

Thermal Decomposition Characteristics of Ammonium Nitrate-Based Energetic Materials

S. Ganesan^{1*}, Dr.B.T.N. Sridhar²

¹Associate Professor,

Department of Mechanical Engineering

Asan Memorial College of Engineering and Technology

Chengalpattu

²Professor

Department of Aerospace Engineering, MIT Campus

Anna University, Chennai,

Tamilnadu, India

*Corresponding author E-mail: ksganeshme@gmail.com

Abstract— This paper describes the thermal decomposition analysis of Ammonium nitrate based composite solid materials. Differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA) were used to investigate the performance of the propellants. Three compositions -Ammonium nitrate (AN)/Hydroxyl terminated polybutadiene (HTPB), AN/HTPB/Ammonium dichromate (ADC), AP/HTPB/ADC/Gunadiene nitrate (GN) were prepared. Calcium stearate, water proofing material was added to AN to resist the moisture absorption from the air, since AN is hygroscopic substance. The thermal decomposition of samples is carried out at the heating rates of 5 K/min, 8 K/min and 16K/min in non-isothermal conditions and the output numerical values are plotted in DSC and TGA curves. The features of the thermal behaviour of phase stabilized AN, phase transition, melting and exothermic peak were studied. The effect of a burning rate catalyst such as ADC and GN on the cure reaction was also studied. For different heating rates, the kinetic parameters i.e activation energy and pre-exponential factor were determined by Ozawa method. For AN/HTPB, AN/HTPB/ADC and AN/HTPB/ADC/GN samples, the activation energies were 145.67, 89.67 and 153.54kJ/mol. Also the pre exponential factors at 16K/min were found to be 8.81×10^{14} , 1.837×10^{12} and 1.13×10^{17} in the same order for the compositions.

Index Terms— Ammonium Nitrate, Ammonium Dichromate, Guanidine Nitrate Differential Scanning Calorimetry, Thermal Decomposition

INTRODUCTION

Ammonium nitrate based energetic materials can be used for gas generator systems. The application of gas generator systems include rocket engine turbo-pump drive power auxiliary or emergency power systems, hydraulic system pressurisation, smoke generator and control actuator systems in space-launch vehicles. The basic formulation consists of polymeric and crystalline materials. The high energy crystalline and low energy polymeric material mixtures make energetic materials. These mixtures play a key role for preparation of gas generator materials. The polymeric materials are used as binding agents so as to adhere crystalline materials. The gas generator material should produce completely gaseous products with chlorine free and smokeless gas. The material for a gas generator is typically a mixture of oxidizers, fuel binders, and catalysts that generates hot gases at low to moderate flame temperatures (1000°C to 1500°C). To

this end, the use of Ammonium nitrate (AN) as a propellant is desirable in a gas generator, given also the fact that its combustion product is environmentally benign. Also, AN is the widely used oxidizer because it yields a non-toxic and non-corrosive exhaust, and exhibits low flame temperature [1-2]. It is relatively cheap, but it has inherent characteristics like low burning rate, phase transition and hygroscopicity problems. This limitation is sorted out and its performance is improved by adding catalyst. Waterproofing materials are used to resist the absorption of moisture from the air, since AN is hygroscopic in nature. Furthermore, its burning rates would be lower than that of other oxidizers. However, a major drawback in AN is that during rapid phase changes while heating, cracks and voids form in it in the absence of an efficient binder. Presently, AN-based materials are popular, despite the major problems, including low burning rate, poor ignitability, and low energy output compared with ammonium perchlorate-based ones. To overcome these limitations, anti-moisture substance and burning rate modifier are added to increase the performance of the AN based materials. Because of low cost and readily available, AN makes an attractive oxidizer in gas generator systems. Thus, addressing the problems of dimensional instability and hygroscopicity of AN through a systematic study may be well appreciated. To overcome the hygroscopicity of AN, waterproofing materials such as calcium stearate kaolin, diethyl phthalate, dinitrotoluene, or shellac was coated to it [3-4]. The addition of ammonium dichromate (ADC) is suggested to improve the burning characteristics of AN-based materials. Many approaches have been proposed to improve the burning characteristics of AN-based propellants, including the addition of catalysts [5-9], metals [10-11], and use of energetic binders based on azide polymers [12-16]. The present investigation has used ADC to improve the performance of AN based composite materials. Thermal decomposition of AN-based composite materials with a hydroxyl-terminated polybutadiene (HTPB)/ polytetrahydrofuran blend has been discussed [17]. DSC is one of the accurate and straight methods to evaluate the kinetics of chemical reactions [18]. The decomposition properties of GN and cupric nitrate-based gas-generating materials by thermogravimetry and differential scanning calorimetry have been studied [19]. Thermal decomposition study of Nitramine based propellant was investigated by DSC and Ozawa method. Using Ozawa method, the kinematic parameters have been determined [20]. The thermal decomposition of AN based composite propellants with a HTPB /PTHF-blend binder are discussed in [21-23]. The effects of potassium fluoride on AN was investigated. The results show that potassium fluoride served as phase stabilizer and

good stability of AN [24]. The thermal decomposition of AP/HTPB composite solid propellant was studied at different heating rates. The Arrhenius parameters were compared by Kissinger and Ozawa methods [25]. A systematic study on the effect of heating rates on the SHS formation of Al₂O₃-SiC composites has been conducted and this result shows that the exothermic peak increases with increasing heating rate, but this powder mixture does not undergo any exothermic reaction at a lower heating rate [26]. Ozawa and Kissinger methods were used to calculate the activation energy and pre-exponential factor A, after obtaining the slope between $\log \beta$ and $1/T_p$. In eqn. (1), a linear relationship was derived between $\log \beta$ and $1/T_p$ (heating rate β and exothermic peak temperature T_p)

$$\log \beta = a \frac{1}{T_p} + b \quad (1)$$

Where a and b are constants.

$$\frac{d \log \beta}{d \frac{1}{T_p}} = -a = \text{slope}$$

Activation energy (E), Pre-exponential factor A can be calculated after obtaining the slope, and are given in eqn. (2) and eqn. (3).

$$E = 2.19R (-a) \quad (2)$$

$$A = \frac{\beta e^{\left(\frac{E}{RT_p}\right)}}{\frac{1}{RT_p^2}} \quad (3)$$

$$k = A e^{-\frac{E}{RT_p}} \quad (4)$$

In eqn. (4), the specific rate (k) is obtained from E and A

The aim of the present investigation is to develop an AN-based gas-generating material with a chlorine-free exhaust for use in air bag applications. GN and ADC were added to enhance thermal stability, burning performance, and low flame temperature.

I. EXPERIMENTATION

A. Sample preparation

It is well known that particle size determines the performance of propellants. Hence AN and ADC and GN were pulverized into a fine powder using a pneumatic pulverizer. The particle size distribution of AN and GN are shown in Fig. 1 and Fig. 2. As per composition, the measured amount of AN, ADC and GN powder by mass is mixed with HTPB and samples were prepared. The prepared

sample is kept inside the oven for curing for a period of one week at 50°C. After curing, the gas generator material sample is cut into required size for testing Calcium stearate as waterproofing material, 6% is added for sample preparation. The composition of propellant samples is given in Table 1.

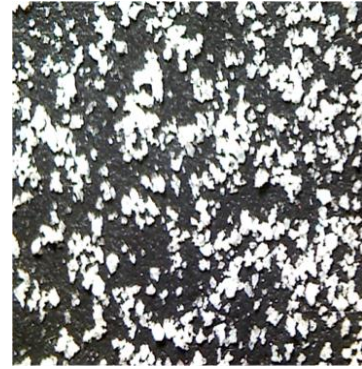


Fig. 1 AN particles (216.31 to 330 μm)



Fig. 2 GN particles (39.13 to 68.89 μm)

B. Simultaneous Thermal Analyzer (STA)

Simultaneous Thermal Analyzer was employed to investigate the thermal decomposition analysis of the prepared gas generator materials in non-isothermal conditions. DSC and TGA plots are the outcome of the experiments. The DSC and TGA studies are accurate techniques to investigate thermal decomposition of the prepared samples. In differential scanning calorimetry, the difference in the amount of heat supplied to increase the temperature of the sample and reference materials is measured as a function of temperature. NETZSCH STA 449C equipment is used for these analyses. Experiments were carried out using alumina crucible under inert conditions (The flow rate of argon gas is 60ml/min) and the heating rates used are 5, 8 and 16K/min. The same conditions were extended to sample. 3mg sample mass was placed in the open alumina crucible

pan. In this experiment, both the sample and reference materials were maintained at nearly the same operating conditions.

II. Results and Discussion

Three different material compositions—AN/HTPB, AN/ADC/HTPB and AN/ADC/GN/HTPB were prepared, and DSC and TGA studies were carried out at different heating rates using an STA. DSC plots for the three samples are shown in Figures 3,4,5, and 6 respectively. Also the TG plots at different heating rates for the three samples are shown in figures 7, 8, 9 and 10 respectively. DSC studies show that endothermic peaks of the three material samples were in the regions of 80–100°C, 120–140°C, and 170–180°C, respectively. The first two endothermic peaks (80–100°C and 120–140°C) were due to the phase transformation of AN and the latter peak (170–180°C) was due to the melting phenomenon (Refer figures 3,4 and 5). This was followed by an exothermic peak during which decomposition occurred. For three heating rate 5, 8 and 16 K/min, the exothermic peak occurred in 222.19°C, 226.66°C and 237.21°C, respectively, for the AN/HTPB sample (Fig 3); 196.16°C, 193.3°C and 214.16°C for the AN/ADC/HTPB sample (Fig 4); and 191.19°C, 194.67°C and 200.67°C for the AN/ADC/GN/HTPB sample (Fig 5). Clearly, the position of exothermic peak varied with the heating rates and composition of the material. When the heating rate increased, the exothermic peak shifted towards higher temperatures. At 16 K/min, the exothermic peak for the sample ADC was $\approx 23^\circ\text{C}$ lower than that of the sample without an ADC (AN/HTPB: 237.21°C; AN/ADC/HTPB: 214.16°C; AN/ADC/GN/HTPB: 200.67°C). However, there was a significant difference between DSC plots of AN/ADC/HTPB and AN/ADC/GN/HTPB.

Also, at a lower heating rate such as 5 and 8 K/min, the exothermic peak did not vary significantly across the samples studied. But 16 K/min, the exothermic peak shifted to higher temperatures. The impact of heating rate on ADC and GN is shown in the DSC and TG curves. It is clear that the addition of ADC and GN remarkably shifted the exothermic decomposition peak to lower temperatures for all the heating rates employed. As per figure 6 and 10, the exothermic peak and mass loss at 16 K/min occurred at lower temperatures for AN/ADC/GN/HTPB compared with other samples, which may be attributed to the presence of GN and ADC. Using Ozawa method, the activation energies for AN/HTPB, AN/ADC/HTPB and AN/ADC/GN/HTPB sample were determined

Table 1.

Composition of gas generator material

S. No	Composition	% by Mass
1	AN	85
	HTPB system	15
2	AN with ADC (6%)	85
	HTPB system	15
3	AN with ADC (6%)	70
	GN	15
	HTPB system	15

as 145.67, 89.67 and 153.54 kJ/mol. Also the pre exponential factors were found as 8.81×10^{14} , 1.837×10^{12} and 1.13×10^{17} for the same composition. On comparing three samples it can be observed that the sample containing ADC requires the least amount of energy to initiate the reaction of the gas generator material.

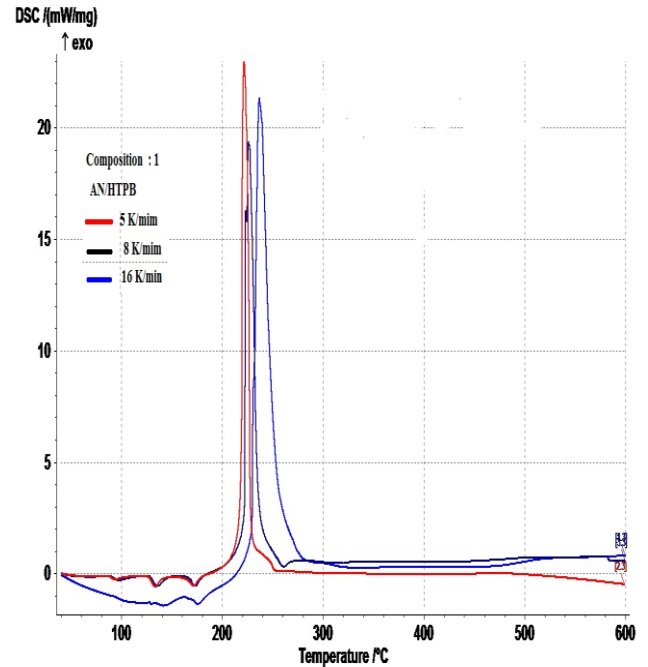


Fig.3 DSC plot of thermal decomposition of solid composite samples, for AN/HTPB system at different heating rates: 5,8 and 16K/min.

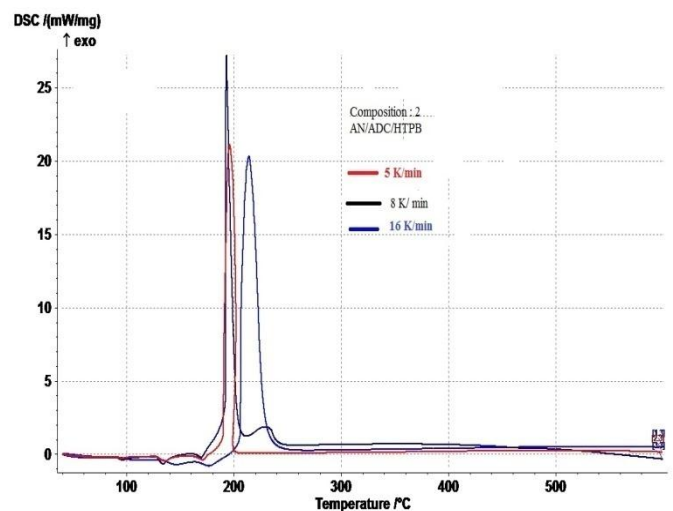


Fig. 4 DSC plot of thermal decomposition of solid composite samples, AN/ADC/HTPB system at different heating rates: 5,8 and 16K/min

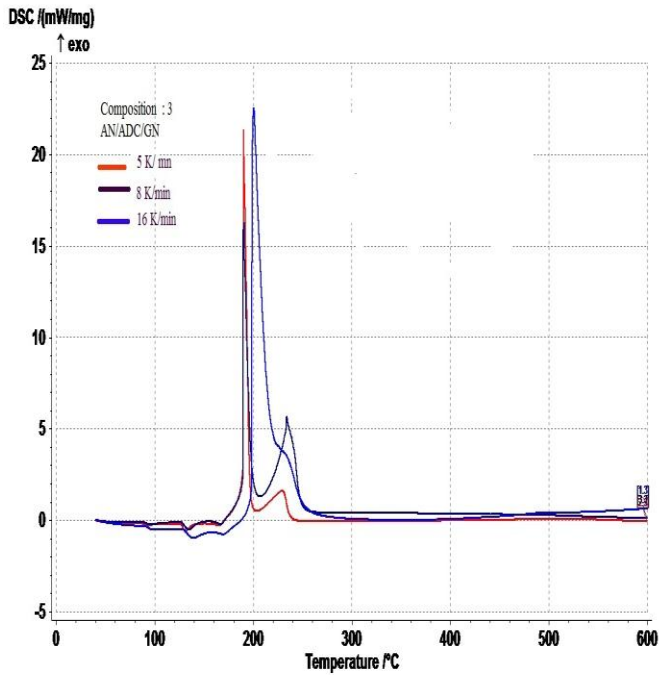


Fig.5 DSC plot of thermal decomposition of solid composite samples, for AN/ADC/GN/HTPB system at different heating rates: 5, 8 and 16K/min.

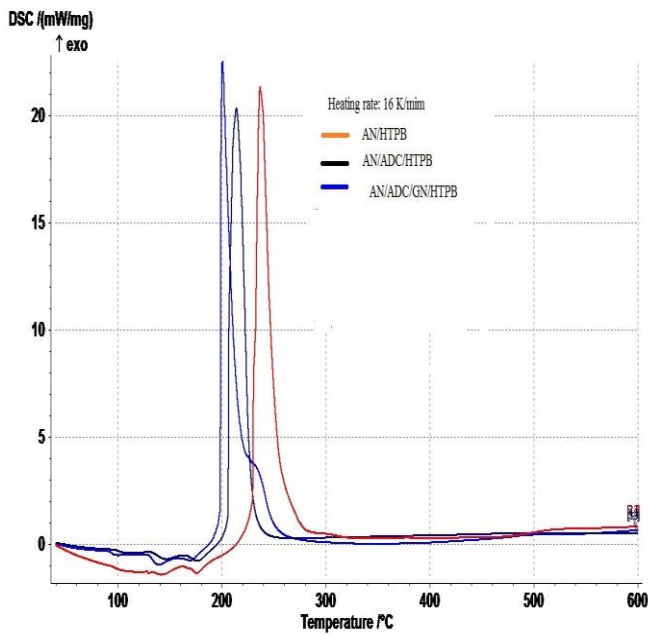


Fig. 6 DSC plots of thermal decomposition of solid composite samples, AN/HTPB, AN/ADC/HTPB and AN/ADC/GN/HTPB at a heating rate of 16 K/min

TGA curves are shown in Figures 7, 8, 9 and 10. For the AN/HTPB sample (Fig 7) at a low heating rate (5 K/min), mass loss occurred uniformly with increasing temperature. But at the highest

heating rate (16 K/min), 40% mass loss occurred between 229°C to 237°C and the next 27% mass loss occurred between 237°C and 247°C. For the AN/ADC/HTPB sample (Fig 8), at the highest heating rate, 35% mass loss occurred between 206.16°C and 207.66°C and 40% major mass loss occurred between 207.66°C and 214.66°C. For the AN/ADC/GN/HTPB sample (Fig 9), at 16 K/min, 47% mass loss occurred between 198.67°C and 200.17°C. This study showed clear evidence of improvement in burning characteristics of the **material** due to the addition of ADC and GN.

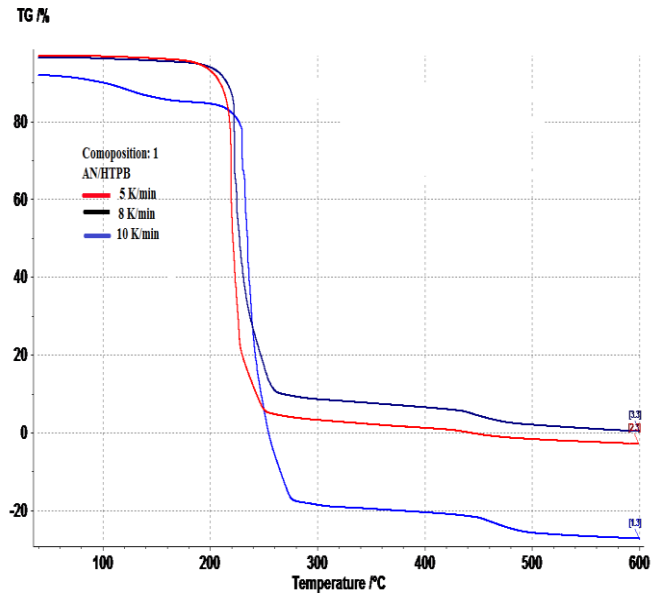


Fig. 7 TG plot for the AN/HTPB at different heating rates

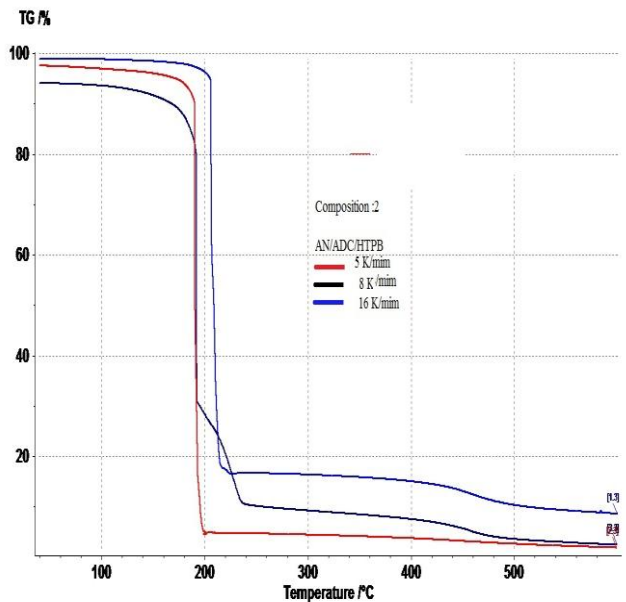


Fig. 8 TG plot for the AN/ADC/HTPB at different heating rates

AN/ADC/GN/HTPB at a heating rate of 16 K/min.

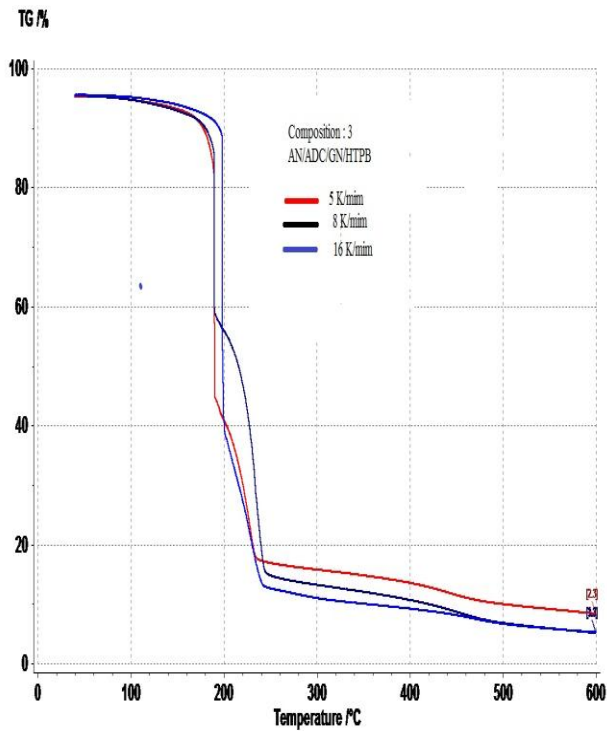


Fig. 9 TG plot for the AN/ADC/GN/HTPB at different heating rates

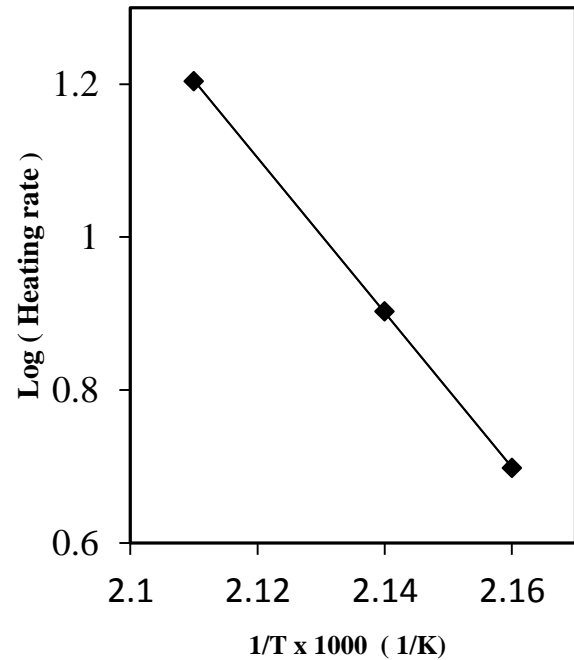


Fig. 11 Ozawa plot for AN/HTPB/ADC/GN samples at 5, 8 and 16K/min

CONCLUSION

Thermal decomposition characteristics of AN based compositions were investigated by DSC and TGA and also the effect of heating rate on decomposition was studied. At higher heating rate, the exothermic peak shifted to a higher temperature for all cases and the sample is thermally stable at a higher heating rate. For AN/HTPB sample, the mass loss occurs uniformly with temperature, but for AN/HTPB/ADC and AN/HTPB/ADC/GN samples, the rapid mass loss occurs by raising even 1°C. Exothermic peak and decomposition occurred at low temperatures for the samples containing ADC and GN. At 16K/min, pure AN showed the exothermic reaction at 237.21°C, whereas the samples containing ADC and GN showed the exothermic reaction at 214.16°C and 200.67°C, respectively, illustrating the superior performance of the sample containing GN. The sample containing ADC/GN material was decomposed at low temperature.

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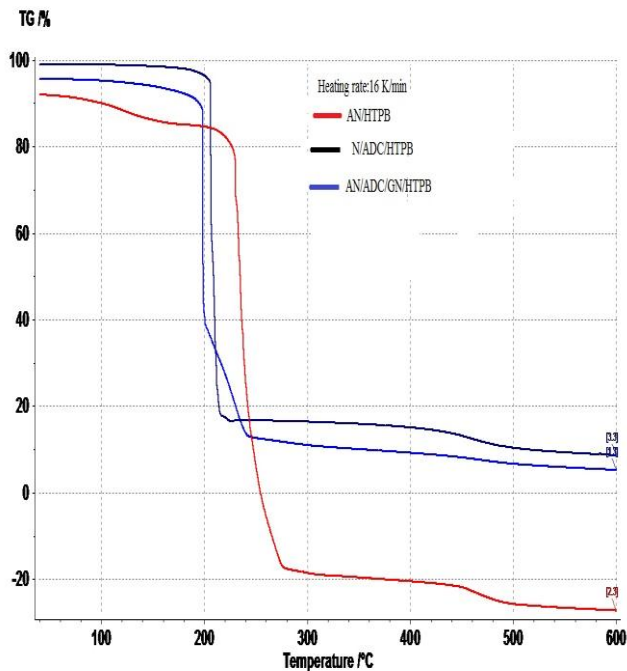


Fig.10 TG plot for AN/HTPB, AN/ADC/HTPB and

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