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# Burning rate of polyurethane composite propellant with energetic nano-composite additives

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**Abstract:** In this study, some improvements in the burning rate of hydroxyl-terminated polybutadiene (HTPB) based composite propellant was performed by introducing innovative fast burning energetic Al-Cu nanocomposites (ACNs). By comparison with the reference composite propellant (based on nano-Al), the results showed the effectiveness of ACNs to improve the characteristics of HTPB composite propellant. The concentration effect of ACNs on the characteristics of HTPB propellant and the possibility of achieving further performance enhancement were studied. The main results have indicated that ACNs based propellants have achieved improvements in the combustion heat, burning rate, ignitability, and mechanical properties.

**Keywords:** composite propellant, Al-Cu nanocomposites, combustion heat, burning rate.

## 1. Introduction

Traditional composite propellant (CP) consists of aluminum powder as a fuel and ammonium perchlorate as an oxidizer where a matrix of hydroxyl-terminated polybutadiene (HTPB) binder is used to bind the fillers and acts as a fuel [1,2].

In the formulation of CPs, some important factors should be considered such as the ease of ignition (ignitability), the rate of burning, and the amount of combustion heat, which are important parameters because they are directly related to the performance of the propellant. Burning rate catalysts, such as transition metal oxides (e.g. Fe<sub>2</sub>O<sub>3</sub>, CuO, MnO<sub>2</sub> and Ni<sub>2</sub>O<sub>3</sub>), are used to enhance the composite propellant burning rate [3]. They are almost inert additives owing to their non-energetic nature. In addition, the effectiveness of these catalysts is concentration dependent. Where, the increase in their concentration decreases the total energy of the propellant, where they added on the expense of the oxidizer or fuel [4]. Therefore, recent work has focused on developing new catalysts or new oxidizers to support better burning rate, while maintaining the propellant energetics [5-7]. This kind of catalysts is termed “energetic catalyst”, where the catalyst could augment the burning rate, and provides added energy to the propellant system [8,9]. Furthermore, in CPs, aluminum is widely used to improve their performance due to increasing the density and the heat release during combustion in addition to its low cost [10]. There are numerous drawbacks to use micron-size Al particles as a fuel in CPs including incomplete combustion, ignition delay and slow burning rate [11,12]. The major challenge of rapid and complete burning of micron-size Al particles has led to generate new approaches to overcome this problem such as increasing the reactivity of Al particles or replacing them by fast burning additives.



Recently, researchers have achieved significant advances in the energetic and catalytic application of nanotechnology [13,14].

In nanomaterials, the reaction rate increases because of increasing the specific surface of the particles [13,14]. For CPs, there is an increase in the research activity of nanomaterial application as burning rate catalysts [15,16]. Metal-metal composites are another category of reactive nanocomposites. It was reported that introducing of another metal (e.g. Ni, or Fe) or non-metal (e.g. carbon) with Al particles could lead to an increase in their reactivity and reducing their ignition temperatures [17-19].

The superior properties of RNCs enable them to be effective additives for a wide range of energy applications (e.g. fuels, propellants, pyrotechnics, and explosives). Typical uses of RNCs include as ignition boosters, initiators, or alternative reactive fuels [20,21]. The utilization of energetic nanocomposites as additives in composite propellant leads to enhance their performance by reducing the ignition delay, increasing the burning rate, improving the heat transfer, and resulting in more effective combustive material [22, 23].

Mechanical and thermal activation (MA) is one of the most reliable methods that used to improve the ignitability and the rate of combustion of metals and metal-composites. This procedure is utilized for manufacturing an extensive variety of fully dense and reactive composites, alloys, ceramics, and other polymeric matrices including the energetic materials [24-26]. The short-term mechanical treatment of exothermic powder mixtures in a high-energy mill can result in: 1) breaking the oxide layer on the metal surface and regenerating more reactive fresh surface, 2) expanding the interface area (reaction-surface) and the degree of intermixing between components, 3) creating surface active sites, and 4) providing particles with high density. All these factors lead to reduce the apparent activation energy of the reactants, i.e., increasing their reactivity and bring it into a high non-equilibrium (activated) state [27, 28].

The present work is to investigate how mechanically activated Al nanocomposites (ANCs) can enhance the performance of HTPB composite propellant by utilizing them as replacements for reference Al nano-particles. Modified propellant formulations based on the new reactive materials were prepared. The prepared ANCs are characterized using X-ray diffractometry (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and particle size analyzer. Additionally, ANCs are examined as energetic catalysts for HTPB composite propellant. The characteristics of ANCs propellants are evaluated, including measurements of combustion heat, burning rate, thermal decomposition, mechanical properties, and safety parameters. The effect of the energy content on the performance.

## 2. Experimental

### 2.1. Preparation of reactive nanocomposite additives

High energy ball mill has been used to prepare Four Al-Cu nanocomposites. They composed of nano-powders of 70 wt. % Al and 30 wt. % of Cu. The average particles sizes of the starting powders are confirmed using Laser diffraction particle size analyzer (Microtrac S3500 SI). The starting mixtures were subjected to short-term (15 min) high-energy ball milling at a rotational speed of 300 rpm. Batch mass 20 g; ball-to-mixture mass ratio was 20:1; 5 mm diameter steel balls in an inert atmosphere (argon). A small amount (10 ml) of hexane was added as a process control agent to hinder the cold welding during milling. An air conditioner was installed to accelerate the cooling of milling vials [13,17].

### 2.2. Preparation of the propellants

Four HTPB based propellants are prepared and formulated with 20% HTPB binder and 80% solid loading. The base propellant, M, was selected for this study contain 75 wt. % ammonium perchlorate, AP (oxidizer, with two average particle sizes: 200 and 10  $\mu\text{m}$ ), 5 wt. % nano-aluminum, Al, powder, and 20 wt. % HTPB binder. The binder system includes HTPB ,76.7 wt%, isophorone diisocyanate (IPDI), 7.1 wt%, dioctyl adipate (DOA), 15.8 wt%, and bonding agent, methyl aziridinyl phosphine oxide (MAPO), 0.4 wt%.

Three modified propellants, M1, M2 and M3, were also prepared and mechanically activated Al-Cu nanocomposite (ACN) with concentrations 1.5, 3.0 and 5 wt. % respectively. They have been formulated by replacing the reference Al with the ACNs. Table 1 shows the propellant compositions which are used in this study.

**Table 1.** Formulations of the propellant mixtures

Ingredients	Propellant, wt. %			
	Ma	M1	M2	M3
HTPB binder	20	20	20	20
AP (200 $\mu\text{m}$ )	50	50	50	50
AP (10 $\mu\text{m}$ )	25	25	25	25
Al/additive	5/-	3.5/1.5	2/3.0	-/5.0
Design variable	Al	Al-Cu	Al-Cu	Al-Cu

### 2.3. Characterization of ACNs additives

The mechanically treated Al nanocomposites, ACNs, were examined for their surface morphologies using field emission Scanning Electron Microscope (SEM, Quanta 250) operated at 20 kV. The crystalline phases were examined using X-ray diffractometer (XRD, Bruker D8) with Cu-K $\alpha$  radiation source. In addition, the particle size distributions of the prepared ACNs were determined using Laser Diffraction Particle Size Analyzer (Microtrac S3500 SI).

### 2.4. Characterization of the propellants

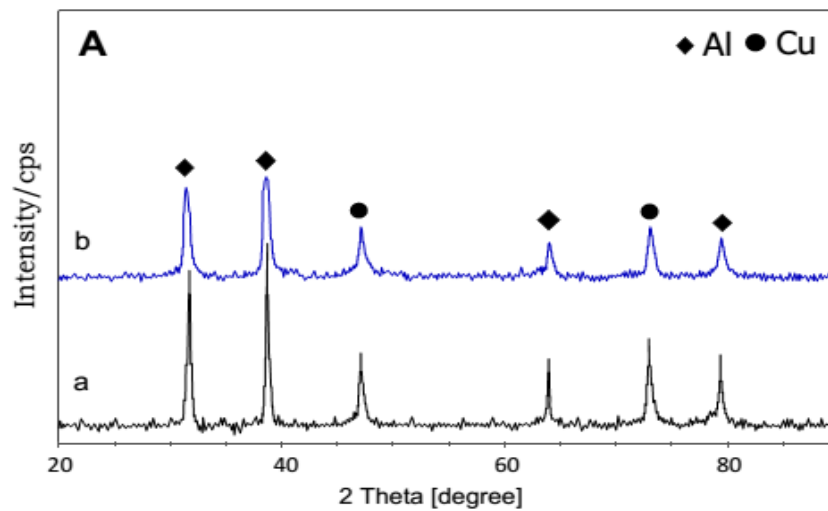
Crawford strand burner method was used to determine the burning Rate (BR) of the propellants at a constant temperature of 20°C and pressure in the limit of 2.0 to 10.0 MPa. Strands of the propellants were cut into 150 mm length and 5 mm square. An inhibitor was used to coat the strands and burned in a bomb in presence of nitrogen. Fusion wires were inserted in the strand and connected to a timing circuit to determine the rate of burning of the samples.

Combustion heat or calorific value of the propellants was measured using Parr isoperibol-6200, one gram of propellant was put into the calorimetric oxygen bomb. The propellant was ignited in the bomb under reduced nitrogen pressure  $\sim 5$  kg/cm<sup>2</sup>, the temperature difference was automatically measured.

## 3. Results and Discussion

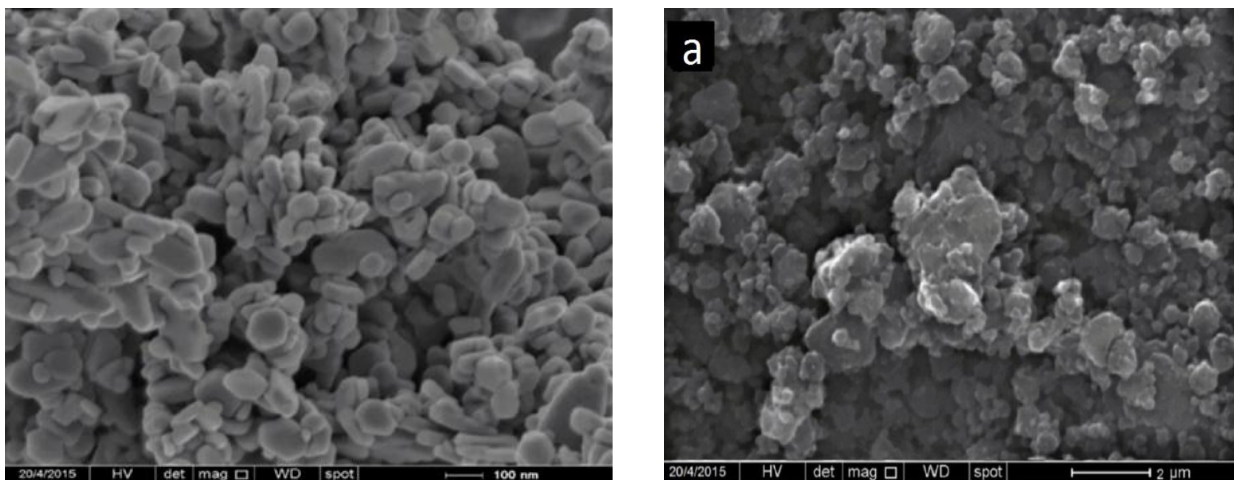
### 3.1. Characterization of ACNs additives

X-ray diffraction analysis was performed to disclose the crystalline phases and to compare between the composition phase of the composite mixtures before and after milling, Figure 1(a,b), respectively. The X-ray diffraction patterns of milled mixtures indicated that there was no formation of new phase. However, some modifications on intensity and shape were observed. In MA process there is no chemical reactions or phase transformations. Therefore, The XRD patterns of activated composites are almost the same as that of the un-milled mixtures [29]. The peaks are broadened and their maximums are shifted to smaller angles, due to a reduction in the crystal size (amorphization) that formed due to the plastic deformation of the milled particles.



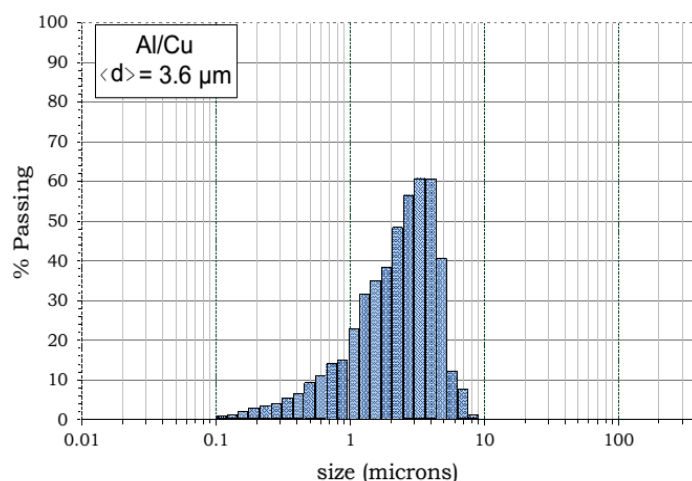
**Figure 1.** XRD of Al-Cu pattern [a represent without milling and b represents 15 min. milling].

The scanning electron micrographs, Figure 2, of the milled ACNs show the modifications in the surface morphology of ACN particles that developed due to MA. A set of characters were observed as: 1) ACNs particles appeared flattened; hence, the formed particles have lamellar structure of successive loosely packed nano-flakes of Al and the inclusion (metal oxides). 2) A considerable amount of inclusions was adhered (contact well) to the surface of Al particles and forming a compact (dense) solid structure. 3) The milled nanocomposite particles were made up of highly irregular aggregates with nearly mean diameters of about 1–3  $\mu\text{m}$ . The new formed surfaces were rough, highly featured (rock-like surfaces), which is a common characteristic for the ball-milled powders [19, 29].



**Figure 2.** SEM images of initial n-Al (at 20,000 $\times$ ), (bar = 100 nm) and a) Al-Cu nanocomposites (at 4000 $\times$ ), (bar = 2.0  $\mu\text{m}$ ).

Results of particle size analysis for ACNs powders are shown in Figure 3. For Al-Cu nanocomposite particles, there were wide distributions of the particle sizes; they ranged from about 0.1 to 6.0  $\mu\text{m}$ , with mean sizes of 2.5  $\mu\text{m}$ .



**Figure 3.** Particle size distributions of ACNs

### 3.2. Characterization of the propellants

#### 3.2.1. Energetic effect

Table 2 reports the combustion heat values of HTPB propellants, M1, M2, and M3, which contained Al-Cu nanocomposite concentrations of 1.5, 3, and 5 %, respectively. It is clear that, the higher the percentage of ACN, the higher is the calorific value of the propellant. The heat of combustion increments that were achieved due to incorporation of different percentages of ACN were in the range of 80, 130, and 170 cal g<sup>-1</sup>, which represented 6, 9, and 11 % of energy increments.

**Table 2.** Combustion heats of ACN propellants

Mix No.	Al-Cu (Composites) [%]	calorific value [cal g <sup>-1</sup> ]	Energy increase [%]
M1	1.5	1498.71	6
M2	3	1547.85	9
M3	5	1570.42	11
M	n-Al, 5	1415.63	-

The combustion heat enhancement, as previously stated, may be due to that the components of ACN can react exothermically and release a considerable amount of heat. Which represents an added energy the propellant system and indicates that the incorporation of more percentage of ACN will achieve an energy enhancement for the HTPB propellant.

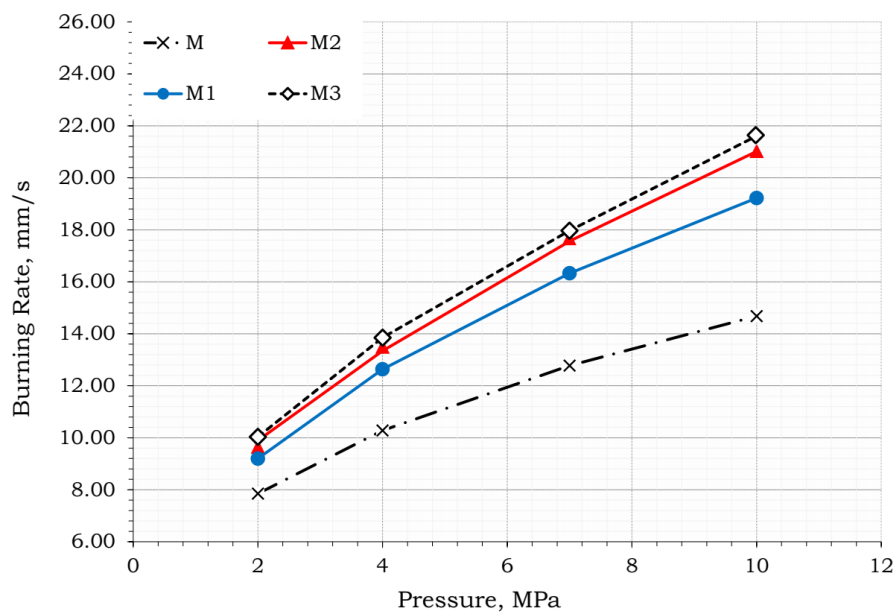
#### 3.2.2. Effect on the rate of burning.

Knowing the burning rate of a propellant, and how it changes under various pressures, is of fundamental importance on the safety of a combustion case. Therefore, the burning rate evaluation was performed at four different values of pressure (2, 4, 7, and 10 MPa). Table 3 shows that the burning rate increased with increasing the content of ACN. It is clear from the table that the burning rate of the propellant increased and at the same time operates with relatively low value of pressure exponent "n" even in the range of 5 % weight concentration. It is also observed that at 1.5 wt. % content of ACN 'n' value was very close to that of the base propellant. The propellants M1, M2 and M3 achieved burning rate increments in ranges of 23 %, 38 % and 40 %, respectively.

**Table 3.** Burning rates of ACN propellants

Samples	Al-Cu (Composites) [%]	R [mm s <sup>-1</sup> ] at pressures [MPa]					Burn Rate increase [%]
		2	4	7	10	n	
M1	1.5	9.19	12.63	16.33	19.22	0.458	23
M2	3	9.64	13.49	17.68	21.06	0.454	38
M3	5	10.97	14.22	17.94	21.29	0.506	40
M	n-Al, 5 %	7.85	10.28	12.78	14.68	0.389	-

Table 3 shows the effectiveness of the ACN additives even at a relatively low concentration and low pressures; the addition of small content of ACN (1.5%) led to a considerable increase in the burning rate of HTPB propellant by about 22 %. On the other hand, further addition of ACN, over 3 %, i.e., 5 % content slightly augmented the propellant burning rate, from 38 % to 40 %, which reveal that the addition of ACN over 5 % may be did not give a further increase in the burning rate. The typical curves of burning rate versus pressure are shown in Figure 4.

**Figure 4.** The burning rate of ACN at different pressures.

Increasing the burning rate of the composite propellant, without very high operating pressures, is one means of increasing the propellant performance without the use of potentially expensive technologies or materials of the combustion case. In view of the above-mentioned facts, the small value of the pressure exponents ( $n \leq 0.5$ ) indicates the ability of ANCs to be reliable and effective catalysts for HTPB propellants. Where, such mechanically activated nanocomposites ignite at temperatures substantially lower than the characteristic temperature of aluminum ignition [20,21]. Therefore, once such nanocomposite powders were ignited, they assisted in a rapid ignition and progressive burning of the complete propellant matrix.



#### 4. Conclusion

A set of reactive Al-Cu nanocomposites (ACNs) were prepared using Cu inclusions. The characterization results of ACNs have indicated that the prepared composites have only the initial phases of the milled components with no formation of new phases. The milled particles were flattened and adhered with each other to form highly featured agglomerate in sizes of 1–2  $\mu\text{m}$ . The energetic and catalytic activities of ACNs were tested by incorporating them as multi-function additives in the HTPB composite propellant formulation. The concentration effect of Al-Cu nanocomposite (ACN) was studied as an example for ANCs. The content effect of ANCs was studied at 3 levels; 1.5, 3, and 5 % of weight concentration. The ACN based propellants were evaluated for their energetic and burning properties. They were examined as both fuel and burning catalyst. The main results have indicated that ACNs based propellants have achieved improvements in the combustion energy and burning rate properties. Therefore, Al-Cu nanocomposites, ACNs, represent promising multi-function additives for HTPB composite propellant as they can perform as highly energetic fuel and fast burning catalysts.

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