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Effects of hydrolysis conditions on the crystallinity, chemical structure, morphology, and thermal stability of cellulose nanocrystals extracted from oil palm biomass residue

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Abstract : Cellulose nanocrystals have the hydrolysis of cellulose-based oil palm biomass residues using hydrochloric acid under sonication-hydrothermal conditions. Characterization of cellulose nanocrystals performed by analysis of FT-IR spectroscopy, SEM microgram, diffraction X-RD, and thermal analysis. FT-IR showed the occurrence elimination of lignin and hemicellulose in cellulose nanocrystals spectrum. Morphology of cellulose nanocrystals show a more compact structure and surface morphology arranged regularly compared with cellulose. High crystallinity can be obtained by hydrolysis using hydrochloric acid3 $molL^{-1}$during reaction time 2 hours. The thermal stability shows the degradation temperature (T_{max}) is high on all cellulose nanocrystals. Treatment parameters such as reaction time, reaction temperature, and the ratio of cellulosic feed stocks-acid affects the yield and crystallinity of cellulose nanocrystals.

Keywords : palm bunches, Cellulose nanocrystals, hydrolysis.

Introduction

Oil palm empty fruit bunches (EFB) is an abundant and renewable biomass in nature. The main content TKKS are cellulose, hemicellulose and lignin. Cellulose can reach 44%, 34% hemicellulose, and lignin reach 17-20%.[1] The content of cellulose contained in TKKS very potential to be produced as cellulose nanocrystals (CNCs).

CNCs present a serious concern in the world of science and technology, this material has a regular atomic arrangement, capable of producing up to 206 GPa or stiffness comparable to steel.[2]CNCs have been successfully used as an organic filler material in the biopolymer nanocomposites.[3,4,5] Remarkable progress has been made in improving the mechanical and thermal properties of biopolymers through the establishment of a network of hydrogen bonds are very solid in the matrix polimer.[6,7,8] CNCs are cellulose crystallites with at least one dimension that is equal to or less than 100 nm. These nanoparticles have received attention because it has a remarkable mechanical properties such as Young's modulus and high tensile strength.[9]

CNCs can be hydrolyzed using a strong acid, acid initially decided amorphous regions of the cellulose chain, further fragmentation to obtain nanocrystals. So far, the common methods used to produce cellulose nanocrystals is the hydrolysis of sulfuric acid, unfortunately many crystalline cellulose degradation and the resulting product shows the low thermal stability with degradation temperature maximum (Tmax) of 250 ° C, to prevent fabrication more they also introduce some processing techniques such as injection molding, mixing twin-screw and extrusion.[10,11,12]Hydrolysis of cellulose using sulfuric acid yields generally achieved less than

30%.[13,14] Hydrolysis of cotton fiber using sulfuric acid to optimize the preparation conditions can only improve the yield becomes 63.8%.[15] In addition, nanocellulose crystallinity index of 72% and particle diameter of 9.1 nm can be achieved through hydrolysis of cellulose-fiber sisal but they still apply H_2SO_4 60% as hidrolisis material.[16]

As an alternative to replace sulfuric acid, mild mineral acids as hydrochloric acid and maleic acid have been used under the ultrasonic conditions or microwave irradiation, the resulting product shows high thermal stability, but leave the liquid suspension tend to flocculation, and this can only be achieved with a yield low of 20%.[17.18] Application of endoglucanase enzymes and microwave heating has been able to improve the crystallinity of cellulose nanocrystals of recycled pulp, but the yield obtained only 38.2%,[14] then Filson and Andoh hydrolyze microcristaline recycle pulp by applying a high-power ultrasonic use maleic acid as a hydrolysis, can be obtained crystallinity 78%, but only 5% yield achieved.[19] Tang et al., reported a yield of 50.04% to 84.26% crystallinity can be achieved by applying a hydrolysis method cation-exchange resin, but the removal of the cation exchange resin with a post-treatment and repeated centrifugations very time consuming.[20]

High yield CNCs to 93.7%, with 88.6% crystallinity only can be achieved by raw materials micro-crystalline cellulose through hydrochloric acid hydrolysis under conditions hidrotermal.[21]they also can maintain the thermal degradation (T_0) up 322.5 ° C, but they use microcrystaline cellulose high crystallinity.The high yield was shown from the use of mild acidic due to the acid is able to penetrates quickly into the deep layers of the network of cellulose and hydrolyze the amorphous regions of cellulose chain, while the crystalline regions are more resistant to mild acid hydrolysis because of the strength of hydrogen bondsbetween adjacent cellulose molecules than the amorphous regions. Hydrolytic reaction is limited by the relatively short reaction time so that the acid can only degrade amorphous regions in the cellulose.[21]

Research on the hydrolysis of cellulose have been carried out as described above, but in this study, we examine the process of hydrolysis of cellulose-based biomass OPEFB.

Cellulose extract obtained in the macro size cellulose is hydrolyzed using hydrochloric acid under sonication-hydrothermal conditions to obtain CNCs. This study focused on assessing the effect of the hydrothermal reaction time and concentration of acid on the quality of CNCs. Technology development and innovation as we showed have produced CNCs with yield and high crystallinity.

Eksperimental

Materials

Biomass residue oil palmwas taken from crude palm oil processing plant. Chemical substance that was used for residue oil palm extraction is NaOH 17,5% from Merck and NaOCl 2%were purchased from PT. Bratachem.Acid solution that was used for cellulose hydrolysis is hydrochloric acid 3 mol.Liter^{-1}from Merck. Aquadest that was used for washing the CNCs is taken from PT. Bratachem.

Preparation of Cellulose

50grams ofdry weight residue oil palm was included in the17.5 wt%NaOH(1:10) w/v, and then it was extracted at 80°C for2hours. Extractthat obtainedbleachingwith250mL of2wt% NaOCl at 70°C for1hour was also performed.Then, producted obtained was filteredandwasheduntilneutrals.

Preparation of Cellulose Nanocrystals

Cellulose1:60 HCl (g/mL) was insertedin theultrasonics bath tipe SU-27 TH capasity 477(W) x 272(D) x 200(H) mm, frequencies 28 kHz, output 300 watts and heater 500 watts, during 30 minutes. After that,sample hydrolyzed in the hydrothermalParr USA pressure batch reactor, then thereactortubewas closedtightly and N_2gas was flowedinto the reactor. The reactionwas runat a temperature of110°Cwitha reaction time of0.5; 1; 2; 3; 4 and 5hours. After reaching thecellulosicsuspensionsamplingtime, the suspensionobtainedis addedsufficientdistilled watertostop theacid reaction, decantedin a bottle1to 2 days toprecipitateparticles ofcrystallinecellulose, and then washed withdistilled water untilneutral, centrifugedanddried.

Characterization

Fourier Transform Infrared Spectroscopy

The chemical structures of OPEFB and the resulting cellulose were characterized on a Nicolet 8700 FT-IR spectrophotometer. FTIR spectra were recorded in the spectral range of 4000–400 cm^{-1}.

Morphological Analysis

Morfologi permukaan dari CNCs di analisa dengan menggunakan SEM-EDX model Oxford INCA 400 voltase 15 KV.

X-Ray Difraction

The crystal structures were characterized on a Philips PZ1200 X-ray difraction (X-RD) by using Cu Kα X-rays with a voltage of 40 kV and a current of 30 mA. X-ray diffraction data were collected over an angular range of 0–50 in steps of 0,02° at room temperature. The crystallinity (Crl) of the samples was determined by Segal's method.[16,19,21,22]

$$Xc = \frac{\mathbf{I}(crystaline) - \mathbf{I}(amorf)}{\mathbf{I}(crystaline)}\ \mathbf{100\ \%}$$

where $I_{(crystalline)}$ is the intensity of the crystalline peak at the maximum at 2θ between 22 and 23 and $I_{(am)}$ is the intensity at the minimum at 2θ between 18 and 19, whereqis the corresponding Bragg angle. The crystallite sizes were estimated from the 110, 110, and 200 lattice planes of cellulose I by using the well-known Scherrer equation. [21]

$$\mathbf{D}hkl = \frac{K.\lambda}{\mathbf{B}hkl\,.\cos\theta}$$

where D_{hkl} is the crystallite size in the direction normal to the *hkl* family of lattice planes, *K* is the Scherrer constant (1.00 for equatorial reflections of rod-like or needlelike crystallites), *λ* is the wavelength of the radiation (1.54 A°), and B_{hkl} is the full width at half-maximum (FWHMLeft) in radians of the reflection of that family of lattice planes.[21]

Thermogravimetric Analysis

The thermal stability was studied using a NETZSCH TG 209 F1 thermogravimetric analyzer. The samples were heated from room temperature to 500°C at a heating rate of 25°C min^{-1} under a nitrogen atmosphere with a flow rate of 30 mL min^{-1}.

Result and Discussion

Physic Analysis

Physically the change of OPEFB may be seen in Figure1, OPEFB colors that has been treated alkali (NaOH 17,5%) becomes clearer. It showed reduced levels of lignin and hemicellulose that contained in OPEFB. Then after the hydrolysis, celullosa nanocrystal showed whiter color.

Figure 1. Physically of (a) OPEFB untreated (b) Cellulose (c) Cellulose nanocrystal

Condition Preparation Cellulose Nanocrystals

Table 1showed the yield, crystallinity, kristalite size (D_{hkl}), T_0 and T_{max}obtained by hydrochloric acid hydrolysis under sonication-hydrothermal conditions. All parameters using the ratio of acid-to-cellulose 60 mL g^{-1}, with a reaction temperature of 110 °C. Hydrolysis uses hydrochloric acid 1 mol L^{-1} and 2 mol L^{-1} at 3 hours of reaction time showed crystallinity decreasesignificantly so that the time parameter is only done up to 3 hours. While hydrolysis with hydrochloric acid 3 mol L^{-1}at the reaction time 3 hours crystallinity obtained tend to be stable so that the reaction time is continued until 4 and 5 hours. Yield CNCs-3A achieved only 74.82%, lower than the yield CNCs-1A, which reached 80.40%, but CNCs have higher crystallinity. The longer the reaction time, the yield obtained showed decreasing trend, this is due to long reaction times hydrochloric acid hydrolysis can attack the cellulose crystalline regions thus lowering the yield CNCs. According to Yu et al., hydrolytic reaction is limited by the relatively short reaction time so that the acid can only be lowered amorphous regions in the cellulose and leavingthe crystal. So that the reaction time is believed to be one of the most important parameters to be considered to improve the quality CNCs.[21]

Table 1. CNCs were prepared through different routes, analyzed by random

Sample name	**Process**	**reaction time (hour)**	**Yield**	***X-Rd***		**Thermal properties**	
				Crystallinity (Crl)	**Crystallite size (D_{hkl})**	**TGA (T_0)**	**DTG (T_{max})**
Cellulose	Ectraction	2	50.04	61.37	29.35	233.43	314.17
CNCs-1A	hydrolysis use HCl 1 mol L^{-1}	1	80.40	70.63	15.64	-	-
CNCs-1B		2	70.20	72.33	3.35	-	-
CNCs-1C		3	49.80	61.68	4.69	-	-
CNCs-2A	hydrolysis use HCl 2 mol L^{-1}	1	79.09	75.87	4.69	305.20	340.15
CNCs-2B		2	63.60	75.78	7.83	-	-
CNCs-2C		3	43.00	71.48	5.87	-	-
CNCs-3A	hydrolysis use HCl 3 mol L^{-1}	1	74.82	78.59	7.83	305.66	339.82
CNCs-3B		2	66.00	77.07	1.81	302.99	328.68
CNCs-3C		3	46.62	76.85	3.91	328.13	361.04
CNCs-3D		4	36.41	76.62	1.81	311.99	337.66
CNCs-3E		5	28.33	73.27	4.70	307.52	334.66

Crystallinity

Figure 2 shows the X-ray diffraction pattern of the cellulose and CNCs are prepared by hydrolysis of hydrochloric acid 3 mol L^{-1} with a reaction time of 1, 2, 3, 4 and 5 h under sonication-hydrothermal conditions. Crystallinity and crystallite size are listed in Table 1. All the diffraction pattern for the cellulose crystals showed peaks around $2\theta = 16^{O}$, 22^{o} and 35^{o}, minimum diffraction pattern for amorphous shows around $2\theta = 18^{o}$ and 19^{o}, which is the characterization of the cellulose structure. [21,23]

Acid concentration and reaction time greatly contributes to the quality of CNCs. Crystallinity CNCs obtained by hydrolysis of hydrochloric acid 3 mol L^{-1} was higher than the crystallinity CNCs obtained by hydrolysis of hydrochloric acid 2 mol L^{-1} and 1 mol L^{-1}, this is due to hydrochloric acid of low concentration has not been able adequately to remove amorphous regions of cellulose so that the crystallinity has not reached the maximum.Crystallinity which reaches 78.59% for CNCs-3A is believed that the hydrolysis of hydrochloric acid at a temperature of 110 °C with a reaction time of 1 hour can help adequately to remove amorphous regions of cellulose. Although crystallinity CNCs-3B dropped to 77.07%, CNCs-3C dropped to 76.85% and CNCs-3D dropped to 76.62%, this is because the reaction time is too long can weaken a small fraction of crystalline cellulose and degraded into glucose so that the crystallinity down. According to Yu et al, an acid treatment with a long time on the cellulose can be debilitatingcrystalline regions, even resulting in carbonization CNCs.[21] Overall CNCs hydrolyzed by hydrochloric acid 3 mol L^{-1} shows the crystallite size is below 7.83 nm, this proves that sonication-hydrothermal processes are applied very effectively to minimize the size of crystalline cellulose.

All CNCs show maximum crystal diffraction peaks located at the angle 2θ = 22.6° ± 0.2 with *002* lattice planes, which shows crystalline cellulose I. Cellulose I indicated at an angle 2θ which is located in a position 22° and the absence doublet at that position. [24,25,26]At an angle of 2θ = 35° all diffraction pattern still shows a low peak of crystalline cellulose, this suggests that the hydrochloric acid is able to retain the crystal region which is at the peak of the weak areas.The high crystallinity CNCs indicates the occurrence of deletion areas amorphous cellulose, which encourages hydrolytic cleavage of glycosidic bonds, finally releasing the individual crystals.[27,28]

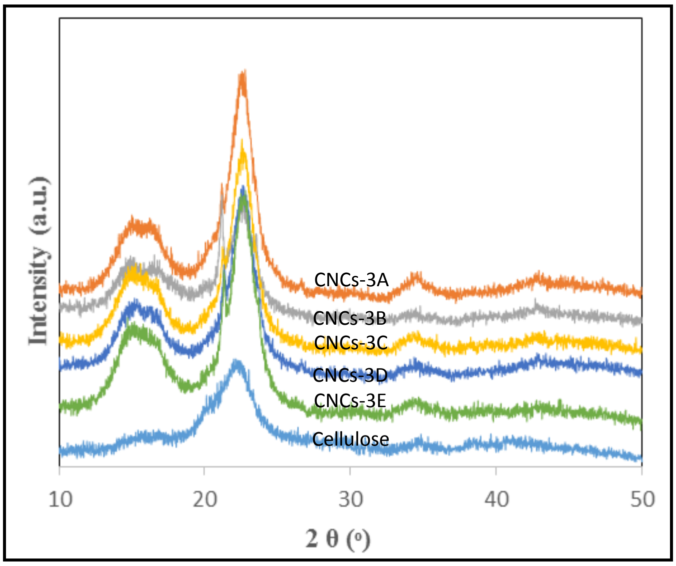


Figure 2. X-RD of cellulose and CNCs are in hydrolysis by different reaction time

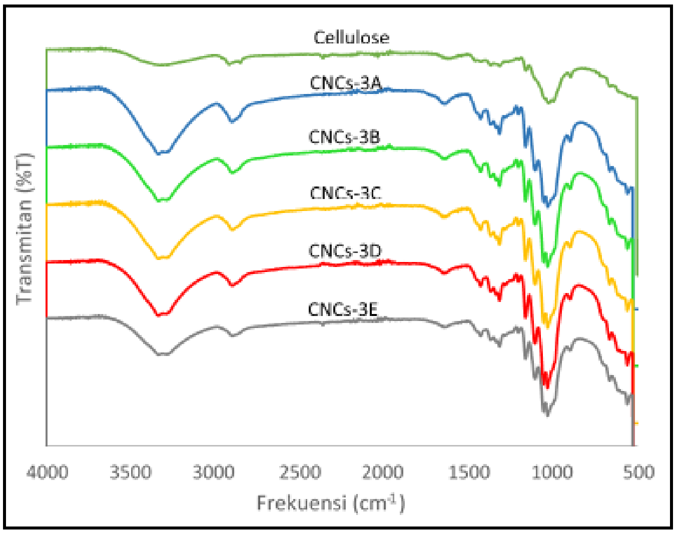


Figure 3. FTIR spectra of cellulose and CNCs hydrolyzed with different reaction times

Chemical Structure

Typical of FT-IR spectra of cellulose and CNCs are shown in Figure 3, and the placement of vibration regions are summarized in Table 2. From the spectrum showed all samples to show a broad absorption peaks located at 3250-3500 cm^{-1} which is a stretch-OH group and peak absorption at 2897-2917 cm^{-1} associated with the group $-CH_2$, whereas the absorption peak of 2847 cm^{-1} and 2844 cm^{-1} is an overlapping of band $-CH_2$, this peak is only found in cellulosic feedstocks, while at the CNCs this peak have been lost due to the amorphous cellulose chain termination.

Table 2. Frequency of FTIR spectra of Cellulose and CNCs

Frekuensi (cm^{-1}) dari TKKS, selulosa dan CNCs	**Nama puncak serapan**
3250–3500	O-H-bending
2917, 2914, 2897	CH_2 groups
1600-1650	O-H stretching
1300-1450	CH_2 aromatik
1238	C-O-C aril
1100 – 1160	C-O-C stretching

Absorption in the 1600-1650 cm^{-1} in the samples cellulose is an indication of the absorption of water or stretch O-H, the samples CNCs absorption peaks are already getting smaller this is because the crystal structure is already happening removal of water so it no longer binds to O-H, according to Joharthis peak indicates the bending form water molecules due to a strong interaction between the cellulose and air.[29]Peak absorption at regionof 1300-1365 cm^{-1} in all samples **is** vibration bandof C-H and C-O were associated with an aromatic ring polysaccharide, an absorption band is in accordance with the analyzed by Nacos.[30]Absorption peaks that has been seen sharp at 1100 cm^{-1}-1160 cm^{-1}, contained in cellulose and CNCs spectrum caused by the deformations of vibration C-H and pyranose C-O-C dominan.[31]The changes of spectrum characteristic in the cellulose and CNCs showed that there has been a removal hemicellulose and lignin. CNCs showed increased intensity in the bands 1050 cm^{-1} which shows the pyranose ring stretching C-O-C, it implies an increase in the value of the crystal selulosa.[18] According to Li Absorption peaks at 896 cm^{-1} is a C-H vibration of the lowest of the cellulose (vibration anomeric, specifically to β-glucosides).[27]

Morphology

The scanning electron micrograph shows the morphological changes of fiber in terms of size and level of smoothness after acid hydrolysis, as shown in Figure 4, which the acid hydrolysis has changed the morphology CNCs compared to cellulose-OPEFB**.**The time and the reaction temperature, the ratio of raw materials; acid and the properties of cellulosic raw material will determine yield and size distribution of CNCs.

Figure 4(a) shows the individual fibers of uniform, this indicates the occurrence removal of hemicellulose and lignin. The fibers are uniformly correlated with evidence pectroscopic to eliminate the cementing material around the bundle of fibers such as hemicellulose and lignin.[32,,29]Cellulose-OPEFB also show a smooth fiber surface. Meanwhile, CNCs-3A showedthat fibrils more regularly shaped comparedto CNCs-3B and CNCs-3C are often formed aggregated and surface morphology are rough. This explains the fact that hydrolysis by hydrochloric acid in a relatively short time can remove amorphous components of cellulose and hold the cellulose crystal region so produce more smoothness dimension CNCs**.** According to previous research roughness of product of nanocrystals often occurs through the acid hydrolysis with long time.[33]Micrographs showing morphological changes as it is influenced by the size and degree of smoothness of the fiber, so that the smoothnessof fibers need to be considered to provide a better surface structure. The fibers are shown in Figure 4 is a typical form of cellulose and CNCs morphology.

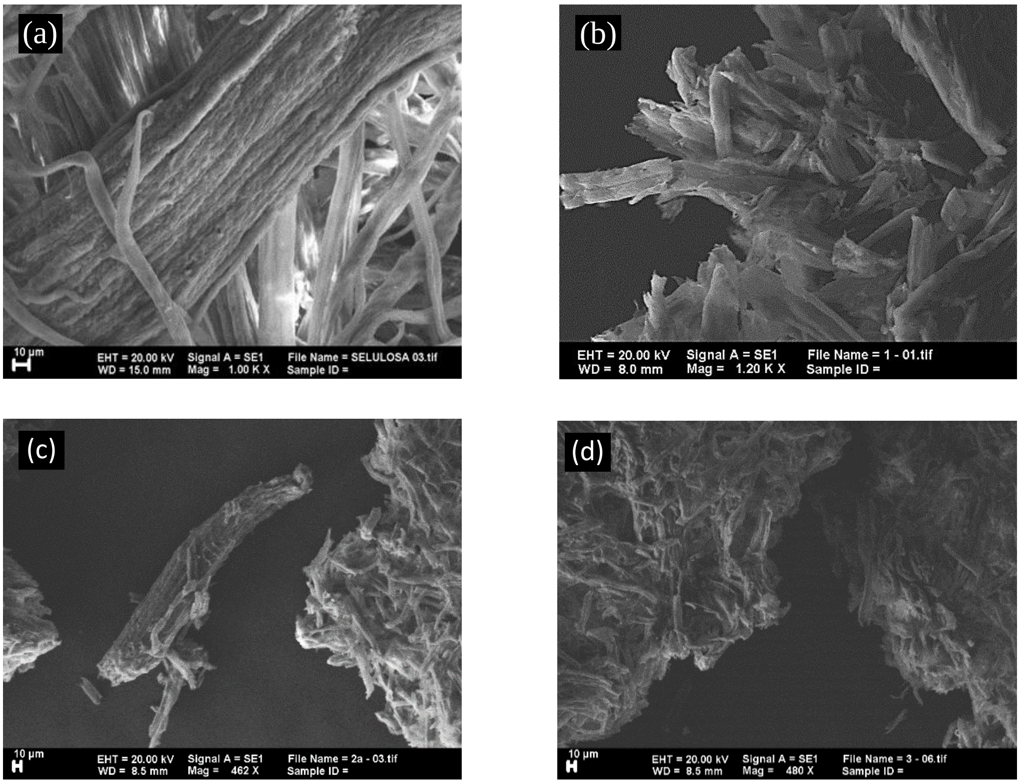
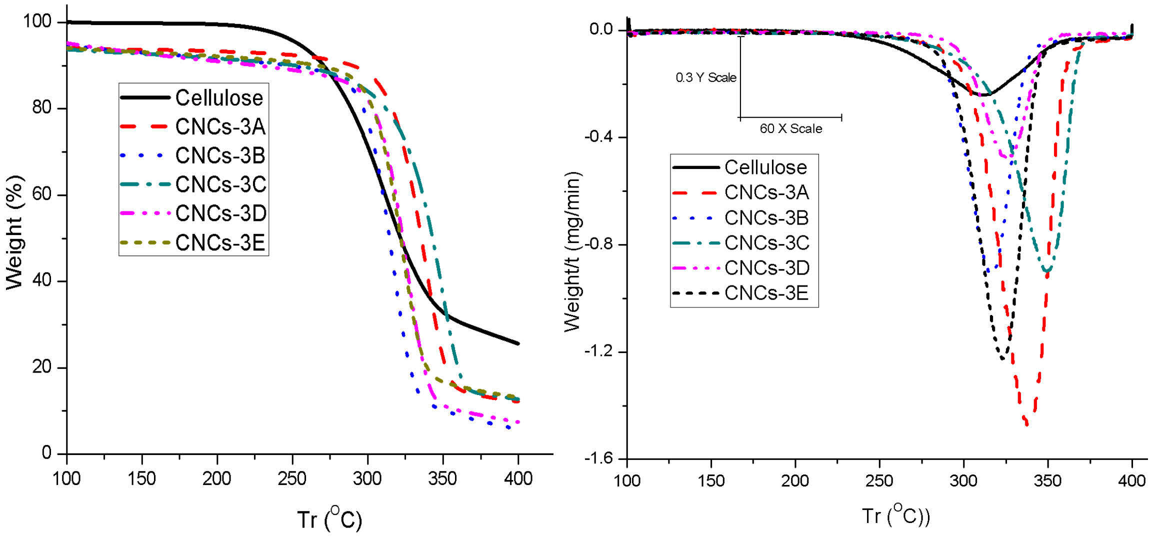


Figure 4. MicrographsSEM of(a) Cellulose-OPEFB, (b) CNCs-3A, (c) CNCs-3B, and (d) CNCs-3C



(a) (b)

Figure 5. Typical (a) TGA and (b) DTG of Cellulose and CNCs obtained through hydrochloric acidhydrolysis with different reaction times

Thermal Stability

Figure 5 displays the curve thermogravimetric analysis (TGA) and derivative calorimetry (DTG) of CNCs were prepared through a different route under sonication-hydrothermal conditions, temperature degradation onset (T_0) and temperature decomposition maximum (T_{max}) are listed in Table 1. Thermal degradation of cellulose involves depolymerization, dehydration and decomposition glycosyl units followed by the formation of residue hangus.[21] Compared with CNCs, phenomena of cellulose degradation temperature started at a lower temperature is 233.43 °C. Temperature degradation CNCs-3A begins at a temperature of 305.66 °C and decomposes at temperatures of 339.82 °C, thermal degradation of CNCs-3B is similar to CNCs-3A namely T_0 = 302.99 °C and T_{max} = 328.68 ^{o}C. Temperature degradation of CNCs-3C increase higher to 328.13 °C and temperature decomposition increase to 361.04 °C. Overall, the third CNCs have high thermal stability. This proves that the cellulose hydrolysis by3 mol L^{-1}hydrochloric acid with reaction time of 1 to 3 hours under sonication-hydrothermal conditions able to increase the temperature degradation and temperature decomposition CNCs. But to CNCs-3D and CNCs-3E temperature degradation fell to 311.99 °C and 307.52 °C, this can be explained by the fact that for the hydrolysis by reaction time is longer acid group will significantly weaken the crystal region of cellulose chain thus lowering the temperature degradation of crystalline cellulose.

The high temperature degradation can reduce the damage in the area of crystalline cellulose and reduce aggregation during netralisasi[21] and hinted CNCs very well be used as a filler to add strength nanocomposite. In addition, Figure 4(b) further shows hydrolysis with hydrochloric acid can result in formation of crystals with a relatively small size distribution, which resulted in a single peak of DTG curves, as described by Correa.[18]

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