

HTPB-Based Polyurethanes for Inhibition of Composite Propellants

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SYNOPSIS

Polyurethanes were synthesized by the reaction of hydroxyterminated polybutadiene (HTPB) and diisocyanates such as toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), hexamethylene diisocyanate (HMDI), and isophoron diisocyanate (IPDI). A number of fillers such as carbon black, kaolin, and antimony trioxide (Sb_2O_3) were used in these formulations. Mechanical and thermal stability of these polyurethanes were studied. Based on its properties, HTPB-MDI derived filled polyurethane was selected and evaluated as an inhibitor for a composite propellant. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

A number of polymeric materials have been reported as inhibitors for a composite propellant such as polyurethanes,¹⁻¹⁰ epoxy resin,^{11,12} phenolic resin, melamine formaldehyde resin,^{13,14} chlorosulfonated polyethylene,¹⁵ thiokol rubber,¹⁶ and nitrile rubber,¹⁷ etc. Among these polymers, hydroxyterminated polybutadiene (HTPB)-based polyurethanes are the most ideal inhibiting materials because its properties could be easily matched with the basic composition of the HTPB-based composite propellant. However, the information regarding its formulation and processing is not available in the literature. Therefore a study was undertaken for the development of an HTPB-based inhibition system using various fillers. We reported inhibition of composite propellants using the fiber reinforced plastics (FRP) technique and polyurethanes as matrix material.¹⁸ The present article reports the data generated on the filled polyurethanes developed from HTPB and various diisocyanates (DI) and the establishment of a new process of its application in the form of sheets. These polyurethanes were evaluated as inhibitors for composite propellants.

EXPERIMENTAL

Chemicals used in the synthesis of polyurethanes are given in Table I. Fillers and additives used for the present study are described in Table II. All chemicals, fillers, and additives were procured from trade sources and used as received.

Synthesis of Polyurethanes

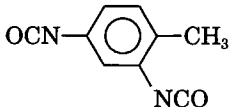
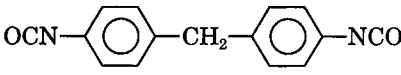
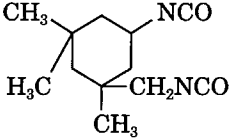
Mixture of HTPB and dioctyl adipate (DOA) as given in the formulation were taken in a sigma blade mixing device (Table III). To this mixture the catalyst dibutyltindilaurate (DBTL) and the processing aid polyethylene glycol monostearate¹⁹ were added and the mixer was allowed to run. This was followed by the sequential addition of carbon black (C-black), antimonytrioxide (Sb_2O_3), kaolin, and wood resin as fillers. The mixer was run for 45 min for better mixing of the ingredients. This formulation was allowed to react with DI in the NCO:OH ratio 1 : 1 at ambient by the addition of DI calculated according to the formula²⁰:

$$\frac{\text{eq. wt. DI} \times \text{OH value HTPB} \times \text{wt. HTPB}}{56.1 \times 1000}$$

This mixture was degassed by application of a vacuum and collected in the form of a highly viscous

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Table I Chemicals in Synthesis of Polyurethanes

Material	Structure	Specification	Source
HTPB	$H-(OCH_2CH=CHCH_2)_n-OH$	Hydroxyl value = 37, $\bar{M}_n = 2600$	NOCIL, Bombay
TDI		80% 2,4 + 20% 2,6 isomeric mixture	Fluka AG, Switzerland
MDI		Mixture of di- and triisocyanates, dark brown viscous liquid	EMERCK
HMDI	$OCN-(CH_2)_6-NCO$	> 99.0% pure	EMERCK
IPDI		> 99.0% pure	Chemisch, Germany
DBTL	$[CH_3(CH_2)_{10}COO]Sn[(CH_2)_3CH_3]_2$	Sp. gr. = 1.047, purity > 97%	EMERCK

and semisolid dough. Polyurethane dough collected was calendered/rolled into 3–4 mm thick sheets. The sheets were kept in an oven at 60°C for optimum postcuring for 15 days.

Characterization

Polyurethane sheets were characterized for tensile strength, percent elongation (E), and shore hardness (A). The thermogravimetric analysis was carried out with a Netzsch simultaneous thermobalance (STA-409) in air from room temperature to 1100°C at a heating rate of 10°C/min.

Inhibition of Composite Propellants

The experiments were carried out by pasting the HTPB-based polyurethane sheets with HTPB-based adhesive to the composite propellants for determination of bond strength/peel strength.^{21,22}

A piece of composite propellant measuring 8.0 cm long and 1.0 cm wide was selected. To this composite propellant piece, a filled HTPB-diphenylmethane (M)DI polyurethane sheet (16 × 1.0 × 0.3 cm) was pasted using HTPB-based polyurethane adhesive. Half the portion of the inhibitor sheet (~ 8 cm) was pasted to the propellant piece and the rest was left as such for clamping during measurements.

Table II Fillers and Additives

Material	Specification	Source
Diocetyl adipate	Viscosity = 10.5 cs at 38°C, sp. gr. = 0.927 Refractive index = 1.447 at 20°C	INDO NIPPON, Bombay
Carbon black	Rubber grade, particle size retained on 200 BSS	Philips Carbon, Calcutta
Hydrated aluminum silicate (kaolin)	Sp. gr. 2.2, particle size retained on 200 BSS purity 99%	MM Suppliers, Pune, India
Antimony trioxide	Sp. gr. = 5.67, particle size retained on 200 BSS purity 99%	UNI Campine Ltd, Pune, India
Wood resin	Particle size 200 BSS pass, purity 98%	MM Supplier, Pune, India
Polyethylene glycol monostearate	Viscosity 2000 cp at 27°C	HICO India, Bombay

Table III Formulation of Polyurethanes

Chemicals	Amount (g)
HTPB	975
DOA	190
Wood resin	150
Fillers	1325
PEGMS	12.5
DBTL	—
Diisocyanates	As per calculation

Fillers = kaolin (5%) + Sb₂O₃ (10%) + carbon black (85%).

The inhibited propellant piece was clamped to the lower jaw and the rubber strip to the upper jaw of an Instron 1185 UK machine at 90°C. Peel strength/bond strength was measured using the formula:

$$\text{peel strength} = \frac{f}{a \times b}$$

where f = peeling load required to pull the inhibitor from the propellant surface; a = length of propellant covered by inhibitor; b = breadth of propellant covered by inhibitor. These polyurethane sheets were also pasted in the rocket motors (OD = 123 mm, ID = 114 mm, L = 210 mm) for their use as liners/inhibitors in the case of the bonded material. A number of rocket motors were lined with the polyurethane sheets. The composite propellant formulation was ammonium-perchlorate (AP) 68%, Al powder 17%, HTPB + toluene(T)DI + DOA 15%. It was cast *in situ* in the motor as a solid cylinder. After the propellant curing, one end was inhibited by giving a precoat of HTPB + MDI mix and pasting the polyurethane sheet over it. Composite propellants were evaluated at ambient, hot (+50°C), and cold (−30°C) temperatures in a “cigarette” burning mode for 20–25 s.

RESULTS AND DISCUSSION

Polyurethanes prepared by reaction of HTPB and DIs (MDI, TDI, etc.), keeping the NCO:OH ratio at 1 : 1 and using DBTL as catalyst at ambient temperature, are highly flexible, sticky, and have poor mechanical properties (tensile strength = 4–6 kg/cm²). To improve mechanical properties of these polyurethanes, inorganic fillers like C-black, kaolin, and Sb₂O₃ were incorporated. C-black is a well known reinforcing filler. Sb₂O₃ and kaolin have also been added in minor amounts to the polyurethanes

to improve flame retardancy in the system. Due to the addition of these fillers, the viscosity of the polyurethanes increased tremendously and it was difficult to process them after the addition of 15 phr (parts per 100 parts of resin) of filler in the resin.¹⁸ Filler level was further increased in the system by the addition of dioctyl adipate plasticizer (16%) and filler amount was increased to the level of 50% in the polyurethane system to achieve the desired level of mechanical properties.

The equivalent stoichiometric amounts of the various DIs were used in each experiment to keep the NCO:OH ratio at 1 : 1 and to enable us to draw conclusions about the effect of molecular structure on physical and mechanical properties. Tensile strength, percent elongation (E), and shore hardness (A) of polyurethanes formed by different DIs were measured (Table IV). The tensile strength of HTPB-TDI polyurethane is high, 15.3 kg/cm², and E is 123.0%. The higher tensile strength is due to the higher rigidity imparted by the direct association of the isocyanate group with the phenyl ring. The higher reactivity of TDI that results from delocalization of a negative charge on NCO by the aromatic structure leads to the higher tensile strength of polyurethane. HTPB-MDI based polyurethanes show highest tensile strength and reduced elongation, 16.3 kg/cm² and 100.5% (Table IV). An increase in tensile strength of HTPB-MDI polyurethanes in comparison to HTPB-TDI polyurethane may be due to higher functionality²⁰⁻²³ of MDI. MDI is a mixture of di- and triisocyanate (55% MDI, 25% TDI, and 20% polymeric isocyanates). Due to this higher functionality, a high degree of cross-linking takes place leading to the highest tensile strength and hardness. Consequently elongation of these polyurethanes decreases due to the higher amount of cross-linking. HTPB-HMDI polyurethanes have low tensile strength due to lack of rigidity in the

Table IV Effect of Diisocyanate on Mechanical Properties of Filled Polyurethanes Derived from HTPB

S. No.	Diisocyanates	TS (kg/cm ²)	% E	A
1	TDI	15.3	123.0	62.0
2	MDI	16.3	100.5	70.0
3	HMDI	14.5	74.3	68.0
4	IPDI	14.6	153.0	54.7

TS, tensile strength; % E , elongation; A , shore hardness.

Table V Thermal Stability of HTPB-Based Polyurethanes

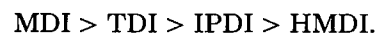
S. No.	Diisocyanate	IDT (°C)	IPDT (°C)	Temp. at Wt. Loss (°C)			Residue at 800°C (%)
				10%	20%	40%	
		I	II				
1	TDI	243	590	460	490	355	68
2	MDI	260	658	450	490	940	70
3	HMDI	220	459	437	465	747	49
4	IPDI	220	482	450	483	770	48

backbone chain. However the presence of the methylene sequence of HMDI forms a tight crystalline structure leading to higher hardness and poor elongation values. Isophoron (IP)DI, which has a cyclic structure, showed inferior properties compared with TDI- or MDI-based polyurethanes because of lack of delocalization of the negative charge on NCO thereby reducing the reactivity of IPDI. Due to this poor relative reactivity of IPDI, HTPB-IPDI polyurethanes have poor cross-linking and hence the highest E , 153.0%. The rigidity was moderate because all cyclic carbon atoms are sp^3 hybridized and they maintain a nonplanar structure. The substituents on the cyclohexane ring reduce the symmetry and cause a general decrease in tensile and hardness properties. However, due to the cyclic structure of IPDI, HTPB-IPDI polyurethanes have slightly higher tensile properties compared to HTPB-HMDI polyurethanes.²⁴

Thermal Properties

Results of thermal analysis of polyurethanes are given in Table V. Initial decomposition temperature (IDT) of HTPB-TDI and HTPB-MDI derived polyurethanes are 243 and 260°C, respectively. However, thermal decomposition starts at 220°C in HTPB-HMDI and HTPB-IPDI polyurethanes in-

dicating a faster degradation in these systems. Integral procedural decomposition temperature (IPDT) as proposed by Doyle²⁵ provides a semi-quantitative means for comparison of relative thermal stabilities of various polymers. HTPB-MDI polyurethane shows the highest IPDT values while HMDI-HTPB polyurethane shows the lowest value. These IPDT values, IDT values, and temperature at various weight losses indicate the relative thermal stabilities of polyurethanes in the order



Thus HMDI polyurethane is the least thermally stable and MDI polyurethane is the most thermally stable.

Inhibition Experiments

Among the polyurethanes synthesized, HTPB-MDI polyurethanes have the best mechanical and thermal properties. Considering these properties, HTPB-MDI based filled polyurethanes in sheet form were evaluated as inhibitor in terms of bond strength/peel strength. This polyurethane sheet pasted to the composite propellant with the help of polyurethane paste (HTPB + MDI + fillers) was allowed to cure at room temperature and subjected to bond strength/peel strength tests.

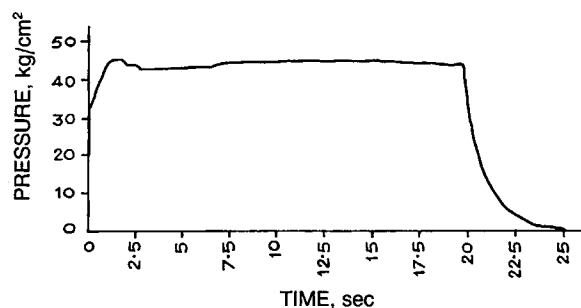


Figure 1 Pressure-time profile for case-bonding technology of inhibition for composite propellant using polyurethane as inhibitor at ambient temperature.

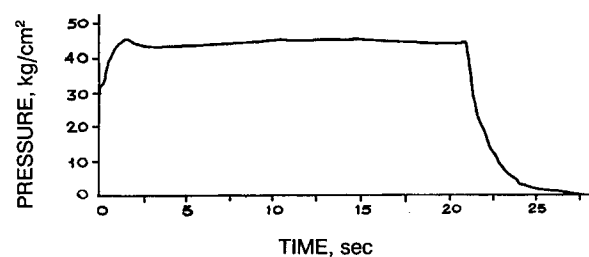


Figure 2 Pressure-time profile for case-bonding technology of inhibition for composite propellant using polyurethane as inhibitor at +50°C.

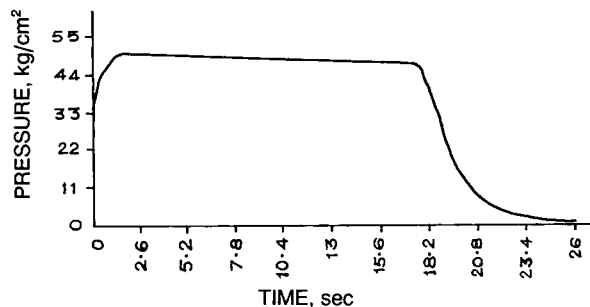


Figure 3 Pressure-time profile for case-bonding technology of inhibition for composite propellant using polyurethane as inhibitor at -30°C .

During the measurements the rubber inhibitor was pulled away along with a thin layer of the propellant indicating good adhesion of the HTPB-based polyurethane sheet to the composite propellant. The mean peel strength/bond strength of the inhibitor on the propellant surface was found to be 12.9 kg/cm^2 . It was observed that break occurs in the composite propellant and not at the propellant inhibitor interface indicating good bonding of the inhibitor with the composite propellant. Static evaluation of composite propellants in a cigarette burning mode using rocket motors lined with HTPB-MDI sheet gives pressure-time profiles at ambient, hot ($+50^{\circ}\text{C}$), and cold (-30°C) temperatures (Figs. 1–3). The pressure-time curve indicates the suitability of (Fig. 1) of HTPB-MDI polyurethane systems as inhibitors/liners because the curves were near neutral. There was no progressivity or regressivity observed in any of the firings.

CONCLUSION

1. Filled polyurethane synthesized from HTPB and various DI's have mechanical properties in the order MDI > TDI > IPDI > HMDI,
2. Thermal stability of these polyurethanes are in the order MDI > TDI > IPDI > HMDI,
3. Due to better mechanical and thermal properties of HTPB-MDI based polyurethane, it was selected as the inhibitors/liners in the case of bonding technology of inhibition for composite propellant. Static evaluation of composite propellants in bonding technology of inhibition in small motors proves the suitability of these polyurethane systems.

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