CRYSTALLIZATION OF INSENSITIVE HMX PARTICLES

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Abstract

In this study HMX was recrystallized from different solvents by a cooling crystallization process to improve the product quality and to produce a more insensitive product. It was found that particles with the best quality were crystallized from propylenecarbonate with a nucleation initiation by dosing a small amount of water as drowning-out substance. This leads to particles with a very high density (near to the theoretical value) and thus to particles with a small amount of inclusions. GAP tests with this product show less sensitivity against shock. A clear linear dependence of the particle density on the shock initiation pressure was found. The particle density is relatively easy to measure so it will be a useful measure to determine the sensitivity of the material.

1. Introduction

The crystallization of any material, so also energetic materials, is subject to increasingly stringent demands regarding crystal size distribution, particle shape, purity, filterability, free-flowing properties and storability. For energetic materials additional demands are required with respect to their hazardous properties, like impact and friction sensitivity, thermal stability and compatibility with other chemical substances. The majority of these properties is influenced by the technique with which these materials are produced. Also the solvents used during the production process may affect these properties. Therefore, it is of great importance to design and improve production processes and equipment in such a way that the product demands are satisfied.

Another important issue related to energetic materials is the fact that the decision whether or not a newly synthesized energetic material is interesting for further development, is based on the thermal stability and sensitivity of the material. The assessment of these properties is often carried out with particles which are not yet optimized with regard to particle shape, mean size and purity and these properties might influence the thermal stability and sensitivity results and hence the decision whether the energetic material will enter a subsequent development step [1, 2]. For this reason, identification of a suitable production technique, where often a crystallization step is the final process, is important not only to further improve already existing energetic materials, but also newly developed materials.

Compared to size reduction in which the particles are subjected to high levels of mechanical stress, crystallization procedures for the preparation of particles of explosives offer substantial advantages. The crystals can be grown relatively slowly and free of stress and they have a well-defined crystalline shape and morphology.

2. Fundamentals

The important energetic materials cyclotrimethylene trinitramine (RDX, hexogen) and cyclotetramethylene tetramine (HMX, octogen) belong to the family of the nitramine explosives, since they contain C-N-NO_2 groups. One of the advantages of HMX compared to RDX is its higher density, resulting in a slightly higher detonation velocity and pressure and hence a higher performance. In contrast to RDX, HMX crystallizes in four different polymorphic forms. Apart from the four polymorphs which have been experimentally identified for HMX, also a large amount of crystal structures has been found consisting of a complex of HMX molecules with solvent molecules. Examples for such complex structures are HMX/NMP (N-methyl pyrrolidone) and HMX/DMF (dimethyl formamide) for which crystallographic data are available [3, 4].

The influence of the crystallization solvent on the crystal morphology was studied for HMX as well as for RDX by several groups. Kinetic data of the crystallization of RDX or HMX in different solvents are only known from few studies in literature.

Xijun et al. present in their paper kinetic data determined by microcalorimetry [5]. They conclude that the measurement of the heat produced and the rate of heat production during the crystallization process is possible in a microcalorimeter and from that data the growth kinetic can be determined. The crystallization kinetics of RDX and HMX from dimethyl sulfoxide (DMSO) and cyclohexanone can be expressed by the BCF dislocation theory model. Moreover, it was shown that the addition of seed crystals of RDX results in an increase of nuclei in the seeded solution compared to the unseeded solution.

Duverneuil et al. investigated the crystallization of HMX from DMSO and cyclohexanone [6]. They concluded that the crystal growth is limited by the diffusion step when cyclohexanone is used as solvent and the integration of the growth unit into the crystal structure is the limited step when DMSO is used. In this study the influence of the solvent on the crystal morphology was also under investigation. It was shown that the crystals of HMX from cyclohexanone are more or less spherical and twinned. Moreover, in certain crystals the presence of cyclohexanone in inclusions has also been observed. In contrast to this results the HMX crystals are sufficiently regular and symmetric and do not contain any inclusions when the crystallization was carried out from DMSO or from a DMSO/acetone mixture. The authors explained the differences with the solvent-solute interactions which are confirmed by the calculation of the entropy factor of the surface defined as:

$$\alpha_s = \frac{4 \cdot \sigma_s \cdot h_c \cdot l_c}{k_b \cdot T} \qquad (1)$$

Here h_c, l_c are the height and width of a monomolecular growth layer, respectively, σ_s is the surface energy, k_b is the Boltzmann constant and T the absolute temperature. The calculation of this surface factor of entropy for the investigated systems showed differences between cyclohexanone and DMSO. For cyclohexanone this factor is 0.60, for DMSO it is 0.26 which shows that there is an absence of ideality which is more pronounced in the solution of dimethylsulfoxide.

Svensson et al. investigated the crystallization of HMX from γ–butyrolactone by cooling and precipitation [7]. They found that HMX can be crystallizaed from γ–butyrolactone in the desired β-modification without any detectable amount of α-HMX. The crystals are well shaped and have a relatively low tendency to form crossed crystals or other irregularities. For the crystallization they used different cooling programmes. With natural cooling, that means with a high cooling rate at the beginning, the resulting mean particle size was found to be consistently around 150 µm. With a more efficient cooling system it is possible to obtain mean particle sizes of 60 – 70 µm.

When long crystallization times are used coarser particles can be produced. Using a cooling period of 6 h a mean particle size of around 500 µm was found, whereas a 3 h cooling period results in a product with a mean particle size of around 320 µm. Seeding the solution changes the particle size to a more coarse product (900 µm).

Very fine particles can be obtained by precipitation of HMX from γ–butyrolactone by adding water to this solution. The mixing can be done either in a static mixer or directly in the crystallization vessel. The crystals obtained usually have mean particle sizes between 5 and

35 µm, depending on the exact conditions used. Similar results can be obtained by the crystallization of RDX from γ–butyrolactone.

The production of superfine RDX particles is described by Ruijun et al. [8]. They used solvent-nonsolvent techniques and the mean particle size was around 0.2 µm. The RDX was dissolved in dimethylformamide and water was used as non-solvent. Two process variations were studied resulting in different mean particle sizes. Both variations are distinct in mixing patterns. In the first process, the solution is fed into the non-solvent, which results in a very rapid dispersion and a high nucleation rate due to the high supersaturation. The particles are very fine, the particle size distribution is narrow and the BET surface area is up to 6 m^2/g. The second way in which the non-solvent is fed into the solution is distinguished by larger particles with a BET surface area of about 4 m^2/g due to the lower supersaturation and therefore a lower nucleation rate. The agitating speed had a tremendous influence on the particle size. Increasing the speed from 300 rpm up to 1300 rpm the mean particle size decreases from 20 µm to 1 µm and the particles became well-distributed and agglomeration was prevented. Best results were obtained if the temperature of the water was as low as possible due to the fact that the growth kinetic rose along with the temperature increasing. The temperature of the solution influences the shape of the RDX particles. At low temperatures (15 °C) needle-like particles were obtained whereas spherical particles will be formed at high temperatures (60 – 70 °C). Between this minimum and maximum temperature plate-like particles were formed.

3. Experimental Section

3.1. Setup and Proceedure

The objective of this study was to find out whether a relationship exists between the solvent and experimental conditions on the one side and the amount of defects in the crystals on the other side. The experimental work was carried out in a batch crystallizer with a volume of 1 l and 2.5 l, respectively. The supersaturation of the solution was achieved by cooling with different linear rates. The experimental setup is shown in figure 1; an example of the temperature during the crystallization process is given in figure 2.

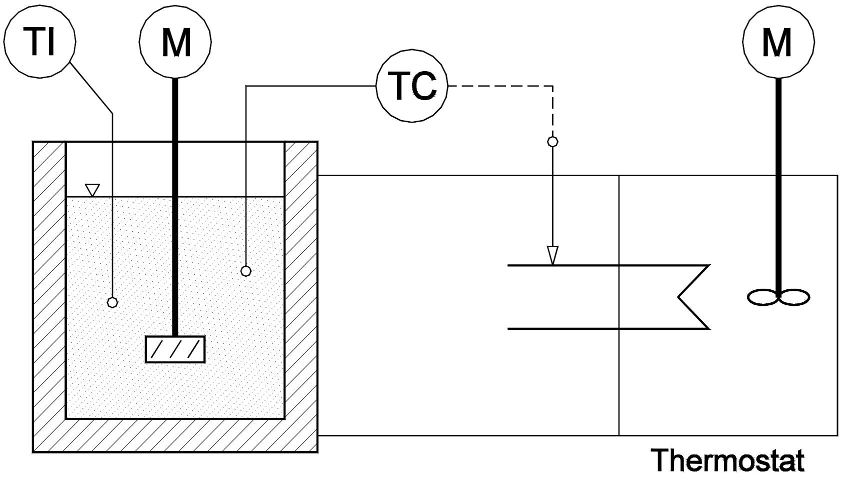

Figure 1: Schematic view of the experimental setup

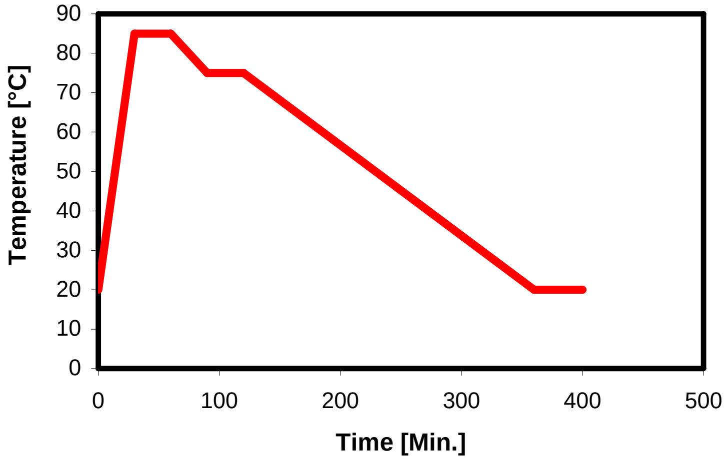

Figure 2: Temperature curve during cooling crystallization

3.2. Solubility Curves

Five different solvents were used in this study. Before starting with the crystallization experiments it was necessary to determine the solubility curves of these binary systems. The following equation (2) describes the results of this investigation. The constants a, b and c are summarized in table 1 for the different solvents [9].

$$\frac{X^*}{g_{HMX} / g_{solvent}} = a + b \cdot \frac{\vartheta}{°C} + c \cdot \left(\frac{\vartheta}{°C} \right)^2 \qquad (2)$$

Due to the very low solubility of HMX in acetone and the very high solubility of HMX in DMSO at low temperatures batchwise cooling crystallization is not the preferred technique for these systems so no experiments were carried out.

Table 1: Summary of the constants a, b and c in equation (2) for different solvents

Solvent	a	b	c
Acetone	$-6.0 \cdot 10^{-5}$	$1.0 \cdot 10^{-5}$	0
N-Methylpyrrolidone	$5.8 \cdot 10^{-3}$	$-9.0 \cdot 10^{-4}$	$7.0 \cdot 10^{-5}$
N,N-Dimethylformamide	$1.9 \cdot 10^{-2}$	$-2.0 \cdot 10^{-4}$	$2.0 \cdot 10^{-5}$
Propylenecarbonate	$-1.6 \cdot 10^{-2}$	$1.8 \cdot 10^{-3}$	0
Dimethylsulfoxide	0.5	$3.7 \cdot 10^{-3}$	0
Cyclohexanone	$4.0 \cdot 10^{-3}$	$7.0 \cdot 10^{-4}$	0

3.3. Results

3.3.1. Cyclohexanone

The crystallization of HMX from cyclohexanone was characterized by the fact that the yield of crystals was very low. Theoretically about 90 % of the material should be recrystallized when the solution is cooled from 80 °C down to 5 °C. In the experiments only 15 % was found what can be explained by a very strong inhibition of the nucleation kinetic. Seeding of the solution was not carried out because of the disadvantages of the seed crystals on the quality of the final product (maybe inclusions in the seed crystals will influence the sensitiveness of the final product). Therefore some evaporative crystallization experiments were carried out with cyclohexanone. The yield was a little bit better than in the cooling crystallization (increasing from 15 up to 30 %) but the crystal shape was very bad so that further experiments with cyclohexanone has not been carried out.

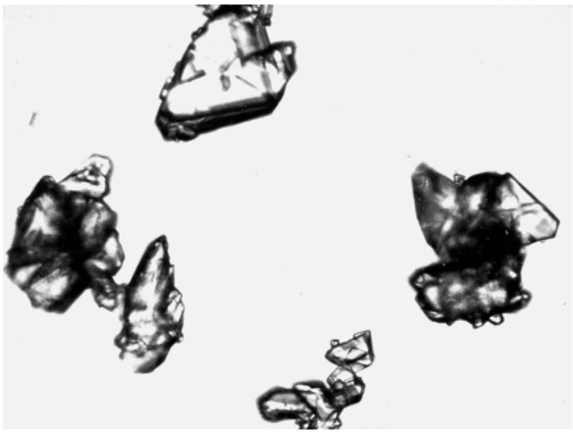

Figure 3: HMX crystals recrystallized from cyclohexanone

Figure 3 shows some crystals from these experiments which are very irregular with no clear morphology.

3.3.2. N-Methylpyrrolidone (NMP)

The crystallization of HMX from N-methylpyrrolidone results in crystals with a bad quality. The surface of the crystals was very rough and the particle shape was irregular (see figure 4). The quality of these crystals was not increased by decreasing the cooling rate which normally results in a slower growth rate and a more regular growth.

Figure 4: HMX crystals recrystallized from N-Methylpyrrolidone

The mean particle size increases by decreasing the cooling rate. Furthermore some crystals were opaque what can be interpreted by solvent inclusions in the crystals. This interpretation can be supported by the measurement of the particle density. These measurements show a particle density of 1.602 gcm^{-3} which is much lower than the theoretical density of HMX (1.903 gcm^{-3}) and of the density of the starting material (1.871 gcm^{-3}). A lower density can be a quantitative measure of the amount of inclusions because the density of the crystalline material is higher than the density of the solvent or a gas. However it is possible that the low density results from the formation of a HMX-NMP complex during the crystallization.

3.3.3. N,N-Dimethylformamide (DMF)

The particles formed by cooling crystallization experiments from DMF are distinguished by their spherical shape and their smooth surface (see figure 5). The influence of the stirrer speed on the mean particle size was investigated. It was shown that an increase of the stirrer speed results in a slight increase of the mean particle size but also in a spreading of the particle size distribution. Both results can be explained: a higher stirrer speed improves the transport of growth units to the crystal surface which results in a higher growth rate. On the other hand the crystal-stirrer collisions are intensified when the stirrer speed is increased, so that attrition is strengthened and the formation of fine particles is enhanced. The influence of the cooling rate on the particle size can be neglected.

In spite of the improvement in particle shape and surface quality no further experiments from DMF solutions were carried out due to the fact that during this crystallization HMX-DMF complexes are formed which have a much lower density (1.612 gcm^{-3}) than the theoretical one. GAP test carried out with this recrystallized material showed a much higher shock sensitivity compared to the sensitivity of starting material.

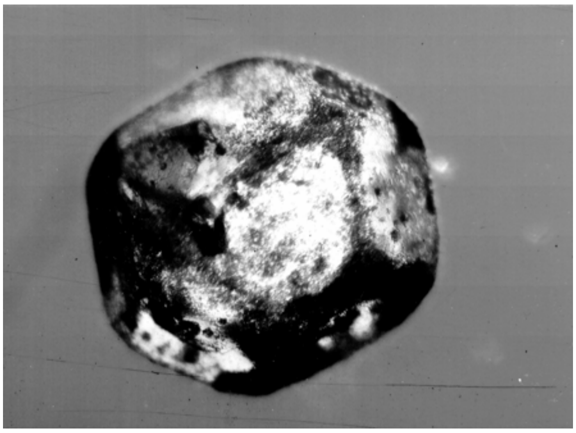

Figure 5: HMX crystals recrystallized from N,N-Dimethylformamide

3.3.4. Propylenecarbonate (PC)

During the crystallization from propylenecarbonate the beginning of the nucleation was much uncontrolled and high supersaturations are caused so that a large amount of fine particles are obtained. Therefore it was decided to start the nucleation at a certain supersaturation ($S = 1.26$) by adding a small amount of water into the supersaturated solution (drowning-out effect). Crystals are formed which are distinguished by a very compact and regular shape (figure 6, left).

However some twinned crystals are produced which show one or several internal cracks or other imperfections, oriented along a diagonal crystallographic plane (figure 6, right). Possibly the crystallographic plane where the two orientations of the twin meet, lead to internal mechanical stresses at or near this boundary. The crystals were mostly transparent which indicates a low amount of internal inclusions. This assumption is supported by the very high particle density which is 1.895 gcm^{-3} and therefore close to the theoretical density but much higher than the density of the starting material. Again the increase of the stirrer speed results in an increase of the mean particle size due to the improvement of the mass transfer from the bulk to the crystal surface. Decreasing the cooling time that means increasing the cooling rate results in a significant smaller mean particle size and the presence of roughness on the crystal surface which are signs of dendritic growth caused by higher supersaturation.

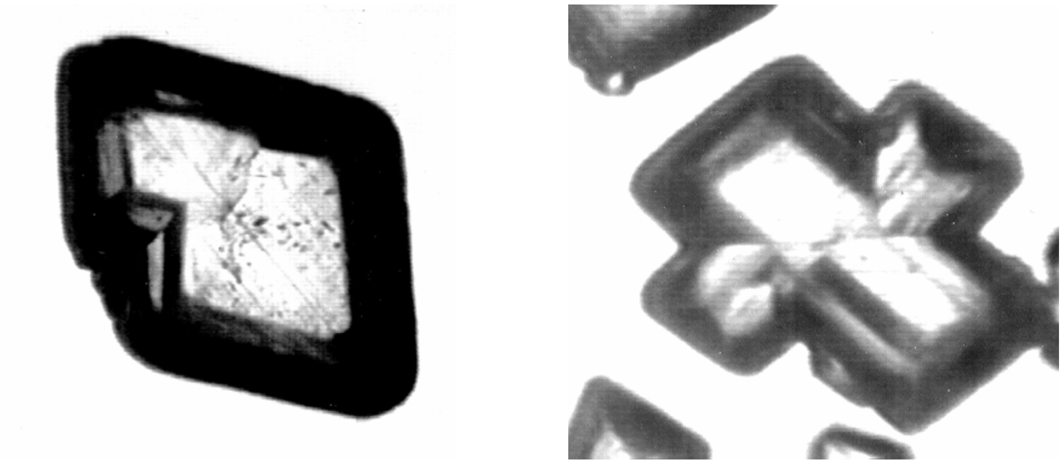

Figure 6: HMX crystal recrystallized from propylenecarbonate

3.4. Characterization

Internal crystal defects like inclusions are responsible for the sensitivity of the energetic material. Inclusions can act as hot spots where shock waves can initiate the reaction. If inclusions are present in a material, this will lead to a small but generally measurable lowering of the density, since the voids are either filled with solution or gases having a lower density than the solid material.

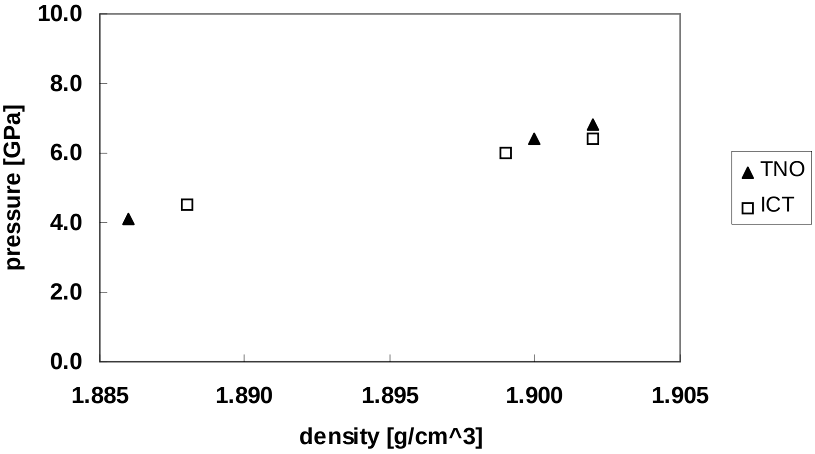

Figure 7: Shock initiation pressure vs. crystal density of HMX embedded in a 70 wt.-% solid load HMX/HTPB based PBX. Data refer to the water gap test as carried out independently by TNO Prins Maurits Laboratory (TNO-PML, The Netherlands) and the Institut für Chemische Technologie (ICT, Germany). The theoretical crystal density of HMX is 1.903 g/cm^3.

The density of the crystals can be regarded as a measure for the internal perfection of the crystals, i.e. the closer this value is to the theoretical maximum density, the more perfect the material. For HMX a clear relationship between mean crystal density and shock initiation pressure was found. An example is shown in figure 7 [9, 10]. The shock initiation pressure is seen to increase from ~ 4 GPa (reference batch) to ~ 6 GPa (recrystallized HMX), with increasing density of the HMX crystals. This is a significant improvement of the shock sensitivity.

4. Conclusions

In this study HMX was recrystallized from different solvents by a cooling crystallization process to improve the product quality and to produce a more insensitive product. It was found that particles with the best quality were crystallized from propylenecarbonate with a nucleation initiation by dosing a small amount of water as drowning-out substance. This leads to particles with a very high density (near to the theoretical value) and thus to particles with a small amount of inclusions. Gap tests with this product show less sensitivity against shock. A clear linear dependence of the particle density on the shock initiation pressure was found. The particle density is relatively easy to measure so it will be a useful measure to determine the sensitivity of the material.

The product quality is influenced by changing some crystallization parameters like stirrer type and rate, cooling rate and supersaturation at which the nucleation is started. Also the method to initiate the nucleation can influence the product quality. Drowning-out, seat crystals or the use of ultrasound are methods to initiate the nucleation. Kröber et al. investigated sonocrystallization of NTO (3-nitro-1,2,4-triazole-5-one) from aqueous solutions [11]. They compared the sonocrystallized material with material crystallized without ultrasound. It was seen that the nucleation starts earlier ($\Delta T = 6.5$ K) when ultrasonic initiation was applied compared to the experiments without ultrasound ($\Delta T = 12$ K). The sonocrystallized material is distinguished by a narrow crystal size distribution and by a smaller mean particle size ($x_{50,3} = 254$ µm) in comparison to the normal crystallized material ($x_{50,3} = 345$ µm). Microscopic pictures show that the use of ultrasound in crystallization processes can result in much regular crystals.

5. Literature

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