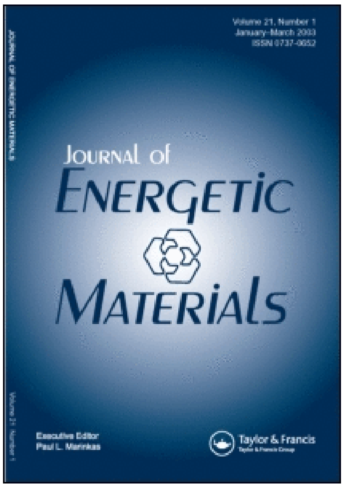

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STUDIES ON THERMOPLASTIC ELASTOMERS BASED RDX-PROPELLANT COMPOSITIONS

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ABSTRACT

This paper presents the results obtained during studies on 80% RDX propellant systems based on thermoplastic elastomers (TPEs) namely ethylene-vinyl acetate (EVA), triblock copolymers of styrene-butadiene/styrene-isoprene (Kraton), poly-urethane-ester-MDI (Estane) and copolymer of polybutylene terephthalate - polyether glycol (Hytrel) as binders, Dioctyl phthalate (DOP), triacetin (TA) and glycidyl azide polymer (GAP) were incorporated as plasticizers in the formulations. An attempt has been made to correlate structural features of TPEs with mechanical properties as well as glass transition temperature (Tg). Results obtained suggest that TPE-based RDX-propellants have the advantage of high insensitivity to impact and friction stimuli vis-à-vis nitrte ester based conventional propellants. EVA based propellants gave the best results in this regard. Ignition temperature for all the compositions was >200°C. EVA, Hytrel and Estane based formulations were found to be more energetic than Kraton based formulations. Incorporation of GAP resulted in the improvement in ballistics (Impetus and burn rates) as compared to DOP plasticised formulations. TA based compositions gave an intermediate value. Thermal decomposition pattern was determined by applying Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC). An attempt has been made to explain the trends observed on the basis of the evidences generated during this study and theories proposed by other researchers.

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INTRODUCTION :

Thermoplastic elastomers (TPEs) offer tremendous advantages to the formulator of solid propellants like simplified processing, greater dimensional stability/control and lower production – losses[1]. Typical structural features are also expected to contribute towards superior insensitivity characteristics (high figure of insensitivity) and mechanical properties of the system. Moreover, inherent elastomeric nature of TPEs results in propellant systems with greater resistance to hyper velocity impact from warhead fragments and charge jets as well as to sympathetic detonation[2]. In view of these advantages, TPE based gun propellants are expected to replace existing double and triple base systems. They are also having scope of application in the field of rocket propellants and explosives[3]. Basically, thermoplastic elastomers are copolymers of ABA or AB type, where A & B are hard and soft segments respectively. The hard segment is capable of crystallisation or association leading to thermoplastic behaviour, whereas the soft segment provides elastomeric characteristic to the copolymer[4]. As a consequence, TPEs offer advantages of desired cohesive strength upto moderately high temperatures and flexibility even at sub-zero temperatures.

During this work, commercially available TPEs namely, ethylene-vinyl acetate (EVA), triblock copolymers of styrene-butadiene/styrene-isoprene (Kraton), poly-urethane-ester-MDI (Estane) and copolymer of polybutylene terephthalate - polyether glycol (Hytrel) were characterised. In the next phase, RDX propellants based on TPE binders were evaluated for their physical, thermal and ballistic characteristics. Effect of incorporation of dioctyl phthalate (DOP), triacetin (TA) and glycidyl azide prepolymer

(GAP) as plasticizer was also studied. An attempt has been made to evolve a mechanism to explain the trends observed.

EXPERIMENTAL :

The TPE binders evaluated during this work i.e.EVA, Kraton (copolymers of styrene-isoprene [S-I-S] and styrene-butadiene [S-B-S]), Estane and Hytrel were procured from trade. TPEs were plasticised with DOP, TA and GAP. RDX of 5μ particle size (80% particles of size ranging from 3-15 μm, 10% particles >15 μm and 10% particles < 3 μm as per spectrum, obtained by Malvern instrument) was selected to obtain propellant formulations of desirable combustion characteristics (elimination of slope break)[5,6,7]. The propellant compositions comprised of 80% RDX, 16% TPE binder and 4% plasticizer. The formulations were prepared by solvent technique. TPEs were solvated with plasticizers and required quantity of solvent (toluene/acetone/chloroform) in a sigma blade mixer. RDX was added in small installments to the solvated binder matrix. Mixing was carried out for two hours. Subsequently, the mix was dried at 40°C to remove the solvent. Dried material was hot rolled at 60-80°C to obtain defect-free extrudable propellant sheets without voids.

The molecular weight of polymers was determined prior to mixing by using gel permeation chromatography (GPC) technique with refractive-index detector where mixed bed columns of Type B were used. The thermochemical parameters were theoretically computed by applying computer software (Therm) developed by HEMRL[8]. The ballistic parameters were obtained by combusting propellant sample in ribbon form in a 100 cc closed bomb at 0.2 g/cc loading density. Data obtained on closed vessel (CV) firing was acquired using piezoelectric gauge in conjunction with indigeneously developed data acquisition system. All the experiments were performed on the propellant samples conditioned at 30°C. The impact sensitivity was determined on a 20 mg sample using 2 kg free-fall weight by applying Bruceton Staircase Method[9]. The drop height corresponding to the 50% probability of initiation (h_{50}) was determined by conducting series of experiments. Figure of Insensitivity (F of I) was computed by selecting tetryl as reference (h_{50} = 104 cm). Friction sensitivity was obtained by testing 5 mg sample in Julius Peter's Apparatus. All the experiments were conducted under controlled R_H (< 60%) and temperature (30 ± 1°C) conditions. Ignition temperature was determined by Julius Peter's Apparatus at a heating rate of 5°C/minute. Thermal studies were carried out on Differential Thermal Analyser (DTA), and Differential Scanning Calorimeter (DSC). DTA was undertaken on indigeneously fabricated instrument (heating rate of 10°C/min in a static air medium) and DSC was carried out (at a heating rate of 10°C/min in N_2 atmosphere) using instrument of Perkin Elmer Make. The mechanical properties i.e. tensile strength TS (maximum stress a material is capable of sustaining) and percentage elongation, %E (percentage increase in length of a sample under tension) of sample (ASTM standard D 638), were determined using Instron Universal Testing Machine Model No.1185.

RESULTS & DISCUSSION :

POLYMERS

Molecular Weight & Mechanical Properties

The molecular weight of EVA, Kraton and Estane ranged from 67051 – 86524. Hytrel was of relatively lower molecular weight (46099). As regards mechanical properties, S-I-S Kraton exhibited the highest %E (1062) but its TS (25 kg/cm^2) was on lower side as compared to other TPEs studied. S-B-S Kraton exhibited almost double TS with 30% less elongation. Relatively superior TS was obtained in case of Estane (124 kg/cm^2) with equally good %E (911). TS of EVA (66 kg/cm^2) was almost half to that of Estane but its % E (904) was comparable. Hytrel gave almost similar TS, however its %E (306) was the lowest among all the TPEs evaluated (Table-1).

DSC

In DSC experiments (Table-1), Tg obtained for S-I-S Kraton was the lowest (-34°C) while that for S-B-S Kraton was found to be the highest (-8°C). Other TPEs gave intermediate values (-14 to -17°C). Softening temperatures for EVA and Estane were found to be ~55°C while those for Kraton and Hytrel were relatively higher (80-89°C). EVA decomposed giving two endotherms at 350 and 479°C while Estane gave an endotherm at 380°C. S-I-S Kraton exhibited single exotherm (379°C). In case of S-B-S Kraton and Hytrel two stage exothermic decomposition was observed in the temperature range of 370 - 380°C and 450 - 550°C.

PROPELLANT FORMULATIONS :

Sensitivity :

F of I of EVA based formulation was 78 with DOP as plasticiser while it was relatively higher for TA plasticised composition (84) and relatively lower (62) for the composition containing GAP as plasticiser. More or less similar trend was observed with other TPEs evaluated during this work. All the formulations were found to be almost insensitive to friction stimuli. Among the TPEs, the best results were obtained with EVA in terms of F of I (Table-2).

In general, TPE-based formulations studied during the work have the advantage of much lower sensitivity (F of I 43-84 and no initiation till 32.4 – 36 kgs) than the conventional double and triple base propellants (h_{50}, 18 – 28 cm and Friction sensitivity 16.8 - 19.2 kg).

Ignition Temperature :

The ignition temperature of all the formulations was found >200°C. DOP plasticized formulations gave ignition temperature in the range of 202-237°C while that for TA based formulations varied in the region of 208-245°C. GAP plasticized formulations gave ignition temperature of the order of 200-230°C. Relatively lower ignition temperature of GAP plasticized composition may be attributed to its relatively lower decomposition temperature than RDX. In all the cases, Kraton based formulations gave relatively lower ignition temperature (Table-2).

The higher ignition temperature of these propellants in comparison to conventional double/triple base propellants establishes their superiority in terms of vulnerability to ignition.

DSC :

TPE based RDX-propellants exhibited single endotherm (196 - 206°C) and exotherm (211 - 244°C). EVA and Estane based formulations liberated 1465 – 1780 J/g during exothermic decomposition while Kraton and Hytrel based formulations liberated 1720 –2650 J/g (Table-3).

Ballistics :

The theoretical computation of ballistic parameters brings out that Kraton based formulations are relatively less energetic (F = 870 – 982 J/g) while Hytrel based formulations are more energetic (955 – 1022 J/g). The results obtained reveal F of I of the order of 870 – 955 J/g for DOP plasticized compositions, while that for GAP plasticized compositions varied from 952-1022 J/g. TA plasticized formulations gave intermediate values (897-983 J/g). The values obtained can be directly co-related with the trend observed for flame temperature (1802-2532 K, 1909-2612 K and 2028-2688 K for DOP, TA and GAP based formulations respectively). CV firing experiments gave F values in close agreement with the theoretically computed data (Table-4). The pressure – burn rate relationships (where r is in cm/s and pressure is in MPa) for various systems obtained during CV firings are summarised below.

$r = 0.0261\ P^{1.08}$ $r = 0.0454\ P^{1.1}$ $r = 0.0733\ P^{1.0}$

DOP TA GAP

EVA Based Formulations

$r = 0.0274\ P^{0.94}$ $r = 0.0664\ P^{0.96}$ $r = 0.0969\ P^{0.87}$

DOP TA GAP

S-I-S Based Formulations

$r = 0.0349\ P^{1.10}$ $r = 0.0594\ P^{1.11}$ $r = 0.0625\ P^{0.97}$

DOP TA GAP

S-B-S Based Formulations

$r = 0.037\ P^{1.13}$ $r = 0.062\ P^{1.15}$ $r = 0.077\ P^{1.05}$

DOP TA GAP

Estane Based Formulations

$r = 0.1813\ P^{1.06}$ $r = 0.2019\ P^{1.08}$ $r = 0.2152\ P^{1.01}$

DOP TA GAP

Hytrel Based Formulations

These results suggest that Hytrel based formulations followed by EVA and Estane give relatively higher burn rates than Kraton based propellants. In all the cases GAP – plasticised formulations gave superior burn rates. The compositions exhibiting pressure index value of the order of 1/<1 can be directly used for practical applications while formulations with higher pressure index value may require tailoring for actual application.

Mechanistic Approach :

Relatively lower TS values of Hytrel may be a direct consequence of low molecular weight of the polymer as compared to other TPEs studied as well as presence of relatively higher proportions of ether units. In case of Kraton, S-B-S system exhibits higher strength than S-I-S system while latter is more flexible. This trend may be attributed to the presence of C=C bonds of butadiene component in the polymer back bone. Flexibility of isoprene units may be due to pendant CH_3 groups. This feature also explains the lowest Tg of S-I-S Kraton among selected TPEs. EVA gives desired TS and elongation combination. This may be due to regular spacing of pendant acetoxy groups. Estane exhibits superior TS and high elongation combination which can be correlated with the presence of aromatic ring in the polymer back bone and involvement of urethane linkages in hydrogen bonding between polymer chains. Low molecular weight chain extender with urethane linkage provides locking units for long chain of soft flexible aliphatic polyether/polyester[10]. Relatively better mechanical properties of EVA and Estane based formulations can also be explained on the basis of these trends.

Superior insensitivity characteristic of TPEs based formulations can be attributed to the elastomeric nature of TPEs conferred-on by soft blocks. Increase in the elasticity of TPEs during hot spot formation by impact/friction stimuli may also be responsible to the reduction of inter crystalline friction. The best results obtained with EVA may be attributed to the lubricity offered by ethylene moiety of optimum chain length[11]. Moreover, vinyl aetate units provide polar groups (Lewis Base) which are attracted to the surface of RDX due to their affinity to nitro groups (Lewis acids) providing effective protective barrier[12]. Basically, plasticisers tend to diffuse between the attached segments of the binder (resulting due to localised physical/polar interactions), thereby weakening the forces of attraction and facilitating the global Brownian motions. These factors result in an increase in the elasticity of the system and, thereby greater capability to withstand impact/friction/shock stimulii. Relatively higher F of I of TA plasticised compositions than that of DOP plasticised composition may be due to its higher plasticisation efficiency. This may be due to the fact that the steric factors arising due to large size of DOP molecule hinder its penetration between binder segments. Lower F of I of GAP plasticized composition may be due to its inherent energetic nature. It may also be having relatively less plasticisation efficiency probably due to the presence of polar centres in its own structures. Higher ignition temperature of systems studied during this work as compared to conventional nitrate ester based propellant is a consequence of high thermal stability of RDX as well as establishes its compatibility with TPE binders.

Two stage endothermic decomposition of EVA observed during DSC, can be explained on the basis of the fact that the deacetylation reaction commences in the first stage followed by the main chain scission in the second stage. These findings are in line with the mechanism proposed by Dutta et.al[13].

Estane undergoes one stage endothermic decomposition probably involving dissociation into free isocyanate and alcohols. However, Hytrel unlike EVA undergoes

2 stage exothermic decomposition. The first stage of decomposition may be involving cleavage of the ester linkage followed by immediate exothermic interaction of decomposition products leading to the formation of stable conjugated aromatic acyl compounds. The second exothermic step may be involving recombination reactions of these products. In case of Kraton, the initial stage of decomposition may be involving cleavage of aromatic and aliphatic units followed by rapid recombination of aromatic degradation products resulting in overall exothermicity. Second prominent exotherm observed in case of S-B-S Kraton unlike S-I-S Kraton may be attributed to the involvement of C = C bonds in further recombination reactions as in case of HTPB[14] The endotherm obtained during DSC of TPE based RDX propellants corresponds to the melting process of RDX while single exotherm can be attributed to the decomposition of RDX and binder mixture.

Relatively lower decomposition temperature was observed for TA and GAP plasticized formulations with Kraton binder as compared to other systems studied. There is a possibility that Kraton being oxygen deficient forms a carbonaceous fine structure on the surface. Higher oxygen balance of TA may be responsible for relatively higher extent of oxidative reactions near the surface. In case of GAP, carbonaceous fine structure may be resulting in the retention of GAP in close proximity of reactions, leading to the catalysis of the overall degradation reaction due to exothermic decomposition of azide structure of GAP[15]. Such factors may also be responsible for an increase in the heat release during decomposition observed in case of GAP plasticised formulations.

The relatively lower energetics of Kraton based formulations may be due to the lack of oxygen in their structure in contrast to EVA, Estane and Hytrel. Wise etal[2] have also reported lower performance of Kraton based formulations. Relatively superior performance of TA based formulations as compared to DOP plasticized compositions can be directly co-related with the superior oxygen balance of the former. Compositions plasticized with GAP gave the best results. This can be explained on the basis of positive heat of formation of GAP (+28 kcal/mol) and release of 170 kcal/mol energy on cleavage of azide bond during combustion[15]. An interesting observation was relatively lower pressure exponent value of GAP based formulations despite high burn rates. It has been established that exothermic cleavage of azide bond occurs in condensed phase/near condensed phase. The energy released during this process may be rendering the combustion relatively less dependant on gas phase reactions and, thereby chamber pressure. These findings are in line with those reported by other researchers[16-18].

CONCLUSION :

Estane followed by EVA offers superior combination of strength and strain capability. TPEs evaluated during this work have desirable Tg except S-B-S Kraton. TPE based formulations offer advantage of low vulnerability and high ignition temperature than current double/triple base propellants. EVA based formulations were found to be superior with respect to insensitivity characteristics. In terms of energetics, Hytrel based formulations followed by Estane/EVA based compositions are superior to Kraton based compositions.. Thermal decomposition pattern brings out that the presence of C=C in the backbone contributes towards exothermic second stage decomposition of polymer. The overall thermal decomposition pattern establishes that RDX and TPE binder undergo decomposition as a mix.

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TABLE-1 :* PHYSICAL & THERMAL CHARACTERISTICS OF TPEs

Properties	EVA	S-I-S	S-B-S	Estane	Hytrel
Molecular Weight	67051	86524	74949	71879	46099
Mechanical Properties					
TS, kg/cm^2	66	25	56	124	63
% E	904	1062	704	911	306
DSC					
Tg, °C	-21	-34	-14	-17	-17
H_f J/g	8	0.5	6	10	12
Softening Temp °C	57	80	81	55	89
H_f J/g	4.1	0.3	0.8	42	
I Endo/Exo, °C	Endo 350	Exo 373	Exo 379	Endo 380	Exo 370
H_f J/g	229	166	415	42	402
II Endo/Exo	Endo 479	--	Exo 477	--	Exo 550
H_f J/g	349		164		183

TABLE-2 : RESULTS OF SENSITIVITY TESTS ON RDX PROPELLANTS WITH TPE BINDERS

	Compositions														
	I			II			III			IV			V		
	EVA			S-I-S			S-B-S			Estane			Hytrel		
Parameters	DOP	TA	GAP	DOP	TA	GAP	DOP	TA	GAP	DOP	TA	GAP	DOP	TA	GAP
Impact Sensitivity (Ht for 50% explosion h_{50}, cm)	117	125	92	100	114	82	87	107	63	90	112	79	82	97	76
F of I	78	84	62	67	77	55	59	72	43	61	75	53	55	65	51
Friction Sensitivity (Insensitive upto, kg)	36	36	36	36	36	36	36	36	32.4	36	36	36	36	36	32.4
Ignition temp, °C	228	236	227	202	215	200	205	208	200	237	245	226	233	235	230

Reference sample : Composition exploding (Tetryl) where h_{50} = 104 cm, R_H = 60%, R_T = 30°C during tests

TABLE-3 : DSC AND DTA OF TPE BASED RDX PROPELLANT

Technique	EVA			S-I-S			S-B-S			Estane			Hytrel		
	DOP	TA	GAP	DOP	TA	GAP	DOP	TA	GAP	DOP	TA	GAP	DOP	TA	GAP
DSC															
Endo, °C	206	206	206	206	206	206	203	197	196	202	203	202	204	204	198
H_f, J/g	110	110	173	136	142	147	147	58	126	94	90	87	100	101	133
Exo, °C	242	244	239	240	211	224	225	219	221	241	241	240	235	236	238
H_f, J/g	1778	1757	1634	1986	2849	2038	2265	1713	2640	1465	1753	1648	2082	2107	2204
DTA															
Endo, °C	210	210	210	215	210	215	210	212	200	215	215	212	212	218	212
Exo, °C	220	225	220	220	205	210	222	205	210	225	225	214	225	223	223

TABLE-4 : BALLISTIC DATA ON TPE BASED RDX PROPELLANT

	Compositions														
	I			II			III			IV			V		
	EVA			S-I-S			S-B-S			Estane			Hytrel		
Parameters	DOP	TA	GAP	DOP	TA	GAP	DOP	TA	GAP	DOP	TA	GAP	DOP	TA	GAP
Theoretical															
Flame Temp, K	2462	2571	2688	1802	1909	2028	1894	2002	2123	2410	2522	2641	2532	2612	2682
Force Constant, J/g	945	983	1013	870	897	952	901	928	982	945	969	1015	955	981	1022
Pmax, MPa	274	276	288	230	235	250	238	243	257	262	264	276	232	241	258
CV Firing															
Force Constant, J/g	951	987	1016	880	909	925	901	911	912	951	975	1011	955	994	1017
Pmax, MPa	264	272	280	227	231	245	227	239	251	256	259	270	228	237	252
β_1, *cm/sec/MPa*	0.026	0.045	0.073	0.027	0.066	0.096	0.034	0.059	0.062	0.037	0.062	0.077	0.181	0.209	0.215
α	1.08	1.1	1.0	0.94	0.96	0.87	1.10	1.11	0.97	1.13	1.15	1.05	1.06	1.08	1.01