Z. Qin, C. Paravan, G. Colombo, F.-Q. Zhao, R.-Q. Shen, J.-H. Yi, L.T. Deluca
Ignition and Combustion of Hydroxyl-Terminated Polybutadiene (HTPB)-based Solid Fuels Loaded with Innovative Micrometer-Sized Metals
International Journal of Energetic Materials and Chemical Propulsion, Vol. 16, N. 2, 2017, p. 139-150
doi:10.1615/IntJEnergeticMaterialsChemProp.2018022772

IGNITION AND COMBUSTION OF HYDROXYL-TERMINATED POLYBUTADIENE (HTPB)-BASED SOLID FUELS LOADED WITH INNOVATIVE MICROMETER-SIZED METALS

Zhao Qin,[1,3] Christian Paravan,[2] Giovanni Colombo,[2] Feng-qi Zhao,[1,*] Rui-qi Shen,[3] Jian-hua Yi,[1] & Luigi T. DeLuca[2]

[1]*Science and Technology on Combustion and Explosion Laboratory, Xi'an Modern Chemistry Research Institute, No. 168 Zhangbadonglu, Yanta District, Xi'an, 710065, China*

[2]*Politecnico di Milano, Department of Aerospace Science and Technology, Via La Masa 34, Milan, 20133, Italy*

[3]*Nanjing University of Science and Technology, Chemical Engineering School, No. 200 Xiaolingwei Street, Xuanwu District, Nanjing, 210094, China*

*Address all correspondence to: Feng-qi Zhao, Science and Technology on Combustion and Explosion Laboratory, Xi'an Modern Chemistry Research Institute, No. 168 Zhangbadonglu, Yanta District, Xi'an, 710065, China; Tel.: +86 29 8829 1663; Fax: +86 29 8822 0423, E-mail: zhaofqi@163.com

This paper discusses experimental investigations on the effects of innovative micrometer-sized metal additives on the ignition and burning of solid fuel formulations based on Hydroxyl-Terminated PolyButadiene (HTPB). Gaseous oxygen was selected as the oxidizer for ignition delay and regression rate tests. A relative grading of solid fuel performance was carried out taking unloaded HTPB as the baseline. Three different micrometer-sized metallic additives were investigated: conventional magnesium (Mg), amorphous aluminum (am_Al,) and magnesium–boron composite (MgB). Ignition delay is highly depending on pressure, while the linear regression rate was not appreciably affected as the pressure increased from 1.0 to 1.9 MPa. All of the micrometer-sized additives have a positive effect on enhancing both linear regression rate and mass burning rate, while amorphous aluminum (am_Al) demonstrated a larger effect than Mg and composite MgB powders.

KEY WORDS: *ignition delay, regression rate, combustion, pressure, micrometer-sized metal*

1. INTRODUCTION

Hybrid-propulsion systems have many advantages over conventional solid- and liquid-propulsion systems, such as low cost, safety, and throttleability, making them very attractive for both military and commercial applications (Chiaverini et al.; 2000; DeLuca et al., 2011). The major drawback of hybrid-propulsion systems is the low regression rate of the gasifying solid fuel that yields low thrust levels for limited burning surfaces. However, this disadvantage can be overcome by loading the solid fuel with energetic additives.

Hydroxyl-terminated polybutadiene (HTPB) is considered one of the most important solid fuels investigated in hybrid propulsion systems due to its relatively large combustion heat, safety in manufacturing and handling, and good mechanical and aging properties (Lu and Kuo, 1996). Risha et al. (2001, 2003) demonstrated that nano-sized particles added into HTPB fuels can provide considerable regression rate enhancement, but proper manufacturing techniques are required to disperse the additive down to nano-scale. On the contrary, the conventional micrometer-sized additives used for solid fuel loading usually proved to be ineffective in enhancing the regression rate (Chiaverini and Kuo, 2007).

A micrometric compound of magnesium–boron (MgB) produced by MACH_I with a proprietary procedure demonstrated that this powder is able to exceed the intrinsic ignition limits of pure boron. Even though the combustion heat of magnesium is not particularly high, it appears an appropriate additive to enhance the combustion temperature in order to allow boron sustained combustion (Kuo et al., 2004; Fanton et al., 2012).

Amorphous aluminum (am_Al) is an alloy of aluminum, iron, and yttrium, which was designed to combine merits of different pure metal.

Ignition is the first step of solid fuel applications for propulsion. However, few works on ignition of hybrid fuel under realistic operating conditions are reported in the open literature. Ohlemiller and Summerfield (1971) were pioneers in ignition tests of polymers and conducted radiative ignition of polystyrene and an epoxy in oxygen/nitrogen mixtures as early as 1971. The effect of radiant flux, pressure, oxygen percentage, and fuel absorption coefficient on ignition delay was discussed. A radiative ignition model of a solid fuel including the gas-phase reaction and the in-depth absorption of the incident radiation in its solid phase was solved by Kashiwagi; however, the pressure effect was not considered (Kashiwagi, 1974).

Regression rate of solid fuel represents the key parameter in the study of hybrid rocket engine. The diffusion model developed during the 1960s by Marxman and co-workers (Marxman and Gilbert, 1963) considers the convective heat transfer as the main mechanism for regression rate determination, and therefore other operating parameters including pressure should exert no (or limited) influence on regression rate. One of the first analyses about pressure effects on solid fuel regression rate was conducted by Smoot and Price (1965, 1966, 1967), during the investigation of rubber and polyurethane fuels using fluorine and mixtures of fluorine/oxygen as oxidizer, at pressure below 1.2 MPa. Results show that in the low mass-flux regime, radiant heat transfer may account for the pressure dependence; however, at the high mass-flux regime, reaction kinetics may become the rate-limiting mechanism. Paravan (2012) reported that pressure exhibits negligible effects on the regression rate of HTPB at the pressure from 0.7 to 1.6 MPa. Nevertheless, Favaró et al. (2013) overall confirmed a negligible dependence of the regression rate on the chamber total pressure under the explored operating conditions, thanks to a theoretical model allowing the possible presence of oxygen below the flame zone.

As mentioned, the major disadvantage of the existing solid fuel for hybrid propulsion is the low regression rate. Adding energetic metal powders to solid fuels has been proved to be efficient in improving fuel's combustion performance. The objective of this investigation is focused on the effects of various innovative micrometer-sized metal additives on the behavior of solid fuel formulations based on HTPB. Ignition of fuels under CO_2 laser radiation was carried out at 0.1 and 1.0 MPa, while ballistic characterization of solid fuel at 1.0 and 1.9 MPa was performed at the same time.

2. EXPERIMENTAL

2.1 Energetic Additives

The types of energetic additives selected in the study, including manufacturer, size, and density are given in Table 1. All of the metal additives are in micrometer size, as it can be seen from the table. MgB is a composite dual metal consisting of magnesium (Mg) and boron (B). The MgB used in this study is composed of 20% Mg and 80% B with 90% purity. Am_Al is an alloy of aluminum (Al), iron (Fe), and yttrium (Y), with mass fraction of 70.30%, 13.54% and 16.16%, respectively.

2.2 Sample Preparation

Details of solid fuel processing procedure were discussed in Paravan (2012). Binder, plasticizer, and curing agent selected for each fuel is HTPB R-45, dioctyladipate (DOA), and isophorone diisocynate (IPDI), respectively. A reference composite fuel consisting of 78.86% of HTPB (mass fraction), 13.04% of DOA, 7.67% of IPDI, and 0.43% of TIN was selected, which was used as HTPB binder in all of the other types of tested formulations. Table 2 shows mass fraction of energetic additives and density of the solid fuel. Although the mass fraction of additives in each fuel is different, the molar content of the main metal (Mg, B, and Al) in each tested formulation is maintained to 0.37 mol/100 g.

The measured density (ρ_{MD}) of the manufactured sample illustrated in Table 2 was obtained thanks to a Gibertini Europe 500 precision balance. The theoretical density (ρ_{TMD}) of the fuel was calculated under consideration of the volume occupied by a certain amount of additives. The quantity M defined in Eq. (1) was used to evaluate the tested compound porosity. As it can be seen from Table 2, the measured densities agree well with the theoretical density.

$$M = \frac{\rho_{MD} - \rho_{TMD}}{\rho_{TMD}} \times 100\% \qquad (1)$$

The sample for ignition tests was cut into a cylinder with diameter of 8 mm and height of 5 mm. The surface to be irradiated was carefully cleaned with acetone before the ignition test. Samples for ballistic tests were manufactured in the shape of cylinders. The cylindrical

TABLE 1: Description of micrometer-sized energetic additives used in this study

Energetic additives	ID	Distributor	Particle size, μm	Density, g/cm^3
Magnesium	Mg	Alfa Aesar	< 47	1.74
Magnesium–boron	MgB	MACH_I	5.2	2.19
Amorphous aluminum	am_Al	CERAM	$38 \sim 212$	3.19

TABLE 2: Composition and density of tested fuels

No.	Additives (by mass %)	ρ_{TMD}, kg/m^3	ρ_{MD}, kg/m^3	M, %
1	None	915	922 ± 2	0.8 ± 0.2
2	8.9% Mg	956	957 ± 2	0.1 ± 0.2
3	2.8% MgB	930	935 ± 1	0.5 ± 0.1
4	14.2% am_Al	1018	1022 ± 1	0.4 ± 0.1

samples are elements of 30 mm length and 18 mm external diameter casted in a metallic case. The cylindrical grain has a central circular port perforation with an internal diameter of 4 mm.

2.3 Experiment Setup

The 2D radial micro-burner was designed in SPLab (Space Propulsion Lab, Politecnico di Milano) as shown in Fig. 1. Flame visualization and time-resolved regression rate can be achieved by this setup. Mass flow rate of oxidizer and chamber pressure can be controlled independently, thus experiments can easily be carried out under different operating conditions.

All of the regression rate tests were conducted in a stainless steel cylinder chamber. Progress of combustion was monitored by a 45° mirror. The oxidizer flow injected into the chamber was controlled by a mass flow meter. The nitrogen injected into the chamber was used to provide combustion pressure and prevent soot from deposition hindering the burning process visualization. The nitrogen flow could also be used to stop combustion when the oxidizer was cut off as well. A quasi-steady pressure of the combustion chamber was achieved thanks to six electro valves.

Ignition was achieved by burning a pyrotechnic primer charge, which was inserted in the central port of the fuel. The primer charge was ignited by a CO_2 laser. The oxygen flow was injected into the center of fuel sample, thus fuel could be ignited quickly as soon as the ignition of primer charge was triggered by laser. The progress of combustion was recorded by a high-speed camera (500 frames per second), and then regression rate could be measured from this video.

A scheme of the implemented setup for ignition test is presented in Fig. 2. The mass flow of oxygen was injected into the chamber and controlled by a flow meter, and it was adjusted to 5

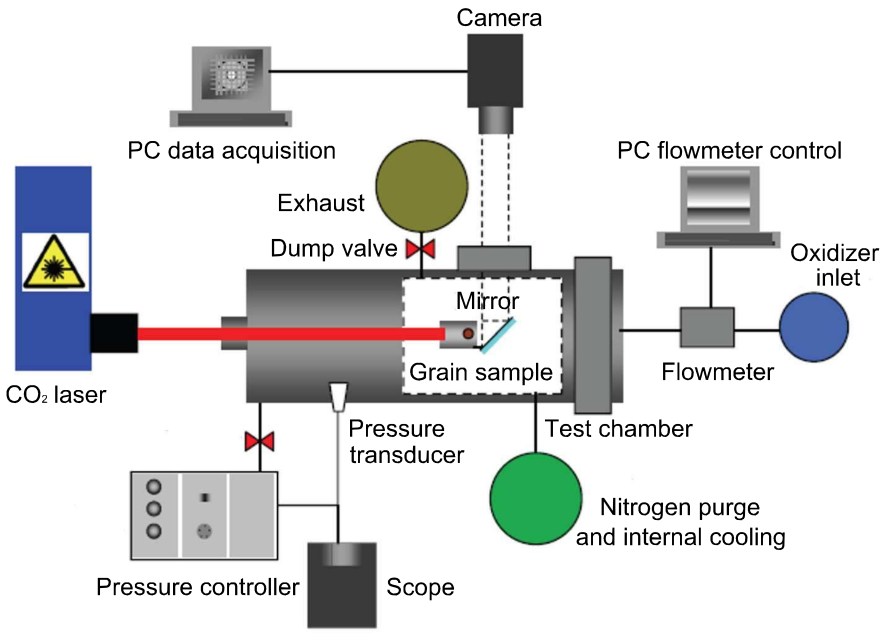

FIG. 1: Scheme of experimental rig for regression tests

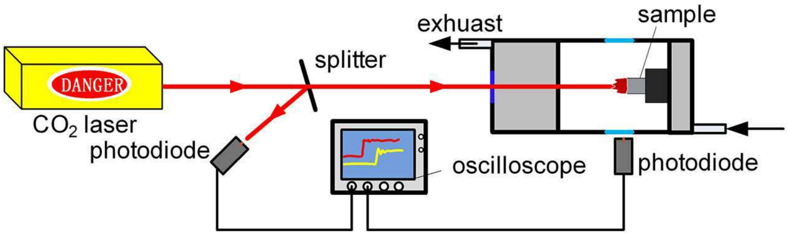

FIG. 2: Scheme of experimental line for ignition tests

NLPM during all of the ignition tests. A continuous CO_2 laser emits a beam with a wavelength of 10.64 μm and spot diameter of 1.5 cm; however, only 4 mm in the center of the beam, which is nearly uniform, was used to ignite the fuel directly. The radiation flux was measured with a dedicated setup for CO_2 laser. Two optical sensors were used in the experiment as shown in Fig. 2, one for the signal of laser and the other one for the ignition of fuel.

3. RESULTS AND DISCUSSION

3.1 Ignition Delay

A typical result of ignition tests is shown in Fig. 3. The beam emitted from the laser source becomes stable in about 5 ms, indicating that it could be used for ignition test of hybrid fuels. The time between the start of stable laser emission and the first flame of the fuel was regarded as ignition delay. The signal for the flame of the fuel after the ignition is nearly a straight line, suggesting that fuel was burned stably as soon as it was ignited.

In Fig. 4, the ignition delays of solid fuels at 0.1 and 1 MPa are presented. Ignition delay of all fuel samples decreased with increasing radiant flux of the laser. The dependence of ignition delay (t_i) on radiant flux (q) can be described by Eq. (2), which is quite similar to that used for solid propellants

$$t_{\mathrm{i}} = \mathrm{A}q^{\mathrm{n}} \tag{2}$$

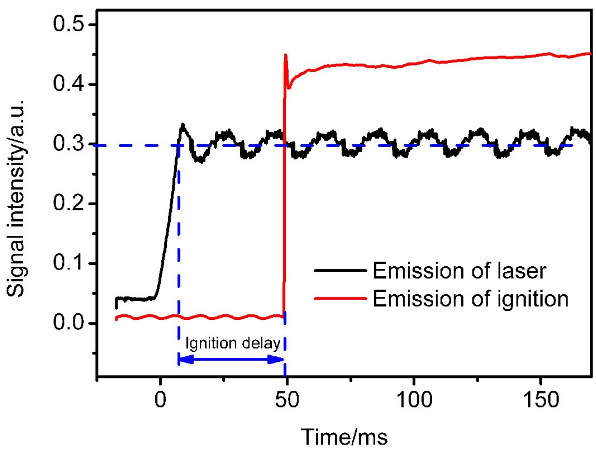

FIG. 3: Typical result of ignition test (HTPB under a radiant flux of 111 W/cm^2 is shown here)

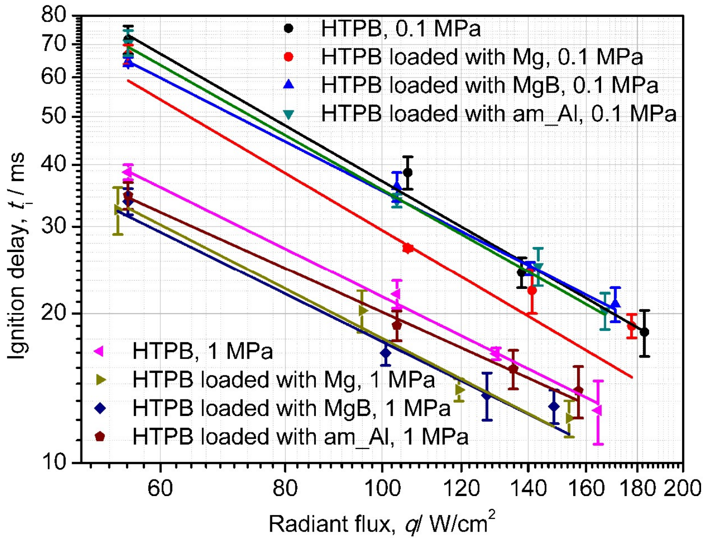

FIG. 4: Ignition delay of solid fuels at 0.1 and 1 MPa under CO_2 laser radiation; O_2, 5 LPM (298 K)

where A and n $<$ 2 are constants. A and n determined for all tested fuels are listed in Table 3. As it can be seen from Table 3, all of the power number n are very close to 1.0, while the multiplicative factor A is quite different for each fuel.

In general, metal additives have a positive effect in decreasing the ignition delay of HTPB fuels; nevertheless, ignition delays were not shortened greatly by the metal additives (less than 30%), indicating that Mg, MgB, and am_Al have a weak effect on decreasing ignition delay of HTPB fuel under CO_2 laser irradiation, and the absorption effect of these metal particles at 10.6 μm wavelength is less than that of carbon black (Ohlemiller and Summerfield, 1971; DeLuca et al., 1976a,b). Magnesium, as a conventional metal additive, shows a larger effect on decreasing ignition delay than all of the other additives due to its lower ignition temperature compared with aluminum and boron.

The ignition delays greatly decreased as the ambient pressure increased from 0.1 to 1 MPa, as shown in Fig. 3. With respect to the reference fuel (HTPB), with radiant flux of 80 W/cm^2,

TABLE 3: Solid fuels ignition in oxygen at 0.1 and 1 MPa, dependence of ignition delay on radiant flux

Fuel	Pressure, MPa	A	n	R^2, Eq. (1)
HTPB	0.1	7702.7 ± 3387.8	1.16 ± 0.10	0.971
	1.0	2130.5 ± 265.2	1.00 ± 0.03	0.997
HTPB loaded with Mg	0.1	7045.2 ± 7738.2	1.19 ± 0.24	0.847
	1.0	1740.2 ± 1194.7	1.00 ± 0.15	0.903
HTPB loaded with MgB	0.1	4038.5 ± 419.8	1.03 ± 0.02	0.998
	1.0	2100.5 ± 1089.4	1.04 ± 0.11	0.951
HTPB loaded with am_Al	0.1	4123.2 ± 1104.7	1.13 ± 0.05	0.993
	1.0	1334.5 ± 264.2	0.91 ± 0.04	0.991

ignition delay decreased from 48.33 ms at 0.1 MPa to 27.04 ms at 1 MPa. The high-pressure dependence of hybrid fuel's ignition delay is consistent with the results of epoxy under CO_2 laser radiation, conducted by Ohlemiller and Summerfield (1971). Since the distance between reaction zone and solid phase decreased with the increasing of pressure, this could be a reason for the pressure dependence. Healy et al. (2010) reported that the ignition temperature of n_C_4H_{10} decreased with increasing ambient pressure. If this is true for hybrid fuel as well, the lower ignition temperature at higher pressure is the main reason for the high-pressure dependence of ignition delay.

3.1.1 BallisticCharacterization

Ballistic characterization was performed in gaseous oxygen with an initial G_{ox} of $\sim$ 390 kg/(m^2·s) at the chamber pressure of 1 and 1.9 MPa. At least three tests were carried out for each fuel at both 1 and 1.9 MPa in order to avoid possible errors. The theory and method for measuring regression rate from recorded video were described in full detail elsewhere (DeLuca et al., 2011; Paravan, 2012). The error bar for each ensemble curve was drawn in the range of G_{ox}, where at least two tests were conducted.

In order to compare the regression rate of fuel at different pressures, the regression rate variation from 1 to 1.9 MPa (R) was defined as

$$R = \frac{r_{1.9} - r_{1.0}}{r_{1.0}} \times 100\% \tag{3}$$

where $r_{1.0}$ is the fuel regression rate at 1 MPa and $r_{1.9}$ is the fuel regression rate at 1.9 MPa.

3.1.2 Pressure Effect

Figure 5 illustrates the regression rate of HTPB loaded with am_Al vs G_{ox} at 1 and 1.9 MPa. Four tests were conducted at 1 and 1.9 MPa. As it can be seen from Fig. 5, the regression rates at

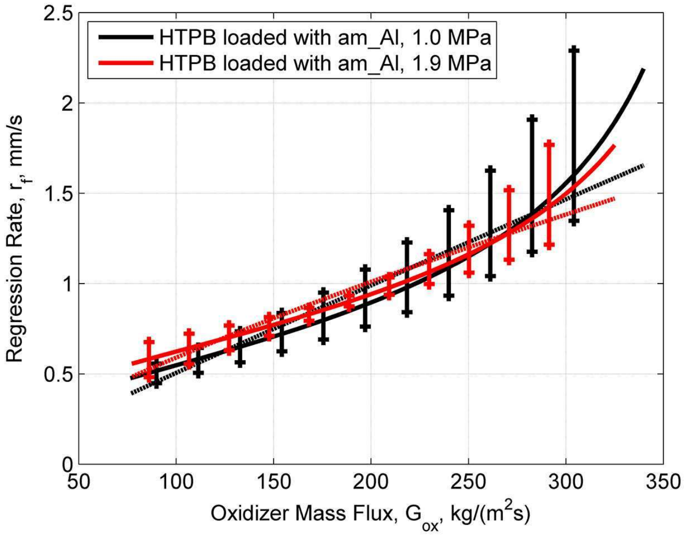

FIG. 5: HTPB loaded with 14.2% am_Al burning in G_{ox} at 1 and 1.9 MPa, vs. G_{ox} (ensemble average)

the two tested pressures are very close over the whole range of the oxidizer mass flux considered in this paper. The average Δr_f is less than 10% over the whole range of G_{ox} tested, and Δr_f decreases to 0 when G_{ox} comes to 262 kg/(m^2·s). Thus, we can come to the conclusion that the regression rate of HTPB loaded with am_Al is essentially independent of pressure.

The experimental variation of regression rate of all of the fuels, over the whole range of G_{ox} investigated in this study, is presented in Table 4. Table 5 demonstrates the regression rate variation of fuels from 1 to 1.9 MPa. In general, the regression rate of fuel increased a little as the ambient pressure increased from 1 to 1.9 MPa [except HTPB loaded with am_Al with the G_{ox} of 250 kg/(m^2·s)]; however, almost all of the R are less or close to 10% as indicated in Table 5. The biggest R is (16.83 ± 2.49)% as HTPB loaded with Mg with the G_{ox} of 250 kg/(m^2·s). Thus, the conclusion can be drawn that the regression rates of HTPB and HTPB loaded with micrometer-sized metal particles have a weak pressure dependence

3.1.3 Additives Effect

Regression rate and mass burning rate of fuels at 1.9 MPa are similar to that at 1 MPa since regression rate did not increase greatly as the ambient pressure increased from 1 to 1.9 MPa, as previously stated. Therefore, additives effect on ballistic characterization will be focused on the pressure of 1 MPa.

In Fig. 6, the linear regression rate of all of the fuels at 1 MPa is presented. In addition, the mass burning rate of fuels at 1 MPa is presented in Fig. 7. All of the energetic material additives

TABLE 4: Regression rate of fuels under different pressure

G_{ox}, kg/m^2·s	Pressure, MPa	HTPB, mm/s	HTPB loaded with Mg, mm/s	HTPB loaded with MgB, mm/s	HTPB loaded with am_Al, mm/s
100	1.0	0.44 ± 0.04	0.53 ± 0.07	0.51 ± 0.07	0.54 ± 0.06
	1.9	0.48 ± 0.03	0.59 ± 0.10	0.48 ± 0.03	0.62 ± 0.09
150	1.0	0.54 ± 0.03	0.66 ± 0.05	0.62 ± 0.07	0.71 ± 0.10
	1.9	0.59 ± 0.05	0.74 ± 0.06	0.61 ± 0.02	0.77 ± 0.05
200	1.0	0.65 ± 0.04	0.81 ± 0.06	0.76 ± 0.08	0.93 ± 0.16
	1.9	0.72 ± 0.08	0.92 ± 0.03	0.77 ± 0.16	0.95 ± 0.04
250	1.0	0.80 ± 0.09	1.01 ± 0.10	0.93 ± 0.11	1.24 ± 0.26
	1.9	0.90 ± 0.13	1.18 ± 0.13	0.96 ± 0.15	1.19 ± 0.13
300	1.0	1.04 ± 0.18	1.32 ± 0.22	1.19 ± 0.18	1.76 ± 0.45
	1.9	1.17 ± 0.22	N/A	N/A	N/A

TABLE 5: Regression rate variation of fuels from 1 to 1.9 MPa

G_{ox}, kg/m2·s	HTPB	HTPB loaded with Mg	HTPB loaded with MgB	HTPB loaded with am_Al
100	9.09 ± 1.00	11.32 ± 2.43	–5.88 ± 0.89	14.81 ± 2.71
150	9.26 ± 0.94	12.12 ± 1.35	–1.61 ± 0.19	8.45 ± 1.31
200	10.77 ± 1.37	13.58 ± 1.10	1.32 ± 0.31	2.15 ± 0.38
250	12.50 ± 2.29	16.83 ± 2.49	3.23 ± 0.63	–4.03 ± 0.95
300	12.50 ± 3.19	N/A	N/A	N/A

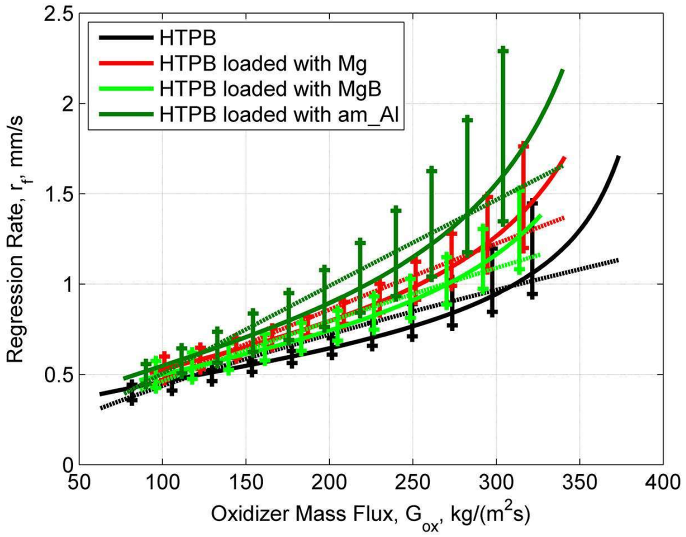

FIG. 6: Comparison of linear regression rate for various fuel formulations at 1 MPa (ensemble average)

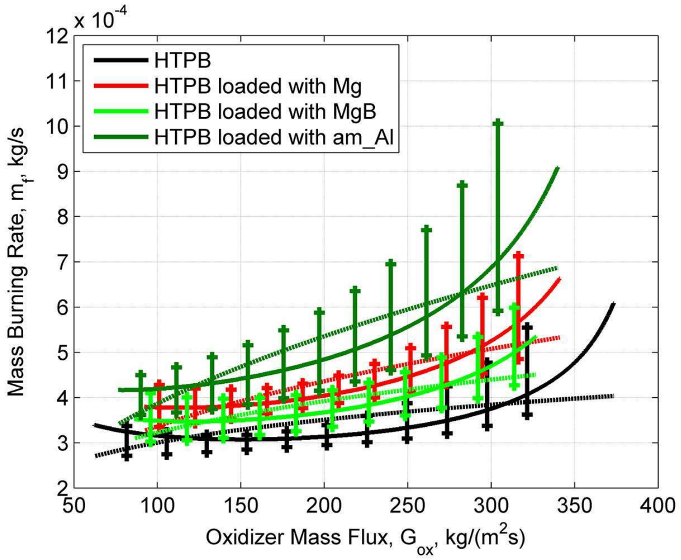

FIG. 7: Comparison of mass burning rate for various fuel formulations at 1 MPa (ensemble average)

have a positive effect on enhancing regression rate. While Mg is a conventional material, MgB and am_Al are innovative micrometer-sized additives. As it can be seen from Fig. 6, HTPB loaded with am_Al demonstrated higher regression rate over the whole range of G_{ox} investigated in this study, while the regression rate of HTPB loaded with MgB is a little lower than that of HTPB loaded with Mg.

As shown in Fig. 7, similar to linear regression rate, HTPB demonstrated the lowest average mass burning rate. The average mass burning rate of HTPB loaded with Mg is a little higher than that of HTPB loaded with MgB over the whole range of oxidizer mass flux. As expected, HTPB loaded with am_Al demonstrated higher mass burning rate than all of the other fuels. Because of the small size of the fuel used in our study, the mass burning rate of fuels here is much lower than that of Risha (2001, 2003).

The percentage increase of linear regression rate of the fuels loaded with energetic additives compared to HTPB, at different oxidizer mass flux, is presented in Fig. 8. The comparison between the percentage increase of mass burning rate of fuels loaded with micrometer-sized additives and HTPB without additives is shown in Fig. 9. Both the percentage increase of regression rate and that of mass burning rate of all the fuels increased with increasing oxidizer mass flux. HTPB loaded with am_Al demonstrated mass burning rate 35% higher than HTPB at the G_{ox} of 112 kg/(m^2·s), which is lower than the value of 61% of HTPB loaded with 13% nano_Al at the G_{ox} of 112 kg/(m^2·s) conducted by Risha (2003). However, when G_{ox} comes to 300 kg/(m^2·s), the percentage increase was increased to 83%, suggesting that am_Al is a promising micrometer-sized material to enhance both linear regression rate and mass burning rate of HTPB-based fuels. The percentage increase of mass burning rate of HTPB loaded with Mg is in the range of 10 to 25%. HTPB loaded with MgB demonstrated less than 40% increase of mass burning rate compared to HTPB in the range of G_{ox} tested. However, pay attention to the fact that Fanton et al. (2012) from SPLab demonstrated that the mass burning rate of HTPB loaded with 2.8% MgB (mass fraction) was increased by 51.7% with G_{ox} of 100 kg/(m^2·s) compared to pure HTPB fuel in 2012. The effect of MgB on enhancing regression rate here is quite lower than the result obtained by Fanton probably because of its aging problem, as we can see from the series study at different time in SPLab (Viscardi, 2008; Fanton et al., 2012; Paravan, 2012).

4. CONCLUSIONS AND FUTURE WORK

Ignition and ballistic characterization of HTPB loaded with micrometer-sized energetic materials have been carried out. All of the micrometer-sized powders showed a positive effect in

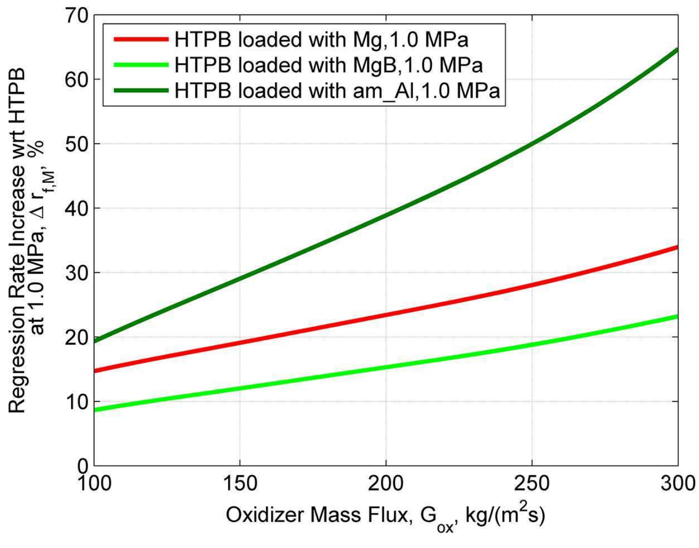

FIG. 8: Percentage increase of regression rate of fuels loaded with additives compared to HTPB at 1 MPa

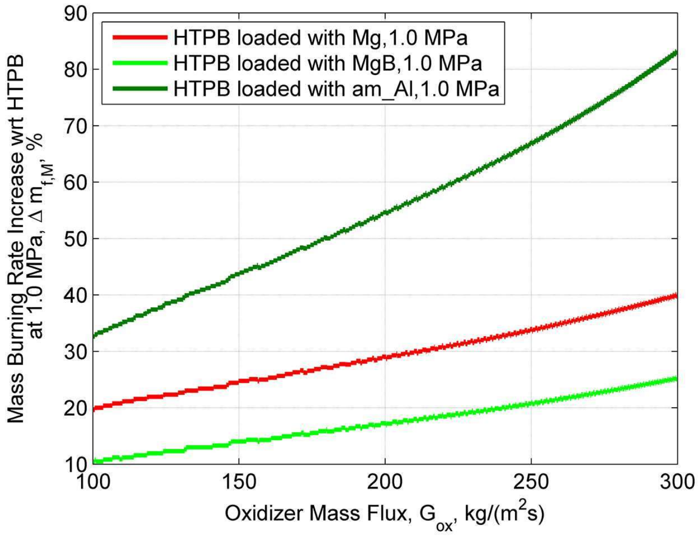

FIG. 9: Percentage increase of mass burning rate of fuels loaded with additives compared to HTPB at 1 MPa

shortening the ignition delay, which decreased with increasing radiant flux. Ignition delay of fuels is dependent on pressure, and the ignition delay of fuels at 1 MPa is nearly 1/2 of that at 0.1 MPa.

Regression rate of fuels increased a little when the test pressure increased from 1 to 1.9 MPa, and almost all of the variation of regression rate is at most 10%, suggesting that regression rate of HTPB and HTPB loaded with micrometer-sized particles have a weak pressure dependence. Micrometer-sized additives have a positive effect on enhancing both regression rate and mass burning rate of the fuel. Am_Al is the best material to increase the mass burning rate of fuel, and the corresponding mass burning rate increased by 83% at the G_{ox} of 300 kg/(m^2·s) compared to that of HTPB. Probably due to aging problem, the innovative micrometer-sized material MgB demonstrated a weaker effect on enhancing both regression rate and mass burning rate compared to Mg powder.

An interesting further work would be an extended study on regression of fuels loaded with am_Al, especially for its capability to enhance regression rates.

ACKNOWLEDGMENTS

The authors would like to thank MACH_I, USA for providing MgB samples. The first author wishes to thank Chinese Scholar Council (CSC) for its living support while in Italy.

REFERENCES

Chiaverini, M.J. and Kuo, K.K., Fundamentals of hybrid rocket combustion and propulsion, *AIAA Progress in Astronautics and Aeronautics*, vol. 218, pp. 413–456 (AIAA, Reston, VA, 2007).

Chiaverini, M.J., Serin, N., Johnson, D.K., Lu, Y.-C., Kuo, K.K., and Risha, G.A., Regression rate behavior of hybrid rocket solid fuels, *J. Propuls. Power*, vol. **16**, no. 1, pp. 125–132, 2000.

DeLuca, L.T., Caveny, L.H., Ohlemiller, T.J., and Summerfield, M., Radiative Ignition of double-base propellants: I. Some formulation effects, *AIAA J.*, vol. **14**, no. 7, pp. 940–946, 1976a.

DeLuca, L.T., Galfetti, L., Colombo, G., Maggi, F., Bandera, A., Boiocchi, M., Gariani, G., Merotto, L., Paravan, C., and Reina, A., Time-resolved burning of solid fuels for hybrid rocket propulsion, *Prog. Propuls. Phys.*, vol. **2**, pp. 405–426, 2011.

DeLuca, L.T., Ohlemiller, T.J., Caveny, L.H., and Summerfield, M., Radiative ignition of double base propellants: II. Pre-ignition events and source effects, *AIAA J.*, vol. **14**, no. 8, pp. 1111–1117, 1976b.

Fanton, L., Paravan, C., DeLuca, L.T., Testing and modeling fuel regression rate in a miniature hybrid burner, *Int. J. Aero. Eng.*, vol. **2012**, pp. 1–15, 2012.

Favaró, F.M., Sirignano, W.A., Manzoni, M., and DeLuca, L.T., Solid-fuel regression rate modeling for hybrid rockets, *J. Propuls. Power*, vol. **29**, no. 1, pp. 205–215, 2013.

Healy, D., Donato, N.S., Aul, C.J., Peterson, E.L., Zinner, C.M., Bourque, G., and Curran, H.J., n-Butane: Ignition delay measurements at high pressure and detailed chemical kinetic simulations, *Combust. Flame*, vol. **157**, no. 8, pp. 1526–1539, 2010.

Kashiwagi, T., A radiative ignition model of a solid fuel, *Combust. Sci. Technol.,* vol. **8**, pp. 225–236, 1974.

Kuo, K.K., Risha, G.A., Evans, B.J., and Boyer, E., Potential usage of energetic nano-sized powders for combustion and rocket propulsion, *Symp. AA – Synth., Character., and Properties of Energetic/Reactive Nanomat.*, Boston, MA, vol. **800**, pp. 1–12, 2013.

Lu, Y.-C., and Kuo, K.K., Thermal decomposition study of hydroxyl-terminated polybutadiene (HTPB) solid fuel, *Thermochim. Acta*, vol. **275**, no. 2, pp. 181–191, 1996.

Marxman, G., and Gilbert, M., Turbulent boundary layer combustion in the hybrid rocket, *Symp. Combust.*, vol. **9**, no. 1, pp. 371–383, 1963.

Ohlemiller, T.J. and Summerfield, M., Radiative ignition of polymeric materials in oxygen/nitrogen mixtures, *Symp. Combust.*, vol. **13**, no. 1, pp. 1087–1094, 1971.

Paravan, C., *Ballistics of innovative solid fuel formulations for hybrid rocket engines*, PhD Thesis, Politecnico di Milano, Milan, Italy, 2012.

Risha, G.A., Boyer, E., Evans, B.J., and Kuo, K.K., Nano-sized aluminum, and boron-based solid fuel characterization in a hybrid rocket engine, *Symp. AA – Synth., Character., and Properties of Energetic/Reactive Nanomat.*, Boston, MA, vol. **800**, 2003.

Risha, G.A., Ulas, A., Boyer, E., Kumar, S., and Kuo, K.K., Combustion of solid fuels containing nano-sized energetic powder in a hybrid rocket motor, *37th Joint Prop Conf. and Exhibit*, Salt Lake City, UT., 2001.

Smoot, L.D. and Price, C.F., Regression rates of metalized hybrid fuel systems, *AIAA J.*, vol. **4** no. 5, pp. 910–915, 1965.

Smoot, L.D. and Price, C.F., Regression rates of non-metalized hybrid fuel systems, *AIAA J.*, vol. **3**, no. 8, pp. 1408–1413, 1965.

Smoot, L.D., and Price, C.F., Pressure dependence of hybrid fuel regression rates, *AIAA J.*, vol. **5**, no. 1, pp. 102–106, 1967.

Viscardi, M., *Ballistic of solid fuels in gaseous oxygen for hybrid space propulsion*, MSc Thesis, Politecnico di Milano, Milan, Italy, 2008.