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Thermal behaviour of MWCNT/ammonium perchlorate particles

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Abstract. A lot of attention has been given to incorporation of carbon nanomaterials (CNMs) including carbon nanotubes (CNTs) in ammonium perchlorate (APC) based solid propellants to enhance their final performance. (CNTs) has many applications in the energetic material field due to its large surface area and surface energy. This study reports on catalysed ammonium perchlorate (APC) by multi wall carbon nanotube (MWCNT). MWCNTs were successively encapsulated with APC particles by using modified fast-crash solvent–antisolvent technique and characterized by scanning electron microscope (SEM) and Energy dispersive X-ray spectrometer (EDX). The catalytic performance of MWCNT on the thermal behaviour of ammonium perchlorate (APC) was analysed using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). Interestingly, the effect of MWCNTs on the thermal decomposition of APC where the results showed that encapsulated APC with 1% MWCNT show significant decreasing in the high temperature of decomposition APC from 452.8°C to 390.1°C and MWCNTs giving an increase in total releasing heat of APC by 130 %. The results confirmed that MWCNTs are a novel catalysing agent on the thermal degradation of ammonium perchlorate which has a direct impact on the burning behaviour, performance and combustion regime of the solid rocket propellants.

Keywords: Ammonium perchlorate, Scanning electron microscopy, Energy dispersive X-ray spectrometer, Differential scanning calorimeter, Thermal gravimetric analysis

1. Introduction

Research related to nanomaterial are interesting due to their unique physico-chemical characteristics which are different from their bulk size [1, 2]. A bulk material have fixed physical properties irrespective to their size, but the nanoscale particles have different characteristics [3]. In case of the nanoparticles, the effect of the surface area has a great influence on the behavior of the materials. very special interesting research in state of carbon nanomaterials (CNMs), because these nanomaterial have a wide range of applications in chemical sensor, medical applications, decontamination, antibacterial, fillers, triggers, semi-conductor and very special application in a new generation of advanced highly energetic material (explosives and propellant) [1, 4, 5]. CNTs particles, due to its particle is small in size, surface area and energy is very high, therefore, the key of hot point researches to improve the performance of propellants combustion regime is replacing the catalysts (conventional) in solid propellant by CNTs [6, 7].



It had been discovered that the specific properties of carbon nanotubes (CNTs) such as its unique form, high-level thermal stability, high-level mechanical stress and high conductivity let them suitable to be used as a catalyst or a carrier of energetic components by coating or encapsulation [6, 8]. Relevant research topics include potential usage of CNTs as a catalyst on degradation and combustion regime of energetic materials [9, 10]. The main source of power in missiles and space shuttle is a solid propellant [11, 12]. The important and mutual oxidizer that has been utilized in various propellants is APC [12, 13]. APC has been used as the most important and mutual oxidizer in missiles and military weapons and its efficiency in such applications is highly impact by various nanomaterials [14, 15]. Thermal behavior of APC Influence on the combustion characteristics of the solid propellant [16, 17]. lately, thermal behavior of APC and the ballistics characteristics of rocket propellant were examined by making use benefits of the stimulus activities of nanomaterials [18, 19]. Thermal behavior of APC happen in two well-known stages and the burning characteristic of solid propellants based on APC depend on the degradation or the decomposition behavior of APC. Since lower degradation temperature of APC causes increasing in the burning regime, catalysts that decrease the thermal degradation temperature of APC will be a great interest in the field of propellants [11, 20]. There isn't any research published shown the impact of different kinds of CNT (MWCNT, SWCNT) on the thermal degradation of APC. This study reports on catalyzed ammonium perchlorate by MWCNT and catalytic influence of MWCNT on the thermal behavior of ammonium perchlorate.

2. Experimental

2.1. Materials

Ammonium perchlorate (150 μm) was getting from (Aldrich). Multi wall carbon nanotubes (MWCNTs) was synthesized by (CVD) method with 21.75 nm and 7.54 nm of average outer and inner diameters respectively was purchased from (Center of scientific of Egypt). Acetone and dichloromethane (Aldrich) were employed as a solvent and anti-solvent respectively for APC.

2.2. Encapsulation of MWCNTs with ammonium perchlorate

APC were encapsulated with MWCNTs by using a modified fast crash solvent –antisolvent method. The method will be as follow APC (1 gm) was added to the solvent (acetone) and stirred the solution until APC get dissolved. MWCNTs (0.01gm) were added to the solution (APC/acetone) and then sonicated the solution to allow MWCNTs dispersion through (APC/acetone) solution. The weight ratio of APC/MWCNTs was 99:1. After that, the dichloromethane (antisolvent) was added to encapsulate the APC with MWCNTs. the mixture allowed to settle for 10 min. The prepared composite particles were vacuum filtered. The resulting composite particle was 25 μm average particle sizes.

2.3. Characterization of Encapsulated MWCNTs with ammonium perchlorate

APC and Encapsulated APC with 1% MWCNTs (size, shape) were examined using (SEM), ZEISS (EV 10 MA). Elemental analysis of APC and Encapsulated APC with 1% MWCNTs was examined by using (EDX) Quant 200 equipped in SEM.

2.4. Catalytic analysis

The decomposition behavior of pure APC and Encapsulated APC with MWCNTs was examined by DSC (Q20, TA, USA) was operated with the heating rate 5°C /min, N₂ atmosphere, the temperature in range of 20°C to 500°C and the sample weight was 1.0 mg. The effect of MWCNTs on the weight loss of APC with monitoring temperature was examined by (TGA 55, TA). The sample (test) have been heated from 25°C to 500°C with the rate of heating 5°C under N₂ gas with flow rate 25 ml/min.

3. Results and discussions

3.1. Characterization of APC

The starting APC particles (size, shape) were used as reference data for the thermal decomposition study of APC was investigated with SEM. SEM micrographs, as shown in figure 1, demonstrated that the particles were almost oval particles with a main size of particle 150-200 μm , the surface was smooth and no sharp edge or cracks appeared on the surface. Elemental analysis, as shown in figure 2 and table 1, confirmed the chemical structure of APC and no interfering elements were reported.

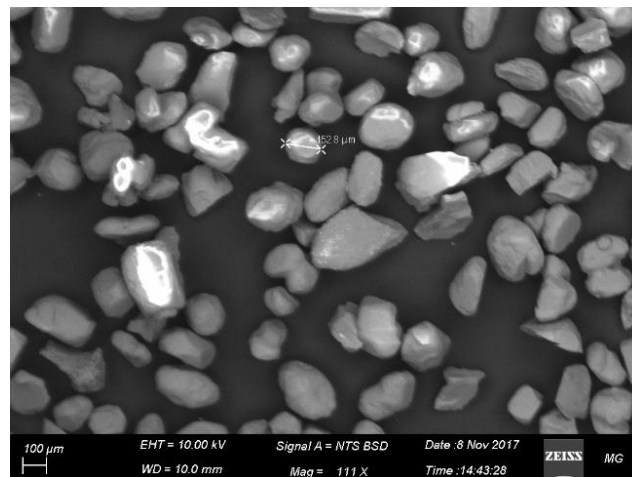


Figure 1. SEM micrograph of APC particles

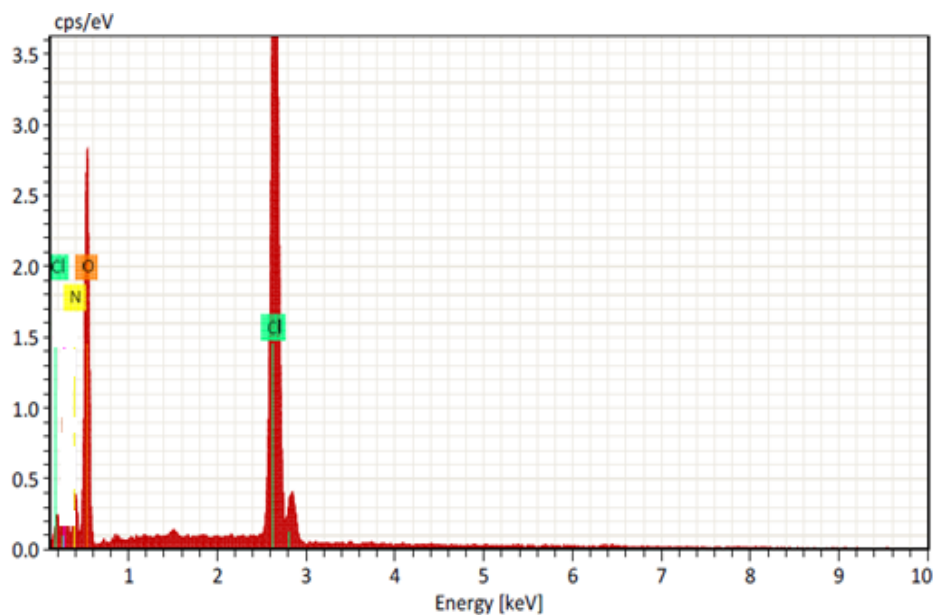


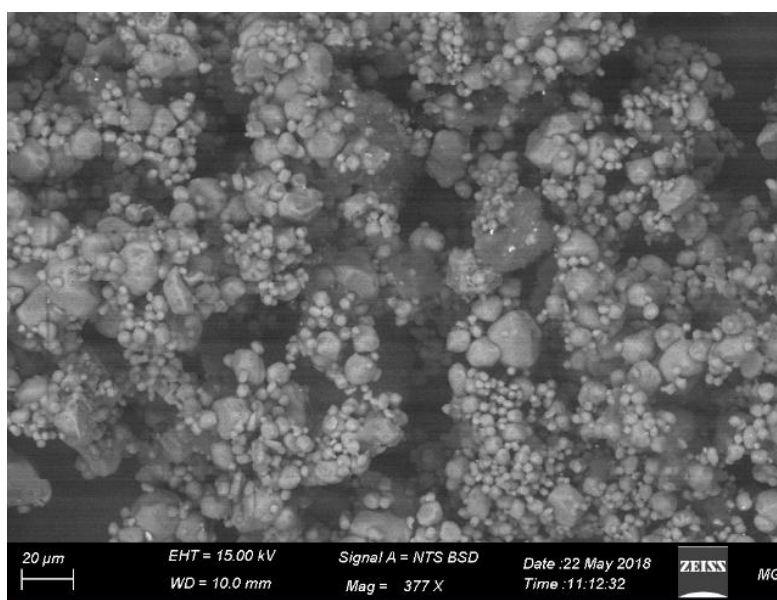
Figure 2. Elemental composition of APC using EDX detector

Table 1. Elemental analysis of APC using EDX detector

Element	Mass Normal [%]	Atom [%]
Nitrogen	11.9	10
Hydrogen	3.5	40
Chlorine	29.9	10
Oxygen	54.7	40

3.2. Characterization of CNTs encapsulated with APC

Encapsulated APC with 1% MWCNTs was investigated with SEM. SEM micrographs, as shown in figure 3, demonstrated that crashed APC particle onto MWCNTs and the average particle size of composite APC with 1% MWCNTs is about 15- 20 μm .

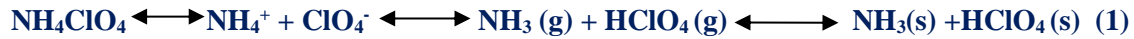
**Figure 3.** SEM micrograph of encapsulated APC with 1% MWCNTs

Elemental analysis of APC encapsulated with 1% MWCNTs was examined by (EDX) Quant 200 equipped in SEM. Elemental analysis, as given in figure 4, confirmed the chemical structure of APC encapsulated with 1% MWCNTs no interfering elements were reported as summarized in table 2.

3.3. Catalytic activity measurements

Figure 5 describes the DSC thermograms for the thermal degradation of pure APC and encapsulated APC with 1% MWCNTs. The analysis showed that the thermal behavior of pure APC particles happens in three main stages: an endothermic decomposition stage and two exothermic decomposition stages [12, 21, 22]. Endothermic decomposition is the first stage which occurs at 242.1°C, This stage could be attributed to the phase of the crystal shifting from orthorhombic to cubic [23-25]. On the other hand, the partial exothermic decomposition is the second stage is which occurs at 297.8°C with the generating of intermediate products (gaseous) such as NH_3 and HClO_4 , as given in Equation 1, via incomplete

dissociation and sublimation[22, 26, 27] (Equation 1). The reaction of the evolved HClO_4 and NH_3 is incomplete at low temperatures; these species (some of them) will be adsorbed onto the surface of APC particles that have not been reacted yet [23, 28, 29]. This partial degradation of APC finished when the surface of APC is completely covered by HClO_4 and NH_3 [15, 23]. This partial decomposition of APC released the amount of heat of 345.5J/g.



The third stage for the complete exothermic decomposition which occurs at 452.8 °C in which reactions between the adsorbed HClO_4 , NH_3 and other species lead to complete decomposition of APC and the production of several terminal volatile molecules such as HCl , H_2O , N_2O , Cl_2 , NO , O_2 and NO_2 [21, 30, 31]. The thermal decomposition of APC is sensitive to MWCNTs, where MWCNT showed high catalytic activity in the thermal behavior of APC particles.

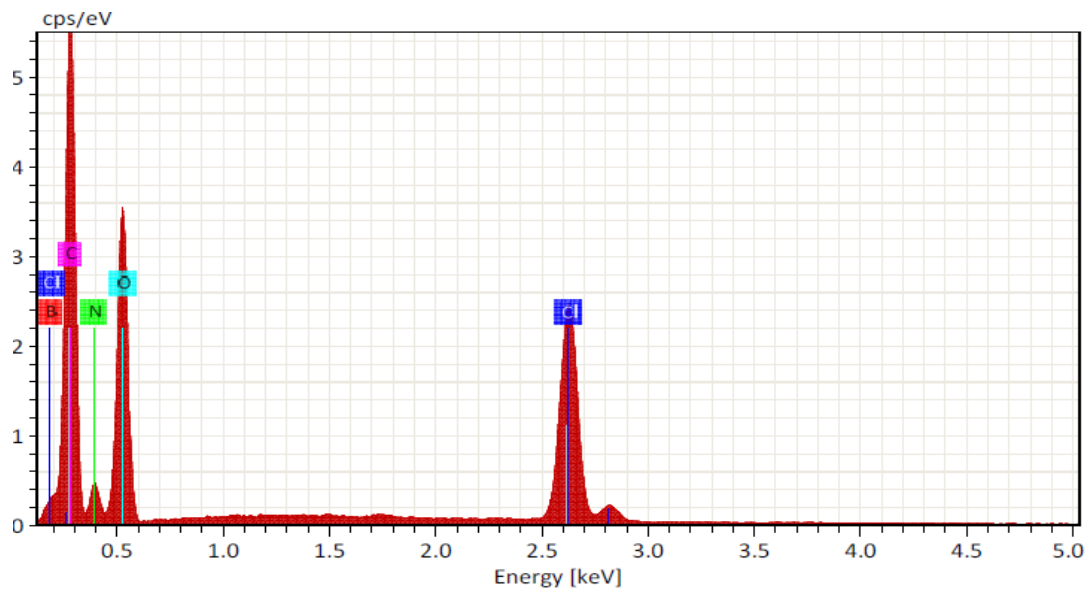


Figure 4. Elemental composition of encapsulated APC with 1% MWCNTs using EDX detector

Table 2. Elemental analysis of encapsulated APC with 1% MWCNTs using EDX detector

Element	Mass Normal [%]	Atom [%]
Nitrogen	11.85	9.9
Hydrogen	3.55	39.62
Chlorine	29.6	9.9
Oxygen	54	39.62
Carbon	1	.96

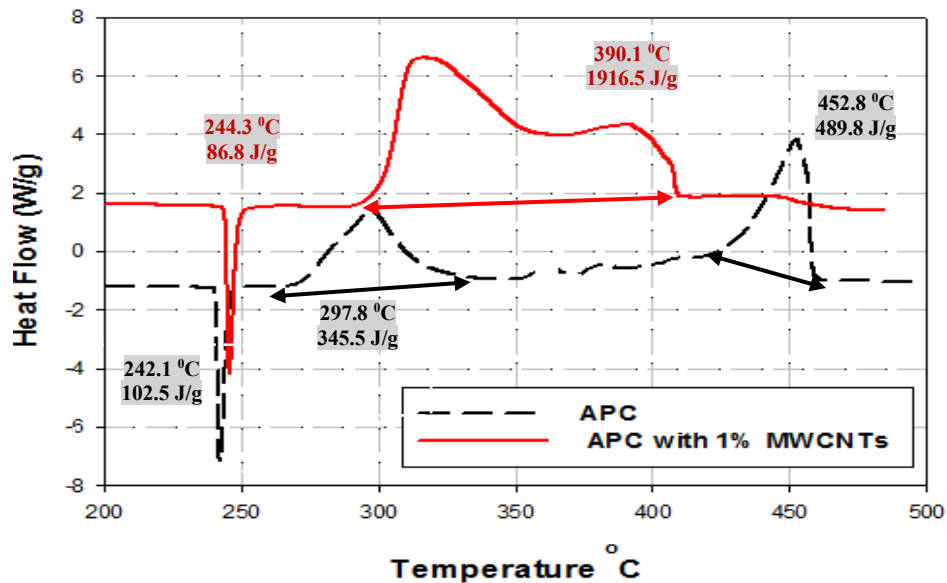


Figure 5. DSC thermogram of encapsulated APC with 1% MWCNTs and pure APC.

The effective of MWCNTs as a catalyst for APC oxidizer is that the high decomposition temperature peak was decreased by 65°C and overlapped with the low decomposition temperature peak with a total heat release of 1916 J/g. MWCNTs increased the total heat release from APC 130%. Thermal behavior of APC (pure) was monitoring with TGA; the weight loss % has been recorded as a function in temperature as given in figure 6. The data showed that two main decomposition stages for pure APC, the first stage is the partial exothermic decomposition which occurs at 298 °C with wt (loss) 30 % This stage of decomposition could be correspond to the initial decomposition peak (exothermic) in DSC 297.8 °C. The second stage is complete exothermic decomposition which occurs at 452 °C with wt % loss of 69.9%; this peak of decomposition could be corresponding to the exothermic decomposition (second main peak) in DSC 452.8 °C.

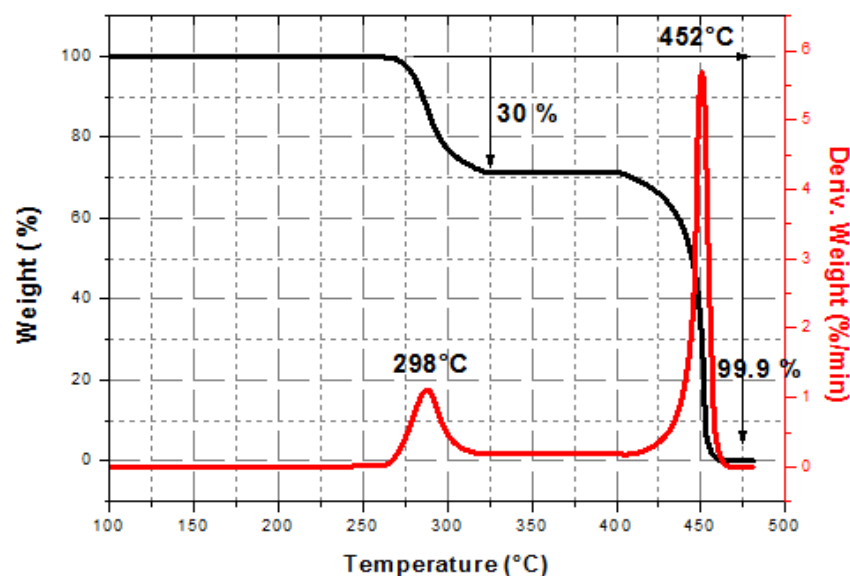


Figure 6. TGA thermogram of pure APC

Upon encapsulated APC with 1% MWCNTs as shown in figure 7, TGA data showed that the exothermic decomposition (two main peaks) for APC were overlapped with wt % loss of 99.3%. DSC and TGA data indicate that the catalytic activity of MWCNTs on the Thermal degradation of APC, which has a direct effect on the burning behaviors of propellant formulations.

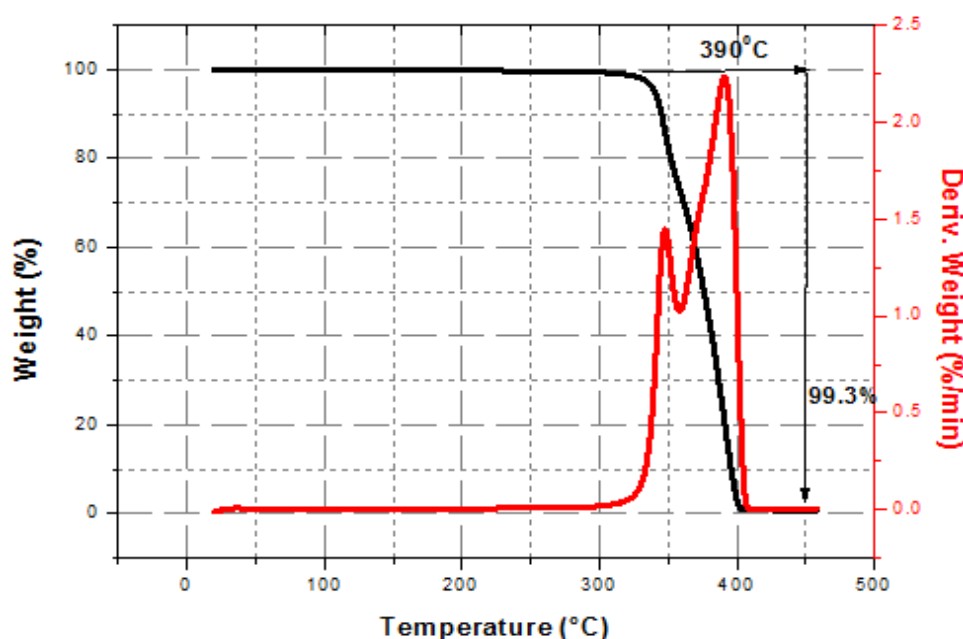


Figure 7. TGA thermogram of encapsulated APC with 1 wt % MWCNTs

4. Conclusion

Successfully encapsulated APC with 1% MWCNTs using the modified fast-crash solvent–antisolvent technique. It was found that encapsulated APC with 1% MWCNTs have good catalytic activity in the thermal behavior of APC, Where the high temperature of decomposition APC decreased from 452.8°C to 390.1°C and increased in total releasing heat of APC 130 %. The results confirmed that MWCNTs are a novel catalyzing agent on the thermal degradation of APC which has a direct impact on the burning behavior, performance and combustion regime of the solid propellants.

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