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Preparation and characterization of cellulose nitrate-acetate mixed ester fibers

Lili Li [a,b], Margaret Frey [a,*]

[a] Department of Fiber Science & Apparel Design, Cornell University, Ithaca, NY 14853, United States
[b] College of Materials Science and Engineering, Jilin University, Changchun 130022, China

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ABSTRACT

Cellulose nitrate-acetate mixed esters (CNA) were synthesized by nitration of cellulose diacetate, using HNO_3/H_2SO_4 as nitration agent. The CNA structures were confirmed and analyzed by IR and ^1H NMR. A decrease in molecular weight and an increase in nitrate group content were observed with increasing H_2SO_4 ratio and reaction time. The highest degree of nitrate substitution, 9.2%, for CNA was achieved with the reaction time of 6h in concentrated HNO_3. Increasing HNO_3 ratio in nitration media resulted in more thermally stable CNA. CNA fibers were prepared by altering the polymer concentration from 15 to 30% in an 85:15 (w/w) acetone:water solvent. The electrospun CNA fibers were characterized by SEM to investigate the influence of different NO_2% on fiber formation, diameters and architectures.

1. Introduction

Cellulose is a linear polysaccharide consisting of β-1,4-linked glucose. Due to its natural abundance, nontoxicity, non-immunogenicity, biocompatibility and degradability, cellulose and its derivatives as cellulose-containing materials have been used in a variety of products including photographic films, fibers, protective films and filters [1,2]. Cellulose acetate (CA) and cellulose nitrate (CN) are two important and commonly used cellulose derivatives [3,4].

CN, a cellulose derivative with over a century of history, has been used in a wide range of applications in both the military and civilian sectors [5,6]. It is produced by nitration of either cotton lint or wood pulp cellulose, where the hydroxyl groups on the cellulose backbone are replaced with nitrate esters. Previous work has explored the optimum conditions for this reaction [7–10]. These studies reveal that H_2SO_4 which added to the nitrating mixture is the best additive and provides stabilization against detonations. The H_2SO_4 also acts as catalyst in the nitration reaction, creating pathways for the nitrate groups provided by HNO_3. In previous papers of this field [5,11–13], the nitration of cellulose nitrate appears to be a fairly simple reaction. However, the comprehensive and theoretical mechanism for this reaction has not yet been developed clearly. In fact, the study of nitrated cellulose indicates that the reaction is not as simple as was believed. The content of nitrogen in the resultant cellulose nitrate indicates that the reaction is irregular nitration [14]. These variations of nitrogen content are used in different applications. For example, CN with 12.6–13.3% nitrogen content can be used as gun propellant and CN with lower nitration content can be used in varnishes and films [15]. Even though it is theoretically possible to have a nitrogen content of 14.14% (where all three hydroxyl groups in the anhydroglucose unit are substituted), the nitrogen content can not exceed 13.8% actually. When CN is used as the fibrous membranes in applications such as universal blotting surfaces for protein research [16], lateral flow immunochromatography testing [17], and immobilization of proteins [18], the nitrogen content should be less than 12.6% to avoid to be classified as an explosive.

Another cellulose derivative, cellulose acetate (CA), is a good candidate for its readily available, inexpensive and biodegradable properties. The hypoallergenic properties guarantee CA can safely contact skin and food. But CA has low oxidation and chemical affinity which limit its further applications [19–22]. Therefore, a blend of these two cellulose derivatives, CA and CN, has been investigated as a potential method of surpassing the individual polymers for improved performance in various applications (i.e. technical films, paint-and-varnish materials, and slow-burning composites). U.S. Patents [23,24] reported the creation of CN-CA blend adsorbent membrane that showed durable adhesion to an absorbent isotropic filter at 323–383 K. The system is unstable outside of this temperature range and results in the phase separation [25].

In this work, a novel method is used to control the NO_2% in anhydroglucose units. Cellulose nitrate-acetate mixed esters (CNAs) is prepared by nitration of the hydroxyl group in cellulose

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* Corresponding author. 299 MVR Hall, Department of Fiber Science and Apparel Design, Cornell University, Ithaca, NY 14853-4401, United States. Tel.: +1 607 255 1937; fax: +1 607 255 1093.
E-mail address: mfw24@cornell.edu (M. Frey).

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diacetate. The modified cellulose diacetate through nitration produce homogeneous cellulose derivatives with both of nitrate and acetate substitution on the backbone. IR and ^{1}H NMR are used to characterize CNA structures. The effects of the nitration agent and the duration on molecular weigh are analyzed by GPC. The tunable nitrate groups were confirmed by elemental analyzer. Electrospinning was used to assess the ability of the CNA polymers to form fibers under typical CA conditions in an acetone/water solvent. The thermal properties and fiber morphology of CNAs were studied for their future applications. CNA possesses higher chemical affinity and better solubility compared with CA; and better thermal stability than CN.

2. Experimental section

2.1. Materials

CA (acetyl content: 39.7%, M_n: 50,000) was purchased from Aldrich Chemical Co. Concentrated HNO_3 (68%), H_2SO_4 (98%) and other chemical reagents were all reagent grades (supplied by VWR scientific, West Chester, PA) and were used without further purification.

2.2. Preparation of cellulose nitrate-acetate mixed ester (CNA)

10 g CA powder was dispersed in only HNO_3 for 1 h, 2 h, 4 h and 6 h or in H_2SO_4/HNO_3 with 2/1, 1/1 and 1/2 (v/v) for 1 h. Distilled water was then added to the mixture under stirring to precipitate out the nitrated CA. The precipitate was filtered, washed repeatedly with distilled water and dried in a vacuum oven at 50 °C for 48 h prior to further characterization.

2.3. IR and ^{1}H NMR

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) technique was utilized to collect IR spectra of the samples, as DRIFTS provides a faster and simpler preparation than traditional FTIR. Samples were filled into the microcup of the diffuse reflectance accessory on a PerkinElmer Nicolet Magana 560 IR spectrometer (Madison, WI), and IR data of samples was collected and processed with OMNIC software.

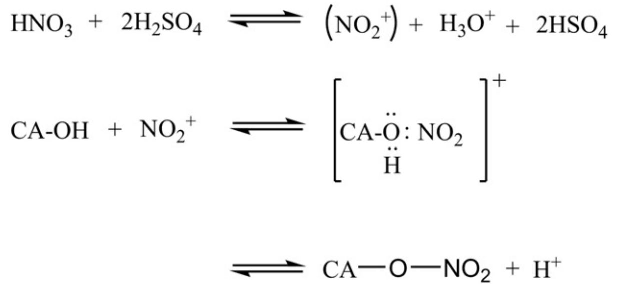
^{1}H NMR spectra were recorded by a Varian Unity INOVA-400 400 MHz spectrometer (Palo Alto, CA) operating at 400 MHz. Deuterated dimethyl sulfoxide (DMSO*d*6, Cambridge Isotope Laboratories, Cambridge, U.K.) was used as the solvent.

2.4. Elemental analysis

Elemental analyses of the prepared polymers were performed on a Carlo Erba NC2500 elemental analyzer. Samples were introduced to the combustion column via a Costech Zero-Blank autosampler.

2.5. GPC

The number and weight averaged molecular weights (M_n and M_w) and the polydispersity index (PDI) of CA and CNA samples were determined using a Model 510 gel permeation chromatographer (Waters Associates Inc. Milford, MA) equipped with a high-pressure liquid chromatographic pump, a Waters 486 UV detector, and a Waters 2410 different refractive index detector. THF was used as the eluent (1.0 mL/min). The columns were calibrated with polystyrene standards having a narrow molecular weight distribution.



Scheme 1. The mechanism of nitration.

2.6. TGA

The thermal properties of CA and CNA were characterized by a Thermogravimetric Analyzer (TGA) model 2920 (TA instruments, New Castle, DE). Weight loss during heating in TGA was measured while heating from 30 to 600 °C at a rate of 10 °C/min under a nitrogen purge.

2.7. Solution experiment

1.5 g CA or CNAs was dissolved in 10 mL acetone. After standing overnight, the precipitate of CA and CNAs in acetone was observed. A digital camera (Canon SD750) was used to record the results.

2.8. Electrospinning

Ultrafine CA fibers were electrospun from a CA solution in a mixed solvent of acetone/water (85/15, w/w) at a concentration of 10 wt% [26].

For electrospinning synthesized cellulose nitrate-acetate mixed ester (CNA) fibers, an appropriate amount of CNA was dissolved in acetone and distilled water (acetone/water = 85/15, w/w). The CNA concentration ranged from 15 to 30 wt%.

Electrospinning was performed at 20 °C in air. The prepared solution was place in a 5 mL syringe and fed by a syringe pump (Harvard Apparatus, MA), and a high voltage at 15 kV was applied. Other electrospinning conditions included 0.6 mm (ID) needle, 2 mL/h feed rate, aluminum foil collector, and 10 cm collection distance. The electrospun samples were dried in a vacuum oven at 40 °C for 24 h and then removed from the aluminum foil before testing.

2.9. Morphology observation

The samples were fixed on aluminum stubs and sputter coated with Au-Pd for 60 s. Scanning electron microscopy (SEM) (Leica 440) with an acceleration voltage of 25 kV was employed to analyze the morphological appearance and size of the as-spun materials.

Table 1
All CNAs which prepared by different condition.

CNA samples	Reaction Condition	
	Nitration agent	Reaction time
CNA 1	2/1 A (v/v)	1h
CNA 2	1/1 A (v/v)	1h
CNA 3	1/2 A (v/v)	1h
CNA 4	HNO_3	1h
CNA 5	HNO_3	2h
CNA 6	HNO_3	4h
CNA 7	HNO_3	6h

A: H_2SO_4/HNO_3.

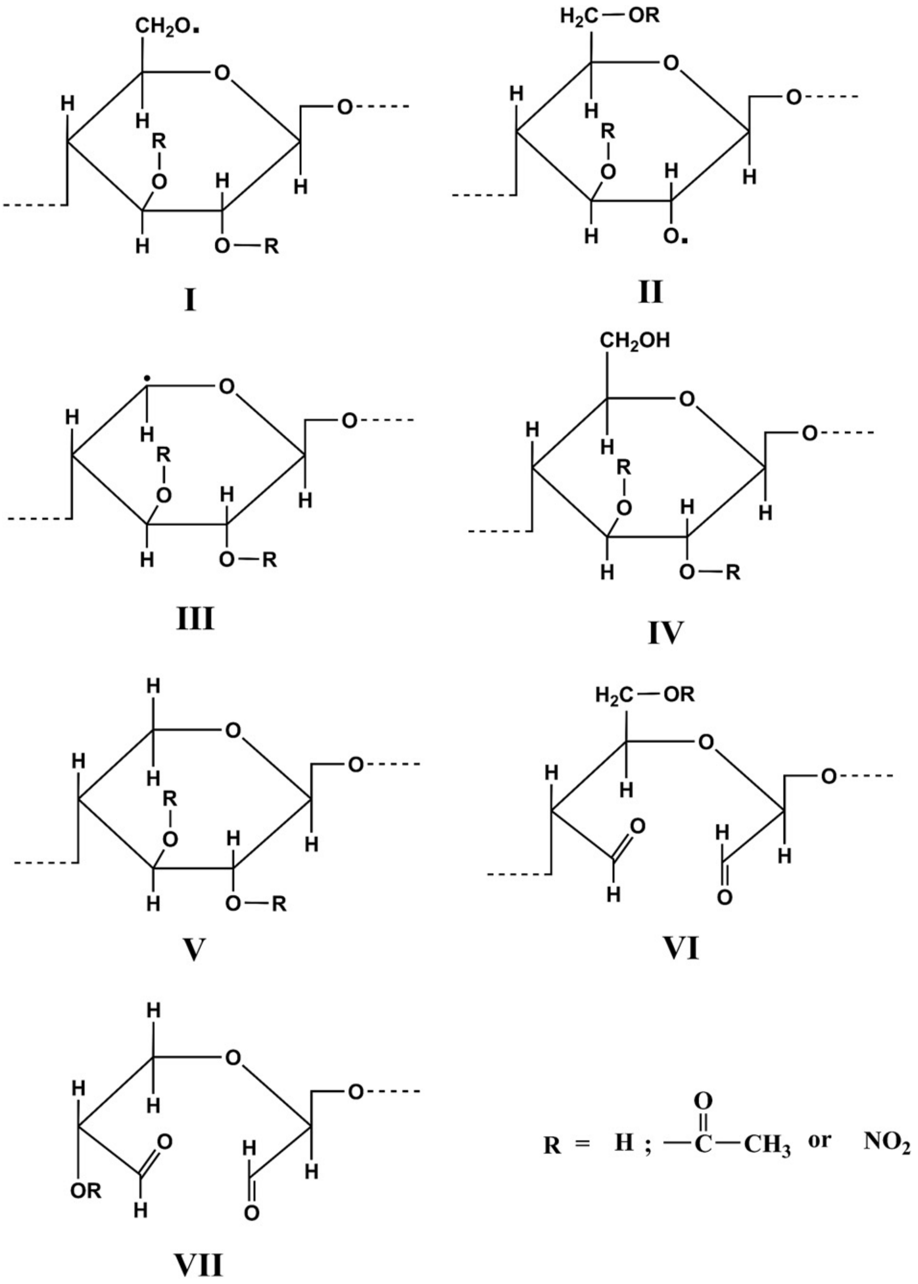
3. Results and discussion

3.1. Nitration of cellulose diacetate

The nitration of cellulose diacetate was conducted using reaction protocols established for the nitration of cellulose [10] which had shown that nitration was affected by the NO_2^+ ion. Physical and chemical evidence confirmed the presence of NO_2^+ ion in the concentrated mixed acid used in nitration reaction [27].

HNO_3/H_2SO_4 with different ratios (2/1, 1/1 and 1/2 v/v) or concentrated HNO_3 alone were used as nitration agents. The nitration reaction was expected to proceed as shown in Scheme 1. By varying the nitration agent and reaction time (Table 1), seven CNAs were produced which resulted in variations of the products and by-products indicated in Scheme 2. The structure of the CNA illustrated in Fig. 1 contained substitutions of acetate, nitrate or hydrogen for R in combination on each anhydroglucose backbone ring. ^1H NMR, IR, elemental analysis, GPC and dissolution experiments were used to identify and characterize the CNAs products.

H_2SO_4 acted as a catalyst in the nitration reaction and swelled the CA, which allowed the nitrate groups to penetrate more easily and uniformly. Nitrate ester formation favored over sulfuric ester formation, so that comparatively few sulfate groups were left to bind with the cellulose nitrate. When HNO_3 alone was used as the nitration agent, the time needed to achieve a certain degree of substitution was longer than in the acid mixture system. Several side reactions were also possible which would result in the decomposition of CA materials (shown in Scheme 2). Previous works on nitration of cellulose [12,13,28,29] presented that homolytic cleavage of R–O bonds occurred to form the nitrogen dioxide or carbon dioxide and intermediates of types I and II. The intermediate I could rearrange to form formaldehyde and



Scheme 2. The decomposition of CNAs in nitration.

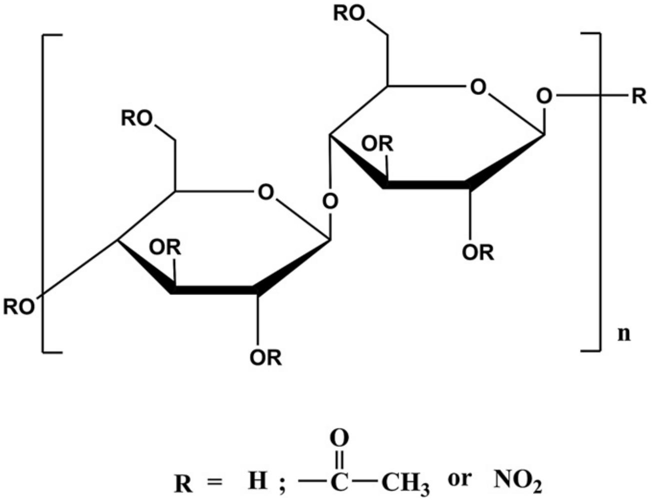


Fig. 1. The structure of CNA.

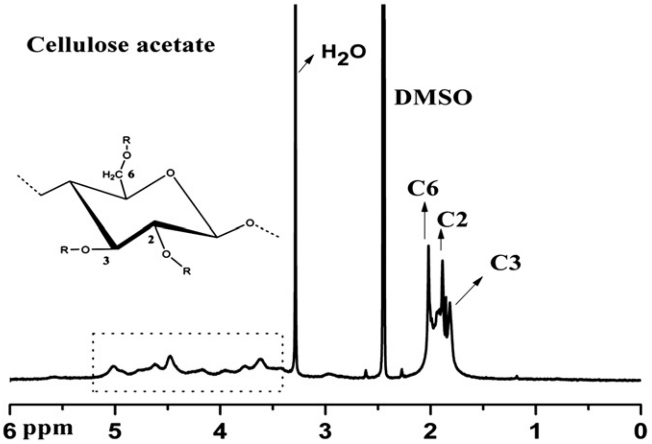


Fig. 2. ^{1}H NMR spectra of CA.

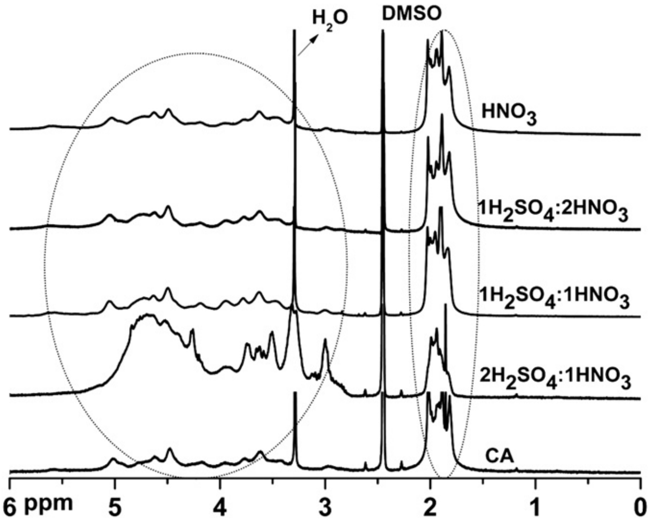


Fig. 3. ^{1}H NMR spectra of CNAs by using acid mixture as nitration agent.

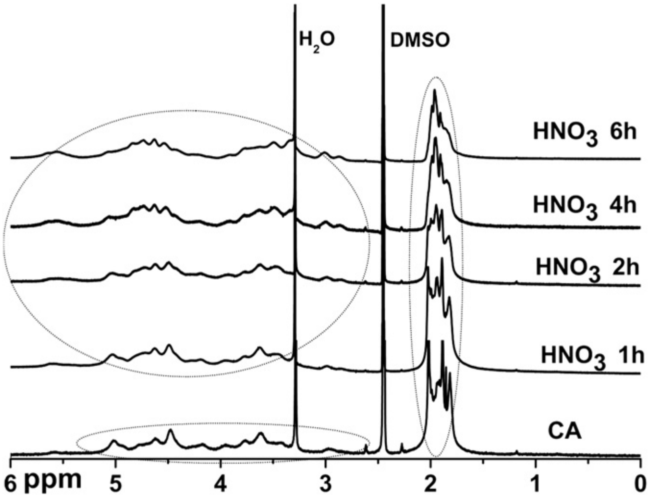


Fig. 4. ^{1}H NMR spectra of CNAs with different reaction time by using HNO_3 as nitration agent.

intermediate III. However, since nitration was the primary reaction, it was likely that the formaldehyde would be destroyed in part by subsequent reactions, and intermediate I alternatively abstracted a hydrogen atom from another position to produce a stable entity IV. If “R” were only an H atom, this could result in formation of the underivatized cellulose. Intermediate III would convert to compound V when similar steps occurred. The rearrangement of II, after the elimination of the ester group, formed the compound VI. If the reactions I–III and II–VI occurred within the same anhydro-D-glucose unit, or anhydroglucose inter chains cleavages occurred, the small molecules produced. These produced structures strongly depended on the reaction conditions and could be characterized in the following discussion from ^{1}H NMR, IR, elemental analysis, GPC and dissolution experiments.

3.2. ^{1}H NMR analysis

Compared with ^{1}H NMR spectra of the starting CA (Fig. 2), it was confirmed that nitrate group had successfully linked with the anhydroglucose backbone to form CNA (Figs. 3 and 4). The

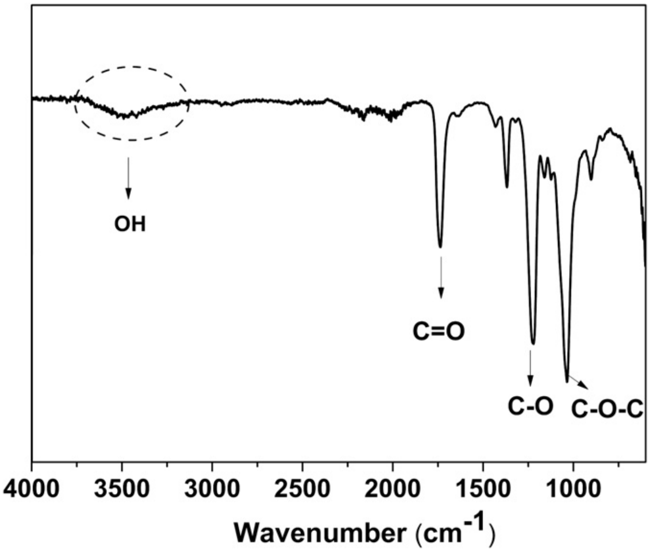


Fig. 5. IR spectra of CA.

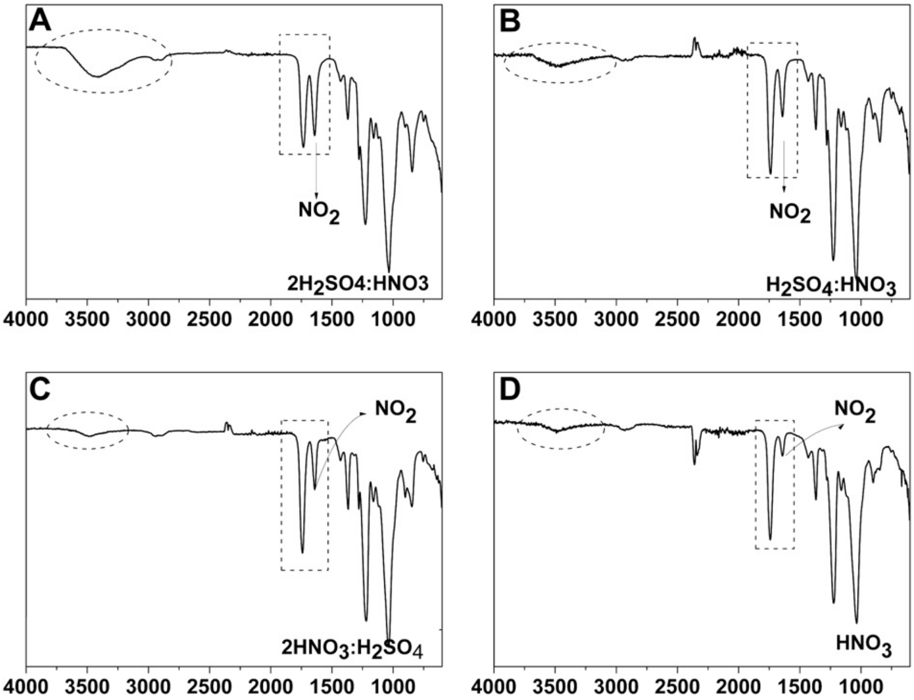


Fig. 6. IR spectra of CNAs by using different volume ratio of H_2SO_4/HNO_3 as nitration agent.

consecutive small peaks between 2.9 and 5.7 ppm were assigned to anhydroglucose units [30–32]. The three clear peaks at 1.6–2.2 ppm corresponded to positions 2, 3, 6 for acetyl substitution in anhydroglucose of CA. The ^{1}H NMR spectra of CNAs after 1 h of nitration in different nitration agent were shown in Fig. 3. Compared with the ^{1}H NMR spectra of original CA, it could be seen that the peaks at 2.9–5.7 ppm became broader and stronger with increasing H_2SO_4 content in the nitration agent, and the three clear peaks at 1.6–2.2 ppm reduced significantly in intensity. One new peak at 1.91 ppm, which assigned to the ester side chain, appeared after reaction with the highest ratio 2:1 (v/v) of H_2SO_4/HNO_3.

Similar results were observed in the ^{1}H NMR spectra of CNAs produced using HNO_3 as the nitration agent and varying reaction time from 1 h to 6 h (Fig. 4). The peaks associated with anhydroglucose units at 2.9–5.7 ppm became broader with increasing nitration time. These observations suggested that carbon–carbon single bond cleavages occurred inside the six-membered rings, as well as the glycosidic scissions, which produced structures VI and

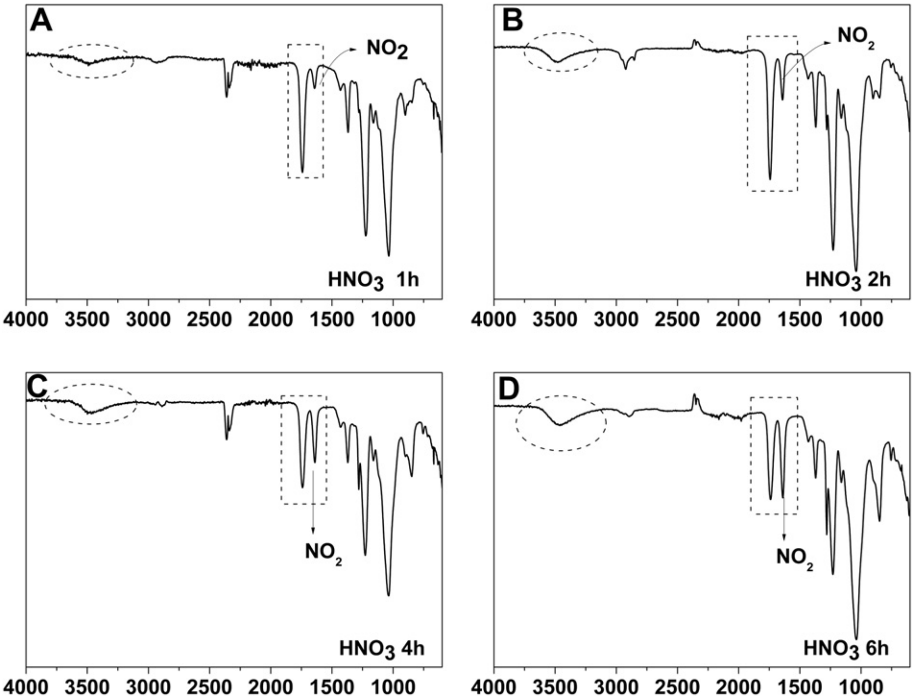


Fig. 7. IR spectra of CNAs with different nitration time by using HNO_3 as nitration agent.

Table 2
Elemental analysis results.

CNA samples	Weight (mg)	N%	C%	$-NO_2\%$
CA	1.06	0	51.0	0
CNA1	1.04	2.3	44.2	7.6
CNA2	1.07	2.1	44.3	6.9
CNA3	1.16	1.7	47.4	5.6
CNA4	1.31	0.6	49.2	2.0
CNA5	1.06	1.2	46.8	3.9
CNA6	1.23	2.2	45.2	7.2
CNA7	1.09	2.8	43.7	9.2

Table 3
GPC data of CA and CNAs.

Samples	M_n (10^4)	M_w (10^5)	M_w/M_n
CA	5.27	1.08	2.05
CNA1	2.51	0.50	1.99
CNA2	3.07	0.54	1.76
CNA3	4.10	1.07	2.61
CNA4	5.31	1.76	3.31
CNA5	3.64	0.97	2.67
CNA6	3.24	0.61	1.89
CNA7	2.98	0.50	1.67

VII. And the esterification which produced structures VI led to the peak increase in this range (see Scheme 2). The three small peaks at 1.6–2.2 ppm reduced to one peak at 1.91 ppm when the nitration time changed from 1 h to 6 h. The data showed that deacetylation and nitration, which produced structures IV or V (Scheme 2) and led to the ester side chain cleavage as well as the main chain scission, had occurred. Nitration and degradation were more significant for the samples using 2/1 (v/v) H_2SO_4/HNO_3 with 1 h reaction time than HNO_3 with 6 h reaction time, which indicating H_2SO_4 acted not only as catalyst but also the primary agent for the degradation reactions.

3.3. IR analysis

As shown in Fig. 5, the main peaks in IR spectra of CA were related to the carboxylate group, and where assigned to $V_{C=O}$ (at 1740 cm^{-1}) and V_{C-O} (at 1228 cm^{-1}) modes. The band at 1168 cm^{-1} corresponded to the glycosidic bond (C–O–C) that linked two pyranose rings. Compared with CA, the IR spectra of the CNAs (Fig. 6) showed clear evidence of nitration. The presence of new peaks at 1646 cm^{-1} and 840 cm^{-1} were attributed to V_{O-NO2} of cellulose nitrate. The band at 1646 cm^{-1} and 840 cm^{-1} became stronger with increasing H_2SO_4 volume ratio in nitration agent. A strong peak at 3446 cm^{-1} appeared to be assigned to the V_{OH} mode, and increased in intensity with increasing H_2SO_4 volume ratios in the nitration agent. The Free OH groups typically had absorbance peaks between 3500 and 3700 cm^{-1}, which suggested that the CA degradation reaction was caused by treatment with H_2SO_4. The shift to 3446 cm^{-1} or lower was due to the formation of hydrogen bonds between the OH and ester groups, as evidence of the presence of IV structure (Scheme 2). These results indicated that H_2SO_4 could accelerate not only the nitration process but also the degradation reaction rate.

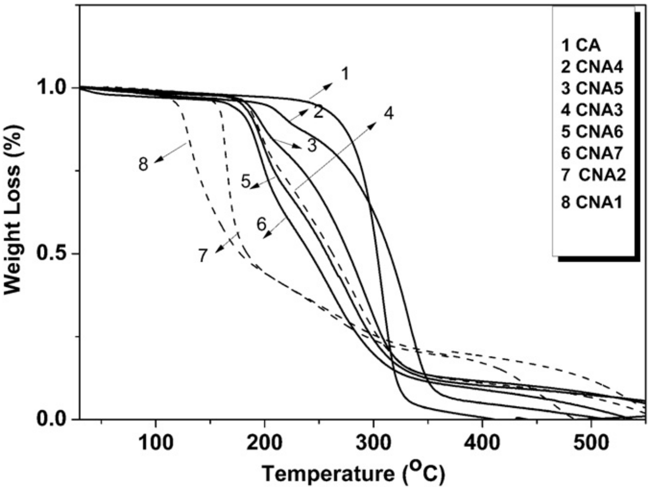


Fig. 9. The thermal degradation properties of CA and CNAs.

Fig. 7 illustrated FTIR spectra of CNAs formed in HNO_3 nitration agent with increasing nitration time from 1 h to 6 h. The V_{O-NO2} peak at 1646 cm^{-1} and 840 cm^{-1} showed increasing intensity with the increase of nitration time. The lower peak of V_{OH} at 3446 cm^{-1} indicated that CNAs treated by HNO_3 with longer time could achieve a higher degree of nitration.

3.4. Elemental analysis

The amounts of nitrogen (N%) presented in CNAs were measured by elemental analyzer. Since the only nitrogen source was from nitrate group in CNAs, the amounts of nitrate group ($-NO_2\%$) would be calculated from these elemental analysis. Table 2 showed N% and calculated $-NO_2\%$ in different CNAs. The results indicated that CNA1 and CNA2 (treated by more H_2SO_4), and CNA6 and CNA7 (treated by HNO_3 with longer time) had higher N%. The highest $NO_2\%$ was 9.2% in CNA7. The percentage of nitrogen in

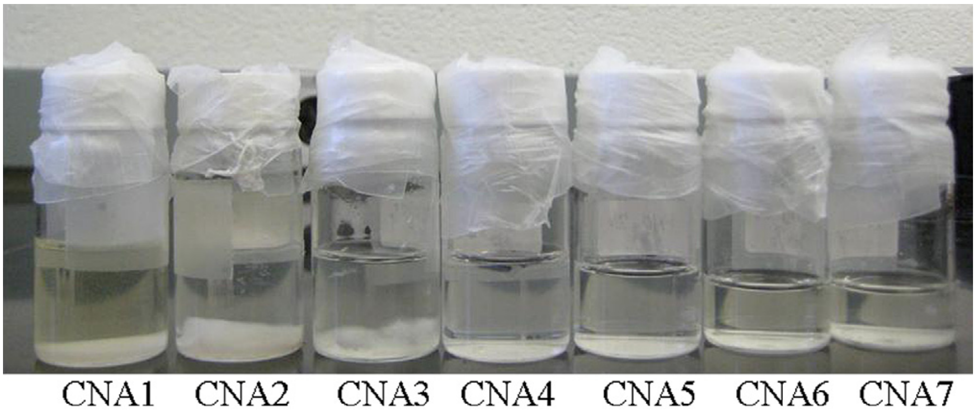


Fig. 8. Solubility images of different CNAs.

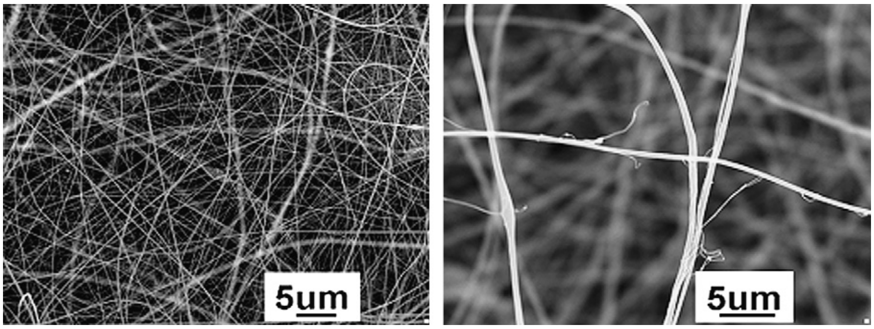


Fig. 10. SEM for CA fibers (CA% = 10%, acetone:water = 80/20, w/w).

the resultant CNAs indicated that the reaction was not stoichiometric. It was believed that the comparatively large sulfate molecules entered the amorphous regions, creating pathways for the smaller nitrate groups. This model would indicate that HNO_3 and H_2SO_4 percentages could vary randomly throughout a fiber and might explain nonstoicheometric nitration [33].

3.5. GPC analysis

M_n, M_w and the polydispersity index (PDI) of CNAs varied with the nitration agent and reaction time (Table 3). The molecular weight of CNA4 and CNA5 both nitrated with only HNO_3 in a relatively shorter reaction time were close to CA molecular weight, indicating that degradation had barely taken place. Both increasing H_2SO_4 content in nitration agent and nitration time resulted in the significant decrease of molecular weight. For 1 or 2 h reaction time and the lower H_2SO_4 ratio in the nitration agent, the polydispersity of the resulting CNA3-CNA5 was broader ($PDI > 2$) than the polydispersity of samples with longer reaction time and higher H_2SO_4 ratio in the nitration media ($PDI < 2$). The CNA6 and CNA7 samples with high NO_2%, low molecular weight and narrow molecular weight distribution were obtained at the optimum conditions of HNO_3 as nitration agent and reaction time longer than 2 h. These also approved the reactions of I–III, II–VI

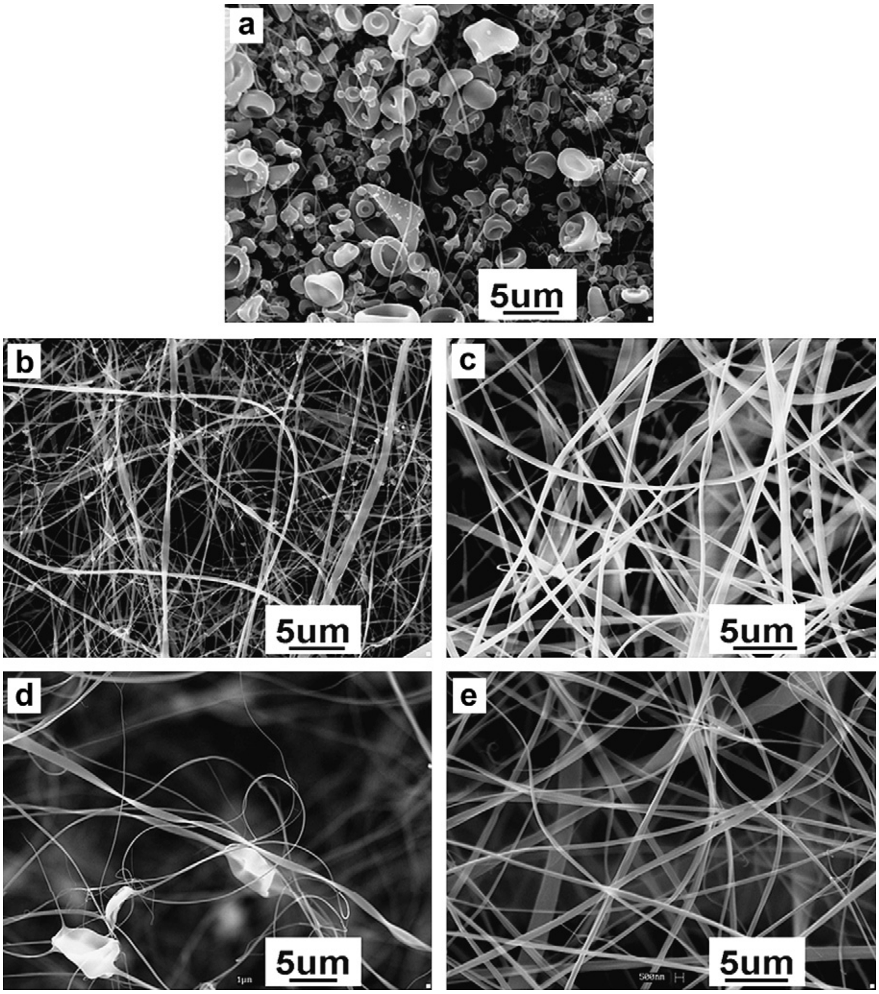


Fig. 11. SEM images of different CNAs concentrations which treated by H_2SO_4/HNO_3: (a) CNA1, 30%; (b) CNA2, 25%; (c) CNA2, 30%; (d) CNA3, 15% and (e) CNA3, 20%.

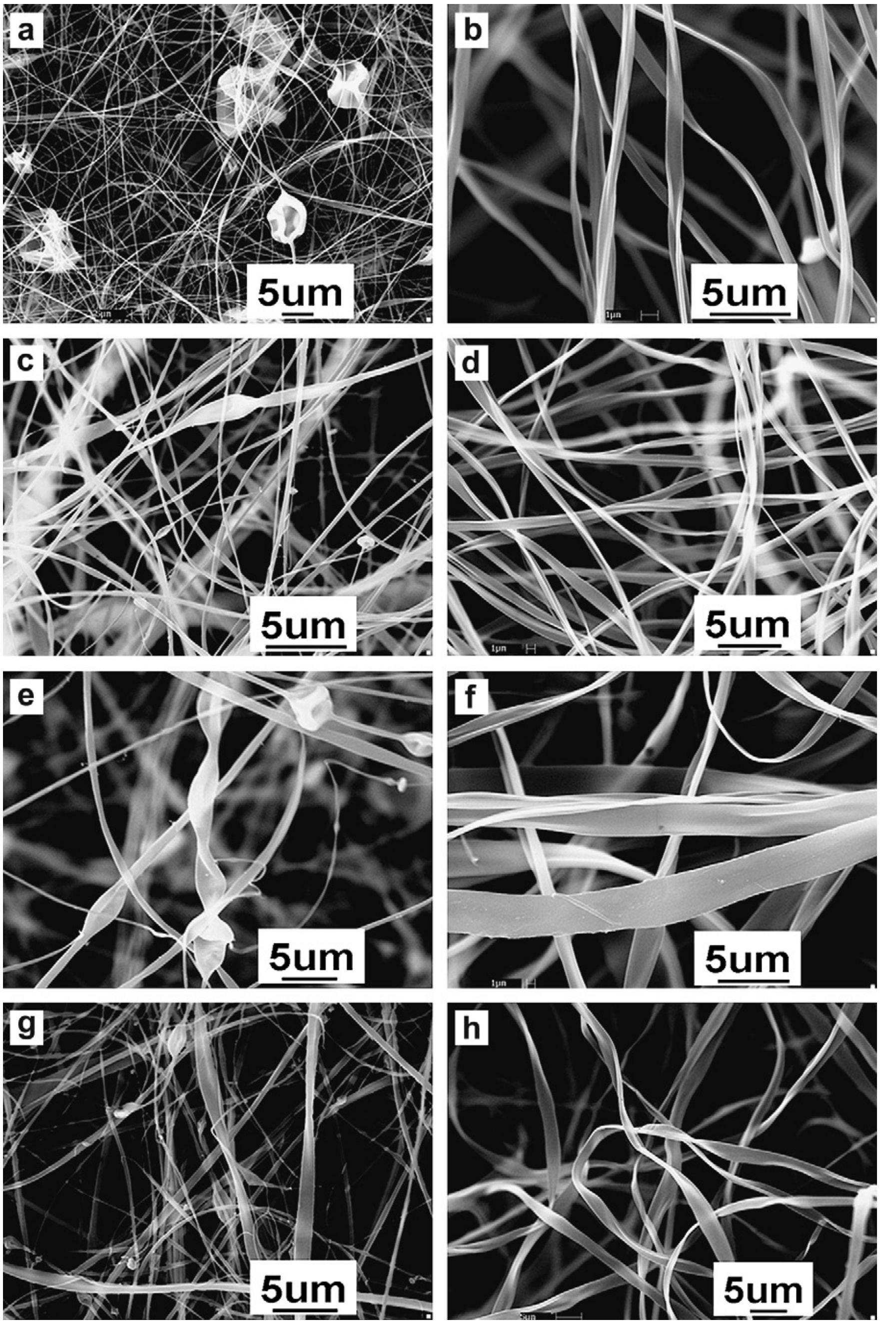


Fig. 12. SEM images of different CNAs concentrations which treated by HNO_3: (a) CNA4, 10%; (b) CNA4, 15%; (c) CNA5, 10%; (d) CNA5, 15%; (e) CNA6, 15%; (f) CNA6, 20%; (g) CNA7, 15% and (h) CNA7, 20%.

occurred within the same anhydro-D-glucose unit, or anhydroglucose inter chains cleavages happened, the small molecular produced (Scheme 2).

3.6. Solubility study

It was found that CNAs created either by nitration with more H_2SO_4 or longer reaction time had higher NO_2% and some degradation. To further assess the nature of degradation during reaction, the CNAs were dissolved in acetone. The precipitate formed (Fig. 8), and was identified as cellulose, since it is not soluble in acetone. CNA prepared with more H_2SO_4 produced more cellulose precipitate, as shown in structure IV when "R" was only an H atom in Scheme 2. CNA prepared with HNO_3 as the nitration agent, and even with longer reaction time, dissolved well in acetone with little or no cellulose precipitate. The use of H_2SO_4 in nitration agent resulted in the conversion of a portion of CA starting material to cellulose rather than CNA.

3.7. Thermal properties

The thermal stability of CNAs and the original CA were analyzed by TGA (Fig. 9). The onset degradation temperature for CA was close to 280 °C. For CNA4, CNA5, CNA6 and CNA7, the onset degradation temperatures were in the range of 210–260 °C. Whereas for CNA1 and CNA2, the onset degradation temperatures were close to 140 °C and 180 °C, respectively (see Fig. 9). These reconfirmed that the presence of H_2SO_4 in the nitration agent resulted in increased

Table 4
The average diameters of CA and CNAs fibers.

Samples	Concentration of electrospinning fibers					
	10%	15%	20%	25%	30%	D (μm)
CA	Y	/	/	/	/	0.73 ± 0.04
CNA2	/	/	/	/	Y	0.85 ± 0.20
CNA3	/	/	Y	/	/	2.07 ± 0.29
CNA4	/	Y	/	/	/	1.28 ± 0.20
CNA5	/	Y	/	/	/	1.43 ± 0.21
CNA6	/	/	Y	/	/	2.70 ± 1.52
CNA7	/	/	Y	/	/	3.72 ± 0.67

Y: could be electrospun to good fibers.
/: could not be electrospun to good fibers.

degradation. For the H_2SO_4/HNO_3 system, the comparatively large sulfate molecules entered the amorphous regions, creating pathways for the smaller nitrate groups. This would produce looser structures than in HNO_3 system [10,13,20], therefore the temperature of oxidative degradation decreased. All CNAs polymers showed the thermal stability lower than 140 °C, while CA/CN blending membrane was only stable in the range of 50–110 °C [23,24]. Therefore, CNAs polymers have applications in a wide range of temperatures.

3.8. Morphology observation

The 85/15 (w/w) acetone/water mixtures were used to electrospin CA and CNAs with different concentration. Representative SEM images of the fiber mats could be seen in Figs. 10–12. Based on these SEM images, the fiber diameters at different CNA concentrations were analyzed by the image visualization software ImageJ produced by Upper Austria University of Applied Sciences, the results were tabulated in Table 4. Electrospinning CA could produce uniform and smooth fibers [3,34] at 10% concentration with an average diameter of 0.73 μm (shown in Fig. 10). Electrospinning of CNA1 (treated by 2/1 H_2SO_4/HNO_3) solutions failed, because the low molecular weight led to low viscoelastic force, which was not enough to counter the higher coulombic stretching force, resulted in total break-up of the charged jet [35,36]. As shown in Fig. 11a, discrete beads with non-uniform shape and rough surface were observed. The rough surface was probably due to rapid evaporation of acetone from the outer surface of the beads firstly, and subsequent evaporation from inside the beads, this caused the collapse of the bead skin. Electrospun CNA2, which was treated by 1/1 H_2SO_4/HNO_3 at the lower concentration of 25%, resulted in the formation of both beaded and smooth fibers (see Fig. 11b). While increasing the concentration of CNA2 to 30%, the uniform fibers formed with average diameter 0.85 μm in Fig. 11c. Electrospinning of 15% CNA3 (1/2 H_2SO_4/HNO_3) solutions produced both beaded and smooth fibers, as seen in Fig. 11d; while the smooth fiber without discrete beads could be formed at the concentration of 20%, the average diameter increased to 2.07 μm (see Fig. 11e). Electrospun CNA4, CNA5, CNA6 and CNA7, which treated by HNO_3 with 1 h, 2 h, 4 h and 6 h respectively, produced both beaded and smooth fibers at the concentration of 10% and 15% (shown in Fig. 12a,c,e and g). Electrospinning of 15% CNA4 (containing 2.0% NO_2) solutions produced uniform and smooth fibers with average diameters of 1.28 μm (see Fig. 12b). Electrospinning of 15% CNA5 (containing 3.9% NO_2) could also produce uniform and smooth fibers with an average diameter of 1.43 μm (see Fig. 12d). While electrospinning of 20% CNA6 (containing 7.2% NO_2) produced smooth fibers with non-uniform diameters from 1.2 to 4.2 μm (see Fig. 12f); and electrospinning of 20% CNA7 (containing 9.2% NO_2) also produced non-uniform diameters from 3.1 to 4.4 μm (see Fig. 12h). Therefore, it was observed that NO_2% had an influence on the morphology of CNA fibers when treated by only HNO_3: the fiber diameters increased with increasing NO_2%. This result could be explained that NO_2 promoted the interactions among molecules and chemical affinity, resulting in an increase of the electrospun CNA fiber diameters.

4. Conclusions

In this work, a novel method was used to prepare a new type of cellulose derivatives which contained nitrate and acetate groups. Cellulose nitrate-acetate mixed esters (CNAs) were prepared by nitration of the hydroxyl group in cellulose diacetate. The different properties of nitration products were compared. All CNAs structures were characterized by ^{1}H NMR, IR, elemental analysis, GPC and solution experiments. The results indicated that a decrease in molecular weight and an increase in nitrate group content were observed with increasing H_2SO_4 ratio and reaction time. The highest degree of nitrate substitution, 9.2%, for CNA was achieved at 6 h in HNO_3 system. Additionally, more homogeneous CNA structures, which dissolved well in acetone/water mixture, were produced in the HNO_3 system. Increasing the ratio of HNO_3 in nitration agent resulted in more thermally stable CNA. The morphology of CNA fibers which were observed by SEM showed that CNAs could be electrospun into fibers at concentrations from 15% to 30%. The NO_2 group promoted the interactions among molecules which resulted in the increase of the fiber diameters.

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