Chapter 2
Effects of Carbon Nanofibers (CNFs) on Combustion and Mechanical Properties of RDX-Based Modified Single Base Propellant

Xiaoxiao Zhang, Xuekun Fan, You Fu, Bin Xu, and Xin Liao

Abstract To improve the properties of the modified single base propellant with RDX, propellant samples with different mass fractions of carbon nanofibers (CNFs) (0, 0.2, 0.4, 0.6, 0.8%) were prepared. The combustion performance of modified single base propellant samples were studied by closed bomb test and the mechanical properties were tested by universal material testing machine and beam impact testing machine. In addition, the microstructure was observed by SEM. Results show that agglomeration occurs when the CNFs content is greater than 0.2%. And the burning rate of the modified single base propellant increases after adding CNFs. The mechanical properties of single base propellant were improved after adding CNFs content of 0.2%, in which the tensile strength increased by 63%, 11.25%, 18% at −40 °C, 20 °C and 50 °C, respectively. The addition of CNFs can improve the stability of modified single base propellant.

2.1 Introduction

The single base propellant mainly consisting of nitrocellulose is widely used in the barrel weapons [1]. The history of the single base propellant is so long that its

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manufacturing technology is mature. It also has excellent mechanical properties, high combustion stability and low ablation. However, its energy is too low to meet the requirement of modern army for the long range power of weapons. RDX is a high energy density substance, which can effectively improve the energy of the propellant [2]. Nevertheless, the addition of RDX has influence on the mechanical properties, combustion properties and thermal decomposition properties of the single base propellant, thus the ballistic and safety properties of the weapon will be affected [3].

Carbon nanofibers (CNFs) are a kind of discontinuous graphite fibers, which are obtained by cracking gas phase hydrocarbons [4]. Carbon nanofibers have many advantages such as large aspect ratio, massive specific surface area and so on. And CNFs also performance well at mechanical strength [5], thermal conductivity and electrical conductivity [6]. CNFs now are widely used in composite materials, energetic materials and other fields. For example, Daniel B. Nileson and Dean M. Lester added carbon nanofibers of different mass fractions to a variety of energetic materials. It is found that the combustion performance of gun propellant and propellant was improved [7]. Zhao Fengqi, Chen Pei and others adding carbon fibers into RDX/AP/HTPB propellant as a kind of burning rate regulator. As a result, the decomposition peak temperature of AP decreases. The initial partial liberation heat of the propellant increases. The peak of liberation heat and the burning rate is increased [8]. Hence CNFs has performed well in improving the properties of energetic materials, but the current researches focus more on combustion performance. While after using RDX to modify the single base propellant, the mechanical properties, combustion properties and thermal decomposition properties of the propellant are affected to some extent. In particular, mechanical properties of the single base propellant will decline. Hence, in this study, different content of CNFs was added to the modified single base propellant to explore its influence on combustion properties and mechanical properties.

2.2 Experimental

2.2.1 Meterials Preparation

The modified single base gun propellants were composed of Nitrocellulose (NC, 12.6 nitrogen percent) from Luzhou Northern Chemical Industry Co., Ltd. (Sichuan, China), RDX from Gansu Yinguang Chemical Industry Co., Ltd. (Gansu, China), 2,4-dinitrotoluene(DNT) and diphenylamine (DPA) from Guoyao Group Chemical Reagent Co., Ltd. (Shanghai, China).

Table 2.1 Formula of modified single base gun propellant with different mass fraction of carbon nanofibers (CNFs)

Sample	*w* (%)				
	CNFs	NC	RDX	DNT	DPA
1#	0	81.0	10	8	1
2#	0.2	80.8	10	8	1
3#	0.4	80.6	10	8	1
4#	0.6	80.4	10	8	1
5#	0.8	80.2	10	8	1

2.2.2 Sample Preparation

Table 2.1 is the formulation of modified single base propellant with different content of CNFs (Aladdin Chemical Reagent Co., Ltd., Shanghai, China). The formulation of total solid mass is 350 g. And the plasticization was dissolved with acetone and ethanol (the volume ratio is 1:1) equivalent to 51% of the total mass of the sample solid. First, CNFs and a certain amount of acetone were mixed (The volume is 40 mL when the CNFs content is 0%. While for every 0.2% increase in CNFs content, acetone volume increased by 5 mL). Second, adding a small amount of OP-10 emulsifier (1/1000 of the volume of the solution) to increase decentralization with magnetic stirring of 30 min and ultrasonic treatment of 30 min to disperse the CNFs. Third, the nitrocellulose, DNT, DPA, RDX, ethanol and acetone were added to the kneading machine to be knead for 30 min. And adding CNFs-acetone mixed solvent to knead for 3 h. Then two different extrusion dies (dumbbell mould and single hole mould) and hydraulic press were used to get the propellant samples. Finally, all the samples put into fume hood to volatilize the solvent for 7 days, then were dried in a wet oven at 40 °C for 3 days and drying oven at 45 °C for 3 days to remove the solvent completely.

2.2.3 Combustion Performance

The closed bomb were tested at 20 °C. And the volume of the closed explosive is 104.97 cm^3 with the ignition pressure of 10.98 MPa. The filling density is 0.12 $g\cdot cm^{-3}$ and 0.20 $g\cdot cm^{-3}$, respectively. While the length of the samples are 40.00 mm.

2.2.4 Mechanical Properties

The impact strength, tensile strength and compression strength are tested according to the GJB 770B-2005 gunpowder test method. The experimental temperature is 20 °C.

The impact strength is tested by se2 simply supported beam pendulum impact tester and the length of the samples are 60.00 mm. The tensile strength and compression strength are tested by instron3367 universal material testing machine and the tensile sample was dumbbell type with the length of 40.00 mm. The ratio of length to diameter of the compression is 1:1.

2.2.5 Microstructure Test

The microstructure was tested by Quanta FEG 250 scanning electron microscope of American FEI company.

2.2.6 DSC Test

The thermal decomposition performance experiment was carried out with differential scanning calorimeter of HPDSC 827 produced by Mettler Toledo company. The samples were tested from 50 to 350 °C with the weight of 1.10 ± 0.02 mg. And the heating rate is 15 °C·min^{-1}.

2.3 Results and Discussion

2.3.1 Microstructure

Figure 2.1a shows the SEM images of carbon nanofibers (CNFs). As you can see, the diameter of the CNFs is at the nanometer level and the length is about 2 μm with a phenomenon of mutual entanglement. Figure 2.1b is a cross-sectional view of the single base propellant. It can be seen from the picture that the nitrocellulose is

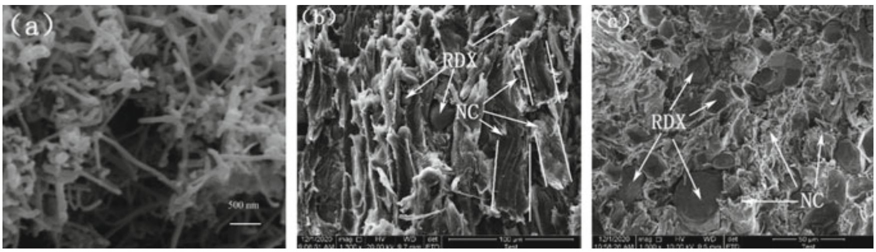
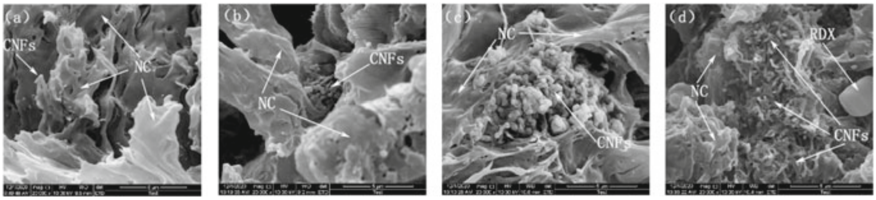


Fig. 2.1 SEM images of carbon nano fibers, modified single base propellant tear and fracture surfaces



(a) 0.2% (b) 0.4% (c) 0.6% (d) 0.8%

Fig. 2.2 SEM images of modified single base propellants with different mass fraction of CNFs

fibrous and twining and the diameter is between 10 and 50 μm. The nitrocellulose still maintains the basic skeleton after a series of processes. Figure 2.1c is a longitudinal fracture surface diagram of a single base propellant. It can be seen from the diagram that the RDX is ellipsoid with a diameter between 2 and 30 μm.

Figure 2.2 is the SEM images of modified single base propellant with different content of CNFs. It can be seen from the images that when the CNFs content is less, CNFs can be "inlaid" in nitrocellulose matrix. While agglomeration occurs when the CNFs content continues to increase.

2.3.2 Combustion Performance

For the purpose of studying the effect of CNFs on the combustion performance of modified single base propellant, the closed bomb was tested at 20 °C. The *u-p* curve was gotten from the closed bomb test, in which *u* is the firing rate of the propellant and *p* is the pressure measured by the closed bomb. It can be seen from the Fig. 2.3 that *u-p* curves were smooth, which shows that the stability of combustion is good. The burning rate of the modified single base propellant with CNFs was higher than that without CNFs, which is due to the good thermal conductivity of the CNFs in the combustion process of modified single base propellant [9]. But the burning rate decreases when the CNFs content is more than 0.2%. The reason is that excessive

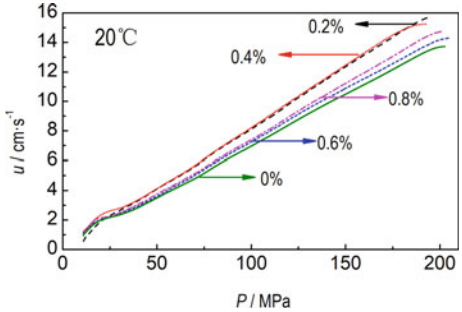


Fig. 2.3 *u-p* curves of modified single based gun propellant with different mass fraction of CNFs

Table 2.2 Combustion performance parameters of modified single base propellant with different content of CNFs

Sample	Parameter	*P* (MPa)				
		50–100	100–150	150-p_{dpm}	50-p_{dpm}	p_{dpm}
1#	u_1	0.0665	0.0610	0.0645	0.0671	203.04
	n	1.0118	1.0306	1.0165	1.0098	
2#	u_1	0.0809	0.0628	0.0869	0.0768	199.13
	n	1.0024	1.0570	0.9905	1.0148	
3#	u_1	0.0787	0.0673	0.0778	0.0756	193.10
	n	1.0105	1.0446	1.0141	1.0199	
4#	u_1	0.0675	0.0664	0.0854	0.0724	205.46
	n	1.0180	1.0209	0.9685	1.0017	
5#	u_1	0.0769	0.0589	0.0680	0.0719	203.37
	n	0.9934	1.0509	1.0200	1.0092	

Note u_1 is the burning rate coefficient, n is the burning rate pressure exponent, p_{dpm} is the pressure when dp/dt reaches its maximum value

CNFs can cause agglomeration [10], which cause that the contact area between the CNFs and the propellant matrix does not increase linearly with the increase of CNFs content. It can be confirmed from Fig. 2.2 that the agglomeration does exist.

Table 2.2 shows the combustion performance parameters of modified single base propellant with different content of CNFs. As can be seen from Table 2.2, the burning rate pressure exponent of the modified single base propellant with a CNFs content of 0.8% is less than 1 when the pressure is from 50 to 100 MPa. While the rest of the propellant are greater than 1. The burning rate pressure exponent of the modified single base propellants are greater than 1 when the pressure is from 100 to 150 MPa. The burning rate pressure exponent of the modified single base propellant with a CNFs content of 0.2% and 0.6% is less than 1 when the pressure is from 150 MPa to p_{dpm} MPa. Considering the whole pressure range (50 ~ p_{dpm} MPa), the burning rate pressure exponent of the sample is more than 1.

2.3.3 Energy Performance

The energy characteristic parameters of propellant are the basic index of propellant design and the important standard to evaluate the work ability of propellant. For the purpose of investigating the effect of CNFs content on the energy performance of the modified single base propellant, 15/1 single-hole tubular propellants were tested with the closed bomb to obtain propellant force (f) and covolume (a). Table 2.3 is the propellant force and covolume data of the samples. It can be seen from the table that propellant force of the samples basically remain unchanged, which indicates that the

Table 2.3 Energy properties of modified single base propellant

Sample	CNFs content (%)	f (kJ kg^{-1})	a (L kg^{-1})
1#	0	997.31	0.78
2#	0.2	997.68	0.80
3#	0.4	980.76	0.76
4#	0.6	989.42	0.75
5#	0.8	986.38	0.75

Note f is the propellant force, a is the covolume

addition of a small amount of CNFs has little effect on the energy performance of the modified single base propellant.

2.3.4 Mechanical Properties

The mechanical properties of the modified single base propellant were tested at different temperatures (−40, 20 and 50 °C). The results show in Table 2.4. As can be seen from Table 2.4, the mechanical properties all show increase first and then decrease as the CNFs content increases. The mechanical properties reach the maximum value at 0.2%. And the impact strength of 2# increases 21% from

Table 2.4 Effects of CNFs on the mechanical properties of modified single base propellant

Sample	T (°C)	α_k (kJ m^{-2})	σ_m (MPa)	δ_m (MPa)
1#	−40	11.10 ± 2.47	102.72 ± 2.73	58.59 ± 1.47
	20	18.18 ± 2.70	91.56 ± 2.53	54.44 ± 1.78
	50	27.05 ± 2.73	87.55 ± 3.09	39.28 ± 2.53
2#	−40	11.40 ± 1.60	104.13 ± 4.42	95.36 ± 1.55
	20	22.00 ± 2.35	99.01 ± 4.73	60.55 ± 1.68
	50	28.92 ± 2.71	96.81 ± 3.95	46.16 ± 1.17
3#	−40	10.00 ± 2.09	99.39 ± 3.58	80.52 ± 0.67
	20	18.16 ± 2.86	97.67 ± 5.78	59.24 ± 2.41
	50	25.78 ± 1.53	91.04 ± 1.61	40.93 ± 2.41
4#	−40	9.30 ± 1.76	98.43 ± 3.04	74.50 ± 2.43
	20	18.06 ± 1.94	94.59 ± 5.63	59.07 ± 2.73
	50	22.69 ± 2.38	90.07 ± 3.66	40.02 ± 2.89
5#	−40	8.64 ± 1.71	97.78 ± 4.87	64.84 ± 1.28
	20	12.78 ± 2.67	93.76 ± 2.76	57.21 ± 2.29
	50	22.44 ± 2.66	87.00 ± 1.78	39.21 ± 1.58

Note α_k is the impact strength, σ_m is the compressive strength, δ_m is the tensile strength

18.18 kJ·m^{-2} to 22.00 kJ·m^{-2} at 20 °C. While at −40 °C and 50 °C, it only increased by 3% and 7%, respectively. Compressive strength increased by 8% over 1# at 20 °C, 1.4% at −40 °C and 10.6% at 50 °C. The tensile strength increases by 11.2% at 20 °C, 63% at 40 °C and 18% at 50 °C, respectively.

Above all, when the content of CNFs is 0.2%, the mechanical properties of the modified single base propellant reach the maximum value, in which the impact strength, tensile strength and compressive strength are greatly improved at 20 °C, the impact strength changes little at 50 and 40 °C. And the tensile strength is greatly improved at −40 °C. The reason is that the CNFs and nitrocellulose matrix become a more uniform mixture after mixing (Fig. 2.2). When the external stress propagates in the propellant, the structure composed of nitrocellulose and CNFs can improve the effect of stress transfer. So the nitrocellulose matrix were strengthened to enhance the mechanical properties.

2.4 Thermal Decomposition Performance

The thermal decomposition performance at the heating rate of 5 °C·min^{-1}, 10 °C·min^{-1}, 15 °C·min^{-1} and 20 °C·min^{-1} are shown in Table 2.5 and Fig. 2.4. As can be seen from Table 2.5 and Fig. 2.4, the initial decomposition temperature and the exothermic peak temperature are basically unchanged after adding CNFs. While the exothermic heat increases first and then decreases with the increase of CNFs content and reaches the maximum when the CNFs content is 0.2%. The main reasons caused the decreasing trends are catalytic effect and high thermal conductivity of CNFs [7].

The activation energy of thermal decomposition kinetic parameters is obtained by using the Kissinger Eq. (2.4.1) through DSC experiments at the heating rate of 5 °C·min^{-1}, 10 °C·min^{-1}, 15 °C·min^{-1} and 20 °C·min^{-1}, respectively. The results of the temperature of the exothermic peak are shown in Table 2.6.

Table 2.5 Summarized results for DSC experiments of modified single base propellant with different mass fraction of CNFs at 5 °C·min^{-1}

Sample	CNFs content (%)	Tonset (°C)	T_{exo} (°C)	ΔH (J g^{-1})
1#	0	187.80	195.61	1933.02
2#	0.2	187.40	195.89	2008.24
3#	0.4	187.65	195.84	1940.87
4#	0.6	187.99	195.29	1910.05
5#	0.8	188.23	195.09	1922.37

Note T_{onset} is the temperature of the exothermic peak, T_{exo} is the temperature of the exothermic peak, ΔH is the enthalpy of decomposition

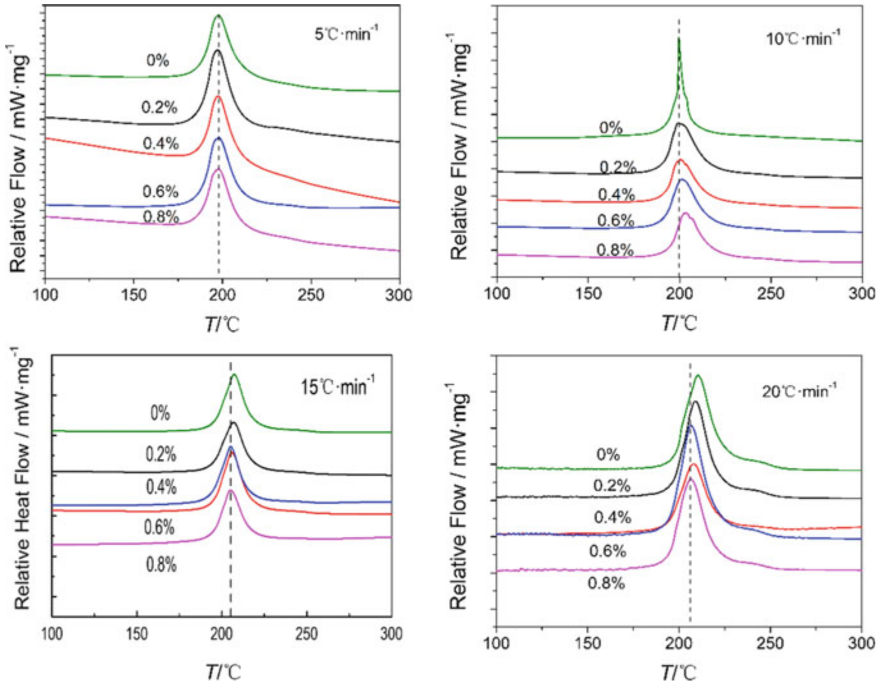


Fig. 2.4 DSC images of modified single base propellant with different mass fraction of CNFs at 5 °C·min^{-1}, 10 °C·min^{-1}, 15 °C·min^{-1} and 20 °C·min^{-1}, respectively

Table 2.6 Results of the temperature of the exothermic peak at the heating rate of 5 °C·min^{-1}, 10 °C·min^{-1}, 15 °C·min^{-1}, 20 °C·min^{-1}, respectively

Sample	CNFs content (%)	T_{exo} (°C)			
		5 °C·min^{-1}	10 °C·min^{-1}	15 °C·min^{-1}	20 °C·min^{-1}
1#	0	195.61	202.19	207.20	210.53
2#	0.2	195.89	201.99	206.90	210.12
3#	0.4	195.84	203.72	205.85	209.40
4#	0.6	195.29	201.43	205.33	208.44
5#	0.8	195.09	203.15	205.17	207.98

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\frac{AR}{E_a} - \frac{E_a}{RT_p} \tag{2.4.1}$$

A is the preexponential, s^{-1}. *R* is the molar gas constant, 8.314 J·mol^{-1}·K^{-1}. β is the heating rate, K·min^{-1}. T_p is the temperature of the exothermic peak, K. *E*a is the activation energy, kJ·mol^{-1}.The Ozawa equation is also a method of calculating kinetic parameters that can be used to verify the accuracy of the data obtained by the

Table 2.7 Results of activation energy of samples with different CNFs contents

Sample	CNFs content (%)	E_a/kJ·mol^{-1}	
		Ozawa equation	Kissinger equation
1#	0	177.34	174.29
2#	0.2	184.98	182.25
3#	0.4	187.39	187.09
4#	0.6	190.22	190.80
5#	0.8	191.37	192.65

Note E_a is the activation energy

Kissinger equation, as shown in (2.4.2)

$$\lg\beta = \lg\left(\frac{AE_a}{RG(a)}\right) - 2.315 - 0.4567\frac{E_a}{RT} \quad (2.4.2)$$

In the formula, G(a) is the function of conversion rate. The activation energy data obtained by Kissinger equation and Ozawa equation are shown in Table 2.7. It can be seen from the table that the activation energy data obtained by Kissinger equation and Ozawa equation are similar and can be considered to be accurate. After the addition of CNFs, the activation energy of the modified single base propellant increase with the increase of CNFs content. The activation energy was 175.82 kJ·mol^{-1} without CNFs, and 192.01 kJ·mol^{-1} with 0.8% CNFs. It shows that the addition of CNFs improves the stability of modified single base propellant. In conclusion, the addition of CNFs has little effect on the decomposition peak temperature of nitrocellulose and RDX, but it can improve the activation energy of propellant combustion process which shows the improvement of the thermal stability of modified single base propellant.

2.5 Conclusion

The burning rate of the modified single base propellant is increased with the addition of the CNFs. And the burning rate pressure exponent of the sample is greater than 1 in the whole pressure range (50 ~ p_{dpm} MPa). The propellant force basically decreases with the increase of CNFs content, but the variation range is little. The propellant force is basically unchanged when the CNFs content is 0.2%. With the increase of CNFs content, the mechanical properties of the modified single base propellant samples increase first but then decrease, and reach the maximum value when the CNFs content is 0.2%. The impact strength increases 21% at 20 °C and the tensile strength increases 63% at −40 °C. And the addition of CNFs can improves the stability of modified single base propellant.

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