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Novel Membranes Regenerated from Blends of Cellulose/Gluten Using Ethylenediamine/Potassium Thiocyanate Solvent System

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Abstract: Current industrial methods for dissolution of cellulose in making regenerated cellulose products are relatively expensive, toxic and dangerous and have environmental problems coming with the hazard chemical wastes. To solve these problems, a novel ethylenediamine and potassium thiocyanate (ED/KSCN) solvent system was developed, that is economical, ecofriendly, and highly efficient. The ED/KSCN solvent system was proven to be a suitable solvent for fabricating cellulose (blended with other polymers) membranes. In this study, gluten was used to develop nonporous membranes with cellulose. The method of casting these membranes provided better ones than the former researchers' techniques. These composite membranes' physical and mechanical properties were studied by analysis of morphology, viscosity, crystallinity, thermal behaviors, tensile properties and water absorption of membranes. Results showed that membranes are nonporous, uniform, strong, flexible, ecofriendly and renewable. Mechanical and physical properties were influenced by the ratio of cellulose/gluten. By blending 40% gluten, the tensile strength of cellulose membrane dropped to 15.89 MPa from 35.11 MPa. However, its elongation at break increased from 35.3% to 57.02% accordingly.

Keywords: Cellulose; gluten; blended film; novel; ED/KSCN solvent; physical and mechanical properties

1 Introduction

A membrane is a thin layer of material that acts as a selective barrier between different phases to allow the chosen materials to pass through but to stop the others. Such "chosen materials" can be specific particles, molecules, ions or other substances [1]. Membranes can also be called films or coating to protect one thing from another. Membranes have a very broad range of end uses in daily life and industry, such as packaging and protector for food, coating on furniture and books, dialysis, ultrafiltration and fractionation of mixtures. Most membranes made from polymers such as polyethylene, polypropylene, polyvinylchloride, polyamide, and polyurethane, which are all petroleum-based polymers. Those polymers consume great amount of petroleum resources and are nondegradable in the landfill which causes severe environmental problems. Because of the limitation of petroleum resources and environment problems, biopolymers have been considered as alternatives to nondegradable petroleum-based polymers because of their abundance, renewability, low cost, and good biodegradability [2]. The strong need for development of new eco-friendly materials has led scientists to study the properties of membranes made of degradable biopolymers. In this work, cellulose and gluten protein were chosen as raw materials to produce membranes.

Cellulose is the most common polymer on the earth which exists in primary cell wall in plants serving as the structural component. It is considered as a promising and recommended material with good biodegradability, cost-effectiveness, abundance and excellent physical and mechanical properties.

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Cellulose is a kind of glucose polymer with a molecular structure with linear 1-4-β linkage [3]. However, the potential applications of cellulose are limited because it cannot be melted to fabricate into a desired form or to be dissolved in a common solvent. Because of existence of strong intra- and intermolecular hydrogen bonding, cellulose usually degrades before melting [4]. Therefore, scientists have paid more attention to finding new efficient solvents for cellulose. Many solvent systems, including N-methylmorphorine-N-oxide (NMMO), LiCl/dimethylacetamide (LiCl/DMAC), and aqueous base ones, are very popular with high efficiency [5-7]. However, these solvent systems could produce chemical waste which can cause environmental problems. Especially, the NMMO solvent system is a thermal instable and strong oxidizing agent, which poses a hazard to environment and human health [8]. To solve these problems, a new solvent system composed of ethylenediamine and potassium thiocyanate (ED/KSCN) was developed [9]. This solvent system allows for dissolution of cellulose in a relatively short period of time at a relatively low temperature, which was also verified by other researchers [10,11]. This ED/KSCN solvent system was used in this work to dissolve raw materials.

Gluten is the name of a special kind of protein which can be found in grains, e.g. wheat. Gluten proteins play a vital role in determining the unique baking property and mechanical properties of wheat flour by controlling water absorption capacity, cohesivity, viscosity and elasticity on dough [12]. Because large amount of disulfide bonds exists between molecular chains, gluten proteins are water-insoluble. There is no specific chemical structure of gluten proteins because they are all mixtures and have extremely long molecular chains. Gluten consists of two main components, gliadin and glutenin, with the similar proportions. Both have unique properties [13]. Gliadins have little elasticity and they are less cohesive than glutenins but they strongly contribute to the viscosity and extensibility of the dough system. Compared to gliadins, glutenins are cohesive and elastic and are responsible for strength and elasticity of the dough system [12,13].

Blending is a useful and important method to develop new materials for polymers. When cellulose is combined with other polymers, hydroxyl groups in cellulose facilitate the formation of intermolecular hydrogen bonds between molecular chains of cellulose and other polymers leading to good miscibility and novel functions and properties [14]. In this work, membranes were made from cellulose/gluten blend, which was dissolved in ED/KSCN solvent system. The objective of this work is to develop a novel cellulose/gluten blended membrane and study the relationship between the concentration of cellulose/gluten and physical and mechanical properties of membrane. The potential of this membrane is also discussed. The physical and chemical properties of membranes were characterized by using different analytical instruments and procedures.

2 Materials and Methods

2.1 Materials

The Buckeye VFC wood pulp was used as the raw material with a degree of polymerization (DP) of around 600. The gluten protein was Arise® 8000 (gluten protein ≥ 94%), provided by MGP. Reagent grade methanol (≥ 99.8%) provided by Sigma-Aldrich was used coagulant.

Membrane-casting tools: a casting board with a glass plate, polyester films for holding substrate, and a casting bar with thickness ranging from 5-50 mil.

Solvent dissolution tools: a Pyrex® three-neck round bottom flask to perform the dissolution of gluten protein and other polymers, a water-cooled condenser for condensation of ED, a stirring system consisted of a Teflon© blade, a glass rod and an electric motor.

2.2 Dissolution of Cellulose

Before dissolving cellulose, 6 g of fine and dried cellulose powder and 94 g ED/KSCN solvent was weighted. Then the dried powder was added into a three-neck round bottom flask followed by the addition of ED/KSCN solvent. The left neck was connected to water-cooled condenser. A Teflon© blade attached to a long ground glass rod connected with an elector motor was inserted into the center neck for the purpose of stirring and mixing the solvent thoroughly. The right neck was plugged by a glass (or

rubber) stopper. During stirring, the flask was immersed and heated in glycol oil bath at 90°C, which was proved the best temperature for cellulose dissolution. Thermometer was used to monitor the temperature from time to time. The mixture was stirred for 3-4 hours until complete dissolution was achieved. When cellulose was dissolved completely, the heater was turned off and the solution was poured it into a glass container for film-forming use.

2.3 Dissolution of Cellulose/Gluten Protein Blend

The first step of dissolution of cellulose/gluten protein blend was preparation of the physical mixture of cellulose and gluten protein powder. Four 6 g samples with different ratio of cellulose to gluten protein, namely 90/10, 80/20, 70/30 and 60/40 were prepared. Dried cellulose and gluten protein powder were weighed out separately and mixed together before adding to the three-neck round bottom flask. It was important to avoid the aggregation of gluten protein that increased the dissolution time. The equipment and temperature set up were the same as used for cellulose dissolution. Dissolving time, around 3 hours. A clear polymer solution was poured into a glass container for storage. The procedure for cleaning the flask was the same as for cellulose.

2.4 Preparation of Membranes

All membranes were always casted with a casting bar on the casting board followed by coagulation in methanol bath and drying in a vacuum oven.

The casting board was placed on the flat workbench. A polyester film was put on the surface of casting board for holding the substrate. Air bubbles between polyester film and casting board surface was eliminated. The casting bar had a casting thickness range from 5 to 50 mil. The best casting thickness for casting cellulose/gluten protein blended films was 20-25 mil and 25 mil was used in the experiments. However, the best casting thickness for casting cellulose-only films is 30 mil that was used in the experiments. It was noted in the study of Douglass [10] that if the thickness of cellulose-only film was lower than 30 mil, the membrane was too brittle and broke when coagulated; if the thickness was higher than 30 mil, the film was too thick to coagulate completely and the ED/KSCN solvent was trapped in the film and it could not be extracted completely.

Prior to pouring on the polyester (PET) film, the glass container with film-forming solution was heated in the oil bath to 90°C allow it to flow smoothly. The solution was poured into the casting bar on the PET film carefully from left to right with the constant speed. Then, the bar was dragged slowly from top to bottom also with the constant speed. This produced a thin and flat wet membrane on the film. The PET film with wet membrane was peeled off from casting board and immersed in the prepared methanol bath for coagulation. Another membrane with PET film was laid on the top of immersed membranes to provide uniform pressure thus to prevent the curls on four sides and to make membranes flat.

The cast membranes were placed on top of each other with PET film in the bath. The coagulation of solvent layers could be observed after 30 seconds. To coagulate the films thoroughly, they were immersed in methanol for about 20 minutes and the coagulated films were separated from PET films automatically. Then, PET films were removed and disposed. To remove the trapped ED/KSCN solvent after initial coagulation, those films were placed into a new methanol bath and soaked for another 20 minutes. After repeating this step 3 times and soaking membranes in a new methanol bath overnight any ED/KSCN residue could be completely eliminated.

After extracting any traces of ED/KSCN solvent, membranes were removed from methanol bath and packed between glass plates. Films were separated by thin sheets of Teflon film. Air bubbles were squeezed out carefully. Films were packed neatly to avoid wrinkles. A sandwich like structure was formed from bottom to top: glass plate/Teflon film/samples film/ Teflon film/samples film/ Teflon film/samples film/……/glass plate. To provide a more uniform pressure, more glass plates could be used in this structure. Finally, this sandwich structure was laid between two bricks with extra weight on the top.

The packed films were left and dried at ambient temperature for 24 hours and then moved to a vacuum oven and dried at 50°C for 2 or 3 days. When drying was finished, the packed films were cooled to the ambient temperature for another 24 hours before separating sample films from the "sandwich". If separating films were immediately moved out from the oven, those films shrank very fast and a number of wrinkles were formed. Wrinkles must be avoided because they create weak and stress concentration points thus lowering mechanical properties.

2.5 Membrane Characterization

2.5.1 Viscosity Measurement

The DV-E Brookfield viscometer was used to determine viscosity of film-forming solutions with different compositions. Containers with solution were heated in an oil or water bath, at around 95°C, to maintain the liquid state. During measuring, containers were kept in the bath to maintain constant temperature. Because the solutions were very viscous, the number 7 spindle (for the highest viscosity range) was chosen and the speed was set up at 100 rpm. Each solution was measured 3 times. The test was used to study the variation of viscosity of film-forming solutions with an increasing amount of gluten protein mixed with cellulose.

2.5.2 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) was utilized to characterize the surface and cross-sections (before and after break) of membranes. Porosity, thickness and any surface/cross-sections characteristics were studied. The SEM micrographs were obtained on a Hitachi S-3200 Scanning Electron Microscope under standard vacuum conditions of 5 kV potential difference. Representative micrographs are reported from 500x to 10,000x magnification. The Revolutions software used was used to analyze the resulting micrographs.

2.5.3 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) was carried out to characterize the chemical components of the membranes. The test was performed on a FTIR Thermo Fisher iS50 machine with a diamond sensor. The ORBIT/OMNI ATR software was used to measure peak intensity and examine the chemical components of membranes.

2.5.4 Thermogravimetric Analysis

The thermo-gravimetric analysis (TGA) was performed for characterizing the thermal behavior of raw materials and produced membranes. The TGA test was performed on a Perkin-Elmer TGA device, under a Nitrogen atmosphere, and a heating rate of 20 °C/min from 25°C (initial ambient condition) to 700°C. 5-8 mg samples of each material were prepared for testing. The final TGA curves were analyzed using the Pyris software package that came with the Perkin-Elmer device.

2.5.5 X-ray diffraction

X-ray Diffraction (XRD) was performed on Philips XLF ATPS XRD 1000 machine with OMNI Instruments from 5 to 40°2θ, to give a graphic representation of the results. It was used to characterize the crystalline structures of raw materials and membrane with different compositions.

2.5.6 Tensile Properties

Tensile tests were performed in the conditioned (65 ± 5% RH, 21 ± 2°C) physical testing laboratory. All tests were completed on a MTS Q-Test/5 Universal Testing Machine with a 113 kg (250 lb) load cell,

set at 50 mm gauge length, a speed of 10 mm/min, following an adapted method for the appropriate ASTM test method for polymer films (ASTM D882). Membrane samples were prepared into a 70 mm long and 12.7 mm (½-inch) wide strips. All samples were conditioned in the lad for 24 hours before testing. Prior to tensile testing, the thickness of each sample was measured by a Thwing-Albert Thickness tester following ASTM D1777 test method to obtain the proper thickness for the Q-test software. Samples were held between rubber grips to prevent slippage during testing.

2.5.7 Water Absorption

Water absorption test was conducted to study the hydrophilicity of dried membranes and calculate the amount of absorbed water. Dried membranes were soaked in deionized and distilled water for 24 hours. Membranes were weighed before (dry weight) and after (wet weight) soaking. The weight percent of water uptake could be calculated by the ratio of the gained weight to the dry weight. Samples made by different formulations were tested. Each of them was tested at least three times. The trend of water absorption of membranes with increasing gluten concentration could be observed.

3 Results and Discussions

3.1 Viscosity measurement

There are many parameters or factors that play important roles in dissolution of cellulose, for instance, salt type, salt concentration, cellulose molecular weight and cellulose concentration. The molecular weight is also related to several properties of materials. Generally, cellulose materials with a higher molecular weight have better mechanical properties like higher tensile properties and modulus [9]. If the cellulose material is in liquid state, higher molecular weight can cause higher viscosity because of the entanglement of polymer chains which limit chains' mobility.

In this work, the solution viscosity of cellulose with increasing gluten concentration of 0%, 10%, 20%, 30% and 40%, were measured. The data were collected and are shown in Tab. 1.

Table 1: Viscosity of cellulose solutions with different gluten concentration

Cellulose/gluten ratio	Torque (%)	Viscosity (cP)
100/0	65.30	26120
90/10	58.70	23480
80/20	47	18800
70/30	36.10	14440
60/40	28.80	11520

The spindle #7, the smallest one for the highest range of viscosity was chosen. The rotation speed was set at 100 rpm. In Tab. 1 "torque" represents the resistance of spindle while rotating in the polymer solution. Higher torque values mean a higher resistance in the solution. The cP is the unit for viscosity; 1 cP = 1 mPa*s. The value of torque and cP are proportional to each other.

As seen in Tab. 1 and Fig. 1, the cellulose-only solution showed the highest torque of 65.30% and viscosity of 26120 cP. With the increase concentration of gluten, the torque and cP value dropped gradually. In the end, the cellulose solution with 40% gluten showed the lowest torque of 28.80% and the viscosity of 11520 cP. Both torque and viscosity decreased by 36.5% and 55.9%, respectively. It can be explained that as the gluten concentration increased the average molecular weight of the blended material or crystallinity decreased. As a result, the polymer chains in the solution became less entangled and the solution viscosity reduced accordingly. The decrease of viscosity can lead to a decrease in mechanical properties of membranes which will be discussed later.

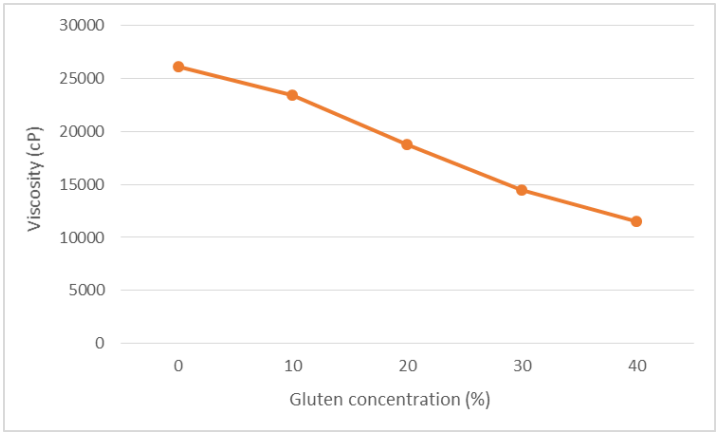
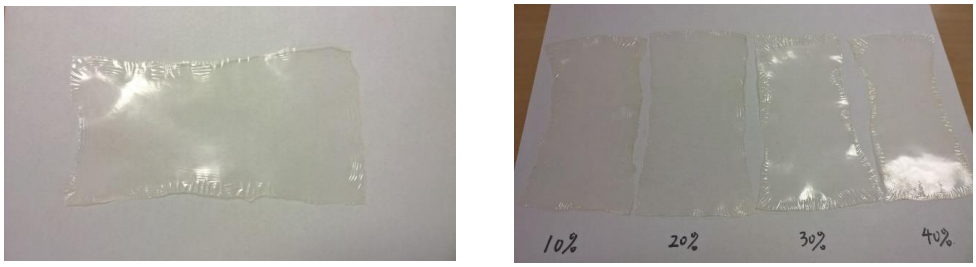


Figure 1: Viscosity of cellulose/gluten solutions with different gluten concentration

3.2 Morphology

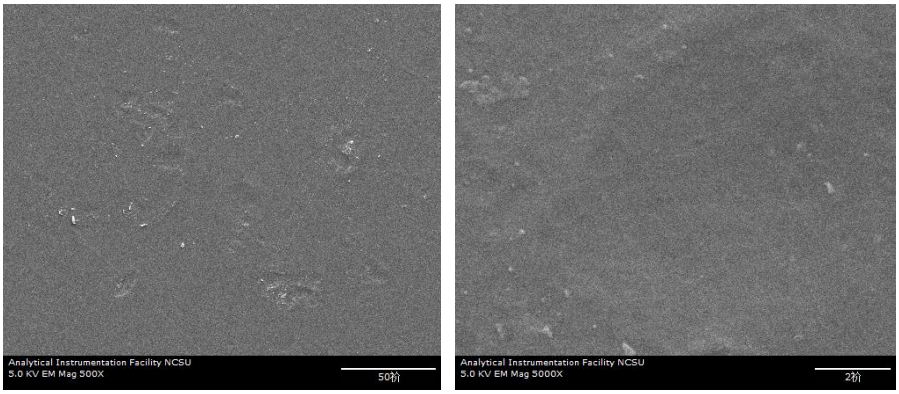
Figs. 2(a) and 2(b) show the cellulose-only membrane and cellulose/gluten blended membranes. All of them are thin, flat and colorless.



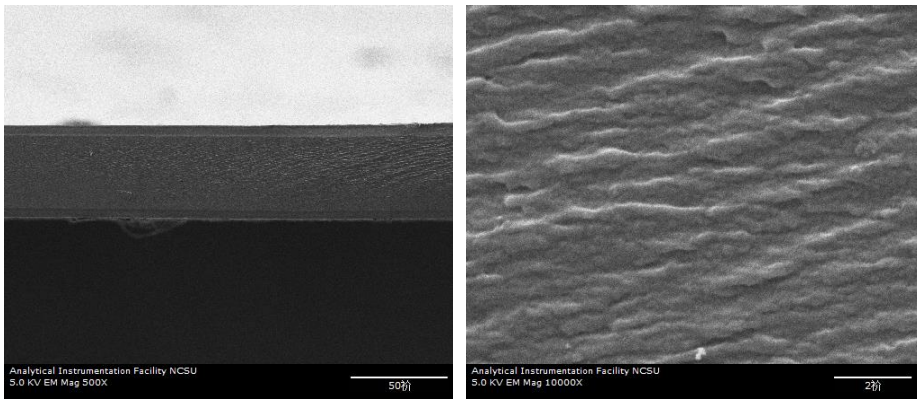
(a) (b)

Figure 2: (a) cellulose-only membrane and (b) cellulose/gluten blended membranes (10%, 20%, 30%, and 40% gluten from left to right)

Scanning electron microscopy (SEM) was performed to characterize the morphology of the cellulose membranes and to verify that they were uniform and nonporous. Both surface and cross-section were taken at various magnifications and shown in Figs. 3(a-d).



(a) (b)

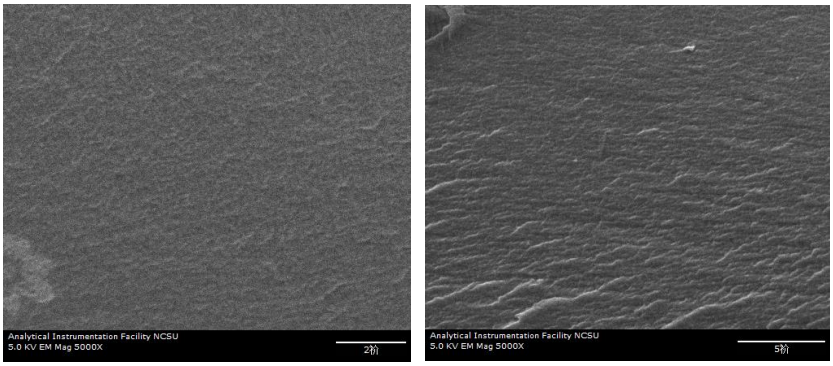


(c) (d)

Figure 3: SEM images of surface of cellulose membranes (unstretched) at (a) 500x and (b) 5000x magnifications and cross-section of cellulose membranes at (c) 500x and (d) 10000x magnifications

As shown in Figs. 3(a)-3(d), the surface of the cellulose membranes was flat, and no pores were visible. The Figs. 3(c) and 3(d) show the morphology of the cross-section of unstretched cellulose membranes at 500x and 10000x magnifications. Those cross-sections were also very even and nonporous. Therefore, it can be concluded that cellulose membranes made in this work were uniform and nonporous, which verify the conclusion drawn by Douglass [10], and Zhu et al. [11].

Figs. 4(a) and 3(b) show very even cross-section areas which represent blended membranes with all different gluten concentration that were uniform and nonporous.



(a) **(b)**

Figure 4: SEM images of cross-section of cellulose/gluten membranes (unstretched) with (a) 10 and (b) 40% gluten at 5000x magnification

As seen in Fig. 5, the stretched-to-break cross-section of membranes become rougher and the fibrous fractures formed on the cross-section area, especially for membranes with 40% gluten. This can be attributed to a decrease in membrane crystallinity which was caused by addition of gluten. This could also be confirmed by XRD tests. Furthermore, the decrease in crystallinity of membranes could influence the tensile properties of membranes which will be discussed later.

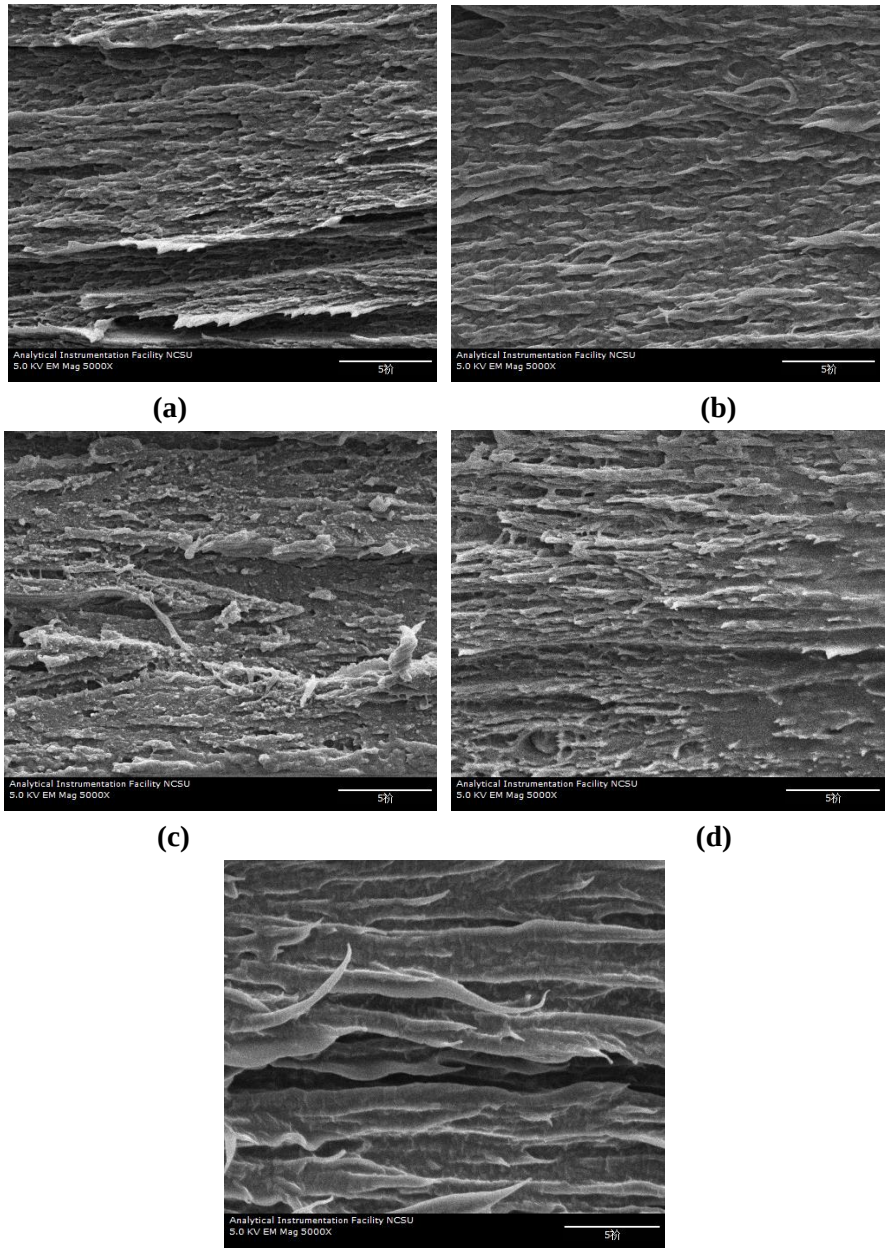


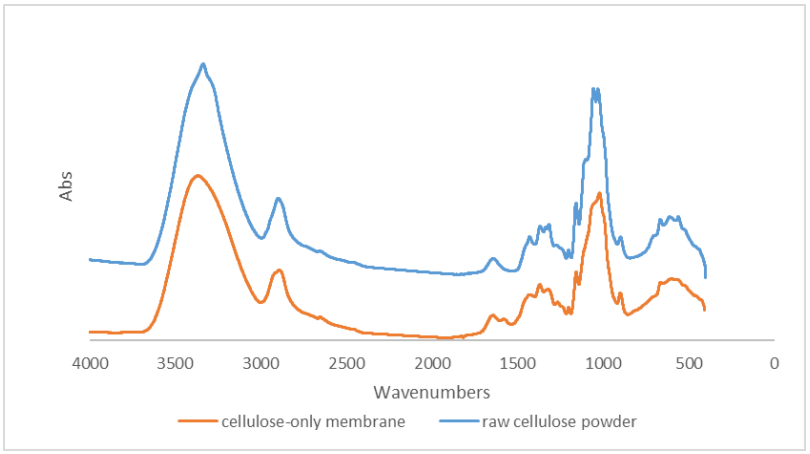
Figure 5: SEM images of cross-section of cellulose/gluten membranes (stretched to break) with (a) 0, (b) 10, (c) 20, (d) 30 and (e) 40% gluten at 5000x magnification

It is very important to point out that the fractured surface of all membranes in these SEM images, there was no fibrous cellulose present and no separation of cellulose and gluten was visible at a high gluten content. As the evidence indicates for the complete dissolution of cellulose and gluten in ED/KSCN solvent system, SEM images exhibited that both polymers are compatible and perfectly blended together.

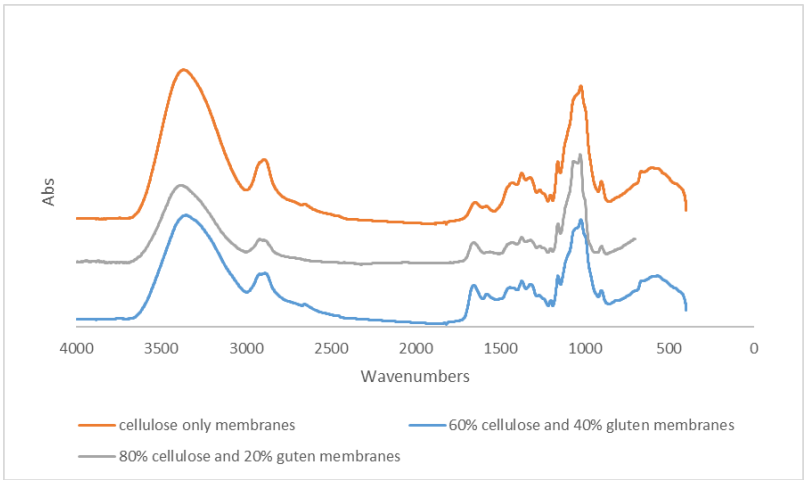
3.3 Fourier Transform Infrared Spectroscopy

The same predominantly functional groups of cellulose and gluten protein are -NH, -OH, -CH and C-C. In addition to these, gluten protein has also amide groups. The FTIR spectra of cellulose powder,

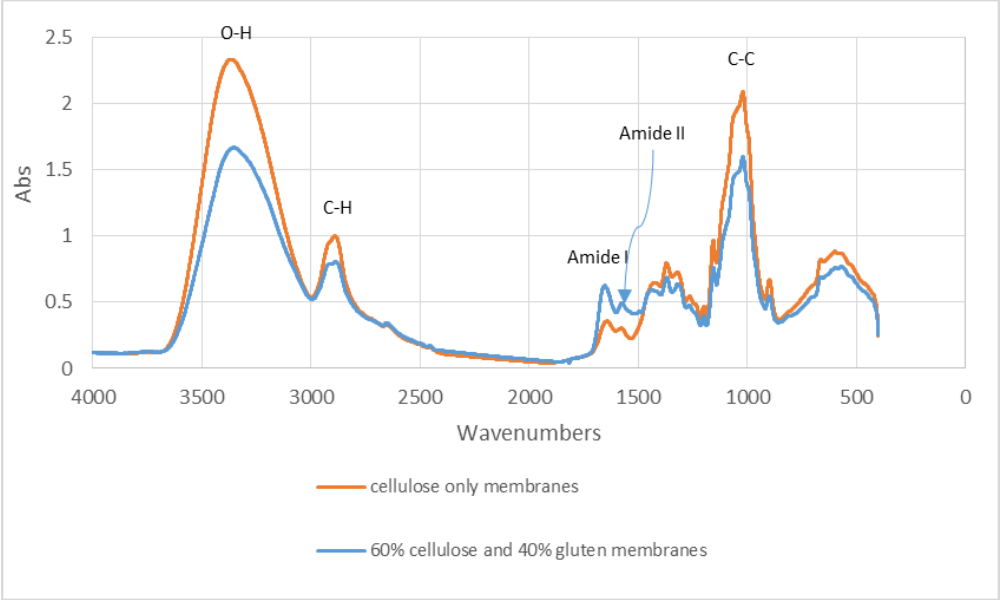
cellulose-only and cellulose/gluten blended membranes with different composition were obtained and used to compare with that one of cellulose-only membrane. To obtain more obvious differences, the FTIR spectra of membranes with the highest amount of gluten were used to compare. Additionally, it was necessary to verify whether any chemical reactions occurred in systems during membrane forming process. Because spectra of membranes with different gluten concentration are very similar to each other, to show the differences between pure cellulose and cellulose/gluten blended membranes, the FTIR spectra of cellulose membranes with 0, 20% and 40% gluten are shown in Fig. 6.



(a)



(b)



(c)

Figure 6: FTIR spectra of (a) cellulose membranes and raw cellulose powder; cellulose membranes with (b) 100/0, 80/20 and 60/40 cellulose-gluten membranes and (c) 100/0 and 60/40 cellulose-gluten membranes

Fig. 6(a) show the FTIR spectra of cellulose-only membranes and cellulose/gluten membranes. The same number of peaks with different intensities and the very similar shapes are present in these Figures. It is very clear from Fig. 6(b), that all peaks are almost at same wavenumbers and no new peak appeared. As shown in Fig. 6(c), with the increasing of gluten concentration, the intensity of most peaks decreased without shifting but two obvious peaks present at 1651 cm^{-1} and 1537 cm^{-1}. Those two peaks represent amide I and amide II groups which belong to gluten, because gluten is a kind of protein, which is made of amino acids. Hameed and Guo [15], and Sashina et al. [16] indicated similar peaks at close wavenumbers. Cellulose does not have amide group as gluten does. The addition of gluten increased intensity of the peaks of amide I and amide II groups. There are no new peaks appearing which means no new bonds formed and no undesired side reactions occurred during dissolution and coagulation processes.

The decrease of peak intensity can be attributed to the decrease of cellulose concentration. The decrease by a small amount in broadening of -OH peak can also be attributed to the hydrogen bonding between -OH and -NH groups.

3.4 Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) was performed to study the thermal degradation of the membranes. The decomposition behavior could be related to the compatibility and miscibility of cellulose and gluten. Depending on the ratio of gluten, TGA thermograms could show more than one peak if the two polymers are not compatible.

Membranes with 0, 10, 20, 30 and 40% gluten were tested. The TGA data is shown in Tab. 2.

Table 2: Onset and offset decomposition temperatures and char levels of the TGA curve

Cellulose/gluten ratio	Onset temperature (°C)	Offset temperature (°C)	Char level (%)
100/0	291.73	377.03	25
90/10	297.39	388.43	26
80/20	293.6	380.47	24
70/30	297.09	393.42	23
60/40	280.82	381.56	26

The onset and offset temperature of wood pulp (264.34°C and 403.38°C) are higher than those of gluten (199.69°C and 391.23°C). As shown in Tab. 2, with the increase of gluten concentration the onset and offset temperature increased but they were still very close to each other. Comparing the char level, membranes with the different gluten concentration had very close char levels which means cellulose and gluten are compatible and likely miscible.

3.5 X-Ray Diffraction

X-ray Diffraction was performed to detect morphological features of cellulose/gluten blended membranes with different gluten concentration and to show the structural differences. The degree of crystallinity is an important parameter which influences the physical and mechanical properties of materials. The XRD spectra of membranes with 0%, 10%, 20%, 30% and 40% gluten were shown in Fig. 7.

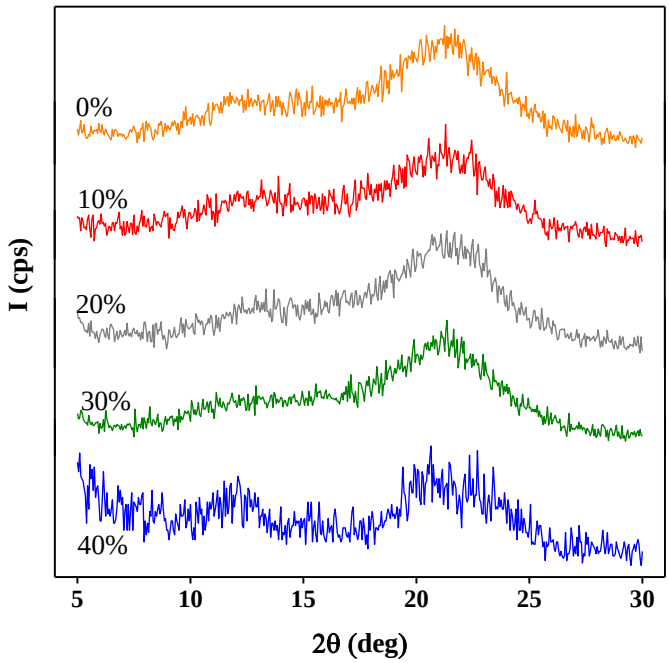


Figure 7: XRD curves of cellulose/gluten blended membranes with 0- 40% gluten

Generally, with the increase of gluten concentration, the crystallinity of membranes decreased. Figure 7 shows the XRD curves of cellulose/gluten blended membranes with different gluten concentration. Cellulose-only (0% gluten) sample showed the curve of cellulose II which was converted from cellulose I by dissolution and then coagulation, which was verified by Douglass [10], and Cao and Tan [7]. XRD curves of all the membranes with different gluten concentration had the same peaks at around 13 and 21-22°2θ that mean cellulose II exists in all these membranes. However, the peaks were spread out with an increase of gluten concentration. We could assume that the sharper the peaks were the higher the crystallinity of membrane [17]. With the increasing concentration of gluten, the crystallinity of membranes decreased, because of the rearrangement of macromolecules during dissolution and regeneration. The ED/KSCN solvent dissolved crystalline form of cellulose by destroying inter- and intramolecular hydrogen bonds between the cellulose molecules [17]. During the regeneration (coagulation), (some of) hydrogen bonds reformed. The addition of gluten prevented the formation of hydrogen bonds; consequently, the crystallinity decreased and the amorphous area increased. Compared to all blended membranes, the intensity for 40% gluten membrane was too low to form a curve which means the crystallinity of the membrane was very low.

3.6 Tensile Properties

Tensile properties are essential to study the potential utilization of the cellulose/gluten blended membranes. Cellulose membranes with different amount of gluten of 10%, 20%, 30% and 40%, were tested. During the analysis, tensile modulus, break stress and elongation at break were taken into consideration. The data was collected and shown in Tab. 3.

Table 3: Comparison of tensile properties of cellulose membranes with different gluten concentration

Cellulose/gluten ratio	Tensile modulus (MPa) & CV (%)	Break stress (MPa) & CV (%)	Elongation at break (%) & CV (%)	Thickness (mm) & CV (%)
100/0	2348.69 ± 151.91 (6.47)	35.11 ± 3.82 (10.98)	34.3 ± 0.09 (25.96)	0.076 ± 0.005 (6.35)
90/10	1210.53 ± 119.64 (9.88)	21.87 ± 2.35 (10.68)	38.64 ± 0.08 (21.94)	0.066 ± 0.002 (3.3)
80/20	759.23 ± 61.29 (7.81)	14.51 ± 0.98 (6.72)	39.16 ± 0.07 (16.6)	0.062 ± 0.001 (1.12)
70/30	321.17 ± 27.07 (8.42)	15.79 ± 1.18 (7.66)	44.6 ± 0.05 (11.59)	0.050 ± 0.001 (2.44)
60/40	338.62 ± 43.15 (12.73)	15.89 ± 1.77 (11.03)	57.02 ± 0.08 (14.38)	0.046 ± 0.003 (6.08)

The cellulose-only membranes had the highest tensile modulus of 2348.69 ± 151.91 MPa and break stress of 35.11 ± 3.82 MPa but the lowest elongation at break of 34.3%. By adding low ratio of gluten, the modulus and stress dramatically decreased. This is because, the addition of gluten increased the amorphous phase content and decreased the degree crystallinity. At last, the blended membranes with the highest gluten ratio (40%), showed the lowest tensile modulus (338.62 ± 43.15 MPa). The membranes with 20% and 30% gluten showed mechanical properties between the cellulose-only and the 40% gluten membranes.

It is plausible to draw a conclusion that with the increase of gluten, tensile modulus and break stress decreased and the elongation at break increased. This means that the addition of gluten can alter the mechanical properties and increase the processability of cellulose membranes because of the increased

elongation at break. In Tab. 3, the elongation at break of all groups of samples show high coefficient of variation. This outcome was obviously influenced by the sample morphology. Wrinkling and air bubbles could be responsible for that. Air bubbles in polymer solutions were difficult to eliminate during membranes casting.

3.7 Water Absorption

Water absorption is an important property for studying cellulose/gluten blended membrane which is related to the potential usages. Water absorption test was conducted to study the hydrophilicity of dried cellulose membranes and water absorption. Gluten proteins have been reported to be water-insoluble. Samples were prepared and tested in the same way as testing cellulose-only membranes. All data of different samples were collected and shown in Tab. 4.

Table 4: Comparison of water absorption results of cellulose-only and cellulose/gluten blended membranes

Cellulose/gluten ratio	Dry mass (g)	Wet mass (g)	Wet mass increase (%)
100/0	0.3547	0.5147	45
90/10	0.3966	0.5380	36
80/20	0.2932	0.3965	35
70/30	0.2827	0.3715	31
60/40	0.2951	0.3588	22

The data in both Tab. 4 and Fig. 8 show a decreasing trend of water pick up by cellulose membranes with an increasing gluten amount. After soaking for 24 hours, the wet mass increase of cellulose-only membranes was 45%. At the gluten content of 40% water absorption decreased 51% to 22%. This indicates that gluten was not as hydrophilic as cellulose and a higher percentage of gluten can cause a lower water absorption. This is because of the decrease in the amount of -OH (cellulose concentration decreases) and the increase in hydrophobic chains (increase of gluten).

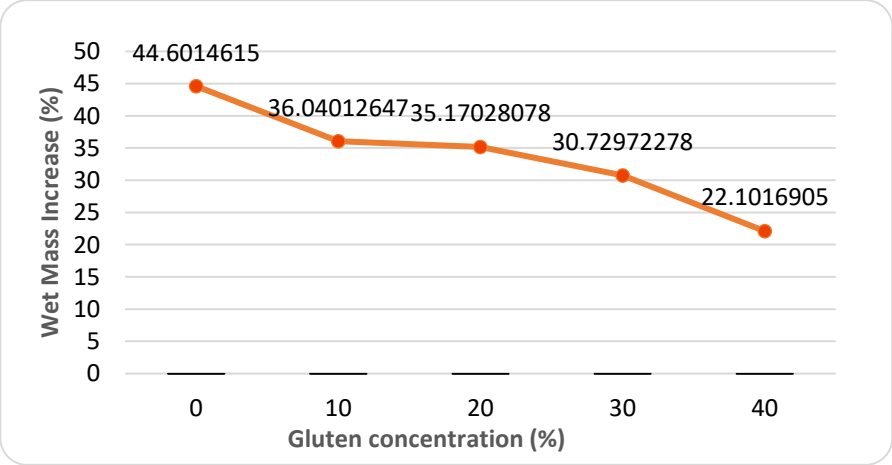


Figure 8: Wet mass increase of cellulose membranes with different gluten concentration

It was noticed that all membranes were intact after soaking in water for 24 hours or even 48 hours, and some strength was kept. Since gluten is water-insoluble, there was no traces of gluten in water. All

wet membranes were dried and were intact with good physical and mechanical properties. The water absorption test showed the potential of cellulose/gluten membranes to serve as a food packaging films.

4 Conclusions

The influence of the ratio of cellulose/gluten to the properties of membrane was systematically studied. Cellulose and gluten can be efficiently dissolved by the ED/KSCN solvent system. With the increase of gluten ratio, the dissolution time decreased. In addition, methanol was an effective coagulant for cellulose/gluten blended membranes. It can remove ED/KSCN from membranes substantially. The membrane casting method can make uniform and nonporous membrane which was confirmed by SEM. FTIR showed no chemical side interactions occurred during membrane production. Cellulose and gluten were compatible and perfectly blended together that was supported by FTIR and TGA. The tensile testing and water absorption test indicated that blended membranes have higher percent of elongation at break and improved water barrier properties, respectively. The properties of blended membranes were related to the ratio of cellulose/gluten blend which can influence the molecular weight, crystal structure and other factors. Therefore, the properties of blended membranes can be controlled by adjusting the ratio of cellulose/gluten concentration. Based on the results discussed above, the cellulose/gluten blended membranes can have potential applications in food packaging, and medical applications because of their sustainability, low cost, biodegradability and ecofriendliness.

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References

1. Zeman LJ, Zydney AL. *Microfiltration and Ultrafiltration: Principles and Applications.* Marcel Dekker, New York, USA. **1996**.
2. Wu RL, Wang XL, Wang YZ, Bian XC, Li F. Cellulose/soy protein isolate blend films prepared via room-temperature ionic liquid. *Industrial & Engineering Chemistry Research* **2009**, 48: 7132-7136.
3. Klemm D, Heublein B, Fink HP, Bohn A. Cellulose: fascinating biopolymer and sustainable raw material. *Angewandte Chemie International Edition* **2005**, 44: 3358-3393.
4. Chen Y, Zhang L. Blend membranes prepared from cellulose and soy protein isolate in NaOH/thiourea aqueous solution. *Journal of Applied Polymer Science* **2004**, 94: 748-757.
5. Dawsey T, McCormick CL. The lithium chloride/dimethylacetamide solvent for cellulose: a literature review. *Journal of Macromolecular Science-Reviews in Macromolecular Chemistry and Physics* **1990**, 30: 405-440.
6. Cuissinat C, Navard P. Swelling and dissolution of cellulose part 1: free floating cotton and wood fibres in N-methylmorpholine-N-oxide-water mixtures. *Macromolecular Symposia* **2006**, 244: 1-18.
7. Cao Y, Tan H. Preparation and properties of microporous cellulose membranes from novel cellulose/aqueous sodium hydroxide solutions. *Journal of Applied Polymer Science* **2006**, 102: 920-926.
8. Manian AP, Ruef H, Bechtold T. Spun-dyed lyocell. *Dyes and Pigments* **2007**, 74: 519-524.
9. Lee HJ. Novel Cellulose Solvent System and Dry Jet Wet Spinning of Cellulose/ED/KSCN Solutions (Ph.D. Thesis). *North Carolina State University*, Raleigh, NC, USA. **2008**.
10. Douglass E.The Development of Cellulose Blend Membranes using Cellulose and other Natural Biopolymers using a Novel Solvent System (Ph.D. Thesis). *North Carolina State University*, Raleigh, NC, USA, **2010**.
11. Zhu Y, Douglass E, Theyson T, Hogan R, Kotek R. Cellulose and soy proteins based membrane networks. *Macromolecular Symposia* **2013**, 329: 70-86.
12. Wieser H. Chemistry of gluten proteins. *Food Microbiology* **2007**, 24: 15-119.

13. Shewry PR, Lookhart GL. *Wheat Guten Protein Analysis.* American Association of Cereal Chemists. **2003.**
14. Yang G, Zhang L, Han H, Zhou J. Cellulose/casein blend membranes from NaOH/urea solution. *Journal of Applied Polymer Science* **2001**, 81: 3260-3267.
15. Hameed N, Guo Q. Blend films of natural wool and cellulose prepared from an ionic liquid. *Cellulose* **2010**, 17: 803-813.
16. Sashina E, Vnuchkin A, Novoselov N. Properties of films prepared from solutions of fibroin-cellulose blends in N-methylmorpholine N-oxide, *Russian Journal of Applied Chemistry* **2006**, 79: 806-810.
17. Mohamed MA, Salleh W, Jaafar J, Ismail A, Jamil SM. Feasibility of recycled newspaper as cellulose source for regenerated cellulose membrane fabrication. *Journal of Applied Polymer Science* **2015**, 132: 42684.