Defence Science Journal, Vol. 61, No. 6, November 2011, pp. 534-539, DOI: 10.14429/dsj.61.594

Nanocrystalline Pentaerythritoltetranitrate using Sol-Gel Process

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ABSTRACT

The secondary explosives developed with reduced particle size tend to be more insensitive for mechanical stimuli and may release energy with faster rate and gaining more importance nowadays. Therefore, aiming to reduce the particle size of one of the popular explosives, viz., pentaerythritoltetranitrate (PETN) to the nanometer range, a method for preparation of nanocrystalline PETN in the silica (SiO_2) gel matrix using sol-gel process has been demonstrated. The PETN-SiO_2 xerogels were prepared containing PETN content ranging from 50 per cent to 90 per cent (w/w) and the xerogels were characterised using different techniques. An exothermic peak at around 185 °C preceded by an endotherm in thermal analysis accompanied with weight loss in the temperature range from 150 °C to 200 °C for the xerogel confirmed the presence of PETN in xerogel. Infrared spectra of xerogels showed peaks at around 1285 cm^{-1} and 1700 cm^{-1} assigned to O-NO_2 and C-O bond representing PETN. Small angle x-ray scattering measurements on xerogels indicated that PETN entered in the pores of silica matrix. Transmission electron microscopy revealed that cystalline PETN with particle size of around 15 nm dispersed in silica xerogel. The specific surface area for the PETN-SiO_2 (90:10) xerogels was found to be 75 m^2/g.

Keywords: Explosives, sol-gel process, pentaerythritoltetranitrate, xerogel, TEM, PETN

1. INTRODUCTION

Pentaerythritol tetranitrate (PETN 1,3-Propanediol, 2, 2-[bis-(nitroxy) methyl]–dinitrate) is a white crystalline aliphatic nitrate ester with melting point 141 °C. Figure 1 shows molecular formula of PETN($C(CH_2ONO_2)_4$)[1].

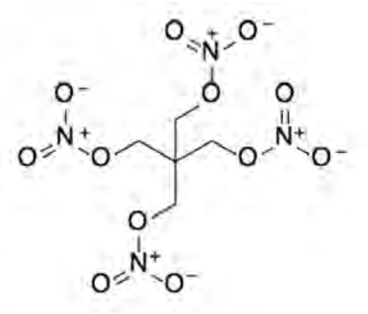


Figure 1. Molecular formula of PETN.

It is the most sensitive among secondary explosives and its sensitivity is attributed to the nitrate ester group. It is used in the most of the booster explosives, detonating fuses, demolition charges and initiation devices. PETN is also commonly used secondary explosive in exploding bridge wire (EBW) detonators[2] due to its low critical energy fluence. In EBW, the crystalline powder is pressed into granular low density compact that can be initiated by an exploding wire. Its high sensitivity to mechanical and frictional stimulations pose hazard in its handling. It is well studied that particle size and surface area affect the initiation properties of explosives[3,4]. Secondary explosives with reduced particle size tend to be more insensitive for mechanical stimuli and release energy with faster rate[5]. However, the effect of particle size on the friction sensitivity of secondary explosives is not well understood[4,6,7]. PETN with reduced particle size shows less sensitivity to ignition in drop weight system[8], flyer plate impact[9], and electrical spark initiation[10]. For these reasons, the development of secondary explosives like PETN with superfine particle size is gaining importance.

There are various methods reported for the preparation of small-sized explosives using various techniques of aerosol production[11], solution and centrifugation[12], rapid expansion of supercritical solution[13], ultrasonication[7], and sol-gel method[14].

One of the popular methods to produce superfine size explosives is solvent/non-solvent recrystallisation method[15] in which PETN solution in dimethylformamide is added to deionised water to recrystallise PETN. The mean particle size achieved for PETN using this method is 3 μm with particle size ranging from 2 μm to 10 μm but the parameters of temperature, agitating speed, solvent, and concentration for recrystallisation significantly affect the particle size.

Tillotson[16], *et al.* have processed PETN using sol-gel process with compositions having 45 per cent of energetic materials and 55 per cent silica. These authors have studied impact sensitivity of xerogels containing PETN but they have not mentioned the analysis of the size of explosives particle in the xerogel.

Received 31 August 2010, revised 16 August 2011, online published 28 October 2011

In the present work, nano-sized PETN- SiO_2 xerogels containing around 50 to 90 wt per cent PETN content in silica matrix using sol–gel process has been prepared. The presence of PETN in resulting xerogel was confirmed by differential thermal analysis (DTA), thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR) studies. The microstructure of PETN-silica xerogel was studied using small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM).The specific surface area of PETN-SiO_2 xerogel was found to be 75 m²/g.

2. EXPERIMENTAL STUDIES

2.1 Preparation of Xerogel

PETN, conforming to specifications JSS 1376-06:1986, was obtained from Ammunition Factory, Khadki, India. The other chemicals used were tetramethoxysilane (Purum grade) from Fluka Chemicals, Switzerland; acetone and hydrofluoric acid (HF) of analytical grade from Thomas and Bakers. Double distilled water was used for preparation of the catalyst.

PETN was dissolved in acetone and to this solution tetramethoxysilane (TMOS) and 0.5M HF were added. The amount of PETN dissolved in acetone was chosen so as to achieve desired content of PETN (ranging from 50 per cent and 90 per cent) in final xerogel. The molar ratio of TMOS: acetone: water: HF was 1: 80: 4: $8x10^{-3}$. The solution was stirred for 15 min. The solution was poured into the test tubes and the test tube was sealed. The gelation of silica into clear and transparent gel took place within 36 h. The wet gels were dried at room temperature, by the evaporation of all internal solvent, which included the alcohol generated from the TMOS hydrolysis, as well as acetone from the gel pores. This resulted in PETN-SiO_2 xerogel containing recrystallised PETN in the pores of silica matrix. Solvent extraction using supercritical CO_2 method, which involves exchanging the acetone solvent in the pores of gel with ethanol and then with liquid CO_2, was not preferred because the solubility of PETN in ethanol and CO_2 supercritical fluid may affect the final composition of PETN-SiO_2 xerogel.

Silica xerogels were prepared with the same molar ratio mentioned above without adding PETN to the solution. The silica xerogels, thus prepared, were used as reference material for TGA, DTA, IR and SAXS analysis for comparison with PETN-SiO_2 xerogels.

2.2 Characterisation of Xerogels

DTA and TGA measurements on the xerogels within the temperature range from room temperature to 700 ˚C were carried out in an Argon atmosphere using Setaram Thermal Analysis System – Model No. 92-16.18. FTIR spectra of the PETN, SiO_2 xerogel and PETN-SiO_2 xerogels were recorded in the wave number range 400 cm^{-1} to 4000 cm^{-1} on a spectrophotometer (Model No.610 of JASCO). SAXS measurements were carried out using Rigaku small angle goniometer mounted on rotating anode x-ray generator ($CuK\alpha$). Scattered x-ray intensity $I(Q)$ was recorded using a scintillation counter with pulse height analyser by varying the scattering angle 2θ where Q (= $4\pi.\sin(\theta)/\lambda$) is the scattering vector, λ is the wavelength of incident x-rays. Data were recorded on pure silica xerogel and PETN-SiO_2 xerogels. For TEM analysis, the samples were prepared by crushing xerogels into powder and then dispersed in methanol. The resulting methanol–powder mixture was dispersed on a carbon-coated copper grid of 200 mesh size. A JEOL 2000FX TEM operating at 160 kV was used to carry out microscopy. Specific surface area of the xerogel sample was measured using a BET surface area analyser (Quantachrome, model: Autosorb-1). The amount of N_2 gas adsorbed at 77 K at various partial pressures ($0.05 < p/p_0 < 0.3$, nitrogen molecule cross-sectional area = 16.2 A°²) was used to determine the specific surface area.

3. RESULTS AND DISCUSSION

Figure 2 show typical DTA curves for silica xerogel (a); PETN (b); and PETN-SiO_2 xerogel with 90 per cent PETN content (c). A sharp endothermic peak at temperature around 140 °C and a broad exothermic peak at temperature around 185 °C were noticed in the DTA curve recorded for the PETN-SiO_2 xerogel matching to the characteristic peaks observed for pure PETN[17].

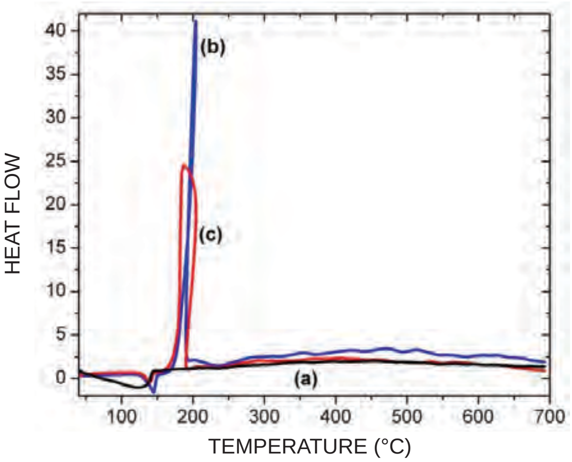


Figure 2. DTA curves of : (a) silica xerogel, (b) PETN, and (c) PETN-SiO_2 xerogel with 90 per cent PETN content.

An endothermic peak at around 140 °C is attributed to the melting of PETN whereas the exothermic peak next to the endotherm noticed at around 185 °C is attributed to the decomposition of PETN and formation of gaseous products. The slight shift in DTA curve of PETN- SiO_2 xerogel to the lower value wrt virgin PETN can be clearly noticed and this could be attributed to reduced particle size of PETN in PETN-silica xerogel as compared to pure PETN. An observed difference in the nature of exotherm of PETN-SiO_2 xerogel than that of recorded for pure PETN could be due to local environment provided by silica matrix to the PETN particles in the xerogel.

In Fig. 3, the results of TGA for silica xerogel (a), PETN (b), and PETN-SiO_2 xerogel with 90 per cent PETN content (c) are summarised. Figure 3 indicates a major weight loss of around 85 per cent in PETN-SiO_2 xerogel within a temperature range from 150 °C to 200 °C. This weight loss is attributed to decomposition of PETN resulting in gaseous products like H_2O, NO_2, NO, N_2, CO and CO_2[18]. The confirmation of PETN content in the xerogels can be verified from the thermogravimetric analysis as the mass loss has occurred mainly

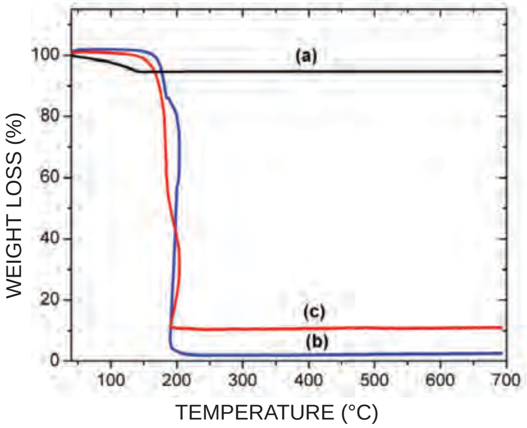


Figure 3. TGA curves for: (a) silica xerogel, (b) PETN, and (c) PETN-SiO_2 xerogel with 90 per cent PETN content.

due to decomposition of PETN and the amount of mass loss matches well with the expected PETN content in the xerogel. The weight loss in silica xerogel at around 100 °C is attributed to loss of adsorbed moisture and acetone residues in the sample. The water loss found in the silica xerogel is mainly due to water adsorbed on the silica due to its hydrophilic nature resulted from the surface –*OH* groups[19]. In case of PETN –silica xerogel the silica content is much low and PETN shows the hydrophobic nature, therefore in PETN-Silica xerogel water loss is much less as compared to pure silica xerogel but is comparable to the results obtained for pure PETN samples. The results from DTA and TGA confirmed survival of PETN through sol-gel processing and its presence in the resulted silica xerogel matrix.

The FTIR spectra are shown in Fig. 4 for silica xerogel (a), neat PETN (b), and PETN-SiO_2 xerogel with 90 per cent PETN content (c). FTIR spectra of PETN and PETN-SiO_2 xerogel (Fig. 4, curves *b* and *c*), show peaks at 2900 cm^{-1} and 1400 cm^{-1} corresponding to *C-H* stretch vibrations from aliphatic compounds. The absorbance band at 1285 cm^{-1} corresponds to NO_2 symmetric stretching vibration of $O\text{-}NO_2$ band, characteristic of nitrate ester like PETN. The peak observed at 1700 cm^{-1} is due to *CO* from the formaldehyde structural group[18]. FTIR spectra of silica xerogel and PETN-SiO_2 xerogel (Fig. 4, curves *a* and *c*) show peaks at 1100 cm^{-1} and 450 cm^{-1} assigned to *Si-O* vibration from silica and band at 3550 cm^{-1} corresponds to vibration of structural *OH* group of the silica[20]. FTIR spectra of PETN-SiO_2 silica xerogel show peaks from both the spectra of PETN and silica indicating that resulted xerogel contain PETN and silica.

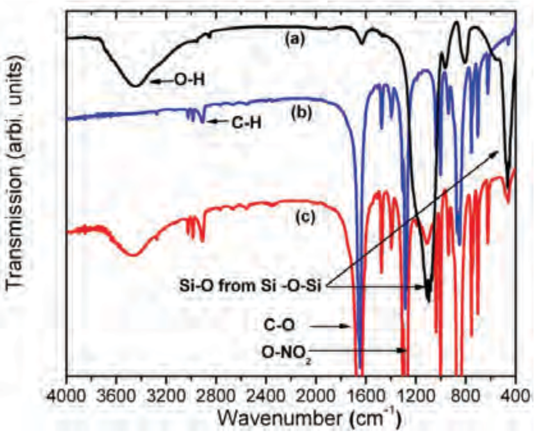


Figure 4. FTIR spectra of (a) silica xerogel (b) PETN and (c) PETN-SiO_2 xerogel with 90 per cent PETN content.

The profiles obtained for SAXS measurements on silica xerogels and PETN-SiO_2 xerogels containing 70 weight per cent and 90 weight per cent PETN are presented in Fig. 5 as curves *a*, *b* and *c*, respectively. The scattering profiles plotted on log-log scale are straight lines over wider Q-range with change of slope at low-Q regions (Guiner region) as marked in the Fig. 5. The profile in the low Q region gives the average pore/particle radius of the xerogel.

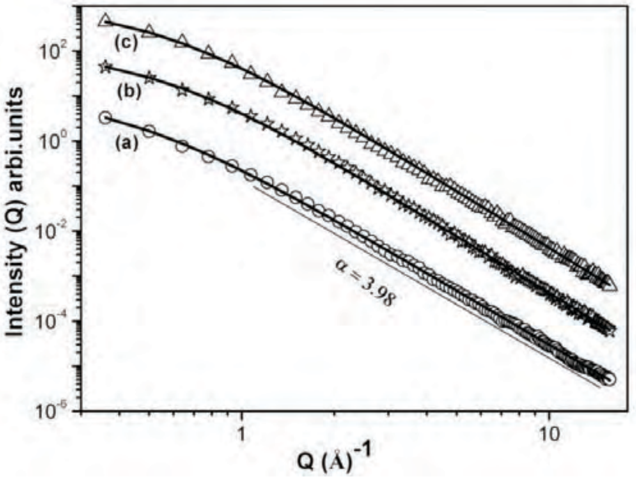


Figure 5. Small angle x-ray scattering profiles for (a) silica xerogel, (b) PETN-SiO_2 xerogel with 70 per cent PETN, and (c) PETN-SiO_2 xerogel with 90 per cent PETN content. Symbols are observed data and lines are fits of the data.

The linear behaviour of the plot indicates that the SAXS profiles follow a power-law $I(Q) \sim Q^{-\alpha}$ with $\alpha = 3.98$, 4.0 and 4.1 for SiO_2 xerogel, PETN-SiO_2 (70:30) xerogel and PETN-SiO_2 (90:10) xerogel, respectively.

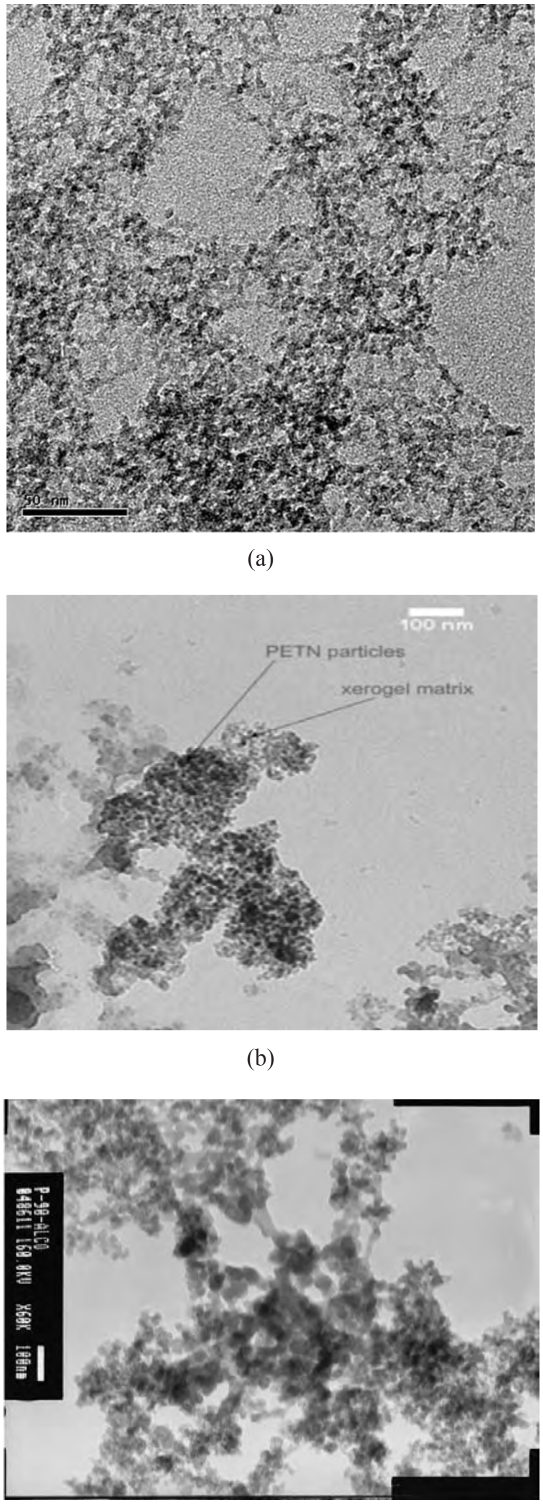
The SAXS profiles were fitted to the function

$$I(Q) = I(0)/[1+(\xi q)^2]^{-\alpha/2} \quad (1)$$

where $\alpha = 4$ for smooth surface of the pores and ξ is the correlation length. For nearly spherical scattering object, ξ represents average radius (*R*). However, for the scattering profiles with the slope $\alpha \neq 4$, this function can be modified[21] as

$$I(Q) = I(0)/[1+\frac{1+\alpha}{3}(RQ)^2]^{-\alpha/2} \quad (2)$$

The average pore size for the xerogels was derived using Eqn(1) and Eqn (2). The pore size reduced considerably to a minimum of 199Å in the PETN-SiO_2 xerogel with 90 per cent PETN content from the value of 247 Å obtained for pure silica xerogel. This suggests that the PETN particles have entered in the pores, thus reducing the average pore size of the original matrix. The surface morphology of the pores is marginally affected. The value 4.1 of the exponent for the xerogel sample with PETN content indicates a slightly diffuse interface



(a)

(b)

(c)

Figure 6. TEM image of: (a) silica xerogel, (b) xerogel with 70 per cent PETN content, and (c) xerogel with 90 per cent PETN content showing PETN nano-particles embedded in a silica xerogel matrix.

between the pores and the matrix[22]. This suggests that, at least some parts of PETN remains at the interface between the pore and the matrix causing a change in the surface morphology. The effect on pore/particle interface at silica xerogel pore boundary on incorporation of PETN and TNT in gel matrix has been discussed in details in one of earlier publication[23].

The TEM pictures of silica xerogel, PETN-SiO_2 xerogels prepared with 70 weight per cent and 90 weight per cent PETN content in silica matrix are shown in Fig. 6 (a), 6 (b), and 6 (c), respectively. TEM pictures of the xerogel samples revealed that PETN particles are dispersed in the xerogel matrix and the typical particle size of PETN particles was estimated to be around 10-15 nm. The results obtained from the SAXS measurements are in concurrence with that derived from TEM studies.

Figure 7 is the SEM micrograph showing the surface morphology of the pores in the PETN-Silica (90/10) xerogel. It shows the uniform pore morphology for the xerogel.

The specific surface area calculated using BET method for silica xerogel was found to be 512 m^2/g, whereas for PETN-SiO_2 xerogel it was 75 m^2/g. This is quiet high specific surface area for PETN-SiO_2 xerogel. The reduced surface area for PETN-SiO_2 xerogel as compared to silica xerogel is due to occupation of silica gel pores by PETN.

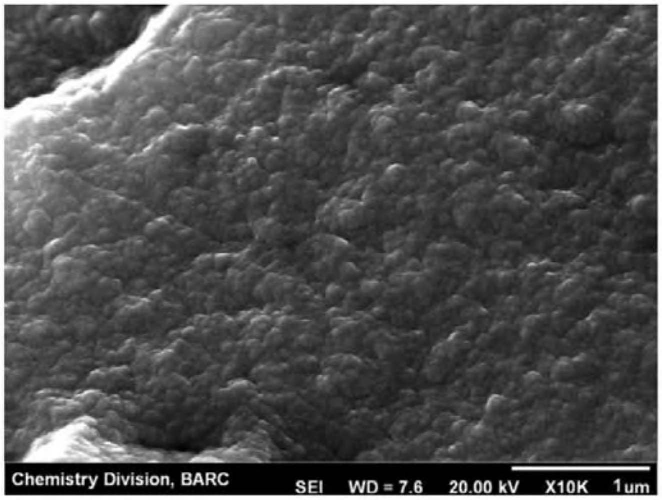


Figure 7. SEM image of PETN- silica xerogel containing 90 per cent PETN.

4. CONCLUSIONS

It has been demonstrated that sol-gel method can be used for preparing nanocrystalline PETN material. The capability of the sol-gel process to load the higher content of solid in to porous gel matrix is used to prepare PETN-SiO_2 xerogels of PETN content ranging from 50 per cent to 90 per cent with 50 per cent to 10 per cent silica. The gel matrix restricts the growth of PETN particles crystallised out of solvent to the nanometer size. The presence of PETN in the PETN-SiO_2 xerogel was confirmed by DTA, TGA and FTIR studies. SAXS measurements made on the xerogels revealed the reduction in average pore size of PETN-SiO_2 xerogel compared to that of silica xerogel which indicated that PETN particles entered in the pores of silica gel network. The PETN-SiO_2 xerogels thus prepared showed high specific surface area of 75 m^2/g with reduced particle size of PETN crystallites of around 15 nm and could be promising candidates for devices like electric bridge wire detonators.

ACKNOWLEDGEMENTS

Authors are thankful to Mr Ratanesh Kumar, Mr Sandip Virnak and Mr Sonu Gavit, APD, BARC, for experimental assistance. Authors are also thankful to Mr V.S. Kamble, Chemistry Division, BARC, for their help in FTIR characterisation.

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