Effect of ball milling on the production of nanocellulose using mild acid hydrolysis method

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ABSTRACT

Nanocellulose was extracted from two kinds of general cellulose feedstocks, *i.e.*, cellulose paper and cellulose powder, by coupling planetary dry ball milling with mild acid hydrolysis. The effect of ball milling time on the yield and properties of nanocellulose obtained by mild hydrolysis in lower concentration (47 wt%) of sulfuric acid was investigated in details. The obtained nanocellulose was characterized by scanning electron microscopy (*SEM*), Fourier transform infrared spectroscopy (*FTIR*), X-ray diffraction (*XRD*), and thermogravimetric analysis (*TGA*). It is found that the crystallinity and crystal size of ball-milled cellulose decreased with the increase of ball milling time, and the mild acid hydrolysis of the ball-milled cellulose resulted in the crystallinity and thermal stability of nanocellulose at the high temperature range increased but without any changes of chemical structure. It indicates that the appropriate ball-milling of cellulose feedstock could be benefit for the mild hydrolysis process for the production of high quality nanocellulose with high yield.

Keywords Nanocellulose; Cellulose; Sulfuric acid; Ball milling; Mild acid hydrolysis.

1.# Introduction

In our daily life, fabrics, ropes, paper and many other consumer goods are made of natural fibers. Most of natural fibers from plants basically consists of cellulose [1], which is the main structure of plant cell wall. Cellulose fiber generally contains two types of structures, i.e., highly ordered (crystalline) and disordered (amorphous) ones [2, 3]. Extraction of the crystalline region from microfibrillated cellulose generally results in nanocellulose.

Nanocellulose is considered as a new class of eco-material with many advantages, such as nanoscale dimension, renewability, high surface area, specific high strength and modulus, unique morphology and good optical properties. Thus, it can be used in many fields such as nanocomposite materials, drug delivery, food additive, and filling materials in rubber industry [2, 4]. That is why nanocellulose extraction from biomass is an interesting study field nowadays. To date, acid hydrolysis is one of preferential processes to remove the amorphous regions within the cellulose microfibrils, in which sulfuric acid is the most generally used acid because it produces negative charges on the particles, leading to more stable suspension [3, 5].

Many previous studies indicate that the typical concentration of sulfuric acid in hydrolysis reaction for extraction of nanocellulose is near 65 wt% [4]. Dong *et al.* extracted cellulose microcrystallite from Whatman No.1 filter paper powder (cotton cellulose) using 64 wt% of sulfuric acid with a pulp to acid ratio of 1:8.75 at 45 °C for 1 h [6]. Haafiz *et al.* isolated

cellulose nanowhiskers from microcrystalline cellulose (MCC) of oil palm biomass by using 64 wt% sulfuric acid hydrolysis with an acid to MCC ratio of 8.75 mL/g at 40 °C for 1 h [7]. Using lower concentration of sulfuric acid hydrolysis will be more attractive for nanocellulose extraction due to more environmentally friendly and less wastewater from washing step, which will decrease the production cost.

Mechanical process is one of approaches to diminish cellulosic fibers into nanocelluloses, by which the cellulose size can be reduced by splitting along the longitudinal axis of the cellulose structures via the mechanical stress [3, 8]. Planetary ball mill is such mechanical techniques, in which the artificial gravity generated by the centrifugal force can be applied to the grinding medium. It is found that the crystallinity of cellulose decreases with the dry ball mill, and as such the nanocellulose could be more easily extracted from the ball-milled cellulose[9-13].

In this study, two general kinds of cellulose, i.e., cellulose paper and cellulose powder, were selected as the raw materials for nanocellulose extraction. To improve the extraction efficiency, the raw materials were pretreated by planetary ball mill at first and then, mild hydrolysis of the ball-milled cellulose with lower concentration of sulfuric acid at lower reaction temperature for a shorter reaction time was performed. The obtained nanocellulose was characterized by using SEM, FTIR, XRD and TGA for investigation of its morphology, the change of chemical composition, crystalline allomorph, crystallinity and crystal size, and thermal stability,

respectively. It is expected that such a kind of method can effectively extract nanocellulose from cellulose feedstock.

2.# Material and methods

2.1 Materials

Grade 3MM Chr cellulose chromatography paper (Whatman), 38 μm (400 mesh) size of cellulose powder (Wako), and sulfuric acid aqueous solution (47 wt%) were purchased from Wako Pure Chemical Industries *Ltd.*, Japan. The cellulose paper (*CPP*¹) was crushed by blender for 30 seconds to small pieces prior to use while the cellulose powder (*CPD*²) was used as received.

2.2 Ball milling pretreatment

Cellulose materials were ball-milled with an ITO LP-1 Planetary pot mill. 80 mL of jar with the three different diameters of zirconia ball (10, 5, and 2 mm) was used, in which the ball to material weight ratio (*BMR*) was 12:1 and the weight ratio of the balls with 10, 5, and 2 mm diameters was 5:4:3. In the preliminary experiments, it is found that high rotation speed resulted in very low nanocellulose yield. Thus, in this study, a relative low rotation speed of 300 rpm was

¹ *CPP*: Cellulose Paper

² *CPD*: Cellulose Powder

selected. The ball milling was carried out for 0.5, 1, 2, and 3 h at room temperature in order to investigate the effect of ball milling time. The pretreated cellulose materials are defined as Ball-milled Cellulose Paper ($BMCP P_x$ ³) or Ball-milled Cellulose Powder ($BMCP D_x$ ⁴) corresponds to the type of material, while x is the ball milling pretreatment time ($x = 0.5, 1, 2$, or 3 h).

2.3 Acid hydrolysis

Acid hydrolysis was performed by using a low concentration of sulfuric acid aqueous solution (47 wt%). 8.8 mL of acid/1 g of cellulose materials was used in each case. The reaction temperature was controlled at 45 °C with a water bath and the mixing speed was set at 600 rpm. The reaction time is fixed at 90 minutes.

The sulfuric acid hydrolysis was stopped by adding 10-fold cold distilled water (4 °C). The suspension was centrifuged at 8500 rpm for 10 minutes to get the precipitates and simultaneously remove out the excess acid. The precipitate was then suspended in distilled water, followed by centrifugation. This process was repeated until the neutral pH was achieved. Subsequently, the suspension was frozen in freezer at -30 °C, then dried in freeze-dryer. The dried product was stored in vacuum for further characterizations. The obtained products are

³ $BMCP P_x$: Ball-milled cellulose paper at x h of ball milling time

⁴ $BMCP D_x$: Ball-milled cellulose powder at x h of ball milling time

defined as Nanocellulose from cellulose materials; Nanocellulose from cellulose paper (*NCCPP*⁵), Nanocellulose from cellulose powder (*NCCPD*⁶), Nanocellulose from ball-milled cellulose paper at x *h* of ball milling pretreatment time (*NCBMCPP_x*⁷), and Nanocellulose from ball-milled cellulose powder at x *h* of ball milling pretreatment time (*NCBMCPD_x*⁸).

2.4 Characterization

Surface morphologies of samples were examined by a scanning electron microscope (*SEM*, SU8010, Hitachi) at an acceleration voltage of 1.0 *kV*. A drop of diluted product suspension was deposited on the carbon tape and air-dried at 50 °C oven for 2 *h*. Then, the sample was sputter-coated with Pt at 15 *mA* for 20 seconds to avoid charging.

Fourier transform infrared spectroscopy (*FT-IR*) was recorded by using Jasco *FT/IR*-4200 infrared spectrophotometer with wavelengths in the range of 500-4000 cm^{-1} , in which the sample was ground into fine powder and mixed with KBr followed by pressing the mixture into thin pellet.

To study the crystallinity, X-ray diffraction (*XRD*) was carried out on a Rigaku Smartlab X-ray diffractometer with *Cu K α* radiation at 45 *kV* and 200 *mA* from 10-50° (2θ angle range).

⁵ *NCCPP*: Nanocellulose from cellulose paper without ball milling pretreatment

⁶ *NCCPD*: Nanocellulose from cellulose powder without ball milling pretreatment

⁷ *NCBMCPP_x*: Nanocellulose from ball-milled cellulose paper at x *h* of ball milling time

⁸ *NCBMCPD_x*: Nanocellulose from ball-milled cellulose powder at x *h* of ball milling time

The crystallinity was calculated using peak height method. It is calculated from the height ratio between the intensity of the crystalline peak and the total intensity after the subtraction of the background signal (non-crystalline) according to the following equation:

$$C (\%) = 100 \times \frac{I_{200} - I_{non-cr}}{I_{200}} \quad (1)$$

where C is the apparent crystallinity [%], I_{200} is the maximum intensity of the peak corresponding to the plane in the sample with the Miller indices 200 at a 2θ angle between 22-24 degrees and I_{non-cr} represents the intensity of diffraction of the non-crystalline material, which is taken at an angle of about 18° (2θ) in the valley between the peaks [14].

The Scherrer equation was used to calculate the crystallite size, t (nm), which is determined perpendicular to the (200) planes for both cellulose I and cellulose II samples:

$$t = \frac{0.9\lambda}{\beta \cos \theta} \quad (2)$$

where λ is the radiation wavelength for Cu, θ is the diffraction angle, and β is the corrected angular width at half maximum intensity in radians [15].

The thermal stability of sample was determined by using a thermogravimetric analyzer (DTG-60H, Shimadzu). An average mass of 10 *mg* of the sample was put in an alumina cup and heated from room temperature to 600 °C at a heating rate of 10 °C/*min* under a nitrogen flow of

50 cm^3/min . Differential thermal gravimetry (DTG) was calculated based on TGA values using a forward finite difference method as the following equation:

$$\text{DTG} = \frac{(w_{t+\Delta t} - w_t)}{\Delta t} \quad (3)$$

where $w_{t+\Delta t}$ and w_t are the residual weight of sample at time $t+\Delta t$ and t , respectively, and Δt is the time interval for reading residual sample weight [16].

3.# Results and discussion

3.1 Product yield

The weight of final product was recorded and calculated as product yield based on 100% of raw cellulose or ball-milled cellulose materials for acid hydrolysis. The yields of all final products were tabulated and shown in **Table 1**. The average yield of nanocellulose from CPP and BMCP_{P_x} was 85.1%, while the average yield of nanocellulose from CPD and BMCPD_x was 83.7%. It is found that these obtained nanocelluloses yields are higher than those reported in other previous work with similar condition. Bondeson *et al.* isolated nanocellulose from microcrystalline cellulose by hydrolysis in 63.5 wt% sulfuric acid at 45 °C for 2 h. The yield of their obtained product was only 30% [17]. As such, mild acid hydrolysis of ball-milled cellulose can extract nanocellulose with a relative high yield. It is possible that hydrolysis of cellulose in a

higher concentration acid could result in some nanocellulose further converted to soluble molecules.

3.2 Morphological investigation

The surface morphologies of *CPP*, *BMCP_x*, *NCCPP*, and *NCBMCP_x* are shown in **Fig. 1**. Raw cellulose paper (*CPP*, **Fig. 1(A)**) showed the significant of single microfibril shape in micro scale. After ball milling pretreatment (**Fig. 1(B-E)**), the microfibril of raw cellulose paper was cracked in longitudinal axis and became to microfibril shape with smaller diameter and the size decreased with the increasing of ball milling time. As stated above, ball milling can produce high shear force from the collision between different sizes of balls as well as the friction of balls to wall [10] which leads to the extraction of long cellulose fibrils in longitudinal axis [3, 18]. From the morphologies of nanocellulose products (*NCBMCP_x*) after mild acid hydrolysis (as shown in **Fig. 1(F-I)**), the single fibril obviously became to nanoscale size, suggesting that nanocellulose was successfully extracted from cellulose paper by using the present method. However, the morphology of *NCBMCP₃* in **Fig. 1(J)** was found to be different from other *NCBMCP_x*. It is possible due to its less crystallinity as indicated in the following sections.

The surface morphologies of *CPD*, *BMCPD_x*, *NCCPD*, and *NCBMCPD_x* are shown in **Fig. S-1** in the supplementary material. Cellulose powder (*CPD*, **Fig. S-1(A)**) shows irregular shape

in micrometer scale. After ball milling pretreatment (**Fig. S-1(B-E)**), the length of cellulose powder ($BMCPD_x$) became shorter. Furthermore, after the mild acid hydrolysis, nano-sized products ($NCBMCPD_x$, **Fig. S-1(F-J)**) were obtained. It also indicated that nanocellulose can be effectively extracted from cellulose powder using the present method.

3.3 FT-IR Spectroscopic Analysis

To investigate the change of chemical compositions occurred during the extraction process, FTIR spectroscopy was measured. **Fig. 2** shows FT-IR spectra of (A) CPP, (B) $BMCP_3$, (C) $NCCPP$, (D) $NCBMCP_{0.5}$, (E) $NCBMCP_1$, (F) $NCBMCP_2$, and (G) $NCBMCP_3$. It should be noted that all spectra showed the same absorption peaks at around 3600-3100, 2900, 1430, 1369-1330, 900 cm^{-1} , which are associated with the native cellulose type I. The broad peak at around 3600-3100 cm^{-1} attributed to the free O-H stretching vibration of the OH groups while the absorption peak at around 2900 cm^{-1} indicated the CH₂ groups of cellulose molecules. The peak appearing at 1430 cm^{-1} related to CH₂ bending of the intermolecular hydrogen attraction at the C₆ group. The absorption peaks in the region of 1369-1330 cm^{-1} corresponded to the C-H and C-O groups of polysaccharides. The detected peak at 900 cm^{-1} associated with the C-H rocking vibration of β -glycosidic linkages between glucose units in cellulose [7, 19]. From all FTIR spectra, one can see that there is no significant differences in chemical compositions among cellulose paper (**Fig. 2(A)**), ball-milled cellulose paper (**Fig. 2(B)**), and nanocellulose products

(**Fig. 2(C-G)**). It indicated that the mechanical ball milling pretreatment **had** no effect on the change of chemical composition. Moreover, the chemical compositions of nanocellulose products were also not changed after **the mild acid hydrolysis reaction**.

FTIR spectra related to cellulose powder are shown in **Fig S-2** which describes the chemical compositions of (A) *CPD*, (B) *BMCPD*₃, (C) *NCCPD*, (D) *NCBMCPD*_{0.5}, (E) *NCBMCPD*₁, (F) *NCBMCPD*₂, and (G) *NCBMCPD*₃. All spectra also showed the similar chemical composition peaks of the native cellulose type I, which are the same as cellulose paper (**Fig. 2**). Moreover, there are also no significantly new compositions found in ball-milled cellulose powder and nanocellulose products. These results are agreement with the results obtained by **other** researchers. For example, Li *et al.* studied sulfuric acid hydrolysis of mulberry branch-bark cellulose, **and found that the** chemical composition of cellulose whiskers had no difference when compared with that of raw cellulose fibers [20].

3.4 X-ray diffraction

The crystalline allomorphs, crystallinity, and crystal size of samples can be examined by X-ray diffraction. **Fig. 3** shows *XRD* patterns of (A) *CPP*, (B) *BMCPP*_{0.5}, (C) *BMCPP*₁, (D) *BMCPP*₂, and (E) *BMCPP*₃. From *XRD* patterns of cellulose paper and its various ball-milled ones, the characteristic peaks were revealed at $2\theta = 15^\circ$, 16.7° , 22.9° , and 34.7° which

corresponded to the crystalline planes of -110, 110, 200 and 004 of the cellulose type I [21, 22]. The crystallinity and crystal size **were** calculated by *Eqs. 1 and 2*, respectively, and the results were tabulated in **Table 2**. Comparing with raw materials, the crystallinity and crystal size of ball-milled cellulose paper decreased with the increasing of ball milling time. The materials were cracked to smaller size after ball-milling, as supported by *SEM* results, which decreased the crystalline region, but increased the amorphous region [12]. For nanocellulose from cellulose paper obtained from the mild acid hydrolysis, the *XRD* patterns are shown in **Fig. 4**. All five nanocellulose products, i.e., (A) *NCCPP*, (B) *NCBMCPP*_{0.5}, (C) *NCBMCPP*₁, (D) *NCBMCPP*₂, and (E) *NCBMCPP*₃, also showed the similar characteristics of cellulose type I. This implied that the crystalline allomorphs was not changed after the mild acid hydrolysis. From the calculated crystallinity and crystal size **shown** in **Table 2**, it is found that the crystallinity and crystal size of products increased to some extent when compared with the raw materials. This can be ascribed to the reduction and removal of amorphous cellulosic part during the acid hydrolysis reaction [23]. Thus, **the remaining part in the nanocellulose should be** mainly consisted of crystalline region **which led to** the increasing of crystallinity when compared with the ball-milled cellulose paper.

For the nanocellulose obtained from cellulose powder, **Fig. S-3** shows *XRD* patterns of (A) *CPD*, (B) *BMCPD*_{0.5}, (C) *BMCPD*₁, (D) *BMCPD*₂, and (E) *BMCPD*₃. One can see that all peaks showed the characteristic peaks at $2\theta = 16^\circ$, 22.8° , and 34.7° which **also** indicated the crystal

structure of cellulose type I [7]. In contrast, the characteristic peak of cellulose type I at $2\theta = 22.8^\circ$ significantly decreased with the increase in the ball-milling time. This significant decrease is also shown by the calculated crystallinity and crystal size in **Table 2**. It can be found that, for the products related to the ball milling time longer than 2 h, the crystallinity decreased more than 50% when compared with that of cellulose powder. This should be also resulted from the ball-milling since the mechanical energy from the friction of balls could transfer to the cellulose and affect its crystalline structure [10, 11]. Moreover, this result is in agreement with the study of Avolio *et al.* in which they used the dry ball milling to treat Arbocel *BWW40* cellulose fibers for 2, 4, 8, 15, 30, and 60 *min*, and found that the cellulose I crystallinity index and cellulose crystallinity decreased with the increase in ball milling time [11]. For nanocellulose products from cellulose powder, the *XRD* patterns are shown in **Fig. S-4**, which describes the characteristic peaks of (A) *NCCPD*, (B) *NCBMCPD_{0.5}*, (C) *NCBMCPD₁*, (D) *NCBMCPD₂*, and (E) *NCBMCPD₃*. The crystal structure of cellulose type I was also found in all nanocellulose products. Furthermore, the crystallinity and crystal size of all products increased when compared with those of raw material (**Table 2**). These results showed the same trend as those nanocelluloses extracted from cellulose paper.

From these *XRD* results, it can be summarized that nanocellulose from cellulose paper as well as cellulose powder showed the identical crystalline peak as the original celluloses but with higher intensity. This can be clarified that the ball-milling pretreatment followed by the mild acid

hydrolysis can preserve the cellulose allomorph, while the crystallinity and crystal size can be improved from the effective removal of the amorphous region. This could result in higher strength and modulus of elasticity in the obtained nanocellulose [22, 24].

3.5 Thermogravimetric analysis

To investigate the thermal stability of samples, thermogravimetric analysis (*TGA*) was used. The obtained *TG* and *DTG* curves of *CPP*, *BMCPP*₃, *NCCPP*, *NCBMCPP*_{0.5}, *NCBMCPP*₁, *NCBMCPP*₂, and *NCBMCPP*₃ are shown in **Figs. 5** and **6**, respectively. The thermal degradation data and the residual weight at 600 °C are tabulated in **Table 3**. For all samples, the initial weight loss started from room temperature (30 °C) to 125 °C with a mass loss about 5 wt%. This small weight loss corresponded to the evaporation of adsorbed water and/or the low molecular weight compounds on the surface [25]. For cellulose paper (*CPP*), the main thermal decomposition occurred at around 270-410 °C with the maximum degradation temperature of 370 °C and 87 wt% of weight loss. This stage related to the degradation of cellulosic material. The remaining residue at 600 °C was about 6 wt%. For *BMCPP*₃, the characteristic of thermal degradation peak was similar to that of *CPP*, which consisted of one decomposition stage at 360 °C. This can be concluded that the ball milling had no significant effect on the thermal stability of cellulose paper. In contrast, for nanocellulose products, *NCCPP*, *NCBMCPP*_{0.5},

NCBMCPD₁, *NCBMCPD₂*, and *NCBMCPD₃*, the decrease in the temperature of the maximum mass loss rate was found at around 200-420 °C with the maximum degradation temperature around 340-350 °C and around 75 wt% of weight loss. This is because the cellulose paper and ball-milled cellulose before acid hydrolysis contains more amorphous region when compared to its nanocellulose products, as supported by *XRD* results. In other way, the decreasing of particle size to nanometer led to the increasing of surface area which made thermal degradation easily occurred at lower temperature [26]. Moreover, the remaining residues at 600 °C for nanocellulose products were about 11-15 wt% which are higher than those of cellulose paper and its ball-milled product. This implied that most of the crystalline region of nanocellulose product performed as a flame resistant at high temperature. It is similar as the results reported by Mandal and Chakrabarty, in which the *TG* of nanocellulose from sugarcane bagasse showed the main thermal degradation at 373 °C, while that of cellulose started degradation at 385 °C [19]. Moreover, the remaining residues were 15.58 wt% for nanocellulose and 7.68 wt% for cellulose.

TG and *DTG* curves of *CPD*, *BMCPD₃*, *NCCPD*, *NCBMCPD_{0.5}*, *NCBMCPD₁*, *NCBMCPD₂*, and *NCBMCPD₃* are also shown in **Fig. S-5** and **Fig. S-6**, respectively. The thermal properties are also tabulated in **Table 3**. The characteristic curve of *CPD* had no significantly different from that of *CPP* because of their similar cellulose-based structure. The main thermal degradation occurred at 200-410 °C with the maximum decomposition temperature

of 372 °C and a mass loss of 80 wt%. Meanwhile, *BMCPD*₃ showed the parallel curves with a little lower value of 360 °C in the maximum thermal degradation peak and the mass loss of 80 wt%. From this result, it can be also concluded that the pretreating of cellulose powder by planetary ball-milling with 300 rpm in 3 h had no significant effect on the thermal stability of cellulose powder. For the nanocellulose, the maximum decomposition temperature was decreased to 300-330 °C with the mass loss around 75 wt%. The remaining of residue at 600 °C was around 14 wt% which was higher than that of raw cellulose powder due to the higher crystallinity of nanocellulose.

From *TG* and *DTG* results, it can be concluded that nanocellulose from hydrolysis of cellulose or ball-milled cellulose by using 47 wt% sulfuric acid in mild condition had higher thermal stability at high temperature when comparing with the raw cellulose material. This phenomenon should be resulted from the higher of crystallinity of nanocellulose which acted as the flame resistant at high temperature [19].

4. Conclusions

Ball milling pretreatment followed by mild acid hydrolysis can extract nanocellulose from cellulose paper and cellulose powder with a high yield. The pretreated cellulose with ball milling showed the smaller diameter size which can promote the mild acid hydrolysis. The morphologies

of nanocelluloses were significantly different from cellulose materials by decreasing to nanometer scale without any new chemical composition occurred. Comparing with the cellulose and ball-milled cellulose materials, the crystallinity and crystal size of nanocellulose increased due to the removal of amorphous phase from the cellulose structure. The maximum decomposition temperature of nanocellulose became lower but the remaining residue over 600 °C was higher than those of cellulose and ball-milled cellulose materials. The present method was identified to be useful for the extraction of nanocellulose from cellulose with high yield and quality.

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Table captions

Table 1 Nanocellulose product yields

Table 2 Crystallinity and crystal size of samples

Table 3 Thermal properties of samples

Figure captions

Fig. 1 SEM images of (A) CPP, (B) BMCPP_{0.5}, (C) BMCPP₁, (D) BMCPP₂, (E) BMCPP₃, (F) NCCPP, (G) NCBMCP_{0.5}, (H) NCBMCP₁, (I) NCBMCP₂, and (J) NCBMCP₃.

Fig. 2 FTIR spectra of (A) CPP, (B) BMCPP₃, (C) NCCPP, (D) NCBMCP_{0.5}, (E) NCBMCP₁, (F) NCBMCP₂, and (G) NCBMCP₃.

Fig. 3 XRD patterns of (A) CPP, (B) BMCPP_{0.5}, (C) BMCPP₁, (D) BMCPP₂, and (E) BMCPP₃.

Fig. 4 XRD patterns of (A) NCCPP, (B) NCBMCP_{0.5}, (C) NCBMCP₁, (D) NCBMCP₂, and (E) NCBMCP₃.

Fig. 5 TG curves of CPP, BMCPP₃, NCCPP, NCBMCP_{0.5}, NCBMCP₁, NCBMCP₂, and NCBMCP₃.

Fig. 6 DTG curves of CPP, BMCPP₃, NCCPP, NCBMCP_{0.5}, NCBMCP₁, NCBMCP₂, and NCBMCP₃.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Table 1

Products	Yield (%)
<i>NCCPP</i>	89.3
<i>NCBMCPP</i> _{0.5}	84.8
<i>NCBMCPP</i> ₁	87.9
<i>NCBMCPP</i> ₂	86.0
<i>NCBMCPP</i> ₃	77.5
<i>NCCPD</i>	81.1
<i>NCBMCPD</i> _{0.5}	83.5
<i>NCBMCPD</i> ₁	83.1
<i>NCBMCPD</i> ₂	83.7
<i>NCBMCPD</i> ₃	87.1

Table 2

Materials	Crystallinity (%)		Crystal size (nm)	
	Raw materials	NC Products	Raw materials	NC Products
<i>CPP</i>	91.1	94.4	12.3	12.9
<i>BMCPD_{0.5}</i>	89.0	93.3	11.2	12.1
<i>BMCPD₁</i>	87.4	92.7	10.5	10.8
<i>BMCPD₂</i>	81.0	89.5	9.5	10.4
<i>BMCPD₃</i>	68.6	84.8	8.5	11.1
<i>CPD</i>	81.8	82.7	8.1	8.1
<i>BMCPD_{0.5}</i>	67.9	79.2	5.6	7.6
<i>BMCPD₁</i>	56.1	69.5	3.8	5.3
<i>BMCPD₂</i>	33.6	65.5	2.7	4.7
<i>BMCPD₃</i>	18.0	59.8	1.6	3.8

Table 3

Materials	Main thermal degradation range (°C)	Max decomposition temperature in each stage (°C)	Weight loss in each stage (%)	Residual weight (%) at 600 °C
<i>CPP</i>	270-410	370	87	6
<i>BMCPP₃</i>	270-410	360	83	7
<i>NCCPP</i>	200-420	350	74	15
<i>NCBMCPP_{0.5}</i>	200-420	350	76	12
<i>NCBMCPP₁</i>	200-400	345	76	9
<i>NCBMCPP₂</i>	200-420	345	78	11
<i>NCBMCPP₃</i>	200-290	250	22	14
	290-420	340	51	
<i>CPD</i>	200-410	372	80	12
<i>BMCPD₃</i>	200-400	360	80	10
<i>NCCPD</i>	220-450	315	62	18
<i>NCBMCPD_{0.5}</i>	210-470	330	74	15
<i>NCBMCPD₁</i>	210-470	325	78	12
<i>NCBMCPD₂</i>	200-290	270	26	14
	290-470	325	48	
<i>NCBMCPD₃</i>	210-340	300	50	12
	340-470	365	25	

Graphical abstract