Journal of Membrane Science 315 (2008) 141–146

Contents lists available at ScienceDirect

Journal of Membrane Science

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

New applications of kenaf (*Hibiscus cannabinus* L.) as microfiltration membranes

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ARTICLE INFO

Article history:
Received 28 September 2007
Received in revised form 11 February 2008
Accepted 13 February 2008
Available online 19 February 2008

Keywords:
Kenaf
Hibiscus cannabinus L.
Cellulose acetate
Microfiltration membrane

ABSTRACT

An attempt to explore the possibility of kenaf (*Hibiscus cannabinus* L.) as microfiltration membrane has been carried out in this work. The pulp was acetylated by anhydride acetic acid to produce cellulose acetate with an acetyl content of 40.40%. Membranes were prepared by phase inversion method using polymer concentrations varied between 14% and 18% (w/w). It was found that membrane composed of 14% (w/w) cellulose acetate, 27% (w/w) formamide and 59% (w/w) acetone showed a water flux of 122.29 L/m^2 h under an applied pressure of 1 kgf/cm^2, while the rejection towards dextran T-2000 solution was 96.17%. Due to its lower crystallinity index and molecular weight, the acetylated kenaf membrane shows a more porous structure than the one prepared from a commercial cellulose acetate. On the other hand, the Young modulus of acetylated kenaf membrane is higher than the one of commercial cellulose acetate. It is concluded that kenaf as a non-wood plant can be used as alternative raw materials for preparing cellulose acetate microfiltration membranes.

1. Introduction

Membrane technology has been developed for several decades after Loeb and Sourirajan discovered the asymmetric membrane preparation for sea water demineralization using cellulose acetate membranes [1]. Until present, cellulose acetate membranes are still made from hardwood. In order to find alternative materials from non-wood plants, this research has been conducted. Compared with hard woods with equivalent cellulose content, non-woods are generally lower in lignin, but higher in silica and ash [2]. So, less chemicals are used in the cooking and bleaching processes. Moreover, in terms of growth rate, non-wood plants take only a few months to reach their full growth while hard wood trees take years.

The renewable and sustainable non-wood materials considered in this work is kenaf (*Hibiscus cannabinus* L.). Kenaf is used for soft fiber, ropes, textiles, paper and automobile industry [3–6]. The American Kenaf Society as well as Japan Kenaf Society reported various new applications of kenaf. This plant is adapted to a wide range of soils and climatic conditions. It grows at temperatures ranging from 15 to 25 °C and can be harvested in 3–4 months from seed.

According to Basta et al., membranes prepared from non-wood fibrous materials are still limited [7]. The exploration of non-woods as basic materials should be done in order to find suitable materials for specific membrane applications. So far, no research on the use of kenaf as basic material for synthetic membranes has been published. Therefore, the objective of this work is to study the possibility of using kenaf (*H. cannabinus* L.) as the basic material for preparing cellulose acetate membranes used in microfiltration processes.

2. Experimental

2.1. Materials

Acetic anhydride 98%, acetone, formamide, glacial acetic acid, hydrochloric acid, sodium hydroxide and concentrated sulfuric acid were obtained from Merck, while dextran T-10, T-40, T-70, T-500 and T-2000 were from Sigma. The numbers in the dextran's code indicate their number–average molecular weight in kg mol^{-1}. Kenaf was taken from an agricultural experimental station and the pulp was supplied by the Center for Pulp and Paper. Kenaf chips were cooked at 165 °C with a soda-anthraquinone process and bleached with five-stage elemental chlorine free (ECF) bleaching process using oxygen at 95 °C, chlordioxide at 60 °C, extraction and two steps of dioxide at 75 °C. The resulting pulp contained 64.46% alpha-cellulose and 1.22% hemicellulose. The commercial grade cellulose acetate with 40.11% acetyl content was procured from Brataco Ltd., a local trading company. All chemicals were used without further purification.

2.2. Preparation of acetylated kenaf

In this experiment, the activation stage was carried out by mixing and stirring 10 g of bleached kenaf pulp and 24 mL of glacial

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doi:10.1016/j.memsci.2008.02.012

Table 1
Variation of dope composition

Cellulose acetate (wt.%)	Acetone (wt.%)	Formamide (wt.%)
14	59	27
16	57	27
18	55	27

acetic acid at 40 °C for 60 min. Then 40 mL of glacial acetic acid and 0.09 mL of concentrated sulfuric acid as catalyst were added and stirred again for 45 min at the same temperature. The mixture was then cooled until its temperature reached 18 °C and 27 mL of acetic anhydride 98% was added. Another mixture containing 40 mL of glacial acetic acid and 0.6 mL of concentrated sulfuric acid was added into the first mixture and stirred at 40 °C for 20 h. This acetylation stage was then followed by the hydrolysis stage. A solution of 30 mL of acetic acid 67% was added drop by drop within 2 h at 38 °C. The hydrolysis reaction was allowed to continue for 20 h. The product was poured into water with strong agitation and the precipitate was washed with water until the pH became neutral and finally dried at 50 °C.

2.3. Characterization of cellulose acetate

The acetyl content of the synthesized cellulose acetate was determined by volumetric method using sodium hydroxide and hydrochloric acid solutions described previously [8]. The viscosity–average molecular weight (M_v) of cellulose acetate was determined in acetone as solvent by viscometry method using the Mark–Houwink–Sakurada equation:

$$[\eta] = KM_v^a$$

with $K = 1.33 \times 10^{-3}$ and $a = 0.616$ [9].

The functional groups of the obtained cellulose acetate were analyzed by Fourier Transformed Infra Red (FTIR) spectroscopy using PerkinElmer Fourier Transformed Infra Red spectrophotometer. The crystallinity index and the mean hydrogen bond strength (MHBS) have been calculated according to the method described by O'Connor et al. [10]. So, the crystallinity index was calculated from the ratio of the absorbance of the band maximum at about 1430 cm^{-1} to the absorbance of the maximum about 900 cm^{-1}. Meanwhile, the MHBS was calculated from the ratio of the absorbance of O—H stretching at about 3390 cm^{-1} to the absorbance of C—H stretching at about 2940 cm^{-1}. The diffraction pattern was observed by a Jeol diffractometer using a reflection method with a Cu Kα line.

As comparison, similar characterizations were also carried out for purchased cellulose acetate, called afterwards as commercial cellulose acetate.

2.4. Preparation of cellulose acetate membranes

Based on our previous results, casting solutions composed of cellulose acetate, acetone and formamide were used in this work [11]. The compositions of the mixtures are varied according to Table 1. Each mixture was stirred for 24 h at room temperature until it became a homogeneous dope solution. The dope was allowed to stand for several hours in air tight condition to get rid of air bubbles, then cast on a glass plate and after a partial evaporation for 10 s in the atmospheric condition, the glass plate was gently immersed into cold water at 4 °C. The membrane was gradually formed and, after a complete precipitation, washed with deionized water for several hours until all the solvent and additive have been removed.

Casting and gelation conditions were kept constant through all membrane preparations since thermodynamic conditions would largely affect the morphology and performance of the resulting membranes [12,13]. The thickness of the produced membranes were about 0.22 ± 0.02 mm and kept constant for all formulations. The membranes were subsequently stored in 1 ppm sodium azide solution to prevent microbial growth.

2.5. Characterization of acetylated kenaf membrane

The flux and rejection of the produced membranes were measured in a dead-end test cell under a constant applied pressure ranging from 1 to 3 kgf/cm^2. The method of these measurements has been described previously [14]. In order to obtain the molecular weight cut-off (MWCO), the rejection of each dextran was plotted against the logarithm of corresponding dextran's molecular weight. The MWCO value is determined as the molecular weight at which the rejection is 95%. Membrane cross-sections were observed by scanning electron microscope Jeol JSM-6360LA using gold as the coating agent. The mechanical properties of the obtained membranes were measured by using Autograph Shimadzu AGS-500D.

3. Results and discussion

3.1. Characterization of acetylated kenaf pulp

The FTIR spectrum of both commercial cellulose acetate and acetylated product of kenaf pulp in Fig. 1(A) and (B), respectively, show qualitatively the existence of characteristic carbonyl peaks at 1752 and 1237 cm^{-1}. So, as the spectra of the original kenaf in Fig. 1(C) has no peaks at those regions, it shows that acetyl groups appeared after acetylation. This result is also confirmed by the acetyl content of acetylated kenaf which is 40.40%, while the commercial cellulose acetate has 40.11%. According to Baker, this value refers to cellulose diacetate with acetyl contents ranging from 35% to 43.5% [15]. It can be concluded that the acetylation condition of kenaf pulp is suitable for obtaining cellulose diacetate.

It is known that cellulose is a very crystalline substance due to its linear structure and multiple intermolecular hydrogen bonds [16]. During the acetylation process, the swelling agent diffuses

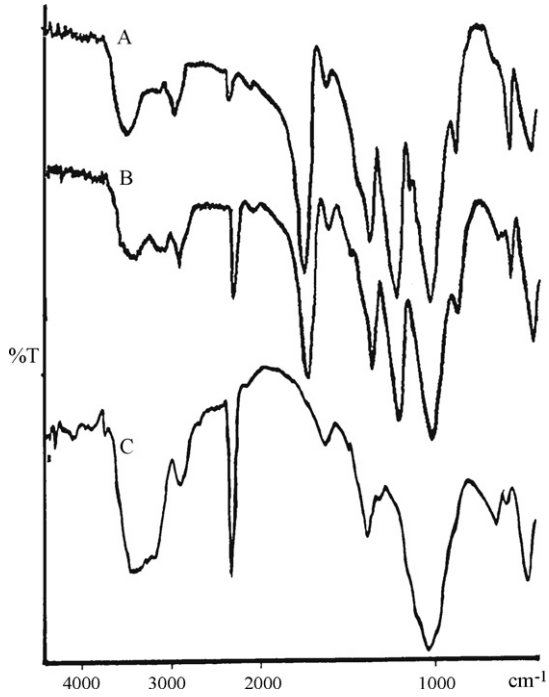

Fig. 1. FTIR spectrum of: (A) commercial cellulose acetate, (B) acetylated kenaf and (C) kenaf pulp.