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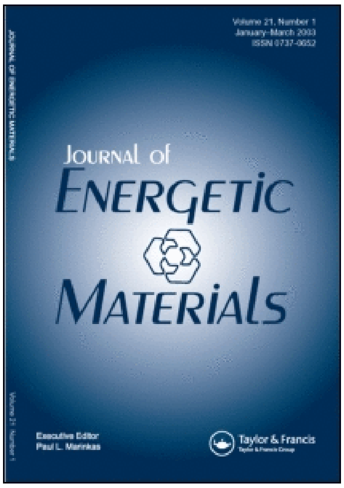

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Studies on Interface Properties of Propellant Liner for Case-Bonded Composite Propellants

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For ensuring a good bond between the insulator and the propellant, a thin layer of liner is applied. Liner compositions should preferably be based on the same binder system used in the propellant formulations. As the liner is to hold the propellant and insulator without debond in all the environmental conditions, the interface properties are very important. Studies were carried out on the effect of particle size of ammonium perchlorate (AP) and the R value on the interface properties. It was found that interface properties highly depend upon the particle size of AP and the coarse-fine ratio of AP in the propellant formulation. As the percentage of fine AP increases, peel value decreases. Liner compositions are developed with aziridine-based compounds to improve the interface properties for compositions containing a large amount of very fine AP. Aging properties of the interface bonding have also been undertaken.

Keywords: insulator, liner, interface property

Key to Abbreviations

Al	Aluminium
AP	Ammonium perchlorate
APES	3-Aminopropyl triethoxysilane

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BR	Burn rate
C:F	Coarse : fine
CNSL	Cashew nut shell liquid
Comp	Composition
DDI	Dimeryl di-isocyanate
EPDM	Ethylene propylene dienemonomer
HEMRL	High Energy Materials Research Laboratory
HTPB	Hydroxyl terminated poly-butadiene
IDP	Isodecyl pelargonate
IPDI	Isophorone di-isocyanate
IPES	Triethoxy (3-isocyanatopropyl) silane
MAPO	Methyl aziridinyl phosphine oxide
NDT	Nondestructive testing
−OH value	Hydroxyl value
PBAN	Polybutadiene acrylonitrile
Prop	Propellant
PU	polyurethane
RH	Relative humidity
R value	−NCO : −OH ratio
TBS	Tensile bond strength
TDI	Tolune di-isocyanate
VSSC	Vikram Sarabhai Space Centre

Introduction

Solid rocket propellants are basically of two types: cartridge-loaded and case bonded. Cartridge loaded systems are simple and are preferred in defence rockets when the requirements are in large number. However, for meeting the requirements of longer ranges and higher payload-carrying capacity, large-sized case-bonded propellants are being used. The case-bonded motor basically consists of a motor case, an insulation, and a liner as major subsystems. The liner is basically an elastomeric material applied between the insulation and the propellant to improve interface properties between insulator and propellant and to hold the propellant to the insulated motor case without debond in all the environmental conditions.

Usually, to have compatibility with the propellant, liner compositions should preferably be based on the same binder system used in the propellant formulations. Hydroxy terminated polybutadiene

(HTPB)-based composite propellants are widely used in present-day rocket motors, and their aging characteristics have been well established. The use of HTPB-based polyurethanes as a liner, insulator, or inhibitor for rocket propellants has not been studied to a great extent.

A German patent by Maucourt [1] describes HTPB/IPDI-based polyurethane (PU) composition for coating the inner surface of a propulsion unit. This has been used for a ''butalene'' propellant by spraying the diluted solution on an insulator. An Aerospace Corporation report by T. W. Giants [2] describes a liner system for case-bonded rocket motors. This liner composition consists of HTPB (RM-45), dimeryl diisocyanate (DDI), C-black as a filler, and an aziridine-based bonding agent. This mixture is coated on an ethylene propylene diene monomers (EPDM) insulator. The authors have claimed that the developed liner system prevents plasticizer migration from propellant to insulator. A German patent by Probster Manfred [3] also reports liner composition based on HTPB-IDP-HMDI and oxamide for rocket motors insulated by EPDM or polybutadiene acrylonitrile (PBAN) rubbers. Haska et al. [4] have reported the studies on adhesion properties of an HTPB-IPDI-based liner elastomer with a composite matrix and metal case. The effects of ***R*** values, triol-diol ratio, and methyl aziridinyl phosphine oxide (MAPO) concentration on the adhesive nature of the metal-elastomer-matrix system were investigated by tensile and peel test methods. Many other publications by Hemminger [5], Wrightson [6, 7], and Pierce [8] report HTPB-based composition of liners for case-bonded rocket motors. But a detailed study with propellant formulations, performance at extremes of propellant operating temperatures, and aging has not been reported in any of the publications.

A liner formulation based on HTPB as a basic resin with fillers, cross-linking agent, and a tackifier was developed at the High Energy Materials Research Laboratory to suit the varieties of composite propellant formulations having burn rates ranging from 5 to 40 mm/sec. A study was undertaken on interface properties between propellant and the liner developed based on HTPB. Interface properties have been studied with different propellant formulations and have been corelated with the percentages of coarse and fine ammonium perchlorate (AP) in the propellant. Coupling agents and aziridine-based bond promoters have been used to improve the interface properties.

As a minimum 10 years of shelf life is mandatory for defence applications, an aging program for interface properties has also been undertaken.

Experimental

Materials

HTPB, M. Wt. (Mn̄) 2200−3000 and −OH value 40−50 mg KOH/g was used as a basic polymeric binder. The filler combination was antimony trioxide (Sb_2O_3, purity min 98%) and C-black (rubber grade, N-550) with capolyte CP-70 as a tackifier. Pyrogallol (purity $>$ 98%) was used as a cross-linking agent cum antioxidant in the polyurethane formulations. Toluene-di-isocyanate (TDI) and isophorone-di-isocyanate (IPDI) have been used as curatives with $>$ 99% purity. Dichloromethane (CH_2Cl_2, AR grade) was used as a solvent for dilution of the liner material. Two different silane compounds, 3-aminopropyl triethoxysilane (APES, purity $>$ 95% Aldrich) and triethoxy-3isocyanatopropyl silane (IPES, purity $>$ 95% Aldrich), were used as coupling agents. MAT-O-BOND (an in-house 3-(isocynatopropyl compound synthesized from MAPO−adipic acid−tartaric acid (−OH value = 380−390 mg of KOH/g) was used as a bond promoter. A nitrile rubber-based insulator has been used during the studies.

Characterization

The liner formulation was characterized by using following techniques:

1. Mechanical properties: Tensile test specimens tested according to ASTM-D-638 using a tensile testing machine, Instron 1185.
2. Glass transition temperature (T_g): Determined by differential scanning calorimetry (DSC) studies using a Mettler DSC-30 machine.
3. Thermal conductivity: Measured by heat flow meter thermal conductivity tester model TCHM-DV (R/R Company, USA).
4. Shore hardness A: Measured by shore hardness tester model SHR-4111 (Blue Steel Engineering Pvt Ltd., Mumbai).
5. Bond strength: The propellant pieces (50 × 20 × 10 mm) were kept in an aluminium mold 10 mm apart, and the liner formulation was filled in the gap and cured. The samples were tested on an Instron universal testing machine for bond strength.
6. Peel-off strength: Measured by the wheel-peel (90° peel) method. The method was established in association with VSSC, and the samples were tested on a universal testing machine, Instron 1185.

Preparation of Liner

HTPB was deaerated under vacuum (<10 torr), and all solid ingredients were dried in an air oven at 100°C for a minimum 6 hr (moisture content <0.1% by Karl Fischer).

HTPB was deaerated under vacuum in a vertical planetary mixer with continuous hot water circulation (60°C) for 30 min. The additives and fillers were mixed following a particular sequence, specific time of mixing, and in requisite installments. After complete addition, mixing was continued for 60 min without vacuum and 60 min with vacuum. Isocyanate is added whenever required. All the above operations have been carried out under controlled humidity (RH 55 ± 5%).

Application of Liner and 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 70°C for 2–3 hr for evaporation of solvent. The liner composition was diluted with dichloromethane in 1:1 proportion and mixed well with a mechanical stirrer for 5 min. A thin layer is applied on the insulation layer manually with a brush or spray gun depending upon the size of the rocket motor. The liner-coated sheets/motors are preserved under a vacuum till the propellant is cast. The liner coat remains tacky from 16 to 120 hr of application. The propellant has to be cast during its tacky condition.

The HTPB-AP-Al–based composite propellant was cast in the rocket motors and interface property molds, cured, and NDT tested. The samples for wheel-peel are cut into specified dimensions and tested on an Instron universal testing machine.

Results and Discussion

The liner formulation was characterized for mechanical, thermal, and interface properties. The results of characterization of isocyanate-cured, optimized liner composition are summarized in Table 1.

Effect of NCO/OH Ratio (R Value) on Liner Properties

The –NCO/–OH ratio was optimized for the typical liner formulation. The results are summarized in Table 2.

To study the effect of the –NCO index (R value) on the mechanical properties of the matrix, experiments were carried out

Table 1
Characteristics of liner

Characteristic	Value
Tensile strength, kg/cm^2	18–20
Percentage elongation	40–50
Density, g/cc	1.18–1.20
Hardness, Shore A	58–60
Thermal conductivity W/m/°K	0.0743
Glass transition temperature, °C	−75 to −77
Pot life, hr	16–120

by varying the −NCO/−OH ratio from 1.0 to 2.4. The base liner composition was kept the same throughout the studies. The formulations were cured in sheet form (2.5–3 mm thick) using TDI at room temperature. The values reported in Table 2 are the average of five measurements for each composition in all sets of experiments.

In general as the *R* value increases, the tensile strength increases with an increase in shore A as expected. It reaches a maximum at an *R* value of 2.0 and again decreases. The cured matrix becomes porous after the R value 1.8. In the present HTPB-TDI polyurethane system the cross-link density and in turn mechanical strength depends on the presence of triols, average functionality of HTPB, it's distribution in HTPB, etc. Cross-linking at higher *R* value is reported to proceed through the formation of isocyanurate linkages, and allophanate

Table 2
Effect of *R* values on mechanical properties of liner

Sr. no.	*R* value	Hardness Shore A	Tensile strength (kg/cm^2)	Percentage *E*	Modulus	Remarks
1	1.0	60	15.5	112	78	Good sheet
2	1.4	70	22.5	105	81	Good sheet
3	1.8	75	31.0	78	84	Porous
4	2.0	80	38	60	86	Porous
5	2.4	80	28.1	57	70	Porous

linkages, which are the possible side reactions, thereby increasing the mechanical properties. Our results are in agreement with the studies carried out by Haska et al. [4]. Observation of higher tensile strength at higher R values might also be attributed to the consumption of excess diisocyanate by the functional groups on the filler surface, especially fine powdered C-black.

The hardness and the modulus increase with increasing R value. Hardness is governed by the polyurethane structures formed. At very high R values (2.4) the matrix becomes highly porous, resulting in lowering of tensile strength.

Taking into consideration the method of application of liner in large-sized motors, the R value is kept around 1.3 (Table 2). The liner is diluted using a requisite amount of CH_2Cl_2 and sprayed using oil- and moisture-free compressed air or nitrogen.

The basic requirement for a good liner is an excellent bond between propellant and liner. For defence applications the bond should not be affected at extremes of propellant operating temperatures (-20 to $+50$°C) and different environmental conditions. In the case of HTPB-based liners in addition to electrostatic dipolar adhesion, a chemical covalent bonding is also achieved. There are free $-OH$ groups available in the propellant matrix as the curative index for propellant formulations are generally around 0.7–0.75. The excess $-NCO$ groups in the liner matrix react with the free $-OH$ groups, and a urethane linkage ($-NH-COO-$) is easily formed across the liner-propellant interface. This urethane reaction is quantitative and goes to completion at a convenient rate, giving good mechanical properties. The urethane linkage formed is very stable, ultimately leading to an excellent bond between propellant and liner. Hence whenever extreme environmental conditions are required, a covalent bonding [9] is necessary. This fact has also been proved by extreme temperature studies and aging studies carried out by us.

Effect of Propellant Formulation on Interface Properties

The liner formulation was studied with five different composite propellants having varying burn rates. The interface properties (W-peel and tensile bond strength) achieved with different propellant formulations are summarized in Table 3.

The results clearly indicate that the interface properties depend on the coarse-fine ratio of ammonium perchlorate, which is the major oxidizer used in composite propellants. It can be seen from the data that as the percentage of fine AP increases from composition C_1 to composition C_5, the W-peel strength decreases significantly (1.62−0.15 kg/cm). The interface properties are the measure of adhesion/bonding across propellant liner interface. As the percentage of fine AP increases, the exposed surface area of AP goes on increasing. Consequently the amount of HTPB available for formation of polyurethane linkages across the liner-propellant interface goes on reducing, ultimately with a reduction in W-peel strength and tensile bond strength (TBS).

The same liner composition gave the highest peel strength (>1.6 kg/cm) with composition C_1 repeatedly. The graph of load V/s displacement is also uniform, and a uniform layer of propellant is always found on the insulator strip. This propellant composition contains a coolent burn rate retarder having the $-NH_2$ end group as one of the ingredients, which also might be taking part in formation of a covalent bond with −NCO from TDI, which is in excess in liner formulation. The reaction can be shown as follows, giving urea linkages that further strengthen the interface bonding:

$$\underset{\text{Burn rate retarder}}{R-NH_2} \quad + \quad \underset{\text{Curative}}{O=C=N(TDI)} \rightarrow \underset{\text{Urea linkage}}{R-NH-CO-NH-(TDI)}.$$

The peel strength at −20°C increases significantly (e.g., from 1.54 to 2.45 for Composition 2) and decreases at +50°C (e.g., from 1.54 to 0.96 for Composition 2) as expected. The observations are similar for all the remaining compositions. For Composition 5, the bonding properties were found to be very low (0.15 kg/cm). This actually resulted in debonds of the case-bonded propellant and failures in small experimental static firings.

Composition 2 and liner were further studied for the effect of propellant mechanical properties on peel strength in case bonded applications. The propellant composition was slightly tailored to get higher mechanical properties. The results of six batches are as shown in Table 4. The results reported in this table clearly show that as the propellant tensile strength increases, elongation decreases and modulus increases, and the peel strength decreases. Hence for case-bonded applications to get good interface bonding, propellant formulation is required to be of low tensile strength and low modulus.

Table 3

Effect of propellant composition on interface properties

Sr. no.	Propellant composition	AP			AP particle size (μ)			W-peel strength (kg/cm)			Tensile bond strength (kg/cm^2)
		C		F	C		F	Hot +50°C	Ambient	Cold (−20°C)	
1	C_1	85		15	310		80	1.32	1.62	2.01	8−10
2	C_2	67		33	310		60	1.04	1.54	2.45	7−8
3	C_3	65		35	310		60	0.96	1.51	2.24	7−8
4	C_4	50	25	25	300	10	4	0.45	0.73	1.4	6−8
5	C_5	10		90	200		4	0.02	0.15	0.25	2−3

Note: For all samples the mode of failure is cohesive in propellants.

Table 4
Variation of peel strength with propellant mechanical properties

Batch no.	Tensile strength (kg/cm^2)	Percentage E	Modulus	Peel strength (kg/cm)
B_1	7.1	36.8	36.1	1.26
B_2	8.8	37.1	43.2	1.20
B_3	10.3	33.0	62.3	0.98
B_4	11.2	25.3	81.8	1.01
B_5	6.5	38.0	30.5	1.46
B_6	6.3	46.5	26.0	1.54

Aging Studies

The aging program was carried out for Composition 2 at 50°C and at room temperature (RT). The Batch No. 1 after 1 yr at room temperature and 6 months at 50°C storage showed no significant change in peel strength (original = 1.26, 1 yr at RT = 1.27 kg/cm, 6 months at 50°C = 1.12 kg/cm). For batch No. 3, drastic reduction in peel strength at 50°C is shown after 6 months' storage (original 0.98, 6 months at RT = 0.73 kg/cm, 6 months at 50°C = 0.58 kg/cm). This fact again proved that for case-bonded applications propellant formulation has to be of low modulus and low tensile properties.

Static Evaluation

The efficacy of interface properties of the developed liner formulation was studied at extremes of propellant operating temperature from −20 to +50°C, as shown by the data in Table 3. In all the cases failure observed is cohesive in the propellant. It is further confirmed by NDT testing and proved by static testing of rocket motors in end-burning mode with a composite propellant of BR 8.3 mm/sec up to 175 sec as well as in radial modes for 35 sec in actual missile applications.

Composition C_2 has been test fired at +50°C, −20°C, and after 2000 km road trials in radial mode, proving the efficacy of interface properties.

Efforts to Improve the Interface Properties

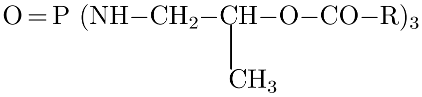
Very low peel strength (0.02–0.15 kg/cm) was observed for propellants that contain a large amount of fine ammonium perchlorate (C_5

in Table 3). Hence a research plan was carried out using different curatives, additives based on epoxy, aziridines, and silane coupling agents to improve the peel strength for this class of propellants. The basic binder-filler-cross-linking agents formulation was kept the same, and additives were added to check the improvement in properties. The results are summerized in Table 5.

The change of curative from TDI to IPDI gave slightly higher peel strength (from 0.15 to 0.35 kg/cm). TDI is an aromatic isocyanate and has higher reactivity due to delocalization of the lone pair of nitrogen on aromatic nucleus as compared to IPDI, which is a cycloaliphatic diisocyanate. Because of slower reactivity, it might have formed better bonding with HTPB in the fine AP-rich propellant matrix. Epoxy resin based on CNSL, a well-known adhesive, could not be used in the present liner formulation because the rates and pot life of HTPB-IPDI reaction and epoxy-amine reaction did not match.

MAT-O-BOND is an in-house-developed compound synthesized from MAPO-adipic acid and tartaric acid and is used as a bonding agent in composite propellants to improve the mechanical properties.

Table 5
Effect of curatives/additives on peel value

Sr. no.	Liner formulation	Structure of additive	Peel strength (kg/cm)
1	Basic liner (L) + TDI	–	0.15
2	L + IPDI	–	0.30–0.35
3	L + MAT-O-BOND (5 pts) + IPDI	 $O=P\ (NH-CH_2-\underset{CH_3}{CH}-O-CO-R)_3$	0.9–1.0
4	L + APES (1.5 pts) + IPDI	$H_2N(CH_2)_3Si(OC_2H_5)_3$	0.7–0.8
5	L + IPES (1.5 pts) IPDI	$(C_2H_5O)_3Si(CH_2)_3NCO$	0.5

Note:
APES: 3-aminopropyl triethoxy silane.
IPES: triethoxy (3-isocyanatopropyl) silane Curative index: 1.3.
1.5 pts: 1.5 parts over base composition.

MAT-O-BOND was added in five parts to the liner, and IPDI was used as a curative. This combination gave a good enhancement in peel strength from 0.15 to 0.9 kg/cm. The properties, synthesis, compatibility with composite propellants, and aging behavior of MAT-O-BOND is very well established in HEMRL. Aziridine-based bond promoters are well reported in the literature [10] for improvement in interface properties. These compounds assist in the interfacial bonding between the liner and propellant by improving the interaction at the binder oxidizer interface and thus also improve the mechanical properties. Their presence in the liner renders the surface of the liner more active for adhesion with the propellant by making hydrogen bonding with ammonium perchlorate at the interface [10]. It is also known to react with the hydroxyl groups of HTPB to form amides, which is accelerated by catalytic effect of ammonium perchlorate particles.

Silane coupling agents $[R^1{-}Si(OR^2)_3]$ are well-known compounds used to improve adhesion. Coupling agents are materials with two chemical functions, one of which is reactive with the inorganic phase, and the other of which is reactive with the organic phase. The mechanism has been reported [11], which might be taking place when these materials are used.

Silanes in the presence of traces of moisture hydrolyze to silanols, which spontaneously condense to yield silanol oligomers. The silanols will also condense with the free $-OH$ groups available in the matrix. The R^1 group also reacts with the matrix, for example, APES the R^1 group $CH_2CH_2CH_2NH_2$ can react very well with the $-NCO$ group in the liner-propellant matrix. The two silane compounds, when used linear formulations, have shown improvement in the peel strength up to 0.8 kg/cm. Further research is in progress for all the above combinations.

The improved liner formulation containing the MAT-IPDI combination has been successfully evaluated in end burning mode upto 5 sec in actual missile application. The surveillance and aging at 50°C for this liner has shown no deterioration in peel strength.

Conclusion

The studies carried out regarding the effect of propellant properties, additives, and oxidizer on interface properties reveal that there cannot be a universal liner formulation suitable for various types of composite case-bonded propellants. The interface properties highly depend on a coarse-fine ratio of oxidizer. As the percentage of ammonium perchlorate increases, the peel strength decreases. Also, peel strength can be increased by organic ingredients having reactive end groups such as amino or hydroxyl in the propellant composition used as ballistic modifiers or bonding agents, which can have covalent bonding with liner ingredients. The −NCO/−OH ratio also plays a vital role in realizing the required interface properties.

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