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Enhancement in the yield and properties of cellulose nanocrystals by two-batch addition of ammonium persulfate

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Abstract

The yield, properties and the reinforcement performance of the resultant CNCs under different modes of adding ammonium persulfate (APS) were investigated. In the two-batch mode, the rate coefficient of the APS decomposition was a bit twice as great as the one in single-batch mode for a specific amount of APS, and the second addition of aliquot portion of APS at 4 h resulted in the most significant enhancement in yields and quality of the resultant CNCs of all two-batch modes. At this condition, the total CNC yield could increase by 36%. Meanwhile, the expected lengths and their aspect ratios of the CNC1 and the CNC2 increased by 20.7 and 40.0%, 103.5 and 141.0%, respectively. Furthermore, the dimension polydispersity in their length and width decreased significantly. Their crystalline index of the CNC1 and the CNC2 decreased by 6.3 and 1.5% %, but the onset degradation temperature increased by about 5 °C. Additionally, the tensile modules, strength and toughness of PVA film increased by 16.0, 20.0, and 70.5 % for the CNC1, by 41.3, 36.0, and 78.2% for the CNC2 from the two-batch mode at incorporation of 1% the CNCs compared to the responding CNCs obtained in single batch mode. Therefore, these findings suggested

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that the batched addition of APS could efficiently improve the extraction of high-quality CNCs.

Keywords:

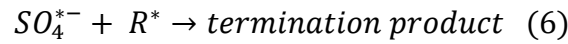
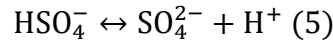
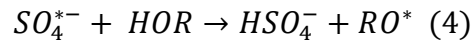
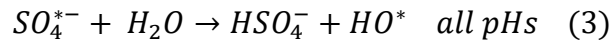
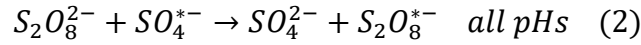
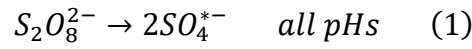
ammonium persulfate, addition mode, cellulose nanocrystal, yield, properties

Introduction

Ammonium persulfate (APS), a mild, cheap, an environmentally nontoxic oxidant, has been used as an initiator in free-radical polymerization in aqueous medium (Block 2005, Syuji, Soichiro et al. 2010). In recent years, there has been a growing interest in using APS for the extraction of nanocellulose from cellulosic materials because the method needs no removal of non-cellulosic contents such as lignin and hemicellulose using alkaline or bleaching agents as pretreatment (Jiang, Wu et al. 2017, Khanjanzadeh and Park 2021, Haunreiter, Dichiaro et al. 2022). Additionally, the side-products, commonly formed under strong acids, has been shown to not be present in the spent APS liquor (Leung, Hrapovic et al. 2011). All literatures reported above indicated that CNCs were commonly extracted under the temperature from 60 to 80 °C, the reaction time from 16 to 24 h, and the APS concentration from 1 to 2 M. Additionally, it was reported that APS concentration had an important influence on the CNCs properties, such as their diameter, aspect ratio, crystallinity, and thermal stability (Zaini, Febrianto et al. 2019). Meanwhile, the formation of the CNCs from cellulosic materials using APS was a liquid-solid reaction in series. The APS accessibility to the starting materials affected the yield and the properties of the resultant CNCs. In our previous work, the reaction time was

decreased to 10 h, and APS concentration declined to 0.6 M by optimizing APS accessibility to the starting materials (Chen, Xie et al. 2023).

It is well-known that multiple reaction steps (presented immediately below) are involved in the entire process for persulfate group conversion. However, the primary reaction step (1), being rate determining (House 1962), is characteristic of all persulfate oxidations and may be initiated by impurities in the solution, dust, or light and heat. And then, a sequence of reactions (2-6) may follow it.



The persulfate reaction in an unbuffered solution usually lowers the solution pH due to the reactions 3 and 5. (House 1962, Goulden and Anthony 1978, Liang, Huang et al. 2008)

It was reported the rate coefficient of the reaction 2 was $7.31 \times 10^5 \text{ L.mol}^{-1}.\text{s}^{-1}$, but the one of the reaction 1 only was $2.25 \times 10^{-5}.\text{s}^{-1}$ (Herrera-Ordonez 2022). It was suggested that higher concentration of $S_2O_8^{2-}$ in reaction medium was more favorable for the reaction 2 than for the reaction 1, eventually, decreasing the efficiency of APS and affecting the properties of the obtained CNCs. The reaction kinetics for the release of CNCs from cellulosic materials using APS was too difficult to be

investigated at present. However, it was known the amount of used APS had an important influence on the CNC yield and its properties (Haunreiter, Dichiara et al. 2022). A certain amount of redox potential was needed to oxidize a given amount of cellulose. When a given amount of APS was introduced to the reaction system in several separate batches, $S_2O_8^{2-}$ could be maintained at a relatively lower concentration, reducing the side-reaction of persulfate radicals and the overreaction of the existing CNC particle. Therefore, it was assumed that the CNCs yield and their properties could also be improved. To the best of our knowledge, research has not been reported about engineering the CNCs yield and their properties by the different modes of adding PAS so far. Therefore, this research would give us more insight into the relationship between the method of adding APS with the CNCs yield and their properties.

This paper aims to investigate if lowering the concentration of APS in reaction medium could improve the yield and properties of the CNCs. To achieve this purpose, the APS decomposition kinetics was investigated at different modes of adding APS, and then the yield and properties of the CNCs were examined carefully in these modes. The properties, including the carboxyl content, the zeta potential, the dimensions, and the size dispersity, play a significant role in their commercial applications. Additionally, their reinforcement performance was primarily evaluated.

2. Experimental section

2.1 Material

The dried hard-wood pulp (HWP) board (α -cellulose, 95.5 %; hemicellulose, 3.2 %, residual lignin, 0.8 %, ash, 0.5 %) was supplied by Kunshan Paper Industry Co. (Jiangsu, China). Hydrochloric acid (HCl; 36–38 %), sodium hydroxide (NaOH; $\geq$ 96 %), and ammonium persulfate (APS; $(\text{NH}_4)_2\text{S}_2\text{O}_8$; $\geq$ 98 %) were supplied by Nanjing Chemical Reagent Co., Ltd. (Nanjing, Chain). A beaten HWP with a beating degree of $25 \pm 2.1^\circ\text{SR}$ (Chen, Xie et al. 2023) was used as a starting material.

2.2 Kinetics of APS decomposition

In the two-batch modes a specific amount of the solid APS (for 0.6 mol.l^{-1} based on our previous work (Chen, Xie et al. 2023)) was divided into two parts in preset mass ratios and separately added to the reaction system in two stages. All experiment schemes are listed in Table 1.

Table 1 Reaction schemes

Schemes	APS concentration in 1 st stage ($\text{mol}\cdot\text{L}^{-1}$)	Reaction time in 1 st state (h)	Increment in APS concentration ($\text{mol}\cdot\text{L}^{-1}$)	Reaction time in 2 nd stage (h)
A	0.6	10	0	0
B2	0.4	2	0.2	8
B4	0.4	4		6
B6	0.4	6		4
C2	0.3	2	0.3	8
C4	0.3	4		6
C6	0.3	6		4
D2	0.2	2	0.4	8
D4	0.2	4		6
D6	0.2	6		4

The flowchart for APS addition modes is presented in Fig.S1, which shows the times for adding APS and for sampling.

A given mass of the beaten pulp and a part of the APS were added into a 250 mL breaker, and then a given mass of deionized water was introduced into the breaker to

keep a mass ratio of solid / liquid of 1/100, and APS initial concentration of 0.4, 0.3, and 0.2 mol.l⁻¹, respectively. Finally, the suspension was stirred and dispersed completely.

The reaction was carried out at a given temperature in a water bath with continuous stirring. Evaporation was prevented by covering the reactor with an aluminum foil. When the reaction times were 2, 4, and 6 hours in the first stage, another part of the solid APS was introduced to the respective reaction systems. Then, the reaction then continued at the same temperature for 8, 6 and 4 hours, respectively, to keep the total reaction time to be 10 hours.

During the reaction, about 3-5 ml reaction suspension was taken out from the reactor every 1 hour. However, the extra sampling was taken at 15 and 30 min during the 1-hour period immediately after the second adding APS. The sampled suspension immediately was put in the ice-water bath to stop the reaction and then centrifuged at Allegra 64R centrifugator (Beckman Coulter, USA.) with 16,000 rpm for 15 min. The supernatant was collected and stored in 5-mL brown EPA glass vials for the determination of the S₂O₈²⁻ concentration.

2.3 Determination of the residual S₂O₈²⁻ concentration

A UV-2802 spectrophotometer (Unic, Shanghai, China) was used for the determination of the residual S₂O₈²⁻ concentration at 352 nm. The test procedure for the calibration line was used with water/KI/NaHCO₃ solution (Liang, Huang et al. 2008), and provided in the supporting information (SI). A volume of 200 μl of

supernatant with drawn from the reacting system was used for the residual concentration.

2.4 Preparation of CNCs at different reaction schemes

Detailed procedures were the same as the ones in section 2.2. At the end of each reaction, the reactor was placed in an ice bath to terminate the oxidation.

Then, the reaction slurry was centrifuged at 1000 rpm for 10 min to remove bigger particles from the reaction medium, and the supernatant was dialyzed against deionized water until its conductivity was consistent with that of deionized water. After the dialysis, the suspension was centrifuged at 8000 rpm for 15 min. And the CNCs in this supernatant with Tyndall effect were designated as CNC1. The remaining sediment was again dispersed in deionized water and diluted to a solid content of 1 %. Then, the diluted suspension was ultrasonicated with a 13 mm probe sonicator (Q-700, Qsonoca, USA) until the appearance of the Tyndall effect. The obtained CNCs were designated as CNC2. The preparation of CNCs at the same conditions was repeated at least three times.

The colloidal suspensions of the CNC1 and CNC2 were lyophilized with Heto Powerdry LL3000 freeze dryer (Thermo, Denmark). The CNC yield was defined as the ratio of the mass of the obtained CNCs to the one of the celluloses in starting pulps. The procedures for the separation of the CNCs from the reaction suspension were presented in Fig. S2 in SI.

2.3 Characterization of the CNCs

Conductometric titrations were conducted to determine the carboxylic acid content on the CNCs (Habibi, Chanzy et al. 2006, Zhang, Sun et al. 2016), and provided in M1 in SI.

The CNCs suspension of 0.01 wt% was ultrasonically dispersed for 10 min. Their zeta potential was measured using a Zetasizer Nano ZS (Malvern Instrument, UK).

The X-ray diffraction was conducted and crystallinity index (CrI) was calculated from the ratio of the sum area of all crystalline peaks to the total area (Garvey, Parker et al. 2005, Park, Baker et al. 2010), and provided in M2 in SI.

Transmission Electron Microscopy (TEM) micrographs of CNCs were obtained by a transmission electron microscope (JEM-1400, JEOL, Japan) operating at 80 kV. At least 10 TEM images were taken for each example. The length and the width of at least 100 CNC particles were measured using Image-J software for each example. The average dimensions were reported.

Thermal stability of all CNCs samples was carried out using thermogravimetric analysis (TGA, Q5000IR, TA, USA) under a nitrogen atmosphere from 30 to 600 °C with a heating rate of 10 °C·min⁻¹.

2.4 Reinforcement performance

The PVA and its CNC composite films were prepared according to the procedures (Jahan, Niazi et al. 2019). The mechanical performance of these film was determined using INSTRON 5565 universal testing machine (INSTRON, MA, USA) (Xie, Li et al. 2024). The built-in software was used to calculate tensile strength, elongation at break, and Young's modulus.

All characterization and all measurements were repeated three times for each sample, and the averages were reported with stand errors of less than 5%.

3 Results and discussion

3.1 Decomposition kinetics of APS and its rate constants

Figure 1 shows the kinetics of the decomposition of $S_2O_8^{2-}$ (a, b, c) and its decomposition rate (d, e, f) in the different reaction schemes.

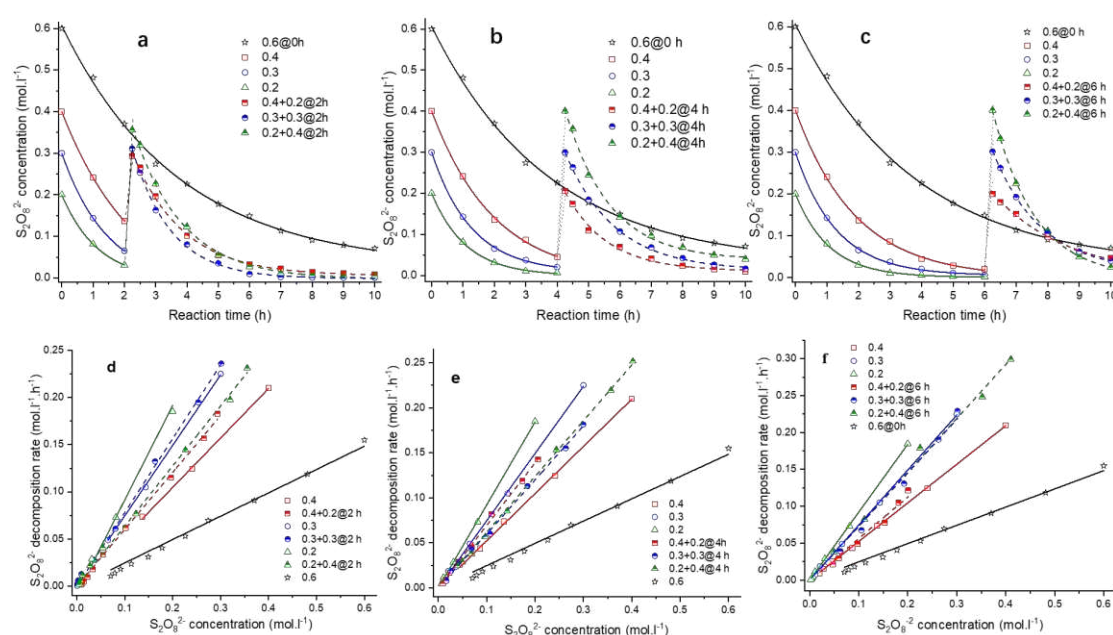


Figure 1. The kinetics of the decomposition of $S_2O_8^{2-}$ (a, b, c) and its decomposition rate (d, e, f) in the different reaction schemes, ☆: A single-batch; all outline legends: period before adding the second batch of APS; all the half-filled legends: after adding the second batch of APS; x+y@z h: x for the initial APS concentration, y for the increment in APS concentration after adding the second batch of APS, z for the reaction time before the second adding APS.

As shown in Fig. 1a, 1b, and 1c, the $S_2O_8^{2-}$ concentration decreased with the reaction time in the single scheme A (0.6@0h), and it decreased to 0.1 mol.l⁻¹ at 10 h.

Furthermore, analogous changes were observed in various two-batch schemes, yet the

concentration rapidly escalated to approximately the increased concentration following the second addition of APS. Subsequently, it quickly declined in the previously observed manner again. The ExpDecay function could be used to describe the decrease in $\text{S}_2\text{O}_8^{2-}$ concentration over time for the various schemes under consideration with the determination coefficient greater than 0.995, and the reduced Chi-Sqr value below 10^{-5} .

The decomposition rate equation was fitted based on the data in Fig. 1a, 1b, and 1c, and the fitted curves were presented in Fig. 1d, 1e, and 1f, respectively, with a determination coefficient of greater than 0.995 at 0.05 level, and the statistics and ANOVA analysis were presented in Table. S1 in SI. A linear relationship was observed between the decomposition rate of $\text{S}_2\text{O}_8^{2-}$ ($d[\text{S}_2\text{O}_8^{2-}]/dt$) and the concentration of $\text{S}_2\text{O}_8^{2-}$, indicating the decomposition rate can be adequately described by the first-order rate equation. Additionally, it was showed that the lines correlating the $d[\text{S}_2\text{O}_8^{2-}]/dt$ with the concentration of $\text{S}_2\text{O}_8^{2-}$ in the two-batch modes were all always above that in the single mode across the APS concentrations. Furthermore, the apparent rate constants were presented in Table 2.

Table 2 showed the K_{app} values were 0.52, 0.75 and 0.95 h^{-1} when the initial $\text{S}_2\text{O}_8^{2-}$ concentration was 0.4, 0.3 and 0.2 mol.l^{-1} , respectively, across the time for the second addition. It was suggested that decreasing the initial APS concentration accelerated its decomposition, thereby increasing the rate of the formation of $\text{SO}_4^{\bullet-}$. Additionally, Table 2 showed that the K_{app} values in the second stage were not identical to those in the first stage, even though the amounts of APS added in both

stages were the same. This was attributed to the component difference in the reaction medium at the beginning of two stages. Nevertheless, the K_{app} values in all the second stages were still more than twice as high as those in the single-batch mode.

Table 2 The apparent rate constants for the decomposition of $S_2O_8^{2-}$

Initial $S_2O_8^{2-}$ concentration mol.l ⁻¹	Scheme	Time at adding 2 nd batch of APS h	K_{app}	
			1 st stage	2 nd stage
			h ⁻¹	
0.6	A	\	0.25±0.005	
	B2	2	0.52±0.004	0.61±0.008
0.4	B4	4	0.52±0.004	0.7±0.009
	B6	6	0.52±0.004	0.52±0.019
	C2	2	0.75±0.005	0.78±0.007
0.3	C4	4	0.75±0.008	0.6±0.006
	C6	6	0.75±0.007	0.69±0.005
	D2	2	0.97±0.004	0.63±0.007
0.2	D4	4	0.95±0.007	0.61±0.005
	D6	6	0.95±0.007	0.77±0.02

As indicated in reactions 1 and 2, reaction 1 formed the persulfate free radicals, but these radicals could disappear due to the reaction 2 in any pHs. It was also reported that the rate of the reaction 1 was profoundly lower than the one of the reaction 2 (Herrera-Ordóñez 2022). Hence, in the single-batch mode, net $SO_4^{\bullet-}$ concentration became less than in the two-batch modes. On the contrary, in the two-batched mode, a greater pulse rate of formation of $SO_4^{\bullet-}$ relatively enhanced its adsorption on the celluloses, favorable for the APS oxidation of cellulose. Therefore, compared to the single mode, $S_2O_8^{2-}$ could be utilized at greater efficiency in two-batch mode.

3.2 Yield

The yields of the CNC1 and the CNC2 in different reaction schemes are presented in Figure 2 and the total yields (the sum of their average yields) also are displayed in Figures 2.

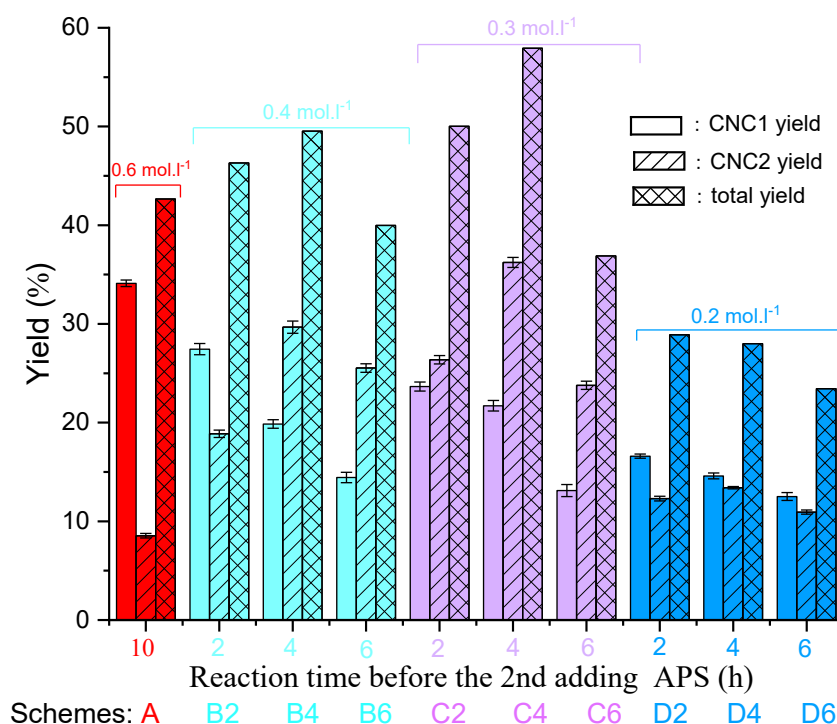
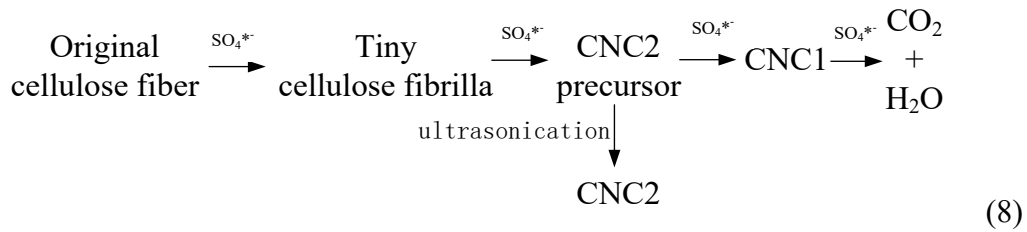


Figure 2. The CNC yields at the different addition modes and legends with or without hatches being for the types of CNCs.

As shown in Fig. 2, for scheme A, the CNC1 and CNC2 yields were 34.1 ± 0.4 , and 8.5 ± 0.3 %, respectively, obtaining a total yield of 42.6 %. However, the CNC1 yield always decreased in the two-batch modes and did more significantly with the increasing reaction time during the first stage. In contrast, the CNC2 yield significantly increased in the two-batch modes compared with the single-batch. It was shown that a maximum CNC2 yield occurred for schemes B4, C4 and D4. The CNC2 maximum yields were up to 29.7 ± 0.7 , 36.2 ± 0.6 and 13.4 ± 0.1 %, respectively, for the two-batch modes. Concurrently, the maximum total CNC yields were up to 49.5 and

57.9 %, respectively, in the schemes B2 and C2, much greater than that in the single-batch (being 42.6%). It was indicated that the total CNC yields increased by 16.2 and 35.9 %, respectively, in B4 and C4 modes. It was suggested that two-batch mode enhanced the APS efficiency.

To explain the CNC1 and the CNC2 yields shown in Fig.2, the release of CNCs was simplified to be series reactions (8) although it is overly complex.



In the single-batch, most of sulfate free radicals (SO_4^{*-}), from the thermal decomposition of APS, rapidly disappeared due to their slower formation rate and greater disappearance rate, as mentioned above, hence less residual SO_4^{*-} preferentially adsorbed on existing CNC2 precursors due to their greater surface areas, facilitating the formation of the CNC1. On the contrary, in the two-batched modes, the simultaneous local concentration of SO_4^{*-} was high, and part of the SO_4^{*-} penetrates the amorphous region of the cellulose chain to hydrolyze the β -1,4 bonds between glucose units, resulting in tiny cellulose fibrilla, thereby releasing more CNC2 precursors, favorable for the formation of the CNC2. Meanwhile, relatively less SO_4^{*-} attacked the existing CNC2, forming the CNC1. Therefore, a lower amount of CNC1 and a greater amount of CNC2 were obtained in two-batch mode than in single-batch mode.

In the scheme Ds, A significantly greater amount of APS (0.4 mol.l^{-1}) was introduced into the reaction system in the second stage, leading to a substantial reduction in the total APS reaction time throughout the entire process. Consequently, the lowest CNC1 and CNC2 yields were obtained of all two-batch modes. The total CNC yield was less than 30%. It was reported the reaction time significantly affected the yield (Marwanto, Maulana et al. 2021). Moreover, as for scheme Bs and Cs, Fig.2 showed the CNC1 yields decreased with the delay of the second addition of APS. All these decreases might contribute to the shortened reaction time for the CNC2 into CNC1 during the entire process, as previously mentioned. However, Fig.2 displayed that the CNC2 yields were up to the maximum values, 29.7 and 36.2 %, respectively, at scheme B4 and C4. Meanwhile, the total CNC yields also reached the maximum values, 49.5 and 57.9 %, respectively, for them. These results might be attributed to the balance of formation of CNC2, its conversion into CNC1 and the further mineralization of the CNC1. Therefore, it was suggested that proper mode of adding APS could lead to an optimal CNC yield.

3.3 Oxidation degree and Zeta potential

Figure 3 displays the carboxyl content and the zeta potential of the CNCs in different reaction schemes.

Fig.3a showed that the carboxyl content of the CNC1 was 1.12 mmol.g^{-1} CNCs in a single-batch. However, the carboxyl content of the CNC1 decreased in two-batch modes. Furthermore, this decrease was more pronounced with the increasing reaction time in the first stage. There might be two reasons for this: The two-batch modes led

to decrease in the total reaction time of APS. Additionally, SO_4^{*-} in the single-batch mode preferentially adsorbed on the existing CNC2 due to its greater surface area, as mentioned above, expanding the oxidation.

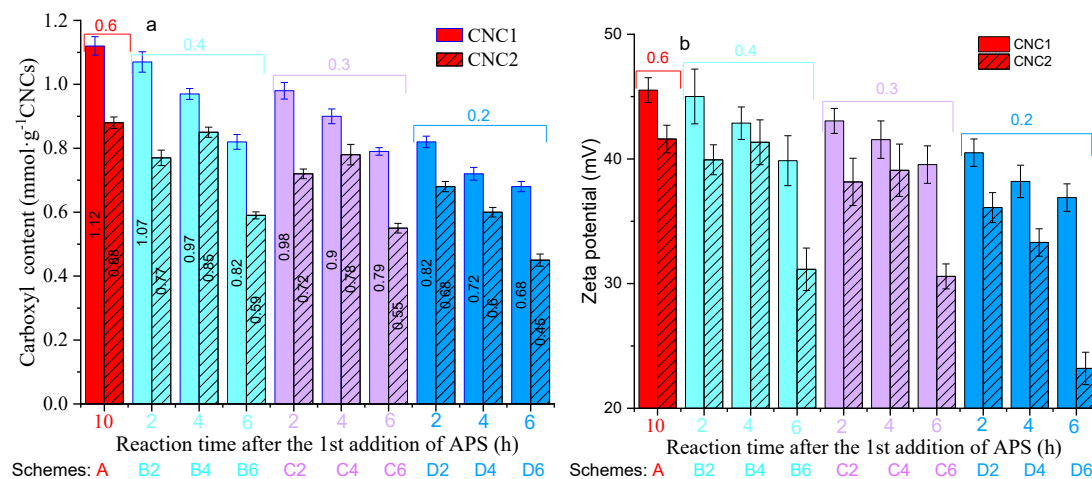


Figure 3. The carboxyl content (a), and zeta potential (b) at the different addition modes and legends with or without hatches being for the types of CNCs.

Furthermore, Figure 3a displayed the carboxyl content of CNC2 were 0.85 and 0.78 mmol.g⁻¹, respectively, being maximum of schemes B4 and C4. They were comparable to 0.88 mmol.g⁻¹ in the single-batch. The results indicated that the two-batch modes marginally decreased the carboxyl content. However, for scheme Ds, the carboxyl content of the CNC2 always decreased with the increasing time of the first phase and its maximum value was only 0.68 mmol.g⁻¹. It was attributed to the reduced total oxidation time for the specific amount of APS. It was reported that increasing APS oxidation time produced more carboxyl groups (Marwanto, Maulana et al. 2021).

Fig.3b shows the zeta potential of CNCs at various reaction schemes. The zeta potential of the CNC1 and the CNC2 were -45.5 and -41.6 mV, respectively, in a single-batch. In two-batch modes, the zeta potential profiles of the CNCs were just

like the ones of the carboxyl contents shown in Fig.3a due to the potential created by the carboxyl groups. Fig.3b showed that the zeta potential of all the CNCs was greater than -30 mV with the exception of the CNC2 at scheme D6. It exhibited a zeta potential of -23.3 mV. In general, CNC particles with zeta potential exceeding -25 mV are deemed colloidally stable due to the presence of sufficient electrostatic repulsion, hereby hindering aggregation (Mirhosseini, Tan et al. 2008, Morais, Rosa Mde et al. 2013) . Here, most CNCs from the two-batch schemes exhibited a zeta potential range of -30 to – 45.5 mV, indicating that they all formed colloidally stable suspensions in water. Therefore, it was suggested that the batched addition of APS could extract CNCs with colloidal stability.

Based on the above results, the two reaction schemes B4 and C4 created higher CNCs yields than that in a single-batch, and their zeta potential almost approached that in a single-batch. Therefore, these CNCs obtained in these two reaction schemes would be further characterized.

3.4 TEM and dimension

Fig.S3 shows the TEM images of the CNCs from A, B4 and C4 modes. Fig.S3 showed that all the CNCs showed rod-like appearance, characteristic of the CNCs, regardless of the reaction schemes. The distribution of measured length and width for each sample is displayed in Figs.4I, 4II.

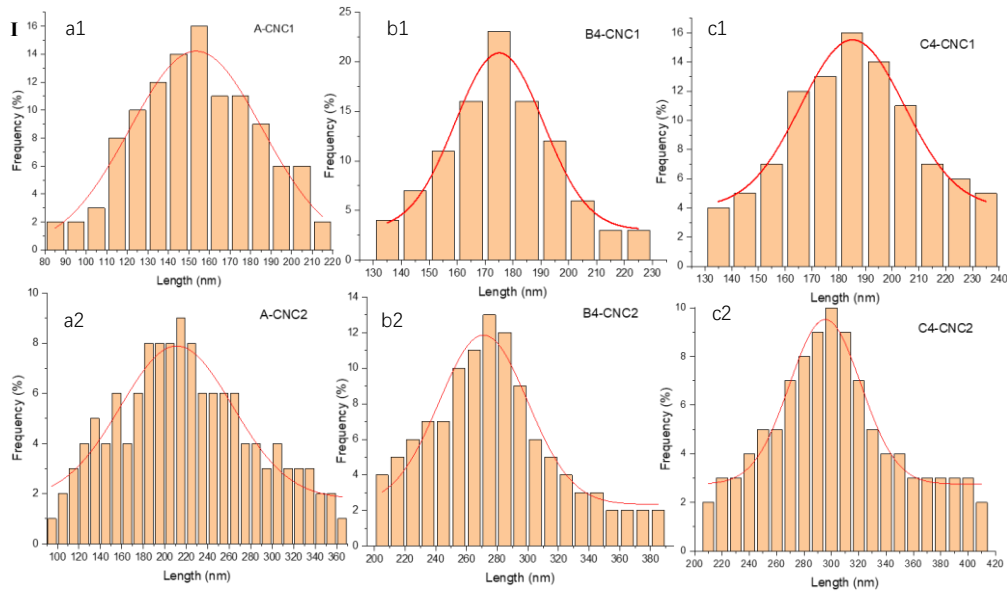


Figure 4I. The length distribution of the CNCs from the schemes A, B4, and C4

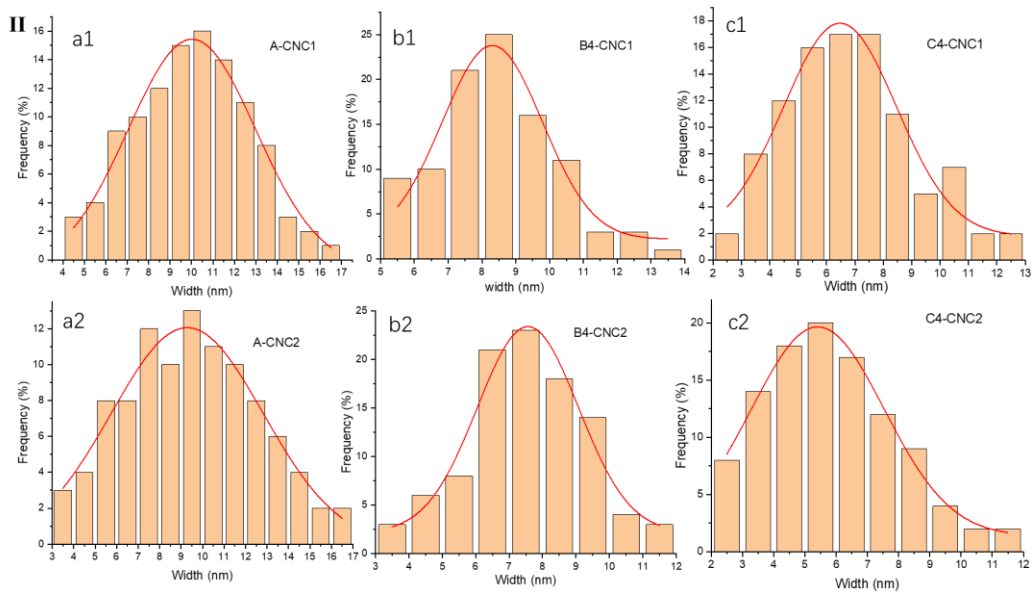


Figure 4II. The width distribution of the CNCs from the schemes A, B4, and C4

Fig. 4I shows the length distribution of the CNCs from the reaction schemes A, B4, and C4. Fig. 4I a1, b1, and c1 displayed that the length of the CNC1 varied from 80 to 220 nm for the single-batch mode, and 130 to 240 nm for two-batch modes, respectively. Similarly, Fig. 4I a2, b2 and c2, the length of CNC2 was from 100 to 360 nm for single-batch mode, and 200 to 410 nm for two-batch modes, respectively.

Fig.4II shows the width distribution of the CNCs in these reaction schemes. It exhibited that the width of the CNCs in the single-batch mode ranged from 3 to 17 nm, and the width of the CNCs in the two-batch mode ranged from 3 to 14 nm. These findings indicated that the two-batch mode can produce the CNCs with a greater length and a narrower width than the single mode.

For further investigating the effect of the APS addition mode on CNCs morphology, the length and width distribution of them was fitted using the Gauss function built-in OriginPro. The fitted curves are also presented in red in Fig.4I and 4II. All adjusted-square values exceeded 0.95 at 0.05 level. Therefore, Gauss function could be used to describe the distribution of the length and width of the CNCs. After fitting, the values of the corresponding expected length, width, and the variance (Sigma) are presented in Fig.4III and Fig.4IV, respectively. In addition, the aspect ratio, the ratio of the expected length to the expected width, of all these CNCs was also displayed in Fig.4III.

Fig. 4IIIa showed that the expected length of the CNC1s was 153.5 ± 1.8 , 175.1 ± 1.1 , and 185.2 ± 1.0 nm in schemes A, B4, and C4, respectively. Meanwhile, their expected width was 10.8 ± 0.1 , 8.3 ± 0.1 and 6.4 ± 0.2 nm, respectively. As a result, it was shown that their aspect ratio was 14.2, 21.1 and 28.9. It was indicated that schemes B4 and C4 achieved a 48.6 and 103.5 % increase in CNC1 aspect ratio, respectively, in comparison to scheme A. Similarly, as illustrated in Fig. 4III b, the expected CNC2 length increased to 271.1 and 295.5 nm from 211.1 nm when two schemes B4 and C4 were used instead of scheme A. Meanwhile, the expected CNC2

width decreased to 7.56 ± 0.13 and 5.40 ± 0.06 nm from 9.28 ± 0.15 nm, respectively. Consequently, an increase in the aspect ratio was observed to 35.9 and 54.7 from 22.7. It was indicated that schemes B4 and C4 achieved 58.1 and 140.1% increase in CNC2 aspect ratio, respectively, in comparison to scheme A. The increased aspect ratio was helpful to CNC applications in many fields such as reinforcement and barrier performance.

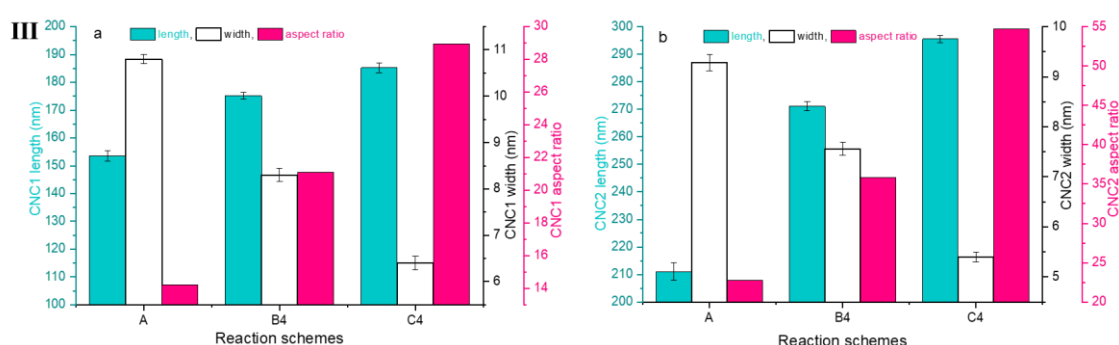


Figure.4III the expected length, width and aspect ratio of the CNCs

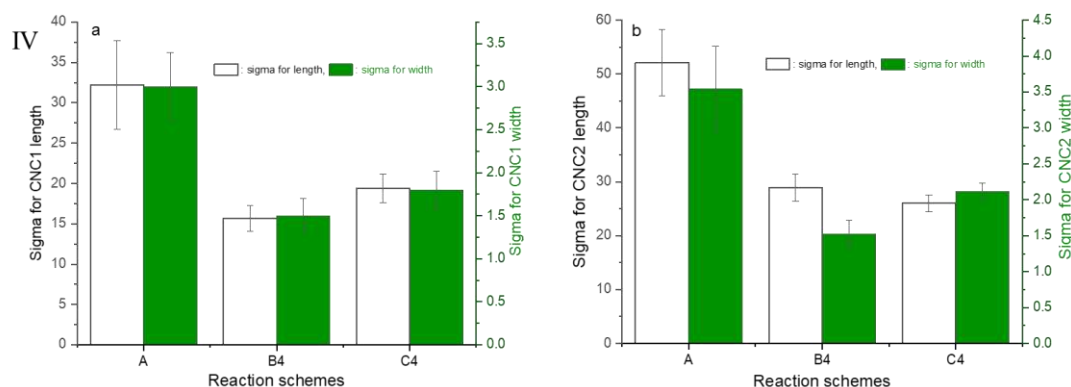


Figure.4IV the Sigma (Variance) of the length and the width of the CNCs

The variance (Sigma) is used as a sign of polydispersity of the CNCs' characteristics. Fig.4IVa shows the Sigma values of CNC1 length and its width at different schemes. Fig.4IVa showed that the Sigma values of the CNC1 length were 32.2 ± 5.2 , 15.7 ± 1.6 , and 19.4 ± 1.9 , meanwhile, the width Sigma values were 3.0, 1.5 and 1.8, at scheme A, B4 and C4, respectively. Analogously, Fig.4IVb shows the

Sigma values of CNC2 length and its width at different schemes. Fig. 4IVb displayed the Sigma values of the CNC2 length were 52.1 ± 6.1 , 28.9 ± 2.3 , and 26.0 ± 1.0 , meanwhile, the width Sigma values were 3.6, 1.5 and 2.1, in the scheme A, B4 and C4, respectively. It was shown that the sigma values of CNC1 and CNC2 in both their length and width were much smaller in the two-batch mode than in the single-batch mode. This result suggested that the two-batch modes were favorable to increasing uniformity of the CNC1 and the CNC2 in both their length and their width.

In the single-batch mode, the residual $\text{SO}_2^{\cdot*}$ free radicals preferentially adsorbed on the existing CNC2 and facilitated the formation of CNC1, as mentioned before, meanwhile, the released CNC1 might be further oxidized and even mineralized. On the other hand, More $\text{SO}_2^{\cdot*}$ were required for disruption of these H-bonds than for the cleavage for the β -glycoside bonds due to the greater number of interchain hydrogen bonds in the I β -cellulose (Moon, Martini et al. 2011). Finally, the obtained CNCs decreased more significantly in length than in their width, decreasing the aspect ratio. On the contrary, in two-batch mode, higher local concentrations of $\text{SO}_2^{\cdot*}$ had a greater advantage in disruption of the H-bonds between molecule interchains than in single mode. Therefore, the CNCs of greater aspect ratio were obtained in the two-batch modes than in the single mode.

3.5 XRD

Fig. 5 shows the XRD patterns of the CNCs in the three reaction schemes. It was shown that all diffractograms exhibited significant similarity. A broad diffraction peak was observed at 2θ between 14° and 17° , comprised of two overlapping peaks at $2\theta =$

14.6 and 16.7°, an intense, sharp peak at $2\theta = 22.4$, and a low-intensity peak at 34.5 °. All these peaks are assigned to the (1-10), (110), (200) , and (040) Bragg planes, respectively, characteristic of the crystallographic form of cellulose I- β (Kargarzadeh, Ahmad et al. 2012). To further investigate the effect of the adding mode of APS on the crystal structure, all these X-ray diffraction curves were deconvoluted using Voigt built-in Jade. All fitted peaks are presented in Fig.S4 in color. Based on the Bragg's angle, the area and the FWHM of each fitted peak in Fig.S5, the crystal structure parameters of all samples were calculated using the Scherrer's and Bragg's equations (Garvey, Parker et al. 2005) (seen in M2 in SI), and the crystalline index were calculated and displayed in Table 3.

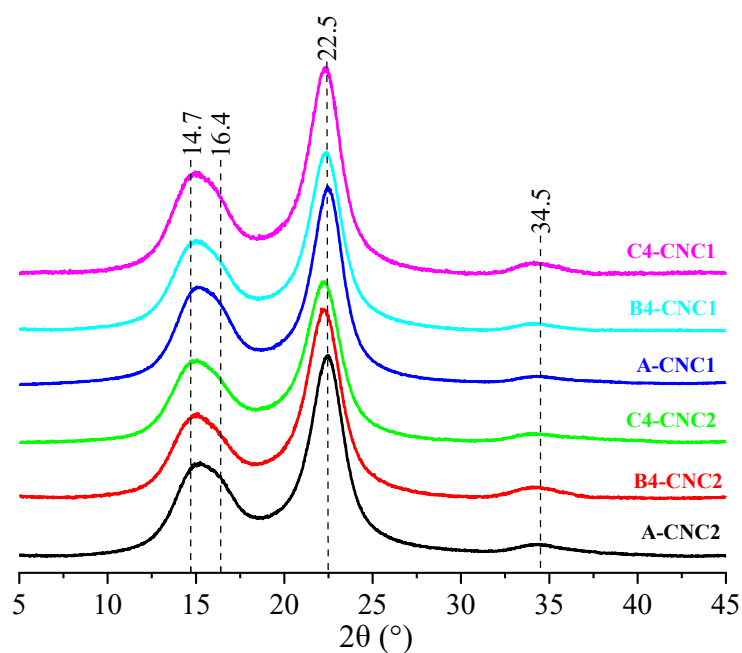


Figure 5. The XRD patterns of the CNCs from the schemes A, B4 and C4

Table 3 displayed that the sizes of the Bragg planes (1-10) and (110) were nearly equivalent, approximately being 3.4 and 3.1 nm for the CNC1 and CNC2, respectively. Additionally, the dimensions of the plane (200) of the CNC1 and the

CNC2 were about 4.5 and 4.3 nm, respectively. The results indicated that the cross-section of the CNC1 was always marginally greater than that of the CNC2 irrespective of the schemes. The result was in agreement in the expected width in Fig.4III. This was attributed to the disruption of the hydrogen bonds within cellulose chains during the ultrasonication of the CNC2 (Guo, Guo et al. 2016, Szymańska-Chargot, Cieřla et al. 2018). Furthermore, it was indicated that the shape of the cross-section of the CNCs remained constant across different reaction schemes. Furthermore, Table 3 showed that the d-spacing of the Bragg planes (1-10), (110), and (200) of the CNC1 and the CNC2 were 0.60, 0.54 and 0.4 nm, respectively, indicating that the d-spacing remained also constant across these different reaction schemes. It was suggested that the two-batch mode almost preserved the shape and dimension of the CNC crystallite cross-section shape.

Table 3. Crystal structure parameters of the CNCs using the schemes A, B4 and C4

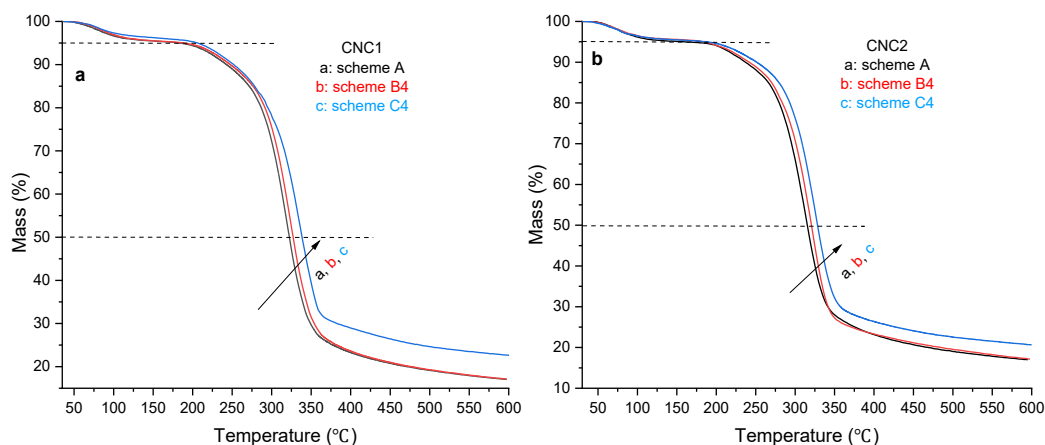
Samples	Crystalline Index (%)	Crystallite size (nm)			d-spacing (nm)		
		1-10	110	200	1-10	110	200
A-CNC1	81.07	3.38	3.39	4.54	0.59	0.54	0.40
A-CNC2	75.42	3.13	3.14	4.30	0.60	0.54	0.40
B4-CNC1	74.57	3.36	3.36	4.49	0.60	0.55	0.40
B4-CNC2	73.45	3.10	3.09	4.25	0.61	0.55	0.40
C4-CNC1	75.92	3.40	3.39	4.50	0.60	0.55	0.40
C4-CNC2	74.26	3.15	3.17	4.27	0.61	0.55	0.40

Moreover, Table 3 showed that the CrI values of all the CNC1 samples were 81.07, 74.57, and 75.92%, respectively. Similarly, the CrI values of all the CNC2 samples were 75.42, 73.45, and 74.26% in schemes A, B, and C. It was displayed that the CrI of the CNC1 samples was always slightly higher than that of the CNC2 samples. The reason for this was the prolonged retention of CNC1 in reaction medium

containing SO_2^{*-} , It was reported that an extended oxidation period led to a higher crystalline index during the extraction of CNCs by APS oxidation (Marwanto, Maulana et al. 2021). Meanwhile, Table 3 showed that the CNCs achieved a higher CrI in scheme A compared to schemes B4 and C4, respective of the CNC1 and the CNC2. This resulted from the fact that the existing CNC2 was preferentially oxidized and removed residual amorphous portions around the released CNC1 in the single mode.

3.6 Thermal stability

The pathway of thermal decomposition of the cellulose is influenced by many physical and chemical factors such as, size and texture of the cellulose sample, crystallinity, and other parameters (Adel, El -Wahab et al. 2010, Popescu, Popescu et al. 2011).



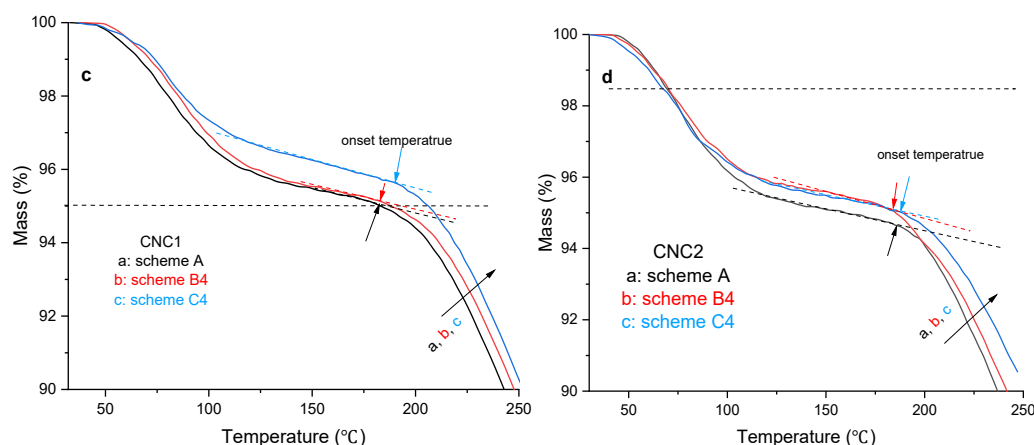


Figure 6 The thermogravimetric profiles (a and b) of the CNCs at different schemes and their parts (~250°C) of these profiles (c and d)

The TGA curves of the freeze-dried CNCs at different schemes are shown in Figs. 6a and 6b. They showed that each TGA curve can be divided into three regions, typical of the cellulose decomposition (Camarero Espinosa, Kuhnt et al. 2013). The initial mass loss portion was located from 30 to about 200 °C, caused by the evaporation of water from the CNC samples. After that, the decomposition of CNCs occurred between 200 and 350 °C, and in last region, the char formed after the 350 °C.

Fig. 6c and 6d showed that the mass loss rate significantly decreased after about 110 °C. The decrease was due to the solidly packed surface layers, which reduced residual moisture diffusion from between the CNCs to their surface. And then, the CNCs began to degrade at a faster rate due to the dehydration and depolymerization of the CNCs. The temperature at which the mass loss rate started to increase again was defined as the onset temperature of thermal degradation, as shown in Figs. 6c and 6d. This onset temperature of thermal decomposition is vital for the applications of CNCs in reinforcing thermoplastics.

Table 4 Thermal stability parameters of the CNCs from the schemes of A, B4 and C4

Samples	T _{onset} (°C)	T _{50%} (°C)
A-CNC1	182.6	321.4
A-CNC2	185.3	315.0
B4-CNC1	183.9	327.5
B4-CNC2	186.1	322.2
C4-CNC1	187.5	338.2
C4-CNC2	189.1	327.3

The temperatures at onset decomposition of the CNCs and at their mass loss of 50% (T_{50%}) are presented in Table 4. Table 4 showed that the onset temperature of decomposition increased to 183.9 and 187.5°C for the CNC1 in the schemes B and C from 182.6 °C for the one in scheme A, respectively. Similarly, the onset temperature of the CNC2 from the scheme A were 185.3°C, and they increased to 186.1 and 189.1 °C for the CNC2 in the schemes B and C, respectively. As for T_{50%}, the same trend was observed, and the minimum T_{50%} values were 321.4 and 315.0 °C for A-CNC1 and A-CNC2, respectively. It was suggested that the CNCs in scheme A had slightly lower thermal stability than these in schemes B4 and C4.

The CNCs from the two-batch mode showed a lower crystallinity than the ones from the single mode, as previously reported. Hence, these CNC surfaces had more amorphous microfibrils, which could aggregate together along their longitudinal direction through H-bond interactions, resulting from the exclusion from the ice particles during the freeze-drying. These aggregated microfibrils might cocrystallize due to the evaporation of the water molecules during the thermal analysis, just like the hornification observed during the drying of wet pulp (Mo, Chen et al. 2022). These

cocrystallized microfibrils increased the resistance to heat transfer during the heating process, leading to the thermal stability of the CNCs. Furthermore, as previously reported, the CNCs from scheme A exhibited a greater number of COOH groups than the ones from schemes B4 and C4. the presence of more carboxyl groups on the microfibrils surface has proved to be responsible for the lower thermal stability of TEMPO-oxidized nanocellulose (Lichtenstein and Lavoine 2017). Additionally, the decomposition of the CNCs was catalyzed by the more acidic groups to a greater extent (Kargarzadeh, Ahmad et al. 2012). Furthermore, the CNCs from the scheme C4 had the smallest content of carboxyl groups. Hence, the CNCs from the scheme C4 achieved the greatest thermal stability among the three types of CNCs. Consequently, it was proposed that the CNCs from two-batch mode had higher onset degradation temperatures than the one from single-batch mode, increasing the temperature widows during the thermal processing.

3.7 Reinforcement performance

Figure 7 displays the mechanical performance of the neat PVA and its composite films at a load of 1% different CNCs.

Tensile fracture energy is an important parameter typical of material tensile toughness, defined as the area enclosed by a stress–strain curve (Xu and Qu 2009). The tensile toughness of the neat PVA and its composites based on data in Figure 7A was calculated and presented in Figure 7B.

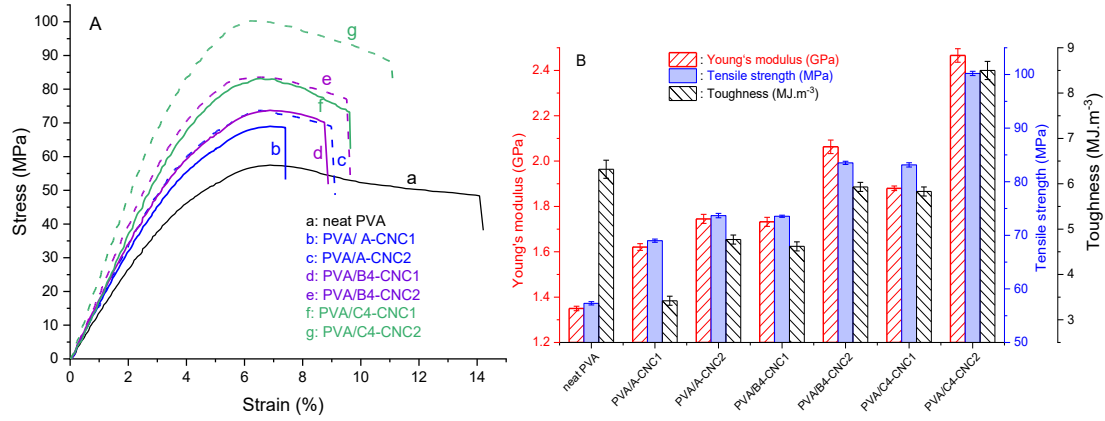


Figure 7 The mechanical performance of the neat PVA and its composite films at a load of 1% different CNCs

Figure 7A shows the stress-strain relationship of all the samples. Fig 7A exhibited the tensile strength and Young's modulus of the PVA composite films always increased, but the elongation at break for these composite films decreased after the incorporation of 1% CNCs compared with the neat PVA film, as expected (Mishnaevsky, Mikkelsen et al. 2019). And these changes were dependent on the types of CNCs.

Fig. 7B shows the Young's modulus, tensile strength and toughness of the neat PVA and its composites after addition of 1% various CNCs. As shown in Fig. 7B, for all the CNCs, the CNC2 always improved the Young's modulus and the tensile strength of the resultant composites more effectively than the CNC1. As for all CNCs from the two-batch modes, the CNCs from C4 scheme exhibited the most efficient reinforcement capability.

Fig. 7B displayed the Young's modules and tensile strength increased to 1.62 GPa and 69.0 MPa from 1.35 GPa and 57.3 MPa, respectively, after incorporation of

1% A-CNC1 in PVA, meanwhile, this A-CNC1 decreased its toughness to 3.42 from 6.32 MJ.m⁻³. Similarly, the A-CNC2 increased the Young's modules and tensile strength to 1.74 GPa, 73.68 MPa, respectively, but it decreased its toughness to 4.77 MJ.m⁻³. Additionally, Fig. 7B showed the Young's modules and tensile strength increased to 1.88 GPa and 83.1 MPa, respectively, after incorporation of 1% C4-CNC1 in PVA, but the corresponding toughness decreased to 5.83 MJ.m⁻³, indicating a decrease by 7.7 % in toughness.

On the contrary, the tensile modules, strength and toughness of this composite PVA film were up to 2.47 GPa, 100.2 MPa, 8.5 MJ.m⁻³, respectively, increasing by 83.0, 74.9, and 34.9 % after incorporation of 1% C4-CNC2. Therefore, the C4-CNC2 created the greatest reinforcement benefits in all mechanical performance. All these results illustrated that the CNCs from the two-batch mode created more reinforcements than the ones from the single-batch mode, and especially, the C4-CNC2 still toughened the PVA. All these observations were attributed to the fact the B-CNCs and C-CNCs had greater aspect ratio and smaller width compared to the A-CNCs. Smaller width and greater aspect ratio were favorable to facilitating the increase in interaction sites and adhesion between the CNC particles with the matrix (PVA), increasing the load transfer in matrix, and then Young's modulus and tensile strength, as reported (Boufi, Kaddami et al. 2013, Lee, Aitomäki et al. 2014). In addition, for all CNC2 particles, lower crystallinity gave some amorphous regions on their surface. These amorphous regions provided more free hydrogen groups, enhancing the formation of H-bonds between the CNC particles with PVA chains.

This observation was similar to the one that a higher beating degree resulted in a greater mechanical strength of paper. Hence, all CNC2 particles had greater reinforcement capacity than the CNC1 ones.

Conclusion

In the two-batch modes, APS decomposed at a bit twice as great as in the single-batch mode, and the addition of aliquot portion of APS at 4 h resulted in the most significant enhancement in yields and quality of the resultant CNCs of all two-batch modes. At this condition, the total CNC yield was increased from 42.6% to 57.9%. The resulting both CNCs exhibited a zeta potential of about -40 mV. Notably, the modes significantly enhanced the aspect ratio of the CNCs, achieving increases in 103.5% for CNC1 and 141.0% for CNC2, while their length and width variance (defined as dimension polydispersity) declined to 19.4 and 2.1 from 32.2 and 3.6, respectively, improving the uniformity of both length and width distributions. Furthermore, the two-batch modes produced CNCs with higher thermal stability and greater reinforcement performance despite a slight reduction in their crystalline index. Therefore, it was proven that the two-batch addition of APS could significantly enhance the yield and properties of the CNCs compared with the single-batch mode.

CRedit authorship contribution statement

Zhangyun Chen: Data curation; investigation; writing – original draft.

Hua Jiang: Funding acquisition; methodology; writing – review and editing.

Zhongyuan XIE: Methodology ; software.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

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