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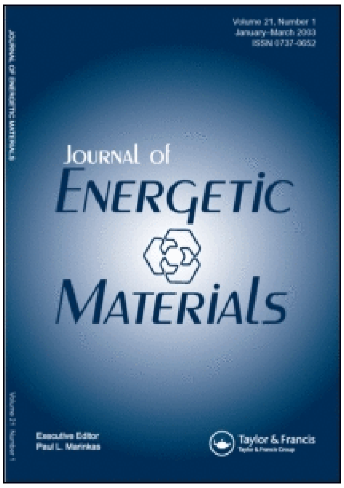

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Studies on a Novel Thermoplastic Polyurethane as a Binder for Extruded Composite Propellants

K. S. Mulage[a]; R. N. Patkar[a]; V. D. Deuskar[a]; S. M. Pundlik[a]; S. D. Kakade[a]; M. Gupta[a]
[a] High Energy Materials Research Laboratory, Pune, India

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K. S. MULAGE
R. N. PATKAR
V. D. DEUSKAR
S. M. PUNDLIK
S. D. KAKADE
M. GUPTA

High Energy Materials Research Laboratory,
Pune, India

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Extruded composite propellant (ECP) is an entirely new thrust area in the development of composite propellants within India. These are based on high-density thermoplastic elastomers as a propellant binder with ammonium perchlorate (AP) as an oxidizer and aluminum (Al) as a metallic fuel. Thus, this class of propellant not only provides higher energy but also yields higher density impulse. There are no pot life problems as with conventional slurry cast composite propellants because the binder used is thermoplastic in nature and hence can be recycled. ECP can take up solid loadings up to 90% and have very good dimensional stability.

The present article reports evaluation of a thermoplastic polyurethane, viz. Irostic, as a binder for extruded composite propellants. The polymer was characterized completely before use. The feasibility of propellant processing has been studied and processing parameters have

Address correspondence to S. D. Kakade, High Energy Materials Research Laboratory, Sutarwadi, Pune 411 021, India. E-mail: sd_kakade@yahoo.co.in

been established. Around 50 propellant formulations are processed for selection and optimization of plasticizer and to investigate the effect of variations in binder content. The results of the propellant characterizations have shown that the binder is capable of imparting significant improvements in mechanical properties and high density. Data generated on burning rate and static evaluation has confirmed that the binder imparts mesa-burning characteristics to the propellant with relatively low temperature sensitivity of burn rate.

Keywords: binder, polyurethane, propellant, thermoplastic elastomer

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Introduction

Composite propellant, by virtue of its high performance, finds wide applications in rocket and missile propulsion. Castable propellants of this class primarily use liquid prepolymer binders, such as hydroxy terminated polybutadiene/carboxy-terminated polybutadiene (HTPB/CTPB), to yield solid propellant grain when cured with a suitable curing agent. Here the pot life/castable life of slurry is limited, as its viscosity starts building up after the addition of curative. However, a slurry casting technique is not production friendly, in terms of economics and time, for small-sized grains required in large numbers; hence, the obvious choice is an extrusion technique [1].

The application of thermoplastic elastomers (TPEs) in the development of extruded composite propellants for rocket motors with performance and physical properties superior to those of conventional slurry cast composite propellant resulted as a spin-off of progress in processing and development of LOVA propellant. Gun propellants containing 80% RDX and thermoplastic elastomers (TPEs) such as ethylene-vinyl acetate (EVA), triblock copolymers of styrene-butadiene/styrene-isoprene (Kraton), polyester MDI urethane (Estane), and copolymer of polybutylene terephthalate-polyether glycol (Hytrel) have been reported to possess superior physical strength and strain capabilities [2,3]. The potential applications of extruded composite propellants are in rockets produced in large numbers for use as gas generators, starter cartridges, source for on-board power supply, etc. The only limitation of this class of propellant is the restriction on outer diameter ($\sim$200 mm) and longer length.

Extruded composite propellant consists of ammonium perchlorate as an oxidizer, aluminum as a metallic fuel, and thermoplastic elastomer as a binder. The development of composite propellants based on high-density thermoplastic elastomers is an entirely new thrust area in the field of rocket propellant.

Extruded composite propellants containing thermoplastic elastomers as polymeric binders have been studied [4]. Due to the thermoplastic nature of the binder, the propellant can be reprocessed and recycled. These propellants have good dimensional stability and the processing time is relatively short. Irostic, a polyester polyurethane, is a thermoplastic elastomer and, because of its favorable density and softening point, it can be used as fuel binder. Irostic as a fuel binder was studied for establishment of process parameters, optimization of binder percentage, and selection of a suitable plasticizer for propellant manufacture and subsequent data generation. The performance parameters of the propellant were evaluated by static firing. In view of higher density impulse [5], a propellant of this kind can find greater use in the system where the propellant burnout mass is very large compared to the propellant volume.

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Experimental

Materials

The TPE binder Irostic used was obtained from M/s. Huntsman International India Pvt. Ltd., Navi Mumbai, India (opaque white-pale yellow pellets, d = 1.20 g/cc,). Ammonium perchlorate (AP, average particle size: 9 μm) received from Tamilnadu Chlorates Ltd., Madurai, India was used as an oxidizer. Aluminum powder procured from Metal Powders Company Ltd., Madurai, India (Madurai; purity 98%, particle size 16 micron) was used as a metallic fuel. Ethyl methyl ketone (MEK) and ethyl acetate (EA) were used as solvents (AR grade).

Characterization

The TPE binder Irostic was characterized by IR spectroscopy (Perkin Elmer FT-IR Spectrometer) and gel permeation chromatography (GPC-Chromline). Thermal analysis was carried out in static air at the heating rate of 10°C/min with alumina as reference standard using Mettler Toledo star system. Glass transition temperature was determined by differential scanning calorimetry (DSC) using a Mettler DSC-30. Mechanical properties of the propellant sample were determined according to ASTM-D-638 using a Hounsfield tensile testing machine. Burn rate was determined in an acoustic strand burner, with a nitrogen atmosphere, in the pressure range of 70–90 kg/cm^2. The density of the propellant was determined via the Archimedes principle. The calorimetric value (cal-val) was evaluated on a Parr adiabatic bomb calorimeter (l00 cc capacity) using 1 g sample in the presence of air. Impact sensitivity was determined by a Fall hammer apparatus using a 2-kg drop weight with a sample weight of 20 mg (Bruceton staircase method) [6]. Friction sensitivity was measured on Julius Peter sensitivity apparatus (BAM, Berlin, Germany).

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Propellant Processing

Binder Solvation and Mixing. The propellant mixing was carried out using a 5-L capacity planetary mixer for batch size of 2 kg. Weighed quantity of Irostic was loaded into the mixer bowl and soaked overnight in MEK+EA (90:10) mixture with binder-to-solvent ratio of 1:3 by weight. The binder was dispersed uniformly in the solvent by mixing for 30 min. A requisite quantity of AP was added in two increments with 15 min intermittent mixing. Weighed quantity of Al was added and mixed for 15 min. Dioctyl adipate (DOA) was added and again mixed for 15 min. The total solid content was varied from 82 to 87%. After complete addition, the slurry was mixed for 30 min, unloaded from the mixer bowl, and spread in aluminum trays in a thin and uniform layer. Solvent was completely evaporated by keeping the slurry in water oven at 70°C for 12–14 h.

Rolling. The resultant rubbery hard dry mass of propellant was then passed through the warm rollers maintained at 70–75°C. Uniform sheets were obtained after 20–25 passes. Propellant discs of 60 mm diameter were then punched from the sheets.

Extrusion. A hand-operated vertical extrusion press of 60 T capacity was employed for the extrusion using two different die configurations: (i) 40 mm diameter and pin size of 20 mm; (ii) 3 mm diameter for propellant strand. Both the dies were made of brass. The jacketed press cylinder and die/pin assemblies were preheated by steam to 65–70°C; the punched discs, also preheated to 50°C, were loaded into the press cylinder and extruded. The extrusion pressure recorded was 60–70 kg/cm^2 for 40 mm × 20 mm grain and 80–85 kg/cm^2 for strands. Propellant flow during extrusion was uniform and no irregular flow patterns were observed. The extrusion rate was observed to be 12–15 mm/min. The extruded grain was tough and found to have a smooth finish and uniform appearance.

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Results and Discussion

Characterization of Polymer

Irostic was completely characterized to ascertain its utility as a propellant binder. The characteristics are summarized in Table 1. The trade polymer is a pure polymer containing no additives or fillers, which has been proved by complete solubility of polymer in acetone forming a true solution.

The high tensile strength of pure polymer (TS = 260 kgf/cm^2, elongation = 800%); relatively higher density (1.20 g/cc), cf. that of HTPB; and softening point are some of the attractive features of Irostic. The polymer has a glass transition temperature (Tg) of −51°C, which can give excellent lower temperature flexibility to the propellant.

Commercial thermoplastic polyurethanes normally consist of three basic components: a polyester or polyether macrodiol, a chain extender such as short chain diol or a diamine, and a bulky diisocyanate.

Table 1
Characterization of TPE binder polymer—Irostic

Chemical class	Linear thermoplastic polyurethane
Density (g/cc) (at 20°C)	1.20
Solubility	MEK, EA, acetone, toluene
M.Wt. (GPC)	
$Mw = 115{,}586$	
$Mn = 12{,}011$	
$PI = 3.16$	
Activation temperature (°C)	80–85
Softening point (DSC) (°C)	52
Glass transition temp (DSC) (°C)	−51
IR Spectra	
Sharp $3347\,cm^{-1}$	$-NH-$ or NH_2
Sharp $2936\,cm^{-1}$	$-CH_2-$
Sharp $2271\,cm^{-1}$	$-N{=}C{=}O$
Sharp $1729\,cm^{-1}$	$-C{=}O$ from ester
peaks around $1600\,cm^{-1}$	Aromatic
1527, 1405, 1173, 1073, 820, 737, & 512	Ester stretching and overtones
NMR Spectra	
7.0 to 7.5 δ	Aromatic protons
3.5 to 4.5 δ	$-O-CH_2$ and $-NH-$ protons
1.8 to 2.5 δ	$-CH_2$ protons
Solubility test	Soluble in acetone forming true solution
Flame test	Yellow flame & drips: Polyester polyurethane
Mechanical properties	
TS (kgf/cm^2)	260
Elongation (%)	800

The IR spectrum has proved that this is a polyester polyurethane (1527, 1405, 1173, 1073, 820, 737, $512\,cm^{-1}$) with MDI as an isocyanate (sharp $2271\,cm^{-1}$ for $-N{=}C{=}O$). NMR spectrum showed chemical shift of aromatic protons at 7.0 to 7.5 and δ,$-O-CH_2$ and $-NH-$ protons around 3.5 to 4.5 δ. Hence, it can be concluded that the polymer is a linear

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polyester polyurethane based on diphenyl methane diisocyanate and is considered a suitable TPE binder for propellant. The simple flame test (yellow flame and polymer drips) also indicate that it is polyester polyurethane elastomer. The IR spectrum can be used as a QC tool for future batches of the polymer.

Selection of Suitable Plasticizer

Three different plasticizers, viz. dioctyladipate (DOA), diethyl phthalate (DEP), and polypropylene adipate (PPA), were tried, keeping the binder percentage constant. Propellant formulations containing AP, Al, and Irostic as binder were processed. It was found that processing with DOA (3%) was easy and improved relative mechanical properties (TS 42–60 kgf/cm^2, elongation of 10–16%) could be obtained compared to those of DEP (TS 30–32 kgf/cm^2, elongation 8–10%) and PPA (TS 35–38 kgf/cm^2, elongation 10–12%). Hence, DOA was selected as a plasticizer for further studies. The plasticization effect was confirmed by lowering Tg by 2–3°C.

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Optimization of Binder Percentage

The effect of binder concentration on physical parameters was studied to optimize the binder percentage in the propellant composition. Variation in Irostic concentration was adjusted

Table 2
Effect of binder percentage variation on physical properties of propellant

		Mechanical properties			
Percentage of Irostic	Density (g/cc)	TS (kgf/cm^2)	%E	E-Mod	Processibility
10	1.82	42	10–12	2500	Very good
12	1.78	51	12–14	2500	Very good
15	1.72	60	15–16	2324	Excellent

by part substitution of AP. The results are summarized in Table 2.

It is clearly seen from Table 2 that this binder is capable of imparting very good mechanical strength to the propellant (of the order of 42 to 60 kgf/cm^2) compared to its HTPB-based analogue manufactured by a slurry cast method. The tensile strength and percentage elongation increase as percentage of binder polymer increases. In all three cases, process parameters were kept constant to study the processibility; in each case, smooth and flawless propellant grains were obtained.

Further, the density decreased from 1.82 g/cc to 1.72 g/cc as the percentage of polymer increased and percentage of solid decreased. The binder polymer can take up to 87% solids and the propellant formulations remain easily processible. The reproducibility was confirmed by repeating the batches three times.

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Energetic and Sensitivity Aspects

The results of burning rates, calorimetric values, and sensitivity are summarized in Table 3. The data generated on burning rate indicate lowering of burn rate with increase in binder content. The pressure index values were remarkably low, and 15% binder content mesa (negative pressure index) burning characteristic was noticed.

Cal-val also shows the similar trend being maximum (1760 cal/g) for the formulation containing Irostic 10%. The values of impact sensitivity (30–34 cm) and friction sensitivity (12–16 kg) are comparable to conventional HTPB-based slurry cast composite propellants (impact 25 cm; friction 10 kg); thus, these propellant compositions are safe for handling and processing. Ignition temperature ranged between 270 and 275°C.

Thermal Analysis

The results of thermal analysis of pure polymer and propellant formulations are summarized in Table 4.

The pure polymer shows two distinct exotherms at 406°C and 506°C. The initial exotherm at 406°C can be assigned to

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Table 3
Energetics and sensitivity

	Burn rate (mm/s)					
Binder percentage	70 kgf/cm^2	90 kgf/cm^2	Cal-Val (Cal/g)	Impact* (cm)	Friction (kg)	Ignition temp. (°C)
10	12.6	12.8	1760	30	12.8	275
12	11.5	11.7	1640	32	14.4	274
15	9.8	9.3	1530	34	16.0	270
CE	—	—	—	46	36.0	—

*Ht. of 50% explosion.

Table 4
Thermal analysis of polymer and propellant composition

	DTA		TGA	
	Exotherm (°C)	Endotherm (°C)	Temp. range (°C)	%Wt. loss
Irostic (pure polymer)	406	—	300–420	72
	506	—	420–600	26
Propellant (AP+Al+Irostic +DOA)	310 362	242	226–380	70

the decomposition of flexible $-CH_2-$ linkage of the polymer and the second exotherm at 506°C can be attributed to the decomposition of hard polyurethane linkage (−NHCOO−). This is in agreement with the decomposition pattern of common polyurethane polymers [7]. This also confirms the stability of polymer up to 400°C. The TGA shows corresponding weight loss of 72% in the temperature range of 300–420°C and of 26% in the temperature range of 420–600°C.

An endotherm at 242°C observed with propellant formulation may be attributed to the phase transition of ammonium perchlorate. A sharp exothermic peak at 310°C can be attributed to the evolution of HCl gas. The decomposition of polymer shifts to lower temperature in the presence of oxidizer and fuel. The corresponding weight loss in the temperature range of 226–380°C is around 70%.

Static Evaluation

The formulation containing 12% binder was selected for further evaluation, and propellant grains of size OD 40 mm, ID 20 mm, and length 65 mm were extruded. After radiographic examination and conditioning at extremes of temperature (+50°C and −20°C), these grains were statically evaluated in a ballistic

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Table 5
Propellant characteristics from BEM firings

η (Pressure range kg/cm^2)	r·, mm/s at 70 kg/cm^2
−0.29 (60–70)	11.6
−0.17 (70–80)	11.9

evaluation motor (BEM). The p-t profile obtained indicates smooth combustion. The data obtained from static evaluation are summarized in Table 5. The performance at extremes of temperature is summarized in Table 6.

The temperature sensitivity of burn rate is of the order of 0.15%/°C between +50 and −20°C. These results also indicate that $(\Pi r)_P$ value between ambient to cold is very low; i.e., 0.04%/°C. The propellant has been further evaluated by cluster firing (cluster of 7 grains of size 40 mm × 20 mm × 180 mm each) and the experimentally determined values of charactersistic velocity (C*) and specific impulse (Isp) are found to be 1576 m/s and 239 s, respectively. The negative pressure index value obtained during BEM firings confirms the observed low η value in the strand burner measurement for the same pressure range.

To study the effect of binder on thermal decomposition of AP, thermal analysis of pure and AP-coated with binder was carried out. DTA analysis showed two-stage decomposition of

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Table 6
Burning rate behavior at extremes of temperature

Sr. no.	Temperature (°C)	r·, mm/s at 70 kg/cm^2	$(\prod r)_P$ %/°C between temperature
1	+50	13.0	0.38 (50°C to amb)
2	Amb (+27)	11.9	0.15 (50°C to −20°C)
3	−20	11.7	0.036 (Amb to −20°C)

pure AP with exothermic peaks at 300 and 410°C and corresponding two-stage weight loss in TGA. In the case of AP coated with Irostic binder, single-stage exothermic decomposition occurred at 300°C and corresponding TGA showed single-stage weight loss. These facts indicate that Irostic definitely plays a significant role in influencing the decomposition of AP. This phenomenon also explains the observed lowering of burn rate in all three compositions and may also be responsible for lowering of η value in the pressure range mentioned earlier. However, detailed study of this phenomenon is under progress and will be reported separately.

Conclusion

TPE-based ECP technology has been established. This technology is more suitable for small diameter grains required in large numbers. This class of propellant offers various advantages, such as very good dimensional stability and relatively short processing time. These have better mechanical properties, higher density, and higher density impulse. Due to the thermoplastic nature of the binder, the propellant can be reprocessed, leading to very low wastage and less environmental pollution. Irostic-based ECP have excellent mechanical properties and very low $(\mathrm{IIr})_{\mathrm{P}}$ value, exhibit mesa-burning in the useful pressure range of 60–75 kg/cm^2, and delivered Isp of 239 s. These features underline the potential Irostic-based ECP hold for futuristic applications.

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