Original Article

Thermomechanical investigation on the effect of nitroguanidine on the thermal expansion coefficient and glass transition temperature of double-base gun propellant

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Glass transition temperature

Abstract

Thermal expansion coefficient (CTE) is a critical parameter of gun propellant because of its major role in fabrication, storage and combustion performance of the propellant. Further, controlling the CTE of the propellant is an effective solution to improve its loading density. Therefore, it is important to understand the thermal expansion of the propellant. To obtain the linear CTE of insensitive gun propellant, different weight percentages of NQ are added to the B# double-base absorbent propellant, the thermal mechanical analyzer (TMA) is employed to estimate their dimensional change over the temperature range of 213–323 K. The pure NQ flaky gun propellant exhibits a negative thermal expansion with a linear CTE of $-2.006 \times 10^{-4}$ mm/mm K$^{-1}$. The results show that the linear CTE of the B# double-base absorbent propellant is decreased by 53.74% as the concentration of NQ is increased to 30%, whereas the glass transition temperature increases with increasing the NQ content.

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1. Introduction

Nitroguanidine (NQ) is a standard energetic additive that has been widely used as propellant and explosive because of its capability to reduce the flame temperature without any adverse effect on the force constant [1,2]. Furthermore, it is less sensitive than other conventional insensitive high explosives such as N-guanyl urea dinitramide, 1,1-diamino-2,2-dinitroethylene and 1,3,5-triamino-2,4,6-trinitrobenzene [3]. Thermal expansion of the gun propellant is an important factor that significantly influences the molding process, deformation of ampoules, or even makes a disastrous excursion in the rigorous applications [4–9]. Earlier studies revealed that the energetic materials such as 2,6-Diamino-3,5-dinitropyrazine-1-oxide and 1,3,5-Trinitro-1,3,5-Triazacyclohexane exhibited a positive thermal coefficient along their α-, β-, and γ-axis [4,10]. Zhang et al. demonstrated that the NQ crystals exhibited an anisotropic thermal expansion coefficient with a negative CTE along β-axis using X-ray diffractometer (XRD) in the temperature range of 30–160 °C [11]. Although the thermal decomposition and thermal behavior of NQ-based gun propellant have been studied extensively [12–14], thermal expansion coefficient in view of their unique negative thermal coefficient is needed to be explored to be used as a gun propellant. This study investigates the influence of NQ on the linear thermal expansion coefficient of a double-base gun propellant. Generally, NQ exists in two forms such as acicular α form and long flaky β form whose decomposition temperatures are 187 and 205 °C, respectively [15]. As an additive and energetic material in the double-base gun propellant, NQ enhances its thermal stability while decreasing the mechanical sensitivity, thereby improves their energy performance [16]. Moreover, NQ has a low explosion temperature which can reduce the effect of smoke on gun chamber [17].

The thermal expansion coefficient (CTE) of metallic, non-metallic and organic compounds is mostly investigated using XRD and Rietveld refinement techniques [18–21]. Recently, our group obtained a reliable linear thermal expansion coefficient for the three-layered double-base gun propellant using the thermal mechanical analyzer [22]. The thermal analysis offers the advantages such as absolute determination of the thermal expansion coefficient, interpretation of glass transition temperature, reduced emission of gases, etc. over the XRD and Rietveld techniques [23,24]. There is a close relationship between CTE and glass transition temperature for the double-base gun propellant and hence it is important to study the glass transition temperature by measuring the CTE [25–30]. In this work, the linear thermal expansion coefficient of pure NQ propellants extruded at different pressures was obtained to understand their influences on the linear thermal expansion coefficient and glass transition temperature of the double-base gun propellant. The thermal mechanical analyzer was employed to calculate the linear thermal expansion coefficient by estimating the dimensional change in the temperature range between 213 and 323 K.

2. Experimental

2.1. Material

NQ (purity, 99%) was provided by the Institute of Chemical Material in China, B# double-base absorbent propellant (mass percentage of Nitrocellulose (NC): 64.4%, Nitroglycerin (NG): 34.6%, Dimethyl phenyl Urea (C2): 1.0%, nitrogen content is 13.0%) was received from North Xingan Chemical Industrial Company in China. The mean particle size was about 20 μm. The mixture of ethyl alcohol and acetone (1.0.9 v/v) was used as a solvent. The ethyl alcohol and acetone were supplied by Shanxi Jiangyang Chemical Industrial Company in China.

2.2. Sample preparation

2.2.1. Flaky sample with NQ only

Firstly, the as-obtained pulverous NQ was dried at 313 K for 24 h, followed by their extrusion as flaky sample using a powder tabling machine (769YP-15A, Tianjing KEQI Co., China). The flaky NQ samples obtained under the pressure of 0.1, 3 and 5 MPa, respectively were denoted as 0.1 NQ, 3 NQ, and 5 NQ, respectively. Finally, pure flaky NQ samples were dried at 303 K for 96 h.

2.2.2. Flaky gun propellant containing NQ

The B# double-base absorbent propellant and NQ were dried at 313 K for 24 h before being made into a paste. The pastes containing B# double-base absorbent propellant and NQ mixture in different mass ratios (10:0, 9:1, 8:2, 7:3) were blocked in the hydraulic machine and the flaky gun propellant was extruded under 8 MPa. The flaky gun propellant was cut into a suitable length and dried by blowing hot air at 303 K for 96 h. The content of NQ in flaky gun propellant was 0, 10, 20, and 30% were denoted as 0 NQ, 10% NQ, 20% NQ, 30% NQ, respectively.

2.3. Measurement of linear CTE

The thermal expansion coefficient of the sample was measured by TMA-Q 400 (TA instrument, USA) with a 5 K/min heating (cooling) rate under a dry nitrogen atmosphere over the temperature range from 213 to 323 K, and the initial thickness was measured at 293 K. The linear CTE can be expressed as Eq. (1) [22];

$$\alpha = \frac{\Delta L}{L_0(T_2 - T_1)} = \frac{\Delta L}{L_1 \cdot \Delta T}$$  \hspace{1cm} (1)

where \(\alpha\), \(\Delta L\), \(L_0\), \(\Delta T\) are the linear CTE, dimensional change, original length of the material, and corresponding temperature change, respectively. The samples were smooth flaky shaped cuboid of dimensions, 5 mm in length and width, and 0.1–1 mm in thickness.

2.4. Scanning electron microscope (SEM)

Morphological studies were carried out using a Scanning electron microscope (VHX-2000; Keyence Company, China).
Fig. 1 – (a, b) SEM image of pure NQ flake compacted under the pressure of 0.1 MPa (0.1 NQ).

Fig. 2 – (a) SEM and (b) 3D image of pure NQ flake compacted under the pressure of 3 MPa (3 NQ).

Fig. 3 – (a) SEM and (b) 3D image of pure NQ flake compacted under the pressure of 5 MPa (5 NQ).

3. Results and discussion

3.1. Scanning electron microscope (SEM) analysis

Morphological studies were carried out by using SEM to confirm the flaky structures of the prepared NQ samples. Fig. 1a, b shows the structure of pure NQ flakes obtained under a low pressure of 0.1 Mpa (0.1 NQ). It can be observed that the flakes are loosely packed and have numerous voids (or) space between them. In contrast, pure NQ flakes compressed under a pressure of 3 MPa (3 NQ) and 5 MPa (5 NQ) show no voids (or) space between them (Figs. 2a and 3a). It also clearly depicts that pure NQ flakes obtained under different pressures possess the same acicular structure, indicating that the high-pressure changes the density of samples without affecting the structure of NQ.

From the 3D images of 3 NQ (Fig. 2b) and 5 NQ (Fig. 3b), the thickness of both the samples is found to be about 100 μm. This indicates that the increasing pressure has a less pronounced effect on the thickness of samples. It can also be observed that pure NQ flaky sample is close-grained under 3 MPa. The surfaces of 3 NQ sample and 5 NQ sample are smooth and flat, and hence suitable for TMA.

3.2. The linear CTE for the flaky NQ samples compacted under different pressures

The thermal expansion curves and their linear fitting curves of pure NQ samples compacted under three different pressures (0.1 MPa (0.1 NQ), 3 MPa (3 NQ) and 5 MPa (5 NQ)) are shown in Fig. 4a–c, respectively and their corresponding values are given in Table 1. It can be found that the linear correlation...
Fig. 4 – Thermal expansion curves and linear fitting curves of pure NQ samples compacted under the pressure of (a) 0.1 MPa (0.1NQ), (b) 3 MPa (3 NQ) and (c) 5 MPa (5 NQ).

<table>
<thead>
<tr>
<th>Samples label</th>
<th>Mean thickness l_0/mm</th>
<th>Linear correlation R</th>
<th>Thermal expansion coefficient (the mean value) α/10^-4 mm/mm K^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating up curves of 0.1 NQ</td>
<td>0.1456</td>
<td>0.99921</td>
<td>-1.501371</td>
</tr>
<tr>
<td>Cooling curves of 0.1 NQ</td>
<td>0.1448</td>
<td>0.99383</td>
<td>-1.466850</td>
</tr>
<tr>
<td>Heating up curves of 3 NQ</td>
<td>0.2239</td>
<td>0.99903</td>
<td>-1.956230</td>
</tr>
<tr>
<td>Cooling curves of 3 NQ</td>
<td>0.2275</td>
<td>0.99710</td>
<td>-2.066811</td>
</tr>
<tr>
<td>Heating up curves of 5 NQ</td>
<td>0.2244</td>
<td>0.99644</td>
<td>-2.071299</td>
</tr>
<tr>
<td>Cooling curves of 5 NQ</td>
<td>0.2240</td>
<td>0.99871</td>
<td>-1.939731</td>
</tr>
</tbody>
</table>

The coefficient of the fitted straight line is greater than 0.99, which indicates that all the three samples follow a linear law in the temperature range from 213 to 318 K. As shown in Fig. 4a–c, the thermal expansion curves of 0.1 NQ, 3 NQ and 5 NQ show a downward trend, and the curves are an almost straight line in the temperature range from 213 to 353 K. The negative thermal expansion and the linear CTE of 0.1 NQ are found to be $-1.501 \times 10^{-4}$ mm/mm K$^{-1}$ and $-1.467 \times 10^{-4}$ mm/mm K$^{-1}$, respectively. It can be observed that the linear CTEs are nearly the same for both heating and cooling curves in the measured temperature range.

The mean value of linear CTE of 3 NQ is $-1.956 \times 10^{-4}$ mm/mm K$^{-1}$ and $-2.067 \times 10^{-4}$ mm/mm K$^{-1}$ for heating and cooling process, respectively. The higher linear CTE of 0.1 NQ than that of 3 NQ is due to the presence of voids and can be explained using the Gay-Lussac’s law as follows. The law states that at a constant pressure, the volume of a certain mass of gas is proportional to the thermodynamic temperature. The linear CTE of air is $0.114 \times 10^{-2}$ mm/mm K$^{-1}$ at 293.15 K, which is higher than that of the linear CTE of 0.1 NQ. As the 0.1 NQ sample contains many voids and space (Fig. 1a, b), the CTE of air contributes significantly to the increase of its linear CTE. However, the result clearly indicates that 0.1 NQ sample with a linear CTE shows a negative thermal expansion. In the test of 0.1 NQ samples, the negative thermal expansion could also be caused by the pressure of the probe. The structure of 0.1 NQ samples is loose and there is a chance for the probe to press the 0.1 NQ sample. Therefore, it is needed to make sure that pure NQ flaky is compacted. 3D image of 3 NQ sample in Fig. 2b shows that the mean thickness of 3 NQ samples is greater than 0.1963 mm, which is nearly equal to the mean thickness of test samples. This further confirms that the 3 NQ samples have no void (or) space in it, as depicted in Fig. 2a.

Further, the thermal expansion behavior of the 5 NQ sample was investigated to understand the effect of extruding
pressure on the linear CTE of the NQ flakes. The mean value of linear CTE of 5 NQ is $-2.071 \times 10^{-3}$ mm/mm K$^{-1}$ and $-1.940 \times 10^{-4}$ mm/mm K$^{-1}$ for heating and cooling process, respectively. The mean linear CTE of 5 NQ samples is nearly the same as that of 3 NQ samples. This result signifies that an increase in the extruded pressure beyond 3 MPa has less effect on the linear CTE of test samples. From the above test results, it is found that the linear CTE of pure NQ flaky sample is negative in the temperature range of 213–323 K, and the linear CTE of pure NQ flaky sample is about $-2.006 \times 10^{-4}$ mm/mm K$^{-1}$ (the mean value of 5 NQ samples).

3.3. **The mechanism for negative thermal expansion of NQ**

The negative thermal expansion of pure NQ flaky samples can be attributed to the molecular packing of NQ. In a NQ molecule, a single carbon atom is bonded with three nitrogen atoms by the conjugate effect. The presence of strong hydrogen bond acceptors (amino groups) and strong hydrogen bond donors (nitro groups) contributes the formation of strong hydrogen bond networks easily and thus the molecules of NQ are packed in the two-dimensional layers by the intermolecular hydrogen bonding (Fig. 5). With an increase in the temperature, the space hindrance between the layers will be decreased because of the hydrogen bond relaxing and hence the perpendicular distance between the layers gets decreased. In addition, the wrinkles caused by the lateral thermal vibrations (known as the tension effect) at a higher temperature also contribute to the decrease in the distance perpendicular to the wrinkling direction (Fig. 6) [11,31–33]. The decrease in the perpendicular distance is observed to result in a negative thermal expansion, macroscopically.

3.4. **The linear CTE for the B# double-base gun propellant containing different weight percentages of NQ**

Fig. 7 shows the thermal expansion curves of the B# double-base gun propellant containing different weight percentages of NQ and their corresponding glass transition temperature ($T_g$). The thermal expansion curves of double-base propellant are different from other solid materials. There are obviously two stages in its thermal expansion curves. In the first stage (about 243 to 300 K), the dimension increases with increasing the temperature, whereas, in the second stage (about 300 K above), the dimension decreases with increasing the temperature. In the second stage, the double-base propellant will turn soft with the rise in temperature and the probe gets

**Fig. 5** – Geometric representation of molecular packing in NQ.

**Fig. 6** – Schematic illustration representing the mechanism of negative thermal expansion in NQ.

**Fig. 7** – Thermal expansion curves and glass transition temperature for B# double-base gun propellant containing different weight percentages of NQ.
pressed into the material. Hence, there is a negative dimension in the curves. The point of intersection of the rising and declining curve denotes the glass transition temperature of double-base propellant. Thus, the glass transition temperature of double-base propellant reflects its soft temperature. It is being observed that the glass transition temperature of the B# double-base gun propellant increases with the increase in the weight percentage of NQ (Fig. 7). This implies that the addition of NQ provides the sample materials with a better linear CTE. The glass transition temperature of the NQ added double-base propellant is 5–10 K higher than that of pure double-base propellant. This phenomenon can be explained by the Free Volume theory proposed by Fox and Flory.

The Free Volume theory states that there are two parts in the macroscopic volume constituents. One is the molecules and the other is the voids created during the formation of molecules. The free volume gives space for the molecular rearrangement and movement. In the glassy state, the movement of molecules is frozen. Upon increasing the temperature, the amplitude of molecular vibration and bond length increases and further the frozen state is converted to the movement state beyond Tg. However, the molecules and voids of NQ shrink with the increase in temperature because of its negative linear CTE. So, there is less space for molecular movement or in other words, the system needs a higher temperature (high glass transition temperature) to get into a high elastic state. According to Free-Volume Theory, at T = Tg, the free volume Vf at Tg can be expressed as Eq. (2):

\[ V_{Tg} = V_f^g + V_0 + \left( \frac{dV}{dT} \right)_g T_g + V_f^g \]  

(2)

When T > Tg, the free volume Vr can be expressed as Eq. (3):

\[ V_r = V_{Tg} + \left( \frac{dV}{dT} \right)_r (T - T_g) \]  

(3)

The free volume at a high elastic temperature (T) can be written as Eq. (4):

\[ V_f^T = V_f^g + \left( \frac{dV}{dT} \right)_r (T - T_g) \]  

(4)

When T ≥ Tg, Vr = Vf(Tg), fr can be expressed as Eq. (5):

\[ f_r = \frac{V_f^T}{V_r} \approx \frac{V_f^T}{V_{Tg}} = V_f^g + \left( \frac{dV}{dT} \right)_r - \left( \frac{dV}{dT} \right)_g \right] (T - T_g) \]  

(5)

\[ f_r = f_{Tg} + \frac{1}{V_{Tg}} \left[ \frac{dV}{dT} \right]_r - \left( \frac{dV}{dT} \right)_g \right] (T - T_g) \]  

The thermal expansion coefficient of free volume is shown as Eq. (6):

\[ \alpha_f = \alpha_r - \alpha_g = \frac{1}{V_{Tg}} \left[ \frac{dV}{dT} \right]_r - \left( \frac{dV}{dT} \right)_g \]  

(6)

Therefore, the free volume fraction (fr) at a high elastic temperature can be written as Eq. (7):

\[ f_r = f_{Tg} + \alpha_f (T - T_g) \]  

(7)

From Eq. (2), it can be concluded that the free volume (fr) increases with increasing the temperature above the glass transition temperature (Tg). This increase in the free volume reduces the strength of the sample, resulting in a decreasing tendency toward deformation. The transition from the glassy state to a high elastic state occurs with a change in the shape variable and it is between 5% and 10% for the NQ samples.

The thermal expansion curves and linear curves for the B# double-base propellant containing different weight percentages of NQ are shown in Fig. 8 and the corresponding parameters are given in Table 2. The linear CTE of the double-base gun propellant (0 NQ) is found to be 2.864 × 10^{-4} mm/mm K^{-1}. Upon addition of NQ, the linear CTE is decreased and reduced by about 53.74% (1.325 × 10^{-4} mm/mm K^{-1}) at 30% of NQ. This phenomenon

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**Table 2 – Calculated linear CTE for B# double-base gun propellant containing different weight percentages of NQ.**

<table>
<thead>
<tr>
<th>Samples label (5 samples in each group)</th>
<th>Mean thickness L0/mm</th>
<th>Linear correlation R</th>
<th>Thermal expansion coefficient (the mean value) α/10^{-4} mm/mm K^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 NQ sample</td>
<td>0.9174</td>
<td>0.99782</td>
<td>2.864398</td>
</tr>
<tr>
<td>10% NQ sample</td>
<td>1.0032</td>
<td>0.99775</td>
<td>2.180819</td>
</tr>
<tr>
<td>20% NQ sample</td>
<td>0.9378</td>
<td>0.99712</td>
<td>1.504584</td>
</tr>
<tr>
<td>30% NQ sample</td>
<td>0.9197</td>
<td>0.99358</td>
<td>1.324997</td>
</tr>
</tbody>
</table>
can be attributed to the lower linear CTE of NQ compared to that of the flaky B# double-base gun propellant.

### 4. Conclusions

The linear CTE curves of pure NQ propellant and the B# double-base propellant containing different weight percentages of NQ was studied by TMA measurement. It was found that pure NQ flakes exhibited a negative thermal expansion with a linear CTE of about $-2.071 \times 10^{-5}$ mm/mK$^{-1}$ for the samples obtained under the pressure of 5 MPa. The main reason for the negative thermal expansion is the lateral thermal vibration in the layers of NQ molecule, which decreases the distance between NQ layers, so pure NQ propellant shows a negative thermal expansion. The thermal expansion coefficient of B# double-base gun propellant is decreased, whereas its glass transition temperature is increased with an increase in the weight percentage of NQ. This was attributed to the negative thermal coefficient of the pure NQ flakes. These results revealed that the addition of NQ enhances the energy property and decreases the sensitivity of the B# double-base gun propellant. Thus, this study significantly contributes to a better understanding of physical properties and their influence on the design of double-base gun propellant and other products to be made of polymers [34–41], metals [42–46], ceramics [47–58], carbon [59–63] and their composites [64–72].

### Conflicts of interest

The authors declare no conflict of interest.

### References


