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Effect of Additives on Liner Properties of Case-bonded Composite Propellants

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ABSTRACT

A thin layer of liner is applied to ensure a good bond between the insulator and the propellant in case-bonded rocket motors. It also acts as a protective shield for the insulator by providing a limited fire protection effect. Liner compositions should preferably be based on the same binder system used in the propellant formulations. As the liner has to hold the propellant and the insulator without debond under all the environmental conditions, it plays a key role in predicted performance of a rocket motor. Hence, studies were carried out to improve the liner properties using various hydroxyl compounds, such as butanediol, cardanol, trimethylol propane, pyrogallol, etc as additives. Butanediol and phloroglucinol combination gave the best results in terms of mechanical properties and interface properties for the liner compositions. The effect of filler content on the liner properties was also studied. The results showed that higher filler content does not affect interface properties. Considering the fire retardancy effect and reinforcement of antimony trioxide (S£$_2$0$_3$), the formulation containing higher Sb_2O_3 was selected. The studies on pot life/castable life of liner showed that propellant could be cast up to 6 days after liner coating, without adversely affecting the bonding and the bond strength.

Keywords: Insulator, liner, interface property, composite propellant, castable life, case-bonded rocket motor, liner compositions, solid rocket propellants, case-bonded composite propellant additives, polyurethanes, peel-off strength

1. INTRODUCTION

Solid rocket propellants are basically of two types, cartridge-loaded and case-bonded. Cartridge-loaded systems are simple and are preferred for defence applications when dimensions are small and the requirement is for large numbers. However, for meeting the requirements of longer ranges and higher payload-carrying capacity, large sized, case-bonded propellant is a preferred choice. The case-bonded motor primarily consists of a motor case, an insulator, a liner, and a propellant as major subsystems. Liner is basically an elastomeric material applied between the insulator and the propellant to improve the interface properties between the two and to hold the propellant to the insulated motor case without debond under all the environmental conditions.

To ensure better compatibility and improved bonding with the propellant, liner compositions should preferably be based on the same binder system, used in the propellant formulation. Hydroxyl-terminated polybutadiene (HTPB)-based composite propellants are widely used in present-day rocket motors and their ageing characteristics

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have been well-established. Nowadays, HTPB-based polyurethanes are finding applications in liner compositions.

Maucourt[1] has patented HTPB-IPDI-based polyurethane composition for coating the inner surface of a propulsion unit. This has been used for a butalene propellant by spraying the diluted solution on the insulator. Giants[2] has described a liner system for case-bonded rocket motors. This liner composition consists of HTPB (RM-45), dimeryl diisocyanate (DDI), and carbon black as a filler, and aziridine-based bonding agent. The mixture is coated on an ethylene propylene diene monomer (EPDM) insulator and it has been claimed that this liner system developed prevents plasticiser migration from the .propellant to the insulator. Probster[3] also reported the liner composition based on HTPB-IDP-HMDI and oxamide for rocket motors insulated by EPDM or PBAN rubbers. Haska[4], *et al.* have reported the studies on adhesive properties of HTPB-IPDI-based liner elastomers with composite matrix and metal case. The effects of *R* values, triol/diol ratio, and methyl aziridine phosphine oxide (MAPO) concentration on the adhesive nature of the metal-elastomer-matrix system have been investigated by tensile and peel test methods. Hemminger[5], Wrightson[6]-[7], and Pierce[8] reported the HTPB-based composition of liners for case-bonded rocket motors. A detailed study of effect of propellant formulations on liner properties, performance at extremes of the propellant operating temperatures, and ageing has been reported by Kakade[9]. The effect of various additives and filler quantities on liner properties has also been reported in this paper.

A liner formulation based on HTPB as a basic resin with different fillers and crosslinking agent along with a well-known tackifier and curative was developed. The effect of filler quantities and different additives on liner properties and peel-off strength has been studied on a typical composite propellant used for a case-bonded booster. The pot life/castable life of the liner has also been evaluated with the same propellant composition.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

The hydroxyl-terminated poly butadiene (mol.wt. *Mn:* 2200-3000 and *-OH* value: 40-50 mg *KOHIg)* was used as the basic polymeric binder. The filler combination was antimony trioxide (Sb_2O_3) (purity 98 %) and carbon black (rubber grade, N-550) with capolyte (CP-70) as a tackifier. Trimethylol propane (TMP), pyrogallol, phloroglucinol (AR grade, purity > 98 %) were used as a crosslinking agent in the polyurethane formulations. Toluene-diisocyanate (TDI) was used as a curative with 99 per cent purity. Dichloromethane ($C7/_2C7_2$, AR grade) was used as a carrier solvent for dilution of the liner material. A nitrile rubber-based insulator was used.

2.2 Characterisation of Liner Material

Mechanical properties of the liner formulation were tested according to ASTM- D-638 using tensile testing machine (Instron 1185). Peel-off strength was measured by wheel peel or drum peel (90° peel) method[10] using tensile testing machine. Shore hardness A was measured by Shore hardness A tester (SHR-4 111). Thermal conductivity was measured using heat flow meter thermal conductivity tester (TCMH-DV), and the glass transition temperature was determined by differential scanning calorimetry studies (Mettler DSC-30). The limited oxygen index number values were determined using oxygen index tester (CS-1788).

2.3 Preparation of Liner Material

All-solid ingredients were dried in an oven at 100 ± 2 °C for minimum 4 h (moisture content < 0.1% by Karl Fischer). HTPB was deaerated under vacuum (<10 torr) in a vertical planetary mixer with continuous hot water circulation (60 °C) for 30 min. The minor additives, such as crosslinking agent, tackifier, and chain extender were added and mixed for 30 min. Carbon black was added in two equal installments and mixed for 10 min. Antimony trioxide was added in two equal installments and mixed for 10 min. The mixing was continued for 60 min without vacuum and then for 60 min in

Table 1. Castable life/pot life of liner formulation

Castable life/pot life of liner (h)	24	48	72	96	120	144	168
Peel-off strength of liner (kgf/cm)	1.56	1.48	1.52	1.50	1.48	1.42	1.36

vacuum. The isocyanate is to be added when the liner is required to be applied on the insulator. All these operations were carried out under controlled humidity 55 ± 5 per cent.

2.4 Application of Liner/Casting of Propellant

The insulator sheets/insulated rocket motors were abraded, cleaned by trichloroethylene to remove oily or greasy matter and kept in an oven at 80 ± 2° C for 2-3 h for evaporation of the,«olvent. The liner was diluted with dichloromethane (CH_2C1_2) in 1:1 proportion and mixed thoroughly for 5 min using a mechanical stirrer. Thin layer of the liner was applied on insulator using a brush or a spray gun, depending upon the size of the rocket motor. The liner coated sheets/motors were preserved under vacuum till casting of the propellant*.

HTPB-AP-A/-based composite propellant was cast in the rocket motors and control moulds, cured and subjected to nondestructive testing.

A study on the pot life/castable life of the liner was carried out by coating the insulator sheets with the liner for 7 days at uniform time intervals of 24 h. The coated sheets were preserved under vacuum. The propellant was cast and the peel values determined after curing of the propellant was complete. The propellant composition was kept the same throughout.

3. RESULTS & DISCUSSION

3.1 Pot Life/Castable Life of Liner

The liner formulation must be in a semi-cured condition (ie, tacky) at the time of propellant casting so that the optimum bonding between the insulator and the propellant is achieved. If the liner is partially cured and is in a fluid state, it may flow along with the propellant slurry during casting of the propellant, resulting in poor interface bonding.

Sometimes, propellant casting may be unduly delayed due to unforeseen reasons. In such situations, liner must remain in a semi-cured condition for sufficiently long period to ensure satisfactory bonding, inspite of the delayed propellant casting. Hence, the study on the pot life/castable life of a liner is necessary.

The liner was coated on the insulator surface keeping a fixed time interval of 24 h up to 7 days. Propellant was cast, cured, and interface properties were determined. The results are summarised in Table 1.

The results of peel-off strength show that up to 144 h, there is no adverse effect on the peel value and the load versus displacement graph was smooth. After 144 h, the peel-off strength decreased marginally but the load versus displacement graph showed some variations. The failure was always cohesive in propellant. Hence, it can be concluded that propellant can be safely cast up to 6 days of liner coating without affecting the interface properties.

The reproducibility and repeatability of the peel-off strength was confirmed by repeating the experiment. The liner used for this experiment contained nBD-pyrogallol combination. Pyrogallol and phloroglucinol are isomers and the trend of peel-off strength observed will not change-off, and hence, the same experiment was not repeated with other formulations like nBD-phloroglucinol combination. The basic criteria for castable life is the maximum peel-off strength and the excellent processibility where the liner is in tacky condition and does not flow along with the propellant.

3.2 Effect of Additives on Liner Formulation

To increase the mechanical properties of liner formulation and interface bond strength between the propellant and the insulator, various combinations of hydroxyl containing compounds were evaluated

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*The propellant must be cast before the liner loses its tackiness.

Table 2. Effect of additives on liner properties/interface properties

Ingredients	Tensile strength (kgf/cm^2)	°?£V°^{n} *(%)*	Peel-off strength (kgf/cm)*
Cardanol-TMP	21-25	57- 75	1.21
Cardanol-pyrogallol	24-29	79- 84	1.32
Cardanol-phloroglucinol	29-34	97-107	1.38
nBD-TMP	22-26	70- 90	1.30
nBD-pyrogallol	25-30	80-95	1.45
nBD-phloroglucinol	41-43	100-119	1.68

* Propellant was cast after 24 h of liner coating. Failure always cohesive within the propellant.

using toluene-diisocya/nate as^a curative. The results are summarised in Table 2. Cardanol is a long chain phenol, which acts as a reactive plasticiser for the basic HTPB matrix of the liner. Cardanol in combination with phloroglucinol showed the highest tensile strength (29-34 kgf/cm^2, percentage elongation = 97-107) with the maximum peel-off strength (1.38 kgf/cm) with the propellant. Trimethylol propane is an aliphatic hydroxy compound, which is more hygroscopic and has limited solubility in HTPB matrix as compared to pyrogallol and phloroglucinol, and hence, gave lower peel-off strength and mechanical properties. Pyrogallol is a 1,2,3-trihydroxy benzene, and phloroglucinol is a symmetric isomer (1,3,5-trihydroxy benzene). Phloroglucinol showed higher mechanical properties and higher peel-off strength probably because of symmetric polyurethane network formation. Both the isomers have better solubility in HTPB matrix and are less hygroscopic as compared to trimethylol propane. The same trend was observed for these crosslinkers in combination with nBD. Mechanical properties and peel-off strengths are on the higher side as compared to formulations using cardanol. This may be attributed to the two hydroxyl groups of nBD acting as chain extenders in the polyurethane matrix. «BD and phloroglucinol gave the best results in terms of the mechanical properties and interface properties for the liner formulations (tensile strength = 41-43 kgf/cm^2, percentage elongation = 100-119, and peel-off strength = 1.68 kgf/cm).

Table 3. Characteristics of liner formulations L_1 and L_2

Characteristics of linear formulation	*L,	**L2
Tensile strength (kgf/cm^2)	29-34	27-30
Elongation (%)	97-107	110-120
Density (g/cc)	1.20	1.06
Hardness (Shore A)	75-80	70-75
Peel-off strength (kgf/cm)	1.3	1.3
Thermal conductivity (w/m/°k)	0.0743	0.0923
Limited oxygen index (LOI) (number)	17	18
Glass transition temperature(°C)	-77	-77

* L, = Filler content (24 % Sb_2O,+ 10 % carbon black)
** L_2= Filler content (10 % $Sb.f>_3$ + 10 % carbon black)

3.3 Study of Filler Content

The liner formulation contains HTPB as base polymer, hydroxyl-terminated additives, fillers, and a curative. Combination of carbon black and Sb_2O^ was used as a filler. Carbon black acts as a reinforcing filler and Sb_2O_3 gives fire retardancy as well as reinforcement to the formulation. The formulation L, contained 34 per cent filler (24 % Sb_2O_3 + 10 % carbon black) and cardanol-phloroglucinol combination. Due to higher Sb_2O_3 content, this formulation had settling problems, hence, a formulation L_2 was tried. L_2contains 20 per cent filler (10 % Sb_2O_3+ 10 % carbon black) and cardanol-phloroglucinol combination. The properties of both the liner formulations, L_t and L_2 are reported in Table 3.

It was observed that tensile strength decreased (L, = 29-34 kgf/cm^2, L_2 = 27-30 kgf/cm^2) with increase in percentage elongation (L, = 97-107 %, L_2=110-120 %). This may be attributed to reinforcing effect of Sb_2O_y

The lower values of hardness (Shore A) and density for the formulation L_2 can be very well explained by lower percentage of high density filler Sb_2O_3 (d = 5.67 g/cc). The values of peel-off strength with propellant remains the same (1.3 kgf/cm) for both the liner formulations.

The limited oxygen index (LOI) number values also showed marginal change (L,: 18, L_2: 17). The effect on fire retardancy was studied in depth by thermal analysis of both the liner formulations.

Table 4. Thermal analysis of liner compositions

Liner Comp	DTA exotherm (°C)	TGA		
		Stage	(%) Wt loss	Temp range (°C)
L,	360	I	6.0	248-337
	451	II	46.3	427-497
	523	III	22.8	500-557
L2	404	I	7.5	248-337
	446	II	17.6	407-437
	516	III	61.0	447-528

3.4 Thermal Analysis

The results of thermal analysis of the liner formulations L_1 and L_a are summarised in Table 4. The DTA curves for both the liner formulations showed two small exotherms and one big sharp exotherm. The first two exotherms can be assigned to the decomposition of flexible polybutadiene part of HTPB and flexible part of indene-coumarone resin (capolyte) (ie, exotherms at 360 °C, 451 °C for L_l and 404 °C and 446°C for L_2). The major exotherm (at 523 °C for L, and 516°C for L_2) can be assigned to decomposition" of the hard urethane linkage *(-NH-COO).* The decomposition pattern of both the liner formulations is similar. Both showed three-stage weight loss. In case of L_p the second stage showed maximum weight loss of 46.5 per cent within temperature range 427-497 °C, while L_2 shows maximum weight loss of 61 per cent around 447-528 °C.

The overall results show that the decomposition patterns of both the formulations are similar as the basic ingredients are the same. Antimony trioxide is a well-known fire retardant filler and fire retardancy can be very well explained. Antimony trioxide reacts with the decomposition products of the composite propellant like *HCl* and $C1_2$ to produce antimony trihalide or antimony oxyhalide, which are the flame retardant antimony species. The studies reported above pertain to the effect of filler content (Sb_2O_3) on the liner properties and fire retardancy, which will not be affected by additives, such as nBD or cardanol.

Hence, considering the above facts and observing no change in the interface properties, (peel-off strength 1.3 kg/cm for both the formulations) the formulation L, was finalised and evaluated in 40 kg ballistic evaluation motors and in full-scale motors.

3.5 Static Evaluation

The efficacy of interface properties of the liner formulation with 34 per cent filler and nBD-phloroglucinol was studied at extremes of propellant operating temperatures (from -20 ° C to + 50 °C). The peel-off strength observed was 2.0 kg/cm at - 20 °C and 1.3 kg/cm at + 50 °C. In all the cases, failure observed was cohesive within the propellant. It was further confirmed by nondestructive testing and proved by static testing of rocket motors in end-burning mode with a composite propellant up to 175 s as well as in radial modes for 35 s in actual missile applications.

4. CONCLUSION

A liner formulation based on HTPB-carbon black-S£$_2$(9$_3$-nBD-phloroglucinol and toluene-di-isocyanate as a curative has been developed. The study of castable life/pot life showed that propellant can be cast up to 6 days of liner coating without affecting the interface properties. n-Butanediol and phloroglucinol combination increases the mechanical strength of the liner as well as enhancement in the interface properties. This enhancement in peel-off strength is an achievement for case-bonded motors. The effect of filler content was studied by thermal analysis, mechanical strength and limited oxygen index studies. The higher Sb_2O_3 content (24 %) was selected considering the reinforcement in mechanical properties and fire retardancy effect. The efficacy of the liner formulation was proved by static evaluations at extremes of propellant operating temperatures in radial as well as end-burning grains.

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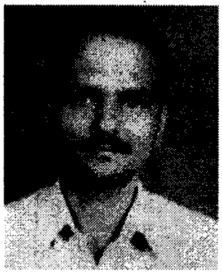

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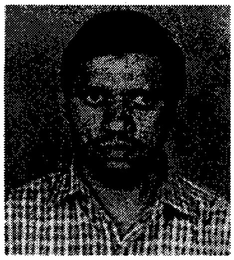

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