Carbohydrate Polymers 88 (2012) 417–421

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Preparation and characterization of alkyl ketene dimer (AKD) modified cellulose composite membrane

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ARTICLE INFO

Article history:
Received 21 September 2011
Received in revised form 21 October 2011
Accepted 26 October 2011
Available online 1 December 2011

Keywords:
AKD
Cellulose
Lithium chloride/N,N-dimethylacetamide
Membrane

ABSTRACT

Cellulose was dissolved in 8 wt.% lithium chloride/N,N-dimethylacetamide. Under the homogeneous conditions, alkyl ketene dimer (AKD) was added to react with the dissolved cellulose. The mixed solvent was utilized to form composite membrane by phase transfer technique. The supermolecular structure, morphology, thermal and physical properties of the membrane were investigated by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TG), scanning electron microscope (SEM), wide-angle X-ray diffraction (WAXD), etc. The results showed that AKD reacted with cellulose under the homogeneous conditions. Moreover, the water absorption and water flux of composite membrane noticeably decreased compared with unmodified cellulose membrane.

1. Introduction

After the paper industry made a decisive change from acid papermaking to neutral papermaking, alkyl ketene dimer (AKD) was frequently used as a neutral sizing agent. AKD was widely used in the paper industry to increase the paper hydrophobicity and improve its printability. Superhydrophobic surfaces were prepared of AKD by casting the AKD melt in a specially designed mold (Garnier, Bertin, & Smrckova, 1999; Minami, Mayama, & Tsujii, 2008; Mohammadi, Wassink, & Amirfazli, 2004; Yoshimune, Yusuke, & Takako, 2010). Sizing mechanism of AKD considered that the lactone ring of AKD reacted with hydroxyl groups of the cellulose surface to generate β-keto esters. The β-keto esters fixed on the surface of the fiber gave the paper water resistance (Garnier & Wright, 1998; Neimo, 1999).

Cellulose is one of the most widely and abundantly available polysaccharides. The annual net yield of cellulose amounts to about several hundred billion tons (Kuo & Hong, 2005). Various polymeric materials are widely applied to the preparation of membranes, such as regenerated cellulose, cellulose acetate, polysulfone, polyacrylonitrile, nylon, polymethylmethacrylate, and ethylene–vinyl alcohol copolymer, among which the most popular material is regenerated cellulose. Now it has been used in dialysis (Makarand & Bhonde, 2001), ultrafiltration (Abe & Mochizuki, 2003; Zhang, Shao, & Shen, 2000), and other membrane areas.

Lithiumchloride/N,N-dimethylacetamide (LiCl/DMAc) is one of the most efficient solvent system for cellulose. Its dissolving capacity could reach 13 wt.% (Potthast, Rosenau, & Buchner, 2002). The mechanism of dissolution involves hydrogen bonding of the hydroxyl protons of cellulose with the chloride ion, which is in turn associated with the Li^+(DMAc) macrocation complex. The resulting charge–charge repulsions or a bulking effect would tend to allow further solvent penetration into the polymer structure (McCormick, Callais, & Hutchinson, 1985). LiCl/DMAc dissolves cellulose with high molecular weight (>10^6) molecularly at the ambient temperature without noticeable degradation. This feature makes the solvent system suitable for processing, characterization, or derivatization of cellulose. All cellulose composites were prepared by partly dissolving microcrystalline cellulose in an 8.0 wt.% LiCl/DMAc solution, then regenerating the dissolved portion (Benoit, Duchemin, Roger, & Mark, 2007; Daisuke, Daisuke, & Takayoshi, 2006; Daisuke Ishii, 2008; Omar, Guilherme, & Gabriela, 2000; Takayoshi, Daisuke, & Nobutake, 2001).

Ideal high-performance asymmetric membranes would combine the excellent fouling resistance of hydrophilic membranes with the high chemical resistance of hydrophobic membranes, which is best achieved through modifying the hydrophilic membranes to be rendered hydrophobic. In this study, cellulose was dissolved in 8 wt.% LiCl/DMAc. Under the homogeneous conditions, AKD was added to react with the dissolved cellulose. The mixed solvent has been utilized to form membrane by phase transfer technique. The asymmetric composite membranes had the water resistance comparing with the pure cellulose membrane. At the same time, the reaction between AKD and cellulose was also

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0144-8617/$ – see front matter © 2012 Published by Elsevier Ltd.
doi:10.1016/j.carbpol.2011.10.062

verified. To the best of our knowledge, no report related to the methods outlined here has been published.

2. Experimental

2.1. Chemicals and instruments

Commercial bleached kraft pulps prepared from hardwood were used as cellulose samples. The alkyl ketene dimer, lithiumchloride, N,N-dimethylacetamide, potassium permanganate and methylbenzene were commercially available and used without further purification.

Infrared (IR) spectra were recorded using a TENSOR27 FTIR spectrometer in the range of 4500–400 cm^{-1}. The phase transformation analysis of the samples was conducted by X-ray diffraction (XRD) using an X-ray diffractometer (*D*/max-2500/PC, Rigaku Co. Ltd., Tokyo) with CuKα radiation (40 kV, 60 mA) in the $2\theta = 5–60^{\circ}$ range. SEM images were taken on a JSM-6700F scanning microscope. The sample was coated with a thin layer of gold in a vacuum before examination. Thermogravimetric (TG) analysis and differential thermal analysis (DTA) of the samples were carried out on a Pyris Diamond TG/DTA analyzer (STA449C/3/F, German). The TG/DTA analyses were performed with a sample weight of 14.2 mg, a heating rate of 10 °C/min, and flowing nitrogen (20 mL/min).

2.2. Preparation of the casting solution

Cellulose was pretreated as follows: 5 g pulp was preswelled in 150 ml DMAc at 160 °C for 0.5 h. 15 mg potassium permanganate was added to the mixture as the active agent. Then the mixture was filtered to obtain the preswelled cellulose.

Stock solution of LiCl in DMAc (8%, w/w) was prepared by dissolving 7.4 g LiCl in 100 ml DMAc in a 250 ml Schott bottle. The bottle was immediately sealed to prevent moisture absorption. The mixture was stirred for 24 h until the salt appeared to be completely dissolved.

LiCl/DMAc solvent was added in three-necked flask equipped with a thermometer and magnetic stirrer under nitrogen atmosphere. When the mixture was heated to 100 °C, the preswelled cellulose was added. The mixture was stirred at 100 °C for 2 h to obtain the cellulose solution; the solution was placed under vacuum for 24 h at room temperature to the casting solution I.

5 g AKD was added in the above mentioned cellulose solution and stirred at 100°C for 2 h. Finally, the solution was placed under vacuum for 24 h at room temperature to the casting solution II.

2.3. Preparation of membrane

The membranes were prepared by the phase inversion technique. The casting solution 1 or 2 was cast on a glass plate using a doctor blade. The glass plate was quickly immersed in the gelation bath. Membrane sheets were subsequently stored in water for 24 h to remove the residual LiCl/DMAc completely to obtain the membrane. Then the composite membrane sheets were soaked in methylbenzene to remove the unreacted AKD.

2.4. Measurement of water absorption and water flux

The water absorption, *Q*, of the membranes was calculated by the following equation (Liang, Zhang, Li, & Xu, 2007; Xiao, Lu, & Jing, 2002):

$$Q = \frac{m_n - m}{m_0} \times 100\%$$

where m_n is the equilibrium weight of the swollen membrane which is obtained by soaking in water for 5 h and m_0 is the weight of the dried membrane. Three replicates were performed to obtain an average value of *Q*.

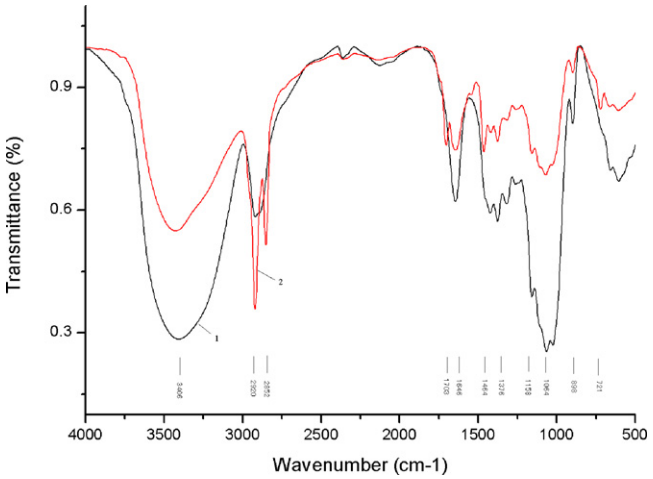

Fig. 1. The FTIR spectra of cellulose (1) and composite membranes (2).

The pure water flux, *F*, was measured under a pressure difference of 0.2 MPa at ambient temperature. The pure water flux was calculated by the following equation (Yu, Qiu, & Tian, 2010; Zhang, Shao, & Wu, 2001):

$$F = \frac{V}{At}$$

where *V* is the total volume of the water permeated during the experiment, *t* is the operation time, and *A* is the membrane area.

2.5. Measurement of mechanical properties

The tensile strength and elongation of the membranes were measured with an TTM testing instrument using a 500 N load cell, and the rate used in the test was 25 mm/min. Five replicates were performed to obtain an average value.

3. Results and discussion

3.1. FTIR analysis

Fig. 1 showed the FTIR spectra of cellulose membrane and composite membrane. As can be seen from the figure, the spectrum of cellulose membrane showed the O–H stretching vibration of hydroxy at 3406 cm^{-1} and the characteristic absorption peak of C–O at 1063 cm^{-1}. Moreover, the spectrum also showed the β-glycosidic bond characteristic absorption peak at 898 cm^{-1} and cellulose characteristic peaks at 2920 cm^{-1}, 1645 cm^{-1} and 1376 cm^{-1}. Different infrared spectrum was observed from the FTIR spectra of cellulose membrane and composite membrane. This indicated that the molecular structure of cellulose had changed. There was no absorption peak of lactone ring at 1840 cm^{-1}. This indicated that unreacted AKD was removed from the composite membrane completely. Characteristic absorption peak of β-ketone ester at 1703 cm^{-1} indicated that lactone ring reacted with hydroxyl groups on the surface of cellulose. The FTIR spectrum of composite membrane also showed the C–H stretching vibration of CH_2 at 2825 cm^{-1}, 1465 cm^{-1}, and absorption peak at 721 cm^{-1} indicated that the molecular structure of the composite membrane contains at least four CH_2. AKD contains two kinds of groups: one is long-chain alkyl that contains 12–20 carbon atoms which can give the AKD good hydrophobicity. Therefore, in the spectra of composite membrane, the occurrence of new peaks at 1703 cm^{-1} and 721 cm^{-1} was due to the reaction product of AKD and cellulose.

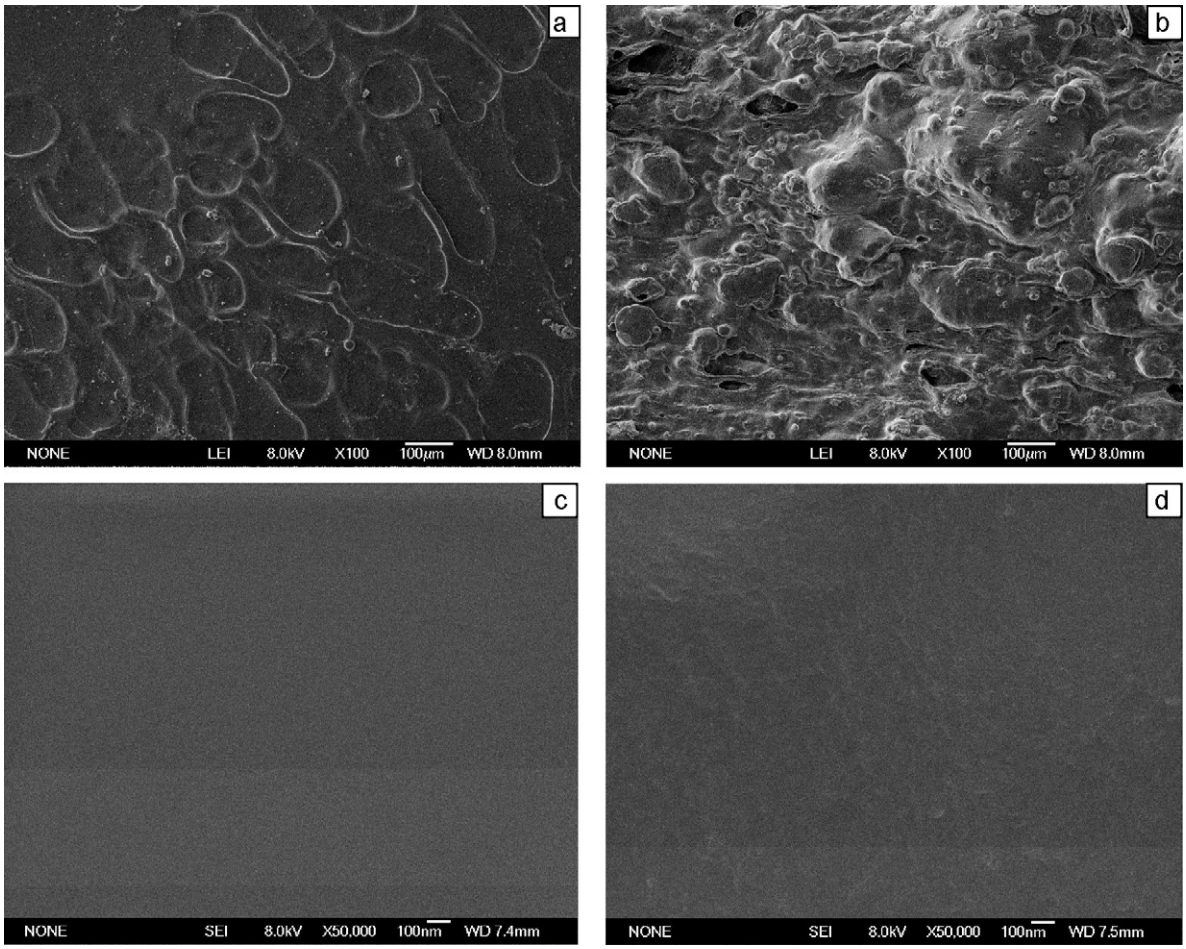

Fig. 2. The SEM images of cellulose membrane and composite membrane.

3.2. SEM analysis

The SEM images of the cellulose membrane and composite membrane are shown in Fig. 2. As can be seen from Fig. 2(a), surface of cellulose membrane has some circular deboss. The main reason of forming the deboss was that the solvent in the casting solution could exchange with the water in coagulation bath during film-forming process. From Fig. 2(b), it could be seen that there were plenty of granular substances. Because the solvent and the unreacted AKD have been removed completely, the granular substances were considered to be the reaction product, β-ketone esters, of cellulose and AKD. The β-ketone esters were also confirmed by FTIR analysis (Fig. 1). The magnified SEM images (Fig. 2(c) and (d)) showed a dense and smooth surface morphology. During the film-forming, the speed of the solidification process will affect the morphology of the membrane. Slow process of delamination and fast process of solidification will lead to dense surface morphology. Because water was used as the coagulation bath, solidification process must be faster than delamination process. Therefore, the membranes showed a dense structure.

3.3. The thermostability of membranes

The TG and DTA curves of membranes are shown in Fig. 3. As can be seen from the TG curves of cellulose, at the low temperature, 4.02 wt.% in weight loss was observed owing to slight dehydration. However, composite membrane did not have any weight loss. The pure cellulose membrane had a high hydrophillicity that could absorb moisture from the surrounding air. In the composite membrane, long chain hydrophobic alkyl of β-keto esters arranging outward resulted in the water resistance. Therefore, weight loss of cellulose membrane was observed at the low temperature. On further heating there was a sharp weight loss, and the decomposition occurred at 290 °C both for cellulose membrane and composite membrane, with about 63.25 wt.% and 67.54 wt.% of weight loss respectively. Thermopositive peaks of cellulose membrane and composite membrane occurred at 665.5 °C and 568 °C, respectively. This thermopositive peak was caused by some reactions with cellulose. Endothermic peak of composite membrane occurred at 710 °C due to decomposition or cracking reactions. This process was accompanied by a 3.35 wt.% in weight loss. Decomposition reaction of β-ketone esters at the higher temperature results in weight loss.

3.4. The X-ray diffraction analysis of membrane

The molecular structure of cellulose is a linear-chain polymer with a large number of hydroxyl groups. The degree of linearity enables the molecules to approach each other. These are responsible for the stiff and straight chain nature of the cellulose molecules as well as the cause of the considerable tendency of the chains to organize in parallel arrangements into crystallites and crystallite strands. As can be seen from Fig. 4, The X-ray diffraction patterns of cellulose membrane showed the characteristic crystalline peaks at $2\theta = 21.59^\circ$ and 23.50°. It was the cellulose I crystal, indicating the cellulose membrane recovered the cellulose I by recrystallization. However, the characteristic crystalline peaks at $2\theta = 21.59^\circ$ and 23.50° disappeared in composite membrane, which indicated

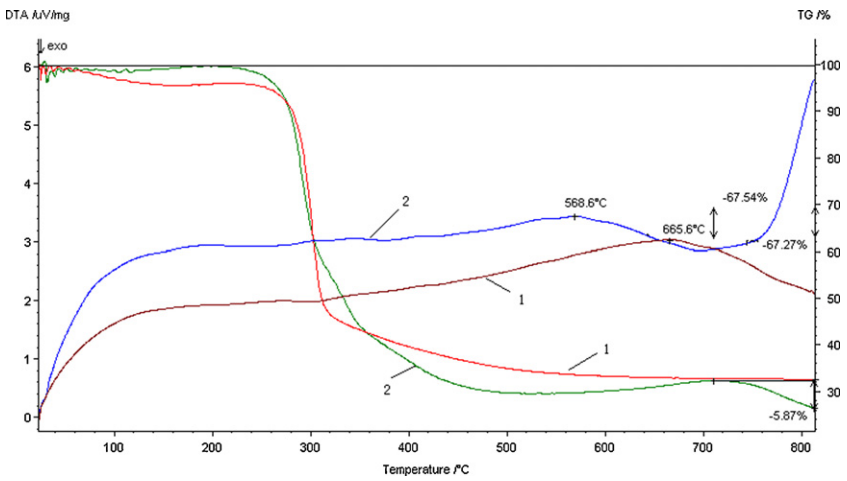

Fig. 3. The thermograms of cellulose membrane (1) and composite membrane (2).

that AKD reacted with cellulose. The reaction product destroyed the original crystalline structure of cellulose; therefore, cellulose molecules cannot reform highly regular arrangement of hydrogen bonds.

3.5. Water absorption and water flux of the membranes

Water absorption and water flux of cellulose membrane and composite membrane are shown in Table 1. As can be seen from the table, cellulose itself is a highly hydrophilic material, the membrane prepared by pure cellulose had higher water absorption and water flux, 124.87%, and 546 L/m^2 h, respectively. However, for the composite membrane, water absorption and water flux noticeably decreased compared with cellulose membrane. The reason was that AKD was added to the cellulose and reacted with cellulose in the homogeneous system. The accessibility and activity of cellulose in the homogeneous system was much higher than the heterogeneous conditions. Consequently, this reaction generated a large number of β-keto esters. The β-keto esters in the composite membrane helped create water resistance. So, water absorption and water flux of composite membrane decreased significantly.

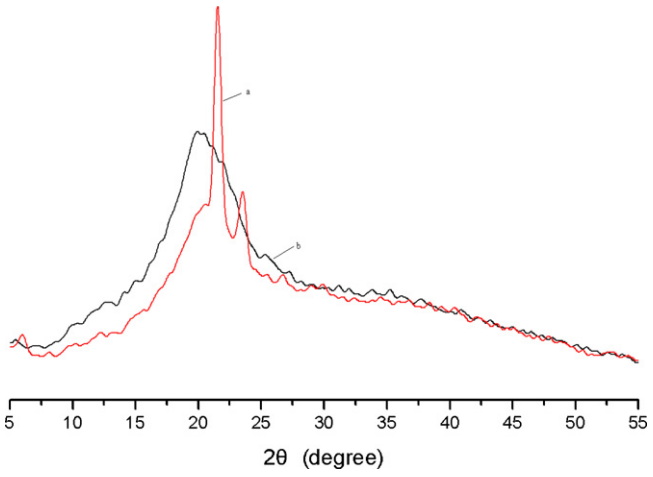

Fig. 4. The X-ray diffraction of cellulose membrane (a) and composite membrane (b).

Table 1
Water absorption and water flux of the membrane.

	Water absorption (%)	Water flux (L/m^2 h)
Cellulose membrane	124.87	546
Composite membrane	98.81	317

Table 2
Tensile strength and elongation of the membrane.

	Tensile strength (MPa)	Elongation (%)
Cellulose membrane	16.67	54.29
Composite membrane	4.67	22.86

3.6. Mechanical properties of the membranes

The tensile strength and elongation of cellulose membrane and composite membrane are shown in Table 2. As can be seen from the table, the cellulose membrane had higher tensile strength and elongation, 16.67 MPa, and 54.29%, respectively. But the composite membrane lower tensile strength and elongation. The reason was that the β-keto esters in the composite membrane destroyed parts of hydrogen bonds. So, the tensile strength and elongation of composite membrane were lower than cellulose membrane.

4. Conclusion

Under the homogeneous conditions, the hydrogen bonds between the cellulose molecular chains were destroyed. AKD could react with cellulose under these conditions. Based on this, the composite membrane modified by AKD was prepared by phase transfer technique. The β-keto esters could be detected in the composite membrane by FTIR, TG, SEM, WXRD, etc. Moreover, water absorption and water flux of composite membrane noticeably decreased comparing with cellulose membrane. The tensile strength and elongation of composite membrane were lower than cellulose membrane due to the destruction of hydrogen bonds.

Acknowledgements

The authors greatly appreciate financial support from China National Natural Science Foundation (Grant Nos.: 20976087 and 21176131).

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