

Characterization of Energetic Materials

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Introduction

Energetic materials (EMs) play a vital role in various applications, ranging from military munitions to civilian explosives for construction and resource extraction. The continuous enhancement of these materials is driven by the demand for higher performance, safety, and stability. Owing to their composition and properties, energetic materials can generally be divided into categories based on their chemical makeup and intended use (Badgujar, Talawar, Asthana, & Mahulikar, 2008).

Energetic materials can be broadly classified into several categories. The primary distinction lies between low explosives and high explosives. Low explosives, like black powder, deflagrate, burning relatively slowly and producing a rapid expansion of gases. In contrast, high explosives, such as TNT or RDX, detonate, resulting in a supersonic shockwave. Further distinctions can include:

- Propellants: used in rockets, propellants burn to produce thrust. Solid propellants consist of a fuel and an oxidizer mixed into a solid form, whereas liquid propellants combine liquid fuel with an oxidizer.
- Explosives: high explosives induce rapid combustion a detonation that produces a shockwave capable of causing destruction.
- Pyrotechnics: these include materials that burn or explode and are often used for signaling (e.g., flares, fireworks) (Klapötke, 2025).

Properties of EMs

Energetic materials (EMs) represent a critical class of chemical compounds that undergo rapid exothermic reactions, generating heat and gas—predominantly nitrogen—essential for various applications such as explosives, propellants, and pyrotechnics. Their utility spans a wide range of fields, including military uses (e.g., munitions and missiles), aerospace applications (e.g., rocket fuels), and civilian activities (e.g., construction and mining explosives). As the demand for EMs continues to evolve, the field relies on advancements that strike a careful balance between high energy density and the paramount concerns of safety, stability, and environmental impact (Chen et al.,

2021; Chun et al., 2020). Recent research efforts have intensified, focusing on various classes of energetic materials, such as high-nitrogen compounds, ionic liquids, and advanced organic frameworks, which are tailored to meet these evolving requirements (X. Liu, Ortmeyer, Bodach, Petersen, & Felderhoff, 2025; Zhou et al., 2014). This trend highlights the significance of ongoing innovations in EMs, ensuring that they remain safe and effective for both military and civilian applications (S. Zhang et al., 2020), while addressing challenges associated with environmental sustainability (Goncalves, Iha, & Rocco, 2018). Thus, the quest for novel energetic compounds continues, with an emphasis on synthesizing materials that not only enhance performance but are also safer and more environmentally friendly (An et al., 2009; Feng, Qiu, Yang, Du, & Zhang, 2016).

One of the significant trends in the development of high-performance EMs is the incorporation of nitrogen-rich compounds. Materials rich in nitrogen are desirable due to their high heat of formation, which leads to increased energetic performance. For instance, Du et al. highlight that compounds based on 1,3,4-oxadiazoles present excellent candidates for high-performing EMs due to their stability and favorable oxygen-balance properties (Du, Qu, Wang, Cui, & Wang, 2021). Similarly, Zhang et al. emphasize the role of fused triazole-tetrazine compounds that showcase versatile energetic performance, reflecting the growing trend towards advanced organic chemistry in EM development influenced by military and civilian needs (H. Zhang et al., 2024). Additionally, the focus on dinitrophenyl and tetrazole derivatives illustrates the continual exploration of new frameworks with optimized performance attributes (Zhao et al., 2024).

High-nitrogen compounds are a significant focus within the realm of EMs due to their favorable energy profiles and environmentally friendly byproducts, primarily nitrogen gas upon decomposition. Ionic liquids have emerged as promising alternatives to traditional solid explosives and propellant fuels, possessing unique properties that allow for tunable energy densities and mitigated volatility (Q. Wang, Wang, Zhou, & Gao, 2023; Q. Zhang & Shreeve, 2014). The adoption of such materials can potentially reduce the sensitivity associated with conventional explosives, offering safer handling without compromising performance. Recent advancements demonstrate that integrating high nitrogen content in energetic salts can yield materials with enhanced stability and performance traits (He et al., 2016; Q. Wang et al., 2023).

Another area of significant interest is the advancement of fused heterocycles, particularly those constructed through innovative synthetic methodologies. Studies indicate that incorporating fused-ring systems contributes to improved energetic performance while addressing safety concerns linked to traditional materials (Gao, Zhang, & Jean'ne, 2020; L. Yang et al., 2022). Fused compounds typically present a structurally resilient framework, which can stabilize the energetic content without the high sensitivity

often observed in their linear counterparts (Bu, Xiong, Zhang, & Design, 2020). The exploration of new synthetic pathways continues to provide fresh insights into designing advanced EMs that meet the rigorous demands of modern applications.

The focus has also been directed towards using metal-organic frameworks (MOFs) and nano-sized composite materials. MOFs are recognized for their tunable porosity and functionality, allowing for the encapsulation of energetic materials and optimized release profiles (Li et al., 2013; J. Liu et al., 2022). Research indicates that MOFs can serve as platforms for high-performance EMs, enhancing properties such as stability, energy output, and lower sensitivity to external stimuli (Gettings, Zeller, Byrd, & Piercey, 2019; J. Liu et al., 2022). Similarly, nano-sized composite energetic materials (nano-CEMs) present a breakthrough, leveraging their high surface area and reactivity to refine detonation characteristics and reduce the environmental impact of EMs (Jiang, Cai, Mao, & Wang, 2019; Pang et al., 2020).

Recent advancements in material science, particularly through the development of metal-organic frameworks (MOFs) and composite materials, have facilitated the production of EMs with enhanced properties. For example, Yang et al. explore the potential of multifunctional materials based on 1-aminotetrazol-5-one ligands, highlighting their broad range of sensitivities and reactivity (J. Yang et al., 2018). Furthermore, the incorporation of nanoscale additives has been shown to improve the performance of existing EMs, as demonstrated by Cheng et al., whose work reveals the positive effects of boron powders on the detonation performance of explosives (Cheng, Yao, Li, Li, & Yao, 2023).

Safety remains a paramount concern in the design of energetic materials. The challenge lies in balancing high energy density with sufficient thermal and mechanical stability, crucial for safe handling and storage. For example, Lin et al. and Liu et al. underscore the importance of developing heat-resistant EMs that can perform reliably at elevated temperatures, particularly in applications like oil and gas extraction where thermal stability is vital (Lin, Chen, Xu, Zheng, & Wen, 2019; N. Liu et al., 2020). Alongside this, the development of insensitive materials has become a focal area of research, as reflected in the studies of Dippold and Klapötke, which investigate the design of high-performance insensitive EMs through strategic molecular modifications (Dippold & Klapötke, 2013).

The importance of thermal stability in EMs cannot be overstated, as it directly influences their performance across various operational environments. The development of heat-resistant energetic materials, such as those derived from specific heterocyclic structures, has been pivotal in ensuring reliability at elevated temperatures (Stolarczyk & Jarosz, 2022; Z. Zhang et al., 2021). Advancements have led to the discovery of heat-resistant

compounds that maintain stability in ascent scenarios experienced in aerospace applications, thus meeting modern equipment demands designed for extreme conditions (Stolarczyk & Jarosz, 2022).

Thermal stability of EMs is a critical factor determining their usability in extreme conditions. Stability depends significantly on the molecular structure and the presence of stabilizing agents. Extensive studies have focused on creating heat-resistant EMs through structural modifications (Bu et al., 2020). For instance, the addition of halogens or the strategic placement of nitrogen-rich groups within molecular frameworks often results in improved stability (Li et al., 2013; J. Liu et al., 2022).

Compounds like 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) have gained attention for their thermal stability, able to resist initiation under high temperatures while maintaining good energetic outputs (Gettings et al., 2019). These findings underscore the importance of material innovations focused on retaining performance under varied environmental conditions.

Collaboration between chemists and material scientists has facilitated a better understanding of the underlying mechanisms governing impact sensitivity, stability, and energetic performance of these materials. As new compounds are synthesized, cheminformatics approaches are being integrated to model and predict the behaviors of these substances under various conditions, which is imperative to enhancing safety profiles and improving predictability in applications (Fayet & Rotureau, 2022; B. Wang et al., 2018).

The field of energetic materials is rapidly evolving, driven by the need for improved performance, safety, and environmental considerations. The synthesis of high-nitrogen compounds, exploration of ionic liquids, utilization of complex frameworks such as MOFs, and advancements in heat-resistant materials exemplify the dynamic nature of this research area. As new methodologies and materials continue to emerge, the implications for both military and civilian applications could be substantial, transforming how energetic materials are utilized across multiple industries.

Another critical aspect of EMs is the characterization of their performance characteristics under various operational conditions. Various studies have consistently demonstrated that structural modifications can significantly impact the thermal stability and detonation performance of EMs. For instance, Yao et al. discussed the effectiveness of micro-encapsulation to enhance the thermal safety of high-energy emulsion explosives (Yao et al., 2021), while Lei et al. explored integration of pyrazole compounds that have shown promise in yielding new classes of insensitive EMs without compromising safety (Lei, Yang, & Cheng, 2020; Yin, Mitchell, Parrish, & Shreeve, 2017).

In conclusion, the evolution of energetic materials is characterized by an intricate interplay of chemical innovation, safety considerations, and performance optimization. Continued research efforts aim to balance these factors while addressing the specific demands of both military and civilian applications. The synthesis of nitrogen-rich compounds, the development of heat-resistant formulations, and advances in composite materials demonstrate the dynamic nature of this field, positioning it as a critical area of both fundamental chemistry and applied sciences.

Structural, Mechanical, and Thermal Characterization of EMs

Energetic materials (EMs) are vital for various applications, including military munitions, propellants for aerospace applications, and demolition explosives in civil engineering. An accurate and comprehensive characterization of these materials is essential for ensuring their reliability, performance, and safety. Characterization encompasses a range of physical and chemical techniques aimed at understanding the materials' structure, sensitivity to external stimuli, mechanical behavior, thermal properties, and overall stability.

Structural characterization techniques such as X-ray Crystallography and Nuclear Magnetic Resonance (NMR) are pivotal in determining the molecular and crystal structures of energetic materials. These methods help elucidate the arrangement of atoms within the material, which directly relates to its energy release mechanisms during detonation. For example, Wozniak et al. highlighted the importance of identifying structural motifs by employing NMR and infrared spectroscopy coupled with crystallography to validate the structural integrity of newly synthesized energetic compounds (Wozniak, Salfer, Zeller, Byrd, & Piercey, 2020).

Additionally, infrared (IR) spectroscopy can be employed to identify functional groups and study bond formations in energetic materials, offering insights into intermolecular interactions and assessing the stability of particular chemical functionalities within the material (Pedreira et al., 2016).

The mechanical properties of EMs significantly influence their performance, particularly in terms of shock sensitivity and internal defect management. Nanoindentation provides a means to measure hardness and elastic modulus at the nanoscale, allowing researchers to understand how EMs respond to mechanical loads. Olokun et al. explored the mechanical anisotropy of β -HMX crystals through nanoindentation and small-scale dynamic impact tests, emphasizing the importance of understanding deformation mechanisms that could alter the safety parameters of explosives (Olokun, Dillard, Dhiman, & Tomar, 2021).

Dynamic mechanical analysis (DMA) provides additional insights into the elastic properties of EMs under varying temperature and frequency conditions. It helps determine

the materials' responses to dynamic loads, which is essential for evaluating potential failure under high-stress conditions (Kaneshige, Rabbi, Mach, Catzin, & Stewart, 2017).

Thermal analysis techniques, such as Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA), provide critical information regarding the thermal stability, decomposition temperatures, and energetic performance of EMs. These techniques help ascertain the temperature ranges within which the materials are stable and their decomposition profiles during thermal exposure. For instance, Gaur et al. utilized TGA and DSC to analyze the thermal stability and gas evolution of triazole-based energetic motifs, allowing for an understanding of their energetic properties (Gaur et al., 2017).

Accelerated aging tests involve subjecting EMs to elevated temperatures and humidity to simulate long-term storage conditions. By monitoring performance changes, researchers can predict shelf life and operational stability, guiding formulations for military and commercial applications (Tsyshevsky et al., 2015).

Examples of novel characterization techniques such as multiaxial testing, energetic coordination polymers, and cocrystallization. Kaneshige et al. introduced novel methods for modeling the multiaxial constitutive and damage responses of energetic materials, facilitating a thorough understanding of their behavior under various loading conditions, which is essential for practical applications (Kaneshige et al., 2017).

The synthesis and characterization of Energetic Coordination Polymers (ECPs) have gained momentum, especially in achieving a balance between high energy density and low sensitivity. These materials present unique opportunities due to their tunable mechanical and energetic properties (Qu et al., 2015; J. Yang et al., 2018).

Cocrystallization has emerged as a promising method for tuning the physicochemical properties of EMs. Wiscons and Matzger discussed the challenges of characterizing cocrystals compared to physical mixtures, underscoring the necessity for comprehensive methods such as single-crystal X-ray diffraction to ensure accurate analysis (Wiscons, Matzger, & Design, 2017).

Performance Characterization of EMs

To ensure the reliability of EMs across various applications, robust performance characterization becomes essential. Standard tests typically assess crucial characteristics of EMs, such as detonation velocity, brisance (shattering capability), sensitivity (impact, friction, and thermal), and thermal decomposition temperatures.

Detonation tests measure the speed at which the shock wave travels through an explosive; higher velocities indicate more powerful explosives. The characterization often employs

empirical correlations and thermochemical calculations to determine performance (Pang et al., 2020). The detonation velocity (Dv) is a crucial property for assessing the energetic performance of explosives. Various experimental setups, employing detonators and pressure gauges, facilitate the measurement of Dv, yielding critical insights into the efficiency and power of the material (Yan et al., 2021).

Impact Sensitivity testing methods that simulate impacts and friction provide insights into the stability and safety associated with specific EMs. Areas of interest include how structural modifications affect the energetic material's propensity for accidental detonation (Jiang et al., 2019). Impact sensitivity tests measure the threshold energy required for detonation or deflagration when exposed to mechanical shock. For instance, Wozniak et al. characterized newly developed N-amino compounds for their impact sensitivity, classifying them among primary explosives (Wozniak et al., 2020).

Friction sensitivity tests, testing the response of EMs to friction, involve applying various loads and assessing the resulting frictional interactions, which guide the design of formulations that minimize the risk of unintended initiation during handling and storage (Lal, Staples, & Jean'ne, 2024).

With increasing environmental awareness, the development of “green” energetic materials is crucial. Assessments focus on the byproducts of explosions, emphasizing formulations that yield minimal ecological damage. This has led researchers to explore eco-friendly additives and greener chemical processes to reduce toxicity (Z. Zhang et al., 2021).

Future Directions in Energetic Materials Research

The future of EMs holds immense potential as new synthetic strategies and materials continue to be developed. Much research will focus on: Computational modelling, machine learning approaches, collaboration across disciplines, and sustainability-environmental conditions.

Advances in computational chemistry have led to the development of predictive models that can simulate the performance and stability of EMs before synthesis. For example, Tsyshevsky et al. described a comprehensive approach combining synthesis, characterization, and quantum-chemical modeling to design novel energetic materials effectively (Tsyshevsky et al., 2017). This predictive capability can significantly expedite the design process by circumventing the costly synthesis of ineffective compounds.

Recent efforts have integrated machine learning techniques to enhance screening processes for EMs. Utilizing thermochemical data and properties such as cohesive energy and oxygen balance enables machine learning to predict energetic performance efficiently, aiding in the identification of promising compounds (Kang, Liu, Abou-Rachid, & Guo, 2020). This approach holds potential for optimizing formulations tailored to

specific performance metrics while reducing trial-and-error methodologies in physical laboratories. The application of machine learning algorithms can expedite the discovery of new EMs by predicting the performance of molecular structures based on existing databases, optimizing formulations based on historical data (Stolarczyk & Jarosz, 2022).

The future of EMs will likely see heightened cooperation among chemists, material scientists, and engineers, culminating in innovative approaches to EM design, synthesis, and performance testing (Fayet & Rotureau, 2022). Finding sustainable paths for the synthesis and application of EMs will become increasingly essential, pushing research towards utilizing renewable resources and minimizing hazardous waste production.

Conclusion

The field of energetic materials is evolving rapidly, reflecting the complex interplay of performance demands, safety requirements, and environmental issues. Innovations driven by high-nitrogen chemistry, advanced composite materials, synthetic pathways, and a vigorous focus on safety are shaping the future of both military and civilian applications. The ongoing exploration of materials with tailored properties, enhanced stability, and reduced sensitivities promises a new era for the development of EMs, catering to the diverse and dynamic needs across multiple sectors.

The characterization of energetic materials is a multifaceted process encompassing various techniques tailored to understanding the materials' structural, thermal, mechanical, and energetic properties. Advances in computational modeling and machine learning further enhance the research landscape, allowing predictions of performance outcomes that inform the design of next-generation EMs. Continuous innovation in analytical techniques not only aids in developing safer and more efficient energetic materials but also ensures compliance with stringent safety regulations, paving the way for broader applications in both military and civilian domains.

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