Current Applied Science and Technology Vol. 18 No. 2 May-August 2018
DOI: 10.14456/cast.2018.6

UV Shielding Properties of Cellulose/TiO_2 Composite Film

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Received: 4 November 2017, Revised: 12 January 2018, Accepted: 4 July 2018

Abstract

Cellulose/TiO_2 composite film was prepared for UV shielding applications. Cellulose was extracted from sugarcane bagasse by ball milling process. The cellulose/TiO_2 composite film with different concentrations of cellulose showed a synergic feature of optical transparency and UV-blocking. The crystalline structure of cellulose was characterized by X-ray diffraction (XRD). The treated cellulose has higher crystallinity than the untreated cellulose. Fourier transform infrared spectroscopy (FT-IR) analysis shows the evidence of chemical treatment hemicellulose and lignin removal from sugarcane bagasse. The optical properties were measured by UV-Vis spectrometer, the results of TiO_2 and cellulose solution correspond to UV-A and UV-C absorbance regions with high transparent of cellulose composite films. The revealed results are essential for UV protecting materials application.

Keywords: nanocellulose composite, TiO_2, UV-shielding, ball milling

1. Introduction

Cellulose is the most abundant resource material on earth. Cellulose is natural, renewable and biodegradable polymers [1, 2]. It is a linear homo-polysaccharide composed of (1 → 4) linked D-glucose units. Cellulose can be found in wood, cotton, rice straws, and sugarcane bagasse [2-5]. Sugarcane bagasse is a residue from sugar and alcohol industries. Many industries have used sugarcane bagasse as a raw material for electronic sensor, paper production, fermented products, and packaging [3]. In general, sugarcane bagasse contains 40-50% cellulose, 25-35% of hemicellulose and 18-24% of lignin [3, 5]. Various methods, such as acid hydrolysis, ionic liquid treatment, enzymatic hydrolysis and mechanical treatment, can be used to obtain cellulose. As a mechanical treatment, ball milling is a top-down technique from micro to nano-scale materials. Ball milling is widely used for the preparation of nanoparticles because of its simple operation, use of relatively inexpensive equipment, and its broad applicability to most types of biomass [6-7].

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Hybrid inorganic/organic materials constitute a new class of functional nano-composites that exhibit high optical, thermal, and mechanical properties due to synergistic effects [8-9]. Natural cellulose is a linear polymer of β-(1→4)-D-glucopyranose with abundant surface hydroxyl groups forming plentiful inter- and intra-molecular hydrogen bonds. These hydroxyl groups provide suitable substrate for metal oxide incorporation onto the cellulose surface. Moreover, the extensive hydrogen bond network builds up a defined hierarchical order of supra-molecular organization for providing a chamber with the formation of inorganic nano-materials. Incorporation of TiO_2 to polymer casting solution could greatly affect the morphologies and properties of the resulting composite. Consequently, a wide range of applications can be obtained such as antimicrobial, anti-fungal, UV protective or self-cleaning properties. TiO_2 is a promising metal oxide that is extensively utilized in many industrial processes due to its stability, biocompatibility, non-toxicity and low cost [5–8].

In this work, cellulose was extracted from sugarcane bagasse by ball milling with mild acid hydrolysis and cellulose/TiO_2 composite films were prepared for an ultraviolet protecting material candidate.

2. Materials and Methods

2.1 Materials

Sugarcane bagasse was collected from plantations located at Sing Buri province, Thailand and used as a starting source of cellulose. Other reagents used were sulfuric acid, sodium hydroxide and hydrogen peroxide.

2.2 Methods

2.2.1 Isolation of cellulose

For extraction of cellulose, sugarcane bagasse was dried in sunlight and then cut into small pieces. The cut bagasse was milled into a powder. The bagasse powder (100 g) was dewaxed using 5% (v/v) sulfuric acid solution (2000 mL) for 2 h with constant stirring at 60 °C. The water-soluble components were removed with 50% (v/v) ethanol solution. The dewaxing process was repeated for 4 times. The residue was consequently washed with distilled water until the pH of the washed water became neutral. This step was conducted to remove lignin. In order to remove hemicellulose, the residual was bleached using 24% hydroogen peroxide and 4% sodium hydroxide solution with mechanical stirring at 60 °C for 2 h, filtered, and washed with distilled water to neutrality. After that, the slurry of 1% (wt/wt) purified cellulose in water was processed by grinding with ball milling process with the two different diameters size of zirconia balls (2 and 5 mm), in which the ball to material weight ratio was 3:1. The milling was performed for 24 h at 275 rpm with distilled water. The product was filtered and washed with distilled water until the pH of the washing water became neutral

2.2.2 Preparation of cellulose and cellulose/TiO_2 composite films

For preparing cellulose and cellulose/TiO_2 composite films, poly vinyl alcohol (PVA) was used for solution preparation. The 5% (wt/wt) PVA solution was prepared by dissolving in distilled water. Cellulose (0.05, 0.5, and 1% (wt/wt)) was added to the PVA solution. The stirring was performed at 80 °C for 2 h. After that, the mixed precursor was dispersed by sonication for about 5 min. For the preparation of cellulose/TiO_2 composite films, the 0.01% (wt/wt) TiO_2 solution was prepared by dispersed it in distilled water then added to the 5% (wt/wt) PVA solution using mechanical stirrer for 1 h. After that cellulose of 0.05, 0.5, and 1% (wt/wt) was added to the PVA/TiO_2 solution then stirring at 80 °C for 2 h and the resulting mixture was dispersed by sonication for 5 min. The final suspension was casted in PET plates and dried at 55 °C for 4 h to remove water before characterization.

2.3 Characterization

The chemical constituents of sugarcane bagasse and cellulose composite were investigated by FTIR spectroscopy (Thermo Scientific Nicolet 6700). The FTIR spectra were recorded in the region between 4000 and 400 cm^{-1}. The crystalline structure and phase identification of the cellulose composites were investigated by X-ray diffraction (Rigaku, Smartlab). The optical transmittance of the prepared films was measured from 200 to 700 nm using UV-Vis spectrometer (PG, T90+).

3. Results and Discussion

3.1 FTIR spectroscopic analysis

FTIR spectra of sugarcane bagasse and extracted cellulose are shown in Figure 1. Accordingly, all samples have three main absorbance regions (Figure 1(a)) in the ranges of 800-1200 cm^{-1}, 1200-1800 cm^{-1} and 2500-3900 cm^{-1} which are assigned to different vibrations mode of various functional groups as observed in Figure 1(b)-(d). The peak at 832 cm^{-1} indicates the bending vibration of the arene C-H bond in lignin. The peak was not found after the bleaching and extracted cellulose by ball-milling in sample (3) and (4). The peak at 897 cm^{-1} in sample (3) and (4) is associated with β-glycosidic linkages between glucose units in cellulose/hemicellulose [10]. This characteristic peak was not found in lignin structure (sample (1) and (2)) indicating that the bleached and extracted samples contain greater amount of cellulose and hemicellulose. The strong peaks observed in the spectra of all samples between the ranges of 1034, 1051 and 1160 cm^{-1} are related to the C-O stretching of cellulose, in plane aromatic C-H deformation vibration of lignin, and C-O antisymmetric stretching vibration of glucosidic ring in cellulose/hemicellulose and pyranose ring C-O-C asymmetric stretching of cellulose/hemicellulose, respectively [12]. The peak at 1105 cm^{-1} can be assigned to the C-O-C glucosidic ring vibration in cellulose. The absorption peaks at 1200 cm^{-1} is O-H deformation vibration mode of cellulose, while the 1240 cm^{-1} peak is aryl C-O out of plane stretching vibration in lignin. After bleaching process, the lignin peaks are not found in samples (3) and (4), revealing the complete removal of lignin. The absorption peaks at 1320 cm^{-1} which are present in all samples are assigned to CH_2 wagging. The peak at 1365 cm^{-1} and 1450 cm^{-1} correspond to the bending vibrational mode of C-H and C-O bonds in polysaccharide aromatic rings and the C-H asymmetric deformations, respectively [10 - 12]. The peak at 1513 cm^{-1} is derived from vibration mode of C=C aromatic ring skeletal in lignin. After bleaching process and extraction in sample (3) and (4), this characteristic peak of lignin vanished. The peak at around 1600 cm^{-1} in raw bagasse and dewaxed sample is due to C=O stretching vibration. This peak also disappears in extracted and blenched samples. The wide absorbance peak at around 1634 cm^{-1} in the extracted and blenched samples is associated with absorbed water in cellulose. Moreover, the peak positioned at 1728 cm^{-1} is correlated to C=O stretching vibration of carboxylic group of lignin and hemicellulose [10-12]. The cellulose samples after bleaching process do not have the peak at 1728 cm^{-1}, indicating that lignin and hemicellulose are totally removed from sugarcane bagasse [13-15]. The absorption peak at around 2900 cm^{-1} is due to the C-H stretching vibration. The broad peak at around 3340 cm^{-1} is attributed to the O-H stretching vibration of the OH groups.

From the FTIR analysis, it is shown that sample (1) and (2) contain lignin and hemicellulose. After bleaching process with hydrogen peroxide solution and extraction of cellulose by ball-milling, the characteristic peak of hemicellulose and lignin vanished. The cellulose was purified by chemical and mechanical treatments to remove of lignin and hemicellulose during cellulose isolation process.

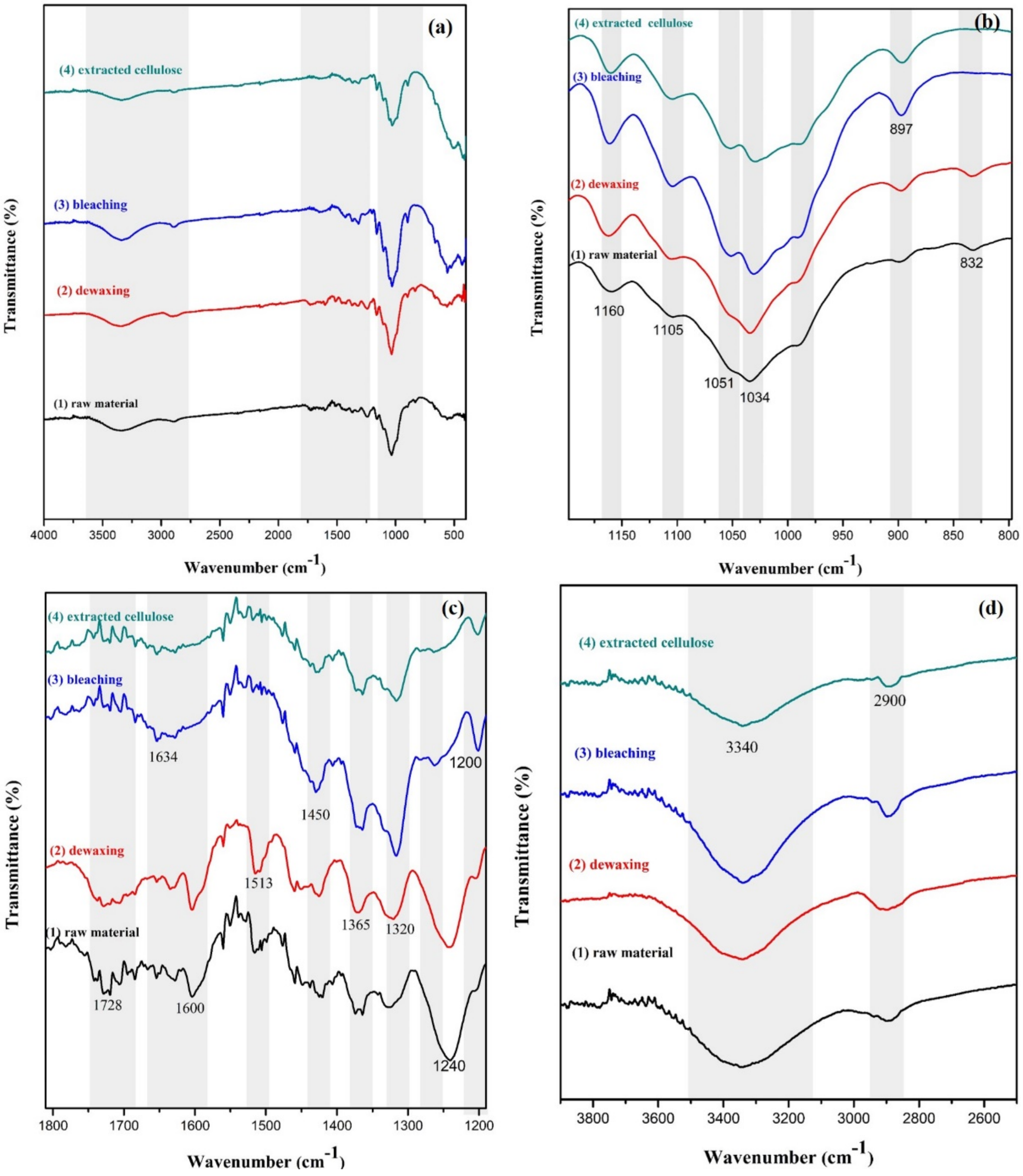

Figure 1. (a) FTIR spectra of lignocellulose, (b) FTIR spectra in the region between (800-1200 cm^{-1}), (c) between (1200-1800 cm^{-1}) and between (2500-3900 cm^{-1}).

3.2 X-ray diffraction

X-ray diffraction was used to analyze the cellulose structure and crystalline. There are several polymorphs of cellulose (I, II, III and IV). Typically, cellulose in natural such as trees, plants, tunicates, algae, and bacteria is cellulose I polymorph with monoclinic and triclinic structures. The

XRD pattern of cellulose I contains the main diffraction peaks at 2θ are around 16.5°, 22.5° and 34.5° which correspond to the (110) (200) and (004) lattice planes [16]. The XRD results were shown in Figure 2 in which sample (a) is untreated cellulose and sample (b) is treated cellulose by ball-milling 24 h. There are two main peaks at 16.5°, 22.5° in the XRD pattern of untreated cellulose with broadening base peak due to the amorphous nature. After the cellulose was treated by bleaching and ball-milling process, the flat base line in (110) and (200) peaks with the small peak at 2θ = 34.5° are observed. From the XRD results, it can be summarized that the bleaching and ball-milling processes increased the crystallinity of cellulose because the hydrolysis in bleaching process removed the amorphous lignin and hemicellulose [11, 17].

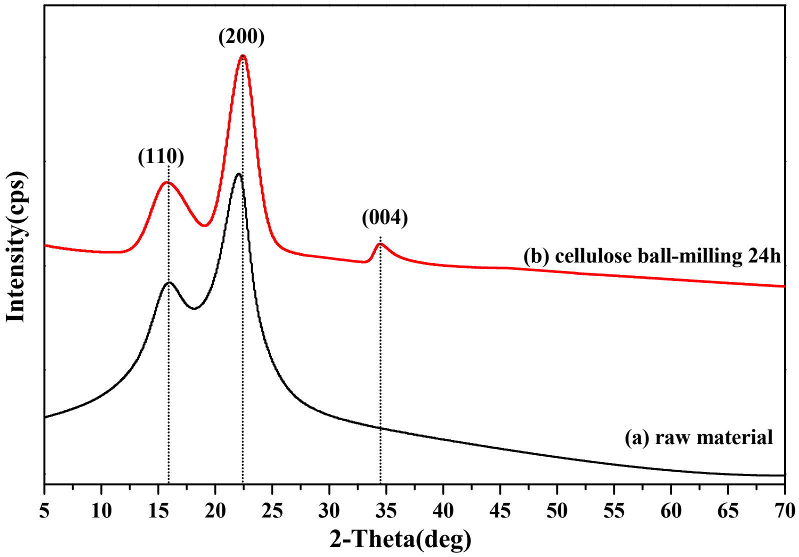

Figure 2. XRD patterns of (a) sugarcane bagasse, (b) cellulose ball-milling 24 h

3.3 Transmittance

The UV absorbance spectra of TiO_2 and cellulose solution were measured from 200 to 700 nm. The absorbance of TiO_2 and cellulose solution shown in Figure 3 exhibits its UV-blocking ability. The strong absorbance peak at around 200 nm and 350 nm of cellulose and TiO_2 solution correspond to UV-C and UV- A regions, respectively. UV- Vis spectra in transmission mode was recorded for PVA/ cellulose without TiO_2 and PVA/ cellulose with TiO_2 composite films with different concentrations of cellulose (0.05, 0.5 and 1 wt %). The results of transmittance were shown in Figure 4. Bare PVA/cellulose without TiO_2 and PVA/cellulose with TiO_2 composite films have rather high transparency in visible region implying that these films are able to transmit visible light while shielding UV radiation. As the same time, when increasing the concentration of cellulose composite films, the UV transmittance decreased (Figure 4). Meanwhile, as the film was incorporated with TiO_2-P25 nanoparticles, their transparencies in UV region ranging from 250-350 nm drastically decreased but their values in visible region insignificantly decreased. The feature can be related to the typically strong UV absorbance character of cellulose and TiO_2.

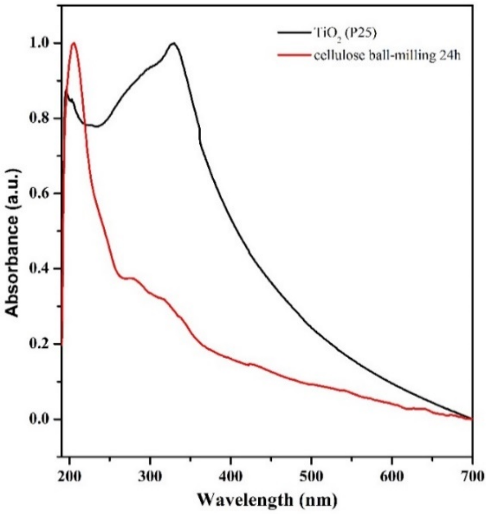

Figure 3. The UV absorbance spectra of TiO$_2$ and cellulose solution.

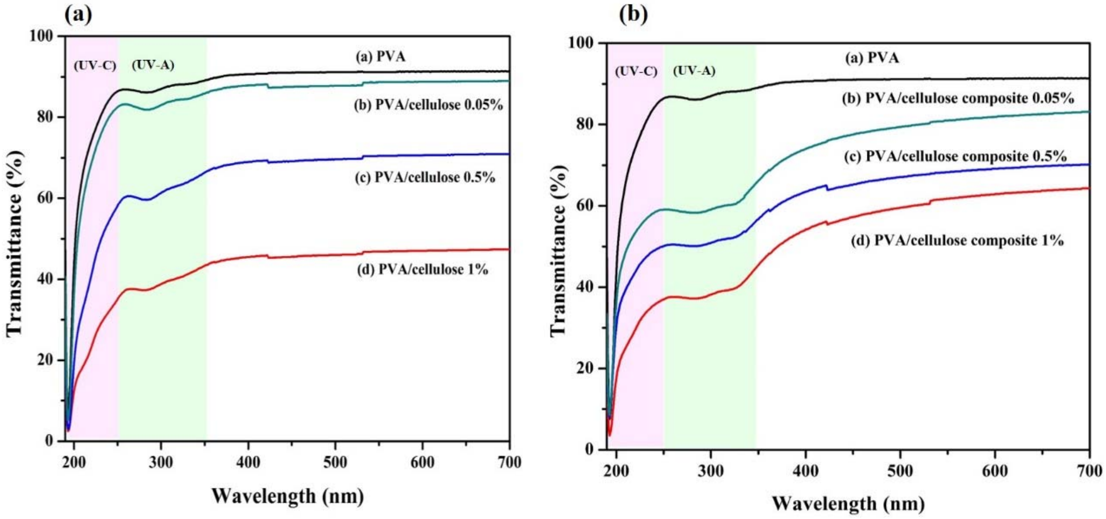

Figure 4. UV-Vis spectra of PVA/cellulose films (a) and PVA/cellulose composite films (b)

4. Conclusions

In this study, cellulose was successfully isolated from sugarcane bagasse by ball-milling process and acid leaching. The FTIR spectra analysis shows that the chemical treatment could remove most of hemicellulose and lignin from the sugarcane bagasse as shown by the disappearance of characteristic peaks of hemicellulose and lignin. The XRD pattern revealed that the treated cellulose by bleaching and ball-milling process has a higher crystallinity than the untreated cellulose. The absorbance regions of of TiO$_2$ and cellulose solution correspond to UV-A and UV- C while the optical transparency of cellulose composite films are high transmittance.Thus the composite films have the optical properties of UV protecting with high transparency. Under these conditions, the obtained results show that the cellulose composite films could be applied for the realization of transparent, low-cost, lightweight, and flexible substrates in UV-blocking fields.

5. Acknowledgements

This work has partially been supported by the National Council of Thailand (Grant No 488072) and College of Nanotechnology, King Mongkut's Institute of Technology Ladkrabang.

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