Energetic Materials with New Structures

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Sammanfattning

Nanomaterial för tillämpningar inom energetiska material (EM) är intressanta då partikelstorleken påverkar materialegenskaperna. Det finns idag studier som tyder på att stötkänsligheten skulle kunna minska med minskande partikelstorlek för EM, dock krävs ytterligare studier med fullständig statistisk utredning för att med säkerhet kunna fastslå, ifall och hur detta gäller. En fördel med energetiska nanomaterial skulle kunna vara att göra känsliga material så som till exempel CL-20 mindre känsliga, ifall materialets känslighet minskar med partikelstorleken. Energetiska nanomaterial är således intressanta ur lågkänslig ammunitions perspektiv. Det finns ett flertal studier som producerar energetiska nanomaterial genom en mängd olika metoder och karakteriserar de energetiska materialen med avseende på storlek och form samt stötkänslighet. Området har dock, trots att forskning nu pågått i ca 10-20 år inte fått något av författarna känt genombrott på den kommersiella marknaden, med undantag för nano-aluminium. Det finns ett fåtal studier där en sammansatt komponent eller formulering produceras, detta kan indikera svårigheter med formuleringar innehållande nanopartiklar. Nanopartiklar påverkar viskositeten och processbarheten av formuleringen. En annan fråga som kvarstår inom området är uppskalningsmöjligheterna av de olika metoderna som använts för att producera energetiska nanomaterial. FOI bör samarbeta med laboratorier som bedriver forskning inom området energetiska nanomaterial, samt bevaka forskningen som sker genom publicerad litteratur.

Nyckelord: nano, nanomaterial, energetiska material, energetiska nanomaterial

Summary

Nanomaterials for applications within energetic materials (EM) are interesting since the particle size affects the properties of a material. There are today studies which indicate that the impact sensitivity could decrease with decreasing particle size, however there is a need for more studies and comprehensive statistic investigation in order to establish that the sensitivity is really decreasing with decreasing particle size. A benefit of using nano-sized EMs would thereby be to make sensitive materials such as CL-20 less sensitive, if the sensitivity is decreasing with decreasing particle size. Energetic nanomaterials are thereby interesting from an insensitive munitions perspective. There are today a number of studies where nano-sized EMs are produced by a number of different methods and then characterized by size, shape and impact sensitivity. The area has however, even if research has been going on for about 10-20 years not had any by the authors known commercial breakthrough, except for nano-sized aluminium. There are few studies where composite materials or complete formulations of energetic nanomaterials are produced. This could indicate the problem of producing a formulation containing nano-sized EMs. Nanoparticles do affect the viscosity and processability of the formulation. Another question within the area is the upscalability of the methods which have been applied. FOI should keep contact, have a dialog and possibly collaborate with research facilities already established within the field. FOI should in addition follow the literature and development of the field.

Keywords: nano, nanomaterial, energetic materials, energetic nanomaterial

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1 Introduction

An ideal energetic material (EM) combines high performance and high thermal stability on the one hand and low sensitivity on the other. Nanocrystallization of EMs has gained attention due to the possibility of achieving reduced sensitivity. Existing theoretical models and experimental data reveal that decreasing crystal size can reduce the sensitivity to impact initiation of explosives [1-3]. The experimental studies showing decreased impact sensitivity do however, in most of the cases, lack statistical certainty and more studies are needed in order to prove that the impact sensitivity do decrease with decreasing particle size. The explanation for why energetic nanomaterials could provide lower sensitivity is that the reduced particle size provides lower degree of defects in the crystal structure such as inclusions, dislocations, grain boundaries etc. [4]. There has however been reports where the opposite is reported. It has been shown that the sensitivity to shock is related to the quality of the explosive particles; the higher the average density of the individual particles, the lower the number of defects like inclusions and voids and the higher the shock initiation pressure [5]. It should also be noted that the shape of particles affect the sensitivity.

It is rare to use only the energetic material, most often formulations are produced. Other ingredients except for the energetic material are; polymeric binders (which can be a wax, paraffin or rubber materials), curing agents, plasticizers, curing catalysts, stabilizers, burning rate modifiers and metals. These other ingredients are applied to tune the performance, mechanical, thermal and ballistic properties of energetic formulations. Lower sensitivity of the energetic material is beneficial, making nanocrystals of energetic materials interesting. However, it can be problematic to process a formulation containing energetic nanomaterials since the particle size affects the mixing viscosity and casting properties of composite materials, e.g. propellants and plastic bonded explosives. As a consequence, it is not straight forward whether energetic nanomaterials do provide a propellant or an explosive with better properties compared to an energetic micromaterial.

Apart from the impact sensitivity, the particle size also affects the melting and/or decomposition temperature. The reason for why the melting/decomposition temperature decreases for nano-sized substances compared to micro-sized substances could be the increase in the number of surface-molecules. The surface area increases when going to smaller particle size. The number of neighboring molecules is larger for a bulk-molecule compared to a surface-molecule, meaning that the surface-molecules will be less bound to the structure than the bulk-molecules.

There are numbers of publications where nanoparticles of energetic, as well as non-energetic materials are produced and characterized. Energetic nanomaterials have been produced by spray drying [6], electrospray [7], sol-gel [8], milling [9], anti-solvent method [2, 10], hydrothermal method [11] and other methods. There is no doubt that energetic nanoparticles can be produced, the question is whether the production methods can be scaled-up and if the final composite nanomaterial show better performance in total compared to a composite micromaterial? The sol-gel method provides an additional degree of safety since the nanocomposites are wet during the production. This could allow the production of a large quantity of energetic nanomaterial which could be stored safely for some time and dried shortly before use [8]. Bayat and Zeynali have published papers where they apply an anti-solvent method for production of nano-HMX [2, 10]. As the sol-gel method, the anti-solvent method provides the process with safety since it occurs in solvent.

Nano-sized aluminium has been applied in energetic formulations for some time [8, 12-14]. The addition of nano-sized aluminium particles have been found to enhance the burning velocity of the propellant, however only when the propellant contains oxidizers with a positive oxygen balance [12]. When the particle size decreases, as a result, the surface area of the particle increases, and this provides better contact with oxidizer and oxygen, which causes faster burning process.

The scope of this report is to investigate and evaluate the literature within the area. The majority of the current literature within the field of energetic nanomaterials focus on the production and characterization of single component nano-sized EMs. So far very little has been published on formulations and applications, such as incorporation of energetic nanomaterials in propellants or explosive compositions.

2 Organic Energetic Nanomaterials

Nano-HMX was produced by Spitzer et al. by applying a Spray Flash Evaporation (SFE) method [15]. The resulting particles were analyzed by Scanning Electron Microscopy (SEM) and X-ray powder diffraction (XRD) and were about 100 nm. The method could be applied for producing nano-TNT, RDX and CL-20 and other materials according to the authors [15].

Bayat and Zeynali prepared nano-HMX and nano-CL-20 by an anti-solvent method and the particles were characterized by SEM and XRD [2, 10]. Both studies investigate factors which affect the particle size such as surfactant and anti-solvent temperature, compressed air flow rate and nozzle diameter. In the paper from 2011 the particles showed to be of spherical or ellipsoid shape with an average diameter of 95 nm [2].

Nano-TATB was produced by a solvent/non-solvent method by Pang et al. [16]. The nano-TATB particles were of spherical or ellipsoidal shape and the particle size was about 60 nm, the particles tended to agglomerate. The nano-TATB showed lower thermal decomposition temperature compared to micro-TATB. Lower thermal decomposition temperature could indicate that the material is less stable towards thermal stress.

Qiao et al. reported a spray freezing into liquid (SFL) method for producing nano-NTO particles [17]. The nano-NTO particles had an elongated shape with a size of 70-90 nm. As the nano-TATB particles, the nano-NTO particles decomposed at a lower temperature compared to micro-sized NTO.

Castro-Rosario et al. produced nano-RDX by exposure of glass substrate surfaces to an aerosol jet containing RDX [18]. The glass substrates were exposed to five shots of the RDX aerosol jet and analyzed by SEM. The result showed about 130 particles scattered on the substrate, the average diameter of the particles was 400 nm.

Li et al. produced nano-CL-20 by ball milling [9]. The particles were characterized by SEM and showed that the particles were pseudo-spheres with an average particle diameter of 200 nm. As for nano-TATB and nano-NTO, the nano-CL-20 showed lower decomposition peak temperature compared to micro-sized CL-20 [9].

The research on carbon nanomaterials (CNMs), such as fullerenes, expanded graphite (EG), carbon nanotubes (CNTs), graphene and graphene oxide (GO) has been widely applied within energy storage, electronics, catalysts and biomaterials, as well as medical applications during the last couple of years. In a review article by Si-Ping Pang et al. the possibility of functionalizing CNMs with energetic moieties and thereby producing energetic additives was investigated [19]. In particular functionalized fullerenes, CNTs and GO are appropriate candidate components in nanothermites, solid propellants and gas generators due to the catalytic properties and easy preparation methods.

Since TATB and NTO already are insensitive it could be questioned whether it is necessary to make these compounds even more insensitive. CL-20 on the other hand is sensitive and powerful as an energetic compound, which would make it beneficial to produce CL-20 in nano-size.

The particle size seems to affect the sensitivity, as previously stated in the introduction. This could be indirect since smaller particle diameter is argued to decrease the primary void space between the particles. As mentioned, the smaller particle size could also provide lower probability to defects in the crystal structure such as inclusion, dislocations etc. In other words the quality of the crystal structure affects the sensitivity. There are studies where different crystallization paths and methods are investigated with concern on the particle quality [5].

As already mentioned there is no lack of articles presenting production of different energetic nanomaterials. The question to ask is whether the methods are upscalable. The methods where the material is in solvent during the production could be beneficial from safety point of view. Sol-gel and solvent/anti-solvent methods are both solvent-based methods which could be feasible to scale-up.

3 Non Organic Energetic Nanomaterials

3.1 Nanothermites

Thermites are compositions of fuel and metal oxides. Upon ignition by heat, thermites undergo an exothermic reduction-oxidation reaction. Below is an example of a thermite reaction.

$Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3$

Thermites are commonly used for welding. When one of the components, the fuel and/or the metal oxide are applied in nano-size the material is called nanothermites [20, 21], superthermites or metastable interstitial composite (MIC). Nanothermites react orders of magnitude faster than conventional thermites. Due to their fast reaction rates, nanothermites have been proposed for use in a variety of contexts such as igniters, actuators, micro-thrusters, micro- and nanoelectromechanical systems as well as lead-free primers for ammunition. Energetic nanomaterials may allow the replacement of toxic substances, lead and mercury salts as primary explosives for example, while being less expensive than other replacements, such as silver azide or fulminate.

Aluminium is a common fuel in nanothermites since it has a high boiling point and low cost. The upscalability of production of nano-aluminium has however been questioned [22]. Spitzer et al. did therefore investigate red phosphorous as fuel in a nanothermite mixture. The CuO/P combination led to the second best combustion potential, PbO_2 showed the best but since the combustion residues are toxic, CuO is considered to be the best option. The sensitivity to impact of CuO/P nanothermites is moderate (27–39 J), but their sensitivity to friction (<5–8 J) and sensitivity to electrostatic discharge (<0.12–0.21 mJ) show that the substance is extremely sensitive [22].

In another study by Spitzer et al. propellant grains (Vectan A1) were coated with a “green” sulfate-based nanothermite (Na_2SO_4/Al) [23]. The nanothermite was used as a pyrotechnic lighter to accelerate the ignition and the combustion of the propellant. Within the study, combustion tests were performed and showed that the combustion of pure Vectan A1 propagates by a conductive mechanism, from one burning grain to its closest neighbor. When Vectan A1 is coated by nanothermite the heat produced by the nanothermite accelerates the reaction. The difference in time for burning plain Vectan A1 or Vectan A1 coated with nanothermite in a Polymetylmetakrylat (PMMA) tube was 11 seconds versus 1 millisecond. The coated Vectan A1 was insensitive to friction (> 360 N) and to electrostatic discharge (> 105 mJ), however relatively sensitive to impact (1.56 J) [23].

Rossi et al. have developed a miniature rocket where a chip with nanothermite is used to ignite a RDX charge, which cuts and propel a stainless steel flyer in a barrel [24]. In the same study Rossi et al. prove that the impact of the flyer can initiate detonation of RDX, which is promising for removing primary explosives in detonators.

Nanothermites show faster burning rates compared to micro-sized counterparts. If nanothermites could replace toxic substances such as silver and lead azid in igniters this would be most beneficial for the community. However, since some countries already use igniters of PETN, this could be a questionable application for nanothermites.

Piercey and Klapötke write “there are many thermite systems incompletely characterized and with no studies yet carried out for practical application feasibility, so this field can only grow” [25]. It should be pointed out that a practical application is however most essential for the research field, without applications it could be discussed how useful the research could be.

Reactive materials (RMs) [26] is a research area which attract a lot of attention today. RMs most often consist of thermite-like compositions of two or more non-explosive solid materials, which stay inert and do not react with each other until subjected to a sufficiently strong thermal, mechanical, electrical or laser stimulus. Upon this stimulus the RM undergoes fast burning or explosion with release of high amount of chemical energy in addition to kinetic energy [27]. The application could be projectiles, shells etc. where the container for the EM in itself is a RM and thereby could add to the total effect of the shell. The materials which are investigated are thermites, intermetallic compounds, metal-polymer mixtures etc. The materials must be strong enough to act as structural components, be sufficiently stable to survive handling and launch, to penetrate a target, but sufficiently reactive to reliably ignite upon impact.

The 20th Biennial APS Conference on Shock Compression of Condensed Matter (July 2017) indicated a continued interest in RMs. Several presentations dealt with methods for producing various RMs, such as vapour-deposition and ink-jet printing of thin films and 3D-printing of bulk material. K. Sullivan gave an overview of how reactive properties may be tailored by precise control over the architecture of an RM [27]. Another invited presentation by S. Peiris (AFRL) highlighted the potential of RMs in future weapon systems [28], e.g. enhanced lethality from reacting warhead fragments.

4 Composite Energetic Nanomaterials

Composite materials are combinations of more than one component which form one material. Within the field of EMs a composite energetic material consists of fuel and oxidizer (e.g. propellants).

Composite energetic nanomaterials have been produced by for example sol-gel method. In the sol-gel method nano-sized primary particles ("sols") are produced by a reaction of two or more chemicals in solution. The nano-sized primary particles can be linked to form a three-dimensional solid network ("gel") containing pores filled with the remaining solution. The remaining solution is thereafter evaporated and a dense, highly uniform porous solid is formed. Simpson et al. produced a skeleton of fuel based on resorcinol-formaldehyd (RF) with nano-sized ammonium perchlorate (AP) particles as oxidizer trapped within the pores [29]. There are different modifications of the sol-gel method. Using the sol-gel method, the following nanocomposite EMs have been reported in literature: AP in a RF matrix [29], CL-20/Nitrocellulose (NC) [30], AP/RDX/SiO_2 [31], AP/SiO_2 [32], RDX/AP in a matrix of phloroglucinol (P) and nitrophloroglucinol (NP) as precursors and formaldehyde as regent [33], RDX/Glycidy azide polymer (GAP) [34] and NC/RDX/AP [35]. The above mentioned studies of nanocomposite EMs are briefly summarized in the following text.

In the study by Simpson et al. where AP was incorporated in an RF matrix, the resulting nanocomposite material was characterized by transmission electron microscopy (TEM) and small-angle neutron scattering (SANS) [29]. The surface area of the RF-AP nanocomposite was measured applying Brunauer Emmett Teller theory (BET) adsorption isotherm technique. In total, TEM, SANS and BET proved the material to be nanostructured. The material was determined energetic by differential scanning calorimetry (DSC). The sensitivity to impact was tested for the four classes of sol-gel derived EMs and compared to analogous conventional materials. As an example a 90w% PETN/10% SiO_2 xerogel made by the powder addition method resulted in a drop hammer H_{50}-value of 133 cm, which results in significant lower sensitivity to impact, compared to neat PETN, which has an H_{50}-value of 17 cm.

Brill and Tappan produced spherical nano-dimensional particles of CL-20 uniformly coated with HDI-cross-linked NC by a sol-gel to cryogel method [30]. Up to 90% solid loading was achieved. The particle size of CL-20 was determined to be in the range of 20 ± 200 nm by TEM, atomic force microscopy (AFM), and XRD. The decomposition characteristics of the composite was investigated by DSC and T-jump/ Fourier-transform infrared (FTIR) spectroscopy. The decomposition properties were controlled mostly by NC until the percentage of CL-20 was well above 50%. The drop weight impact sensitivity of the cryogels was essentially independent of the composition. This is explained by the fact that pure NC and pure CL-20 have comparable drop heights of 30-35 cm and 29 cm, respectively (on the same impact machine) and the fact that the NC was not plasticized. In the study a sensitivity to impact of about 30 cm is measured for pure CL-20, consistent with 29 cm. It should however be noted that both CL-20 and NC are relatively sensitive and the composition of CL-20 and NC is sensitive, NC is in addition unstable.

Also Chen et al. used sol-gel processing in order to achieve a nano-composite material of AP/RDX/SiO_2 [31]. The structure and its properties were characterized by SEM, BET, XRD, thermogravimetric analysis (TGA)/DSC, and impact sensitivity measurements. The structure of the AP/RDX/SiO_2 cryogel was of micrometer scale powder with numerous pores of nanometer scale and the mean crystal size of AP and RDX was approximately 200 nm. According to impact sensitivity tests, the sensitivity of the AP/RDX/SiO_2 cryogel was lower than that of the pure energetic ingredients and their mixture.

Cong et al. produced an AP-based nano-limit growth energetic material (NLGEM) [32]. A SiO_2 gel was used as a nano-limit growth skeleton material, a sol-gel method, in combination with a solution crystallization in order to make AP recrystallize in the nanopores of the SiO_2 gel skeleton, which resulted in AP/SiO_2 NLGEM. The material was characterized, the AP particle size showed to depend on the AP concentration however, in the study ranging between 69 nm to 108 nm. The sensitivity of AP/SiO_2 NLGEM was lower than those of the pure energetic components and physical mixtures according to the impact sensitivity test.

Wuillaume et al. published a study where RDX/AP nanoparticles were incorporated in a matrix of phloroglucinol (P) and nitrophloroglucinol (NP) as precursors and formaldehyde as regent [33]. According to the results obtained using the closed-vessel experiment or the ultrasonic method (ONERA), 80w% AP nanocompositions showed a stable increase in the burning rate compared to the micro equivalent. By small scale gap tests (SSGT) it showed that nano-sized 90w% RDX compositions, free of binder, were less sensitive to shock compared to micro equivalent.

Li et al. [36] produced a RDX/GAP composite and found the heat of explosion (Q) higher for the nano-composite compared to the physical blend, as well as the impact sensitivity lower for the RDX/GAP nano-composite compared to the physical blend and pure RDX. The finding of the Q is however questionable since the Q should be constant for the same chemical structure, no matter of the dimensions of the consisting particles.

Jin et al. published an article where submicrometer AP particles and nanoparticles of RDX were uniformly dispersed in cross-linked NC, prepared by sol–gel method [35]. The authors claim that the heat-of-explosion tests showed that the composite produced more energy during explosion, this is as noted before, questionable since the Q should be constant for the same chemical structure, no matter of the dimensions of the consisting particles. As in other published studies, the authors find the sensitivity of the composite lower than that of the physical mixture according to the impact sensitivity test.

Lin et al. [37] produced nano-nitramine explosives (RDX, HMX, CL-20) by bi-directional ball mining. The PBX samples were consisting of RDX/DNT/polyvinyl acetate (PVAc)/stearic acid (SA) and HMX/fluororubber Viton/PMMA/vax. Compared with the micron-sized samples, the nano-products, both plain particles and PBX compositions showed decrease in shock sensitivities.

In a study by Stepanov et al, where RDX was incorporated in a binder (wax), the crystal size and shock sensitivity was investigated, the result showed that there seems to be a minima of sensitivity for the investigated RDX particles at 500 nm [38]. The 200 nm RDX particles showed a markedly elevated sensitivity compared to the 500 nm particles. The authors explains this by that there may be a transition to an initiation mechanism which is perhaps not hot-spot based. Instead of hot-spot based initiation, a thermal explosion take place after a given delay following the passage of the initial shock wave. The authors also argue that the elevated reactivity due to the higher surface area is responsible for the higher impact sensitivity. This is however one study, more studies showing the same result would be needed in order to draw any conclusions.

In the European project HISP, nano-sized aluminium in different dimensions and amounts was evaluated in terms of burning velocities and ignition delays of HTPB-based propellants [39]. For the applied propellant mixtures, increase in performance is obtained for a nano-sized aluminium content between 1.5% and 3% (18% aluminium in total, leaving the rest of the aluminium to be of micro-size). Further increase of nano-sized aluminium content, above 3%, leads to reduced gain in both burning velocity and ignition delay. Moreover, the performance of the formulation containing 4.5% nano-sized aluminium are almost levelled with behavior of propellant containing only nano-sized aluminium (18%) [39].

As a final note worth mentioning, it is not possible to predict or give a correlation between the particle size and the density of a material or formulation. This is since small size particles have a tendency to form low-density agglomerates.

5 Amorphous Energetic Nanomaterials

The vast majority of EMs are made up of crystalline grains. In these grains, relatively small molecules are ordered, according to a specific space group, into a crystal. The grains are subsequently made up of a single crystal, or a collection of crystals. The size of the grains is typically in the range tens to hundreds of micrometers, but they can also be grown into nanoparticles, as explained in the previous sections of this report. Most EMs thus have a propensity to crystallize upon condensation. Nevertheless, depending on the thermodynamic path, other states can be reached. Recent studies [40-42] have shown that amorphous structures can be attained through rapid cooling. In general, an amorphous state material has different properties than its crystalline counterpart. It is hence of interest to investigate how critical properties for EMs differ in the amorphous state.

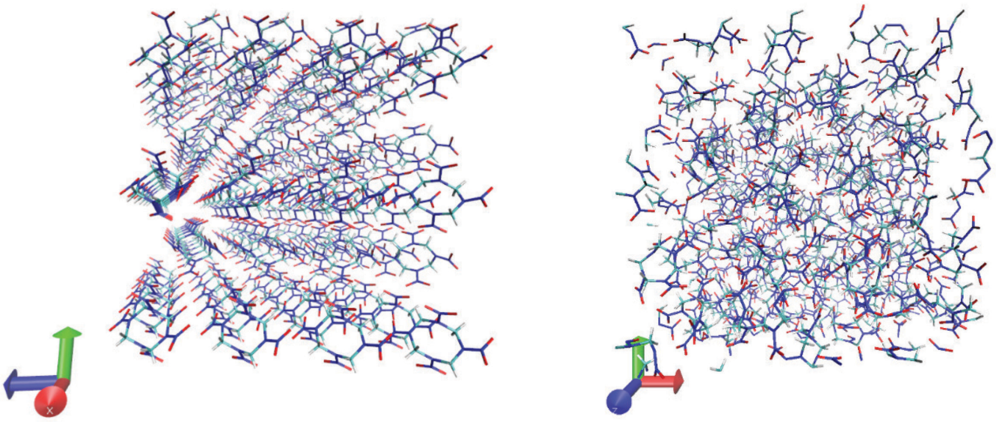

Figure 1. Snapshots from Molecular Dynamics simulations showing the molecular structure of HMX under crystalline (left) and amorphous (right) conditions after equilibration at ambient conditions.

The density of the material can be expected to be somewhat lower in the amorphous state. In order to investigate this, a Molecular Dynamics model has been constructed at FOI. In this model, NPT-simulation[I] were performed, first on HMX and RDX in their ambient crystal form and secondly in an amorphous state created by compression of randomly oriented molecules in the gas state. Snapshots from these simulations are shown in Figure 1. For both these materials, the predicted density is close to 3% lower for the amorphous structure compared to the crystal structure. This decrease can be evaluated in terms of explosive performance. For RDX, the thermochemical program Cheetah predicts a decrease in detonation velocity of 2.3% and detonation pressure of 6.9%. These calculations provide an estimate of the performance that has to be sacrificed assuming that full amorphous density can be obtained. In an application, such a decrease has to be weighed against potential advantages that an amorphous structure could offer.

One important property that possibly could be improved is the shock sensitivity. Since the presence of primarily inter-granular voids but also imperfections (dislocations, nano-voids, grain boundaries etc.) has a strong influence on sensitivity, a homogeneous amorphous structure can be expected to lead to a reduction in sensitivity. This is since an ideal homogeneous amorphous structure would be devoid of imperfections on the nano/micro-scale where energy can accumulate to form hot spots. Another feature of an amorphous structure close to theoretical maximum density (TMD) is optical transparency. Transparent explosives is something that potentially could be utilized in novel weapons and protection systems. On ARDEC's homepage [43], potential applications are mentioned: "clear,

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[I] Simulation with constant number of particles, pressure (1 bar) and temperature but with variable volume. The simulations were performed with GAFF and ReaxFF force-fields.

reactive armor, self-destructible optics, invisible mines and new types of fuzing applications”

Stepanov et al. [41] reported on preparation of samples of amorphous state CL-20/HMX/PVAc 50/45/5 where PVAc was an additive in order to increase the stability of the amorphous phase. Pellets were obtained by spray-drying technique. The high amorphous degree of this composition was confirmed by XRD. At close to full density (around 1.7 g/cm^3) optical transparency was confirmed. Impact sensitivity test of this material (proportions 72/18/10) with a 2.5 kg drop-weight (on 35 mg sample) yielded a H_{50} value of 45 cm. As a reference, the H_{50} value of the precursor CL-20 was 26 cm. These results show that some phase stability can be achieved and that the amorphous state explosive concept may be worth investigating further. Several critical issues, such as phase stability, upscalability and optimization of critical properties remain however to be investigated and solved.

6 Novel Molecular Structures

Exotic molecular structures such as cyclo-N_5 have been intriguing researchers for many years. A Chinese group recently managed to synthesize cyclo-N_5^- and stabilize it by means of $(N_5)_6(H_3O)_3(NH_4)_4Cl$ [44]. In addition just some time after, another group published the synthesis of five metal pentazolate hydrate complexes $[Na(H_2O)(N_5)]\cdot 2H_2O$, $[M(H_2O)_4(N_5)_2]\cdot 4H_2O$ (M = Mn, Fe and Co) and $[Mg(H_2O)6(N_5)_2]\cdot 4H_2O$ [45].

The pentazole HN_5 and its anion (cyclo-N_5^-) are in many ways ideal as EM. They would impose no/low levels of toxic fumes since N_2 would be the major product upon decomposition. The performance of an energetic material is dependent on its density, the chemical elements present in the molecule and the heat of formation (ΔH_f). An all nitrogen containing molecule provides high performance due to that upon decomposition only N_2 is produced, which contains one of the strongest bonds in nature.

7 Conclusions

Both nano-size crystalline and amorphous state EMs are interesting however, both have several aspects which need to be clarified. Those aspects are for example possibility to scale up the production process, stability and processability. Many of the published articles today involve spraying using nozzles, since the diameter of the nozzle determines the particle size the nozzle limits the production volume. More nozzles can of course be applied but the question is, if this is sustainable and economical, as a production method. The nano-size materials have shown a decrease in melting and decomposition temperature compared to the micro-sized materials. Whether this is an issue has not been investigated. Due to the lack of full-scale polymer matrix nano-size particle composite studies there is no knowledge about how the processability of nano-composites would work. Or, there are no studies since it is an issue which has not been solved, yet. Studies within the area of nano-size crystalline materials have been reported for some 10-20 years now. Most studies so far are focused on exploring the possibilities, the number of different particles to produce, different production methods and different processing conditions etc. However, except for nano-size aluminium it is not known, by the authors, whether nano-size crystalline EMs are applied within commercial products. This could be seen as an indication of the complexity of the issues.

A number of the published articles included in this review state questionable arguments and results, such as that the heat of explosion (Q) would increase for a nano-composite material compared to a micro-sized counterpart. Since the Q is dependent on the constituent chemical elements and the bonds between them, a difference in the Q for two samples of the same chemical elements is questionable. Many of the studies showing the difference in impact sensitivity for nano-sized substances compared to micro-sized materials do not use standards (e.g. STANAG etc.) for measuring the impact sensitivity and provide, most often, only one value without a confidence interval or standard deviation.

Amorphous state energetics is a novel field where basic studies on properties and manufacturing are necessary. Critical questions that should be addressed are stability of the amorphous state, as well as, quality and density of bulk material. Moreover, it is still an open question to what degree properties such as insensitivity to shock can be improved.

It is recommended that FOI collaborate with other laboratories and research institutes regarding nano-size crystalline and amorphous state EMs. It would be of interest to investigate the effect of particle size on impact sensitivity in a throughout statistical way. FOI should follow the development of these research fields in the literature. This in order to increase our knowledge and understanding of the field and the development within novel energetic materials.

8 References

1. Siegert, B., M. Comet, and D. Spitzer, *Safer energetic materials by a nanotechnological approach.* Nanoscale, 2011. **3**(9): p. 3534-3544.
2. Bayat, Y. and V. Zeynali, *Preparation and Characterization of Nano-CL-20 Explosive.* Journal of Energetic Materials, 2011. **29**(4): p. 281-291.
3. Lefrancois, A., et al., *Nanostructured HE based on nano-RDX and nano-RDX/AI Detonation Properties*, in *47th Intenrational Annual Conference of ICT* June 28 - July 1, 2016: Karlsruhe, Germany.
4. Armstrong, R.W., *Dislocation mechanism for shock-induced hot spots.* Journal of Physics IV. Colloques, 1995. **5**: p. C4-89-C4-102.
5. Heijden, A.E.D.M.v.d. and R.H.B. Bouma, *Crystallization and Characterization of RDX, HMX, and CL-20.* CRYSTAL GROWTH & DESIGN, 2004. **4**(5): p. 999-1007.
6. An, C., et al., *Preparation and Properties of 2,6-Diamino-3,5-dinitropyrazine-1-oxide based Nanocomposites.* Propellants, Explosives, Pyrotechnics, 2013. **38**(2): p. 172-175.
7. Mei, X., et al., *Ignition and combustion characteristics of Al/Ni(IO3)2*4H2O nanothermite*, in *48th International Annual Conference of ICT* 2017, ICT: Karlsruhe, Germany.
8. Teipel, U., *Energetic Materials - Particle Processing and Characterization* 2005: WILEY-VCH Verlag GmbH & Co. KGaA.
9. Guo, X., et al., *Massive Preparation of Reduced-Sensitivity Nano CL-20 and Its Characterization.* Journal of Energetic Materials, 2015. **33**(1): p. 24-33.
10. Bayat, Y., M. Eghdamtalab, and V. Zeynali, *Control of the Particle Size of Submicron HMX Explosive by Spraying in Non-Solvent.* Journal of Energetic Materials, 2010. **28**(4): p. 273-284.
11. Zhou, W.-L., et al., *Preparation and Properties of Nano-Al/MoO3 Thermite*, in *48th International Annual Conference of ICT* 2017 ICT: Karlsruhe, Germany.
12. Luman, J.R., et al., *Development and characterization of high performance solid propellants containing nano-sized energetic ingredients.* Proceedings of the Combustion Institute 2007. **31** p. 2089–2096.
13. Gromov, A., L.T. DeLuca, and U. Teipel, *Aluminium nanoparticles application to energetic systems - new horizons or sunset?*, in *5th International Annual Conference of ICT* 2014, ICT: Karlsruhe June 24-27, 2014.
14. Yarrington, C.D., et al., *Nano Aluminum Energetics: The Effect of Synthesis Method on Morphology and Combustion Performance.* Propellants, Explosives, Pyrotechnics, 2011. **36**(6): p. 551-557.
15. Pichot, V., et al., *Elaboration of pure nano HMX and nano composite by Spray Flash Evaporation Process*, in *48th International Annual Conference of ICT* 2017, Fraunhofer ICT: Karlsruhe, Germany.
16. Yang, G., et al., *Preparation and Characterization of Nano-TATB Explosive.* Propellants, Explosives, Pyrotechnics, 2006. **31**(5): p. 390-394.
17. Yang, G., et al., *Preparation and Characterization of Nano-NTO Explosive.* Journal of Energetic Materials, 2007. **25**(1): p. 35-47.
18. Mercado, L., et al., *Synthesis and Characterization of High-Energy Nanoparticles.* The Journal of Physical Chemistry B, 2004. **108**(33): p. 12314-12317.

19. Yan, Q.-L., et al., *Highly energetic compositions based on functionalized carbon nanomaterials.* Nanoscale, 2016. **8**(9): p. 4799-4851.

20. Weismiller, M.R., et al., *Dependence of flame propagation on pressure and pressurizing gas for an Al/CuO nanoscale thermite.* Proceedings of the Combustion Institute, 2009. **32**(2): p. 1895-1903.

21. Comet, M., et al., *Elaboration and Characterization of Manganese Oxide (MnO2) Based "Green" Nanothermites*, in *39th International Annual Conference ICT* 2008: Karlsruhe, Germany.

22. Comet, M., et al., *Phosphorus-Based Nanothermites: A New Generation of Pyrotechnics Illustrated by the Example of n-CuO/Red P Mixtures.* Propellants, Explosives, Pyrotechnics, 2010. **35**(3): p. 220-225.

23. Berthe, J.-E., et al., *Propellants Reactivity Enhancement with Nanothermites.* Propellants, Explosives, Pyrotechnics, 2016. **41**(6): p. 994-998.

24. Glavier, L., et al., *Nanothermite/RDX-Based Miniature Device for Impact Ignition of High Explosives.* Propellants, Explosives, Pyrotechnics, 2017. **42**(3): p. 308-317.

25. Piercey, D.G. and T.M. Klapötke, *Nanoscale Aluminum - Metal Oxide (Thermite) Reactions for Application in Energetic Materials.* Central European Journal of Energtic Materials, 2010. **7**(2): p. 115-129.

26. Nechitailo, N.V., *Enhanced performance reactive composite projectiles*, 2007, Google Patents.

27. Sullivan, K. *Controlling material reactivity using architecture*. in *20th Biennial APS Conference on Shock Compression of Condensed Matter*. 2017. St Louis, US: APS.

28. Peiris, S. *Enhancing Energy in Future Conventional Munitions*. in *20th Biennial APS Conference on Shock Compression of Condensed Matter*. 2017. St Louis, US: APS.

29. Simpson, R.L., et al., *Nanostructured Energetic Materials Derived From Sol-gel Chemistry*, in *31st International Annual Conference of ICT* 2000, ICT: Karlsruhe, Germany.

30. Tappan, B.C. and T.B. Brill, *Thermal Decomposition of Energetic Materials 86. Cryogel Synthesis of Nanocrystalline CL-20 Coated with Cured Nitrocellulose.* Propellants, Explosives, Pyrotechnics, 2003. **28**(5): p. 223-230.

31. Chen, R., et al., *Preparation and Properties of an AP/RDX/SiO2 Nanocomposite Energetic Material by the Sol-Gel Method.* Propellants, Explosives, Pyrotechnics, 2012. **37**(4): p. 422-426.

32. Li, G.P., et al., *The Preparation and Properties of AP-Based Nano-Limit Growth Energetic Materials.* Advanced Materials Research, 2014. **924**: p. 105-109.

33. Wuillaume, A., et al., *Formulation and Characterizations of Nanoenergetic Compositions with Improved Safety.* Propellants, Explosives, Pyrotechnics, 2014. **39**(3): p. 390-396.

34. Li, G., et al., *Synthesis and properties of RDX/GAP nano-composite energetic materials.* Colloid Polym Sci, 2015. **293**: p. 2269–2279.

35. Jin, M., et al., *Preparation and properties of NC/RDX/AP nano-composite energetic materials by the sol–gel method.* Journal of Sol-Gel Science and Technology, 2015. **76**(1): p. 58-65.

36. Li, G., et al., *Synthesis and properties of RDX/GAP nano-composite energetic materials.* Colloid Polym Sci 2015. **293**: p. 2269–2279.

37. Liu, J., et al., *Study of nano-nitramine explosives: preparation, sensitivity and application.* Defence Technology, 2014. **10**: p. 184-189.

38. Stepanov, V., et al., *Initiation properties of nanocrystalline rdx-based explosive compositions.* 2010: p. 23-29.

39. Maggi, F., et al., *Optimization of ignition properties and agglomeration features of the main metal-based fuel candidates*, 2013: The European project HISP. Deliverable no: D5.4.

40. Knepper, R., et al., *Microstructure Evolution during Crystallization of Vapor-Deposited Hexanitroazobenzene Films.* Propellants, Explosives, Pyrotechnics, 2012. **37**(4): p. 459-467.

41. Stepanov, V., et al., *Investigation of Nitramine-Based Amorphous Energetics.* Propellants, Explosives, Pyrotechnics, 2016. **41**(1): p. 142-147.

42. Stepanov, V., H. Qui, and H. Surapeneni. *Production and Characterization of Novel Energetic Compositions by Spray Drying*. in *ICT*. 2012. Karlsruhe.

43. ARL. *At molecular level, Picatinny Arsenal seeks to develop versatile, transparent explosives*. 2016.

44. Zhang, C., et al., *Synthesis and characterization of the pentazolate anion cyclo-N5- in (N5)6(H3O)3(NH4)4Cl.* Science, 2017. **355**(6323): p. 374-376.

45. Xu, Y., et al., *A series of energetic metal pentazolate hydrates.* Nature, 2017. **549**(7670): p. 78-81.

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