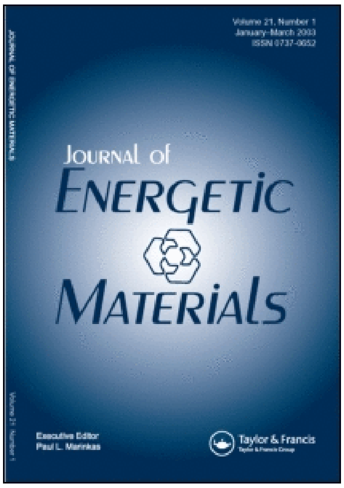

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

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To cite this Article Sun, Dong-Ping , Ma, Bo , Zhu, Chun-Lin , Liu, Chang-Sheng and Yang, Jia-Zhi(2010) 'Novel Nitrocellulose Made from Bacterial Cellulose', Journal of Energetic Materials, 28: 2, 85 — 97

To link to this Article: DOI: 10.1080/07370650903222551

URL: http://dx.doi.org/10.1080/07370650903222551

Journal of Energetic Materials, 28: 85–97, 2010

ISSN: 0737-0652 print/1545-8822 online
DOI: 10.1080/07370650903222551

Novel Nitrocellulose Made from Bacterial Cellulose

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Nitrocellulose (NC) is useful in several industrial segments, especially in the production of gun, rocket, and missile propellants. The conventional way to prepare NC is done through the nitration of plant cellulose with nitric acid. In this work, bacterial cellulose nitrate (NBC) is synthesized by bacterial cellulose (BC) and nitro-sulfric acid under heterogeneous conditions. NBC with the degree of substitution (DS) of 1–2.85 was obtained, and the effects of sulfuric to nitric ratio, reaction temperature, and reaction time on the value of DS of NBC are discussed. The samples are also characterized by elemental analysis, thermal analysis, Fourier transform infrared (FT-IR) spectroscopy, and X-ray diffraction.

Keywords: bacterial cellulose, nitrocellulose, optimization conditions

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Introduction

Nitrocellulose (NC) was first prepared in 1833 with cotton and nitric acid. Since then, it has been used in a wide range of products including plastics, paints and lacquers, and smokeless gun propellants [1]; these are all related to each other by virtue of their production from cellulose that has been nitrated to a higher or lower degree. Cellulose is usually found in a number of plant sources. But unfortunately, it does not exist in pure form. It is closely associated with lignin, hemicellulose, pectin, starch, and other plant materials. Therefore, the nitration of the plant generation raw materials is difficult to control. This is important, because the properties of the finished NC are affected considerably by the characteristics of the raw linters, as determined by such factors as climate and soil conditions where the plants are grown and by the completeness of the linter purification process.

The linter purification is accomplished by pressure digestion in caustic solutions. After digestion under specified conditions, the linters are washed hot and then cold and then are bleached. A second wash follows the bleaching, after which the purified and bleached lint passes through a continuous drying process and is then rolled into sheets and stored. A requisite of the linter purification process is a supply of pure water. Approximately 30,000 gallons of water are used per ton of material [2]. New environmental regulations, public concerns, and growing environmental awareness have triggered the search for new products that are compatible with the environment.

A new source of NC, bacterial cellulose (BC), is produced through fermentation using *Acetobacter xylinum*. The primary structure of BC is similar to that of plant cellulose: an unbranched polymer of β-1,4-linked glucopyranose residues. However, the fibrous structure of BC is different from that of plant cellulose. BC is composed of microfibrils, which have a ribbon-like structure, and the thickness (0.01×10^{-6} m) is two orders of magnitude smaller than that of plant cellulose (1×10^{-6} m). In addition, the microfibrils retain a fine network structure. Because of this characteristic macrostructure, BC has various advantageous properties, such as high tensile strength and ultrafine and highly pure fiber network structure. Due to these unique characteristics, attention has been drawn to BC to make novel industrial materials in recent years, including in foods, in acoustic diaphragms for audio speakers and headphones, in making unusually strong paper, and in medical applications [3]. This article describes the synthesis of bacterial cellulose nitrate (NBC) from BC in laboratory conditions. NBC is examined under various conditions to enhance the degree of substitution (DS) and its properties have been determined by transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectroscopy, and X-ray diffraction (XRD).

Experimental

Instruments

The nitrogen content (N%) was determined by an elemental analysis (Vario EL III, Elementar, Hanau, Germany) and the DS value was calculated by the following equation [4]: $DS = (1.62 \times N)/(14 - 0.45 \times N)$. The sample was homogenized in distilled water by the ultrasound treatment, and a drop of suspension thus obtained was put onto a Formvar/carbon-coated Cu grid for TEM. After being slightly dried, the specimen was examined on a JEM-2100 (JEOL, Ltd., Tokyo, Japan) TEM at 200 KV. X-ray diffraction spectra were recorded using a Bruker D8 ADVANCE to analyze the sample's crystalline structure. Scans were performed over the 5–40° 2θ range using step 0.1° width. A Bruker EQUINOX55 remote-sensing FT-IR spectroscope was used to collect transmission spectra with a KBr wafer. The thermal behaviors of NC and NBC were studied by simultaneous thermo-gravimetric/differential thermal analyzer (TG-DTA) (TGA/SDTA851^{e}, Mettler, Toledo, Ohio) under nitrogen atmosphere from 50 to 400°C at a heating rate of 10°C/min.

Materials

A BC pellicle was produced by *Acetobacter xylinum* NUST4.1 [5]. NC was obtained from the Institute of Chemical Engineering, Nanjing University of Science and Technology. The BC pellicle was then crushed in a pulverizer (GQF-1, JEOL, Ltd., Tokyo, Japan) to obtain the required particle fractions (size <40 µm) as BC powder. Sulfuric acid and nitric acid (China Medicine Group Shanghai Chemical Reagent Co., Shanghai, China) was chemical grade and used in various concentrations.

Preparation of BC Powder

When *Acetobacter xylinum* NUST4.1 was grown in a suitable statically incubated surface culture medium, a thick, white pellicle was formed at the air–liquid interface of the culture. The BC pellicle was taken from the medium and treated with 4% (w/v) NaOH at 80°C for 2 h to solubilize impurities and cells and then thoroughly washed in tap water until the pH of water became neutral. The purified BC pellicle was dried to constant weight at 80°C and then crushed in an air flow pulverizer to obtain the required particle size fractions as BC powder.

Preparation of NBC

The BC powder was placed in nitrating solutions with different mixing ratios of sulfuric acid at controlled temperature for some time. The reaction was quenched by addition of excessive cold water. The deposit was filtered through a vacuum filter and then stabilized by three cycles of washing and boiling in water for 5 min for each operation. NBC was vacuum dried at 60°C to ensure complete dryness.

Results and Discussion

Effect of Ratio of Sulfuric Acid to Nitric Acid on DS of NBC

The effect of ratio of sulfuric acid to nitric acid on DS was investigated, and the results are shown in Fig. 1. It can be seen that the reaction time, reaction temperature, water content of the mixture acid, and esterification coefficient (mass ration (r) of mixture acid to BC) are fixed at 30 min, 30°C, 8% water

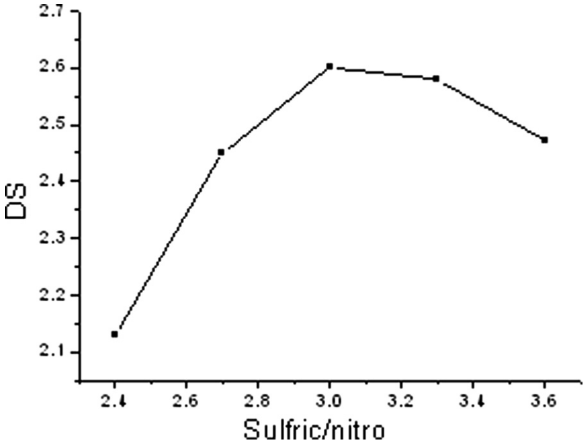

Figure 1. Effect of ratio of sulfuric acid to nitric acid on DS.

content, and r = 54, respectively, with the change of the ratio of sulfuric acid and nitric acid. As shown in Fig. 1, the DS increased with the increase of the sulfuric acid/nitric acid ratio from 2.4 to 3. The increase of the sulfuric acid concentration improves the swelling of BC molecule, allowing nitric acid to diffuse into the BC molecule easily. However, as the ratio of sulfuric acid to nitric acid increased, a decrease in DS was observed, which suggests that the higher ratio of sulfuric acid to nitric acid would go against the reaction. The data listed in Fig. 1 indicate that an optimum ratio of sulfuric acid to nitric acid is 3.

Effect of Water Content of the Mixture Acid on DS

Figure 2 shows the effect of water content on DS. Reaction time, reaction temperature, ratio of sulfuric acid to nitric acid, and esterification coefficient are fixed at 30 min, 30°C, r = 3, and esterification coefficient of 54, respectively, the water content is changed. As shown in Fig. 2, DS decreases as water content increases, possibly because the active nitrating agent in the system of nitro-sulfuric acid is nitronium ion, whose concentration decreases as water content increases [6].

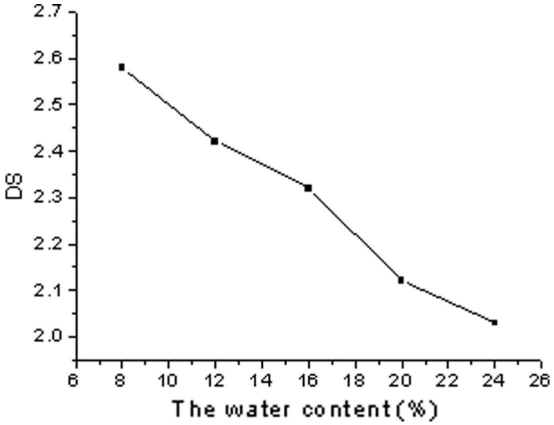

Figure 2. Effect of water content of the mixture acid on DS.

Effect of Esterification Coefficient on DS

The effect of the esterification coefficient on DS is shown in Fig. 3. First, the esterification coefficient is set at 51, 54, 57, 60, 63 and the other parameters are as follows: reaction time 30 min, reaction temperature 30°C, ratio of sulfuric acid to nitric acid equal to 3, and water content 8% DS due to the reversible reaction [7]. However, the influence of esterification

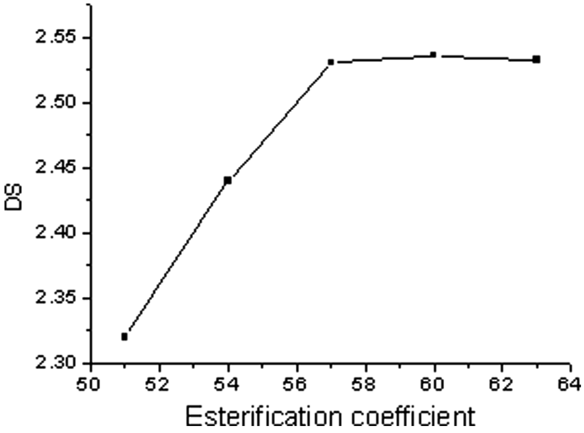

Figure 3. Effect of esterification coefficient on DS.

coefficient to DS became weaker when the mixture acid was excessive.

Influence of Reaction Temperature on DS

In order to determine the reaction temperature necessary to achieve an appropriate DS, a number of attempts to synthesize NBC were made. First, the reaction temperature was set at 20, 25, 30, 35, 40°C and other parameters are given as follows: reaction time 30 min, ratio of sulfuric acid to nitric acid equal to 3, esterification coefficient of 57, and water content 8%. As shown in Fig. 4, the DS increases with increasing temperature. Due to side reactions with temperature increases, the optimum temperature was determined to be 30°C.

Influence of Reaction Time on DS

The effect of reaction time on DS is shown in Fig. 5. First, reaction time was set at 20, 25, 30, 35, 40 min and the other parameters are given as follows: ratio of sulfuric acid to nitric acid equal to 3, esterification coefficient of 57, reaction temperature 30°C, and water content 8%. With the increase

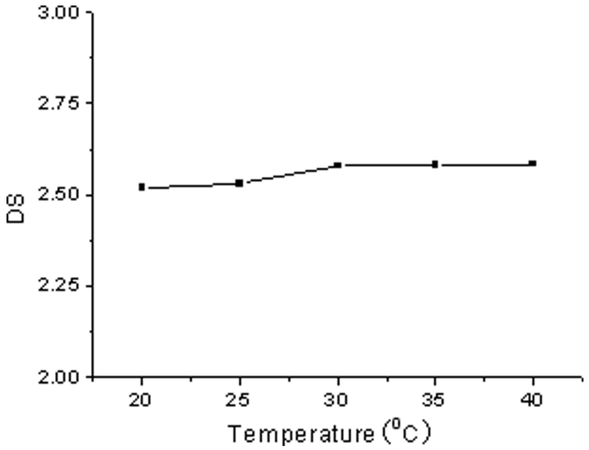

Figure 4. Influence of reaction temperature on DS.

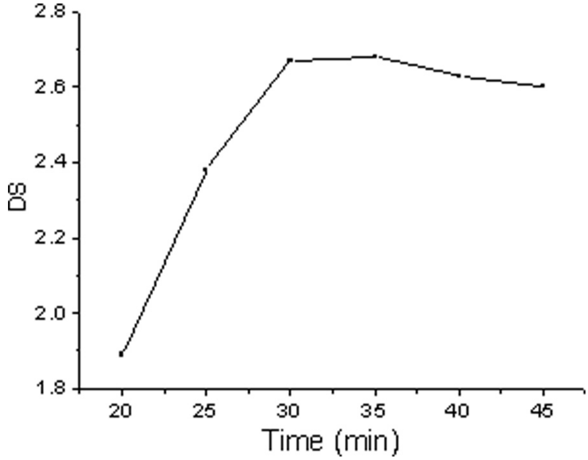

Figure 5. Influence of reaction time on DS.

of time from 20 to 30 min, the DS increased from 1.89 to 2.67. However, because DS decreases with longer time, the present work adopted 30 min for the reaction.

Optimization of Experimental Conditions

To optimize the experimental parameters of the preparation techniques, an orthogonal experiment $L_{16}(4^5)$ was designed with DS as referring index. Sixteen experiments were carried out at reaction temperatures of 26, 28, 30, and 32°C; esterification coefficients of 54, 56, 58, and 60; water contents of 6, 8, 10, and 12%; ratios of sulfuric acid to nitric acid 2.7, 2.9, 3.1, and 3.3; and reaction times of 26, 28, 30, and 32 min. Considering the results of a range analysis, the reaction temperature of 30°C, esterification coefficient of 58, water content 8%, and ratio of sulfuric acid to nitric acid 3.1 were determined; a reaction time of 30 min was the most favorable condition and DS reached 2.85 under such conditions. The result of variance analysis indicates that the content of water has a remarkable influence on DS, and the order of influence is water content $>$ ratio of sulfuric acid to nitric acid $>$ esterification coefficient $>$ temperature $>$ time.

Characterization of the Sample (TEM)

TEM is a frequently used method to analyze fibers. Figure 6 shows TEM of NBC (DS = 2.3) and BC. Significant changes in appearance of the ribbon assemblies are observed. BC is characterized by a more compact and more parallel structure than that of NBC. In contrast, NBC contains nets with many holes and ribbon in disorder. Such changes suggest that the solid-phase nitration proceeded with some drastic reorganization of the microfibrils.

Characterization of the Sample (XRD)

To obtain further information, a wide-angle X-ray diffractometer was also measured for NBC (DS = 2.3) and BC. As shown in Fig. 7, the diffraction diagram indicates that BC has three characteristic diffraction peaks standing for crystal

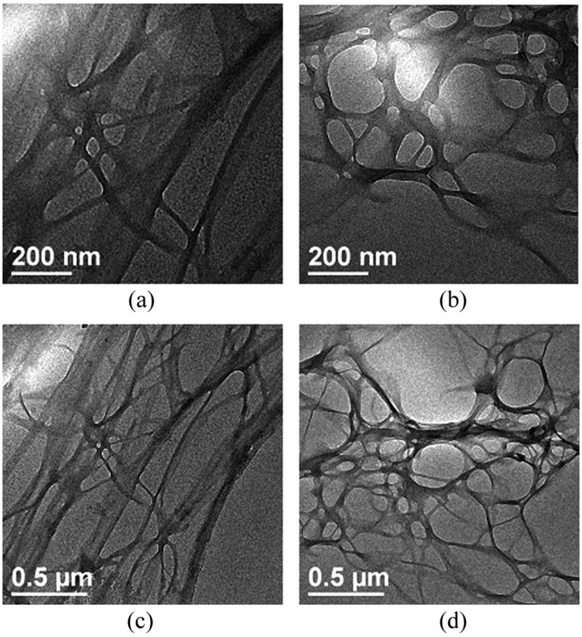

Figure 6. TEM of BC (a, c) and NBC (b, d).

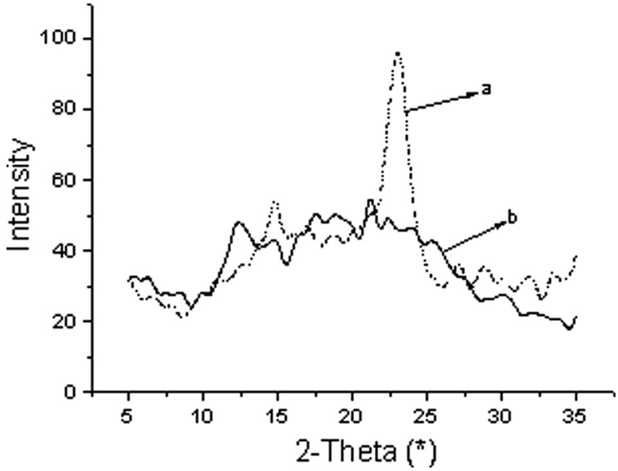

Figure 7. XRD curves for BC (a) and NBC (b).

planes (ī10), (110), (200), respectively, which revealed that BC was I crystal cellulose [8]. However, these specific peaks disappeared in the NBC as a result of nitration. These results might support the presumption that the present solid-phase nitration proceeded from the surface to the core of microfibril with increasing amorphism portions [4].

Characterization of the Sample (FT-IR)

Infrared spectra of NBC (DS = 2.3), NC (DS = 2.3), and BC are shown in Fig. 8. There were no obvious variations at 2,924.98 cm^{-1} for C–H stretching vibration and 1,049.93 cm^{-1} for C–O–C and C–O–H stretching vibration of sugar ring in all spectra. Furthermore, almost no difference between NBC and NC is observed in both spectra. However, the appearance of characteristic of the –NO_2 stretching vibration (1,272.25 cm^{-1}), N–O stretching vibration (820.30 cm^{-1}), and –NO_2 bending vibration (729.01 cm^{-1}) in the FT-IR spectrum of NBC and NC established conformation of the nitryl. In addition, comparing the FT-IR spectrum of the NBC and NC to that of the BC, the stretching peak of hydroxyl groups on

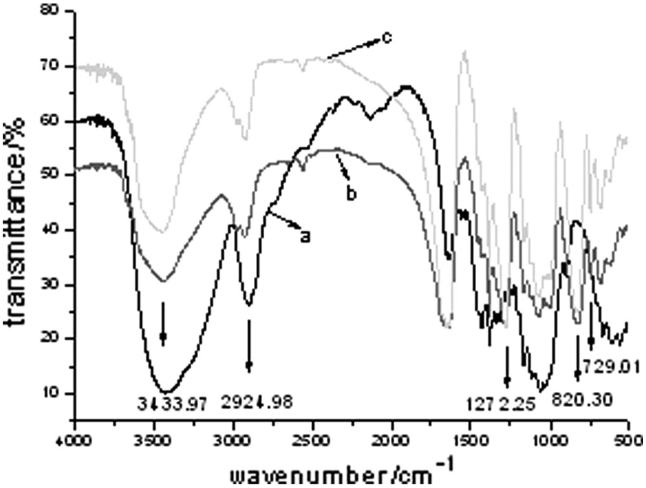

Figure 8. FT-IR spectra of BC (a) and NBC (b).

the glucose rings around 3,500 cm^{-1} was greatly reduced, which signifies that the hydroxyl groups are partly substituted by the nitryl group.

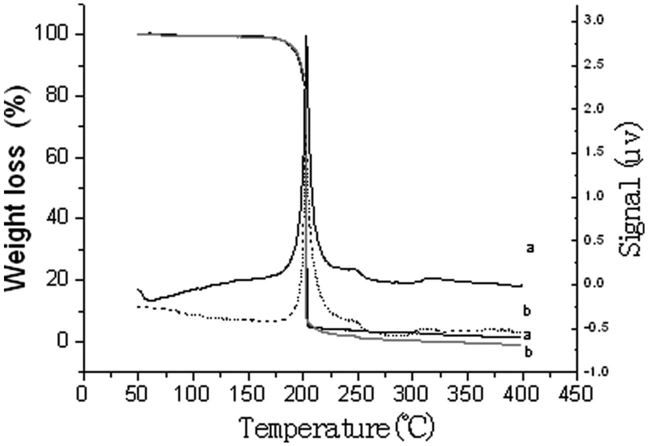

Figure 9. TGA/DTG curve of NBC (a) and NC (b).

Characterization of the Sample (TGA/DTG)

As shown in Fig. 9, NBC (DS = 2.3) starts its decomposition at 198.5°C and continues up to 238°C. The decomposition peak reaches the maximum mass loss at 200.7°C and shows 0.9431 wt% of solid residuals at 385°C. Decomposition of NC (DS = 2.3) starts around 199°C, the exothermic hump in the differential thermal analysis (DTA) curve is 202.4°C, and solid residues of NC at 385°C are close to 0.03 wt% as reported in the literature [8]. Therefore, similar thermal behaviors are observed.

Conclusion

The present study is concerned with the synthesis of NBC under laboratory conditions. By means of elemental analysis, FT-IR, XRD, TEM, and DTA-TG, it is possible to characterize the product. From TEM, different morphologies are observed between BC and NBC. XRD tests show that the crystallinity of BC is severely broken through nitration, which is consistent with the TEM analysis and confirms previous conclusions [4]. FT-IR studies reveal the presence of nitryl. Furthermore, when comparing NBC and NC in terms of thermal behaviors, almost no differences are observed.

NBC, which would appear to have different physical properties and explosive performance compared to conventional NC, is expected to perform as an advanced energetic material. Due to exceptionally promising results of the investigations into the properties of NBC, broader interest and deeper research of the issue merits seems to obtained.

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