Development of MTV Compositions as Igniter for HTPB/AP Based Composite Propellants

Ahmet Göçmez, Gürkan A. Yilmaz, and Fikret Pekel

Defense Industries Research and Development Institute, TÜBITAK, P.K. 16 Mamak, 06261 Ankara (Turkey)

Saim Özkar*

Department of Chemistry, Middle East Technical University, 06531 Ankara, (Turkey)

Entwicklung von MTV-Kompositionen als Anzünder für HTPB/AP-haltige Komposit-Treibstoffe

MTV-Kompositionen wurden hergestellt bei Konstanthaltung des Magnesium/Teflon-Verhältnisses und Zunahme des Viton-Gehalts der Mischung bis auf 14% bei einer Steigerung um 2%, um die Wirkung des Bindergehalts auf die Explosionswärme zu untersuchen. Diese nimmt zu mit zunehmendem Viton-Prozentgehalt während der Magnesiumgehalt gleichzeitig zurückgeht gegen den stöchiometrischen Wert. Im zweiten Teil der Untersuchung werden brennstoffreiche MTV-Kompositionen hergestellt durch Änderung des Magnesiumgehalts und Konstanthalten des Vitonanteils bei einem spezifischen Wert, um die Wirkung des Magnesiumgehalts auf die Explosionswärne und Verbrennungscharakteristik zu untersuchen. Der allgemein beobachtete Trend ist, daß die Explosionswärme von MTV-Kompositionen abnimmt während der Magnesiumgehalt zunimmt. Alle MTV-Kompositionen wurden in der Ballistischen Bombe getestet, um den maximal erreichten Druck zu messen und die Geschwindigkeit, diesen Druck zu erreichen. Das Anzündverhalten von drei ausgewählten MTV-Kompositionen wurde in einem 2,75-inch Raketenmotor geprüft bei Verwendung derselben Anzündladung und desselben HTPB/AP-Komposit-Treibstoffs mit derselben Menge in jedem Test. Zwei von ihnen haben eine hervorragende Anzündleistung und können deshalb als Anzünder für HTPB/AP-haltige Komposit-Treibstoffe verwendet werden.

Développement de compositions MTV en tant qu'allumeurs pour propergols composites à base de HTPB/AP

Des compositions MTV ont été synthétisées en maintenant à un niveau constant le rapport magnésium/téflon et en augmentant la proportion de viton du mélange jusqu'à 14 % avec un incrément de 2% pour étudier l'effet de la proportion de liant sur la chaleur d'explosion. Cette dernière augmente avec le pourcentage de viton alors que la teneur en magnésium diminue simultanément pour s'approcher de la valeur stœchiométrique. Dans la seconde partie de l'étude, on synthétise des compositions MTV riches en combustible en modifiant la teneur en magnésium et en maintenant la proportion de viton à une valeur spécifique, en vue d'étudier l'effet de la teneur en magnésium sur la chaleur d'explosion et les caractéristiques de combustion. La tendance générale observée est que la chaleur d'explosion des compositions MTV diminue lorsque la teneur en magnésium augmente. Toutes les compositions MTV ont été testées dans la bombe balistique en vue de mesurer la pression maximale obtenue et la vitesse qui permet d'atteindre cette pression. Le comportement d'allumage de trois compositions MTV sélectionnées a été examiné dans un moteur de fusée de 2,75 pouces en utilisant la même charge d'allumage et le même propergol composite HTPB/AP avec la même quantité lors de chaque test. Deux d'entre elles possèdent une excellente performance d'allumage et peuvent donc être utilisées en tant qu'allumeurs pour des propergols composites à base de HTPB/AP.

Summary

MTV compositions were prepared by keeping the magnesium/Teflon ratio constant and increasing the Viton content of the mixture up to 14% by an increment of 2% to investigate the effect of binder content on the heat of explosion, which is found to increase with the increasing Viton percentage as the magnesium content concomitantly goes down toward the stoichiometric value. In the second part of the study, fuel-rich MTV compositions were prepared by changing the magnesium content and keeping the Viton fraction constant at a specific value to investigate the effect of magnesium content on the heat of explosion and combustion characteristics. The observed general trend is that the heat of explosion of MTV compositions decreases as the magnesium content increases. All the MTV compositions were tested in a closed vessel to measure the maximum pressure achieved and the rate of reaching this pressure. The ignition performance of three selected MTV compositions was examined in 2.75 inch rocket motor by using the same charge of igniter and the same HTPB/AP composite propellant of the equal amount in each test. Two of them have excellent ignition performance and, therefore, can be used as igniter for the HTPB/AP based composite rocket propellants.

* to whom correspondence should be addressed,
e-mail:sozkar@metu.edu.tr

1. Introduction

Magnesium based pyrotechnic compositions are widely known in the pyrotechnic community for their effectiveness and performance in flare applications. Of particular interest are the pyrotechnic compositions based on the magnesium-Teflon (MT) formulations which are high energy materials used in rocket and ramjet propulsion systems[1]. MT Pyrolants produce high combustion temperatures and generate hot solid particles which can be easily used to ignite propellants and to produce luminous flame. Accordingly, MT pyrolants have been used as igniters for solid rocket motors and pyrotechnics. MT Formulations are characterized by some advantageous properties as rocket motor igniter materials[2]: high energy content (high caloric output), low hygroscopicity, high degree of safety in preparation, adjustable burning rate, low temperature and pressure dependence of the burning rate, ease of igniter pellet or grain fabrication, favorable aging characteristics, stable burning at low pressures, and low production costs. Viton A copolymer is frequently added into the binary MT mixture to improve its characteristic properties[3]. It increases, for example, the homogeneity of the igniter mixture and, therefore, facilitates product fabrication

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without substantial effect on combustion thermochemistry. Magnesium-Teflon-Viton (MTV) mixtures are highly efficient and thermally stable materials with performance characteristics which make them desirable for use in many applications. MTV mixtures have already been recognized as very effective igniters for solid propellant rocket motors. In recent applications, they have been replacing the traditional pyrotechnic ignition compositions. In general, the MTV based pyrotechnic compositions possess many properties suitable for their use as rocket motor igniter materials. In particular, they have very good igniter material characteristics, due to the existence of hot solid and liquid particles and reactive condensable species in their combustion products[4]. The existence of hot and reactive particles enables fast ignition of solid propellant surface by almost all possible modes of heat transfer. Thus, the MTV based pyrotechnic compositions have very high ignition effectiveness[5]. MTV mixtures have also been used for base bleed systems which are normally very difficult to ignite[6], and in the fabrication of Decoy Flares which can be processed in a continuous way by using a twin screw extruder[7].

Most of the studies on MTV compositions are about their ballistic properties which are of great importance in designing igniters for new solid rocket propellants[8]. It has been shown that the burning rate of MTV igniter depends on the porosity of the composition, its charge length, and the size of its particulate components[9]. Size of the magnesium particles used in MTV formulations affects not only the burning rate, but also the sensitivity of the igniter[10]. The influence of the density, reduced pressure (to simulate high altitude conditions) and high rotation speeds (to simulate spinning projectiles) on the burning rate of MTV composition has been well investigated[11], and the relationship between the combustion and sensitivity characteristics has been established[12]. Another important characteristic of MTV mixture is its aging caused mainly by the reaction of magnesium with water[13]. An accelerated aging study by using IR, X-ray, and bomb calorimeter has shown that the energy and mechanical properties of MTV igniters are deteriorated during the aging depending on the temperature and relative humidity of the air, and the binder system provides only partial protection against aging[14].

The aim of this study is to develop a pyrotechnic MTV igniter composition for HTPB/AP based composite propellants by studying the heat of explosion and combustion characteristics. For this purpose seven different MTV compositions were prepared by keeping the magnesium/Teflon ratio constant and varying the Viton content of the mixture to study its effect on the heat of explosion. According to the results obtained from the first part of the study, twenty new compositions were prepared by changing the magnesium content and keeping the Viton content at a certain value of 4, 6, 8, 10, or 12% by weight to investigate the effect of magnesium content on the heat of explosion and combustion characteristics. After the experiments, three MTV compositions were selected to be used as igniters for the HTPB/AP based composite propellants and their performance were tested by 2.75 inch rocket motor.

2. Experimental

Magnesium powder, purchased from Magnesium and Metallic Powders Ind. and Trade A.S., Istanbul, Turkey, was used as a metallic fuel with the average particle size of 100 μm and the density of 1.74 g/cm^3. Teflon granular powder of the type 7A and Viton A (copolymer of vinylidene fluoride and hexafluoropropylene) were purchased from DuPont, Long Beach CA, USA. The latter one was used as a binder to increase the homogeneity and facilitate product fabrication. Its density and Mooney viscosity at 100°C were 1.82 g/cm^3 and 71 Mooney, respectively.

In production of MTV igniter compositions, acetone is used to solve the binder, providing good processability during the mixing period. A solution of Viton in acetone is poured onto a solid premix of magnesium and Teflon in a beaker and stirred by using a spatula. The whole mass is then transferred into a 0.3 L, horizontal mixer. The solvent is evaporated slowly at 25°C under vacuum while mixing continued until the igniter is obtained in the granular forms. The igniter granules are dried in an oven at 70°C for 12 hours.

The work was carried out in two parts. In the *first part*, seven different MTV compositions (Table 1) were prepared by keeping the magnesium/Teflon ratio constant and varying the Viton content of the mixture to study its effect on the heat of explosion. In the *second part* of the study, magnesium-rich MTV compositions (Table 2) were prepared by changing the magnesium content and keeping the Viton content at a certain value of 4, 6, 8, 10, or 12% by weight to investigate the effect of magnesium content on the heat of explosion and combustion characteristics.

Heat of explosion of MTV igniters was measured by using a Parr 1261 Bomb Calorimeter under nitrogen atmosphere according to MIL-STD-286[15]. The pressure versus time relation was obtained by means of a closed vessel equipped with a firing electrode, pressure gage, and a vent valve. The volume of the bomb was 100 ml. Electronic Signal Acquisition Module (ESAM) system consisting of AT 2023(P8/S) acquisition board and an appropriate software was used for the acquisition and processing the data. For the ignition of samples, a squib was used.

Some of the igniter compositions, V8b, V10d, and V12d (Table 2) were tested in 2.75 inch rocket motor containing an HTPB/AP based composite propellant[16]. The grain config-

Table 1. MTV Formulations in the First Part of the Experiment

Composition	% Viton	% Mg	% Teflon
V2	2	59.21	38.79
V4	4	58	38
V6	6	56.79	37.21
V8	8	55.58	36.42
V10	10	54.38	35.62
V12	12	53.17	34.83
V14	14	51.96	34.04

Table 2. MTV Formulations in the Second Part of the Experiment

Composition No	% Viton	% Mg	% Teflon
V4a		43	53
V4b	4	49	47
V4c		54	41
V4d		60	36
V6a		41	53
V6b	6	47	47
V6c		52	42
V6d		58	36
V8a		39	53
V8b	8	45	47
V8c		50	42
V8d		56	36
Vl0a		37	53
V10b	10	43	47
V10c		48	42
Vl0d		54	36
V12a		35	53
V12b	12	41	47
V12c		46	42
V12d		52	36

uration of the rocket motor was the star type. The igniter system was placed at the exhaust nozzle end of the motor.

3. Results and Discussion

In the first part of the study, the ratio of magnesium to Teflon was kept constant at 1.526 (58/38, based on a theoretical calculation[8a]) and the percentage of Viton increased up to 14% by an increment of 2% to investigate the effect of binder content on the heat of explosion. Figure 1 shows the variation in the heat of explosion with the Viton content of MTV composition at a constant magnesium to Teflon ratio of 1.526. Theoretical studies[2,8b] have shown that the heat of explosion of magnesium rich compositions decreases with the increasing fractions of both magnesium and Viton in the mixture. The reason for the latter case is that the replacement of Teflon by Viton increases the carbon fraction in the mixture and introduces small amounts of HF and MgH as combustion products. The experimental results of this study (Fig. 1) show that the heat of explosion increases first with the increasing Viton percentage as the magnesium content concomitantly goes down toward the stoichiometric value. In other words, the effect of magnesium content on the heat of explosion is dominant up to a certain Viton fraction (12%). However, after this Viton fraction the heat of explosion starts to decrease with increasing Viton content. It implies that the heat of explosion is predominantly affected by the increasing Viton content beyond the value of 12%.

A homogeneous mixture could not be obtained for the MTV compositions containing %2 and %14 Viton. In the former composition the amount of Viton seems to be insufficient for the encapsulation of the magnesium particles and the latter one could not be produced in the granular form under the processing conditions given in the experimental part. The remaining five compositions containing 4, 6, 8, 10,

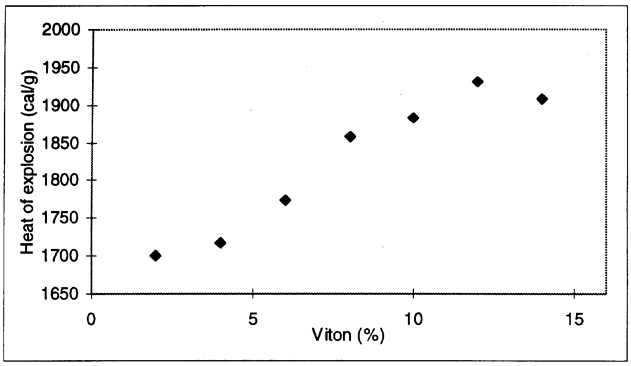

Figure 1. Effect of Viton content on the heat of explosion.

or 12% Viton by weight were selected for the further investigation. In the second part of the study, MTV compositions (Table 2) were prepared by changing the magnesium content and keeping the Viton fraction constant at a certain value to investigate the effect of magnesium content on the heat of explosion and combustion characteristics. For all MTV compositions, magnesium was used in excess to obtain easy ignition and consistency in ballistic performance. Figure 2 shows the variation in the energy of MTV compositions with the increasing magnesium content. Although the magnesium/Teflon ratio was changed, the heat of explosion was plotted against magnesium content for a better understanding. The observed general trend is that the heat of explosion of MTV compositions decreases as the magnesium content increases. This is not unexpected when magnesium is used in excess (higher than stoichiometric value; magnesium amount required for the complete conversion of fluorine to magnesium fluoride). However, the individual compositions at constant Viton percentage show various slopes of the decreasing line. The slope decreases with the increasing Viton fraction. The increasing Viton fraction causes the heat of formation to be less affected by the magnesium content, in consistence with the theoretical studies[2,8b].

All the MTV compositions were tested in a closed vessel with a capacity of 100 ml to measure the maximum pressure achieved and the rate of reaching this pressure. The results are listed in Table 3. Both the maximum pressure and the rate of reaching the highest pressure value show a decreasing tendency with the increasing magnesium content for compositions containing 4%, 6% and 8% Viton A.

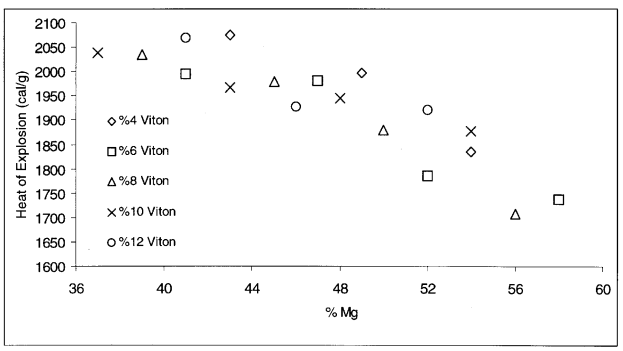

Figure 2. Effect of magnesium content on heat of explosion.

Table 3. Maximum Pressure and Rate of Reaching Maximum Pressure

Composition	Maximum pressure (bar)	dP/dt (max. (bar/s)
V4a	41.9	1586
V4b	32	1287
V4c	26.5	1432
V6a	32.6	1537
V6b	29.9	1169
V8a	35.1	1240
V8b	32	1237
V8c	30	1150
Vl0a	25.9	320
V10b	28.9	687
V10c	29	676
Vl0d	40.6	851
V12b	23.8	361
V12d	27	607

However, such a tendency is not observed for the other compositions containing 10% and 12% Viton A.

Among the twenty MTV compositions tested, V8b, Vl0d, and V12d (Table 2) were selected as candidate igniters for HTPB/AP based composite propellant, by considering the granulation quality, energy, and magnesium content. The ignition performance of the three MTV compositions was examined in 2.75 inch rocket motor by using the same charge of igniter and the same HTPB/AP composite propellant of the equal amount in each test. The pressure versus time graphs are given in Figure 3 for all the three MTV compositions obtained from the 2.75 inch rocket motor test. The MTV composition V8b shows an ignition delay of 0.3 s while the other two, Vl0d and V12d do a perfect ignition job without delay. The ignition delay observed for the composition V8b can be attributed to its lower magnesium content compared to that of the others. The two MTV compositions Vl0d and V12d have excellent ignition performance and, therefore, can be used as igniter for the HTPB/AP based composite rocket propellants.

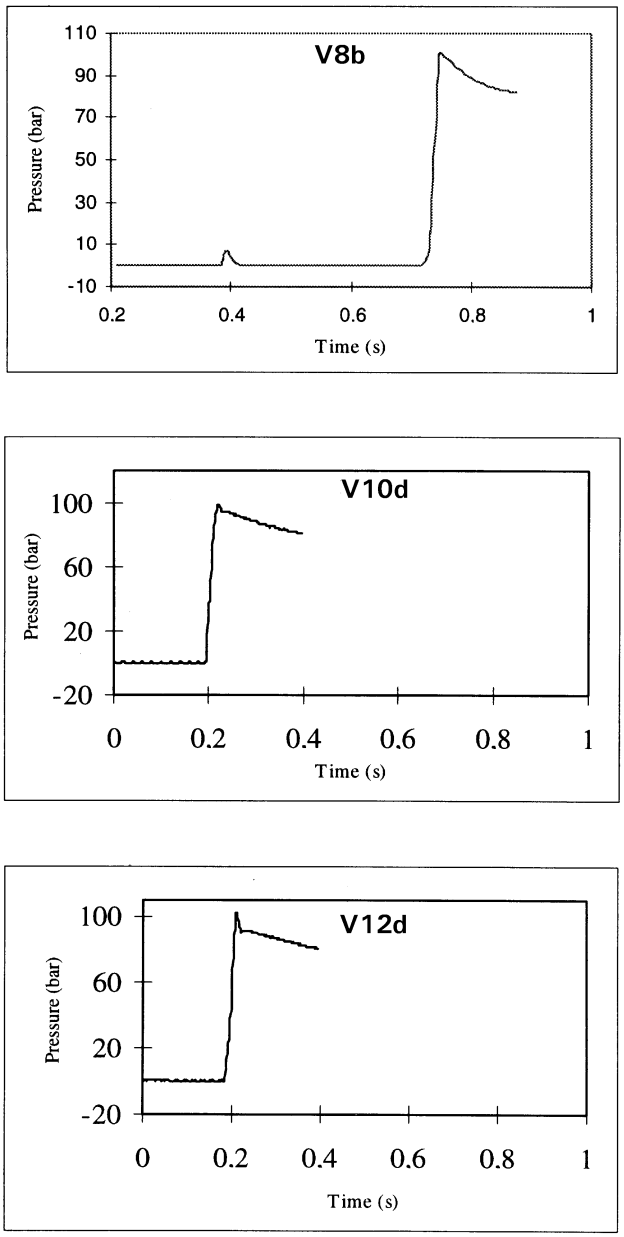

Figure 3. Results of 2.75 inch motor tests.

4. Conclusion

For the MTV compositions prepared at constant magnesium to Teflon ratio, the heat of explosion is found to increase with the increasing Viton content of the mixture. For the fuel-rich MTV compositions prepared by keeping the Viton content constant at a specific value, the heat of explosion is found to decrease with the increasing magnesium content. In other words, the heat of explosion can be increased by decreasing the magnesium content, though being still higher than the stoichiometric value. This seems to be a favorable phenomenon. However, the motor testing shows that increasing the heat of explosion by decreasing the magnesium content causes an ignition delay in rocket motors. All the experimental results enable one to suggest that the compositions, Vl0d and V12d, are suitable igniter materials for HTPB/AP based composite propellants.

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