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Preparation and Characterization of Nitrocellulose Nanofiber

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Abstract: A novel procedure for the preparation of nano-sized nitrocellulose (NC) was developed. Cellulose nanofiber (CNF) water suspension was obtained by disk-milling of cotton powder. CNF was first pretreated using sulfonic acid to enhance the esterification process using HNO_3 and H_2SO_4. The esterification process generated nitrocellulose nanofiber (NCNF) with a nitrogen content of 9.0%–13.7%. The Brunauer-Emmett-Teller (BET) specific surface area of NCNF was ten times larger than that of NC, and the burn-ing rate of NCNF was 3.5 times faster than that of NC. Differential scanning calorimetry (DSC) was conducted to assess the difference between the thermal stability of NCNF and NC. NCNF and NC exhibited the same onset exothermic temperature (200 °C), the height of the exothermic peak of NCNF was 20% higher than that of NC. Thus, NCNF has great potential to be used in explosives due to its high combustion performance.

Keywords: nitrocellulose · cellulose nanofiber · esterification · specific surface area · burning velocity

1 Introduction

Nitrocellulose (NC) is used as smokeless gunpowder for munitions and firearms and in other industries such as paints, medicines, adhesives, and celluloids. However, it is considered a hazardous substance. NC is a hazardous substance, as spontaneous combustions are known to cause explosion accidents. Studies on thermal stability [1] and the relationship between spontaneous ignition and climatic conditions [2] have also been conducted. In recent years, the spontaneous ignition of NC caused a massive explosion in Tianjin [3] 2015. NC is typically prepared by mixing sulfuric acid and nitric acid and placing a dried piece of cotton in the mixture. Cellulose consists of β-1,4 linked glucose units. At most three hydroxyl groups of the anhydrous glucose units are esterified using the mixed acids. The esterification reaction is very rapid and is followed by washing the processed NC with water and removing the acid. NC is then dried under vacuum or ambient air. It is used in the manufacture of gun cotton, which is highly flammable (nitrogen content > 13%, lower nitrogen content = 11%–12%). NC with lower nitrogen content < 10% is used in paint industries.

Recently, investigations of NC to improve its environmental suitability, cost, thermal stability, and sensitivity have been reported. Some research has focused on manufacturing NC from materials other than wood and cotton. For example, studies investigated producing NC from *Miscanthus* cellulose [4] and grass [5]. Other studies investigated the treatment of NC with isophorone diisocyanate to obtain ladder-like NC [6], whose mechanical sensitivity is less than that of raw NC. Nanosized spherical NC composite crystals (diameter = 15–30 nm) were obtained through the pretreatment, hydrolysis, and nitration of microcrystalline cellulose. The impact sensitivity of the nanosized spherical NC decreased by 44.6% in comparison with traditional NC [7].

In this study, the synthesis of nanosized NC was investigated. Yan et al. [8] used electrospinning (ES) approach to preparing thermite-based nitrocellulose nanofibers. Nanothermite in the nitrocellulose polymer matrix results in a significant increase in the total energy release and combustion propagation velocity. Similarly, Sovizi et al. [9] prepared two different types of nanofiber NC (diameter: smooth nanofiber = 90–150 nm, diameter: porous nanofiber = 400–500 nm) using electrospinning of ethyl methyl ketone solution In another study, NC dissolved in an organic solvent was dropped on a glass substrate and dried to produce particulate NC (diameter = 200–900 nm) Also, nanosized NC has attracted the attention, because it has higher reactivity than micronsized NC. Zhang et al. [10] also prepared submicron NC particles (diameter = 500 nm) using dimethylformamide (DMF) solvents, which generated NC with a

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higher burning rate. The electrospinning and dropping methods have several shortcomings, which are listed below (a–d).

(a) The diameter of NC generated by the ES method ranges from 90 to 500 nm, and its specific surface area ranges from 4.8 to 26.9 m^2/g. Thus, NC nanofiber (NCNF) with a diameter of 50 nm or less and a specific surface area of 80 m^2/g or higher cannot be prepared using this method.

(b) In the ES method, high voltage is used for the manufacturing process. Thus, a safety counterplan is required to mitigate explosion risks.

(c) In the ES method, it is necessary to dissolve NC in a solvent before spinning and a special solution is required. However, NC with low nitrogen content is difficult to dissolve; thus, it is difficult to produce NC with various nitration levels to suit different applications.

(d) The dropping method is not suitable for mass production because the dropped amount was too small. Additionally, the specific surface area of the manufactured NC was only 4.0–18.2 m^2/g.

Cellulose nanofiber (CNF) water suspension was used as a raw material for NC. To the best of the authors' knowledge, this material has not been used for this purpose in the past. CNF water suspension was subjected to sulfuric acid pretreatment before esterification to promote the swelling of CNF and increase the nitration rate.

2 Experimental

2.1 Preparation of CNF

Cotton-based cellulose powder (40–100 mesh, Advantech, Tokyo, Japan) was disk-milled using the method reported by Iwamoto et al. [11,12] A water suspension of the cellulose powder (5%) was passed through a disk mill (Supermasscolloider, MKCA6-2, Masuko Sangyo Co., Ltd, Saitama, Japan) equipped with two stone grinding disks rotating at a speed of 1800 rpm. The gap between the two disks was narrowed from 300 to 150 μm. This fibrillation treatment was repeated 17 times to obtain a CNF water suspension.

2.2 Pretreatment and Nitration of CNF

First, the as-prepared CNF water suspension was centrifuged at 3,500 rpm ($2,330 \times g$) for 10 min using a Kubota 5420-type centrifuge (Tokyo, Japan). The water content in the suspension was determined using a moisture analyzer (HB43 Mettler-Toledo) and a 0.5 g sample heated to 120 °C to remove water. The moisture content was found to be $< 95\%$. Next, CNF was pretreated with H_2SO_4 by mixing the CNF water suspension (7 g) and H_2SO_4 (50%, 7 ml) using a hybrid mixer (ARE310, THINKY, Japan), which is also known as a self-rotating or orbital mixer. This mixer is capable of evenly mixing

viscous materials, which is important because CNF water suspension is a highly viscous substance. The mixture of CNF water suspension and H_2SO_4 was then centrifuged at 3,500 rpm ($2,330 \times g$) for 10 min to remove the diluted H_2SO_4 solution from the mixture. These steps reduced the water content in the CNF water suspension. Using a more powerful centrifuge and removing larger quantities of water from CNF can increase the nitrogen content in the NCNF produced. Water removal by physical compression could not be used because it causes CNF aggregation. Thus, mixed acids were prepared by mixing H_2SO_4 (98%, 25 ml) and HNO_3 (70%, 10 ml). Esterification was conducted using the prepared mixed acid solution, which consisted of H_2O (8.6%), HNO_3 (16.6%), H_2SO_4 (74.8%). The process involved mixing for 10 min using a hybrid mixer at 40 °C and was left to cool for 5 min using crashed ice with sodium chloride. Thus, the total mixing time was 50 min (i.e., 10 min mixing $\times 5$ times) using a hybrid mixer. The H_2SO_4 pretreatment promotes the swelling of the CNF water suspension and consequently enhances the esterification treatment. In fact, NCNF was synthesized with different nitrogen contents by changing the above-mentioned conditions, concentrations, and volumes.

2.3 Washing Treatment and Freeze-Drying Treatment

After esterification, the mixture of NCNF and the acid solution was mixed with a large volume of water and decanted for 1 h to precipitate NCNF. The precipitate was washed several times with water and then $NaHCO_3$ (5%) was added to neutralize the pH to approximately 7. It should be noted that $NaHCO_3$ should be used in small amounts for neutralization because it can degrade NCNF. Next, boiling washing was conducted for more than 40 h followed by decantation. A centrifuge was used to remove excess water from NCNF, and then freeze-drying was performed. Equal amounts of tertiary butyl alcohol (TBA) and NCNF suspension were stirred in a hybrid mixer and then centrifuged. This operation was repeated several times to replace the water in NCNF with TBA. It was then frozen at 0 °C, and solid TBA was sublimated at room temperature under a vacuum of 0.5 Pa in a handmade freeze-dryer consisting of a cold trap (VT-400, Advantec, Japan) and an oil rotary vacuum pump (GVD-165, ULVAC, Japan). Feather-like NCNFs were obtained after the freeze-drying process.

2.4 Characterization of CNF, NC, and NCNF

2.4.1 Scanning Electron Microscopy (SEM)

The surface morphology of the samples was observed using a field-emission scanning electron microscope (FE-SEM, Hitachi FE-SEM S-4800, Hitachi Ltd., Tokyo, Japan) operated at an accelerating voltage of 1 kV. All samples were coated with osmium before SEM analysis.

2.4.2 Brunauer-Emmett-Teller (BET) Surface Area Analysis

The surface area of CNF and NCNF were determined using BET analysis. Before the measurements, dried CNF and NCNFs were degassed under reduced pressure for 6 h using BELPREP VAC II (BEL Japan, Inc., Tokyo, Japan) at 105 °C and 50 °C, respectively. The adsorption isotherms of nitrogen at 77 K were measured using BELSORP-max (BEL Japan, Inc., Tokyo, Japan). The specific surface area (SBET) was calculated according to the BET equation using BEL master analysis software (BEL Japan, Inc., Tokyo, Japan).

2.4.3 Nitrogen Content Measurements Using FT-IR/ATR

The FT-IR/ATR (Fourier Transform Infrared Spectroscopy/Attenuated Total Reflection) measurements were performed using an FT-IR spectrometer (SpGX/Raman FT-IR system, PerkinElmer Inc.) and a DuraScope diamond ATR accessory (Smith Detection, USA) that fits into the sample compartment of the spectrometer. The spectra were recorded at a constant ambient temperature of 25 °C with a spectral resolution of 4 cm^{-1} over ten scans. The FT-IR/ATR data were acquired in the range of 600–1800 cm^{-1}. Among them, the peaks specific to CNF [13] (*a*: 930–1190 cm^{-1}) and the three peaks of the nitro group (*b*: 768–905 cm^{-1}, *c*: 1190–1350 cm^{-1}, *d*: 1575–1710 cm^{-1}) were focused on (Figure 1).

Since the quantity of NCNF obtained from synthesis is extremely small, it is difficult to determine the nitrogen content by ordinary CHNO elemental analysis and titration methods. Thus, the nitrogen content was estimated on the basis of the adsorption peak obtained by FT-IR/ATR method, which can determine nitrogen contents in the mg order. Since the CNF-specific peak barely changed before and after nitration, the peak area is used to normalize the s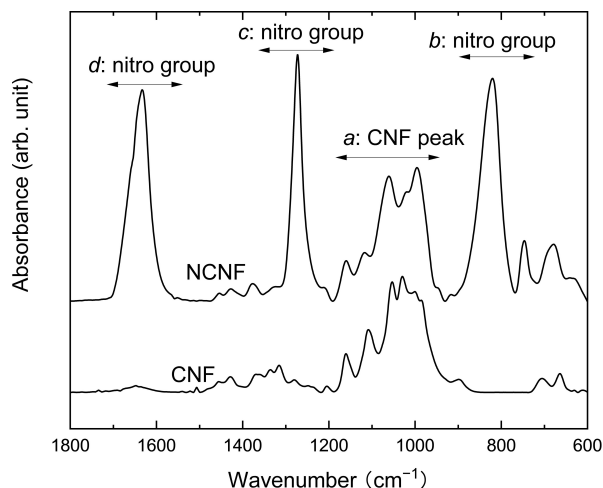pectrum. The obtained spectrum was baseline corrected, smoothed, the peak intensity between 1360 and 1380 cm^{-1} was set to one, and the peak intensity at 600 cm^{-1} and 1800 cm^{-1} was set to zero. Seven comparative samples were prepared, including CNF as raw material and six NCs with different nitrogen contents which are determined by titration method (i.e., 11.53, 11.76, 12.6, 13.0, 13.15, 13.4 %) The relationship between the *b/a*, *c/a*, and *d/a* ratios and the nitrogen content was based on the known nitrogen content. The nitrogen content was calculated from the average value of these three ratios.

2.5 Differential Scanning Calorimetry (DSC) Measurements and Pressure Vessel Test (PVT)

DSC measurements were conducted using EXSTAR DSC 7020 (SII Nano Technology, Inc.). A sample (1 mg) was sealed in a stainless steel container and heated from 25 °C to 500 °C at a rate of 10K/min. To evaluate the burning behavior in a closed environment, we prepared a pressure vessel (SUS 316, 100 mL-PV, Nitto high pressure, Japan) with an inner volume of 100 mL; outer and inner diameters of 55 and 40 mm, respectively; and an inner height of 90 mm (Figure 2). The inner pressure was measured using a pressure sensor (PE-100KWS, Kyowa Co.). The sample (0.2 g) was wrapped with a plastic film and an electric fuse (Kayaku, Japan) typically found in the igniters used for launching fireworks. NC and NCNF were molded into 14–17 mm and 20–30 mm spheres, respectively (Figure 2 (b)-1 and (b)-2). NCNF has a larger bulk and lower bulk density than NC. In this closed vessel, the sample was ignited by the electric fuse, and then the increase in the inner pressure and temperature was measured.

2.6 Burning Behavior of NCNF

Samples (1 g, width = 5 mm, length = 14 cm) of NC and NCNF (1 g) were placed on the green screen and their burning behavior was recorded using a high-speed camera (SA-X, Photron Co. Ltd., Japan) at a recording speed of 1000 frame/s. Under atmospheric conditions, NC and NCNF were ignited by an incense stick placed on one side of the samples.

3 Results and Discussion

3.1 Nitrogen Content and Yield of NCNF

Firstly, the novel method to calculate the nitrogen content of NC was investigated. The nitrogen content of NC was calculated by different methods of FT-IR/ATR and titration respectively. The amount of synthesized NCNF was low because of the low yields. Therefore, it was difficult to evaluate the amount of nitrogen using the titration method. FT-IR could be used to evaluate the amount of nitrogen at lesser
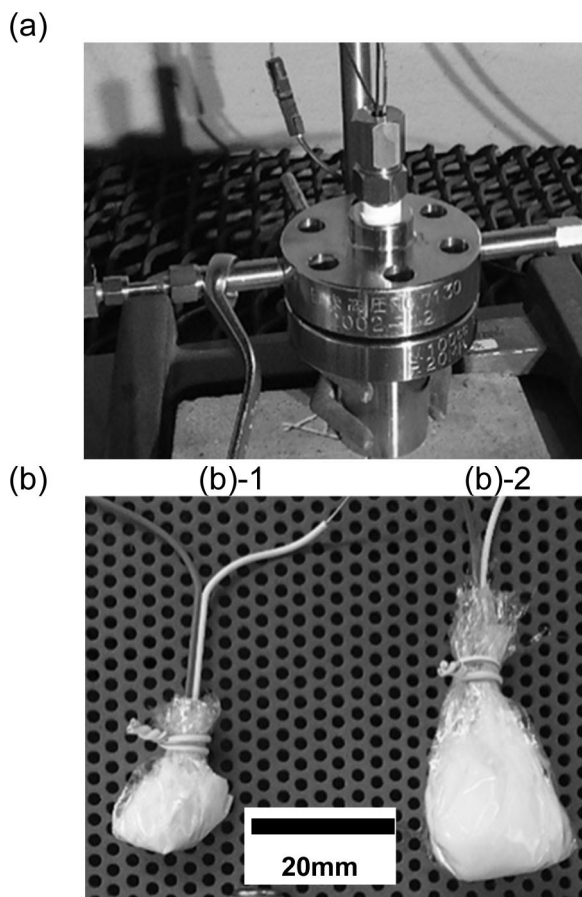

Figure 1. Fourier transforms infrared spectroscopy results of CNF and NCNF.

(a)

(b) (b)-1 (b)-2

Figure 2. (a) pressure vessel (100 ml) (b) sample (0.2 g) of (b)-1: NC and (b)-2: NCNF.

Figure 3. The relationship between water and nitrogen contents in NCNF.

amounts compared with the titration method, and the method of Levitsky et al. [14] was improved to evaluate the amount of nitrogen. The result of the nitrogen amount of NC (13.14%, titration) was $13.09 \pm 0.07\%$ (FT-IR), and the correspondence was good, thus, the FT-IR method was used to evaluate the nitrogen content. Nitrogen content evaluation by FT-IR/ATR showed reasonable results although it was the simplified method. Thus, we determined the nitrogen content of NCNF by FT-IR/ATR method. Figure 3 shows the relationship between the water content in CNF, NCNF yield (NCNF weight/CNF weight), and nitrogen content in NCNF. The effects of H_2SO_4 content (20–25 mL, concentration 98%), HNO_3 content (6.7–10 mL, concentration 60%–90%), pretreated CNF (5%) quantity (7–20 g) on the synthesis process were studied. With no H_2SO_4 pretreatment, nitration hardly proceeded, the nitrogen content in NCNF was 3%, and the yield was low. When the H_2SO_4 pretreatment was performed and the water content was reduced to 70% or less, the yield increased and the nitrogen content was 10% or more. At the CNF water content of 50%–70%, it was possible to obtain a 20%–28% yield and nitrogen content of 10% or more. At a water content of 50% or less, it became impossible to sepa-
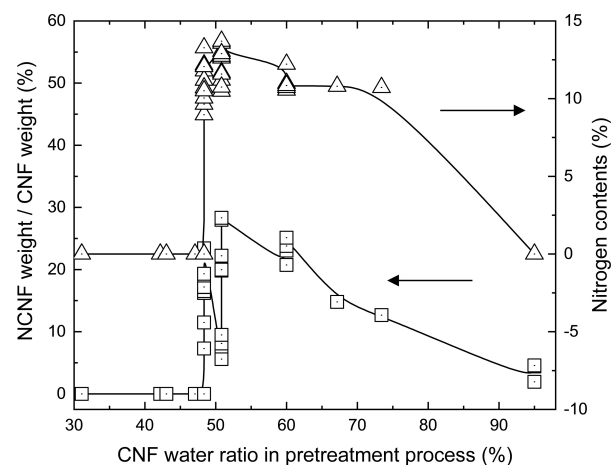
rate sulfuric acid and CNF, which hinders the synthesis. The change in the synthesis and mixed acid conditions resulted in a very wide range of results. At a water content of 50.8% in CNF, maximum values of nitrogen content (13.7%) and the yield (28.3%) were obtained. Thus, this should be selected as a synthesis condition.

The results of the pretreatment with H_2SO_4 showed that the water concentration should be within the range of 50%–70%. At a water concentration of lower than 50%, the effect of advanced nitration was small. At a concentration higher than 80%, CNF decomposed during the pretreatment step or nitration step, and the apparent yield decreased. When H_2SO_4 pretreatment was not performed, CNF almost decomposed during nitration and effective NCNF could not be obtained. Though CNF has large water content, it decomposes if a large volume of mixed acids is added. Similarly, CNF decomposes at high nitric acid concentrations. As a result, nitration of CNF was revealed to proceed after the appropriate pretreatment. This procedure does not expose the NC to high voltage conditions. Also, it is expected that NCNF with low N content can be produced by changing the water content of CNF because this procedure does not require the step of dissolving NC in an organic solvent.

3.2 BET Specific Surface Area and SEM Analysis

The results of BET showed that the specific surface areas of NC, CNF, and NCNF were 9.8, 107.2, and 103.0 cm^2/g, respectively. This result shows that NCNF and CNF exhibited a specific surface area ten times that of NC. It should be noted that the specific surface area of CNF did not change during nitration. The diameter of NC fiber was in the range of 12–28 μm because this is approximately the diameter range of the cellulose of the cotton raw material. The diameter of the CNF and NCNF was 40–90 nm and 30–50 nm, re-

spectively. CNF exhibited a linear structure, and NCNF had a fiber diameter comparable to CNF but with curved fibers forming a network structure (Figure 4).
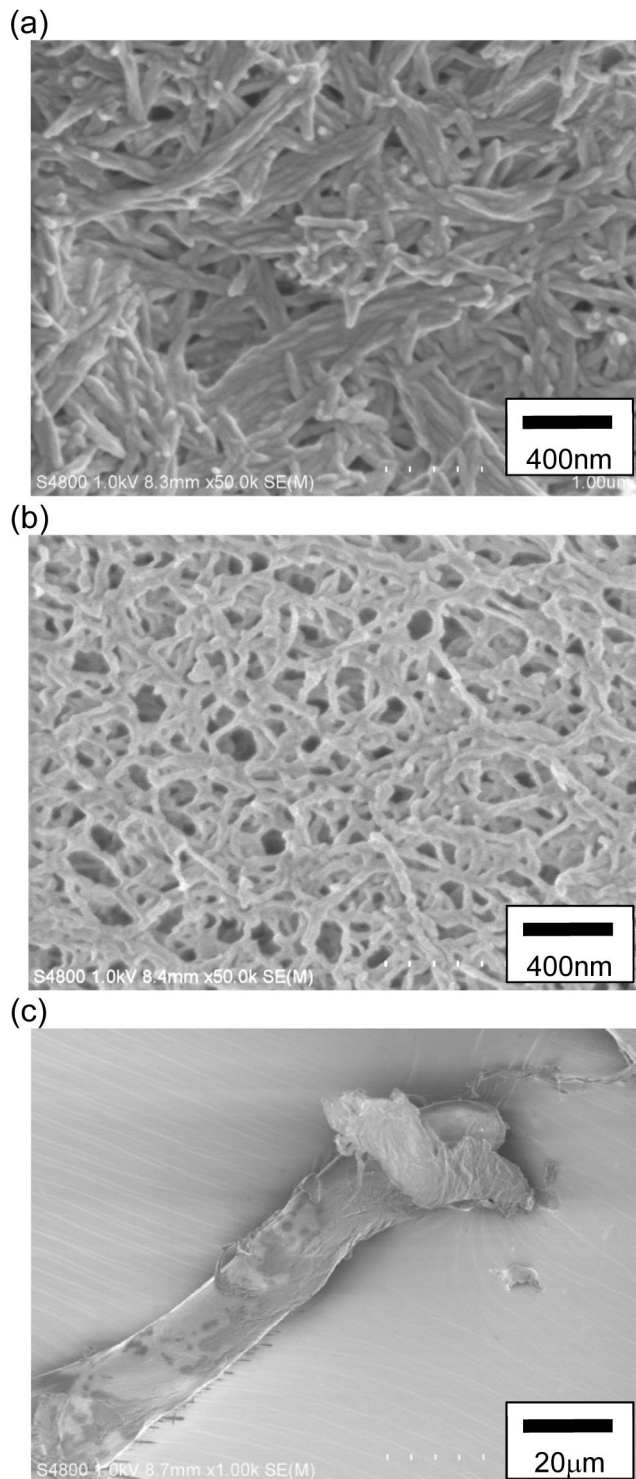

(a)

(b)

(c)

Figure 4. SEM image of (a) CNF, (b) NCNF, and (c) NC.

3.3 Thermal Analysis of NCNF and NC Using DSC

Table 1 and Figure 5 show the results of thermal analysis. The nitrogen contents in NC and NCNF were 13.4% and 12.6%, respectively. The peak heat flow of NCNF was higher than that of NC. The extrapolated exothermic onset temperature (T_o) of NCNF was 2.4 °C lower than that of NC. Both materials exhibited almost the same exothermic onset temperature, but because of the large specific surface area of NCNF, it was more oxygen-dependent than NC. The oxidation reaction of NCNF may proceed at low temperatures. The total calorific value of NC was found to be larger than that of NCNF because NC had a larger nitrogen content. The heat flow of NC and NCNF was 73.4 and 87.7 mW, respectively, and NCNF exhibited a heat generation peak of 20% or larger than that of NC. Besides, high instantaneous heat generation was observed. The Q_{DSC} values of NCNF and NC were 3.9 and 4.2 kJ/g, respectively. This value is not dependent on the specific surface area or the reaction rate, but the amount of nitrogen. Based on the DSC results, NCNF has a high potential for synthesizing high-performance explosives with a faster energy generation rate than that of NC.

3.4 PVT Results and Burning Behavior of NCNF

Figure 6 shows the change in vessel pressure as a function of time after the start of the ignition. NCNF (N = 13.7%) exhibited a higher maximum pressure and a shorter time to

Table 1. DSC data summary of NC and NCNF.

Sample	Nitrogen Content (%)	QDSC (kJ/g)	Heat flow (W/g)	To (°C)
NCNF	12.6	3.9	87.7	196.5
NC	13.4	4.2	73.4	198.9
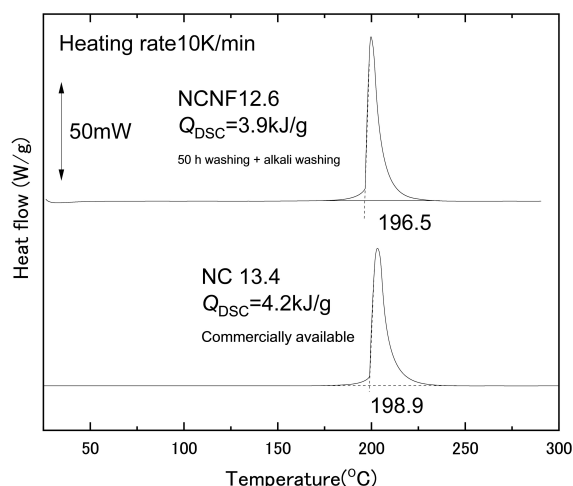
Figure 5. DSC results of NC13.4 and NCNF12.6.

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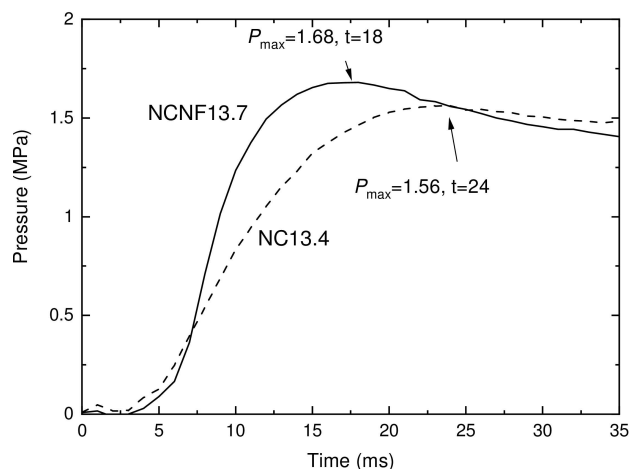

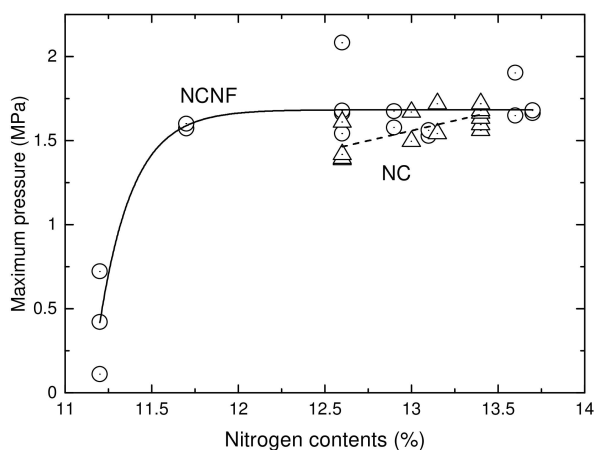**Figure 6.** The pressure vessel test results of NC13.4 and NCNF13.7.

Figure 7. The relationship between maximum pressure (P_{max}) and nitrogen content in NC and NCNF.
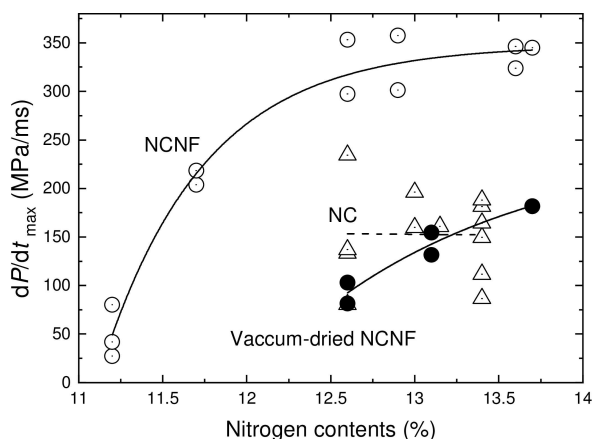

Figure 8. The relationship between the maximum pressure slope (dP/dt_{max}) and nitrogen content in NC, NCNF, and Vaccum-dried NCNF.

reach the maximum pressure compared to NC (N = 13.4 %). The experiments were carried out several times using samples with different nitrogen contents to precisely determine whether this was due to the difference in the nitrogen content or the effect of the specific surface area.

Figure 7 shows the results of the pressure vessel test. For both NCNF and NC, the maximum pressure increased with the nitrogen content. NCNF and NC exhibited approximately the same maximum pressure value. These similar values of maximum pressures can be attributed to the fact that NC and NCNF differ only in their specific surface area. An NCNF with a nitrogen content of 11.2 % exhibited almost no increase in pressure and showed poor performance as an explosive.

Figure 8 shows the relationship between the nitrogen content and dP/dt_{max} (maximum pressure gradient). Vacuum-dried NCNF was prepared using a vacuum desiccator (As one, Japan) for 8 h at 25 °C. NCNF shows more than twice the dP/dt_{max} compared with NC. The burning rate increased with the specific surface area. Moreover, dP/dt_{max} increased with an increase in the nitrogen content. Typically, vacuum-dried NCNF shows a dP/dt_{max} value equal to or less than that of NC. Besides, vacuum-dried NCNF aggregates and has a specific surface area equal to or less than that of NC. The maximum dP/dt_{max} value and adequate combustion performance were obtained at a large nitrogen content and high specific surface area. At a nitrogen content of 13.4 %, the dP/dt_{max} values of NCNF and NC were 339 and 152 MPa/ms, respectively. Therefore, NCNF showed a maximum pressure gradient 2.2 times larger than that of NC.

Figure 9 shows the burning behavior of NCNF12.6 and NC12.6. The time ranges for (a, b)-1, (a, b)-2, and (a, b)-3 were 50, 150, and 300 ms from the start of the ignition, respectively. The burning speed was analyzed using a high-speed camera, burning front, (i.e., the direction of the left-
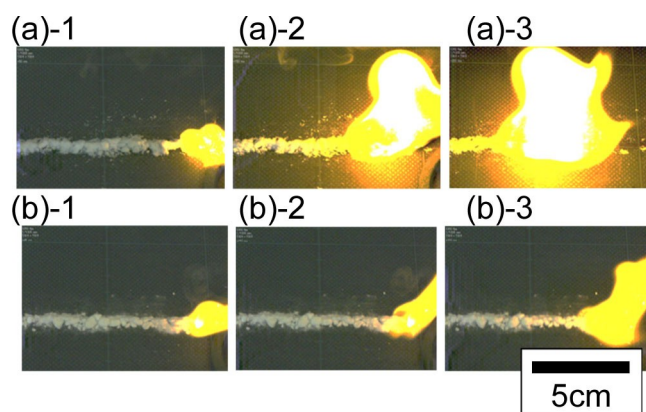

Figure 9. The burning behavior recorded by the high-speed photography of NCNF12.6 after (a)-1 50 ms, (a)-2 150 ms, and (a)-3 300 ms from the ignition start and of NC12.6 after (b)-1 50 ms, (b)-2 150 ms, (b)-3 300 ms from the ignition start.
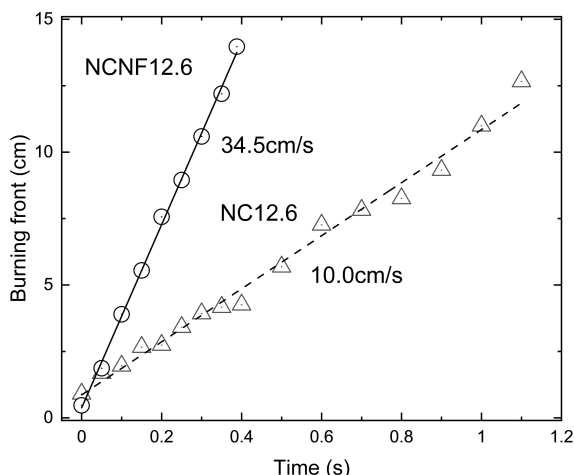
Figure 10. The burning rates of NCNF12.6 and NC12.6.

most tip of the flame) and time exhibited a nearly linear relationship. The burning speed of NCNF and NC was 34.5 and 10.0 cm/s, respectively (Figure 10). The burning speed of NCNF was 3.5 times higher than that of NC. NC burning speed experienced some fluctuations because NC contained some condensed parts and was not homogeneous.

4 Conclusions

Nanosized cellulose was obtained using a disc mill to synthesize CNF. CNF was pretreated and esterified to synthesize NCNF. NCNF had a nitrogen content of 10%–14% and preformed well as an explosive. NCNF exhibited a BET-specific surface area approximately 10 times that of the commercially available NC and the same thermal stability. The pressure increase rate and burning rate were 2 and 3.4 times, respectively, higher than those of NC. Thus, NCNF is expected to be used as an explosive and in other applications.

Data Availability Statement

No Data available.

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