

Grafting Nanocellulose With Diethylenetriaminepentaacetic Acid and Chitosan As Additive for Enhancing Recycled OCC Pulp Fibres

Ao Li

Fujian Agricultural University: Fujian Agriculture and Forestry University

Dezhong Xu

Fujian Agricultural University: Fujian Agriculture and Forestry University

Mengnan Zhang

Fujian Agriculture and Forestry University

Shengzhong Wu

Agriculture and Forestry University

Yu Li

Fujian Agriculture and Forestry University

Jiuping Rao

Fujian Agriculture and Forestry University

Omar Abo Madyan

University of Cambridge

Mizi Fan (✉ Mizi.fan@brunel.ac.uk)

Brunel University <https://orcid.org/0000-0002-6609-3110>

Research Article

Keywords: Nanocellulose, Old corrugated container (OCC), NC-DTPA-CS, Additive, Paper property

Posted Date: September 27th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-904686/v1>

License:  This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

This paper is to develop a novel paper additive for effectively recycling old corrugated container (OCC) by functionalizing nanocellulose (NC) with diethylenetriaminepentaacetic acid (DTPA) and chitosan (CS), and investigate the reinforcing mechanisms and effect of the developed additive on the physical properties of recycled OCC pulp handsheets. The tensile, tear and bursting strength, whiteness, air permeability, tensile energy absorption of the recycled OCC handsheets are examined. Fourier transform infrared (FTIR) spectroscopy, thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM) are used for the chemical and microstructure characterization of both NC based additives and recycled OCC pulp paper. The results show that the functional groups, such as carboxyl, amino and hydroxyl groups on the NC based additives, can combine with the hydroxyl groups on the recycled OCC fibres to generate chemical bonds, which increase the crosslinks between fibres as well as the bonding area, thus enhancing their tensile strength and improving their recycling rate. SEM shows that the paper with NC based additives had tighter inter-fibre bonds and smaller paper pore structure. Addition of 0.2% NC-DTPA-CS additive results in optimal properties of the recycled OCC paper with an increase by 32%, 188%, 19% and 35% of tensile strength, tearing degree, breaking resistance and air permeability respectively.

1 Introduction

Recently, nanocellulose (NC) has received increasing attention due to its attractive inherent properties such as biodegradability (Mishra et al., 2018), low density (Dufresne, 2010), high surface area (Klemm et al., 2018), stiffness (Hubbe et al., 2017), flexibility (Tanaka et al., 2015), high aspect ratio and unique rheology as well as the ability to form effective hydrogen bonds within the entire cellulose chain or other polymeric matrix (Li et al., 2021). The polyhydroxy chemistry of NC offers many derivatization opportunities for many industries and researchers. NC and its derivatives-based materials have been widely used in food (Velasquez-Cock et al., 2019), paper (E. Espinosa et al., 2016), and composite materials (Pei et al., 2011), especially in the paper industry. As NC is derived from natural fibres themselves, it has the inherent property of being compatible with pulp fibres. Nevertheless, it could cause some negative effects during the papermaking process, such as the poor retention of NC (Hollertz et al., 2017); forming a tightly entangled network structure of the slender filaments is favour for recycling but may cause drainage problems (Ahola et al., 2008; Onur et al., 2019); its limited adsorption capacity to pulp fibres and moderate reinforcement effect, which often makes it difficult to achieve specific strength requirements (Yang et al., 2017). Some researchers have addressed these negative effects by modifying the NC, adding fillers or multi-reinforced systems by considering the complex interactions between cellulose pulp, NC, mineral fillers and various commonly used additives (Eduardo Espinosa et al., 2019; He et al., 2017; Khalil et al., 2014). The molecular structure characteristics of NC itself, which is a linear polymer composed of D-glucans linked by β -1,4-glycosidic bonds and two D-glucans forming a cellobiose as a repeating unit of the cellulose polymer, each D-glucans unit having six carbon atoms and three hydroxyl groups (C2, C3 and C6 atoms, respectively), can confer a high degree of functionality to its biomolecules (Mahfoudhi et al., 2017; Poletto et al., 2013). The presence of abundant primary and

secondary hydroxyl groups on the surface of NC can be easily used to modify the biopolymer and produce cellulose derivatives or grafted to different materials. The abundant -OH groups on surface can also be attracted to each other electrostatically (through hydrogen bonding), leading to chain building ordered structures (Hubbe et al., 2015; Kalia et al., 2011). This hydrogen bonding across polysaccharides has a key role in adhesive applications related to the adhesion between NC and other materials (Gardner et al., 2008). This role is particularly prominent in the composite and paper industries (Amini et al., 2017).

Old Corrugated Container (OCC) is a major component of the recycling market. The fibres of OCC pulp are degraded shorter and weaker than the original fibres, and the bond between the short fibres is significantly weaker, which results in a very poor mechanical strength of the paper in addition to relatively weak strength of short fibres themselves compared to that of long/virgin fibres. Reusing OCC also requires dealing with pulp contaminants, the composition and types of which are extremely complex, such as adhesive impurities, inks, certain anions, etc. (Holbery et al., 2000). These adhesive impurities can generate deposits in paper-making equipment and also cause paper breakage phenomena, which prolongs production time and reduces productivity (Wu et al., 2010). The presence of anionic litter could cause the original strength agent to lose its efficiency and has a certain electrostatic repulsion between the fibres (Sheikhi et al., 2011; Zhao et al., 2014). Therefore, in the OCC recycling process, the removal and utilization of various impurities and the improvement of paper strength are the keys for the quality of recycled OCC pulp and decide whether the recycling of OCC can be further developed. In this paper, a novel paper additive nanocellulose derivative (NC-DTPA-CS) was developed by modifying NC with diethylenetriaminepentaacetic acid (DTPA) and cross-linking it with chitosan (CS). It is then applied as a paper reinforcement to enhance the tensile properties of recycled paper, and to improve the recyclability of OCC by forming chemical bonds as well as producing hydrogen bonding to bind the fibres to the OCC by making them cross-linked to a complex degree. The additive also bridges the pulp fibres with anion. The development could lead to improving the efficient recovery of waste paper resources, reducing greenhouse gas emissions, alleviating environmental pressure, and implementing a low-carbon economy with low energy consumption, low emissions, and low pollution, which has tremendous economic and social benefits.

2 Materials And Methods

2.1 Materials

The old corrugated container (OCC) used in this study was obtained from Qingshan Paper Co Ltd. The moisture content of OCC was 8.48%. The OCC was pulped to 37 °SR and stored for uses. Nanocellulose (NC) with high molecular weight, 20 ~ 50 nm diameter, $\geq 1\mu\text{m}$ length, 1.02mmol/g carboxyl content, and $2.5 \pm 0.5\%$ solid content was used as the raw materials for NC additive production. NC and chitosan (CS) were provided by Sinopharm Chemical Reagent Co Ltd., DTPA by Shanghai Maclean Biochemical Technology Co Ltd., sodium hydroxide (NaOH) by Xilong Technology Co Ltd., and sodium hypophosphite (SHP) and acetic acid (CH_3COOH) by Tianjin Zhiyuan Chemical Reagent Co Ltd.

2.2 Fabrication of advanced NC additives

5 g of DTPA was dissolved in 20 mL of NaOH solution with pH = 12 and 1 g of SHP was added and heated to make it fully reacted. The reaction mechanism is shown in Fig. 1a. After 5 g of NC was added, the mixture was stirred vigorously by hand with a glass rod and placed in an electric thermostatic blast dryer at 130 °C for 4 h. The product was washed with distilled water and filtered several times to remove the unreacted material, and then air-dried overnight at 50 °C in an electric thermostatic blast dryer to obtain a product called NC-DTPA. The reaction mechanism is shown in Fig. 1b. After dissolving 1 g of CS in 50 mL of 1.5% acetic acid solution and 1 g NC-DTPA in 50 mL of deionized water, both solutions were mixed together and reacted in a magnetic stirrer at 80 °C for 90 min to obtain the product called NC-DTPA-CS. The reaction mechanism is shown in Fig. 1c.

Chemical reaction and structure of NC-DTPA-CS

2.3 Preparation of recycled OCC pulps

The pulp concentration was adjusted to 1.57% and the pulp temperature was (20 ± 5) °C. The pulp was sparged in a Valley pulping machine (T06-23, Xianyang Tongda Light Industrial Equipment Co., Ltd, China) for 30 min until no small pulp pieces appeared. The pulping was carried out under a lever arm load of (29.4 ± 1) N and the pulping degree was tested by taking samples every 5 min until the pulping degree of 37 °SR. The pulp was finally removed, and wrung out to balance the water and refrigerated.

2.4 Handsheets preparation

The wet OCC pulp equivalent to 2 g of absolute dry pulp is diluted with 1000 mL of deionized water and dissociated in the fibre standard dissociator (T075-A, Xianyang Tongda Light Industrial Equipment Co., Ltd., China) for 5 min. The required NC-DTPA-CS was added, including the compositions with 0%, 0.1%, 0.2%, 0.3%, 0.5%, 1.0%, 1.5%, 2.0% of the absolute dry volume of pulp respectively. The same NC was also added in the same ratio as above. The pulps with the additives were again dissociated in the fibre standard dissociator at 30,000 rpm for 5 min. The handsheets was then copied with a sheet former (200-1, Labtech Canada, Ltd., Canada) with nominated weight of 60 g/m². The obtained wet paper sheets were dried at 105 °C for 15 min. The final dried handsheets were then stored at a humidity of 45% and a temperature of 25 °C. The experimental flow diagram is shown in Fig. 2.

Schematic diagram of NC-DTPA-CS and paper preparation process

2.5 Characterizations

2.5.1 Tensile strength test

The tensile strength of OCC handsheets was tested using the L&W tensile strength tester (Code 066, L&W Sweden, Sweden) according to the TAPPI T 494 method. The samples were cut from the handsheets with a rectangular dimension of 15 mm × 180 mm and tested with a tensile rate of 10 mm/min. 10 specimens

were tested in each group and the average value was taken as the final result. The tensile index is defined as the quotient of the tensile strength (N/m) of the handsheets and the weight (g/m²).

2.5.2 Tear strength test

Tear strength of OCC pulp hand-crafted handsheets was tested using L&W tear tester (Code 009, L&W Sweden, Sweden) according to TAPPI T 414 method. The samples were cut from the handsheets with a rectangular dimension of 63 mm × 75 mm. 5 test pieces were cut in each direction and tested, and the average value was taken as the final result.

2.5.3 Bursting strength test

The burst strength of OCC pulp hand-crafted handsheets was tested using the L&W paperboard bursting tester (Code, L&W Sweden, Sweden) according to the TAPPI T 403 method. The dimension of samples was 70 mm × 70 mm. 10 valid data were obtained on each side and the average value was taken as the final result.

2.5.4 Whiteness test

The whiteness of OCC pulp hand-crafted handsheets is tested using the whiteness tester (YQ-Z-48B, Hangzhou Qingtong Boke Automation Technology Co., China) according to the TAPPI T 525 method. The dimension of samples was 6 mm × 6 mm. Six specimens per group of samples were used and the average taken as the final result.

2.5.5 Air permeability test

The air permeability of OCC pulp hand-crafted handsheets was tested using the paper and board air permeability tester (J-TQY10, Sichuan Changjiang Paper Instrument Co., China) according to the TAPPI T 460 method. 5 mm × 5 mm samples were used to cover the lower probe of the instrument. Each test sample was measured three times on both sides and the average taken as the final result.

2.5.6 Tensile energy absorption

Tensile energy absorption (TEA) is a comprehensive function of handsheets strength and elongation, which is an indicator of handsheet toughness. The TEA was calculated according to the following Eq. (1) (Balan et al., 2015):

$$\text{TEA} = \frac{1000A}{b*c}$$

1

Where, A is the integral area of the tension-elongation curve (mJ), b is the Original spacing between the two clamping ports (mm) and c is the original width of test strip (mm). Dimension of the samples was 15 mm × 180 mm. 10 specimens were tested in each group and the average value was taken as the final result.

2.5.7 FTIR Analysis

Dried handsheets, namely NC (F1), NC-DTPA (F2), NC-DTPA-CS (F3), OCC pulp sheet (F4), OCC-NC-DTPA-CS pulp sheet (F5), of 1–2 mg mixed with 100 mg of potassium bromide were scraped and ground well with a razor blade, placed in a mold and pressed at 15 MPa pressure for 2 min to produce FTIR samples. The FTIR spectra were measured with Fourier transform infrared spectroscopy (Nicolet 380, American Thermoelectric Corporation, USA). Test conditions: resolution 4 cm^{-1} , 32 scans, scan range $4000 - 400\text{ cm}^{-1}$.

2.5.8 Thermal Gravimetric Analysis (TGA)

The thermal stability of the NC, NC-DTPA, NC-DTPA-CS, OCC pulp sheet, OCC-NC-DTPA-CS pulp sheet were determined by taking 6 mg of dried handsheets samples into the DSC simultaneous thermal analyzer (STA449C, NETZSCH Germany Ltd., Germany). Test conditions: nitrogen atmosphere, scanning temperature $25 \sim 800\text{ }^{\circ}\text{C}$, temperature rise rate $10\text{ }^{\circ}\text{C}/\text{min}$.

2.5.9 Scanning Electron Microscope (SEM)

Scanning electron microscopy was performed on OCC pulp handsheets treated with NC-DTPA-CS derivatives. The pre-prepared handsheets samples were sprayed with gold using a vacuum ion sputtering instrument (JFC-1600, JEOL Corporation, Japan). The structures were then observed and photographed using a Hitachi cold field emission scanning electron microscope (SU 8010, Ko Min International Trade Co., China).

3 Results And Discussion

3.1 Surface functional groups

3.1.1 FTIR of NC additives

The FTIR spectra of NC (F1), NC-DTPA (F2) and NC-DTPA-CS (F3) are shown in Fig. 3. It is apparent that the spectra of F1, F2, and F3 all have a strong absorption peak at 3438 cm^{-1} , which is the superposition of symmetric and asymmetric stretching vibrations from O-H or N-H. The absorption peak at 1635 cm^{-1} is attributed to DTPA by the C = O stretching vibration and the bending vibration of N-H. It can be seen that the F1 has no absorption peak at $1700 - 1800\text{ cm}^{-1}$, indicating that there is no carbonyl group in the NC. However, there was an absorption peak at 1736 cm^{-1} in the spectrum of F2 (Fig. 3a) and this peak refers to the C = O double bond stretching vibration absorption peak in the ester group, indicating that the esterification reaction between NC and DTPA occurred and NC was successfully chelated to DTPA (Salam et al., 2010). The dehydration of DTPA catalyzed by sodium hypophosphite (SHP) generates DTPA dianhydride and the hydroxyl group of the reactive group on the surface of NC may undergo esterification with DTPA dianhydride. The spectrum of F3 shows an absorption peak at 1416 cm^{-1} attributed to the C-N

stretching vibration absorption peak. There is an absorption peak at 1635 cm^{-1} attributed to N-H bending vibration absorption peak (Fig. 3b).

3.1.2 FTIR of modified OCC paper

The FTIR Spectra of OCC pulp sheet (F4) and OCC-NC-DTPA-CS pulp sheet (F5) are shown in Fig. 3. It is apparent that the spectra of F4 and F5 all have a strong absorption peak at 3438 cm^{-1} which may be attributed to the hydroxyl group on the OCC pulp sheet as well as the OCC pulp sheet treated with NC-DTPA-CS derivative (Fig. 3a). Compared to the blank OCC pulp sheet (F4), the NC-DTPA-CS derivative treated sheet has a smaller absorption peak at 3438 cm^{-1} which may be due to the chemical bonding of a large number of hydroxyl groups on the OCC pulp sheet with the reactive groups such as hydroxyl, carboxyl and amino groups on the NC-DTPA-CS derivative. An absorption peak with high intensity at 1635 cm^{-1} was attributed to the complexation reaction of the NC-DTPA-CS derivative with the OCC pulp after incorporation into the OCC pulp matrix and drying at $105\text{ }^{\circ}\text{C}$, which increases the intensity of this amide band compared to the NC-DTPA-CS derivative. An absorption peak with high intensity at 1635 cm^{-1} is attributed to the amide group in the NC-DTPA-CS (F3) derivative itself and the amide reaction of the NC-DTPA-CS derivative with the hydroxyl group on the OCC pulp after incorporation into the OCC pulp matrix by drying at $105\text{ }^{\circ}\text{C}$, which leads to a significant increase in the intensity of the amide band. It is further illustrated that the polyelectrolyte complexes interacting between the carboxyl group of NC-DTPA and the amino group of CS may be converted into amide bonds when the NC-DTPA-CS derivatives were incorporated into the OCC pulp matrix.

3.2.1 Thermal behaviour of NC additives

The thermogravimetric analyses of NC, NC-DTPA, and NC-DTPA-CS are given in Fig. 4a. Their thermogravimetric behavior was evaluated at a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ under nitrogen. It can be seen that the thermal decomposition of the three samples, namely NC, NC-DTPA, and NC-DTPA-CS, can be divided into four main stages. The first stage is from room temperature to $100\text{ }^{\circ}\text{C}$, which is mainly the stage of removal of certain volatile groups, the main component of which is water. The second stage was from $100\text{ }^{\circ}\text{C}$ to around $200\text{ }^{\circ}\text{C}$. The sample mass was either constant or modest decrease depending on the materials, where NC-DTPA lost more weight than both NC and NC-DTPA-CS, and this may be due to the fact that DTPA has a lower degradation temperature than both NC as well as CS. The third stage is from $200\text{ }^{\circ}\text{C}$ to $400\text{ }^{\circ}\text{C}$. The significant decomposition and rapid weight loss took place, caused by the decomposition, oxidation and combustion of the sample components. The differential thermal thermogravimetric analysis (DTG) of the three samples of NC, NC-DTPA, and NC-DTPA-CS can be further scrutinized as a decomposition rate (Fig. 4b). It can be seen that the weight loss peak of NC was at $318\text{ }^{\circ}\text{C}$ and the maximum thermal decomposition rate was reached at this temperature. The maximum thermal decomposition rate was reached at $208\text{ }^{\circ}\text{C}$ for NC-DTPA and at $203\text{ }^{\circ}\text{C}$ for NC-DTPA-CS. The specific thermal decomposition is shown in Table 1. The fourth stage is from $400\text{ }^{\circ}\text{C}$ to $500\text{ }^{\circ}\text{C}$, where the sample is further decomposed and gradually reaches weight loss equilibrium.

Table 1
Parameters of pyrolytic properties

Samples	Residuals at 100 °C (%)	Residuals at 400 °C (%)	Residual carbon at 500 °C (%)	Start weight loss temperature (°C)	Maximum weight loss temperature (°C)	DSC melting point (°C)
NC	93.15	27.14	20.85	200	318	106
NC-DTPA	96.81	35.87	28.23	180	236	112
NC-DTPA-CS	93.07	36.82	31.57	188	203	121

While the maximum weight loss temperature of all NC derivative additives decreases compared to that of NC, the residual mass for the former is significantly higher than that for the latter when heated to 500 °C. This may be due to the lower degradation temperature of the NC modifiers, which are attached to the NC surface through ester bonds (Ferrer et al., 2012). As can be seen from Table 1, the melting temperatures for the NC derivative additives are elevated, which may be due to the robustness of the chemical structure resulted from the increased hydrogen bonding and higher molecular organization obtained by cross-linking. The introduction of carbonyl group after the modification of NC by esterification reaction may lead to an increase in the number of intermolecular hydrogen bonds, which makes the crosslinking between NC and DTPA molecules more stable. The NC-DTPA grafted with CS is in the form of ionic bonds and more hydrogen bonds could be formed. Therefore, the melting temperature of NC derivative additives is gradually increasing. NC has the highest thermal stability with modest weight loss rate. This is due to the introduction of substituents such as carbonyl and hydroxyl groups on the surface of NC, which destroys the structure of NC and makes NC derivative additives less stable than NC.

The maximum weight loss temperature of NC-DTPA-CS additive is lower than that of NC-DTPA. This is because the generation of NC-DTPA-CS is equivalent to the introduction of carbonyl and hydroxyl groups on NC by esterification reaction; the introduction of CS on NC-DTPA by complexation reaction, which is connected by ionic bonding, the chance of hydrogen bonding generated is reduced and the structure of NC-DTPA may be destroyed, which makes the maximum weight loss temperature of NC-DTPA-CS lower.

3.2 Thermal behaviour

3.2.2 Thermal behavior of NC modified OCC sheet

The TG profiles of NC-DTPA-CS modified OCC sheet are shown in Fig. 5. It can be seen that the thermal decomposition of the control OCC handsheet and the NC-DTPA-CS derivative-treated handsheet can be divided into four main stages. The first stage is the loss of fibre weight caused by the physical adsorption hydrolysis of fibres in the paper. Water physically adsorbed in the paper is desorbed from room temperature to 105 °C. The nature of the paper remains largely unchanged at this stage. The second stage is almost constant in mass, although the production of small molecule gases and some volatile

components may take place. The thermo-gravimetric curve was basically horizontal from 105 °C to 250 °C, which is higher than those of NC derivative additives themselves. This is because the main components of the OCC pulp sheet have cellulose, and NC has all the properties of cellulose. NC derivatives are based on NC with the introduction of DTPA and CS, which destroy the structure of NC making its derivatives less thermally stable than NC, therefore the pyrolysis temperature of cellulose at this stage is higher than that of the NC-derived additive itself. The third stage is the main part of the thermal degradation of the sheet, the decomposition of the material is very rapid, the OCC pulp sheet and the sheet treated with NC-DTPA-CS derivatives lose weight sharply, the mass loss is the largest, the glycosidic bonds may open and break to generate some new low molecular weight volatile products. The loss of paper quality is significant from 250 °C to 380 °C. The fourth stage is the gradual decomposition of the product, causing further weight loss up to almost constant mass. The start weight loss temperature was slightly increased and the initial weight loss mass is reduced even lower in the NC-DTPA-CS derivative-treated sample group compared to the control blank group, and the temperature at the fastest degradation rate was similar. This may be due to the introduction of substituents such as carbonyl and hydroxyl groups on NC, which increase the chance of hydrogen bonding, the initial degradation weight loss temperature was increased and the temperature at the fastest degradation rate was basically the same. The specific thermal decomposition of the OCC pulp sheet paper and the OCC-NC-DTPA-CS pulp sheet paper were shown in Table 2. When the temperature reached 600 °C, more residues remained in the sample group modified with NC-DTPA-CS additives, which may be due to the cross-linking of NC-DTPA-CS with pulp fibres.

Table 2
Pyrolysis characteristic parameters of OCC handsheets

Samples	Start weight loss temperature (°C)	Maximum weight loss temperature (°C)	Residual carbon at 600 °C (%)
OCC pulp sheet (control)	251	328	19.54
OCC-NC-DTPA-CS pulp sheet	254	320	23.57

3.3 Strength enhancement of recycled OCC based paper with nanocellulose derivative additives

In packaging paper applications, the paper substrate requires sufficient resistance to external stress to ensure that it does not break easily, which is generally attributable to the adequate development of hydrogen bonds at the molecular level in addition to the fibre strength itself, and also depends on the number and area of bonding sites, which are closely related to the geometry of the fibre. Unfortunately, fibres undergo irreversible damage during secondary fibre recycling and without enhancement, this damage eventually affects the mechanical properties of the paper. An enhancement should and could be carried out for an effective recycling and quality paper pulp (Fig. 6). It can be seen that the mechanical

properties of the paper could be improved significantly with NC based additives studied. The paper burst strength significantly increased by 17.81% with an addition of 0.1% NC-DTPA-CS and then gradually increased from 152.20 kPa to 155.5 kPa when NC-DTPA-CS increased from 0.1–0.3%. However, a continuous increase of additive did not result in an increase rather gradually decrease from 155.5 kPa to 135.8 kPa when the additive increased from 0.3–2%. There was a similar trend of change in the burst strength for the addition of NC additive though with much lower magnitude. The reactive groups on NC and NC-DTPA-CS can produce hydrogen bonding with hydroxyl groups on pulp fibres, increasing the number and area of bonding points between pulp fibres, which could increase the bonding strength between fibres, and therefore the burst strength of paper increases. Because there are more reactive groups on NC-DTPA-CS than NC, the number and area of its bonding points with pulp fibres will be higher, leading to greater burst strength for NC-DTPA-CS than NC enhanced fibres. The tensile force of the handsheets with the addition of NC and NC-DTPA-CS is shown in Fig. 6 (b). With the increase in the amount of NC and NC-DTPA-CS added, the paper tension shows a trend of rising and then decreasing, because a certain amount of NC and NC-DTPA-CS can cross-link with the pulp fibres. The force is strengthened during the curing and drying process of the paper, and the bonding between the fibres is increased, thus increasing the tension resistance of the paper.

Tensile strength of paper and paperboard is one of the parameters that determine their applications. The main factors that affect the tensile strength of paper include the bond strength between fibres, the strength of the fibres themselves, and the interweaving between fibres (Ferrer et al., 2012). The tensile strength and tensile index of the NC and NC-DTPA-CS enhanced papers are shown in Fig. 6(c) (d). The tensile strength and tensile index both increased and then decreased as the amount of NC and NC-DTPA-CS increased. When NC-DTPA-CS was added at 0.2%, the tensile strength reached 0.91 KN/m, an increase of 31.82% compared with the blank OCC handsheet. This may be due to the fact that the structural molecules of NC-DTPA-CS derivatives contain basic amino groups, which could generate positive charges in slightly acidic media and may form covalent or ionic bonds with negatively charged fibres in pulp fibres during the papermaking process (Mucha et al., 2000). The DTPA in NC-DTPA-CS derivatives is rich in free carboxyl groups, which could also form ionic bonds with the fibres on the surface of pulp fibres and increase the relative bonding area of the fibre facultative (Duker et al., 2008). The increase for NC-DTPA-CS modified fibres were significantly higher compared to that for the same content of NC. This is probably due to the high surface area/volume ratio of the NC derivatives and the relatively strong chemical bonding between the OCC pulp fibres through the large number of carboxyl and amino groups on the derivatives. NC and their derivatives can become very thin films and distributed in the fibres during the drying and heating of the paper. Therefore, by increasing the generation of contact area, more hydrogen bonds can be formed between the fibres and the NC derivatives, and there are more opportunities for freely bonding of the fibre hydroxyl groups. The free carboxyl groups of NC also contribute to interfibre bonding, thus improving paper strength (Bernabe et al., 2005). Therefore, the increase in tensile strength can be attributed to the carboxyl, amino, and hydroxyl groups, increasing the inter-fibre bonding area as well as the number of bonds during the paper forming process. When the

additives exceed 0.2%, the bonding of NC-DTPA-CS with pulp fibres may reach saturation, and the number of bonding and bonding area reaches the limit.

Physical properties of paper with NC and NC-DTPA-CS content (a: Burst, b: Force, c: Tensile Strength, d: Tensile Index, e: Breaking Length, f: TEA, g: Tearing Strength, h: Whiteness, i: Air permeability.)

Tensile energy absorption (TEA) is a paper physical property index that combines tensile strength and tensile rate (strain) into one consideration, which can indirectly reflect the strength and toughness of packaging paper or recycled paper. It can be seen that NC and NC-DTPA-CS modifications resulted in significant effect on the TEA (Fig. 6(f)). When the stretch rate is increased or the tensile strength is increased, the tensile absorption energy of the paper is increased. An addition of 0.3% NC-DTPA-CS gave rise to about 35% increase in TEA, but further increase in additives resulted in a decrease in TEA. NC modification has a much modest effect on TEA, which gradually increases with the increase of NC and then level off after 0.5% addition. This may be because the addition of NC and NC-DTPA-CS makes the inter-fibre bond stronger, which leads to an increase in the f breaking length. The changes of paper breaking length with the addition of NC and NC-DTPA-CS are shown in Fig. 6(d). With the increase of NC and NC-DTPA-CS, the breaking length of paper showed a trend of rising and then leveling off.

The changes in paper tearing strength with the addition of NC and NC-DTPA-CS are shown in Fig. 6(g). It is evident that the tearing strength of papers increases and reached a maximum at 0.3% NC-DTPA-CS and at 1.5% NC additions respectively, but the maximum increase rate takes place at 0-0.2% for both types of additives. Paper whiteness refers to the ability of the paper to be fully reflected by light irradiation, and the higher the whiteness of the paper, the more its surface can make the characteristic of the ink color accurately (Bristow, 1994; Jimenez Rezende et al., 2016). The whiteness of the paper did not change significantly with the increase in the content of the additive NC-DTPA-CS (Fig. 6h). This may be because the amount of NC-DTPA-CS added is relatively small to the absolute dry weight of the paper, which did not cause changes in the whiteness of the OCC.

The sheet is a laminated material with porosity formed by the interweaving of fibres, and the paper permeability can reflect the paper pore size as well as the tightness of the paper (Jimenez Rezende et al., 2016). It is interesting that the air permeability of the developed paper decreased and then levelled off with the additive content. When the content of NC-DTPA-CS was 0.2 %, the paper air permeability showed a minimum value of $29.44\mu\text{m}/(\text{Pa}\cdot\text{s})$. This means the paper pore structure became smaller and the paper tightness increased, which was attributed to the increase in bonding and networking of fibres, especially fine fibres after NC-DTPA-CS or NC modifications.

OCC refers to pulp with fibres that have passed through at least two recycling processes, which are shorter and weaker than the original fibres, resulting in poor quality in terms of paper strength. OCC contains a large amount of anionic trash and more fine fibres, where the presence of these anions prevents the bonding between pulp fibres (Zhao et al., 2014). It is apparent that NC or NC-DTPA-CS modifications help improve the efficiency of the utilization of anionic waste and fine fibres in the slurry. Some reactive groups on the auxiliary are reactive suitable for forming agglomerates with anionic trash

and fine fibres, which can prevent contact with each other. The basic groups (-NH_2) on each ring in the NC-DTPA-CS can become positively charged in sufficiently acidic media and thus may form ionic or covalent bonds with negatively charged cellulose or anionic trash in paper fibres during papermaking. NC-DTPA-CS acts as a bridge between the OCC and the anion (Fig. 7(a)). The hydroxyl, carboxyl, amino and other reactive groups on NC-DTPA-CS can produce chemical bonding with pulp fibres and generate stable chemical bonds by curing and heating (Fig. 7(b)). Hydrogen bonding can also be generated to enhance the bonding area of the inter-fibre bond and this can be further confirmed from SEM analyses which is presented in next section. The mechanical properties of paper are thus enhanced (Fig. 7).

3.4 Structure of enhanced OCC paper

The SEM images of the paper fibre surface are shown in Fig. 8 (a: no addition of NC-DTPA-CS, b: addition of 0.2% NC-DTPA-CS). It can be seen that the paper fibres without NC-DTPA-CS addition were loosely interwoven without tight arrangement. There existed various spaces between the fibres (Fig. 8a1) and on the fibre surface, there were local splits and irregular sparse morphology (Fig. 8a3). This may be due to the low degree of cross-linking between the fibres and among fibrils on the fibre surface. The fibres with 0.2% NC-DTPA-CS addition have a thin film with smooth surface compared with those untreated (Fig. 8a), which can adhere to the fibre surface uniformly. The deposits appeared on the fibre surface may be due to the cross-linking phenomenon on the OCC pulp fibres with the NC additives. The fibres interlocked and interpenetrated each other and arranged closely. It is evident that the surface of paper fibres after the addition of 0.2% NC-DTPA-CS is flatter and smooth compared to those without treatment (Fig. 8a3 and 8b3), which shows slight cracks without the addition of NC-DTPA-CS. This may be due to the fact that NC-DTPA-CS is attached to the pulp fibres and the multifunctional groups on the NC-DTPA-CS derivatives form chemical bonds with the hydroxyl groups on the pulp fibres, which increases the number of fibre-to-fibre bonds and the bonding area, thus making the paper structure more compact. The hydrogen bonding force between paper fibres is transformed into chemical bonding, which improves the chemical bonding between fibres and fibres and fibres and additives. A high-strength semi-interpenetrating network structure may also be formed in the paper, which improves the bond strength between fibres, and the fibres interpenetrate with each other and are arranged more closely.

4 Conclusions

1) NC was confirmed by Fourier infrared spectroscopy (FTIR) to produce ester bonds by esterification with DTPA and amide bonds by amide reaction with CS to successfully formulate a novel paper reinforcing agent, NC-DTPA-CS.

2) NC-DTPA-CS has been successfully applied to recycled OCC pulp as a reinforcing agent with rapid paper forming and drying.

3) NC-DTPA-CS significantly improved various physical properties of used OCC handsheet and enhanced the recyclability of OCC pulps; NC-DTPA-CS could react with the hydroxyl groups of pulp fibres to form chemical bonds that were attached to the paper, increasing the cross-linking between fibres as well as the

bonding area. The surface of paper fibres modified with NC-DTPA-CS was smooth with interpenetrating interlacing fibres and compact structure. The paper modified with NC-DTPA-CS exhibited higher thermal stability than that of untreated and higher mass retention when the temperature reached 600 °C partly due to the cross-linking of NC-DTPA-CS with the pulp fibres. The optimal addition of NC-DTPA-CS at 0.2% resulted in an increase in the tensile strength by 32%, tearing degree by 188%, breaking resistance by 19%, and permeability by 35% compared with the untreated recycled OCC handsheets.

Declarations

CrediT authorship contribution statement

Ao Li: Investigation and original draft. Dezhong Xu: Data acquisition. Mengnan Zhang: Investigation. Shengzhong Wu: Methodology. Yu Li: Concept and design. Jiuping Rao: Concept and supervision. Mizi Fan: Supervision, review and editing.

Declaration of Competing Interest

The authors report no declarations of interest.

Acknowledgements

This work was supported by the National Natural Science Foundation of China [Grant number 31971592]; the National Key Scientific Research Project of China [Grant number 2016YFD060070504].

References

1. Ahola S, Osterberg M, Laine J (2008) Cellulose nanofibrils-adsorption with poly(amideamine) epichlorohydrin studied by QCM-D and application as a paper strength additive. *Cellulose* 15:303–314. <https://doi.org/10.1007/s10570-007-9167-3>
2. Amini E, Tajvidi M, Gardner DJ, Bousfield DW (2017) Utilization of Cellulose Nanofibrils as a Binder for Particleboard Manufacture. *Bioresources* 12:4093–4110. <https://doi.org/10.15376/biores.12.2.4093-4110>
3. Balan T, Guezennec C, Nicu R, Ciolacu F, Bobu E (2015) Improving barrier and strength properties of paper by multi-layer coating with bio-based additives. *Cellul Chem Technol* 49:607–615
4. Bernabe P, Peniche C, Arguelles-Monal W (2005) Swelling behavior of chitosan/pectin polyelectrolyte complex membranes. Effect of thermal cross-linking. *Polym Bull* 55:367–375. <https://doi.org/10.1007/s00289-005-0439-5>
5. Bristow JA (1994) The calibration of instruments for the measurement of paper whiteness. *Color Research Application* 19:475–483
6. Dufresne A (2010) Processing of Polymer Nanocomposites Reinforced with Polysaccharide Nanocrystals. *Molecules* 15:4111–4128. <https://doi.org/10.3390/molecules15064111>

7. Duker E, Lindstrom T (2008) On the mechanisms behind the ability of CMC to enhance paper strength. *Nord Pulp Pap Res J* 23:57–64. <https://doi.org/10.3183/npprj-2008-23-01-p057-064>
8. Espinosa E, Rol F, Bras J, Rodriguez A (2019) Production of lignocellulose nanofibers from wheat straw by different fibrillation methods. Comparison of its viability in cardboard recycling process. *Journal of Cleaner Production* 239. <https://doi.org/10.1016/j.jclepro.2019.118083>
9. Espinosa E, Tarres Q, Delgado-Aguilar M, Gonzalez I, Mutje P, Rodriguez A (2016) Suitability of wheat straw semichemical pulp for the fabrication of lignocellulosic nanofibres and their application to papermaking slurries. *Cellulose* 23:837–852. <https://doi.org/10.1007/s10570-015-0807-8>
10. Ferrer A, Quintana E, Filpponen I, Solala I, Vidal T, Rodriguez A, Laine J, Rojas OJ (2012) Effect of residual lignin and heteropolysaccharides in nanofibrillar cellulose and nanopaper from wood fibers. *Cellulose* 19:2179–2193. <https://doi.org/10.1007/s10570-012-9788-z>
11. Gardner DJ, Oporto GS, Mills R, Samir MASA (2008) Adhesion and surface issues in cellulose and nanocellulose. *J Adhes Sci Technol* 22:545–567. <https://doi.org/10.1163/156856108x295509>
12. He M, Yang G, Cho B-U, Lee YK, Won JM (2017) Effects of addition method and fibrillation degree of cellulose nanofibrils on furnish drainability and paper properties. *Cellulose* 24:5657–5669. <https://doi.org/10.1007/s10570-017-1495-3>
13. Holbery JD, Wood DL, Fisher RM (2000) Analysis and characterization of contaminants in OCC recycle furnishes. *Tappi journal* 83:57
14. Hollertz R, Duran VL, Larsson PA, Wagberg L (2017) Chemically modified cellulose micro- and nanofibrils as paper-strength additives. *Cellulose* 24:3883–3899. <https://doi.org/10.1007/s10570-017-1387-6>
15. Hubbe M A, Rojas O J, Lucia L A (2015) Green Modification of Surface Characteristics of Cellulosic Materials at the Molecular or Nano Scale: A Review. *Bioresources* 10: 6095–6206. Retrieved from < Go to ISI>://WOS:000364199800173
16. Hubbe MA, Tayeb P, Joyce M, Tyagi P, Kehoe M, Dimic-Misic K, Pal L (2017) Rheology of Nanocellulose-rich Aqueous Suspensions: A Review. *Bioresources* 12:9556–9661. <https://doi.org/10.15376/biores.12.4.Hubbe>
17. Jimenez Rezende D, Eslami S, Mohamed S, Battaglia P, Jaderberg M, Heess N (2016) Unsupervised learning of 3d structure from images. *Advances in neural information processing systems* 29:4996–5004
18. Kalia S, Dufresne A, Cherian BM, Kaith BS, Averous L, Njuguna J, Nassiopoulos E (2011) Cellulose-Based Bio- and Nanocomposites: A Review. *International Journal of Polymer Science* 2011. <https://doi.org/10.1155/2011/837875>
19. Khalil HPSA, Davoudpour Y, Islam MN, Mustapha A, Sudesh K, Dungani R, Jawaid M (2014) Production and modification of nanofibrillated cellulose using various mechanical processes: A review. *Carbohydr Polym* 99:649–665. <https://doi.org/10.1016/j.carbpol.2013.08.069>
20. Klemm D, Cranston ED, Fischer D, Gama M, Kedzior SA, Kralisch D, Kramer F, Kondo T, Lindstrom T, Nietzsche S, Petzold-Welcke K, Rauchfuss F (2018) Nanocellulose as a natural source for

- groundbreaking applications in materials science: Today's state. *Mater Today* 21:720–748. <https://doi.org/10.1016/j.mattod.2018.02.001>
21. Li A, Xu DZ, Luo L, Zhou YL, Yan W, Leng X, Dai DS, Zhou YH, Ahmad H, Rao JP, Fan MZ (2021) Overview of nanocellulose as additives in paper processing and paper products. *Nanotechnology Reviews* 10:264–281. <https://doi.org/10.1515/ntrev-2021-0023>
 22. Mahfoudhi N, Boufi S (2017) Nanocellulose as a novel nanostructured adsorbent for environmental remediation: a review. *Cellulose* 24:1171–1197. <https://doi.org/10.1007/s10570-017-1194-0>
 23. Mishra RK, Sabu A, Tiwari SK (2018) Materials chemistry and the futurist eco-friendly applications of nanocellulose: Status and prospect. *Journal of Saudi Chemical Society* 22:949–978. <https://doi.org/10.1016/j.jscs.2018.02.005>
 24. Mucha M, Miśkiewicz D (2000) Chitosan blends as fillers for paper. *J Appl Polym Sci* 77:3210–3215
 25. Onur A, Ng A, Gamier G, Batchelor W (2019) The use of cellulose nanofibres to reduce the wet strength polymer quantity for development of cleaner filters. *J Clean Prod* 215:226–231. <https://doi.org/10.1016/j.jclepro.2019.01.017>
 26. Pei A, Malho J-M, Ruokolainen J, Zhou Q, Berglund LA (2011) Strong Nanocomposite Reinforcement Effects in Polyurethane Elastomer with Low Volume Fraction of Cellulose Nanocrystals. *Macromolecules* 44:4422–4427. <https://doi.org/10.1021/ma200318k>
 27. Poletto M, Pistor V, Zattera AJ (2013) Structural Characteristics and Thermal Properties of Native Cellulose. *Cellulose - Fundamental Aspects*
 28. Salam A, Pawlak JJ, Venditti RA, El-tahlawy K (2010) Synthesis and Characterization of Starch Citrate-Chitosan Foam with Superior Water and Saline Absorbance Properties. *Biomacromol* 11:1453–1459. <https://doi.org/10.1021/bm1000235>
 29. Sheikhi P, Talaeipour M (2011) Comparison mechanical and chemical treatments on properties of low yield bagasse pulp during recycling. *World Academy of Science, Engineering and Technology* 57: 490–494
 30. Tanaka R, Saito T, Hondo H, Isogai A (2015) Influence of Flexibility and Dimensions of Nanocelluloses on the Flow Properties of Their Aqueous Dispersions. *Biomacromol* 16:2127–2131. <https://doi.org/10.1021/acs.biomac.5b00539>
 31. Velasquez-Cock J, Serpa A, Velez L, Ganan P, Gomez Hoyos C, Castro C, Duizer L, Goff HD, Zuluaga R (2019) Influence of cellulose nanofibrils on the structural elements of ice cream. *Food Hydrocolloids* 87:204–213. <https://doi.org/10.1016/j.foodhyd.2018.07.035>
 32. Wu S, Tang Y, Xue G, Zhao Y (2010) *INFLUENCE OF CPAM/CMC LAYER-BY-LAYER SELF-ASSEMBLY ON OCC FIBER PHYSICAL STRENGTH AND SURFACE PROPERTIES*
 33. Yang W, Bian H, Jiao L, Wu W, Deng Y, Dai H (2017) High wet-strength, thermally stable and transparent TEMPO-oxidized cellulose nanofibril film via cross-linking with poly-amide epichlorohydrin resin. *Rsc Advances* 7:31567–31573. <https://doi.org/10.1039/c7ra05009g>
 34. Zhao Y, Li J, Rao QL, Cheng W (2014) Furnish pretreatment to improve paper strength aid performance in papermaking. Google Patents

Figures

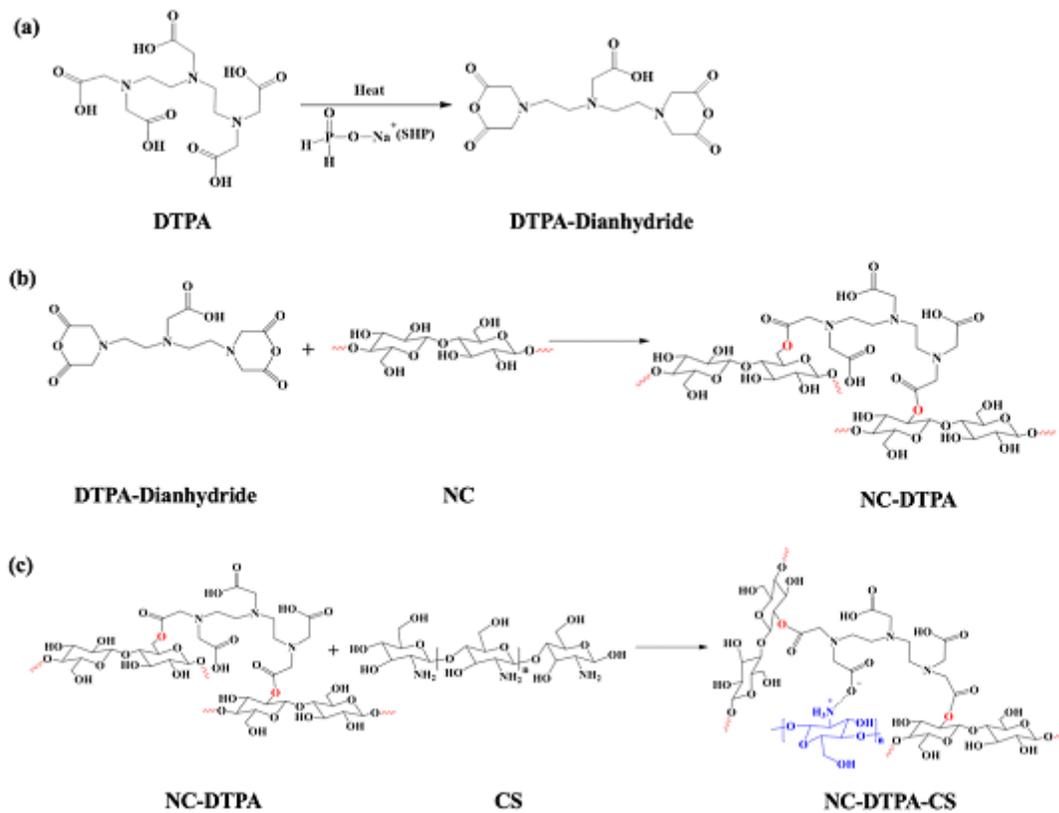


Figure 1

Chemical reaction and structure of NC-DTPA-CS

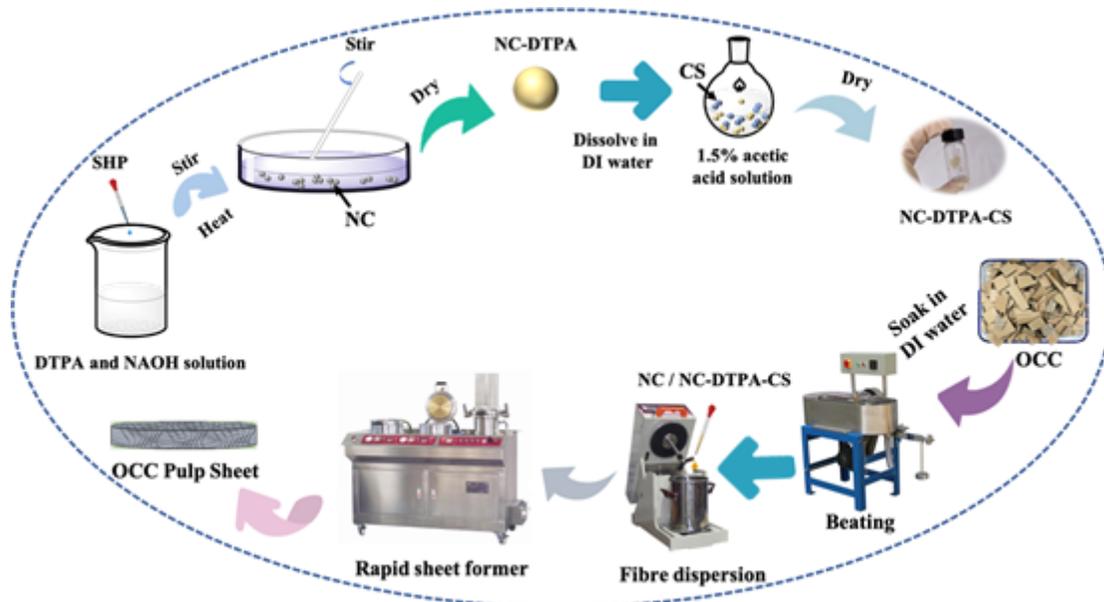


Figure 2

Schematic diagram of NC-DTPA-CS and paper preparation process

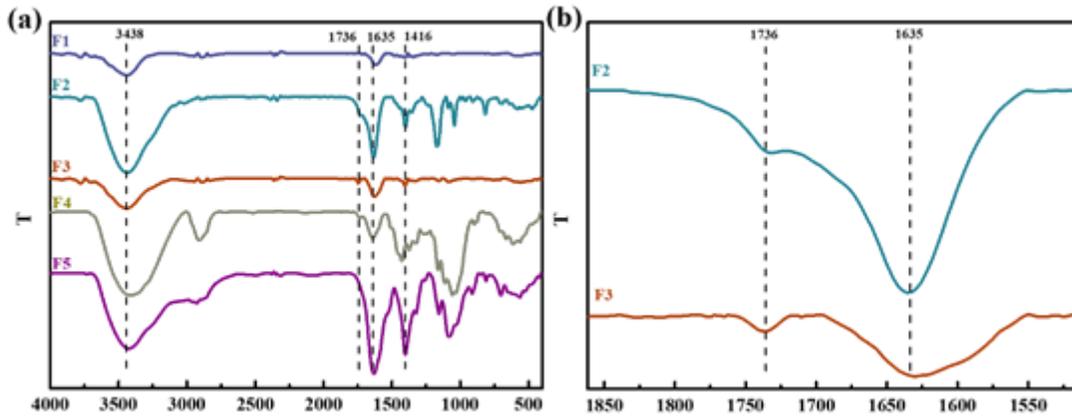


Figure 3

FTIR Spectra of various handsheets (F1: NC, F2: NC-DTPA, F3: NC-DTPA-CS, F4: OCC pulp sheet, F5: OCC-NC-DTPA-CS pulp sheet)

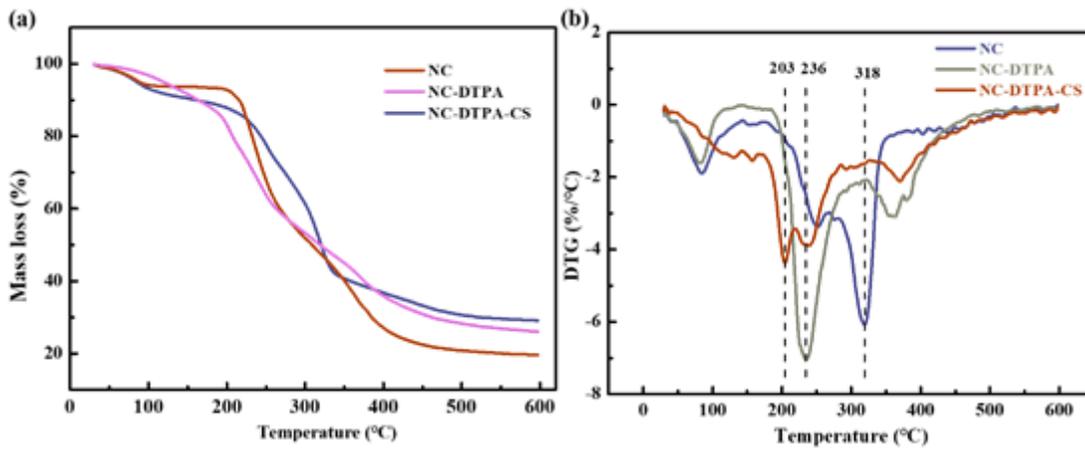


Figure 4

Schematic diagram of TG and DTG profiles of NC additives

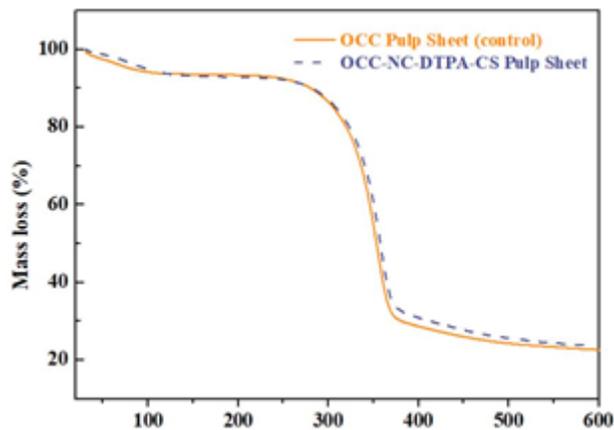


Figure 5

TG of OCC handsheets

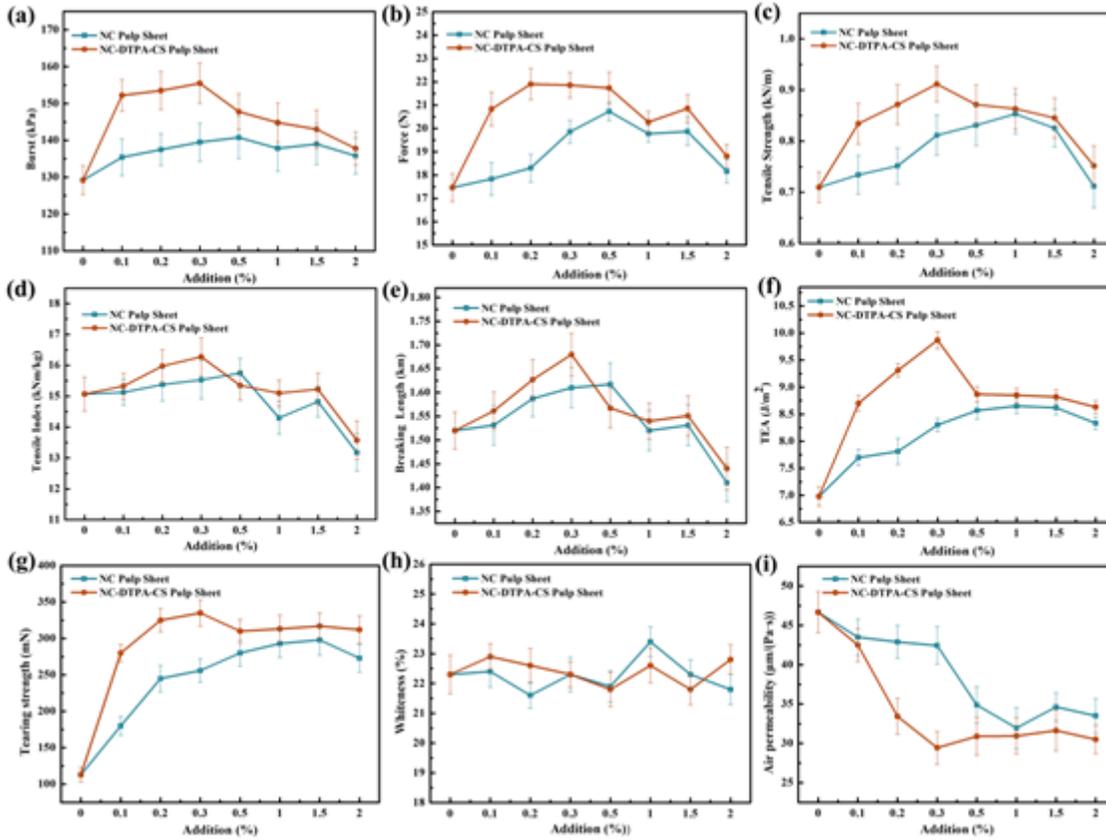


Figure 6

Physical properties of paper with NC and NC-DTPA-CS content (a: Burst, b: Force, c: Tensile Strength, d: Tensile Index, e: Breaking Length, f: TEA, g: Tearing Strength, h: Whiteness, i: Air permeability.)

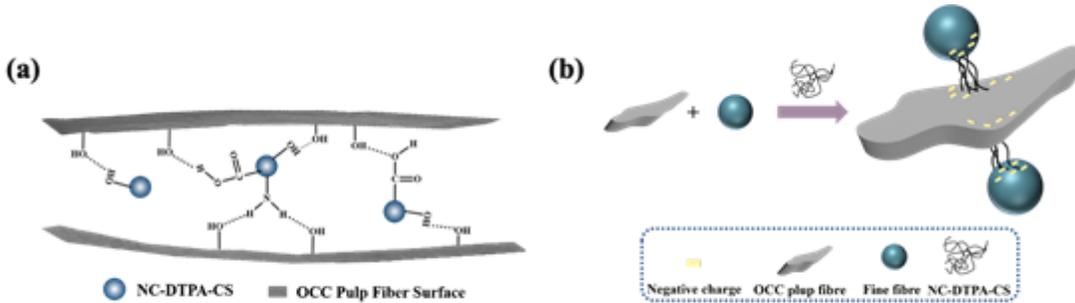


Figure 7

Schematic of NC-DTPA-CS enhanced OCC paper sheet

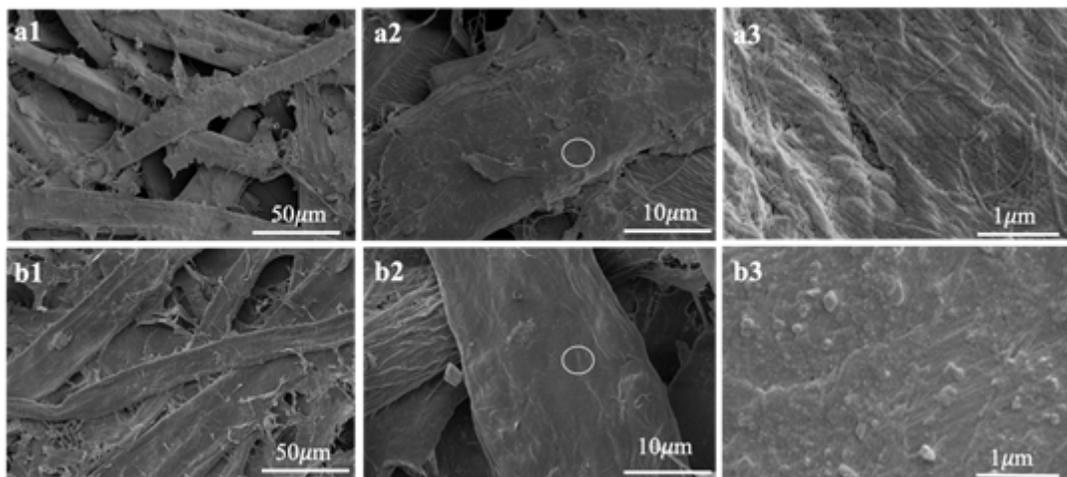


Figure 8

Morphology of recycled OCC handsheet without NC-DTPA-CS (a) and with 0.2% NC-DTPA-CS (b)