Chemical modification of nitrocellulose by grafting sodium carboxymethyl

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Abstract Introducing deterrents improves the thermal stability of nitrocellulose of propellant surface, but is accompanied with inevitable problems, such as migration, residue, smoke flame, and so on. In this paper, sodium carboxymethyl function groups were chemically grafted to nitrocellulose molecular chains by reaction of denitration and following etherification, which provided thermal stability, flame suppression ion without detergent migration. Various structure characterizations were conducted and confirmed the sodium carboxymethyl-nitrocellulose (CMNC) was prepared successfully. The number of sodium carboxymethyl groups linked to nitrocellulose chains was affected by both denitration and etherification. The results of thermal analysis showed that the thermal stability of CMNC improved with the increase of bearing sodium carboxymethyl groups and was better than that of original NC sample. Meanwhile, the thermal decomposition behaviors and decomposition products of CMNC are similar to that of NC at temperature of the first DTG peak $T_{\text{max}}$ and that of CMC at temperatures of the second DTG peak $T_2$. This work provided a way for designing gun propellant with progressive burning, anti-migration and flame suppression simultaneously.

Keywords Nitrocellulose · Sodium carboxymethyl-nitrocellulose · Thermal stability · Flame suppression ion

Introduction

Nitrocellulose is obtained from esterification between hydrogen groups on cellulose and nitrate groups in an acidic medium. The number of hydroxyl groups replaced by nitrate groups determines the nitrogen content of nitrocellulose, which is usually more than 12.5% when used in military (Alinat et al. 2015; Onwukamike et al. 2019). Presently, nitrocellulose is an irreplaceable binder of gun propellants for small and medium caliber weapons. In practical application, improved thermal stability of nitrocellulose of gun propellant surface often has to be required to reduce the chamber pressure and increase the muzzle velocity of projectile, usually realized by adding deterrents with low molecular weight such as phthalate ester, camphor or dinitrotoluene (Liang et al. 2021; Li et al. 2021; Yang et al. 2020). However,
the thermal stability could become worse due to the migration of these deterrents in nitrocellulose, causing high firing pressure and the risk of explosion in application (Steve et al. 2011; Boulkadid et al. 2016). Meanwhile, the low oxygen balance of deterrents often causes intense flame during shooting, which not only exposes the position, but also reduces the aiming accuracy (Aurell et al. 2019; Liang et al. 2021). Hence, it is urgent to develop a novel strategy to address both migration and flame of deterred propellant.

In order to solve or alleviate the migration of deterrents in nitrocellulose, polymeric deterrents were developed as alternative (Liang et al. 2021). However, the migration of polymeric deterrent could not be inhibited completely. Our team also made some attempts to solve the migration of deterrents in nitrocellulose. Li et al. (2020b, 2021) conducted denitration strategy to improve the thermal stability of nitrocellulose at the molecular level, which solved the migration problem by reducing the nitrogen content of nitrocellulose on the surface of propellant without introduction of any deterrents.

However, the denitration strategy reduces the oxygen balance of nitrocellulose matrix by removing part of the nitrate groups from nitrocellulose, which could cause intense flame during shooting. As we all know, it is an effective means to inhibit the flame by adding inorganic alkali metal salts such as sodium salt and potassium salt (Jiang et al. 2019; Sridhar Iya et al. 1975; Birchall 1970). The inorganic alkali metal salts are decomposed into M· radicals during burning, which react with H· and OH· radicals in gas, terminating the chain reaction of flame generation (Hindiyarti et al. 2006; Babushok et al. 2017; Shen et al. 1991; Omar et al. 2022). However, the inorganic alkali metal salts are difficult to decompose and easy to convert into smoke in the burning process. Previous reports presented that the smoke problem of inorganic alkali metal salts could be effectively relieved by organometal salts due to their low decomposition temperature (Bracuti et al. 1983).

Inspired by the flame retardancy of cellulose modified by carboxymethyl metal salt (Guo et al. 2021; Hu et al. 2019), a strategy of combining denitration and etherification of nitrocellulose was proposed. Specifically, nitrocellulose was denitrated by reacting with hydrazine hydrate to transform part of the nitrate groups into hydroxyl groups, followed with carboxymethylation that these hydroxy groups were carboxymethylated in the presence of chloroacetic acid, leading to sodium carboxymethyl-nitrocellulose (CMNC) finally. The effect of the preparation process on the structure and thermal properties of CMNC were studied. As expected, CMNC with chemically grafted sodium carboxymethyl groups exhibited improved thermal stability of nitrocellulose without adding any deterrents. Meanwhile, CMNC could be considered as an organic sodium salt, which eliminates the flame without increasing smoke concentration. This paper not only presents an effective way of preparing CMNC, but also provides a foundation of designing a gun propellant with progressive burning, anti-migration and flame suppression.

Materials and methods

Materials

Nitrocellulose (nitrogen content: 13.15 wt%) was obtained from Luzhou North Chemical Industries Co., Ltd. Sodium carboxymethyl cellulose (average MW: 250000, DS: 0.9) was purchased from Acros Organics Co., Ltd. Sodium hydroxide (99.5 wt%) was obtained from Sigma Aldrich Co., Ltd. Chloroacetic acid (99 wt%) was purchased from Shanghai Bailingwei Chemical Technology Co., Ltd. Anhydrous ethanol, hydrazine hydrate (85 wt%) and hydrochloric acid (36 wt%) were obtained from Sinopharm Chemical Reagent Co., Ltd. All the above reagents were of analytical purity (AR) and used as received without further purification. Deionized water was used throughout the experiments.

Methods

Sodium carboxymethyl-nitrocellulose (CMNC) was prepared by removing part of the nitrate groups in nitrocellulose and subsequently introducing sodium carboxymethyl (–CH₂COONa) functional groups through etherification reaction. The CMNC preparation process is illustrated in Scheme 1.

Preparation of low nitrogen nitrocellulose (LNNC)

Initially, the NC was dried in a 60 °C water bath oven for 12 h. Anhydrous ethanol and 85 wt% hydrazine
hydrate were used to prepare hydrazine hydrate ethanol solutions with different mass fractions. The hydrazine hydrate solutions were prepared with 3 wt%, 9 wt% and 15 wt% for comparative study. 3 g dried NC was added into a three-necked flask containing 40 mL of hydrazine hydrate ethanol solution. The denitration reaction of NC was conducted at a constant temperature of 65 °C for 2 h with magnetic stirring. Subsequently, the mixture was transferred to an ice bath to stop the reaction quickly. Then, the denitrated NC was washed with deionized water and anhydrous ethanol in turn for 3 times, followed by drying in a water bath oven at 65 °C for 24 h. After that, LNNC sample was obtained.

Preparation of sodium carboxymethyl-nitrocellulose (CMNC)

Typically, take the molar ratio of 6.1:2.4:1 (sodium hydroxide/chloroacetic acid/NC) as an example, the LNNC sample (before drying) and 10 mL NaOH aqueous solution with 1.5 wt% were added to a 100 mL three-necked flask. LNNC was alkalized at 35 °C in water bath for 1 h with continuous magnetic stirring. Then, the water bath temperature was raised to 48 °C and a solution prepared previously with 25 mL 3.96 wt% NaOH anhydrous ethanol solution, 1.637 g chloroacetic acid and 10 mL anhydrous ethanol was added to start etherification reaction. The water bath heating program during etherification was divided into three stages: 48 °C for 30 min, 63 °C for 45 min, and 73 °C for 15 min. After the reaction, the three-necked flask was transferred to an ice bath quickly. The mixture was then transferred to a beaker containing 100 mL 2.72 wt% hydrochloric acid anhydrous ethanol solution and stirred magnetically for 20 min to neutralize the excess NaOH. After that, the product was washed with ethanol several times. Finally, sodium carboxymethyl-nitrocellulose (CMNC) samples were obtained by drying in a 60 °C water bath oven for 12 h. The number of introduced sodium carboxymethyl (–CH₂COONa) functional groups can be easily and effectively regulated by changing the molar ratio of sodium hydroxide/chloroacetic acid/NC, and a series of CMNC samples were prepared. The labels and experimental parameters of samples were listed in Table 1. The chemical mechanism of CMNC preparation was summarized as the follows:

\[
(C_6H_7O_2(OH)_{(3-x)}(ONO_2)_x)_n + nN_2H_4 \rightarrow (C_6H_7O_2(OH)_{(3-x)}(ONO_2)_{x-1}O^\ominus)_n + nH_2N - NH_2 - NO_2
\]  

\[
(C_6H_7O_2(OH)_{(3-x)}(ONO_2)_{x-1})_n + nH_2N - NH_2 - NO_2 \rightarrow (C_6H_7O_2(OH)_{(4-x)}(ONO_2)_{x-1})_n + nH_2N - NHNO_2
\]

\[
(C_6H_7O_2(OH)_{(4-x)}(ONO_2)_{x-1})_n + nNaOH \rightarrow (C_6H_7O_2(Na)_{(4-x)}(ONO_2)_{x-1})_n + nH_2O
\]  

\[
\text{ClCH}_2\text{COOH} + \text{NaOH} \rightarrow \text{ClCH}_2\text{COONa} + \text{H}_2\text{O}
\]
Characterization

Structural characterization and elemental analysis

The functional groups of the samples were characterized by Fourier transform infrared spectrometer (FTIR, Thermo Fisher Nicolet iS20, America). The spectral resolution was 4 cm⁻¹ and the range of measurement was 4000–700 cm⁻¹. Scanning electron microscope equipped with energy dispersive X-ray spectroscopy (SEM, FEI Quanta 250 FEG, America) with 5 kV accelerating voltage was used to characterize the microstructure and elemental mapping image of the samples. Surface elemental analysis of the samples were performed by an X-ray photoelectron spectrometer (XPS, Thermo Scientific ESCALAB 250Xi, America) probed with a monochromatic Al Kα radiation source (hν = 1486.65 eV) in a vacuum chamber. The binding energies of the spectra were calibrated according to the C 1s peak at 284.6 eV. The nitrogen (N) elemental analysis was undertaken with an Elemental Analyzer (EA, Elementar UNICUBE, Germany). The Sodium (Na) content was evaluated by ICP-OES (Agilent 7700, America).

Thermal analysis

The thermal decomposition properties were investigated by thermogravimetric analysis (TG, Mettler Toledo SDTA 851E Instruments, America). TG experiments were carried out under Ar atmosphere (20 mL·min⁻¹) at a heating rate of 10 °C·min⁻¹ from 50 to 700 °C. TG-FTIR measurements were carried out by using a TG analyzer (TG, Netzsch STA 449F5, Germany) coupled with a FTIR spectrometer (Bruker VERTE X80, Germany), providing a continuous detection of the gaseous products in the thermal decomposition process. The experiments were performed in Ar at a purge rate of 20 mL min⁻¹ and heated at 10 °C min⁻¹ from 50 to 700 °C. The scanning range of the FTIR spectra varied between 4500 and 650 cm⁻¹ at a resolution of 4 cm⁻¹ with 8 scans per sampling.

Results and discussions

Structural characterization and elemental analysis

The FTIR spectra of CMNC, NC, and commercial CMC samples were shown in Fig. 1a and the absorption bands of functional groups were summarized as shown in Table 2. All IR spectra of samples were normalized, on the basic of that, the peak intensity at around 1160 cm⁻¹ attributed to the asymmetric vibration of the C–O–C in β-glycosidic linkage was believed to be unchanged, which was convenient for comparing the change of characteristic peaks of samples obtained from different experiment conditions. From Fig. 1a, there are different offsets near 1730–1490 cm⁻¹ for five CMNC samples. Those characteristic peaks of different samples were fitted and deconvoluted into two peaks: ≈1639 cm⁻¹ (–ONO₂) and 1587 cm⁻¹ (COO⁻ or COONa in –OCH₂COONa), as shown in Fig. 1b and c. From Fig. 1b, with the increase of the degree of denitration, the number of –OCH₂COONa introduced to (C₆H₇O₂(ONa)₄₋₃(NO₂)₃₋₄(ONa)ₙ)ₙ + nClCH₂COONa
→ (C₆H₇O₂OCH₂COONa(ONa)₃₋₄(NO₂)ₙ)ₙ + nNaCl
(5)
LNNC samples increases under the same subsequent etherification reaction conditions. As seen in Fig. 1c, the degree of etherification gradually decreases with the decrease of the degree of denitration. Under the same degree of etherification, the nitrocellulose molecular chain with high denitration degree is more likely to react with carboxymethyl groups. This may be because the sequence of $-\text{ONO}_2$ removed from the glucose units in nitrocellulose molecule is $\text{C}_3 > \text{C}_6 > \text{C}_2$, while in the process of etherification, the order of $-\text{OCH}_2\text{COONa}$ introduced into glucose ring is $\text{C}_2 \approx \text{C}_6 > \text{C}_3$ (Shukla and Hill 2012; Shui et al. 2017). From the spectra of the samples in Fig. 1, the CMNC sample presents both characteristic peaks of $-\text{ONO}_2$ and peaks of introduced $-\text{OCH}_2\text{COONa}$, which proves the CMNC has been successfully prepared.
XPS experiments were employed to support the FTIR data and to further understand the chemical property and chemical bonding of the surface region of CMNC samples and their precursors. The full surface survey and individual spectra of samples were shown in Fig. 2. The total intensity for each sample has been normalized to unity. It can be seen that the characteristic peaks of NC, LNNC, commercial CMC and CMNC samples are C 1s, O 1s, N 1s, Na 1s, O Auger and Na Auger (Yu et al. 2013; Wang et al. 2017). Meanwhile, under the same degree of etherification, with the increasing degree of denitration, the characteristic peak intensity of Na element gradually increases and the characteristic peak of N element gradually disappears. Under the same degree of denitration, with the increasing degree of etherification, the characteristic peaks of Na element are gradually enhanced. The curve fitting with a high resolution of C 1s and O 1s spectra revealed that the functional compositions were carbon and oxygen species for samples, as shown in Fig. 2b and c. The C 1s peak of the CMNC (1, 2 and 3) samples were fitted to five Gaussian curves. Among them, the Gaussian peak at 283.1 eV is belonged to C–C and C–H; the Gaussian peak at 284.4 eV is assigned to the characteristic peak of C–O; the characteristic peak at 285.3 eV corresponding to the characteristic peak of C=O or O–C–O was observed (Mansur et al. 2017; He et al. 2020); the peak at 286.3 eV is attributed to the characteristic peak of O=C–O− (Samadder et al. 2020; Liu et al. 2017). Under the same etherification conditions, the characteristic peak of C–ONO2 gradually weakened and the characteristic peak of O=C–O− gradually elevated with the increasing denitration degree. From Fig. 3c, the O 1s peak of the CMNC sample is fitted to four Gaussian peaks. Among them, the characteristic peak at 529.3 eV is assigned to the O=C characteristic peak; the characteristic peak at 530.5 eV is belonged to the characteristic peak of O–C (Hu et al. 2018; Bai et al. 2020; Yuan et al. 2021); the characteristic peak at 531.3 eV is correspond to the characteristic peak of O–NO2 (Lu et al. 2019b). Under the same etherification conditions of CMNC (1, 2 and 3) samples, with the increase of denitration degree, the characteristic peak of C–OO− gradually increased and the characteristic peak of O–NO2 gradually weakened. The above results are consistent with the FTIR results, which confirm that the –OCH2COONa groups have been introduced in nitrocellulose chemically and the CMNC samples have been prepared successfully.

The morphologies of the original NC and CMNC-3 samples were observed by SEM, as shown in Fig. 3a and b, respectively. From the SEM images, the CMNC sample exhibits a fiber structure similar to NC and a rougher surface, which indicated that the NC may have undergone a chemical reaction that did not destroy its fiber structure. Meanwhile, the local element content analysis for CMNC was performed and presented in Fig. 3b, indicating that the content of N and Na was 1.30 wt% and 6.23 wt%, respectively. Furthermore, the distribution of C, O, N and Na elements was showed in form of elemental mapping image (Fig. 3c–f), the N element mapping signal is weak due to the large loss of nitrate groups, consistent with the results of N element analysis (Fig. 2b inset), and the C, O, N and Na elements were distributed on the fiber surface uniformly. The results of SEM–EDS indicated that the CMNC have been prepared successfully combined with the results of FTIR and XPS.

The elemental analyses of NC, LNNC, CMC and CMNC samples were displayed in Fig. 4. The nitrogen content of NC and LNNC was 12.152 wt% and 6.225 wt%, respectively. The CMNC samples do not contain nitrogen. For CMNC (1, 2 and 3) samples, the nitrogen content of the samples decreased gradually with the increase of denitration degree.

| No. | Absorption range/cm−1 | Characteristic groups |
|-----|-----------------------|-----------------------|
| 1   | 3375                  | –OH stretching vibration |
| 2   | 2900                  | –CH2– stretching vibration |
| 3   | 1160                  | Asymmetric oxygen bridge stretching vibration |
| 4   | 1587                  | COO− or COONa stretching vibration |
| 5   | 821                   | –ONO2 stretching vibration |
| 6   | 1273                  | –ONO2 symmetric stretching |
| 7   | 1639                  | –ONO2 asymmetric stretching vibration |

Table 2 Identification of prevalent bands in FTIR spectra of samples (Casaburi et al. 2018; Golbaghi et al. 2017; Zhao et al. 2016; You et al. 2016; Luo et al. 2019a; Kumar et al. 2018; Wongvitwichot et al. 2021; Wang et al. 2018, 2021; Mu et al. 2016).
The nitrogen content of the samples of CMNC (2, 4 and 5) gradually increased with the decrease of the degree of etherification under the same degree of denitration, which could be caused by the introduction of \(-\text{OCH}_2\text{COONa}\) into the NC molecular chains. Another reason for this result is that sodium hydroxide was used to provide an alkaline environment during the etherification reaction, which had a certain alkaline hydrolysis effect on NC as a strong base (Christodoulatos et al. 2001). Both NC and LNNC samples contained a small amount of sodium, which may be attributed to the alkalizing step during nitrocellulose production (Urbanski et al. 1965). For the CMNC (1, 2 and 3) samples, the sodium content of CMNC samples increased gradually with the increase of denitration degree. For the CMNC (2, 4 and 5) samples, the Na element content gradually decreased with the decreasing degree of etherification under the same denitration conditions. The results of the elemental analysis were consistent with that of FTIR and XPS, which proved that the structure construction of CMNC
could be controlled precisely. Hopefully, the introduction of sodium-containing functional groups (–OCH₂COONa) will provide a significant flame suppressant effect on CMNC samples (Jiang et al. 2019).

Thermal decomposition behavior

The curves of thermogravimetric analysis (TG) and its differential thermogravimetric analysis (DTG) during thermal decomposition at the heating rate of 10 °C min⁻¹ were shown in Fig. 5. \( T_{\text{in}} \) and \( T_{\text{f}} \) are the initial and ending temperature of main weight loss zone, respectively. The decomposition process of samples can be divided into three stages (Wu et al. 2016). The initial stage is from the beginning of heating to \( T_{\text{in}} \), during which a slight weight loss phase, the glass transition and dehydration occur. The yield of

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**Fig. 3** SEM images of the NC and CMNC samples (a,b) and corresponding element mapping (c–f) for CMNC-3 (the inserted table in image (b) is the result of local element content analysis for CMNC).

**Fig. 4** Elemental composition analyses of samples.
volatiles is extremely low at this stage (Zhang et al. 2019). The second stage starts from $T_{\text{in}}$ to $T_{\text{f}}$, featuring main weight loss because the thermal reaction becomes intensive and a large amount of volatiles are produced (Tudorachi et al. 2012). When the temperature reaches $T_{\text{max}}$ (temperature of the first DTG peak), the weight loss rate achieves the peak value. Then the DTG curve starts to decrease with increasing temperature until the thermogravimetric process ends at $T_{\text{f}}$. The third stage is carbonization stage where the TG and DTG curves are almost flat and the residues from the second stage are carbonized (Xu et al. 2020).

The thermal characteristic parameters were presented in Table 3. The $T_{\text{max}}$, $T_{\text{f}}$ and $M_r$ (the weight fraction of final residue) values of the CMNC sample are higher than those of the original NC sample. Combing the thermal characteristic parameters and the results of FTIR and XPS of different CMNC samples, a clear trend can be concluded that the more $-\text{OCH}_2\text{COONa}$ was introduced into the NC molecular chain, the better thermal stability of CMNC was obtained (Guo et al. 2021). Remarkably, CMNC sample exhibited two maximum decomposition rate peaks from the DTG curves. The first at near 210 °C is close to the maximum decomposition temperature of NC. The other is near 290 °C, which is close to the maximum pyrolysis temperature of CMC (Wu et al. 2016). The above experimental results indicated that CMNC presented similar thermal decomposition characteristics to both NC and CMC.

The TG-FTIR simultaneous analysis technique was employed to investigate the thermal degradation process of NC and CMNC-2 samples with real-time detection at a heating rate of 10 °C min$^{-1}$. There is apparent variation in the IR characteristic absorption peaks of the gaseous decomposition products of samples during thermal decomposition process at typical temperatures, including the temperature before decomposition ($T_x$, select 125 °C as $T_x$ temperature), $T_{\text{in}}$, $T_{\text{max}}$, $T_2$, and $T_{\text{f}}$, as shown in Fig. 6. Most gases produced during sample pyrolysis could be identified through their FTIR peaks, as shown in Table 4.

Figure 6a showed the real-time FTIR spectrum of NC sample. The FTIR absorption peaks of $\text{H}_2\text{O}$ and $\text{CO}_2$ were detected at $T_x$ and $T_{\text{in}}$. The initial

Table 3 Thermal behavior parameters of NC, CMC and CMNC samples with $\beta=10$ °C min$^{-1}$

| Parameters     | NC   | CMNC-1 | CMNC-2 | CMNC-3 | CMNC-5 |
|----------------|------|--------|--------|--------|--------|
| $T_{\text{in}}$ (°C) | 179.5 | 155.8  | 175.8  | 188.8  | 166    |
| $T_{\text{max}}$ (°C) | 205.6 | 206.3  | 222.5  | 225    | 214    |
| $T_2$ (°C) | –    | 296.8  | 292.5  | 280    | 261.3  |
| $T_{\text{f}}$ (°C) | 245.8 | 325.2  | 320.2  | 326.7  | 385.17 |
| $M_r$ (%) | 15.70 | 29.74  | 51.61  | 61.40  | 17.46  |

$T_{\text{in}}$: initial devolatilization temperature; $T_{\text{max}}$: temperature of the first DTG peak; $T_2$: temperatures of the second DTG peak; $T_{\text{f}}$: temperature at the end of the DTG peak; $M_r$: weight fraction of the final residue.
characteristic gas-phase CO₂ peaks at 669 cm⁻¹, 2342 cm⁻¹ and 2360 cm⁻¹ were attributed to the air flow fluctuation found within the air vent inside the FTIR beam chamber (due to the presence of CO₂ in the laboratory atmosphere). Additionally, in this temperature range, the structure of nitrocellulose was relatively stable and there was no thermal damage. When the temperature increased to $T_{\text{max}}$, the gaseous products such as H₂O, HCHO, CO₂, N₂O, CO, NO, NO₂ and HCOOH were detected. The peak at 1760 cm⁻¹ was attributed to the C=O stretching bands of HCHO, generated from the -CH₂ONO₂ group. Evolution of the HCOOH gas was due to the secondary autocatalytic reactions of NC. At the end of the decomposition process ($T_f$), the FTIR absorption peaks of H₂O and CO₂ were still easily identifiable in Fig. 6a (Chai et al. 2020; Zhao et al. 2021). Figure 6b presented the FTIR spectra of CMNC-2 at typical temperatures in the thermal decomposition. At the temperature of $T_x$ and $T_{\text{in}}$, the peaks of H₂O and CO₂ were assigned to the same event with the previous discussion. At the temperature of $T_{\text{max}}$ and $T_2$, the main evolved gases were H₂O, CO₂, NO₂, HCOOH, etc. The generation of nitrogen oxides were attributed to the decomposition of –ONO₂ in the molecular chain during heating. This is similar to the thermal decomposition characteristics of NC (Zhao et al. 2021). At $T_2$, the absorption bands in the FTIR spectrum were corresponding to H₂O, CO₂, HCHO, etc. In addition, a wide absorption band between 3200 and 3400 cm⁻¹, corresponding to νOH vibrations, could be attributed to ethanol fragments. The decomposition products at this temperature are similar to the decomposition process of CMC (Tudorachi et al. 2012). At $T_f$, H₂O and CO₂ were observed, which might be due to the residual organic matrix. According to the real-time detection of gas generation by TG-FTIR during thermal decomposition, CMNC exhibited a similar thermal decomposition behavior with NC and CMC to some extent and a better thermal stability than NC, leading to potential applications in propellant with certain flame retardant properties through chemical modification. Furthermore, the chemical grafting of sodium carboxymethyl groups through partly

Table 4: Reported FTIR characteristic peaks from gases generated during thermal degradation (Tudorachi et al. 2012; Chai et al. 2020; Zhao et al. 2021)

| No | Products | Wavenumbers of IR absorption peaks/cm⁻¹ |
|----|----------|----------------------------------------|
| 1  | H₂O      | 3600–4000                              |
| 2  | CO₂      | 2300–2380, 660–670                      |
| 3  | HCHO     | 2700–2900, 1720–1740                    |
| 4  | N₂O      | 2200–2300                              |
| 5  | CO       | 2109–2195                              |
| 6  | NO       | 1760–1965                              |
| 7  | NO₂      | 1593–1639                              |
| 8  | HCOOH    | 1080–1128                              |
| 9  | C=O      | 1760                                  |
| 10 | –OH      | 3200–3400                              |
denitration and etherification provides an inspiration of designing a new type of cellulose derivative with burn progressive, flame suppression and anti-migration properties simultaneously. It is expected to become a new type of cellulose derivative with energy containing and anti-migration properties.

Conclusions

According to the chemical modification method, we used hydrazine hydrate as a denitration reagent to remove part of the nitrate groups in nitrocellulose with high nitrogen content and converted nitrate groups into hydroxyl groups. Then sodium hydroxide and chloroacetic acid were employed as etherification reagents to introduce the sodium carboxymethyl functional groups into the molecular chains of nitrocellulose to prepare sodium carboxymethyl-nitrocellulose (CMNC) successfully. The results were shown as follows:

(1) The design strategy of denitration and then etherification was adopted, and CMNC was prepared successfully. Structural characterization and elemental analysis of the as-prepared CMNC samples were performed by FTIR, XPS, SEM, EA and ICP-OES. The results showed that the denitration reaction in the first step transformed part of the nitrate groups (–ONO₂) in nitrocellulose into hydroxyl groups (–OH), and the etherification reaction in the second step introduced the sodium carboxymethyl groups (–OCH₂COONa) into the nitrocellulose successfully. All results confirmed that CMNC was prepared successfully.

(2) The thermal decomposition behavior and thermal decomposition products of NC, CMC and CMNC samples were compared by TG-FTIR. The results of TG-FTIR showed that CMNC exhibited a higher thermal stability than original NC and similar thermal decomposition behavior to NC and CMC to a certain extent. CMNC was expected to provide progressive burning, anti-migration and flame suppression for gun propellants.

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Declarations

Competing Interests  There are no conflicts of interests/competing interests.

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