Research paper

Exploring the Influence of NC on the Crystallization of HTPE

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Abstract: A series of polymer blends of nitrocellulose (NC) and hydroxy terminated polyether (HTPE) in different proportions were prepared by a solution mixing method. The diffraction peak positions and peak intensities of the blends were analyzed by X-ray diffraction. The relative crystallinity of HTPE in the blends was analyzed by differential scanning calorimetry. The crystal morphology of the NC/HTPE blends was observed with a polarizing microscope. The results demonstrated that there is a certain degree of crystallinity in pure HTPE, while the crystallinity of NC/HTPE blends was gradually decreased as NC was added. In addition, when the mass fraction of NC in the blends was more than 40%, the crystallinity of the blends was hardly observed by these characterization methods, which demonstrated that the crystallinity of HTPE could be easily inhibited by NC.

Keywords: materials science, nitrocellulose, hydroxy terminated polyether, blending, crystallize

1   Introduction

Nitrocellulose (NC) is one of the most important components of double base and modified double base propellants [1, 2], in which it mainly plays the role of adhesive, constitutes the structural skeleton of the propellants, and has a great influence on the mechanical properties. However, nitrocellulose is a kind of semi-rigid polymeric material [3] with poor flexibility of the molecular chain segment, so its glass transition temperature is relatively high [4-6], making double base propellants brittle at low temperature and soft at high temperature [7], and limiting its application in solid propellants [8]. Physical [9-11] and chemical modification [12] of NC were the most significant methods for improving the properties [13] of double base propellants [14-16] in recent years. A novel energetic binder, named nitric acid ester of cellulose glycidyl ether (NGEC), with different esterification and etherification degrees, was synthesized by nitrating cellulose glycidyl, which was prepared by basification and etherization reactions of cellulose. The mechanical performance of two propellants based on NGEC and NC were tested and analyzed. The results demonstrated that the propellant based on NGEC has better mechanical performance than that based on NC [17]. Wei *et. al.* [18] substituted NGEC for NC and prepared NGEC based propellant samples by an absorption-extrusion method and then studied their basic physical and chemical properties. The results demonstrated that with the addition of NGEC, the burning rate was increased and the high and low-temperature properties were improved to different degrees compared to the NC based propellant. A series of blends of GAP-based polyurethane elastomers (GAPE) and NC were prepared by a solution mixing method by Hai-qing Ding *et. al.* [19] and the resulting mechanical properties were analyzed on a universal material tensile testing machine. The results showed that when the mass fraction of GAPE was 30%, the elongation at break of the blends was five times more than that with NC, while the tensile strength decreased slightly. However, both of these researches focused on modification of the NC molecule itself by chemical methods that have a long preparation process, or used the GAPE elastomer synthesized in the laboratory, where the batch stability of the synthesized product is not controllable, so that there are many difficulties in practical application. The crystallization behaviour and morphology of PEG in NC/PEG blends with different mass ratios was studied by Wang *et. al.* [20] and found that the crystallization of PEG was greatly influenced by NC because of the strong interaction between the NC and PEG molecular chains, which result in defects in the PEG crystals and a significant decrease in the crystallinity of PEG. However, the molecular chains of PEG used in this research were regular

and crystallinity was more than 90%. When the NC content was greater than 60%, PEG crystallization can be better inhibited, while when the NC content is too high, it is not conducive to improving the low temperature mechanical properties of the blends.

In the present study, a type of polymer that has already achieved industrial production in small batches [21, 22], called hydroxy terminated polyether (HTPE), was used to modify NC. HTPE is a block copolymer composed of polytetrahydrofuran and polyethylene glycol [23] with two and four adjacent methylene groups in the molecule, therefore the molecular chain segments rotate relatively easily and the flexibility of the molecule is good, so that its glass transition temperature is low. Additionally, HTPE has significant benefits in terms of compatibility with nitrate plasticizers and a low response in the slow cook-off test. Consequently, it is used to improve the low temperature mechanical and insensitivity properties of solid propellants [24]. Researchers have made a profound study of the application of HTPE in propellants. Lü *et. al.* [25] tested the explosion heat, density, and mechanical sensitivity of an HTPE insensitive propellant, compared it with HTPB propellant, and evaluated the bullet impact and fast cook-off properties of HTPE insensitive propellant. The results showed that the measured explosion heat and density of HTPE propellant are higher than those of HTPB propellant. Its friction sensitivity is 0, and its impact sensitivity (characteristic drop height H_{50}) is higher than 77 cm. The 12.7 mm bullet impact test and fast cook-off test both showed a combustion reaction and low vulnerability. Yoo, Kim *et. al.* [26, 27] studied the slow cook-off and impact sensitivity of HTPE insensitive propellants, and compared them with the impact sensitivity of HTPB propellants. The results indicated that the slow cook-off response temperature of HTPE propellant reaches 250 °C. Caro and Bellerby [28] conducted in-depth research on the slow cook-off properties of two types of HTPE propellants. It is believed that the softening and even liquifaction of the organic phase in HTPE propellants has an important influence on the slow cook-off response. In addition, Caro and Bellerby [29] also characterized and compared two kinds of HTPE prepolymers to determine their molecular weight, molecular structure, glass transition temperature (T_g), melting temperature (T_m), impurities and viscosity. Wu *et. al.* [30] studied the effect of two kinds of ammonium perchlorate (AP) with different content and particle size on the slow cook-off behaviour of HTPE propellant, and the results indicated that as the AP content increased from 52% to 67%, or the diameter of the AP particles decreased from 400 to 5 μm, the violence of the slow cook-off response all increased, and possible mechanisms were proposed. The above researches focused on the mechanical sensitivity and slow or fast cook-off properties of HTPE propellants,

while the study of the crystallization behaviour of HTPE as a propellant binder was largely ignored. However, due to the regular molecular chain of HTPE there is a relatively high degree of crystallization, which will have a negative effect on the low temperature mechanical performance of propellants. While NC is an amorphous polymer with low crystallinity, the blending a modification of NC and HTPE can produce a blend with both advantages [31]. On the one hand, it can improve the flexibility of NC molecular chains and mechanical properties at low temperature [32], and on the other hand, it can inhibit the crystallization of HTPE, thus eliminating the negative effects of HTPE crystallization on the mechanical properties of the propellant. Different mass ratios of NC/HTPE blend films were prepared by a solution mixing method in the work reported here. The crystallization properties of HTPE as influenced by NC was studied by XRD and DSC methods, and the crystallization morphology of the blends was observed with a polarizing microscope (POM). This was expected to provide theoretical references for improving the mechanical properties of double base propellants and for preparing insensitive modified double base propellants.

2   Experimental Section

2.1 Materials
NC (Nitrogen content = 12%, properties meet the requirements of GJB 3204-1998 [33]), produced by Sichuan North Nitrocellulose Co., Ltd. Hydroxy terminated polyether (HTPE, average molecular weight = 4380), produced by Liming Research Institute of Chemical Industry; Acetone, analytically pure, Rionlon Bohua Pharmaceutical Chemical Company.

2.2 Preparation of NC/HTPE blend and its films
NC and HTPE were placed separately in a 60 °C water bath and dried to constant weight. The dried NC was dissolved in acetone with a mass fraction of 12%, and HTPE was also dissolved in acetone with a mass fraction of 20%. These two solutions were then mixed in different mass ratios. After standing at room temperature to eliminate air bubbles, the blended solution was placed in an oven and heated to 60 °C to partially remove the acetone. After cooling naturally, the blended solution was slowly poured into a PTFE mold, and the desired dense film required for the following tests was formed after slow evaporation. The sample obtained was exposed in a 60 °C oven and dried to a constant weight.

2.3 Analysis and characterization

X-Ray diffraction analysis: Empyrena, Netherlands PANalytical B.V.:
– working voltage: 40 kV,
– tube current: 40 mA,
– radiation source: Cu Kα radial,
– incident light wavelength: 1.54 Å,
– scan range: $2\theta = 5\text{-}90°$ and scan speed: 9 °C/min.

Differential scanning calorimetric analysis: TA2910, US TA Company:
– heating rate: 5 °C/min,
– temperature range: 0-145 °C,
– protected by a nitrogen atmosphere at a gas inlet speed of 5 mL/min.

The melting point (T_m) is defined as the temperature corresponding to the intersection of the tangent of the point with the maximum slope on the leading edge of the complete endothermic peak and the epitaxial baseline.

Polarizing microscopic analysis: DM2500M, German Leica Company. The crystal morphology of HTPE in the NC/HTPE blends was observed; the magnification was 100X.

3   Results and Discussion

3.1 XRD analysis of NC/HTPE

The diffraction pattern of the NC/HTPE material was obtained by polycrystalline X-ray diffractometry, and the peak positions, peak types and relative intensities were used to analyse the material phase or amorphous structure.

The XRD diffraction pattern of a pure NC sample is shown in Figure 1. It can be seen in this figure that the XRD diffraction curve of pure NC is a wide dispersion peak with weak intensity in the range of $2\theta = 15\text{-}30°$. This demonstrated that the crystallinity of NC is relatively low, but there may be a small quantity of crystalline regions, therefore it is considered as an amorphous polymer in this paper.
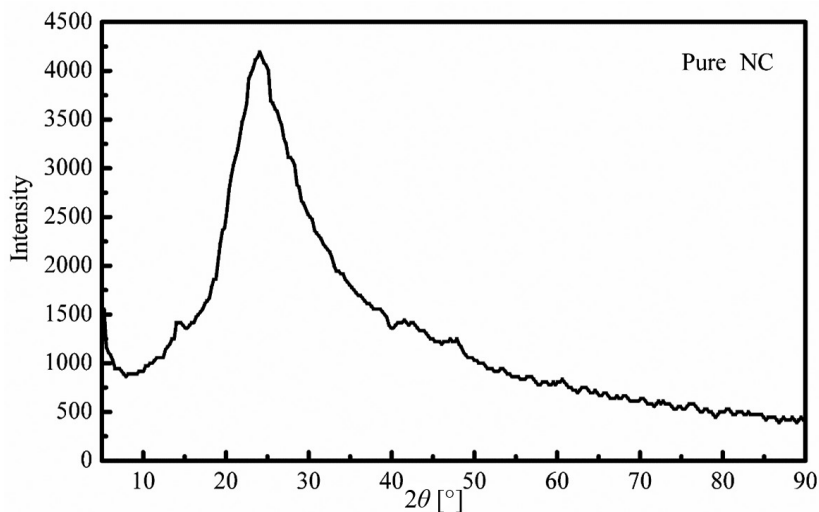
Figure 1.   XRD pattern of pure NC

The XRD diffraction pattern of a pure HTPE sample is shown in Figure 2. As can be seen in this figure. the diffraction peaks of pure HTPE are sharp and the baseline is relatively flat, which is typical for a crystalline diffraction pattern. Pure HTPE has four crystal diffraction peaks with relatively high intensity, and the 2θ angles are located at 19.01°, 19.80°, 23.16° and 24.18°. In addition, in the range of $2\theta = 5\text{-}90°$ there are several diffraction peaks with relatively low intensity, located at 10.37°, 37.52° and 38.34°, together with a broad peak at 10.37° of low intensity, which indicates that HTPE is not completely crystalline; there are still certain amorphous regions.
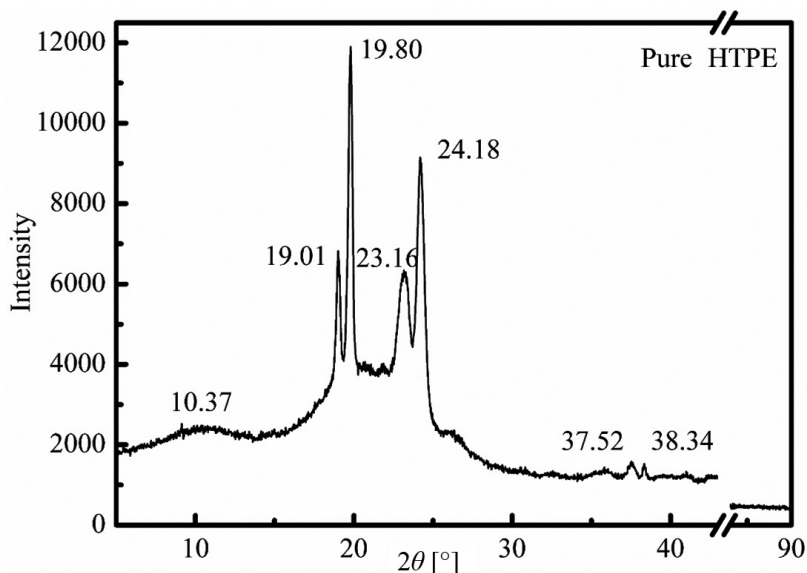
Figure 2.   XRD pattern of pure HTPE

Figure 3 shows the XRD diffraction pattern of NC/HTPE blends in different ratios. It can be seen in this figure that when the mass fraction of NC is 30%, the intensity of the crystal diffraction peaks are obviously weakened, while the peak positions were unchanged. There were relatively high intensity diffraction peaks located in 19.14°, 19.80°, 23.24° and 24.24°, which demonstrated that a small amount of NC, with mass fraction less than 30%, does not cause a transformation of the HTPE crystalline form. However, the peak intensities are weakened, and indicated that the addition of NC inhibited the growth of HTPE crystal grains, thus causing a decrease in crystallinity. The sharp diffraction peaks of HTPE are overlapped by the wide dispersion peak, indicating that there are obvious differences between the crystalline and amorphous phases in the blends. When the mass fraction of NC was more than 40%, the diffraction patterns of the blends appeared as two fairly broad peaks, which are typical amorphous diffraction curves, the peak located in 2θ 8-12° is a relatively low intensity wide dispersion peak, which belongs to the amorphous area of HTPE, while the peak located in 2θ 15-30° is a relatively high intensity wide dispersion peak, which belongs to NC. Additionally, there is still a very low intensity but relatively sharp peak at 38.34°, which indicates that there is a small amount of crystalline region of HTPE in the blends when the mass fraction of NC is equal to or more than 40%. However this peak is very weak and superposed on the wide dispersion peak

of NC, indicating that crystallinity is very low and the crystalline phase is very incomplete. Furthermore, when the mass fraction of NC is between 40-70% the diffraction peak types and peak positions are hardly changed and only the peak intensities are decreased. This behaviour shows that the crystallinity of HTPE in the blends is close to zero when the mass fraction of NC is more than 40% and a further increase in NC has little influence on the crystallinity of the HTPE. In summary, the crystallinity of HTPE in the blends has already approached a minimum value when the mass fraction of NC is 40%.
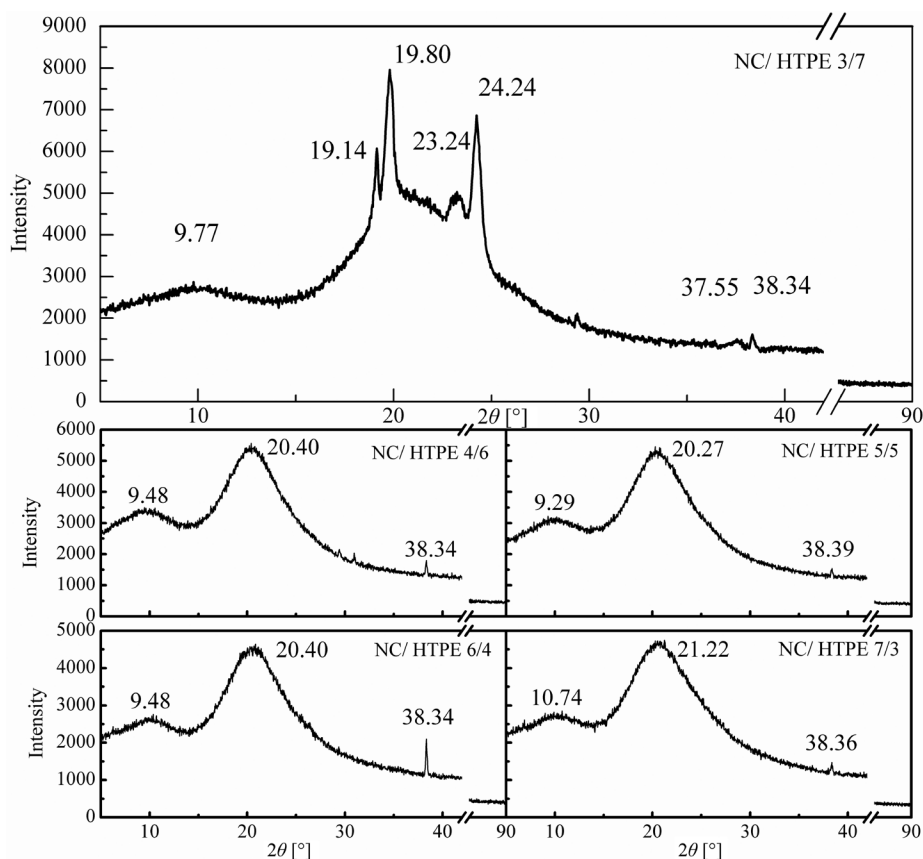

Figure 3. XRD patterns of NC/HTPE blends

There are many models describing polymer crystallization, mainly including the fringed micelle model, the folded chain model, the switchboard model and the tunnel-folded chain model [34, 35]. These models all propose that crystalline regions and amorphous regions coexist in crystalline polymers [36]. In order

to quantitatively describe this phenomenon, the concept of crystallinity is proposed as a measure of the crystalline content of the polymer . Crystallinity is the percentage of the crystalline part of a substance or material in the total mass or volume. The degree of crystallinity is a clear characterization of the aggregated state structure of the system, in which the order degree of crystalline and amorphous parts is obviously different, but due to the complexity of the polymer structure, it is difficult to clearly divide the two states in the crystalline polymer. The mass crystallinity (X_C) of the two distinct state systems with sharp diffraction peaks encompassed by the wide dispersion peak can be calculated using Equation 1. The diffraction pattern of the two distinct state systems is simply the superposed crystalline and amorphous parts. As shown in Figure 3, the diffraction curve of the blend with 30% NC mass fraction consists of two parts, one is the crystal diffraction peaks and the other is the amorphous wide dispersion diffraction peak. The mass crystallinity formula deduced theoretically is as follow [37]:

$$X_C = I_C / (I_C + kI_a) \tag{1}$$

where I_C is the diffraction intensity of the crystalline regions, I_a is the diffraction intensity of the amorphous regions and k is the relative ray coefficients of amorphous and crystalline states per unit mass. I_C is obtained from the area of each diffraction peak after correction. I_a is obtained from the area of the wide dispersion diffraction peak after correction. Theoretically, k is approximately equal to 1, so it is considered as 1 in practical calculations.

In order to correct the peak areas, the diffraction peaks should be resolved from each other, but the calculation of the correction coefficient is complicated. So, the correction is often omitted when comparing a series of samples and the sum of diffraction peak areas and wide dispersion diffraction peak areas is substituted directly into Equation 1 in order to calculate the approximate crystallinity $<X_C>$, which is a kind of crystallinity index. The calculation formula is as follow:

$$<X_C> = S_C / (S_C + S_a) \tag{2}$$

where $<X_C>$ is the crystallinity index, S_C is the sum of diffraction peak areas and S_a is the wide dispersion diffraction peak areas.

The diffraction peak area from 19-25° of NC/HTPE = 3/7 blend was calculated from Figure 3 and the wide dispersion diffraction peak area from the same angle range for pure NC was calculated from Figure 2, the crystallinity index of the NC/HTPE = 3/7 blend was then calculated through Equation 2. The

result was 20.54%. This result was close to the crystallinity calculated by the DSC method in Section 3.2.

3.2 DSC analysis of NC/HTPE

The DSC heating curve of a pure HTPE sample is shown in Figure 4, from which we can see that there is an obvious endothermic peak from 30-45 °C. Due to the good flexibility and symmetry of pure HTPE, the molecular chains fold into the lattice to form crystalline regions. During the heating process, the crystalline regions melt giving the endothermic peak. The melting point of pure HTPE is 29.63 °C, the melting limit is 4.51 °C and the crystallization melting heat is 66.97 J/g.
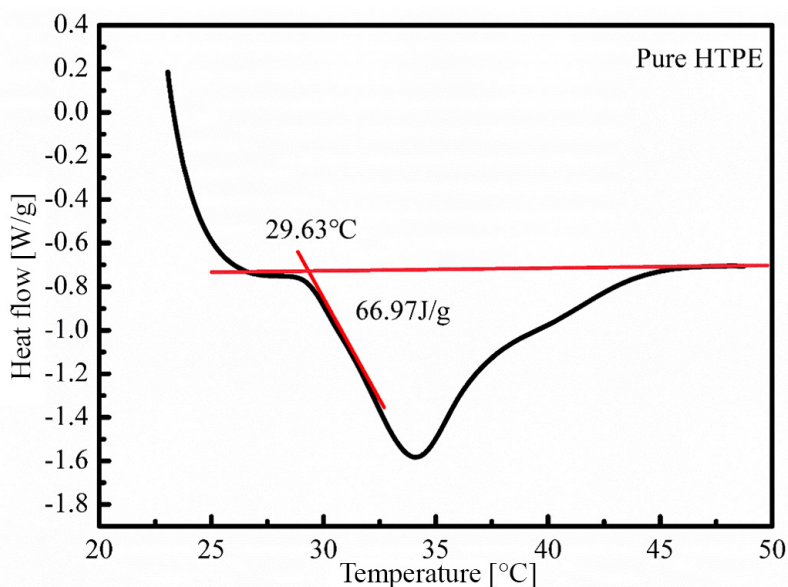

Figure 4.   DSC curve of pure HTPE

Figure 5 is the DSC heating curve of a pure NC sample, which is almost a straight line. Because there is no change in the specific heat capacity of NC during the heating process, there will be no inflection point change in the baseline. As a result, the glass transition temperature of NC cannot be observed. Moreover, within the experimental temperature range, NC did not reach its decomposition temperature, so the decomposition peak cannot be observed either. In addition, NC has few crystalline areas and therefore could not melt. Its DSC curve is close to a straight line with a small slope.
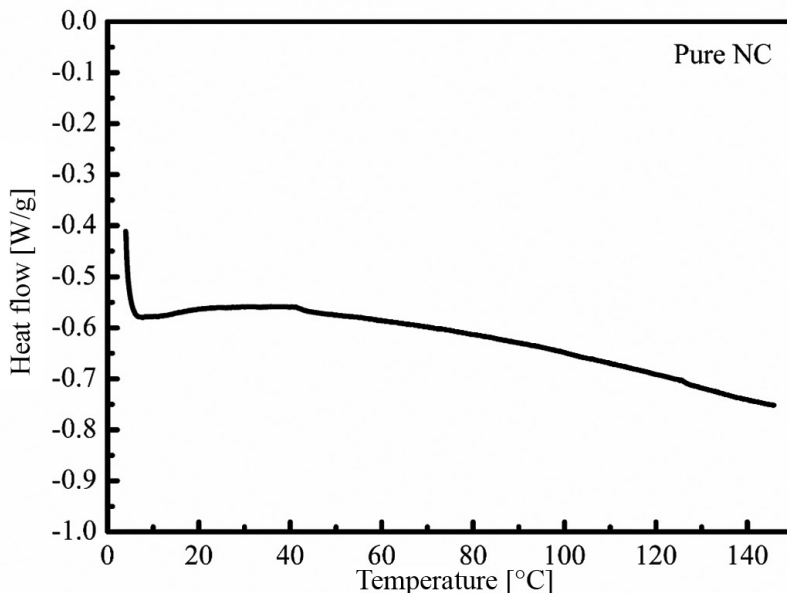
Figure 5. DSC curve of pure NC

The DSC heating curves of NC/HTPE blends with NC mass fractions 10-30% are shown in Figure 6, and demonstrate that the DSC curve of HTPE is obviously changed after blending with NC. With an increase in the NC content, the melting endothermic peak of the blends becomes smaller and smaller, so the melting enthalpy gradually decreases, while the melting point and melting peak temperature gradually increase. It can be seen in Table 1 that when the NC/HTPE mass ratio is 30/70, the melting enthalpy has decreases to 10.03 J/g, while T_m and T_p have increased from 29.63 and 34.14 °C for pure HTPE to 32.69 and 42.83 °C, respectively. The analysis shows that with the gradual increase in the number of NC molecules, the HTPE and NC molecular chains diffuse with each other, resulting in entanglement and the formation of intermolecular hydrogen bonds, which reduces the free volume of the HTPE molecules, limits the regular arrangement of molecular chains, and the process of chain segments entering the lattice is affected, thus inhibiting the crystallization of HTPE. At the same time, the further growth of crystal nuclei is also limited. The presence of NC also increases the number of crystal defects and irregular microcrystals, reduces the degree of crystal perfection and the crystallinity, resulting in a decrease in the melting enthalpy of HTPE in the blends. On the other hand, the increase in T_m and T_p may be due to the rigidity of NC molecules, and the movement of molecules

in the crystalline regions is restricted by the amorphous regions formed from NC, so that HTPE molecules in the crystalline regions need a higher energy to escape the lattice, thus causing the increase in T_m and T_p.
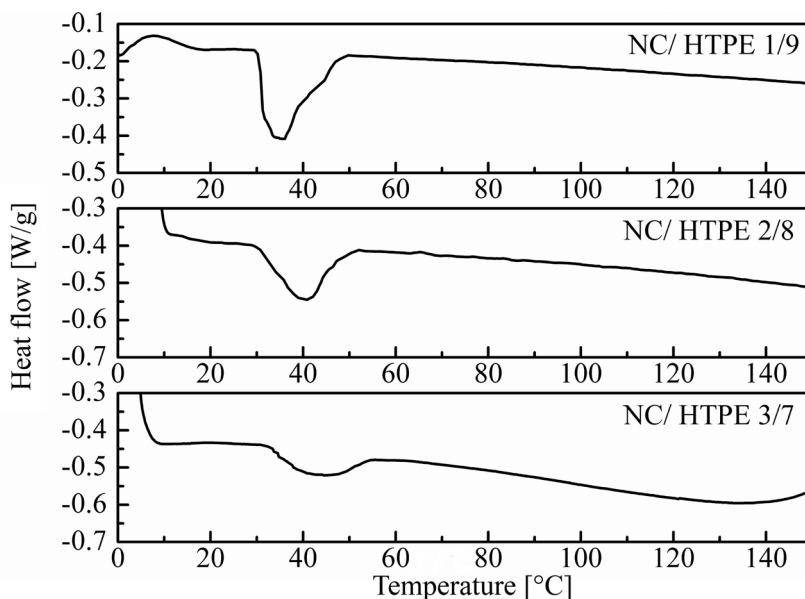

Figure 6.   DSC curves of NC/HTPE blends (NC content 10-30%)

Table 1.   DSC parameters of NC/HTPE polymer blends in different mass ratios

NC/HTPE	T_m [°C]	ΔH [J/g]	ΔS [J/(g·°C)]	X_C [%]
100/0[a)]	—	—	—	0
30/70	32.68	10.03	0.3069	21.40
20/80	31.88	17.74	0.5565	33.11
10/90	30.53	28.03	0.9181	46.51
0/100	29.63	66.97	2.260	100.0

[a)] The melting point of pure NC is still controversial [38, 39], so it is not listed in Table 1.

The DSC curves of NC/HTPE blends with NC mass fraction 40-70% are shown in Figure 7 and are all similar to the DSC curve of pure NC, that is a straight line with a very small slope. It can be seen in this figure that there are no crystalline regions of HTPE in the blends with these ratios or the crystallinity

has been already reduced below the sensitivity of the DSC test method, so that the phase transition in the microcrystalline regions cannot be reflected in the DSC curves. This conclusion is basically consistent with the XRD method in Section 3.1.
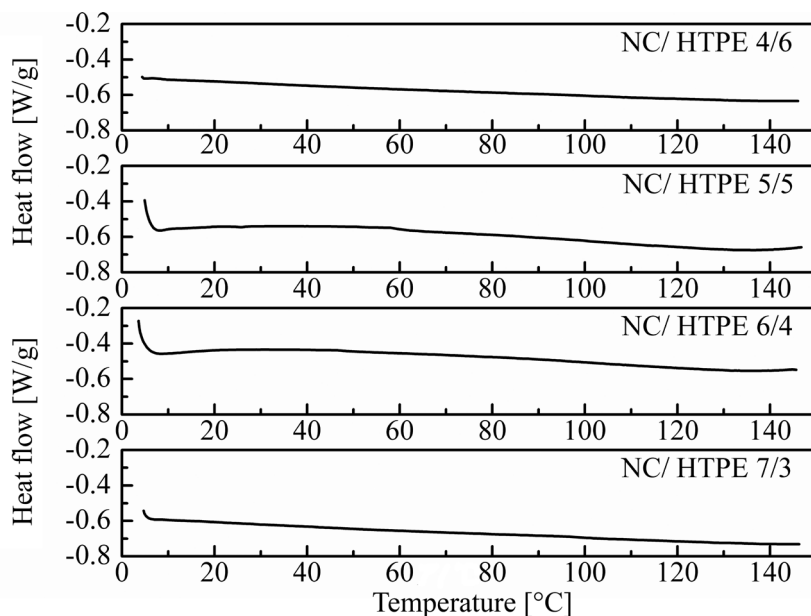

Figure 7. DSC curves of NC/HTPE blends (NC content 40-70%)

The DSC analysis parameters of NC/HTPE blends are listed in Table 1, and the relative crystallinity of HTPE in the blends was calculated by Equation 3 [40, 41]:

$$X_C = \Delta H/(\chi \cdot \Delta H_0) \tag{3}$$

where ΔH is the crystallization melting heat of the blends, X_C is the relative crystallinity of HTPE, χ is the mass fraction of HTPE and ΔH_0 is the melting enthalpy of pure HTPE, calculated based on the measured value of 66.97 J/g.

Entropy is a physical quantity that reflects the chaotic degree of system motion. The entropy change can reflect the components' interactions in the blends to a certain extent. The crystallization entropy change of the blends (ΔS) is calculated by Equation 4.

$$\Delta S = \Delta H / T_m \tag{4}$$

where ΔH is the crystallization melting heat of the blends and T_m is the melting point of the crystalline regions in the blends.

Figure 8 shows that the relation between the crystallinity, the crystallization entropy change of HTPE in the blends and the mass fraction of NC. As shown in Table 1 and Figure 8, compared with pure HTPE, the crystallinity of HTPE in NC/HTPE blends was rapidly decreased as the mass fraction of NC was gradually increased. When the NC content was 10%, the relative crystallinity of HTPE was only 46.51%. Thereafter the decrease of crystallinity is relatively gentle and basically decreases linearly with a certain slope. When the NC content was 30%, the relative crystallinity of HTPE had decreased to only 21.40% and when the NC content reached 40%, the crystallinity of HTPE in the blends could not be measured by the XRD or DSC methods, which illustrated that the crystallinity of HTPE in the blends above this ratio is too small to be detected.
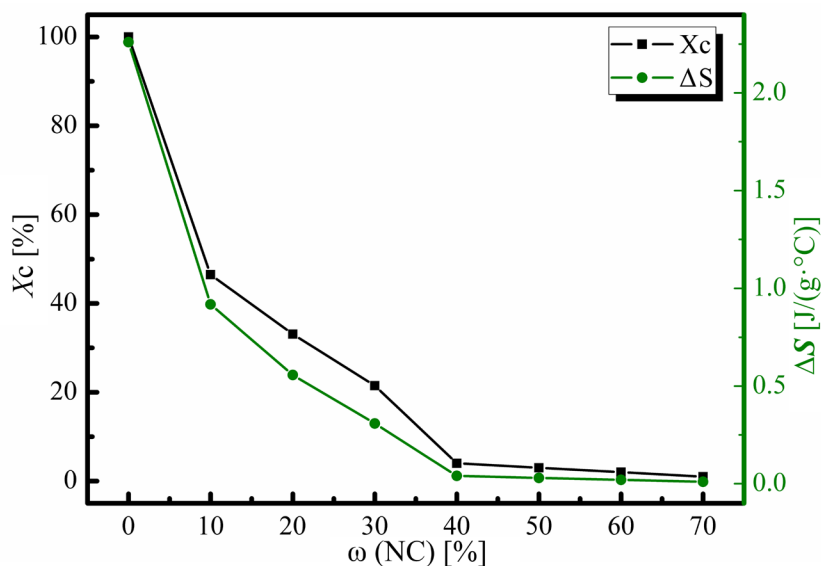

Figure 8. Relation between the relative crystallinity, crystallization entropy change of HTPE in the blends and the mass fraction of NC

It can also be seen from Table 1 and Figure 8 that, after the blending of NC and HTPE, the changing trend of crystallization entropy and relative crystallinity of the blend are generally consistent. When the mass fraction of NC is less than 10%, the two parameters decrease rapidly as the NC content increases. While

the mass fraction of NC is between 10-40%, the crystallinity and crystallization entropy changes decrease steadily, that is both decrease linearly with a certain slope. While NC in the blends exists as amorphous phases, so the crystallization entropy change is only for HTPE. The results indicate that the free movement of HTPE molecules are restricted by the rigid structure of NC molecules, and there are hydrogen bonds between the incompletely nitrated hydroxy groups in NC and HTPE molecules, which restricts the molecular movement of HTPE to a certain extent, resulting in the decrease in crystallization entropy in the blends.

3.3 Crystal morphology analysis of NC/HTPE

The NC/HTPE blends can be distinguished by a polarizing microscope when there are two phases: crystalline and amorphism. The basic structure of a polarizing microscope is to add two polarizers on the sample table of an ordinary optical microscope. The lower polarizer is the polarizer and the upper polarizer is the analyzer. The vibration directions of the two polarizers are usually placed perpendicular to each other, which is called an orthogonal polarizing microscope.

The polymer is optically isotropic in the molten state and the amorphous state, that is, the refractive index is the same in all directions. Only one beam of light with the same vibration direction as the polarizer passes through the sample, and cannot pass through the analyzer at all. Therefore, the field of vision in the eyepiece is completely dark. When the polymer has crystalline or orientation regions, the optical properties vary with direction and when light pass through it, it will be decomposed into two beams whose vibration directions are perpendicular to each other. If the vibration directions of the crystal are inconsistent with the upper and lower polarizers, the field of vision is bright and the structural morphology of the polymer can be observed [42].

The microstructure of NC/HTPE blends in different mass ratios were observed by POM. It was found that after the blending of NC and HTPE by the solution mixing method, the crystal morphology of HTPE changes greatly. With the increase in NC mass fraction, the crystal morphology of HTPE underwent a process from larger broken crystals to smaller broken crystals, and then gradually disappeared. POM images of NC/HTPE blends in different mass ratios are shown in Figures 9-11.
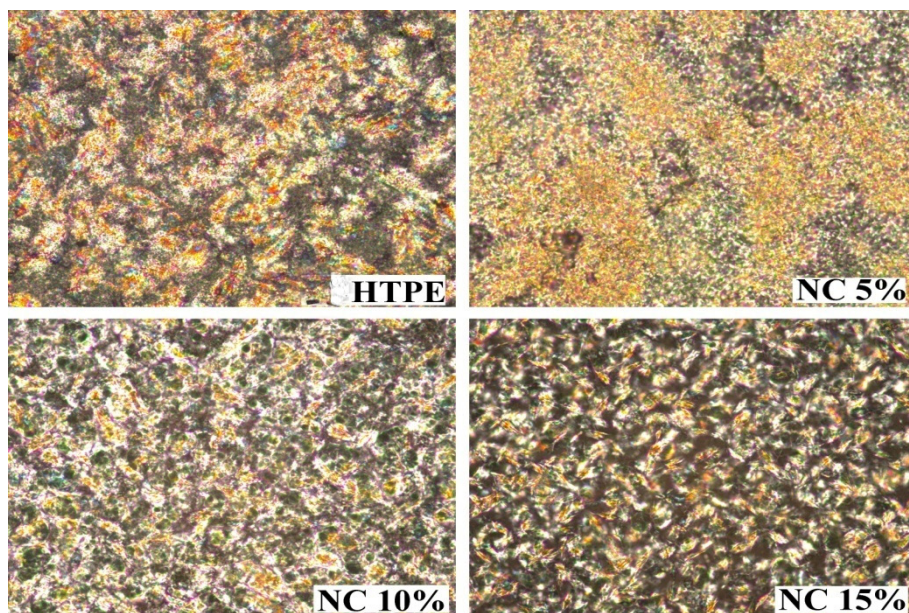
Figure 9.   POM images (×100) of NC/HTPE blends (NC content 0-15%)

POM images of pure HTPE and NC/HTPE blends with the NC mass fractions of 5-15% are shown in Figure 9, and demonstrate that pure HTPE is irregular radial crystals, alternating between light and dark. The irregular crystal morphology shows that the crystalline region of HTPE begins to grow from the pre-existing heterogeneous nuclei. Because the crystals grow at the same time and finally start to contact each other to a certain extent, the radial crystals are formed through incomplete growth of spherocrystals.

When the mass fraction of NC was 5%, the bright areas in the POM image of the blend increase and relatively complete spherocrystals are formed in some regions, while other regions showed the phenomenon of collision and fusion, indicating that the addition of a small amount of NC made it become the crystal nuclei of HTPE that began to grow in different phases with these NC as the crystal nuclei. Therefore, extremely irregular broken spherocrystals will not exist in pure HTPE. However, as the mass fraction of NC continues to increase to 10% or more, the content of NC has greatly inhibited the crystal growth of HTPE, so the bright area in the POM image of the blend is reduced, and irregular strip or radial crystals begin to appear again, which indicates that the growth of HTPE spherocrystals is inhibited and the crystal integrity is destroyed. In summary, a very small amount of NC, $\omega(\text{NC}) \leq 5\%$, contributes to

the heterogeneous nucleation of HTPE crystals to a certain extent, which makes HTPE spherocrystals more perfect. When the content of NC exceeds a critical value, ω(NC) = 10%, NC begins to inhibit the growth of HTPE crystals and obviously leads to a crystallinity decrease.

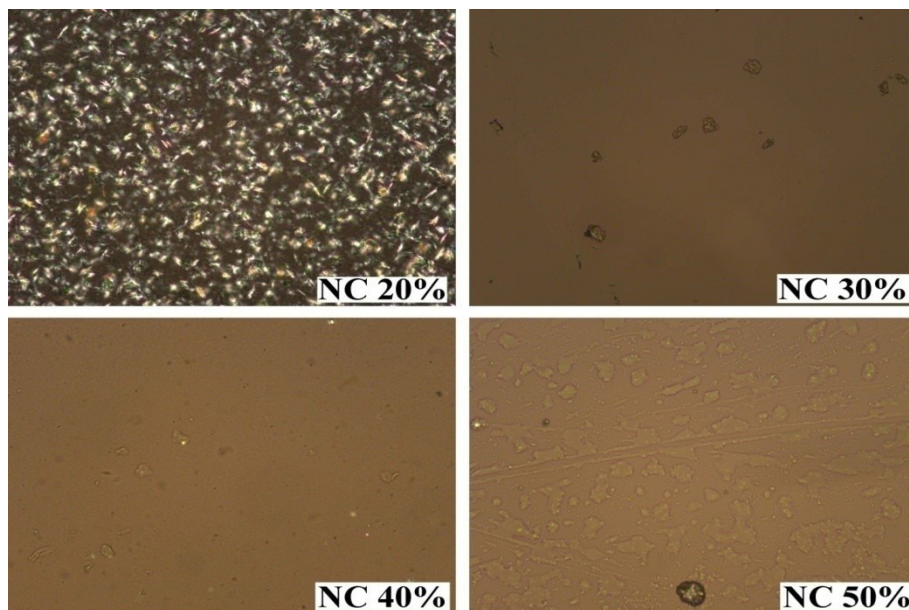**Figure 10.** POM images (×100) of NC/HTPE blends (NC content 20-50%)

Figure 10 shows the POM images of NC/HTPE blends with the NC mass fractions of 20-50%, which demonstrate that when the mass fraction of NC was 20%, the bright areas in the POM image of the blend decreased significantly and could no longer be merged into a large area, indicating that the growth of HTPE crystals was greatly inhibited by NC of this content and its crystallinity was greatly reduced, consistent with the conclusion of the DSC method in Section 3.2.

When the mass fraction of NC was 30%, most of the visual field became gray, and only a few small areas have bright and dark crystal area extinction phenomenon. This shows that the crystallization region of HTPE in the blend has been reduced to such an extent that the POM method is difficult to observe, which is consistent with a crystallinity of about 21% calculated by the XRD method in Section 3.1 and the DSC method in Section 3.2.

As the NC content continues to increase, the bright areas in POM images are fewer and fewer, and most of them are dark areas of amorphous states. This indicates that when the mass fraction of NC is greater than or equal to 40%, the

crystallization region of HTPE in the blend has been reduced to such an extent that it cannot be observed by the POM method, consistent with the conclusions of the XRD and DSC methods in the previous two sections.
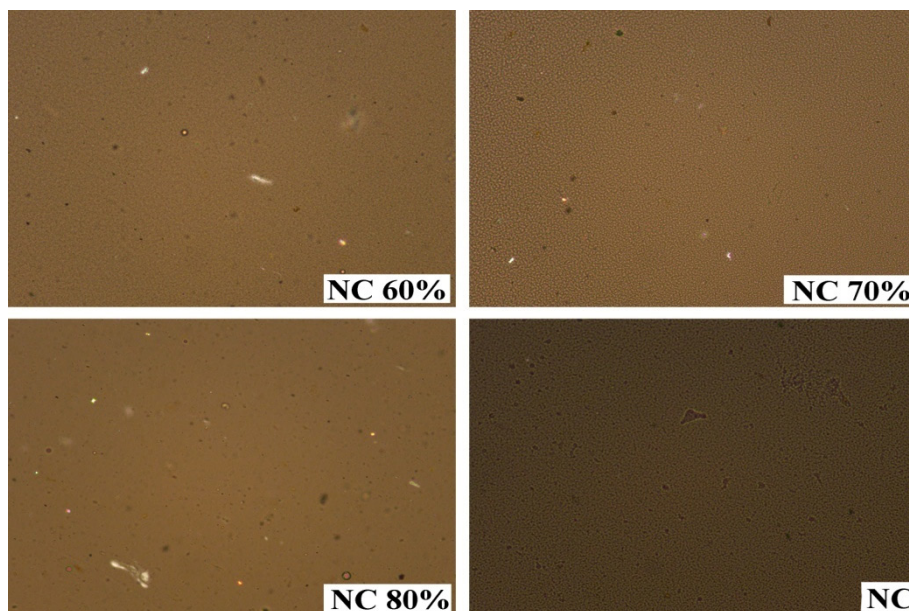

Figure 11. POM images (×100) of NC/HTPE blends (NC content 60-100%)

POM images of pure NC and NC/HTPE blends with the NC mass fraction of 60-80% are shown in Figure 11, and demonstrate that when the NC mass fraction is greater than or equal to 60%, the HTPE crystals in the blends could no longer be observed in the POM images. The POM image of pure NC is gloomier than that of these blends, indicating that NC is a kind of amorphous polymer and has almost no crystalline regions, which is the same conclusion drawn by the XRD and DSC methods in the previous two sections.

4   Conclusions

♦   Pure HTPE is a semicrystalline polymer and the crystal morphology is mainly incomplete spherocrystals and broken crystals. The melting point of the crystalline region is 29.63 ℃ and the melting limit is 29.63-34.14 ℃. Pure NC is an amorphous polymer with few crystalline regions. There is no endothermic peak or decomposition peak under 150 ℃.

♦ When the mass fraction of NC is 30%, the diffraction peak position of the NC/HTPE blend and pure HTPE appear at the same position, which demonstrates that the type of HTPE crystal has not changed. In addition, XRD analyses indicate that the crystallinity index of HTPE is 20.54% when the mass fraction of NC is 30% in the blend.

♦ The relative crystallinity of HTPE is significantly reduced and the melting point of the crystalline region moves to a high temperature with an increase of the NC content. DSC analyses indicate that when the NC content is 10%, the crystallinity of HTPE in the blend is 46.51%. Then, the crystallinity decreases relatively steadily as the NC content is increased 10-30%, almost linearly with a certain slope. When the NC content is 30%, the relative crystallinity of HTPE in the blend has decreased to 21.40%. When the NC content reaches 40%, the relative crystallinity of HTPE in the blends has decreased to such an extent that it cannot be detected by either XRD and DSC analysis.

♦ When the mass fraction of NC is 5%, a small amount of relatively complete spherocrystals of HTPE appeared in the blends, which demonstrates that the addition of a small amount of NC made it become the crystal nuclei of HTPE, and is conducive to the formation of HTPE crystals. When the mass fraction of NC is 10-30%, the crystallisation of HTPE is inhibited by the NC in some extent, as can be seen in the POM images that HTPE crystals are strip or radial crystals, the growth of HTPE spherocrystals is inhibited and the crystal integrity is destroyed. When the mass fraction of NC is 40-80%, crystals of HTPE could not be observed in the POM images, which demonstrates that crystalline regions do not exist or cannot be detected by these analytical methods.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] Liu, J. *Physical and Chemical Properties of Gunpowder.* Beijing Institute of Technology Press, Beijing, **1997**, pp. 9-17; ISBN 7-81045-287-8.
[2] Ren, W.; Wang, Z. *Theory and Practice of Explosives & Propellants.* China North Chemical Industries Corporation, Beijing, **2001**, pp. 540-560.

[3]   Hu, Y.-W.; Zheng, Q.-L.; Zhou, W.-L.; Xiao, L.-Q. Preparation and Performance of GAP-ETPE/NC Polymer Blends. (in Chinese) *Chin. J. Energ. Mater.* **2016**, *24*(4): 331-335; https://doi.org/10.11943/j.issn.1006-9941.2016.04.003.

[4]   Zhang, D. *Properties and Preparation of Raw Materials for Gunpowder.* Beijing Institute of Technology Press, Beijing, **1995**, pp. 11; ISBN 7-51491-312-5.

[5]   de Paula, A.C.; Uliana, F.; da Silva Filho, E.A.; Soares, K.; Luz, P.P. Use of DMA-Material Pocket to Determine the Glass Transition Temperature of Nitrocellulose Blends in Film Form. *Carbohydr. Polym.* **2019**, *226*: paper 115288; https://doi.org/10.1016/j.carbpol.2019.115288.

[6]   Wang, H. Research and Development on Binders for Propellants. *J. North Univ. China, Nat. Sci. Ed.* **2007**, (S1): 97-99.

[7]   Ren, Z.; Li, X. Research Situation and Prospect of Nitrocotton Modification. (in Chinese) *Chem. Propellants Polym. Mater.* **2014**, *12*(5): 48-51.

[8]   Zhang, D. *Solid Rocket Propellant.* Ordnance Industry Press, Beijing, **1991**, pp. 43; ISBN 7-80038-266-4/TQ9.

[9]   Kang, B.; Wang, L.; Li, X. Investigation on the Compatibility of NC/PEG Blended System. (in Chinese) *Chin. J. Explos. Propellants* **2014**, 37(6): 75-78.

[10] Yang, L.; Shi, X.; Li, Z,; Duan, X.; Wu, B.; Pei, C. Effect of 3-Methyl-4-nitro-furoxan on Morphology, Thermal Stability, Rheological and Mechanical Properties of Nitrocellulose (NC)-based Energetic Materials. *FirePhysChem* **2021**, *1*(2): 90-96; https://doi.org/10.1016/j.fpc.2021.04.004.

[11] Touidjine, S.; Karim Boulkadid, M.; Trache, D.; Belkhiri, S.; Mezroua, A.; Islam Aleg, M.; Belkebiche, A. Preparation of Ammonium Nitrate-based Solid Composite Propellants Supplemented with Polyurethane/Nitrocellulose Blends Binder and Their Thermal Decomposition Behavior. *Def. Technol.* **2022**, *18*(11): 2023-2033; https://doi.org/10.1016/j.dt.2021.12.013.

[12] Zhang, Y. *Study on Solid Propellant Based on Modified Nitrocellulose and Its Gel/Composite Gel.* Beijing Institute of Technology, Beijing, **2015**, pp. 6-19.

[13] Tomaszewski, W.; Gołofit, T.; Ostrowski, M. Thermochemistry of the Binary System Nitrocellulose + Dimethyl 4,4´-dinitroheptanedioate. *Thermochim. Acta* **2022**, *707*: paper 179103; https://doi.org/10.1016/j.tca.2021.179103.

[14] Hu, T. *Experimental Study on the Chemical Modification of Nitrocellulose.* North University of China, Taiyuan, **2020**, pp. 9-13.

[15] Ding, H. *Study on Synthesis, Modification and Properties of Polymers for Ammunition.* Nanjing University of Science and Technology, Nanjing, **2013**, pp. 4-11.

[16] Meng, X.; Xiao, Z. Synthesis, Thermal Properties and Sensitivity of Ladder-Like Nitrocellulose Grafted by Polyethylene Glycol. *Propellants Explos. Pyrotech.* **2018**, *43*(3): 300-307; https://doi.org/10.1002/prep.201700193.

[17] Wang, F.; Yang, F.; Wang, J. Preparation and Performance of Double Base Propellant Modified by NGEC. (in Chinese) *Chin. J. Explos. Propellants* **2006**, *29*(6): 51-53.

[18] Wei, X.; Zhou, J.; Zhao, G.; Manyi, Q.; Junbo, C.; Zhiwei, W. Study on the Application of NGEC in Modified Double Base Propellant. (in Chinese) *New Chem. Mater.* **2020**, *48*(6): 232-235.

[19] Ding, H.; Xiao, L.; Jian, X.; Zhou, W. Research of Blends of GAP-based Polyurethane Elastomer and NC. (in Chinese) *J. Solid Rocket Technol.* **2012**, *4*: 495-498.

[20] Wang, L.; Li, X.; Kang, B. Research on Crystallization Behavior of NC/PEG Blends. (in Chinese) *Initiators Pyrotech.* **2012**, *5*: 44-47.

[21] Zhang, B. *Synthesis and Characterization of HTPE Hydroxyl Terminated Polyether and Study on Its Reaction with Isocyanate.* Masters Dissertation, Henan University of Science and Technology, Henan, **2017**, pp. 6-10.

[22] Fu, X.; Jiang, L.; Yu, H. Research Situation and Prospect of HTPE Propellants. *Aerodynamic Missile J.* **2020**, *10*: 82-90.

[23] Song, X.; Zhou, J.; Wang, W.; Li, X. Review on HTPE Propellants. (in Chinese) *Chin. J. Energ. Mater.* **2008**, *16*(3): 349-352.

[24] Zhi, R.; Li, X.; Wang, H.; Liu, M.; Study on Preparation and Its Compatibility of Nitrocotton/Hydroxyl-terminated Polyether Polyblend. (in Chinese) *China Adhes.* **2015**, *24*(3): 6-9.

[25] Lü, X.; Pang, W.; Li, J.; Wang, K. Bullet Impact and Fast Cookoff Characteristics of HTPE Insensitive Solid Propellant. (in Chinese) *Chin. J. Explos. Propellants* **2019**, *42*(1): 79-83.

[26] Yoo, J.C.; Kim, C.K.; Kim, J.H.; Lee, D.H.; Min, B.S. Slow Cook-Off Test and Evaluation for HTPE Insensitive Propellants. (in Korean) *J. Korean Society Propulsion Engineers* **2010**, *14*(6): 31-37.

[27] Kim, C.K.; Yoo, J.C.; Min, B.S. Impact Sensitivity of HTPE & HTPB Propellants using Friability Test. (in Korean) *J. Korean Soc. Propulsion Engineers* **2011**, *15*(1): 29-34.

[28] Caro, R.I.; Bellerby, J.M. Behavior of Hydroxyl-terminated Polyether (HTPE) Composite Rocket Propellants in Slow Cook-off. *Int. J. Energ. Mater. Chem. Propul.* **2008**, *7*(3): 171-185; https://doi.org/10.1615/IntJEnergeticMaterialsChemProp.v7.i3.10.

[29] Caro, R.I.; Bellerby, J.M. Characterization and Comparison of Two Hydroxyl-terminated Polyether Prepolymers. *Int. J. Energ. Mater. Chem. Propul.* **2010**, *9*(4): 351-364; https://doi.org/10.1615/IntJEnergeticMaterialsChemProp.v9.i4.50.

[30] Wu, W.; Jing, P.; Zhao, S.; Luo, Y. Mechanism of AP Effect on Slow Cook-Off Response of HTPE Propellant. *Thermochim. Acta* **2022**, *715*: paper 179291; https://doi.org/10.1016/j.tca.2022.179291.

[31] Wang, G. *Principle and Application of Polymer Blending Modification.* China Light Industry Press, Beijing, **2011**, pp. 134; ISBN 978-7-5019-5741-5.

[32] Ren, Z.; Li, X.; Liu, M.; Wang, H.; Wu, X. Modification of Crosslink NC by HTPE. (in Chinese) *Chin. J. Energ. Mater.* **2015**, *23*(7): 638-643.

[33] National Military Standard of P.R. China GJB 3204-1998. *General Specification for Army Nitrocotton.* **1998**, p. 3.

[34] He, M.; Zhang, H.; Chen, W. *Polymer Physics.* 3rd Ed., Fudan University Press, Shanghai, **2011**, pp. 160; ISBN: 978-7-309-05415/O·391.

[35] Sperling, L.H. *Introduction to Physical Polymer Science.* 4th Ed., John Wiley & Sons, Inc., Hoboken, **2005**, pp. 256-260; ISBN 978-0-471-70606-9.

[36] Strobl, G. *The Physics of Polymers.* 3rd Ed., Springer-Verlag, Berlin/Heidelberg, **2007**, pp. 165-173; ISBN 978-3-540-25278-8.

[37] Mo, Z.; Zhang, H. Measurement of Crystallinity of Polymers by X-ray Diffraction Method. *Polym. Mater.: Sci. Eng.* **1988**, *4*(3): 9-20.

[38] Zhang, W.; Chen J.-N.; Fan, H.-J. Combustion Characteristics of Smokeless XLDB Propellant at Low and High Pressure. (in Chinese) *Chin. J. Explos. Propellants* **2003**, *26*(4): 27-29.

[39] Shao, Z. *Structure and Properties of Nitrocellulose.* (in Chinese) National Defence Industry Press, Beijing, **2011**, pp. 189; ISBN 978-7-118-07426-0.

[40] Bai, S.B.; Liu, J.-L.; Wang, Q. Effect of PEO on Nonisothermal Crystallization of POM in POM/PEO Blends. *Polym. Mater. Sci. Eng.* **2007**, *23*(6): 136-139.

[41] Xu, B.; Man, J.; Wei, C. Methods for Determining Relative Crystallinity of Plant Starch X-ray Powder Diffraction Spectra. (in Chinese) *Chin. Bull. Bot.* **2012**, *47*(3): 278-285.

[42] Zhang, M.; Liu, B.; Gu, X. *Polymer Research Methods.* (in Chinese) China Light Industry Press, Beijing, **2011**, pp. 178-184; ISBN 978-7-5019-2626-8.