

Synthesis, Characterization, and Propellant Binder Studies of New Polyurethanes

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Synopsis

Hydroxy-terminated ether- and ester-based prepolymers more suitable for propellant binder applications were prepared from tetrahydrofuran, propyleneoxide, and various dicarboxylic acids. Polyurethanes were prepared from these prepolymers with various diisocyanates such as hexamethylenediisocyanate, toluene diisocyanate, and diphenylmethanediisocyanate, and the mechanical properties such as hardness, tensile strength, and elongation of these polyurethane elastomers were compared. The thermal degradation study of these polyurethanes was studied in the atmosphere of oxygen. Composite propellants were formed using these prepolymers as binder resins, toluene diisocyanate as the curing agent, ammonium perchlorate as the oxidizer, and aluminum as the fuel. Propellants having two different solid loadings (85 and 82%) were made and compared with respect to their unloading slurry viscosity and mechanical properties. The tensile strength, elongation, and ballistic performance parameters (theoretical) of these new propellant systems were promising.

INTRODUCTION

The binder part of the composite propellant contributes to the rocket motor assembly in three ways: fuel value, compatibility with energetic oxidizers, and good mechanical properties. The last mentioned contribution is usually the most important.^{1,2} In brief, the mechanical properties of the propellant are influenced largely by the type and volume fractions of the oxidizer and the adhesion between the binder and the filler. Crosslinked polyurethanes are used as a binder component to produce propellants of superior physical properties and performance characteristics.³⁻⁶ Hydroxy-terminated polybutadiene-toluenediisocyanate-based binder system is commonly used in practice.^{7,8} Mishuck and Carleton⁹ prescribed that to attain maximum specific impulse, hydrocarbon binders should have comparatively higher oxidizer loading. The extremely high volume fraction of oxidizer necessary for maximum energy release in rubber-based composite propellant places serious restrictions on the selection of the original liquid binder. If the solid loading exceeds 80% by volume (approximately 90% by weight) the resulting mixture might be

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difficult to cast and, further, the resulting propellant would have undoubtedly poor mechanical properties, especially the ultimate elongation. The solution to the problem is attempted by selecting oxygen containing binders that would reduce the amount of oxidizer required to achieve the maximum performance for the particular binder-oxidizer system.

Polyethers exhibit low viscosity and proper rate of cure, and the oxygen included in the binder results in a higher energetic performance even with a limited oxidizer loading.¹⁰ Both polytetramethyleneglycol- and polypropyleneglycol-based polyurethanes have T_g lower than -40°C ; hence the propellants based on this can be operated over a wide range of temperature.^{4, 11, 12} Generally polyester-urethane-based propellants exhibit excellent mechanical properties and superior aging stabilities compared to that of polyether-urethane-based propellant whereas the ballistic performance is comparatively poor. A mixture of both polyether and -ester components in polyurethane make possible a large variety of changes both in the mechanical and ballistic properties of the resultant propellant.¹³⁻¹⁶

The viscosity of the propellant slurries as related to the solid loading is a problem of much complexity. Sweeny and Geckler¹⁷ initiated this study by investigating a simplified model consisting of concentrated suspensions of glass spheres in nonreactive resins. The greater complexity exhibited by propellants results from many distinct and additional factors like sedimentation, interfacial effects, flocculation-deflocculation effects, chemical reactions, polymerizations, solubilities, etc. Hence it is necessary to rely on systematic empirical observations and good engineering judgment. The development of binders with higher oxygen content, a recognized target in the propellant chemistry, was approached with the new urethane-based ether- and ester-containing polymer system. The effect of solid loading on the slurry viscosity and the resultant mechanical properties of the propellants were studied.

EXPERIMENTAL

Materials

Tetrahydrofuran (AS, SDs), Xylene, (AR, SDs), were dried before use. Adipic acid (Loba Chemie), maleic anhydride (Loba Chemie), phthalic anhydride (Sarabhai M. Chemicals), propylene oxide (Ag, Fluka), acetic anhydride (AR, SDs), and toluenediisocyanate (AG, Fluka) were used as received. Hexamethylene diisocyanate (AG, Fluka) and diphenylmethane diisocyanate (AG, Fluka) were purified by distillation under reduced pressure. Perfectly dried ammonium perchlorate having the average particle size $325\ \mu\text{m}$ (coarse) and $50\ \mu\text{m}$ (fine) were used as the oxidizer in the propellant. Dry aluminum powder having the average particle size $16.5\ \mu\text{m}$ was used as the metallic fuel in the propellant.

Preparation of Prepolymer Diols

Hydroxy-terminated linear polyoxytetramethyleneglycol (POTMG) of high molecular weight (MW 1500) and low molecular weight (MW 540) were prepared by the cationic ring opening polymerization of tetrahydrofuran (THF)

in the presence of acetic anhydride and by the subsequent hydrolysis of the acetate end.^{18,19}

A copolymer of THF and propylene oxide with hydroxyl end was prepared by doing the polymerization in presence of 1,4-butanediol, a chain transfer agent, and using $\text{BF}_3 \cdot \text{O}(\text{CH}_2)_4$ as initiator.^{20,21} Polyoxytetramethyleneoxypropyleneglycol (POTMOPG) of two different molecular weights 1550 and 620 were prepared.

Linear polyesters with hydroxyl endcapping were best achieved by the polycondensation of low molecular weight polyether diols (both POTMG of MW 540 and POTMOPG of MW 620) and diacids taking excess of diol. The solution polymerization procedure reported by Brown et al.²² was adopted but using xylene as the solvent. The extent of polyesterification was followed by estimating the decrease in carboxyl number of the polymer.²³ The polymerization was continued till the acid number goes below 1.0 and the solvent was removed under vacuum. No catalyst was used in the process except in case when phthalic anhydride was used. Paratoluenesulfonic acid (PTS) in small amount was used (0.2 g PTS for 500 g of monomer) to increase the rate of the reaction. Polyoxytetramethylen adipate (POTMAA), polyoxytetramethylenemaleate (POTMMAO), and polyoxytetramethylenephthalate (POTMPA) are the condensation products of low molecular weight POTMG (MW 540, 0.9 mol) with adipic acid (0.6 mol), maleicanhydride (0.6 mol), and phthalicanhydride (0.55 mol), respectively. Similarly polyoxytetramethyleneoxypropylen adipate (POTMOPAA), polyoxytetramethyleneoxypropylenemaleate (POTMOPMA) and polyoxytetramethyleneoxypropylenephthalate (POTMOPPA) are the condensation product of low molecular weight POTMOPG (MW 620, 0.9 mol) with adipic acid (0.6 mol), maleicanhydride (0.6 mol), and phthalic anhydride (0.55 mol). The structure of these prepolymers is given in Figure 1.

Characterization of the Prepolymers

The hydroxyl and carboxyl numbers of the prepolymers were found out by standard procedures.^{23,24} The molecular weight of the prepolymers was found out from its hydroxyl and carboxyl numbers.²⁵ The viscosity of the prepolymer was determined by the Brookfield viscometer (Brookfield Engineering Laboratories, Inc.) at 25°C.

Preparation of Polyurethane Elastomers

A resin kettle, fitted with a sealed stirrer, a nitrogen inlet, and a thermometer, was charged with a requisite amount of prepolymer under study and degassed for about 10 min. An equivalent amount of toluenediisocyanate (TDI) or hexamethylene diisocyanate (HMDI) or diphenylmethanediisocyanate (MDI) was added and mixed thoroughly by stirring. Dry nitrogen gas jacketing was maintained throughout the mixing. Temperature rise observed reached a maximum and started decreasing. At this point, the viscous syrup was degassed under vacuum and transferred into a square tray coated with silicone oil to form a film of approximately 3–4 mm and cured in an oven at 60–65°C for 5 days. While preparing polyurethane from MDI, after the

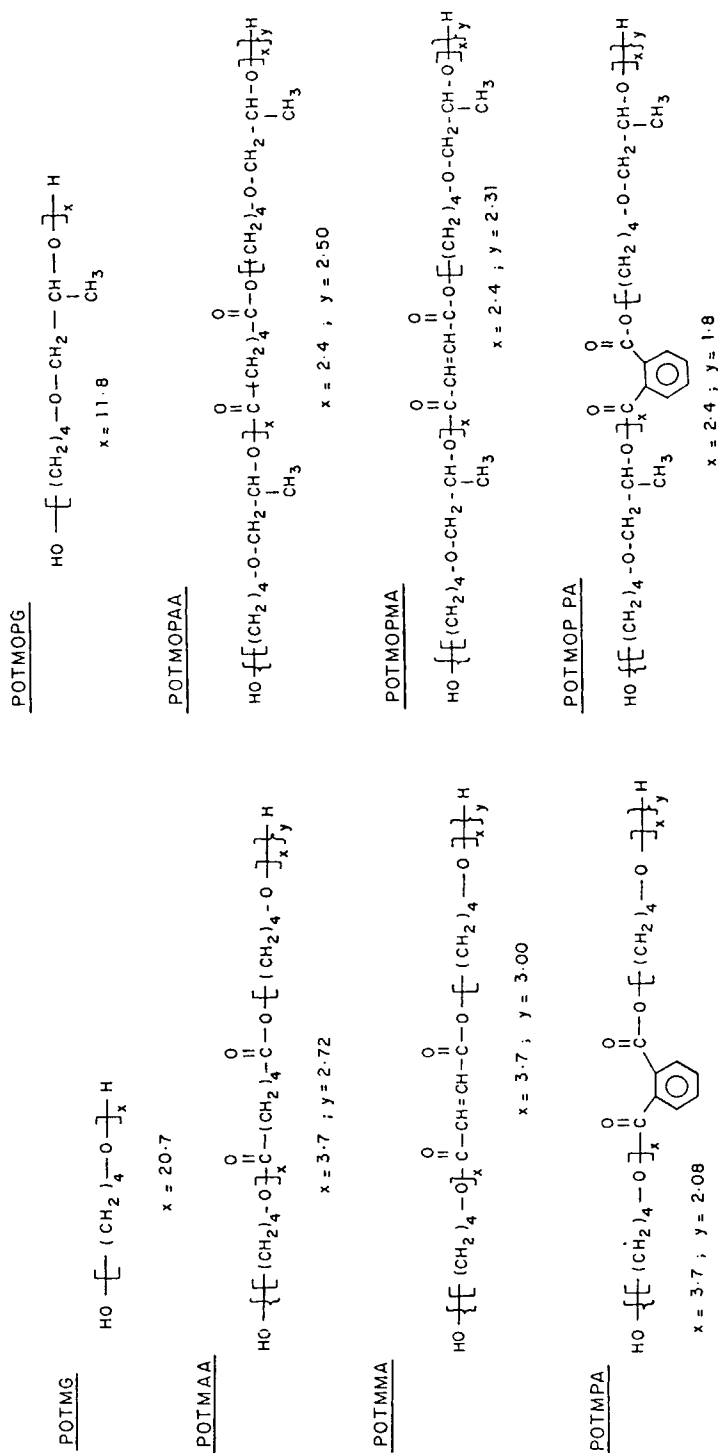


Fig. 1. The structure of prepolymers with average stoichiometry of each segment.

addition of both ingredients, the mixture was heated to 50–55°C to enhance perfect mixing.

Characterization of Polyurethane

The inherent viscosity values (η_{inh}) of the polyurethanes were found out for 0.5% solution in dimethyl formamide (DMF) using Ubbelohde viscometer at 30°C. The infrared spectra of the polymers (film) were recorded in a Perkin-Elmer IR instrument (Model 983). Mechanical properties such as tensile strength and elongation (at break) of the polyurethane elastomers were measured by using Instron Model 1122 (U.K.) by the standard procedures²⁶ at the crosshead speed of 20 mm/min. Thermal degradation (TGA) of the polyurethanes was carried out using Mettler TA 3000 system in an oxygen atmosphere at the heating rate of 20 K/min. The temperature at the degradation maximum was obtained from the differential curves (DTG).

Propellant Binder Studies

Propellants were cast with 82 and 85% solid loading with various prepolymers such as POTMG, POTMAA, POTMMA, POTMPA, POTMOPG, POTMOPAA, POTMOPMA, and POTMOPPA as binders with TDI (80% 2,4 isomer and 20% 2,6 isomer) as curing agent. The composition of the 85% solid-loaded propellant was fixed as ammonium perchlorate (APC) 67%, aluminum power 18%, and the rest 15% polymeric binder. APC of two different particle size 325 μm (coarse) and 50 μm (fine) were used in the ratio 3 : 1. The polymeric binder consisted of the prepolymer, plasticizer (dioctyladipate), and trimethylol propane (cross-linker) in the ratio 100 : 35 : 4 (by weight) and the required equivalent of TDI. The composition of the 82% solid-loaded propellant was fixed as APC 67% (bimodal, coarse : fine 3 : 1), aluminium power 15%, and the rest 18% polymeric binder. The composition of the polymeric binder is similar to that of the 85% solid loaded propellant.

The mixing of the propellant was carried out in a stainless steel sigma blade mixer having a capacity of 0.8 kg as per the standard procedure. The homogeneity of dispersion of ingredients in the slurry was found out by estimating the amount of APC and aluminum at various locations.^{27,28} The propellant slurry was vacuum cast by pouring into a plastic carton and curing at 60°C in an air oven for 5 days. The cured propellant cast was cut into slabs having the dimensions 10 × 10 × 0.6 cm with the aid of nonsparking cutting tools. The dumbbell-shaped specimens used for mechanical testings were cut out from these slabs. Tensile strength, elongation (at break), and modulus (initial) of the propellant were found out using an Instron Model 1122 by the standard procedures with the crosshead speed of 50 mm/min. The performance parameters such as specific impulse, flame temperature, and specific heat ratio were theoretically evaluated for the 82% solid loaded propellants by the commonly accepted method.²⁹

RESULTS AND DISCUSSION

The properties of the prepolymers are given in Table I. The molecular weight of the prepolymers were controlled to have comparable values and the

TABLE I
Properties of Prepolymers

Properties	POTMG	POTMAA	POTMMA	POTMPA	POTMOPG	POTMOPAA	POTMOPMA	POTMOPPA
Specific gravity (25°C)	0.970	0.994	1.014	1.018	0.987	1.007	1.027	1.025
Viscosity (Pa s 25°C)	1.580	2.180	1.898	1.632	1.160	1.485	1.718	1.418
Hydroxyl number	74.5	61.0	58.8	79.0	72.1	59.8	66.2	87.0
Carboxyl number	0	0.6	1.1	0.9	0	0.3	1.2	1.3
Molecular weight	1506	1821	1873	1404	1556	1866	1665	1271

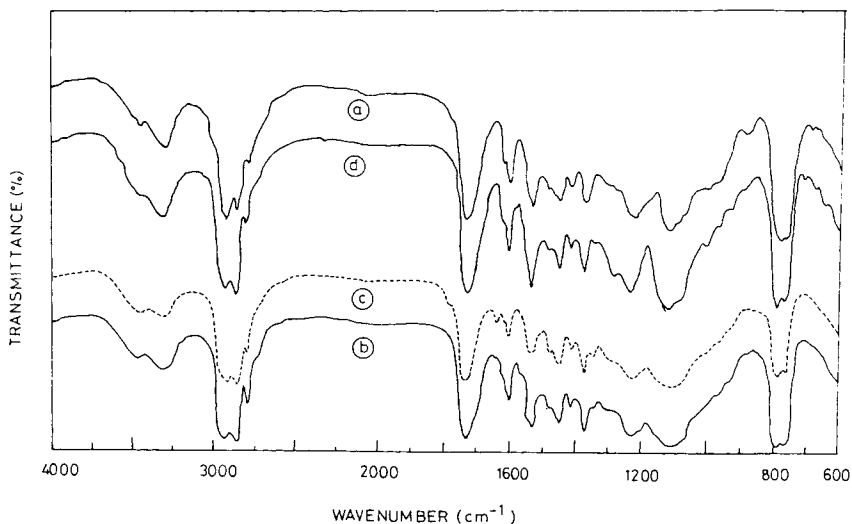


Fig. 2. The IR spectra of the polyurethane elastomers: (a) POTMOPG-TDI; (b) POTMOPAA-TDI; (c) POTMOPMA-TDI; (d) POTMOPPA-TDI.

viscosity was varied as it mainly depends on its chemical structure. The viscosity of the prepolymer has a telling effect on the efficiency of mixing and also on the rheological behavior of the uncured propellant. It should not be so high as to render it difficult to disperse the oxidizer and should not be so low as to allow the oxidizer to settle down rapidly in the uncured mix. The viscosity of the prepolymers was found to be optimum for better mixing and curing.

Polyurethanes were prepared from these prepolymers with HMDI, TDI, and MDI. The IR spectra of the representative polyurethanes are given in Figure 2. The identification of the individual constituents of the polyurethane in IR spectroscopy is difficult.³⁰ However, the formation of the urethane bond and the presence of some other constituent groups can be seen in the spectra. A broad band characteristic of N—H stretching was observed in the region 3300–3350 cm^{-1} . The amide I band (due to C—O stretching of the urethane group) and amide II band (due to N—H deformation) of polyurethane were observed in almost equal intensity in all the spectra in the regions 1720–1730 cm^{-1} and 1525–1540 cm^{-1} , respectively. All the polyurethanes exhibited a strong band at 1100 cm^{-1} due to the aliphatic ether group.

Mechanical properties like hardness, tensile strength, elongation, and also the solution viscosity (inherent viscosity) of the polyurethanes are given in Table II. From the table it is observed that the HMDI-based polyurethanes show poorer mechanical properties than those based on MDI and TDI. This property is attributed to the lower reactivity of HMDI³¹ and the less effective intermolecular interaction in the resulting polymer as the $-\text{CH}_2-$ group is having very low molar cohesive energy.³² Mechanical properties of TDI- and MDI-based polyurethanes are better and comparable. The structure, molecular weight, and reactivity of the ingredients play a larger role in determining the mechanical properties obtained with the polymers based on POTM derivatives (POTMG, POTMAA, POTMMA, and POTMPA) than those of

TABLE II
Mechanical Properties and Inherent Viscosity Values of HMDI-, TDI- and MDI-Based Polyurethanes

Prepolymer base	HMDI-cured polymers				TDI-cured polymers				MDI-cured polymers			
	Hardness (Shore A)	Tensile strength $\sigma \times 10^{-4}$ ($N m^{-2}$)	Elongation at break (%)	η_{inh} (DMF, 30°C)	Hardness (Shore A)	Tensile strength $\sigma \times 10^{-4}$ ($N m^{-2}$)	Elongation at break (%)	η_{inh} (DMF, 30°C)	Hardness (Shore A)	Tensile strength $\sigma \times 10^{-4}$ ($N m^{-2}$)	Elongation at break (%)	η_{inh} (DMF, 30°C)
POTMG	10	37.3	420	0.280	14	140.2	854	0.316	15	109.8	710	0.480
POTMAA	10	20.6	524	0.220	12	45.1	712	0.394	12	30.4	924	0.322
POTMMA	12	47.1	320	0.415	12	37.3	1757	—	14	66.7	1025	—
POTMPA	—	—	—	0.290	6	8.8	135	0.298	—	—	—	0.348
POTMOPG	—	—	—	0.247	—	—	—	0.203	—	—	—	—
POTMOPAA	—	—	—	0.315	13	22.6	510	0.191	12	30.4	610	0.230
POTMOPMA	10	21.57	180	0.305	12	31.4	754	0.408	14	39.2	588	0.480
POTMOPPA	—	—	—	0.119	—	—	—	0.139	—	—	—	0.215

POTMOP derivatives (POTMOPG, POTMOPAA, POTMOPMA, and POTMOPPA). This is partly due to the less reactivity of the secondary hydroxyl groups. The presence of pendant methyl group in the POTMOP-based polymers is also responsible for the poor mechanical properties,³³ since these groups reduce the intermolecular forces by keeping apart the mutually attracting groups like urethane or ester groups. Among the polyester series maleic-acid-based (POTMMA and POTMOPMA) polyurethane showed higher tensile value than that of adipic-acid-based polyurethane (POTMAA and POTMOPAA). This might be due to the ease of rotation of the $-\text{CH}_2-$ groups favoring softness and flexibility to the adipic-acid-based polyurethane chain, unlike those derived from maleic acid wherein the fraction of double bonds present stiffen the chain. Unexpectedly, the polyetherphthalates (POTMOPPA)-based polyurethanes have poorer mechanical properties, even though the aromatic group is expected to favor chain stiffness. This is due to the bending of the polymer chain resulting with the phthalic group. The lower reactivity of this aromatic-group-containing prepolymer resulted in low molecular weight polyurethanes as evidenced from its inherent viscosity values. The prepolymer-isocyanate reaction rate should be comparatively low; otherwise the reaction exotherm, which is the measure of the extent of the isocyanate alcohol reaction, will be high, leading to shrinkage problems and also explosion hazard. Less reactive prepolymers only will give enough potlife during propellant mixing. But very low reactivity is not desirable as it affects the curing process and the final mechanical properties of the propellant. The mechanical properties of most of the polyurethane elastomers derived from phthalic-anhydride-based prepolymers (POTMPA and POTMOPPA) are so poor as to prevent testing. Such a poor reactivity prevents its applications as a propellant binder, which was reflected in the inability of the propellant to cure.

Thermal degradation studies of the selected polyurethanes (POTMOPG-TDI, POTMOPAA-TDI, POTMOPMA-TDI, POTMOPPA-TDI, and POTMMA-TDI) were made. Figures 3 and 4 show the continuous weight loss curves (TGA) and the differential curves (DTG) of the polymer. The decomposition of all the polymers took place in two stages. The first stage is the major decomposition process and nearly 80–90% of the polyurethane degraded at this stage with the remaining polymer degrading in the second stage. The first degradation process, which is due to the decomposition of polyurethane, starts at 475 K and continued up to 758 K. The second stage can only be the oxidation of the residual carbonaceous material (combustion) since the degradation was carried out in an atmosphere of oxygen. There is no notable difference in the decomposition pattern or decomposition temperature as all the polymers are structurally comparable containing ether, ester, and urethane groups in common. The degradation stage and the temperature at which maximum decomposition took place are tabulated in Table III.

The propellant properties will be drastically affected by the extent of solid loading. This is shown in this study on propellants with 82 and 85% solid loading. It was observed that increasing the solid loading even by 3% considerably increased the slurry viscosity, which may even become unprocessable. TDI-cured POTMAA-based binder with 85% solid loading (APC = 67%, Al = 18%) after 3 h of mixing resulted in a slurry having the viscosity of 300 Pa s,

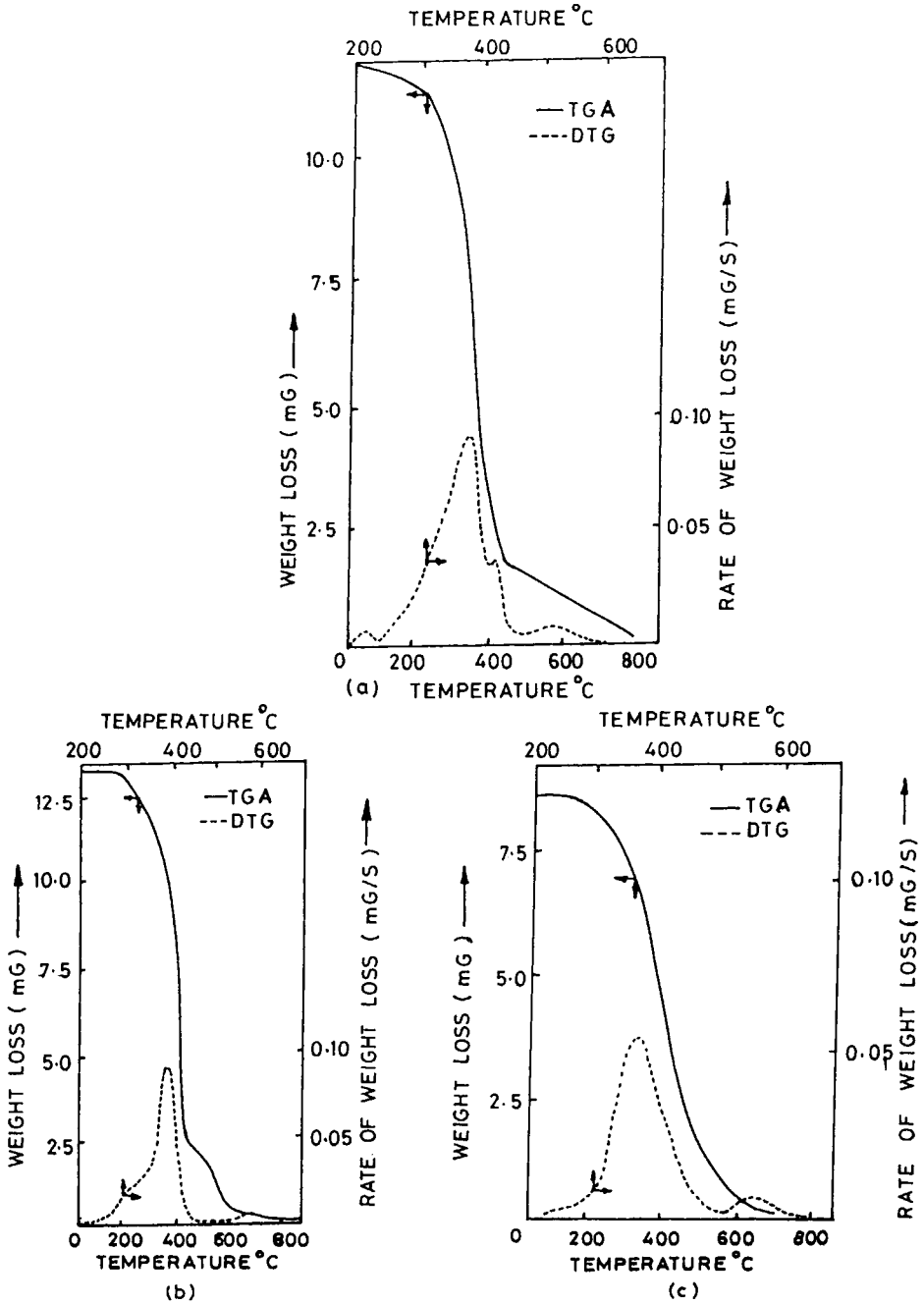


Fig. 3. The thermogravimetric analysis (TGA) and its derivative (DTG) curves of polyurethanes: (a) POTMOPG-TDI; (b) POTMOPAA-TDI; (c) POTMOPMA-TDI.

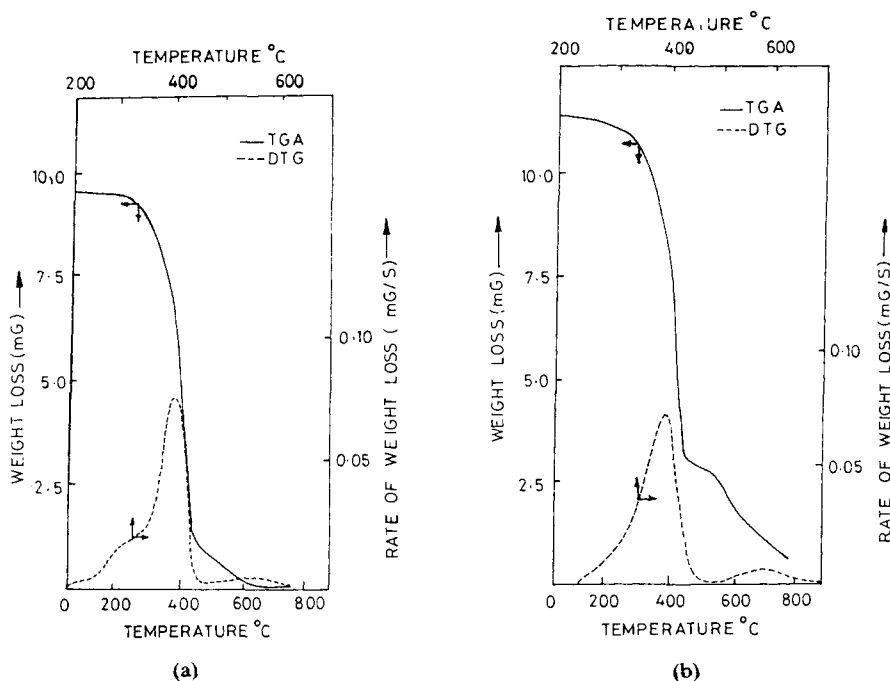


Fig. 4. The thermogravimetric analysis (TGA) and its derivative (DTG) curves of polyurethanes: (a) POTMOPPA-TDI; (b) POTMMA-TDI.

which is too high for casting. But the same binder with 82% solid loading gave the propellant slurry with the viscosity of 128 Pa s only, which is castable and cured to give a propellant of good tensile strength ($156.9 \times 10^4 \text{ N m}^{-2}$). In all the propellant systems up to a threefold increase in slurry viscosity was observed by increasing the loading from 82 to 85% (Tables IV and V). Small changes in solid loading affects the slurry viscosity considerably. Sweeny³⁴ studied the rheological effect of the addition of crystalline inorganic oxidizers in Aeroplex propellants, containing uncured polyester-styrene based binder loaded with 75% oxidizer. Increasing the oxidizer content of this propellant by 3% sharply increased the viscosity to the extent of a thixotropic breakdown. The extent of solid loading has been shown in the present study to have an

TABLE III
Degradation Stages of Different Polyurethanes and the Characteristic Temperature with Weight Loss

Polymer	First stage decomposition			Second stage decomposition		
	Temperature range (K)	T_{\max} (K)	Weight loss (%)	Temperature range (K)	T_{\max} (K)	Weight loss (%)
POTMOPG-TDI	478-728	653.0	85.1	728-938	783	14.1
POTMOPAA-TDI	484-736	672.3	89.5	736-960	832	10.2
POTMOPMA-TDI	475-758	693.0	85.3	758-958	828	13.6
POTMOPPA-TDI	476-740	664.0	90.5	740-940	808	8.5
POTMMA-TDI	493-738	683.0	74.1	738-933	843	20.1

TABLE IV
Properties of 85% Solid Loaded Propellant^a

Prepolymer	Unloading slurry viscosity (Pa s)	Tensile strength $\sigma \times 10^{-4}$ (N m ⁻²)	Elongation at break (%)	Hardness (Shore A)	Modulus (initial) $k \times 10^{-4}$ (N m ⁻²)
POTMG	92.8	73.5	6	60-80	1882
POTMAA	300.8	Not castable	—	—	—
POTMMA	960.0	89.2	16	—	1804
POTMPA	144.0	Brittle	—	—	—
POTMOPG	102.4	62.8	5	83	1480
POTMOPAA	288.0	Too hard	—	—	—
POTMOPMA	156.8	69.6	3	86	2461
POTMOPPA	198.4	Uncurable	—	—	—

^aR value = 1.0; APC = 67 wt % (bimodal, coarse: fine = 3:1); Al = 18 wt %; prepolymer, plasticizer (DOA) TMP = 100:35:4 (wt ratio).

adverse effect on the ultimate elongation (Tables IV and V). It was found that the POTMMA-based binder, on loading to 85%, resulted in a propellant having an elongation of 16% while the tensile strength was 89.2×10^4 N m⁻². But on reduction of solid loading by 3%, the elongation increased to 36% without an appreciable change in the tensile strength. POTMPA-based binder with 82% solid loading resulted in a propellant with 12% elongation but loading to 85% resulted in a hard brittle mass.

The maximum performance with good mechanical properties with the stipulated solid loading can be attained by using bimodal or trimodal particle-size distribution with ratios between the mean particle sizes of roughly 10:1. In the present propellant systems, bimodal APC of particle sizes 325 μ m and 50 μ m were used in the weight ratio 4:1 to ensure compact packing. The voids produced by the APC coarse will be occupied by the APC fine, leading to compact packing.

TABLE V
Properties of 82% Solid Loaded Propellant^a

Prepolymer	Unloading slurry viscosity (Pa s)	Tensile strength $\sigma \times 10^{-4}$ (N m ⁻²)	Elongation at break (%)	Hardness (Shore A)	Modulus (initial) $k \times 10^{-4}$ (N m ⁻²)
POTMG	32.0 at 49°C	68.6	5.5	83	1814
POTMAA	128.0 at 33°C	156.9	17.5	85	2559
POTMMA	640.0 at 29°C	73.5	36.0	70	284
POTMPA	35.2 at 32°C	24.5	12.0	60	510
POTMOPG	35.2 at 32°C	68.6	11.0	75	843
POTMOPAA	230.4 at 35°C	—	Not castable	—	—
POTMOPMA	76.8 at 37°C	70.6	3.0	80	—
POTMOPPA	67.2 at 32°C	—	Uncurable	—	—

^aR value = 1.0; APC = 67 wt % (bimodal, coarse: fine = 3:1); Al = 15 wt %; prepolymer, plasticizer (DOA) TMP = 100:35:4 (wt ratio).

Compact packing of the solid ingredients have a beneficial effect on the ballistic performance of the rocket also. Among the binder systems loaded with 82% solids (APC = 65%, Al = 17%), POTMMA results in a propellant having 36% elongation with the tensile strength of $73.5 \times 10^4 \text{ N m}^{-2}$, which is comparable to the systems that are under current use. Even though the elongation that resulted with the POTMAA binder-based propellant was only 17.5%, it is associated with a higher tensile strength of $156.9 \times 10^4 \text{ N m}^{-2}$. Since the tensile strength of this propellant is very high, and elongation is low, by the reduction of crosslinker (TMP) and R value (NCO/OH ratio) and/or by the use of excess plasticizer, the elongation can be increased with a limited decrease of the tensile strength. Even though the other polymeric binder systems based on POTMG, POTMOPG, and POTMOPMA impart enough tensile strength (ranging from 68.6×10^4 to $70.6 \times 10^4 \text{ N m}^{-2}$), the elongation is not sufficient (3–12%). Even then, by doing variations with the crosslinker, R value, and plasticizer or by the reduction of solid loading, better elongation can be achieved. POTMOPPA was the least reactive prepolymer diol which gave a poor elastomer and the resulting propellant slurry was not castable even with an extended curing period. Generally, the observed mechanical properties of the propellant are comparable to those of the unfilled binder systems. Among the binder systems, POTMMA–TDI gave better elongation and this persisted in the propellant also. But POTMG–TDI, which gave maximum tensile strength, did not exhibit the same property in the propellant. Thus the same trend in mechanical properties was not observed in all the cases. This is due to the effect of other factors like binder–filler interaction and binder–plasticizer compatibility, which may differ, depending upon the prepolymer type. Modulus of a propellant can be relatively low, but it must be large enough to ensure that the flight acceleration forces do not deform the grains sufficiently to modify the internal configuration. If the propellant has a significant tensile strength, it is usually true that the modulus will also be adequately high.³⁵

Presence of crosslinking sites in the binder has a considerable effect on the propellant mechanical properties. Among the two ways of achieving crosslinking, either by using polyol or excess diisocyanate, crosslinking through polyol is preferred since any excess isocyanate might form carbodiimide with the evolution of carbon dioxide gas. Moreover, the allophanate and isocyanurate linkages, which are responsible for crosslinking in polyurethane by excess diisocyanate, are thermally unstable.³⁶ Hence, in the present system also,

TABLE VI
Effect of R Value and Crosslinker Concentration on Propellant Properties Solid Loading^a

Prepolymer	Prepolymer DOA : TMP (wt ratios)	NCO/OH ratio (R value)	Unloading slurry viscosity (Pa s)	Tensile strength $\sigma \times 10^{-4}$ (N m^{-2})	Elongation (%)	Hardness (Shore A)
POTMG	100 : 35 : 4	1.0	92.8 at 35°C	73.5	6.0	60–80
POTMG	100 : 35 : 4	0.8	86.4 at 35°C		Uncurable	
POTMG	100 : 35 : 1.35	0.8	64.0 at 34°C		Uncurable	

^a 85 wt %; APC = 67 wt % (bimodal, coarse : fine = 3 : 1), Al = 18 wt %.

TABLE VII
The Performance Parameters (Theoretical) of the 82% Solid Loaded Propellant Systems^a

Property	POTMG	POTMAA	POTMMA	POTMPA	POTMOPG	POTMOPAA	POTMOPMA	POTMOPPA
Specific impulse at sea level (s)	257.4	257.4	257.2	255.8	257.9	257.7	257.6	256.4
Specific impulse in vacuum (s)	280.1	280.6	280.5	278.9	281.1	281.1	281.1	279.7
Flame temperature (K)	3081	3149	3178	3157	3133	3178	3205	3188
Vent temperature (K)	2885	2957	2988	2966	2940	2988	3016	2998
Ejection temperature (K)	1828	1922	1963	1936	1898	1962	2000	1978
Mean molecular weight (g mol ⁻¹)	26.2	27.0	27.3	27.4	26.7	27.2	27.5	27.6
Specific heat ratio	1.151	1.147	1.146	1.147	1.148	1.140	1.140	1.140
Thrust coefficient	1.633	1.635	1.636	1.635	1.634	1.636	1.636	1.636
Characteristic velocity (m s ⁻¹)	5071	5065	5058	5033	5078	5070	5066	5043
Expansion ratio (AE/AT)	9.8	10.0	10.1	10.0	9.96	10.1	10.2	10.1
H (kcal/mol)	-1495.1	-1807.9	-1858.5	-1398.9	-1544.8	-1852.6	-1653.0	-1261.8

^aAPC = 67%, polymer = 18%, Al = 15%, pressure = 70 KSC.

crosslinking was attained through trimethylolpropane only. But using R values below 1.0 did not result in good mechanical properties, especially when they are derived from soft elastomeric prepolymers. In the POTMG-based propellant, a reduction of the R value from 1.0 to 0.8 was found to reduce the propellant slurry viscosity from 92.8 to 86.4 Pa s and rendered the propellant uncurable (Table VI). Reduction of the TMP content reduced the viscosity further (up to 64 Pa s) and made the propellant uncurable.

The energy release or the specific impulse of a propellant composition can either be calculated thermodynamically or determined by experiment. Since the polymeric binders of all the solid propellants serve chiefly as the primary source of gases, the contribution of the binder to the energetics is important. Specific impulse is simply defined as the thrust per unit weight of the propellant that burns per second and this is the most important measure of the propellant's effectiveness. With rubbery or plastic binders having groups like fluorine, nitrogen, hydrazides, and exotic perchlorates, a maximum specific impulse of 275 has been obtained.³⁷ The specific impulses calculated for the present propellant systems are in the range of 255.8–257.9 (Table VII), which are quite promising. Even though the flame temperature of the polyether polymers (POTMG and POTMOPG) was lower, these systems have higher impulse power, which may be due to the lower mean molecular weight of the evolved gases. Values of the calculated specific impulse will necessarily be higher than those obtained from firing actual propellants in rocket motors. In practice, it has been found that the experimental values are in general 3–12% lower than those calculated. This is partly due to nozzle design and combustion inefficiencies.

Thus the new ether-ester based polyurethanes are more suitable for propellant binder applications. The higher oxygen content of these prepolymers confer on them a higher specific impulse with limited solid loading. A high solid loading (85%) has been achieved in the case of POTMMA- and POTMAA-based binder systems with the required mechanical properties, showing promise in actual applications. The crucial effect of the extent of solid loading on the rheological and mechanical properties has been brought out in these binder systems.

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