PRELIMINARY STUDY OF CELLULOSE EXTRACTION FROM OLD CORRUGATED CARDBOARD

Aina Fatini Ahmad Fisal[a], Waheedah Abdul Hakeem[b]*, Najwa Mohamad[c]

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Abstract: Old corrugated cardboards (OCCs) that is known as lignocellulosic waste are one of the large by-products of commercial and industrial activities. Thus, the alternative uses for such waste are currently being sought. The aim of this study was to extract cellulose from OCC by using chemical treatment. The method includes alkaline treatment, washing, bleaching treatment, and drying to produce final product of OCC cellulose (OCCC) powder. The yield of OCCC obtained was 39.28%. OCCC was then characterised by Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), and thermogravimetry analysis (TGA). FTIR exhibits the functional groups of cellulose in both IR spectrum of OCCC and CC, and no sign of hemicellulose and lignin. DSC results showed endothermic peaks were more profound in OCCC compared to CC. Endothermic peak corresponds to the removal of water. TGA results showed the highest degradation profile exhibited from CC TG curve with 80% weight loss, compared to OCCC which has 35% weight loss. The residue of CC was around 14% whereas OCCC was 41%. In conclusion, this study have isolated cellulose by removing most hemicellulose and lignin from OCCC. OCCC is a potential to be developed as a functional cellulosic molding in pharmaceutical field, which may eventually reduce the environmental problem that is caused by OCC waste.

Keywords: Old corrugated cardboard; cellulose extraction; alkaline treatment; bleaching treatment

[a]. Department of Pharmaceutical Sciences, Faculty of Pharmacy, University of Cyberjaya, 63000 Cyberjaya, Selangor, Malaysia.
[b]. Department of Pharmaceutical Sciences, Faculty of Pharmacy, University of Cyberjaya, 63000 Cyberjaya, Selangor, Malaysia.
[c]. Department of Pharmaceutical Sciences, Faculty of Pharmacy, University of Cyberjaya, 63000 Cyberjaya, Selangor, Malaysia.

***Corresponding Author**

E-mail: waheedah@cyberjaya.edu.my

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INTRODUCTION

In the 21st century, there has been an increase in the consumption of papers and packaging materials, which eventually caused serious consequences to the natural environment all over the world. The used boxes and cardboard produced are decomposed in the landfill and this led to the released of methane gases followed by the increased in greenhouse effect [1]. To de-escalate the impact of box-making process toward environment issue and to attenuate the number of used boxes, papers and cardboards, recycling will take the edge off the environmental problem. Recycling of used boxes is defined as recycle without additional reagents, additional processes, or additional pretreatment [2]. As an alternative of recycling used boxes into cardboard, a functional cellulosic molding could be constructed instead, resulting in a biodegradable and environmentally friendly products. Thus, this study will be using a sample from old corrugated cardboard (OCC) to investigate the physical properties, characteristics, and feasibility of cellulose extracted from OCC toward its contribution as a functional cellulosic moldings.

OCC was the post-use or waste of corrugated packaging material which usually comes from boxes. It consists of a defensive inner framework which functions as the structural robustness of cell wall, preserve a protection against microbial and have hydrolytic stability [3]. The major components of these OCC fibers consist of 3 primary biopolymers; carbohydrate polymers (cellulose, hemicellulose) and an aromatic polymer (lignin) [3].

It is a matter of fact that an extraction process is generally difficult under mild treatment conditions attributed to the stiff structure and extensive intra and intermolecular hydrogen bonding network in cellulose [4]. Recently, some of the alternative approach include the used of sodium hypochlorite (NaClO) and sodium hydroxide (NaOH) to simultaneously remove lignin and hemicellulose from wood on the study of cellulose extraction from sugarcane bagasse, using a cost-effective method combining physical treatment (high pressure steaming) and repeated chemical treatments (alkali and bleaching) [5]. This remarkable achievement has improved the processing time of cellulose extraction, minimised physical sample manipulation and potential errors, increased sample throughput, and reduced the number of chemicals and analytical costs. However, to our limited knowledge, we have found no reports on the study of cellulose extraction from OCC in Malaysia. Thus, it is a commencement of research work on cellulose extraction concerning of waste from OCC, as the first study conducted in Malaysia.

The extraction of cellulose from OCC by using chemical method could serve as an alternative way of managing the largely produced wastes. The chemical method used were alkaline and bleaching treatments concerning NaOH and

NaOCl, respectively. Then, the extracted cellulose was characterized by using Fourier transmission infrared (FTIR), differential scanning calorimetry (DSC) and thermogravimetric analyser (TGA).

METHODOLOGY

Materials

OCC was collected from waste boxes at a local market in Cyberjaya, Malaysia. Chemical reagents used were sodium hydroxide (NaOH) pellets (R&M Chemicals, UK) and sodium hypochlorite (NaOCl) (Systerm Chemicals Malaysia). Reference sample used was commercial cellulose (CC) by (R&M Chemicals. UK).

Preparation of OCC as a Sample

A sample of 25 g of OCC was weighed and then cut into smaller pieces. It was then soaked in water for 24 hours. Then, OCC was filtered with muslin cloth and thoroughly washed with distilled water. After that, it was air-dried in ambient temperature and was kept in a polyethylene bag until further use.

Extraction of Cellulose from OCC

Alkaline Treatment

OCC was then subjected to 4% of NaOH; 4 g of NaOH dissolved in 100 ml of distilled water at 80℃ for 2 hours [6] with mechanical stirring. This treatment was performed 3 times to produce suspension. Then, it was filtered and washed with distilled water until neutral pH was obtained.

Bleaching Treatment

OCC sample then underwent bleaching treatment at the same concentration, which was 4% NaClO; 4 g of NaClO was dissolved in 100 ml of distilled water, at pH 4 and 100℃ for 4 hours with mechanical stirring [5]. Like the alkaline treatment, bleaching treatment steps were also repeated 3 times for a more effective extraction. After each treatment, the OCC suspension was filtered and washed with distilled water until neutral pH was obtained. Finally, OCC suspension was dried via freeze-dryer to obtain OCCC powder as a final product of cellulose extraction.

Analysis

Extraction Yield

The raw sample were weighed and recorded beforehand. Then, the final samples were weighed with analytical balance after being recovered to room temperature. The yield was calculated as follows:

$$Yield\ (\%) = \frac{(m_1 - m_2)}{\mathrm{M}} \times 100\% \qquad \text{Equation (1)}$$

M = Total mass of raw materials (g)
m_1 = Mass of OCCC including container after dried (g)
m_2 = Mass of container (g)

Fourier Transform-Infrared Spectroscopy

FTIR spectra were recorded on a model of Nicolet iS10 FT-IR spectrometer, Thermo Electron, USA. The wavenumber recorded was in the region of 400 – 4000 cm^{-1}.

Differential Scanning Calorimetry

DSC analyses were conducted on both OCCC and CC samples. Mettler-Toledo/TGA DSC 1 model was used under argon atmosphere at a heating rate of 20°C/min. The operating temperature was elevated from 30℃ to 600℃.

Thermogravimetric Analysis

TGA analyses were conducted on both OCCC and CC samples. TGA was carried out by using a Mettler-Toledo/TGA DSC 1 model at the operating temperature elevated from 30°C to 600°C with a constant heating rate of 20°C/min. All measurements were performed under argon gas atmosphere.

RESULTS AND DISCUSSION

Physical Appearance of OCCC

The effectiveness of alkaline and bleaching treatment on the removal of hemicellulose and lignin was observed clearly based on colour change in Figure 1. Alkaline treatment was conducted using 4% NaOH to eliminate hemicellulose from OCC [6]. Alkaline treatment prominently expand the hemicellulose matrix, resulting in the reduction of intermolecular hydrogen-bonding and eventually removes the hemicellulose. During the first NaOH treatment, it has been observed that the OCC suspension, which appeared as dark brown in colour turns yellowish brown. This may indicate the removal of hemicellulose and impurities that exist on the surface of the OCC. This is supported by a study of Sutan et al. [7] on the effect of alkali treatment of sugarcane bagasse. The changing of fibre colour treated with alkali to yellowish may be due to the removal of hemicellulose and impurities from the fibre surface. This finding was similar to OCC suspension as it turns to yellowish brown in colour. The treatment was repeated 3 times to increase the effectiveness of the elimination process. It can be seen that the discolouration of the OCC suspension becomes more visible after the third treatment.

In bleaching treatment, 4% of NaOCl played its role on eliminating lignin as there was a notable sign of discoloration after the treatment. The OCC suspension which appeared yellowish brown prior to the treatment turned yellowish, similar with the result of another study by Khenblouche et al. [3]. The treatment was repeated 3 times to ensure the efficacy on removing lignin from OCC. During the third treatment, OCC turned white in colour which indicates that hemicellulose, lignin and other impurities was completely removed from the sample. Finally, white powder of OCCC was obtained after being dried with freeze dryer.

Figure 1. Figure shows the observations on each process of cellulose extraction: (a) OCC during first NaOH treatment; (b) Removal of hemicellulose; (c) OCC during first NaOCl treatment (d) Removal of lignin; (e) OCC after 3 repeated times of NaOH and NaOCl treatment; (f) OCCC formation upon drying

Extraction Yield of OCCC

The result on the percentage yield of extracted cellulose was calculated by using Equation 1. The dry weight of the raw sample (M) was 25 g. The mass of extraction after drying with container (m_1) and the mass of container (m_2) was recorded as 43.58 g and 33.76 g respectively. The calculated percentage yield of cellulose extracted from OCC was 39.28 %.

Based on the extraction yield from this study, it was slightly lower than that in the literature data [8] which reported a yield of 48 % on the same sample of OCC, yet using acid hydrolysis procedure. However, it is comparable with [9] which was 38 %, on the study of cellulose extraction from laser printed paper by using acid hydrolysis. The dissimilarity of cellulose yield between the current study and those reported in literature may be due to the type of cellulosic sample used for the extraction of cellulose and the efficacy of treatment conducted for each studies.

Characterisation of OCCC and CC

The characterizations of OCCC as a sample and CC as a reference were conducted. The results were compared between each other and previous studies.

FTIR Spectroscopy

FTIR spectroscopic analysis was performed to investigate the changes of chemical composition as well as the purity of cellulose in OCCC as compared to CC. The identification of each band was based on CC spectrum (Figure 2), OCCC spectrum (Figure 3) as well as on the literature data.

There are several functional groups which happened to fall in range with the wavenumber reported in literature data [10]. These includes C-O-C stretching, O-H bond, fiber-OH and C-H stretching vibration, which correspond to cellulose. The C-O-C stretching was observed in CC spectrum at 1024 cm^{-1}. Similarly, in OCCC spectrum, the C-O-C stretching was also present at 1031 cm^{-1}. Next, O-H bond was seen in CC spectrum at 3331 cm^{-1}, likewise, it was also observed in OCCC spectrum at 3333 cm^{-1}. Fiber-OH was identified in CC spectrum at 1651 cm^{-1}, whereas in OCCC it was at 1643 cm^{-1}. Moreover, C-H stretching vibration in CC spectrum was observed at 2893 cm^{-1}, which was also quite identical to the OCCC spectrum which showed C-H functional group at 2900 cm^{-1}. Based on these results, it was proven that OCCC and CC have similar functional groups that are identified as cellulose.

Based on FTIR spectra, hemicellulose can usually be found around 1765–1715 cm^{-1}, that is assigned as C=O band, whereas lignin was usually observed at 1500 cm^{-1} to 1600 cm^{-1}, that is assigned as aromatic group [11]. In CC, there was no hemicellulose identified. However, there was a peak of weak intensity at 1537.51 cm^{-1} which is not profound to indicate lignin, thus was assumed as negligible value. Meanwhile, in OCCC, there was no notable sign of both hemicellulose and lignin detected. This result was similar with another study [12], where C=O band acetyl stretching was no longer observed in the treated wastepaper spectrum. Therefore, the treatment of NaOH with the help of NaOCl removed hemicellulose and lignin from OCCC, which is supported in a study [13] on the effectiveness of both treatments.

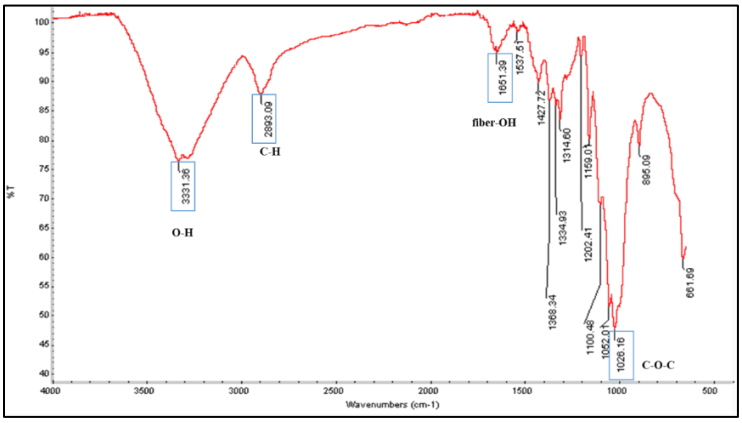

Figure 2. FTIR spectrum of CC

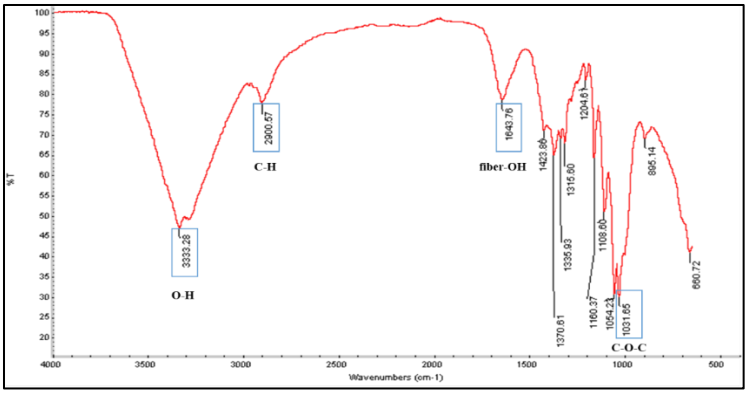

Figure 3. FTIR spectrum of OCCC

Thermal analysis

Differential Scanning Calorimetry Analysis

DSC was conducted to study the endothermic and exothermic reaction of CC and OCCC as shown in Figure 4 and Figure 5 respectively.

Initially, both thermograms showed an endothermic characteristic at the beginning of the process. In CC (Figure 4) the peak onset was between 30 ℃ to 45 ℃, whereas for OCCC (Figure 5), the peak onset was between 41.7 ℃ to 62.48 ℃. Weight loss for cellulose fibers observed up to 100 ℃ was due to the water removal [14].

Hemicellulose started its decomposition at 220 ℃ and continued up to 315 ℃ [10]. Based on both thermograms, there was no notable sign of hemicellulose observed. Thus, hemicellulose was absent in both CC and OCCC. On the other hand, lignin decomposition was extended to the temperature of above 700 ℃ and thus not being able to be detected in this study due to the limitation of heating system of DSC that only reached up to 600℃ maximum temperature.

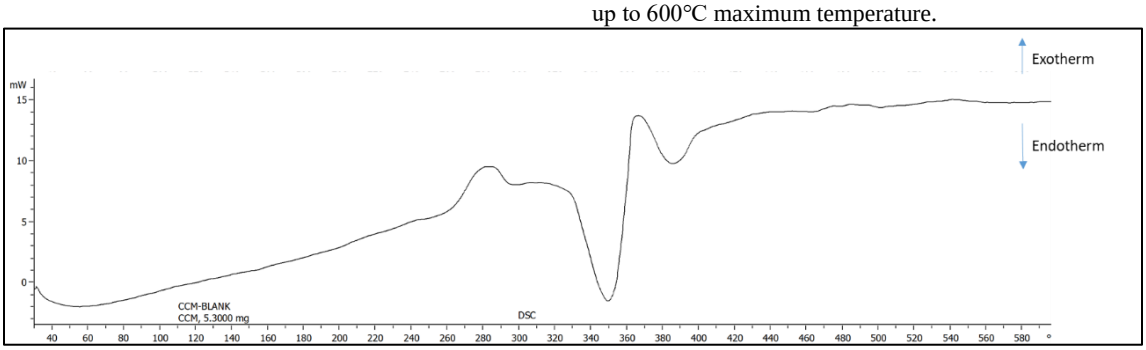

Figure 4. DSC thermogram of CC

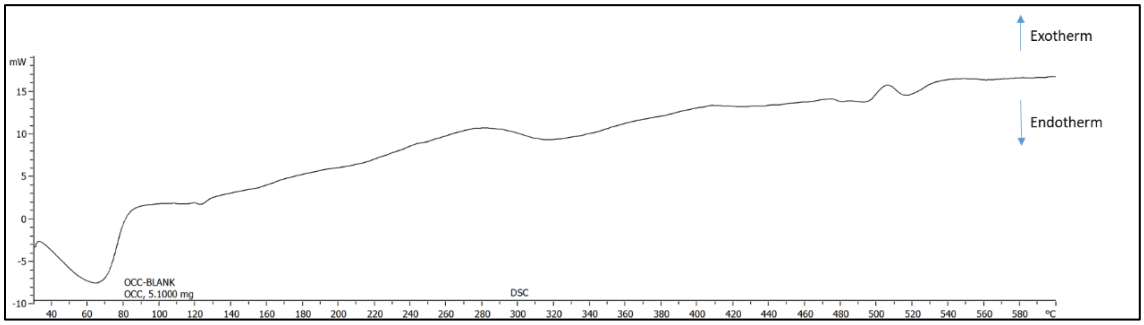

Figure 5. DSC thermogram of OCCC

Thermogravimetric Analysis

TGA studies the decomposition of CC as well as OCCC. The results were shown in Figure 6 and Figure 7 respectively.

Decomposition of CC and OCCC showed several stages, which indicated the presence of different components at different temperature. From previous study, a small weight loss was found in the range of 25 ℃ to 150 ℃ due to the evaporation of the humidity of the material [10]. Based on CC thermogram in Figure 6, there was no notable sign of percentage loss or decomposition at that range. Conversely, it was clearly seen in Figure 7 of OCCC, where the removal of water takes place from 30 ℃ until 88 ℃. In fact, this removal of water happened to be similar with DSC results, which strongly suggest that OCCC contains high amount of water compared to CC.

CC has a sharp decomposition starting from 222 ℃ to 420 ℃, which was responsible for about 80% of the total mass loss of

the sample. However, OCCC started to decompose at 223 ℃ to 310 ℃, with a total of 35% mass loss lesser than CC. Cellulose decomposition started at 315 ℃ and persisted until 400 ℃ [10]. This shows that CC has higher cellulose content compared to OCCC.

OCCC has a degradation peak at the temperature ranges from 190 ℃ to 320 ℃. Hemicellulose decomposes at 220 ℃ and continued up to 315 ℃ [10]. Thus, this result might indicate the presence of hemicellulose in OCCC. However, it is difficult to compare the results between this experiment and in the literature due to the difference in heating rate in this study (20 ℃/min), whereas in previous studies, the heating rate used were mostly at 5 ℃/min or 10 ℃/min.

Moreover, in a study of cellulose extraction from sisal fibers [10], the lignin decomposition started at 200 ℃ until 700 ℃. Based on this result, it may indicate that OCCC and CC contains quite an amount of lignin. However, it is difficult to justify it due to the temperature of TGA conducted was at 600°C maximum. Hence, no observable sign of lignin can be concluded.

Finally, the residue of CC was around 14% whereas OCCC was around 41%. In a study of cellulose extraction from sisal fibers [10], the solid residue left from lignin decomposition was reported as 48%. This may indicate that OCCC contains quite an amount of lignin compared to CC.

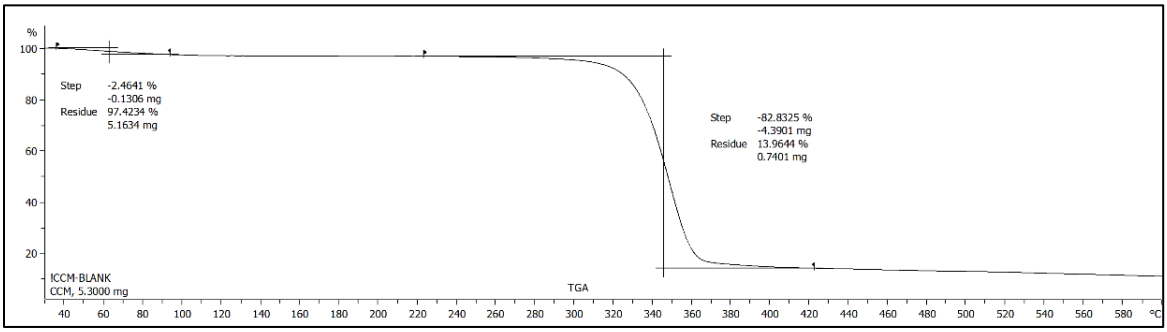

Figure 6. TG curve of CC

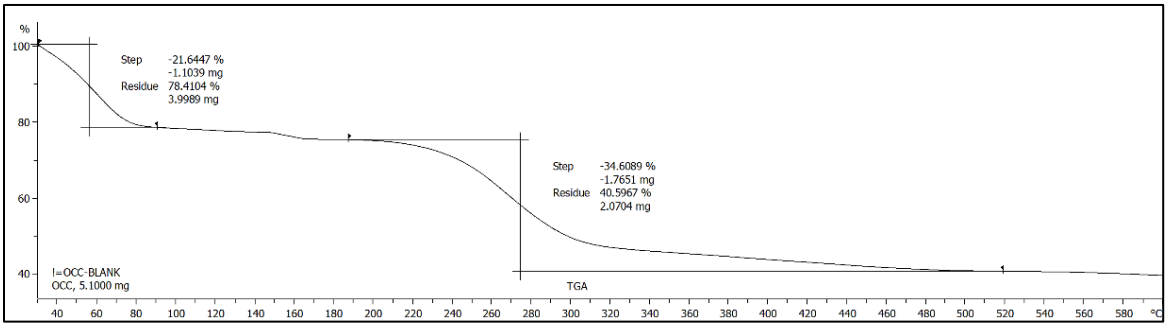

Figure 7. TG curve of OCCC

CONCLUSION

In conclusion, it is seen that cellulose can be extracted from OCC by dissolving it in NaOH treatment followed by NaOCl treatment. There was a gradual discolouration observed in OCC along the process until whitish OCCC powder was obtained as a final product. The OCCC final yield was 39.28% and this was quite comparable with previous studies. FTIR spectra proved that a stepwise of chemical treatments have essentially removed hemicellulose, lignin and other impurities in OCC. However, this study has found that there are some limitation in thermal analysis of the samples where the heating rate was not in the optimum range.

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