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Comparative ballistic efficiency of solid composite propellants: which plasticizer/polymer combination is the energetically preferred binder?

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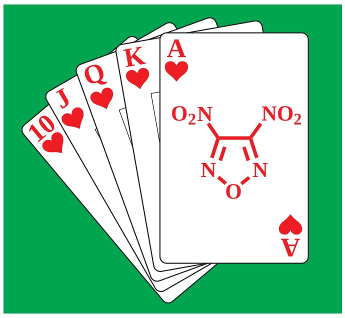
The relative efficacy of real energetic plasticizers and polymers for model solid composite propellants comprising 25% aluminum hydride, 50% dinitramide ammonium salt and 25% binder (20% a plasticizer and 5% a polymer) has been estimated. The quantitative dependence of the efficiency of plasticizers on the value of their enthalpy of formation ΔH_f^0, the oxygen coefficient α, percentage of hydrogen %H and density *d* has been revealed. 3,4-Dinitrofurazan tested as a plasticizer for the binder provides effective impulse values at the 3rd stage up to ~2 s higher than those for other plasticizers.

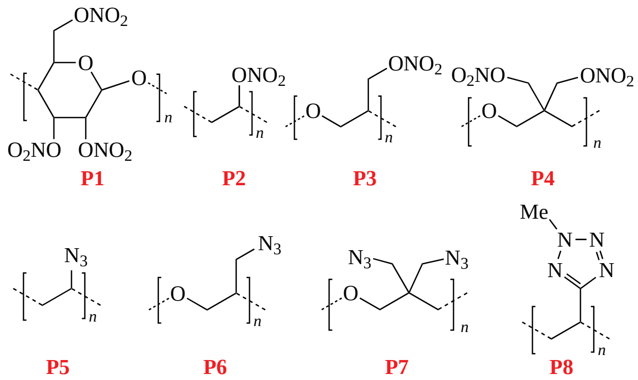


Keywords: solid composite propellant, binder, polymer, plasticizer, specific impulse, effective impulse.

A multicomponent system of solid composite propellants (SCP) usually includes an oxidizer (50–80%, oxygen-rich inorganic and/or organic compounds), combustible (up to 25%, high-calorific metals or their alloys, metal hydrides, boron and its derivatives, high nitrogen compounds, *etc*.), binder (10–25%, plasticized polymers), catalysts and processing aids.[1] All these components complementing each other should provide the required effect, namely, the development of the maximum thrust and the maximum increase in the speed of the aircraft in the process of propellant burning. Formulations based on aluminum hydride AlH_3 are characterized by the highest values of specific impulse in comparison with both metal-free formulations and formulations based on metallic aluminum.[2]

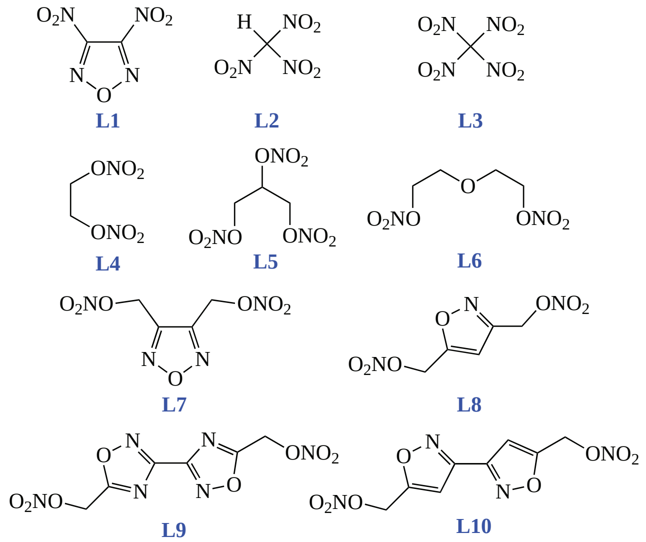
Since AlH_3 contains ~10% hydrogen, the use of 20–25% AlH_3 in combination with the usual percentage of hydrocarbon binder (10–15%) significantly increases the hydrogen content in the composition. In this case, an oxidizer with a higher oxygen content is required than is available in ammonium perchlorate (AP, NH_4ClO_4) or ammonium dinitramide, (ADN, $NH_4N_3O_4$).[3] To eliminate this imbalance, a so-called active binder, that is, containing oxidizing units such as ONO_2, NO_2, N–NO_2, *etc*., can be used instead of a hydrocarbon binder. Such a binder requires less oxidizer for complete gasification. Moreover, binders created on the basis of a polymer and a plasticizer enriched with explosophoric groups[4] gave a significant increase in the specific impulse for metallized SCPs, especially for SCPs with AlH_3.[5] It should be noted that up to 80% of the binder can be occupied by a plasticizer, which, thereby, has a more significant effect on the ballistic performances of the propellant composition than the polymer. The creation of a binder with an optimal chemical content, which in combination with an oxidizer and other components would be suitable for processing both an uncured propellant mass and a hardened charge with the desired physical and mechanical properties, is a rather difficult task.

Here, the results of evaluating the energetic capabilities of SCPs created using various binders based on energetic polymers and oxygen-rich plasticizers are described. The weight ratio of polymer/plasticizer was invariably 1 : 4, which is close to that actually used in active binders.[6] A formulation containing AlH_3 (25%)/ADN (50%)/polymer (5%)/plasticizer (20%) was considered as a model propellant. The combined binder consisted



Polymer	Formula	α	*d*/g cm^{-3}	ΔH_f^0/kJ mol^{-1}
P1	$C_6H_7N_3O_{11}$	0.71	1.66	–658.1
P2	$C_2H_3NO_3$	0.54	1.5	–144.8
P3	$C_3H_5NO_3$	0.35	1.46	–284.1
P4	$C_5H_8N_2O_7$	0.5	1.54	$–450.6_{calc}$
P5	$C_2H_3N_3$	0	1.18	283.7_{calc}
P6	$C_3H_5N_3O$	0.12	1.29	160.2_{calc}
P7	$C_5H_8N_6O$	0.07	1.29	468.5
P8	$C_4H_6N_4$	0	1.28	216.7

Figure 1 Energetic polymers of this study (for details, see Online Supplementary Materials, Table S1).



Compound	Formula	Mp/°C	d/g cm^{-3}	ΔH_f^0/kJ mol^{-1}	α	%H
L1	$C_2N_4O_5$	–15	1.62	+235.14	1.25	0.0
L2	CHN_3O_6	26	1.47	–45.1	2.4	0.66
L3	CN_4O_8	14	1.64	+38.00	4.0	0.0
L4	$C_2H_4N_2O_6$	–22	1.49	–242.76	1.0	2.6
L5	$C_3H_5N_3O_9$	13	1.59	–370.70	1.06	3.3
L6	$C_4H_8N_2O_7$	2	1.385	–418.99	0.58	4.1
L7	$C_4H_4N_4O_7$	–6	1.57	–47.7	0.7	1.8
L8	$C_5H_5N_3O_7$	–76	1.494	-214.7_{calc}	0.67	2.28
L9	$C_6H_4N_6O_8$	84.5	1.832	-62.6_{calc}	0.57	1.4
L10	$C_8H_6N_4O_8$	92	1.585	-183.1_{calc}	0.42	2.1

Figure 2 Energetic plasticizers of this study (for details, see Online Supplementary Materials, Table S2).

of one of eight polymers shown in Figure 1 and one of ten plasticizers grouped in Figure 2.

The values of the effective specific impulses $I_{ef}(3)$ at the third stage of multi-stage rocket systems[7] are taken as a measure to compare the prospects of energetic polymers and plasticizers combinations to create SCP.

$$I_{ef}(3) = I_{sp} + 25(d - 1.7)$$

The specific impulse values, I_{sp}, were calculated at pressures in the combustion chamber of 4.0 MPa and at the nozzle exit of 0.1 MPa using the TERRA Code.[8]

To select new binder components for SCPs, their characteristics such as the enthalpy of formation, ΔH_f^0, the coefficient of supply with oxidizing elements, α, hydrogen content, %H, and density, d, should be analyzed. The question is how the basic characteristics of the plasticizer affect the I_{sp} value of a propellant. The growth of any of these characteristics, as is known, leads to an increase in I_{sp}.[9,10]

We estimated I_{sp} values for all 80 formulations containing 25% AlH_3, 50% ADN and 25% of various binders. All binders contain polymer and plasticizer in a weight ratio of 1 : 4, which is close to optimal. In fact, the actual polymer/plasticizer ratio which provides the best rheological and physico-mechanical characteristics for a particular propellant may differ. The I_{sp} values for the polymer–plasticizer combinations of this study range from 273.8 to 279.2 s (for details, see Table S3).

We have shown that a simple and visual estimation of I_{sp} can be carried out if it represented as a function defined by the above parameters. It can be expressed by a simplified empirical relation given by equation (1):

$$I_{sp} = k_0 + k_1\%H + k_2\alpha + k_3\Delta H_f^0, \qquad (1)$$

where k_0–k_3 are the required coefficients.

We assume that the value of I_{sp} is described by a linear dependence (1) on each of their characteristics, %H, α and ΔH_f^0. Statistical analysis of the I_{sp} value for 80 compositions from Table S3 makes it possible to determine to what extent this assumption is justified and to find the values of the coefficients k_0, k_1, k_2 and k_3 (see Tables 1 and S4). For example, when evaluating a binder based on polymer **P1**, the correlation coefficient r for values of k_0, k_1, k_2, and k_3 is equal to 0.97 ± 0.005, 0.98 ± 0.005, 0.88 ± 0.005, and 0.94 ± 0.005, respectively.

For polymer **P1**, the average deviation of the I_{sp} values calculated using the simple empirical equation (1) from the corresponding values calculated using the TERRA Code[8] is 0.9 s. This is a rather noticeable deviation, which indicates that equation (1) only approximately describes the dependence of I_{sp} on H%, α and ΔH_f^0. Nevertheless, due to its simplicity and minimal investment of time, it can be used for preliminary assessment of the effectiveness of plasticizers, including hypothetical ones. With approximately the same deviation, I_{sp} can be estimated for similar SCP formulations based on other polymers (see Table S3).

The calculated averaged values of k_1, k_2 and k_3 roughly characterize the quantitative effect on the I_{sp} value of the characteristics of the plasticizer, such as the percentage of hydrogen (%H), α and the enthalpy of formation (ΔH_f^0), respectively. For example, the values of k_2 correcting the contribution of oxygen content α in the polymer, for polymers of this study range from 0.6 to 1.4. The dependence of k_2 on α of polymers is close to linear (see Online Supplementary Materials, Figure S2); the values of k_2 (as well as I_{sp}) increase with decreasing value of α.

As noted above, the values of $I_{ef}(3)$ can be used to compare the ballistic effectiveness of different compositions. For all 80 model SCPs comprising 5% polymer **P1**–**P8** + 20% plasticizer **L1**–**L10**, $I_{ef}(3)$ were computed (see Table S5 and Figure 3). Both diagrams show the same set of calculated $I_{ef}(3)$ values. However, the diagrams are drawn in such a way that part *a* visualizes the relative effectiveness of plasticizers, while part *b* – polymers. Thus, for plasticizers, the order of relative effectiveness efficiency is **L1** > **L7** > **L3** > **L4** > **L5** > **L2** > **L9** > **L6** > **L8** > **L10**. Figure 3 clearly illustrates that 3,4-dinitrofurazan **L1** is the most energetic plasticizer.

For more detail, it is useful to compare the values of $I_{ef}(3)$ that can be achieved for all ten plasticizers with each of the polymers, as well as those that can be achieved for all eight polymers with each of the plasticizers (Table S5). For example, Figures 4 and 5 show the ranking of the effectiveness of polymers and plasticizers. Replacing the polymer can lead to a gain on average up to 1.2 s,

Table 1 Values of k_0 – k_3 of the equation (1).

Coefficient	**P1**	**P2**	**P3**	**P4**	**P5**	**P6**	**P7**	**P8**
k_0	274.6	273.12	272.7	273.1	274.0	273.6	273.9	272.9
k_1	1.05	1.75	1.71	1.66	1.73	1.66	1.74	1.70
k_2	0.57	1.03	1.04	0.83	1.21	1.17	1.19	1.38
k_3	0.000858	0.0020	0.00194	0.00190	0.00197	0.00190	0.00202	0.00194

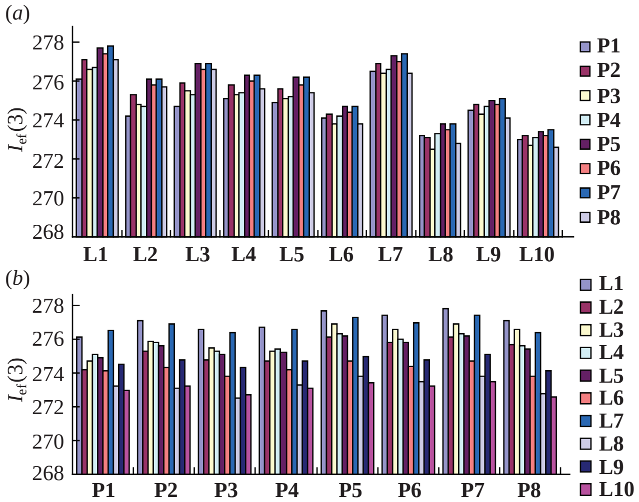


Figure 3 Comparison of $I_{ef}(3)$ values of model SCP depending on (*a*) the plasticizer and (*b*) the polymer used.

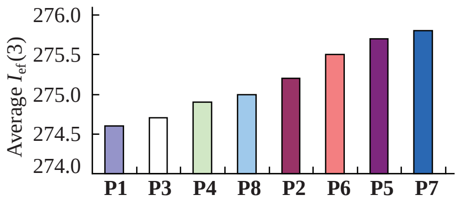


Figure 4 Average values of $I_{ef}(3)$ for model SCPs with 10 plasticizers, when using the specified polymer.

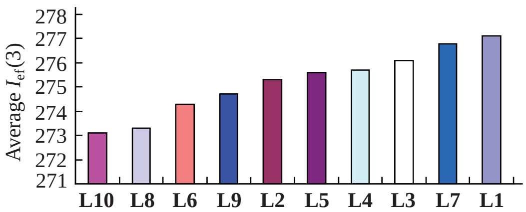


Figure 5 Average values of $I_{ef}(3)$ with 8 polymers, when using the specified plasticizer.

while replacing the plasticizer up to 4 s (for additional information, see Online Supplementary Materials, Figure S3).

In general, model SCPs with 3,4-dinitrofurazan **L1** paired with any of the eight polymers provide higher $I_{ef}(3)$ values, which exceed the others by an average of 2.1 s.

In conclusion, the quantitative dependences of the influence of plasticizer properties such as enthalpy of formation ΔH_f^0, oxygen coefficient α, percentage of hydrogen %H and density d on the ballistic efficiency have been found for model SCPs containing 25% AlH_3/50% ADN/5% polymer/20% plasticizer. As a result, a simple and intuitive method for preliminary quantitative assessment of the effectiveness of plasticizers has been proposed. The relative efficiencies of various combinations of real energetic polymers and plasticizers were evaluated. The maximum value of $I_{ef}(3)$ is shown by a model SCP where poly[bis(azidomethyl)oxetane] **P7** is used as the polymer, and 3,4-dinitrofurazan **L1** as the plasticizer. 3,4-Dinitrofurazan is a promising plasticizer of a SCP since its use allows one to increase the effective impulse value at the third stage by about 2 s in comparison with other plasticizers.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.09.010.

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