

HTPB-Based Polyurethanes for Inhibition of Composite-Modified Double-Base (CMDB) Propellants

D. C. GUPTA, P. K. DIVEKAR, V. K. PHADKE

High Energy Materials Research Laboratory, Pune-411008 India

Received 6 August 1996; accepted 30 December 1996

ABSTRACT: Polyurethanes were synthesized by the reaction of hydroxy-terminated polybutadiene (HTPB) and diisocyanates such as toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), hexamethylene diisocyanate (HMDI), and isophorone diisocyanate (IPDI). Carbon black and antimonytrioxide (Sb_2O_3) were incorporated into these formulations as fillers. Dioctyladipate (DOA) and trimethylolpropane (TMP) were also added as a plasticizer and crosslinker, respectively. These polyurethanes were investigated as inhibitors for composite-modified double-base (CMDB) propellants. Due to superior mechanical properties, thermal properties, and low nitroglycerine absorption, HTPB-MDI-TMP-derived filled polyurethane was selected and evaluated as an inhibitor for a CMDB propellant. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 355–363, 1997

INTRODUCTION

The major ingredients of composite-modified double-base (CMDB) propellants are ammonium perchlorate (AP), metal powder, Research and Development Explosive (RDX-cyclotrimethylene trinitramine), in addition to nitro-cellulose (NC) and nitroglycerine (NG), which are also present, in double-base (DB) propellants. The migration of NG from the double base as well as CMDB propellants to the inhibitor is a serious problem and requires special attention at the time of development of the inhibition system. Initially, cellulose acetate and ethyl cellulose were tried as inhibitors for double-base (DB) propellants.^{2,3} However, cellulose acetate absorbs a higher amount of NG (>20–80%) and was stripped off from the propellant. Ethyl cellulose has a poor softening point. To overcome the problem of inhibition, attempts have been made to use rigid thermosetting polymers. Filled polyester resin^{2–6} has been claimed to be a good inhibitor for DB propellants.

This resin has a very good bond strength with DB propellants but NG migration was still observed. A barrier coat of fast-setting polyester resin followed by inhibition with polyester resin (EP-4) was developed and reported at HEMRL.⁶ Inhibition of CMDB propellants was carried out by giving a coat of Desmodur R (triphenylmethane trisocyanate solution in methylene chloride) followed by final inhibition by a HEMRL-EP-4 polyester resin containing 30% alumina as a filler. However, polyester resin as an inhibitor has a limited shelf life and becomes delaminated after a period of 6 months to 1 year.⁶ This led to the search for newer types of polymeric materials for their use as inhibitors. A number of polymers have been reported as inhibitors for CMDB propellants such as the epoxy resin-butadiene-acrylic copolymer,⁷ polyester resin,⁸ and silicones.⁹ Recently, we reported on epoxy resin¹⁰ as an inhibitor for CMDB propellants. However, bond failure occurs during storage-aging trials of epoxy resin-inhibited CMDB propellants at 60°C. A literature survey revealed that filled polyurethanes^{11–13} have better low-temperature properties and very good aging characteristics as compared to polyester resins and epoxy resins. Filled polyurethanes were thus thought to be ideal in-

Correspondence to: D. C. Gupta at Defence Research & Development Establishment, Jhansi Road, Gwalior-474002 India.

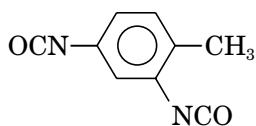
© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/020355-09

hibitors for CMDB propellants. We have already reported on HTPB-based polyurethanes¹³ for the inhibition of composite propellants. We are now reporting the synthesis, formulation, and characterization of various polyurethanes and their application as inhibitors for CMDB propellants.

EXPERIMENTAL

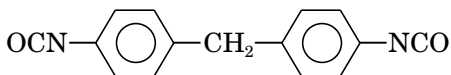
The following chemicals, fillers, and additives were used in the synthesis of polyurethanes¹³:

- (i) HTPB, $\text{H}-(\text{OCH}_2\text{CH}=\text{CHCH}_2)_n\text{OH}$, hydroxyl value = 37, $M_n = 2600$, NOCIL, Bombay, India.
- (ii) TDI,



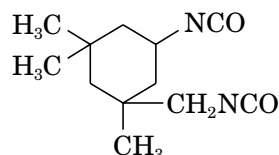
80% 2,4 + 20% 2,6 isomeric mixture, M/s Fluka AG, Switzerland.

- (iii) MDI,



mixture of di- and triisocyanates, dark brown viscous liquid, E. Merck, Germany.

- (iv) HMDI, $\text{OCN}-(\text{CH}_2)_6\text{NCO} > 99.0\%$ pure, E. Merck, Germany.
- (v) IPDI,



> 99.0% pure, Chemisch, Germany.

- (vi) TMP, $\text{CH}_3\text{CH}_2-\text{C}-(\text{CH}_2\text{OH})_3$, mp = $61 \pm \text{ic}$, > 99.0% pure, E. Merck, Germany.
- (vii) DBTL, $[\text{CH}_3(\text{CH}_2)_{10}\text{COO}]\text{Sn}[(\text{CH}_2)_3\text{CH}_2]_2$, sp gr = 1.047, > 97% pure E. Merck, Germany.
- (viii) DOA, $[-\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}(\text{C}_2\text{H}_5)-$

$(\text{CH}_2)_3\text{CH}_3]_2$, viscosity = 10.5 CS at 38°C, sp gr = 0.927, ref. index = 1.447 at 20°C, Indo Nippon, Bombay, India.

- (ix) Carbon black (C-black), rubber grade, particle size retained on 200 BSS, Philips Carbon, Calcutta, India.
- (x) Sb_2O_3 (antimony trioxide), sp gr 5.67, particle size retained on 200 BSS, purity 99.0%, UNI Campine, Pune, India.

All chemicals, fillers, and additives were used as received from the trade.

Synthesis of Polyurethanes

A number of formulations were made of a mixture of HTPB and DOA in an RB flask under an inert atmosphere.¹⁴ To this mixture, the catalyst DBTL and crosslinker TMP were added. This was followed by the addition of fillers, i.e., C-black and Sb_2O_3 . The formulation was stirred well for better mixing of the ingredients. This formulation was allowed to react with diisocyanate in an NCO : OH ratio of 1 : 1 at ambient, calculated according to the formula¹⁵

$$\frac{\text{Equiv wt of diisocyanate} \times \text{OH value of HTPB} \times \text{wt of HTPB}}{56.1 \times 1000}$$

This mixture was degassed by application of a vacuum and cast into a dumbbell shape by pouring it into a dumbbell-shaped mold. These samples were postcured at 60°C for 10 days for further characterization. A number of formulations were prepared as given in Table I and then evaluated as inhibitors for CMDB propellants.

Characterization

Polyurethane samples were characterized for tensile strength, % elongation, bond strength with CMDB propellants, Shore hardness, gel time, nitroglycerine absorption, flame retardance, and thermal analysis as reported^{16,17} earlier.

Inhibition of CMDB Propellants

Polyurethane with superior mechanical, thermal, and low NG migration was evaluated as an inhibitor for CMDB propellants. The CMDB propellant (id = 129.0 mm, L = 160 mm, and weight = 3.250 kg) surface was roughened by rubbing with an

Table I Formulations of Polyurethane Composition

Composition	Formulation (g)			
	1	2	3	4
HTPB	100	100	100	100
C-black	—	10	10	10
DOA	—	—	10	10
Sb ₂ O ₃	—	—	45	45
TMP	—	—	—	1
DI	As per calculations (—NCO : OH = 1 : 1)			

emery paper and the propellant dust was removed by a brush. The propellant was coated with Desmodur-R and kept for 3 h. This was followed by a thin brush coat of the formulation given to the CMDB propellant surface and the propellant was assembled on the base plate of the inhibition mold.¹⁰ A thin brush coat of DBTL was given to the inside wall of the mold and the mold was assembled along with the propellant (Fig. 1). Finally, the polyurethane formulation was poured into the mold at room temperature. The mold was evacuated for 5 min. The propellant was extracted from the inhibition mold after 24 h. The inhibited propellant was machined to an od = 135 mm and $L = 170$ mm, X-rayed, and statically evaluated after conditioning for 24 h at low (-30°C), ambi-

ent, and hot ($+50^{\circ}\text{C}$) temperatures for a burning duration of 3–12 s.

Storage aging trials were also carried out at ambient and hot temperatures ($+50^{\circ}\text{C}$) by putting an inhibited charge at ambient and at 60°C in a constant temperature water-jacketed oven and observed for bond failure between the propellant and inhibitor.

RESULTS AND DISCUSSION

A number of polyurethane formulations (Table I) were planned and executed to develop a polyurethane-based inhibitor for nitramine-containing CMDB propellants. Moreover, the geometry of the CMDB propellants demands a casting technique of inhibition. Therefore, the formulation developed for this purpose should be a free-flowing polyurethane resin and pourable.

Mechanical Properties

Polyurethanes synthesized using different formulations were characterized for their mechanical properties, i.e., tensile strength (TS), % elongation (E), and Shore hardness. Polyurethanes prepared by the reaction of HTPB and DI's (TDI, MDI, etc.), keeping the NCO : OH ratio at 1 : 1 and using DBTL as a catalyst at ambient temperature, are highly flexible and sticky and have poor mechanical properties (Table II, Formulation No. 1, TS = 2–6 kg/cm²). To improve the mechanical properties of these polyurethanes, C-black, a well-known reinforcing filler, was incorporated into these formulations (Formulation No. 2, Table I). Due to the addition of C-black, the viscosity of the polyurethanes increased tremendously¹⁴ and it was difficult to process or pour them after the addition of 10 phr of the filler to the resin. The

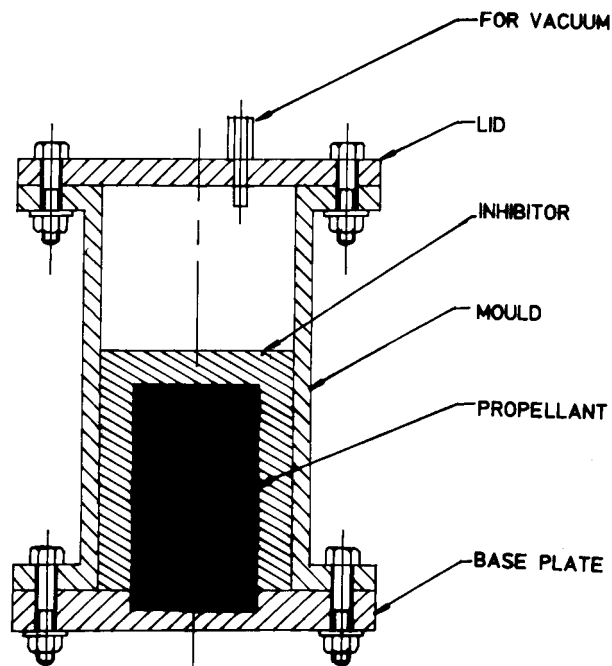


Figure 1 Assembly for inhibition of CMDB propellants.

Table II Mechanical Properties of Formulation No. 1

Sample No.	DI	Tensile Strength (kg/cm ²)	<i>E</i> (%)	Shore A
1	TDI	4.15	74.8	20.0
2	MDI	5.92	124.4	21.0
3	HMDI	2.79	216.5	18.0
4	IPDI	2.23	168.2	18.0

filler level was further increased in the system by the addition of dioctyladipate (DOA) plasticizer (Formulation No. 3) and the filler amount was increased to the level of 55 phr in the polyurethane system to achieve the desired level of mechanical properties. Thus, Sb₂O₃ was incorporated into the formulation (Formulation No. 4, Table I) to the level of 45 phr to improve the mechanical properties, which increased to the level of 5–10.4 kg/cm² (Table IV). The mechanical properties were further improved by the addition of the crosslinker TMP in the formulation (Formulation No. 4, Tables I and V). The mechanical properties, particularly tensile strength, were increased to the level of 8.8–15.6 kg/cm² (Table V). The higher tensile strength achieved in this formulation may be due to the increased level of crosslinking in this formulation as explained by the reaction mechanism of curing of polyurethanes.¹⁵

The tensile strength of filled HTPB–TDI polyurethane is 13.6 kg/cm² and the elongation is 74.4% (Table V). 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, which results from the delocalization of a negative charge on NCO by the aromatic structure, leads to the higher tensile strength of polyurethane.¹³ Filled HTPB–MDI-based polyurethanes show the highest tensile strength, 15.6 kg/cm², and reduced elongation, 56.8% (Table V). An increase in tensile strength of HTPB–MDI polyurethane in com-

parison to filled HTPB–TDI polyurethane may be due to the higher functionality of MDI. MDI is a mixture of di- and trisocyanates¹⁸ (55% MDI, 25% MTI, and 20% polymeric isocyanates). Due to this higher functionality, a high degree of crosslinking takes place, leading to the highest tensile strength and hardness. Consequently, elongation of these polyurethanes decreases due to the higher amount of crosslinking. Filled HTPB–HMDI polyurethanes have low tensile strength due to the lack of rigidity in the backbone chain. However, the presence of the methylene sequence of HMDI forms a tight crystalline structure, leading to higher hardness and poor elongation. IPDI, which has a cyclic structure, showed inferior properties compared with TDI- or MDI-based polyurethanes because of a lack of delocalization of the negative charge on —NCO, thereby reducing the reactivity of IPDI.¹⁸ Due to this poor relative reactivity of IPDI, HTPB–IPDI polyurethanes have poor crosslinking and, hence, the highest *E*, 93.0%. The substitutes on the cyclohexane ring reduced the symmetry and caused 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. The same trend as that of the tensile properties is shown by the bond strength studies (Table V). The HTPB–IPDI polyurethane gave the lowest (6.2 kg/cm²) and the HTPB–MDI polyurethane gave the highest (13.3 kg/cm²) values of the bond strength.

Table III Mechanical Properties of Formulation No. 2

Sample No.	DI	Tensile Strength (kg/cm ²)	<i>E</i> (%)	Shore A
1	TDI	5.3	83.4	25.0
2	MDI	6.6	71.9	30.0
3	HMDI	3.2	147.7	27.0
4	IPDI	3.6	62.0	26.0

Table IV Mechanical Properties of Formulation No. 3

Sample No.	DI	Tensile Strength (kg/cm ²)	<i>E</i> (%)	Shore A
1	TDI	8.1	70.7	24.0
2	MDI	10.4	80.5	35.0
3	HMDI	4.8	156.6	26.0
4	IPDI	4.9	202.1	20.0

Thermal Degradation Studies

DTA and TGA studies were carried out with a Netzsch simultaneous thermobalance (STA-409) in static air from room temperature to 1100°C at a heating rate of 10°C/min. The results of the thermal analysis of polyurethanes (Formulation No. 4) are given in Table VI. DTA thermograms gave two exothermic peaks which correspond to the thermooxidative degradation or decomposition temperature of these polyurethanes¹⁹ (Fig. 2). HTPB-TDI polyurethanes have decomposition temperatures of 490 and 585°C, respectively. The first exotherm may be ascribed to be due to thermooxidative degradation at the rubbery HTPB part of the polymer. The second exotherm similarly may be due to the thermooxidative degradation at the aromatic hard part of the polyurethane. These decomposition temperatures shift to higher temperatures of 500 and 600°C, respectively, when TDI is replaced by MDI. Thus, filled HTPB-MDI polyurethane is more stable thermally. The higher decomposition temperature in MDI-based polyurethanes may be due to a higher degree of crosslinking, since it is a mixture of di- and triisocyanates. Decomposition temperatures of HTPB-HMDI polyurethane, however, decreased to 430 and 510°C, respectively, due to the lack of rigidity and maximum flexibility in the polyurethane structure.¹⁹ DTA thermograms for filled HTPB-IPDI were observed at 475 and 550°C. These temperatures are higher than are

those observed for filled HTPB-HMDI polyurethanes, indicating the higher thermal stability of these systems (HTPB-IPDI polyurethanes).

Thermal analyses of polyurethanes are given in Figure 3 and Table VI. The DTA data are further supported by the TGA thermograms. Temperatures at various weight losses are given in Table VI for HTPB-based polyurethanes (Formulation No. 4, Table I). The initial decomposition temperatures (IDTs) of HTPB-TDI- and HTPB-MDI-derived polyurethanes are 240 and 250°C, respectively. However, thermal decomposition starts at 210 and 220°C in HTPB-HMDI and HTPB-IPDI polyurethanes, indicating a faster rate of degradation in these systems (Table VI). MDI-based polyurethanes are the thermally most stable as given by the amount of residue left at 800°C and the IDT values. The highest thermal stability of HTPB-MDI polyurethanes may be due to the higher functionality¹³ of MDI and, hence, the higher amount of crosslinking in these systems. Similarly, HTPB-HMDI polyurethane is the least thermally stable, as indicated by the IDT and the amount of residue left at 800°C.

Nitroglycerine (NG) Absorption

NG absorption of HTPB-based polyurethane was studied and recorded with respect to time (days) as given in Table VII. It was observed that as the time increases (1–7 days) NG absorption also

Table V Mechanical Properties of Formulation No. 4

Sample No.	DI	Tensile Strength (kg/cm ²)	<i>E</i> (%)	Shore A	Bond Strength (kg/cm ²)
1	TDI	13.6	74.4	50.0	10.8
2	MDI	15.6	56.8	58.4	13.3
3	HMDI	8.8	51.9	55.2	7.6
4	IPDI	9.4	93.0	43.7	6.2

Table VI Thermal Behavior of HTPB-based Polyurethanes

Sample No.	DI	Exotherm Temp on DTA		IDT (°C)	Temp at Wt Loss			Residue at 800°C (Wt %)
		I	II		10%	20%	40%	
1	TDI	490	585	240	460	485	860	63
2	MDI	500	600	250	450	490	920	70
3	HMDI	430	510	210	425	450	730	50
4	IPDI	475	550	220	450	480	765	57

increases and, finally, it reaches 3–4% for HTPB–TDI polyurethanes and 3.0% for HTPB polyurethanes after immersion in a casting liquid for 7 days. The reduced amount of NG absorption by MDI-based polyurethanes may be due to the higher functionality of MDI (MDI is a mixture of di-, tri-, and polymeric isocyanates) which is responsible for the higher amount of crosslinking in the polyurethanes. Due to this higher crosslinking in HTPB–MDI polyurethane, migration or absorption of NG is difficult in the three-dimen-

sional polyurethane network and a very much less amount of NG is able to penetrate into the structure (Table VII). However, HTPB–HMDI and HTPB–IPDI polyurethanes absorb only 4.0 and 4.4%, respectively, after a period of 7 days. Thus, HTPB–MDI polyurethane absorbs 3.0% NG, a minimum among all the polyurethanes. Since its NG absorption is low, it is expected that its migration during storage of the inhibited propellant will not adversely affect the ballistics of propellants as well as mechanical properties of the inhibitor.

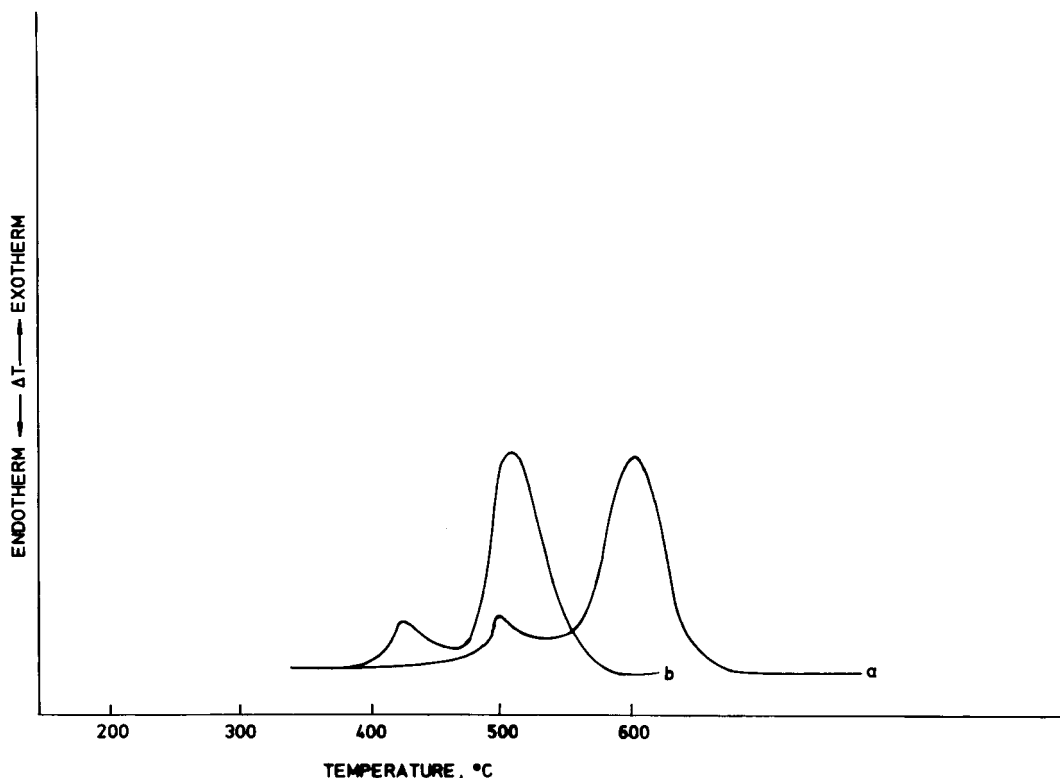


Figure 2 DTA thermograms of filled polyurethanes: (a) HTPB–MDI; (b) HTPB–HMDI.

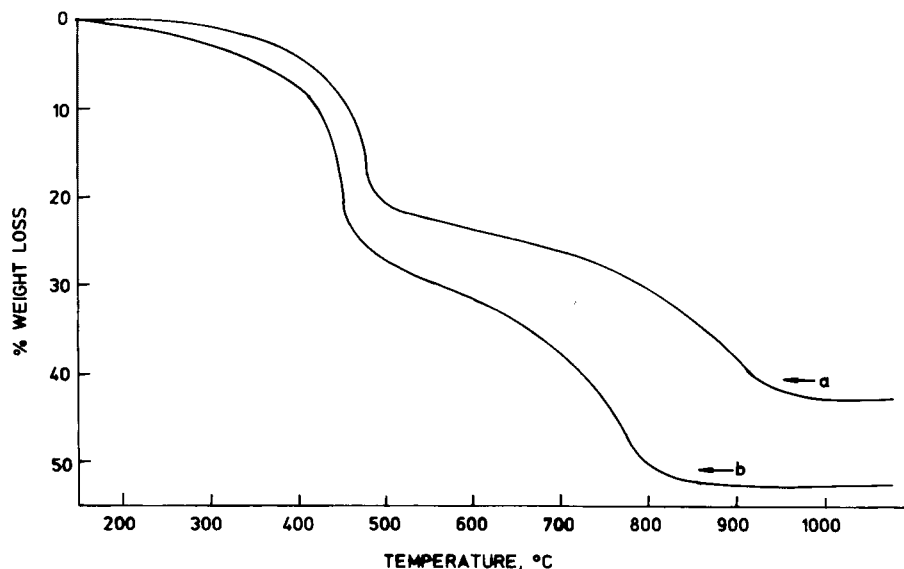


Figure 3 TGA thermograms of filled polyurethanes: (a) HTPB-MDI; (b) HTPB-HMDI.

Inhibition of CMDB Propellants

Among the polyurethanes synthesized, filled HTPB-MDI polyurethanes have the best mechanical and thermal properties. These polyurethanes also have very low NG absorption (3% NG in 7 days). The characteristic properties of HTPB-MDI polyurethanes such as gel time and burning rate (relative measure of flame retardancy) are given in Table VIII. The gel time of these polyurethanes is < 10 min. Further, polyurethanes have very good flame-retardance properties as indicated by the burning rate data (HTPB-MDI polyurethanes, 0.625 mm/s, and polyester resin, 0.971 mm/s).

Considering these properties, HTPB-MDI-based filled polyurethane was evaluated as an inhibitor. CMDB propellants containing RDX were machined and inhibited with polyurethanes using

a casting technique of inhibition. These inhibited propellants were assembled in a rocket motor along with a venturi and igniter and statically evaluated at ambient, hot (+50°), and cold (-30°C) temperatures. The static evaluation in a cigarette-burning mode gave a smooth and neutral pressure-time curve with the desired performance (Figs. 4-6). The pressure-time curve indicates the suitability of filled HTPB-MDI polyurethane as an inhibitor for nitramine-containing CMDB propellants. Thus, polyurethane (HTPB-MDI) was considered suitable for the inhibition of CMDB propellants. Further, a full sustainer charge ($L = 160$ mm, $od = 129$ mm) was inhibited in a similar way by HTPB-MDI polyurethane and statically evaluated in a sustainer mode at ambient temperature for a burning duration of 12 s. The pressure-time curve was neutral (Fig. 7), indicating the suitability of polyurethane

Table VII NG Absorption Data of Filled HTPB-based Polyurethane (Formulation No. 4)

Sample No.	DI	NG Absorption % (Days)						
		1	2	3	4	5	6	7
1	TDI	1.7	2.2	2.4	3.2	3.3	3.4	3.4
2	MDI	1.4	1.8	2.6	2.8	2.9	3.0	3.0
3	HMDI	1.8	2.6	3.0	3.3	3.8	4.0	4.0
4	IPDI	2.3	3.2	3.6	3.9	4.2	4.4	4.4

Table VIII Characteristics of Polyurethane Inhibitor (Formulation No. 4)

Gel time	10.0 min
Burn rate	0.625 mm/s
NG absorption	3.0% in 7 days
TS	15.6 kg/cm ²
<i>E</i>	56.8%
Shore A	58.4
Bond strength	13.3 kg/cm ²
Wt loss	30% at 800°C

(HTPB–MDI) as an inhibitor for CMDB propellants.

Storage–aging Trials

Having established the efficacy of polyurethane as an inhibitor, storage–aging of this inhibitor and inhibited CMDB propellants were also carried out. HTPB–MDI polyurethane-inhibited propellant charges were kept at 60°C in a water-jacketed oven and bond failure between the propellant and inhibitor was monitored.

The propellant–inhibitor bond remained intact (Jan. 1994 to Jan. 1995) at 60°C after a period of 1 year. This is contrary to observations that EP-4 polyester-based inhibitors debond after a period of 45 days at 60°C. Epoxy resin-based inhibitor, however, starts debonding and cracking¹⁰ after a period of 5 days at 60°. This indicates that filled HTPB–MDI-based polyurethane behaves satisfactorily during storage–aging as an inhibitor for nitramine-containing CMDB propellants in comparison to polyester- and epoxy resin-based inhibitors.

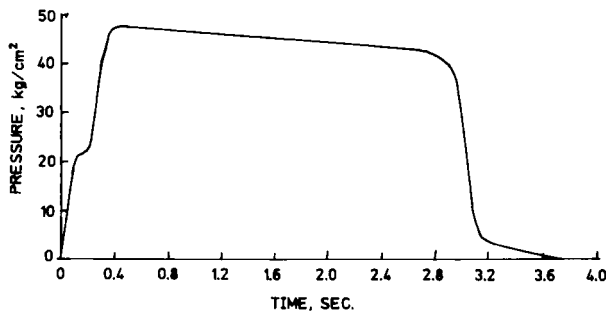


Figure 4 Pressure–time profile for CMDB propellants inhibited with polyurethane at ambient temperature in cigarette-burning mode.

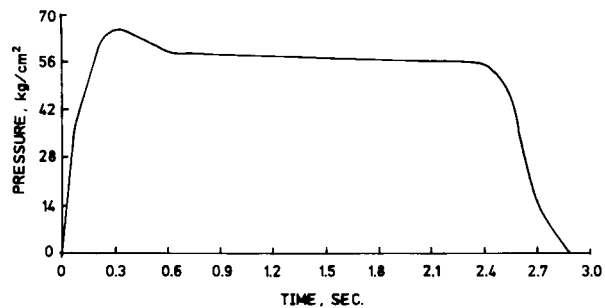


Figure 5 Pressure–time profile for CMDB propellants inhibited with polyurethane at hot (+50°C) temperature in cigarette-burning mode.

CONCLUSIONS

- Filled HTPB–MDI polyurethane has the best mechanical and thermal properties compared to polyurethanes synthesized by the reaction of HTPB with various DIs.
- Filled HTPB–MDI polyurethanes have low NG absorption.
- Due to better mechanical and thermal properties and low NG absorption, filled HTPB–MDI polyurethane was selected and evaluated as an inhibitor for CMDB propellants. The static evaluation of the inhibited CMDB propellant (by HTPB–MDI polyurethane) at ambient, hot (+50°C), and cold (–30°C) temperatures proves the suitability of this polyurethane system as an inhibitor for CMDB propellants.
- Storage–aging trials at ambient and hot (+60°C) temperatures suggested that the inhibitor–propellant bond remains intact for

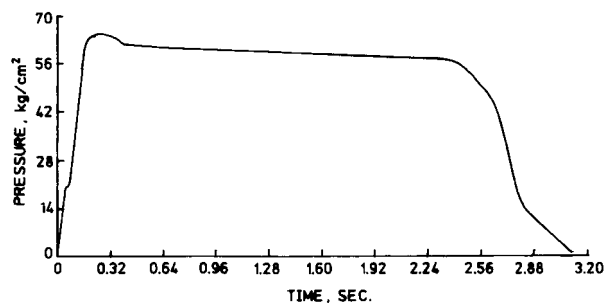


Figure 6 Pressure–time profile for CMDB propellants inhibited with polyurethane at cold (–30°C) temperature in cigarette-burning mode.

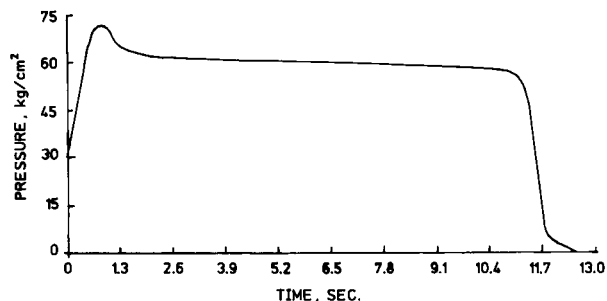


Figure 7 Pressure-time profile for CMDB propellants inhibited with polyurethane at ambient temperature in sustainer mode.

more than 1 year and thus is suitable as a long-lasting inhibition system for CMDB propellants.

The authors are thankful to the director, HEMRL Pune, for permission to publish this manuscript. Thanks are due to Shri P. G. Shrotri, associate director and scientist G, Hemrl, for encouragement and suggestions. We are also thankful to Dr. (Mrs.) Seema D. Kakade, Scientist C, for her help in the preparation of the manuscript.

REFERENCES

1. R. F. Gould, *Propellants, Manufacture, Hazards and Testing*, American Chemical Society, Washington, DC, 1969.
2. C. W. Lawson, ERDE (UK)m, Tech. Memo 14/M/65 (1965).
3. R. Stenson, ERDE (UK), Tech. Note No. 48 (1971).
4. A. Schwartz, Symposium on chemical problems connected with the stability of explosives, ed. J. Hansson. *Sektionen for Detonik och Förbränning*. Sundbyberg, Sweden **4**, 65 (1976).
5. B. Hans, Ger. Offen. 1,206,340 (1965); *Chem. Abstr.*, **64**, 6395 (1966).
6. S. K. Sinha, K. Bahadur, and S. B. Patil, Unpublished, ERDL, India.
7. O. G. Schaffling, U.S. Pat. 3,947,523 (1976); *Chem. Abstr.*, **60**, 3522 od (1976).
8. J. P. Agarwal, M. P. Chouk, R. S. Satpute, and V. C. Bhale, *J. Polym. Sci. Part A*, **27**, 409 (1989).
9. S. Venugopalan and J. Ather, Paper presented at the *High-energy Material Society*, Trivendrum, India, 1994.
10. D. C. Gupta, M. V. Vaidya, S. S. Raomare, V. K. Phadke, and P. K. Divekar, *Macromol. Rep.*, **A32**(Suppl. 8), 1245 (1995).
11. E. Mesmer, Ger Offen, 2,444,930 (1976); *Chem. Abstr.*, **85**, 48938 (1976).
12. B. Wasserman and W. H. Thielbahr, U.S. Pat. 4,009,231 (1977); *Chem. Abstr.*, **86**, 157832 (1977).
13. D. C. Gupta, S. S. Deo, D. V. Wast, S. S. Raomare, and D. H. Gholap, *J. Appl. Polym. Sci.*, **55**, 1151 (1995).
14. J. P. Agarwal, P. G. Shrotri, D. C. Gupta, and M. P. Chowk, *Compos. Manuf.*, **2**(1), 48 (1991).
15. J. H. Saunders and K. C. Frisch, *Polyurethane Chemistry and Technology*, Wiley, New York, 1964, Part II, Vol. 54.
16. J. P. Agarwal, D. C. Gupta, M. P. Chouk, and Y. Khare, *Propell. Explos. Pyrotechn.*, **18**, 155 (1993).
17. J. P. Agarwal, D. C. Gupta, Y. Khare, and R. S. Satpute, *J. Appl. Polym. Sci.*, **43**, 373 (1991).
18. M. V. Pandya, D. D. Deshpande, and D. G. Hundiwale, *J. Appl. Polym. Sci.*, **32**, 4959 (1986).
19. D. C. Gupta, D. V. Wast, M. A. Tapaswi, and B. N. Nigade, *Macromol. Rep.*, **A31**(Suppl. 5), 613 (1994).