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Properties of hydrophilic chitosan network membranes by introducing binary crosslink agents

Huang-Shian Tsai, Yen-Zen Wang (✉)

Graduate School of Engineering Science and Technology (Doctoral Program), National Yunlin University of Science & Technology, Yunlin, 640 Taiwan
E-mail: wangzen@yuntech.edu.tw; Fax: 886-5-5312071

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Summary

In this investigation chitosan (CS) was crosslinked using mixtures of sulfosuccinic acid (SSA) and glutaraldehyde (GA) as the binary crosslinking agents to form hydrophilic chitosan network membranes. GA and SSA improve the tensile strength and contribute to hydrophilicity of the membranes, respectively. The membranes prepared by varying the crosslinking agent ratios are also characterized using FT-IR, X-ray diffraction, and tensile testing, and their swelling ratio and thermal properties were measured. Experimental results reveal that the contact angle of the membrane decreases from 84.54° to 69.83° and the maximum stress rises from 39.62 MPa to 133.66 MPa as the increase of the binary crosslinking agent content. These resultant membranes not only maintain its hydrophilicity and but also enhance the mechanical strength.

Introduction

Interest in the production and use of new materials from renewable sources is growing. Natural polymers are replacing synthetic polymers in numerous applications, for example, solving numerous problems in environmental and biomedical engineering [1-2]. Over the last few years, interest in the naturally available class of polymers known as polysaccharides has been increasing rapidly, because of their abundance in nature [3]. Chitosan is a basic polysaccharide that is easily prepared from the shells of crabs, shrimp and prawns. Furthermore chitosan is an environmentally benign compound. The advantages of being non-toxic, antibacterial and biodegradable have led chitosan and its derivatives to have been attracted increasing attention. Recently, active researches have been conducted on the use of chitosan and it derivatives in water and wastewater treatment, including their use as coagulants [4], biomaterials [5-6] and membrane materials [7-8], as well as for extracting heavy metal ions from aqueous solution [9-10] etc.

A key disadvantage of chitosan membranes is its poor tensile strength, which limits its use. Chitosan contains active amino groups and hydroxyl groups that can produce hydrogen bonds with water. These two active functional groups enable chitosan to be

chemically modified. Polysaccharides can be crosslinked by a reaction between the hydroxyl and amino groups of the chains with an appropriate agent to generate water-insoluble crosslinked networks [11] and to improve its mechanical strength and physicochemical properties. Chitosan can be crosslinked by various chemicals, including glutaraldehyde [12-15], formaldehyde [16-19], sulfuric acid [17-18, 20] and multicomponent carboxylic acid [21-22].

Glutaraldehyde (GA) has been the most frequently used crosslinking agent that forms a Schiff base when reacted with CS [23]. The crosslinking reactions of general organic crosslinking agents such as GA, normally increase the mechanical strength, but make the CS membranes less hydrophilic, causing a loss of amino binding sites by reaction with aldehyde [24] and consisting long hydrophobic alkyl chains without hydrophilic groups. The resulting membranes had poor permselectivity. Hydrophilicity is a very important characteristic of this material, especially when used in affinity membranes.

Therefore, a hydrophilic crosslinking agent is expected to improve the hydrophilicity of the membrane except crosslinkage. Sulfosuccinic acid (SSA) has three crosslinkable sites (two carboxylic acid groups and one sulfuric acid group) and a relatively bulky chemical structure. The three acidic groups effectively crosslink with chitosan molecules, and help to keep the membrane hydrophilic [25].

The crosslinked polymers are obtained under homogenous or heterogeneous conditions by reticulation with bi- or polyfunctional crosslinking agents. Crosslinked heterogeneous conditions improve partial mechanical strength. Homogeneous conditions are more effective in improving bulk strength. A hydrophilic crosslink agent, SSA, can not form a film when crosslinked was performed under homogeneous conditions.

For hydrophilicity membrane applications, mechanical strength can be improved by crosslinking and without reducing hydrophilicity, using a binary crosslinking agent such as sulfosuccinic acid (SSA) and glutaraldehyde (GA) in homogeneous condition to keep the membrane hydrophilic and improve its mechanical strength in this study.

Experimental

Materials

Chitosan was purchased from Fluka Chemical Co.. The degree of deacetylation was approximately 85%. Acetic acid (J. T. Baker), glutaraldehyde (25% aqueous, GA)(JASSEN), sulfosuccinic acid (75% aqueous, SSA)(Aldrich) and ethanol(Riedel-DeHaën) were also used. All of the reagents and solvents were of reagent grade.

Membrane preparation

Chitosan membranes were prepared from 2 wt % aqueous solution of chitosan, which was formed by dissolving 2 g of chitosan in 100 mL of distilled water that contained 2 mL of acetic acid. Aqueous 2:1 GA/SSA solution was prepared as a crosslinking agent. The crosslinking agent and the polymer solutions were mixed and then stirred

for at least a half-day at room temperature to produce a homogeneous solution. The degree of crosslinking was controlled by varying the crosslinking agent content. The resulting crosslinked membrane was designated as CS*x*GASSA, where *x* denotes the weight percentage of binary crosslinking agent, based on the weight of chitosan, in the crosslinked membranes. Homogeneous membranes were cast onto a Petri dish. The membranes were placed in a vacuum to remove air pockets and dried in a thermostat oven at 50°C for 12 h. The resulting membranes were 0.03-0.05 mm thick that measured at least five times with a Vernier Caliper and the averaged value was used as the thickness.

Membrane characterization

FT-IR spectroscopy

FT-IR spectra of the crosslinked chitosan membranes were obtained using a Perkin Elmer FT-IR spectrometer (Fourier-Transform Infrared Spectroscopy-mode: spectrum one). A homogeneous polymer solution containing crosslink agent was cast directly on CaF surface followed by the same drying procedures used in the membrane preparation. Sixteen scans from 900 to 4000 cm^{-1} were performed on each sample with a resolution of 2 cm^{-1}.

Density and fractional free volume (FFV) measurement

A quantity frequently used to compare the free volume in polymers is the fractional free volume (FFV), which is defined: [26]

$$FFV = \frac{V_{sp} - V_0}{V_{sp}} \qquad (1)$$

where V_{sp} is the polymer bulk specific volume and V_0 is the volume occupied by polymer chains. The value of V_0 may be calculated using

$$V_0 = 1.3V_W \qquad (2)$$

where V_w is the van der Waals volume, which can be estimated using group contribution methods. The method of Bondi [27] is adopted herein.

The bulk density of the chitosan and the crosslinked chitosan membrane were measured using a Mettler Toledo Excellent XS Analytical Balance with octane as the auxiliary liquid at 25°C.

The true density of the chitosan and the crosslinked chitosan membrane were measured using an AccuPyc™ 1330 Pyconometer.

Measurement of contact angle

The contact angle (θ) between the water and the chitosan films was measured using a First Ten Ångstroms (FTA 200) contact angle meter at room temperature. Water was carefully dropped onto the chitosan films and contact angles were determined before the swelling of the films using the auto pump program procedure. The auto pump is controlled by a computer and set with constant drop rate and volume. In our study, the automatic dropping rate is set at 2.0000 ul/s and automatic pumped volume is 25 ul.

Mechanical testing
Samples of size 30 x 10 x 0.05 mm^3 were prepared for testing in a tension machine (mode TCF-RC) that was made by Yashima Works Ltd. The speed of the testing machine crossheads was controlled at 10 mm/min. The wet non-crosslinked chitosan is too brittle to be able to measure its tensile strength.

Swelling ratio measurement
The pre-dried samples were carefully weighed and submerged under deionized water or 95 wt. % ethanol aqueous solution at room temperature. After 24 hours, the swollen samples were removed from the water; excess water was wiped off, and the samples were weighed. The swelling ratio was calculated as follows.

$$\text{Swelling ratio} = \frac{(W_s - W_d)}{W_d}$$

where W_s and W_d are the weights of the swollen and dry samples, respectively.

XRD analysis
A Siemens D 5000 X-ray diffractometer was applied to investigate the solid state morphology of crosslinked chitosan film. X-rays of 1.5406Å wavelength were generated using a CuK α source. The angle of diffraction was varied from 5 to 45°.

Thermal analysis
The thermal stability of the polymer films was studied using DuPont Q500 TGA instrument ranged from 25 to 600°C at 20°C/min, with nitrogen flushed at 40 ml/min. Modulated differential scanning calorimetry (MDSC) was performed using a DuPont Q100 DSC system with a refrigerated cooling accessory (RCS) and modulated capability. Samples were analyzed under continuously flowing dry nitrogen gas (40 ml/min) at 3°C/min from -50°C to 200°C. The amplitude and the period of the MDSC were 0.8°C and 60 s, respectively.

Results and discussion

Characterization

FT-IR spectroscopy
Figure 1 displays FT-IR spectra of chitosan and the crosslinked chitosan films. Figure 1 (a) shows the IR bands of the chitosan film, including a characteristic band at 1644 cm^{-1}, which corresponds to the stretching of amide C=O (amide I) and at 1550 cm^{-1} ,which corresponds to the N-H deformations of a primary amine (amide II). The band at 1380 cm^{-1} is attributed from the C-H of group CH_3 of the acetamide group, which demonstrates that chitosan is not completely deacetylated. The band at 1078 cm^{-1} corresponds to the C-O stretching of a primary alcohol. Comparison of natural chitosan and crosslinked chitosan spectra indicate that a new band at 1712 cm^{-1} and the band at 1260 cm^{-1} became clearer. These results correspond to the C=O stretch peak and the $S(=O)_2$ stretch peak from SSA, respectively. The significant band at 1644 cm^{-1} is associated an imine bond (N=C), which is formed by the reaction of the amino group in chitosan with the aldehyde groups in glutaraldehyde to form a Schiff

base. According to the literature [28-29], the 1548cm^{-1} - 1560cm^{-1} peak corresponds to the symmetric deformation of -NH_3^+, formed by the ionization of primary amino groups. The peak at 1550cm^{-1} is split into 1550cm^{-1} and 1548cm^{-1} peaks after crosslinking by the binary crosslink agent (Fig. 1 (a): crosslinked CS), because of the amino group in the chitosan side-chain following ionization by reaction with SSA.

The same behavior was exhibited by the C-H stretching vibration at 2936 cm^{-1}, because the glutaraldehyde and SSA molecule in the chitosan–glutaraldehyde/SSA reaction strengthens the crosslinking chain (Fig. 1 (b)).

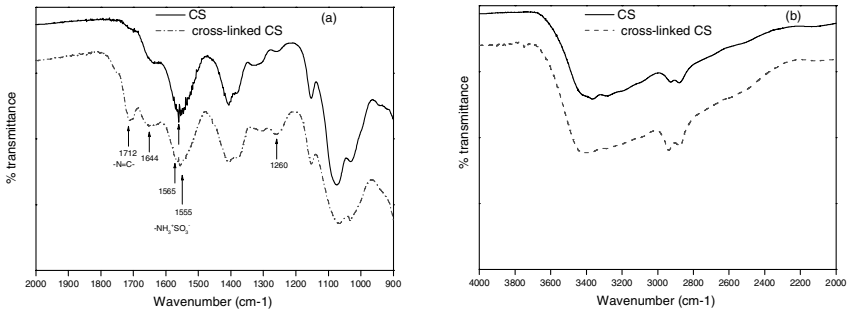

Figure 1. The FT-IR spectrum of wavenumber rang of 900 cm^{-1} to 2000 cm^{-1} (a), and 2000 cm^{-1} to 4000 cm^{-1} (b)

Density and fractional free volume (FFV)

Table 1 presents the bulk density, true density and FFV of the crosslinked chitosan membranes as functions of the crosslink agent content in the membrane. As is well known, the crosslinking density of a crosslinked material is expressed as bulk density. Bulk density can be increased by increasing the degree of crosslinking. However, with respect to the structure of the material, the inter-molecular distance may increase when a crosslinking agent is introduced and the resultant higher free volume reduces the bulk density with the increase of the crosslinking agent. Introducing the crosslinking agent into the chitosan molecule reduced the bulk density of the membrane, revealing that the introduce crosslinking agent can create a rougher structure to the membrane.

The FFV of crosslinked chitosan increased in the order, CS < CS3GASSA < CS6GASSA < CS10GASSA <CS20GASSA < CS30GASSA. Because of there are more inter-molecular hydrogen bonding present in chitosan, the hydroxyl groups are

Table 1. Density and FFV result of chitosan and crosslinking chitosan membranes

Samples	bulk density (g/cm^3)	true density (g/cm^3)	FFV
CS	1.4257 ± 0.0042	1.4514 ± 0.0022	0.0510
CS3GASSA	1.4187 ± 0.0032	1.4209 ± 0.0174	0.0557
CS6GASSA	1.4124 ± 0.0015	1.4489 ± 0.0020	0.0599
CS10GASSA	1.4106 ± 0.0038	1.4602 ± 0.0035	0.0610
CS20GASSA	1.3999 ± 0.0049	1.5120 ± 0.0038	0.0682
CS30GASSA	1.3796 ± 0.0038	1.5736 ± 0.0175	0.0817

thought to be close to the amino group. However, the crosslinking can suppress the formation of hydrogen bonding and improved the FFV [30].

The true density defined as the ratio of the weight of the bulk polymer to the volume occupied by the polymer chains increased with the degree of crosslinking. Hence, crosslinking can reduce the volume occupied by the polymer chains.

Contact angle

Table 2 presents the contact angles of the crosslinked membranes. The hydrophilicity of chitosan is known to come from the hydrophilic groups as –OH and $–NH_2$ of the chitosan chain. The reaction of glutaraldehyde with primary amino groups result in formation of two Schiff bases involving both aldehyde groups of the glutaraldehyde molecule [31]. Therefore, the decline in the $–NH_2$ group content and the hydrophilicity of the crosslinked chitosan membrane enable the increasing contact angle which can be regarded as the enhancing of the hydrophobicity of a membrane surface. Table 2 reveals that the advancing contact angle decreases as the binary crosslink agent content increases, indicating that the sample treated with more crosslinking agent is more hydrophilic. This result indicates that the binary crosslink agent in the SSA increases the surface hydrophilicity and results in hydrophilic chitosan network membranes.

Table 2. Contact angle of crosslinked chitosan membrane (25°C)

	Membrane					
	CS	CS3GASSA	CS6GASSA	CS10GASSA	CS20GASSA	CS30GASSA
Contact angle (°)	84.54	82.38	80.45	78.75	71.09	69.83

Mechanical properties

Table 3 presents the tensile strength of the crosslinked membranes. The results reveal that the crosslinked membrane is stronger than natural chitosan. This enhancement is attributable to the GA/SSA reaction with the chitosan, and the formation of a network structure that maintains the crystal structure, thus increasing the tensile strength and reducing the elongation at breakage. Table 3 present the Young's modulus and the elongation at breakage of the crosslinked chitosan films with the various crosslinking agent ratios. The mechanical characteristics of the material change from hard and tough to hard and brittle. The Young's modulus of the crosslinked membranes increased with the addition of the crosslinking agent. For a crosslinking agent content of 30%, the Young's modulus increased from 1233 MPa to 7344 MPa – by a factor of more than six. The elongation-at-breakage values of the crosslinked membrane declined as the content increased. According to the literatures, water in the materials is responsible for the 'plastic effect' that reduces the tensile strength and increases the elongation at breakage. The results herein contradict this suggestion, perhaps because the binary crosslinking agent increased the water content and the hydrophilicity of the surface only. Therefore, no plastic effect occurred and the tensile strength and elongation at breakage did not decrease. This result shows that the binary crosslinking agent not only increased the hydrophilicity but also generated the crosslinking effect increasing the tensile strength. In particular, the water content and hydrophilicity of the surface can be increased more than that inside, according to the results of the swelling tests.

Table 3. Mechanical properties of chitosan and crosslinking chitosan membranes

Samples	Young's modulus (MPa)	Max. stress (MPa)	Breaking elongation (%)
CS	1233	39.622	74.31
CS3GASSA	1961	41.535	41.48
CS6GASSA	2105	67.847	30.31
CS10GASSA	2340	76.487	28.71
CS20GASSA	4431	110.675	13.74
CS30GASSA	7344	133.659	4.03

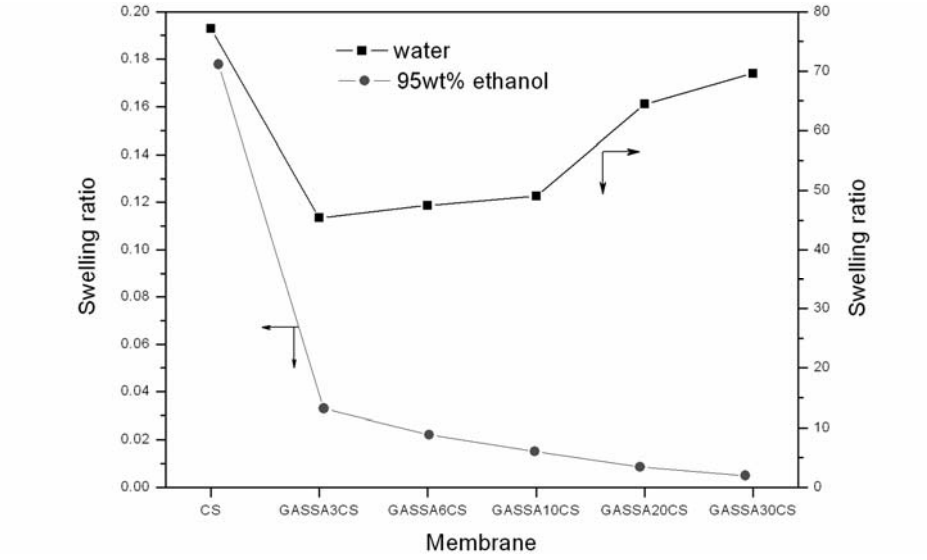

Figure 2. Swelling ratio of chitosan membranes of different crosslink agent contents

Swelling characteristics

Figure 2 displays the swelling behavior of the crosslinked membrane in deionized water and 95 wt. % aqueous ethanol. The swelling ratio in water decreased as the crosslink agent content increased, revealing that an increase in the crosslinking of the membrane reduces the hydrophilicity of the internal structure of the membrane the group increases the hydrophobility. It indicates that the water content inside the membrane does not increase and no water effect can reduce the mechanical tensile strength or increase the elongation at breakage. The degree of swelling in 95 wt.% ethanol aqueous slightly increased with the degree of crosslinking, suggesting that the membrane inside the structure is more hydrophobic. Since the water molecules are adsorbed and stayed around the sulfonic groups to produce so-called water clusters, and ethanol is amphiphilic, and so can dissolve in both hydrophilic and hydrophobic environments in the membrane [22].

X-ray diffraction

Figure 3 presents wide-angle X-ray diffractograms of pure chitosan and crosslinked chitosan membranes. Chitosan (Fig. 3(a)) exhibits peaks at 2θ = 11, 18, 21 and 23°, while the crosslinked membrane does not appear to have more amorphous domain

than the pure chitosan membrane. The diffraction peaks at approximately 11° (2θ) and 18° (2θ) were attributed to the hydrated and anhydrous crystals, respectively [32]. In addition, the intensity of the hydrated crystal at approximately 18° (2θ) was weaker. It seemed that all chitosan films were in the amorphous state to partially crystalline state [33]. Specifically, the crystalline peak of chitosan at $2\theta = 11°$ (Fig. 3(b, c, d)) does not disappear as the crosslinked chitosan membranes were formed from pure chitosan, potentially increasing the tensile strength with the degree of crosslinking.

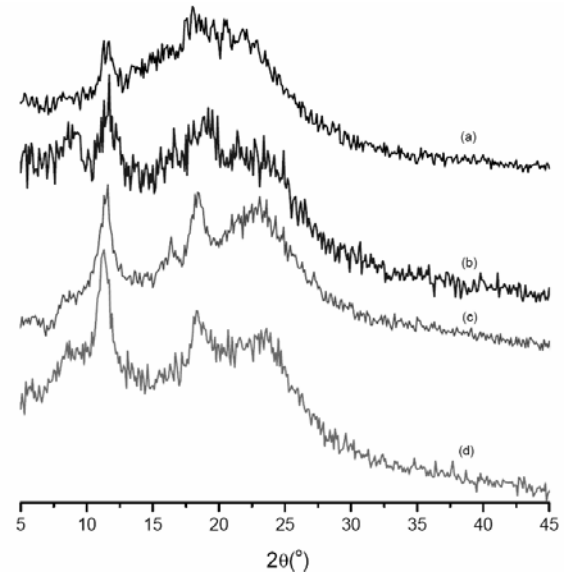

Figure 3. X-ray diffraction patterns of chitosan membrane of different crosslink agent content: (a) CS, (b) CS10GASSA, (c) CS20GASSACS, (d) CA30GASSACS

Thermal analysis

Figure 4 plots TGA curves of pure chitosan (a) and crosslinked chitosan membranes (b, c, d). The thermograms of both samples exhibited similar, two-stage weight loss trends. The first stage is assigned to the loss of water. The second stage corresponded to the thermal decomposition of chitosan, and the vaporization and elimination of volatile products. The differential TGA diagram did not show any degradation peak at the boiling point of acetic acid of 100.1°C.

The change in weight loss at lower temperature increased with the crosslinking agent content of the membrane. The surfonic groups in the membrane matrix, which are responsible for the membrane hydrophilicity, and water molecules may have been trapped inside these aggregates when the membrane was exposed to water [34]. This suggestion agrees with the contact angle results herein.

As presented in Fig. 5, the DSC thermograms of all chitosan membranes exhibited broad endothermic peaks that are attributable to water loss at 35–160°C. The endothermic peak position shifts toward higher temperature as the crosslinking agent content increased, indicating a possible relationship between the water binding

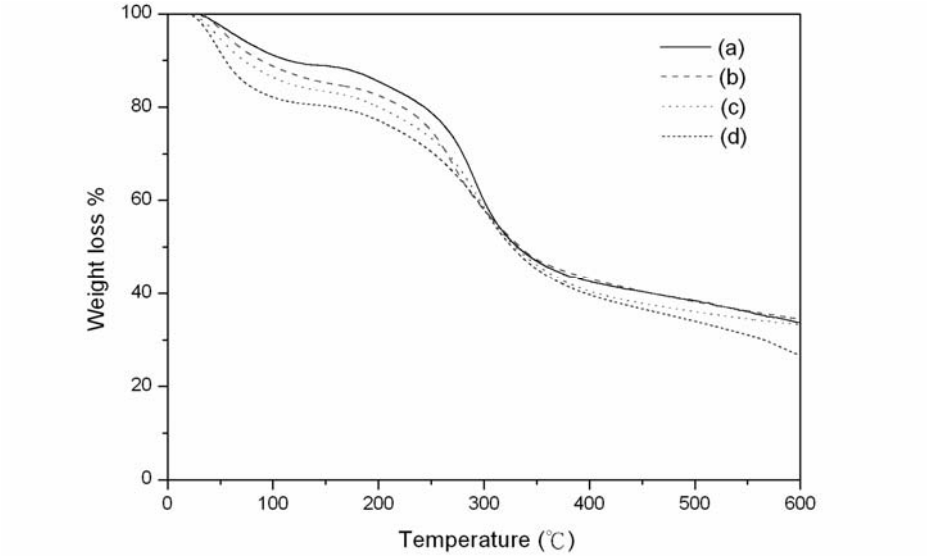

Figure 4. TGA thermograms of chitosan membranes of different crosslink agent contents: (a) CS, (b) CS10GASSA, (c) CS20GASSACS, (d) CA30GASSACS

capacity and the chemical and supra-molecular structures of these polymers [35-36]. This result supports that of TGA observations. Increasing the degree of crosslinking increases the hydrophilicity of the polymer. Most of the bound water is associated with the interaction of the hydroxyl group with water molecules, increasing the difficulty of removal and elimination [35,37].

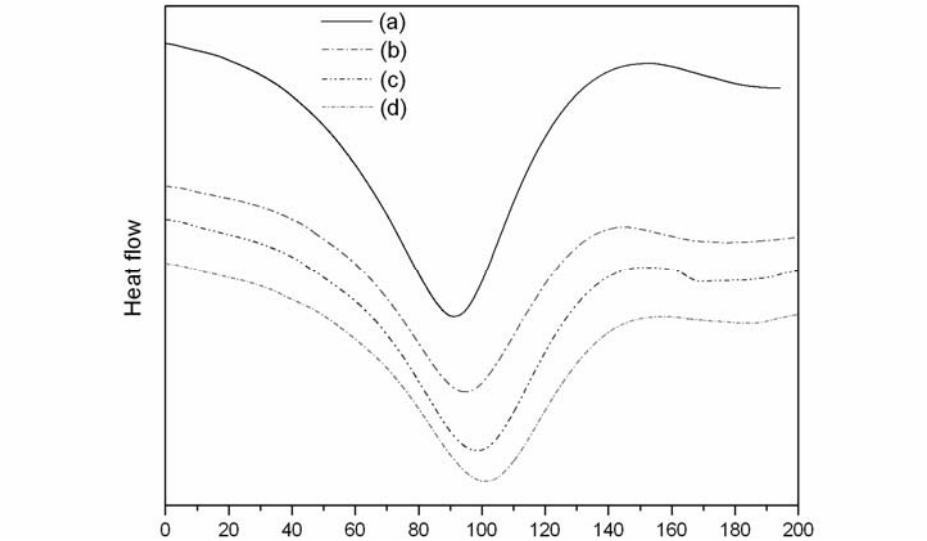

Figure 5. DSC thermograms of chitosan membranes of different crosslink agent contents: (a) CS, (b) CS10GASSA, (c) CS20GASSACS, (d) CA30GASSACS

Conclusions

This investigation studied the properties of hydrophilic chitosan network membranes by introducing a binary crosslinking agent. Characterization of the crosslinked membrane by FTIR proved the crosslinking. As the bulk density and FFV increased, and the true density and contact angle decreased as the degree of crosslinking increased. Mechanical testing demonstrated that the crosslinked membrane efficiently enhanced mechanical performance. The degree of swelling in water declines significantly and that in 95% ethanol increases slightly as the degree of crosslinking increases. The presence of all X-ray peaks demonstrated the retaining crystallinity of the polymer, but their intensities fell.

Finally, TGA and MDSC indicated that the evaporation temperature of water from chitosan crosslinked degree increased to around 120-150°C less than that from chitosan, suggesting that there are more water on the surface than that in the bulk after crosslinking.

The results demonstrate that hydrophilic chitosan network membranes were prepared and may be useful in applications that require membranes with high tensile strength and hydrophilicty

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