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TA OF HTPB MIXTURES WITH SOME OF THE ENERGETIC MATERIALS

Determination of effective factors

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Abstract

The heat of reaction of HTPB mixtures was measured by calorimetric method. The mixtures were prepared according to 'ruggedness testing [1]'. The effect of the factors was calculated and it was found that the quantity of the energetic materials in the mixture was the most effective factor in the mixing process and it had the greatest effect on the response.

Keywords: effective parameters, heat of reaction, HTPB mixtures, ruggedness testing

Introduction

Composite propellants are essentially composed of a binder, metallic fuel, and an oxidizer. The binder must be chemically and physically stable during storage and operating conditions, and must be capable of bonding to insulating materials and the metallic parts of rocket. Among conventional binders for composite propellants hydroxyl terminated polybutadiene (HTPB), has been regarded as the most suitable binder for composite propellants [2–20]. However, it is an inert binder. For increasing the energy, it is necessary to mix HTPB with an energetic material for example cyclo-tetramethylenetetranitramine (HMX) or cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX) [21–28]. In this work, the effective factors in mixing process of HTPB with HMX and 2,6-diamino-4-phenyl-1,3,5-triazine (DAPTA) have been investigated by 'ruggedness testing'.

Experimental procedures

The experimental design was arranged for seven factors at two levels (uppercase and lowercase levels). The following parameters have been known to be effective in the quantity of heat of reaction:

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A,a: mixing time (min); B,b: temperature of the mixture (°C); C,c: speed of the stirrer (rpm); D,d: quantity of the energetic material (g/mass of HTPB); E,e: type of the stirrer; F,f: type of the diluting agent; G,g: quantity of diluting agent (g/mass of HTPB).

It is predicted that by increasing the mixing time and temperature the probability of breaking of the polymeric chains will be increased. Increasing the speed of the stirrer will also have similar effect. So these factors will influence on the quantity of the heat of reaction. Furthermore, the quantity of the energetic material will affect on the heat of reaction. Since by increasing the quantity of the energetic material in the mixture, the viscosity will be increased and consequently the tendency of the mixture to accept the solid fillers will be reduced, low molecular mass polymers (for example PPG-2000 and PPG-1200) has been added to the mixture (as a diluting agent) to decrease the viscosity. Polypropyleneglycols have been selected for this reason as they have reactive OH groups to form urethane linkages via reaction with isocyanate. In quantitative factors the upper limit for each factor is shown by a capital letter and a small letter shows the lower limit for each factor. The experiments were performed according to Table 1. The amounts used for high and low levels are given in Table 2. Mass of HTPB in all of the mixtures were 20 g. The mass of sample used for calorimetric measurement was 0.5 g and duplicate analysis was performed at each case.

Table 1 Experimental design according to 'ruggedness testing'

Run	Factors combination							Response
1	A	B	C	D	E	F	G	R_1
2	A	B	c	D	e	f	g	R_2
3	A	b	C	d	E	f	g	R_3
4	A	b	c	d	e	F	G	R_4
5	a	B	C	d	e	F	g	R_5
6	a	B	c	d	E	f	G	R_6
7	a	b	C	D	e	f	G	R_7
8	a	b	c	D	E	F	g	R_8

Table 2 The amounts used for high and low levels

A: 15 min	a: 10 min
B: 35°C	b: 25°C
C: 70 rpm	c: 60 rpm
D: 1 g	d: 0.5 g
E: metallic stirrer	e: glassy stirrer
F: PPG-2000	f: PPG-1200
G: 1 g	g: 0.8 g

Specification of materials and instruments

Materials

Preparing the mixtures:

a. HTPB having the microstructure: Trans; 62%, Vinyl; 20%, Cis; 18%.
b. Granular HMX [21, 25], its average particle sizes were 150 micron.
c. Polypropyleneglycol (P-2000) from Fluka.
d. Polypropyleneglycol (P-1200) from Fluka.
e. DAPTA from Merck.

All materials were characterized in our laboratory [2–5].

Instruments

a.'IKA-Calorimeter system, C4000A'
b. 'RW-20' mixer.

Results and discussion

The results obtained by calorimetry are summarized in Table 3.

Table 3 Results of calorimetric experiments

Responses	Reaction heat/J g^{-1}	
	HTPB/HMX mixtures	HTPB/DAPTA mixtures
R_1	42458	42576
R_2	42560	42674
R_3	42473.5	42920
R_4	42575	42856
R_5	42642	42798
R_6	42800	42802
R_7	42300	42624
R_8	42414	42486

In our calculations, only the critical effects have been considered and the experiments were performed according to Table 1.

Designs on the bases of two levels for each factor are called 'ruggedness-testing or screening designs [1]'. Uppercase and lowercase letters identifies two-factor levels. This design is similar to that for 2^k Fractional Factorial Design and provides information about the first order effect of each factor [29]. The experimental design for 'ruggedness-testing' is balanced in that each factor level is paired on equal number of times with uppercase and lowercase levels for every other factor.

The effect of changing the level for anyone factor, E_f, is determined by subtracting the average response when the factor is at its uppercase level from the average value when it is at its lowercase level

$$E_f \quad \frac{(\quad R_i)_{\text{Upper case}}}{4} \quad \frac{(\quad R_i)_{\text{Lower case}}}{4} \tag{1}$$

For example, the effect of changing the level for factor *A* is determined by averaging the responses from runs 1 through 4 and subtracting the average response from runs 5 through 8. The effect of a change in level for each factor is calculated using Eq. (1).

$$E_A = (R_1+R_2+R_3+R_4)/4 - (R_5+R_6+R_7+R_8)/4$$
$$E_B = (R_1+R_2+R_5+R_6)/4 - (R_3+R_4+R_7+R_8)/4$$
$$E_C = (R_1+R_3+R_5+R_7)/4 - (R_2+R_4+R_6+R_8)/4$$
$$E_D = (R_1+R_2+R_7+R_8)/4 - (R_3+R_4+R_5+R_6)/4$$
$$E_E = (R_1+R_3+R_6+R_8)/4 - (R_2+R_4+R_5+R_7)/4$$
$$E_F = (R_1+R_4+R_5+R_8)/4 - (R_2+R_3+R_6+R_7)/4$$
$$E_G = (R_1+R_4+R_6+R_7)/4 - (R_2+R_3+R_5+R_8)/4$$

The effects have been calculated and listed in Table 4.

Table 4 Effects for HTPB mixtures

Effects		Ordered effects (by absolute values)	
HTPB/HMX	HTPB/DAPTA	HTPB/HMX	HTPB/DAPTA
E_A=–22.375	E_A=79	E_D=189.625	E_D=254
E_B=174.375	E_B=–9	E_B=174.375	E_A=79
E_C=118.875	E_C=25	E_C=118.875	E_F=76
E_D=–189.625	E_D=–254	E_A=22.375	E_E=42
E_E=17.125	E_E=–42	E_E=17.125	E_C=25
E_F=2.125	E_F=–76	E_G=10.875	E_B=9
E_G=10.875	E_G=–5	E_F=2.125	E_G=5

The estimated standard deviation for the analysis is given by

$$S \quad (2/7 \quad E_i^2)^{1/2} \tag{2}$$

For HTPB/HMX mixtures:

$$S=\{2/7[(-22.375)^2+(174.375)^2+(-118.875)^2+(-189.625)^2+(17.125)^2+(10.875)^2+ +(-2.125^2]\}^{1/2}$$

$$S=152.514$$

which is 0.363% with respect to the average of response.

Similarly for HTPB/DAPTA mixtures we obtain S=150.264. This standard deviation is 0.352% with respect to the average of the responses.

Ordering the effects by their absolute values (Table 4) indicates that in both systems the quantity of energetic material (factor D) has the greatest effect on the response and the quantity of 'the diluting agent' (factor G) has the least effect on the response. The least effect of factor G can be explained by considering the chemical structure of polypropyleneglycols, which are chiefly hydrocarbonic materials, and their structures are similar to HTPB. Also in both systems, speed of the stirrer (factor C), type of the stirrer (factor E), and mixing time (factor A) has substantial effect on the responses.

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