

Fabrication of cellulose membrane with “imprinted morphology” and low crystallinity from spherulitic [Bmim]Cl

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ABSTRACT: In the present study, regenerated cellulose membrane with “imprinted morphology” and low crystallinity was fabricated from the crystal cellulose/[Bmim]Cl solution. Spherulites of 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) and cellulose/[Bmim]Cl solution were observed using polarized optical microscopy under certain condition. The fabricated cellulose membranes presented some particular characteristics compared with the membrane prepared from traditional cellulose/[Bmim]Cl solution. All the fabricated membranes were characterized by optical microscope, Wide-angle X-ray diffraction (WAXD), thermo-gravimetric analysis, and mechanical testing. The images showed that the resulting membranes prepared from crystal cellulose/[Bmim]Cl solution were “imprinted” with patterns which originated from the crystalline structure of [Bmim]Cl. The results of WAXD showed that the obtained cellulose membrane exhibited low diffraction peaks and crystallinity of approximately 24.57%. Furthermore, the low crystallinity led to the low mechanical property (27.5 MPa), thermal stability (315.4 °C), and high moisture regain (9.5%). © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43798.

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INTRODUCTION

Cellulose is a very important renewable biopolymer, consisting of crystalline and amorphous regions. The proportion of the two regions has an important influence on the physical and chemical properties of cellulose materials.¹ The property of amorphous cellulose is totally different from its crystalline counterpart. Most reactants only penetrate into the amorphous region of cellulose, which is more susceptible to water.² This endows the amorphous cellulose with special properties, such as excellent hygroscopic power and solubility in 1N sodium hydroxide,^{3,4} which makes it significant to prepare this kind of cellulose. However, it is difficult to isolate amorphous cellulose from the native microfibrils. At present, amorphous cellulose has been prepared by ball-milling,⁵ regeneration with ethanol from their solution,⁶ or precipitation from nonaqueous solvent,⁷ where SO₂-diethylamine-dimethylsulfoxide and ionic liquid (IL) 1-ethyl-3-methylimidazolium were used as the solvent, respectively.

ILs is a kind of salt consisted of cation and anion, has been proposed as a powerful green solvent for dissolving cellulose,^{8,9} and the field has been highly developed in decades.^{10,11} From

the literatures, amorphous and partially crystallized cellulose has been prepared using imidazole ILs as solvent and water or ethanol as coagulant, and the formed crystalline cellulose mainly depended on the regeneration kinetics. There is no doubt that ILs provides a new way for preparing cellulose materials with special properties.¹² 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) with the melting point of 64 °C was the first confirmed IL for fabricating various cellulose materials.^{13–15} There are many researches concerning the properties of [Bmim]Cl and its solutions.^{16–18} For example, Huddleston *et al.* compared the physical properties of various imidazolium ILs and Xia *et al.* investigated the rheological behaviors of cellulose/[Bmim]Cl solution.^{19,20} However, few researches have been conducted on the crystallization of cellulose/[Bmim]Cl solution. In this work, the spherulitic structures of [Bmim]Cl and cellulose/[Bmim]Cl solution were observed under polarized optical microscope. Furthermore, the regenerated cellulose membrane with low crystallinity and “imprinted morphology” was fabricated using the spherulitic structures of [Bmim]Cl, their thermal stability, mechanical property, and moisture regain were investigated as well.

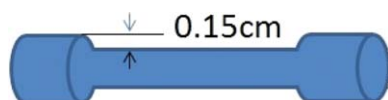


Figure 1. The schematic of scraper used for casting the solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EXPERIMENTAL

Materials and Reagents

Commercial microcrystalline cellulose (MCC) was purchased from Sinopharm Chemical Reagent. Its degree of polymerization (DP) in cupriethylenediamine hydroxide solution was 350 as determined by an Ubbelohde viscometer. The analytical grade N-methylimidazole, 1-chlorobutane and ethyl acetate were also purchased from Sinopharm Chemical Reagent. N-methylimidazole and 1-chlorobutane was distilled before use.

Synthesis and Purification of [Bmim]Cl

The IL [Bmim]Cl was synthesized according to the method described by Huddleston with slight modification.¹⁹ About 139.4 g N-methylimidazole and 165.1 g 1-chlorobutane with molar ratio of 1:1.05 were added to a round-bottomed flask fitted with reflux condenser. The mixture was stirred for 24 h at 90 °C until two phases were formed. The upper phase, containing unreacted raw reagents, was decanted and ethyl acetate was added and mixed thoroughly. The ethyl acetate was decanted followed by the addition of fresh ethyl acetate and this step was repeated twice. After the third decanting of ethyl acetate, the product was purified under rotary evaporator to remove the remaining ethyl acetate. The obtained product, [Bmim]Cl, was a viscous solution with amber color. ¹H NMR, FT-IR, ion chromatography, and AgNO₃ titration were used to determine its purity, it was above 99%.

Preparation of [Bmim]Cl Sample for Spherulite Observation

The prepared [Bmim]Cl was cast onto a glass slide which was covered to avoid absorbance of moisture in air. The thickness of the [Bmim]Cl solution is controlled by the gap of scraper, as shown in Figure 1. The sandwiched [Bmim]Cl sample was sealed with plastic wrap and refrigerated at -16 °C for 12 hours to form the crystal nucleus. Then, polarizing optical microscope (POM) was used to observe the crystal growth at room temperature.

Cellulose Membrane Fabrication

One g of MCC was added to 32.4 g [Bmim]Cl and dissolved at 80 °C to form a homogeneous 3 wt % cellulose/[Bmim]Cl solution. In the same way, the solution was cast onto a glass slide, and covered. The sample was also sealed and put in a -16 °C refrigerator until it was fully crystallized. The crystallized cellulose/[Bmim]Cl solution sample was immersed in water to

obtain the cellulose membrane, named as RCM-1. As comparison, the noncrystalline cellulose/[Bmim]Cl solution was directly immersed in water to obtain the regenerated cellulose membrane, named as RCM-2. The fabrication process of RCM-1 and RCM-2 is presented in Figure 2. Before vacuum drying, both RCM-1 and RCM-2 were washed thoroughly until no Cl⁻ was detected using AgNO₃.

Characterization

Crystallization of [Bmim]Cl was observed under Nikon 50I polarized optical microscope at room temperature and the photographs were captured at a certain time interval. The inverted microscope Nikon TI-S with phase-contrast (Nikon, Japan) was used to observe the crystallization of cellulose/[Bmim]Cl solution and morphology of RCM-1 and RCM-2.

Wide angle x-ray diffraction (WAXD) and Thermo Gravimetric Analyzer (TGA) were used to investigate the crystallinity and thermal stability of MCC, RCM-1, and RCM-2. WAXD of all samples were obtained from Rigaku D/Max-2550 (Rigaku, Japan) with Cu radiation operated at 40 kV and 200 mA, from 5° to 60° in steps of 0.02°. TGA of all samples were obtained from TG 209 F1 Iris (Netzsch Gertebau GmbH, Germany) under nitrogen atmosphere, from 50 °C to 600 °C at a heating rate of 10 °C/min.

Mechanical property was measured using a WDW3020 Materials Testing System (Changchun Kexin Instrument Co. Ltd, China) at room temperature with a crosshead speed of 5 mm/min, the samples were cut into strips of 40 mm × 5 mm, and ten strips were measure for each sample.

Moisture regains trials: a certain weight of MCC, RCM-1 and RCM-2 were dried at 105 °C for 1 h, and weighed on a Mettler XS105 balance. The weights were recorded at certain time interval until constant weight under equilibrium condition (25 °C and 65% relative humidity). The collected data was used for further calculations and analysis.

RESULTS AND DISCUSSION

It is well known that [Bmim]Cl is a powerful solvent for cellulose, its melting point is 64 °C determined by DSC. Although this value is different from the literature reports because of different measurement standard,^{19,21} there is no doubt that the [Bmim]Cl will be solidified in cooling process in theory. We observed the solidification process of [Bmim]Cl, and presented the formation of spherulite, as shown in Figure 3. It is obvious that [Bmim]Cl presents birefringence and Maltese cross, which are typical properties of spherulite. Spherulite is a common form of self-assembly during crystallization, particularly from

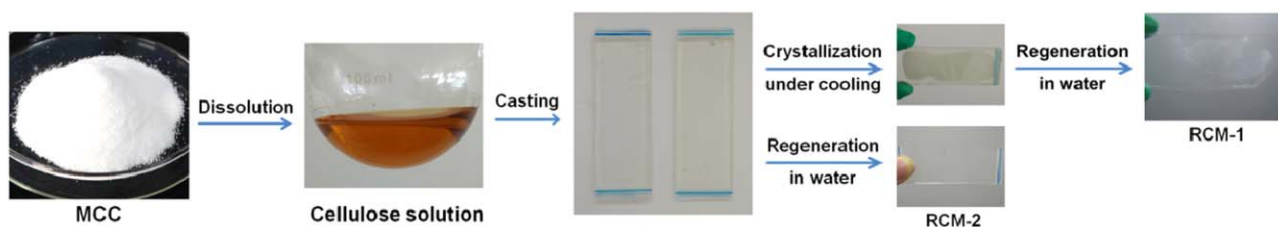


Figure 2. Fabrication process of RCM-1 and RCM-2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

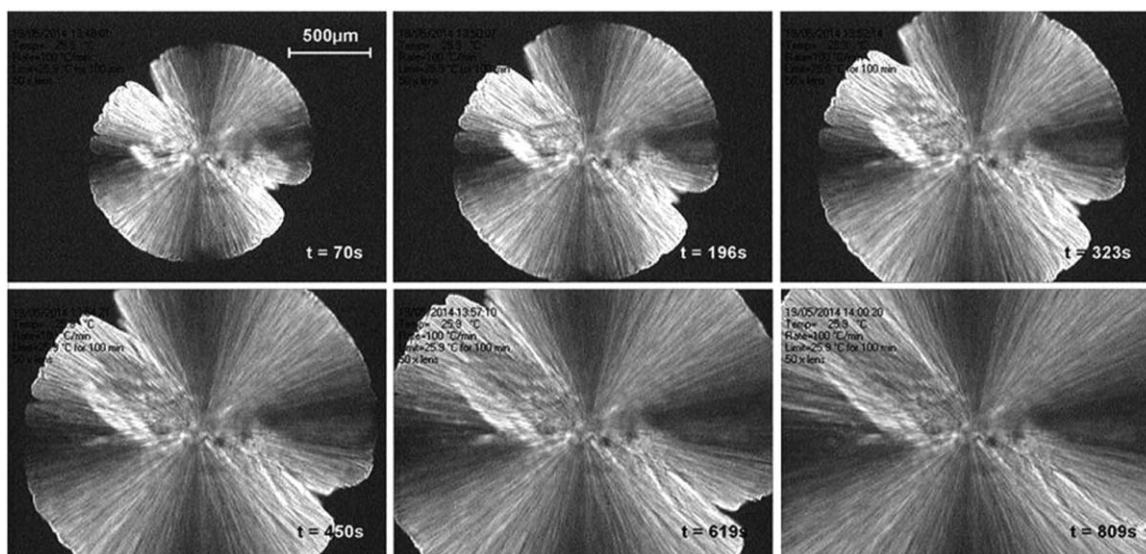


Figure 3. Crystallization process of [Bmim]Cl under polarized optical microscopy.

the melts of synthetic polymers. The growth rate of spherulitic [Bmim]Cl is closely associated with temperature.²² According to our previous experiences, the formation of crystal nucleus is easy under low temperature. Therefore, we put the [Bmim]Cl samples in refrigerator to form the crystal nucleus.

The spherulitic texture of [Bmim]Cl endowed the crystal cellulose/[Bmim]Cl solution and regenerated cellulose membrane with special properties. As shown in Figure 4, it can be seen that crystal

cellulose/[Bmim]Cl solution presents a regular arrangement on the surface of the solution. Furthermore, when the IL was removed during the regeneration process, it leaves the cellulose surface with an “imprinted morphology”, which originates from the crystalline structure of [Bmim]Cl, as shown in Figure 5. For comparison purposes, the optical micrograph of RCM-2 prepared from traditional cellulose/[Bmim]Cl solution was presented and did not show the “patterned morphology”. The whole process has been

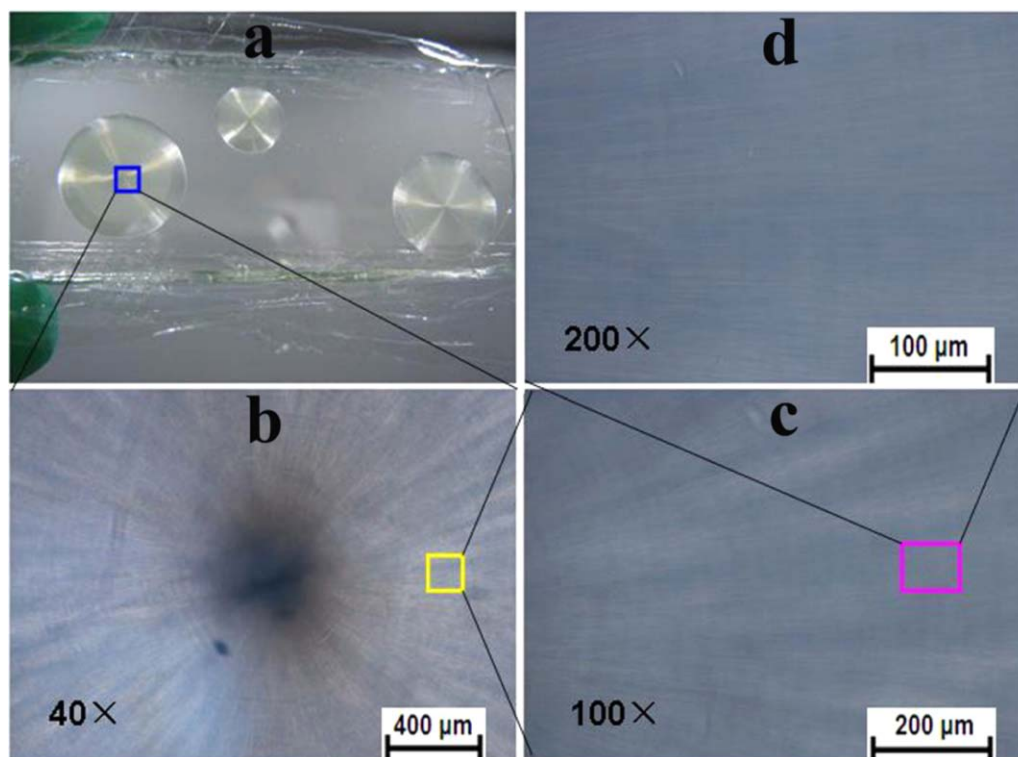


Figure 4. Optical micrograph of the crystallized cellulose/[Bmim]Cl solution under different magnification [Figure 4(a) was captured at the beginning of crystallization, a total homogeneous spherulitic structure was formed in the end]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

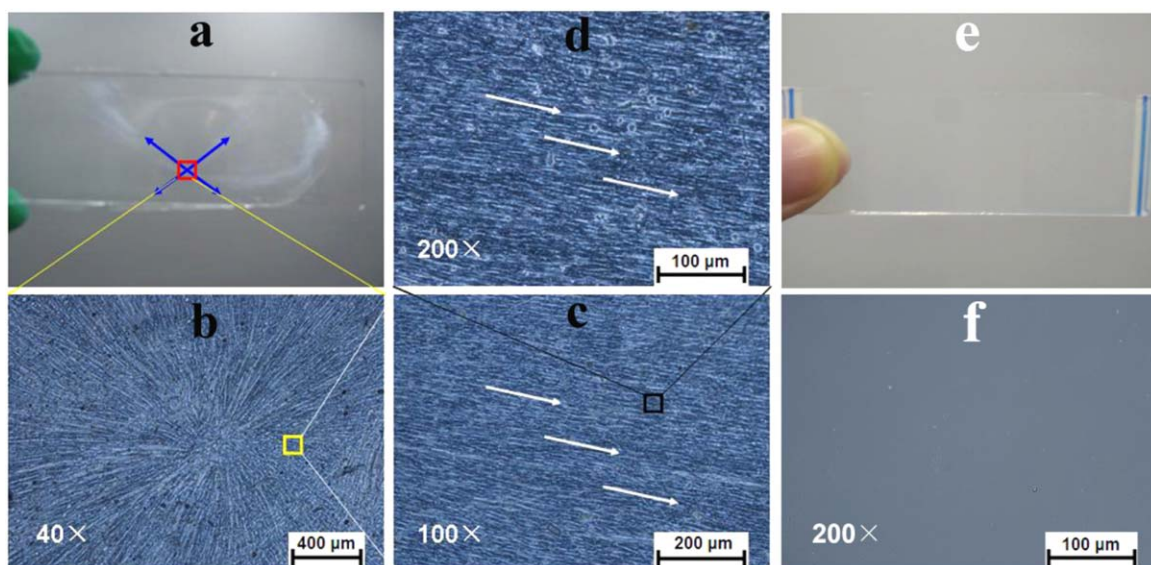


Figure 5. Optical micrograph of the RCM-1 (a,b,c,d) and RCM-2 (e,f) under different magnification. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

illustrated in Figure 6. [Bmim]Cl is a powerful solvent which completely dissolves the cellulose under 80 °C, the cellulose macromolecular chains are dispersed in the solvent and forms a viscose solution. As the solution temperature decreases, [Bmim]Cl begins to form the spherulites, that compels the cellulose macromolecular chains to arrange as the pattern of IL spherulites.^{7,23} When the IL was replaced by the nonsolvent in coagulation bath, the crystal cellulose/[Bmim]Cl solution was regenerated leaving the cellulose membrane a special texture as shown in Figure 5.

Biganska *et al.* prepared this kind of cellulose morphology using N-methylmorpholine-N-oxide (NMMO) as the solvent.²² And they claimed that the crystallization of cellulose/NMMO/water solutions was only because of the crystallization of the solvent, not the cellulose, which is totally different from the classical polymer solutions. Song *et al.* prepared four types of microcrystalline cellulose spherulites by the vapor precipitation procedure using 1-allyl-3-methylimidazolium chloride.²⁴ Here, we observed the spherulites of [Bmim]Cl and cellulose/[Bmim]Cl solution, and prepared the regenerated cellulose membrane with “imprinted morphology”. Both [Bmim]Cl and NMMO hydrates can be crystallized upon cooling, confirming that the crystallization of cellulose solution is driven by crystallization of the solvent, not the cellulose.

Based on the above experimental results, the properties of MCC, RCM-1, and RCM-2 were investigated. Their crystallinity, thermal stability, and moisture regain were characterized using WAXD, TGA, and gravimetric method, respectively. Figure 7(a) presents the WAXD profiles of the original MCC powder, and RCM-1 which was regenerated from crystal cellulose solution, RCM-2 was regenerated from the traditional cellulose solution. It can be seen that the WAXD curve of MCC powder exhibited three major peaks at 14.8°, 16.3°, and 22.6°, which are the characteristic peaks of cellulose I.^{25,26} However, the crystal structure and crystallinity of regenerated cellulose membranes changed significantly. The characteristic peaks of RCM-2 at 12.2°, 20.6°, and 22.3°, which are indexed as the cellulose II. For the RCM-1, a broad peak at about 20.8° was observed, and the peak at approximately 12° disappeared. All this confirmed that the crystal transformation from cellulose I to II occurred. The crystallinity of the three samples was compared as follows: 71.46%, 41.34%, and 24.57% for MCC, RCM-2, and RCM-1, respectively. The decreased crystallinity was because of the fact that the solvent [Bmim]Cl destroyed the crystal region during dissolution, and the destroyed crystal region could not be totally restituted during the regeneration process. Furthermore, the crystallinity of RCM-1 was lower than that of RCM-2. This is because of the regeneration process of liquid–solid exchange for RCM-1, but liquid–liquid exchange for

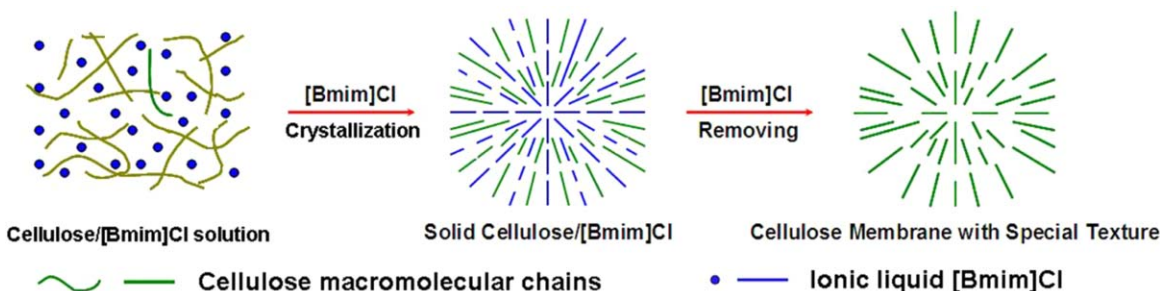


Figure 6. Schematic of formation of “imprinted morphology” in cellulose membrane solidified from [Bmim]Cl. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

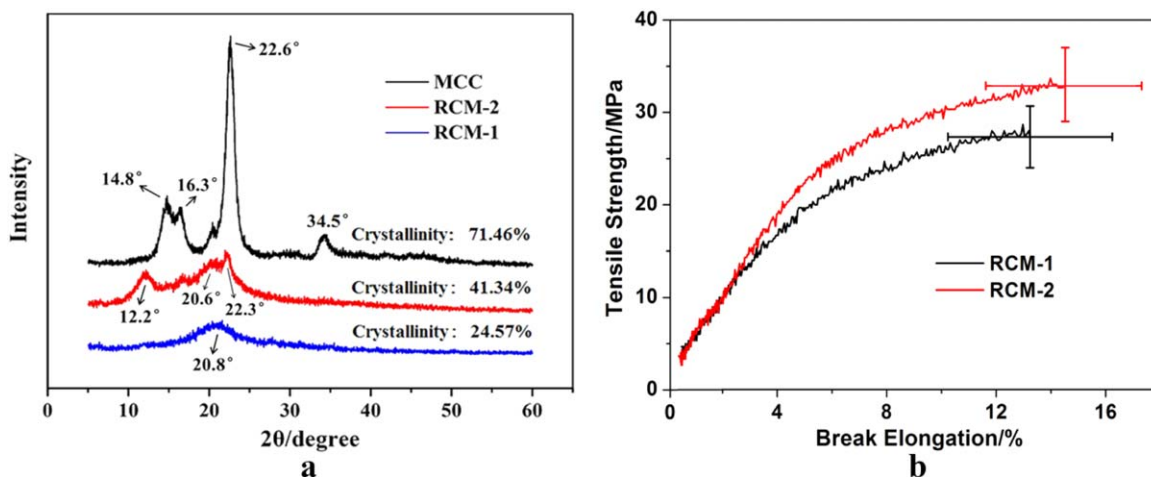


Figure 7. (a) WAXD profiles and crystallinity for the original MCC, RCM-1 and RCM-2, respectively; (b) mechanical property of the fabricated RCM-1 and RCM-2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RCM-2. Liquid–liquid exchange leaves space for cellulose macromolecular chains to be restituted. However, there was no space left for the liquid–solid exchange process. This led to the low crystallinity of RCM-1, which further demonstrates the crystallization of cellulose solution because of the crystallization of solvent, not the cellulose. Since the crystallinity of RCM-1 was low, its tensile strength was a little lower than that of RCM-2. Their strength is a significant difference while the breaking elongation is no obvious difference from the statistical results. Specifically, the strength of RCM-1 was 27.5 MPa with breaking elongation of 13.2%, and that of RCM-2 is 33.4 MPa with breaking elongation of 14.8%, as shown in Figure 7(b). Mechanical property of the cellulose membrane mainly depends on the degree of polymerization and crystallinity. Degree of polymerization is closely associated with the dissolving temperature and dissolving times, the cellulose was dissolved under the same conditions when RCM-1 and RCM-2 were fabricated. Therefore, the different strength of RCM-1 and RCM-2 is mainly ascribed to their different crystallinity.

Figure 8 shows the thermo-gravimetric results of MCC, RCM-1, and RCM-2, which was investigated by TGA from 30 °C to 600 °C at 10 °C/min. From the TGA profile, all the three curves

present weight loss before 130 °C, which is because of the evaporation of free water and bound water in the samples. The decreasing weight loss for the three samples are 1.8%, 7.0%, and 6.5% for MCC, RCM-1, and RCM-2, respectively, which is associated with their moisture regain. From the DTG profile, MCC began to decompose after 280 °C and had a faster decomposition rate of 349.5 °C. While RCM-1 and RCM-2 began to decompose after 220 °C and reached a faster decomposition rate of 315.4 °C and 329.5 °C, respectively. This indicates that the thermal stability of regenerated cellulose membrane was poor compare to that of the original MCC, which can be ascribed to the decreasing crystallinity during the dissolution and regeneration processes.

Moisture regains of the three samples were investigated by putting them under certain conditions (25 °C and 65% relative humidity). The percentage weight of water as a function of time was recorded, as shown in Figure 9. It can be seen that the three curves were similar and present a rapid initial moisture absorption followed by a leveling off. Specifically, moisture regain of RCM-1 (9.5 wt %) was higher than that of MCC (4.3 wt %), and moisture regain of RCM-2 (8.2 wt %) is between the two values. This tendency is opposite to that of crystallinity. It is well known that the equilibrium water

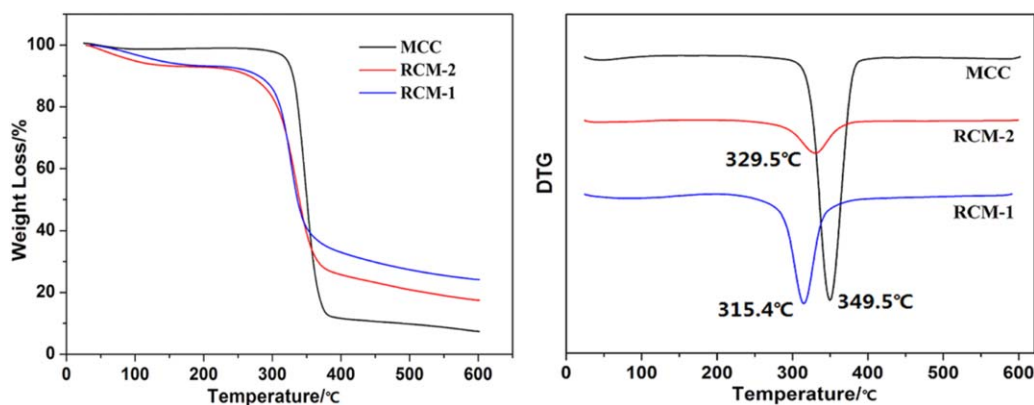


Figure 8. TGA and DTG profiles for the original MCC, RCM-1 and RCM-2, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

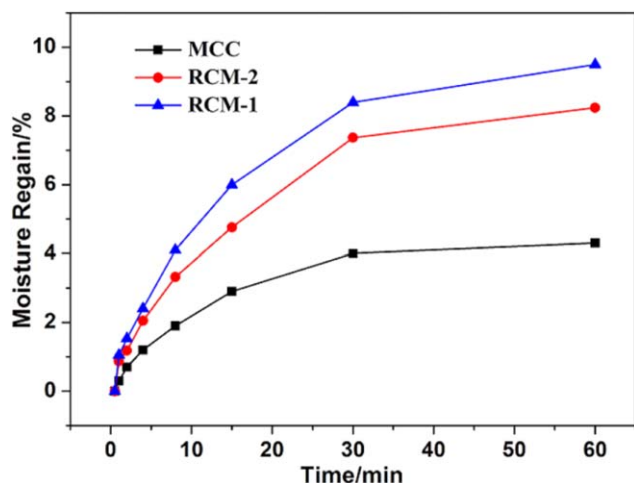


Figure 9. Moisture regain for the original MCC, RCM-1, and RCM-2 under equilibrium conditions at 25 °C and 65% relative humidity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

uptake of any materials involves sorption, diffusion, and permeation process,²⁷ and the three steps occur easily in the amorphous region than that in crystal region. Crystallinity of MCC was the highest among the three samples, therefore, its moisture regain is lowest. On the contrary, Crystallinity of RCM-1 was the lowest, but its moisture regain is the highest. RCM-1 possesses the lowest crystallinity, which gives it an excellent hygroscopic power.

CONCLUSIONS

The crystallization of [Bmim]Cl was observed under polarized optical microscopy, it presented a spherulitic structure. The cellulose membranes regenerated from crystal cellulose/[Bmim]Cl solution exhibited special “imprinted morphology” and some other characteristics compared to the membranes regenerated from traditional cellulose solution. Specifically, the crystallinity of resulting cellulose membranes decreased to 24.57%, which is lower than that of the usual cellulose membranes and the original MCC powder. The low crystallinity led to its low mechanical property (27.5 MPa), thermal stability (315.4 °C), and high moisture regain (9.5%). However, this provides a new method for preparing cellulose membrane with special morphology and properties.

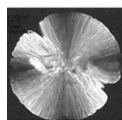
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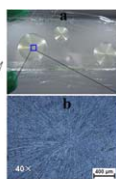
REFERENCES

- Isogai, A.; Atalla, R. H. *J. Polym. Sci. Part A: Polym. Chem.* **1991**, *29*, 113.
- Kontturi, E.; Suchy, M.; Penttila, P.; Jean, B.; Pirkkalainen, K.; Torkkeli, M.; Serimaa, R. *Biomacromolecules* **2011**, *12*, 770.
- Hermans, P. H.; Weidinger, A. *J. Am. Chem. Soc.* **1946**, *68*, 2547.
- Mazeau, K. *Carbohydr. Polym.* **2015**, *117*, 585.
- Shimura, R.; Nishioka, A.; Kano, I.; Koda, T.; Nishio, T. *Carbohydr. Polym.* **2014**, *102*, 645.
- Ciolacu, D.; Ciolacu, E.; Popa, V. I. *Cell Chem. Technol.* **2011**, *45*, 13.
- Sundberg, J.; Toriz, G.; Gatenholm, P. *Polymer* **2013**, *54*, 6555.
- Zakrzewska, M. E.; Bogel-Lukasik, E.; Bogel-Lukasik, R. *Energ. Fuel* **2010**, *24*, 737.
- Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. *J. Am. Chem. Soc.* **2002**, *124*, 4974.
- Wang, H.; Gurau, G.; Rogers, R. D. *Chem. Soc. Rev.* **2012**, *41*, 1519.
- Isik, M.; Sardon, H.; Mecerreyes, D. *Int. J. Mol. Sci.* **2014**, *15*, 11922.
- Bowlas, C. J.; Bruce, D. W.; Seddon, K. R. *Chem. Commun.* **1996**, *14*, 1625.
- Olsson, C.; Westman, G. *J. Appl. Polym. Sci.* **2013**, *127*, 4542.
- Stefanescu, C.; Daly, W. H.; Negulescu, I. I. *Carbohydr. Polym.* **2012**, *87*, 435.
- Turner, M. B.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. *Biomacromolecules* **2004**, *5*, 1379.
- Chen, X.; Zhang, Y. M.; Cheng, L. Y.; Wang, H. P. *J. Polym. Environ.* **2009**, *17*, 273.
- Siedlecka, E. M.; Czerwicka, M.; Stolte, S.; Stepnowski, P. *Curr. Org. Chem.* **2011**, *15*, 1974.
- Kamavaram, V.; Reddy, R. G. *Int. J. Therm. Sci.* **2008**, *47*, 773.
- Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. *Green Chem.* **2001**, *3*, 156.
- Xia, X.; Yao, Y.; Gong, M.; Wang, H.; Zhang, Y. *J. Polym. Res.* **2014**, *21*, 1.
- Heinze, T.; Schwikal, K.; Barthel, S. *Macromol. Biosci.* **2005**, *5*, 520.
- Biganska, O.; Navard, P.; Bédué, O. *Polymer* **2002**, *43*, 6139.
- Biganska, O.; Navard, P. *Cellulose* **2008**, *16*, 179.
- Song, H.; Niu, Y.; Yu, J.; Zhang, J.; Wang, Z.; He, J. *Soft Matter* **2013**, *9*, 3013.
- Gao, Q.; Shen, X.; Lu, X. *Carbohydr. Polym.* **2011**, *83*, 1253.
- Cai, T.; Zhang, H. H.; Guo, Q. H.; Shao, H. L.; Hu, X. C. *J. Appl. Polym. Sci.* **2010**, *115*, 1047.
- Mathew, A. P.; Laborie, M. P. G.; Oksman, K. *Biomacromolecules* **2009**, *10*, 1627.

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Spherulitic structure of [Brim]/Cl



40 μ m
Morphology of the fabricated cellulose membrane