drying was thoroughly washed with water. All membranes before spectral measurements and swelling experiments were thoroughly dried under vacuum at 60°C.

2.3. FTIR spectroscopy analysis
FTIR spectra of non-crosslinked and crosslinked chitosan in KBr disc form were recorded on Perkin-Elmer 2000 FTIR spectrometer from 4000 to 400 cm^{-1} with a resolution 4 cm^{-1} and 100 scans. The polymer samples were ground into a fine powder using liquid nitrogen and thoroughly dried under vacuum at 60 °C before milling with anhydrous KBr.

2.4. Swelling measurements
Dynamic swelling experiments were performed in three buffer solutions (pH 1.0, 7.4, 9.0) at constant ionic strength I=0.145 M and at 37ºC. pH of swelling solutions was measured with pH-meter (Elmetron, Poland) and their ionic strength was adjusted to 0.145 M with the addition of sodium chloride. The degree of membrane swelling (S) was measured by gravimetric method. The

completely dry membrane sample of known mass (m_o) was immersed on definite time period t in buffer solution. After time t the sample was taken out from the buffer, wiped quickly with filter paper and weighed (m_t) The swelling degree S at time t was calculated in grams of water per grams of dry membrane using the following formula:

$$S = (m_t - m_o)/m_o \qquad (1)$$

where: m_o -mass of the dry sample in g, m_t -mass of the swollen sample in g at time t.

The swelling kinetics were followed by measuring the membrane sample mass until equilibrium was reached. The swelling degree at equilibrium S_{eq} is given by

$$S_{eq} = (m_{eq} - m_o)/m_o. \qquad (2)$$

3.   Results and Discussion
3.1. Structural characterization of membranes by FTIR spectroscopy

FTIR spectra of non-crosslinked chitosan, chemically crosslinked chitosan and chemically and physically crosslinked chitosan are presented in Fig. 2. In FTIR spectrum of chitosan characteristic bands at 1656 cm^{-1} (C=O stretching in amide group, amide I vibration), 1598 cm^{-1} (N-H bending in aminoglucose primary amine) and 1560 cm^{-1} (N-H bending in amide group, amide II vibration) [10, 11] are observed. After chitosan crosslinking with GA these bands shift to 1648 cm^{-1}, 1695 cm^{-1} and 1566 cm^{-1} respectively. As we discussed earlier [7], the band at 1648 cm^{-1} is composed of amide I band of chitosan and C=N stretching band of Schiff's base and confirms the reaction of chitosan and GA with formation of imines (Schiff bases). The new absorption bands at 1645 cm^{-1} and 1203 cm^{-1} in the spectrum of Ch/GA/TPP can be assigned to asymmetric N-H deformation vibrations in NH_3^+ ion and P=O stretching vibrations in tripolyphosphate ion [12], respectively.

The spectral changes observed in the FTIR spectrum of chitosan crosslinked with glutaraldehyde or glutaraldehyde and sodium tripolyphosphate indicate the formation of covalent and ionic crosslinking bonds, as schematically presented in Fig. 3.
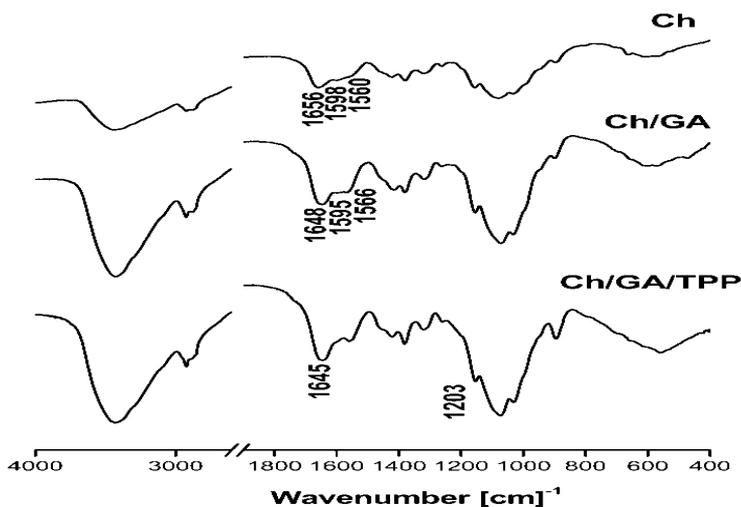
Figure 2. FTIR spectra of Ch, Ch/GA and Ch/GA/TPP
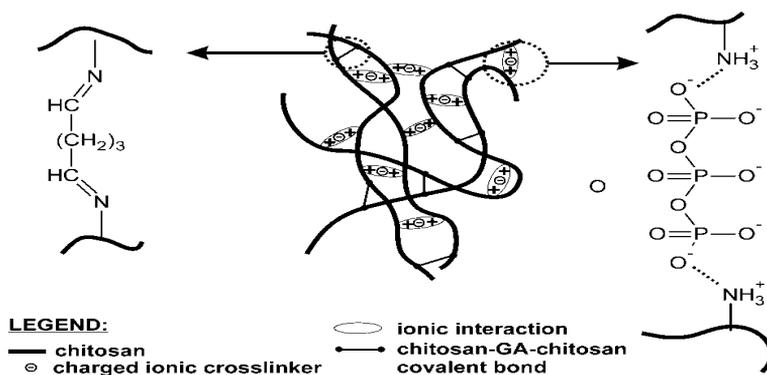
Figure 3. Schematic representation of chemical structure of crosslinked chitosan membranes.

3.2. Swelling properties of membranes

Swelling isotherms for non-crosslinked and crosslinked chitosan membranes in analysed buffer solutions are presented in Fig. 4.
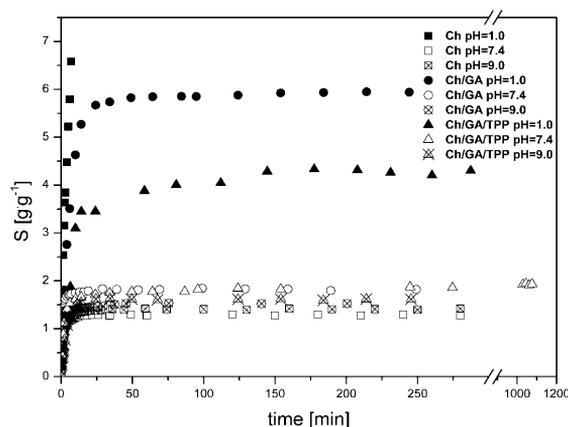
Figure 4. Swelling isotherms of noncrosslinked and crosslinked chitosan membranes.

As can be seen, non-crosslinked chitosan membrane swelled and disintegrated quickly at pH=1.2, but it was stable at pH=7.4 and 9.0. Ch/GA and Ch/GA/TPP membranes were stable in all buffer solutions. Swelling isotherms for Ch (in solutions of pH=7.4 and 9.0), Ch/GA and Ch/GA/TPP are similar by shape. The water content in the membrane and/or degree of swelling S increase with time up to certain level, then they level off and reach an equilibrium water content m_{eq} or a swelling degree at equilibrium S_{eq}. For each membrane value of S_{eq} decreases with an increase of pH (Fig. 5). The observed decrease of degree of swelling of chitosan membrane with increase of pH of swelling solution results from the decrease of the degree of ionisation of chitosan [13].
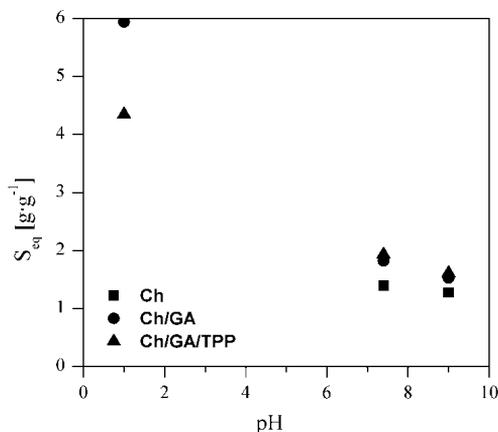
Figure 5. Equilibrium swelling degrees of noncrosslinked and crosslinked chitosan membranes in different buffer solutions (I = 0.145 M, T = 37ºC).

Using the values of the degree of swelling at any time t and equilibrium degree of swelling it is possible to analyze the kinetic order of the swelling process [14, 15].

For the first order kinetics the rate of swelling at any time may be expressed by Eq. (3):

$$\frac{dS}{dt} = k_1(S_{eq} - S) \qquad (3)$$

where: S is degree of membrane swelling at time t, S_{eq} is degree of swelling at equilibrium, k_1 is a first-order rate constant.

This equation after integration between limits S=0 at t=0 and S=S at t=t results in

$$\ln\frac{S_{eq}}{S_{eq} - S} = k_1 t \qquad (4)$$

A plot of the left-side term of this equation vs t should lead to a straight line. However, none of the hydrogel chitosan membrane studied obeyed Eq. (4). As an example, the variation of $\ln(S_{eq}/(S_{eq}-S))$ as a function of time is plotted in Fig. 6A for Ch, Ch/GA and Ch/GA/TPP membranes in buffer solution of pH=9.0.
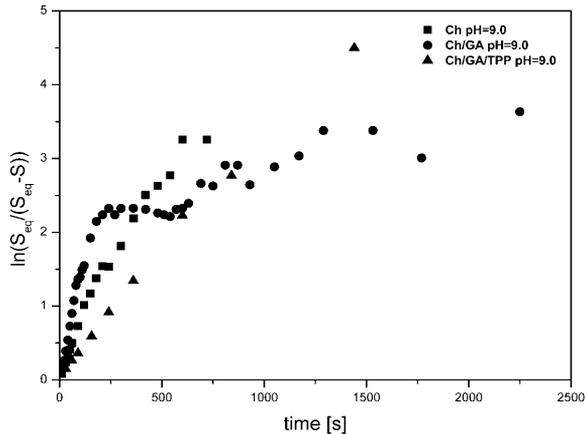
Figure 6A. Plots of $\ln(S_{eq}/(S_{eq}-S))$ vs time for Ch, Ch/GA and Ch/GA/TPP membranes.

If we assume that the swelling processes of hydrogel membranes in buffer solutions follow the second-order swelling kinetics, then the swelling rate at any time may be expressed as

$$\frac{dS}{dt} = k_2 (S_{eq} - S)^2 \qquad (5)$$

where: k_2 is a second-order rate constant.

After integration between the limits S=0 at *t*=0 and S=S at *t*=t the following integrated equation is obtained

$$S = \frac{k_2 S_{eq}^2 t}{1 + k_2 S_{eq} t} \qquad (6)$$

which after rearrangement yields the well known Schott′s equation [16]

$$\frac{t}{S} = \frac{1}{k_2 S_{eq}^2} + \frac{t}{S_{eq}} \qquad (7)$$

According to Eq. (7), if the swelling process of hydrogel follows a second-order kinetics, then the swelling data must fit a straight line with a slope of $1/S_{eq}$ and an ordinate $1/k_2 S_{eq}^2$. Application of swelling data for the studied membranes to Eq. (7) resulted in a series of plots presented in Fig. 6B.
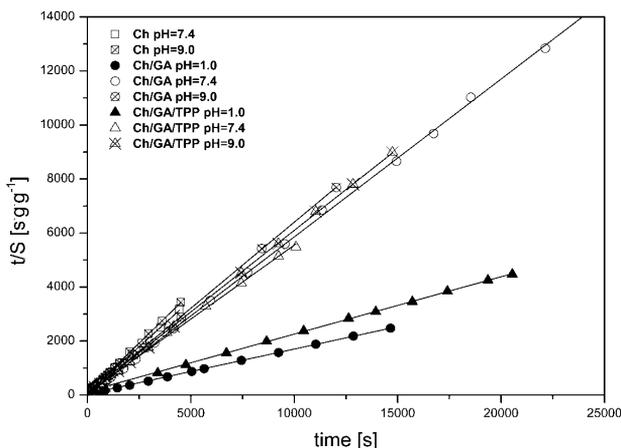
Figure 6B. Plots of t/S vs time for Ch, Ch/GA and Ch/GA/TPP membranes buffers of different pH.

For each membrane the experimental data fit Eq. 7 over the whole range of values. Values of rate constants k_2, equilibrium swellind degrees $S_{eq}^{calc.}$ and determination coefficients R^2 are gathered in Table 1. As can be seen, the values

of determination coefficients are very good, in each case $R^2 > 0.999$. So, the results indicate that the swelling processes of chitosan membranes in the buffer solutions follow Schott′s second-order kinetics equation. Data presented in Table 1 indicate that both for non-crosslinked chitosan membrane, as well as for crosslinked membranes, values of swelling rate constants were lower in acidic swelling media than in alkaline solutions.

Table 1. Second-order kinetic parameters for non-croslinked and croslinked chitosan membranes.

	pH	$S_{eq}^{calc.}$ [g·g⁻¹]	$k_2 \cdot 10^3$ [s⁻¹]	R^2
Ch	**1.0**	-	-	-
	7.4	1.45	8.62	0.9995
	9.0	1.34	10.80	0.9991
Ch/GA	**1.0**	6.27	0.67	0.9998
	7.4	1.89	15.15	0.9999
	9.0	1.57	13.31	0.9999
Ch/GA/TPP	**1.0**	5.04	0.19	0.9985
	7.4	2.00	3.82	0.9999
	9.0	1.66	5.90	0.9996

Our results are in agreement with findings of the others for different ionic hydrogels. The dynamic swelling of the anionic and cationic hydrogels is in good agreement with a second-order kinetics [14, 15, 17-20].

4. Conclusions

Modified hydrogel membranes were prepared by chemical crosslinking of chitosan with glutaraldehyde followed by physical crosslinking with sodium tripolyphosphate. FTIR spectroscopy of non-crosslinked chitosan membrane, chitosan membrane crosslinked with GA and chitosan membrane crosslinked with GA and TPP confirmed the formation of covalent crosslinks between glutaraldehyde and chitosan or simultaneously covalent and ionic bonds between chitosan, glutaraldehyde and sodium tripolyphosphate

The swelling properties of Ch, Ch/GA and Ch/GA/TPP membranes in swelling media of different pH (pH=1.0, 7.4 and 9.0) has been studied. It has been found that the swelling behaviour of each chitosan membrane depended on pH of the surrounding medium. The S_{eq} values of the studied chitosan membranes decreased with increasing pH of swelling medium. The experimental

data suggested that the swelling process followed a second-order kinetics. The apparent swelling rate constants were lower for acidic swelling media then for alkaline solutions. It means, that swelling processes of chitosan hydrogel membranes became somewhat faster in alkaline swelling media.

5. References

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