

CHARACTERIZATION OF WATER STATE IN CHITOSAN HYDROGEL MEMBRANES

Zofia Modrzejewska

*Faculty of Process and Environmental Engineering
Technical University of Łódź,
ul. Wólczańska 175, 90-924 Łódź, Poland
e-mail: zmodrzej@wipos.p.lodz.pl*

Abstract

In this study, the structure of hydrogel chitosan membranes was investigated. To determine the structure of hydrogel membranes the Differential Scanning Calorimetry (DSC) was used. On the basis of DSC spectra the enthalpy of the character of water in the structure were determined.

Key words: *chitosan membranes, hydrogel, DSC.*

1. Introduction

Polysaccharides are in the group of materials that are designed mainly for biomedical applications. Chitosan and its complexed forms are used in many branches of biomedical engineering, mainly as athrombogenic coatings, biomaterials in dressings, auxiliary substances in the controlled drug release systems and as packing of implants. Biological activity is revealed mainly by polysaccharides in the form of hydrogels. They are formed by hydrogen and ionic bonds. The stable, crystalline structure causes that chitosan is insoluble in water solutions at pH up to 7. However, in the medium of dissolved acids the free amino groups are protonated and at pH about 5 chitosan is dissolved. In order to convert it into a gel, pH is changed (increased), solvents of low polarity are used as precipitating substances (e.g. methanol) or they are complexed with water-soluble natural anionic polysaccharides (heparin, alginate) or synthetic polyanions (poly(acrylic) acid, phosphates) [1 - 11].

The aim of this study was to produce highly porous chitosan membranes and to recognise the possibility of their application in biomedical engineering as dressings with immobilised pharmacological materials.

In this study, the structure of hydrogel chitosan membranes was investigated. In the case of hydrogels, methods of structural investigations are limited. The usually applied methods such as mercuric porosimetry and the method of adsorption-desorption of nitrogen, benzene or CO₂ (on the basis of BET, BJH or GET isotherms) are inadequate for hydrogels because they require dry samples. Of interest are the methods Differential Scanning Calorimetry (DSC) and Raman spectroscopy. To determine the structure of hydrogel membranes the (DSC) was used. The DSC technique enabled the determination of thermal effects of particular phase transitions related to physical or chemical transformations being a function of time or temperature [12-22].

On the basis of DSC spectra the enthalpy of phase transitions and the character of water in the structure were determined.

2. Materials and methods

2.1 The method of formation of gel chitosan membranes

Hydrogel membranes were produced in the processes of phase inversion, due to changes in the pH of a precipitating medium. The membranes were formed from chitosan acetate, formate, chloride and lactate. The concentration of polymer in the membrane-forming solution ranged from 6 to 12% wt. To dissolve chitosan, a stoichiometric amount of acid was added in relation to amino groups present in a polymer molecule. A coagulant was the water solutions of 5% NaOH. Chitosan salts were distributed over a flat surface by means of an applicator with slit height 0.9 mm and immersed in a coagulation bath for 20 min. Next, the surface was washed with distilled water until a membrane of pH = 7 was formed on it.

For comparison, chitosan membranes were produced in the system where polyanion – sodium triphosphate was used instead of a basic coagulation bath. The membranes were formed from chitosan acetate and lactate of polymer concentration reaching 8%. After

distributing the salt solution on a flat surface as described above, it was placed in 20% sodium triphosphate for 1 h, and next washed.

2.2 The characteristics of gel chitosan membranes

The microporous membrane structure was determined by the DSC method using a Perkin-Elmer calorimeter V3 1E TA Instruments. DSC data were recorded over the temperature range from -100 °C to +300 °C. Samples were rapidly cooled and then heated (10 °C/min).

3. Results and discussion

The effect of polymer concentration and type of solvent on the structure of chitosan hydrogel membranes is presented in this study. The structural characteristics were determined on the basis of DSC spectra analysis. The analysis of subsequent peaks for water of membranes formed by the phase inversion method is given in Table 1. From the obtained curves the enthalpy of semi bound water evaporation (from the peak area at the temperature 110 - 120 °C) and the enthalpy of ice melting (from the peak area at the temperature 2 - 3 °C) and enthalpy of free water evaporation (from the peak area at the temperature 80 - 100 °C) were determined. Results are shown in *Figures 1 to 7*.

In membranes formed from chitosan formate, the enthalpies of ice melting and water evaporation depend linearly on polymer concentration in the initial solution, i.e. as expected they decrease with an increase of the concentration. For membranes formed from chitosan chloride the melting enthalpy reaches a minimum at polymer concentration in the solution being 8%, while the enthalpy of water evaporation is as expected, i.e. it decreases with the concentration increase. For membranes formed from chitosan acetate the enthalpy of melting achieves a slight maximum at 8% polymer concentration in the solution, while the

Table 1. The analysis of curves DSC for membranes formed by the phase inversion method.

Solvent type	Polymer concentration, %	Enthalpy of ice melting		Enthalpy of free water evaporation		Enthalpy of semi bound water evaporation		Enthalpy of water evaporation	
		Temperature, °C	Enthalpy, J/g	Temperature, °C	Enthalpy, J/g	Temperature, °C	Enthalpy, J/g	Total, J/g	Free + Semi bound water, J/g
Formic acid	6	3.49	300.9	97.92	740.6	112.27	1330	2372	2071
	8	3.10	280.1	95.69	374.1	117.53	1550	2204	1924
	10	2.93	267.5	88.56	348.7	120.47	1602	2218	1951
Hydrochloric acid	6	3.63	307.7	93.6	791.2	110.18	1105	2204	1896
	8	2.07	241.7	90.39	504.5	114.80	1290	2036	1795
	10	2.60	284.6	86.07	277.7	110.44	1517	2080	1795
Lactic acid	6	3.96	288.8	97.88	1009	112.36	1028	2326	2037
	8	3.18	268.9	96.37	507.1	110.58	1350	2126	1857
Acetic acid	6	3.09	286.0	93.30	781.7	110.14	1176	2291	1998
	8	2.31	305.3	80.48	368.0	119.15	1788.0	2461	2156
	10	2.86	264.2	78.25	400	107.67	1483	2197	1933
	12	2.93	250.6	78.59	289.6	113.75	1367	1939	1688

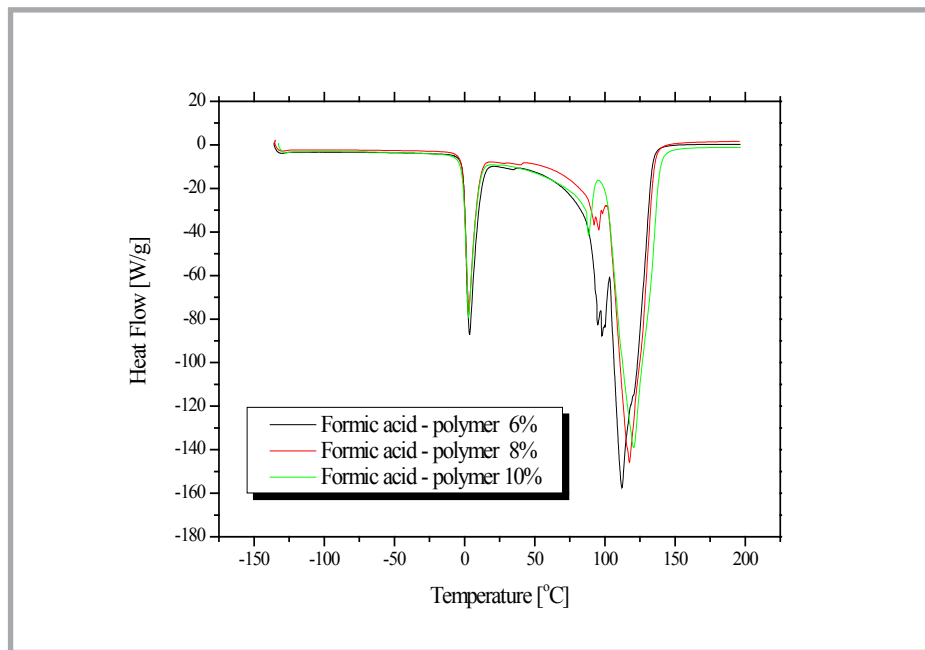


Figure 1. DSC spectra – membrane from chitosan formate / coagulation NaOH.

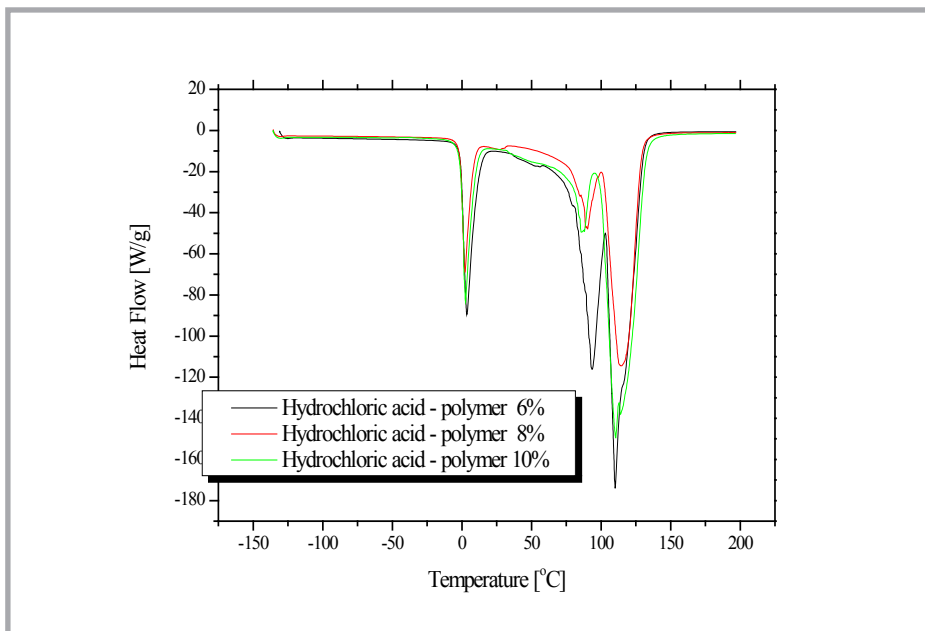


Figure 2. DSC spectra – membrane from chitosan chloride / coagulation NaOH.

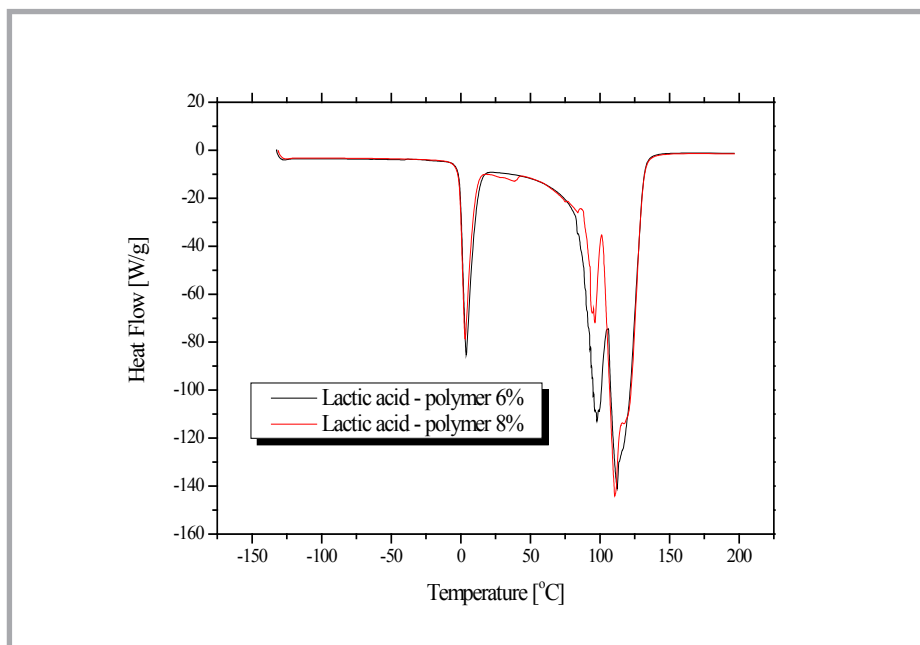


Figure 3. DSC spectra – membrane from chitosan lactate / coagulation NaOH.

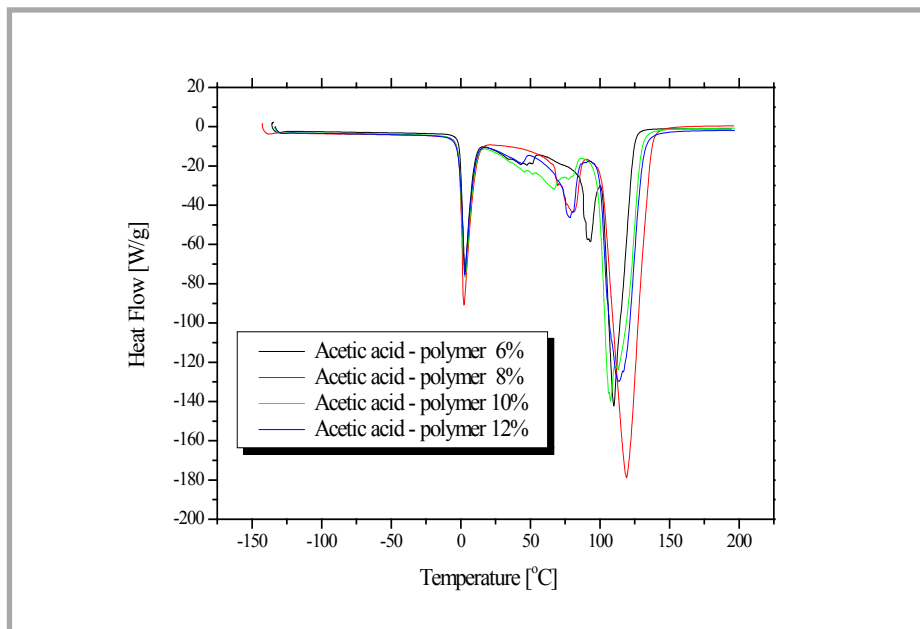


Figure 4. DSC spectra – membrane from chitosan acetate / coagulation NaOH.

enthalpy of water evaporation reaches a small minimum at this concentration; however, in general the character of changes is correct – it decreases with the increase of concentration.

Membranes from chitosan lactate were produced at 2 initial concentrations, hence it is difficult to formulate conclusions. The enthalpies of melting and evaporation decrease with the increase of concentration.

While determining semi bound water, for membranes formed from chitosan chloride, lactate and formate a relation was obtained where, as expected, with an increase of polymer concentration in the initial solution the enthalpy of semi bound water grows, while non-typical interesting properties are obtained in the case of chitosan hydrogels formed from chitosan acetate, at the polymer concentration in the solution being 8%. Then, the enthalpy of semi bound water grows abruptly.

To determine the character of water present in the structure, Mansor and Malcolm's method was applied. In the analysis peaks appearing at 2 to 3°C were used (they were related to the presence of water that froze out, i.e. water that was unbound or very weakly bound to a polymer molecule) and a number of peaks that appeared at the temperature from 80 to 103°C (related to the enthalpy of water evaporation from subsequent layers). The bound water is represented as a difference between the total water present in the struc-

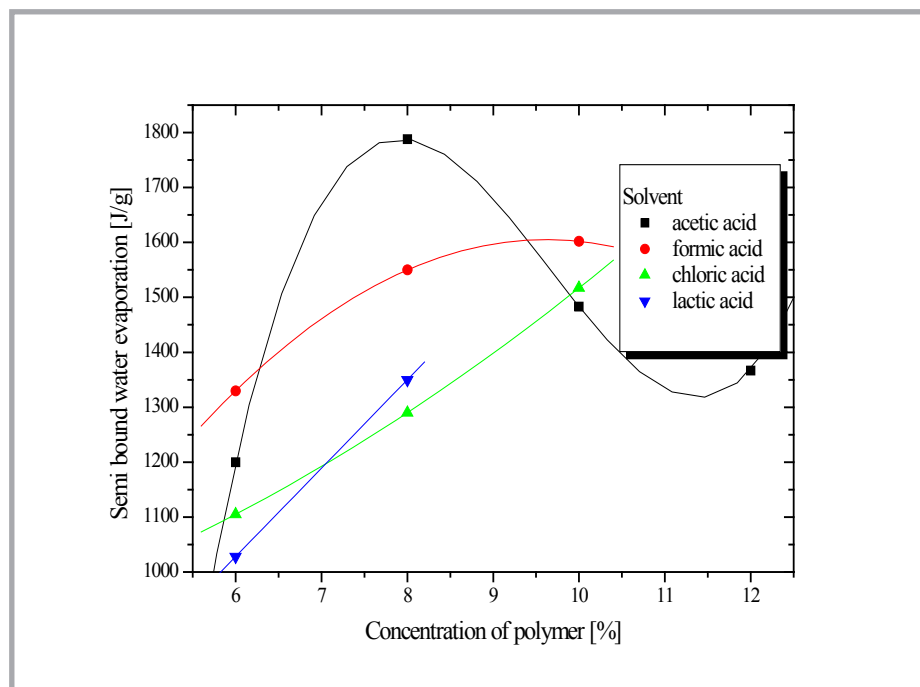


Figure 5. The effect of polymer concentration in the film-forming solution on the enthalpy of semi bound water evaporation.

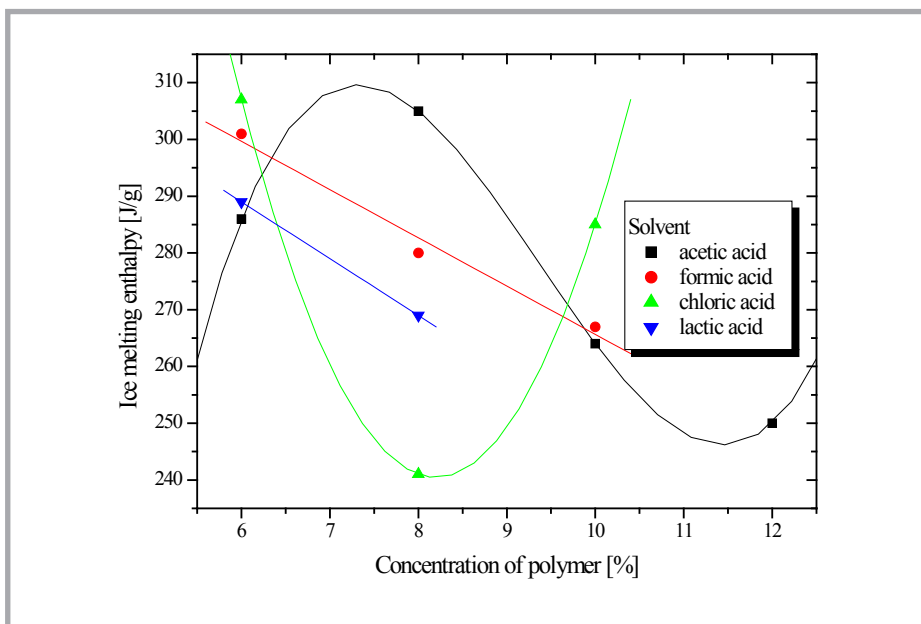


Figure 6. The effect of polymer concentration in the film-forming solution on the enthalpy of ice melting.

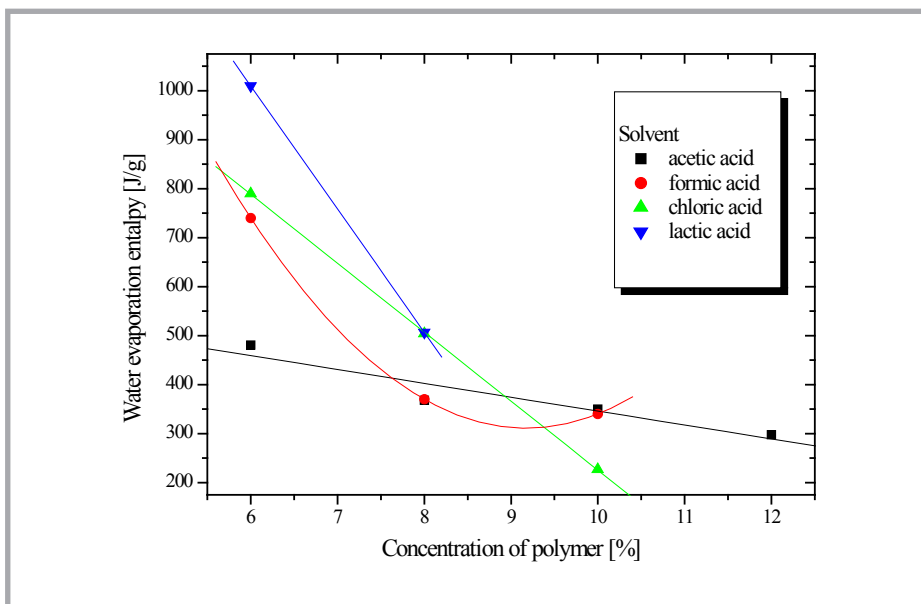


Figure 7. The effect of polymer concentration in the film-forming solution on the enthalpy of water evaporation.

Table 2. Character of water contained in the chitosan hydrogel structure

Sample type		Percent of water in the membrane W_t , %	$\frac{Q_{endo}}{Q_f} \cdot 100$	Percent of bound water W_b , %
Type solvent	polymer content, %			
Acetic acid	6	92.83	87.46	5.37
	8	89.02	91.19	0.12
	10	86.10	78.92	7.18
	12	82.91	74.85	8.06
Formic acid	8	88.33	83.67	4.66
Hydrochloric acid		87.88	72.20	15.68
Lactic acid		87.67	80.32	7.35

ture and water that freezes. Taking the melting enthalpy for pure water ($Q_f = 334.78 \text{ J/g}$), the amount of water bound in the hydrogel structure was calculated from the equation:

$$W_b (\%) = W_t - (W_f + W_{fb}) = W_t - (Q_{endo} / Q_f) \cdot 100$$

where: W_t – total amount of water in hydrogel, W_b – bound water in hydrogel – the water does not freeze, W_f and W_{fb} – unbound or partly bound water – it freezes; and given in **Table 2**.

It follows from the studies that from chitosan acetate containing 8% polymer in the solution, membranes are formed that contain almost exclusively unbound water. Most bound water is in the membranes formed from chitosan chloride, where polymer concentration in the initial solution was also 8%.

Comparative studies were performed for the membranes formed by the phase inversion method and those obtained in the polyanion – sodium triphosphate system. Results are given in **Table 3** and **Figures 8 & 9**.

When polyanion is used instead of basic bath, membranes with a lower content of water in the structure were obtained. This is confirmed by a remarkable decrease of the enthalpy of water evaporation (1.4 - 2.5x) and a reduction of the ice melting enthalpy.

4. Conclusions

- The method for structure determination of hydrogel chitosan membranes on the basis of DSC spectra enables specification of the character of water contained in the membrane structure.
- Interesting results were obtained for chitosan membranes formed from chitosan acetate containing 8% polymer. The membranes contain a very small amount of bound water, while semi bound water reaches a maximum value. This is probably due to the formation of an ordered structure already in the initial solution.
- Membranes formed from chitosan chloride reveal some deviations from expected properties also in the case of 8% solutions, the enthalpy of melting attains certain minimum at this polymer concentration in the solution, while the enthalpies of water evaporation and semi bound water have a character which is in agreement with theory.

Table 3. The analysis of curves DSC for membranes formed by polyanion – polycation system.

Initial salt		Enthalpy/temperature of phase transition			
Solvent	Coagulant	Semi bound water	Ice melting	Water evaporation	Related to the presence of TRI
Acetic acid	NaOH	119/1788	2.31/305	64-/368	
	TRI	102/1425	2.05/244	75/143	41/74
Lactic acid	NaOH	110/1350	3.18/268	92.2/507	
	TRI	111.5/1185	2.54/252	88/349	48/75

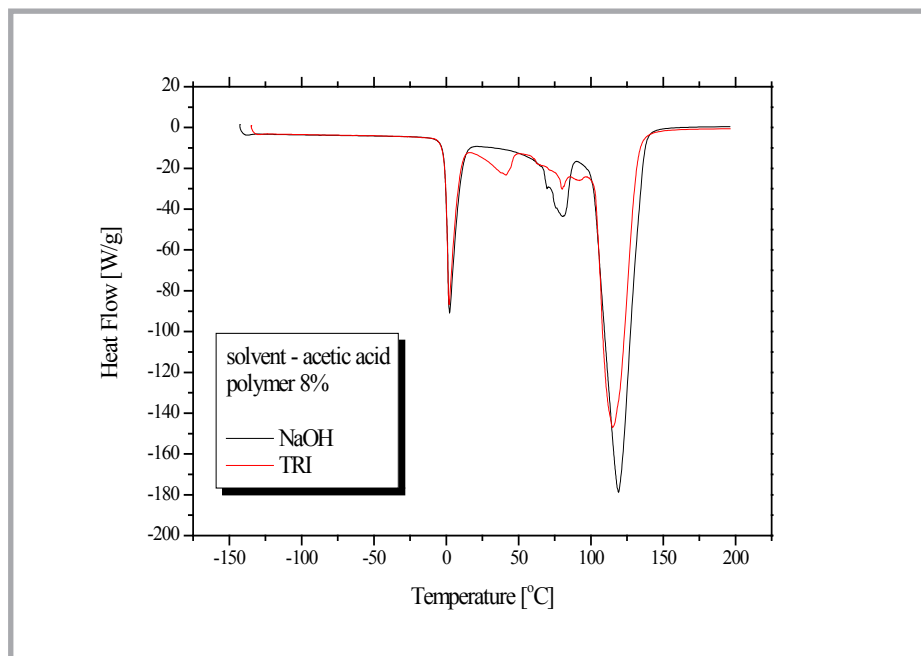


Figure 8. Comparative - the membranes formed by the phase inversion method and those obtained in the polyanion - sodium triphosphate system - solvent acetic acid.

- Membranes formed from formate show typical properties, in agreement with theoretical predictions. The enthalpies of melting and water evaporation decrease with an increase of polymer concentration in the initial solution, while the enthalpy of semi bound water increases.
- Membranes formed in the presence of polyanion have less water in their structure than the membranes formed by the phase inversion method and their semi bound water is lower.
- Interesting for further studies can be the membranes formed from chitosan acetate at the concentration around 8%. A significant increase of semi bound water and lack of bound water in the structure can suggest ordering of the polymer molecules in the film-forming solution.

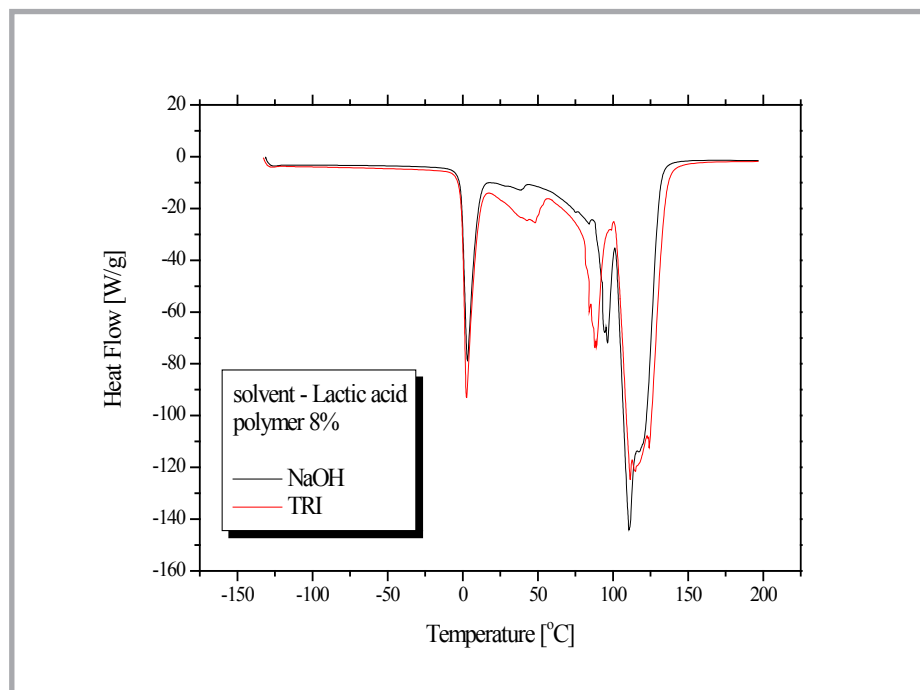


Figure 9. Comparative - the membranes formed by the phase inversion method and those obtained in the polyanion - sodium triphosphate system - solvent: lactic acid.

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