Research paper

Using polymeric additives in microcrystalline wax based hybrid rocket fuel

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Abstract

This study examined addition of polymeric fuel powder to hybrid rocket fuel to improve its mechanical properties. Microcrystalline wax is attractive as a hybrid rocket fuel: its regression rate is about 2−4 times higher than that of hydroxyl-terminated polybutadiene (HTPB). Unfortunately, cracks in fuel grains are caused and promoted by the low tensile strength of microcrystalline wax. Therefore, to improve the microcrystalline wax tensile strength, we added polymethyl methacrylate (PMMA) powder. We conducted experiments to ascertain the tensile strength and ignitibility while observing effects of PMMA powder added to microcrystalline wax. Results demonstrated that increasing the added amount increases tensile strength and decreases ignitibility.

Keywords: hybrid rocket, ignitibility, microcrystalline wax, PMMA powder, tensile strength

Nomenclature

EVA	Ethylene vinyl acetate
HTPB	Hydroxyl-terminated polybutadiene
I_{sp}	Specific impulse
PMMA	Polymethyl methacrylate
λ_w	Thermal conductivity of microcrystalline wax
K	Thermal conductivity ratio of PMMA powder and microcrystalline wax
P	Volume ratio of PMMA powder in solid fuel

1. Introduction

Hybrid rockets have several beneficial features of liquid and solid rockets: controllable thrust, reignition, and simple piping comparable to that of liquid rockets[1]. Furthermore, hybrid rockets have high safety because these propellants have different phases and storage in different spaces. In fact, the oxidizer and fuel are not explosive mixtures. Because of these features, hybrid rocket development has attracted many researchers. Nevertheless, hybrid rockets have a low regression rate because of boundary-layer combustion. In fact, a diffusion flame appears in boundary layer combustion. Therefore, the distance between the flame and the solid fuel surface is greater than that which occurs with solid rocket combustion. Consequently, the heat flux from the flame to the solid fuel is lower.

It is noteworthy that microcrystalline wax improves the low regression rate. Actually, the regression rate of microcrystalline wax is about 2−4 times higher than that of hydroxyl-terminated polybutadiene (HTPB)[2], a commonly used hybrid rocket fuel. Nevertheless, microcrystalline wax has low tensile strength, which causes and promotes cracks in fuel grains during hybrid rocket combustion. For an earlier study, ethylene vinyl acetate (EVA), a polymeric material, was added to microcrystalline wax to improve its tensile strength[3),6]. This study confirms the effects of polymethyl methacrylate (PMMA) powder addition to microcrystalline wax to improve its tensile strength. Similarly to EVA, PMMA is a polymeric material that has been studied for use as a hybrid rocket fuel. In general, the tensile strength of PMMA is about 10 times higher than that of EVA. Accordingly, PMMA is useful as a fuel additive and to improve tensile strength. Furthermore, PMMA has low environmental loading because it comprises carbon, oxide, and hydrogen. However, PMMA

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has a low regression rate[4]. Also, PMMA addition affects the combustion characteristics. This study investigates PMMA powder effects on tensile strength and combustion when PMMA powder is added to microcrystalline wax.

2. Experiment

2.1 Properties of microcrystalline wax and PMMA powder

Tables 1 and 2 present properties of the microcrystalline wax and PMMA powder used for this experiment.

Actually, PMMA has high tensile strength in polymeric materials. We selected PMMA powders of two kinds with different fluidity (melt flow rate). Fluidity affects the regression rate because the heat transfer coefficient is reportedly reversely proportional to viscosity[3]. Table 3 presents a comparison of PMMA and EVA properties.

The tensile strength of PMMA is about 10 times higher than that of EVA, with a melting point that is about twice that of EVA. Actually, PMMA's higher tensile strength is particularly attractive for our purposes.

Table 1 Microcrystalline wax properties.

Microcrystalline wax	
Supplier	Nippon Seiro Co. Ltd.
Model number	Hi-Mic-2095
Carbon number	30–60
Molecular weight	300–550
Melting point [°C]	101
Flash point [°C]	350
Density [kg m^{-3}]*	935
Thermal conductivity [W m^{-1} K^{-1}]	0.325

*25 °C

Table 2 PMMA powder properties.

Poly methyl methacrylate (PMMA)		
Supplier	Kuraray Co. Ltd.	
Product name	Parapet	
Model number	GF-P	HR-LP
Tensile strength [MPa]	67	77
Melt flow rate [g 10 min^{-1}]*	15	2
Density [kg m^{-3}]**	1190	1190
Particle diameter [μm]	270	310
Thermal conductivity [W m^{-1} K^{-1}]	0.2	0.2

*230 °C, 37.3 N JIS K7210
**25 °C, JIS K7112

Table 3 Material properties. (nominal values from suppliers)

	PMMA		EVA[6]
	GF-P	HR-LP	EV210ETR
Melting point[°C]	(160)*	(160)*	73
Tensile strength [MPa]	67	77	5
Density [kg m^{-3}]	1190	1190	950
Melt flow rate [g 10 min^{-1}]	15	2	400

*Reference values.

2.2 Added amount

Added amounts were 0 mass %, 10 mass %, and 20 mass %, expressed as an internal percentage of the total mass. We referred to results of I_{sp} theoretical calculations by NASA-CEA[5]. For this calculation, the oxidizer was oxygen gas, the combustion chamber pressure was 0.46 MPa (4.5 atm), the exit pressure was standard atmosphere, the pressure ratio was 4.5, O/F was 2.0, the opening ratio was 8 and the condition of flow was equilibrium flow. Figure 1 presents I_{sp} calculation results. Furthermore, theoretical I_{sp} of the solid fuel with added EVA is about 260 s (EVA 20 mass %, $O/F = 2.0$)[6].

Table 4 presents the rate of decrease of I_{sp} with addition of PMMA or EVA[6].

The rate of decrease of I_{sp} with added PMMA is higher than that with added EVA. In the future work, propulsion characteristics must be investigated by combustion experiments.

2.3 Tensile strength test

Figure 2 portrays the tensile test piece shape, which was referred from a standard of the tensile testing machine (5500R; Instron Corp.). Microcrystalline wax was melted by mantle heating at 120 °C with addition of PMMA powder. The PMMA powder does not melt at 120 °C. We poured melted microcrystalline wax with the added PMMA powder into a silicone mold. The cooling time was 10 min at room temperature (about 25 °C).

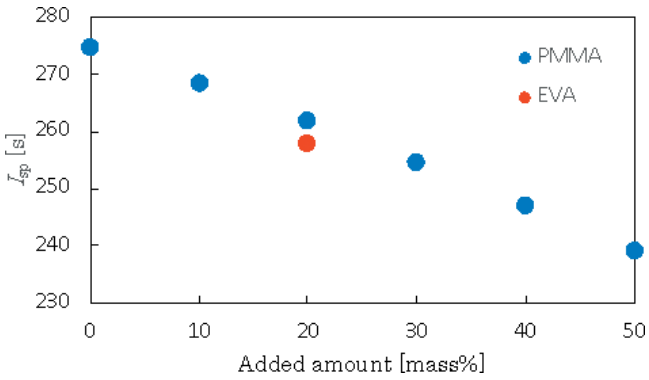

Figure 1 Calculation of I_{sp}.

Table 4 PMMA and EVA on I_{sp}.

Added amount [%]	Rate of decrease [%]	
	PMMA	EVA[6]*
10	2.3	0.3
20	4.7	0.6

*Calculation conditions were not reported.[6]

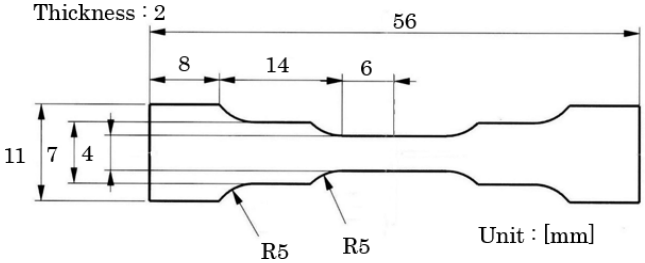

Figure 2 Tensile test piece.

The tensile speed was 0.5 mm min^{-1}. We conducted experiments five times for each added amount.

2.4 Ignition test

We executed ignition tests to observe the effects of added PMMA powder. Ignition characteristics such as the ignition delay time affect the solid fuel combustion characteristics in hybrid rocket engines. Figure 3 portrays a 6-mm-diameter ignition test piece. Its height was 6 mm. We molded microcrystalline wax with added PMMA powder into a disk. Then we cut out a test piece using an aluminum pipe of 6 mm internal diameter.

The ignition test piece was recorded by camera (300 fps frame rate) through a mirror when inside the electric furnace (MINI BS-1; Nitto Kagaku Co. Ltd.). We set the electric furnace to the microcrystalline wax flash point: 350 °C. After putting the test piece into the furnace, we observed its ignition. Experiments were conducted five times for each added amount.

3. Results and discussion

3.1 Tensile strength

Figure 4 presents tensile strength test results. We selected three data, excluding maximum and minimum data from five data.

As this figure shows, the tensile strength improved as the PMMA powder added amount was increased. The rate of increase was 24 % in HR-LP 10 mass %, 28 % in HR-LP 20 mass %, 31 % in GF-P 10 mass %, and 33 % in GF-P 20 mass %. The error of a test piece with added PMMA powder is larger than that of a pure microcrystalline wax test piece because the test piece mixture is not homogeneous during test piece preparation. From experiment results, we compared the two PMMA powders, which revealed that GF-P is better than HR-LP. However, the tensile strength of PMMA powder HR-LP was greater than that of GF-P, as shown in Table 2. Results show that the tensile strength of PMMA powder does not influence that of the solid fuel.

Table 5 presents a comparison of PMMA and EVA[6] according to the rate of increase on tensile strength.

The rate of increase of PMMA is lower than that of EVA. Results show that the tensile strength of PMMA itself is higher than that of EVA, but the effect of PMMA addition was lower, probably because of the mixing method. Unlike EVA, PMMA was not melting in microcrystalline wax, and PMMA was added as particles. Therefore, the PMMA effects were thought to be reduced.

We observed properties of adhesion between microcrystalline wax and the PMMA powder surface using a scanning electron microscope (SEM, FE2000; Hitachi Ltd.). Figures 5 and 6 are SEM micrographs. The left panel shows pure PMMA powder. The right panel shows test piece sections in Figures 5 and 6.

As these figures show, no void space exists between microcrystalline wax and PMMA powder surfaces. We confirmed a close bond between microcrystalline wax and PMMA powder. Interface shear stress occurs mainly between microcrystalline wax and the PMMA powder surface.

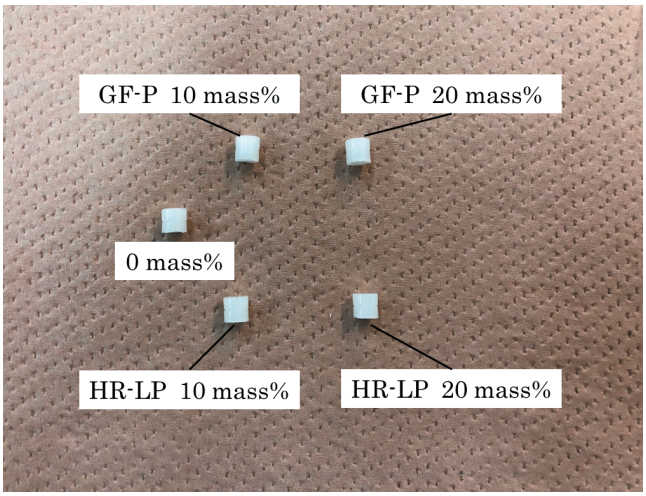

Figure 3 Ignition test piece.

Table 5 PMMA and EVA tensile strength.

Added amount [%]	Rate of increase [%]		
	PMMA		EVA[6]
	GF-P	HR-LP	
10	31	24	50
20	33	28	100

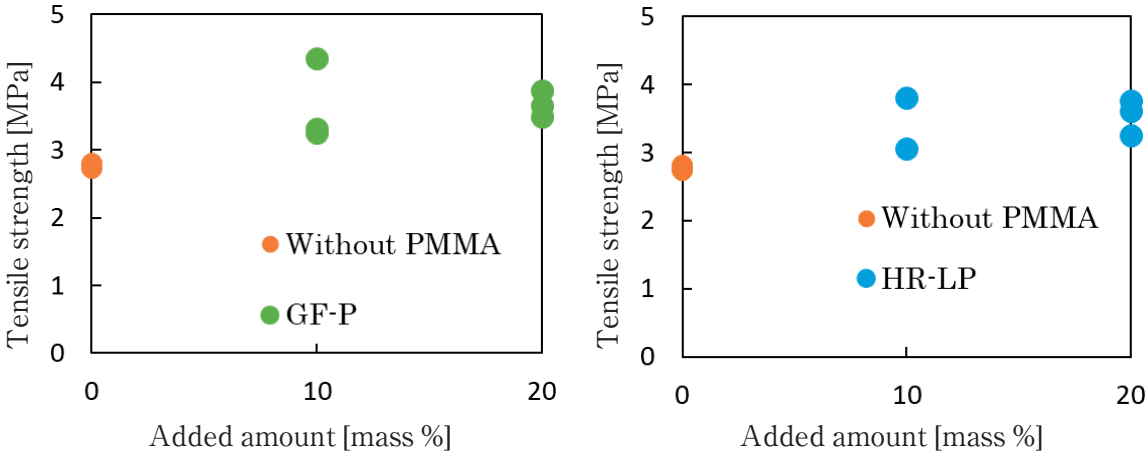

Figure 4 Tensile test results.

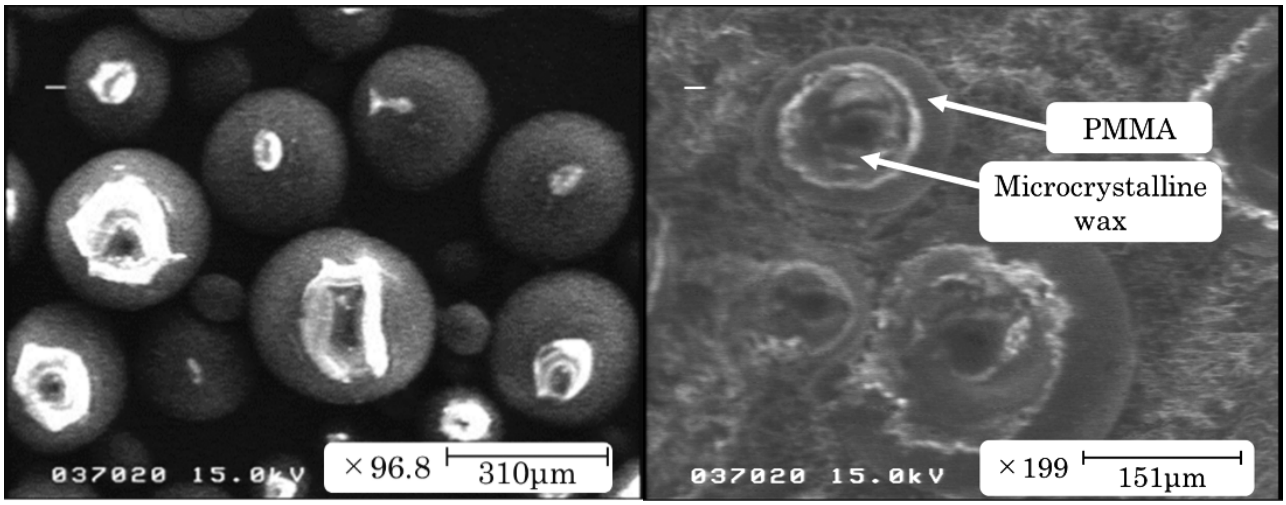

Figure 5 SEM image of HR-LP.

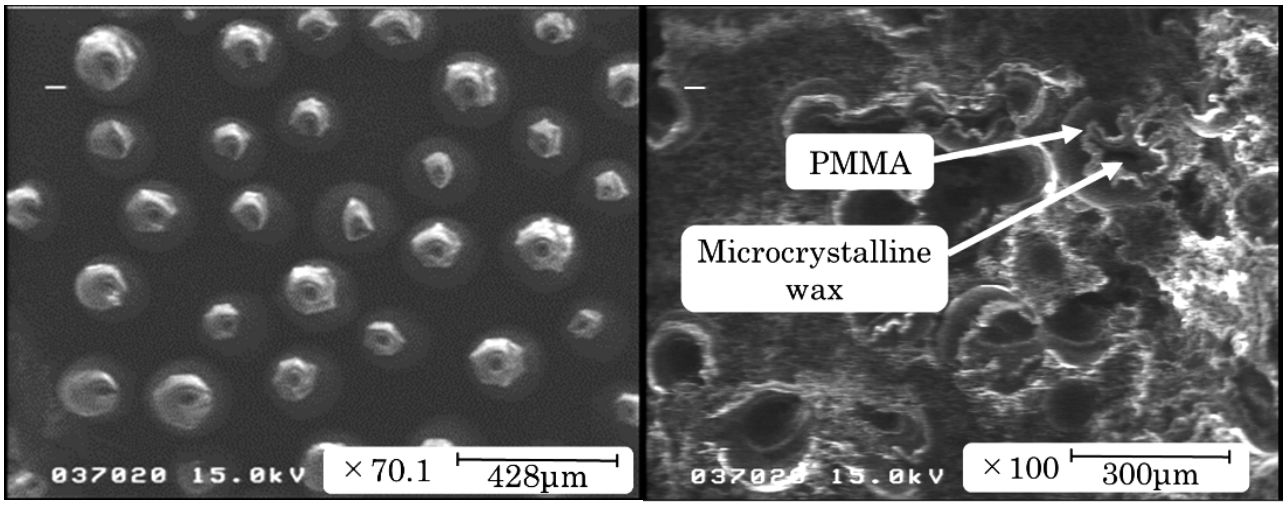

Figure 6 SEM image of GF-P.

Table 6 Total surface area of 1 g PMMA powder.

	GF-P	HR-LP
Particle diameter [μm]	270	310
Total surface area [m^2]	9337	8132

Table 6 presents the total surface area of 1 g PMMA powder particles from calculations. For these calculations, we assumed that PMMA powder particles were true spheres and that all PMMA powder particles lined up equally. We calculated the particle number based on the particle diameter and PMMA powder density. Then the total surface area was calculated using the particle number and surface area of PMMA powder particles.

According to Table 6, the total surface area was greater for smaller particles. Therefore, the GF-P particle surface is affected more easily by the interface shear stress than HR-LP. We confirmed the PMMA powder particle size as the reason for the superior tensile strength of microcrystalline wax with added GF-P to that with added HR-LP. An earlier study of a wood plastic combination (WPC) showed that sawdust added to plastic produced higher tensile strength for smaller particles[7]. These results resemble our results.

3.2 Ignition test

Figure 7 presents ignition test results. We selected three data by excluding maximum and minimum data from five data.

The ignition delay time increases along with the increased added amount of PMMA powder, as shown in Figure 7. The rate of increase was about 70 % in HR-LP 10 mass %, about 220 % in HR-LP 20 mass %, about 140 % in GF-P 10 mass %, and about 240 % in GF-P 20 mass %. The ignition delay time might affect complete combustion of solid fuel droplets in the combustion chamber, thereby affecting the combustion efficiency of hybrid rocket combustion.

This result is explained by the difference of thermal conductivities and melting point of microcrystalline wax and PMMA. The melting point of PMMA is about 160 °C. That of microcrystalline wax is 101 °C. The gas component of vaporized microcrystalline wax with added PMMA is almost identical to that of pure microcrystalline wax. Therefore, PMMA consists of carbon, oxygen, and hydrogen. Therefore, we are unconcerned about the influence of gas components. Melting behavior is affected by thermal conduction of the solid fuel. Tables 1 and 2 present the thermal conductivity of microcrystalline wax as 0.325 W m^{-1} K^{-1}, whereas that of PMMA is 0.2 W m^{-1}

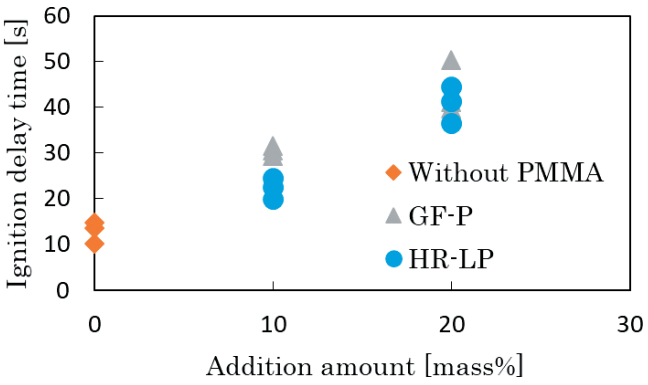

Figure 7 Ignition test results.

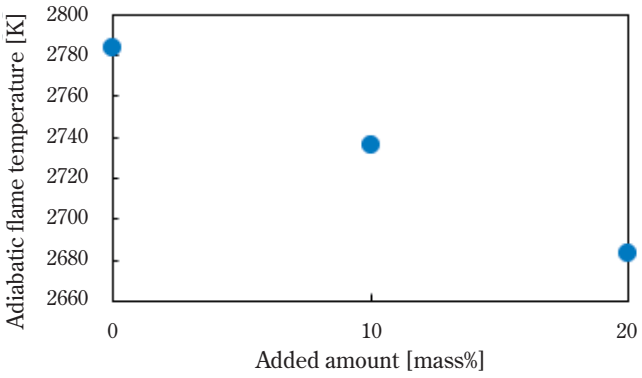

Figure 8 Adiabatic flame temperature.

Table 7 Thermal conductivity of PMMA-containing microcrystalline wax.

	10 mass %	20 mass %
Thermal conductivity [W m^{-1} K^{-1}]	0.310	0.295

K^{-1}. The following equation is a Maxwell equation, which is used to calculate the theoretical thermal conductivity λ for low volume percentage composite materials[8].

$$\lambda = \frac{2+K-2P(1-K)}{2+K+P(1-K)}\lambda_w \quad (1)$$

Using that equation, we calculated the thermal conductivity of microcrystalline wax with added PMMA. Table 7 presents the theoretical calculation results.

Table 7 shows that thermal conductivity decreases as the added amount is raised. Therefore, the ignition delay time is lengthened because of thermal conduction hardening due to added PMMA powder. In hybrid rocket engine combustion, the solid fuel liquid phase thickness is proportional to thermal conductivity[9]. The liquid phase of the solid fuel becomes thinner by thermal conduction hardening. This thinning decreases the entrainment of fuel droplets. Therefore, the regression rate of the solid fuel is thought to decrease because the entrainment of fuel droplets is known as an important factor affecting the regression rate in boundary layer combustion[2].

This experiment revealed a large difference in ignition delay times with change of the added amount of PMMA powder. Furthermore, we confirmed that the temperature of the combustion chamber on an actual hybrid rocket is higher than that used for this experiment. Figure 8 is calculated for the theoretical adiabatic flame temperature of microcrystalline wax with added PMMA. For this calculation, the chamber condition was the same as described before. (Section 2.2)

According to Figure 8, the adiabatic flame temperature is much higher than 350 °C, which is the temperature of the electric furnace used for this experiment. Actually, the ignition delay time becomes shorter in an actual combustion chamber.

According to the ignition test results, when PMMA powder is added to the solid fuel, the combustion time of fuel droplets might lengthen. Then, the combustion efficiency is thought to decrease. The effects on the combustion efficiency with added PMMA powder must be investigated by combustion experiments conducted with a hybrid rocket engine.

4. Conclusion

This study was conducted to assess the effects of adding PMMA powder to microcrystalline wax. We specifically measured the tensile strength and ignitibility. Results demonstrated that the tensile strength was improved by adding PMMA powder because the interface shear stress affects the relation between microcrystalline wax and PMMA particles. Results confirmed that the tensile strength increased as smaller PMMA particles were used. Nevertheless, the ignitibility decreased because of the thermal conductivity of PMMA. Future studies must assess the optimum amount of PMMA powder addition. Future studies will include combustion experiments using a combustor to investigate the regression rate and combustion efficiency of microcrystalline wax with addition of PMMA powder.

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