Study on Various Polyesters as Binders for Pyrotechnic Composition

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ABSTRACT

Two tracer compositions were formulated based on magnesium, strontium nitrate and sodium nitrate with unsaturated non-halo and halo polyesters as binders. They were characterized for mechanical properties, thermal behaviour, burning rate, luminous output, and impact, friction and spark sensitivities. The data show that the composition with chloropolyester as binder is better for tracer compositions.

Keywords: polyester, halopolyester, binder, tracer composition

Introduction

Polymeric binders play multiple roles in pyrotechnic compositions and, in general, contribute towards better mechanical strength[1,2] and moisture-absorption resistance, which leads to improved shelf-life.[3,4] They also contribute significantly to the performance of tracer compositions by increasing the reaction rates. A literature survey reveals that a number of synthetic binders such as polyesters, epoxies, silicones, thiokols, have been studied in place of natural binders in search of more luminous efficiency.[5] The use of halogenated resins as binders in various tracer compositions has recently been reported,[6] and it has been concluded that the polyester resins give higher luminosity, while fluorinated polymers contribute to the combustion exothermicity leading to faster burn rates.

The literature on binders for tracer compositions indicates that polyester resins are promising,[7] but a comparative account of non-halo and halo polyesters has not yet been reported. This study was therefore undertaken with a view to make the comparison. This article reports the data generated on pyrotechnic compositions based on magnesium, strontium nitrate and sodium nitrate with unsaturated non-halo and halo polyesters as binders.

Experimental

Materials

Chemicals conforming to the following specifications were used for the study.

i) Magnesium [Mg] (Grade V) conforming to Commonwealth Specification (CS) 5035A having an average particle size of 63 µm with a purity of 98%.

ii) Strontium nitrate [$Sr(NO_3)_2$] conforming to Joint Services Specification (JSS) 1052 (1964) passing Indian Standard (IS) 125 µm sieve, purity of 97% with moisture content 1% (maximum) and insoluble matter in water 0.25 % (maximum).

iii) Sodium nitrate [$NaNO_3$] conforming to JSS 1095 (1968) passing IS 125 µm sieve, purity of 97% with moisture content 1% (maximum) and total impurities 1% (maximum).

iv) Polyvinyl chloride [Caliplast 370] conforming to Indian/Military Explosives (IND/ME) 741(a) (1977) passing IS 75 µm sieve, with bulk density 0.4 g/cm^3 (minimum) and volatile matter 0.5% (maximum).

v) Tetrachlorophthalic-anhydride- and phthalic-anhydride based unsaturated polyesters were synthesized in the High Energy Materials Research Laboratory by a process given elsewhere.[8]

Preparation of Tracer Composition:

i) ***Chemical Composition***: The composition formulation in percent and the amount for a 200 g batch is as follows:

Ingredient	%	g
Magnesium	53	106
Strontium nitrate	22	44
Sodium nitrate	13	26
Polyvinyl chloride	2	4
Resin (binder)	10	20

ii) ***Drying of ingredients***: Oxidizers [$Sr(NO_3)_2$ and $NaNO_3$] were ground, sieved and dried in an electric oven at 100±2 ºC for 8 hours. The ingredients were again sieved through IS 125 µm sieve. Polyvinyl chloride (PVC) was dried in a water-jacketed oven at 60±2 ºC for three hours and sieved through IS 300 µm sieve.

iii) ***Coating of Mg Powder***: The coating of Mg with polyester resin was done as given below. Either Polyester resin or chloropolyester resin (20 g) was premixed with catalyst (2%) and accelerator (1%). Mg powder Grade V (106 g) was placed in a bowl and coated with polymeric binder. Premixed ingredients as stated above were added to coated Mg and hand mixed for half an hour. The whole mixture was then passed through IS 600 µm sieve five times to get a homogenous composition. The composition was finally dried/cured for 18 hours by spreading in aluminium trays.

Characterization

Mechanical Properties:

The compositions were consolidated into pellets of 20 mm diameter and 20 mm height under the load of 3 tons with a dwell time of 15 seconds. The compression strength and percent compression of the pellet were recorded using Instron UTM (Model–1185) as per the American Society for Testing and Materials (ASTM) method.[9]

Thermal Characterization:

i) The heat of combustion was determined by PARR Bomb Calorimeter (300 ml volume) by igniting 1 g of the sample in air as per the ASTM method.[10]

ii) Differential Thermal Analysis (DTA) was carried out using an apparatus fabricated in this laboratory; the details are described elsewhere.[11] Five milligrams of pyrotechnic composition were placed in an open platinum cup and heated simultaneously with an equal amount of reference sample (calcined alumina) in another cup. The temperature difference between the test and reference sample was measured as a function of temperature. To calculate the activation energy of the ignition process of the pyrotechnic composition, DTA runs were recorded at five different heating rates (i.e., 5, 10, 15, 18 and 20 ºC/min). The peak maxima (T_m) thus obtained at different heating rates for various pyrotechnic compositions are given in Table 2. The energy of activation of ignition was determined using the Ozawa[12] and the Kissinger[13] methods. In the Ozawa method, a curve was plotted between the logarithm of the heating rates (β) versus the reciprocal of the peak maxima temperature (i.e., $\log \beta$ vs. $1/T_m$), which gave a straight line, and the energy of activation (E) was calculated from its slope;

$$\text{Slope} = 0.4567/1.987 \times E$$

In the Kissinger method, the energy of activation was calculated by plotting the curve between $\ln \beta/T_m^2$ vs. $1/T_m$, which is also a straight line. The activation energy was then calculated from the slope, similar to the Ozawa method.

Burning Rate and Luminous Output:

The compositions were pressed in paper-lined steel tubes of 20 mm diameter and 30 mm length, under 15 tons of dead load with a dwell time of 15 seconds. The tracer compositions were electrically ignited, and their luminous outputs and burning times were measured using a photometer, (Photometer, Model 550 from M/s EG & G, Massachusetts, USA).

Table 1. Mechanical Properties, Burn Rate and Luminosity of NHP and CP Based Tracer Compositions.

Composition based on	Compression strength (MPa)	Compression (%)	Linear Burn Rate (mm/s)	Mass Burn Rate (g/s)	Luminosity (cd × 10^4)	Efficiency [(cd·s/g)× 10^4]
NHP	32.0	5.8	4.7	3.48	6.329	1.81
CP	41.23	6.7	4.3	3.19	3.692	1.167

Sensitivity:

i) ***Impact sensitivity*** was determined by the fall-hammer method using a 2 kg weight on 20 mg samples, and the height for 50% explosion was recorded.[14]

ii) ***Friction Sensitivity*** was determined on the Julius Peter apparatus using 10 mg samples, and the minimum weight, for which five samples did not ignite, was recorded.[15]

iii) ***Spark sensitivity*** was determined by placing 10 mg samples between two electrodes that were spaced at a distance of 2 to 2.5 mm. The energy of the spark was varied from 15 mJ to 5 J, and the ignition or non-ignition of the samples was recorded.

Results and Discussion

The data on mechanical properties (Table 1) indicate that the tracer composition based on chloropolyester (CP) has higher compression strength and percent compression than the one based on non-halo polyester (NHP). This is attributed to greater tensile strength of CP compared to NHP[16,17] and is reflected in the compression strength of the tracer composition.

Differential thermal analysis data reveals that the T_i and T_m are less for the CP-based composition than the NHP-based composition at all the heating rates. This may be due to the involvement of chloropolyester in the ignition process of the composition. It is consistent with the activation energy of the CP-based composition being less than that of the NHP-based composition (Table 2). Further, heat of combustion data on show that both the compositions release approximately the same amount of heat (Table 3).

The impact, friction, and spark sensitivity data (Table 3) suggest that both compositions are reasonably safe with respect to impact, friction and electrostatic charge. However, the CP-based composition is more sensitive to impact and friction as compared to the NHP- based composition. This is because chloropolyesters are generally rigid as compared to their coun-

Table 2. Peak Inception Temperature (T_i), Peak Maxima Temperature (T_m) and Activation Energy of NHP and CP Based Tracer Compositions.

Composition Based on		Heating Rate (ºC/min)					Activation Energy (kcal/mol)	
		5	10	15	18	20	Ozawa Method	Kissinger Method
NHP	T_i	436	442	451	462	457	34.27	33.1
	T_m	453	458	463	476	479		
CP	T_i	424	429	445	443	447	31.0	29.8
	T_m	442	446	458	465	469		

Table 3. Sensitivity and Heat of Combustion of NHP and CP Based Tracer Compositions.

Composition based on	Friction Sensitivity (kg) (does not ignite until)	Impact Sensitivity (cm) (height for 50% Explosion/Ignition)	Spark Sensitivity (J) (does not ignite until)	Heat of Combustion (cal/g)
NHP	28.8	162.5	3.5	2029
CP	24.0	127.0	3.5	1982

terpart non-halo polyesters.[16,17] As a result, they behave like grit particles in pyrotechnic compositions leading to increases in their impact and friction sensitivity. Similar behaviour is observed in differential thermal analysis.

The data on luminosity and luminous efficiency (Table 1) indicate that the NHP-based composition gives more luminous output. But, as a practical matter, flares filled with NHP-based compositions do not ignite easily, probably due to the higher activation energy of NHP. Further, the CP-based composition intensifies the red colour of the flame, presumably due to the presence of chlorine atoms, which aid in the formation of the red-colour-emitting species.

Conclusions

Tracer compositions are required to give bright red light for better visibility of the tracer both during day and night; therefore, chlorinated binders are preferred, as chloro groups enhance the red colour of the flame. Moreover, the CP-based tracer composition has better mechanical properties than the NHP-based composition. As the tracer compositions have to burn under spin and mechanical stresses, compositions with higher mechanical strength are preferred. While the NHP-based tracer composition gives higher luminous output, it is difficult to ignite, and hence the composition may fail to burn.

On balance, the more intense red colour of the CP-based composition, coupled with its greater mechanical strength, make it the better choice for tracer use.

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