Central European Journal of Energetic Materials
ISSN 1733-7178; e-ISSN 2353-1843

Cent. Eur. J. Energ. Mater. 2018, *15*(4): 554-571; DOI: 10.22211/cejem/93601

Research paper

System and Method for Simultaneous Measurement of Nitrogen Content and Uniformity of Nitration of Nitrocellulose

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Abstract: Nitrocellulose (NC) is a common, commercially available, cellulose-derived material and has been functionalized and widely applied in microfluidic technology, immunoassays and biochemical analyses. However, existing testing parameters always fail to completely and accurately reflect its inherent quality. In this study, we have designed and assembled a novel automatic polarizing microscope test system (PMTS) to scientifically test the nitrogen content and uniformity of nitration of NC based on the chromogenic principle of a polarization microscope. The advantages of this system are: (i) the PMTS requires less sample (only a few micrograms); (ii) the test period is shorter and the results can be obtained within 20 min; (iii) the method belongs to the nondestructive testing group, and the NC sample is not burned, dissolved, or damaged; and (iv) this method has increased accuracy, and the deviation of the nitrogen content is less than ±0.05%. The properties of various NC samples prepared by different nitric-sulfuric acid systems from raw materials with diverse maturities were determined *via* PMTS. Five NC samples with different nitrogen contents (10.9%, 11.5%, 11.8%, 12.6% and 13.5%) were tested, and the variance of the corresponding uniformity of nitration of these samples were 3.17, 1.61, 1.15, 1.76, and 2.83. The uniformity of nitration initially decreased and then increased with increasing nitrogen content, and the best uniformity of nitration appeared at a nitrogen content of 12%. We also found that fibre maturity has a positive effect on the uniformity of nitration. This testing device and method, with its cost-effectiveness and field-portability, can significantly improve the accuracy of nitration content and uniformity, and has an important value in practical applications.

Keywords: nitrocellulose, uniformity of nitration, nitrogen content, mixed acid nitration, cotton maturity

1 Introduction

As a type of conventional chemical product, nitrocellulose (NC) has been widely used in civil and military fields, for example as printing inks, paints, putty, lacquers, varnishes, filter membranes, plastics, propellants, high explosive formulations, *etc*. [1-3]. In recent years, its areas of application have been extended to biosensors [4, 5], oil/water separation [6], electrospun nanofibres [7], emulsions [8], microfluidic devices [9], microelectronics [10, 11] and microbiology [12-14], and these fields have huge demands for NC of special and dedicated quality [15]. Generally, to measure the quality of NC, eight indexes, which have been widely accepted, are set. These include the nitrogen content, solubility, viscosity, solubility in ethanol ether (Pinkevitch degrees), fine fault degree, stability, alkalinity and ash [16, 17]. Several approaches have even been established to test individual indicators, for example methods including the ferrous sulphate titration method, nitrometer method (Du Pont), interferometer method, electrical potential titration, and volume method have been developed to determine the nitrogen content [18, 19]. However, with NC applications expanded to biomedicine and high performance propellants, the existing eight indexes cannot fully reflect the quality of NC [20-23]. Prior studies have failed to objectively and conveniently evaluate and test the uniformity of nitration of NC [24-26].

As is known, the esterification of cellulose and nitric acid is a rapid, heterogeneous chemical process [27, 28]. The degree of nitration (nitrogen content) depends mainly on the penetration rate of the nitrating agent and the reaction degree between the fibre and the nitrating agent [29, 30]. Raw cotton cellulose is a natural polysaccharide, in which obvious inhomogeneity usually exists at multiple structural levels [31-33]. Firstly, the molecular weight of cellulose is polydispersed because the molecular chain length of the cellulose macromolecule has obvious heterogeneity, and the dispersion coefficient of the molecular weight distribution is about 3.0 [34]. Secondly, there exists a high density of intramolecular and intermolecular hydrogen bonds in cellulose [35]. Thirdly, the aggregation structure of cellulose includes crystalline and non-crystalline regions [36, 37]. At the same time, factors that include growth environment, picking time and dissection degree of refined cotton, have a certain impact on its maturity, and which further affect the uniformity of nitration. Finally,

the composition of the mixed acid, the contact time between the cotton fibres and the mixed acid during nitration can also directly affect the nitrogen content and the uniformity of nitration [38, 39]. In a word, all of the inhomogeneity in the first order, two-stage structure, the aggregation structure and the macroscopic structure of cellulose can cause inhomogeneity of nitration in the product [40]. Thus, inhomogeneous nitration with different degrees can be observed at different *C*-sites in the same glucose ring, different glucose rings on the same cellulose macromolecular chain, different basic fibrils, micro fibrils and fine fibres [41].

The uniformity of nitration of NC can refer to the distribution of $-ONO_2$ groups at different positions along the long macromolecular chain [42]. It can also reflect the uniformity of the degree of nitration at different physical locations of a NC fibre, as well as the difference in nitration between different cellulose fibre bundles [43]. Moreover, the uniformity of nitration of NC has a direct impact on its application performance, such as its solution properties, rheological properties, plasticizing properties and mechanical properties, especially in the fields of propellants, explosives and non-traditional application areas [44]. Thus, many efforts have been dedicated to exploring new methods and techniques to determine the uniformity of nitration of NC. Kamide [45] studied characterization of cellulose nitrate by thin-layer chromatography. Miles [46-49] recorded sample images before and after dissolving and grading using microscopes, demonstrating that the inner and outer surfaces of the fibre cavity were dissolved, which suggested that the amount of luminous flux increased after dissolving and grading. This indicated that there is an uneven distribution of nitrogen in the thickness direction of the fibre wall. A study of the surface properties of fibres of NC by chemical analysis photoelectron spectroscopy (ESCA) [42, 43, 50], showed a discrepancy between the surface degree of substitution and the average degree of substitution. The distribution of nitration degree in various kinds of NC as obtained by thin-layer chromatography (TLC) further indicated the uneven distribution of nitrogen in NC [19]. Clark [42, 43, 50] analyzed the degree of esterification of NC and the distribution of nitrate groups at different positions on the glucose rings and different glucose units using high resolution ^{13}C NMR, which reflects the average distribution of the nitrate ester groups on the glucose rings in the molecular chain. However, these methods cannot achieve the product quality control in an industrial process. In the 1980s, Wu [16] tested the nitrogen content homogeneity of NC by the Micro Dumamy Nitrogenous Method (MDNM). However, this method is tedious, time-consuming, difficult to operate, and can be easily affected by human factors. Lewis [51] and Kohlbeck [52-53] developed a polarizing microscope for the determination of nitrogen distribution, but this method failed to be of practical

use due to the lack of manoeuvrability and stability.

In summary, the development of accurate methods and instruments for measuring the uniformity of nitration of NC for industrial application still remains a great challenge. Our previous work analyzed the nitrogen content and nitrate group distribution of NC by polarization microscopy, and found that a linear relationship can be established between the nitrogen content and the optical path difference of NC [2, 33, 35]. Based on this, the purpose of the present study was to establish the relationship between the uniformity of nitration of NC and its optical index at a molecular level and to develop a set of fast automatic test systems for the determination of nitrogen content and uniformity. Furthermore, the effects of the nitrating agent and raw materials on the distribution of the nitrogen content and its uniformity were also studied.

2 Experimental

2.1 Reagents and instruments

Sulfuric acid, nitric acid, sodium carbonate, naphthalene bromide kerosene (analytical reagent) were provided by the Beijing Tongguang Fine Chemical Company. In order to study the effect of maturity on the nitration results, refined cotton samples with maturities of 73.2%, 71.2%, 68.7%, 64.9% and 59.6% (alpha cellulose content ≥96.5%, the degree of polymerization was about 960) were selected. A 2000 mL vertical glass reaction kettle and a 3000 mL stainless pressure kettle were used (homemade). The refractive index of the NC immersion solution was determined with an automatic Abbe refractometer (2WA-J, Shanghai Optical Instrument Factory). A scanning electron microscope was used to determine the morphology of the samples (ProX, Phenom-World). A PMTS (BIT-II), assembled in our laboratory, was used to test the nitrogen content and uniformity of nitration of the NC samples.

2.2 Preparation of NC

The mixed H_2SO_4-HNO_3-H_2O system was chosen as the nitrating agent. NC samples with different nitrogen contents were prepared by changing the ratio of sulphate and nitrate in the H_2SO_4-HNO_3-H_2O system with a bath ratio of 50 and a nitration time of 30 min at 30 °C. After nitration, the NC product was filtered off, washed with gradient acid 3 times, then boiled in a high pressure cooking vessel at 120 °C for 60 min, followed by alkaline cooking in aqueous sodium carbonate (mass concentration no more than 0.15%) at 120 °C for 120 min. Subsquently, the NC obtained was milled with a mechanical fine

grinding machine. After grinding, the length of the NC fibres was less than 2 mm. The products were washed and filtered 3 times and then dried in a vacuum oven at 85 °C for 2 h.

2.3 The establishment of PMTS

2.3.1 Testing mechanism

The nitrogen content and uniformity of nitration of the NC samples were investigated using a polarizing microscope. The principle of measurement is based on the quantitative relationship between the molecular structure of cellulose and the optical information obtained by interference with polarized light. Before nitration, the raw material has a complex structure. The fibrils form a fascicular orientation along the fibre axis, which belongs to a typical heterogeneous body with optical anisotropy. The basic cell of cellulose (crystal cell) is composed of five cellobiose groups arranged along the axis, which can be considered as a uniaxial crystal. Thus, the birefringence would not appear when the light enters the crystal along this axis, but it would appear in other directions.

The scheme for light propagation in the sample is shown in Figure 1. When light enters the heterogeneous body, it would be decomposed into perpendicular vibration directions, *o*-light and *e*-light; *e* is along the optical axis direction of vibration, and *o*-light is perpendicular to the optical axis direction of vibration. When the material refraction rate of *e*-light (n_e) is greater than that of *o*-light (n_o), the materials are referred to as positive crystals; when the n_e is less than n_o, the materials are referred to as negative crystals. Cellulose raw material is generally a positive light substance. After nitration, it can be transformed into a negative light material. The structure of the introduced $-ONO_2$ groups on the glucose ring is similar to the NO_3^- structure. In this structure, the N atom is bonded *via* sp^2 hybrid orbitals and three sigma bonds are formed. Moreover, its valence electron (VP_{NO3}) is 0, thus it belongs to the isoelectronic species with a plane triangular structure. As a result, a large number of $-ONO_2$ triangular plane structures perpendicular to the fibre axes are formed on nitration of the cellulose molecular chain. When the *e*-light passes through the $-ONO_2$ triangular planar structures, its polarizing action is less than that of the *o*-light. So n_e is less than n_o, and negative light property can be observed.

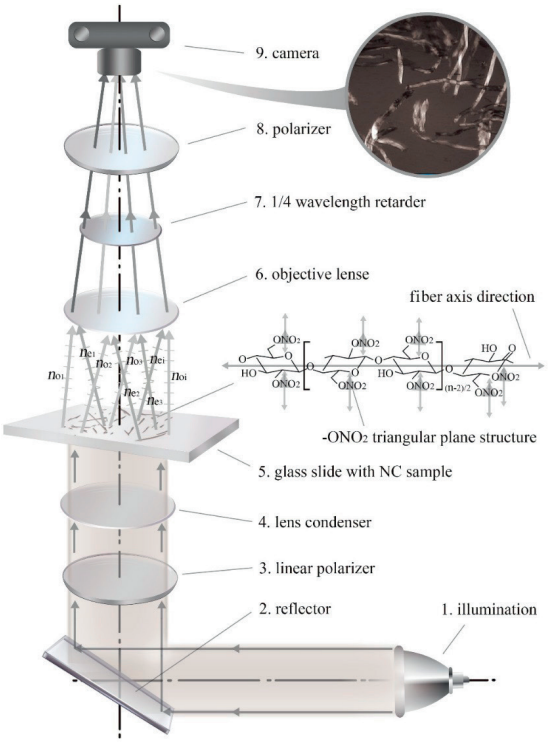


Figure 1. Scheme for light propagation in the sample

Because of the different refractive indexes of the NC fibres for *o*-light and *e*-light, their transmission speeds are different. When light exits from the fibre, the optical path difference between the two beams will interfere with each other. Under natural light, some wavelengths are enhanced and other wavelengths are offset. If a certain wavelength of light is missing from the white light, the polarizing colour can be observed as its complementary colour.

Figure 2 shows the sequence structure of cellulose and the mechanism for polarizing microanalysis of the nitration.

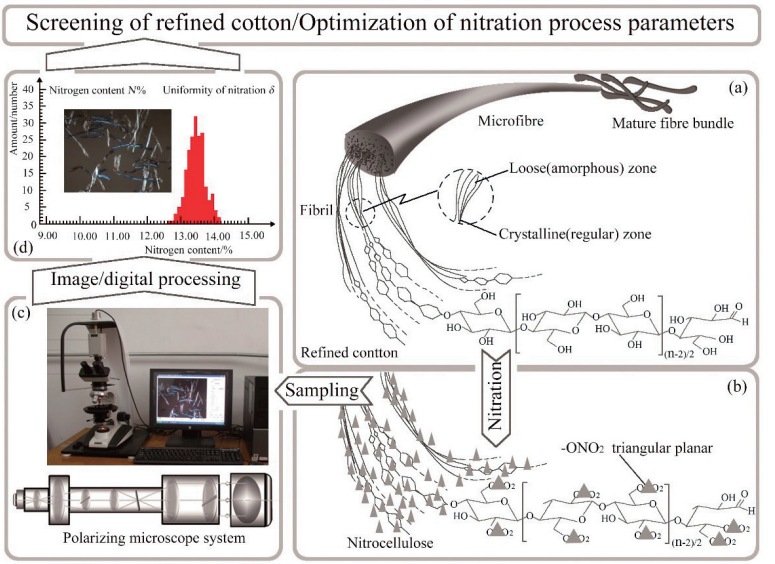


Figure 2. The structure of cellulose and the mechanism for polarizing microanalysis of the nitration

In 1976, Kohlbeck [52, 53] used a suitable immersion liquid to determine the mathematical relationship between the nitrogen content of NC fibres and the polarizing colour. The nitrogen content of NC showed an optically neutral point at 12.3%, while it did not produce a polarizing colour. He also pointed out that NC with different nitrogen contents had obvious spectral selectivity, that is, the spectral absorption curves of NC varied with different nitrogen contents. This is the theoretical basis for determining NC nitrogen content and its homogeneity by an optical method. The 1/4 wave plate method is used in the PMTS. The optical path difference can be converted to the compensation angle (β) because of the quantitative relationship between the compensation angle and the optical path difference. The conversion formula is:

$$\Delta = \frac{\beta}{180} \cdot \lambda \tag{1}$$

where Δ is the mean source wavelength (nm), β is the compensation angle (°), and λ is the mean wavelength of lambda as a light source (nm).

2.2.2 Construction and testing procedure of the system

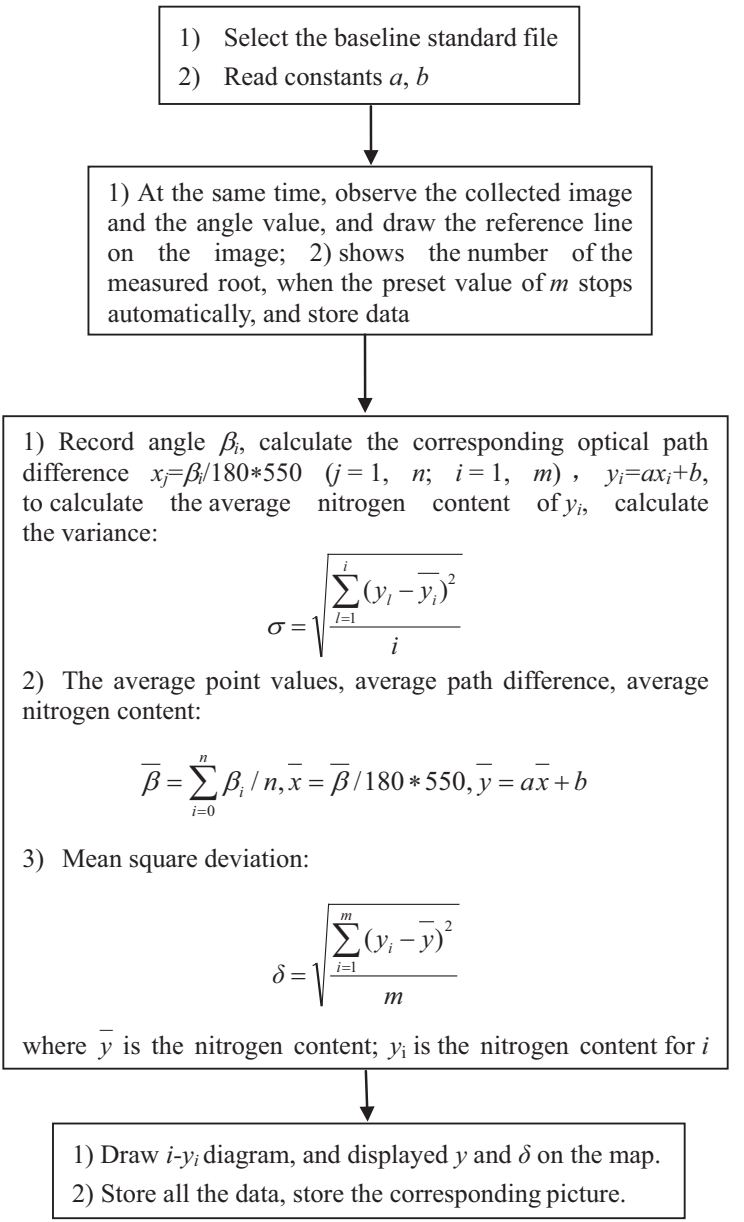
The PMTS was composed of a 1/4 wave plate, an average light wavelength

of 550 nm, a detection mirror deviation of 0.01 degrees, a digital image camera system, and a detection image processing system and its software. The polarizing microscope was fixed on a bracket pedestal. A video-camera shaft of the angle sensor was integrated with a polarization analyzer of the polarizing microscope by a connecting rod, so that the angle sensor is synchronously rotated with the polarization analyzer of the polarizing microscope, which in turn is connected with a computer by a data wire, to transmit the rotating and compensation angle data to the computer. This instrument, named BIT-II, was able to give the average nitrogen content and the nitrogen content of every fibre in the NC sample, as well as the mean square deviation (δ); δ can be taken as quantitative criteria for the uniformity of NC; the larger the value of δ, the worse the uniformity of NC will be. The data processing program for the system is displayed in Scheme 1.

2.2.3 Test process

1) Preparation of samples: In order to eliminate the internal stress and adhesion of organic impurities, the slides and coverslips were soaked in chromic acid for 12 h. About 10 μg NC sample (the NC samples were dried in an oven at 110 ±2 °C for 60 min before the determination, and the samples were of solid powder whose length was less than 2 mm) was spread evenly in the middle of the slide, soaked with the immersion liquid (composed of α-brominated naphthalene and kerosene in a certain proportion, and its refractive index adjusted to 1.51~1.53 using an Abbe refractometer), covered with a coverslip, and gently pressed in order to drive out air bubbles between the slide and coverslip. The sample to be measured was placed on the carrier platform of the polarizing microscope. The optical path difference of 200 NC fibre bundles in the NC samples was tested with the polarizing microscope test system, and the nitrogen content and the uniformity of nitration were calculated by the software.

2) Establishment of the standard curve: 8 NC standard samples with different nitrogen contents (tested by the Derwald alloy method, an absolute and standard test method) were selected. The average optical path difference for each sample was measured by the polarizing microscope. The standard curve was obtained by linear regression between the nitrogen content and the average optical path difference.



Scheme 1. Data processing program for the system

3) Sample test: About 200 fibres in each NC sample were tested randomly, the optical path difference of each fibre was measured, and the nitrogen content

of the NC sample can be obtained. The mean square deviation δ of the NC sample was calculated by the method of statistics for standard deviation.

3 Results and Discussion

3.1 Application of the test system

The nitrogen content of various types of standard NC samples and their homogeneity of nitration were tested by BIT-II PMTS. The standard curve for the NC nitrogen content versus optical path difference is shown in Figure 3.

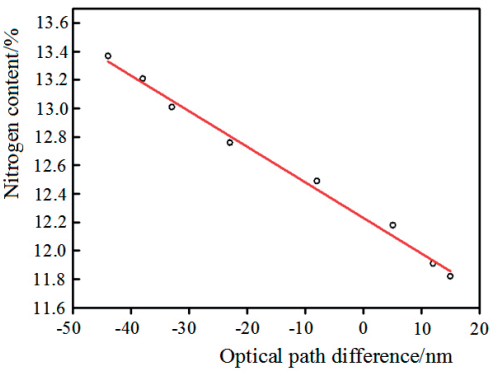


Figure 3. Typical standard curve for the test system

The results for several typical NC samples, including their fibre polarizing colour diagrams, nitrogen contents and the contrast diagrams for uniformity of nitration, are shown in Figure 4. As shown, different NC samples demonstrated different polarizing colours, which further correspond to different nitrogen contents and uniformity of nitration. Therefore, a facile method was established, and the advantages of this system may be summarized as follows: (i) compared with results from the interferometer method, the accuracy of this method is higher, and the absolute error for nitrogen content is less than 0.05% (Table 1); (ii) the nitrogen content and the uniformity of nitration of an NC sample may be obtained simultaneously; (iii) parameters such as viscosity, molecular weight, nitrogen content, ambient temperature and ambient humidity have no effect on the test results; (iv) the amount of samples used is very small (a few micrograms), and the process is nondestructive; (v) the system has a short test time, within 20 min.

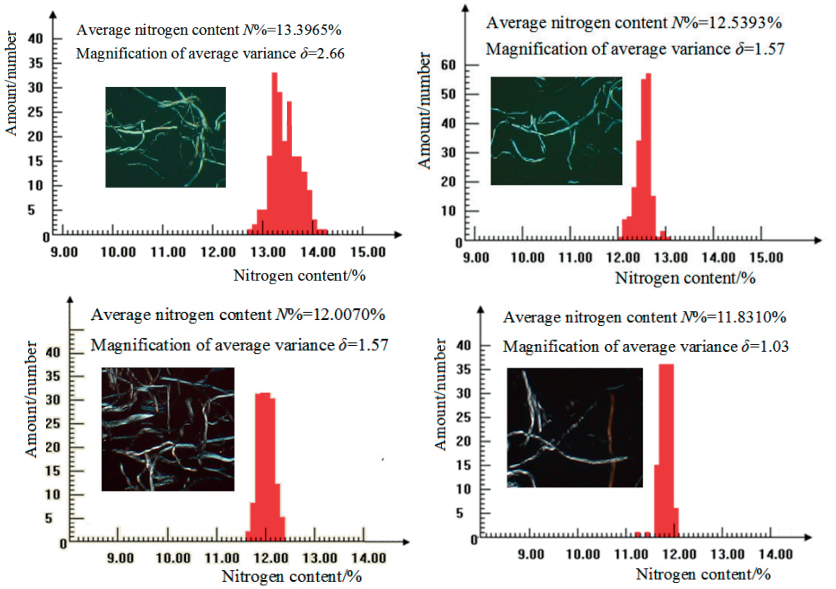


Figure 4. Comparison of polarizing colour, nitrogen content and uniformity of nitration for various NC samples

3.2 Effects of mixed acid composition

Refined cotton with a maturity of 71.2% was selected as the raw material. NC samples with different nitrogen contents were obtained by changing the ratio of nitric acid/sulfuric acid/water in the mixed acid. The traditional interferometer method and the BIT-II PMTS method were used for the same samples. Table 1 shows the differences in nitrogen content and uniformity of nitration *versus* mixed acid composition.

As shown, using different nitration systems, NC with five levels of nitrogen, 10.9 ±0.05%, 11.5 ±0.05%, 11.8 ±0.05%, 12.6 ±0.05% and 13.5 ±0.05% were obtained; their corresponding uniformity of nitration was significantly different, the mean square deviations δ were 3.17, 1.61, 1.15, 1.76 and 2.83, respectively. From the data we can see that the NC samples with different nitrogen contents showed different uniformity of nitration. When the nitrogen content of the product was reduced from 13.5% to 11.8%, the mean square deviation of the product was gradually reduced. However, when the nitrogen content was below 11.8%, the mean square deviation increased with the decrease in nitrogen content, and the uniformity of nitration decreased. When the nitrogen content was 11.8%, the NC showed the best uniformity of nitration, and the mean square deviation was only 1.15.

Table 1. Nitrogen content and uniformity of nitration of NC samples from different H_2SO_4-HNO_3-H_2O nitration systems

Serial number	Nitration system			Nitrogen content [%]			Mean square deviation δ
	Nitric acid [%]	Sulfuric acid [%]	Water [%]	Traditional method [a]	Polarizing method	Test deviation	
1	24.0	66.0	10.0	13.4834	13.4732	−0.0102	2.80
2				13.4534	13.4577	+0.00437	2.77
3				13.4709	13.4486	−0.0223	2.93
Ave.				13.4692	13.4598	−0.0094	2.83
4	24.0	60.2	15.8	12.5563	12.5393	−0.0170	1.70
5				12.5188	12.5450	+0.0262	1.73
6				12.6188	12.6234	+0.0046	1.85
Ave.				12.5646	12.5692	+0.0046	1.76
7	24.0	59.2	16.8	11.8563	11.8310	−0.0253	1.09
8				11.8313	11.8208	−0.0105	1.15
9				11.8413	11.8202	−0.0211	1.20
Ave.				11.8430	11.8240	−0.0190	1.15
10	18.8	65.6	15.6	11.4605	11.4512	−0.0093	1.58
11				11.4722	11.4752	+0.0030	1.61
12				11.4677	11.4589	−0.0088	1.63
Ave.				11.4668	11.4618	−0.005	1.61
13	16.7	62.5	20.8	10.9470	10.9510	+0.004	3.23
14				10.9290	10.9423	+0.0133	2.93
15				10.9556	10.9420	−0.0136	3.36
Ave.				10.9439	10.9451	+0.0012	3.17

[a] Traditional method: The nitrogen content of the NC samples was calibrated and determined by interferometer and the ferrous sulphate titration method, *i.e.* the result tested by CPEMS (Chinese Professional Explosive Metrology Station)

From the morphological analysis we can see that the structure of the raw cellulose is a multi-sequence structure. Obvious cross folding and fibre bundles can be observed, thus it is difficult to achieve the same degree of nitration at each physical point. Normally, most cellulose fibres can react quickly with the nitrating acid in the available area within 5 ~ 10 min. An extension of the nitration time under the stirring conditions can promote the acid entering the unreacted areas of the fibres, but within a limited reaction period, the degree of nitration and its uniformity depend mainly on the permeability of the nitrating acid, the degree of exposure, and the swelling of the cellulose fibre bundles. In the mixed

acid, an increase in the amount of nitric acid and a decrease in the proportion of water can produce two effects: firstly, the surface tension of the mixed acid is reduced, the diffusion capacity of the mixed acid is increased and the contact area between the mixed acid and the fibres is enlarged; secondly, as a moistening agent, an increase in water content can increase the moisture content of the fibre (expanding the diameter of the fibre). The production of NC with a nitrogen content of less than 11.8% is usually dominated by these two factors. However, when NC has a nitrogen content above 11.8%, the surface of the fibres would be dissolved. The thin film layer formed by dissolution hinders the further diffusion of HNO_3 into the fibre, which weakens the effect of the increase in surface tension. In addition, the swelling of cellulose also decreases under this condition, thus decreasing the uniformity of nitration.

3.3 Effect of maturity of refined cotton

On a global scale, the cellulose raw materials of NC are mainly wood pulp and cotton cellulose. As a fast-growing plant, the growth cycle of cotton is about 6 months, and there is a certain difference in the maturity of the fibre bundles due to differences in the producing area, planting mode, sunshine, picking time and different processing methods. Based on this, samples of refined cotton with different maturities (73.2%, 71.2%, 68.7%, 64.9% and 59.6%) were selected for nitration. The nitrating mixing acid ratio was nitric acid/sulphuric acid/ H_2O = 24.0/60.2/15.8.

Figure 5 shows the nitrogen content and uniformity of nitration of NC for a variety of refined cottons with different maturities. As shown, the NC samples prepared from different maturities of refined cotton under the same nitration process exhibited different uniformity of nitration. The nitrogen contents of these NC samples were 12.58%, 12.57%, 12.56%, 12.57% and 12.55%, and the corresponding variances in uniformity of nitration (mean square deviations δ) of these samples were 3.17, 1.61, 1.15, 1.76 and 2.83, respectively. That is, the nitrogen contents of the NC products obtained from refined cotton with different maturities were similar, but a significant difference was observed in the uniformity of nitration. The uniformity of nitration increased with increased maturity.

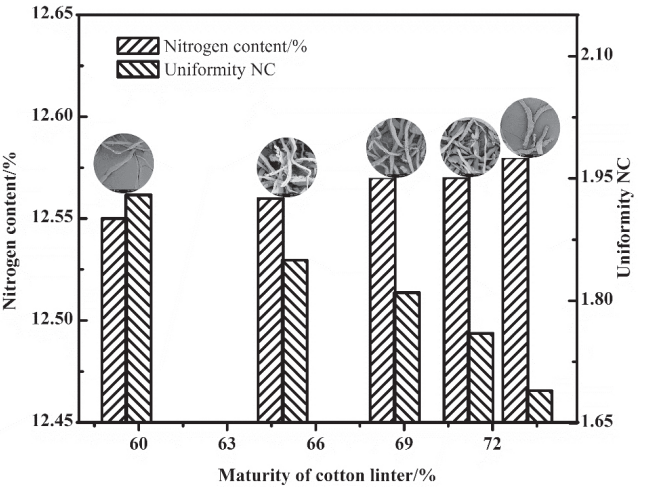


Figure 5. The nitrogen content and uniformity of nitration of NC from a variety of refined cottons with different maturities

Compared to mature cotton fibres, the contents of pentose, protein, fat, wax, water-soluble substances and ash in immature cotton fibres is higher (see the SEM diagrams in Figure 5). Meanwhile, the content of the primary wall in immature cotton fibres is higher. Thus, the ability to react for immature cotton fibres is poor. When the maturity of a refined cotton reached 73.2%, the uniformity of nitration index (δ) was reduced to 1.69, which can be considered as a product with superior uniformity.

4 Conclusions

Based on the polarization changes of cellulose before and after nitration, a test system with improved accuracy and operability for the determination of nitrogen content and uniformity of nitration of NC has been established. The test results for NC samples prepared by different nitric-sulfuric acid systems from raw materials with diverse maturities demonstrated that the uniformity of nitration of samples with high nitrogen content (above 13%) and low nitrogen content (below 11.5%) was relatively poor, while the medium nitrogen NC products had good uniformity. The maturity of refined cotton has little effect on the nitrogen content of the NC produced, but has an obvious effect on the uniformity of nitration. Cotton fibres with high maturity are beneficial to permeation of the nitrating agent and for the preparation of an NC product with good uniformity.

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Received: February 22, 2017
Revised: July 16, 2018
First published online: December 17, 2018