

## Research progress in thermal expansion characteristics of TATB based polymer bonded explosives

Cong-mei Lin<sup>a,\*\*</sup>, Liang-fei Bai<sup>b</sup>, Zhi-jian Yang<sup>a</sup>, Fei-yan Gong<sup>a</sup>, Yu-shi Wen<sup>a,\*</sup>

<sup>a</sup> Institute of Chemical Materials, CAEP, Mianyang, 621999, China

<sup>b</sup> Institute of Nuclear Physics and Chemistry and Key Laboratory of Neutron Physics, CAEP, Mianyang, 621999, China

### ARTICLE INFO

#### Keywords:

TATB  
Irreversible thermal expansion  
Shape stability  
Structural evolution  
Suppression methods

### ABSTRACT

Under complex temperature variations, the irreversible thermal expansion of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) based polymer bonded explosives (PBXs) results in decreased shape stability, directly impacting mechanical properties, safety performance during storage and use. In recent years, extensive and thorough researches have seen carried out on the thermal expansion characteristics of TATB based explosives. This paper summarizes the thermal expansion characteristics of TATB based PBXs, the influencing factors, as well as their suppression methods. Starting with the distinctive crystal structure of TATB, the thermal expansion mechanism of TATB based PBXs is introduced, the microstructural evolution during the thermal expansion process is summarized, and the effects of thermal expansion on comprehensive performance are analyzed. More attention to the influencing factors of thermal expansion and control methods are paid. Existing challenges are summarized with the recommendation for further exploration into the irreversible expansion mechanism of TATB based PBXs. It points out several key directions for future development: design and control of TATB crystal structure, construction and development of novel composites with integrated structural-functional properties, as well as the application of negative thermal expansion functional materials.

### 1. Introduction

1,3,5-Trinitro-2,4,6-triaminobenzene (TATB) is currently the only single-component explosive that meets the U.S. Insensitive high explosive (IHE) standard. It demonstrates significant insensitivity to external stimuli, such as light, heat, static electricity, shock waves, mechanical friction, and impact, making it an excellent high-energy explosive with superior comprehensive properties.<sup>1–4</sup> In recent years, TATB based polymer bonded explosives (PBXs), such as the formulations LX-17 (92.5% TATB/7.5% Kel-F800) and PBX 9502 (95% TATB/5% Kel-F800) developed by Lawrence Livermore National Laboratory (LLNL) and Los Alamos National Laboratory (LANL), respectively, have been widely applied in the main charge of strategic weapons.<sup>5</sup>

During processing, assembly, transportation, and usage, TATB based PBXs may be subjected to varying environmental temperatures and thermal stresses, including fluctuations from seasonal changes and diurnal shifts in desert climates. Compared with cubic structured explosive crystals like octogen (HMX) and cyclotrimethylenetrinitramine (RDX), TATB crystals present a planar layered  $\pi$ -stacked structure. This

unique anisotropy gives rise to distinctive irreversible thermal expansion phenomena.<sup>6,7</sup> Under the effect of temperature change, the irreversible thermal expansion of TATB based PBX leads to a decrease in material dimension accuracy, consequently affecting the mechanical and safety performance of the explosives. It has become an important issue of concern in weapons system design.

For decades, extensive researches have been carried out domestically and internationally on the thermal expansion characteristics, mechanisms, structural evolution, influences on usability, influencing factors, and control methods of TATB based PBX. This paper reviews the recent progress in the research of thermal expansion characteristics of TATB based PBX, starting from the crystal structure characteristics of TATB. The mechanism of thermal expansion, the microstructural evolution of during thermal expansion, the influences of thermal expansion on comprehensive performance, the influencing factors of thermal expansion and its control methods were summarized. The objective is to provide insights and technical pathways for the design of high shape-stability PBX.

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [linmei2009@caep.cn](mailto:linmei2009@caep.cn) (C.-m. Lin), [wenys@caep.cn](mailto:wenys@caep.cn) (Y.-s. Wen).

<https://doi.org/10.1016/j.enmf.2023.09.003>

Received 3 June 2023; Received in revised form 14 August 2023; Accepted 14 September 2023

Available online 16 September 2023

2666-6472/© 2023 The Authors. Publishing services by Elsevier B.V. on behalf of KeAi Communications Co. Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

## 2. Irreversible thermal expansion characteristics and its mechanism

### 2.1. Crystal structure and its fundamental influence on irreversible thermal expansion

TATB molecules possess a planar structure, as shown in Fig. 1a.<sup>8</sup> Based on the benzene ring structure, TATB molecules exhibit conjugation characteristics. On one hand, it enhances the stability of the TATB molecule. On the other hand, it allows electrons on the benzene ring to readily delocalize, forming large  $\pi$  bonds. This leads to the formation of  $\pi$ - $\pi$  interactions within TATB crystals, enhancing the stability of the TATB crystal structure.

TATB crystals are in the triclinic system<sup>8</sup> with group [P-1], whose cell parameters are shown in Table 1.<sup>9</sup> A TATB unit cell contains two molecules, totaling 48 atoms and a  $2 \times 2 \times 3$  TATB supercell is shown in Fig. 1b. TATB forms graphite-like layers due to  $\pi$ - $\pi$  interactions, hydrogen bonding, and van der Waals forces. Amino and nitro groups facilitate strong N-H...O hydrogen bonds between TATB molecules in the same layer, ensuring tight bonding. Between layers, TATB has mainly weak  $\pi$ - $\pi$  and van der Waals interactions. This causes TATB's interlayer slippage and higher thermal expansion. Its structure and interactions promote lamellar crystal formation during crystallization.<sup>10,11</sup> TATB's stable structure, hydrogen bonds, and  $\pi$ - $\pi$  interactions enhance its chemical stability and safety, when its planar layered structure causes its significant thermal expansion anisotropy and other directional property differences.<sup>12</sup>

TATB molecules exhibit a planar structure, forming  $\pi$ - $\pi$  interactions within their benzene ring structures. This characteristic not only guarantees the stability of TATB molecules and their crystalline structures but also leads to a high degree of thermal expansion anisotropy in TATB. Structurally, TATB crystals adopt a graphite-like layered architecture, sustained by potent N-H...O hydrogen bonds alongside weaker  $\pi$ - $\pi$  and van der Waals interactions. This arrangement ensures tight bonding between molecules within the same layer while relying mainly on weaker interactions to maintain structure between different layers. Consequently, during thermal cycling, the significant disparity in the interaction forces within and between the layers of TATB crystals makes them prone to uneven expansion and contraction, coupled with interlayer slippage, resulting in irreversible thermal expansion.

### 2.2. Irreversible thermal expansion characteristics and their microscopic mechanisms

Heat motion is a macroscopic manifestation of the disorderly motion of microscopic particles. Under a certain heat action, all parts within the crystal have the same outward diffusive power, leading to a statistical tendency to move away from each other. In other words, thermal expansion is the result of increase in the thermal vibrational amplitudes of molecules which leads to an 'outward pressure'. Generally, thermal

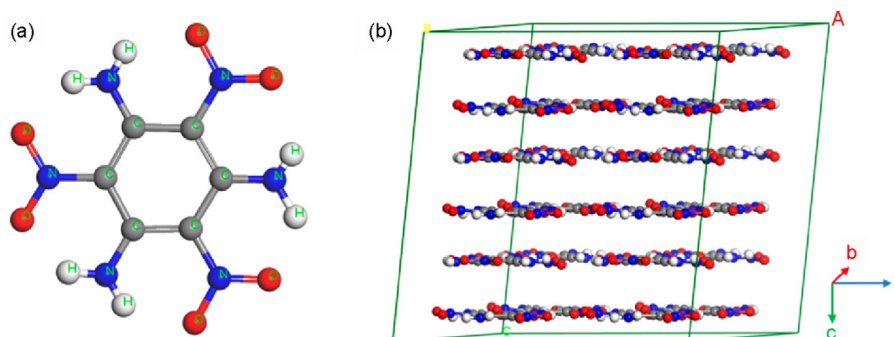
**Table 1**  
Lattice parameters of TATB.<sup>9</sup>

Crystals	Expt (Room-temperature)
Crystal system	Triclinic
Space group	P-1
$a / \text{\AA}$	9.01
$b / \text{\AA}$	9.028
$c / \text{\AA}$	6.812
$\alpha / (^\circ)$	108.580
$\beta / (^\circ)$	91.820
$\gamma / (^\circ)$	119.970
$V_0 / \text{\AA}^3$	442.524
$\rho / \text{g}\cdot\text{cm}^{-3}$	1.9374

expansion is stabilized by entropic contributions and therefore (within DFT framework) cannot lead to a more stable structure unless a phase transformation is observed to change the local enthalpic minimum. While thermal expansion is a ubiquitous phenomenon for materials, irreversible thermal expansion remains a rather distinctive occurrence, closely associated with the material's structural attributes. For instance, one prevailing theory posits that irreversible expansion might be related to the unique structure of graphene-like materials. The unique graphene-like layer stacking crystal structure of TATB leads to a much higher coefficient of thermal expansion (CTE) for the  $c$  axis when heated, compared with that of  $a$  and  $b$  axes.<sup>6,13,14</sup> The averaged coefficients of thermal expansion for  $a$ -axis,  $b$ -axis and  $c$ -axis are  $1.04 \times 10^{-5}/^\circ\text{C}$ ,  $0.98 \times 10^{-5}/^\circ\text{C}$  and  $16.9 \times 10^{-5}/^\circ\text{C}$ ,<sup>14</sup> respectively. Thus, the thermal expansion coefficient of  $c$ -axis is about 17 times of that of  $a$ -axis and  $b$ -axis, indicating obvious anisotropic expansion of TATB crystals, as shown in Fig. 2. In the  $a$ - and  $b$ -axes within the layer, the strong hydrogen bond network restricts the movement of TATB molecules away from each other, thus greatly limiting the CTE. Whereas between different layers, the  $\pi$ - $\pi$  interactions and van der Waals forces acting on TATB molecules are relatively weak, offering limited restriction on the disorderly movement, resulting in a relatively larger CTE of  $c$  axis.<sup>14</sup>

It has been found that TATB single crystals do not undergo irreversible expansion at the molecular level, but pure TATB and PBX 9502 demonstrate typical irreversible thermal expansion behavior, as shown in Fig. 2b. Irreversible expansion refers to the phenomenon of significant growth in the size of TATB based PBXs after temperature cycling, also known as ratcheting growth, as shown in Fig. 3<sup>15-16</sup>. Under heat cycling, TATB based PBXs experience irreversible size growth. As the number of cycling increases, the size of the PBXs first increases significantly, then the growth rate decreases, and finally stabilizes. Rizzo et al.<sup>17</sup> pointed out that high-density pure TATB and its PBX produce 1.5–2.0 vol% irreversible volume expansion after multiple heat cycles at  $-54$ – $74$  °C. Mulford et al.<sup>18</sup> found that the average irreversible volume expansion of PBX 9502 was 3.24 vol% after at least five heat cycles (from room temperature to over 200 °C).

Regarding the mechanism of irreversible expansion of TATB and its PBX cylinder, various assumptions have been put forward: (1)



**Fig. 1.** Structural characteristics of TATB explosive: (a) TATB molecular structure; (b) TATB crystal layered structure.

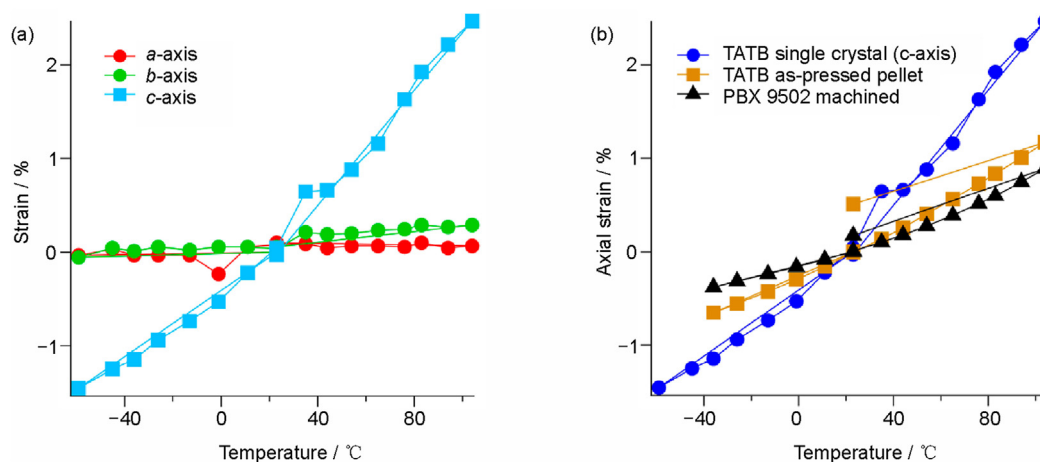


Fig. 2. (a) Strain versus temperature curves of TATB single-crystals measured at various temperatures between  $-59$  and  $104$  °C for the  $a$ ,  $b$ , and  $c$  axes; (b) Single-crystal  $c$ -plane measurements compared to axial growth (predominately  $c$ -plane orientation) of neat TATB and PBX 9502.<sup>6</sup>

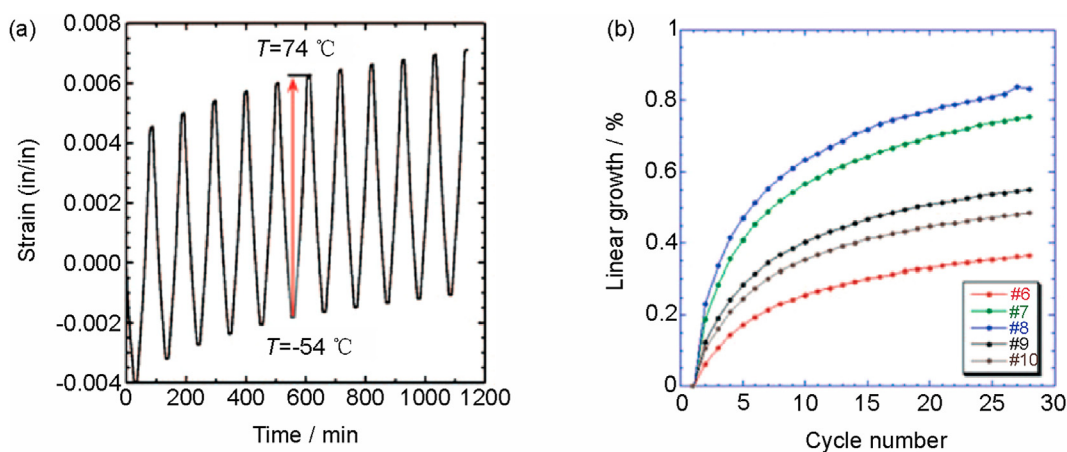


Fig. 3. Irreversible growth of polymer-bound TATB powder upon repeated thermal cycling between  $-54$  and  $74$  °C for five different cylindrical samples cut (at different angles) out from the same TATB billet: (a) Plot for one of the samples showing length variation within each thermal cycle; (b) Room-temperature length for all five samples within each thermal cycle.<sup>15</sup>

anisotropic thermal expansion of TATB crystals during the thermal expansion process generates internal stress, leading to crystal fracture<sup>13</sup>; (2) graphite-like structure characteristics of TATB crystals,<sup>19</sup> for example, graphite and boron nitride (BN) materials also show similar ratcheting growth behaviors<sup>20,21</sup>; (3) new loose structures, voids, and cracks are generated between TATB in the cylinder<sup>14,22</sup>; (4) the plasticity of the binder and the detachment and cracking of the interface due to stress concentration.<sup>23</sup> Although numerous mechanisms have been proposed to date, there remains controversy among these theories, and a consensus has not been reached. Further research and exploration are required.

### 2.3. Theoretical simulation for the analysis of irreversible thermal expansion mechanisms

Ji et al.,<sup>24</sup> employing periodic density functional theory methods, observed hydrogen bonds within TATB crystal layers and larger distances between layers connected by weak van der Waals forces. Electrons within the same layer are highly delocalized with limited inter-layer interaction. This accounts for the observed anisotropy and irreversible TATB expansion along the  $c$ -axis after heat cycling. Analyzing TATB crystal structure reveals that anisotropy in thermal expansion stems from molecular layer stacking. Due to weak interlayer interactions, the  $c$ -axis has a high thermal expansion coefficient. The  $a$ - $b$  plane, defined by  $a$  and  $b$  axes, has numerous hydrogen bonds limiting its expansion, resulting in lower coefficients for both axes. Zhang et al.<sup>25</sup> theorized on the

irreversible expansion of TATB crystals, suggesting they typically exist in a high potential energy state. Temperature shifts reduce potential energy through size increase, stabilizing the system. This elucidates the irreversible growth of heated TATB-based PBX. Cunningham et al.<sup>26</sup> attribute the irreversible growth of TATB to its anisotropic expansion. Gee et al.<sup>15,27,28</sup> employed mesoscopic simulations to study TATB's irreversible expansion. Their findings indicate that TATB's irreversible expansion results from crystal breakage during heating and cooling. The DPD model examined TATB crystal structural changes, depicted in Fig. 4. They observed that specific thermal stimuli break TATB crystals, causing irreversible expansion, with reversible expansion only at the mesoscale. Their detailed analysis revealed that micron-sized TATB powder underwent irreversible volume growth during heating and cooling cycles. They used the mesoscale DPD Hamiltonian simulation to replicate powder materials' irreversible growth quantitatively. Their study confirmed that irreversible growth happens with intrinsic crystal anisotropy and is driven by particles smaller than average microcrystals.

Schwarz et al.<sup>29</sup> investigated the irreversible growth of TATB and PBX 9502 explosives under temperature cycling, introducing a model for internal stress in TATB polycrystals to explain this growth. The model links irreversible growth to cracks from internal stress during thermal cycling and accurately captures the growth in TATB and PBX 9502. Yet, the model doesn't consider the polymer binder's role or crystal orientation's influence. Future studies should delve into the polymer binder and orientation to better understand irreversible growth. Ritter et al.<sup>30</sup> noted



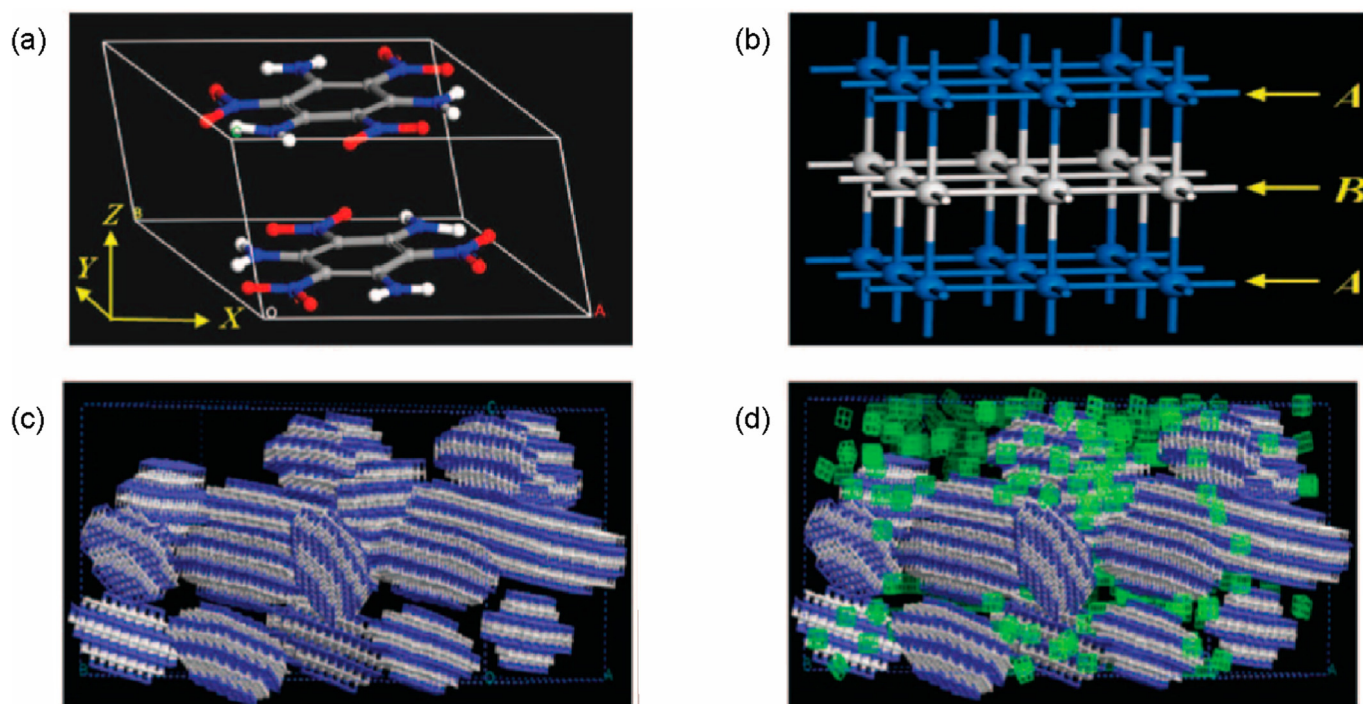


Fig. 4. (a) Experimental crystal structure of TATB. There are two molecules in each unit cell. Spatially extended models reveal a layered structure, with layers parallel to the plane of the aromatic rings. Color scheme: C (gray), N (blue), O (red), and H (white). (b) An equivalent crystal of “mesobeams,” with alternating planes of A and B beads parallel to the XY planes of (a). (c) An ensemble of large TATB particles, each shaped according to its equilibrium morphology. (d) Packing of small TATB particles (cubes) within interparticle voids of (c).<sup>15</sup>

that thermal cycling reduces TATB's density, creating more voids that might become detonation hotspots, amplifying shock wave sensitivity. Wang et al.<sup>23</sup> tackled the irreversible deformation in PBX 9502 from thermal cycling, accounting for TATB grain anisotropy and grain/binder thermodynamic differences. They employed a three-phase microstructure model and XFEM for their simulations. During thermal cycling, they observed misaligned deformations and stress concentrations causing damage like binder breakage and grain-binder detachment (Fig. 5), resulting in irreversible deformation.

Lei et al.<sup>31</sup> detailed the PBX's irreversible strain from  $-30\sim 60$  °C thermal cycling using the Gurson-Tvergaard-Needieman (GTN) model. By fine-tuning the yield strength, hardening index, and GTN parameters, the model quantifies PBX's irreversible expansion under thermal cycling. Buechler et al.<sup>32</sup> researched how TATB structure impacts PBX 9502 pressing outcomes using modeling. They formulated a component-level model for compressing TATB powder into explosives, which predicts explosive deformation during pressing.

Luscher et al.<sup>33,34</sup> developed an algorithm rooted in March (1932)

theory to generate discrete crystal orientations for any deformation history. This algorithm simulates the anisotropic thermal expansion of polycrystalline TATB explosives. Using this method, the relationship between TATB's thermal expansion and microstructure was studied, and a model was created that factors in particle aspect ratio, porosity, and texture, linking discrete orientation to macroscopic expansion. The results reveal that porosity and particle aspect ratio influence TATB's thermal expansion; preferred crystal orientation causes anisotropy; and predicted textures, strains, and temperature distribution align with experiments. This method has practical value in integrating microstructures into macro models. Future research will study polymer binders' impact on TATB and asymmetric slip to understand polycrystalline growth during thermal cycles.

This section extensively delineates the theoretical simulation studies undertaken by various research groups on the irreversible thermal expansion and its mechanisms in TATB and PBX 9502. Ji et al. utilized periodic density functional theory and mesoscopic simulations to unravel the structural characteristics of TATB crystals, precipitating observed

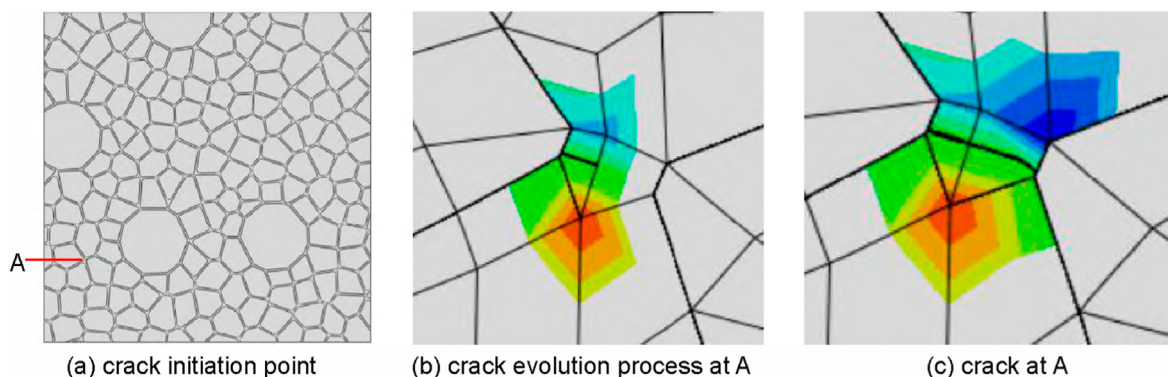


Fig. 5. Numerical simulation of crack initiation and evolution in PBX 9502 thermal cycle process.<sup>23</sup>

anisotropy and irreversible expansion along the c-axis. Other researchers have examined the relationship between internal stresses and crack initiation during thermal cycling, although these studies have elucidated valuable insights, they also reveal the restrictions of the current theoretical models, which insufficiently consider the role of polymer adhesives and crystal orientation. This signals the necessity for future investigations to delve deeper into these aspects for a better understanding of irreversible growth, as well as the impact of thermal cycling on the density and shock sensitivity of TATB. The research presented herein underlines the importance of augmenting theoretical and simulation studies, necessitating interdisciplinary approaches and innovative models to surpass existing limitations and spearhead advancements in this field.

#### 2.4. Microstructural evolution and its role in irreversible thermal expansion mechanisms

At the macroscopic level, the apparent volume of TATB based PBXs undergoes thermal expansion and irreversible growth with temperature variation. At the microscopic level, on one hand, TATB crystals and polymer binders undergo intrinsic thermal expansion at the atomic, molecular, and crystal or aggregated structural levels, mainly manifested as the evolution of TATB lattice parameters and the morphology of the binder polymer with temperature.<sup>22,35</sup> On the other hand, some TATB grains may experience fracture, bending, straightening, displacement, and stacking rearrangement, due to thermal stress.<sup>7</sup> Some binders may soften and flow, causing their redistribution between TATB grains and on their surface. Interfacial debonding may also be caused by thermal stress.<sup>35</sup> These phenomena mainly manifest as the evolution of micro and mesoscale pore and interfacial structures with temperature.<sup>35–38</sup> This is also one of the direct causes of irreversible growth of TATB based PBX under temperature cycling.

Small angle scattering (SAS) technology is highly sensitive to the evolution of micropores, making it a powerful tool for revealing irreversible thermal expansion behaviors.<sup>39</sup> Similar to other composite explosives,<sup>40</sup> the pore structure within TATB based PBX is extremely complex.<sup>36,41</sup> Consequently, the study of the evolution of the pore structure in TATB based PBXs is closely related to the theoretical models and characterization methods used. Most of the reported literature<sup>21,35,37,38</sup> employs the isolated spherical pore model, and a series of studies based on SAS characterization methods have presented the evolution of pore size distribution and content in TATB based PBXs with temperature cycles.

TATB-based PBXs show significant pore structure changes under temperature cycling from  $-54^{\circ}\text{C}$  to  $74^{\circ}\text{C}$ , leading to a notable increase in pore sizes within 10 nm–20  $\mu\text{m}$ . Studies on samples from LX-17, PBX 9502, and isotropically pressed PBX 9502 systems confirm this, as seen in Table 2. Willey et al.<sup>38</sup> employed USAXS and a data fitting method to analyze pore structure changes in LX-17 and PBX-9502 samples after 12 temperature cycles. After cycling, pores within 2–10 nm (from intra-TATB grains) in TATB-based PBXs stay consistent, but those between 10 and 1000  $\mu\text{m}$  (inter-TATB grains) grow and become more numerous. Pore content detected by USAXS in LX-17 and PBX-9502

surged by roughly 60%, from initial 1.5–1.6% to 2.4–2.5%. This suggests thermal cycling enlarges pores beyond the USAXS detection limit (over 2.5  $\mu\text{m}$ ). Willey et al.<sup>36,37</sup> used USAXS, USANS, and X-ray imaging to analyze LX-17 samples pre and post-thermal cycling, shown in Fig. 6. Results show thermal cycling boosts pore content between 1  $\mu\text{m}$  to tens of micrometers. Damage from these larger pores, detectable by CT, mainly surfaces in the mold powder's center where TATB is concentrated. Thompson et al.,<sup>20</sup> using USANS, found 30 thermal cycles between  $-65^{\circ}\text{C}$  and  $85^{\circ}\text{C}$  made pores in PBX 9502 samples larger and more numerous. Pore content in the 0.1–10  $\mu\text{m}$  range rose from 2.3% to 3.1%. Hence, thermal cycling might produce a more interconnected pore structure in TATB-based PBXs.

The pore structure of TATB based PBXs exhibits another characteristic during thermal cycling: the evolution of the microstructure with temperature is significantly affected the range of the cold-hot cycling temperature zone,<sup>35</sup> the order of the alternation of the cold-hot cycling temperature zone (thermal history),<sup>7</sup> the glass transition temperature of the binder,<sup>35</sup> and the adhesive characteristics of the interface between the binder and TATB crystals.<sup>35,42</sup> Willey et al.<sup>35</sup> applied in situ temperature-variable USAXS to comparatively study the in situ evolution of the small angle scattering signal during the alternating temperature cycling process between  $-55$  and  $70^{\circ}\text{C}$  in four TATB/fluoroelastomer formulas (Kel-F 800, Cytop M, Cytop A, and Hyflon AD60). During the thermal cycle, the pore changes in the LX-17 sample mainly occurred during the heating and cooling cycle from  $20^{\circ}\text{C}$  to  $70^{\circ}\text{C}$  and then back to  $20^{\circ}\text{C}$ , while the changes in the small angle scattering signal during the cycle from  $20^{\circ}\text{C}$  to  $-55^{\circ}\text{C}$  and back to  $20^{\circ}\text{C}$  were not significant. This suggests that pore changes in the LX-17 sample mainly occur in the cycle temperature zone above the glass transition point of Kel-F 800 ( $T_g \sim 28^{\circ}\text{C}$ ).

Comparing changes in the pore volume fraction tested by USAXS after temperature cycling, it was found that for the same cycle temperature range, fluoroelastomer binders with a high glass transition temperature, good adhesion to TATB crystals, and good wettability all contribute to suppressing an increase in pores after alternating temperature cycling, i.e., they suppress the phenomenon of irreversible thermal expansion. More detailed information will be discussed in latter section. Recent research by Thompson et al.<sup>7</sup> based on a static thermal mechanical analyzer (TMA) also indicated that the evolution of the TATB based PBX pore structure is not only related to the current temperature cycle range but also to its thermal history (the range of the previous temperature cycle). Research by Lin et al.<sup>42</sup> using in situ temperature-variable small angle neutron scattering (SANS) on TATB based PBX samples before and after PDA coating in the range from room temperature to  $120^{\circ}\text{C}$  demonstrated that PDA coating also significantly suppresses the formation of pores during the heating process due to its strengthening effect on the interface between TATB crystals and the binder.

In addition, Armstrong et al.<sup>43</sup> applied in situ temperature-variable USANS/SANS technology and a numerical dendritic fractal network structure model to study the evolution of the pore structure in PBX 9502 during the heating and cooling process. The change in these fractal characteristics of the pore structure indicates that phenomena such as material thermal expansion, rearrangement, and fracture of TATB

**Table 2**  
Comparison of the void volume of TATB based PBXs before and after thermal cycling.

Samples	Density (g.cm <sup>-3</sup> )	Thermal cycle condition	Porosity measured by density		Porosity measured by SAS	
			Before thermal cycling	After thermal cycling	Before thermal cycling	After thermal cycling
Uniaxially pressed LX-17 <sup>38</sup>	1.898	$-54\sim 74^{\circ}\text{C}$ ,	2.0%	3.7%	1.5% (2nm-2.5 $\mu\text{m}$ )	2.4% (2nm-2.5 $\mu\text{m}$ )
Uniaxially pressed PBX-9502 <sup>38</sup>	1.895	12 cycles	2.0%	3.8%	1.6% (2nm-2.5 $\mu\text{m}$ )	2.5% (2nm-2.5 $\mu\text{m}$ )
Isostatically pressed PBX-9502 <sup>20</sup>	1.891	$-65\sim 85^{\circ}\text{C}$ ,	2.2%	3.2%	2.3% (0.1–10 $\mu\text{m}$ )	3.1% (0.1–10 $\mu\text{m}$ )
Isostatically pressed PBX-9502 <sup>20</sup>	1.871	30 cycles	3.2%	–	3.3% (0.1–10 $\mu\text{m}$ )	–

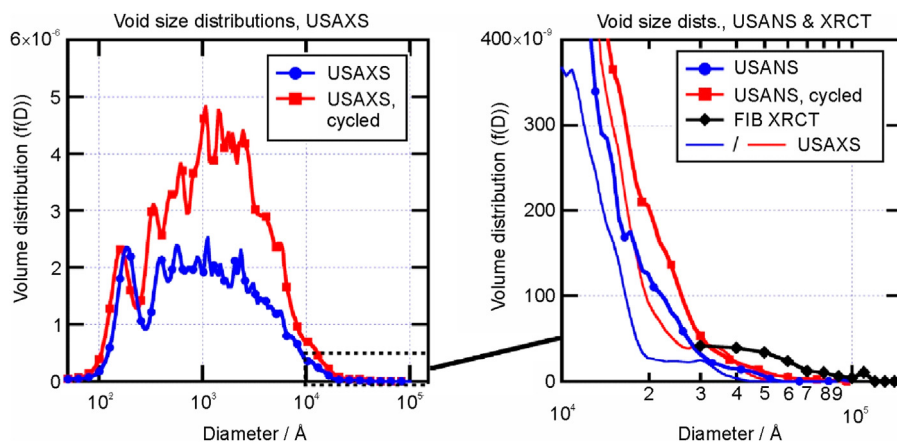


Fig. 6. Void volume distribution in LX-17 before and after high and low temperature cycling.<sup>37</sup>

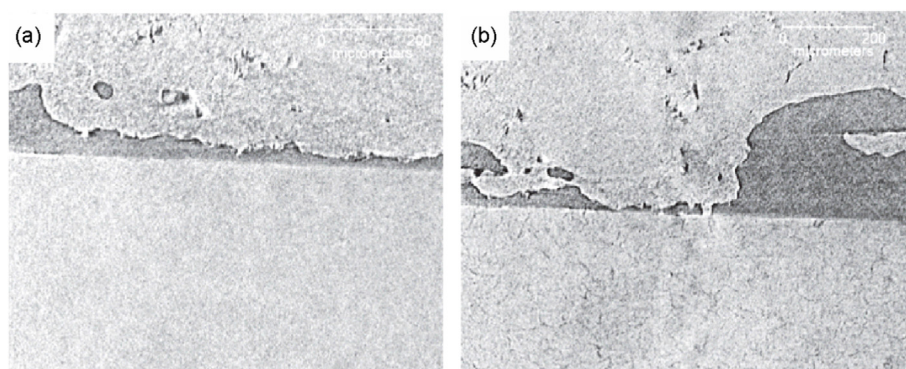


Fig. 7. Micro X-Ray CT images (a) before and (b) after thermal cycling at 20× magnification.<sup>44</sup>

crystals occur simultaneously during the high-temperature cycle in PBX 9502.

It has found that after undergoing 18 cycles (−43–153 °C), TATB samples showed noticeable pores as observed by micro X-ray computed tomography (micro X-ray CT), as shown in Fig. 7<sup>44</sup>. These pores were interconnected, forming a fractal network. During the compression process, the layered TATB crystals break, creating a network of pores. After ratchet growth, this network of pores expands.

In this section, the evolution of the microscopic structure of TATB-based PBXs during thermal expansion processes is explored in depth through a review of the literature, unveiling changes on both macroscopic and microscopic scales. The discussion emphasizes the intrinsic thermal expansion of TATB crystals and polymer binders, manifesting in alterations at the atomic, molecular, and crystalline or polymeric structure levels, primarily reflected in the variations in TATB lattice parameters and the morphology of the binder polymers with temperature changes. Concurrently, it describes the potential transformations TATB granules might undergo due to thermal stress, including fracturing, bending, straightening, displacement, and stack rearrangement. Additionally, the evolution of the porous structure receives substantial discussion, encompassing notable increases in pore size and number, and heightened complexity in the porous architecture. This segment also elaborately details studies employing Small Angle Scattering (SAS) technology and other pertinent techniques in investigating the evolution of porous structures, offering detailed insights into pore size distribution and content variations during temperature cycling.

Despite the profound insights afforded by existing studies into the microscopic structural evolution of TATB-based PBXs during thermal expansion, there are still existing deficiencies. Primarily, most research relies on isolated spherical pore models, potentially curtailing a full

understanding of the actual porous architecture. Moreover, current characterization techniques might be insufficient in capturing all microscopic structural alterations, particularly under more extreme temperature cycling conditions. For future research directions, it is suggested to delve deeper into how the glass transition temperature and interfacial adhesion properties of binders influence the evolution of porous structures. Furthermore, there is a call to incorporate more physical and chemical factors, and to develop refined and intricate porous structure models for a better understanding of the evolution of pore structures. Additionally, there is scope for designing new experiments to comprehend better the impact of different temperature cycling conditions on porous structures, and exploring avenues to control the evolution of porous structures through the manipulation of these conditions.

### 3. Influence factors of thermal expansion and inhibition methods

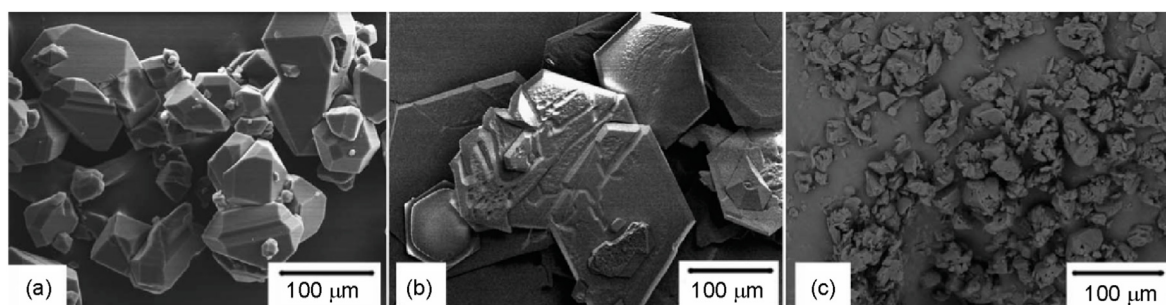
#### 3.1. Internal factors affecting thermal expansion of TATB based PBXs

##### 3.1.1. TATB crystals

Numerous factors affect the thermal expansion characteristics of explosives, which are also the main direction for the regulation of the stability of explosive formulations. Among them, the chemical properties of TATB crystals and polymer binder, as well as interfacial adhesion properties are the internal factors determining the thermal expansion characteristics of PBX.

The morphology and orientation of TATB explosive crystals, particle size, and molecular structure of the binder are all key factors affecting the linear expansion coefficient of the explosives.<sup>45,46</sup> Sun et al.<sup>47</sup> studied the impact of TATB crystal orientation on thermal expansion characteristics.





**Fig. 8.** SEM images of TATB samples with different morphologies (a. gem-like TATB, b. platy TATB, c. TATB raw materials).<sup>48</sup>

The results show that the linear expansion coefficient of TATB based PBXs increases with the increase of crystal orientation. This is mainly because the thermal expansion coefficient of TATB crystal *c* axis is far stronger than that of *a* and *b* axes. The greater the degree of crystal orientation is, the more crystal *c* axis are parallel to the testing direction, and the greater the degree of thermal expansion in the testing direction.

The degree of orientation of TATB crystal is closely related to the crystal morphology. By controlling the crystal morphology and thereby the crystal orientation, anisotropic expansion of the cylinder can be suppressed, improving the stability of TATB explosives. Zhang et al.<sup>48</sup> prepared gem-like and platy TATB through recrystallization, as shown in Fig. 8. The results show that the higher the crystal quality, the lower the irreversible volume growth. With the same crystal quality, crystal preferred orientation leads to anisotropic irreversible dimension growth. Therefore, controlling the morphology of TATB can control the orientation to some extent, but gem-like TATB crystals do not achieve the expected effect of reducing the orientation of the cylinder. If spherical TATB can be obtained, the degree of orientation during the pressing and forming process would be greatly reduced.<sup>49</sup> In specific terms, by adjusting the short-range anisotropy (the anisotropy of each nanoparticle) and agglomerating to form long-range isotropy, the irreversible macro-scale expansion (e.g., at the pellet level) of TATB crystals is effectively prevented. If we envision that each crystallographic axis is populated with nanoparticles of different orientations, then the anisotropy of a single nanoparticle is apparent. However, in aggregate, if the average expansion size in each direction is nearly consistent with the expansion sizes in other directions, then from a macro perspective, the entire system will necessarily display isotropy. This novel form of spherical TATB crystal, due to its lack of a preferred direction, can to some extent suppress the anisotropy of the expansion coefficient, thus effectively preventing irreversible expansion.

Li et al.<sup>50</sup> investigated the influence of the grain size of TATB crystals on the thermal expansion of PBX. When the average grain size of the TATB crystals increases from 0.73  $\mu\text{m}$  to 78.08  $\mu\text{m}$ , the linear expansion coefficient of PBX reduces by 12.5%. Research conducted by Jiang et al.<sup>51</sup> indicates that the size stability of coarse-grained TATB under thermal conditions is superior to that of fine-grained TATB. With an increase in the number of cycles, the average linear expansion coefficient of

coarse-grained TATB is less than that of fine-grained TATB. Rizzo et al.<sup>17</sup> found that the average linear expansion coefficient of fine-grained TATB in a relatively low-temperature range is 10% higher compared to TATB with a grain size of 50  $\mu\text{m}$ . In addition, they recorded the linear expansion coefficients of different types of TATB, as shown in Table 3. Dry-aminated TATB and wet-aminated TATB correspond to ordinary TATB and chlorine-free TATB, respectively. It can be seen that the shape stability of ordinary TATB is better than that of chlorine-free TATB. Moreover, the particle size of TATB and the molding process are also crucial influencing factors.

This section delves deeply into the effects of various characteristics of TATB crystals (including morphology and orientation) on the thermal expansion properties of PBXs. The research illustrates that irreversible thermal expansion of PBXs can be curtailed to a certain extent through the control of TATB crystal morphology and orientation. However, the question of precisely manipulating crystal orientation to optimize thermal expansion properties remains not fully addressed. Future studies can further explore different crystal growth conditions and methods to better control the morphology and orientation of TATB crystals, thereby effectively regulating their thermal expansion properties.

### 3.1.2. Polymer binder

Although the content of the polymer binder in PBX is relatively small (5–10 wt%), it acts as a continuous phase, exerting a restraining effect on the thermal expansion of TATB particles. Rizzo et al.<sup>17</sup> conducted a systematic study on the effects of multiple polymer binders with high glass transition temperatures ( $T_g$ ), such as aromatic diamine cured epoxy resin, polystyrene/polyphenyl ether, Kraton block copolymers, and phenoxy resin, on the thermal expansion of TATB based PBX. Among them, the Phenoxy PRDA 8080 binder, with the value of  $T_g$  as high as 96  $^{\circ}\text{C}$ , has the most significant inhibition effect on TATB expansion and exhibits excellent mechanical properties. In the 40–70  $^{\circ}\text{C}$  range, the linear expansion coefficient of the PBXs with Phenoxy PRDA 8080 as a binder is 32% lower than LX-17. Li et al.<sup>52</sup> have found that acrylonitrile-styrene copolymers (AS) with high  $T_g$  can inhibit the movement of TATB particles and decrease the thermal expansion coefficient of the material.

From a mechanical viewpoint, binders can be thought of as a matrix that encapsulates the TATB particles. When the binder has a high  $T_g$ , it remains rigid and maintains its form over a wider temperature range. This rigidity can physically constrain the movement and expansion of TATB particles within the matrix. Furthermore, when a binder undergoes a glass transition at a certain temperature, it changes from a brittle, glassy state to a more flexible, rubbery state. This change can also affect the thermal expansion of the TATB particles. Before the glass transition temperature is reached, the high  $T_g$  binder would be in a glassy state, and it would be stiff and brittle, providing a strong restraint on the TATB particles and preventing them from expanding. After the glass transition temperature is exceeded, the binder would be in a rubbery state, and its restraining effect on the TATB particles would be reduced, leading to an increased thermal expansion of the PBX.

This subsection principally discusses the role of polymer binders in

**Table 3**  
Linear CTE data of TATB.<sup>17</sup>

Sample description (TATB type, median particle size [ $\mu\text{m}$ ], consolidation method)	Percent of theoretical maximum density	Bulk linear CTE ( $\mu\text{m}\cdot\text{mK}^{-1}$ ) 223–263 K	Bulk linear CTE ( $\mu\text{m}/\text{mK}$ ) 313–343 K
Dry-aminated, 50, uniaxial	97.1	55	91
Dry-aminated (different lot), 50, isostatic	96.3	43	68
Wet-aminated, 100, uniaxial	97.7	95	150
Micronized wet-aminated, <10, uniaxial	97.3	110	142

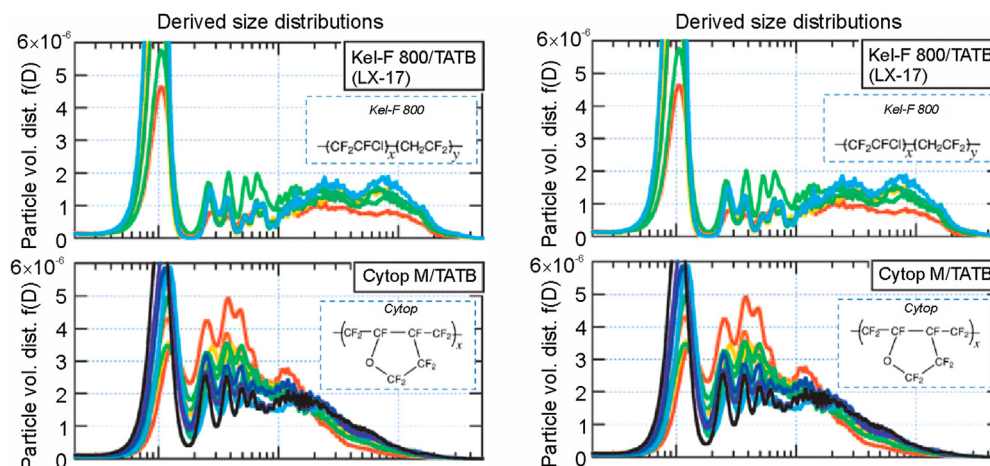


Fig. 9. Maximum entropy derived USAXS size distributions.<sup>35</sup>

controlling the thermal expansion of TATB based PBXs. Binders with specific high  $T_g$  can significantly suppress the thermal expansion of TATB. However, the section does not comprehensively examine the influence of various types of binders on TATB thermal expansion, particularly under different temperature and environmental conditions. Future research should further consider the influence of different binders, possibly delving into a greater variety of high  $T_g$  binders and their interactions with TATB. Moreover, a more detailed investigation into the behavior of binders under varying temperatures and environmental conditions will be essential to better understand and manage the thermal expansion characteristics of PBXs.

### 3.1.3. Interfacial adhesion properties

Since PBX is a polymer-based composite material highly filled with explosive particles, its performance is primarily determined by the properties of the internal binder and the interface between the explosive and binder.<sup>3</sup> As mentioned before, Willey et al.<sup>35</sup> used ultra-small-angle X-ray scattering to detect the microstructure of TATB based explosive formulations with four kind fluoropolymers during temperature cycling. Compared to TATB/Kel-F800, Cytop M and Cytop A show relatively small increases in void volume from 0.9% to 1.3% and 0.6%–1.1%, respectively, while Hyflon fails to prevent irreversible volume expansion (1.2–4.6%), as shown in Fig. 9.

Gee et al.<sup>53</sup> adopted atomistic simulations to study the adhesion properties of amorphous perfluoro- and fluoropolymers onto two different TATB crystal surfaces 001 and 100. It has been found that Kel-F800 and Cytop polymers except Hyflon show a propensity to readily wet the two TATB surfaces. This study could be helpful in determining polymeric binders suitable for use with TATB.

Good adhesion and wetting properties between the binder and the TATB particles can help suppress irreversible thermal expansion for the following reasons. Good adhesion means that the binder effectively “sticks” to the TATB particles, creating a strong interface between them. This interface acts as a mechanical barrier that can restrict the movement and expansion of TATB particles when heated, thus limiting thermal expansion. About wetting, if a binder has good wetting properties, it means it can thoroughly and evenly coat the TATB particles, minimizing gaps or voids. This complete coverage can provide a more uniform restraint on the TATB particles, again contributing to the suppression of thermal expansion. Therefore, by achieving good adhesion and wetting properties, the binder can more effectively restrain the TATB particles, helping to limit their thermal expansion and thereby reducing the irreversible expansion of the material.

This section primarily addresses the significance of interfacial adhesion properties in controlling the thermal expansion of TATB based PBXs. It points out that good adhesion and wetting properties can effectively restrain the thermal expansion of TATB particles, mainly attributed to their capacity to establish a strong interface that restricts the movement and expansion of TATB particles upon heating. However, existing research does not thoroughly explore how to achieve these optimal adhesion and wetting conditions or other factors that might influence these properties. Future endeavors should focus on optimizing this interfacial adhesion to control TATB thermal expansion more effectively. Additionally, it is advisable to validate the theoretical and simulated outcomes through experiments, which would facilitate a better understanding of the behavior of these binders in applications and might spearhead the development of new and more efficient binders.

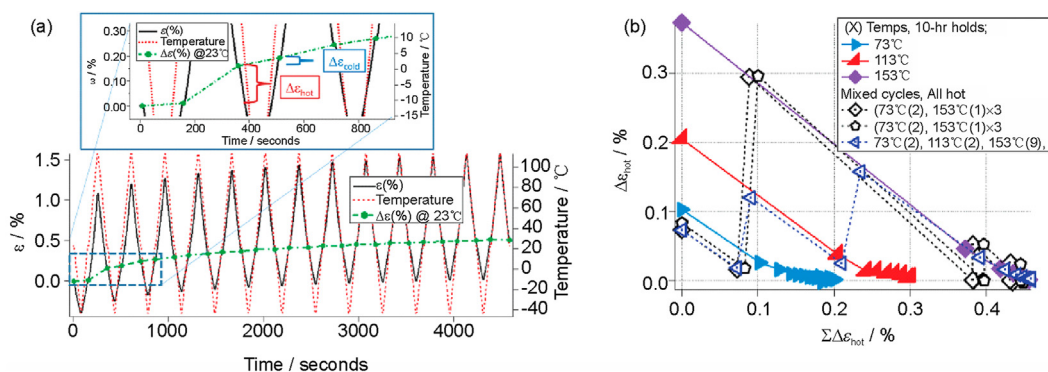


Fig. 10. TMA data, temperature (dotted) and strain (solid) versus time where X alternates between  $-43$  and  $113$  °C; (b) Values of  $\Delta\epsilon_{hot}$  plotted versus  $\Sigma\Delta\epsilon_{hot}$  for PBX 9502<sup>7</sup>



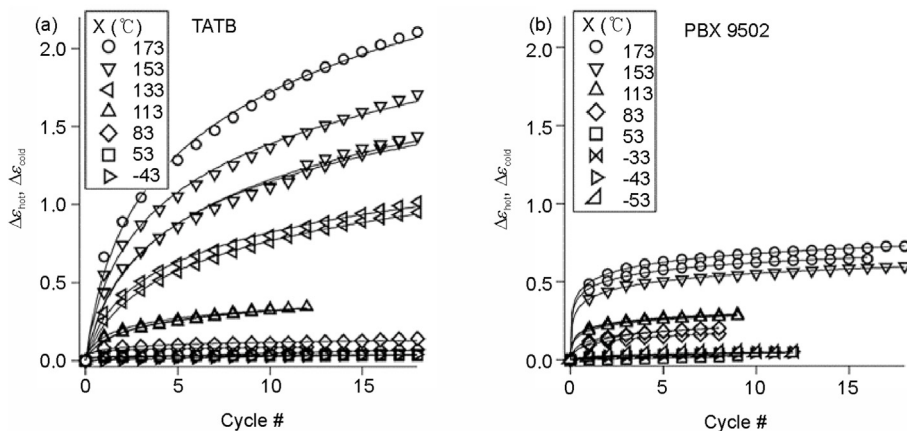


Fig. 11. (a,b) For TATB and PBX 9502, values of  $\Delta\epsilon_{hot}$  and  $\Delta\epsilon_{cold}$  plotted versus cycle number, along with Eq. (2) best fits.<sup>7</sup>

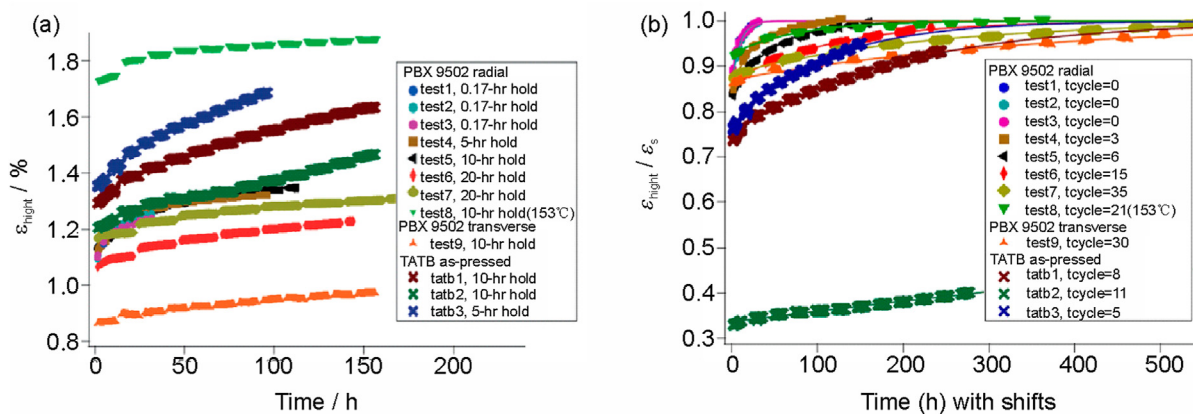


Fig. 12. (a) Strain response of high-temperature holds for PBX 9502 and for the TATB tests; (b) Same strain data as in Fig. a but with time axes for each test shifted using the  $t_{cycle}$  values.<sup>4</sup>

### 3.2. External factors affecting the thermal expansion of TATB based PBXs

#### 3.2.1. Thermal cycling conditions

Thompson et al.<sup>7</sup> used TMA to study the thermal expansion behavior of TATB and PBX 9502 under different thermal cycle conditions. Under the same conditions, compared with pure TATB, the size growth of PBX 9502 is significantly reduced. The length of time at high or low temperature endpoints has little effect on irreversible growth performance. The size increase  $\Delta\epsilon_{hot}$  during the thermal cycle (room temperature and above) is significantly higher than that during the cold cycle (below room temperature),  $\Delta\epsilon_{cold}$ , as shown in Fig. 10a. The greater the applied stress on the sample, the smaller the  $\Delta\epsilon_{hot}$  value is, but  $\Delta\epsilon_{cold}$  is not related to the applied stress. Compared to the alone cold cycle, the alternating cold and hot cycle significantly increased the contribution of the cold cycle. In the thermal cycle test, TATB based explosives follow different irreversible growth paths in different temperature ranges, and the wider the temperature range is, the greater the irreversible growth value is. After temperature cycling within a narrow temperature range, and then experiencing wider temperature range conditions, the PBX 9502 continues to grow, as shown in Fig. 10(b).<sup>7</sup> However, after experiencing a wide temperature range cycle, then experiencing narrow temperature range conditions, the explosive will no longer grow, and the contribution to irreversible growth is close to 0.

The higher the temperature in the explosive thermal cycle is, the greater the irreversible expansion value is. According to the fitting results in Fig. 11, the irreversible growth of TATB and PBX 9502 with the change of cycle numbers ( $n$ ) follows the following formula:

$$\sum \Delta\epsilon(n) = A * \ln[1 + B * n] \tag{1}$$

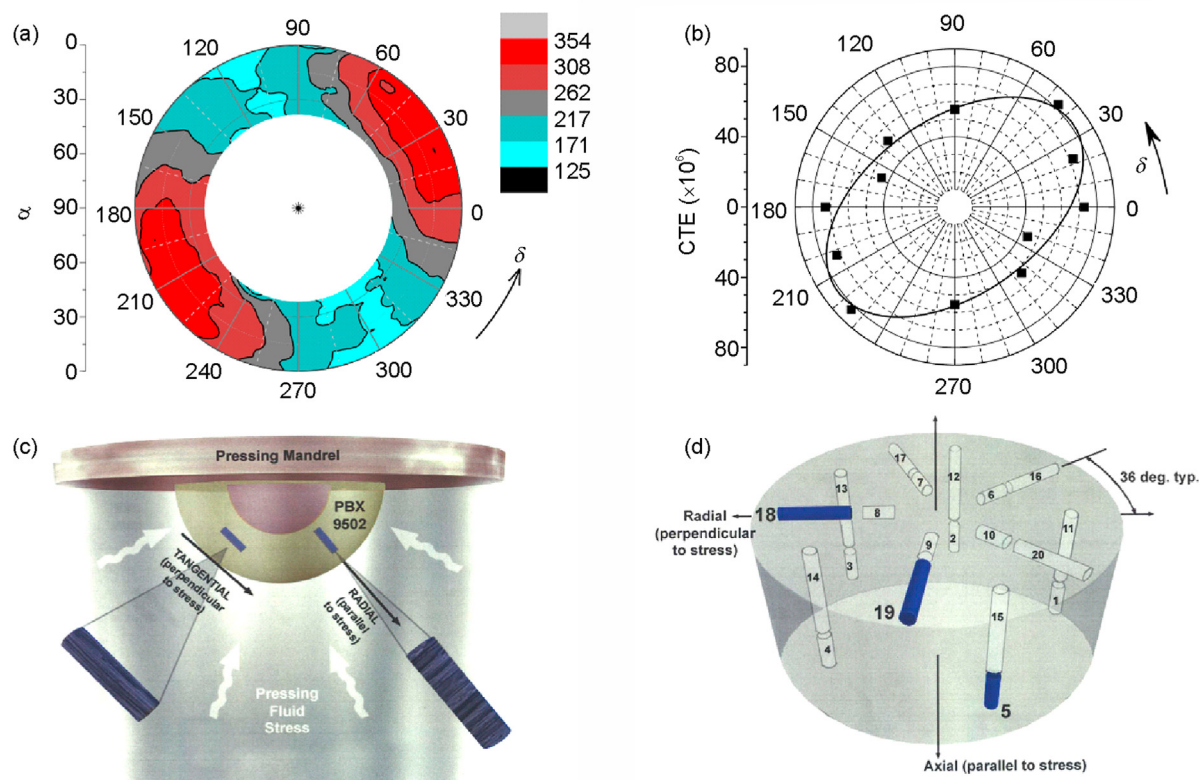
In this equation, A and B are the parameters obtained by fitting.

Thompson et al.<sup>4</sup> studied the irreversible thermal expansion of TATB and PBX 9502 using a time-evolution method, and established a time-temperature equivalence relationship. The effect of temperature cycling can be replaced by prolonging the high temperature holding time, as shown in Fig. 12. Due to the local anisotropy of CTE, local internal stress is formed during the thermal history, leading to local strain, which is macroscopically manifested as thermal expansion. During the high temperature holding process, stress release and thermal expansion show exponential time dependence:

$$\epsilon_{high}(t) = \epsilon_s + A \times \exp(-t/\tau) \tag{2}$$

In this equation,  $\epsilon_{high}(t)$  is the strain value at time  $t$  during the constant period at a specific high temperature,  $\epsilon_s$  is the saturation strain value after a prolonged infinite time at a specific high temperature, parameter A is the offset of  $\epsilon_s$  at  $t = 0$ , and  $\tau$  is the time parameter.

In this section, the focus is primarily on the research of the thermal expansion behaviors of TATB and PBX under various thermal cycling conditions. The research indicates that higher temperature cycles are more prone to induce irreversible thermal expansion compared to lower temperature cycles. Moreover, the study successfully formulated two equations to describe the irreversible thermal expansion behaviors of TATB and PBX. However, the literature falls short of delving deeply into the reason why such effects are observed during high and low-temperature cycles. Furthermore, despite presenting several equations



**Fig. 13.** (a) (002) Pole figure for the PBX 9502 disc specimen; (b) CTE measured across the diameter of the PBX 9502 disk; (c) Schematic diagram of the semi-isostatic consolidation process; (d) Transparent model that shows the orientation of specimens with respect to the mother derby.<sup>16,56</sup>

to account for the observed phenomena, these formulations are primarily empirical, leaving room for future studies to explore models grounded more solidly in first principles to better comprehend the fundamental driving forces behind these phenomena. Looking forward, research can seek to understand more profoundly the specific mechanisms through which high and low-temperature cycles affect irreversible expansion, and to explore ways to control irreversible expansion by adjusting the thermal cycling conditions.

### 3.2.2. Pressing technology

The pressing process is also an important factor influencing the thermal expansion performance of TATB based PBXs. Skidmore et al.<sup>16</sup> studied the thermal expansion of TATB based PBXs produced by different processes, and the results showed that the thermal expansion coefficients varies with different processes. Rizzo et al.<sup>17</sup> found that the CTE of uniaxially pressed samples is significantly higher than that of isostatically molded samples, 62% higher at low temperatures and 18% higher at high temperatures. Rainbolt et al.<sup>54</sup> reported that steel mold uniaxially pressed samples show extremely high CTE values compared to isostatically molded samples.

During the pressing process, TATB crystals exhibit an orderly orientation, leading to anisotropic expansion of TATB based PBXs.<sup>55</sup> The difference in the degree of orientation of the 002 crystal plane of the PBX 9502 disc samples leads to the anisotropy of the linear expansion coefficient of samples taken from different positions, with a range of variation from  $51 \times 10^{-6}$  to  $81 \times 10^{-6} \text{ K}^{-1}$ , as shown in Fig. 13.<sup>56</sup> The CTE in the direction of the 002 crystal plane orientation is the smallest, and the CTE perpendicular to the 002 crystal plane orientation direction is the largest. For uniaxially pressed TATB based PBXs, the a-b planes of most TATB crystals are perpendicular to the pressure direction, and more than 19% of the crystals display an ordered orientation.<sup>57</sup> Maienschein et al.<sup>58</sup> found that the axial expansion of mold-pressed LX-17 samples is 1.4–1.7 times the radial expansion, which is because TATB exhibits a certain

degree of orientation under uniaxial compression. Zhang et al.<sup>59</sup> studied the influence of mold pressing parameters on the expansion characteristics of TATB based PBX and analyzed its influence mechanism. Under the condition of constant pressing temperature (110 °C), the irreversible axial expansion of the cylinder increases with increasing the pressing pressure, while the irreversible volume expansion of the cylinder decreases. With a constant pressure (170 MPa), both the axial height and overall volume irreversible expansion of the cylinder reduce with decreasing the temperature. This could be ascribed to the fact that different pressing parameters lead to different degrees of crystal orientation and fragmentation during the molding process. Isostatically pressed PBXs still exhibit a certain degree of orientation due to inconsistent internal stress directions. For isostatically pressed hemispheres, the ratcheting growth of specimens in the radial direction (parallel to the stress direction) is larger than in the transverse direction (perpendicular to the stress direction).<sup>7,16,56</sup> The test results of thermal expansion properties of PBX 9502 hemispherical samples taken in different directions show that the thermal expansion in the radial direction of the hemisphere is 16%–19% greater than that in the tangential direction along the surface of the hemisphere.<sup>16</sup> With the increase of isostatic pressure, the size and density changes of the samples after temperature cycling reduced.<sup>60</sup>

In this section, a deep exploration is undertaken into the effects of different pressing process on the thermal expansion properties of TATB based PBXs. The ordered orientation of TATB crystals during the pressing process leads to anisotropic features in the expansion of the PBXs. Moreover, pressing parameters, including pressure and temperature, play a pivotal role in determining the expansion characteristics of PBXs. However, existing research appears not to delve sufficiently into how to optimize the thermal expansion properties of PBXs through fine control of these parameters. Future directions could focus more on how to optimize the pressing process through more precise simulations and experimental techniques.

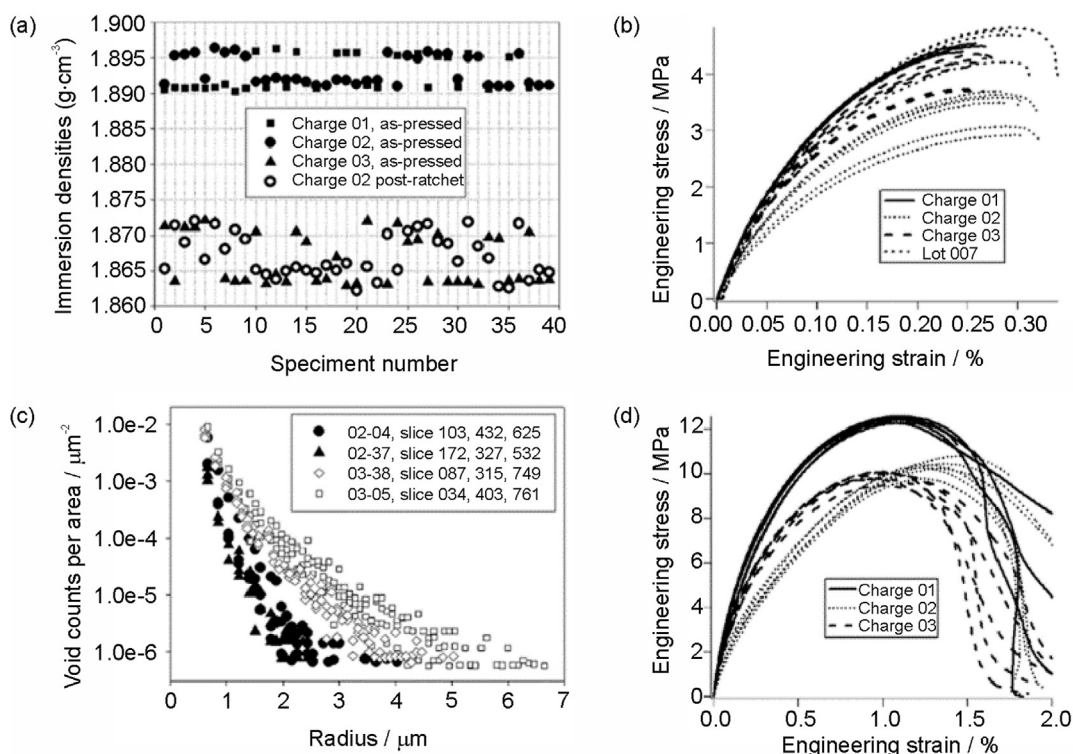


Fig. 14. (a) Immersion density values for PBX 9502 cores; (b) Pore-size distribution results from X-ray CT image analysis using Clemex software; (c) Stress-strain curves for 50 °C tension tests; (d) Stress-strain curves for 50 °C compression tests.<sup>20</sup>

### 3.2.3. Thermal aging

In order to study the size stability of materials after exposure to heat and radiation environments, Tu et al.<sup>61</sup> investigated the thermal expansion properties of TATB based PBXs after high temperature aging, and  $\gamma$  and neutron irradiation. The results showed that after aging at high temperatures of 55 °C, 65 °C, and 75 °C for 60 days, the thermal expansion coefficient of TATB based PBXs decreased. The higher the aging temperature is, the smaller the thermal expansion coefficient is. This is mainly due to the growth of internal pores in TATB based PBXs after high temperature aging. In addition, no significant changes in thermal expansion properties occurred after  $\gamma$  and neutron irradiation tests under certain conditions.

In this section, the research on the thermal expansion properties of TATB based PBXs post high-temperature aging as well as  $\gamma$  and neutron radiation is outlined. The research illustrates that high-temperature aging can reduce the thermal expansion coefficient of TATB based PBXs, primarily attributed to the increase in the internal porosity of the material following aging. Moreover, it is noted that under certain conditions,  $\gamma$  and neutron radiation tests did not lead to significant alterations in thermal expansion properties. Future investigations can delve deeper into understanding the impacts of high-temperature aging and radiation on the internal structures of TATB based PBXs, and how these alterations influence thermal expansion performance. Additionally, considerations should be extended to testing under a wider range of radiation and temperature conditions, with a view to establishing a more comprehensive and detailed framework of thermal aging effects.

### 3.3. Influences of thermal expansion on the performance

Under thermal cycling, irreversible thermal expansion of TATB based PBXs occurs due to the anisotropy and preferred orientation of TATB crystals. It results in macroscopic size changes, directly affecting the performance of TATB based PBXs, such as mechanical properties, safety performance, and detonation performance.

#### 3.3.1. Mechanical properties

During thermal expansion, the binder detaches from the TATB crystals, leading to the reduced mechanical properties. After 32 cycles (−54 °C–74 °C), the density of LX-17 explosive decreased from 1.895 g cm<sup>-3</sup> to 1.871 g cm<sup>-3</sup>, and the maximum tensile strength decreased from 9.2 MPa to 5.2 MPa.<sup>17</sup> Research by Li et al.<sup>62</sup> showed that the thermal cycling produce stress at the interface between TATB particles and the binder of TATB based PBXs, which weakens the interfacial interaction. After thermal cycling, the mechanical properties showed a certain degree of decrease, with a decrease in strength and modulus and a deterioration in creep properties. Li et al.<sup>63</sup> found that after 28 thermal cycles (−40 °C–75 °C), interfacial debonding of TATB based PBXs results in a reduction in interface bonding strength and a decrease in tensile strength by 13.0%. Thompson et al.<sup>20</sup> conducted a 30 cycle thermal cycling test (−55 °C–80 °C) on high-density PBX 9502 samples (1.8932 ± 0.002 g cm<sup>-3</sup>), which resulted in a 1.4% decrease in density to 1.8671 ± 0.003 g cm<sup>-3</sup>. Fresh samples prepared under low pressure were used to compare the differences in microstructure and mechanical properties under the same density conditions as thermally cycled samples, as shown in Fig. 14. Micro X-ray CT and USANS techniques revealed that, compared to low-density fresh samples, the thermally cycled samples display more and smaller pores, leading to a decrease in tensile strength and modulus at high temperature (50 °C) and an increase in tensile strain. Similarly, the compression modulus decreased and the compression strain increased at high temperature. However, mechanical properties at low temperature (−20 °C) which are mainly related to sample density are insensitive to thermal history. This means that the low-density samples after thermal cycling and the fresh samples produced under low pressure with the same density exhibit similar mechanical responses at low temperature. The results further demonstrated that irreversible thermal expansion not only causes a change in density, but also leads to changes in the porosity distribution and the generation of microdamage in TATB based PBXs.



### 3.3.2. Safety performance

The irreversible volume expansion of explosives under thermal cycling can lead to friction and collision between munitions and their casings in the environments subjected to vibration, shock, and thermal loading, thereby affecting the safe usage of weapon systems.<sup>23</sup> Moreover, the irreversible volume expansion of TATB crystals leads to a trend towards larger pore sizes and higher porosity.<sup>35,38</sup> The defects become hotspots influencing the sensitivity of explosives.<sup>64,65</sup> When TATB based PBXs are heated to 250 °C or subjected to thermal cycling, the sensitivity to shock waves increases, which might be due to the creation or change of pores during the ratcheting growth process, leading to more hotspots and faster reaction growth.<sup>66–68</sup> Mulford et al.<sup>69</sup> studied the ratcheting growth phenomenon in PBX 9502 and its effect on explosive sensitivity. With an increase in the number of cycles, the volume of the explosive continues to expand, the porosity increases, leading to increased sensitivity. Mulford et al.<sup>70</sup> also explored the irreversible growth phenomenon caused by thermal cycling and investigated the changes in the sensitivity of PBX 9502 to shock waves under heating conditions. It was found that as the temperature increased, the volumetric expansion and increase in internal energy of PBX 9502 enhanced the sensitivity to shock waves. The study revealed the influence of the increased chemical reaction rate of TATB and changes in material morphology on the detonation behavior of explosives.

Numerous studies indicate that the sensitivity of TATB to shock waves increases significantly after thermal expansion. Schwartz et al.<sup>71</sup> found that the minimum flyer velocity required to initiate detonation of TATB explosives at an initial temperature of 260 °C is significantly lower than at ambient temperature. Seitz et al.<sup>72</sup> found that under the same shock conditions, the distance to detonation of PBX 9502 explosives at –55 °C is approximately 50% longer than at room temperature. Scheloske et al.<sup>73</sup> determined that the flyer energy required to initiate detonation of TATB based explosives at 250 °C is significantly lower than at room temperature. In particular, the flyer energy required for TATB explosives with a density of 1.8 g cm<sup>-3</sup> is reduced by 33%, while that for LX-17 is reduced by 50%. Dallman et al.<sup>74</sup> studied the relationship between the distance to detonation and initiation pressure of PBX 9502 and LX-17 explosives at different temperatures and found that at 75 °C and 252 °C, the distances to detonation are only half and one-tenth of those at room temperature, respectively. Combining the studies of the performance changes of explosives at high temperatures, researchers believe that the reason why TATB becomes more sensitive to shock after being heated is that thermal expansion leads to a decrease in density and an increase in porosity, generating more potential hotspots. These hotspots trigger reactions in the surrounding heated explosive particles, leading to rapid reaction growth. Similar research has been conducted domestically, such as the Fang et al.'s<sup>75</sup> study using the impact initiation method on the changes in the initiation performance of TATB based explosives at 20 °C, –30 °C, and –54 °C. Chen et al.<sup>76</sup> conducted impact initiation experiments on TATB based PBX at five different heating temperatures of 14 °C, 100 °C, 140 °C, 160 °C, and 180 °C, and obtained the POP relationship diagram of the explosive at these temperatures. The patterns obtained in these works are consistent with foreign research results.

In this section, the variations in the safety performance of TATB-based PBXs under the influence of thermal cycles are elaborately described, with a special emphasis on the irreversible volumetric expansion and the role of thermal cycling in influencing the formation and growth of material pores, consequently affecting its sensitivity to shockwaves. Multiple research findings indicate an increased shock sensitivity of TATB-based PBXs under high-temperature conditions, a phenomenon principally attributed to the reduction in density and augmentation in porosity due to thermal expansion, fostering a greater number of potential hot spots and hastening the reaction rate. Despite the insights the current research offers into the impact of thermal expansion of TATB based PBXs on their safety performance, a deeper understanding of this phenomenon necessitates further detailing. To foster safer utilization moving forward, upcoming studies should focus predominantly on mitigating the adverse

effects induced by thermal cycling, possibly through advancements in PBX manufacturing processes or the development of novel materials. Simultaneously, given the limited volume of relevant research literature, there is a call for intensified research efforts in this domain to refine and augment our understanding of this phenomenon, furnishing more theoretical backing and empirical grounds to enhance the safety credentials of TATB based PBXs.

### 3.3.3. Detonation performance

Detonation characteristics depend on temperature fluctuations and resulting density changes, and usually, the detonation performance of PBX changes with increasing temperature and decreasing density. Research has shown that although some detonation characteristics change after TATB undergoes irreversible expansion, it has no significant impact on the overall detonation performance. Stephen et al.<sup>77</sup> studied the detonation performance characteristics of original and regenerated batches of PBX 9502, where 50 wt% of TATB in the regenerated batches came from mechanical chips recycled from old PBX 9502 explosive samples, leading to a higher proportion of fractured and damaged TATB crystals compared to the original batches. The results showed that the detonation speed of the original batches is slower compared to the regenerated ones, but their performance was similar. That is, the microstructural changes between different batches of PBX 9502 influence the reaction rate but not the total energy. Thompson et al.<sup>78</sup> found that TATB's irreversible growth has a significant impact on the thermal anisotropy of PBX 9502, but it has little impact on its detonation performance (enhanced corner-turning tests (ECOT)). Li et al.<sup>62</sup> assessed the impact of temperature cycling on the detonation performance of TATB based PBX. After 11 and 20 cycles of thermal cycling (–40~75 °C), the detonation speed did not change significantly. Some studies also suggest that ratchet growth does indeed affect detonation performance. Salyer et al.<sup>79</sup> used the detonation destruction cone test to distinguish the minor detonation performance differences caused by microstructural changes in PBX 9502 before and after thermal cycling. The results showed that besides the density differences affecting the detonation performance, explosives that have undergone thermal cycling have more fine-grain crystals, resulting in a shorter action zone and therefore a smaller critical diameter. The performance of uniformly ratcheted growth material was superior to low-density compressed material. Moreover, ratchet growth impacts the distribution of void spaces in the material, which in turn influences the morphology of hot spots and thus has a direct impact on the critical diameter of the material.

In this section, the detonation characteristics of TATB-based PBXs under varying temperature conditions are discussed. Despite the significant microstructural alterations triggered by thermal cycles and irreversible growth, numerous studies suggest that these changes have a relatively limited impact on the overall detonation performance. In this context, while some studies point to a certain influence on the detonation velocity and critical diameter, others argue that the total energy output remains unchanged. The existing research offers a preliminary understanding, illustrating a degree of stability in the detonation performance of TATB-based PBXs, which appears to be relatively unaffected by temperature cycles. However, given the scant amount of related research literature, many aspects in this domain remain unexplored. Future studies necessitate a more comprehensive grasp of how various microstructural alterations affect detonation characteristics, investigating how and to what extent the microstructure influences detonation velocity and critical diameter. This not only can provide theoretical support for the safe application of TATB-based PBXs but also guide the development of optimized material design and preparation methodologies.

### 3.4. Suppression methods for thermal expansion

TATB based PBXs exhibit a large CTE, which has a substantial impact on the performance of weapon charges. Therefore, technologies to reduce the CTE and improve shape stability are urgent need. Numerous studies

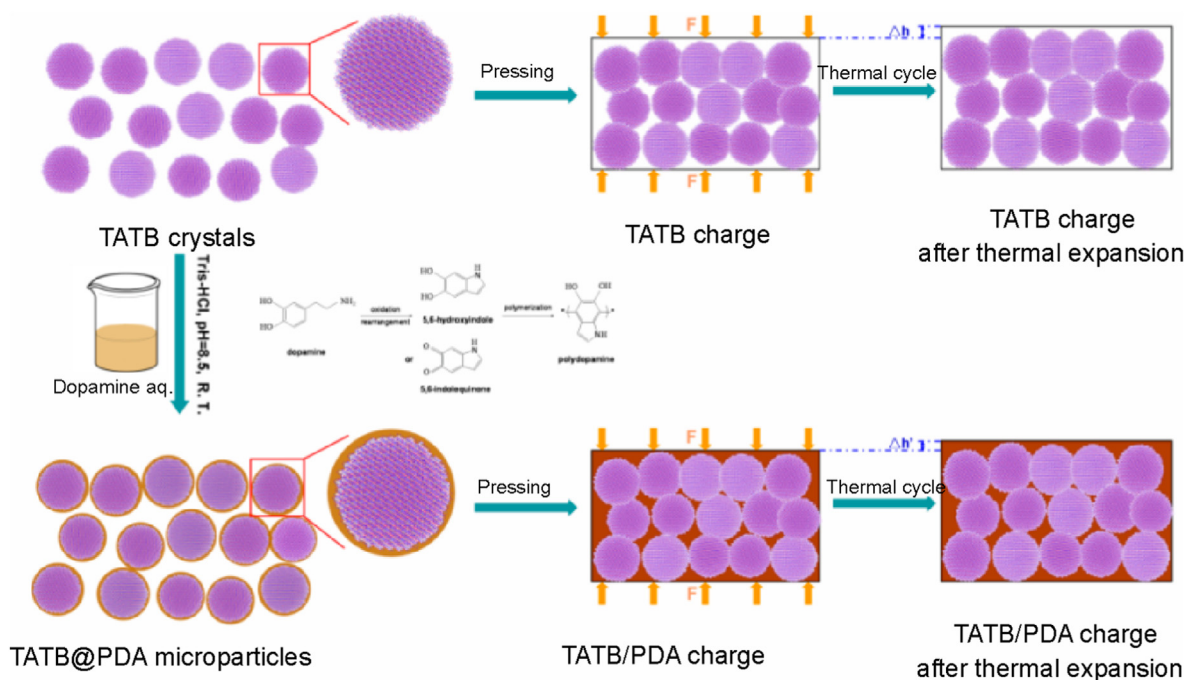


Fig. 15. Schematic depiction of the processes of TATB@PDA core@shell microparticles formation, pressing, and thermal expansion.<sup>81</sup>

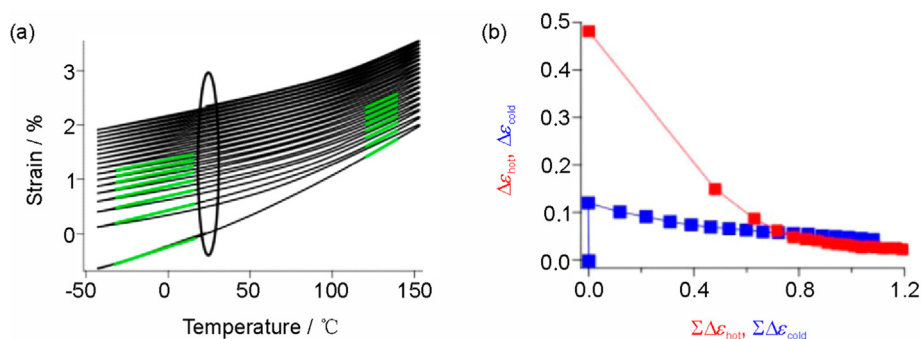


Fig. 16. (a) Strain versus temperature TMA data for TATB showing nonlinear ratchet growth; (b) The irreversible strain per cycle is plotted versus the total accumulated strain for hot (red) and cold (blue) cycles.<sup>82</sup>

have been conducted domestically and internationally on suppressing the irreversible expansion of TATB based PBXs, and several methods to control thermal expansion have been developed.

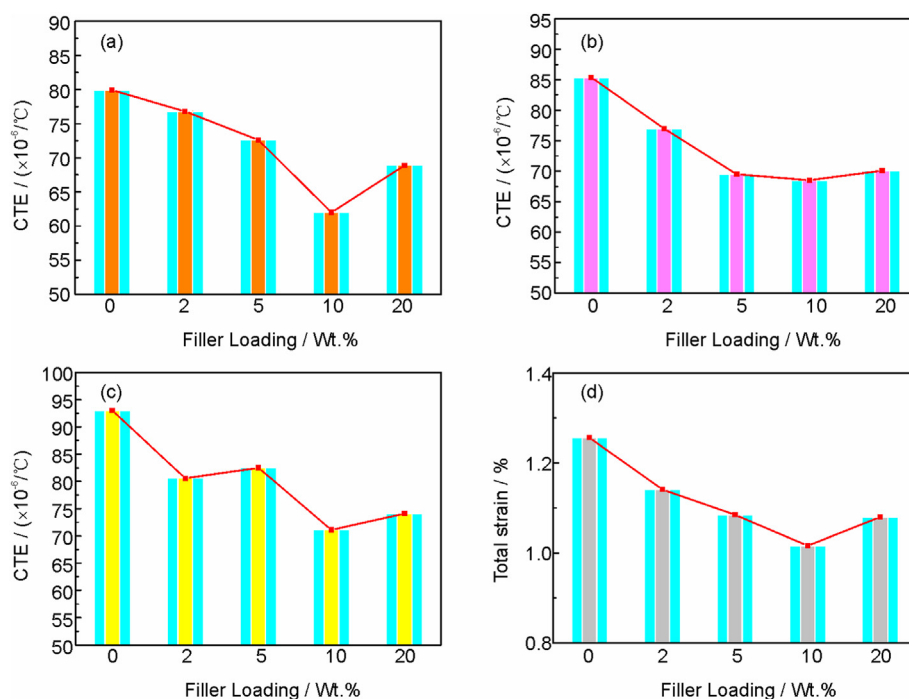
Based on assessments and analyses of influencing factors, current technologies to improve the stability of TATB based PBXs mainly include: 1) regulating the crystal structure of TATB; 2) using high  $T_g$  binders; 3) optimizing molding techniques; 4) adopting temperature cycling as post-processing techniques; 5) introducing negative expansion functional materials.

Regulation of TATB crystal structure primarily includes two methods. The first method involves increasing the average grain size of the explosive crystal to prepare coarse-grained TATB explosives, reducing the residual stress in the pellets and shortening the stress release period.<sup>51,52</sup> The second method involves controlling crystal orientation by recrystallizing to prepare sphere crystals, thereby suppressing the anisotropy expansion and improving the shape stability of PBXs.<sup>50</sup>

From the perspective of modifying the polymer binder system, adjusting the structure and composition of the binder system and increasing the rigidity of the binder system is an effective way to regulate the thermal expansion performance of PBXs. Currently, it is mainly achieved through polymer copolymerization, blending, or direct replacement to increase the  $T_g$  of the binder system and enhance

molecular rigidity.<sup>17,53</sup> The modified polymer matrix enables the binder to exist as a glass state at the test temperature range, with the free volume reaching the minimum value. There is no sufficient space for molecular chain conformation adjustment, with molecular chain segment movement frozen, and the movement of the polymer chain is obstructed. At the same time, a highly rigid binder system has strong constraining force on the movement of TATB particles, reducing the thermal expansion. In the traditional PBX granulation process (such as water suspension method), the binder coating is completed with a simple dissolution-precipitation physical process, leading to low encapsulation of the explosive crystals and weak interface interaction.<sup>3,80</sup> The in-situ polymerization method of dopamine can form a dense, rigid polydopamine (PDA) cross-linked network on the TATB surface and form a strong chemical adhesion. After 9 h of dopamine coating, the irreversible expansion strain of fine and coarse grain TATB@PDA decreased by 27.7% and 32.2% compared to pure TATB, as shown in Fig. 15.<sup>81</sup>

Isostatically pressed molding technology effectively inhibits the preferred orientation of TATB crystals and reduces the CTE value of TATB based PBXs. The CTE value of the charge column prepared by isostatical pressure is about  $60\sim70 \times 10^{-6} \text{ K}^{-1}$ , while the CTE value of the charge column obtained by steel mold pressing is about  $100\sim110 \times 10^{-6} \text{ K}^{-1}$ , the former is only 55%~70% of the latter.<sup>52</sup>



**Fig. 17.** The CTE for  $ZrW_2O_8$  modified composites at different stages: (a) the cooling stage (23 °C ~ -54 °C); (b) the heating stage (-54 °C ~ 74 °C); (c) the cooling stage (74 °C ~ 23 °C); (d) the total strain over a -54 ~ 74 °C cycle.<sup>85</sup>

The CTE of TATB based PBXs decreases gradually with the increase in the number of temperature cycles and then stabilizes, as shown in Fig. 16<sup>82</sup>. After 20 cycles, the CTE value of TATB based PBXs decreases by 12% ~ 20%.<sup>55</sup> After multiple cold-heat cycles, the samples exhibit irreversible volume expansion, thereby generating more voids. TATB particles can freely expand within these voids, resulting in the overall expansion of the sample smaller than before the cycles. Additionally, the size expansion of TATB based PBXs charge column mainly occurs during the initial few cycles.<sup>83</sup> Therefore, using multiple rounds of temperature cycling pretreatment can effectively reduce the irreversible expansion during usage.

Negative thermal expansion (NTE) materials are a type of functional materials with unique heat-shrink and cold-expansion properties, which have attracted significant attention in the field of material science.<sup>84</sup> Lin et al.<sup>85</sup> introduced materials with NTE characteristics to adjust the thermal expansion of TATB based PBXs. Through the combination of negative expansion zirconium tungstate ( $ZrW_2O_8$ ) filler and the positive expansion of TATB explosives, the linear expansion coefficient of PBXs is reduced, and thermal expansion was suppressed, as shown in Fig. 17. Compared with PBX-Raw without  $ZrW_2O_8$ , the CTE of the modified material initially decreases and then increases with the filler content. When the  $ZrW_2O_8$  content is 10 wt%, the CTE and strain decrease by 19.8% and 19.1% respectively. The successful application of negative expansion functional materials in the field of energetics provides a novel strategy for constructing new energetic composites with controllable thermal expansion properties. In addition, other NTE functional materials, such as scandium fluoride ( $ScF_3$ ),<sup>86</sup> certain metal-organic frameworks (MOFs),<sup>87</sup> as well as NTE polymers<sup>88,89</sup> also have potential for application. Moreover, we would also like to address that, while these materials can be beneficial for thermal management, excessive amounts may indeed adversely affect the energetic performance of PBX. For instance, an addition of 20% could significantly influence the energy output. Furthermore, if the negative thermal expansion materials possess high chemical reactivity or hardness, safety performance could be compromised. These concerns underscore the importance of carefully optimizing the PBX formulation.

In this section, a systematic exploration of methods to mitigate thermal expansion of TATB based PBXs is presented, encompassing

strategies such as manipulating the crystal structure of TATB, employing high  $T_g$  binders, optimizing molding technologies, applying temperature cycle post-processing techniques, and introducing NTE functional materials. These strategies aim to reduce the CTE values, thereby enhancing the shape stability and performance of TATB based PBXs. Notably, utilizing NTE materials not only facilitates control over the thermal expansion of TATB based PBXs but also inaugurates avenues for investigating new energy composite materials with controllable thermal expansion attributes. Despite the diversity of current approaches to curbing thermal expansion, research has predominantly focused on materials and molding techniques, with insufficient consideration given to environmental factors and long-term stability. Future endeavors could delve deeper into the safety of NTE materials and their impact on the energy output of PBXs, ensuring that these novel materials do not compromise the overall system's safety and performance. Moreover, developing more efficient testing methods to evaluate the effectiveness of various approaches in thermal expansion mitigation stands as a pivotal direction moving forward. In summary, future research should undertake a multifaceted deep dive into this issue, with the ambition to pinpoint the most optimized solutions. The endeavor encompasses not only further insights into materials' synthesis and processing but also a holistic approach considering external conditions and long-term implications to foster advancements in this field.

#### 4. Conclusion and future perspectives

Under temperature cycling, the irreversible expansion of TATB based PBXs leads to a decrease in mechanical properties, safety performance, and deterioration in usability during assembly and storage, directly affecting the safety and reliability of the weapon system. Suppressing the irreversible thermal expansion of TATB based PBXs and improving the shape stability of the explosive under temperature cycling environment is of great importance. Although related researches have carried out on the irreversible expansion characteristics to obtain certain theoretical understandings and experimental results, due to the complexity and diversity of structure, process, and environment, the understanding of the thermal expansion mechanism of TATB based PBXs is still insufficient.



How to effectively suppress thermal expansion of TATB based PBXs remains a significant challenge.

In future research work, the author believes that the following points should be the focus:

- (1) The irreversible expansion mechanism of TATB based PBXs. Although extensive research has been conducted, the origin of irreversible expansion is still in dispute. It is necessary to combine new characterization techniques, numerical simulations, and experimental research to further explore the irreversible expansion mechanism at the microscopic scale.
- (2) TATB crystal structure design and control. Starting from the perspective of crystal design, the construction of macroscopic spherical crystal morphology can reduce anisotropic thermal expansion and crystal orientation. Although the effect of TATB spherical crystals on thermal expansion has not been reported yet, the effect remains to be experimentally verified.
- (3) The design and development of new structural-functional integrated polymers. The use of high  $T_g$  polymer binders has, to some extent, reduced the irreversible thermal expansion of TATB charges, but has not yet been applied practically. The interface bonding, density, aging performance, and mechanical properties of high  $T_g$  polymer binders are certainly different with fluoropolymers. The development of new structural-functional integrated fluoropolymers to synchronously solve the problems of interface bonding, high  $T_g$ , and mechanical properties is expected to be applied in TATB based PBXs.
- (4) The application of new negative thermal expansion functional materials. In recent years, significant progress has been made in negative thermal expansion fillers and intrinsic negative thermal expansion polymers. Designing a new structure of negative thermal expansion binding system, through the design of negative thermal expansion polymers or fillers and positive expansion TATB crystals, can reduce the linear expansion coefficient of PBXs, suppress material thermal expansion, and has broad application prospects. The development of structural design of TATB and binder system and the application of negative thermal expansion functional materials will bring new opportunities to suppress the thermal expansion of TATB based PBXs and enrich the modification techniques of energetic composites.

#### Author contribution

Cong-mei Lin formulated the core ideas and direction of this review, wrote the initial draft of the manuscript, participated in its review and editing, and secured the necessary funding for the research. Liang-fei Bai was instrumental in conducting extensive literature reviews and analyses, and also participated in the review and editing of the manuscript. Zhi-jian Yang took charge of compiling and organizing relevant research data and information, handled data visualization and the creation of charts, and contributed to the review and editing of the manuscript. Fei-yang Gong assisted in reviewing and analyzing the literature, and participated in the manuscript's review and editing process. Yu-shi Wen oversaw the entire review writing process and the team, and played a key role in reviewing and editing the manuscript. All authors have read and agreed to the published version of the manuscript.

#### Declaration of competing interest

I would like to declare, on behalf of all authors of the manuscript titled "Research Progress in Thermal Expansion Characteristics of TATB Based Polymer Bonded Explosives", that there are no conflicts of interest related to this submission to Energetic Materials Frontiers.

We confirm that there have been no financial or personal relationships with any individuals or organizations that could inappropriately influence or bias our work.

We understand the implications of this declaration and that any discovered violation of the journal's conflict of interest policy may result in serious consequences.

#### Acknowledgments

The authors gratefully acknowledge the project supported by National Natural Science Foundation of China (Grant No. U213020030).

#### References

1. Steele BA. Initial decomposition mechanisms of 2,4,6-triamino-1,3,5-trinitrobenzene (TATB) and their kinetic isotope effect. *J Appl Phys*. 2023;133:075902.
2. Boddur VM, Viswanath DS, Ghosh TK, et al. 2,4,6-Triamino-1,3,5-trinitrobenzene (TATB) and TATB based formulations-A review. *J Hazard Mater*. 2010;181:1–8.
3. He G, Lin C, Liu J, et al. Review on interfacial bonding improving of TATB based PBX. *Chin J Energetic Mater*. 2016;24(3):306–314.
4. Thompson DG, Schwarz RB, Brown GW, et al. Time-evolution of TATB based irreversible thermal expansion (ratchet growth). *Propellants, Explos Pyrotech*. 2015; 40:558–565.
5. Souers PC, Lewis P, Hoffman M, et al. Thermal expansion of LX-17, PBX 9502, and ultrafine TATB. *Propellants, Explos Pyrotech*. 2011;36:335–340.
6. Woznick CS, Thompson DG, Scott SJ. Coefficient of thermal expansion evolution during ratchet growth of PBX 9502 and neat TATB. *Propellants, Explos Pyrotech*. 2022; 47:70–77.
7. Thompson DG, Woznick C, DeLuca R. Thermal cycling and ratchet growth of TATB and PBX 9502. *Propellants, Explos Pyrotech*. 2019;44:850–857.
8. Cady HH, Larson AC. The crystal structure of 1,3,5-triamino-2,4,6-trinitrobenzene. *Acta Crystallogr*. 1965;18:485–496.
9. Huang XN, Guo F, Yao KG, et al. Anisotropic hydrogen bond structures and orientation dependence of shock sensitivity in crystalline 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). *Phys Chem Chem Phys*. 2020;22:11956–11966.
10. Zhang CY. Investigation of the slide of the single layer of the 1,3,5-triamino-2,4,6-trinitrobenzene crystal sliding potential and orientation. *J Phys Chem B*. 2007;111: 14295–14298.
11. Szczepan R, Richard HG, Balasubramanian K, et al. Molecular interactions of TATB clusters. *Chem Phys Lett*. 2003;374:286–296.
12. Rosen JM, Dickenson C. Vapor pressure and heats of sublimation of some high melting organic explosives. *J Chem Eng Data*. 1969;14:120–124.
13. Kolb JR, Rizzo HF. Growth of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) I. Anisotropic thermal expansion. *Propellants Explos*. 1979;4:10–16.
14. Sun J, Kang B, Xue C, et al. Crystal state of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) undergoing thermal cycling process. *J Energetic Mater*. 2010;28(3):189–201.
15. Gee RH, Maiti A, Fried LE. Mesoscale modeling of irreversible volume growth in powders of anisotropic crystals. *Appl Phys Lett*. 2007;90:254105.
16. Skidmore CB, Butler TA, Sandoval CW. *The Elusive Coefficients of Thermal Expansion in PBX 9502. LA-14003*. 2003.
17. Rizzo HF, Humphrey JR, Kolb JR. Growth of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) II. Control of growth by use of high  $T_g$  polymeric binders. *Propellants Explos*. 1981;6:27–36.
18. Mulford RN, Romero JA. Sensitivity of TATB based explosive PBX 9502 after thermal expansion. In: *Shock Compression of Condensed Matter; Amherst, Massachusetts*. 1997.
19. Thompson DG, Brown GW, Olinger B, et al. The effects of TATB ratchet growth on PBX 9502. *Propellants, Explos Pyrotech*. 2010;35:507–513.
20. Naum RG, Jun CK. Thermal expansion of polycrystalline graphite. *J Appl Phys*. 1970; 41:5092–5095.
21. Fredrickson JE, Redanz WH. Boron nitride for aerospace applications. *Met. Prog*. 1965;87(2):97–101.
22. Sun J, Kang B, Zhang H, et al. Investigation on irreversible growth of 1,3,5-triamino-2,4,6-trinitrobenzene cylinder. *Cent Eur J Energ Mater*. 2011;8(1):69–79.
23. Wang Y, Huang XC. Numerical simulation analysis of irreversible deformation mechanism caused by thermal cycling of PBX-9502. *Chin J Energetic Mater*. 2021; 29(12):1152–1159.
24. Ji G, Xiao H, Ju X, et al. Periodic DFT studies on the structure of crystalline TATB. *Hua Hsueh Hsueh Pao*. 2003;61(8):1186–1191.
25. Zhang C, Shu Y, Zhao X. DFT study on non reversible expansion of TATB crystal. *Proc. Sino-Russ. Sem. on New Prog. Energetic Mater*. 2004.
26. Cunningham B, Weese R, Lewis P, et al. *CTE and Ratchet Growth Measurements on LX17-1 and Constituents*. UCRL-JC-147447; 2002.
27. Gee RH, Roszak SM, Fried LE. *Theoretical Studies of Interactions between TATB Molecules and the Origins of Anisotropic Thermal Expansion and Growth*. UCRL-JC-; 2022:148607.
28. Gee RH, Roszak S, Balasubramanian K, et al. Ab initio based force field and molecular dynamics simulations of crystalline TATB. *J Chem Phys*. 2004;120(15): 7059–7066.
29. Schwarz RB. Model for ratchet growth in PBX 9502. *Acta Mater*. 2019;180:170–179.
30. Ritter B. *A Literature Review of Shock Sensitivity Changes of TATB Due to Thermal Cycling*. LA-UR-16-26390. 2016.
31. Lei S, Wang S, Chen R. Ratchet growth of PBX in simulation based on GTN damage model. *Acta Armamentarii*. 2021;42(S1):74–81.
32. Buechler MA, Miller NA, Luscher DJ, et al. Modeling the effects of texture on thermal expansion in pressed PBX 9502 components. In: *ASME 2016 International Mechanical Engineering Congress and Exposition*. American Society of Mechanical Engineers; 2016.

33. Luscher DJ. *Modeling the Thermal Deformation of TATB Based Explosives. Part I: Thermal Expansion of "Neat-pressed" Polycrystalline TATB.* LA-UR-14-23072. 2014.
34. Luscher DJ, Buechler MA, Miller NA. Self-consistent modeling of the influence of texture on thermal expansion in polycrystalline TATB. *Model Simulat Mater Sci Eng.* 2014;22:075008.
35. Willey TM, Hoffman DM, Buuren T van, et al. The microstructure of TATB based explosive formulations during temperature cycling using ultra-small-angle x-ray scattering. *Propell. Explor. Pyrotech.* 2009;34:406–414.
36. Willey TM, Lauderbach L, Gagliardi F, et al. Comprehensive characterization of voids and microstructure in TATB based explosives from 10 nm to 1 cm: effects of temperature cycling and compressive creep. In: *14th International Detonation Symposium.* United States: Coeur d'Alene, ID; 2010.
37. Willey TM, Overturf G. Towards next generation TATB based explosives by understanding voids and microstructure from 10 nm to 1 cm. In: *40th International Annual Conference of ICT; Karlsruhe, Germany.* 2009.
38. Willey TM, Buuren T van, Lee JRI, et al. Changes in pore size distribution upon thermal cycling of TATB based explosives measured by ultra-small angle X-ray scattering. *Propellants, Explos Pyrotech.* 2006;31:466–471.
39. Tian Q, Yan G, Bai L, et al. Progress in the applied research of small-angle scattering technique in polymer bonded explosives. *Chin J Energetic Mater.* 2019;27:434–444.
40. Bai LF, Li XX, Li H, et al. A review of small angle scattering, neutron reflection, and neutron diffraction techniques for microstructural characterization of polymer-bonded explosives. *Energ. Mater. Front.* 2023 <https://doi.org/10.1016/j.enmf.2023.01.001>.
41. Mang JT, Hjelm RP. Fractal networks of inter-granular voids in pressed TATB. *Propellants, Explos Pyrotech.* 2013;38(6):831–840.
42. Lin C, Gong F, Qian W, et al. Tunable interfacial interaction intensity: construction of a bio-inspired interface between polydopamine and energetic crystals. *Compos Sci Technol.* 2021;211:108816.
43. Armstrong CL, Mang JT. Thermally-driven changes to porosity in TATB based high explosives. *Propellants, Explos Pyrotech.* 2021;46(8):1304–1312.
44. Woznick CS, Thompson DG, DeLuca R, et al. Thermal cycling and ratchet growth of as-pressed TATB pellets. *AIP Conf Proc.* 2018;1979:060011.
45. Pietron JJ, Mirkarimi PB. Review of the effects of polymer binder properties on microstructure and irreversible volume growth of plastic bonded explosives formulations. *Propellants, Explos Pyrotech.* 2022;47:e202100379.
46. Maiti A, Gee RH, Hoffman DM, et al. Irreversible volume growth in polymer-bonded powder systems: effects of crystalline anisotropy, particle size distribution, and binder strength. *J Appl Phys.* 2008;103:053504.
47. Sun J, Zhang H, Wen M, et al. Influence of crystal preferred orientation on thermal expansion of die pressed TATB based PBXs. *Chin J Energetic Mater.* 2012;20(5):545–550.
48. Zhang H, Xu J, Liu Y, et al. Effects of crystal quality and preferred orientation on the irreversible growth of compact TATB cylindrical explosives. *AIP Adv.* 2013;3:092101.
49. Zhang H. *Control of TATB Crystal Morphology and its Impact on the Preferred Orientation.* Mianyang: China Academy of Engineering Physics; 2011.
50. Li Y, Shen M, Li J. Thermal expansion of TATB filled polymeric material. *Chin J Energetic Mater.* 2003;11(1):24–27.
51. Jiang K, Pang W, Zhou Z, et al. Study on thermal expansion of two TATB. *J Ordnance Equip. Eng.* 2016;37(6):149–152.
52. Li Y, Zheng X, Shen M, et al. Study on thermal expansion coefficient of TATB based PBX. *Chin J Explos Propellants.* 2003;26(1):23–26.
53. Gee RH, Maiti A, Bastea S, Fried LE. Molecular dynamics investigation of adhesion between TATB surfaces and amorphous fluoropolymers. *Macromolecules.* 2007;40:3422–3428.
54. Rainbolt M, Hatler L. CTE value for PBX 9502. In: *Technical Report ESA-WE-98-0422U to Brian Aubert.* USA: Los Alamos National Laboratory memorandum: Los Alamos, NM; 1998.
55. Xu Y, Tian Y, Wang H, et al. Crystal orientations of 1,3,5-triamino-2,4,6-trinitrobenzene-based polymer bonded explosives during the pressing process by neutron diffraction. *Powder Technol.* 2023;413:118044.
56. Schwarz RB, Liu C, Thompson DG, et al. *Anisotropy in the Ratchet Growth of PBX 9502.* LA-UR-15-21827. 2015.
57. Cady HH. *WX-3 Monthly Report.* Los Alamos, NM, USA: Los Alamos Scientific Laboratory; 1975. Technical Report WX-3-MR-75-4.
58. Maienschein JL, Garcia F. Thermal expansion of TATB based explosives from 300 to 566 K. *Thermochim Acta.* 2002;384:71–83.
59. Zhang Q, Huang J, Sun J. Effects of pressing parameters on irreversible growth of TATB based PBX. *Chin J Explos Propellants.* 2010;33(5):5–7.
60. Woznick CD, Thompson DG, Luca RD. TATB ratchet growth and hydrostatically confined PBX 9502. *AIP Conf Proc.* 2020;2272:100023.
61. Tu X, Shen M, Zheng C, et al. Effect of thermal aging and irradiation on thermal expansion property of TATB based PBX. *Chin J Energetic Mater.* 2016;24(6):614–617.
62. Li J, Wen M, Huang Y. Effect of thermal cycling test on the properties of TATB based PBX. *Chin J Energetic Mater.* 2005;13(4):208–210.
63. Li YB, Nie FD, Sun J, et al. Influence of irreversible growth of PBX on interface of TATB/binder. *Chin J Explos Propellants.* 2001;24(4):15–16.
64. Willey TM, Lauderbach L, Gagliardi F, et al. Mesoscale evolution of voids and microstructural changes in HMX-based explosives during heating through the  $\beta$ - $\delta$  phase transition. *J Appl Phys.* 2015;118:055901.
65. Grebenkin KF. Comparative analysis of physical mechanisms of detonation initiation in HMX and in a low-sensitive explosive (TATB). *Combust Explos Shock Waves.* 2009;45(1):78–87.
66. Urtiew PA, Tarver CM, Maienschein JL, et al. Effect of confinement and thermal cycling on the shock initiation of LX-17. *Combust Flame.* 1996;105:43–53.
67. Dallman JC, Wackerle J. Temperature-dependent shock initiation of TATB based high explosives. In: *10th Symposium (International) on Detonation; Boston, MA, USA.* 1993.
68. Vlasov YA, Kosolapov VB, Fomicheva LV, et al. Effect of temperature, density, and technical factors on the shock-wave sensitivity of plastic TATB. *Combust Explos Shock Waves.* 1998;34:467.
69. Mulford RN, Swift DC. Sensitivity of PBX-9502 after ratchet growth. *AIP Conf Proc.* 2012;1426:311.
70. Mulford RN, Alcon RR. *Shock Initiation of PBX-9502 at Elevated Temperatures.* LA-UR-95-2761. 1995.
71. Schwartz AC. *Flyer Plate Performance and Initiation of Insensitive Explosives by Flyer Plate Impact.* 1975. SAND75-0461.
72. Seitz WL, Wacherle J. Prompt initiation studies of PBX-9502 and PBX-9503. In: *5th Annual Joint Firing System Conference.* 1980.
73. Scheloske R, Green L, Weingart R. Sensitivity of triaminotrinitrobenzene (TATB) at elevated temperature. *UCRL.* 1980:18336.
74. Dallman JD, Wackerle J. Temperature-dependent shock initiation of TATB based high explosives. In: *Paper Summaries of the Tenth International Detonation Symposium; Boston, MA.* 1993.
75. Fang Q, Wei YZ, Wen SG. Temperature effects on the initiation of plastic bonded TATB by divergent shock wave. *Explos Shock Waves.* 2000;20(2):121–124.
76. Chen L, Liu Q, Wu JY. On shock initiation of heated explosives. *Explos Shock Waves.* 2013;33(1):653–655.
77. Voelkel SJ, Anderson EK, Short M, et al. Effect of lot microstructure variations on detonation performance of the triaminotrinitrobenzene (TATB)-based insensitive high explosive PBX 9502. *Combust Flame.* 2022;246:112373.
78. Thompson DG, Hill LG. Effects of TATB texture and ratchet growth on PBX 9502 corner turning. In: *Proceedings of the 16th International Detonation Symposium; Cambridge, MA, USA.* 2018.
79. Salyer TR. The effects of PBX 9502 ratchet growth on detonation failure as determined via the LANL failure cone test. *AIP Conf Proc.* 2012;1426:243–246.
80. Yeager JD, Dattelbaum AM, Orlor EB, et al. Adhesive properties of some fluoropolymer binders with the insensitive explosive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). *J Colloid Interface Sci.* 2010;352:535–541.
81. Lin C, Cheng B, Zhang H, et al. Tailoring the irreversible thermal expansion of 1,3,5-triamino-2,4,6-trinitrobenzene crystals by bioinspired polydopamine coating. *J Appl Polym Sci.* 2019;37:48695.
82. Thompson DG, Woznick CS, DeLuca R, et al. Coefficient of thermal expansion during ratchet growth of TATB compactions. *Propellants, Explos Pyrotech.* 2020;45:1877–1883.
83. Li Y, Zhou Y, Nie F, et al. Study on the growth rules of PBX TATB charges. *Chin J Energetic Mater.* 2001;9(3):139–141.
84. Liang E, Sun Q, Yuan H, et al. Negative thermal expansion: mechanisms and materials. *Front. Phys.* 2021;16:53302.
85. Lin C, Bai L, Wei L, et al. Zirconium tungstate reinforced energetic composites with inhibited thermal expansion and reduced thermal stress. *Chem Eng J.* 2023;461:141986.
86. Kasatkin IA, Gulina LB, Platonova NV, et al. Strong negative thermal expansion in the hexagonal polymorph of ScF<sub>3</sub>. *CrystEngComm.* 2018;20:2768–2771.
87. Burtch NC, Baxter SJ, Heinen J, et al. Negative thermal expansion design strategies in a diverse series of metal-organic frameworks. *Adv Funct Mater.* 2019;29:1904669.
88. Wang Z, Huang Y, Guo J, et al. Design and synthesis of thermal contracting polymer with unique eight-membered carbocycle unit. *Macromolecules.* 2018;51:1377–1385.
89. Shen X, Viney C, Johnson ER, et al. Large negative thermal expansion of a polymer driven by a submolecular conformational change. *Nat Chem.* 2013;5:1035–1036.



Cong-mei Lin is now an assistant professor. She is working in the field of energetic composites and her research focuses on structure design and the structure-property relationships of polymer-bonded explosives (PBXs). So far, she has published more than 30 academic papers in ACS Applied Materials & Interfaces, Composites Part B, Composites Science and Technology, among others. Email: [lincm2009@caep.cn](mailto:lincm2009@caep.cn)



Yu-shi Wen is a Ph.D. in Engineering Mechanics. His research interests include the ignition mechanism of explosive experiments and related computer simulations. He has published over 60 papers in relevant research fields, granted 6 patents. ORCID: 0000-0001-9452-7150. Email: [wensy@caep.cn](mailto:wensy@caep.cn)