PREPARATION OF CELLULOSE HYDROGEL FILMS FROM SUGAR CANE BAGASSE

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Abstract

Several million dry tons of sugar cane bagasses are annually produced throughout the world. Bagasse is a waste product mainly deriving from sugar cane production. Thus, sugar cane bagasse is a big problem of their production. As a result, convertion of bagasse to valuable products like cellulose hydrogel films is important issues to be concerned. In the present work, sugar cane bagasse was used as a cellulose resource which was chemically treated using sulphuric acid (H_2SO_4) and sodium hydroxide (NaOH).When this pretreated sample was bleached by sodium hypochlorite (NaOCl), treated bagasse cellulose fiber was obtained. FTIR, SEM and XRD measurements were used to characterize the properties of raw and treated fiber samples. Following this, solvent exchange processes were performed by use of water, ethanol and Dimethylacetamide (DMAc) respectively. Using (DMAc/LiCl) system was possible to obtain cellulose hydrogel solution and cellulose hydrogel film was prepared by phase inverse method without cross linker. The resultant hydrogel film was found to be transparent and flexible.

Keywords: cellulose hydrogel film, sugar cane bagasse, cellulose, phase inverse method

Introduction

In recent years, there has been an increase in the level of research on the development of new biodegradable materials for use in packaging, agriculture, medicine and other areas. Generally, biodegradable polymer materials are increasingly important as environmental contamination and waste disposal problems associated with plastics and related products from synthetic polymers become more severe. Natural polymers have various advantages over synthetic polymers due to their low-cost, great availability and biodegradability (Zhou, *et al.,* 2008).

Cellulose hydrogel has become especially attractive to "tissuse engineering" as matrices for repairing and regenerating a wide variety of tissue and organs. Hydrogels consisted of hydrophilic polymer networks

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which can absorb from 10-20 % up to thousands of times of their dry weight in water. Various hydrogels from natural polymers were fabricated by using hyaluronate, chitosan and its derivatives, and cellulose in which there is a potential application in the biomaterials field. Among them, cellulose is the most abundant renewable resource on earth and may become a main chemical resource in the future. Therefore, this sustainable material in plants has numerous functional possibilities and can be expected with the demand for environmentally and biocompatible products (Svensson *et al.,* 2005). A wide range of lingocellulosic agricultural by-products has successfully been converted into cellulose hydrogel film including agave tequilana Weber bagasse (Karla Lizette Tovar Carrillo *et al*., 2013), sugar cane bagasse (Kazuki Nakasone *et al*., 2016).

Sugarcane bagasse (SB), as the fibrous by-product remaining after sugar extraction from sugarcane, is one of the most important byproducts. About 54 million dry tons of SB are produced annually throughout the world (Ren *et al.,* 2006). Bagasses offer the advantages of being a cheap, plentiful and low polluting fuel (Mothe and Miranda, 2009). Commonly, all plant biomass consists of cellulose, hemicellulose, lignin, pectin and protein. Most of the plant biomass consists of about 33 % of cellulose as the major component of the rigid cell walls. Table 1. shows the percentage composition of sugarcane bagasse.

Table 1: Percentage Composition of Sugarcane Bagasse

Component	**%Composition***
Cellulose	43.6
Hemicellulose	33.5
Lignin	18.1
Ash	2.3
Wax	0.8
Other	0.7

Sun *et al.,* 2004

Cellulose is a linear and high molecular weight polymer as well as natural, renewable and biodegradable material (Rachtanapun, 2009). Cellulose is aligned parallel to each other in fibrils, which are surrounded by a matrix of lignin and hemicellulose (Figure 1). In addition, cellulose has properties such as low density, good mechanical properties as well as biodegradability. Cellulose, the major chemical component of fiber wall and contributing 40-45% of the dry weight. It is composed of linear chain of D-glucose linked by β-1,4-glycosidic bond with the degree of polymerization (DP) from 10,000 in native wood to 1,000 in bleached kraft pulps. Each D-anhydroglucopyranose unit possesses hydroxyl groups at C2, C3, and C6 positions, capable of undergoing the typical reactions known for primary and secondary alcohols. The molecular structure imparts cellulose with its characteristic properties: hydrophylicity, chirality, degradability, and broad chemical variability initiated by the high donor reactivity of hydroxyl groups.

Cellulose has a strong tendency to form intra - and inter-molecular hydrogen bonds by the hydroxyl groups on these linear cellulose chains, which stiffen the straight chain and promote aggregation into a crystalline structure and give cellulose a multitude of partially crystalline fiber structures and morphologies. Crystalline cellulose has very limited accessibility to water and chemicals (Edgar *et al.,* 2001).

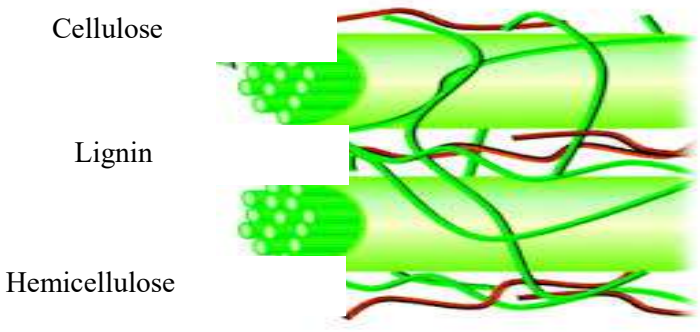


Figure 1: Components of primary cell wall

It is well known that native cellulose is very difficult to dissolve in common solvents. This is due to formation of strong hydrogen bond between abundant hydroxyl groups in the polymer chains. In addition, crystalline and

aggregated fibers of the cellulose also make it difficult in the solubilization. For this reason, studies on native cellulose hydrogel are fewer than cellulose derivatives. Therefore, solvents such as alkali-based aqueous system, N-methylmorpholine-N-oxide (NMMO), lithium chloride (LiCl)/ N, N-dimethylacetamide (DMAc) and ionic liquids (ILS) were developed for cellulose dissolutions. These solvent system provides great opportunities to prepare native cellulose hydrogel through physical cross-linking (Striegel, 1997).

For cellulose hydrogel films preparation has been reported by which a DMAc/LiCl system enables flexible cellulose hydrogel films using phase inversion processes. Hydrogels are networks of hydrophilic polymer chains in natural or synthetic polymers. They are highly water absorbent without being soluble in water. Here, the phase inversion process involves transformation from a liquid phase polymer solution to a solid state of the polymer (Kazuki and Kobayashi, 2016). In the present study, sugar cane bagasse was used to obtain cellulose hydrogel solution and the hydrogel film.

Materials and Methods

Collection of Sugar Cane Bagasse

Sugar cane bagasse was collected from Nawaday Sugar Mill, Pyay Township, Bago Region.

Bagasse Treatment

The bagasse was firstly washed with distilled water to remove remaining sugar components and then heated in oven at 50˚C. For acid treatment, 10 g of bagasse was added into 300 mL of 4 vol% H_2SO_4 aqueous solution and stirred for 2 h at 90 ˚C. Then, sample was washed with abundant distilled water five times to eliminate residues of the H_2SO_4 solution. And then 300 mL of 10 wt% NaOH solution was added and kept under stirring for 12 h at 90 ˚C until a black liquor solution was obtained. The residues of fiber were washed with excess distilled water until neutral pH. After that the fiber was added into 300 mL of 10 vol% NaOCl solution and stirred for 3 h at 40˚C. NaOCl was used as bleaching agent to obtain light colored fiber for

preparation of cellulose solution. Figure 2 shows sugar cane bagasse raw sample, acid treated sample, base treated sample and cellulose fiber. The obtained cellulose fiber was used for preparation of cellulose solution in DMAc/LiCl system.

(a) (b) (c) (d)

Figure 2: (a) Sugar cane bagasse raw sample (b) acid treated sample (c) base treated sample and (d) cellulose fiber

Preparation of Cellulose Solution

The treated bagasse cellulose fiber (1 g) was stirred in 300 mL of distilled water at room temperature for 24 h to swell the fiber. After the swelling fiber was filtered by an adapter glass filter under vacuum, ethanol (300 mL) was added to the swelled fiber and the mixture was stirred for 24 h at room temperature. Ethanol was removed and the swelled fiber was added to 300 mL of DMAc. The mixture was then left overnight under stirred condition. Both dried LiCl and DMAc were added to the swelled bagasse fiber to dissolve the cellulose fiber and stirred at room temperature for 3 days. About 1 wt% cellulose in DMAc/LiCl containing 8 wt% LiCl was obtained.

Preparation of Cellulose Hydrogel Films

For preparation of cellulose hydrogel films, 10 g of cellulose solution was poured into glass dish (9.1 cm diameter), and kept for 24 h in a plastic container filled with ethanol. In this step, cellulose was gradually progressed in the vapor at room temperature. Finally, the cellulose hydrogel film was obtained by the phase inversion process from liquid to solid gel. The resultant transparent film as shown in Figure 3 was washed with excess distilled water and then placed in distilled water for 24 h to remove DMAc. The obtained

hydrogel films were kept in plastic container filled with distilled water until further experiments.

Figure 3: Transparent cellulose hydrogel film from sugar cane cellulose fiber

Characterization

The formation of prepared samples was monitored by FTIR, SEM and XRD. The structural changes of samples were analyzed by FTIR spectrometer (FTIR – 8400 SHIMADZU, Japan). FTIR analysis was in a range of wave number from 4000 to 400 cm^{-1}. Surface morphology of the samples was investigated by SEM (JSM-5610 LV Scanning Microscope, JEOL, Japan). X-ray diffraction pattern of the sample was recorded on X-ray diffractometer (Rigaku, Tokyo, Japan), using CuK_{α} radiation (λ= 1.54 Å) at 40 kV and 40 mA. The diffraction angle ranged from 10˚ to 70˚ of 2θ.

Results and Discussion

Figure 4 shows FTIR spectra of the sugarcane bagasse, treated fibers and cellulose fibers at different treatment conditions. The FTIR spectra of all sample show the strong broad band around 3400 cm^{-1}which is due to the O-H stretching vibration. The strong band at around 2900 cm^{-1} which is due to C-H stretching vibration referred to CH_2 group. The absorption band at around 1730 cm^{-1} indicates the C=O stretching in carbonyl group of pyrone. Appearance of the band around 1600 cm^{-1} is a relative pure ring stretching mode strongly associated with the aromatic ring C=C in benzene as well as in pyrone ring. From the comparison of the FTIR spectra, the appeared peaks around 1510 cm^{-1} showed the presence of lignin and lignocellulose in the initial raw sample. Moreover, the band around 1200 cm^{-1} disappeared in

treated fiber which is assigned the removal of hemicelluloses. This clearly indicated that the amount of lignin from the sugar cane bagasse raw sample was successfully reduced by the chemical and temperature treatments.

SEM microphotographs of treated samples indicated the clearly appearance surface morphologies of the samples. Figure 5(a) is SEM micrograph of sugar cane bagasse sample which shows the major constituents of natural fibers such as cellulose, hemicelluloses and lignin. The SEM images of treated samples in Figures 5(b) and (c) have been changed in their morphologies due to the removal of lignin and hemicelluloses. Finally Figure 5(d) can be seen that the main structural unit of cellulose in the plant wall consists of cellulose microfibrils bonded together in a polymeric matrix.

XRD measurement was carried out to evaluate the effect of treatment condition on the crystalline structure of bagasse, treated fibers and cellulose fibers. Figure 6 shows the XRD patterns of the bagasse and the purified fibers. The patterns of (a) – (d) exhibited typical crystalline lattice of cellulose with peaks at 22.3˚ and 16.4˚. The crystalinity indexes of sugar cane bagasse raw sample, acid treated sample, base treated sample and cellulose fiber were 44.1%, 58.8%, 59.1% and 60.2% respectively. The increment of crystalinity in cellulose fiber was due to the removal of hemicelluloses and lignin by NaOH and NaOCl treatment.

The crystalinity index (CI) was calculated by using following equation:

$$CI\ (\%) = (I_{002} - I_{am}) / I_{002} \times 100$$

I_{002} = the maximum intensity of the peak (002) lattice diffraction

I_{am} = the intensity of diffraction attributed to amorphous cellulose

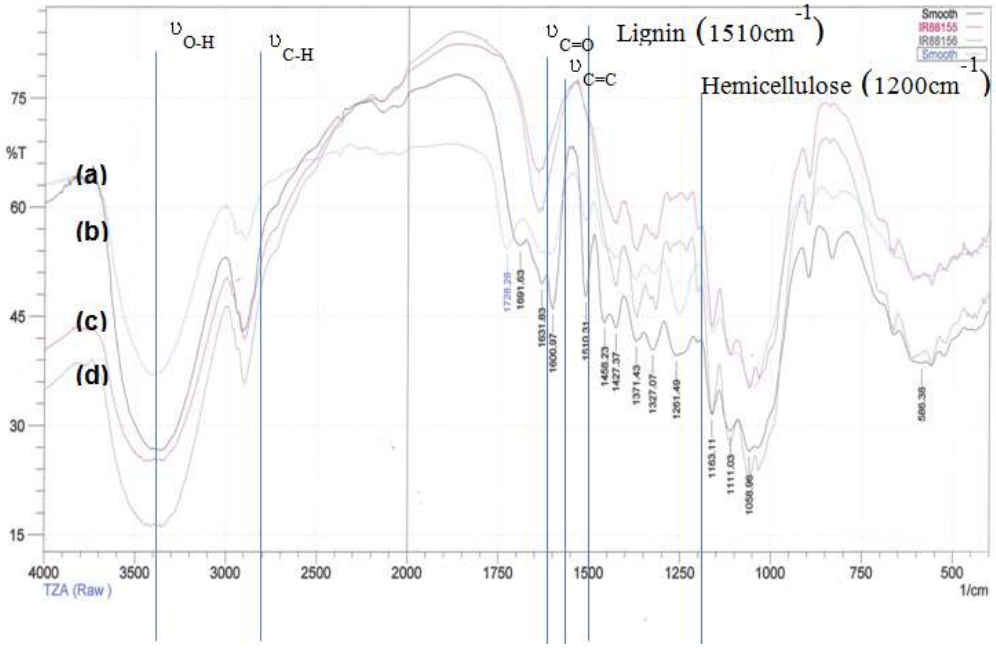
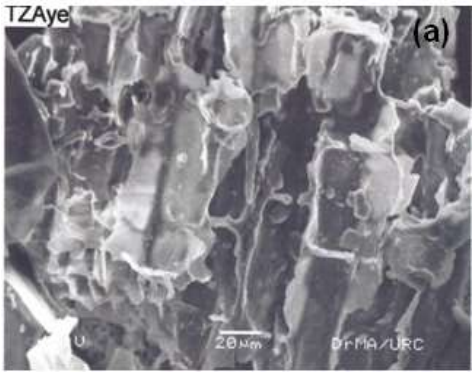


Figure 4: FTIR spectra of (a) sugar cane bagasse raw sample (b) acid treated sample (c) base treated sample and (d) cellulose fiber



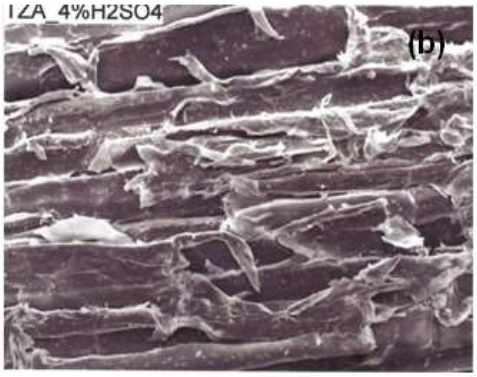


Figure 5: SEM photographs of (a) sugar cane bagasse raw sample (b) acid treated sample (c) base treated sample and (d) cellulose fiber

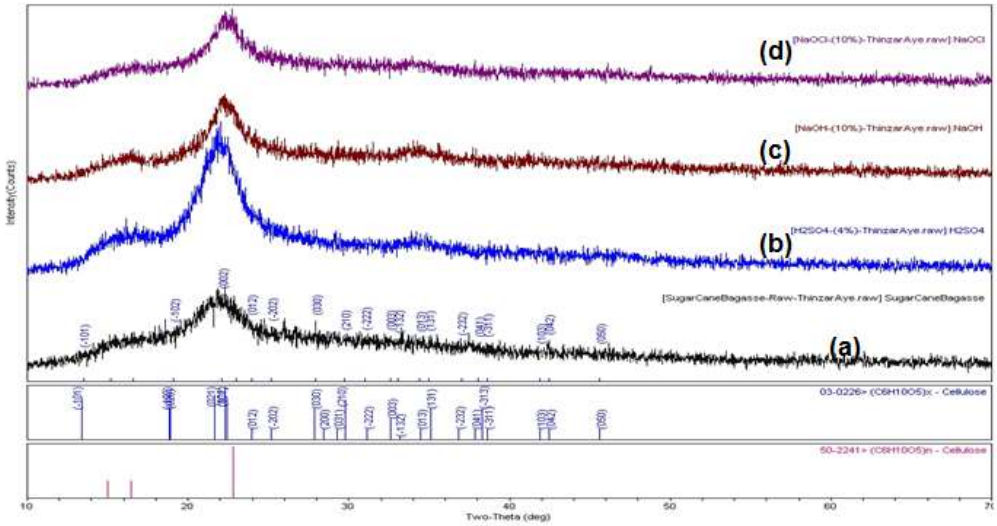


Figure 6: XRD patterns of (a) sugar cane bagasse raw sample (b) acid treated sample (c) base treated sample and (d) cellulose fiber

Conclusion

The sugar cane bagasse was used as starting material which was treated using sulphuric acid, sodium hydroxide and then bleached with sodium hypochlorite. The treated samples were characterized by FTIR, SEM and XRD. From the XRD data, crystalinity indexes of sugar cane bagasse raw sample, acid treated sample, base treated sample and cellulose fiber were 44.1%, 58.8%, 59.1% and 60.2% respectively. SEM and FTIR analyses clearly showed that the amount of liginin and hemicellulose from sugar cane bagasse sample was successfully reduced by chemical treatment and also proved that the final product was cellulose fiber. From the observation, obtained bagasse fiber was pure cellulose fiber which was used for preparation of cellulose hydrogel films. Sugar cane bagasse hydrogel films were successfully prepared by phase inversion of the DMAc solution with LiCl. Later, sugar cane bagasse cellulose hydrogel films will be utilized for biomedical applications.

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