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Characterization of HTPB-based Fuel Containing Multi-wall Carbon Nanoturbes (MWCNTs) for Hybrid Propellant

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Abstract

In order to investigate the effects of MWCNTs on the combustion performance of HTPB-based fuel for hybrid propellant, based on high speed photography recording the radical regression process of fuel grain under oxygen flow. The regression rate of HTPB-based fuel containing different kind of MWCNTs respectively were analysed. The regression of HTPB-based fuel containing 1 wt% >50nm, 1 wt% 20-40nm MWCNTs, 1 wt% 50nm, 1 wt% 20-30nm, 1 wt% <8nm MWCNTs-OH and 1 wt% carbon black respectively are increased by 57.2%, 52.4%, 24.6%, -15.6%, -2.9%, -33.0% at Gox=375 kg/m^{2}s while decreased by -29.5%, -35.0%, -16.0%, -22.8%, -17.3%, -12.7% at Gox=150 kg/m^{2}s. HTPB-based fuel containing MWCNTs increases regression to some extent but shows more sensitive to oxygen flux. MWCNTs form a three-dimensional heat conducting network to increase thermal conductive and heat radiation.

1. Introduction

Hybrid propulsion is becoming a promising emerging technology for suborbital space tourism like SpaceShipOne[1] and space exploration mission due to its inherent safety for non-explosive nature, potential low-cost, throttleability, less complex and environment friendly. However, hybrids fuel is subject to their low regression rate which is due in part to the decrease of the heat transfer from the flame zone to the fuel surface[2, 3], resulted in complicated fuel grain design like port geometries and multi-port limiting their application. This low-fuel regression rate is the inherent limitation of diffusion flames. Fuel consumption rate is expressed as $\dot{m}_f = A_b \dot{r} \rho_d$, A_b- burning area(m^2), $\dot{r}$- regression rate(mm/s), ρ_d-density of hybrids fuel(kg/m^3). One method is to increase combustion area. Armold D M[4] designs a series of multi-port grain such as cylindrical port ,double-D, cruciform wagon wheel of acrylonitrile–butadiene–styrene copolymer(ABS) hybrid fuel grains, it definitely improves fuel mass burning rate but bringed a lot of problems such as complex design/fabrication, excessive unburned mass, uneven burning. Porous hybrid grains increase combustion area with the limitation of control difficultly and low density. The other method is to increase regression rate. Adding the energetic materials such as micron-sized metal particles, nano-sized metal particles[5-7], metal hydride such as $NaBH_4$[8] or self-decomposing oxidizer to fuel can enhance heat release near the regressing surface improving the heat feedback. Frederick[8] has done many work in the addition of self-decomposing oxidizer (ammonium perchlorate) and iron(III) oxide(Fe_2O_3) to the fuel. The regression rate of HTPB with mass fraction of 25% AP increases by 200％ compared to pure HTPB at Gox=160 kg/m^{2}s , but reduced safety and increased pressure dependency. Using fuel with low effective heat of gasification such as paraffin[9-11], but the paraffin is poor of mechanical properties and is prone to brittle deformation.Using swirling oxidizer flow[4, 12] and insertion of mechanical devices to increase the turbulent intensity ,but subjected to complexity, scaling, axial uneven burning. However, none of these methods is free from shortcomings. Almost all propellants are bad conductors of heat , embedded metal wires, graphite fibers, and carbon black was added to increase heat conduction, but the effect is not very good. Carbon nanotubes (CNTs) are the ideal fillers for improving thermal conductive and heat radiation from flame zone to fuel surface. Theoretical calculation and practical measurement show that the thermal conductivity of multi-walled carbon nanotube (MWCNTs) is 3000W/mK. MWCNTs has disorganized distribution in HTPB-based fuel, formed a three-dimensional heat conducting network in space in statistical under ideal conditions compared to a granular heat conductive filler such as carbon black. High speed photography was used to evaluate HTPB-based fuel regression of radical burning surface in oxygen flow through a radical regression rate test stand based on SPlab 2D radical hybrid burner.

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2 Experiment setup and fuel preparation

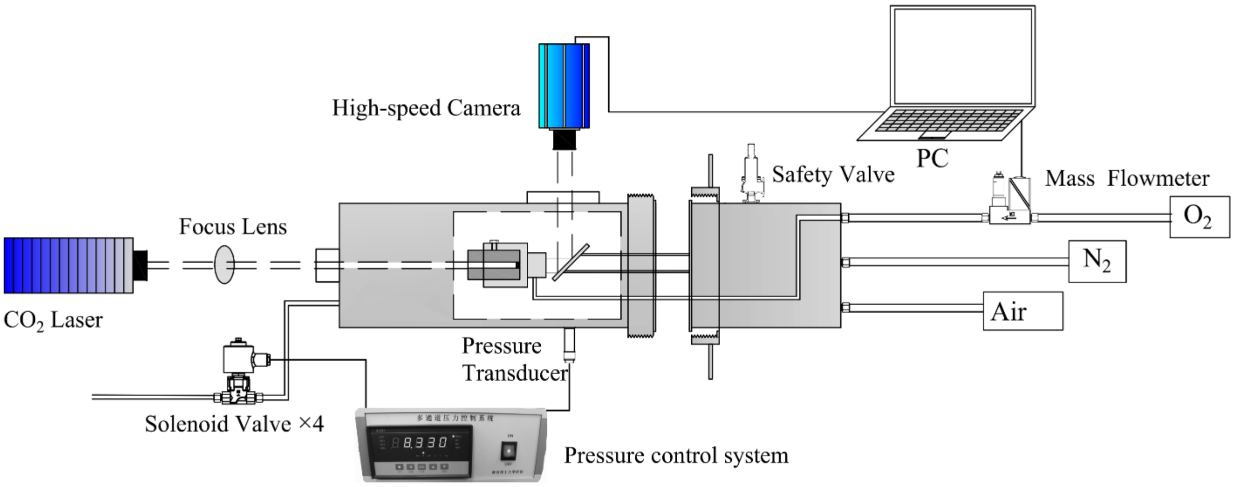

Fig 1 Schematic of radical regression rate test stand

Fig 1 showed schematic of radical regression rate test stand, The experiment setup is based on SPLab 2D radial hybrid burner[13-15]. This system include gasous oxygen ,gasous nitrogen, compressed air.Air is used to save nitrogen before the combustion chamber reaching setting pressure 1MPa.Gaseous nitrogen keep the chamber pressure under the desired pressure and took combustion gas out of chamber when fuel burned. Gasous oxygen was measured by bronkhorst F202 Mass Flowmeter, Check valve and filter prevented combustion gas backflow into mass flowmeter.pressure transducer , solenoid valve and electromagnetic relay control the system in quasi-steady state. The fuel grains were casted inside 19mm OD×16mm ID 304 steel pipe. Each fuel grain had a length of 30mm and initial central port diameter of 4mm. After the CO_2 laser ignited the B/KNO_3 (40/60) ignition powder at the fore of central port.The high-speed camera recorded the regression of inner port of burning fuel grain in 1500fps/s under 45 degree flat mirror as a video.

2.1 fuel preparation

Table 1 Formulation of Pure HTPB

Ingredient	*Function*	*wt/%*	*ρ(g/cm3)*
HTPB R45	*Binder*	*79.97*	*0.901*
DOA	*Plasticizing agent*	*13.04*	*0.920*
IPDI	*Curing agent*	*6.56*	*1.06*
TIN	*Curing catalyst*	*0.43*	*1.31*

Formulation of Pure HTPB is showed as table 1, determined by the curing coefficient. Di (2-ethylhexyl)adipate (DOA)is plasticizing agent, Isophorone Diisocyanate (IPDI) is used as curing agent reacting with hydroxyl groups(-OH) in HTPB molecular to extend molecular chain of HTPB. Dibutyltin Diacetate (TIN) is used as curing catalyst. MWCNTs additives improves combustion characteristics of the formula. Table 2 shows physical properties of hydroxylate MWCNTs and MWCNTs additives. The outer diameter (OD) of CNTs used in this study include (<8)/（20-30)/(>50) nm hydroxylate MWCNTs and (20-40)nm/(>50)nm MWCNTs, all added mass fractions were one percent to determine which kind and OD is best additives to improve HTPB-based fuel regression rate.

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Table 2 Hydroxylate MWCNTs and MWCNTs additives

MWCNTs nm	Manufactor	Purity wt%	-OH Content wt%	Tap density g/cm^3	ID nm	OD nm	Length µm	SSA m^2/g
<8	Chengdu TIME-NANO	>98	5.58	0.27	2-5	<8	10-30	>400
20-30		>98	1.76	0.28	5-10	20-30	10-30	>110
>50		>98	0.71	0.18	5-15	>50	10-20	>60
>50		>98	0	-	-	>50	10-20	60
20-40	Shenzhen Nanotech Port Co. Ltd	>95	0	-	-	20-40	>5	80～140

Fig 2 showed a HTPB-based fuel mixing device with ultrasonic and vacuum. Mixing is under vacuum by vacuum pump to remove air bubbles and CO_2 reacted by hydroxyl groups(-OH) and isocyanate groups(-N=C=O) under 20℃. Ultrasound dispersed the additives uniformity in HTPB system. Firstly mixing 79.97 wt %HTPB, 13.04 wt %DOA with 0.43 wt %TIN approximately 30 minutes under vacuum at 20 ℃. Additives was sonicated for 15 minutes simultaneously. Secondly mixing 1wt%MWCNTs additives with above mixture 15 minutes, later mixing 7.76wt %IPDI with above mixture 10 minutes under ultrasound and vacuum. Casting into 19mm OD×16mm ID 304 steel pipe after standing uncured HTPB-based fuel 10 minutes under vacuum.

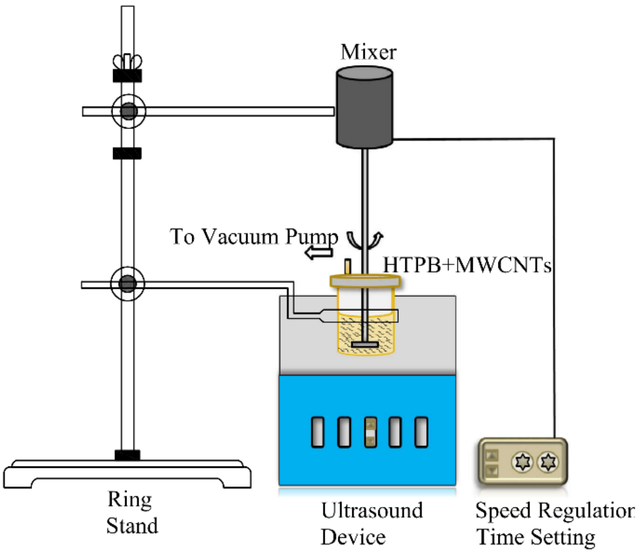

Fig 2 HTPB-based fuel mixing device with ultrasonic and vacuum

Fig 3 shows SEM images of pure HTPB and HTPB-based fuel containing MWCNTs. It can be seen that pure HTPB had smooth face without air bubbles decreasing mechanical strength on face. MWCNTs has chaotic orientation in all directions (horizontal, vertical, sideling et.) in HTPB system. The mass fraction is too little to form a three-dimensional heat conducting network in space in statistical under ideal conditions. We need to increase mass fraction, but the heat of vaporization of MWCNTs is high, there must be an optimum mass fraction compromised by increasing heat conducting and high heat of vaporization.

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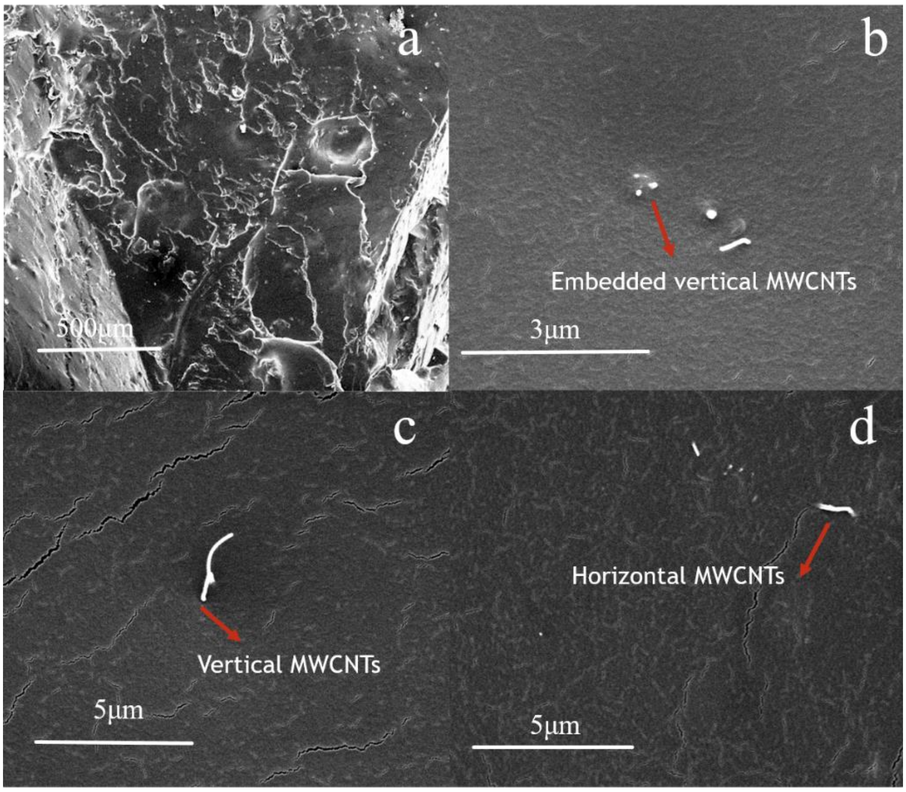

Fig 3 SEM images of the (a) pure HTPB,HTPB-based fuel with, (b) 1% >50nmWCNTs-OH, (c) 1% <8nmWCNTs-OH, (d) 1%20-40nmWCNTs

3 Results and Discussions

Fig4 showed a)regression rate vs. oxygen mass flux, b)mass burning rate vs. oxygen mass flux, c)percentage increase in regression rate vs. oxygen mass flux, d)percentage increase in mass burning rate vs. oxygen mass flux of HTPB-based fuel containing 1wt %>50nm , 1wt %20-40nm MWCNTs ; 1wt % 50nm, 1wt %20-30nm, 1wt %<8nm MWCNTs-OH and 1wt % carbon black respectively. Operating pressure 1.0MPa. The rate of regression of radical burning surface in oxygen flow was regression rate defined as d(Δr)/dt for central port fuel grain.The mass flow rate of oxygen was 210 Nlm. As the radical regression went on, radical burning diameter was growing, the oxygen mass flux decreased continuously, Gox=375 kg/m^{2}s was the beginning of radical regression, Gox=150 kg/m^{2}s was the end of burning. One fuel grain can get one smooth fitting curve of instantaneous regression rate vs. oxygen mass flux by experiment dates, the solid line in Fig 4 is the average between three to five fuel grains which was same formula. The regression rate $\dot{r}(t)$ fitted in G_{OX} as a power function $\dot{r}(t) = \text{a}\, G_{OX}(t)^n$ showed by dotted line in Fig 4(a). The mass burning rate of central port fuel grain can be expressed as $\dot{m}_f(t) = A_b\dot{r}(t)\rho_f$ showed by solid line in Fig 4 (b), fitting as $\dot{m}_f(t) = \pi\rho_f L\text{D} * \text{a}\, G_{OX}(t)^n$ showed by dotted line in Fig4 (b). Table 3 shows regression rate and mass burning rate at Gox=375 kg/m^{2}s and Gox=150 kg/m^{2}s,The regression rate of HTPB-based fuel containing 1 wt % >50nm MWCNTs is 1.140 mm/s at Gox=375 kg/m^{2}s, has a significantly improve compared to pure HTPB' regression rate (Gox=375 kg/m^{2}s)= 0.725 mm/s. Table 4 shows percentage increase of regression rate and mass burning rate compared to pure HTPB at Gox=375 kg/m^{2}s and Gox=150 kg/m^{2}s, The regression rate of HTPB-based fuel containing 1% >50nm MWCNTs and 20-40 nm MWCNTs have an increase of 57.2% and 52.4% compared to pure HTPB at Gox=375 kg/m^{2}s while have a decrease of -29.5% and -35.0 % compared to pure HTPB at Gox=150 kg/m^{2}s because of low oxygen flux. HTPB-based fuel containing MWCNTs are more sensitive to oxygen flux, the regression rate at Gox=375 kg/m^{2}s is approximately 7 times as the regression rate at Gox=150 kg/m^{2}s. As showed in Fig 4(c), larger out-diameter (OD) MWCNTs is advantageous to increase the regression rate. >50nm OD MWCNTs-OH show better performance than 20-30nm OD MWCNTs-OH and <8nm OD MWCNTs-OH. Smaller OD MWCNTs is easy to agglomerate and poor to disperse. Table 5 Coefficients obtained for the $\dot{r}_f$ / G_{OX} curves of HTPB-based fuel containing 1 wt % >50nm ,20-40nm MWCNTs, 50nm, 20-30nm, <8nm MWCNTs-OH and carbon black respectively. Table 5 shows coefficients obtained for the $\dot{r}_f/G_{OX}$ curves of HTPB-based fuel containing 1wt %>50nm , 1wt %20-40nm MWCNTs ; 1wt % 50nm, 1wt %20-30nm, 1wt %<8nm MWCNTs-OH and 1wt % carbon black respectively. HTPB-based fuel showed lower fitting degree due to erosive burning to some extent at the beginning of burning. HTPB-based

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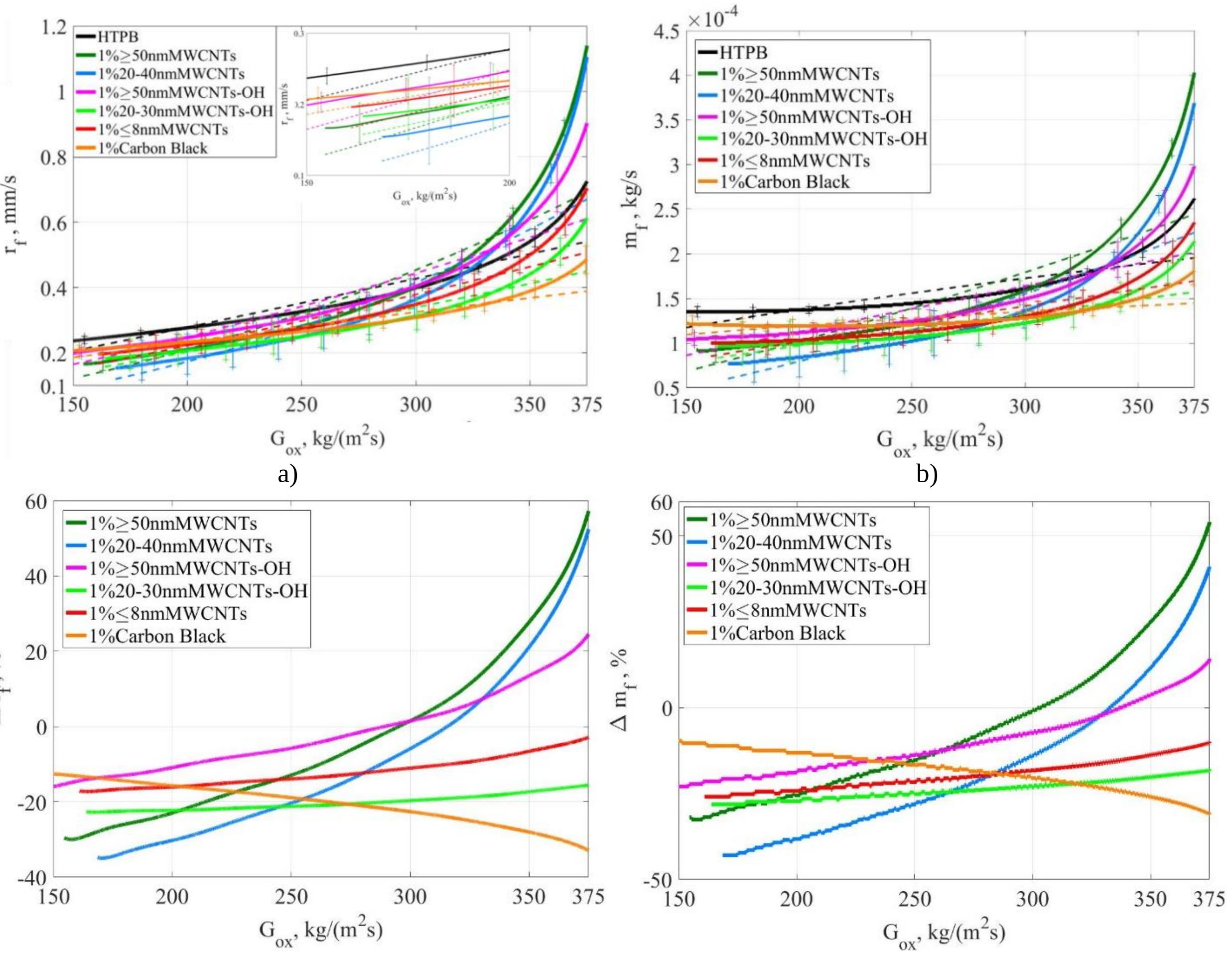

Fig 4 a)regression rate vs. oxygen mass flux, b)mass burning rate vs. oxygen mass flux, c)percentage increase in regression rate vs. oxygen mass flux, d)percentage increase in mass burning rate vs. oxygen mass flux of HTPB-based fuel containing 1wt %>50nm , 1wt %20-40nm MWCNTs ; 1wt % 50nm, 1wt %20-30nm, 1wt %<8nm MWCNTs-OH and 1wt % carbon black respectively.

Table 3 Regression rate and mass burning rate of HTPB-based fuel containing 1wt %>50nm , 1wt %20-40nm MWCNTs ; 1wt % 50nm, 1wt %20-30nm, 1wt %<8nm MWCNTs-OH and 1wt % carbon black respectively at Gox=375 kg/m^{2}s and Gox=150 kg/m^{2}s

	Density kg/m^3	$\dot{r}$(Gox=375 kg/m^{2}s) (mm/s)	$\dot{r}$(Gox=150 kg/m^{2}s) (mm/s)	$\dot{m}_f$ (Gox=375 kg/m^{2}s) (10^{-4}) (kg/s)	$\dot{m}_f$ (Gox=150 kg/m^{2}s) (10^{-4}) (kg/s)
HTPB	930	0.725	0.237	2.62	1.35
1% >50nm MWCNTs	957	1.140	0.167	4.03	0.92
1% 20-40 nm MWCNTs	909	1.105	0.154	3.69	0.77
1% >50nm MWCNTs-OH	956	0.903	0.199	2.98	1.04
1% 20-30nm MWCNTs-OH	933	0.612	0.183	2.14	0. 97
1% <8nm MWCNTs-OH	964	0.704	0.196	2.35	1.00
1% carbon black	950	0.486	0.207	1.81	1.22

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Table 4 Percentage increase of regression rate and mass burning rate of HTPB-based fuel containing 1wt %>50nm , 1wt %20-40nm MWCNTs ; 1wt % 50nm, 1wt %20-30nm, 1wt %<8nm MWCNTs-OH and 1wt % carbon black respectively compared to HTPB at Gox=375 /150 kg/m²s

	$\Delta\dot{r}$(Gox=375 kg/m²s) %	$\Delta\dot{r}$(Gox=150 kg/m²s) %	$\Delta\dot{m}_f$(Gox=375 kg/m²s) %	$\Delta\dot{m}_f$(Gox=150 kg/m²s) %
1wt% >50nm MWCNTs	57.2	-29.5	53.8	-31.8
1wt% 20-40nm MWCNTs	52.4	-35.0	40.8	-43.0
1wt% >50nm MWCNTs-OH	24.6	-16.0	13.7	-23.0
1wt% 20-30nm MWCNTs-OH	-15.6	-22.8	-18.3	-28.1
1wt% <8nm MWCNTs-OH	-2.9	-17.3	-10.3	-25.9
1wt% carbon black	-33.0	-12.7	-30.9	-9.6

Table 5 Coefficients obtained for the $\dot{r}_f/G_{OX}$ curves of HTPB-based fuel containing 1wt %>50nm , 1wt %20-40nm MWCNTs ; 1wt % 50nm, 1wt %20-30nm, 1wt %<8nm MWCNTs-OH and 1wt % carbon black respectively.

Test	Regression rate vs. oxygen mass flux	
	Analytical	Data fitting(R^2)
HTPB	$\dot{r}_f = (1.040 * 10^{-3}) {G_{OX}}^{1.059}$	0.882
1wt% >50nm MWCNTs	$\dot{r}_f = (9.405 * 10^{-6}) {G_{OX}}^{1.891}$	0.786
1wt% 20-40nm MWCNTs	$\dot{r}_f = (1.974 * 10^{-6}) {G_{OX}}^{2.160}$	0.856
1wt% >50nm MWCNTs-OH	$\dot{r}_f = (1.288 * 10^{-4}) {G_{OX}}^{1.428}$	0.832
1wt% 20-30nm MWCNTs-OH	$\dot{r}_f = (2.472 * 10^{-4}) {G_{OX}}^{1.266}$	0.817
1wt% <8nm MWCNTs-OH	$\dot{r}_f = (2.113 * 10^{-4}) {G_{OX}}^{1.313}$	0.845
1wt% carbon black	$\dot{r}_f = (1.780 * 10^{-3}) {G_{OX}}^{0.916}$	0.902

fuel containing 1wt% carbon black and HTPB show a coefficient quantity level of 10^{-3}. HTPB-based fuel containing MWCNTs-OH show a coefficient quantity level of 10^{-4}. HTPB-based fuel containing MWCNTs show a coefficient quantity level of 10^{-6}. High coefficient quantity level shows more sensitive to oxygen flux.

The mass burning rate of HTPB-based fuel containing 1wt% >50nm MWCNTs , 1wt%20-40 nm MWCNTs and 1wt%>50nm MWCNTs-OH have an increase of 53.8%, 40.8% and 13.7% compared to pure HTPB at Gox=375 kg/m²s while have a decrease of -31.8% , -43.0%, -23.0%compared to pure HTPB at Gox=150 kg/m²s because of low oxygen flux. Regularity is similar to the regression rate vs. oxygen mass flux.

4 Conclusion

1) HTPB-based fuel containing MWCNTs increases regression to some extent but shows more sensitive to oxygen flux.
2) The mass fraction is too little to form a three-dimensional heat conducting network. Next work need to increase mass fraction, there must be an optimum mass fraction compromised by increasing heat conducting and high heat of vaporization.

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3) The regression of HTPB-based fuel containing 1wt %>50nm , 1wt %20-40nm MWCNTs ; 1wt % 50nm, 1wt %20-30nm, 1wt %<8nm MWCNTs-OH and 1wt % carbon black respectively are increased by57.2%, 52.4%, 24.6%, -15.6%, -2.9%, -33.0% at Gox=375 kg/m^{2}s while are decreased by -29.5%, -35.0%, -16.0%, -22.8%, -17.3%, -12.7% at Gox=150 kg/m^{2}s due to lack of oxygen flux.
4) HTPB-based fuel containing 1wt % >50nm OD MWCNTs-OH show better performance than 1wt % 20-30nm OD MWCNTs-OH and 1wt % <8nm OD MWCNTs-OH. The regression rate of HTPB-based fuel containing larger OD is higher relatively because of more easy to disperse.
5) The regression of HTPB-based fuel containing 1wt% MWCNTs is increased by 50% while 1wt% MWCNTs-OH is increased by 20%. MWCNTs shows better performance than MWCNTs-OH.

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