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Mechanical Behavior of Nanostructured and Microstructured Explosives

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Abstract: Nanostructured hexolites (40/60), (60/40), (80/20) and microstructured hexolite (60/40) powders are pressed by uniaxial compression to obtain explosive charges. This kind of composition is often used for the synthesis of detonation nanodiamonds. The morphology, density and cohesion of the resulting pellets are analyzed in the light of the different used compression parameters. This study allows optimizing the compression parameters to obtain well suited explosive charges from nanostructured explosive components. A good cohesion of the nanostructured explosive pellets could be obtained with increasing the temperature used for the compression. Another very important point is that the nanostructuring of the composites is maintained for every compression.

Keywords: Nanostructured · Microstructured · Explosives · Hexolite · Uniaxial compression

1 Introduction

Research on materials is going toward the miniaturization through the nanostructuring. In the energetic material domain, some studies reports about the nanostructuring of explosives by using different techniques [1–4]. These techniques are rather expensive and only allow synthesizing small quantities of product (i.e. mg to a few g) and mainly with only one explosive. In our laboratory, we have developed a new process, namely the Spray Flash Evaporation (SFE), which permits to synthesize nanosized explosive particles in large amounts (up to 100 g per h) and to produce composites (hexolite, octolite…) [5–7].

These nanostructured compounds should lead to a lot of breakthroughs in various domains of pyrotechnics. The reactive properties should be changed for numerous explosives by decreasing their size and modifying their morphology. Even the classical detonation theory may have to be revised to model and predict the reactive behavior of these new materials. The characterization of the morphological and reactive properties of nanometric explosives or explosive mixtures requires large samples, which can be easily produced by the SFE technique. One of the applications for high explosives is the synthesis of materials by top-down or bottom-up approach. For instance, detonation nanodiamonds are classically synthesized by detonation of hexolite compositions prepared from micrometer-sized explosive particles [8–10]. By using a nanostructured explosive charge, a striking result was obtained, the synthesis of ultrafine nanodiamonds, smaller than those usually synthesized by using a microstructured explosive charge could be performed [7, 11]. These experiments require knowledge about the shaping of nanostructured explosive powders in order to obtain charges with a high density and a good cohesion.

In this article, the behavior of nanostructured and microstructured hexolites during uniaxial compression was investigated. Their density, microstructures, cohesion, and homogeneity were extensively studied according to different compression parameters such as pressure, temperature, or aspect ratio.

2 Results and Discussion

2.1 Results

2.1.1 Particle Size

The size of the starting material was investigated by Scanning Electronic Microscopy (SEM) and Atomic Force Microscopy (AFM) (Figure 1). While SEM is very interesting because it can give valuable information on the morphology at micrometric and nanometric scale, it has the disadvantage to modify slightly the explosive particles due to the

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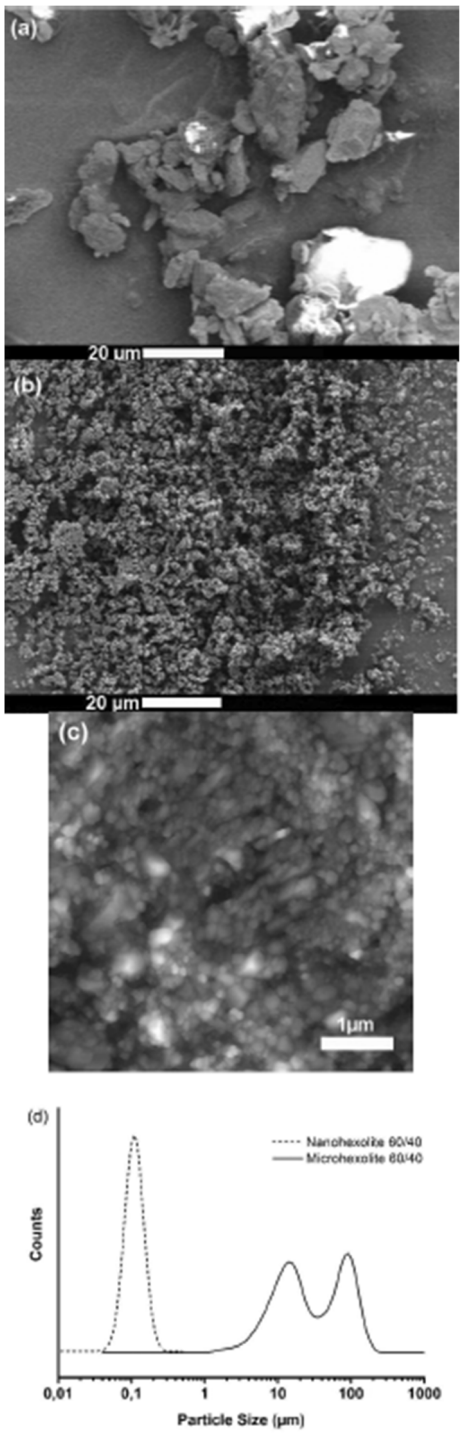

Figure 1. Observation by SEM at the same magnification of the starting materials: microhexolite (60/40) (a), nanohexolite (60/40) (b), AFM image of nanohexolite (60/40) (c), size distribution curves obtained from both materials (d).

energy provided by the electron beam and the applied vacuum. TNT, which usually melts around 80 °C, moves and melts under the electron beam. AFM measurements were conducted on nanostructured materials because of the small interaction between the sample and the AFM tip, it has the advantage to be non destructive for this kind of sample (i.e. it does not modify the size or shape of the explosive particles). In microstructured hexolite, the particle sizes range from 5 to 100 µm, (Figure 1 a). Conversely, the nanostructured hexolite is made of RDX and TNT particles having a size smaller than 1 µm with a majority around or below 100 nm (Figure 1 b–d).

2.1.2 Aspect Ratio

Different conditions were tested in order to explore the compression behavior of these explosives. In a first time, the nanostructured explosive materials were pressed at room temperature so as to maintain the nanostructuring. In order to perform all experiments with the same lots, the diameter of the pellets was fixed at 15.8 mm.

A preliminary study of the density gradient depending on the aspect ratio (L/Φ) was performed on 60/40 microstructured hexolite in order to determine the best pressing conditions to obtain the most homogeneous density in the pellets. The densities were measured on pellets with aspect ratios of 1 and 2. The pellets pressed at 220 MPa were machined into two and three equal parts for $L/\Phi = 1$ and 2, respectively. The density values are reported in Table 1.

According to the variation of the density between the lower and the upper parts, the length over diameter ratio was set to 1. The densities were measured on numerous pellets, in this case, the standard deviation of the density between the center and an extremity of the pellet was always found to be around 0.01 g cm^{-3} (0.6 %).

The variation of the density was also studied by helium pycnometry to check the porosity of the pellets at different pressures (Table 2).

In both cases, the densities measured by pycnometry are higher than the one measured by immersion in water. Indeed, in the case of pycnometry, the helium can penetrate inside the porosity of the pellets while the water

Table 1. Densities of the different parts of microstructured explosive pellets pressed at 220 MPa.

L/Φ	Density [g cm^{-3}] (immersion in water)			
	Superior	Median	Inferior	Δ
1	1.683	–	1.662	0.021
2	1.681	1.652	1.610	0.071

Table 2. Densities of microstructured explosive pellets pressed at 153 and 220 MPa.

P [MPa]	Density [g cm^{-3}]	
	Helium pycnometry	Immersion in water
153	1.739	1.633
220	1.712	1.678

cannot. For an applied pressure of 153 MPa, the density value is the same as the Theoretical Maximal Density (TMD) (1.738 g cm^{-3}) indicating that all the porosity of the pellet is open. When the pressure is increased to 220 MPa, a slight decrease of the density value is noticed, this is due to the closing of the porosity when applying a higher pressure.

2.1.3 Microstructure and Pressure

A comparison between the densities (measured by immersion in water) depending on the applied pressure was performed on a microstructured and a nanostructured 60/40 hexolite (Figure 2).

The density measurements were achieved after one and three days for both hexolites. For each applied pressure, the nanostructured hexolite reaches a higher density than the microstructured one. After 3 d, for higher pressure than 140 MPa, a relaxation inducing a decrease of the pellets densities is observed for the nanostructured hexolites and some cracks could be detected. At lower pressures, very small cracks were observed, but no break of the pellets occurred. As this study was also performed to fix the optimized compression conditions of such materials, it is obvious that some problems may be encountered. The loose powder densities of both hexolite were measured by helium pycnometry and values of 1.737 g cm^{-3} $\pm$ 0.003 and 1.740 g cm^{-3} $\pm$ 0.003 were found for nanohexolite and microhexolite, respectively. Due to the precision of the measurement, the difference of 0.003 g cm^{-3} that was found cannot be considered as valuable and we cannot conclude that the difference of the density in the pellets is linked to the density of the starting powders.

2.1.4 Composition

Similarly, the evolution of the density vs. the applied pressure for compression of nanohexolites of different compositions was studied (Figure 3).

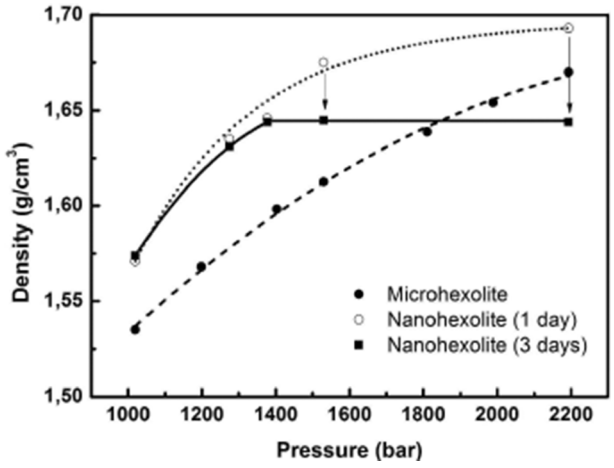

Figure 2. Evolution of the density according to the pelletization pressure for microhexolite and nanohexolite (60/40).

When the TNT content increases, the variation of the density with the increase of the pressure is less pronounced and the compactness of the pellets is higher. All the pellets were visually cracked after 3 d. The cracks were more pronounced for high RDX content.

In order to be able to prevent the formation of cracks in nanohexolite pellets, the effect of the temperature applied during the compression was investigated.

2.1.5 Temperature

According to Meyer et al., micrometer-sized TNT melts at 81 °C [12]. The experiments of compression were conducted with temperatures which did not exceed 60 °C, to avoid the melting of the TNT and the subsequent loss of the nanostructuring. Figure 4 shows the evolution of the density of pellets formed from microstructured and nanostructured hexolites at constant pressure of 100 MPa depending on the temperature applied during the compression.

The increase of the pellet density by pressing at different temperature evolves linearly for the microstructured hexolite. This might be due to the fragmentation of the biggest

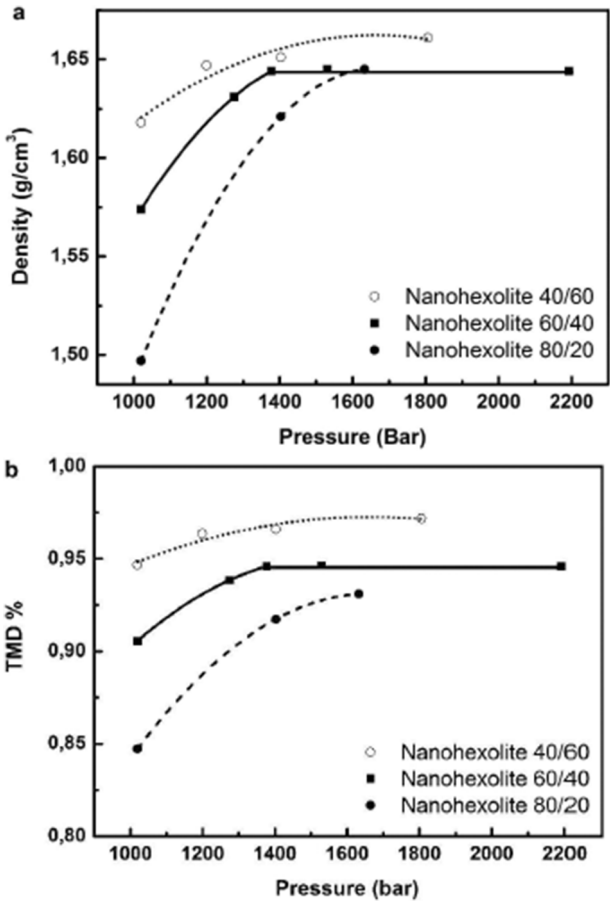

Figure 3. Density (a) and TMD percentage (b) of 40/60, 60/40, and 80/20 nanohexolites depending on the applied pressure during compression.

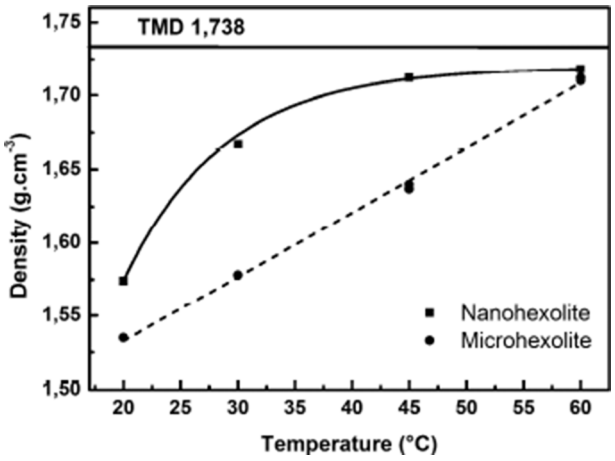

Figure 4. Evolution of the nanohexolite and microhexolite (60/40) density depending on the temperature applied during the compression for a constant pressure of 100 MPa.

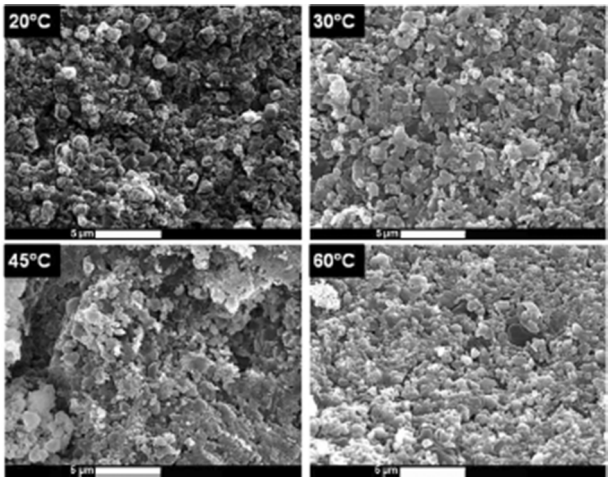

Figure 5. SEM images showing the structure of nanohexolite after compressions at 20 °C, 30 °C, 45 °C, and 60 °C for a constant pressure of 100 MPa.

particles into smaller particles, which will fill the initial intergranular porosity. Concerning nanostructured hexolite, a slight increase of the temperature during the compression allows increasing more efficiently the density than in the case of the microstructured one. For temperatures of 30 °C and 45 °C, 96% (1.667 g cm^{-3}) and 98.5% (1.712 g cm^{-3}) of the TMD, respectively, can be reached for the pellets obtained from the nanostructured hexolite, whereas in the case of the microstructured one, densities of 91% (1.578 g cm^{-3}) and 94% (1.637 g cm^{-3}) of the TMD, respectively, are obtained. For a temperature of 60 °C, both pellets have nearly the same density. The pellets prepared from nanostructured materials pressed at a temperature ranging from 30 °C to 60 °C do not undergo cracking, even after weeks of ageing. To ensure that the nanostructuring was maintained, SEM investigations of the pressed nanohexolite morphology were performed (Figure 5).

For every sample, it can be clearly seen that the nanostructuring was preserved after pressing the compositions under the different conditions, the microstructured hexolite (not shown here) also show no evolution of their microstructure (i.e. no melting). Moreover, XRD patterns revealed that no amorphization of the TNT occurred in any cases.

The homogeneity of the density was also studied (Table 3) on the pellets obtained after pressing at 100 MPa at different temperatures.

In the case of the microstructured hexolite, some density difference can still be noticed between the top and the bottom of the pellets at every temperature, a slight decrease of the variation is still observed for a pressing temperature of 60 °C. Concerning the nanostructured hexolite, for pressing temperature of 45 °C and 60 °C, the variation of density between the top and the bottom of the pellets is zero indicating a good homogeneity of the pellets.

The densities measured by helium pycnometry and immersion in water (Table 4) gives some additional results.

Table 3. Densities of the different parts of microstructured and nanostructured hexolite (60/40) pellets pressed at 100 MPa for pressing temperatures of 30 °C, 45 °C, and 60 °C.

T [°C]	Density [g cm^{-3}]		
	Superior	Inferior	Δ
Microstructured hexolite			
30	1.600	1.554	0.046
45	1.667	1.616	0.051
60	1.721	1.693	0.028
Nanostructured hexolite			
30	1.679	1.645	0.034
45	1.717	1.717	0.000
60	1.724	1.723	0.001

Table 4. Densities measured by helium pycnometry and immersion in water for nanostructured hexolite (60/40) pellets pressed at 100 MPa for pressing temperature of 30 °C, 45 °C, and 60 °C.

T [°C]	Density [g cm^{-3}]	
	Helium pycnometry	Immersion in water
30	1.674	1.668
45	1.704	1.712
60	1.721	1.721

When the temperature increases, the density increases, and the values obtained from both measurements are nearly equal. This indicates that the porosity is closed when the compression temperature is superior or equal to 30 °C for an applied pressure of 100 MPa.

2.1.6 Pressure for Optimized Conditions

Figure 6 shows the density variation for different pressures at a given temperature of 60 °C. While for the microstruc-

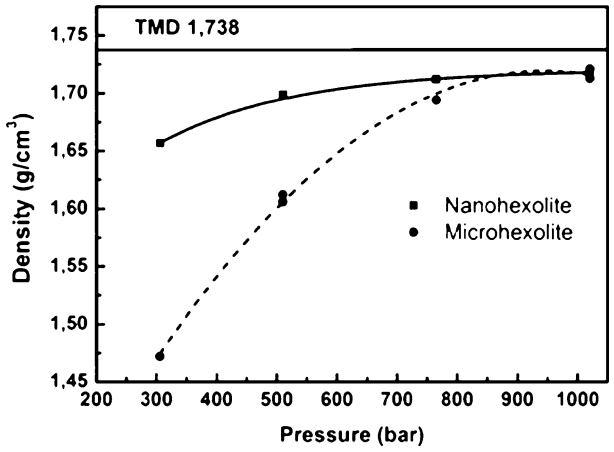

Figure 6. Density vs. pressure for a constant pressing temperature of 60 °C.

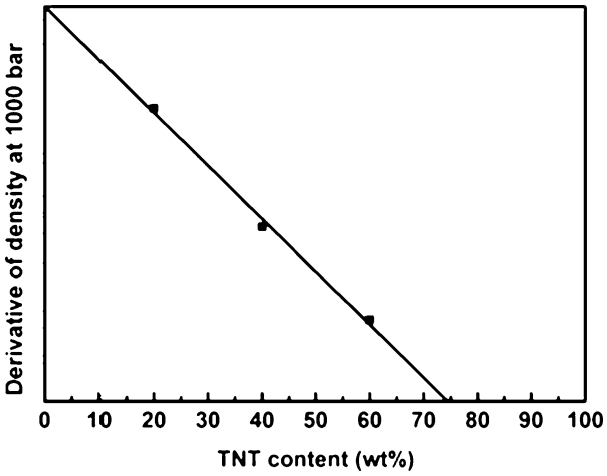

Figure 7. Evolution of the derivative intensity at 100 MPa depending on the TNT content in the nanostructured compositions.

tured hexolite, the density of the pellet falls to 85% (1.472 g cm^{-3}) of the TMD for a pressing of 30 MPa, in the case of the nanohexolite, the density is still above 95% (1.657 g cm^{-3}) of the TMD.

When the pressure is superior to 80 MPa, the densities of both hexolites are the same and equal or slightly superior to 98.5% of the TMD (1.712 g cm^{-3} for microhexolite and 1.718 g cm^{-3} for nanohexolite).

2.2 Discussion

Depending on the aspect ratio, the morphology and the composition of the hexolite, the pressure and temperature of compression, the homogeneity of the density of the pressed pellets can be very different.

The geometric parameter plays a major role in compression and lower L/Φ ratios will favor a better homogeneity of the pellets. Saßmannshausen and co-workers showed that, for a given diameter, inhomogeneities of the density are more pronounced as the height of the pellets increases [13].

The difference in the composition of the nanohexolite has a strong influence on the density and compactness that can be reached. We have shown that an increase of the TNT content in the explosive composition minimizes the variation of the density and increases the compactness of the pellets through the compression. For the different nanostructured compositions (Figure 3a), the derivative value at 100 MPa can be calculated, and it can be found that, at this pressure, the maximum density (derivative = 0) of the pellets will be directly obtained for 75% of TNT content (Figure 7). In other words, the nanohexolites which contain more than 75% of TNT cannot be further densified by increasing the pelletization pressure above 100 MPa, because the maximal apparent density was already reached. The TNT creep and sintering results in the nearly complete filling of the space surrounding RDX nanoparticles in the initial hexolite loose powder. This effect is more difficult to achieve for compositions with low TNT content, and requires higher pressing levels.

The pellets cohesion depends on their microstructure. Concerning the microstructured pellets, a closed porosity is only observed for compression at 220 MPa, while in the case of nanostructured hexolite, a closed porosity is already obtained at a pressure of 100 MPa at ambient temperature. Lamy and Denny have further interpreted the works of Heckel and Kawakita to describe the different steps that occur during uniaxial compression [14–17]. According to these studies, the microstructured hexolites, which are investigated in this article, should follow with no doubt the first and the second step, which mainly consist in the reorganization of the aggregates and the fragmentation of the particles into smaller particles filling the initial intergranular porosity. The third step, which leads to the closing of the porosity is not reached for all used pressures, but only for a pressure of 220 MPa. In the case of the nanostructured hexolites, a first step of reorganization with a fragmentation of the particles aggregates can be invoked, but we assume that the particles will not be broken due to their small size. In both cases, a welding of the particles together may occur due to the sintering of TNT particles, indeed, the Tamman temperature being of −96 °C for TNT, the superficial surface of the TNT particles should lead to sintering or welding of the particles together. The porosity should be closed easier for the nanoparticles rather than for micrometer-sized particles because of the better homogeneity of the nanomaterial.

During the optimization of the compression parameters, some cracks were noticed in nanostructured pellets pressed at room temperature. As noticed by Lamy and co-workers when they studied the modeling of powder compaction, the cohesion of the pellet is mainly driven by the porosity of the pressed powder [18]. As the microstructured powder exhibits a lower porosity than the nanostructured one, it will result in pellets with a better cohesion. Concerning the

pressing of nanoparticles, the quantity of air that will be trapped in the porosity of the pellets will be more important. When the compression ends, the gas trapped in the porosity will have a spring effect that will lead to the relaxation of the pellets inducing cracks in nanohexolite pellets depending on the applied pressure. The relaxation effect is all the more marked that the pelletization pressure is high. This phenomenon is emphasized when the pressure is greater than 140 MPa with breaking of the pellets. When the RDX content is increased, a more pronounced effect is noticed due to the less TNT quantity acting like glue between the particles. When the temperature of compression is increased, two parameters are expected to play a role in the better cohesion and the higher densities of the pellets: First, the elevation of temperature may lead to a slight increase of the air pressure, which is trapped in the porosity favoring its diffusion out of the pellets. Second, a higher temperature may improve the welding and the sintering of the nanoparticles leading to sufficient forces to counter the relaxation effect.

3 Experimental Section

Micrometer-sized RDX and TNT were provided by Dyno and Eurenco, respectively. In order to get the most homogeneous product, micrometer-sized hexolite was obtained by the following procedure: RDX and TNT were dispersed in water and heated at 81 °C in order to melt the TNT. The solution was mechanically stirred and cooled down to room temperature during 30 min and the final product was filtered, grinded, and dried. The nanosized hexolites were prepared by flash evaporation technique. This technique has already been reported elsewhere [5,6]. For the comparison between nanostructured and microstructured explosives, the studied composition was a hexolite (RDX/TNT, 60/40). Additional compositions (hexolites 40/60 and 80/20) were tested in the case of nanostructured explosives in order to compare the compression behavior depending on the explosive composition. These ratios are classically used for synthesizing nanodiamond by detonation. Pellets with a diameter of 15.8 mm were prepared by uniaxial compression. The compactions were achieved using a single load during 10 min at various temperatures and pressures.

Densities of the pellets were determined by immersion in water and helium pycnometry Accupyc 1330 Micromeritics. To ensure the stability of the density measurements, densities determined by immersion in water were measured after 1 and 3 d relaxation for every sample. Morphologies of the pristine products and hexolites were imaged by a Scanning Electronic Microscopy (SEM) DSM 982 Gemini from Zeiss. Atomic Force Microscopy was achieved in the Tapping Mode® with a Nanoscope IV multimode AFM (Digital Instruments, Santa Barbara, USA). The probe used was a "RTESP" (Force Etched Silicon Probe) produced by NanoWorld Ltd. Co.

4 Conclusions

The influence of some parameters through uniaxial compression of microstructured and nanostructured explosives were investigated. It showed the importance of the L/Φ ratio, the structure, and the composition of the hexolite, the pressure and temperature of compression on the homogeneity of the density and the porosity of the pressed pellets.

The main results are the following:

(i) Relaxation of the pellets is noticed in the case of nanostructured explosives, but this can be overcome by adjusting the temperature and pressure parameters.

(ii) Higher densities and good cohesion of the nanostructured pellets were reached for lower applied pressures than for microstructured pellets when increasing the temperature.

(iii) TNT acts as glue between the particles and helps to obtain high quality pellets.

(iv) Nanostructuring was maintained after each compression.

Further studies will be carried out in order to produce nanostructured explosive charges with a bigger diameter.

Symbols and Abbreviations

RDX – Cyclotrimethylenetrinitramine (Hexogen)
TNT – Trinitrotoluene
L – Length
P – Pressure
Φ – Diameter
T – Temperature
AFM – Atomic Force Microscopy
SEM – Scanning Electron Microscopy

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