

Thermal Investigation and Kinetic Evaluation of CuO Coated Carbon Nanofibers in Hybrid Nanocomposite Energetic Composition

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Abstract: Nanomaterial additives have been broadly used in different applications to enhance the energy output of energetic materials. Herein, the carbon nanosized fibrous surfaces (CNF) were subjected to a pretreatment process followed by catalysis to ensure the successful deposition of a thin layer of nano-copper. The obtained Cu-coated layer was then galvanized at 250°C then sonicated with aluminum nanoparticles (120 nm average particle size), producing CuO-coated CNF nanosized thermit colloids in isopropanol. These colloids could act as a recommended oxidizer agent for Al nanoparticles. Finally, the obtained nanosized thermit colloids were combined with trinitrohexahydrotriazine (RDX) crystals. The impact of this combination on the RDX decomposition behavior was investigated utilizing the modified Kissinger-Akahira-Sunose (KAS) method. Interestingly, the average activation value was decreased by 40.5%, which could be attributed to the high reactivity of the developed thermit colloids together with a combination that occurred with RDX nitramine particles.

Keywords: carbon nanofibers; metal nanoparticles; electroless-plating; thermal study.

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1. Introduction

Carbon is considered a high chemical bonding flexible element, which could be the backbone for various organic and inorganic particles. Carbon possesses numeral allotropes such as fullerenes, graphite, and diamond [1]. One from the underscore of carbon is carbon nanofibers (CNFs). It is a promising modern revolution participating in many fields, especially materials science, and is recommended to open new routes into nanotechnology [2]. The low cost of CNFs supported their application in a variety of modern thermal and electrical improvements as well as their usage in electromagnetic protective shielding and composite materials additives [3-5]. CNFs have extensively been employed as a reinforcing material in different polymeric formulations regarding their electrical, mechanical, and thermal properties [6,7]. CNFs can find wide applications in powder rolling and other metallurgic processing via plating with metal particles [8,9].

A unique structure of carbon nanofibers (CNFs) offers a structure full of pores that induce high catalytic proficiencies, enabling nanofibers to work effectively as desirable carriers for communal nanoparticles and energetic fillers [10-12]. CNFs provide an optimum surface for uniformly loading the catalyst [13]. Catalyst active centers on CNF could enhance the uniform contribution in the redox reaction when mixed with energetic fillers [14]. However,

enhancing the CNF characteristics by deposited metal particles is limited because CNFs cannot be deposited by metal particles. Therefore, surface modification techniques are considered for metal deposition. Working at the normal room temperature [15] is considered one of the major advantages of the metal electroless technique over others, such as the molecular-level mixing [16] and the chemical/physical vapor deposition [17]. Moreover, the electroless technique offers the simplicity and feasibility of depositing a wide variety of metals, such as nickel, silver, copper, gold, and cobalt, onto CNFs [18]. This could be attributed to enhancing the CNFs/deposited metal wettability regarding the increased active spots over the surface [19-21].

Energetic Materials (EMs) are well-known in the military field and for their valuable civilian applications such as in airbags, smoke formulations, and pyrotechnics. Moreover, EMs could be mixed with metal powder and metal oxide, which act as fuel-oxidant compositions such as "Thermite" [22]. They can undergo exothermic reduction-oxidation reactions converting metals into stable metals oxide or producing free metals from their oxides based on their oxygen content [23-24]. Alternatively, thermite can be used effectively as gas generator material or in incendiary devices and welding applications regarding its relatively huge amount of heat released during the exothermic reaction. Furthermore, the metals obtained from these redox reactions could be used to produce more energy through the combustion reactions in the presence of additional oxygen content and high temperatures [25-27]. Also, nano-thermites are interested in various implementations such as micro/nano-joining and energy generation devices for modern, energetic materials. These applications depend on their relatively small sizes, high density, and tunable reaction parameters, such as ignition temperature and reaction rate [28-30]. 1,3,5-trinitro-1,3,5-triazinane (RDX) is a traditional high energy material that is used as a shaped charge filler [31,32] and has several applications in composite propellants and explosives [33]. It is still one of the most usable compositions in the energetic materials field [34].

In this study, CNFs coated with copper oxide were successfully synthesized through the electroless plating technique. This enabled the improvement of the interfacial bonding of CNFs with aluminum matrix regarding the molecular-level mixing process. Herein, the CNFs were mixed with the Cu in an optimized plating bath, which encouraged the homogenous distribution of the CuO nanoparticles over the whole surface of the pre-treated CNFs mixed with Al nanoparticles to obtain a hybrid meta-intermolecular nanomaterial based on CNFs. TEM micrographs demonstrated the homogenous coating of CNFs with Cu. The XRD investigation recognized the formation of the highly crystalline material. The effective integration and dispersion into energetic systems were studied for improving (enhancing) the performance. The obtained hybrid material was dispersed in the energetic nitramine RDX using acetone with aluminum nanoparticles. Finally, the impact of the synthesized hybrid material, based on CuO plated CNFs, upon the thermal and kinetic decomposition of RDX was also evaluated.

2. Materials and Methods

2.1. Materials.

Carbon nanofibers were obtained from Pyrograf Products, Inc., Copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was obtained from Sigma-Aldrich, Germany. Sodium Citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$) was purchased from the Bio shop, while Sodium hydroxide (NaOH), Stannous chloride (SnCl_2), Stannous chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 98%), and Hydrochloric

acid were acquired from CALEDON Laboratory Chemicals. Acetone (99.9%) was bought from Penta chemicals. Palladium (II) chloride (PdCl_2 , 100%) was obtained from Artcraft chemicals Inc. RDX crystals were synthesized in our local laboratory. All reagents were utilized as received with no need to perform any additional purification procedures.

2.2. CNFs catalyzation.

CNFs catalyzation is a pretreatment procedure consisting of two consecutive processes; sensitization and surface activation [6]. This procedure improves the surface adhesion to acquire the deposition of metal coatings successfully. Firstly, 2 g of SnCl_2 is used accompanied by 10 ml conc. HCl, in the presence of 90 ml of deionized water, generates active spots on the CNFs surfaces, which is known as "sensitization". The mixture is mixed for 30 min using an ultrasonic probe sonicator (Q500 Qsonica); thus, a surface catalyst would be effectively created. The CNFs were then rinsed with water, filtered, and dried at 70 °C for 1 hr with a vacuum. The obtained CNFs were activated using the mixture of (0.04 g PdCl_2 , 3 ml HCl, and 150 ml water) for 30 minutes with the aid of the sonicator.

2.3. Copper metallization of activated CNFs.

Herein, electroless plating was performed to deposit copper nanoparticles upon the activated CNFs. This process was done through a reduction reaction with a stoichiometric ratio of $\gamma = 16$ (w/w) [37, 38]. This emerging method provides a continual Cu deposition layer through dispersing 0.3 gram of CNF in 200 ml solution; 18.5 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 44 g $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, deionized water, and 55 ml HCHO. Sonication of CNFs was achieved for 1 h by ultrasonic probes. Meanwhile, 500 ml of NaOH solution with a concentration of 2N was added slowly to set the solution at a pH in the range of 9 to 10. The reaction is completed once the black color turns red-brown. Finally, the reaction mixture was washed, filtered, and dried for 4 h at 250 °C to obtain CNFs coated with CuO. Interestingly, this process develops a uniform coating distribution. The whole process is schematically represented in Figure 1.

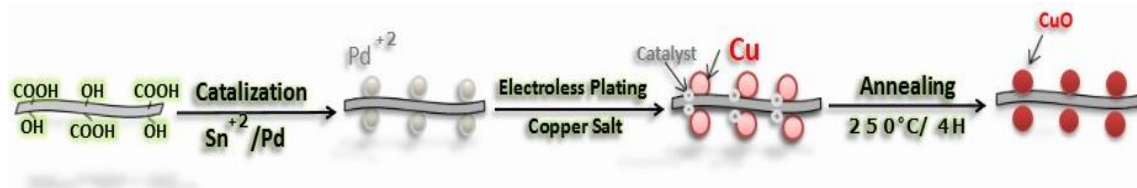


Figure 1. The procedure of obtaining CNFs plated by CuO.

2.4. Characterization of CuO-CNFs.

TEM, JEM-2010F, and XRD, Bruker D8, have been applied to clarify the morphology and the crystalline structure of both CNFs and CuO-CNFs, respectively. XRD was connected with a Davinci diffractometer operating where the experiments were performed at 35 kV, 45 mA, and $\text{Co-K}\alpha$ radiation ($\lambda_{\text{avg}} = 1.79026 \text{ \AA}$). SEM was connected to an energy dispersive X-ray spectrometer (EDX) Bruker Quantax 200 to investigate the elemental analysis.

2.5. Dispersion of CuO-CNFs and Alex into RDX matrix.

The dispersion process for CuO-CNF/Al into the RDX energetic matrix was successfully performed via the solvent blending methodology. Firstly, CuO-CNFs were added to aluminum nanoparticles (Alex) in acetone. The mixture was ultrasonicated to ensure the

effective distribution of solid particles in solvent and to eliminate any physical aggregations. Meanwhile, RDX crystals were dissolved in acetone and then added to the first mixture. The hybrid mixture was subjected to a continuous sonication accompanied by a slowly heating up. This heating guarantees the plenary dispersion of the hybrid mixture into the RDX matrix and evaporates acetone gradually.

2.6. Thermal analysis study.

Thermogravimetric analysis, TGA55, TA Instruments, USA, together with the differential scanning calorimetry technique, DSC Q-2000, TA Instruments, USA, were utilized to clarify the thermal behavior of the obtained compositions. The heating rates were 3, 5, 7, and 10 K min⁻¹ in the case of TGA measurements and 5 K min⁻¹ in the case of DSC measurements. The sample weight ranges between 1.5 and 2 mg for each test at a temperature range between 40 and 350 °C.

2.7. Thermal analysis study.

The kinetic triplet and the reaction model ($f(\alpha)$) were studied. The evaluation of the solid phase reactions could be investigated by various techniques [39]. Different isothermal or nonisothermal methods could be applied to obtain the decomposition kinetics.

The isoconversional method could be investigated depending on the change in the rate of the process.

$$\frac{d\alpha}{dt} = k(T)f(\alpha)$$

In this case, the reaction model is $f(\alpha)$, and $k(T)$ is a rate constant (depending on the temperature) and could be determined by applying the Arrhenius equation

$$k(T) = A \exp\left(\frac{-E}{RT}\right)$$

By adding eq. 2 to eq.1, the kinetic differentiation could be:

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha)$$

By the integration of eq.3, the following equation was obtained

$$g(\alpha) \equiv \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \int_0^t \exp\left(\frac{-E}{RT}\right) dt$$

Here, $g(\alpha)$ represents the integrated order for the model of the reaction.

In the iso-conversional method, the model of the reaction is based on Eq. 1 and does not depend on the temperature. In this study, the modified Kissinger-Akahira-Sunose (KAS) methods were investigated:

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^{1.92}}\right) = \text{const} - 1.0008\left(\frac{E_\alpha}{RT_\alpha}\right)$$

The symbol T_p represents the exothermic peak temperature at the selected rates and β is the selected heating rate. By plotting of $\ln\left(\frac{\beta_i}{T_{\alpha,i}^{1.92}}\right)$ against $\left(\frac{1}{T_\alpha}\right)$ (at the various heating rates), the slope of the obtained straight line represents the activation energy [40].

3. Results and Discussions

3.1. Characteristics of CuO-CNFs.

Figure 2 showed the TEM micrographs for the synthesized CNFs where the average diameter started from 50 to 100 nm, while the particles' average length was 50-200 μm . As given in Figures 2 (c and d), it is also clear that CNFs surfaces were homogeneously coated with CuO particles through the effective electroless plating approach.

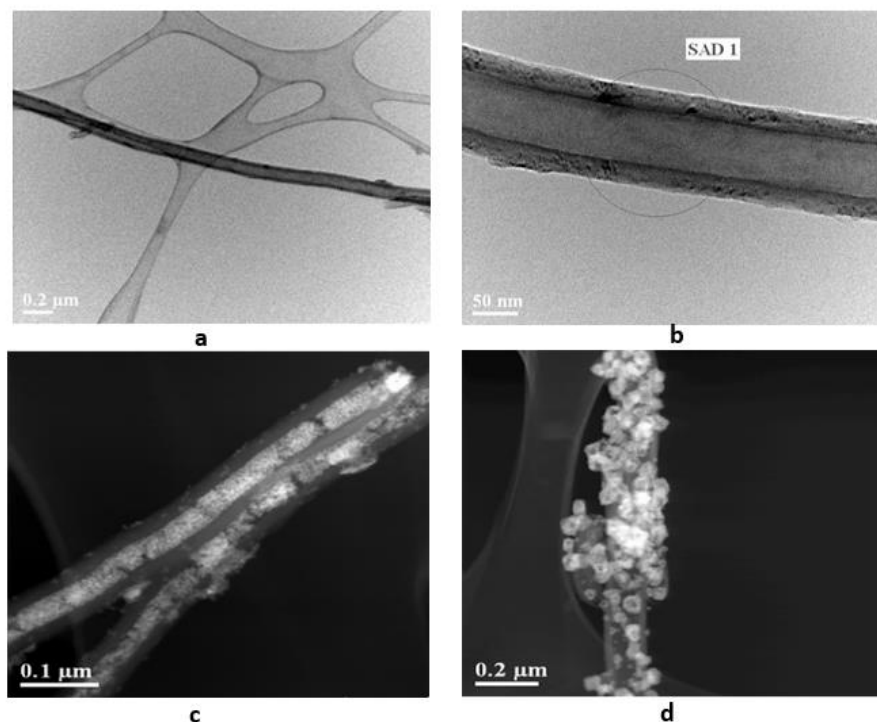


Figure 2. TEM micrographs of synthesized CNF (a) and (b) before catalyzation, (c) and (d) after catalyzation and deposition of CuO onto -CNF.

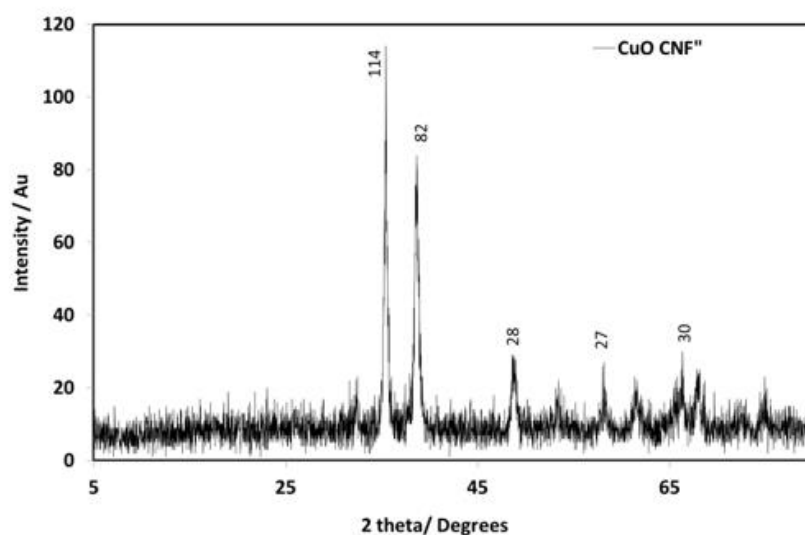


Figure 3. XRD patterns of CuO/CNF composition.

The XRD pattern in Figure 3 indicated ten distinctive CuO peaks, which confirmed the high crystallinity of the synthesized CuO-CNFs. These results coincided with the international JCPDS standard data (PDF-04-007-1375). Also, the XRD results confirmed the high purity of the synthesized CuO-CNF particles regarding the reflection of CuO to CNFs ratio (16:1).

3.2 Thermal decomposition of the prepared nanocomposite and the pure RDX.

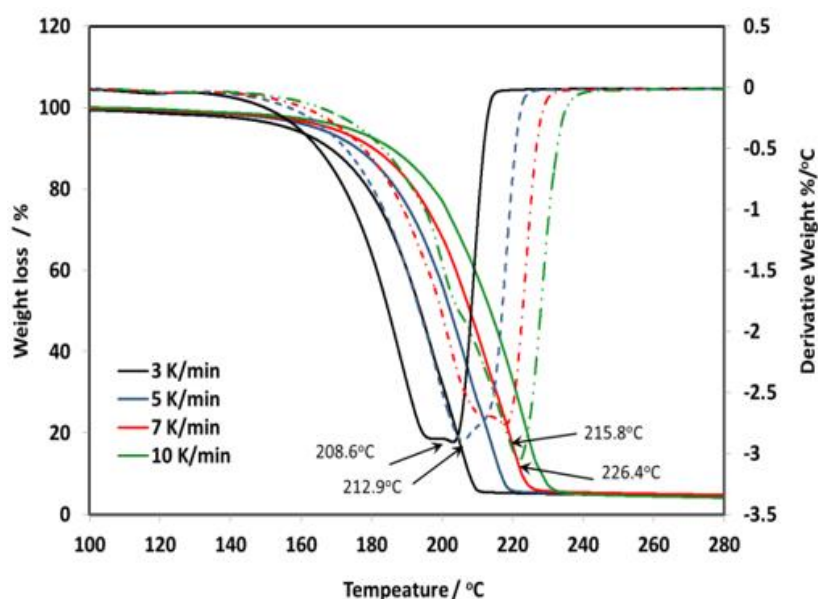
TG/DTG thermograms obtained for pure RDX and CuO-CNF-Al nano-thermite, given in Figure 4 and Table 1, showed that both investigated compositions possessed a single decomposition procedure. However, the onset decomposition temperature at a heating rate of $3\text{ }^{\circ}\text{C min}^{-1}$ was increased from 161.2°C , in the case of pure RDX, to 172.7°C for the synthesized RDX/CNF/Al/CuO colloids.

Table 1. TG/DTG results obtained for RDX/CNF/Al/Cu in comparison to pure RDX.

Type	TG curve			DTG curve	
	$\beta / ^{\circ}\text{C min}^{-1}$	$T_0 / ^{\circ}\text{C}$	Mass loss / %	$T_p / ^{\circ}\text{C}$	$T_{oe} / ^{\circ}\text{C}$
RDX+ 5%Al+1%CuO- CNFs	3	172.7	95.1	208.6	217.1
	5	181.7	95.8	212.9	224.5
	7	190.4	95.5	215.8	224.9
	10	202.2	95.6	226.5	236.7
RDX	3	161.2	99.9	205.6	218.5
	5	168.3	99.0	210.6	224.3
	7	178.3	98.8	213.5	225.7
	10	181.5	99.4	220.2	235.4

Also, the maximum decomposition peak was increased from $205.6\text{ }^{\circ}\text{C}$, for pure RDX, to $208.6\text{ }^{\circ}\text{C}$ for the nano-thermite colloids. Moreover, the RDX decomposition was ended at 218.5°C , while the decomposition was ended at $217.1\text{ }^{\circ}\text{C}$ in the case of the hybrid nano-thermite colloids. The quick finishing of the RDX/CNF/Al/CuO decomposition could be attributed to the ability of new colloids to cover the RDX crystals and prevent heat loss from the surface of the crystals.

As a result, a homogenous distribution of heat occurred, which accelerated the autocatalytic effect of the gaseous pieces and resulted in the quick finishing of the decomposition process. At the end of decomposition, pure RDX was found to leave about 1% of the original mass, which confirms the complete decomposition of RDX into gaseous products. On the other hand, RDX/CNF/Al/CuO remained 4.5% of its original mass regarding Al and CuO residuals. These results confirmed the significant impact of CNF/Al/CuO on the thermal decomposition behavior of RDX crystals.



(a) RDX+ 5%Al+1%CuO-CNFs

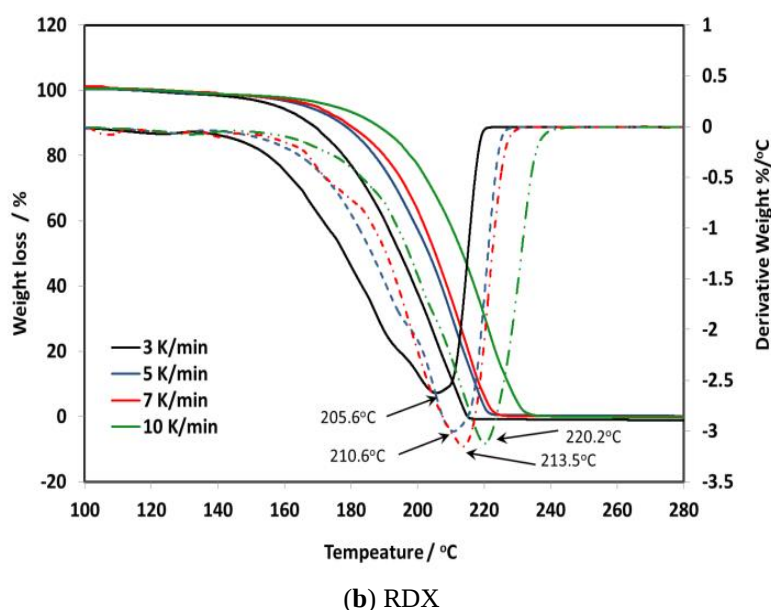


Figure 4. Nonisothermal TG/DTG of the energetic nanocomposite and the individual RDX at 3, 5, 7, and 10 heating rates.

3.3. Kinetic parameters obtained by nonisothermal technique.

Since the synthesized RDX/CNF/Al/CuO hybrid composition is a novel energetic formulation, it is essential to investigate its thermal properties. These thermal characteristics directly relate to the combustion and explosive characteristics of the whole composition [41-45]. Moreover, evaluating this composition's activation energy (E_a) and thermal stability is crucial to fully characterize this novel energetic material [46-50]. In this research, the modified Kissinger-Akahira-Sunose (KAS) was chosen as the most recommended iso-conversional approach to characterize the thermal decomposition behavior of energetic compositions [39]. KAS was performed at conversion rates of 5-90%, and a mean value interval of 0.25-0.85 was selected to avoid the inaccuracy of the tail peaks. As given in Table 2, the E_a of the obtained RDX/CNF/Al/CuO composition was found to be $107.9 \text{ kJ mol}^{-1}$, while the activation energy for the pure RDX crystals was $181.5 \text{ kJ mol}^{-1}$. The obvious decrease in E_a with 40.5% reflects the significant impact of adding the synthesized hybrid colloids to RDX crystals. This could be attributed to the existence of the relatively high surface area regarding the addition of nanosized particles, thus increasing the active site. As more active sites are initiated, more reactivity of RDX exists, and a lower decomposition peak temperature obtains [51]. The addition of the nanoparticles, which developed a higher surface area, together with CNFs, which possess a high heat conductivity, is responsible for the dramatic conversion of the pure RDX decomposition mechanism [52] into a complex nonlinear one. This could be due to the improvement of the conductivity of the reaction surface and the absorption of some of the gaseous products via the higher surface area provided. As a result, the decomposition reaction remains in the condensed phase and thus increasing the overall catalytic ability.

3.4 Effect of the extent of the reaction conversion on the kinetic parameters

In this part, the dependency between the reaction conversion (α) and the reaction temperature was investigated for either pure RDX crystals or the hybrid RDX/CNF/Al/CuO composition. As shown in Figure 5, both curves were found to be similar regarding the reaction conversion. However, a slight change was observed in the case of the reaction temperature.

These results confirmed that the addition of the synthesized nano-thermite colloids did not negatively influence the thermal stability of the RDX crystals.

Table 2. Kinetic parameters of the energetic nanocomposite and the individual RDX.

α reacted	Nanocomposite of RDX			RDX		
	Ea kJ.mol ⁻¹	Log A s ⁻¹	R2	Ea kJ.mol ⁻¹	Log A s ⁻¹	R2
0.05	128.1	16.8	0.9958	186.2	21.0	0.9635
0.10	116.6	15.0	0.9989	184.0	20.7	0.9765
0.15	112.9	14.4	0.9995	182.9	20.6	0.9865
0.20	110.7	14.0	0.9995	181.8	20.4	0.9828
0.25	109.5	13.8	0.9997	172.4	19.3	0.9817
0.30	110.3	13.8	0.9995	171.7	19.1	0.9828
0.35	110.0	13.7	0.9992	173.4	19.3	0.9828
0.40	108.7	13.5	0.9995	174.5	19.3	0.9850
0.45	108.6	13.4	0.9995	174.4	19.3	0.9882
0.50	107.2	13.2	0.9997	172.5	19.0	0.9852
0.55	106.5	13.1	0.9998	178.8	19.6	0.9917
0.60	106.5	13.0	0.9999	182.4	20.0	0.9932
0.65	104.6	12.8	0.9994	188.9	20.6	0.9958
0.70	106.6	12.9	0.9995	189.2	20.6	0.9973
0.75	107.7	13.0	0.9994	189.6	20.6	0.9973
0.80	108.3	13.1	0.9990	190.9	20.7	0.9990
0.85	108.4	13.0	0.9971	189.4	20.6	0.9987
0.90	108.8	13.0	0.9987	190.0	20.6	0.9987
Mean value	107.9±0.54	13.2±0.11		181.6±2.5	20.1±0.22	

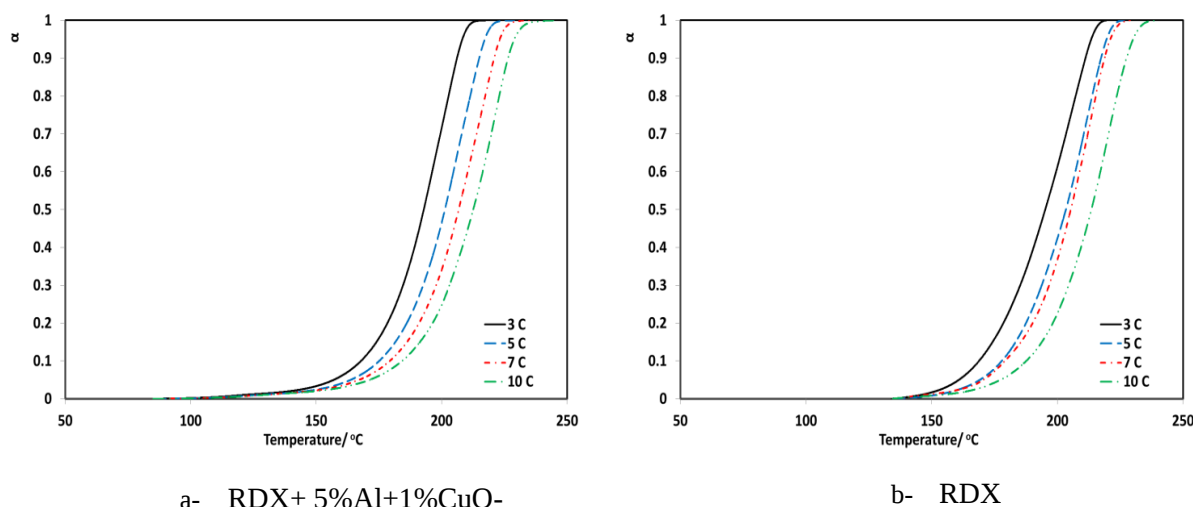


Figure 5. The α -T curves at different heating rates for (a) RDX + 5%Al+1%CuO-CNFs, (b) RDX.

Also, the impact of the conversion extent on the activation energy was examined, as shown in Figure 6. It was found that the activation energy of the RDX/CNF/Al/CuO was constant versus the conversion extent except at the beginning of the conversion, which showed a slight change. On the other hand, the activation energy of pure RDX was constant until it reached the conversion extent of 0.55. Afterward, the activation energy increased by 10 kJ mol⁻¹ then remained constant until the end of the conversion. These results confirmed our previous conclusion that the addition of nanoparticles increases the surface area and the available active sites, thus increasing the molecular energy level [53,54]. Moreover, these outputs coincided with Joseph *et al.*'s results that metal nanoparticles were able to develop physical adsorption, which forms what is known as "hotspots" that promote the HMX thermal decomposition [54]. This explanation could also be used to confirm our conclusion that nano CNF was the reason

behind the thermal conductivity enhancement of the obtained hybrid composition, which leads to the reduction of the activation energy of the energetic nanocomposite.

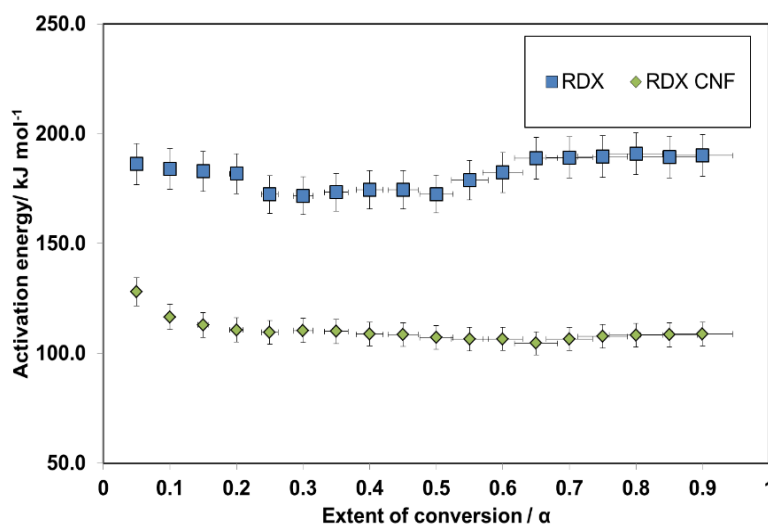


Figure 6. The activation energy and the conversion extent of the nano-thermite composition and the individual RDX through the modified KAS method.

4. Conclusions

The study of nanoscale hybrid thermite compositions represents advanced research in the energetic materials field. The CNFs were successfully catalyzed through a surface pretreatment process. The CNFs surfaces were homogeneously coated with CuO particles through the effective electroless plating approach. The dispersion of the thermite mixture with the catalyzed CNFs was observed by the TEM. According to TGA results, the presence of nano-thermite with the RDX exhibits decomposition behavior similar to the individual RDX. While the nanocomposite has different decomposition kinetics and its activation energy was lower than the RDX. The individual RDX and the nanocomposite have activation energies of $181.6 \text{ kJ mol}^{-1}$ and $107.9 \text{ kJ mol}^{-1}$, respectively. The addition of nanoparticles, which developed a high surface area, together with the CNFs, is responsible for the conversion of the pure RDX decomposition mechanism into a complex nonlinear one. The activation energy of the RDX/CNF/Al/CuO was constant at different extents of the reaction conversion. The thermite mixture was able to perform physical adsorption of the gaseous products, which forms what is known as "hotspots" that promoted the RDX thermal decomposition. The CNFs were the reason behind the enhancement of thermal conductivity, resulting in a great decrease of the activation energy of the energetic hybrid composition.

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Conflicts of Interest

The authors declare no conflict of interest.

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