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Resorcinol-Formaldehyde Ammonium Nitrate Energetic Nanocomposites Processed by Sol-Gel Method

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Abstract

The nanostructure composite of Resorcinol–Formaldehyde (RF) organic gel and ammonium nitrate (AN) oxidizer has been developed using sol-gel method. The composite of RF gel with recrystllized AN in the gel pores, containing about 85% AN offers nearly stoichiometric oxygen balance. X-ray diffraction studies confirmed the presence of ammonium nitrate in the composite. Scanning electron microscopy indicated homogeneous microstructure of RF-AN composite with nanosized particles. Thermal analysis of the composites revealed the decomposition behaviour of RF-AN with sudden and high energy release comparable with monomolecular explosives. The sensitivity studies indicated that RF-AN composite are relatively insensitive as compared to conventional explosives like PETN and RDX and are safer to handle.

Keywords: *Nanostructured composite, explosive, sol-gel process, organic gel, ammonium nitrate.*

1. Introduction

The explosives like trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX) etc., in which the fuel and oxidizer species are incorporated in one molecule are limited in numbers and therefore the class of composite explosives which are mixtures of fuel and oxidizers is being explored so as to obtain a wide range of explosives materials suitable for various applications [1]. Gun powder, Ammonium Nitrate / Fuel Oil (ANFO), Ammonium per chlorate base explosives for rocket propellants etc. are some of the examples of composites explosives in which fuel and oxidizers are physically mixed. The performance of these composites is governed by the particle size of components and homogeneity of resultant explosive mixture [2].

The composite explosives with reduced particle size of component materials to nanometer scale can have better homogeneity in mixture of a fuel and an oxidizer and therefore can offer high energy density with a rate of energy release comparable with monomolecular explosives [3]. Therefore, the focus is mainly on reducing the particle size of constituents to nanometer scale so as to have better energy density of the composite explosives. The sol-gel method is a promising technique in the area to achieve the particle size in nanometer range and have better homogeneity of the components [4]. The gel material consists of a three dimensional porous network and dispersed phase. The energetic nano-composites by using sol-gel method can be developed either with three dimensional network of oxidizer and fuel as dispersed phase or the network made of fuel material and oxidizer in dispersed phase [5]. The thermite mixtures consisting of porous network of metal oxides like iron oxide and Aluminum as metallic fuel have been studied [6] but these mixtures have less power being gasless compositions. The other energetic composites being studied are of nano sized explosives like RDX and HMX with silicon dioxide network [7].

However, in these nano-composites, there is no contribution from the oxide network in the detonation energy and the sensitivity of the energetic materials is also found to be more than raw explosives materials. Organic gels are another class with much potential to be explored as composite explosives by using organic gels as fuels and oxidizers as dispersed phase. A few attempts have been made in this area by using organic components like resorcinol or phenol gel network as fuels whereas inorganic materials like ammonium nitrate, ammonium perchlorate and magnesium chlorates have been used as oxidizers [8,9]. One of the difficulties in the development of such nanocomposites is to prepare a uniform organic/inorganic composite with high oxidizer content which is imperative for good energy output due to highly oxygen deficient organic gel structure [8]. The efficient organic-inorganic nano composites should have nearly stoichiometric oxygen balance for high energy output and sensitivity suitable for safe handling and reliable performance.

In the present work, we have demonstrated a method to prepare nanostructured energetic composite consisting of Resorcinol – Formaldehyde (RF) organic gel and ammonium nitrate (AN) as an oxidizer using sol-gel method. The composite contain more than 85% ammonium nitrate which offers nearly stoichiometric oxygen balance. The physical properties of the nanocomposite material have been studied by using x-ray diffraction, electron microscopy, N_2 adsorption and thermal analysis techniques whereas sensitivity of the composite has been studied by using fall hammer impact test measurements.

2. Experimental

In present works, RF-AN nanocomposite has been prepared by using sol-gel method [10]. All the chemicals used in the present work viz. Resorcinol, Formaldehyde , Ammonium nitrate, acetone, hydrochloric acid are of analytical grade and Merck make. To prepare RF-AN composite, resorcinol and formaldehyde, in molar ratio 1:2, were added to the acetone. To this solution, ammonium nitrate was added in suitable proportion so as to achieve desired composition of RF and AN in final xerogel. The concentrated HCl was used to accelerate the gelation of Resorcinol. The molar ratio of precursor chemicals R: F: Acetone: HCl was maintained at 1:2:35:0.25. The solution turned into gel within half an hour. The solvent from the gel pores was extracted under vacuum at 40^{o}C. This resulted in RF gel with recryastllized ammonium nitrate in the gel pores. The RF-AN composite containing about 85 % AN is designated as RF-AN (15/85). The compositional analysis of the composite materials was carried out by X-ray diffraction (XRD), thermo gravimetric (TG) and differential thermal analysis (DTA). The presence of AN in the gel was confirmed by the X-ray diffraction (XRD) measurements. The XRD data for the resultant RF-AN composite was obtained on a Philips X-ray diffractometer using a PW 1710 goniometer (CuKα, 30 kV, 20 mA). The diffracted X-rays were collected by scanning between 10.01 to 79.99° in a scan step size of 0.02.

Simultaneous Thermo gravimetric (TG) and differential thermal analysis (DTA) studies on RF/AN composites were carried out in inert atmosphere in the temperature range 25 - 500 ˚C by heating the accurately weighed samples (2-5 mg) at the rate of 10 ˚C/min. using Thermal Analyser, Model No. STA 409 PC Luxx (Netzsch Gerateubau, Germany). In this work Pt vs. Pt-10% Rh thermocouples were used as temperature and differential temperature sensors. Recrystallised alumina sample holders were used as sample and reference carriers. The microstructure of the composites was observed in a high resolution scanning electron microscope (Carl Zeiss Auriga Field Emission Scanning Electron Microscope (FESEM)). For FESEM studies, the RF-AN powder was used on carbon substrate and it was subsequently quoted with gold to get rid of charging effect.

The specific surface area, specific pore volume and pore size distribution were measured by nitrogen physisorption method using a Sorptomatic 1990 analyzer from CE Instruments. Prior to measurement, the samples were degassed at 473 K. The specific surface area was calculated using Brunauer-Emmett- Teller (BET) method [11] from the amount of N_2 gas adsorbed at 77 K at various partial pressures (eleven points; $0.05 < p/p_0 < 0.3$).

Impact sensitivity studies were carried out by using Fall Hammer Impact Test with 2 kg weight. For impact sensitivity test, powder sample of about 30 - 40 mg was placed on anvil and the height of impact (2 kg hammer) was varied to arrive at a height where 50 % probability of initiation is found using 'Bruceton up-down' method [12].

3. Results and discussion

3.1 X- ray diffraction studies

The X-ray diffraction data recorded for RF gel and RF-AN composite is shown in Fig. 1.

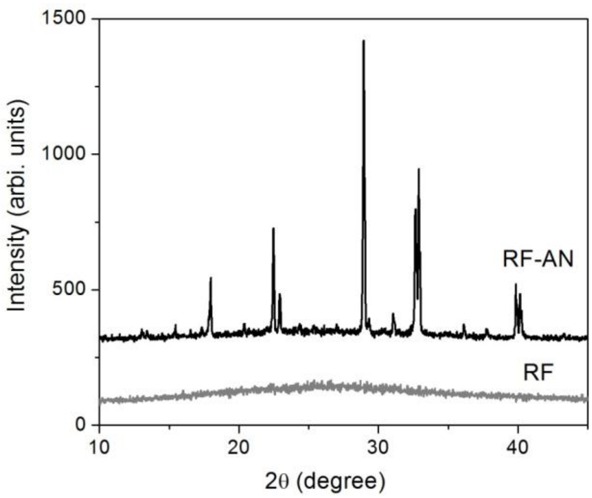

Fig. 1 XRD patterns of RF and RF-AN nanostructured composite processed by sol-gel method

The diffraction peaks from the XRD pattern of RF-AN composite are assigned to ammonium nitrate. Solid ammonium nitrate (NH_4NO_3) exists in five stable polymorphic forms (designated as phases I, II, III, IV, and V) below its melting point at around 170◦C. The results show that theNH_4NO_3 powder sample is in phase IV [13]. XRD studies of the composite materials revealed that the ammonium nitrate survives the sol gel processing and retained in the gel structure.

3.2 Thermal Analysis

The thermo gravimetric (TG) and differential thermal analysis (DTA) of RF-AN (15/85) composite have been shown in Fig. 2. The DTA curve shows an endothermic peak at about 125 ^{o}C attributed to phase transition of ammonium nitrate from II to I [14]. An endothermic peak at about 150 ^{o}C is followed by strong exothermic peak.

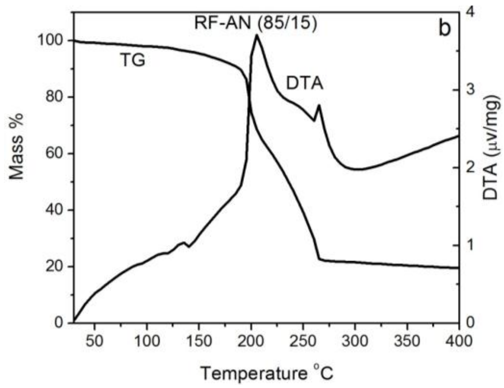

Fig. 2 TG-DTA curves for RF-AN nanostructure composite containing 85 % AN

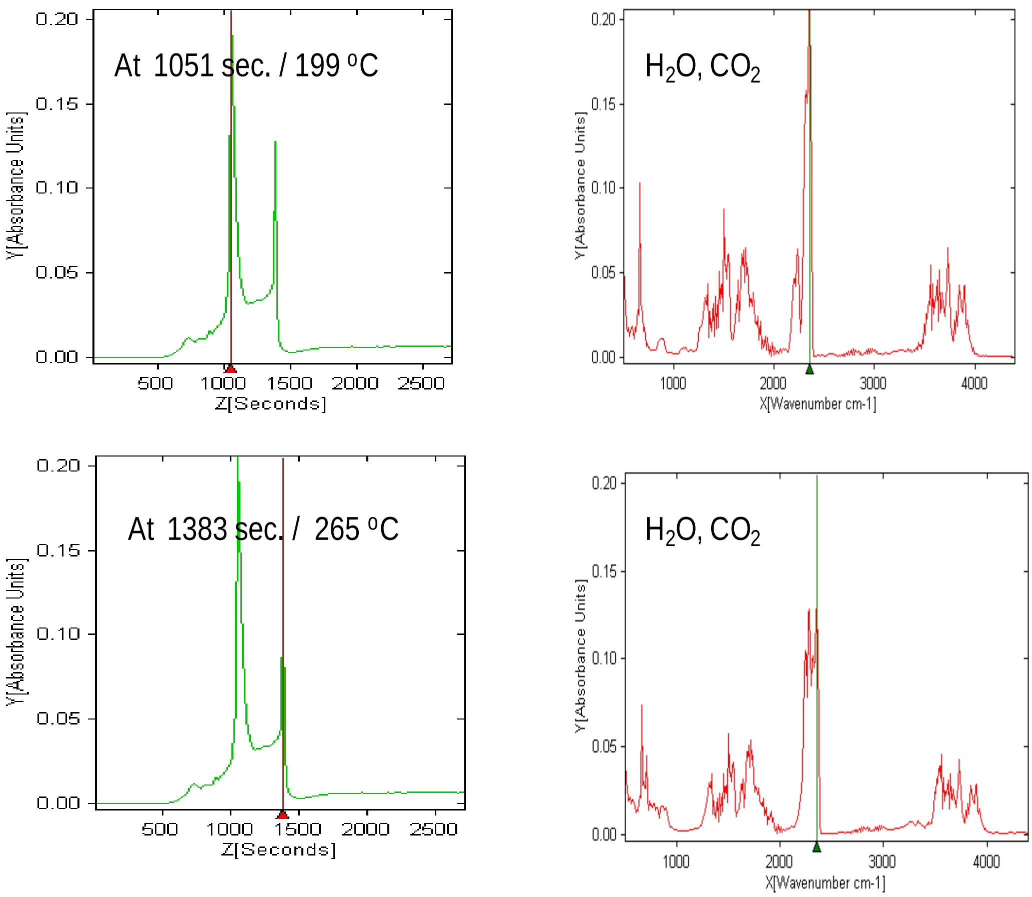

Fig. 3 Evolved gas analysis data during RF-AN (15/85) composite thermal analysis

This exothermic peak is due to the decomposition in the composite. The early onset of decomposition reaction is the result of nanosized particles in the composite. The heat flow is seen to be increased gradually within the temperature range of 150 to 190 °C and increased sharply above 205 °C. The exothermic peak can be attributed to decomposition in RF and AN along with oxidation of organic component of gel with ammonium nitrate. This is revealed by mass loss of about 70 % in the temperature range of 190 to 260 °C accompanied with large amount of heat release associated with formation of oxidized species of carbon and hydrogen from organic gel. The results obtained from evolved gas analysis (Fig. 3) are in consistence with these observations. The gas monitored during decomposition of RF-AN composite associated with exothermic peak in thermal analysis consists of H_2O and CO_2. This shows modification and improvement in decomposition characteristics in RF-AN composite.

3.3 Field Emission Scanning Electron Microscopy

A homogeneneous microstructure was revealed from the SEM micrograph (Fig.4). Pores of nanometer range have been found present all over the samples. The AN recrystllizes in the pores of RF gel confining particle size of AN in the range of nanometers. In RF-AN composite, though the organic and inorganic phases cannot be resolved from one another, the small particle size clearly reveals the distribution of both the constituents in the nanometer range. The particles are nearly spherical in shape with size less than 50 nanometers. The particles are connected to form aggregates resulting in a structure of interconnected clusters and pores are found to be entrapped within this cluster.

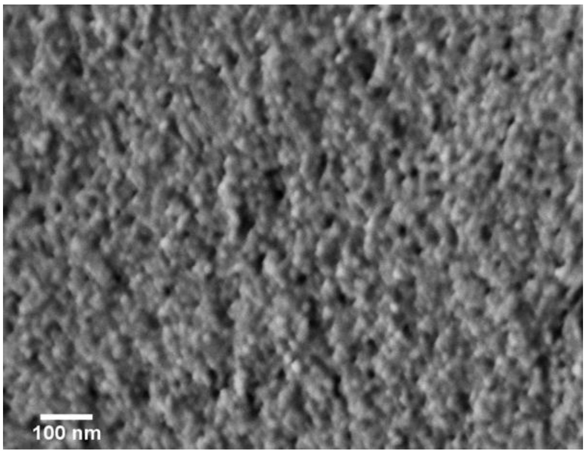

Fig. 4 FESEM of RF-AN (15/85) nanostructure composite processed by sol gel method

3.4 Surface area measurements

The RF xerogel derived by sol-gel process has porous microstructure and the porosity in the gel has been exploited to load the inorganic component of the composite. Specific surface area is an important characteristic of the sol gel process derived materials. The specific surface area of the RF gel and RF-AN (15/85) composite was measured by using low temperature N_2 adsorption method.

The BET specific surface area as determined from the adsorption isotherms for RF xerogel is 136 m^2/g whereas the specific surface area of RF-AN composite is 82 m^2/g. The BET specific surface area has been found to be decreased from 136 to 82 m^2/g for RF-AN composites owing to partial filling up of the pores by AN.

3.5 Impact sensitivity studies

The sensitivity studies on these composites have been carried out by fall hammer impact test apparatus using Bruceton up down method. Fig. 5 shows the data of sensitivity to impact measured for neat PETN, RDX received from ordnance factories and RF-AN (15/85) composites processed by sol-gel method.

The energy required for initiating the RF-AN composite with 50% initiation probability is 9.2 J whereas the initiation energies for RDX and PETN materials are 6.4 and 3.9 J, respectively. The increase in initiation energy indicates the decrease in sensitivity of the material.

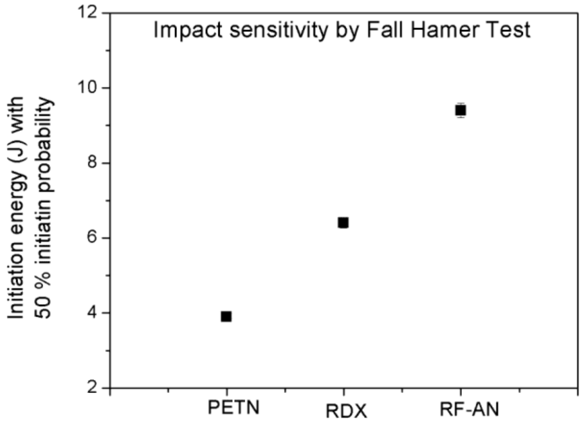

Fig. 5 Impact sensitivity data for PETN, RDX and RF-AN (15/85) nanostructure composite

Our measurements showed that the sensitivity of the RF-AN composite is significantly lower than that of PETN and RDX. This enhances the safety in handling and processing of the composite. The sensitivity of RF-AN composite is lower than that of RDX that ensure safe handling but still is in the range where it can be initiated reliably by using proper initiating source. Thus, the developed RF-AN nano-composite are found to be suitable as a safe and reliable explosive composite. The decomposition of composite on impact was found to be complete with little traces of undetonated material which indicated that oxygen balance is achieved. The oxygen balance in the RF fuel component and AN as oxidizer which are distributed homogeneously at nano meter scale due to sol gel processing may offer better energy density as compared to traditional composites.

Conclusions

The RF-AN (15/85) composites has been developed to optimize the sensitivity and energy output of the composite so as to make it suitable as safe and reliable explosives material. The nanostructure composite of RF-AN processed by sol – gel method contains more than 85% ammonium nitrate. It enables to achieve the desired oxygen balance so as to harness maximum energy from this fuel-oxidizer composite. XRD studies of the composite materials confirmed the presence of ammonium nitrate in the composite. The FESEM indicated homogeneous microstructure of RF-AN composite with nano sized particles. The resultant RF-AN composite was found to be more insensitive than pure RDX but can be initiated reliably with proper initiation source. The thermal anaylsis of the composite revealed the improvement in decomposition characteristics of the RF-AN composite with better energy output as compared to traditional composites. The nanosized particles and homogeneity of mixture at nanometer scale in RF-AN composites are important properties to use these materials in explosive applications.

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