Research Article

Development rheological and thermal properties of a novel propellant RDX/TEGDN/NBC

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Abstract

To meet the high energy and high strength requirements of advanced propellants, a novel propellant RDX/TEGDN/NBC was designed by hexogen that was also called RDX and triethylene glycol dinitrate/nitrated bacterial cellulose (TEGDN/NBC) composite. The basic properties such as structure, morphology and thermal properties were characterized by fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and simultaneous thermal analysis (TG-DSC). The rheological properties were measured by rheometer and the effects of RDX content were studied by steady flow and dynamic test in detail. The results showed the added RDX of RDX/TEGDN/NBC composites solutions could destroy the stable structure of the system. Under the external force, RDX/TEGDN/NBC composite solution exhibit a better fluidity compared with TEGDN/NBC composite solution. And with the RDX increase, the viscosities of the solution systems decreased first and then increased, reached their minimum values when the RDX content was 15 wt%.

Graphic abstract

Keywords RDX · TEGDN/NBC · Rheological properties · Viscosity

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1 Introduction

The practice shows that the advanced nature of propellant and barrel weapon mainly embodies the high energy property of propellant and its charge. But advanced barrel weapons require not only high energy, but also high strength. High energy and high strength have become the characteristics of high performance artillery. In order to increase the energy of propellant, many high energy density particles should be added. However, it leads to the decrease of the relative content of polymer binder in the propellant system, which reduces the mechanical properties of propellant, increases the ablation effect of the propellant combustion process on the bore wall of barrel weapon, and makes the processing of propellant difficult. The propellant with poor mechanical properties will be deformed or broken during the launching process of barrel weapon, which will lead to a sharp increase in surface energy of propellant, abnormal ballistic performance, and even breech blow. As shown in the Table 1, the analysis of the causes leading to exploding accidents indicates that the mechanical properties of propellant, especially its poor low temperature mechanical properties, will make the propellant brittle at low temperature, which will lead to the breakage of propellant particles. In the course of ignition and launching, the intense combustion of propellant leads to a sharp increase in chamber pressure, which is greater than the design strength of chamber, and directly leads to breech blow [1]. So, improve of mechanical properties of propellants is of great significance to the development of advanced and high performance barrel weapons.

To meet the high energy and high strength demands of advanced propellant, a novel propellant contained nitrated bacterial cellulose (NBC), triethylene glycol dinitrate (TEGDN) and hexogen (RDX) was prepared

following the designs of TEGDN propellant and nitramine propellant. TEGDN was used as the energetic plasticizer to improve the processing performance. RDX was acted as the high energy particles to enhance the energy level. NBC was regarded as energetic binder to supply the structure of the propellant [2]. NBC is synthesized from bacterial cellulose (BC), and because of its macrostructural characteristics, it has various advantageous properties, such as a high tensile strength and an ultrafine and highly pure fiber network [3]. According to the reports of Sun et al. [4] and Yang et al. [5], the properties of NBC are more promising than those of NC that is also called nitrocellulose an important and essential energetic material in war production, suggesting that the substitution of NBC for NC as the main component in propellants is possible. In this case, NBC was considered to displace NC as the binder in the propellant. Because the thermal properties of NBC are extremely similar with NC [5], it has to be dissolved in the solvent for processing rather than hot working. Thus, it's necessary to study the novel propellant RDX/TEGDN/NBC composites' rheological properties in solvent before their processing.

The rheological properties of composites are of great importance because they affect the processing performance directly. The work studied by R. Hsissou et al. [6–13] are appreciated because they made great effort on the rheological properties of polymer composite and it's of practical and scientific guiding significance. But, preliminary investigations on the properties of NBC in organic solvents have been reported [14–16]. Luo et al. [14] studied its solution characteristics in acetone, and Zhu et al. [15] studied its rheological properties in acetone. Both articles only studied the rheological properties of pure NBC in solution, but there was no mention about the properties of its composite. Huang et al. [16] designed a novel energetic composite TEGDN/NBC according to the TEGDN propellant and had a detail of its rheological properties. For the

Table 1 Analysis of exploding accidents in various countries

Artillery type	Damage	Cause	Country
M198 155 mm howitzer	Breech blast	The strong bottom ignition Grain fracture at low temperature	U.S.A
M11E203 howitzer	Breech blast	Ignition failure of central tube Grain fracture at low temperature	U.S.A
127 mm naval gun	Early explosion of lead wire Breech blast	Excessive output rate of ignition tube Compaction and fragmentation of powder bed	U.S.A
M1E1 120 mm tank gun	Breech blast	Blasting at low temperature test	U.S.A
125 mm 3rd generation tank gun	Breech blast Tear of chamber	Improper design of ignition system Grain fracture at low temperature	China
125 mm 3rd generation tank gun	Tear of chamber Breakup of projectile	Improper design of ignition system Grain fracture at low temperature	China
120 mm Uranium bomb charge	Breech blast, tear of chamber	Grain fracture at low temperature	China

further utilization of NBC, a novel propellant RDX/TEGDN/NBC was designed in order to meet the high energy and high strength requirement for the modern gun propellant. And the rheological properties must be studied detailedly as the premise of processing and application.

2 Experiment

Nitrated bacterial cellulose (NBC) (nitrogen content: 13.0 wt%) was prepared in our laboratory. TEGDN and RDX were supplied by Luzhou North Ltd. The plasticizing of NBC by TEGDN was carried out by Luzhou North Ltd. considered the safety.

First, NBC was added to deionized water and stirred for 1 h. Then, adequate TEGDN was added, and the mixture was stirred for 1 h at 60 °C to achieve effective absorption of the TEGDN by the NBC. Finally, the TEGDN/NBC composites were prepared after dehydrating the material in an oven at 60 °C. The mass ratio of TEGDN was 23% in the TEGDN/NBC composites according to the quantity change of composites. TEGDN/NBC composites were dissolved in the N,N-dimethylformamide (DMF) at 15 wt% concentration according to our previous researches [16]. The RDX was added and mixed in the solution to form the mixture. By the control of the quantities of added RDX, various RDX/TEGDN/NBC composites solutions of 0, 5 wt%, 10 wt%, 15 wt%, 20 wt%, 25 wt% and 30 wt% RDX content were prepared. Last, the solutions were dried by lyophilization for further test.

The rheological parameters of the samples were measured by using a Haake MARs II Modular Advanced Rheometer System (Thermo Fisher Scientific, USA) which used 20 mm parallel plate geometry at a gap width of approximately 1 mm in air. The temperature was controlled at

25 °C with a Haake test chamber controller to an accuracy of ± 1 °C. The steady state test was in the 0–100 s^{-1} shear rate. Amplitude sweep was tested in the 1–1000 Pa at 1 Hz, 25 °C. Oscillatory sweep was measured in 0.1–10 Hz frequency at 100 Pa, 25 °C.

The Fourier transform infrared spectra of the samples were recorded on a Nicolet 5700 Spectrum One FT-IR spectrometer from American Thermo Scientific using KBr pellets in the 4000 to 500 cm^{-1} range at a resolution of 4 cm^{-1} . The physical phase of the sample was analyzed by using a X'pert Pro X-ray diffractometer (PANalytical B.V., The Netherlands) under 40 kV and 40 mA Cu-K α ($\lambda = 1.540598$ Å) radiation with a monochromatic graphite polarized beam. The morphology of each sample was analyzed by using field emission scanning electron microscope (Ultra 55, ZEISS, German) at an accelerating voltage of 15 kV. TG-DSC analysis was done on a simultaneous thermal analysis (Q160, TA Instruments, USA) with a 10 K/min heating rate in a nitrogen atmosphere. Amounts of 2–3 mg of each sample were placed in small Al_2O_3 cells.

3 Results and discussion

3.1 FT-IR analysis

FT-IR spectroscopy was performed to elucidate the structural features of NBC, TEGDN, RDX, TEGDN/NBC and RDX/TEGDN/NBC composites, and the results are showed in Fig. 1a.

As shown in Fig. 1a, it can be seen from the figure that all samples have a wide range of absorption peak at 3200–3700 cm^{-1} , which is the stretching vibration peak of -OH, which comes from the intermolecular hydrogen bonds of the sample. On the infrared spectrum of RDX,

Fig. 1 FT-IR spectra (a) and XRD patterns (b) of samples

the characteristic peaks of $-\text{CH}_2$ stretching vibration were found in 3085 cm^{-1} , 3003 cm^{-1} and 2943 cm^{-1} , which were relatively weak, and the characteristic peak of $-\text{NO}_2$ stretching vibration was found in 1578 cm^{-1} [17]. For TEGDN and NBC, there are strong peaks at 1650 cm^{-1} , 1280 cm^{-1} and 840 cm^{-1} , which represent the characteristic peaks of stretching vibration of $-\text{O}-\text{NO}_2$. In contrast to that of NBC, the spectrum of TEGDN shows a peak at 905 cm^{-1} , which is associated with the $-\text{C}-\text{O}-\text{C}-$ stretching vibration. The characteristic absorption peaks of TEGDN and RDX are observed in the spectra of RDX/TEGDN/NBC.

3.2 XRD analysis

Figure 1b shows the X-ray diffraction patterns of the initial NBC and RDX, the patterns of TEGDN/NBC and RDX/TEGDN/NBC composites are showed too.

As shown in Fig. 1b, the peaks of X-ray diffraction pattern of RDX are apparent due to its crystal structure. $2\theta = 25.5^\circ$, 29.4° , 32.4° are its characteristic diffraction peaks. It can be seen from the figure that the X-ray diffraction pattern of RDX/TEGDN/NBC mainly shows the peaks positions of RDX, which is basically consistent with the pattern of pure RDX, but slightly deviated. This is because the diffraction peaks of RDX are the main features in the XRD of amorphous cellulose composite with RDX. However, RDX/TEGDN/NBC has wider diffraction peaks compared with NBC, which is caused by the wider diffraction peak of amorphous NBC [18, 19].

3.3 FESEM analysis

Figure 2 shows the FESEM images of NBC, TEGDN/NBC and RDX/TEGDN/NBC composites.

As shown in Fig. 2, NBC has disorderly stacking with obvious folds and rough surfaces (Fig. 2 (a1)) and a three dimensional network structure with interwoven fibers approximately 30 nm in diameter (Fig. 2 (a2)). The surface of TEGDN/NBC is relatively smooth and has wrinkles and micropores, and its network structure is not obviously interwoven (Figs. 1 and 3). These features may be caused by the solvation of TEGDN. RDX is dispersed on the surface of NBC in granular form. It can be seen that RDX is actually attached to NBC fiber in granular form by magnification of electron microscope from Fig. 2 (c1) and (c2). According to the structure and morphology tests of the propellant, the propellant has been proved to be composed of NBC, TEGDN and RDX.

3.4 TG-DSC analysis

Figures 3 and 4 show DSC and TG curves of RDX, TEGDN/NBC and RDX/TEGDN/NBC with different RDX content respectively.

The right figure is the enlarged drawing of the left at 150°C to 350°C . It's observed easily that there are two peaks in the curves of pure RDX corresponding to the endothermic peak during melting and exothermic peak during decomposition respectively from Fig. 3a [20]. As shown in Fig. 3, an obvious exothermic peak appears at range of about 180°C to 200°C in the curve of RDX/TEGDN/NBC composites. And the peak temperature of thermal decomposition of all RDX/TEGDN/NBC composites is lower than the melting temperature of pure RDX. The added RDX in composites have decomposed before melting. By the analysis of the peak temperature of thermal decomposition of the composites with different RDX content, it indicates that a small amount of RDX is added to TEGDN/NBC composite as filler, which is helpful to improve its thermal stability and increase its thermal decomposition temperature. However the thermal decomposition temperature of RDX/TEGDN/NBC composite decreases first and then increases with the increase of RDX content when the RDX content is more than 5 wt%. With the increase of temperature, TEGDN and NBC in composite decompose firstly, producing nitrogen oxide gas, which has catalytic and promoting effect on RDX thermal decomposition [21]. The thermal decomposition of RDX in the composite also produces nitrogen oxide gas, which promotes its own thermal decomposition process. What's more, the changes of microstructure of TEGDN/NBC by the addition of RDX, weakening the interaction force between NBC molecules, which leads to the decrease of its thermal decomposition temperature. When the content of RDX continues to increase to a certain extent (for example $> 20\text{ wt}\%$), the whole system is mainly affected by the thermal properties of RDX. The thermal decomposition of RDX/TEGDN/NBC composite mainly shows the thermal decomposition characteristics of RDX, and its thermal decomposition temperature begins to rise [22]. It's worthy to notice that there is a platform area before the exothermic peak of pure TEGDN/NBC and RDX/TEGDN/NBC with 5 wt% added RDX. Actually, this plateau region corresponds to the glass transition process of NBC with the increased temperature. However, the platform appears behind the exothermic peak of the composites when RDX content $> 5\text{ wt}\%$. It indicates that the glass transition process of NBC is ignored because of the mutual catalysis when RDX is added in. And the appearance of platform behind the peak indicates the decomposition of extra RDX.

As shown in Fig. 4, the mass loss of RDX/TEGDN/NBC and pure RDX is the similar continuous process. The difference is that the initial decomposition temperature of RDX is much higher than that of RDX/TEGDN/NBC composites and TEGDN/NBC.

The difference between the initial degradation temperature of RDX and the temperature at the maximum mass loss

Fig. 2 FESEM images of samples: (a1, a2): NBC, (b1, b2): TEGDN/NBC, (c1, c2): RDX/TEGDN/NBC

is not significant. But the difference between the initial degradation temperature of TEGDN/NBC and RDX/TEGDN/NBC composites and the temperature at the maximum mass loss is large, which indicates the thermal stability of the composites is lower than RDX. TEGDN/NBC and RDX/TEGDN/NBC composites degrade slowly before reaching the maximum mass loss temperature and the mass loss is about 20%. But when the temperature reaches the decomposition temperature, they decompose immediately. The phenomenon of one-step weight loss on the TG diagram is showed in the figure, and the mass loss reaches 100%. When the content of RDX is added to 30%, the TG curves of RDX/TEGDN/NBC composites are similar with RDX, which is caused by too much added RDX. At this case, the catalytic decomposition

of TEGDN/NBC and RDX can not lead to the whole system decompose violently to 100% mass loss at a decomposition temperature and show a relatively slow continuous weight loss process, which is consistent with the results in DSC curves. The initial degradation temperature of RDX/TEGDN/NBC reduces 10 °C to 40 °C from Fig. 4. It also indicates that the added RDX in TEGDN/NBC could destroy the structure of the composite and induce it to degradation more easily.

Fig. 3 The DSC curves of RDX/TEGDN/NBC with different RDX contents **(a)** and **(b)** was the magnification of **(a)**

Fig. 4 The TG curves of RDX/TEGDN/NBC with different RDX contents

3.5 Rheological behavior test

3.5.1 Analysis of steady flow rheological properties

Figure 5 shows rheological properties test curves for RDX/TEGDN/NBC solutions with RDX content at 5 wt%, 10 wt%, 15 wt%, 20 wt%, 25 wt% and 30 wt%.

As shown in Fig. 5a, all the RDX/TEGDN/NBC solutions exhibit shear thinning behaviors and the viscosities have changed with the increase of RDX content. It's also worth to notice that the viscosity of propellant was relatively stable at low shear rate and decreased significantly at high shear rate as it is shown in Fig. 5c, d.

It's found that the shear stress versus shear rate curves shifted downward first and then shifted upward with the increasing RDX content from Fig. 5a. This trend was also shown in Fig. 5c, d. Increasing the RDX content up to 15%, the apparent viscosity versus shear rate curves shifted downward (Fig. 5c), indicating a decrease in the apparent

viscosity below 15%. When the amount of RDX was above 15%, the curves shifted upward (Fig. 5d).

It's an effective method to study the rheological properties by using rheological model to fit the flow curves. A Herschel–Bulkley modified model was used to study rheological properties curves by A. Mortadi [23]. They studied the influence of CaO content on the rheological properties of sludge and well revealed the transition process of sludge coagulation process combined with electrical properties research [24, 25]. In this case, Herschel–Bulkley model was chosen because preliminary attempts in Fig. 5a to fit the experimental data with the model showed a good correlation factor. The equation of Herschel–Bulkley model was:

$$\tau = \tau_y + K\dot{\gamma}^n$$

where, τ , τ_y , K , $\dot{\gamma}$ and n is the shear stress (Pa), yield stress (Pa), consistency coefficient (Pa s^n), shear rate (s^{-1}) and rheological index respectively.

The rheological curves of propellant at 0, 15% and 30% RDX content was studied as typical curves and these fitting parameters were extracted to plot against the RDX content as shown in Fig. 5c. The consistency coefficient K decreases when the propellant was mixed with RDX below 15% but show a slow increase above 15%. In contrast, the rheological index (n) shows an inverse behavior. It starts to increase up to 15% and then start to decrease.

The effect of RDX content on the rheological properties of propellant is similar to that of CaO content on the rheological properties of sludge by A. Mortadi et al. But their internal mechanisms may be different.

When TEGDN/NBC is dissolved in DMF, the molecules of TEGDN and NBC are entangled, forming a net-like construction [26]. When RDX is added to the TEGDN/NBC solution system, RDX dissolves in the solvent and evenly

Fig. 5 The rheological properties test curves of RDX/TEGDN/NBC composites. **(a)** Shear stress-shear rate curves at different RDX content. Solid lines correspond the fit using Herschel Bulkley model. **(b)** Rheological parameters extracted from fit model at 0, 15% and

30% RDX content. **(c)** Apparent viscosity curves at 0, 5%, 10% and 15% RDX content. **(d)** Apparent viscosity curves at 15%, 20%, 25% and 30% RDX content

disperses in the pore space of the net-like construction formed by TEGDN/NBC molecules. Due to the net-like construction, the propellant performs a relatively stable structure and exhibit a newton fluid character at low shear rate as shown in Fig. 5c, d. With the increase of shear rate, the interwoven TEGDN/NBC molecules in the solution begin to disentangle and the orientation motion of TEGDN/NBC molecules starts to take place. Thus, the viscosity of the solution decreases with the increase of shear rate, showing shear thinning [27]. The RDX in the solution will also have orientation movement along with the external force. At this time, the RDX will attack the TEGDN/NBC molecular chains under the force. With the increase of shear rate, the force of attack will be more intense, and the interaction between RDX and TEGDN/NBC will be more intense. This process greatly promotes the disentanglement process of TEGDN/NBC molecular chain and accelerates the destruction process of the net-like structure formed by TEGDN/

NBC molecules in solution [28, 29]. The results show that the viscosity of TEGDN/NBC solution decreases greatly when RDX is added with the increasing shear rate.

As the shear rate continues to increase, the viscosity of the solution added RDX decreases slightly and even remains invariable due to the re-formation of net-like structure between TEGDN/NBC molecules under the effort of hydrogen bond, which is shown as the plateau district of viscosity curve at 10 to 30 s^{-1} of shear rate range in Fig. 5c, d [28, 29]. The net-like structure would be destroyed again with the increased shear rate the orientation motion and the propellant exhibit shear thinning feature again as shown in Fig. 5c, d at high shear rate range.

When the content of RDX is >15%, the viscosity of the solution system increases with the content of RDX, as shown in Fig. 5c, d. It can be seen from the figure that when RDX content is 15%, RDX/TEGDN/NBC solution has a minimum viscosity, and then its viscosity increases

with the increase of RDX content. This is because with the increase of RDX content, the amount of molecules in the whole solution system increases and the internal force and friction between molecules increases too, making the viscosity of the whole solution system increase. However, the viscosity is still less than that of TEGDN/NBC solution without RDX content. It indicates that the damage of RDX to the structure of solution system is stronger than its stabilizing effect.

3.5.2 Analysis of dynamic rheological properties

1. Analysis of amplitude sweep

The dynamic rheological properties of RDX/TEGDN/NBC composites solutions are tested by Haake rheometer. The results of amplitude sweep test of the solutions with different RDX are showed in Fig. 6.

It can be seen from the figure that both the storage modulus G' and loss modulus G'' of TEGDN/NBC composite solution without RDX is significantly higher than that of RDX/TEGDN/NBC composite solution with RDX addition under the same shear stress. This is because when the RDX is dispersed into the net-like structure formed by TEGDN/NBC molecules and under the action of external force, not only the orientation movement of TEGDN/NBC molecules but also the disentanglement between the molecular chains takes place. What's more, the RDX particles constantly attack the TEGDN/NBC molecules, which promotes the disentanglement process of TEGDN/NBC and leads to the instability of the solution structure. It is shown in the figure that the storage modulus G' and loss modulus G'' of RDX/TEGDN/NBC composite solution decreases after adding RDX. With the increase of shear stress, the storage modulus G' of RDX/TEGDN/NBC composite solution

decreases because the process of orientation movement and disentanglement of molecules in the solution become more likely to happen with the increase of external force. Therefore, when RDX content is at 5 wt% to 30 wt% under the shear stress is greater than 100 Pa, the storage modulus G' of RDX/TEGDN/NBC solution decreases greatly. It indicates the addition of RDX will weaken the stability of TEGDN/NBC solution, and even destroy the original structure under external force. When the shear stress is less than 40 Pa, the storage modulus G' and loss modulus G'' of RDX/TEGDN/NBC solution change little with the shear stress, so the linear viscoelastic region (LVR) of the solution is below 40 Pa.

2. Analysis of oscillatory sweep

As stated above, RDX/TEGDN/NBC solutions have a LVR at a shear stress of 40 Pa. Thus, oscillatory measurements of G' and the loss modulus (G'') of RDX/TEGDN/NBC solutions were performed by a frequency sweep from 0.1 to 10 Hz at 25 °C under a shear stress of 40 Pa. The results are presented in Fig. 7.

The complex viscosities (η^* values) also indicated that the polymer solutions showed viscoelastic properties [30]. Figure 7a, b show the curves of complex viscosity in the frequency sweep of RDX/TEGDN/NBC composite solutions at different RDX content. All samples show similar behavior in the frequency range, where the complex viscosity decreases when the frequency increases.

As shown in Fig. 7a, b, the evolution of complex viscosity was split into two graphs to examine the effect of RDX content. Figure 7a shows the evolution of η^* versus frequency (Hz) corresponding to the propellant from 0 to 15% RDX content. Figure 7b shows the evolution of η^* versus frequency (Hz) corresponding to the propellant from 15 to 30% RDX content. It can be seen that the curves of η^* shifted downward with the increase in RDX content up to 15% as it is indicated by the arrow from Fig. 7a. In contrast, Fig. 7b shows clearly that the curves of η^* shifted upward with the increase in RDX content from 15% to 30% as it is indicated by the arrow too. The complex viscosity of RDX/TEGDN/NBC composite solution first decreases and then increases with the increase of RDX content. When the RDX content is 15 wt%, the RDX/TEGDN/NBC composite solution has the minimum complex viscosity value. Therefore, the net transition was occurred at 15% RDX content according this analysis and the above analysis of steady flow tests.

Although the complex viscosity of RDX/TEGDN/NBC composite increases with the increase of RDX content when RDX content is more than 15%, it is still smaller than pure TEGDN/NBC composite solution. It indicates that the damage of RDX to the solution structure is dominant. With

Fig. 6 Shear stress sweep curves of RDX/TEGDN/NBC composites with different RDX contents

Fig. 7 Dynamic rheological tests of RDX/TEGDN/NBC composites. Variation of complex viscosity (**a, b**), G' (**c, d**) and G'' (**e, f**) as a function of frequency sweep at different RDX content

the increase of frequency, the complex viscosity of RDX/TEGDN/NBC solutions decreases shows a similar phenomenon of shear thinning.

A transition at 15% of the RDX was observed according to the analysis of the complex viscosity. The evolution of the storage modulus G' and loss modulus G'' as a function of frequencies has been also separated in two graphs considering the net transition. Figure 7c shows the evolution of G' for 0–15%, whereas Fig. 7d shows the evolution of G' for 15%–30%. It can be seen from the Fig. 7c that the curves of G' shifted downward with the increase in RDX content up to 15% as it is indicated by the arrow. In contrast, Fig. 7d shows clearly that the curves shifted upward with the increase RDX content from 15% to 30% as it is also indicated by the arrow. This analysis also showed that there is a transition which was occurred at 15%.

Figure 7e shows the evolution of G'' for 0–15%, whereas Fig. 7f shows the evolution of G'' for 15%–30%. Similar trend is observed in the evolution of G'' indicating that the existence of two stages below and above 15%. In the first stage, the curves of G'' shifted downward with the increase RDX content up to 15% as it is indicated by the arrow. In the second stage, the curves shifted upward with the increase in RDX content from 15% to 30% as it is also indicated by the arrow.

Both the storage modulus G' and loss modulus G'' of RDX/TEGDN/NBC solutions increase with the increase of frequency [31]. It can also be seen from the Fig. 7 that in the same scanning frequency range, the storage

modulus G' and loss modulus G'' of RDX/TEGDN/NBC composites solutions are smaller than that without RDX. This is because the structure of the whole RDX/TEGDN/NBC solution system is unstable after the addition of RDX and it is easy to be damaged under the stimulation of external forces, resulting in the decrease of the modulus of the solution system. It shows that the structural stability of RDX/TEGDN/NBC composite is worse than that of TEGDN/NBC composite.

The traditional classification system commonly separates solution phase behavior into three categories: the behaviors of viscoelastic solids, gels, and viscous fluids, which can be quantitatively measured by the loss tangent $\tan\delta = G''/G'$ [32]. In principle, fluid characteristics are dominant when $\tan\delta > 1$, while solid characteristics are dominant when $\tan\delta < 1$. According to the storage modulus G' and loss modulus G'' of RDX/TEGDN/NBC composites solutions in Fig. 7, the loss factor $\tan\delta$ of the whole solutions are calculated and the correlation function curves between loss factor and frequency are showed in Fig. 8.

From Fig. 8, it can be seen that the loss factor $\tan\delta$ of RDX/TEGDN/NBC composites are always greater than 1 in the whole frequency scanning range, indicating that the fluid characteristics still play a dominate role in the solution system, showing fluidity. The loss factor $\tan\delta$ of RDX/TEGDN/NBC composite decreases with the increase of frequency indicates that the increase of frequency can weaken the fluidity of the solution system and enhance

Fig. 8 Loss factor vs frequency curves at different RDX content

the cross-linking between molecules in the solution, showing the characteristics of solid gradually.

The behavior exhibited by the dynamic rheological test can reflect the change in the interior structure of propellant and the transition between two different states. The critical amount of RDX (15%) obtained in dynamical rheological tests and it corresponds to the steady flow tests.

3.6 Rheological mechanism of the energetic composites based on NBC

With the addition of TEGDN and RDX into NBC, under the action of solvent and external force, they contact and interact with NBC, which have a great influence on their rheological properties in organic solvent. The interaction process in solution is shown in Fig. 9.

NBC molecular chains are evenly dispersed in the solvent, and the molecular chains are entangled with each other to form a network structure. The added TEGDN are beneficial to the stability of solution structure because of the formation of hydrogen bond between TEGDN and NBC according to their chemical structure as shown in Fig. 9. When RDX are added into the TEGDN/NBC composite solution system, a small amount of RDX will form hydrogen bond with TEGDN and NBC. But most of RDX will be dispersed in the network structure of NBC as filler, which will not make much contribution to the improvement of its mechanical properties. Due to the hydrogen bonding consumption of RDX, the intermolecular forces of NBC has reduced. Thus, the stability of solution structure weakens after the added RDX. The rheological parameters changes in rheological test also prove it. The rheological parameters apparent viscosity, complex viscosity, G' and G'' decrease with the increases in RDX content below 15%. And the apparent viscosity, complex viscosity, G' and G'' increase with the increases in RDX content above 15% because of the enough amount of RDX [16, 27–29].

4 Conclusion

In this paper, a novel propellant based on RDX and TEGDN/NBC composite was prepared to reach the high strength and high energy goal of advanced propellant. The structure, morphology, thermal properties and rheological performance were characterized detailed.

The RDX amount of propellant was important according the analysis of thermal and rheological tests. RDX amount of 15% was seemed as a critical addition value

Fig. 9 Schematic illustrations of solution structure change

both in thermal and rheological tests. With the increase of RDX, the decomposition temperature of the propellant decreased below 15% RDX content. In contrast, the decomposition temperature of the propellant increased with the increase of RDX above 15%. The propellant had a minimum decomposition temperature and thermal stability at 15% RDX content.

With the increase of RDX content, the viscosity of RDX/TEGDN/NBC composite decreased first and then increased. When the RDX content was 15%, the viscosity of the composite solution was the minimum, and the stability of the solution is the worst. After the addition of RDX, the structure of TEGDN/NBC composite solution became unstable. The molecules in the solution are more likely to have orientation movement under the action of external force, and the entanglement between macromolecular chains is more likely to be damaged. It weakened the interaction between molecules and greatly enhanced its fluidity. It will help to the further extrusion molding of propellant especially in respect of the selection of pressure and energetic filler amount. And the relationship between thermal properties and rheological performance of the propellant will be studied further in future.

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Author contribution Jing Zhao and Juan Zhu provided the RDX raw material. Xiaorui Huang and Qingping Luo conceived and designed the experiments. Zhaoqian Li and Chonghua Pei characterized all samples. All authors discussed the experiment results and contributed to the writing of the paper.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

- Weng CS, Jin ZM, Yuan YX, Zhang XB (1996) Numerical studies on the influence of grain fracture on abnormal pressure in guns. *J Ballistics* 4:13–18
- Yamanaka S, Sugiyama J (2000) Structural modification of bacterial cellulose. *Cellulose* 7(3):213–225
- Wan YZ, Hong L, Jia SR, Huang Y, Zhu Y, Wang YL, Jiang HJ (2006) Synthesis and characterization of hydroxyapatite–bacterial cellulose nanocomposites. *Compos Sci Technol* 66(11–12):1825–1832
- Sun DP, Ma B, Zhu C, Liu C, Yang J (2010) Novel nitrocellulose made from bacterial cellulose. *J Energ Mater* 28:85–97
- Yang Q, Peng BH, Liang G, Luo QP, Pei CH (2012) Preparation and characterization of nitrated bacterial cellulose. *Chinese J Exp Pro* 35:88–90
- Hsissou R, Bekhta A, EL Harfi A (2017) Viscosimetric and rheological studies of a new trifunctional epoxy pre-polymer with noyan ethylene: Triglycidyl Ether of Ethylene of Bisphenol A (TGEBA). *J Mater Environ Sci* 8(2):603–610
- Bekhta A, Hsissou R, Berradi M, EL Bouchti M, Elharf A (2019) Viscosimetric and rheological properties of epoxy resin TGEBA and their composite (TGEBA/MDA/TGEMD+TSP). *Results Eng* 4:100058
- Hsissou R, Bekhta A, Dagdag O, EL Bachiri A, Rafik M, Elharfi A (2020) Rheological properties of composite polymers and hybrid nanocomposites. *Heliyon* 6:e04187
- Rachid H, Ahmed E (2020) Rheological behavior of three polymers and their hybrid composites (TGEBA/MDA/PN), (HGEMDA/MDA/PN) and (NGHPBAE/MDA/PN). *J King Saud Univ Sci* 32:235–244
- Hsissou R, Dagdag O, Berradi M, EL Bouchti M, Assouag M, EL Bachiri A, Elharf A (2019) Investigation of structure and rheological behavior of a new epoxy polymer pentaglycidyl ether pentabispheol A of phosphorus and of its composite with natural phosphate. *SN Appl Sci* 1:869
- Hsissou R, Berradi M, EL Bouchti M, EL Bachiri A, EL Harfi A (2019) Synthesis characterization rheological and morphological study of a new epoxy resin pentaglycidyl ether pentaphenoxy of phosphorus and their composite (PGEPPP/MDA/PN). *Polym Bull* 76:4859–4878
- Hsissou R, EL Bouchti M, EL Harfi A (2017) Elaboration and viscosimetric, viscoelastic and rheological studies of a new hexafunctional polyepoxide polymer: hexaglycidyl ethylene of methylene dianiline. *J Mater Environ Sci* 8(12):4349–4361
- Hsissou R, Dagdag O, Berradi M, EL Bouchti M, Assouag M, Elharf A (2019) Development rheological and anti-corrosion property of epoxy polymer and its composite. *Heliyon* 5:e02789
- Luo QP, Zhu J, Li ZQ, Duan XH, Pei CH, Mao CY (2018) The solution characteristics of nitrated bacterial cellulose in acetone. *New J Chem* 42:18252–18258
- Zhu J, Luo QP, Li ZQ, Liu X, Duan XH, Pei CH (2016) Rheological properties of nitrated bacterial cellulose solution. *Chinese J Energ Mater* 24(4):375–379
- Huang XR, Luo QP, Zhu J, Li ZQ, Li CZ, Pei CH (2019) The preparation and rheological properties of novel energetic composites TEGDN/NBC. *Propellants Explos Pyrotech* 45(1):101–110
- Oyumi Y, Brill TB (1985) Thermal decomposition of energetic materials 3. a high-rate, in situ, FTIR study of the thermolysis of RDX and HMX with pressure and heating rate as variables. *Combust Flame* 62(3):213–224
- Robles E, Urruzola I, Labidi J, Serrano L (2015) Surface-modified Nano-cellulose as reinforcement in poly (lactic acid) to conform new composites. *Ind Crop Prod* 71:44–53
- Yu J, Wang C, Wang J, Chu F (2016) In situ development of self-reinforced cellulose nanocrystals based thermoplastic elastomers by atom transfer radical polymerization. *Carbohydr Polym* 141:143–150
- Xu WY, He WD, Zhang Y (2006) Thermal decomposition performance of high-energy TEGDN propellant. *Chinese J Exp Pro* 29(2):63–65
- Batten JJ (1971) The thermal decomposition of RDX at temperatures below the melting point. III. Towards the elucidation of the mechanism. *Aust J Chem* 24(10):2025–2029
- Mcdonald BA (2011) Study of the effects of aging under humidity control on the thermal decomposition of NC/NG/BTTN/RDX propellants. *Propellants Explos Pyrotech* 36(6):576–583
- Mortadi A, EL Melouky A, Cahid E, Nasrellah H, Bakasse M, Zradba A, Cherkaoui O, El Moznine R (2018) Rheological and electrical properties to investigate the coagulation process during sludge treatment. *Water Sci Technol* 77(1):196

24. Mortadia A, Elmeloukya A, EL Chahida G, Essajaib R, Naserllahc H, Chahbia M, Ghyatia N, Zaima S, Cherkaouid O, EL Mozninea R (2020) Effects of calcium oxide on the surface properties of industrial sludge by analyzing rheological and electrical properties. *J Environ Chem Eng* 8:103764
25. Mortadi A, Elmelouky A, Chahbi M, EL Ghyati N, Zaim S, Cherkaoui O, EL Moznine R (2020) Flocculation monitoring of wastewater by using impedance spectroscopy. *Spectrochim Acta A Mol Biomol Spectrosc* 224:117437
26. Jia X, Chen Y, Shi C, Ye Y, Abid M, Jabbar S, Wang P, Zeng X, Wu T (2014) Rheological properties of an amorphous cellulose suspension. *Food Hydrocoll* 39:27–33
27. Ren YL, Chen SZ (1985) Solubility and apparent viscosity of NC concentrate solution system. *Acta Armamentarii* 6(1):51–54
28. Iotti M, Gregersen W, Moe S, Lenes M (2010) Rheological studies of microfibrillar cellulose water dispersions. *J Polym Environ* 19(1):137–145
29. Zhou L, He H, Li MC, Song K, Cheng HN, Wu Q (2016) Morphological influence of cellulose nanoparticles (CNs) from cottonseed hulls on rheological properties of polyvinyl alcohol/CN suspensions. *Carbohydr Polym* 153:445–454
30. Yao Y, Mukuze KS, Zhang Y, Wang H (2014) Rheological behavior of cellulose/silk fibroin blend solutions with ionic liquid as solvent. *Cellulose* 21(1):675–684
31. Ferreira FV, Mariano M, Rabelo SC, Gouveia RF, Lona LMF (2017) Isolation and surface modification of cellulose nanocrystals from sugarcane bagasse waste: from a micro- to a nano-scale view. *Appl Surf Sci* 436:1113–1122
32. Pinheiro IF, Ferreira FV, Souza DHS, Gouveia RF, Lona LMF, Morales A, Mei LHI (2017) Mechanical, rheological and degradation properties of PBAT nanocomposites reinforced by functionalized cellulose nanocrystals. *Eur Polym J* 97:356–365

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