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Preparation of Spherical Particles of 1,1-Diamino-2,2-dinitroethene (FOX-7) Using a Micellar Nanoreactor

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ABSTRACT: The need and preparation of spherical 1,1-diamino-2,2-dinitroethene (FOX-7) particles to meet certain special applications in high explosives and propellant formulation have been illustrated. Preparation of spherical FOX-7 particles by using a microemulsion technique has not been reported in the literature. In the present study, the preparation of spherical FOX-7 particles has been described using the novel concept of a micelle-based nanoreactor. Micelle-based nanoreactors have been prepared using a microemulsion of Triton X-100, cyclohexane, and water. Formation of spherical FOX-7 particles in the reverse micelle reactors have been described in the subsequent sections of this article. It is observed that spherical particles of FOX-7 are formed within 2 h in the microemulsion media. Analysis of the experimental results revealed that the particle size and shape of FOX-7 can be varied by changing the water/surfactant molar ratio in the microemulsion. Spherical particles synthesized by this method have diameters that are generally in the submicrometer to nanometer range. Impact sensitivity (h_{50}) of the spherical particles obtained by the fall-hammer method is around 45 cm compared to regular synthesized FOX-7 (i.e., 50 ± 5 cm) without any change in friction sensitivity, i.e. 36 kg. Loadability of the explosive charges can be enhanced by using these spherical particles of FOX-7.

INTRODUCTION

FOX-7 is a thermally stable insensitive high-energy material developed by the Swedish Defence Research Agency around the year 2000. FOX-7 is considered a futuristic, insensitive high explosive and a potential candidate to replace RDX. Due to its chemical and thermal stability, it has created significant interest in the recent past. Lochert[1] of the Aeronautical and Marine Research Laboratory (AMRL) has also reported details about the synthesis, characterization, and performance evaluation. Studies at AMRL envisaged that FOX-7 can be considered a new explosive ingredient with significant potential for application in high-performance, insensitive munition (IM)-compliant explosive compositions. FOX-7 is prepared by adopting a batch process by nitration of 2-methyl-4,6-dihydroxypyrimidine (MDP) followed by hydrolysis. Morphology of this material shows a hexagonal layer type of crystal structure. However, it was essential to know whether the spherical morphology of FOX-7 can be synthesized for certain applications as the sensitivity of solid explosive materials is closely related to particle size and shape. The requirement of a higher value of impact sensitivity may be met with spherical particles with defined size. Particles tending toward a spherical shape in comparison to nonspherical (needles/plates) shape with the same mean particle size have advantages such as the following:

- higher ratio of surface to volume
- better free-flowing properties
- higher bulk density

This means that the more spherical the outer shape of the particles, the higher the weight proportion of solid energetic particles that can be put in the formulation. Spherical particles, generally, can be made via the dispersion of the liquid phase which then becomes droplets in continuous phase. Literature information revealed that various research activities are being carried out in order to produce spherical FOX-7 particles. Heintz et al.[2] prepared spherical ammonium dinitramide (ADN) particles by emulsion crystallization using molten ADN (as the dispersant phase) and paraffin oil (as the continuous phase). Waldemar et al.[3] attempted spheroidization of FOX-7 crystals by a high degree of agitation of the suspension of nonspherical crystals in various solvents for 6−7 h at different temperatures, but the process produced crystals of a similar shape where the sharp edges/corners became slightly rounded. Since FOX-7 does not have a sharp melting point, it will be preferred to prepare such spherical particles either at the nucleation stage during hydrolysis of the nitrated pyrimidinedione (NMPD) or during recrystallisation in a suitable organic solvent by using the micelles/microemulsions. Micelles are formed through a self-assembling process which represents a tiny template/nanoreactor which is generally used for preparing nano-structured materials of desired sizes and shapes with required functionalities and attributes. Using micellar nanoreactors/microemulsions, various experiments have been reported[4] on nitration of phenol to synthesize *o*-nitrophenol with dilute nitric acid. However, there is no literature available to synthesize spherical FOX-7 particles/nanoparticles of FOX-7 using any other concepts.

Hence, a feasibility study has been carried out to synthesize spherical particles of FOX-7 by using the concept of a micelle-based nanoreactor. The basic aim was to design the experiments followed by conducting the same at laboratory level to prepare spherical particles of FOX-7 and analyze the data by various

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instrument techniques. As an outcome of this study, it is realized that spherical particles of FOX-7 can be synthesized using the concept of a micelle-based nanoreactor. The diameters of these spherical particles are generally in the nanometer to submicrometer range. Details of the study are described in the subsequent sections.

DESIGN OF THE MICELLAR NANOREACTOR

Nanoreactors have been designed using the concept of micelles. Micelles are formed using surfactants that are usually organic compounds that are amphiphilic, meaning they contain a hydrophobic tail as well as a hydrophilic head. Surfactants are classified on the basis of the nature of the hydrophilic group. Different types of surfactants considered during the design of microreactor are given below.

- **Anionic Surfactants:** The hydrophile is a negatively charged group, e.g, $RC_6H_4SO^{3-}$ Na^+ (alkylbenzene sulfonate).
- **Cationic Surfactants**: The hydrophile bears a positive charge, e.g, RNH_3^+ Cl^- (salt of a long-chain amine).
- **Nonionic Surfactants**: The hydrophile has no charge, e.g, $R(OC_2H_4)\cdot OH$ (polyoxyethylenated alcohol).
- **Amphoteric (Zwitterionic) Surfactants**: The molecule contains both a negative charge group and a positive charge group, e.g, $RN^+H_2CH_2COO^-$(long-chain amino acid).

A fundamental property of surfactants (surface-active agents) that has been exploited is to form aggregates, known as micelles. The first-formed aggregates, just above the critical micelle concentration, are reported to be spherical in shape, and the concentration where they start to form is known as the critical micelle concentration (CMC). In addition, on the basis of the arrangement of the hydrophilic groups either towards the centre or away from the centre, two types of micelles, normal micelles and reverse micelles, respectively, were considered while designing the present experimental system of nanoreactors. These nanoreactors provide a unique way for the development of special type of advance materials for a wide variety of applications in electronics, photonics, biomedical, and other areas. The types of nanoreactors are the following:

- **Normal Micellar Nanoreactor:** The oil-in-water micelle is called a normal micelle. Here oil acts as a dispersed phase and water acts as a continuous phase. The size of the nanoreactor by normal micelles can vary from 100 nm to 20 μm.
- **Reverse Micellar Nanoreactor:** Reverse micelles are fine dispersions of water in an organic solvent stabilized by a surfactant molecule. Reverse micelles provide an example of organized self-assemblies of surfactants in solution and are most widely used as reaction media or templates for biomimetic synthesis of various inorganic nanoparticles. The hydrophilic head and hydrophobic tail of surfactants in a polar solvent self-assemble to give reverse micelles where the polar core contains the hydrophilic heads, and the polar shell, the hydrophobic chains.

These nanoreactors can be solubilized in the core, forming water-in-oil droplets (minimum size = 5 nm) which eventually become the water in oil microemulsion with increasing the water content from 5 to 100 nm. Hence, the water/surfactant molar ratio has a decisive influence on the diameter of the reverse micelles. The aggregation number is typically in the range of 20−30, lower than in that in direct micelles due to the hydrophilic core. The shape can be spherical, rodlike, or lamellar, and it also depends on the concentrations of surfactant, cosurfactant, other additives, etc. The droplets undergo continuous collisions and exchange their contents. The shape of nanoparticles synthesized in reverse micelles would normally be spherical unless some system-specific special care is exercised. Microemulsions have been used to control the particle size of many inorganic and organic materials because they induce drastic changes in the reagent concentration, and this can be particularly useful for tuning the reaction rates.[5−7] In a given composition (oil and aqueous phases), the nature of the surfactant molecules determines the exchange rate through the elasticity (or rigidity) of the surfactant shell or interface. Thus, in order to prepare the spherical particles of FOX-7, the design of the spherical nano template has been produced by using selected surfactant and cosurfactant which is discussed in the Experimental Section.

EXPERIMENTAL SECTION

Chemicals. The following chemical composition is used in the present study,

- Surfactant (Triton X-100)
- Cyclohexane (oil media)
- Cosurfactant (*n*-hexanol)
- Water
- Nitrated-MDP

FOX-7 by Normal Synthesis Method Using Nitrated-MDP. Synthesis of FOX-7 has been carried out by adopting the nitration of MDP followed by hydrolysis of the nitrated derivative.[8−10] *Nitration of MDP is a highly exothermic reaction where a mixture of concentrated sulphuric acid, H_2SO_4, and nitric acid, HNO_3, is used as nitrating agent.* MDP was first dissolved in H_2SO_4 followed by slow addition of HNO_3 acid at a mole ratio of $MDP/HNO_3/H_2SO_4$ = 1:5.1:10.1, and the temperature was maintained at the desired level. After completion of each run, the reaction mixture was quenched into the cold water followed by hydrolysis under high speed of agitation to get the product, FOX-7, which was then filtered and washed with water (until removal of acid) to separate the solid product.

Spherical FOX-7 by Microemulsion Method. Microemulsion solution was prepared by using 52 wt % of cyclohexane as the oil phase, 22 wt % of Triton X-100 as surfactant, 11 wt % of *n*-hexanol as cosurfactant. Surfactant/cosurfactant ratio used was about 2:1 by weight along with 15 wt % aqueous phase. The critical micelle concentration was 0.22−0.24 mmol/L. Surfactant along with cosurfactant was added first to cyclohexane as the oil phase, followed by addition of aqueous phases and then stirred at room temperature until an optically clear and stable reverse microemulsion was obtained. To this microemulsion, nitrated intermediate of MDP was added slowly under vigorous stirring, maintaining the temperature of about 25 °C. The microemulsion containing nitrated MDP was kept for 2 h under vigorous agitation and then allowed to settled for 12 h. The precipitated powders were recovered/separated by centrifuge followed by washing with acetone and methanol. The separated FOX-7 material then dried in a vacuum oven at 70 °C for 16 h. All chemicals used for the experiments were from M/s E-Merck, India. Water used was doubly distilled and deionized.

RESULTS AND DISCUSSION

Details of experimental results using microemulsion are shown in Table 1. It can be seen from the table that, as the water/surfactant ratio goes on increasing, the yield of spherical FOX-7 goes on

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Table 1. Details of batches carried out by reverse microemulsion (cyclohexane, 156 g; Triton X-100, 66 g; *n*-hexanol, 33g)

batch No.	wt of NMPD (g)	wt of water (g)	water/surfactant ratio	FOX-7 wt (g)
MCN-1	96	9.18	5	product not formed
MCN-2	96	18.36	10	0.19
MCN-3	96	27.54	15	0.6
MCN-4	96	36.72	20	1.18
MCN-5	96	45	24.5	2
MCN-6	96	55.08	30	2.93
MCN-7	96	100	54.5	3.2
MCN-8	240	150	81.7	8

increasing; However, deviation from the spherical morphology is seen. Nevertheless, beyond this ratio, separation of the organic and aqueous layers is observed. Spherical FOX-7 is then characterized by various analytical/instrumental methods.

A mechanism proposed for the hydrolysis reaction in microemulsion is shown in Figure 1. After mixing 2-dinitro-

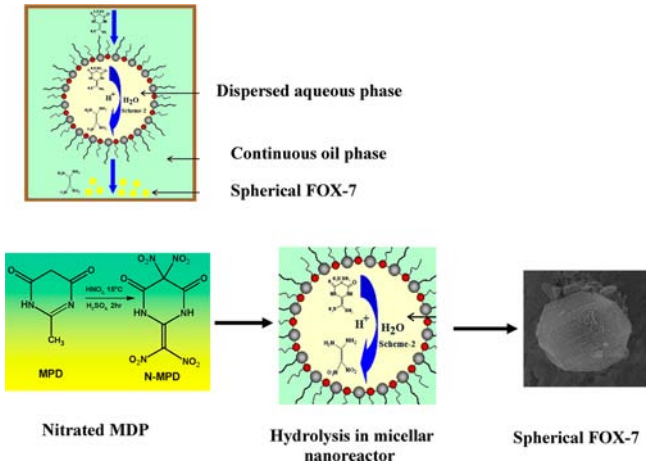

Figure 1. Proposed mechanisms for the formation of spherical FOX-7 in microemulsion.

methylene-5,5-dinitropyrimidine-4-6-dione into the reverse microemulsion, the hydrolysis of the intermediate starts during the mixing process, Figure 2. The hydrolysis, consisting of

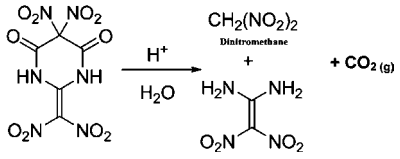

Figure 2. Microemulsion-assisted hydrolysis of 2-dinitromethylene-5,5-dinitropyrimidine-4,6-dione (NMPD) to FOX-7.

nucleation and growth, takes place inside the droplets and controls the final size of particles. This gives the homogeneous particle size distribution of FOX-7 nanoparticles. This is due to controlled hydrolysis in reverse microemulsion. The sizes of the microemulsion droplets can be modified by varying the water/surfactant (R) ratio. The effect of water/surfactant molar ratio on the morphology of FOX-7 particles is seen to be one of the most important parameters that determines the state of aggregation, size, and morphology of the particles and the nature of the solubilized water molecules. The sample prepared in reverse microemulsion containing 15 wt % aqueous phase (water/surfactant molar ratio = 25) shows nearly spherical particles with an average particle size of 200 nm, whereas the sample prepared in microemulsion having a water/surfactant molar ratio of 30 shows spherical particles of FOX-7 with an average particle size of ∼1 μm. The yield is around 30%. This may be due to the presence of a smaller amount of water in reverse microemulsion. The characterization of as-synthesized as well as spherical FOX-7 was confirmed by various analytical tools such as thermal analysis, nuclear magnetic resonance (NMR) spectroscopy, infrared (IR) spectroscopy, differential scanning calorimetry (DSC), scanning electron microscope (SEM), etc.

The common spectroscopic data obtained for FOX-7 in the present study is similar to that reported in the FOI publication.[11] NMR spectroscopy reveals that the behavior of two carbon atoms of FOX-7 is similar, and behaviors of four hydrogen atoms are also identical. Lochert[1] reported that, in DMSO-d_6, the single proton resonance for the amino protons occurs with chemical shift at approximately (δ) 8.8 ppm. The ^{1}H NMR spectrum of the FOX-7 sample (shown in Figure 3) gives a single resonance of four hydrogen atoms of two amino groups with the chemical shift (δ) = 8.78 ppm. Figure 4 shows ^{13}C NMR spectra for signals of carbon (C-1) with chemical shift δ 128.1 ppm and a signal with chemical shift δ 158.2 ppm of carbon (C-2). The measured ^{1}H and ^{13}C NMR chemical shifts are identical to the literature reported values.

The IR spectroscopy of FOX-7 was carried out on a Shimadzu infrared spectroscopy (FTRI-8400) instrument. KBr was mixed with the sample. The powder was placed in the cup of diffused reflectance assembly, and spectra were recorded. The infrared spectrum of FOX-7 shows absorbance in the ∼3160−3409 and ∼1330−1620 wavenumber ranges characteristic of the amino and nitro functionalities and also shows numerous peaks in the fingerprint region, Figure 5.

Thermal analysis of spherical FOX-7 samples was carried out in DSC. The DSC thermogram, Figure 6, has been generated at a heating rate of 10 °C min^{-1}. The single exothermal peaks at 283 °C (maximum peak) was observed. Additional very minor 'endothermic peaks' were observed at 112−115 °C and 165−172 °C, suggesting two thermally induced phase transitions. As a result, thermal analysis provided further evidence of a two-step process of phase transition. No melting point was observed in DSC analysis. Earlier similar observations were also noticed by Lochert of the Defence Science and Technology Organisation (DSTO). The values of decomposition of both as-synthesized and spherical FOX-7 are similar to the results reported in the literature. In addition, small variations in the DSC spectrum of values from different batches of FOX-7 have been partially explained by Ostmark et al.[10] by proposing a relationship between particle size and the decomposition temperature.

SEM image of as-synthesized FOX-7 shows layer structure of rectangular rod-shaped crystal structure shown in Figure 7. The particle size was measured by using scanning electron microscopy (SEM Leica 440). SEM images of dried powders prepared using micelle-based nanoreactor (by varying water/surfactant ratio) are shown in Figure 8.

The particle size distribution of spherical FOX-7 analyzed by Malvern Particle Size Analyzer (model: Mastersizer 2000) is shown in Figure 9. Bimodal distribution of particle are seen with the overall particle size $d(0,5)$ of ∼10.0 μm.

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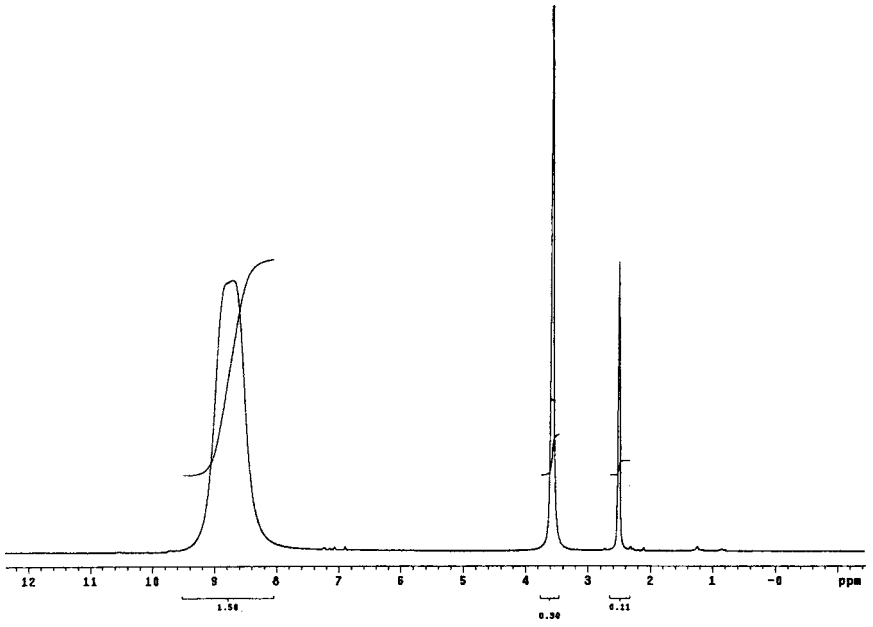

Figure 3. ^{1}H NMR of FOX-7/spherical FOX-7.

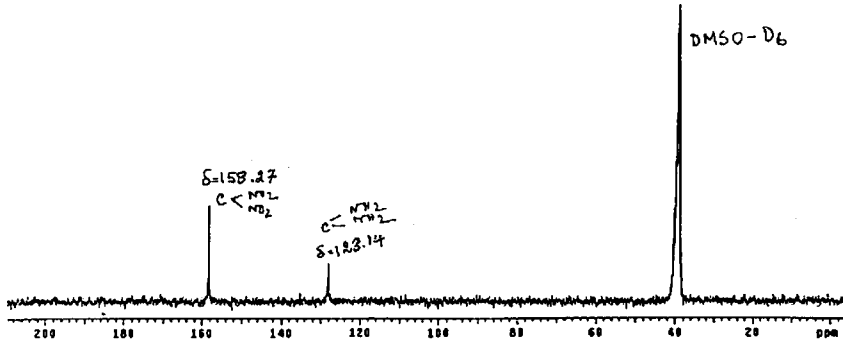

Figure 4. ^{13}C NMR of FOX-7/spherical FOX-7.

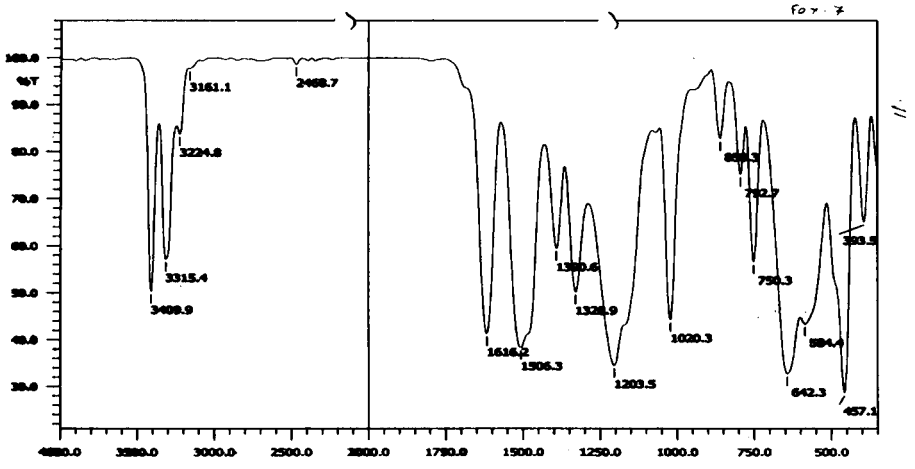

Figure 5. IR spectrum of FOX-7.

CONCLUSIONS

Nearly spherical particles of 1,1-diamino-2,2-dinitroethene (FOX-7) have been successfully prepared in a reverse micelle microemulsion of Triton X-100/cyclohexane/water. The particle size and shape of FOX-7 can be varied by changing the water/surfactant molar ratio in the microemulsion. With this method, formation of FOX-7 particles begins within 2 h. Spherical particles synthesized in this way generally have diameters in the submicrometer-to-nanometer range. Impact sensitivity (h_{50}) by the fall-hammer method is around 45 cm compared to that of regular synthesized FOX-7 (i.e., 50 ± 5 cm), without altering any change in friction sensitivity, i.e., 36 kg. An explanation may be

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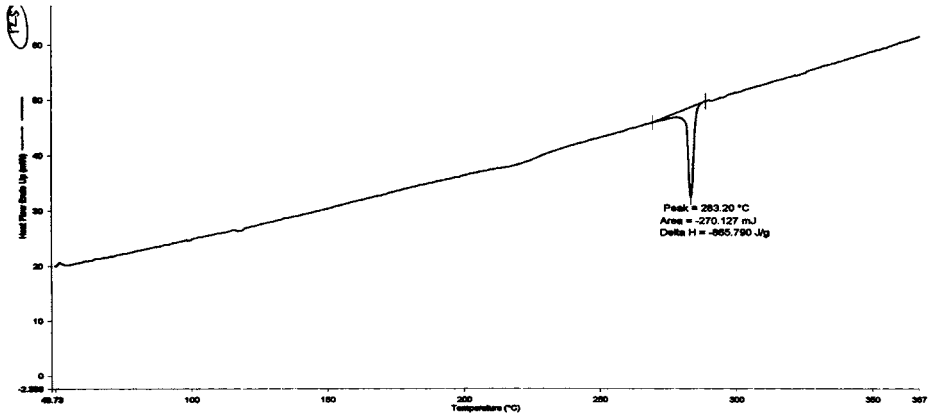

Figure 6. DSC thermogram of FOX-7.

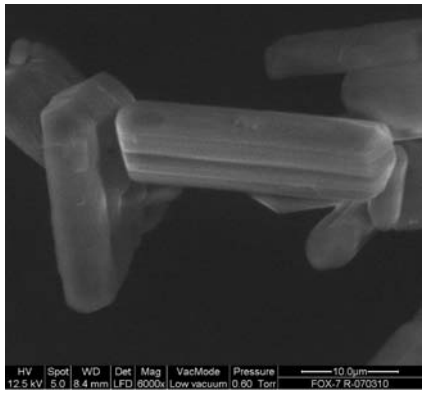

Figure 7. SEM Image of as-synthesized FOX-7.

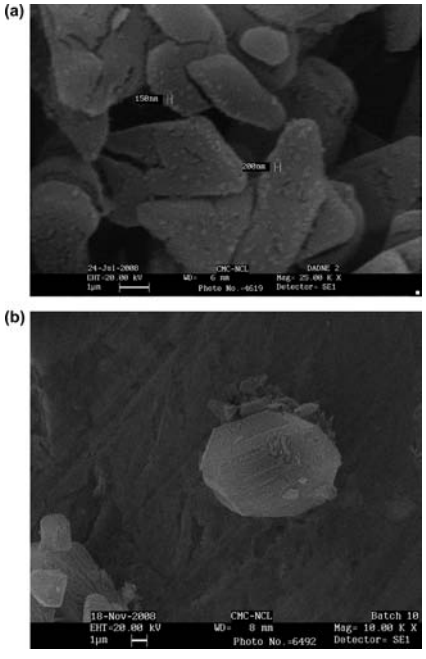

Figure 8. (a) SEM micrograph of spherical FOX-7 embedded on a surface. (b) SEM micrograph of spherical FOX-7 prepared by reverse microemulsion process.

that, as the particle size is reduced, the surface area is increased, which makes the particles more active towards impact. Since the layer structure of the crystal remains unchanged, friction sensitivity remains unaffected. The data collected during the study are helpful for scaling up the process of preparation of spherical particles.

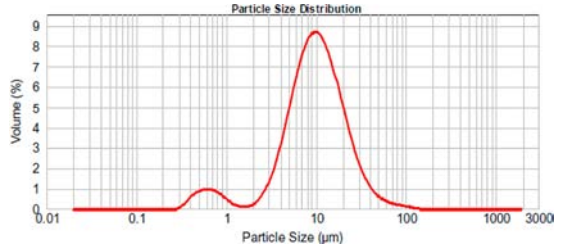

Figure 9. Particle size distribution of spherical FOX-7.

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Notes

The authors declare no competing financial interest.

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