Influence of trans 1,4,5,8-tetranitrosotetraazadecalin on mechanical integrity and microstructure of composite modified double base propellant

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ABSTRACT

This study investigates the influence of trans-1,4,5,8-tetranitrosotetraazadecalin (TNSTAD) (20-30% loadings) on the mechanical properties of composite modified double base (CMDB) propellant. A counterintuitive finding emerged: TNSTAD simultaneously enhances both stiffness (storage modulus) and mechanical damping (tan δ). Dynamic Mechanical Analysis (DMA) revealed a 14% increase in the tan δ peak, signaling new energy dissipation, while the rubbery-state modulus nearly doubled. Notably, the α-transition width (FWHMα) narrowed significantly (36.0 °C to ~ 25 °C), suggesting a more homogeneous relaxation spectrum due to uniform stress fields created by well-dispersed particles. Quasi-static tests confirmed significant reinforcement tensile strength increased by 33.7% and Young's modulus doubled, albeit with a 64% reduction in ductility. SEM fractography identified weak interfacial adhesion and debonding as primary failure mechanisms. We propose that interfacial frictional sliding at these weak interfaces is responsible for the enhanced damping. Despite the damping-ductility trade-off, TNSTAD yields a favorable stiffness-damping balance, promising improved stability and vibration tolerance.

Keywords: Ballistite propellant; Trans-1,4,5,8-tetranitrosotetraazadecalin; Dynamic mechanical analysis (DMA); Composite modified double base propellant; Energetic additives.

1. INTRODUCTION

Nitrocellulose (NC) plasticized with nitroglycerine (NG)—commonly termed ballistite—has long underpinned a wide range of ammunition systems thanks to its high energy content, processability, and stable burning behavior. As performance requirements of modern weapon platforms continue to rise (e.g., very-high-velocity small-caliber rounds and advanced armor-piercing systems), conventional ballistite increasingly reveals limitations: elevated flame temperature, accelerated barrel erosion, limited mechanical integrity, and sensitivity to impulse loading during storage, transport, and ignition [1, 2].

Traditional remedies fall into two classes: (i) energetic plasticizers up to 25% (e.g., Bu-NENA, DEGDN) to improve flexibility and combustion homogeneity, and (ii) about 18-45% crystalline energetic fillers (e.g., RDX, HMX) to raise energy density. These approaches, however, come with trade-offs. Plasticization can reduce strength and thermal stability, whereas dispersed crystals frequently introduce interfacial microvoids and brittleness unless additional surface treatments or compatibilizers are employed [1-5]. The general need remains for propellant modifications that strengthen the load-bearing network without compromising structural uniformity or increasing sensitivity.

Within this context, trans-1,4,5,8-tetranitrosotetraazadecalin (TNSTAD; chemical formula $C_6H_{10}N_8O_4$) has emerged as a promising solid energetic additive for NC/NG matrices. TNSTAD is a polynitroso compound with high nitrogen content, low oxygen balance (-80,56%), enthalpy, sub-5 μm crystal sizes, reduced impact sensitivity, a moderate decomposition temperature, and

thermal breakdown into light gaseous products (predominantly CO and NO) [6, 7]. These attributes suggest the potential to contribute to combustion while mitigating undesirable temperature/pressure spikes. Importantly, TNSTAD is not a plasticizer; rather, it is examined here as a solid energetic filler introduced as a dispersed phase with the expectation of mechanical reinforcement in the composite sense. TNSTAD should be distinguished from its more familiar descendant, trans-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin (TNAD), which is synthesized via the tetranitroso intermediate. The nitroso variant may offer advantages in decomposition behavior or compatibility relative to the nitro analog. TNSTAD has been used as an energetic additive in artillery propelling charges at loadings up to 27% [6, 8].

This study not only evaluates TNSTAD as an additive but also seeks to elucidate the mechanism by which it modulates the mechanical response of the propellant. A series of formulations with increasing TNSTAD content was prepared and characterized by DMA, uniaxial tension and compression, and SEM. Emphasis is placed on a clear paradox in the viscoelastic data, simultaneous increases in stiffness and damping and on linking this behavior to microstructural features and macroscale strength. The objective is to clarify TNSTAD's potential as an alternative route to a more favorable stiffness–damping profile in advanced propellant types.

2. EXPERIMENTAL METHODS

2.1. Materials

Nitrocellulose (NC) with a nitrogen content of approximately 11.94% and nitroglycerin (NG, purity > 99%) were employed as the primary energetic constituents of the ballistite base, offered by Z company of Industrial Defence of Vietnam. Stabilizers and processing additives, including Centralite II, carbon black, and mineral oil and Titanium dioxide, were used at a combined concentration of 4% by mass. Trans-1,4,5,8-tetranitrosotetraazadecalin (TNSTAD) was synthesized and purified in-house via an established protocol at Institute T of the Vietnam General Department of Defence Industry, involving ring-closure and nitrosation steps, followed by recrystallization to ensure high purity and consistent particle morphology. Recrystallized TNSTAD crystals were characterized by laser diffraction to determine particle-size distribution, yielding D10 = 2.87 μm, D50 = 4.65 μm, and D90 = 6.91 μm.

2.2. Sample preparation

The baseline ballistite formulation (M0) consisted of 48% NC, 48% NG, and 4% additives by mass. In order to ensure technological capability and machining safety, the TNSTAD content was selected based on the minimum content of RDX (18%) and the declared TNSTAD (27%) used in ballistite propellants, from which TNSTAD was incorporated into the base propellant at varying mass ratios of TNSTAD/base = 20/80, 25/75, 30/70, resulting in final propellant formulations labeled M1 to M3, respectively. The components were thoroughly mixed in a controlled aqueous environment at approximately (50 ÷ 55) °C for 2.5 hours at a liquid-to-solid ratio of 6:1 (water-to-solids mass ratio). After homogenization, the mixture is rolled into a thin film using a hot rolling mill operating at a temperature of (90 ÷ 95) °C, the thin film is cut into small granules and pressed through a die on a hydraulic press at a temperature of (80 ÷ 90) °C. The propellant is stored at (20 ÷ 25) °C before testing.

2.3. Microstructural characterization

Samples were cryo-fractured by immersion in liquid nitrogen and snap-breaking. Fracture surfaces were sputter-coated with platinum and examined using field-emission scanning electron microscopy (FESEM, Hitachi S-4800) at 5 kV accelerating voltage.

Particle size of TNSTAD powder was analyzed on the Partica Laser Scattering Particle size distribution analyzer LA-950V2 of Horiba.

2.4. Mechanical testing

Dynamic Mechanical Analysis (DMA): Thermomechanical properties are measured according to STANAG 4540 (NATO standard procedure for DMA of explosives. Rectangular samples (~ 30 × 5 × 2 mm) were tested in single cantilever bend mode on the PerkinElmer DMA 8000 analyzer. Temperatures are scanned from – 100 °C to + 100 °C (including sub-Tg to multiple on Tg) at 5 ºC/min, with an oscillating frequency of 1 Hz.

Tensile-compressive strength tests: Tensile and compressive tests are conducted using the M350-10 CT Measuring Machine equipped with a 10 kN force sensor, according to the following standards.

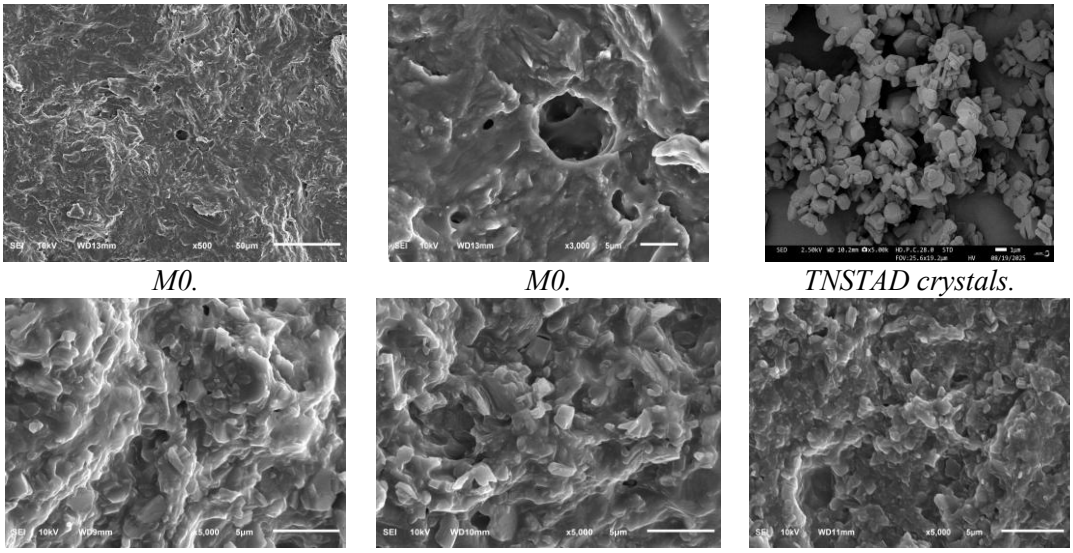
Tensile Tests (STANAG 4506): Tensile tests are performed in accordance with STANAG 4506 guidelines, using dog bone specimens with dimensions approximately 120×50×3.3 mm. A cross-head velocity of 10 mm/min is maintained throughout the test. The recorded parameters include tensile strength at peak load, strain at peak load, and strain at break. Each formula has been tested five times to ensure statistical reliability.

Compressive Tests (STANAG 4443): Compressive strength is determined according to STANAG 4443, using cylindrical specimens with a diameter of approximately 10 mm × a height of 15 mm. Compression tests are performed at a compression rate of 20 mm/min until significant failure or deformation is observed. Five repetitions for each recipe were evaluated to determine the average compressive strength.

3. RESULTS AND DISCUSSION

3.1. Microstructure and fractography

Figure 1 shows the morphological progression from the neat matrix (M0) to TNSTAD-containing formulations (M1–M3). In M0, the NC/NG matrix exhibits intrinsic micro-voids (up to ~5 μm) that act as stress concentrators. SEM images of TNSTAD crystals show not fully rounded polyhedral particles with relatively smooth facets.



M0. *M0.* *TNSTAD crystals.*

M1. *M2.* *M3.*

Figure 1. *The SEM micrographs of the TNSTAD–ballistite formulations.*

In cryo-fractured surfaces of M1, M2, and M3, TNSTAD crystals are relatively well dispersed in the NC/NG binder with no macro-scale agglomerates, also TNSTAD particles fill the inherent micro-voids observed in the base matrix; particle number density rises from M1 to M3, inter-particle spacing decreases, and local particle–particle contacts appear. Thin debonded layers along TNSTAD–NC/NG interfaces are observable at specific locations, indicating imperfect compatibility.

Rugged, torn fracture surfaces characteristic of semi-brittle NC/NG are present. Numerous "imprints/voids" in M1 to M3 mark sites where particles were plucked out during snap-fracture at cryogenic temperature; relatively smooth crystal facets indicate crack paths preferred along filler–binder interfaces (adhesive failure) rather than through the crystals themselves. This implies weak interfacial bonding - a key factor to be discussed in the viscoelastic context.

3.2. Thermo-mechanical response

Table 1. *DMA properties of propellants.*

Sample	**T_β** °C	**Tg_α** °C	**E′** (Tg+20) MPa	**E′** (Tg-20) MPa	**Tanδ** max	**FWHMα** °C	**FWHMβ** °C	**E′** (20 °C) GPa
M0	-40.0	69.2	7.05	78.1	0.325	36.01	11.14	0.345
M1	-39.2	72.7	8.97	80.9	0.346	21.80	10.59	0.445
M2	-38.6	73.8	11.9	112.0	0.370	25.29	10.71	0.531
M3	-38.0	73.8	13.2	115.0	0.369	24.66	10.50	0.583

DMA was performed to quantify the effect of TNSTAD on the viscoelastic spectrum of the NC/NG matrix, with emphasis on determining the shift and broadening (width) of the macroscopic α and microscopic β relaxations.

From DMA data (figure 2, table 1) can be seen that below 0 °C, all samples showed a secondary relaxation near − 40 °C assigned to β transition. The β-peak breadth is nearly unchanged across the series (FWHMβ ≈ 10.5 - 11.1 °C), indicating no meaningful broadening. These results suggest that TNSTAD does not materially alter the sub Tg local motions; any interfacial constraint, if present, is too subtle to resolve at the β scale with the current DMA resolution. On the other hand, the β transition temperature tends to increase from − 40 °C to − 38 °C when the TNSTAD content increases compared to the base sample, indicating that TNSTAD does not plasticize NC, in contrast to Bu NENA, which has been reported to lower this transition (from − 33.8 °C to − 38.1 °C) owing to its plasticization effect on NC [8].

TNSTAD markedly modifies the viscoelastic response of NC/NG. As the TNSTAD content increases from base to 30%, the α transition temperature Tα (defined at the tan δ peak) shifts about 7% from 69.2 °C to 73.8 °C, evidencing a modest restriction of segmental mobility. Simultaneously, the rubbery state storage modulus (E′ at Tg + 20 °C) nearly doubles, glassy at (Tg–20 °C) almost one and a half times, confirming a reinforcing effect of the filler particles.

Most notably, tan δmax increases from 0.325 (M0) to 0.369 (M3), nearly 14%. This behavior is unusual because adding rigid, non-participating crystalline fillers typically reduces the tan δ peak amplitude by constraining chain mobility and decreasing the volume fraction capable of energy dissipation [9]. The concurrent increases in stiffness (E′) and damping (tan δ) in TNSTAD filled CMDB propellants point to a new energy dissipation mechanism that is not governed by polymer segmental motion. It can be proposed that interfacial frictional sliding is the primary mechanism behind the increased tan δ. The hypothesis is supported by SEM evidence of weak bonding. Under cyclic DMA loading, the polymer matrix deforms and weakly bonded TNSTAD particles slide relative to the matrix, dissipating energy through friction. Such sliding boosts the loss modulus (E″) without a commensurate increase in storage modulus (E′), thereby raising the ratio E″/E′ (i.e., tan δ). This mechanism contrasts with well-bonded fillers, where chain immobilization at interfaces dominates and typically diminishes damping [9-11].

In addition, the width of the α transition (FWHM_α) narrows significantly, from 36.0 °C (M0) to ~ 25 °C (M2–M3). This is consistent with a more homogeneous recovery spectrum, possibly because well-dispersed filler particles promote a more uniform stress field and a more homogeneous environment for polymer chains between particles.

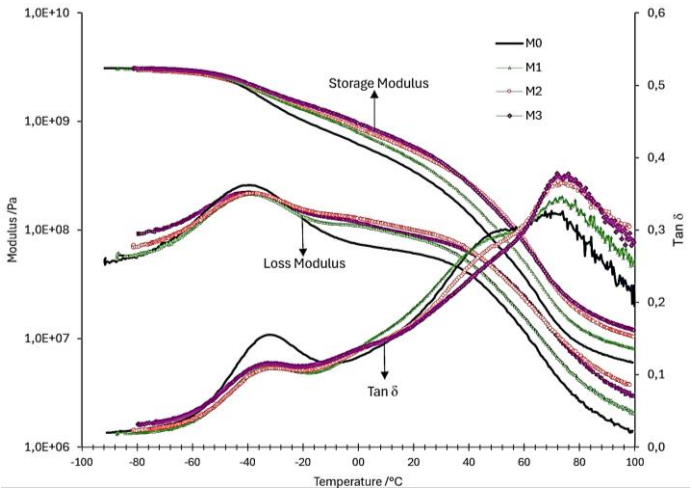


Figure 2. *DMA thermogram of propellants.*

3.3. Mechanical strength properties

Quasi-static mechanical tests (table 2) reveal substantial reinforcement, consistent with the SEM and DMA observations. Tensile strength (σ^a) increases by 33.7% from M0 to M3, and Young's modulus (E) nearly doubles. These gains follow directly from reinforcement by rigid TNSTAD particles and from void mitigation, aligning with the ~ 70% increase in the storage modulus E′ at 20 °C observed by DMA (table 1).

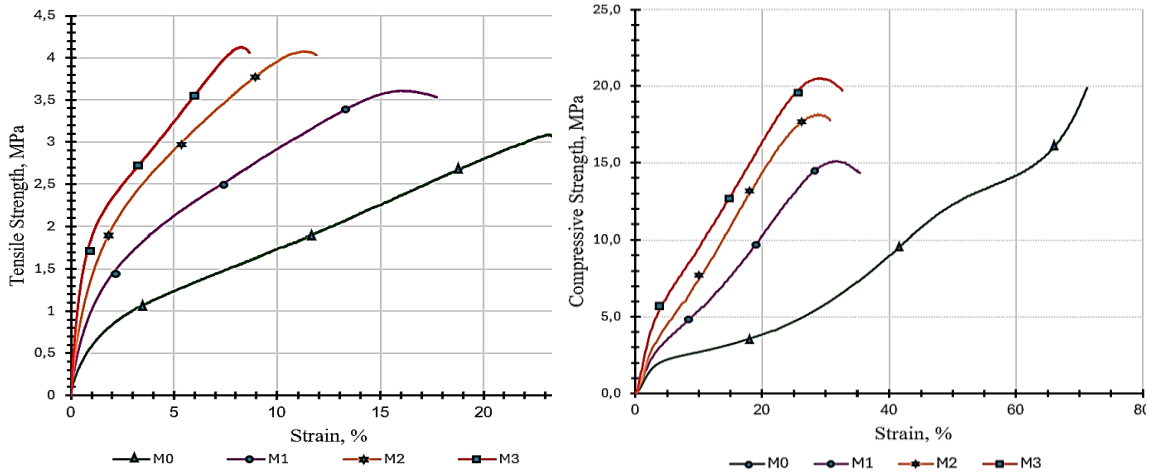


Figure 3. *Mechanical strength of propellants.*

Table 2. *Mechanical strength of propellants.*

Sample	Tensile Strength at Peak		Compressive Strength at Peak		
	σ^a [MPa]	ε^b [%]	σ^c [MPa]	ε^d [%]	E [MPa]
M0	3.09	23.07	-	-	67.46
M1	3.61	15.85	15.21	32.81	80.58
M2	4.08	11.27	18.55	25.78	110.57
M3	4.13	8.23	20.27	24.95	134.82

By contrast, elongation at peak (ε^p) drops sharply by 64%, indicating that reinforcement stiffens the matrix at the expense of ductility. The trade-off can be rationalized by the same weak-interface mechanism proposed above. Propellant failure is governed by micro-damage processes: particle–binder debonding, void nucleation, and crack growth. Under monotonic tensile loading at large strains, stresses concentrate at weak interfaces. Debonding occurs at relatively low strains, generating micro-voids that coalesce into cracks, causing premature failure and thus low elongation. The interfacial weakness that enhances small-amplitude cyclic damping (DMA) thus becomes the origin of failure under large-strain monotonic loading, explaining the observed damping–ductility trade-off.

4. CONCLUSIONS

Incorporating TNSTAD into an NC/NG matrix yields a composite propellant that combines increased stiffness with enhanced mechanical damping - an uncommon outcome for conventional crystalline fillers. This finding has important implications for the design of energetic materials that must withstand dynamic loads and vibration, such as high-performance artillery propelling charges.

It is proposed that the underlying physical mechanism is energy dissipation through interfacial frictional sliding between TNSTAD particles and the polymer matrix at weak interfaces. SEM evidence of adhesive failure, together with concurrent increases in E' and $\tan\delta$ in DMA, supports this hypothesis. However, the same interfacial weakness also serves as a failure initiation site under large deformation, leading to a strength–ductility trade-off.

Future work should focus on improving elongation at break and on physicochemical and ballistic characteristics, to enable application as propelling charges for next-generation munitions.

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TÓM TẮT

Ảnh hưởng của Trans 1,4,5,8-tetranitrosotetraazadecalin lên tính toàn vẹn cơ học và cấu trúc vi mô của thuốc phóng đa gốc

Nghiên cứu này khảo sát ảnh hưởng của trans-1,4,5,8-tetranitrosotetraazadecalin (TNSTAD) (hàm lượng 20-30%) đến các đặc tính cơ học của thuốc phóng đa gốc cải tiến trên cơ sở NC/NG. Một phát hiện trái với trực giác đã xuất hiện: TNSTAD làm tăng đồng thời cả độ cứng (mô đun lưu trữ) và độ giảm chấn cơ học (tan δ). Phân tích cơ nhiệt động (DMA) cho thấy sự gia tăng 14% chiều cao đỉnh tan δ, báo hiệu sự tiêu tán năng lượng mới, trong khi mô đun ở trạng thái cao su tăng gần gấp đôi. Đáng chú ý, độ rộng chuyển tiếp α (FWHMα) thu hẹp đáng kể (từ 36,0 °C xuống ~ 25 °C), cho thấy một phổ hồi phục đồng nhất hơn do các trường ứng suất đồng đều được tạo ra bởi các hạt phân tán tốt. Các thử nghiệm tĩnh xác nhận sự gia cường đáng kể, độ bền kéo tăng 33,7% và mô đun Young tăng gấp đôi, mặc dù đi kèm với sự sụt giảm 64% độ dẻo. Phân tích mặt gãy bằng SEM xác định liên kết bề mặt phân cách yếu và sự tách pha là các cơ chế phá hủy chủ đạo. Chúng tôi đề xuất rằng ma sát trượt tại các bề mặt phân cách yếu này là nguyên nhân dẫn đến sự tăng cường giảm chấn. Mặc dù có sự đánh đổi giữa độ giảm chấn và độ dẻo, TNSTAD mang lại sự cân bằng độ cứng-giảm chấn thuận lợi, hứa hẹn cải thiện độ ổn định và khả năng chịu rung động.

Từ khoá: Thuốc phóng ballistic; Trans-1,4,5,8-tetranitrosotetraazadecalin; Phân tích cơ nhiệt (DMA); Thuốc phóng đa gốc; Chất độn năng lượng.