Preparation of microcrystalline cellulose from Rabdosia rubescens and study on its membrane properties

Tong Wei (1422956327@qq.com)
Zhengzhou University https://orcid.org/0000-0002-2669-1191
Meng Li
Zhengzhou University
Wenrui Shi
Zhengzhou University
Zhengyong Liang
Zhengzhou University

Research Article

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Abstract

Microcrystalline cellulose (MCC) from Rabdosia rubescens was prepared by acid hydrolysis, and the corresponding yield of MCC was about 94% when the hydrochloric acid concentration was 10%, the acid hydrolysis time was 70min and the acid hydrolysis temperature was 70℃. The MCC was dissolved in N-methylmorpholine-N-oxide(NMMO)by phase transformation method to prepare MCC membrane. The structure and mechanical properties of MCC membrane were studied systemically. The results showed that the cellulose structure changed from type I to type II in the process of membrane formation, and the thermal stability also decreased. The content of MCC in the casting solution has a great influence on the mechanical properties of the membranes. The higher the content of MCC, the better the comprehensive mechanical properties of the membranes. When the MCC content is 9%, the tensile strength is 8.38 MPa and the elongation at break is 26.72%. Finally, the separation properties of membrane studed by separation bovine serum albumin (BSA) from water. The results showed that the rejection rate and water flux changed positively and negatively with the change of MCC content. When the content was 5%, MCC membrane showed the best comprehensive performance, its rejection of BSA was 37.23 g/(m^2·h), and the corresponding rejection rate and water flux were 88.87% and 41.89 L/(m^2·h) respectively.

Introduction

Rabdosia rubescens is an important Chinese herbal medicine in China, which has the functions of clearing away heat and detoxification, anti-bacterial and anti-inflammatory, promoting blood circulation and relieving pain, preventing cancer and fighting cancer, etc., and it is well known as "Penicillin in Traditional Chinese medicine"(Han et al. 2015,Ikezoe 2003). Rubescens grows widely in Taihang Mountains, Funiu Mountains and Dabie Mountains. Among them, Jiyuan county, Henan Province has the best quality Rabdosia rubescens which is bred artificially in large quantities(Wang et al. 2008). Rubescens is mainly extracted using water-containing alcohol to prepare medicinal extract in pharmaceutical factory. Statistically speaking, one kilogram of hay can obtain 0.1to 0.12 kilogram extract, accounting for more than 80% of the total extraction residue becomes solid waste, causing a waste of resources. The results from our previous study showed that the residue of rubescens is rich in cellulose, and its fiber quality is also good. If the residue is properly used, it is highly possible to turn waste into valuable resource. So, how to use the residue valuably is a meaningful research project.

Cellulose membranes have the characteristics of wide sources, low cost, biodegradability, diverse properties and easy chemical modification, which have become one of the development directions of functional membrane materials in recent years. In the process of preparing membrane materials, the quality of cellulose raw materials is an important factor that determines the performance of membrane materials. Microcrystalline cellulose (MCC) is a white powder with an average crystallite size of 20–80μm. It has low degree of polymerization, uniform molecular weight and large specific surface area. It is suitable for the preparation of cellulose regenerated membranes. Although there are currently reports that microcrystalline cellulose prepared with corn cob(Shao et al. 2020), banana tree waste(Elanthikkal et al. 2010), wheat straw(Han et al. 2011), oil palm fiber(Xiang et al. 2016), etc., as

fillers used in the preparation of cellulose membranes. However, jute and oil palm fiber are expensive, and the supply of tea dregs and banana tree waste is difficult. Corncobs are mainly used as feed, and their promotion is subject to certain restrictions. The rubescens dregs do not have the above problems and can be used as a rich and high-quality source of cellulose. At the same time, the research on the preparation and performance of rubescens MCC and its membrane materials has not been reported. In this paper, the conventional cellulose was treated by acid-catalyzed hydrolysis to obtain MCC. Depending on the intrinsic properties of MCC to overcome the shortcomings of conventional cellulose membrane such as low strength and uneven membrane pores, a cellulose membrane with better comprehensive properties was successfully prepared .

Experimental

Materials

The Rubescens cellulose (96.28%) :prepare from Rubescens dregs which provided by Jishi Pharmaceutical Company, Jiyuan City, Henan Province; NMMO aqueous solution(50%), hydrochloric acid(37%), gallic acid Propyl ester, glycerin($C_3H_8O_3$:AR), and BSA(AR) all were purchased from Sinopharm Group.

Preparation of Rabdosia rubescens MCC

Cellulose prepared from Rabdosia rubescens dregs was hydrolyzed to obtain MCC, By changing hydrolysis temperature,concentration of HCl and reaction time. When the reaction was terminated, the mixture was filtere and washed with distilled water to neutrality. Finally, dried to constant weight and crushed to obtain microcrystalline cellulose.

Preparation of Rabdosia rubescens MCC membrane

Under the condition of 55°C, 50% NMMO aqueous solution was concentrated to 86.5%, and 0.5% propyl gallate was added to the solution, shaken to store in a cool and dark place for later use (Thomas et al. 2002).

The extracted Rubescens vulgaris MCC was added to NMMO/H_2O in a certain proportion, swelled in the reactor for a certain period of time at 100℃, and then mechanically stirred until the cellulose was completely dissolved, forming a translucent amber gelatinous liquid. Let stand for 4h at 100℃ for deaeration, pour the solution on a thermostatic glass plate at 85℃, and scrape the membrane at a constant speed with an I-shaped coater. After scraping the membrane, quickly put it in the coagulation bath for 24h and change the water every 8h. The solidified Rubescens officinalis MCC membrane was put into a glycerin aqueous solution ($C_3H_8O_3$: H_2O = 30 ml: 100 ml) for plasticization for 1h, then taken out, the surface moisture was absorbed by filter paper, and then placed in an oven at 80°C for drying to constant weight.

FTIR analysis

The prepared oridonin cellulose membrane was vacuum-dried at 80°C for 12 h, then cut into small pieces, ground and compressed with KBr powder, and scanned and analyzed in the interval of 4000-400cm^{-1}.

XRD analysis

X-ray diffraction equipped(D8,Bruker, Germany) with Cu Kα radiation in the 2θ range 3–50° with step size of 0.02° ,was used under the operational conditions of 40 kV and 40 mA, scanning speed 10°/min.

Thermal analysis

6mg sample was put into an alumina crucible, which was heated from 25℃ to 500℃ under the condition of nitrogen flow rate of 20mL /min, and the heating rate was 10℃/min.

Mechanical performance test

The membrane samples were cut into a rectangle of 2.0×6.0cm, and the mechanical properties were tested on a universal tensile testing machine. The tensile speed was 50mm/min and the clamp was 50mm. The experimental method referred to GB/T1040.3-2006.

Separation performance test

The membrane was cut into a circle with a diameter of 4cm, and measured with a prepared 1.00g/L bovine serum albumin aqueous solution, pre-pressured at 0.2MPa for 20 min, and then set the pressure to 0.1MPa for 10 min, and the measurement was collected. The membrane's permeating flux was calculated by formular (1) (Weng et al. 2017), the BSA concentration of the permeate was measured by a spectrophotometer, and compare it with the original solution to obtain the rejection rate(Wang et al. 2017) .

$$\mathrm{J} = \frac{V}{St}$$

1

J : water flux, L/(m^2·h);

S: the effective area of the membrane, m^2;

V :the volume of liquid passing through the membrane in a certain time, L;

t : the test time, h.

$$\mathrm{R} = \left(1 - \frac{\mathrm{C1}}{\mathrm{C0}}\right) \times 100\%$$

2

R: rejection rate,%;

C_0 :concentration of BSA in the stock solution, g/L;

C_1: concentration of BSA in the permeate, g/L.

$$Q = JcoR$$

3

Q: The mass of BSA separated per unit area of membrane material in unit time, g/(m^2·h).

Results And Discussion

The effect of the hydrolysis temperature on yield of MCC

Studies have shown that the hydrolysis of cellulose requires higher energy, so the hydrolysis temperature has a significant impact on the preparation of MCC [6, 12]. It can be seen from Fig. 1 that as the temperature increases, the yield of microcrystalline cellulose first increased and then decreased. When the temperature rose to 70–80℃, the yield of microcrystalline cellulose tends to stabilize and remains at about 87% When the temperature rose to 90℃, the system energy was too high. At this time, the glycosidic bond of cellulose was broken and was hydrolyzed to dissolved glucose, causing MCC loss. Therefore, the hydrolysis temperature should be maintained at 70–80°C. Considering the economics of the process, 70℃ was more appropriate.

Effect of the concentration of hydrochloric acid on yield of MCC

Due to the large activation energy required for the cellulose hydrolysis reaction, the reaction is difficult, and inorganic acid is usually added as a catalyst to reduce the activation energy of the reaction(Han et al. 2015). Considering the improvement of substrate reaction activity, product selectivity and cost, hydrochloric acid is the most suitable, so hydrochloric acid is used as the catalyst in this study. So, The reaction was caried in different concentrations of hydrochloric acid system. It can be seen from Fig. 2 that as the concentration of hydrochloric acid increases, the yield of MCC first increased and then decreased. When the concentration of hydrochloric acid was 5%, the acidity of the system was weak and the number of active sites was insufficient. In this condition, the rate of hydrolysis was much lower, so the product yield was low. With the increasing of the acidity of the solution, the rate of hydrolysis increased significantly. when the mass fraction of hydrochloric acid reached 10%, the yield was the highest. After that, as the concentration of hydrochloric acid increased, the hydrolysis of glycosidic bonds intensifies, exposing more reducing end groups and further accelerating the rate of hydrolysis, which leaded to excessive degradation and dissolution of cellulose, which reduced the yield of MCC.

It can be seen from Fig. 3 that in the early stage of acid hydrolysis (before 70 min), the main destruction of the hydrolysis reaction was the amorphous region of cellulose, which increased the crystallinity of cellulose, so the yield of MCC increased. However, if the reaction time was excessively extended, the crystalline area of cellulose will also be destroyed, that was to say, MCC will also undergo hydrolysis. When the degree of polymerization was reduced to a certain extent, it will be dissolved in the reaction system and lost. Therefore, the acid hydrolysis time was preferably selected as 70 minutes.

Reaction conditions: m(cellulose) = 2g; V(HCl) = 40ml; C(HCl) = 10%;T = 70°C;

FTIR analysis

As shown in Fig. 4, A is the Rubescens cellulose, B is the MCC of Rubescens, and C is the MCC standard sample (purchased from Xi'an Baichuan Biotechnology, purity 99%). It can be seen from the FTIR spectrum that the they all have the absorption peaks at 3400 cm^{-1}, 2920 cm^{-1}, 1634 cm^{-1}, 1370 cm^{-1}, 1040 cm^{-1}, and 897 cm^{-1} in common represent the –OH stretching vibration peak, the –CH stretching vibration peak, and –C = O stretching vibration peak,–CH bending vibration peak, –C–O–C stretching vibration characteristic peak and alienation β-bond [14]. It can be seen that the position of the basic characteristic peak of cellulose has not changed, indicating that the molecular structure of the microcrystalline cellulose was basically unchanged during the process of preparing microcrystalline cellulose, and it's quality was basically consistent with the commercial microcrystalline cellulose.

XRD analysis

It can be seen from Fig. 5 that the positions of the diffraction peaks of the rubescens microcrystalline cellulose and the MCC standard sample are the same, and diffraction peaks appear at 2θ = 15.4°, 22.5°, and 34.6°, and their crystal structure is type I(Wang et al. 2016), indicating that the preparation of microcrystalline cellulose was basically the same as the MCC standard. Analysised with jade software found that the crystallinity was slightly lower than MCC standard sample. The microcrystalline fiber microfilm had a diffraction peak at 2θ = 20.8°, and it was crystal structure was type II(Han et al. 2013), indicating that the crystalline structure of the cellulose has changed after the NMMO/H2O was dissolved into a membrane. After the membrane was formed, the diffraction intensity decreases, and the crystallinity drops to 58.03%. This was due to the strong polar oxygen atoms on the N-O in the NMMO solution attacking the hydrogen bond and breaking it during the dissolution process.

Thermal analysis

The thermal curve of MCC standard sample, Rubescens chinensis MCC and Rubescens chinensis MCC membrane measured at a heating rate of 10°C/min were shown in Fig. 6. The thermal decomposition behavior of the samples can be roughly divided into three intervals. The first stage was the micro-weight loss stage, which was mainly manifested by the volatilization of intermolecular bound water and additives.The second stage was the thermal decomposition stage which caused a significant weight loss. The third stage was the stability of carbon formation, the sample was basically carbonized at this stage,

and the increase in temperature has a relatively small effect on the weight loss of the residue(Fahma et al. 2010)

From Fig. 6(a), we can see the thermal weight loss curve of Rubescens vulgaris MCC. Compared with the standard sample, in the first stage, the weight loss rate of Rubescens vulgaris MCC was slightly lower than the standard sample, indicating that it was more hydrophilic than the standard sample. The initial pyrolysis temperature was about 275℃, which was basically the same as the standard sample. It can be seen from the Fig. 6(b) that its maximum weight loss rate temperature was 327℃ ,which was 22℃ lower than the standard sample and the remaining residue rate was 8.9 %. Overall, the thermal stability of Rubescens vulgaris MCC was not much different from that of MCC standard. In sharp contrast, the initial pyrolysis temperature of Rubescens vulgaris MCC membrane was 151℃, and the maximum pyrolysis rate temperature was 218℃. The thermal stability after membrane formation was lower than before membrane formation, which may be due to the dissolution regeneration process. The hydrogen bond between the cellulose was not completely rebuilt after it was opened, and the decrease in crystallinity after dissolution also affects the thermal stability of the MCC membrane(Weng et al. 2017)

Influence of the content of MCC on the mechanical properties

Figure 7 shown the influence of the content of microcrystalline cellulose in the casting solution on the mechanical properties of the microcrystalline cellulose membrane. It can be seen that with the increase of the content of MCC in the casting solution, the tensile strength and elongation at break of the MCC membrane both show an increasing trend. When the content of MCC increased from 5–9%, the tensile strength of the membrane increased from 3.20 MPa to 8.38MPa, and the elongation at break increased from 13.79–26.72%. This was due to the increase in cellulose content in the casting solution, the increase in the number of molecules per unit volume, forming extrusion with each other, increasing the intermolecular microcrystalline entanglement, and the tighter intermolecular connection, thus increasing the mechanical properties of the membrane. However, as a separation membrane, the concentration of casting solution should not be too high, otherwise the membrane will be too dense, which will reduce the permeability and even lose the separation function.

Influence of MCC Content on the membrane's hydrophilicity

The contact angle is one of the indexes to measure the hydrophilic or hydrophobic properties of the membrane. The hydrophilicity or hydrophobicity of the membrane has a certain influence on the application field of the membrane.

Table 1
Contact angle of membranes with different MCC content

MCC Content(%)	4	5	6	7	8
Contact Angle(°)	18.6	24.7	29.4	31.0	36.8

Therefore, it is of great significance to control the hydrophilic and hydrophobic properties of the membrane. From the perspective of cellulose structure, cellulose was an amphiphilic molecule, which has both a hydrophobic carbon ring and a hydrophilic hydroxyl group. Therefore, the hydrophilic and hydrophobic properties of the membrane are controllable by some means. Here, we examined the membranes formed by different cellulose contents of Rubescens in the casting solution, and the contact angles of water against membrane are also different. The contact angles were shown in Fig. 8 and Table 1. The data in Table 1 shown that as the concentration of cast cellulose increases, the contact angle increases, indicating that the hydrophobicity of the cellulose membrane increases simultaneously. This was because the higher the content of microcrystalline fibers in the casting liquid, the denser the membrane formed, the shrinkage of the membrane pores, the smaller the specific surface area, and the less the number of exposed hydroxyl groups, the weaker the hydrophilicity and the increased hydrophobicity.

The water flux and rejection rate of the membrane are important indicators to characterize the performance of the membrane. In this study, the flux and rejection rate of the membrane formed by the casting liquid with different MCC content to 1.0 g/L bovine serum albumin aqueous solution were determined under the pressure of 0.1MPa. The result was shown in Fig. 9.

The effect of the content of MCC on the separation performance of membrane

It can be seen from Fig. 9 that under the same pressure, with the increased of the cellulose content in the membrane casting solution, the water flux of the formed membrane shown a downward trend, and the rejection rate rate continues to increased. When it reached 7%, the water flux was still decline but the rejection rate hardly changes. This is due to the increase in cellulose content and the increase in the force between cellulose molecules, which will be more tightly bonded to each other when forming a membrane, and the membrane pore size will become smaller, resulting in smaller water molecular channels and reduced water flux. This was consistent with the above conclusion that the higher the cellulose content in the contact angle, the stronger the hydrophobicity of the cellulose membrane.

Therefore, selecting the appropriate cellulose content was of great significance to the separation effect of the regenerated cellulose membrane. Here, under a certain pressure, the solute rejection Q per unit time and unit area of the membrane represents the separation efficiency of the cellulose membrane.

It can be seen from Fig. 10 that the membrane formed when the MCC content was 5% has the highest rejection of bovine serum albumin, and its value can reach 37.23 g/(m^2·h).

SEM analysis of membrane

The cellulose membrane with 5%MCC content with the best performance was taken as the test object, and its microstructure was analyzed using SEM. The plane and section structure were shown in Fig. 11. It can be seen from Fig. (a) that the surface of the membrane was smooth, flat and uniform without obvious structural defects. As can be seen from fig. (b) section, the section of the membrane shows a

high density spongy shape, and the bonding between cellulose molecules was close, thus showing a high mechanical strength and separation performanc.

Conclusions

In this paper, microcrystalline cellulose of rubescens was prepared via hydrolysis in hydrochloric acid solution, and the optimized preparation process was obtained through single factor experiments. The yield of MCC was 94.04% under the optimized conditions of 10% HCl concentration, 70 min acidolysis time and 70°C. The MCC membrane was prepared from the microcrystalline cellulose and characterized by FT-IR, SEM and XRD. The results showed that the dissolution of MCC in NMMO was a pure physical process, the crystalline form of cellulose changed from cellulose I to Cellulose II in the process of cellulose regeneratio. At the same time, the thermal stability of cellulose decreased greatly. It was found that the content of MCC in the casting solution had a great influence on the mechanical properties of the MCC membrane, and the tensile strength and elongation at break increased with the increase of the content of MCC. The relationship between membrane separation performance and MCC content was more complicated. The rejection rate and water flux change with MCC content positively and negatively, when water flux was 43.31 L/(m^2·h), the rejection rate was 83.56% ; the water flux was 21.66 L/(m^2·h) when the maximum rejection rate was 95.80%. In practical application, it was necessary to consider synthetically between rejection rate and energy.

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Figures

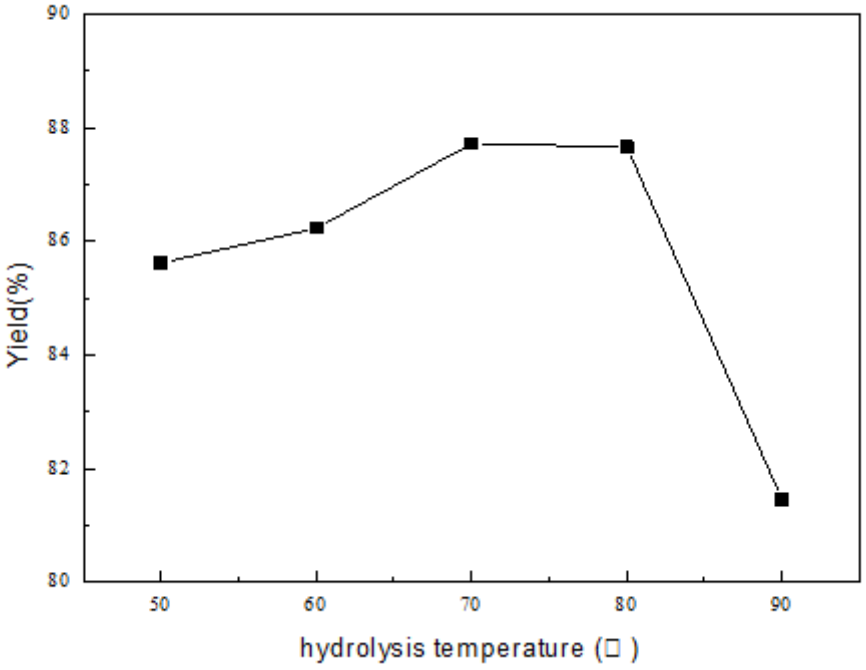

Figure 1

Effect of the hydrolysis temperature on yield of MCC. Note: Reaction conditions: m(cellulose)=2g; V(HCl)=40ml; C(HCl)=20%□t=60min;

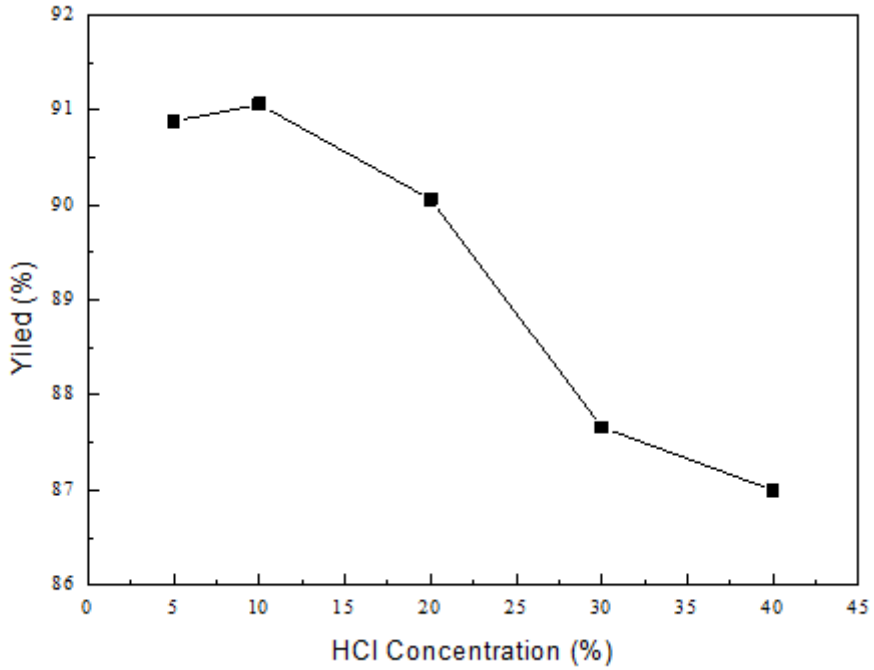

Figure 2

Effect of the concentration of HCl on yield of MCC. Note: Reaction conditions: m(cellulose)=2g;

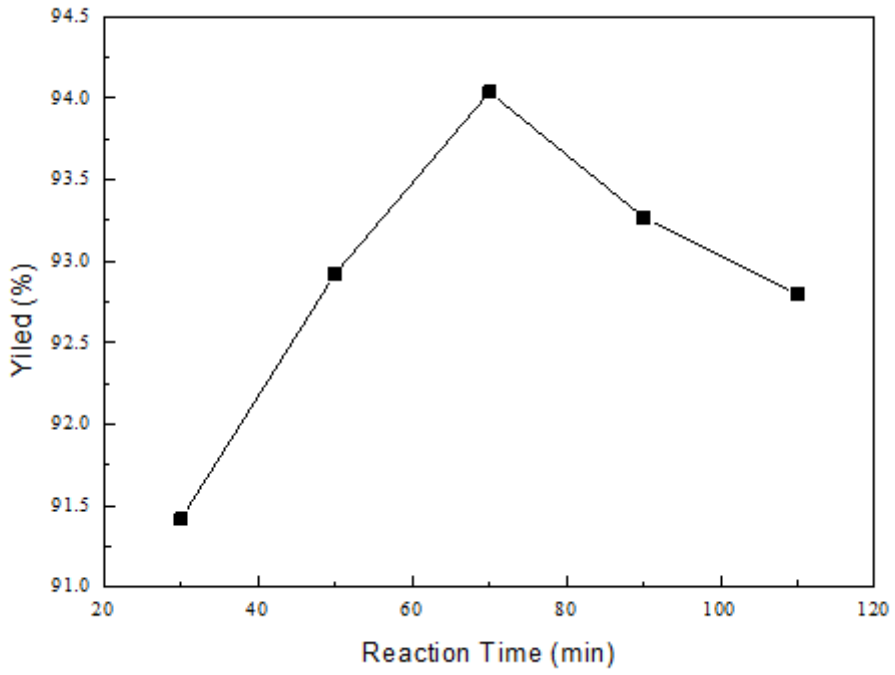

Figure 3

Effect of the hydrolysis time on yield of MCC. Reaction conditions: m(cellulose)=2g; V(HCl)=40ml; C(HCl)=10%;T=70℃;

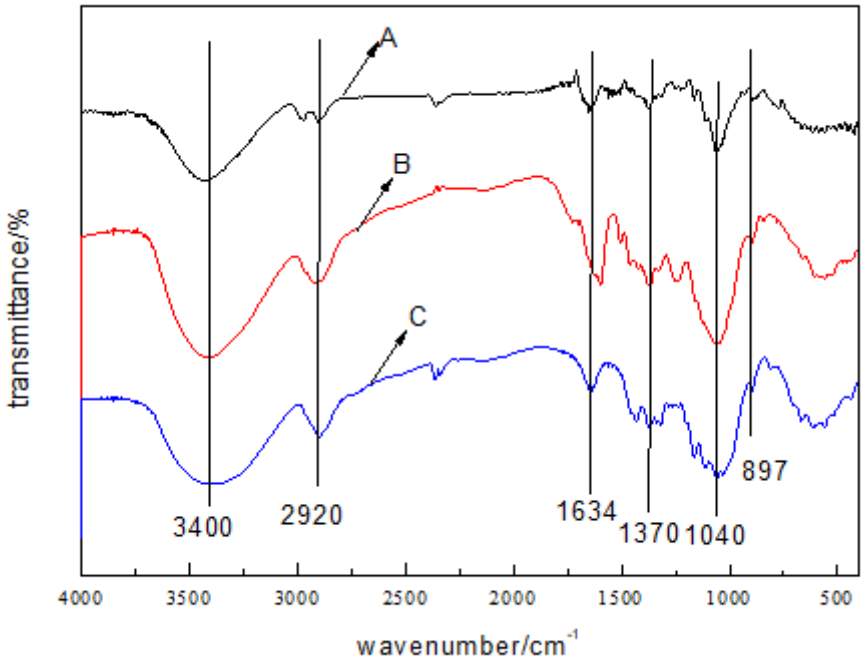

Figure 4

The FTIR of A(Rubescens cellulose), B (Rubescens MCC) and C(MCC standard sample)

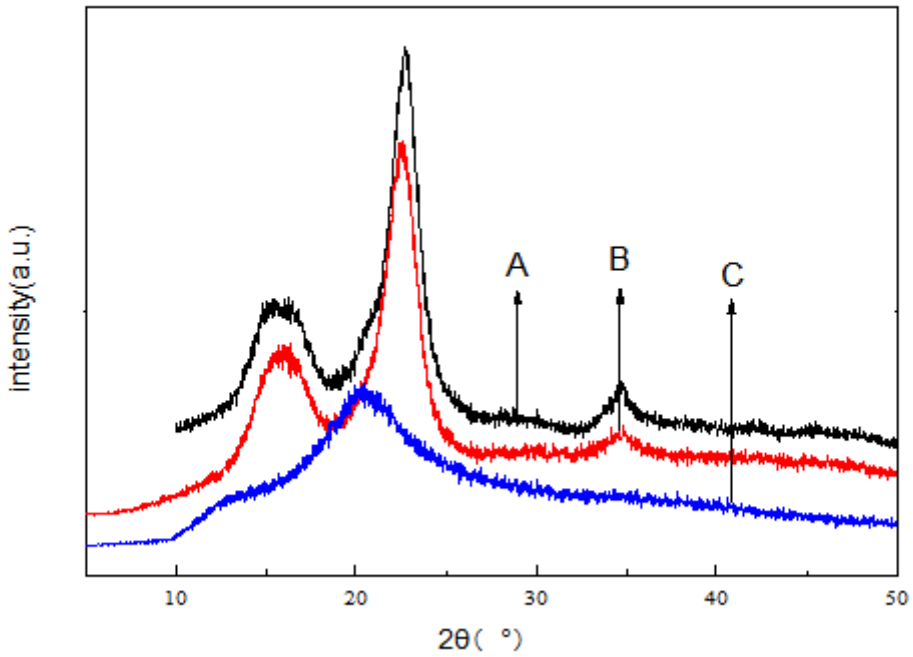

Figure 5

The XRD of A(the MCC standard sampl), B (Rubescens MCC) and C(MCC membrane)

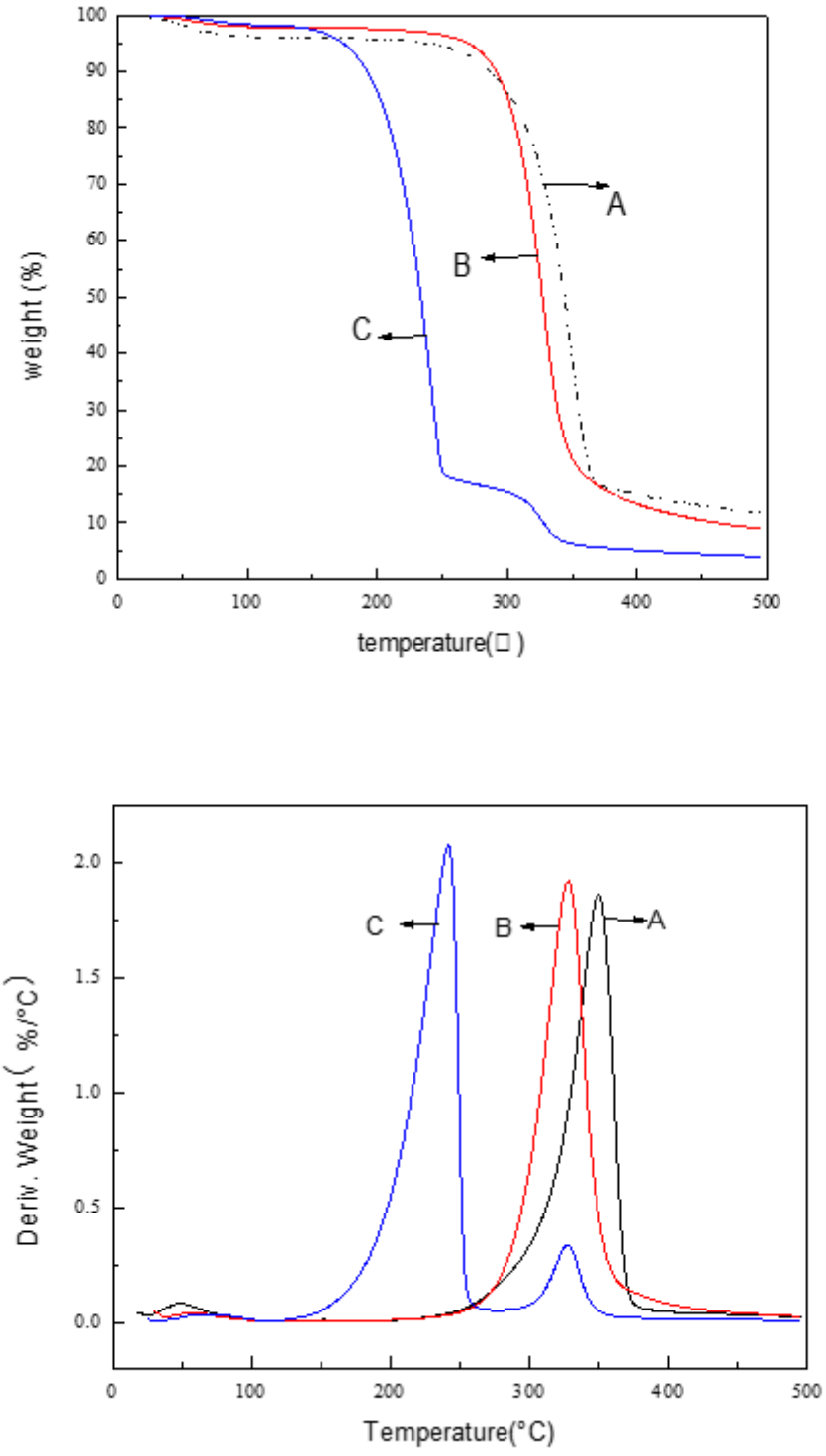

Figure 6

The TG and DTG of A (MCC standard sampl),B (Rubescens MCC) and C(MCC membrane)

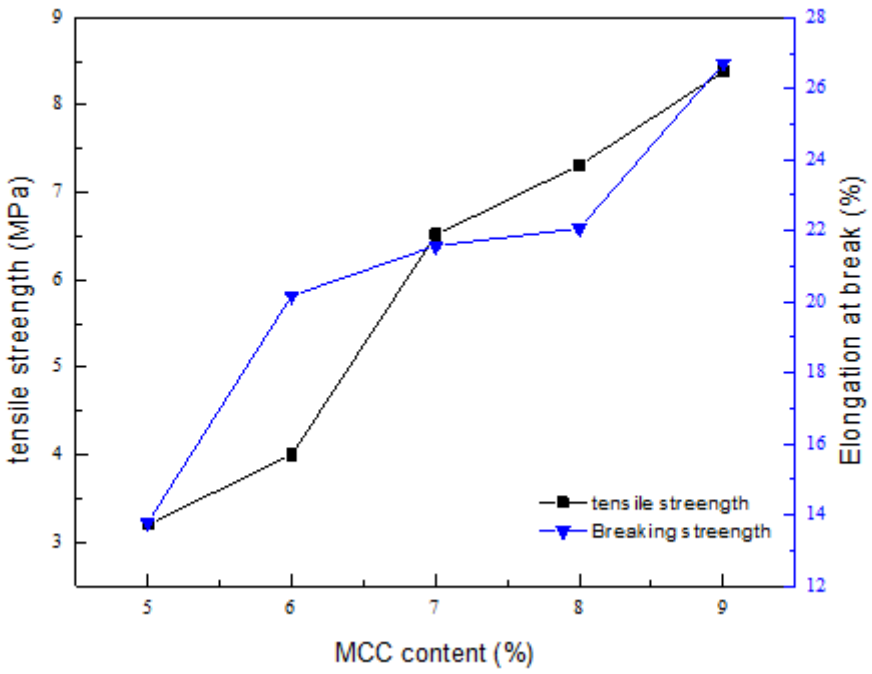

Figure 7

Effect of MCC content on mechanical properties of Membrane

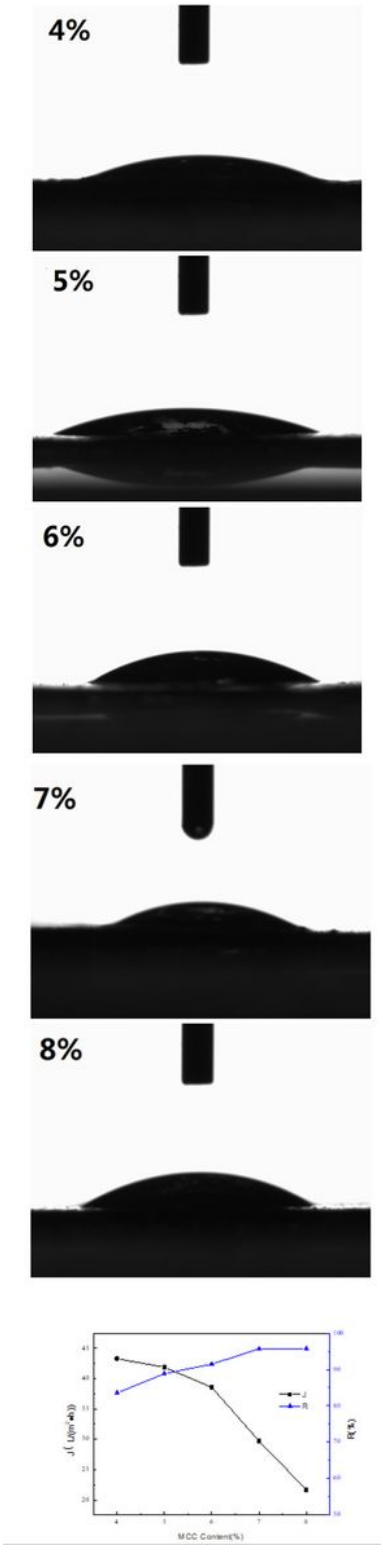

Figure 8

Effect of MCC content on the J and R value of MCC membrane

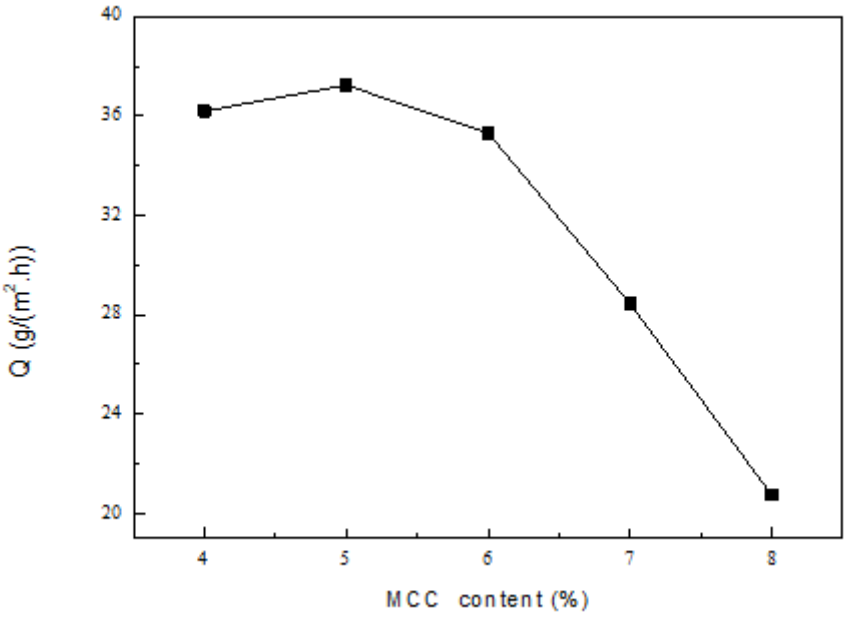

Figure 9

Effect of MCC content on the Q value of MCC membrane

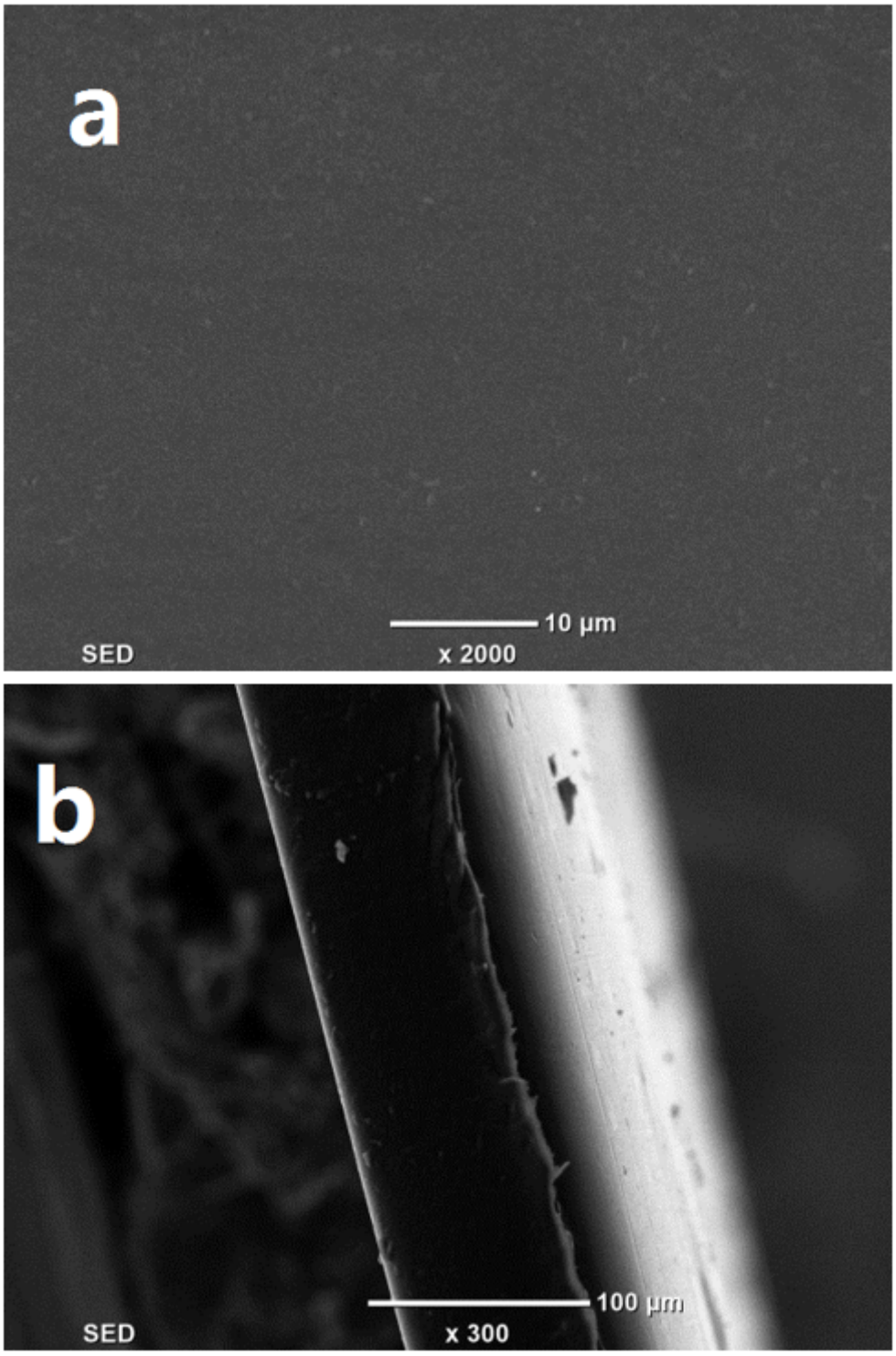

Figure 10

SEM of MCC membrane (5% of the floor plan(a) ; 5% cross section(b))