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# The Effects of Mechanical Modification Additives on the Regression Rate of Paraffin-Based Fuels for Hybrid Rocket

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## Abstract

The applications of paraffin-based fuel for hybrid rocket are seriously hindered by the poor mechanical properties, adding additives in paraffin fuel can increase the mechanical properties but also can affect the regression rate. Therefore, it is important to study the effects of additives on both mechanical properties and regression rate of paraffin-based fuel, which is useful to develop a kind of paraffin-based fuel with excellent performance. In this paper, an experimental investigation focused on the effects of three kinds of additives (stearic acid, polyethylene wax (A-C®6A) and low density polyethylene (LDPE)) on behavior of paraffin-based fuel was carried out. The mechanical properties of the three kinds of formulations were characterized by compressive and tensile experiments at different temperature and the effects of additives on mechanical properties were analysed by scanning electron microscope (SEM). In addition, the influence of additives on the regression rate of paraffin fuel were discussed by viscosity test and DSC analysis. The results show that all the additives can improve the mechanical properties of paraffin-based fuels as well as A-C®6A and LDPE are more effective, and this influence were more obvious at low temperature (increased 121.4% and 132.8% by blending with 5 mass% A-C®6A and LDPE at 12 ℃, respectively). On the other hand, the additives of stearic acid increased the regression rate of paraffin-based fuels owing to decreased melting point and the additives of A-C®6A and LDPE decreased the regression rate due to the increased melted liquid viscosity. The regression rates of three kinds of formulations which mixing with 5 mass% stearic acid, A-C®6A and LDPE were 119.32 %, 82.45% and 61.00% with respect to pure paraffin at 350 kg/($m^2$s), respectively. Thus, taking into consideration both mechanical properties and regression rate, A-C®6A is the best one among these three additives.

## 1. Introduction

Hybrid rocket engines (HREs) have excellent application perspectives owing to the advantages of high safety, low cost and pollution, adjustable thrust and on-off capability. But the low regression rate of the conventional solid fuel is a serious drawback to hinder the development and application of HREs [1-3]. The paraffin-based fuels have the characteristic of high regression rate owing to the entrainment phenomenon[4], which is attractive for hybrid rocket, but its serious weakness is the poor mechanical properties. A commonly used method to improve the mechanical properties is adding additives in paraffin fuel [5-7]. Although additives can increase the mechanical properties, the regression rate of paraffin-based fuel can also be affected. Therefore, it is important to study the effects of additives on both mechanical properties and regression rate of paraffin-based fuel, which is useful to develop a kind of paraffin-based fuel with excellent performance. In this paper, three kinds of additives of stearic acid, polyethylene wax (A-C®6A) and low density polyethylene (LDPE) had been chosen to investigate the effects on paraffin-based fuel. The compressive and tensile tests at different temperature were carried out and the influences of additives on mechanical properties were analysed by scanning electron microscope (SEM). In addition, the combustion tests of pure paraffin and modified paraffin-based fuels were performed with oxygen mass flow and operating pressure was 1MPa, and the influence of additives on the regression rate were discussed by viscosity test and DSC analysis. It is useful to manufacture an excellent paraffin-based fuel both with good mechanical properties and regression rate.

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## 2. Experiment

### 2.1 Investigated materials

An overview of the investigated materials is shown in Table 1. The melting points of the 3 kinds of additives are much higher than 58# paraffin whose melting point is 58.3 ℃, and the combustion heat of A-C®6A and LDPE are similar to 58# paraffin while which of stearic acid is a little lower than paraffin. Tested fuel formulations are presented in Table 2, the modified paraffin-based fuels are manufactured by blending with 5 mass percent additives and the actual density were measured by AccuPyc II 1340 density meter.

Table 1: Properties of 58# paraffin and the 3 kinds of additives

| Materials | Melting point /℃ | Combustion heat /(kJ/g) |
|---|---|---|
| 58# paraffin | 58.3 | 47.36 |
| stearic acid | 69.0 | 40.60 |
| A-C®6A | 108.7 | 47.47 |
| LDPE | 115.8 | 47.16 |

Table 2: Densities of 58# paraffin and modified paraffin-based fuels

| Name | Formulation | Density /( g/cm3) |
|---|---|---|
| 58# paraffin | - | 0.9172 |
| No. 1 | 5 mass% stearic acid | 0.9231 |
| No. 2 | 5 mass% A-C®6A | 0.9216 |
| No. 3 | 5 mass% LDPE | 0.9236 |

### 2.2 Experimental set

Compressive strength and tensile strength tests were performed with a CMT 4254 instrument and the load velocity was 5 mm/min, experimental temperature were 21 ℃ and 12 ℃. A scanning electron microscope (SEM) was used to observe the micromorphology of modified paraffin-based fuels with 300 times magnification, platinum (Pt) was electrodeposited on the surfaces of the samples to impart electrical conduction and the acceleration voltage was set at 5.0 kV [5]. The thermal behaviour of formulations were characterized by a Mettler-Toledo DSC823e thermal analyzer, air (30 ml/min) as cooling gas and the temperature ramp was 10 K/min ranged from 30 ℃ to 100 ℃ [8]. The melted liquid viscosities of modified paraffin-based fuels were measured at 100 ℃ under 60 r/min rotor speed by a NDJ-1 rotary viscometer.

The combustion tests for modified paraffin-based fuels were performed by a 2D-radial burner similar to the setup in SPLab [9], which is shown in Figure 1. And the samples are cylinder with a hole in center (external diameter: 16 mm, inner diameter: 4 mm, length: 30 mm). The $Nd^{2+}$:YAG pulse laser is used to ignite and the combustion cross-section images of the sample are recorded by a HG-100K high-speed camera after reflection of a flat mirror, thereby the combustion characteristics of paraffin-based fuels can be obtained. According to the recorded burning cross-section images, the regression rate ($r_f$) vs. oxidizer mass flow rate ($G$ox) can be obtained as equation (1), (2) and (3) show [10].

$$D(t) - D(t_0) = a_D (t - t_0)^{n_D} \qquad (t > t_0) \tag{1}$$

$$r_f(t) = \frac{1}{2}\frac{d(D(t) - D(t_0))}{dt} = \frac{1}{2} a_D n_D (t - t_0)^{n_D - 1} \qquad (t > t_0) \tag{2}$$

$$G_{OX}(t) = \frac{m_{OX}}{\pi D^2(t)/4} = \frac{m_{OX}}{\pi (D(t_0) + a_D (t - t_0)^{n_D})^2 / 4} \qquad (t > t_0) \tag{3}$$

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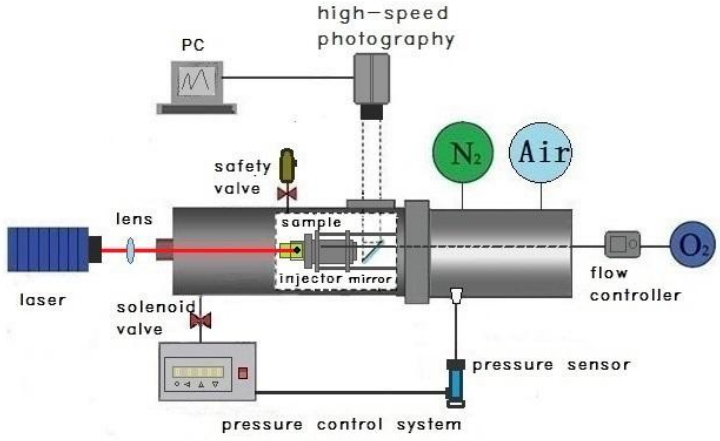


Figure 1: Schematics of a 2D-radial burner

## 3. Result and Discussion

### 3.1 The effects of additives on mechanical properties

The results of mechanical properties for modified paraffin-based formulation fuels are shown in Figure 2. In order to ensure the accuracy, the measurements were repeated three times for each formulation except the test for formulation No. 2 at 12 ℃ (2 times) and none tests for formulation No. 1 at low temperature due to the insufficient samples. It can be seen that stearic acid, A-C®6A and LDPE all improved the mechanical properties of paraffin-based fuels while the effects of stearic acid were indistinctive compared with A-C®6A and LDPE. In addition, the enhancements of mechanical properties were more obvious at low temperature, the most prominent is that the tensile strength of formulations blended with 5 mass% A-C®6A and LDPE increased up to +121.4% and +132.8% relative to pure paraffin, respectively. The reasons were found from the SEM images of pure paraffin and paraffin-based fuel formulations as Figure 3 show. The 58# paraffin is a kind of macrocrystalline paraffin, as Figure 3 (a) shows that the crystal structure were macro-size angular lumps and the connections between lumps were not tight, thus the mechanical properties of pure paraffin were poor. Figure 3 (b), (c) and (d) show the surface microstructure of modified paraffin-based fuels. The crystal structure of formulation blended 5 mass% stearic acid changed into multilayer claviform aggregation and the connections were more tight compared with pure paraffin, thereby blending with stearic acid can enhance the mechanical properties, while the effects were indistinctive which is because that mixing stearic acid only changed the shape of crystals but not shrunk the size. In contrast, blending with A-C®6A and LDPE can reduce crystals size obviously, therefore the mechanical properties of formulation No. 2 and No. 3 raised signally with respect to pure paraffin. And the effects of mixing LDPE were better than that of A-C®6A which is owing to the more dense crystal structure as we can see in Figure 3 (c) and (d), and this is also proven by the measuring result of density (the density of formulation blended with 5 mass% LDPE is bigger than that of formulation blended with A-C®6A). In addition, paraffin-based fuels will shrink when temperatures fall so that the texture can become more tight, which is the reason that the mechanical properties were better at low temperature.

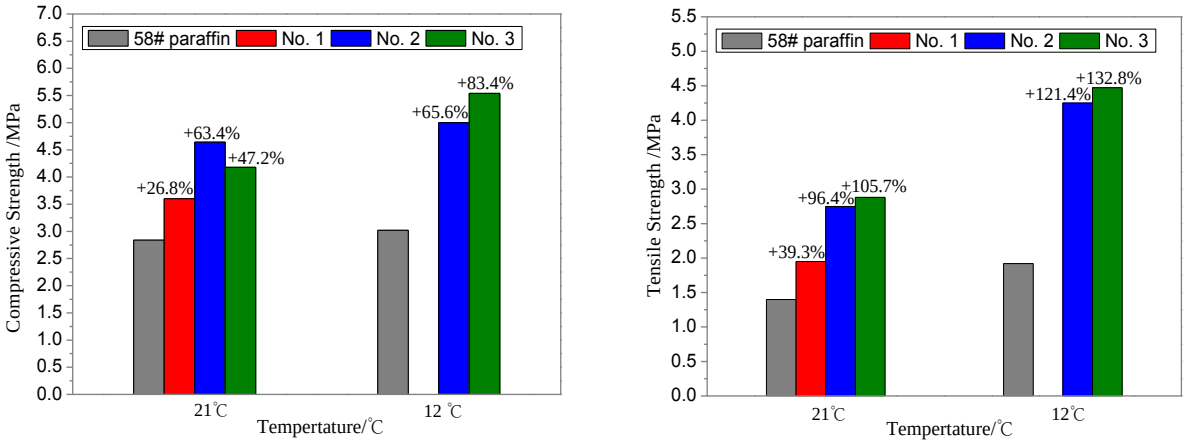


Figure 2: The mechanical properties of 58# paraffin and modified paraffin-based fuels

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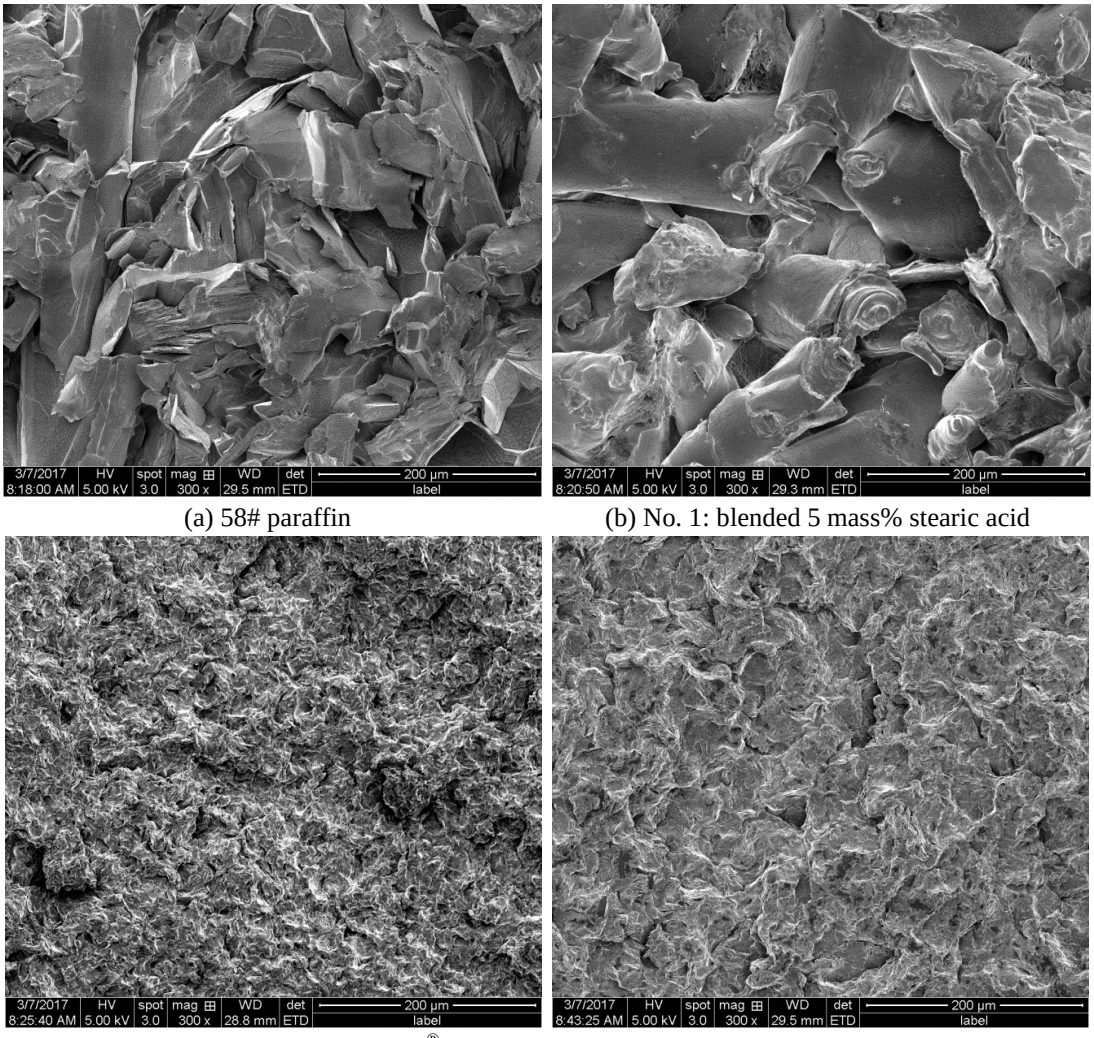


(a) 58# paraffin (b) No. 1: blended 5 mass% stearic acid

(c) No. 2: blended 5 mass% A-C®6A (d) No. 3: blended 5 mass% LDPE

Figure 3: SEM images of 58# paraffin and modified paraffin-based fuels

### 3.2 The effects of additives on regression rate

The combustion tests were implemented under oxygen flow with operating pressure of 1MPa, the $r_f$ and *G*ox of tests were evaluated by Eqs. (2) and (3). Figure 4 shows the $r_f$ of 58# paraffin and three modified paraffin-based fuels vs. *G*ox ranges from 100 kg/(m$^2$s) to 350 kg/(m$^2$s). It can be seen that the regression rate of all the fuels raised with the increase of oxidizer mass flow rate, and the regression rates of formulation blended with 5 mass% stearic acid were higher than that of the pure paraffin, on the contrary, the regression rate of formulations blended with A-C®6A and LDPE were lower. The regression rates increase with respect to 58# paraffin ( $\Delta r_f$ ) at different oxidizer mass flow rate are reported in Table 3. It can be seen that the variations of regression rate for modified paraffin-based fuels were more substantial at high oxidizer mass flow rate, and the $\Delta r_f$ of formulations blended with 5 mass% stearic acid, A-C®6A and LDPE at 350 kg/(m$^2$s) were +23.83 %, -18.36 % and -40.59 %, respectively. In the range of 100 kg/(m$^2$s) to 350 kg/(m$^2$s), the average regression rates of formulation No. 1, No. 2 and No. 3 were 119.32 %, 82.05 % and 61.00 % with respect to pure paraffin, respectively.

In order to analyse the influence on regression rate of different additives, the DSC analysis and viscosity test were carried out for pure paraffin and three modified paraffin-based fuels. The DSC results were reported in Figure 5 and Table 4. It can be seen that there are two endothermic stages for pure paraffin and formulation No. 1 and No. 2 as well as three stages for formulation No. 3. The first stage is softening process while the second and third stages are melting process. The third stage for formulation No. 3 is due to the existence of little undissolved LDPE. Comparing with 58# paraffin, the melting point and endothermic heat of formulaition blended with 5 mass% stearic acid were a little lower while those of formulation No. 2 and No. 3 were opposite. Table 5 described the melted liquid viscosity of pure paraffin and three formulations at 100℃, the viscosity of paraffin blended with 5 mass% stearic acid were

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basically not affected, but the viscosity of paraffin blended with 5 mass% A-C®6A was increased by 39.13% with respect to pure paraffin and that of paraffin blended with 5 mass% LDPE was increased more than 4 times. Therefore, the regression rates of formulation blended with stearic acid were increased owing to the decreased melting points and basically unchanged viscosity, while the regression rates of formulations blended with A-C®6A and LDPE were decreased primarily due to the significantly increased melted liquid viscosity [4,11].

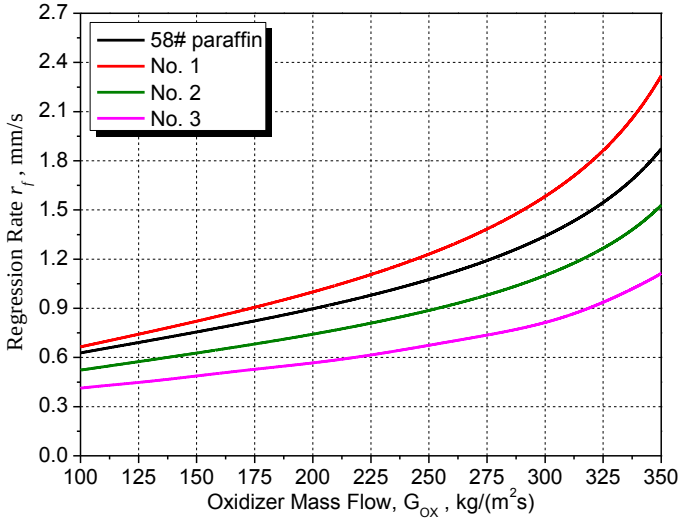


Figure 4: The $r_f$ vs. $G_{OX}$ of 58# paraffin and modified paraffin-based fuels, pressure 1 PMa

Table 3: The regression rate increase with respect to 58# paraffin ($\Delta r_f$) at different $G$ox

| **Name** | $\Delta r_f$ | | |
|---|---|---|---|
| | **100 kg/(m$^2$s)** | **250 kg/(m$^2$s)** | **350 kg/(m$^2$s)** |
| No. 1 | +5.84% | +11.44% | +23.83% |
| No. 2 | -16.74% | -17.28% | -18.36% |
| No. 3 | -34.25% | -36.80% | -40.59% |

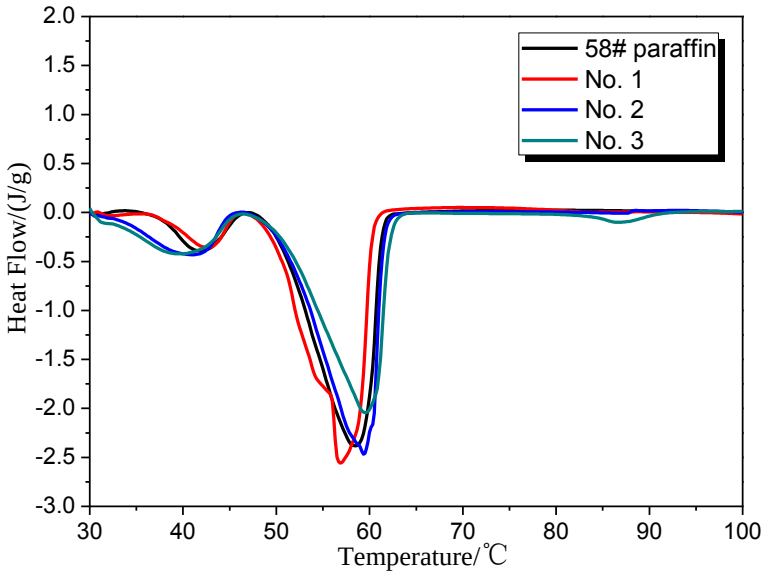


Figure 5: The DSC curves of 58# paraffin and modified paraffin-based fuels

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Table 4: DSC results obtained from 58# paraffin and the 3 kinds of modified paraffin-based fuels ($T_s$ is softening temperature, $T_m$ is melting temperature, $Q$ is endothermic heat)

| Name | First stage | | Second stage | | | Third stage | | $Q$ /(J/g) |
|---|---|---|---|---|---|---|---|---|
| | $T_{s,1}$ /℃ | $T_{s,2}$ /℃ | $T_{m,1}$ /℃ | $T_{m,peak}$ /℃ | $T_{m,2}$ /℃ | $T_{m,3}$ /℃ | $T_{m,4}$ /℃ | |
| 58# paraffin | 33.50 | 46.17 | 46.33 | 58.33 | 64.00 | - | - | 112.98 |
| No. 1 | 35.17 | 45.83 | 46.67 | 56.83 | 62.83 | - | - | 110.16 |
| No. 2 | 31.00 | 46.33 | 46.50 | 59.33 | 63.67 | - | - | 120.96 |
| No. 3 | 30.67 | 46.5 | 46.83 | 59.50 | 63.67 | 80.33 | 92.5 | 115.74 |

Table 5: Viscosity of 58# paraffin and the 3 kinds of additives

| Name | 58# paraffin | No. 1 | No. 2 | No. 3 |
|---|---|---|---|---|
| Viscosity (100℃) | 4.6 | 4.9 | 6.4 | 25.8 |

## 4. Conclusion

The three kinds of additives of stearic acid, A-C®6A and LDPE all can improve the mechanical properties of paraffin-based fuels while the effects of A-C®6A and LDPE were more remarkable than stearic acid owing to reduced crystals size, as well as the enhancements of mechanical properties were larger at low temperature because of the shrink of paraffin-based fuels. In addition, the influence of these additives on regression rate were inconsistent. The melting point of formulation blended with 5 mass% stearic acid were decreased as well as the viscosity was basically unchanged, so the regression rates were increased up to 119.32 % with respect to pure paraffin. While the regression rates of formulations blended with 5 mass% A-C®6A and LDPE were obviously decreased primarily due to the significantly increased melted liquid viscosity, which were 82.05 % and 61.00 % with respect to pure paraffin, respectively. Therefore, synthesizes the influence on mechanical properties and regression rate, A-C®6A is the best one among these three additives.

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