Polymethyl Methacrylate as a Binder for Pyrotechnic Compositions

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ABSTRACT

Studies on polymethyl methacrylate (PMMA) as a binder for igniter and delay compositions are reported. Igniter compositions based on magnesium and boron as fuels and potassium nitrate as oxidiser, and delay compositions comprising ferrosilicon and red lead, have been investigated. These compositions were subjected to various tests, such as linear burning rate, sensitivity, calorimetric value, compatibility, pelleting properties, spark sensitivity, ignition temperatures and performance characteristics. The results indicate that the igniter compositions Mg:KNO_3:PMMA (42:50:8) and B:KNO_3:PMMA (30:70:10) as well as the delay composition comprising $FeSi$:Pb_3O_4:PMMA (25:75:1) have improved properties and therefore could find practical applications.

1. INTRODUCTION

A variety of binders are used for the manufacture of pyrotechnic compositions[1], such as priming, igniter, delay, illuminating, tracer, smoke, etc. Depending upon the type of system/composition, the requirements of the binder may vary. A few binders, like nitrocellulose (NC), HSR-8111, HR-6312, plasticised ethyl cellulose (PEC), etc, are being used in pyrotechnic compositions. HSR-8111 and HR-6312 are proprietary products of Bakelite Hylam, Hyderabad (HSR-8111 is a polyester resin and HSR-6312 is a phenol-formaldehyde resin). Various igniter compositions using PEC as a binder have been developed at the High Energy Materials Research Laboratory (HEMRL), Pune. Binder PEC has a long processing time during batch preparation because of the usage of high boiling point solvent. It also suffers from flame pickup properties. Besides, ethyl cellulose (which is a starting material) is not available indigenously. Two other binders, viz, Bonosol B-40 and Bonosol BS-142, currently used in service compositions are basically solutions of butyl methacrylate, which is of imported origin. To find an indigenous binder having properties similar to acrylates which are soluble in low boiling point solvent, it was decided to synthesise polymethyl methacrylate (PMMA) and study its properties in the pyrotechnic compositions.

Literature survey shows that PMMA has been used as a fuel binder in composite solid propellants[2]. Mixtures of PMMA as a fuel binder with potassium perchlorate[3] are known as aeroplex K and those with ammonium perchlorate go by the name aeroplex N.

2. EXPERIMENTAL METHOD

2.1 Synthesis and Characterisation of PMMA

The polymer was synthesised at HEMRL using free radical polymerisation technique[4]. It was further characterised by IR spectra, NMR spectra, DTA, DSC techniques and molecular weight by intrinsic viscosity.

2.2 Preparation of Igniter and Delay Compositions

Igniter compositions based on boron and magnesium as fuels and potassium nitrate as oxidant were prepared using PEC and PMMA as binders. A delay composition comprising ferrosilicon ($FeSi$) and red lead (Pb_3O_4) was prepared using NC and PMMA as binders.

The compositions were prepared first by mixing the ingredients in the required proportion and passing them together through a 600 micron sieve six times to achieve homogeniety. This dry mixture was granulated by using requisite amount of PMMA dissolved in ethyl acetate. The granules of size 600/300 micron were dried at 70 ± 5 °C for 5 hr and used for further experiments.

3. RESULTS AND DISCUSSION

Two igniter systems, viz., $B:KNO_3$; $Mg:KNO_3$, have been studied using PMMA and PEC as binders; and a comparative account of their characteristics is given in Tables 1 and 2. For the delay composition based on $FeSi:Pb_3O_4$, a comparative account of NC and PMMA as binders has been given in Table 3.

It can be seen from the results that PMMA enhances the buring rate in comparison with PEC and NC in B: KNO_3:PMMA and $FeSi:Pb_3O_4$:PMMA formulations. It has been found that the compositions based on Mg: KNO_3:PMMA fail to propagate the combustion in lead fuze burning test. However, the enhancement of burning rate in the case of $Mg:KNO_3$:PMMA has been supported by lower ignition delay as compared to $Mg:KNO_3$:PEC system, in CV firings. The enhancement in buring rate in the case of PMMA-based compositions can be attributed to many factors, such as the structure of the binder, its decomposition/ignition temperature, available oxygen, products of decomposition, heat output of the compositions, etc. Since the decomposition temperature, available oxygen, heat output of the composition are of the same order

Table Igniter composition based on boron

Test	$B:KNO_3$:PMMA 30:70:5	$B:KNO_3$:PMMA 30:70:10	$B:KNO_3$:PEC 30:70:10
Inverse burning rate (s/cm)	0.76	0.86	1.35
Sensitivity to impact, Ht. of 50 % explosion (cm)	85	91	84
Sensitivity to friction (kg)	>36	>36	>36
Spark sensitivity	5J-NF	5J-NF	5J-NF
Density of pellets (g/cc)	1.81	1.82	1.85
Breaking strength (N)	451 (0.1 % *Zn* stearate)	645	575
Cal. val (cal/g)	1810	1724	1750
Ignition temp (°C)		541	517
Compatibility, (vacuum stability, amount of gas evolved) (cc)	Compatible 0	Compatible 0.003	Compatible 0
Closed vessel firings (comp)			
P_{max} (kg/cm^2)	39	41	42
ID (ms)	12	14	23
Closed vessel firings (pellets)			
P_{max} (kg/cm^2)	38	41	37
ID (ms)	19	20	32

NF: Not fired

Table 2. Igniter compositions based on magnesium

Test	$Mg:KNO_3$:PMMA 45:50:5	$Mg:KNO_3$:PMMA 42:50:8	$Mg:KNO_3$:PEC 42:50:8
Sensitivity to impact. Ht. of 50 % explosion (cm)	100	164	100
Sensitivity to friction (kg)	28.8	>36	28.5
Spark sensitivity	5J-NF	5J-NF	5J-NF
Density of pellets (g/cc)	1.63	1.64	1.74
Breaking strength (N)	207	226	230
Ignition temp (°C)		599	612
Cal. val (cal/g)	1984	2157	2150
Compatibility, (vacuum stability, amount of gas evolved) (cc)	Compatible 0.005	Compatible 0.006	Compatible 0.009
Closed vessel firings (comp)			
P_{max} (kg/cm^2	51	52	55
ID (ms)	27	40	50
Closed vessel firings (pellets)			
P_{max} (kg/cm^2)	49	51	45
ID (ms)	53	60	81

Table 3. Delay composition based on ferrosilicon and red lead

Test	$FeSi:Pb_3O_4$:PMMA 25:75:1	$FeSi:Pb_3O_4$:NC 25:75:1
Inverse burning rate (s/cm)	0.35	0.65
Sensitivity to impact, Ht. of 50 % explosion (cm)	>175	103
Sensitivity to friction (kg)	24	24
Spark sensitivity (mJ)	6.0-NF 9.4-F	18.4-NF 20.5-F
Ignition temperature (°C)	>700	>700
Compatibility (by vacuum stability amount of gas evolved) (cc)	Compatible 0	Compatible 0.006

NF: Not fired, F : Fired

in all the three systems, the enhancement in the burning rate in the case of PMMA is presumably because of the structural differences. PMMA is the only straight chain polymer amongst the three.

This observation has also been supported by ignition delays recorded in CV firings. In the case of igniter compositions based on B-KNO_3 – binder, the ID is observed to be 23 ms with PEC, whereas it is observed to be 14 ms with PMMA as binder. The same trend has been observed in the case of the compositions based on $Mg:KNO_3$ system. As regards Mg-KNO_3 system, the ID is observed to be 50 ms with PEC and 40 ms with PMMA.

The sensitivity to impact, friction and spark is of the same order for the igniter compositions with PMMA or PEC binders. In the case of $FeSi:Pb_3O_4$:binder system, the composition with PMMA is less sensitive to impact but slightly more sensitive to spark though the difference is not significant. In brief, the compositions based on PMMA as a binder are as safe as the current compositions using PEC/NC binders.

The density of the pellets of PMMA-based compositions is slightly less than those based on PEC, although the breaking strength for PMMA binder is higher. For PMMA, it is 645 N whereas for PEC it is 575 N. This reflects on good binding properties of PMMA.

The vacuum stability test indicates that PMMA is compatible with the fuels, viz., boron, magnesium, ferrosilicon, and oxidisers, viz., potassium nitrate and red lead.

The granulation process using PMMA as a binder is quicker compared to that using PEC. For a batch size of 100 g composition, it takes about 4 hr using PEC as a binder, whereas the granulation can be completed in about 2 hr with PMMA.

4. CONCLUSIONS

It can be seen from the results of the tests, that PMMA satisfies many requirements of an ideal binder for pyrotechnic compositions. PMMA is non-toxic[5], easy to synthesise and the raw materials are available indigenously.

The compositions based on PMMA are easy to granulate, possess good binding and pelleting properties and are reasonably safe to handle. They have higher burning rates. The vacuum stability studies indicate good storage characteristics for these compositions.

A work to conduct exhaustive environmental and qualification trials on the components filled with an igniter composition making use of PMMA as binder is already in progress.

REFERENCES

1. Cackett, J.C. Monograph on Pyrotechnic Compositions, special restricted publication by Royal Armament Research & Development Establishment, 1965, pp 35, 37.
2. Rastogi, R.P. & Kishore, K. *J. Sci. Ind. Res.* 1973, **32**(6), 279-99.
3. Urbanskii, T. Chemistry and Technology of Explosives, Vol 3, 1967, 380-81.
4. Ghatge, N.D. ; Shinde, O.M.; & Patil, A.S. *J. Polym. Mater.*, I, 1984, 125.
5. Othmer, Kirk. Encyclopedia of Chemical Technology, Vol. 15, p. 392.