



Cent. Eur. J. Energ. Mater. 2021, 18(4): 448-476; DOI 10.22211/cejem/144708

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Research paper

Structure and Properties of Chain Branched Nitrocellulose

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Abstract: Nitrocellulose (NC) with a semi-rigid polymer chain is one of the typical traditional cellulose derivatives. Optimization of its mechanical properties is of great significance for improving the performance of NC-based propellants. The nitrate glycerol ether cellulose (NGEC) was prepared by introducing glycerol onto the unreacted, free hydroxyl groups on NC through a three-step process (alkalization, etherification, and nitration). The effects of both the nitration process and the degree of etherification on the NGEC nitrogen content were qualitatively explored. By adding NGEC into modified double-base propellant,

a standard engine grain with a diameter of 50 mm was produced by adsorption, granulation, and screw extrusion. The heat of explosion, and other physical properties of NGEC were characterized and the variation in mechanical properties and performance after storage for 6 years was investigated. The results indicated that the sensitivity was improved, and the stability was slightly decreased on increasing the nitrogen content of NGEC. Compared with NC containing similar nitrogen levels, NGEC exhibited a slightly higher heat of explosion, similar compatibility, and lower sensitivity. Additionally, the solubility of NGEC in ethanol/ether exceeded 99.7%. Through branched-chain chemical modification, the glycerol ether played a significant role in achieving internal plasticization among the cellulose chains.

Keywords: nitrate glycerol ether cellulose, NGEC, mechanical properties, compatibility, propellant, energy

Nomenclature

A	Compatibility assessment: <i>Compatible</i>
B	Compatibility assessment: <i>Slightly sensitive, short-term use</i>
C	Compatibility assessment: <i>Sensitive, better not use</i>
D	Compatibility assessment: <i>Dangerous, prohibited use</i>
GE	Glycerol ether
GEC	Cellulose glycerol ether
H ₁	A control blank group
H ₂	Formulation of propellant in which NC is partially replaced by NGEC (NGEC replaced 50% NC in H ₁)
H ₂ -1	Freshly prepared NGEC-based modified double-base propellant
H ₂ -2	The same propellant (H ₂ -1) after storage for 6 years
MS	Molar substitution
N%	Nitrogen content of NC [wt.%]
N%	Nitrogen content of NGEC [wt.%]
NC	Nitrocellulose
NGEC	Nitrate glycerol ether cellulose
Q _v	Heat of explosion [J/g]
G'	Storage modulus
G''	Loss modulus
T _g	Glass transition temperature [°C]
ΔT _p	Decomposition peak temperature difference [°C]
u	Burning rate of propellant [cm/s]
x	Molar degree of substitution for GEC (0 < x < 3)

1 Introduction

The use of an energetic binder in the basic framework of a propellant has an important influence on the energetic performance (content and properties), mechanical properties, and combustibility of the propellant [1-3]. Binders such as glycidyl azide polymer (GAP) [4-6], 3,3-bis(azidomethyl)oxetane (BAMO) [7-9], 3,3-bis(azidomethyl)oxetane-tetrahydrofuran copolyether (BAMO/THF) [10, 11], and thermoplastic elastomers (TPEs) [12] have received extensive attention and inspired in-depth research. However, most of these binders are utilized in modified composite propellants after cross-linking in the casting process.

Currently, the main binder used for double-base or modified double-base propellants that are molded by screw pressing, remains nitrocellulose (NC), which is derived from cotton or wood cellulose. The macromolecular chains of NC are rigid and straight owing to the nature of the β -(1,4)-linkage and the intra-chain hydrogen bonds that facilitate the linear chain morphology [13]. After nitration, NC partially retains some characteristics of cellulose, such as the semi-rigid molecular chain, high crystallinity, and strong intermolecular interactions. As an energetic binder, NC serves as a skeleton in modified double-base propellants. However, NC exhibits several limitations, such as low-temperature brittleness, high-temperature softness, and low output energy, which restrict the application and development of modified double-based propellants.

In order to improve the performance of NC-based propellants, polymers with high flexibility and low glass transition temperatures are often preferentially blended with NC, *e.g.* polyethylene glycol [14], epoxy resin [15], and butylene adipate [16]. Mixing of GAP/NC/N-100 as a binder into a propellant reduced its sensitivity and enhanced its energy density up to 1286 J/g. Furthermore, the compressive strength at room temperature could be significantly increased, by 420% [17]. However, such manufacturing techniques have been limited to small batch experiments on the laboratory scale and are difficult to realize on a production scale.

Compared with other thermoplastic elastomers, NC has several disadvantages, such as high impact sensitivity, brittleness, low combustion temperature, and poor long-term stability. Therefore, it is important to develop new alternative cellulose-based energy-containing polymers with enhanced performance and low induction [18, 19]. As early as 1965, studies were reported on NC grafting. The grafted segments included malonyl malonanilide dimmers (MA) [20], methyl methacrylate (MMA) [21, 22], and ethyl acrylate (EA) [23]. These grafted products have become important synthetic materials that have been widely

applied in the preparation of plastic films, permeable films, and coatings. For instance, a tough “polymer alloy” could be achieved by grafting polyether soft segments onto the free hydroxyl groups of NC macromolecular chains. However, owing to the high cost of modification and the difficulty of batch production, this process ultimately failed in practice [24]. The use of NC grafts in propellants has rarely been reported.

Gilbert [25] used NC directly as a raw material and prepared azidodeoxycellulose containing up to 17.0%N; however, owing to its poor thermoplastic performance it could not meet the standards of high-performance propellants. Li and Frey [26] prepared a modified NC (cellulose nitrate acetate mixture (CNA)), containing cellulose nitrate and cellulose acetate, with high toughness, low temperature fragility, good rigidity and re-elasticity, and good solubility. However, the amount of nitrogen in CNA was low; the maximum was only 2.8%. Grafting glycidyl azide to the original cellulose surface, Yang [27] showed a significant improvement in the energy density and insensitive properties of the cellulose-based nitrogen-containing materials. Tarchoun *et al.* [28] synthesized a new nitrogen-rich energetic polymer tetrazole-acetate modified cellulose, followed by nitration to obtain a tetranitrazole-acetate functional polymer; compared with traditional NC, this polymer had a high nitrogen content, good thermal stability, and low sensitivity characteristics.

During the time of the former Soviet Union, polyhydroxy cellulose ethers, such as:

- methoxy cellulose glycerol ether,
- 3,3-bisazidomethyl epoxybutane cellulose ether, and
- chloroglycerol hydroxyethyl cellulose ether,

were prepared by etherification of cellulose to tailor the flexibility of cellulose macromolecules and increase the number of –OH groups on the macromolecular chains. More importantly, a new cellulose-based energetic binder with good thermoplasticity and high energy was synthesized *via* nitration of polyhydroxy cellulose ether. Adding this to propellants resulted in new composites, which had high specific impulse and excellent mechanical properties [29].

To improve the flexibility of the molecular chains of NC, glycerol ether groups were chemically grafted onto the hydroxyl groups to weaken interactions among the macromolecular chains, thereby reducing the glass transition temperature. Simultaneously, inner plasticization could be achieved by residual glycerol between these macromolecular chains, further enhancing the flexible modified NC (see Figure 1).

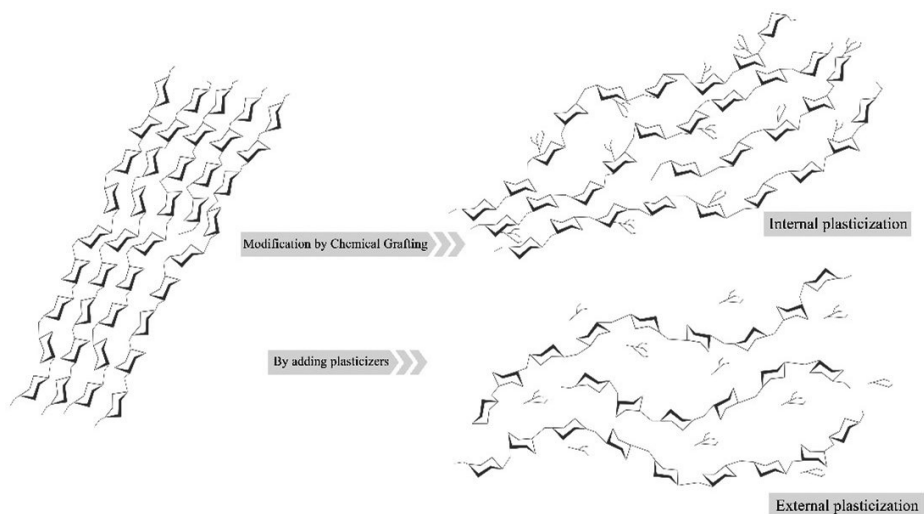


Figure 1. A schematic representation of the mechanism of internal and external plasticization and modification of NC

Cellulose is pretreated by an alkalization process to weaken the hydrogen bonding strength, then the hydroxyl-containing tri-carbon ether branches are introduced by etherification to furnish the nitrate glycerol ether cellulose (NGEC) [30-32]. Figure 2 shows the molecular structure of NGEC. This structure, it is suggested, destroys the crystalline structure of NC by grafting short, 3-carbon branched chains and achieves an internal plasticizing effect among the macromolecules, thereby improving the flexibility of the frame. The aim of this application is to reduce the glass transition temperature of the macromolecular chains and further improve their interaction with NGEC, triethylene glycol dinitrate (TEGN), diethylene glycol dinitrate (DEGN), and ethyl acetate (EA).

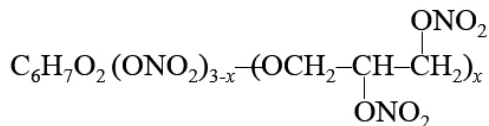


Figure 2. Molecular structure of NGEC, where x is the molar degree of substitution of GEC ($0 < x < 3$)

In the present study, NGEC was prepared, the effects of the nitration system (including the ratio of nitric acid to dichloromethane) and the degree of

etherification on the nitrogen content of NGEC were studied, the basic properties of NGEC were analyzed (*i.e.* heat of explosion, impact sensitivity, compatibility, stability, acetone solubility, ethanol solubility, and glass transition temperature), and the fabricated NGEC was used to modify a double-base propellant through adsorption, calendaring, granulation, and screw extrusion. Furthermore, the mechanical properties and performance changes after 6 years of storage were investigated.

2 Materials

Refined cotton powder (M60), with a fineness of 150 μm , purity of 98.2%, and degree of polymerization of 250 was provided by Beijing North Century Cellulose Technology Development Co., Ltd.

Generally, NC used in modified double-base propellants is pyrocellulose (D-grade) with a nitrogen content of 11.75-12.1%. Therefore, when preparing the NGEC-based modified double-base propellant, NGEC with a nitrogen content close to pyrocellulose (D-grade) was selected. NGEC with 12.41% nitrogen content was selected to replace NC in the modified double-base propellant. The composition of a certain model of modified double-base propellant with NGEC or NC was chosen (see Table 1). As shown in Table 1, H₁ is a control blank group, while H₂ is the formula of propellant in which NC is partially replaced by NGEC (NGEC replaced 50% of NC in H₁). In the experiments, H₂-1 indicates the freshly prepared NGEC-based modified double-base propellant; H₂-2 represents the same propellant after storage for 6 years.

Table 1. Basic composition of propellant

Formula	NC ^(a) [%]	NGEC ^(b) [%]	NG [%]	Other ingredients [%]
H ₁	20.5	–	21	58.5
H ₂	10.5	10		

Note: ^{a)} nitrogen content 12.20%N, ^{b)} nitrogen content 12.41%N

Through absorption, mixing, calendaring, granulation, and screw processes, the propellant powder was compressed into tubular grains with shapes of $\Phi 45/\Phi 8-365$ (the processes are shown in Figure 3; the grains can be used in a $\Phi 50$ mm standard engine). Finally, the performance changes of the propellant after 6 years of storage were investigated.

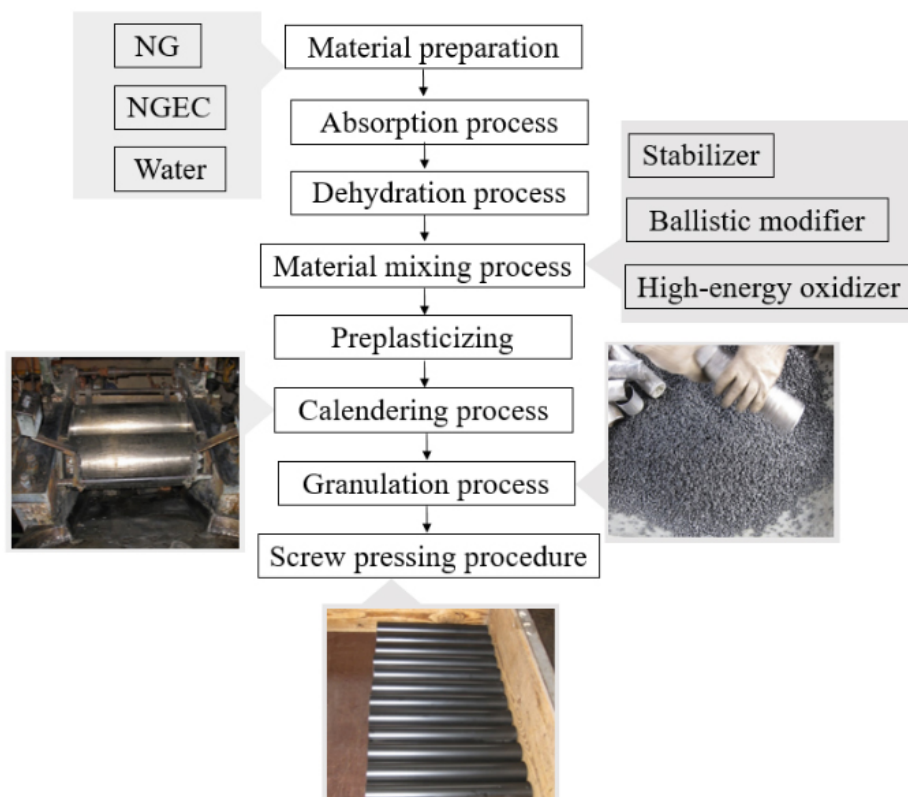


Figure 3. The preparation processes of NGEC-based modified double-base propellant

Common chemical reagents (analytical purity), including sodium hydroxide, propan-2-ol ($\text{CH}_3\text{CHOHCH}_3$, isopropanol, IPA), propylene oxide, adipic acid, glacial acetic acid, ethanol, nitric acid (HNO_3), concentrated sulfuric acid, dichloromethane (CH_2Cl_2), and sodium carbonate, were purchased from China Pharmaceutical Group Co., Ltd., and used without further purification.

3 Test Methods

The following instruments were employed for the measurements:

- Vario EL Element Analyzer, Elementar Company, Germany,
- PARR 6200 Automatic Oxygen Bomb Calorimeter, PARR Company, USA,

- Impact sensitivity: WL-1 Vertical Drop Hammer, Xi'an Modern Chemistry Institute, China,
- Photo-DSC 204 F1, Netzsch Group, Germany,
- WD-4005 Electronic Tension Machine, Shimadzu Company, Hondazin, Japan,
- DMTA Dynamic Thermomechanical Analyzer, Rheometric Scientific Company, Japan.

4 Experimental part

4.1 Preparation of NGEC

Refined cotton was dispersed in 25% NaOH aqueous solution for alkalization. The alkali cellulose obtained was subsequently added to an etherifying agent composed of IPA and glycerol ether (GE) in a specified proportion, for etherification while stirring continuously for 2 h with a magnetic agitator. After neutralization, washing, and drying, cellulose glycerol ether (GEC) with a certain degree of substitution was obtained. Finally, GEC was nitrated in the $\text{HNO}_3/\text{CH}_2\text{Cl}_2$ system at 25 °C for 40 min and the product was filtered off, washed, and dried to obtain the NGEC product. The structure, reaction mechanism and process of preparation of NGEC are shown in Figure 4.

4.2 NGEC structure and performance testing/analysis

4.2.1 Content of glycerol ether groups in intermediate GEC [33]

First the GEC sample was heated in a metal bath incubator, and then the GEC group content was analyzed by gas chromatography. Using adipic acid as the catalyst, the alkoxy groups were quantitatively substituted by hydroiodic acid to generate the corresponding iodides. The mixture was then extracted with *o*-xylene, and the extracted liquid was injected into the gas chromatograph to separate the components. The content of the glycerol ether group (K_2) was calculated by the internal standard method according to Equation 1:

$$K_2 = \zeta_2 \times \frac{Q_2}{A_3} \times A_4 \times \frac{W}{W_2} \times 100\% \quad (1)$$

where K_2 is the percentage content of glycerol ether groups, %; ζ_2 represents the molecular weight ratio of the glycerol ether group to 2-iodopropane ($\zeta_2 = 0.5353$),

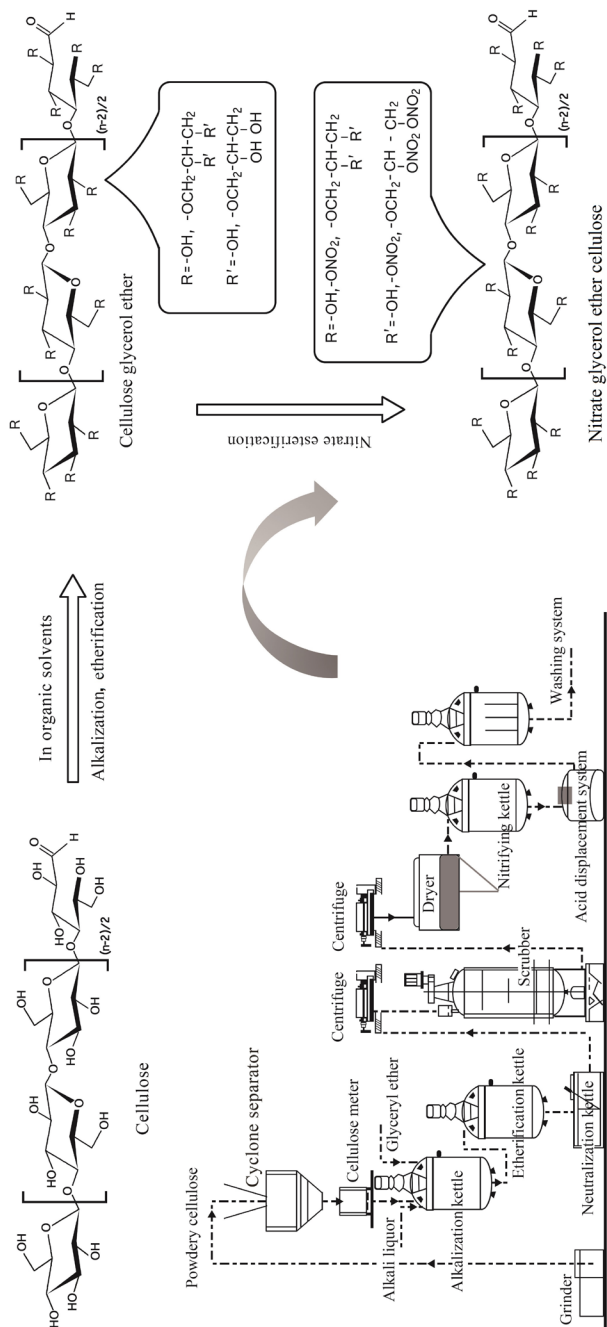


Figure 4. The structure, mechanism, and process for the preparation of NGECE

Q_2 is the mass ratio of 2-iodopropane and toluene in a standard solution (2 mL internal standard solution), A_3 is the peak area ratio of 2-iodopropane to toluene in the standard solution, A_4 is the peak area ratio of 2-iodopropane to toluene in the sample solution, W is the mass in grams of toluene in 2 mL of the internal standard solution, and W_2 is the dried mass in grams of GEC in the sample solution.

4.2.2 Stability of NGEC

The stability of NGEC was tested using the Beckman-Juncker method. Quantitative samples (2.0 ± 0.01 g) were placed in a Beckman-Juncker test vessel, and the content of nitric oxide originating from the decomposition of NGEC was measured by iodometry after heating for 2 h at 132.0 ± 0.4 °C. Finally, the stability of NGEC was determined by the nitric oxide value.

4.2.3 Solubility of NGEC

To determine solubility, dried NGEC (1.00 g) was wetted with ethanol (50 mL) in a conical bottle. Then, ether (100 mL) was added to the system and shaken for 1 h to achieve dissolution. After a further 30 min, the transparent solution was removed by filtration, and the solid residues were collected and dried at 95–100 °C. The solubility of NGEC (s) in ether and ethanol was characterized through Equation 2:

$$s = \frac{m - (m_1 - m_2)}{m} 100 \quad (2)$$

where m is the mass of NC, m_1 is the funnel mass with the dry residues, and m_2 is the mass of the empty funnel.

4.2.4 Q_v of NGEC

Using adiabatic oxygen bomb calorimetry, quantitative pressed samples of NGEC were subjected to determination of the heat of explosion according to the Chinese national military standard method [34].

4.2.5 Impact sensitivity of NGEC

The impact sensitivity was tested, according to [35], using a WL-1 vertical drop hammer at room temperature (15–35 °C), with a hammer mass of 2 kg and propellant quantity of 0.03 g. A schematic diagram of the WL-1 vertical drop hammer is shown in Figure 5. It contains two parallel guide rails, and there is a freely movable drop hammer on the guide rail (the weight of the drop hammer was 2 ± 0.002 kg). Additionally, the striking sleeve on the drop hammer

was intended to fix the impact device, and the steel base was positioned under the drop hammer, as shown in Figure 6. The drop hammer was fixed by a spring clip that was free to move along the guide rail and could be fixed to the desired height with a screw. A scale plate was also fixed on the guide rail to indicate the drop height. When the drop hammer was free to fall, the deviation between the center of the drop hammer and the center of the impact device was no more than 1.5 mm.

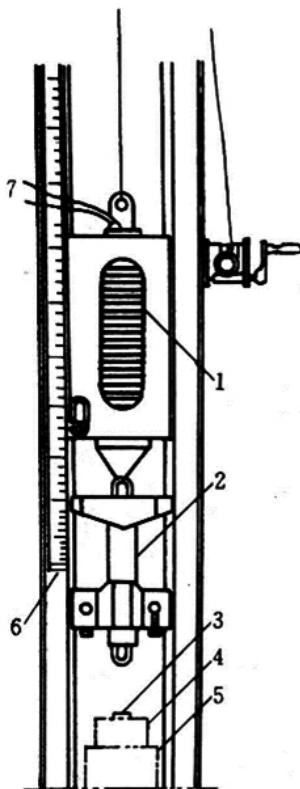


Figure 5. A schematic diagram of the WL-1 vertical drop hammer: 1 – electromagnet, 2 – drop hammer, 3 – upper striking column, 4 – striking sleeve, 5 – pedestal, 6 – scale plate, 7 – pinchcock

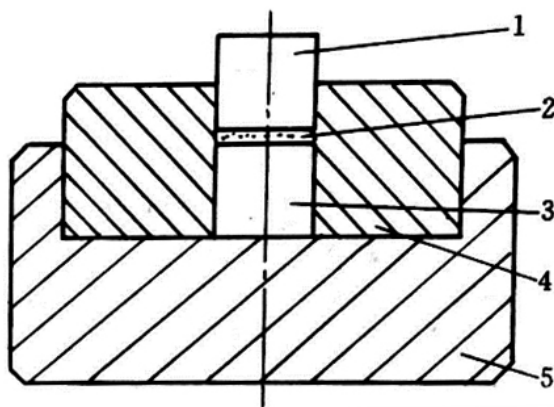


Figure 6. Percussion device: 1 – upper striking column, 2 – test sample, 3 – lower striking column, 4 – striking sleeve, 5 – pedestal

The impact sensitivity was analyzed by its characteristic drop height (H_{50}) with a drop hammer of 2 kg. Experiments were conducted 30 times after removing invalid tests, and the average value of the measured median drop height H_{50} was taken.

4.3 Compatibility between NGEC and NG, and NGEC, and RDX

Both NG and RDX are the main ingredients in modified double-base propellants. To ensure the safety of the NGEC application, the compatibility between NGEC and NG, and NGEC and RDX were evaluated. NGEC and NG or RDX were evenly mixed in mass ratios of 1:1, and DSC experiments were then performed. The compatibility between NGEC and NG or RDX was evaluated based on the difference in the decomposition peak temperatures (Equation 3).

$$\Delta T_p = T_{p1} - T_{p2} \quad (3)$$

where T_{p1} is the decomposition peak temperature of NGEC and T_{p2} is that of the mixture of the NGEC/NG and NGEC/RDX systems). Table 2 shows the standard or criteria for evaluating compatibility with ΔT_p (in terms of the peak temperature drop) [35].

Table 2. Standard or criteria for evaluating compatibility with ΔT_p

ΔT_p [°C]	Compatibility assessment	Compatibility of mixed systems
≤ 2	A	<i>Compatible</i>
3-5	B	<i>Slightly sensitive, short-term use</i>
6-15	C	<i>Sensitive, better not use</i>
≥ 15	D	<i>Dangerous, prohibited use</i>

4.4 NGEC-based modified double-base propellant tests

4.4.1 Liquidity test

To compare the mobility and molding of NC-based and NGEC-based propellants, including a 40×10×3 mm propellant extension plate, cut and prepared at 80 °C. Oil was pressed through a $\Phi 5$ mm mold extrusion at 10 mm/s using an automatic tester to measure the extrusion pressure and delivery speed.

4.4.2 Dynamic thermo-mechanical test

The size of the propellant for this test was 50×10×3 mm (length × width × thickness) (the samples are shown in Figure 7(a)). Under a dynamic load, by using a DMTA (Dynamic Thermomechanical Analyzer), with a 1-Hz frequency and 20- μ m amplitude, the viscoelasticity and glass transition temperature (T_g) of the NGEC-based propellant were measured. The temperature range was from -90 to 120 °C at a heating rate of 3 °C/min.

4.4.3 Mechanical properties

The tensile strength and elongation at break of dumbbell-shaped samples of NGEC-based propellant were measured using a WD-4005 electronic tension machine, at different temperatures (20, 40, and 50 °C), with a 10 mm/min tension application rate (the samples are shown in Figure 7(b)).

4.4.4 Burning rate test

Propellant strips approximately 5-mm wide and 130-mm long (the samples are shown in Figures 7(c) and 7(d)) were evaluated with a Target Line Burning Rate Tester, and under a specified pressure, five splines were tested and their average values were obtained [36].

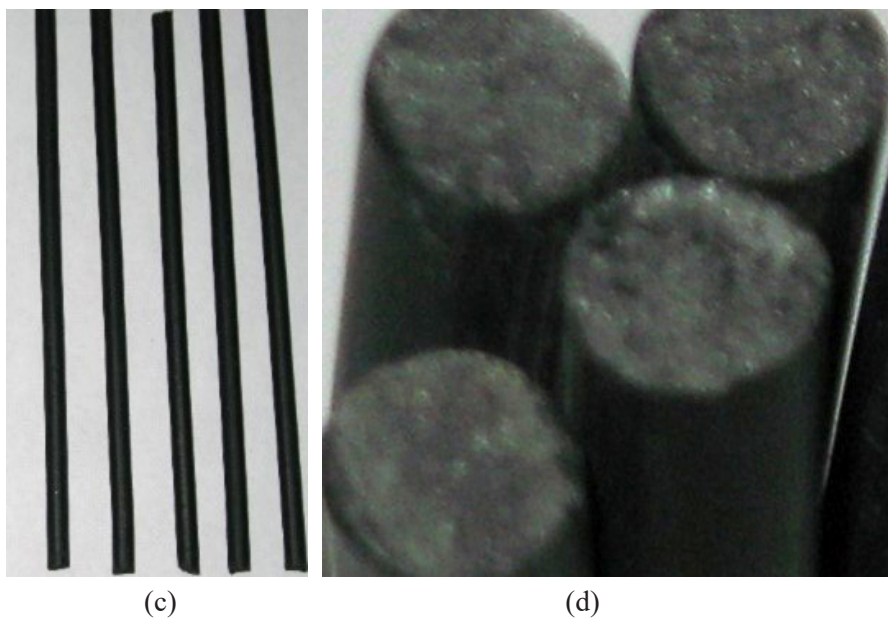
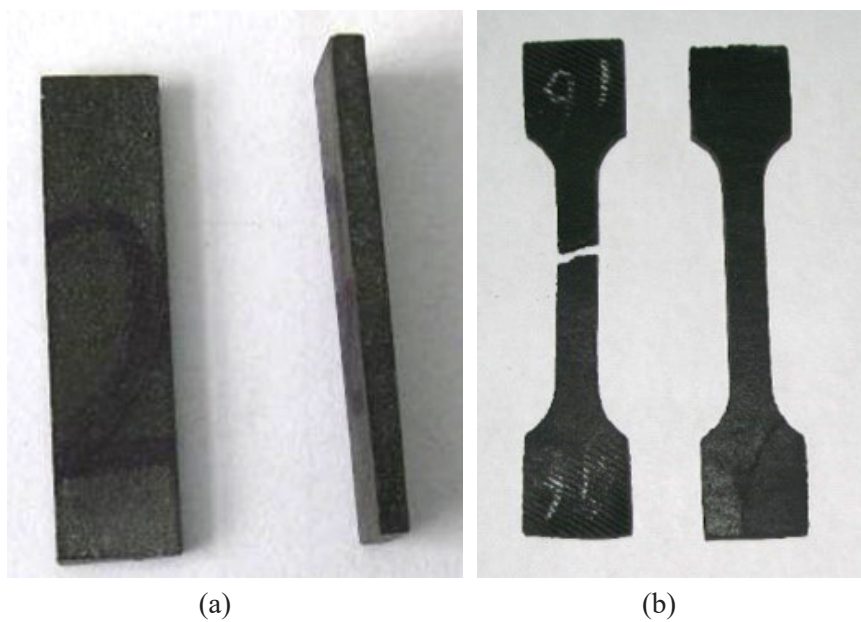


Figure 7. Samples used in the tests: DMTA sample (50×10×3 mm) (a), mechanical tensile sample (b), and burning rate spline and its cross-section (Φ5×130 mm) (c, d)

5 Results and Discussion

5.1 NGEC performance

5.1.1 Basic physical and chemical properties of NGEC

The nitrogen content of NGEC is directly related to its energy level and is the main index characteristic. The theoretical maximum nitrogen content of NGEC ($N\%$) was calculated according to Equation 4.

$$N\% = \frac{14(3+x)}{297+119x} 100 \quad (4)$$

where x is the molar substitution degree of GEC (see Figure 2). The relationship between the nitrogen content in NGEC and the corresponding x value is also shown in Figure 8.

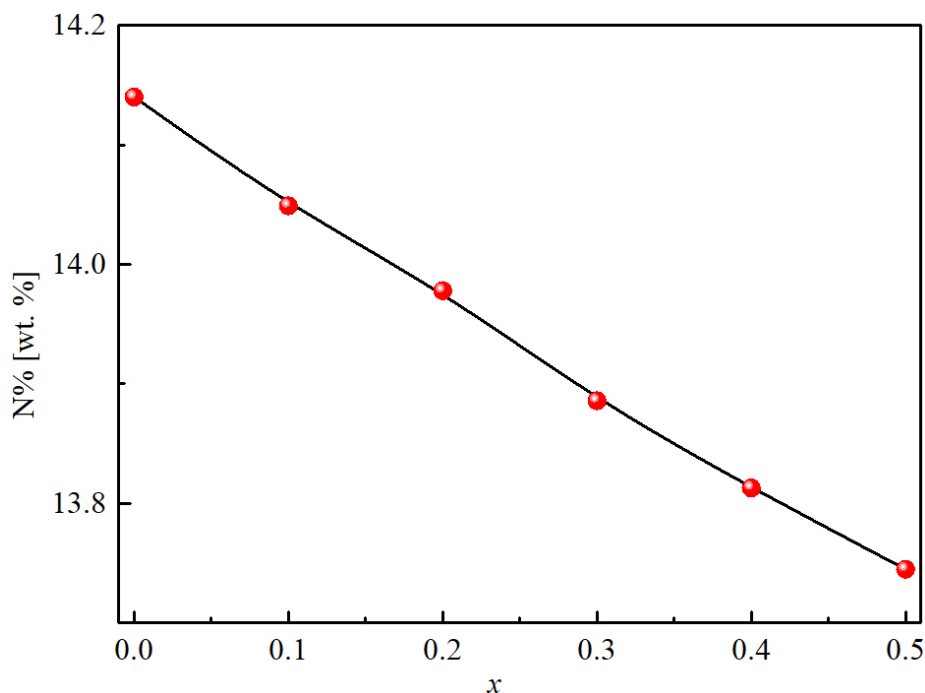


Figure 8. Theoretical maximum nitrogen content corresponding to different molar degrees of substitution of GEC

As shown in Figure 8, as the molar substitution degree of glycerol ether increases, the theoretical maximum nitrogen value and energy decreases. Previous experiments have demonstrated that the nitrating agent could not enter the gel, resulting in incomplete nitration when the x value was more than 0.3 in the normal mixed $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ system. We ascribe this to the hydrophilic glycerol ether group, which quickly combines with water to form a substantial gel. During nitration in the $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ system, cellulose sulfate is an instability factor. Therefore, to improve the stability of the NC, a stabilization treatment is necessary. Similarly, if NGEc is prepared from the $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ system, it also requires stabilization, which is achieved by washing the product three times in the gradient 0.3-0.1% acid, and treating with acid and heating, alkali and heating, fine grinding, and other stabilizing treatments in a high-pressure vessel. Moreover, the recycling of the waste acid is relatively difficult. Therefore, the $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ mixed acid system was not utilized in our study.

In the nitration stage, GEC can be nitrated more effectively using $\text{HNO}_3/\text{CH}_2\text{Cl}_2$. However, when GEC is nitrated, most of the sample is dissolved in the $\text{HNO}_3/\text{CH}_2\text{Cl}_2$ system when x exceeds 0.5, which impedes precipitation. Therefore, the nitration system used in these experiments was $\text{HNO}_3/\text{CH}_2\text{Cl}_2$ and x was controlled from 0.2 to 0.4 to avoid this.

As confirmed by gas chromatography, the molar substitution (MS) degree of GEC prepared in this study was 0.28. The GEC was then nitrated, and NGEc with different $N\%$ was obtained using $\text{HNO}_3/\text{CH}_2\text{Cl}_2$ as the nitration system with various mass ratios. Table 3 shows the basic properties of the product.

Table 3. Basic properties of NGEc obtained from the $\text{HNO}_3/\text{CH}_2\text{Cl}_2$ system with different mass ratios

Test item	Composition of nitrating acid ($\text{HNO}_3/\text{CH}_2\text{Cl}_2$ mass ratio)				
	20:80	30:70	40:60	45:55	50:50
	1#NGEC	2# NGEC	3# NGEC	4# NGEC	5# NGEC
$N\%$ [wt.%]	12.41	12.75	13.36	13.21	13.16
Stability [mL/g]	2.24	2.25	2.79	2.65	<2.5
Alcohol-ether solubility [%]	99.85	99.82	99.79	99.81	99.78

For nitration in the $\text{HNO}_3/\text{CH}_2\text{Cl}_2$ system, the degree of nitration of GEC depends strongly on the permeation of HNO_3 into the GEC. Given that GEC contains branched chains and more hydroxyl groups after etherification, solid particles of GEC are expected to aggregate in the nitration system when the

mass ratio of HNO_3 is lower than 30%, which reduces the nitration efficiency and results in a lower $N\%$. As expected, when the mass ratio of HNO_3 reaches 40%, GEC solid particles could be dispersed in the nitration system. The particle size decreases gradually as the reaction proceeds, leading to homogeneous nitration and higher $N\%$. Although a stronger nitrating ability is capable of improving the reaction rate, the internal GEC is encapsulated by gel after reaction when the concentration of HNO_3 is higher in the system (50%), further inhibiting nitration within the gel and reducing the $N\%$.

It can be seen from Table 3 that the stability of NGEC is low. Compared with NC having the same nitrogen content, the stability of NGEC with different $N\%$ is better than NC, suggesting it exhibits better stability and ability to resist chemical decomposition. Because the molecular flexibility of NGEC is increased, NGEC has better alcohol-ether and acetone solubility.

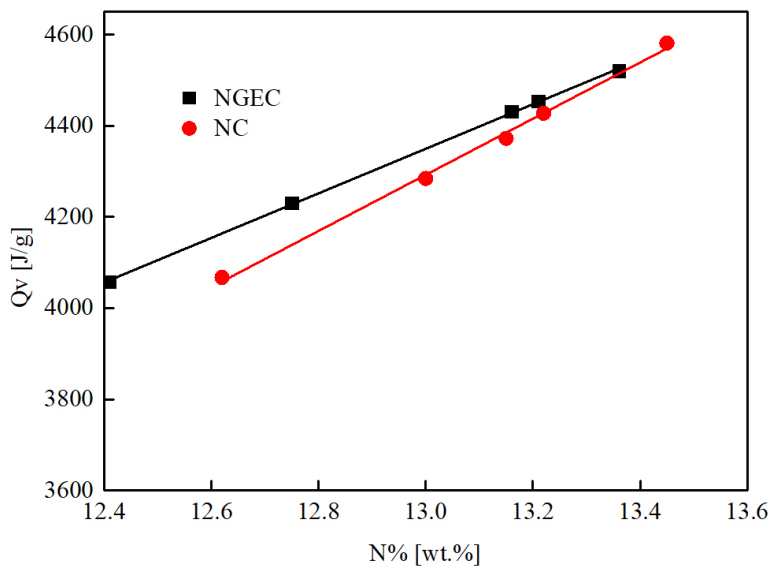
5.1.2 Q_v of NGEC

Figure 9 shows the heat of explosion values (Q_v) of NGEC and NC with different $N\%$, and the relationship between $N\%$ and the nitration bath ratio. As shown in Figure 9, the Q_v of NGEC is linearly correlated with $N\%$, and Q_v increases with the increase in $N\%$. When $N\%$ is 13.36%, the heat of explosion reaches 4520 kJ/kg. The linear relationship, fitted by the least squares method, between Q_v and $N\%$ was:

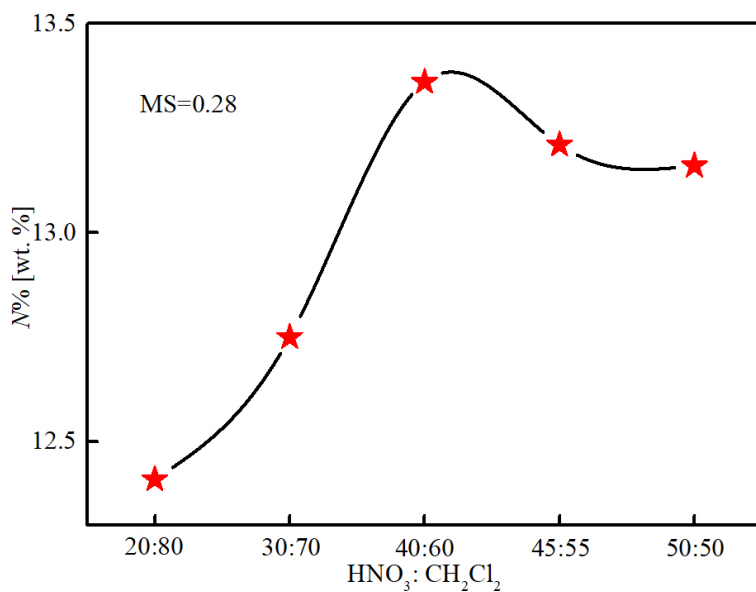
$$Q_v = 488.57 \cdot N\% - 2002.2 \quad (5)$$

When the $N\%$ is greater than 13.40%, the heat of explosion of NC is higher than that of NGEC with an equivalent nitrogen content, but when the nitrogen content is less than 13.40%, the heat of explosion of NGEC is higher than that of NC with an equivalent $N\%$. Because the NC used in solid propellants is mostly from pyrocellulose (D-grade, with an $N\%$ of 11.75–12.10%), the energy of the NGEC-based propellant is higher than that of the NC-based propellant.

It can be seen from Figure 9 that in the $\text{HNO}_3/\text{CH}_2\text{Cl}_2$ system, the $N\%$ exhibits an obvious trend with the change in acid concentration. As the acid ratio increases from low to high, the $N\%$, and the degree of substitution of $-\text{ONO}_2$ exhibits a trend of rising first and then decreasing. Because nitration is a reversible reaction, with the increase of nitric acid ratio, the nitrating ability increases, the reaction degree increases, and $N\%$ increases gradually. When the acid ratio reaches 45%, the dispersion of CH_2Cl_2 is limited. The contact layer between GEC and acid forms a layer of gel, which prevents further nitration. In this way, the degree of nitrate ester substitution is reduced, and the $N\%$ of product is decreased with further increase in the acid ratio.



(a)



(b)

Figure 9. Relationship between Q_v and nitrogen content of NGEC and NC (a), and the relationship between $N\%$ of NGEC and nitration bath ratio (b)

5.1.3 Impact sensitivity of NGEC

Impact sensitivity refers to the degree of difficulty in initiating a reaction (combustion or explosion) when the propellant is subject to physical stress. This has practical significance and serves as a guiding role in preventing accidents. From Table 4, it can be seen that even when NC has 11.9%N, the H_{50} is only 57.5 cm, while that of NGEC with a different N% must be more than 60 cm, since when the H_{50} of the NGEC is 60 cm, the sample has not exploded. In practice, when the H_{50} is 60 cm, this indicates that the impact sensitivity is already low and therefore no further detailed testing has been performed. Clearly, compared with NC, NGEC has a lower impact sensitivity, lower risk factor, and better thermoplasticity, indicating that it is easier to form by thermoplastic processing. Other sensitivity testing may be the subject of future work.

Table 4. Comparison of NGEC and NC impact sensitivities with different N% values

Parameter	1# NGEC	2# NGEC	3# NGEC	4# NGEC	5# NGEC	NC
Impact sensitivity [cm]	>60					57.5

5.1.4 Compatibility of NGEC

The DCS curves for NGEC with 12.41% nitrogen content, NG and RDX are shown in Figure 10. NGEC has a decomposition exothermic peak at 207.25 °C. Due to NG being a kind of liquid and volatile, at high temperature and at atmospheric pressure, it is difficult to observe the apparent decomposition on the DSC curve. There is only a faint form of an endothermic peak at about 197.8 °C, but with NGEC/NG the DSC curve exhibits only an exothermic peak at 206.36 °C, a decrease of 0.9 °C from the exothermic peak of NGEC, a relatively small effect [37]. RDX exhibits a crystal transition peak at 205.2 °C and an exothermic decomposition peak at 240.66 °C. The crystal transition peak of RDX in the mixture NGEC/RDX is at 201.51 °C, clearly lower than the transition temperature of pure RDX. As shown in Figure 10, the difference between the decomposition peak temperature of the NGEC mixed system and that of NGEC alone (ΔT_p) is less than 2 °C. As listed in Table 4, the compatibility of NGEC with NG is grade A, and with RDX is grade B. Thus, the NC binder in some modified propellants could be partially replaced by NGEC without affecting the compatibility with other ingredients.

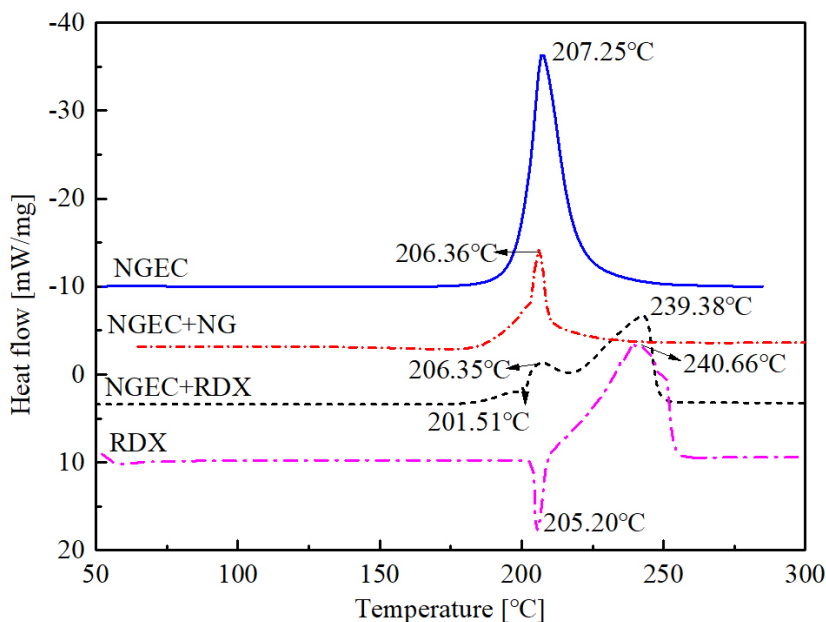


Figure 10. DSC curves of NGEC, RDX, NGEC+NG, NGEC+ RDX

5.2 Test results for NGEC-based modified propellant

5.2.1 Mobility of the particle extrusion process

The plastic processing capacity of the propellant is reflected in the mobility experiment of its propellant grain particles [34].

Table 5. Experimental results of the liquidity test (extrusion area 0.707 m²) of NGEC-based and NC-based propellants

Test items		H ₁	H ₂
Test data sheet	Extrusion pressure [kN]	15.21	6.4
	Time [s]	300	278
	Length [m]	1.6	1.69
Calculation	Pressure [MPa]	21.51	9.05
	Velocity [m/min]	0.25	0.36

The results in Table 5 show that the formability for NGEC-based propellant was improved compared with the NC-based propellant; the extrusion pressure was reduced by 57.9%, the extrusion speed was increased by 44%). It can be seen that compared with the NC structure, the glycerol ether branch chains

in the NGEC molecular structure improve the thermoplastic processing ability of the NGEC-based propellant, which not only ensures uniform component distribution in the NGEC-based propellant and good quality plasticity (glue) in the manufacturing process, but also reduces the processing energy consumption and reduces risks in the processing stage. By contrast, the NC molecular chain is rigid, with a slow NC-based propellant delivery speed and high delivery pressure, thus increasing risks in processing.

5.2.2 Ageing tests

The methyl violet test can quickly and accurately judge the stability of gunpowder. The test method involves heating gunpowder (2.5 g) at 120 °C and recording the time at which the methyl violet test paper changes from purple to orange caused by the gas originating from thermal decomposition [38]. Table 6 shows the physicochemical properties of NGEC-based modified double-base propellant. As can be seen, there is little change in density and heat of explosion of the modified double-base propellant after 6 years; however the methyl violet discoloration time is prolonged by 20 min, indicating that the stability of the grain is somewhat improved.

Table 6. Physicochemical properties of NGEC-based modified double-base propellant

Test item	H ₂ -1	H ₂ -2	
Density [g/cm ³]	1.72	1.73	
Q_v [kJ/kg]	5353	5345	
120 °C Methyl violet test	Discoloration time [min]	90	110
	Explosion time [h]	5.08	5.08

5.2.3 Dynamic thermomechanical properties (DMTA)

In a propellant, the surface of the RDX crystals can be uniformly coated by the mixtures formed by the interaction of NGEC and NG, thus enhancing the mechanical properties. It can be seen from Figure 11 that the positions of two loss factor peaks ($\tan \sigma$) have changed after storage, the low temperature zone being reduced by 6.33 °C, the high temperature zone increased by 6.09 °C, and the storage modulus ($\lg G''$) slightly decreased (indicating a change in the mechanical performance of the NGEC-based propellant after storage), decreasing the low temperature T_g and increasing the high temperature T_g . This is primarily attributed to the flexible chain motion of NGEC, as well as to the mechanical loss caused by the synergy of NGEC with NC and NG molecules. The two loss factor peaks are the low temperature and high temperature relaxation processes,

which also determine the low and high temperature mechanical properties of the propellant itself. The reason this type of change occurs is that the NGEC polymer chain is in a frozen state at low temperature, and only some slight vibrations of small units, such as the branched side groups and chain links, remain; while at high temperatures, there are chain segment movements in the NGEC itself [33].

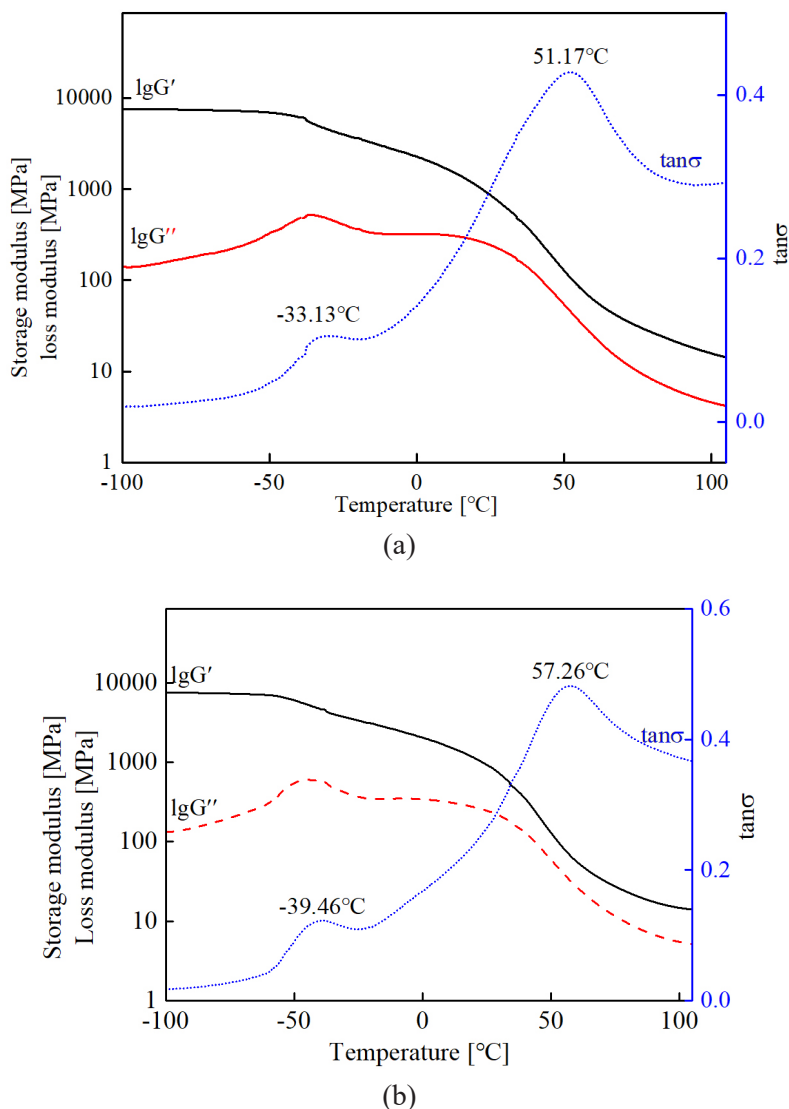
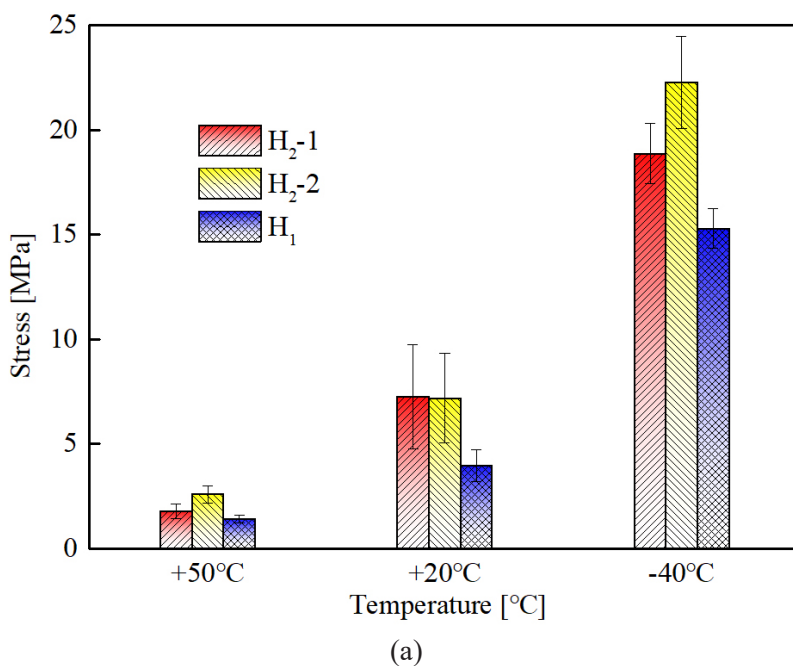


Figure 11. DMTA curves of NGEC-based propellants: H₂-1 (a) and H₂-2 (b)

5.2.4 Mechanical properties

It can be seen from Figure 12 that after 6 years of grain storage, the strength and elongation of NGEC-based propellants before and after storage are better than those of NC-based propellants. In addition, the comparison of stored NGEC-based propellants with fresh NGEC-based propellants revealed that after 6 years of storage, the strength increased by 59% for propellants stored at 50 °C, decreased by 2% when stored at 20 °C, and increased by 15% when stored at -40 °C. The elongation increased by 1% at 50 °C, 3% at 20 °C, and 10% at -40 °C. This shows that the mechanical properties can be improved on storage.



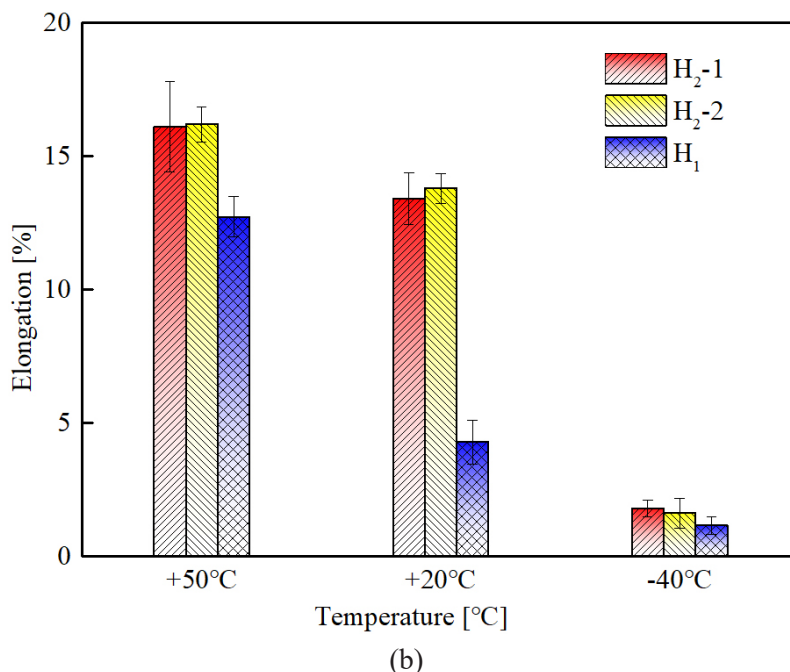


Figure 12. Comparison of strength (a) and elongation at break (b) of NGEC-based and NC-based propellants at different temperatures

NGEC has a 3-carbon branch chain structure; this modification increases the distance between the cellulose large molecular chains [29], weakens the intermolecular hydrogen bonding, and improves the flexibility of the macromolecules, owing to which the rigidity of the propellant is decreased and the glass transition temperature is reduced. Thus, the elongation rate of the NGEC-based propellant is higher than that of the NC-based propellant, improving its low-temperature mechanical performance and molding processing performance.

Compared with NC with a nitrogen content of 12.20%, the tablet prepared by calendering with NGEC has good plasticity and high flexibility, and the number of calendering cycles has been reduced by 2-3 times; indicating that NGEC has a stronger plasticizing ability than NC, which improves the formation process. As can be seen from Figure 12, under the same preparation conditions, the mechanical strength and elongation of the NGEC-based modified double-base propellant are better than those of the NC-based modified double-base propellant, indicating that the addition of NGEC can improve the low-temperature mechanical properties of the propellant. After storage for 6 years, the mechanical

properties of the NGEC-based modified double-base propellant do not decrease and are superior to those of the NC-based modified double-base propellant.

5.2.5 Burning rate test

The value of the pressure index n is viewed as the sensitivity of the burning rate to pressure, which is calculated according to Equation 4. To ensure stable and reliable engine operation, the n value is kept as small as possible.

$$n = \frac{d \ln u}{d \ln p} \quad (6)$$

where u is the burning rate of the propellant and p is the pressure in MPa. The correlative performance test results before and after storage are shown in Figure 13. After grain storage for 6 years, the burning rate pressure index of the NGEC-based propellant was reduced from 0.296 to 0.257 (approximately 13.18% loss). By contrast, the corresponding value for the NC-based propellant was 0.307, which is still higher than for the NGEC-based propellants.

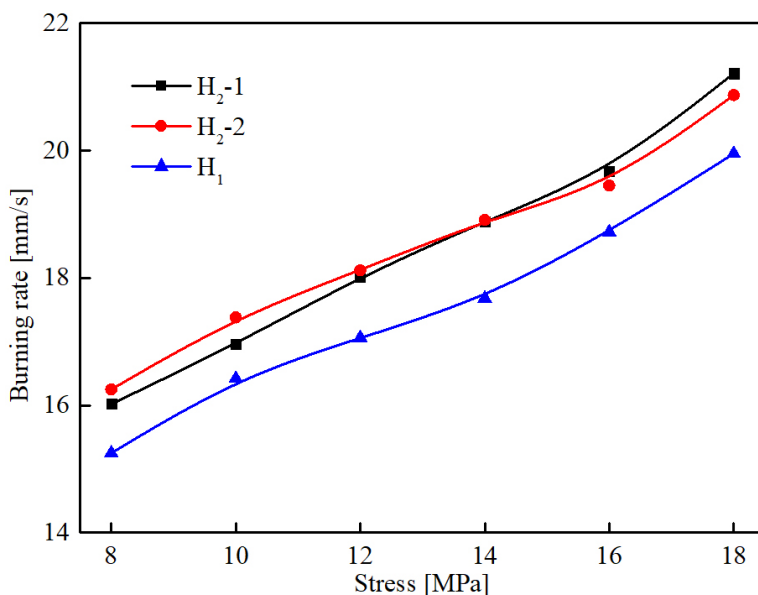


Figure 13. Comparison of burning rate curves of propellants at room temperature: H₁ – fresh NC-based modified double-base propellant; H₂-1 – fresh NGEC-based modified double-base propellant; H₂-2 – NGEC-based modified double-base propellant after 6 years of storage

As shown in Figure 13, in the low-pressure zone (8-14 MPa), the burning rate increases to some extent, H₂-2 becomes larger than H₂-1, and the curve changes more gently; furthermore, as the pressure increases, the burning rate increase decreases, resulting in the burning rate in the high-pressure zone (16-18 MPa) decreasing by 1.0 to 1.3 mm/s. All burning rates are greater than those of the NC-based propellant.

6 Conclusions

- ◆ Several properties of NGEC have been characterized and compared with unmodified NC, including the heat of explosion, impact sensitivity, compatibility, stability, acetone solubility, ethanol solubility, and glass transition temperature.
- ◆ Through branched-chain chemical modification, glycerol ether plays a significant role in achieving internal plasticization among the cellulose chains.
- ◆ The nitrated cellulose glycerol ether exhibited a decreased glass transition temperature and still maintained better stability and compatibility with the other main components in multi-component propellants.
- ◆ These results demonstrated that the addition of NGEC improved the impact sensitivity performance of NGEC-based propellants.
- ◆ The response of the mechanical properties and performance of NGEC after 6 years of storage was investigated and showed that the combustion pressure index was decreased over time while the mechanical properties, such as strength, was improved by as much as 59% for propellant stored at 50 °C.

Statement

No conflict of interest exists in the submission of this manuscript.

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Received: August 7, 2020

Revised: December 8, 2021

First published online: December 21, 2021