Research paper

Habit modification of 1,1-diamino-2,2-dinitroethylene (DADNE) by crystallization

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Received : November 15, 2011 Accepted : January 28, 2012

Abstract

1,1-Diamino-2,2-dinitroethylene (DADNE, FOX-7) is a new promising insensitive high energetic material. The final performance of this material is similar with common high energetic materials such as RDX and HMX. However, DADNE shows the lower sensitivity to impact and friction than those materials. The final applications, which are solid loading, ballistics, shelf-life, and compatibility, and sensitivity of high energetic materials depend on the crystal properties such as morphology, size, size distribution, solvent inclusion, and polymorph. The synthesized DADNE crystals had needle-like morphologies and the mean particle size of 50 μm. In order to control the properties, seed crystals were initially generated by changing the solvent composition adding water as an anti-solvent to DADNE/dimethylacetamide (DMAc) solution, and those crystals were slowly grown by cooling of the solution. The important factor of this research which influenced the crystal properties was a feeding method of the anti-solvent into the solution. Depending of the manner of feeding anti-solvent, the crystals with the desired properties could be obtained. The morphologies of the final products were polygonal and the mean sizes were 35 and 145 μm, respectively. In addition, the impact sensitivities of the products were 26 and > 35 J depending on the mean size, respectively.

Keywords : DADNE, crystallization, morphology, size, sensitivity

1. Introduction

DADNE (or FOX-7, 1,1-diamino-2,2-dinitroethylene) which was first prepared by Latypov et al.[1] shows the similar characteristics of detonation to RDX, but it shows much lower impact and friction sensitivities. These properties of DADNE were explained by the study of its crystal and molecular structures[2]. Most of high energetic materials are not suitable to use directly after synthesized due to properties such as purity, morphology, and size distributions. Crystallization is a well-known process for separation and purification, and it also can be used to enhance the morphology and size distribution of crystals. The DADNE crystals obtained by synthesis show a needle-like shape and the mean particle size of 50 μm. In a present study, DADNE crystals synthesized were recrystallized from the solution to change the properties, especially morphologies and sizes. The driving force for crystallization is supersaturation and the properties of the final products highly depend on the supersaturation during the crystallization process[3]. There are various techniques to generate the supersaturation such as cooling, evaporating, changing the solvent compositions, and reaction[4]. Of these techniques, the combination of drowning-out and cooling was used to generate supersaturation in the solution and to finally produce the DADNE crystals with the desired properties in this study.

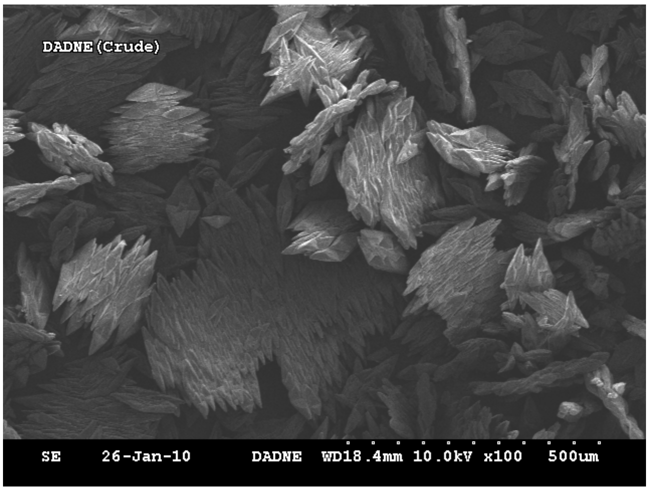

Figure 1 Synthesized DADNE.

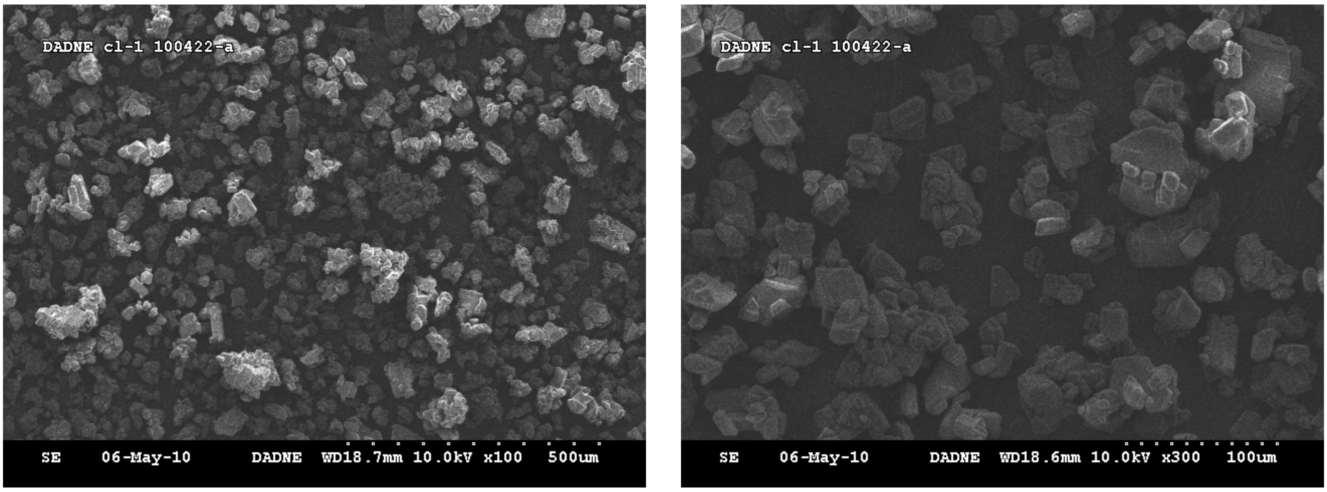

Figure 2 Recrystallized DADNE (38μm).

2. Experimental

DADNE used in this study was synthesized at Hanwha Corporation R & D center as shown in Figure 1. The purity of dimethylacetamide (DMAc) used as a solvent was 98.5% and distilled water used as an anti-solvent. The DADNE/DMAc solution with the concentration of 38 wt% was prepared in a jacketed-vessel at 75°C. After the solute was completely dissolved, water was fed into the solution to generate seed crystals using a peristaltic pump. The amount of water used was the half weight of the DADNE/DMAc solution. The temperature and the feeding rate of water would be different according to the desired particle size. After feeding of water completed, the solution was cooled down at the constant cooling rate. The crystals obtained were analyzed for purity, thermal properties, particle size, density, acidity, and sensitivities.

3. Results

The SEM images of the recrystallized DADNE are shown in Figures 2 and 3 and the mean particle sizes were analyzed by a laser particle size analyzer.

In this study, the desired mean crystal sizes are 30 μm and 150 μm. In order to obtain those crystal sizes, the temperature of the anti-solvent has been changed from 40°C to 90°C and the feeding rate also has been changed. As shown in Figure 2, the crystals show the polygonal shapes and the mean particle size of 38 μm. These crystals were obtained by feeding the anti-solvent whose temperature was maintained at 40°C. On the other hand, the crystals shown in Figure 3 have the mean particle size of 149 μm and have the polygonal shapes. They were obtained with the anti-solvent of the temperature of 90°C. As mentioned above, the mean particle size has been changed depending on the temperature and the feeding rate of water. Those factors are related to the supersaturation condition which is the driving force for crystallization from the solution. In this experiment, supersaturation would be primarily generated by changing the solution composition as the anti-solvent is added. During this process, the metastable zone width would be narrower as the temperature difference between the solution and the anti-solvent becomes lower. Therefore, the spontaneous nucleation occurs at the different point in the metastable zone and the crystal growth rate also can be different depending on the temperature of the anti-solvent. For the effect of the feeding rate of the anti-solvent, it influences the supersaturation generation in the solution in the same manner. In order to generate small crystals, the temperature and the feeding rate of the anti-solvent

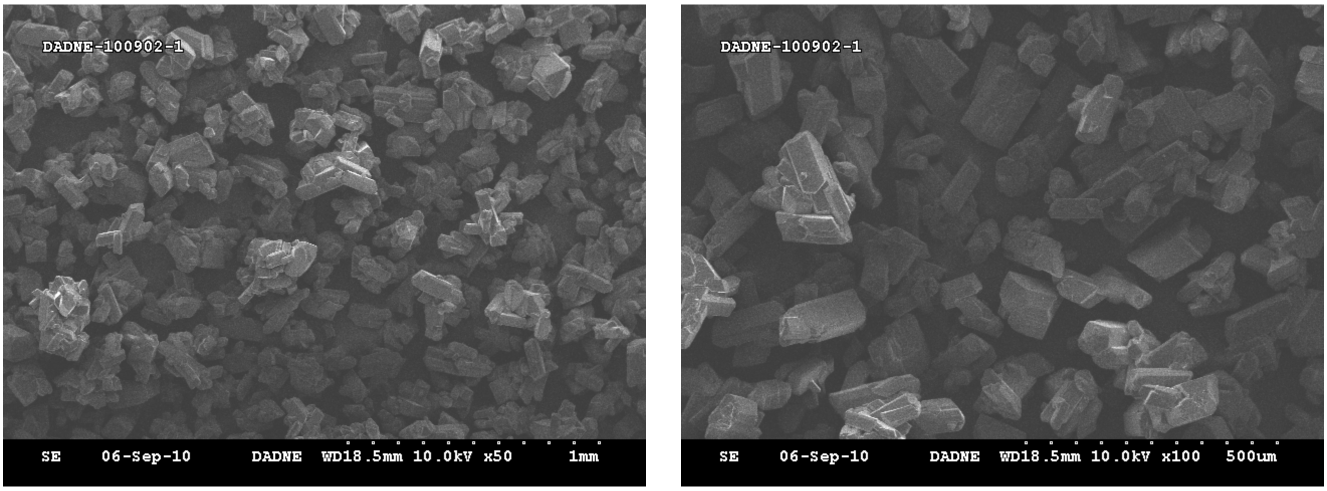

Figure 3 Recrystallized DADNE (149μm).

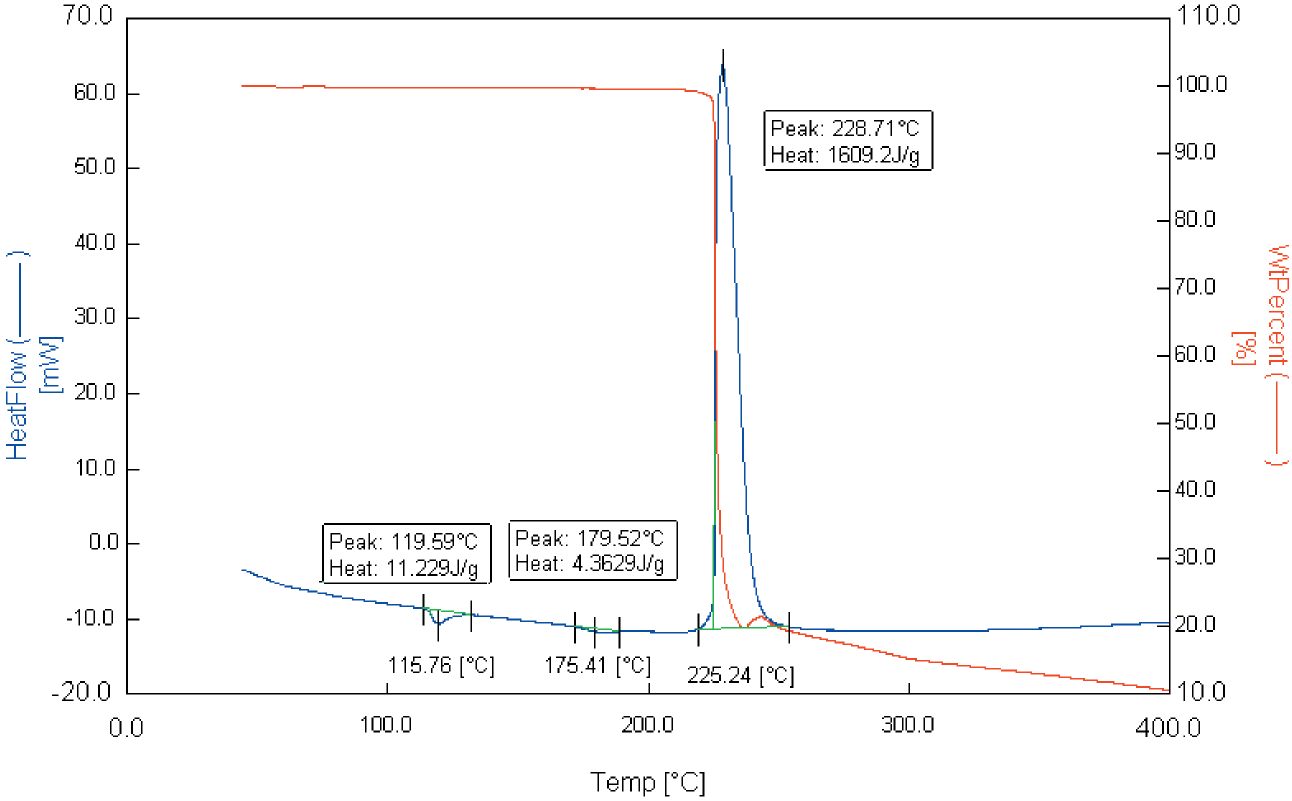

Figure 4 Thermal analysis of DADNE.

should be low and fast depending on the desired final crystal size.

The crystals obtained were analyzed to verify the crystal properties. The DSC/TGA analysis at the heating rate of 10°C min^{-1} is shown in Figure 4. As known as well, the solid phase transitions occur at 115~120°C and at 150~180°C and then the solid decomposition begins at 225~235°C. The transition and decomposition temperatures can be slightly shifted with heating rate, crystal size, morphology, and solvent inclusion. Other analysis results are listed in Table 1.

The impact and friction tests were performed for the final products analyzed. DADNE is well known as a promising insensitive high energetic material with the impact sensitivity of 20~40 J and the friction sensitivity of > 350 N. The test results are listed in the Table 2.

The friction sensitivities of the samples are lower than the values known. This is due to the shape of the crystals. Generally, the edges of the crystals have a higher surface energy than the others. Therefore, the crystals obtained in this study show lower sensitivity to the friction due to their morphologies. Therefore, etching of the edges on the crystals was done to improve the sensitivities. Figure 5 shows the SEM image of the crystals after etching. Those crystals show the impact sensitivity of 45 J and the friction sensitivity of 270 N.

4. Conclusion

In the present study, DADNE synthesized was recrystallized by the combination of drowning-out and

Table 1 Analysis results.

	BT.1	BT.2	BT.3	BT.4	Method
Density [g ml^{-1}]	1.8748	1.8727	1.8792	1.8771	Helium pychnometer
Purity [%]	No impurity detected	No impurity detected	No impurity detected	No impurity detected	HPLC
Acidity [%]	0	0.001	0	0	Titrator
Decomposition [℃]	225.24	224.91	233.72	232.31	DSC (10 K min^{-1})
Mean size [μm]	38.21	39.04	145.9	144.4	Laser analysis
Yield [%]	97	93	88.75	93.64	

Table 2 Impact and friction test results.

	BT.1	BT.3
Impact sensitivity [J]	25.6	35.48
Friction sensitivity [N]	268.5	244.2

cooling method. The mean size of the final products was dominated by the temperature and the feeding rate of the anti-solvent. With this method, the mean size of the final crystals can be controlled without changing the properties of the final products.

Reference

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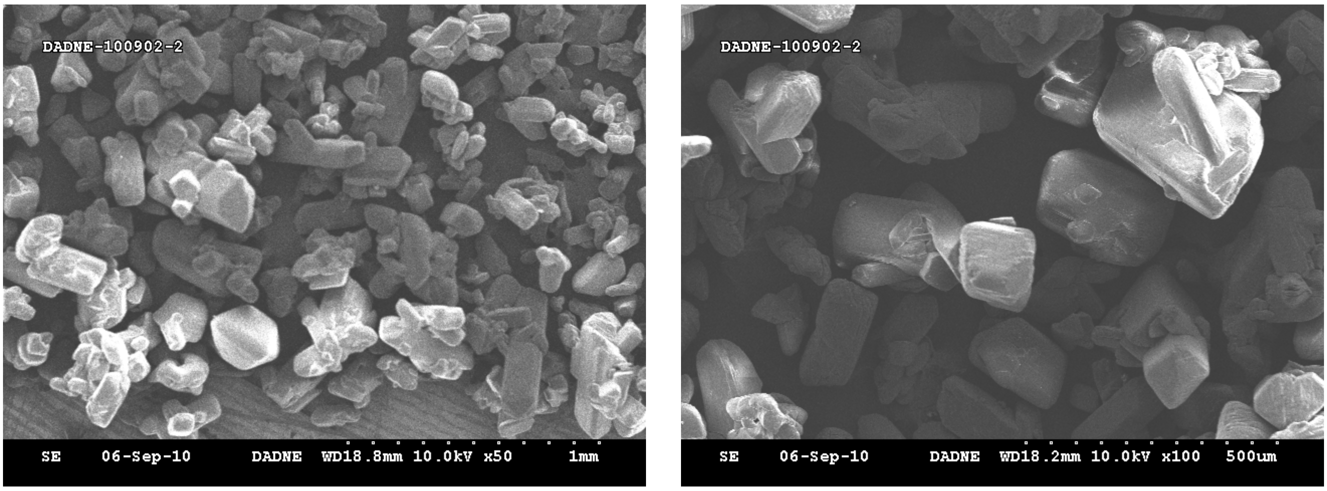

Figure 5 DADNE after etching.