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Development of Cross linked Chitosan/Alginate Polyelectrolyte Proton Exchanger Membranes for Fuel Cell Applications

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In this study, chitosan (CS) was chemically crosslinked with an activated-low molecular weight alginate biopolymer (Alg) with different molar ratios. The activation process of alginate was achieved using glutaraldehyde (GA) as a covalent crosslinker to obtain CS/Alg-GA crosslinked membrane as a potential polyelectrolyte for fuel cell applications. Various instrumental characterizations such as FTIR, TGA, SEM, and tensile machine were applied to verify the changes in the chemical structure, thermal stability, the morphological structure and mechanical properties respectively. Furthermore, both thermal stability and mechanical properties were also investigated. The results were obtained and compared with that obtained using ionic crosslinked CS/Alg membranes. Maximum ion exchange capacity (IEC) was established (5.96meq/g) using CS/Alg-GA with molar ratio (4/1), while, only 3.47meq/g was obtained in case of ionic crosslinked CS/Alg with the same molar ratio. The interaction with water and methanol were investigated via methanol and water uptake studies. Results showed that the covalent crosslinked CS/Alg-GA membranes have a low permeability for methanol ranged from 2.179×10^{-9} to 2.5×10^{-10}cm^2/s compared to that of Nafion membranes (1.14×10^{-9} cm^2/s). Above all, simplicity of the used preparation method and the cost reduction potentials of covalent crosslinked CS/Alg-GA membranes promote their use for DMFC applications as proton exchanger membranes.

Keywords: Fuel cell, Chitosan, Alginate, Covalent crosslinking, Electrolyte membrane.

1. INTRODUCTION

Direct methanol fuel cells (DMFCs) are a simple device which converts chemical energy into electrical energy. Nowadays, it is used as an energy source for transportation and other portable applications such as mobile phones and laptop computers [1]. The enhancements of DMFC via improving the electrolyte membrane and increasing the effectiveness of the catalysts have been studied by many researchers along several decades. To improve the fuel cell performance, the polymer electrolyte membrane should be modified to yield higher proton conductivity. The conventional membrane currently used is Nafion, which is mainly composed of perfluorinated sulfonic acid and is the dominant popular available membrane for PEMFC and DMFC technologies [2, 3]. However, it has some disadvantages. First of all, it is an expensive material costing about 600–1200 $ per square meter [4]. At temperatures above 120 ºC, membranes demonstrate low performance ratings [5]. Production of Nafion membranes was done with emission of hazardous chemicals such as fluorine. Thus, the utility of Nafion membranes enhances environmental pollution. Also, it has relatively high methanol permeability, leading to methanol crossover as much as 40% during the process [6]. Many research workers are investigating low-cost polymers, which produce lower methanol permeability and higher proton conductivity. Composites based on polysaccharide can be excellent in the meaning of the environment and ecosystems.

Till now, the synthetic polymer dominated the composites industry, but recently, their popularity has decreased due to their non-environmental compatibility and degradability [7]. The use of Natural polysaccharides, like cellulose, cellophane [8], cellulose acetate [9, 10], has replaced traditional “green” synthetic polymers, such as poly-3-hydroxybutyrate (PHB) and polylactic acid (PLA). Alginate and chitosan as biopolymers obtained from natural substances and have been employed in polymer networks. Research on biopolymer as a promising membranes materials and systems has focused on the development of beneficial biopolymers and improving their membrane processing capacity and operation. Recently, efficient and eco-friendly biopolymer has been intensively investigated as a new material for applications in fuel cells technology. This sort of biopolymer can be used in both membrane electrolyte and electrode in different fuel cell types such as alkaline polymer electrolyte fuel cells, direct methanol fuel cells, and biofuel cells. One of which is chitosan, which has been investigated widely for this purpose [11–13]. Chitosan as a linear polysaccharide composed of irregularly distributed β-(1–4)-D-glucosamine and N-acetyl-D-glucosamine. It is essentially manufactured commercially by deacetylation of chitin, which is the central component in the exoskeleton structure of crustaceans such as crabs and shrimps. Additionally, CS has excellent properties such as biodegradability, biocompatibility, antimicrobial activity [14-18], antioxidant activity [19-21], and hydrophilic properties [22]. The presence of different function groups in its structure such as the primary amine (–NH_2) and hydroxyl (–OH) groups can act as electron donors. Thereby, owing to their easy modification, it may be applicable in many applications as wastewater treatment [23], drug delivery [24-26], biomedical engineering [27-28], fuel cell [29, 30], and food packaging. Several forms of chitosan have been produced such as Films or membranes, beads or particles, fibers etc. [31].also, chitosan is directly cast into a membrane from the solution of a weak acid. Being dissolved in a weak acid, the amine groups of chitosan could be protonated and these proton scan move in the membrane, leading to the ionic conductivity of the membrane [32]. Despite its advantages chitosan exhibit relatively low mechanical strength and weak electrical conductivity. results of its high glass temperature chitosan form a brittle membrane [33]. On the other hand, the ability of chitosan to be compatible blends with other polymers, doping inorganic fillers in the chitosan matrix, creating chitosan-based organic-inorganic hybrids or chemically modifying chitosan can be utilized to promote its properties [34].

Alginate is a water-soluble polysaccharide obtained by brown Algae. the physical and biochemical structure of alginate enable it to have great potential in various required applications, such as drug and gene delivery, biomedical and tissue engineering, water treatment etc. Alginate can be produced into a difference forms, such as film, microspheres, and fibers, etc [35]. the presence of hydroxyl groups along Alginate backbone simplified crosslinking with glutaraldehyde, 1, 6-hexane diamine, and other bi-functional organic compounds [36]. Like chitosan, alginates have defined limits to their applications due to several defects; include high water solubility and weak mechanical strength. [37]. Reinforced chitosan with alginate was established before by coupling cationic amine groups of chitosan with anionic carboxylic groups of alginate. Chitosan /alginate polyelectrolyte complex was employed in several applications such as drug deliver [24, 25], wound dressing, etc.

In the current study, both covalent and ionic crosslinked chitosan/alginate polyelectrolyte membranes were fabricated with different molar ratios. The membranes were characterized via different characterization tools. In addition, water/methanol uptakes, ion exchange capacity, and methanol permeability were also conducted.

2. EXPERIMENTAL

2.1. Materials

Chitosan (CS) from crab shells highly viscous was purchased from Sigma-Aldrich (USA), Sodium alginate (Alg) was supplied from Sigma–Aldrich Chemicals Ltd., (Germany). Glutaraldehyde (G)(50%), Methanol (purity 99.8%) were purchased from Fluke Chemie GmbH (Switzerland). Hydrochloric acid (purity 37%) obtained from POLSKA ODCZYNNIKI CHIMICZNE S.A. (Finland). Sodium hydroxide, hydrogen peroxide, and phenol phethalin were purchased from El- Nasr Pharmaceutical Co for Chemicals (Egypt).

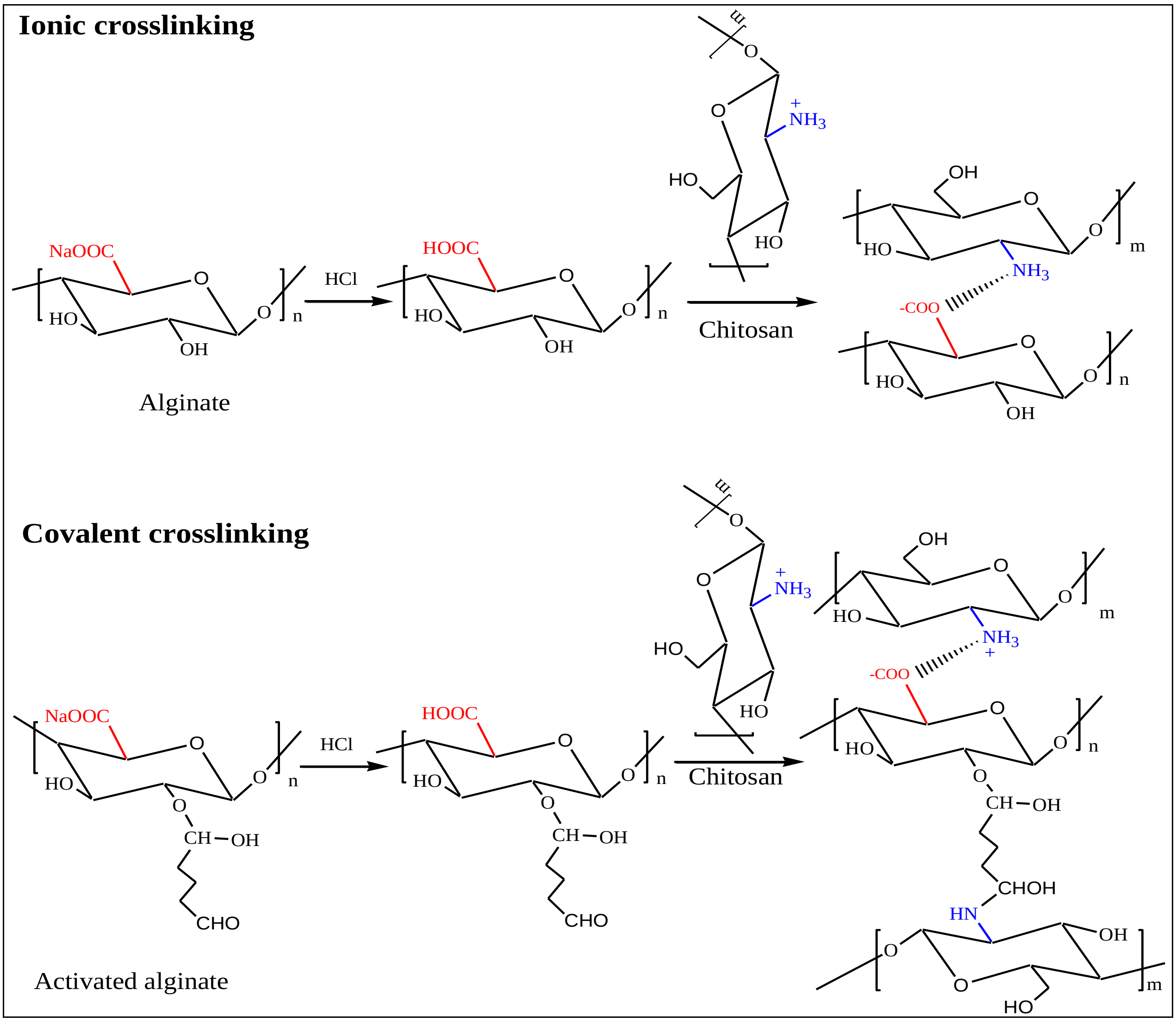
2.2. Methods

2.2.1. Preparation of activated and low molecular weight alginate

In brief, 5 g of alginate (Alg) was dispersed in 84 mL distilled water. After complete dissolving, 16 mL of H_2O_2 (30 %) was added to the solution. Then, the solution was heated to 80 °C for 6 h and the degradation reaction as stopped by cooling. Then, the solution was filtrated and the remains solution complete to 166.67 mL with distilled water to prepare the final concentration (3%) of low molecular weight alginate. Finally, 7 mL of glutaraldehyde (GA; 50%) was added to the solution, followed by heating to 50 ºC for 3 h to prepare the activated low molecular weight alginate (Alg-GA).

2.2.2. Membrane preparation

Chitosan/alginate polyelectrolyte membranes were synthesized using physical blending and covalent crosslinking via solution casting-solvent evaporation technique. A solution of chitosan 3 wt % was prepared by dispersing 3 g of chitosan in 100 ml of 2% glacial acetic acid solution. Then, the solution was mixed with alginate or activated alginate solution in the molar ratio of 4:1, 3:1, 2:1, and 1:1. Next, pH of the mixture was adjusted to 5.5 by adding a drop of HCl (0.05 mL) with stirring for 30 min at room temperature. A solution was slowly cast onto a clean glass plate with bubble-free and allowed to dry in the atmosphere at room temperature. Both physically and covalently crosslinked CS/Alg membranes were split off from the petri dish and washed with methanol for 4–5 times, followed by vacuum drying for 5 h at 40 °C in a closed oven. Membranes so formed were dense, and their thicknesses were estimated with a micrometer. Schematic diagram describes the mechanism of synthesis both covalent and ionic crosslinked CS/Alg membranes as shown in Scheme 1.



Scheme 1: Ionic and covalent crosslinking of chitosan and alginate membranes.

2.3. Membrane characterization

Water/methanol uptakes

The water/ methanol absorption characteristics of membranes were investigated by immersing the samples in pure water or methanol, at room temperature overnight. After that, the swollen samples were separated, and the excess of water or methanol which adhering to the surface was quickly wiped with tissue paper and weighed immediately in a closed-door balance. Liquid uptake (water or methanol) was determined by the following equation:

$$LU(\%) = \frac{W_w - W_d}{W_d} \times 100 \tag{1}$$

Where: W_d and W_w are the dry and the wet weight of the prepared samples.

Infrared spectrophotometric analysis (FTIR)

The FTIR spectra of alginate, chitosan, and the developed membranes were investigated by carrying FT-IR spectroscopic analyses using Fourier Transform Infrared Spectrophotometer (Shimadzu FTIR - 8400 S, Japan).

Thermal gravimetric analysis (TGA)

The samples were subjected to TGA instrument to determine their thermal stability and decomposition characteristics. Thermal stability of the polymer films was examined, using thermogravimetric analyzer (Shimadzu TGA –50, Japan).

Scanning electron microscopic analysis (SEM)

Surface characterization of native chitosan, alginate, and the developed membranes were carried out using energy-dispersive analysis X-ray (Joel Jsm 6360LA), Japan.

X-Ray diffraction analysis (XRD)

A Schimadzu7000 powder X-ray diffractometer was utilized to investigate the solid state morphology of physically and chemically crosslinked blend films. X-rays of 1.5406 A° wavelength were generated by a CuK source. The angle of diffraction was changed from 0° to 65° to distinguish the difference in the crystal structure and intermolecular distances between the inter-segmental chains after crosslinking.

Surface roughness

Surface roughness device (SJ- 201P- Japan) was employed to determine the surface roughness of all the prepared membranes. Tested Samples were mounted onto a glass slide by double-sided tap. The recorded results are the average of six measurements.

Optical properties (Colorimeter)

Colorimeter X-Rite (model (Sp64) - USA) was used to measure the change color values for different sites of the developed membranes. All measurements was measured with a standard white background. Colorimeter produces the three color components; L* (black-white component, luminosity), and the chromaticness coordinates, a* (+red to −green component) and b* (+yellow to −blue component) [8]. Color differences ΔE* were also determined by the following equation:

$$\Delta E = \sqrt{\left(\Delta L^*\right)^2 + \left(\Delta a^*\right)^2 + \left(\Delta b^*\right)^2} \qquad (2)$$

Where: $\Delta L^* = L* - L_0^*$, $\Delta a^* = a* - a_0^*$, $\Delta b^* = b* - b_0^*$ being: L_0^*, a_0^*, b_0^* are the color parameter values of the standard and L^*; a^*; b^* the color parameter values of the sample.

Ion exchange capacity (IEC)

To determine the interactive groups, the samples were immersed in 50 mL of 0.01 N sodium hydroxide solutions for 12 h at room temperature. Next, 10 mL of solution was titrated against 0.01N sulfuric acid. The IEC was calculated according to the equation:

$$IEC = \frac{B - P * 0.01 * 5}{m} \qquad (3)$$

Where; IEC is the ion exchange capacity, B is the volume of 0.01 N sulfuric acid used to neutralize blank. P: the amount of 0.01 N sulfuric acid used to neutralize the membranes, the amount 0.01 is the factor used to estimate the normality of sulfuric acid/NaOH, where amount 5 is factor corresponding to the ratio of the NaOH amount used in dissolving the polymer to the amount used for titration, m is sample mass in g.

Tensile strength measurement

Universal Testing Machine (UTM) was used to estimate the tensile strength of membranes with a working head load of 5 k N. sample dimension measured and recorded. The films were then held between the machine grips. The gap length was 5 cm, where the speed of testing was fixed at the rate of 12.5 mm/min. the recorded measurement was the average of at least three measurements. Tensile strength was calculated using the equation:

$$Tensil\ strength = \frac{Max\ load}{cross - section\ area} N/mm^2 \tag{4}$$

Methanol permeability measurements

The methanol permeability of the developed covalent crosslinked membranes was determined by glass diffusion cell as shown in Figure 1. The cell consists of two sides one of them (A) filled with 100 mL of 2 M methanol aqueous solution and the other side (B) contains 100 mL distilled water. The membrane was placed at the center of the cell. A micro-syringe was used to withdrawn 1 mL before testing and each 15 min for 2 h from the compartment (B) [9]. The concentration of methanol in water compartment was estimated by GC analyzer, and the methanol permeability (P) was calculated from the slope of the linear relationship between the concentration of methanol in the water compartment (CB) and the time (t) according to the next equation [10]:

$$P = \alpha \frac{V_B}{A} \times \frac{L}{C_A} \tag{5}$$

Where: α is the slope of the linear function of CB versus t.

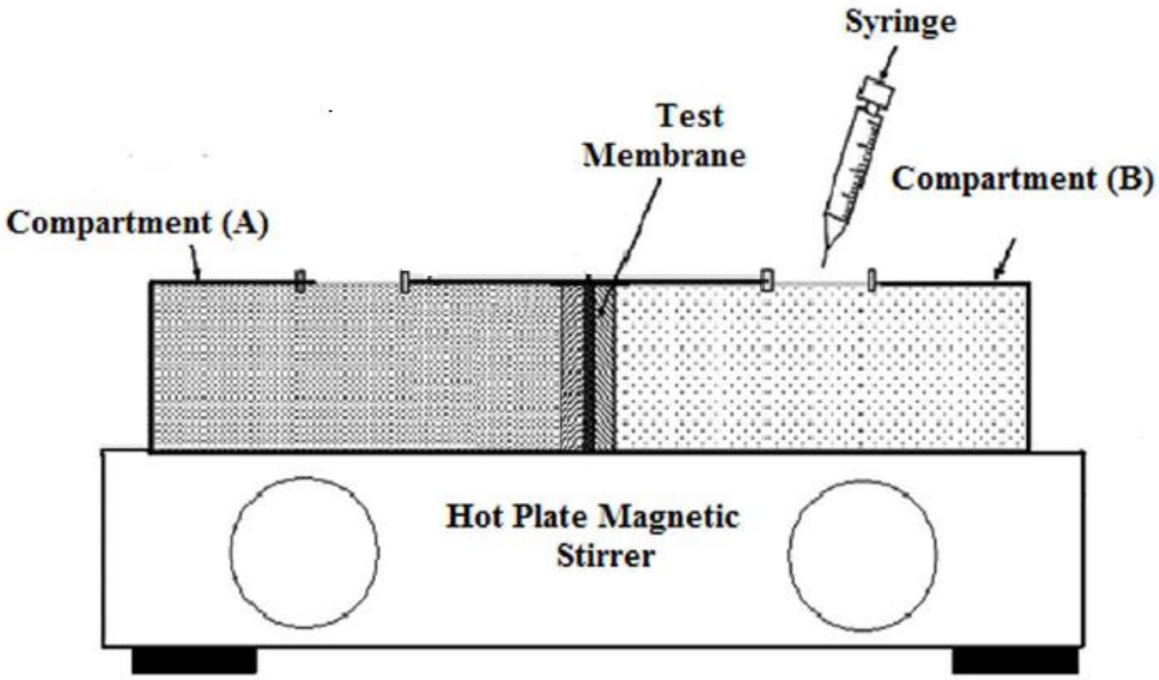


Figure 1. Methanol permeability cell.

3. RESULTS AND DISCUSSION

3.1. Membrane preparation

In the current study, a comparative study of two sets of Chitosan/alginate polyelectrolyte membranes synthesized via two different methods. In the first, physical crosslinked of two polyions are formed through blended two polymers. The addition of HCl helps inform homogenous solution of chitosan and alginates. During the drying process, the free carboxylic groups of the alginic acid interact ionically with protonated amine groups of chitosan; the resulting is the formation of new salt bonds. From the examination, it was verified that the formation of polyelectrolyte complex was performed by the ionic reaction and the formulated membranes are supposed to have a great affinity for water as well as reduced interaction with organic solvents (salting-out effect) [11]. While in the second method, Glutaraldehyde (GA) was used as a chemical coupling agent. In this method, GA was coupled with the free hydroxyl groups of alginate, and then coupled with amine groups of chitosan.

3.2. Membranes characterization

3.2.1. Water and methanol uptake (LU)

Water & methanol uptakes of chitosan/alginate poly electrolyte membranes were determined and illustrated in Table 1. Water sorption characteristics of the two types of chitosan/alginate membranes were attributed to their hydrophilic groups (i.e. carboxylic, hydroxyl, and amine groups) [11]. The first series of membranes – physically bonded membranes- exhibited higher swelling in water, losing its mechanical properties and accordingly the water uptake could not be measured (i.e. NA). These results could be attributed to the low molecular weight of the contributed alginate which leads to form of a weak polyelectrolyte complex network. That result is in contrast with previous published results by other authors [11].

Table 1. Water and methanol uptakes of CS, Alg, and different crossslinked chitosan/alginate membranes

Sample	Water uptake (%)	Methanol uptake (%)
CS	59.8	6.6
CS/Alg (4/1)	NA	5.7
CS/Alg (3/1)	NA	5.2
CS/Alg (2/1)	NA	4.94
CS/Alg (1/1)	NA	1.6
Alg	NA	1.3
CS/Alg-GA (4/1)	371.4	0.1
CS/Alg-GA (3/1)	265.1	0.82
CS/Alg-GA (2/1)	118.5	1
CS/Alg-GA (1/1)	34.19	1.4

On the other hand, the covalent crosslinked membranes show controllable swelling. It was observed that the water uptake increased with increasing the chitosan content due to increasing the hydrophilicity of the membrane with increasing number of the hydroxyl and amine groups. Additionally, increasing the CS content increases the formed covalent bonds via glutaraldehyde (GA) molecules which working as spacer, and so increases the pores volume in the network structure of the covalent crosslinked membrane. On contrast, the methanol uptake took the reverse behavior as it decreased to a great extent with increasing CS concentration. The obtained results are comparable with previous published results by other authors [11].

3.2.2. Surface roughness test

Table 2 represents the surface roughness of CS, Alg, CS/Alg, CS/Alg-GA membranes. It was observed from results that surface roughness of neat polymers (Chitosan or alginate) have a less rough surface compared to the crosslinked membranes. These results could be due to the formed network three dimensions structure as a result of formation of ionic and covalent bonds between carboxylic and amine groups of alginate and chitosan respectively through polyelectrolyte formation. This could reflect negatively on the rate of water evaporation and so the dryness process homogeneity leading to increase of roughness of their surfaces after cast-membrane process [8]. The roughness of the covalent bonded polyelectrolyte membranes is less than that of the ionic polyelectrolyte ones due to the expanded network structure which allows more uniform dryness process and less roughness surface.

Table 2. Surface roughness of chitosan, alginate, ionic and covalent crosslinked membranes at different molar ratios

Sample	**Roughness (μm)**
CS	0.12
CS/Alg (4/1)	0.31
CS/Alg (3/1)	0.35
CS/Alg (2/1)	0.49
CS/Alg (1/1)	0.51
Alg	0.03
CS/Alg-GA (4/1)	0.18
CS/Alg-GA (3/1)	0.25
CS/Alg-GA (2/1)	0.25
CS/Alg-GA (1/1)	0.44

3.2.3. Color measurement

The color of the film is an important index regarding general appearance. The rectangular coordinates (L, a, and b) and the total color difference (ΔE) were calculated and are summarized in

Table 3. By comparing the optical parameters it was evident that the color of membranes changes significantly by changes of the molar ratio of Chitosan. The presence of GA in membranes showing a significant increase in the yellowish color (+ve b value) of membranes that could be attributed to the formation of Schiff base with chitosan amine groups.

Table 3: Color values of chitosan, alginate, and crosslinked membranes at different molar ratios

Sample	L	a	b	ΔE
CS	81.97	9.14	49.94	42.86
CS/Alg (4/1)	84.09	5.14	18.45	35.06
CS/Alg (3/1)	83.18	6.14	22.71	33.92
CS/Alg (2/1)	81.83	5.8	12.73	33.98
CS/Alg (1/1)	71.21	8.02	27.49	22.63
Alg	87.49	2.17	2.02	43.49
CS/Alg-GA (4/1)	84.38	6.20	37.6	38.25
CS/Alg-GA (3/1)	87.66	3.47	22.79	38.46
CS/Alg-GA (2/1)	77.38	15.97	65.7	52.6
CS/Alg-GA (1/1)	72.97	20.26	63.02	49.19

3.2.4. Ion exchange capacity (IEC)

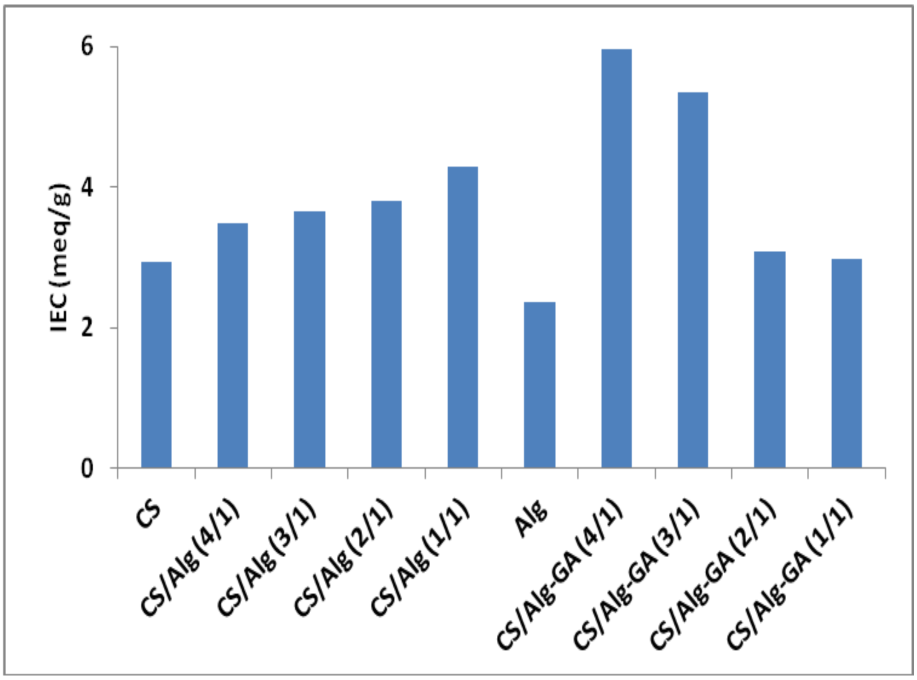


Figure 2. Ion Exchange capacity of chitosan, alginate, and crosslinked membranes at different molar ratios.

IEC of the chitosan, alginate, and polyelectrolyte ionic and covalent crosslinked membranes is indicated in Figure 2. It was evident from the figure that the IEC of polyelectrolyte ionic and covalent crosslinked membranes were higher than the native chitosan and alginate membranes. This is in agreement with other published results [11]. It is worthy to mention here that the IEC values were increased in case of covalent crosslinked membranes with increase in CS ratio, where the highest IEC value (5.96meq/g) was recorded for CS/Alg-GA (4/1). This behavior could be referred to the formed of more open three network structure in case of the chemically crosslinked membranes which leads to reduce the chance of ionic interaction between the carboxylic and the amine groups and increase their contribution in the ions exchange process. In addition the chemical bonding between the activated hydroxyl groups of alginate, instead of carboxylic groups, with the Chitosan amine groups offered more carboxylic groups to contribute in the ions exchange process. An opposite behavior in case of the physically crosslinked membranes has been observed where the IEC decreased with increase the Chitosan ratio. This behavior could be referred to the increase contribution of more amine groups in formation of ionic bonds with carboxylic groups which consequently reduced the free ionic sites for the ions exchange process.

3.2.5. Mechanical properties

Table 4 represented the mechanical parameters maximum stress σmax (Nm^{-2}) and maximum strain λmax of chitosan, alginate, and crosslinked membranes. The obtained results demonstrated a relatively good mechanical property of neat polymers chitosan and alginate, the combination of the two opposite charged polymers exhibit weakness of its mechanical parameters in contrary to other published results [11]. The low molecular weight of alginate may present an explanation.

Table 4. Mechanical parameters of chitosan–alginate membranes

Sample	Max Force (N)	Max Displacement (mm)	Max Stress σ_{max} (N/mm^2)	Max Strain (λ_{max}) (%)
CS	78.13	11.73	39.16	39.1
CS/Alg (4/1)	57.34	0.936	36.07	3.12
CS/Alg (3/1)	32.34	1.0635	23.69	5.32
CS/Alg (2/1)	36.09	1.2585	26.44	4.2
CS/Alg (1/1)	25.35	0.962	20.81	3.21
Alg	80.94	2.657	67.45	8.86
CS/Alg-GA (4/1)	47.5	1.249	28.53	6.25
CS/Alg-GA (3/1)	38.44	0.809	48.35	4.05
CS/Alg-GA (2/1)	30.31	1.464	17.57	7.32
CS/Alg-GA (1/1)	20.94	0.231	13.69	2.31

3.2.6. FTIR Spectroscopy

The FTIR spectra of chitosan, alginate, and crosslinked membranes were illustrated and listed in Figure 3. The spectrum of chitosan exhibit the typical band of chitosan function groups, the characteristic absorption bands at 1651 cm^{-1}, 1587 cm^{-1} for (Amide I) and (Amide II) respectively, and binding band at 1375 cm^{-1} for (–CH_2). Additionally, the characteristics bands of saccharide structure were observed at 1160 cm^{-1} (anti-symmetric stretching of the C–O–C bridge), 1075, and 1040 cm^{-1} (skeletal vibrations involving the C–O stretching) [38]. While, alginate spectrum demonstrate bands at 1416 and 1620 cm^{-1} that assigned to symmetric and asymmetric stretching peaks of carboxylate groups. Also, the stretching bands around 1320 cm^{-1} for (C–O), 1130 cm^{-1} for (C–C), 1090 cm^{-1} for (C–O), 1020 cm^{-1} for (C–O–C), and 950 cm^{-1} for (C–O) are attributed to its poly saccharide structure. On the other hand, the generated bands at 1736 cm^{-1} and 1242 cm^{-1} in the spectrum of crosslinked membranes, due to the asymmetric and symmetric stretching of –COO− groups. Whereas, the band appearing at 1639 cm^{-1} may be assigned to asymmetric –NH_3C deformation and broad bands appearing at 2500 cm^{-1}and 1900 cm^{-1} confirm the presence of –NH_3C group in the polyelectrolyte membranes.

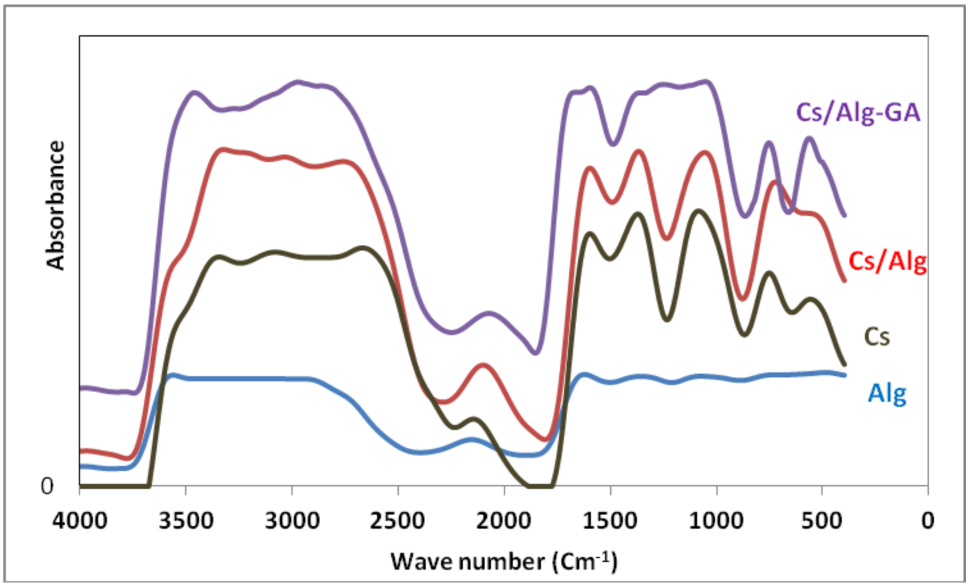


Figure 3. FTIR spectra of CS, Alg, CS/Alg, and CS/Alg-GA crosslinked membranes.

3.2.7. TGA analysis

Figures 4 and 5 represent the thermal gravimetric analysis of native chitosan, alginate, ionic and covalent crosslinked membranes. All membranes exhibit three different degradation steps. The first step was related to evaporation of in piping water that attached to the internal chains. The presence of hydrophilic groups along chain backbone (hydroxyl, amine and carboxylic) facilitate trapping of moisture molecules into the polymer matrix. For ionic crosslinked membranes, samples loss 16.8, 19.1, 16.6, and 15.7 % from CS/Alg (1/1), CS/Alg (2/1), CS/Alg (3/1), and CS/Alg (4/1), while, 15.7, 16.9% were lost for native CS and Alg at temperature up to 150 ºC. Covalent crosslinked chitosan/alginate membranes demonstrate less hydrophilicity compared to the ionic crosslinked membranes. The moisture losses were 10.8, 14.3, 13.5, and 14.6% for CS/Alg-GA (1/1), CS/Alg-GA (2/1), CS/Alg-GA (3/1), and CS/Alg-GA (4/1) respectively. These observations could be explained by the consumption of some hydrophilic groups (hydroxyl or amine) included in the crosslinking process. Elevated temperature displays the second degradation step which starts from 220 ^{o}C which occurred due to the oxidative degradation of pyranose ring in polysaccharide backbone [39-41]. Finally, the third degradation level was observed at the higher temperatures as a result of degradation of the formatted adduct. Furthermore, the temperature required for samples to loss its half weight (T_{50}) recorded 318.9, 266.2, 262.4, 260.9, 264.9, and 271.85 ^{o}C for CS, Alg, CS/Alg (1/1), CS/Alg (2/1), CS/Alg (3/1), and CS/Alg (4/1) ionic crosslinked membranes respectively. Whilst T_{50} of the covalent crosslinked membranes recorded 365.1, 316.4, 313.5, and 304.5 ^{o}C for /Alg-GA (1/1), CS/Alg-GA (2/1), CS/Alg-GA (3/1), and CS/Alg-GA (4/1) respectively. These results indicated that the covalent crosslinked membranes were thermally enhanced than the ionic crosslinked membranes due to the presence of covalent bonds.

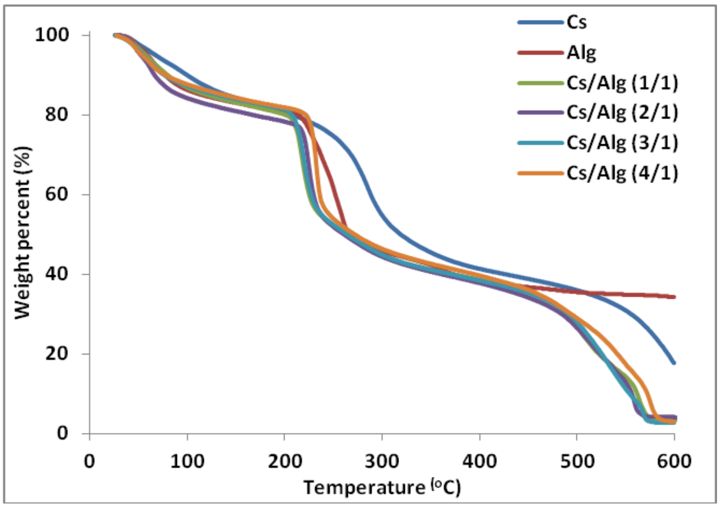


Figure 4. TGA thermographs of CS, Alg, and ionic crosslinked membranes.

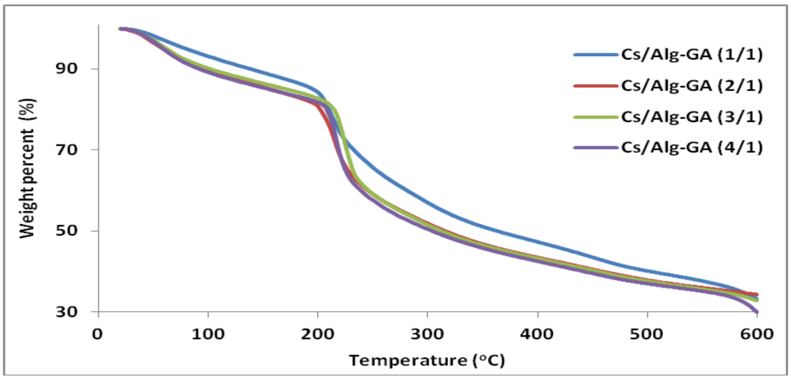


Figure 5. TGA thermographs of covalent crosslinked membranes.

3.2.8. Morphological SEM

Figure 6 displays the microstructure of the surfaces of CS, Alg, CS/Alg, and CS/Alg-GA membranes. It was clear that the morphological structure of neat membranes (i.e., chitosan and alginate) was smooth structure. Conversely, both ionic and covalent crosslinked membranes exhibited to have a rougher structure. However, the obtained results were matched with that obtained from roughness measurements.

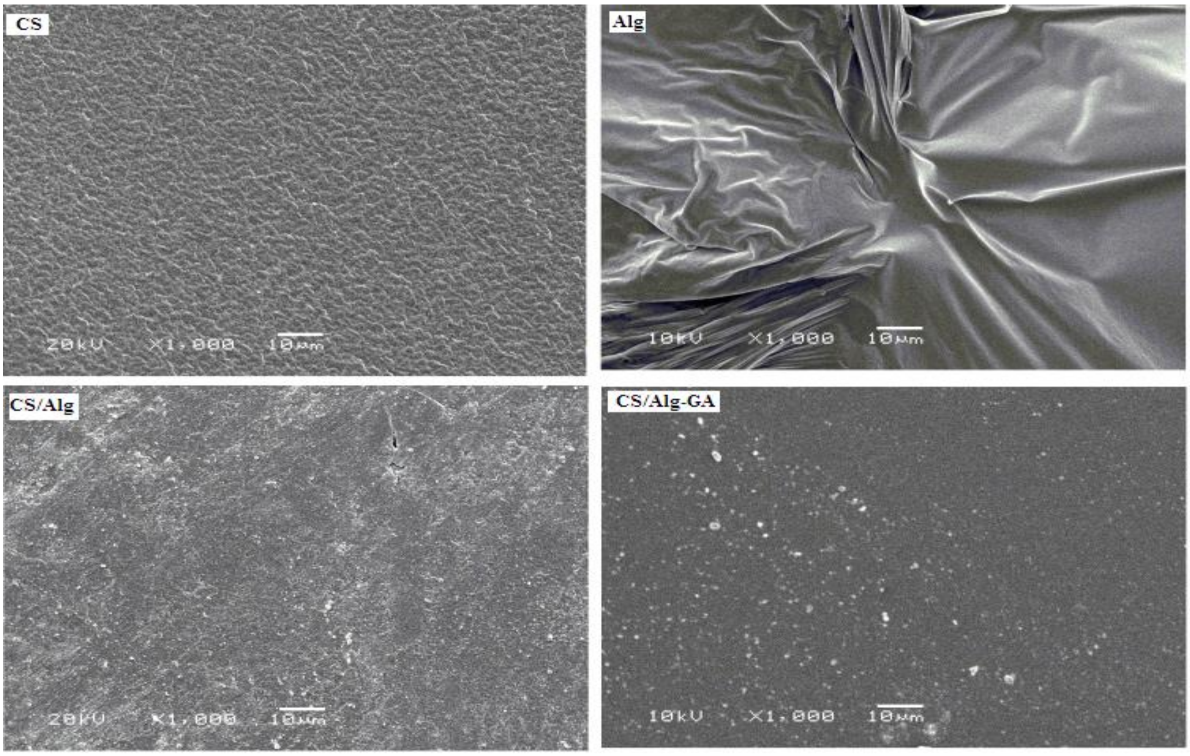


Figure 6. SEM Micrographs of CS, Alg, CS/Alg, and CS/Alg-GA membranes.

3.2.9. XRD analysis

X-ray diffraction (XRD) method was used to analyze CS, Alg, CS/Alg, and CS/Alg-GA membranes with different concentrations. XRD patterns have been studied in the 2Θ range of 5º to 50º as shown in Figures 7 and 8. It was observed that CS exhibit two reflections at 2Θ = 11º, and broad band at 2Θ = 23º. It was reported that the reflection at 2Θ = 11º was associated with the crystal form I. The strongest reflection is at 2Θ = 23º, and corresponds to crystal form II [40]. While, XRD patterns of polyelectrolyte membranes appeared to have a greater amorphous morphological structure. Also, it was noticed that a crystalline peak of CS at 2Θ = 10º in CS/Alg membranes was disappeared as the polyion complex was formed between alginate and chitosan. These results could be attributed to the elimination of hydrogen bonding between amino and hydroxyl groups in chitosan [42].

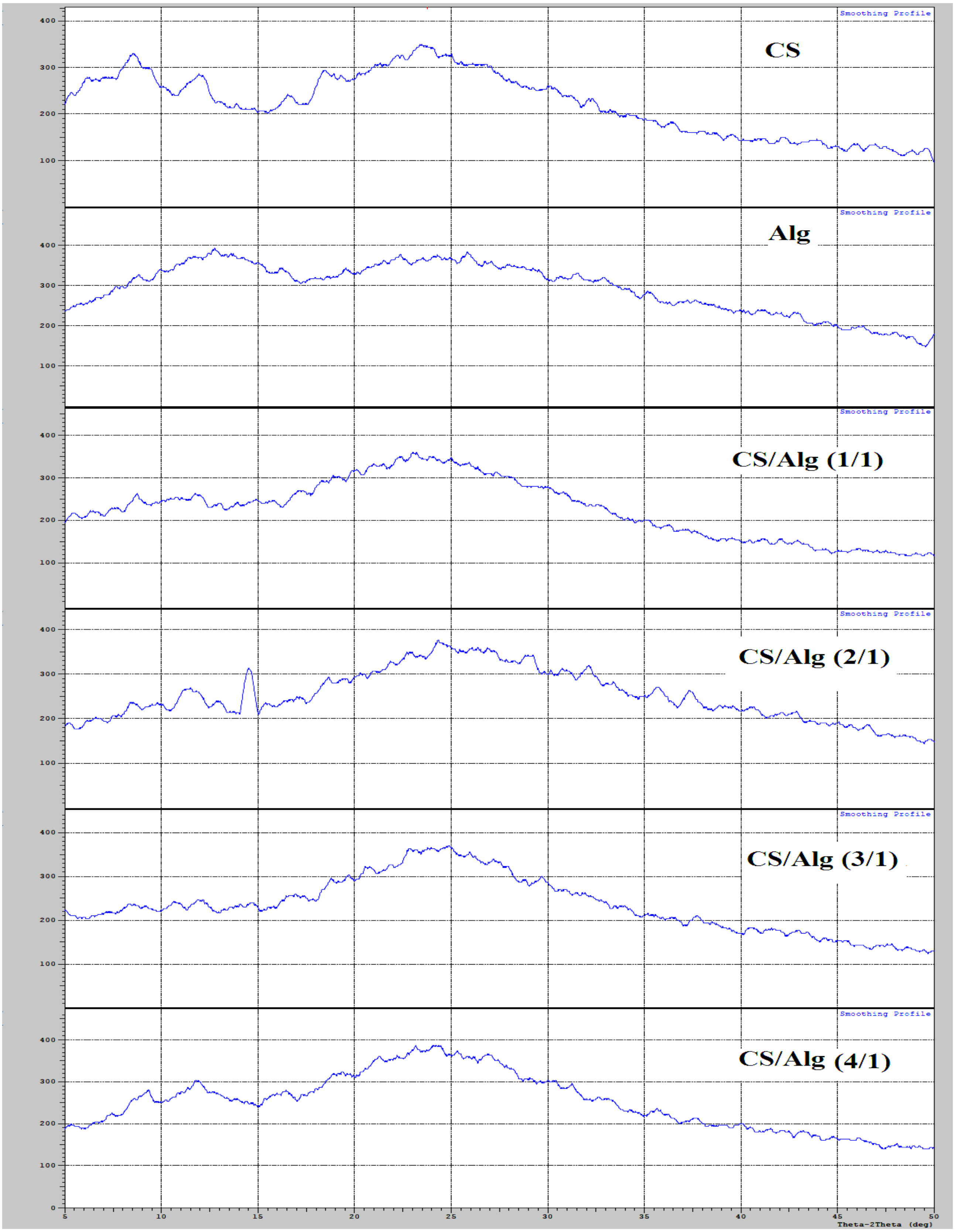


Figure 7. XRD patterns of CS, Alg, and CS/Alg ionic crosslinked membranes.

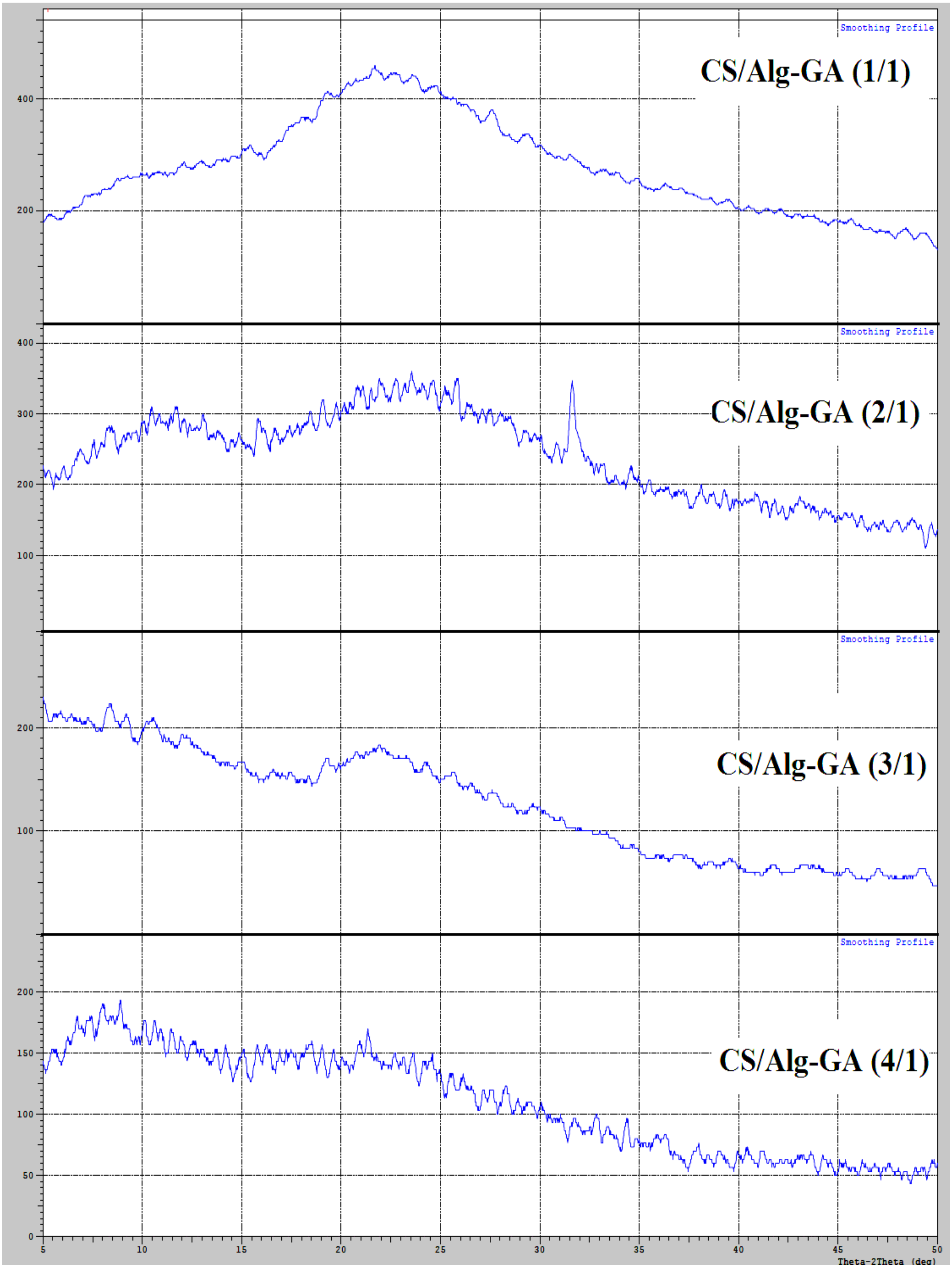


Figure 8. XRD patterns of covalent crosslinked CS/Alg membranes.

3.2.10. Methanol permeability measurements

The values of methanol permeability for the covalent crosslinked membranes are shown in Figure 9. The notable advantage in this figure is that the permeability of Nafion® 117 membrane was (1.14×10^{-9}cm^2/s), which is higher than that of the chemically modified. These results illustrated that the membranes could be used successfully for reducing the methanol crossover. Besides, it was evident that the both native alginate and chitosan membranes in addition to the ionic crosslinked membranes were highly swollen in water, thus it cannot be measured. Furthermore, the methanol permeability coefficient of membranes has the lowest value (2.5×10^{-10}cm^2/s). Hence, the prepared polyelectrolyte membranes can act as an excellent methanol barrier. This is due to the lack of a significant chemical interaction between the methanol molecules and ionic clusters, which introduced through formation of the polyelectrolyte membranes [11].

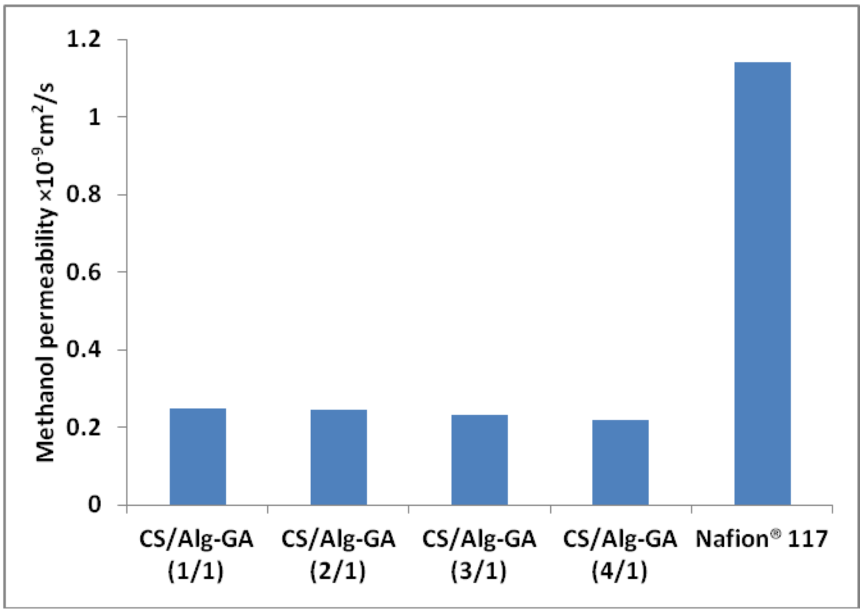


Figure 9: Methanol permeability of CS/Alg-GA and Nafion 117 membranes.

4. CONCLUSION

In this work, two polyelectrolyte membranes were prepared based on chitosan and alginate biopolymers via physical and chemical crosslinking processes. The developed membranes were characterized using different characterization tools, physical characterizations such as surface roughness and optical properties were also investigated. Thermo-mechanical properties revealed adequate mechanical and thermal stability. Additionally, IEC of the covalent crosslinked membranes was increased up to 5.96meq/g with increasing chitosan contents. Moreover, results indicated that the developed membranes have low methanol permeability (2.179×10^{-9}-2.5×10^{-10} cm^2/s) compared to Nafion® 117 membrane (1.14×10^{-9}cm^2/s). These results suggested that covalent crosslinked CS/Alg-GA membranes could be suitable candidates as low-cost polyelectrolyte membranes for direct methanol fuel cell applications.

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