

Polysiloxane-Based Inhibition System for Double-Base Rocket Propellants

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ABSTRACT: Four hydroxy-terminated poly(dimethyl siloxane) (HTPDMS) prepolymers of varying viscosities and molecular weights were prepared and used with and without alumina trihydrate as a filler. The HTPDMS viscosity and filler percentage were optimized to ensure acceptable pot life and mechanical properties. Low nitroglycerine migration from the propellant to the inhibitor, excellent temperature stability, and good bonding between the propellant and inhibitor at temperature extremities (-40 to $+60^{\circ}\text{C}$) are some of the remarkable features of a room-temperature vulcanizing (RTV) silicone inhibitor. Double-base (DB) propellant grains were inhibited by a casting technique using Siloxane-15 and statically fired in a rocket motor. A smooth pressure–time profile infers that Siloxane-15 works satisfactorily as an inhibitor for DB propellants.
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INTRODUCTION

A rocket-propellant inhibitor is an inert polymer which is coated on certain specific surfaces of a rocket-propellant grain to restrict the burning of the propellant and to obtain the desired pressure–time profile during the burning. Some of the vital requirements of an inhibitor are its chemical compatibility with the propellant, acceptable mechanical properties (tensile strength and percentage elongation, etc.), low shrinkage, good bonding with the propellant even at the extremities of temperature (-40 to $+60^{\circ}\text{C}$) during storage, low nitroglycerine (NG) migration from the propellant to the inhibitor, and ease of processability. In the case of double-base (DB) propellants which contain a considerable amount of NG (ca. 40% in some cases) as an explosive plasticizer, ethyl cellulose and unsaturated polyesters have been used for a long time as inhibitors.^{1–4} But the major disadvantage of these inhibitors is the high NG migration from the propellant to the inhibitor dur-

ing storage. This not only causes debonding between the propellant and the inhibitor on storage but also leads to problems such as undesirable ballistics and coning of the burning propellant.^{5–7} The use of silicone rubber has been reported as an inhibitor for composite propellants^{8,9} in order to minimize the extent of NG migration; it was thought that a semiorganic polymer, particularly the one based on a silicone elastomer, could be used as an inhibitor for the DB rocket propellants.

EXPERIMENTAL

Materials

Dimethyl dichlorosilane (DMDCS, (Fluka), tetraethoxysilane; (Fluka), dibutyl tin dilaurate (DBTDL, BDH), sodium chloride (AR), solvent ether (BDH); anhydrous sodium sulfate (AR), and alumina trihydrate (average particle size $\approx 8 \mu$) were used.

Synthesis of HTPDMS Prepolymer

The hydroxy-terminated poly(dimethyl siloxane) HTPDMS prepolymer was prepared by the drop-

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wise addition of DMDCS to a saturated solution of sodium chloride at 40°C over a period of 2 h.^{10,11} The reaction mixture was kept at room temperature for different periods. The HTPDMS present in the mixture was extracted with ether and dried using anhydrous sodium sulfate. Several batches of HTPDMS were prepared by varying the duration and temperature of the hydrolysis and, finally, reaction conditions were optimized.

Characterization of HTPDMS

The prepolymer was characterized by the following:

IR Spectra

IR spectra were recorded using a Perkin–Elmer 683 IR spectrophotometer by the smear technique.

Viscosity

Viscosity was determined at 30°C using an RVTD Brookfield viscometer.

Gel Time

Gel time was determined using a Gel Timer (GT-4, Techne, UK) with tetraethoxysilane as the crosslinking agent in the presence of the DBTDL catalyst as per the reported method.¹²

Molecular Weight

Number-average molecular weight (\bar{M}_n) was determined by a vapor pressure osmometer (Knauer, Germany) using toluene as a solvent and benzil as the standard.

Formulation of Room-temperature Vulcanized (RTV) Silicone Rubber

RTV silicone rubber was obtained by crosslinking HTPDMS with tetraethoxysilane (2% by weight

of the prepolymer) in the presence of a few drops of the DBTDL catalyst. A different amount of alumina trihydrate was added as a filler in the composition and thoroughly mixed. These formulations were cast into sheets and cured at room temperature ($\approx 30^\circ\text{C}$) for about 7 days to ensure complete curing.

Mechanical Properties

Mechanical properties such as tensile strength (TS) and percentage elongation (% *E*) at break were measured on a universal tensile testing machine (Instron) using dumbbell-shaped specimens of 3-mm thickness.¹³

NG Absorption

An NG absorption test was carried out¹⁴ on RTV silicone sheets (50 × 50 × 2 mm). These sheets were dipped in a casting liquid (80% NG, 18% diethylphthalate, and 2% carbamate). After 5 days, the sheets were removed, wiped off thoroughly, and weighed. The percentage absorption of NG was calculated in terms of an increase in the weight of the sheets. The properties of the cured polymer such as thermal conductivity, flammability, brittleness, Shore hardness, and bond strength with the propellant were also evaluated as per the standard methods given elsewhere.¹⁵

Inhibition and Static Firing of Double-base (DB) and Composite-modified Double-base (CMDB) Rocket Propellants

Inhibition of DB and CMDB propellant grains (solid sustainer) was carried out by the casting method. The grains were initially surface-treated followed by the application of a fast curing silicone-based barrier coat. They were kept in the inhibition mold and the composition was poured

Table I Viscosity, Molecular Weight, Gel Time, Tensile Strength, and Elongation of Various HTPDMS Prepolymers

Resin/ Composition	Viscosity at 30°C (cPs)	Number-average Mol. Wt. (\bar{M}_n)	Gel Time at 40°C (Min)	Tensile Strength at Break (kg/cm ²)	Elongation (%)
Siloxane-1	400	6,606	300	2.4	65
Siloxane-2	800	7,147	240	2.7	75
Siloxane-3	1200	7,927	217	2.8	78
Siloxane-4	1600	9,909	205	3.2	80

Table II Effect of Filler on Viscosity and Gel Time of HTPDMS Prepolymers

Resin/ Composition	Filler (%)	Viscosity at 40°C (cPs)	Gel Time at 40°C (Min)	Tensile Strength at Break (kg/cm ²)	Elongation (%)
Control 1	0	260	300	2.4	65
Siloxane-5	10	340	150	3.3	60
Siloxane-6	20	380	112	4.8	55
Siloxane-7	25	955	100	5.6	52
Siloxane-8	30	1280	73	6.1	54
Control 2	0	370	240	2.7	75
Siloxane-9	10	480	121	3.6	72
Siloxane-10	20	620	50	5.4	80
Siloxane-11	25	980	36	7.9	95
Siloxane-12	30	1560	27	8.2	100
Control 3	0	760	217	2.8	78
Siloxane-13	10	1040	81	3.8	80
Siloxane-14	20	1360	46	6.2	85
Siloxane-15	25	1870	31	8.4	105
Siloxane-16	30	2840	22	9.2	107
Control 4	0	1040	205	3.2	80
Siloxane-17	10	1320	49	4.2	84
Siloxane-18	20	1810	32	7.6	96
Siloxane-19	25	3845	21	9.9	120
Siloxane-20	30	4940	17	10.1	124

under a vacuum to remove any entrapped air. To ensure complete curing of the inhibitor, the grains were left undisturbed for about 7 days. The inhibited grains were extracted from the mold and radiographed using a Philips-M151/301 (Germany) X-ray machine to ensure proper bonding between the propellant and the inhibitor. The propellant grains were loaded into rocket motors and fired statically, recording the pressure–time profile. The rocket motor was carefully dismantled about 24 h after the firing to recover the unburnt inhibitor sleeve for visual examination.

RESULTS AND DISCUSSION

The data on the effect of viscosity and molecular weight of the HTPDMS prepolymer on its gel

time, tensile strength, and percent elongation are given in Table I. The gel time data of the HTPDMS prepolymers show that when viscosity increases from 400 to 1600 cPs (at 30°C), the gel time decreases from 300 to 205 min, which is attributed to the decrease in the number of terminal hydroxyl groups per unit weight of the higher viscosity prepolymers which contain HTPDMS molecules of longer chain length. A comparison of the mechanical properties of different cured polysiloxanes shows that tensile strength and elongation marginally increase with the increase in viscosity and molecular weight of the HTPDMS prepolymers (Table I).

To improve the mechanical properties of the cured polysiloxanes, the effect of alumina trihydrate as a filler was studied (Table II). The addition of a filler increases the tensile strength as

Table III Effect of HTPDMS Viscosity on Mechanical Properties

Resin/ Composition	Viscosity Without Filler at 40°C (cPs)	Viscosity with Filler (25%) at 40°C (cPs)	Tensile Strength at Break (kg/cm ²)	Elongation (%)
Siloxane-7	260	955	5.6	52
Siloxane-11	370	980	7.9	95
Siloxane-15	760	1870	8.4	105
Siloxane-19	1040	3845	9.9	120

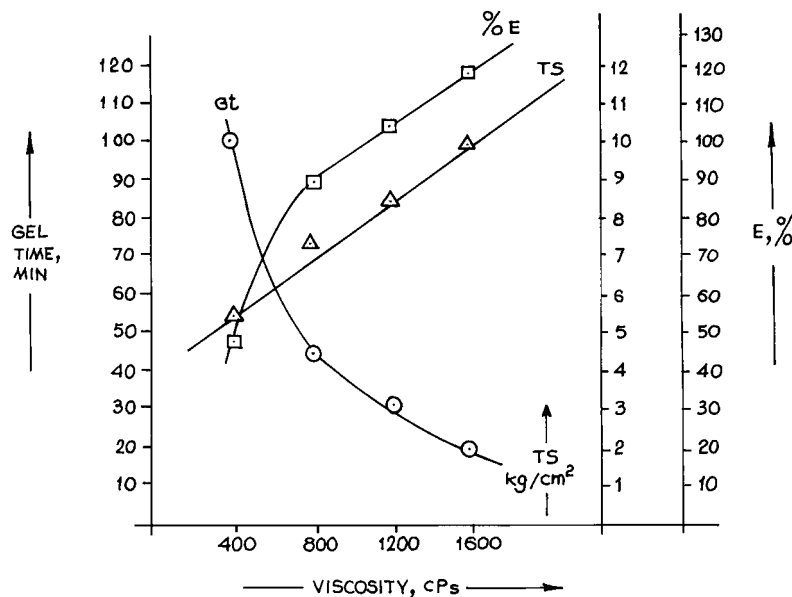


Figure 1 Variation of gel time (Gt), tensile strength (TS), and percentage elongation ($\% E$) of the RTV elastomer with HTPDMS viscosity.

well as the elongation of the cured polymers. The increase in tensile strength is because of the reinforcing action of the filler on the resin matrix.¹⁶⁻¹⁸ However, it decreases the gel time significantly. For example, addition of 25% filler in a given HTPDMS prepolymer (viscosity 1040 cPs) decreases its gel time from 205 to 21 min. However, it not only improves the tensile strength from 3.2 to 9.9 kg/cm² but also increases the elongation from 80 to 120% (Table II).

The viscosity and pot life of polymeric materials are important for the inhibition of rocket propellants from the processing angle. On the other hand, mechanical properties play a vital role at the time of the handling of the inhibited propellants and also at the time of combustion of the rocket propellants during static/dynamic trials. A comparison of various properties, that is, viscosity, gel time, tensile strength, and elongation of

various compositions, indicates that the composition "Siloxane-15" possesses the desired mechanical properties coupled with acceptable pot life. This composition is based on a 75% (by weight) HTPDMS prepolymer and 25% (by weight) alumina trihydrate filler. It has an acceptable pot life (gel time at 40°C: 31 min) and mechanical properties (tensile strength 8.4 kg/cm² and elongation 105%) (Table III).

The variation of gel time, tensile strength, and percent elongation of the cured RTV elastomer (with 25% alumina trihydrate as a filler) with the viscosity of the HTPDMS prepolymer is given in Figure 1.

A comparison of the RTV silicone elastomer with some of the conventional inhibitors for DB/CMDB rocket propellants (Table IV), namely, ethyl cellulose¹⁹ and unsaturated polyesters,²⁰ brings out that

Table IV Comparison of Some Rocket Propellant Inhibitors

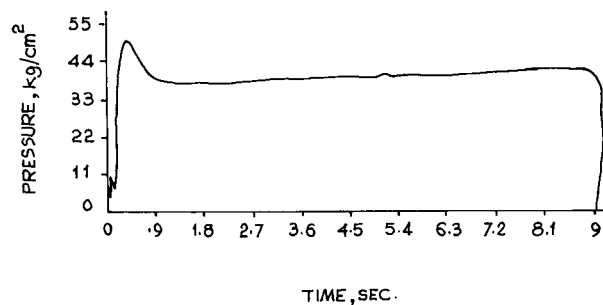
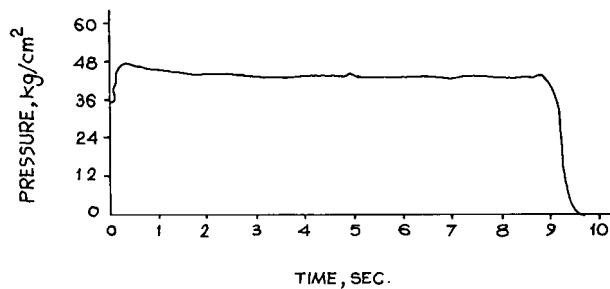
Inhibitor	Tensile Strength at Break (kg/cm ²)	Elongation (%)	MG Absorption (%)	Remarks
Ethyl cellulose	80	20	6	Not castable; low softening point
Unsaturated polyesters	50-300	3-70	3-50	Debonding on storage
RTV siloxane	10	100-120	0.6	Lower T_g (-125°C); excellent stability and compatibility over a wide range of temperatures (-40 to +60°C)

Table V Some Properties of Siloxane-15

Properties	Data
NG absorption (%), after 5 days	0.55
Thermal conductivity (w/mk)	0.80
Oxygen index (n)	Self-extinguishing
Shore hardness (A)	5
Autobrittleness (break at 25°C) (%)	30
Bond strength with propellant (kg/cm ²)	
After conditioning at room temperature	9.0
After conditioning at 60°C for 24 h	10.5

1. Ethyl cellulose (tensile strength 80 kg/cm² and elongation 20%), which is used as a sleeve inhibitor for extruded DB rocket propellants, may not be suitable for cast DB/CMDB propellants, mainly because of the higher NG migration (>6%) from the propellant to the inhibitor and also the low softening temperature. The higher NG migration not only weakens the propellant-inhibitor bond but also decreases the overall energy of the propellant.
2. The unsaturated polyester-based inhibition systems are also used for cast DB propellants. They possess excellent mechanical properties (TS 50–300 kg/cm² and elongation 3–70% depending on the polyester formulation) but NG migration to these polyesters is quite high (3–50%), resulting in debonding.

As compared to these systems, polysiloxane rubber (RTV) has a very low NG migration (0.2–0.6%) which appears to be due to the low polarity of the Si—O—Si chains. One major factor responsible for the migration of polar NG molecules to

**Figure 2** Pressure-time profile for CMDB propellant grain inhibited with Siloxane-15.**Figure 3** Pressure-time profile for DB rocket propellant inhibited with Siloxane-15.

the inhibitor matrix is the polarity of the matrix and it is expected that the tendency for NG migration decreases with decrease of the polarity of the polymer (inhibitor) matrix.²¹

RTV polysiloxanes have a higher elongation (>100%) and possess very low glass transition temperatures (T_g , -125°C).¹⁶ Some other properties of the selected silicone elastomer (Siloxane-15) are given in Table V.

All these properties make the RTV polysiloxane system a promising inhibitor for DB rocket propellants and, accordingly, siloxane-15 has been selected for inhibition trials. Small CMDB propellant grains (length 50–70 mm and diameter 129 mm) were also inhibited with the same composition and statically fired in the cigarette-burning mode. It was observed that the pressure-time profile (Fig. 2) was satisfactory, with the grains having a burning time 8–9 s. However, CMDB grains of longer length and, therefore, longer burning time (>10 s) did not result in flat and neutral pressure-time profiles.

Further, the DB sustainer propellant grains inhibited with Siloxane-15 were also statically fired in a rocket motor and a smooth pressure-time profile was obtained (Fig. 3). A polysiloxane-based system thus appears to have a potential for the inhibition of DB rocket propellants.

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