Tuning the properties of pineapple peel cellulose nanofibrils by TEMPO-mediated oxidation and ball milling

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Received: 6 April 2022 / Accepted: 13 September 2022 / Published online: 23 September 2022
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Abstract In this study, the oxidized cellulose nanofibrils from pineapple peel (PP-TOCNF) were prepared by TEMPO-mediated oxidation followed by ball milling. The influence of oxidation degree on the structure and properties of PP-TOCNF were investigated, including Fourier transform infrared spectroscopy, X-ray diffraction, atomic force microscope (AFM), X-ray photoelectron spectroscopy and thermogravimetry, as well as the potential application in aerogels. The results suggested that TEMPO oxidation facilitated the dispersion of PP-TOCNF due to the strong electrostatic repulsion between –COO− groups. Regulating oxidation degree by varying NaClO concentration could effectively adjust the –COO− content (0.167–0.550 mmol/g), zeta potential (−18 to −34 mV) and rheological properties. The obtained PP-TOCNF showed a long fibrillar structure, whose average diameter and CrI values gradually decreased with the increase of oxidation degree. The PP-TOCNF-based aerogels exhibited a light weight, good porosity, water absorption, and mechanical properties, which also can be easily adjusted by oxidation degree of PP-TOCNF. Furthermore, TEMPO oxidation improved the stability and shape recovery ability of aerogels in water.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10570-022-04851-9.

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Graphical abstract

Keywords Pineapple peel · Cellulose nanofibrils · TEMPO oxidation · Ball milling · Aerogel

Introduction

Tremendous energy consumption has been considered as one of the most serious social problems, showing an urgent need for developing more energy efficient, more affordable and more sustainable resources. Cellulose, as the most abundant renewable biopolymer on Earth, is mainly derived from agricultural and forest residues and considered to be a promising candidate (Dai et al. 2020a, b), due to its superior characteristics of wide source, low-cost and environmental friendliness (Dilamian and Noroozi 2021). Considering the insolubility of natural cellulose, the effective utilization of cellulose is mainly through chemical modification to form cellulose derivatives (Mettu et al. 2021) (e.g., carboxymethyl cellulose (CMC), methylcellulose (MC), hydroxypropyl methylcellulose (HPMC), cellulose acetate (CA), and hydroxyethyl cellulose (HEC) (Cho et al. 2021)), or through micro/nano processing to form microcrystalline cellulose (MCC) or nanocellulose (Dai et al. 2021a, b). Among these, nanocellulose is gaining tremendous research attention due to its superior properties such as renewability, biodegradability, biocompatibility, high aspect ratio, high specific surface area, easy availability, high mechanical strength, and good modifiability (Sun et al. 2021). Generally, nanocellulose can be divided into three main types, namely cellulose nanocrystals (CNCs), cellulose nanofibrils (CNFs) and bacterial cellulose (BC) depending on their sizes, resources and preparation techniques (Feng et al. 2022; Dai et al. 2020a, b). Among these, CNFs as longer semi-flexible fibrils are currently receiving considerable attention due to some attractive features, such as gentle extraction method, high aspect ratio, gel-like behavior, and industrialized production potential (Perumal et al. 2022). Recently, CNFs have been regarded as a promising material for applications in stabilizer (Goi et al. 2019), food packaging (Lee et al. 2017), papermaking (Jele et al. 2021) and nanocomposites (Benítez and Walther 2017).

The application of CNFs mainly depends on their preparation method, which influences their properties such as morphology, crystallinity and surface properties. At present, the common methods for CNF isolation include high pressure homogenization, microfluidization, sonication, mechanical grinding and ball milling (Chen et al. 2021). Among these methods, ball milling is suitable for CNF production due to its less expensive equipment and simple operation steps and conditions (Zhang et al. 2022). It can be used in dry condition to reduce the size of fibers and prepare CNFs under wet condition (Nuruddin et al. 2016). Due to the strong inter- and intra-molecular hydrogen bonds among cellulose chains, the enormous energy and time consumption during mechanical disintegration process are always a challenge in CNF isolation. Recently, some studies have found that effective
pretreatments can reduce energy consumption to facilitate the disintegration and nanofibrillation of cellulose, such as chemical modification, enzymatic pretreatment (Perzon et al. 2020), and alkali treatment (Miao et al. 2016). For CNF production, the TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl)-mediated oxidation of native cellulose stands out amongst the most used chemical methods, showing advantages in terms of individual fibers, uniform size, long length and flexible (Van Hai et al. 2018). Furthermore, the TEMPO-mediated oxidation can result in the regioselective conversion of the hydroxyl groups at the C6 positions of cellulose molecules into carboxylic groups, thus endowing CNFs with improved dispersibility in water (Qu et al. 2021a, b). Recently, a series of studies based on TEMPO-mediated oxidation to prepare CNFs have been reported (Tanpichai et al. 2021; Wen et al. 2019; Xu et al. 2022). In addition, ball milling is considered to be an effective method for the preparation of nanocellulose because it can break the longitudinal axis of cellulose structure (Piras et al. 2019; Sitotaw et al. 2021). Although a number of studies about the production of cellulose by ball milling have been investigated in the literature (Ling et al. 2019; Mattonai et al. 2018; Nagarajan et al. 2019), there is little information available regarding the effect of TEMPO-mediated oxidation on the properties of CNFs prepared by ball milling.

Aerogel is a highly porous nanostructured material with characteristics of high porosity, high surface area and low density (Wan et al. 2019; Wei et al., 2021), which is regarded as a promising material for a variety of applications such as biomedical scaffolds, separation and adsorption, among others (Liu et al. 2021). Cellulose aerogel is known as a new generation of aerogel material following inorganic aerogel and organic polymer aerogel, and it combines the traditional properties of aerogels with the advantages of cellulose and belongs a promising material for making aerogel with flexibility and pressure resistance. The carboxyl groups of CNFs induced by TEMPO-mediated oxidation can improve the properties of CNF aerogel due to the electrostatic repulsion between cellulose fibers, thus preventing the pores from collapsing (Gong et al. 2021). The oxidation degree can effectively dominate the properties of CNFs, which is of great significance for the application of CNF aerogel. However, there is still a lack of information available on the effect of oxidation degree.

Pineapple is the third most important tropical fruit in the world and widely planted in many countries including Philippines, Thailand, Malaysia, Mexico and China (Zakaria 2018). China is one of the major producers of pineapple, and the peak harvesting period of pineapple is March to June. In 2017, there are approximately 670,000 hectares of pineapples in China, accounting for 7.2% of the world’s total planting area. The total annual output is 1.67 million tons, accounting for about 8.1% of the world’s total annual output (Li et al. 2022). Generally, pineapple industries produce major wastes from 50% of total fruit mass, with the peel accounting for 29–40%, the core for 9–10%, the stem for 2–5%, and the crown for 2–4% (Shivamathi et al. 2022). Therefore, developing utilization of pineapple peel can enhance the economics of processing units and reduce environmental pollution issues. Our previous study indicated that the dried pineapple peel approximately contains 24% cellulose, 7% lignin, 16% hemicellulose, and 8% pectin (Dai and Huang 2017).

Recently, our research team has confirmed the feasibility of pineapple peel as a raw material for cellulose and nanocellulose extraction (Dai et al. 2018), whose potential applications involve the fields of hydrogels (Dai et al. 2018), emulsion stabilizer (Dai et al. 2021a, b), adsorbents (Dai et al. 2019a, b), drug carriers (Dai et al. 2019a, b). For the literatures based on pineapple leaves, there have been reports on the preparation of cellulose film (Wei et al. 2020), the extraction of cellulose microfibers by steam explosion (Tanpichai et al. 2019), the isolation of CNFs by ball milling (Ravindran et al. 2019), and the extraction of CNFs by using an oxidative pretreatment with TEMPO followed by mechanical combination of grinding and microfluidization process (Araya-Chavarria et al. 2021). However, the isolation of CNFs from pineapple peel and its TEMPO oxidation have not been reported yet to the best of our knowledge. In this study, the pineapple peel as a raw material was used to prepare CNFs by TEMPO-mediated oxidation followed by ball milling. The influence of oxidation degree on the physical and chemical properties of CNFs was systematically investigated, including zeta potential, functional groups, elemental composition, morphology, crystalline structure, thermal stability, rheological behavior and their application potential in aerogels.
Materials and methods

Materials and reagents

Pineapple peel was freely provided by a pineapple processing factory in Zhanjiang (Zhanjiang, China) in May 2021, and then used to isolate from cellulose (PPC) according to our previous study (Dai et al. 2019a, b). Sodium hydroxide (NaOH), sodium bromide (NaBr), Hydrochloric acid (HCl) and ethanol were purchased from Kelong Reagent Co., Ltd. (Chengdu, China). Sodium chlorite (NaClO₂) and TEMPO were provided by Yuexiang Chemical Co., Ltd. (Chongqing, China). Sodium hypochlorite (NaClO) solution with the available chlorine of 10~15% was purchased from Jiuding Chemical Technology Co., Ltd. (Chongqing, China). All other chemical reagents were of analytical grade without further purification.

Preparation of TEMPO-oxidized pineapple peel CNFs (PP-TOCNF)

PP-TOCNFs was obtained according to TEMPO-mediated oxidation followed by mechanical ball milling (Huang et al. 2020). Briefly, 1 g of PPC was suspended in 100 mL of distilled water containing TEMPO (0.0125 g) and NaBr (0.125 g). Then, the TEMPO-mediated oxidation of the PPC slurry was initiated after adding various amounts of NaClO (2.5, 5 and 10 mmol) at 25°C and pH 10 during 1.5 h reaction at room temperature. Lastly, the resulting slurry was collected and dialyzed at 4 °C for 3 d to gain the oxidized PPC (TOPPC). Afterwards, the obtained TOPPC was further ball milled using a vertical planetary ball mill (XQM-0.4A, Tencan powder, China). Briefly, TOPPC suspension (1.0%, 20 mL) was placed in the zirconia vessel containing zirconia balls (90 g) with different diameters (15, 12, 10, 8 and 5 mm). The ball milling was processed at a speed of 400 rpm for 3 h at room temperature and performed in cycles of 20 min/milling per 10 min/rest. Then, the resulting slurry was collected and washed by three repeated centrifugation (5000 r/min, 10 min) and dispersed by ultrasonic treatment (300 W, 30 min). The obtained suspension was stored at 4 °C for further use or freeze-dried for characterization. According to the addition of NaClO, the obtained PP-TOCNF samples were coded as PP-TOCNF-2.5, PP-TOCNF-5 and PP-TOCNF-10, respectively. As a control, the pineapple peel CNF (PP-CN) was also prepared by directly ball milling method without TEMPO-mediated oxidation. The carboxylate content of PP-TOCNF was determined by a conductometric titration procedure using a conductivity meter (FE38, Mettler Toledo, Switzerland). A fixed amount of PP-TOCNF suspension was dried to a constant weight at 60°C, then the yield of CNFs was calculated using the following equation:

\[
\text{Yield (\%)} = \frac{M_1 \times V_0}{M \times V_1} \times 100\%
\]

where \(M\) is the initial weight of PPC (g), \(M_1\) is the weight of the corresponding PP-TOCNF (g) dried to a constant weight at 60 °C, \(V_0\) is the total volume of initial PP-TOCNF suspension, and \(V_1\) is the volume of PP-TOCNF suspension used for drying.

Zeta potential measurement

Zeta potentials of PP-CN and PP-TOCNF suspensions (0.05%, w/w) were measured by a Zetasizer Nano ZS particle analyzer (Malvern Instrument, UK) at 25 °C. Before analysis, the suspension was ultrasonically treated for 10 min.

UV/visible (UV–Vis) light transmittances

The UV–Vis light transmittances of PP-CN and PP-TOCNF suspensions (0.02%, w/w) were recorded by a UV–Vis spectrophotometer (UV 6100, Metash, China) in the wavelength range 200–900 nm. The transmittance spectra were attained by means of cuvette as background.

Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of samples were recorded using a Fourier transform infrared spectrometer (Thermo Nicolet iS10, Thermo Fisher Scientific, USA) in the attenuated total reflectance (ATR) mode. The measurement was performed in the range of 4000–600 cm⁻¹ with a resolution of 4 cm⁻¹ and 32 scans.
Atomic force microscopy (AFM)

Topographical characterization of PP-CNF and PP-TOCNF was obtained using an atomic force microscope (Cypher ES, Oxford Instruments, USA). Before observation, the diluted suspension (0.01%) was dropped on the mica substrate and air-dried at room temperature. The average value and distribution of diameter were analyzed by the Nano Measurer 1.2 software.

X-ray diffraction (XRD)

The crystalline structure of samples was analyzed by an X-ray diffractometer (X’Pert3 Powder, Malvern Panalytical, Netherlands), with a Ni-filtered Cu-Kα radiation (λ = 0.15444 nm) operating at an anode voltage of 40 kV and a current of 40 mA. The XRD data were collected in the 2θ range from 10° to 40° with a scan rate of 4°/min. XRD data were further analyzed using the MDI JADE 6 software. The background was fitted with a software-generated cubic spline function. Then, the entire pattern was smoothed with a parabolic filter to reduce unwanted noise. The crystallinity index (CrI) was calculated by the Segal’s method (Segal et al. 1959):

\[
CrI(\%) = \frac{I_{200} - I_{am}}{I_{200}} \times 100
\]

where \( I_{200} \) is the maximum intensity of the (200 plane) diffraction peak, and \( I_{am} \) is the minimum diffraction intensity for amorphous region between planar reflections (200) and (110).

X-ray photoelectron spectroscopy (XPS)

XPS spectra of PP-CNF and PP-TOCNF were recorded using an XPS spectrometer (Scientific K-Alpha, Thermo, USA) using an Al Kα X-ray irradiation (hv = 1486.6 eV). Low-resolution survey spectra were recorded in 1 eV steps and pass energy of 100 eV. The high-resolution of the C 1 s spectra (278–294 eV) and the O 1 s spectra (525–545 eV) were recorded in a step size of 0.05 eV and a pass energy of 50 eV.

Thermal stability analysis

The thermal stability of samples was analyzed by a thermogravimetric analyzer (TGA550, TA Instruments, USA) with temperature range from 30 to 600 °C at a constant heating rate of 10 °C/min under a nitrogen flow of 50 mL/min.

Rheological behavior of PP-CNF and PP-TOCNF suspensions.

The rheological properties of PP-CNF and PP-TOCNF suspensions (1.0%, w/v) were measured using a rotational rheometer (MCR 302, Anton Paar Physica, Austria) equipped with a parallel-plate fixture (25 mm diameter). The linear viscoelastic region of samples was measured with a strain sweep (γ) of 0.01–100% in an oscillatory mode, and the viscosity and the dynamic frequency sweep of samples were performed at an increasing shear rate from 0.1 to 100 s⁻¹. All measurements were performed at a gap of 1.0 mm within the linear viscoelastic region at a reference temperature of 25 °C.

Application in aerogel

Preparation of aerogel

The aerogels were simply prepared by a direct freeze-drying method (Manzocco et al. 2022). Briefly, the PP-CNF, PP-TOCNF-2.5, PP-TOCNF-5 and PP-TOCNF-10 suspensions (1.0%, w/w) were respectively poured into a cylindrical mold and pre-frozen by an ultra-low temperature refrigerator (−80 °C, 24 h). Afterwards, the samples were lyophilized at −50 °C in a freeze-drier (Heraeus Multifuge XWR, Thermo Fisher, USA) for 48 h to obtain aerogels. Correspondingly, the obtained aerogels were named as PP-CNF-AG, PP-TOCNF-2.5-AG, PP-TOCNF-5-AG and PP-TOCNF-10-AG, respectively.

Density and porosity measurements

The density of the obtained aerogels can be calculated by the following equation:

\[
\rho = \frac{M}{V}
\]
where ρ (g/cm³) is the density of aerogels, \( M \) (g) and \( V \) (mL) are the weight and geometric volume of aerogels, respectively.

The porosity of the aerogels can be calculated by the following equation (Sanguanwong et al. 2020):

\[
\text{Porosity (\%)} = 1 - \frac{\rho}{\rho_c} \times 100 \tag{4}
\]

where \( \rho \) is the density of PP-TOCNF-AGs and \( \rho_c \) is the bulk density of cellulose (1.527 g/cm³).

**Water absorption measurement**

The water absorption of aerogels was measured by a gravimetric method (Mettu et al. 2021). Briefly, the freeze-dried aerogel was soaked in distilled water at room temperature and taken out until the adsorption equilibrium was achieved. After removing the surface water using a filter paper, the samples were weighed immediately. The water absorption capacity (WA) of aerogels was calculated using the following equation:

\[
WA (g/g) = \frac{M_w - M_d}{M_d} \tag{5}
\]

where \( M_w \) (g) is the weight of the aerogel after water adsorption, and \( M_d \) (g) is the initial weight of the dried aerogel.

**Scanning electron microscopy (SEM)**

The morphologies of the aerogels were observed by a scanning electron microscope (Phenom pro, Phenom-World BV, Netherlands) at an operating voltage of 10 kV. Before observation, the samples were sputter-coated with a gold–palladium.

**Mechanical property analyses**

The mechanical performance of the aerogels was determined by an electronic universal testing machine (E44.104, MTS, USA) equipped with a 1 KN standard load cell. The compression strain was set to 86% on the cylindrical aerogel samples with a crosshead speed of 15 mm/min.

**Statistical analysis**

All measurements were repeated at least 3 times. The obtained data were partially presented as mean values ± standard deviation (SD).

**Results and discussion**

**Carboxylate content and yield**

The carboxylate content and yield of PP-CNF and PP-TOCNF are summarized in Table 1. After TEMPO-mediated oxidation, the carboxylate content of PP-TOCNF-2.5, PP-TOCNF-5 and PP-TOCNF-10 was 0.218 ± 0.011, 0.331 ± 0.041 and 0.550 ± 0.031 mmol/g, respectively, showing an increased oxidation degree with the increase of NaClO concentration. Accordingly, the carboxylate content of PP-TOCNF can be effectively adjusted by controlling oxidation parameters (e.g., NaClO concentration). The yield of PP-CNF, PP-TOCNF-2.5, PP-TOCNF-5 and PP-TOCNF-10 was 73.70 ± 3.11%, 68.25 ± 1.59%, 74.50 ± 2.12% and 75.25 ± 0.18%, respectively. Compared with PP-CNF directly isolated by ball milling, the yield of PP-TOCNF firstly decreased (PP-TOCNF-2.5) and then slightly increased (PP-TOCNF-5 and PP-TOCNF-10) with the increase of oxidation degree. This trend could be caused by a combination of the increases of cellulose degradation and defibrillation degree during TEMPO mediative oxidation and ball milling process (Huang et al. 2020). Under the oxidative conditions, the cellulose can be oxidized and depolymerized into water soluble derived compounds (Isogai et al. 2018). The decrease of yield at low oxidation degree is probably due to the fact that the increased defibrillation degree cannot offset the
increase of amorphous region hydrolysis of cellulose, while higher oxidation degree leads to an easier defibrillation by ball milling, thus resulting in an increase of yield (Liu et al. 2018).

Zeta potential analysis and visual appearance

The zeta potential value and visual appearance of PP-CNF and PP-TOCNF suspensions are shown in Fig. 1a, b. As shown in Fig. 1a, the zeta potential value of PP-CNF, PP-TOCNF-2.5, PP-TOCNF-5 and PP-TOCNF-10 was $-18.13 \pm 1.01$, $-24.20 \pm 1.65$, $-26.67 \pm 0.50$ and $-33.90 \pm 1.71$ mV respectively, corresponding to the change of carboxylate content (Table 1). The increase of oxidation degree resulted in the increase of carboxylate content, thus endowing PP-TOCNF with a better colloidal stability due to stronger electrostatic interaction between carboxyl groups (Yang et al. 2019). As shown in Fig. 1b, after standing for 1 d at room temperature, all samples showed a phase separation at a low concentration (0.1%), implying a poor colloidal stability. However, with the increase of solid concentration (0.5% and 1%), the colloidal stability was visibly enhanced due to the increase of electrostatic repulsion and solution viscosity (Li et al. 2015). Notably, all the PP-TOCNF samples showed a better colloidal stability than that of PP-CNF, mainly attributing to the enhanced electrostatic repulsion.

FTIR analysis

FTIR spectra of PP-CNF and PP-TOCNF are shown in Fig. 1c. All samples displayed the characteristic peaks of cellulose I structure at 3000–3400, 2800–3000, 1620, 1425, 1370, 1160, 1050 and 896 cm$^{-1}$ (Bisla et al. 2020; Krueer-Zerhusen et al. 2017), indicating the chemical structure of cellulose can be maintained after TEMPO oxidation and ball milling process. The wide band at 3000–3400 cm$^{-1}$ and the peak at 1370 cm$^{-1}$ reflected the intramolecular –OH bond stretching and bending vibration (Tarchoun et al. 2019). The peak around 2800–3000 cm$^{-1}$ corresponded to the symmetric and asymmetric stretching vibrations of the –CH$_2$, –CH, and hydroxyl groups (Barbash et al. 2021). The peaks around 1200–1450 cm$^{-1}$ corresponded to bending vibrations of the bonds of the –CH$_2$OH group at C6 of cellulose. The peak at 1425 cm$^{-1}$ represented the bending vibrations of –CH$_2$ (Sai Prasanna et al.
The peak at 1050 cm\(^{-1}\) belonged to the stretching vibrations of the C–O–C group of the glucopyranose ring of cellulose (Ilyas et al. 2017), and the band at 1330 cm\(^{-1}\) belonged to the C–O stretching (Gago et al. 2020). The peak at 896 cm\(^{-1}\) was attributed to the stretching vibrations of the β-glycosidic bond between the glucose units of the cellulose molecule (Hassan et al. 2021). After TEMPO-mediated oxidation, the obtained PP-TOCNF showed an increased intensity of peaks around 1609 cm\(^{-1}\) that belongs to the asymmetric stretching of –COO\(^-\) (Lourenço et al. 2017), implying the increase of oxidation degree, which is consistent with the results of carboxylate content (Table 1).

UV–Vis light transmittances analysis

The light transmittances of PP-CNF and PP-TOCNF suspensions are shown in Fig. 1d. As can be clearly observed from this figure, all PP-TOCNF samples showed a better light transmittance than that of PP-CNF. The increase in light transmittance was positively correlated with the increase in the oxidation degree of PP-TOCNF, showing the highest light transmittance in PP-TOCNF-10. The higher carboxyl groups on the surface of PP-TOCNF can increase the electrostatic repulsion between nanofibrils, thus improving the dispersion properties of suspensions and the light transmittance (Besbes et al. 2011). In addition, the transmittance of the suspension is also closely related to the particle size of the substance (Levanič et al. 2020), implying the decrease of particle size of PP-TOCNF with increasing oxidation degree, which can be confirmed by the following result of AFM (Fig. 2).

Morphological analysis

The AFM images and diameter distributions of PP-CNF, PP-TOCNF-2.5, PP-TOCNF-5, and PP-TOCNF-10 are depicted in Fig. 2. All samples showed a long fibrillar structure in their AFM images, belonging to typical morphological structure of CNFs. After ball milling, the PPC can be separated into individual nanofibril to generate PP-CNF, showing an average diameter of 42 nm. Notably, after TEMPO oxidation followed by ball milling, the average diameter of the obtained PP-TOCNF gradually decreased with the increase of oxidation degree, showing an average value of 32 nm for PP-TOCNF-2.5, 19 nm for PP-TOCNF-5, and 17 nm for PP-TOCNF-10, respectively. The surface carboxyl groups of PP-TOCNF could reduce the adhesion by forming strong electrostatic repulsion among nanofibrils (Lai et al. 2014), thus
promoting the nanofibrils disaggregation (Huang et al. 2019).

**XRD analysis**

After the background treatment, the XRD patterns of PPC, PP-CNF, and PP-TOCNF samples are displayed in Fig. 3a, and their corresponding CrI values are shown in Fig. 3b. All samples showed some similar diffraction peaks at 2θ of around 16.0°, 22.8°, and 34.5°, respectively corresponding to (110), (200), and (004) of the cellulose Iβ crystal structure (Mhd Haniffa et al. 2017), indicating the crystal structure of PP-CNF and PP-TOCNF can be maintained after TEMPO oxidation and ball milling. Compared with the CrI value of PPC (65.97%), the CrI value of PP-CNF, PP-TOCNF-2.5, PP-TOCNF-5 and PP-TOCNF-10 was 75.11%, 76.52%, 88.47% and 87.03%, respectively. The CrI value of PP-TOCNF increased with the degree of oxidation increase, attributed to the destruction of amorphous region during TEMPO oxidation process and ball milling (Tang et al. 2017). In addition, the TEMPO-mediated oxidation can make the structure of PPC loose, thereby resulting in an easier removal of the amorphous region during the ball milling (Qu et al. 2021a, b).
XPS analysis

The surface elemental composition of PPC, PP-CNF, and PP-TOCNF can be reflected by XPS, and the results are shown in Fig. 3c–i. As shown in Fig. 3c, the XPS survey spectra exhibited two main peaks, respectively at 532 eV for O 1s and 286 eV for C 1s. Compared with the O/C ratio of PPC (0.396), the O/C ratio of PP-CNF (0.522) was significantly increased, attributed to the exposure of more hydroxyl groups during ball milling. After TEMPO oxidation followed by ball milling, the O/C ratio of PP-TOCNF-2.5, PP-TOCNF-5 and PP-TOCNF-10 was 0.580, 0.597, and 0.604, respectively, showing a further increase of O/C ratio with the increase of oxidation degree, which can be attributed to the formation of carboxylic groups in PP-TOCNF. Notably, there was no significant difference in O/C values among PP-TOCNF samples. The oxidation occurred at the surface of cellulose at a low NaClO concentration (2.5 mmol), and gradually further occurred at both on the surface and greater depth area of cellulose with a higher NaClO concentration, but it cannot be revealed by surface elemental analysis. As shown in Fig. 3d-h, the C 1s survey spectra of all samples showed four peaks at 284.50, 286.10, 287.60 and 288.30 eV, respectively belonging to C–C/C–H, C–O, O–C–O/C = O and O–C = O groups (Fei et al. 2020). Compared with the peak area of C–O for PPC (44.15%), PP-CNF increased to 64.32%, attributed to more exposure of hydroxyl groups during the defibrillation process by ball milling. The peak area of C–O and O–C–O/C = O for PP-CNF and PP-TOCNF remained almost unchanged. This trend might be due to the combination effects of TEMPO-mediated oxidation and ball milling. As the amount of C–O can be increased during ball milling and the amount of C=O also can be increased by the formation of intermediate aldehyde groups, the relative percentages of these two functional groups will affect each other and influence these peaks. Furthermore, as shown in Fig. 3f–h, the peak area of the O–C = O group for PP-TOCNF increased as the oxidation degree increased. The O 1s survey spectra of all samples is shown in Fig. 3i. The peak at 533 eV for PPC and PP-CNF belonged to the O–C groups, and the peak around 532.5 eV for PP-TOCNF was attributed to the O = C groups, also confirming the introduction of carboxyl groups (Barazzouk et al. 2011).

Thermal stability analysis

The thermal stability of PPC, PP-CNF, and PP-TOCNF samples was analyzed by the thermogravimetric analysis (TGA) and the derivative thermogravimetric analysis (DTG), and the results are shown in Fig. 4a-b. The first peak below 100 °C was due to the weight loss of residual moisture in samples (Dai et al. 2018). PPC and PP-CNF respectively started to decompose at 223 and 207 °C (Tonset), and reached the maximum degradation rate at 327 and 322 °C (Tmax). Compared with PPC, the lower degradation temperature of PP-CNF at high temperature range could be attributed to its more available surface area for chemical reaction and lower CrI value (Sofla et al. 2016). PP-TOCNF also showed a decreased trend in Tonset and Tmax, showing 203 and 305°C for PP-TOCNF-2.5, 184 and 300 °C for PP-TOCNF-5, and 176 and 291 °C for PP-TOCNF-10, respectively. This trend is due to the existence of carboxyl groups in PP-TOCNF (Masruchin et al. 2018). As for PP-TOCNF samples, the thermal degradation involves several chemical reaction, including dehydration,
hydrolysis, depolymerization, decarboxylation and transglycosylation reaction (Gómez et al. 2016). At the second stage, PP-TOCNF showed two thermal decomposition steps. The first degradation peak at 200–250 °C was ascribed to the decarboxylation of the carboxyl groups, and the second degradation peak that occurred at 290–305 °C was due to the thermal decomposition of PP-TOCNF (Kim et al. 2021).

Rheological analysis

Figure 5a shows the curves for elastic modulus (G’) and the loss modulus (G’’) versus the imposed shear strain (γ) of PP-CNF and PP-TOCNF suspensions (1.0%, w/v). The strain sweep test was used to confirm the linear viscoelastic region of samples. As can be seen from this figure, the G’ and G’’ values of all samples were stable at γ = 0.1%, so it was selected in the subsequent test. The shear rate-viscosity curves of PP-CNF, PP-TOCNF-2.5, PP-TOCNF-5 and PP-TOCNF-10 are displayed in Fig. 5b. It can be seen that in shear rates ranging from 0.01 to 100 s⁻¹, as the shear rate gradually increased, the viscosity of suspensions gradually decreased, showing a typical shear thinning behavior as a non-Newtonian fluid (Kim et al. 2021). At low shear rates, all samples presented high viscosities due to the presence of the entangled network formed by PP-CNF or PP-TOCNF (Almeida et al. 2021; Alves et al. 2020). The three-dimensional network structure of the entangled or aggregated CNFs can be destroyed during the shearing process, thus reducing the fluid resistance and its apparent viscosity (Malkin 2013). And it can be obviously observed that the viscosity of PP-TOCNF increased with the increase of oxidation degree, attributed to the fact that viscosity mainly depends on the carboxyl content and morphology (Wei et al. 2017). In addition, the PP-TOCNF samples with higher oxidation degree had a larger aspect ratio, the resulting three-dimensional network structure could be more stable.

The G’ and G’’ of PP-CNF and PP-TOCNF suspensions as a function of angular frequency (ω = 0.1–100 rad/s) are shown in Fig. 5c. The values of G’ and G’’ with the increase of oxidation degree had a larger aspect ratio, the resulting three-dimensional network structure could be more stable.

### Table 2 Density, porosity and water absorption of aerogel (PP-CNF-AG, PP-TOCNF-2.5-AG, PP-TOCNF-5-AG and PP-TOCNF-10-AG)

| Samples               | Density (g/cm³) | Porosity (%) | WA (g/g)  |
|-----------------------|-----------------|--------------|-----------|
| PP-CNF-AG             | 0.0156 ± 0.0001a | 98.96 ± 0.01d | 38.18 ± 0.23a |
| PP-TOCNF-2.5-AG       | 0.0136 ± 0.0003b | 99.09 ± 0.02c | 46.37 ± 1.63c |
| PP-TOCNF-5-AG         | 0.0097 ± 0.0001d | 99.35 ± 0.01a | 71.71 ± 0.76a |
| PP-TOCNF-10-AG        | 0.0120 ± 0.0003c | 99.20 ± 0.02b | 56.28 ± 1.86b |
frequency. At low frequency (0.1–10 rad/s), the $G'$ values of all samples were higher than $G''$ values, showing a gel network structure formation in the suspensions. At high frequency (10–100 rad/s), the $G'$ values of PP-TOCNF were still higher than their $G''$ values, but the PP-CNF sample had a cross-over point, displaying a quasi-liquid behavior at high frequency. In general, it is a sign of gelation that existing a cross-over point where $G' = G''$ (Ding et al. 2018). Therefore, PP-CNF and PP-TOCNF can form the elastic 3D network and have the potential of gelation. As depicted in Fig. 5d, the PP-CNF sample exhibited a higher flowability. With the increase of oxidation degree, the flowability of PP-TOCNF samples gradually decreased, showing an obvious gelation behavior (especially in PP-TOCNF-10).

Application in aerogel

Density, porosity and water absorption of aerogel

The density, porosity and water absorption (WA) values for PP-CNF-AG and PP-TOCNF-AG are summarized in Table 2. Compared with the density of PP-CNF-AG (0.0156 g/cm$^3$), the density of PP-TOCNF-AG samples showed a decreased trend (0.0097–0.0136 g/cm$^3$). It can be observed that the density of PP-TOCNF-AG samples firstly decreased and then increased with the increase of oxidation degree, attributed to the electrostatic interaction between the nanocellulose filaments in the suspension (Silva et al. 2012). The increase in the density of PP-TOCNF-10-AG might be due to the high carboxyl content and more entangled network structure because of smaller size of nanofibers, which could result in a dense structure (Gong et al. 2021). Compared with PP-CNF-AG, the porosity of PP-TOCNF-AG increased, and the porosity of PP-TOCNF-AG samples increased firstly and then decreased with the increase of oxidation degree, among which PP-TOCNF-5-AG showed the highest porosity. The water absorption values of PP-CNF-AG, PP-TOCNF-2.5-AG, PP-TOCNF-5-AG and PP-TOCNF-10-AG aerogel were 38.18, 46.37, 70.71 and 56.28 g/g, respectively, showing an inverse relationship with aerogel densities, which was also reported in other study (Zhang et al. 2016).

SEM analysis

The surface morphological structure of PP-CNF-AG, PP-TOCNF-2.5-AG, PP-TOCNF-5-AG and PP-TOCNF-10-AG; Digital images (d) of water solubility and compressed rehydration of aerogel.
PP-TOCNF-10-AG is shown in Fig. 6a. As can be clearly observed from this figure, the surface morphologies of aerogels can be influenced by TEMPO oxidation with different oxidation degree. Obviously, PP-CNFF-AG exhibited a randomly stacked structure of fragments, while the PP-TOCNF-AG samples showed an obvious entangled porous network structure. Notably, as the oxidation degree increased, the network structure and surface of PP-TOCNF-AG became tighter. The reduced particle size of PP-TOCNF enables the formation of an entangled network structure for PP-TOCNF-AG, thus leading to the smaller pores. Some aggregation might be occurred thus forming the lamellar structure (Gong et al. 2021). However, due to the formation of lamellar structure, some properties of aerogel such as water absorption will be limited to a certain extent. Thus, the proper use of TEMPO-mediated oxidation to introduce negative charge is necessary for the further application of CNFs.

**Mechanical property analyses**

Figure 6b is a digital photograph of the appearance of the obtained aerogel, showing a typical light weight characteristic of aerogel that can be placed smoothly over the flower. The compression test was used to analyze the mechanical characteristics of the obtained aerogels, and the results are shown in Fig. 6c. There was no yield occurred at a strain of up to 86%, which was a typical deformation behavior of porous materials (Mirtaghavi et al. 2020). When the strain reached 86%, the compressive stress of PP-CNFF-AG was 37.67 kPa, the compression stress values of PP-TOCNF-2.5-AG, PP-TOCNF-5-AG and PP-TOCNF-10-AG were 34.16, 18.13 and 14.45 kPa, respectively. It can be demonstrated that TEMPO oxidation may regulate the mechanical characteristics of aerogel, showing a decreased compressive strength and an increased flexibility with the increase of oxidation degree (Chen et al. 2019). That might be because CNFs tend to be ordered, making the aerogel structure fluffy and thereby decreasing its compression resistance. As can be obviously seen in Fig. 6d, all aerogel samples maintained their initial shape after being soaked in water for 1 h. However, after prolonging to 12 h, PP-CNFF-AG showed a disintegration while PP-TOCNF-AG samples still remained their initial shape, showing a better structural integrity in aqueous solutions. In addition, compared with PP-CNFF-AG, the PP-TOCNF-AG samples had better rehydration performance after being pressed. These results suggest TEMPO oxidation endows CNF aerogel with better structural stability and shape recovery ability, providing tuning potential for their aerogel applications.

**Conclusion**

CNFs were successfully defibrillated from pineapple peel using TEMPO-mediated oxidation treatment followed by ball milling. TEMPO oxidation endowed CNFs with desirable dispersion and suspension stability in water and good gel-forming ability. With the increase of oxidation degree, the content of carboxyl group increased from 0.218 to 0.550 mmol/g, and the zeta potential values gradually decreased from −18 to −34 mV. The results of FTIR, XPS and XRD implied that the basic chemical structure of PP-CNFF can be maintained after TEMPO oxidation procedure. The obtained PP-TOCNF showed a long fibrillar structure and the average diameter gradually decreased from 40 to 17 nm with the increase of oxidation degree. In addition, TEMPO-mediated oxidation and ball milling process resulted in the reduction of the thermal stability of PP-TOCNF. Furthermore, controlling TEMPO oxidation can effectively adjust the porosity and density, water absorption and mechanical properties of PP-TOCNF aerogels. This work emphasized that TEMPO oxidation and ball milling could be an effective approach on the adjustment of the properties of CNFs.

**Author contributions** TL: Methodology, Investigation, Visualization, Writing-Original Draft. YL: Investigation, Resources. YC: Investigation, Resources. DD: Investigation, Resources. XF: Formal analysis. HC: Visualization. YY: Visualization. LM: Supervision, Project administration. YZ: Conceptualization, Funding acquisition. HD: Conceptualization, Funding acquisition.

**Funding** This study was supported by the National Natural Science Foundation of China (No. 31901683), Natural Science Foundation of Chongqing, China (No. cstc2020jcyj-msxmX0087), Fundamental Research Funds for the Central Universities (No. SWU-KT22046), the Ecological Fishery Technological System of Chongqing Municipal Agricultural and Rural Committee under Grant (No. 4322000102), and
Chongqing Postgraduate Research and Innovation Project (No. CYB2131).

Data availability All the data used to support the findings of this study are included within the article.

Declarations

Conflict of interest The authors declare that they have no conflicts of interest.

Ethical approval This study does not contain any studies with human participants or animals performed by any of the authors.

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