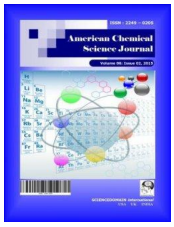

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Characterization of Micro-fibrillated Cellulose Produced from Sawmill Wastage: Crystallinity and Thermal Properties

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Authors' contributions

This work was carried out in collaboration between all authors. Authors MSA and SYP designed the study, performed the Instrumental analysis, wrote the protocol and wrote the first draft of the manuscript. Authors GMAK and MHU managed the analyses of the study. Author MAAM managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

In this work, micro-fibrillated cellulose (MFC) was prepared from sawdust and characterized by FTIR, WAXRD, and TGA. The MFC was synthesized by several steps such as alkali treatment, followed by $NaClO_2$ bleaching and acid hydrolysis. The acid hydrolysis was performed by three different H_2SO_4 concentrations (1N, 3N and 5N) whereas other conditions were remained unchanged. MFC were exhibited the identical peaks in FTIR spectra. The oxidation reaction took place during the MFC preparation by using high concentrations of acid which was detected by FTIR spectra. The crystallinity index of prepared MFC was measured by peaks at 16.2º and 22.2º (2θ

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angles) of WAXRD curves. The crystallinity index was increased with acid concentration up to 1N H_2SO_4 and thereafter decreased. The TGA results showed that the MFC degrade earlier temperature compare to the bleached pulp. The peaks of differential thermo-gravimetric curves (DTG) were shifted to lower temperature with the increase of acid concentration during hydrolysis of bleached pulp.

Keywords: Sawdust; Micro-fibrillated cellulose; FTIR; WAXRD; TGA.

1. INTRODUCTION

The increasing interest in nanomaterials and their unique properties have led to intensive research in the area of nanocellulosic materials, such as cellulose nanocrystals (cellulose whiskers), electro-spun cellulose nanofibers and microfibrillated cellulose (MFC) [1-4]. MFC is a man-made substance which is obtained from the naturally occurring compound i.e. cellulose. It is a renewable and biodegradable substance which provides a cheap source of quality fiber that can be used in many manufacturing process. On account of its small size, very high surface area and high aspect ratio, MFC is a potential reinforcing material with the advantages of being derived from renewable resources, biodegradable and biocompatible. MFC networks have been used in the field of biomedical applications and in transparent materials for different purposes such as, manufacture of, biocomposite for bone repair, nanoarchitechture, nanostructured foams and membranes, flexible electronic displays, magnetic films, switchable optical films novel bioplastics, additives for paints, cosmetic products, pharmaceutical products, recyclable structural and interior components for transport industry, hygiene and adsorbent products etc [5-6].

MFC can be prepared from native fibers, giving rise to highly crystalline and rigid nanoparticles [7]. Gong et al. [8] were prepared nanocellulose with high aspect ratio from wood. Abrahama et al. [9] were intended to study the extraction of nanocellulose from lignocellulosic fibers. In the preliminary analysis, they were investigated three different fibers: Banana (pseudo stem), jute (stem) and pineapple leaf fiber (PALF). Cotton fiber also been used as a raw materials for MFC [10]. The saw dust is mainly composed by cellulose is now used as a fuel for burning. As like cotton and other lignocelluloses fiber it might be a potential source of MFC. In the present investigation, this wastage sawdust has been received interest as the raw materials for cellulose as well as MFC.

Plenty of methods have been investigated to isolate nano-cellulose for different species such as mechanical methods, enzyme hydrolysis, chemical methods etc [5,10,11]. Chemical processes were frequently practiced due to easy and quick extraction, low cost, and to obtain shortest crystalline fiber diameter. Mandal and Chakrabarty [11] were isolated more crystalline nanocellulose by acid hydrolysis from sugarcane bagasse (SCB) by the acid hydrolysis of native cellulose fibers using a concentrated inorganic acid, commonly sulfuric or hydrochloric acid. Abrahama et al. [9] were tried to extract MFC by steam explosion technique along with mild chemical treatment. Their processes were consisted usual chemical procedures such as alkaline extraction, bleaching, and acid hydrolysis. However, several chemical treatment and acid hydrolysis caused the partial cleavage of the elementary crystallites and recrystallization of cellulose during hydrolysis [8]. Cellulase and Xylanase enzyme often used to find superior quality nanocellulose from cellulose [12]. Satyamurthy and Vigneshwaran [13] were established a novel process for the synthesis of spherical nanocellulose by hydrolysis of microcrystalline cellulose using anaerobic microbial consortium. Now a day, combined techniques were more popular to get homogeneous MFC. Li et al. [14] were prepared of entangled nanocellulose fibers from alkaline peroxide mechanical pulp and physical ultrasonication method. Hassan et al. [15] were isolated of nanofibers from bleached bagasse and rice straw pulps using high-shear ultrafine grinder. The pulps were refined using high-shear ultrafine grinder and then homogenized using high-pressure homogenizer and resulted in nanofibers with diameters ranging from 3.5 to 60 nm. Panthapulakkal and Sain [6] were prepared cellulose nano fibrils from wood pulp fibers by mechanical defibrillation, and diameter distribution of the fibers produced was in the range of 1–100 nm. Nanocelluloses are rod like highly crystalline particles with a regular cross section and their dimensions depend on 1) The native cellulose source material, 2) Hydrolysis time and 3) Temperature. Jiang and Hsieh [16]

were isolated from pure rice straw cellulose through sulfuric acid hydrolysis, mechanical blending and TEMPO-mediated oxidation to 16.9%, 12% and 19.7% yields, respectively.

In this work, bleached pulps from sawdust was used as cellulose sources to prepare MFC. Normally waste sawdust obtained from sawmills as a byproduct which is used as domestic fuel. High cellulose and low lignin percentage of saw dust can be the potential raw materials for nanocellulose production. The aim of this work is to isolate microfibrillated cellulose from bleached sawdust pulp by combined methods i.e., acid hydrolysis and ultrasonication. MFC were characterized by Fourier Transform Infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and wide angle X- ray diffraction (WAXRD).

2. MATERIALS AND METHODS

The saw dust of *Leucaena leucocephala* (Lam.) plant was collected from local wood industries (sawmill) at Kushtia, Bangladesh. All the chemicals used in the present investigation were analytical reagent grade purchased from Sigma-Aldrich.

2.1 Preparation of Micro-fibrillated Cellulose from Sawdust

Sawdust was clarified by using several physical methods such as sieving and washing to remove large particles like as stone, concrete, bark etc. The dry sawdust was immersed in 17% (w/v) sodium hydroxide (NaOH) solution at room temperature for 3 h with occasional stirring by glass rod and liquor ratio was maintained at 1:50 (w/v). The alkali treated sawdust was washed several times thoroughly by distilled water and neutralized with very dilute acetic acid. The alkali treated sawdust was dried in air filled by an electric oven at 105°C for 6 h and stored in poly bag.

The alkali treated fibers were bleached with 1 wt% sodium chlorite ($NaClO_2$) solution for 90 min at 85-95°C. The fiber-liquor ratio was maintained at 1:50 (w/v). In this process the pH was controlled at 4. A buffer mixture of pH 4 (acetic acid-sodium acetate) are prepared and added to the chlorite solution in the proportion of 1 ml of buffer solution for every 10 ml of chlorite solution. After the treatment, bleached pulps were filtered over a sintered funnel and washed thoroughly with distilled water. The pulp was then treated with 0.2% (w/v) sodium meta-bi-sulfite ($Na_2S_2O_5$) solution for 20 min with fiber-liquor ratio 1:20 (w/v). The pulps were filtered and washed thoroughly with distilled water, dried in an electric oven.

10 g of each bleached pulps were added in the solutions of 1N, 3N and 5N sulfuric acid. The fiber-liquor ratios were maintained at 1:50 (w/v). The pulp suspensions were then placed on a magnetic stirrer and continued stirring up to 6 h by a magnetic bar. After 6 h acid hydrolysis, the white powder like MFCs were formed and then MFCs were filtered and washed thoroughly with distilled water. The obtained MFCs are insoluble in water, ethanol, DMF and other organic solvents. MFCs were kept in acetone and sonication was performed for 12 h in an ultrasonic bath.

2.2 Characterization

The Infrared spectra of bleached pulp and MFCs were recorded with FTIR 8400S Shimadzu spectrophotometer in the range of 4000-400 cm^{-1} using KBr pellet technique. The sample pellets was prepared by mixing approximately 0.5 mg of powdered sawdust and 100 mg of dried KBr in small agate mortar pestle. For better resolution 30 times scans were taken.

The surface morphology of prepared MFCs and reference bleached pulp were also examined by an Olympus microscope using a drop of dilute suspension of the samples. A computer was integrated with the machine with relevant software.

Wide-angle X-ray diffractogram (WAXD) pattern were obtained with BRUKER D8 ADVANCE wide angle X-ray diffractometer using Cu Kα radiation (α=0.154 nm), voltage of 50 KV and current of 40 mA with 2θ ranges from 5° to 45° increased in step of 2º/min. The data was analyzed by origin 8 software.

The thermo gravimetric analyses (TGA) of MFCs were conducted by thermal gravimetric analyzer supplied by TA Instrument (EXTAR 6000 STATION, Seiko Instrument, Inc. Japan). 20 mg of sample was taken for every analysis. The sample were heated up steadily at a rate of 20°C/min from 25°C to 600°C under continuous flow of nitrogen at 50 ml/min. To get perfection, analysis was carried out twice for each sample.

3. RESULTS AND DISCUSSION

The morphology, structure and thermal properties of MFC and reference bleached pulp prepared from sawdust have been studied by optical microcopy (OM). Fourier transform Infrared spectroscopy (FTIR), wide angle X-ray diffractogram (WAXRD) and thermogravimeteric analysis (TGA). The optical images of prepared MFC are shown in Fig. 1. It is observed that the particle size of MFC was decreased with the increases of acid concentration.

The FTIR spectra of bleached pulp, MFC-1N, MFC-3N and MFC-5N are presented in the Fig. 2. The FTIR spectra of fibers contain the typical vibration bands of the components mainly corresponding to cellulose, hemicellulose, and lignin. The hydrophilic tendency of the cellulose and nanocellulose samples is reflected in the broad absorption band in the 3700–3100 cm-1 region, which is related to the –OH groups present in their main components. In the 1600–900 cm-1 region, it is possible to appreciate in fibers vibrations of chemical components of the lignin at frequencies of 1514 cm-1 for guaiacyl and 1468, 1433 and 1214 cm-1 associated with syringyl. These absorptions are consistent with those of the typical cellulose backbone. Furthermore, almost the same absorption peaks as shown in the cellulose fibers were observed in the spectrum of the MFCs. This indicated that the structure of cellulose had not been damaged after the treatments.

On acid hydrolysis, the hydroxyl group of cellulose is oxidized to aldehyde (-CHO) or carboxylic acid (-COOH) group thus gives the identical peak at 1736 cm-1. As the concentration of acid hydrolysis increases, the intensity of the peak at 1736 cm-1 of the samples increases. From the Fig. 2, it is seen that the very low intensity of the peak which negligible for bleached pulp, but it gradually increases in case of MFC-1N, MFC-3N and very high in MFC-5N. On the other hand, the peak centered at 1643 cm-1 in the FTIR spectrum of cellulose and MFC may be due to the C=O bond of hemicellulose. The intensity of the peak decreases from cellulose to MFC as the hemicellulose is removed gradually by acid hydrolysis.

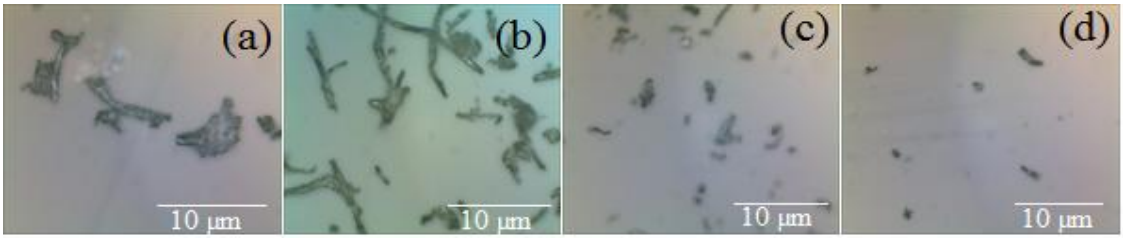

Fig. 1. Optical micrograph of (a) bleached pulp, (b) MFC-1N, (c) MFC-3N and (d) MFC-5N

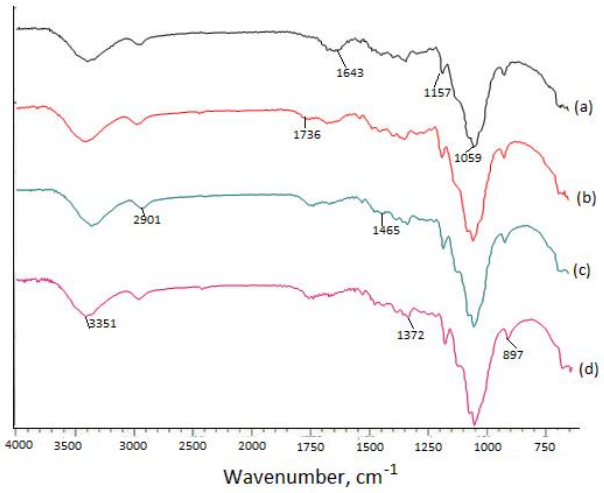

Fig. 2. FTIR spectra of (a) bleached pulp, (b) MFC-1N, (c) MFC-3N and (d) MFC-5N

The crystallinity index (*crI%*) of bleached pulp and MFC has been analyzed by X-ray diffractometry. From the Fig. 3, it is seen that all the cellulose peaks near 2θ = 16.2°, 22.2°, and 34.2°. Compared with the bleached pulp, there was no crystalline transformation of the crystalline structure in the MFC samples due to invisible changes in the diffraction angle (2θ). It is also observed that after acid treatment the *crI%* of MFC was increased. Moreover, the diffraction intensity of relative diffraction angle was increased after acid hydrolysis. The increase of diffraction intensity indicated that the acid hydrolysis induced the *crI%* due to the removal of amorphous materials like hemicellulose, lignin, and some other non-cellulosic materials, which is revealed by the results in Table 1. It can be noted that the increases orientation of cellulose along a particular axis with the non-cellulosic polysaccharides which are removed by hydrolysis and the amorphous zones are dissolved. All the four diffractograms displayed a strong intensity peak at around 2θ = 22.2° and other weak diffractions at 2θ = 16.2°, and 2θ = 34.2°. These figures were corresponded to the structure of cellulose. The percentage of crI of MFC-1N is higher than the bleached pulp and others MFC. It can be noted from Table 1 that the *crI%* decreases in case of MFC-3N and MFC-5N. This may be due to higher acid concentration, degradation of cellulose occurs which decrease the crystallinity index.

The thermal behavior of bleached pulp, MFC-1N, MFC-3N and MFC-5N are presented in the Fig. 4. The summary of weight loss in different temperature is also depicted by Table 2. For convincing explanation, four different temperature ranges (30-170, 171-270, 271-400 and above 400) were considered on the basis of the degradation of the constituent of fibers. The first weight loss at the range 30-170°C is found due to removal of moistures. The further degradation is occurred at the range of 171-270°C for removal of hemicellulose and final weight loss is happened for degradation of cellulose and lignin together at the range of 271-400°C. From the table, it is seen that bleached pulp content less amount of moisture then MFC-1N, MFC-3N and MFC-5N. Therefore, after acid hydrolysis fiber becomes more hydrophilic. For MFC-5N the weight loss at 170°C is seems unusual. Probably the loss of low molecular weight carbohydrate is caused by hydrolysis with higher concentration of acid. The further degradation is occurred at the range of 171-270°C. The bleached pulp and MFC-1N shows very trace loss in weight. These values proved that bleached pulp has neglected quantity of hemicelluloses and MFC-1N pulp is not degraded into lower molecular weight carbohydrate. However, MFC-3N and MFC-5N shows huge weight loss at this temperature range. This weight loss may be due to degradation of low molecular weight fraction of carbohydrates. The final degradation is occurred at the range of 271-400°C and respective weight loss is due to degradation of cellulose. The order of weight loss in this range MFC-1N>bleached pulp>MFC-5N> MFC-3N. The results indicate that MFC-1N content higher amount of cellulose fraction and then bleached pulp. MFC-3N and MFC-5N shows early degradation and therefore their weight loss at the range of 271-400°C is lower than bleached pulp and MFC-1N. The char content at above 450°C are followed by the order: MFC-3N>bleached pulp>MFC-5N> MFC-1N.

Table 1. Crystallinity index of bleached pulp and MFCs

Sample	Full width of half maximum of 2θ = 22.2	Peak ratio of peaks at 2θ = 22.2 and 16.2	Peak Intensity at 2θ = 22.2	Crystallinity index, %
Bleached pulp	1.0	1.47	7.9	77
MFC-1N	1.0	1.90	8.0	86
MFC-3N	0.9	1.56	8.1	81
MFC-5N	0.8	1.60	7.8	76

Table 2. Weight loss of bleached pulp and MFCs at various temperatures

Sample	Wt. loss (%) at 30-170°C	Wt. loss (%) at 171-270°C	Wt. loss (%) at 271-400°C
Bleached pulp	4.2%	0.30%	56.5%
MFC-1N	8.1%	0.90%	90.4%
MFC-3N	8.2%	28.3%	18.2%
MFC-5N	18.0%	38.7%	25.4%

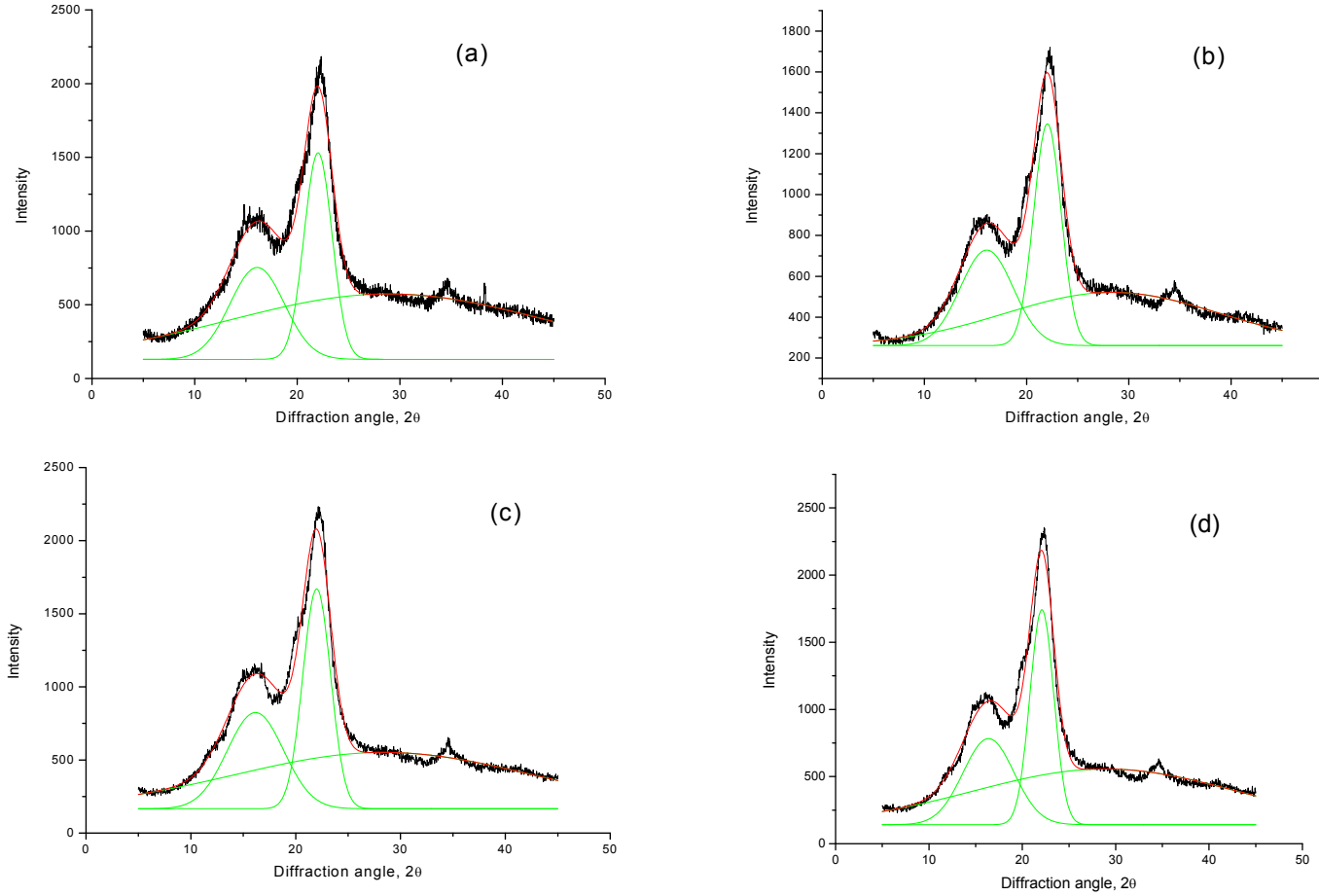

Fig. 3. WAXRD of (a) bleached pulp, (b) MFC-1N, (c) MFC-3N and (d) MFC-5N

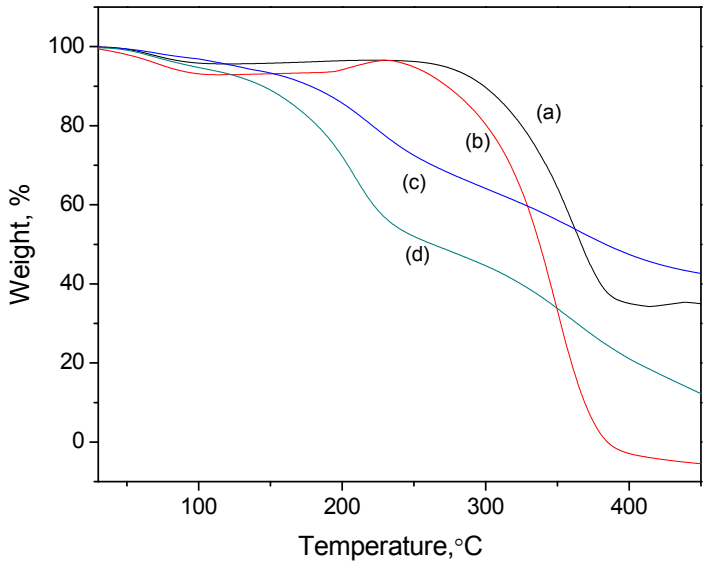

Fig. 4. TG of (a) bleached pulp, (b) MFC-1N, (c) MFC-3N and (d) MFC-5N

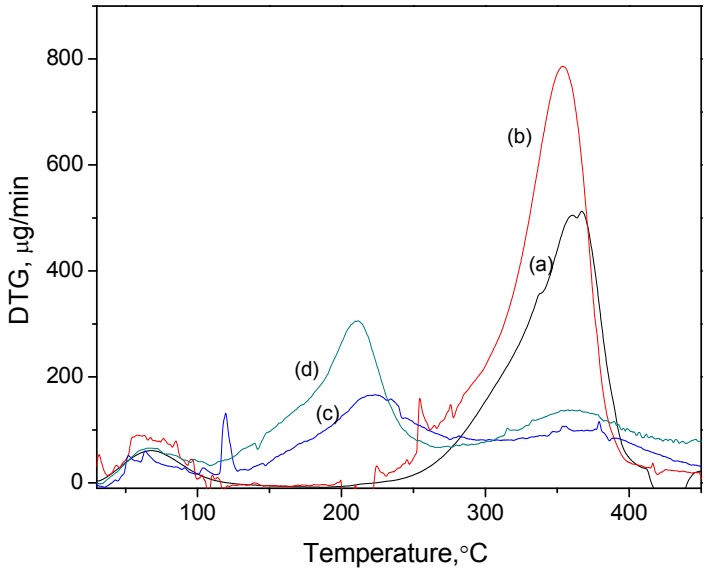

Fig. 5. DTG of (a) bleached pulp, (b) MFC-1N, (c) MFC-3N and (d) MFC-5N

The DTG curves (Fig. 5) above shows the differential form of TG curves. The peaks reveal the different stages of degradation of the pulp and MFC. The bleached pulp and MFC-1N has mainly two degradation stage at the around 67 and 360°C is due to moisture removal and cellulose degradations. Whereas the other two curves of MFC-3N and MFC-5N shows multiple peaks at 67.5, 125, 210 and 361.4°C due to the removal of moisture and degradation of low molecular carbohydrate and cellulose respectively.

4. CONCLUSION

Sawdust, the byproduct of wood industry has no economic value now, can be used to produce micro-fibrillated cellulose (MFC). Morphological and thermal experimental data are proved that the prepared MFC has identical characteristics

and quite different to cellulose. The concentration of acid during hydrolysis reaction of bleached pulp is affected on the crystallinity and thermal stability of MFC. The further work would attempt to do to modify the MFC for improving thermal resistance.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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