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CARDANOL-BASED EPOXY FLEXIBILIZERS FOR INHIBITION OF COMPOSITE PROPELLANTS

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ABSTRACT

Five epoxy flexibilizers based on cardanol, epichlorohydrin, and several glycols have been synthesized. These have been characterized for epoxide equivalent, number-average molecular weight ($\overline{M}_n$), and viscosity, and their structures have been established with the help of IR and NMR. The flexibilizing effect of these flexibilizers on the properties of novolac epoxy resin has been studied by preparing different formulations of flexibilizers and Dobeckot E-4 (in different proportions) and curing them with the polyamide hardner EH-411. The resulting cured specimens have been characterized for tensile strength, percent elongation, nonexplosive plasticizer (emolein) absorption, heat resistance, Oxygen Index, brittle temperature, and thermal conductivity. Based on the data for various characteristics, Formulation 7 (Flexibilizer 1:Dobeckot E-4: Hardner EH-411, 1:2:1.5) has been selected for inhibition and static evaluation of composite rocket propellants at ambient, hot, and cold temperatures. The nature of the *p–t* profiles suggest that Formulation 7 with 30% filler is a potential inhibition system for composite propellants.

INTRODUCTION

Because of their unique combination of properties and innumerable applications, epoxy resins are regarded as one of the most versatile innovations of chemistry and have become an integral part of various industries. They possess a number

of unusually valuable properties immediately amenable for use in diverse applications. Their major fields of applications are lamination (glass-fiber reinforced laminates for fuel-cell backing-board in aircrafts, helmets, etc.), potting (encapsulation of electronic circuits, insulating sleeves, parts for TV assemblies and capacitors, etc.), molding (fabrication of large radar housings with complex aerodynamic shapes, big boats, etc.), and surface coating. The most recent expansion of their applications is in the field of inhibition of composite rocket propellants because of chemical inertness, toughness, better bonding with a variety of substrates, negligible shrinkage on curing, etc.

The inhibition of rocket propellants demands higher elongation and moderate tensile strength. Unfortunately, novolac epoxy resins are reported to possess elongation of medium order, which make them unsuitable for this purpose. The addition of external or internal plasticizers improves their elongation [1, 2]. The added advantage of an internal plasticizer/flexibilizer is that they take part in three-dimensional network formation, eliminating their migration in addition to improving the elongation of novolac epoxy resins.

Our literature survey indicates that no work appears to have been done on cardanol and glycol-based epoxy flexibilizers. This article aims at synthesizing epoxy flexibilizers based on cardanol, epichlorohydrin (ECH), and various glycols (ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, and polyethylene glycol-200), establishing their probable structures, and studying their effect on various properties of the novolac epoxy resin Dobeckot E-4 which is used for the inhibition of composite rocket propellants.

MATERIALS AND METHODS

Materials

The materials, their specification, and their sources of supply are as follows.

Novolac Epoxy Resin, Dobeckot E-4

This is a novolac epoxy resin based on cashew nut shell liquid (CNSL). It is an amber colored clear liquid. Its density at 25°C is 1.062–1.066 g/cm^3 and its viscosity at 25°C is 17,120 ± 50 cP.

Hardner, EH-411

This is a room temperature curing polyamide hardner. It is a yellowish brown clear liquid. Its density at 25°C is 0.97–0.99 g/cm^3 and its viscosity at 25°C is 17,750 ± 50 cP.

Dobeckot E-4 and the polyamide hardner EH-411 are proprietary products of Dr. Beck & Co. (India) Ltd., Pune.

Antimony Trioxide

It conforms to IS 38-1976, its purity is 99.5%, its specific gravity at 25°C is 2.67–2.70 g/cm^3, and it passes through 200 BSS.

Composite Propellant

Composite propellant has the composition ammonium perchlorate (66%), aluminum powder (19%), and hydroxy-terminated polybutadiene (HTPB) binder (15%) and was made by the "casting technique." This propellant possesses a density at 25°C of 1.75–1.76 g/cm^3, a burning rate at 70 kg/cm^2 of 8.4–8.5 mm/s, a tensile strength of 12–13 kg/cm^2, an elongation of 4–5%, and it was used for inhibition and static evaluation trials.

Cardanol ($OH \cdot C_6H_4:C_{15}H_{27}$)

This was made from CNSL by steam distillation. Its density at 25°C is 0.9272–0.9350 g/cm^3, its viscosity at 30°C is 52–58 cP, and its hydroxyl value 180–190 mg KOH/g. It was supplied by Mercury Resins and Polymers Pvt Ltd., Hyderabad.

Epichlorohydrin

This has a boiling point of 115–117°C, $n_D^{20} = 1.4380$, its density at 25°C is 1.183 g/cm^3, and its purity is not less than 99%. It was supplied by Thomas Baker and Co., Bombay.

Glycols

Ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, and polyethylene glycol of molecular weight 200 (PEG-200). These were procured from BDH and used as received.

Miscellaneous chemicals such as sodium hydroxide (AR), solvents, and acids were procured from the trade and used without further purification.

Methods

Methods for the synthesis of epoxy flexibilizers, characterization of uncured epoxy flexibilizers, characterization of cured Dobeckot E-4 flexibilizer formulations, and inhibition and static evaluation of composite propellants are given below.

Synthesis of Epoxy Flexibilizers

The novolac epoxy flexibilizers were synthesized by following a two-step process in a three-necked flask equipped with a stirrer, condenser, and thermometer pocket.

In the first step, glycol, freshly distilled cardanol, and 1:1 H_2SO_4 (2%) were charged in a three-necked flask placed in a heating mantle. The mixture was refluxed for 6 h. The product obtained was washed with water till it was free of SO_4^{2-} ions.

The prepolymer obtained in the first step was treated with epichlorohydrin in the presence of 40% NaOH aqueous solution which was added drop by drop in order not to exceed a temperature of ~15°C.

The liquid flexibilizer and solid NaCl formed during the reaction were separated by using a separating funnel. At this stage, the flexibilizer was washed with

distilled water several times. Finally, water was removed by applying vacuum at ~55°C.

Similarly, five flexibilizers were prepared by using different glycols such as EG, PG, DPG, and PEG-200. Their compositions are shown in Table 1.

Characterization of Uncured Epoxy Flexibilizers

These flexibilizers were characterized for the following properties: epoxide equivalent, viscosity, IR, NMR, and number-average molecular weight.

Epoxide Equivalent. This is defined as the weight of resin in grams which contains a 1-gram equivalent of epoxide. It was determined by reacting a weighed quantity of sample with an excess of HCl. The amount of HCl consumed was found by back-titration using standard KOH solution.

Viscosity. The viscosity was measured at room temperature with a Brookfield viscometer, Model RVTD.

IR, NMR, and Number-Average Molecular Weight. The IR spectra of all prepolymers and flexibilizers were recorded on a Perkin-Elmer Model 683 by the smear method. The NMR spectra were recorded in $CDCl_3$/TMS solution by using a Varian FT-80 NMR Spectrometer.

The number-average molecular weight ($\overline{M}_n$) was determined by a vapor pressure osmometer (Wescan Model 233) as described in the literature [3]. Double distilled toluene was used as the solvent to prepare solutions of different prepolymers and flexibilizers, and benzil was taken as the standard.

TABLE 1. Compositions of Flexibilizers

Flexibilizer	Glycols[a]	Cardanol, moles	Epichlorohydrin, moles	Sodium hydroxide, mol
1[b]	Ethylene glycol	2.0	1.1	1.0
1	Ethylene glycol	2.0	2.1	1.0
2	Diethylene glycol	2.0	2.1	1.0
3	Polyethylene glycol-200	2.0	2.1	1.0
4	Propylene glycol	2.0	2.1	1.0
5	Dipropylene glycol	2.0	2.1	1.0

[a]The molar proportion of glycols was 1 mol in all flexibilizers.

[b]The Dobeckot–flexibilizer–polyamide formulation does not cure properly, and pieces remained tacky even after 1 week. Therefore, further work was not undertaken.

TABLE 2. Various Formulations of Dobeckot E-4 with Flexibilizers

Formulation	Nomenclature of flexibilizer	Composition (by weight)		
		Flexibilizer + Dobeckot	E-4 + hardner	EH-411
1	–	0	1	0.5
2	Flexibilizer 1	1	1	1
3	Flexibilizer 2	1	1	1
4	Flexibilizer 3	1	1	1
5	Flexibilizer 4	1	1	1
6	Flexibilizer 5	1	1	1
7	Flexibilizer 1	1	2	1.5
8	Flexibilizer 2	1	2	1.5
9	Flexibilizer 3	1	2	1.5
10	Flexibilizer 4	1	2	1.5
11	Flexibilizer 5	1	2	1.5

Characterization of Cured Dobeckot E-4 Flexibilizer Formulations

The formulations of Dobeckot E-4 flexibilizers are shown in Table 2. These were cured at 30°C and postcured at the same temperature for 1 week before their properties were measured. The test methods for these properties are listed in Table 3.

The plasticizer absorption [4] and heat resistance [5] were determined as reported in the literature.

Inhibition and Static Evaluation of Composite Propellants

The HTPB-based composite propellant (i.d. 40 mm, o.d. 200 mm, length 600 mm) was placed on a lathe and machined to o.d. 180 mm. The propellant surface thus prepared was free of such contaminants as oily substances, grease/foreign particles, etc. A resin composition (Formulation 7) was prepared, mixed thoroughly, and applied to the propellant which was revolving at a speed of 40 rpm on

TABLE 3. Test Methods

Property	Method
Tensile strength and percent elongation	ASTM D-638
Brittle temperature	ASTM D-746
Oxygen Index	ASTM D-2863
Thermal conductivity	ASTM D-433
Hardness	ASTM D-2240

a lathe. This coat was allowed to cure partially at room temperature (27–30°C) before final inhibition. Freshly prepared Formulation 7 was then placed in the tray which was mounted on the lathe. The dried rayon thread was passed through the resin and wound on the propellant by selecting a suitable pitch, so that there were no gaps between adjacent circular thread windings. The assembly is shown in Fig. 1a.

The number of windings was based on the inhibition thickness which was 3.0 to 3.5 mm. The propellant was allowed to rotate until the resin became immobile. After 24 h the propellant was machined to 187 mm o.d., cut into pieces of 200 mm length, and slots cut as shown in Fig. 1b. The end inhibition of these inhibited propellant pieces was done by the casting technique.

These propellants were x-rayed and statically evaluated after conditioning at ambient, cold (−30°C for 20 h), and hot (+50°C for 16 h) temperatures.

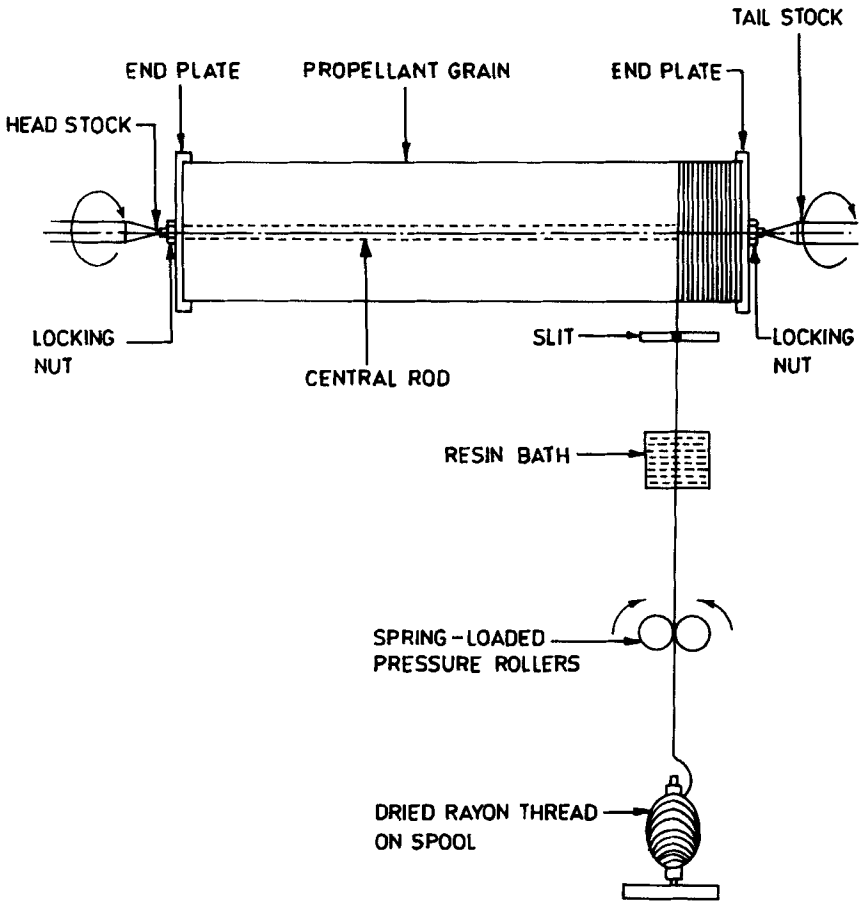


FIG. 1a. Assembly for thread-winding technique of inhibition.

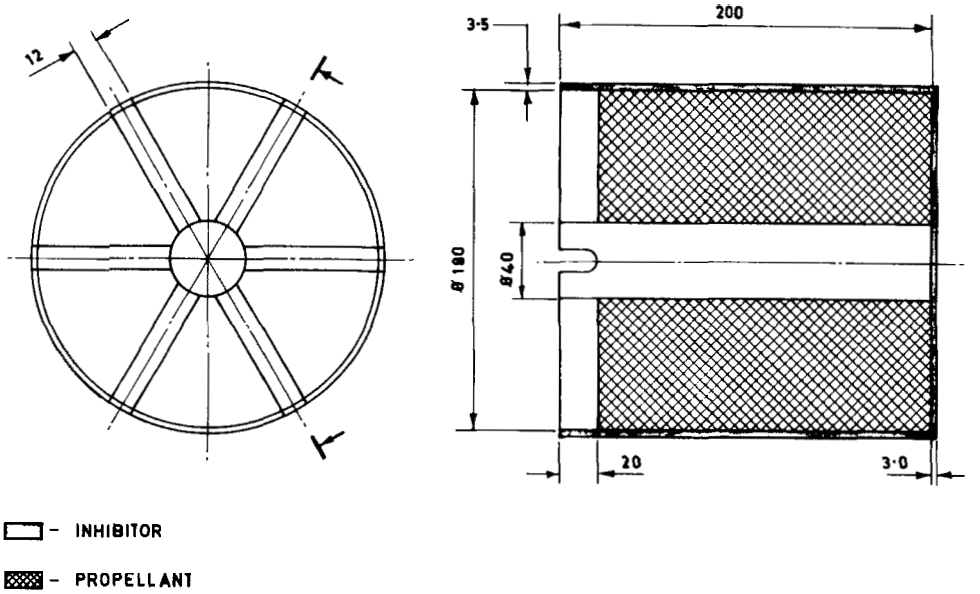


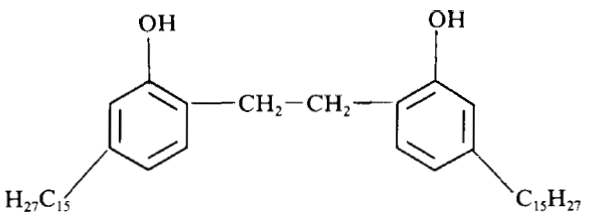
FIG. 1b. HTPB-based composite propellant inhibited with Formulation 7 and configuration of slots.

RESULTS AND DISCUSSION

Structural Aspects

These flexibilizers have been synthesized by a two-step process, i.e., the reaction of cardanol with glycol in the presence of an acid catalyst, and the reaction of a prepolymer with ECH in the presence of an alkali.

The molecular weight ($\overline{M}_n$) of cardanol-glycol (EG) prepolymer is 640. The IR spectra of the prepolymer suggests the presence of $-OH$ (3400 cm^{-1}), $-C=C-H$ in the side chain (2900 cm^{-1}), $-C=C-$ in the side chain (1600 cm^{-1}), aromatic $-C-H$ (1450 cm^{-1}), and three free aromatic H (720-790 cm^{-1}) groups/linkages [6]. The NMR spectra (Fig. 2a) of this prepolymer [7] shows chemical shifts at 0.9 δ ($-CH_2-$, $-C-CH_2-C-$, $-CH_2-C=C-$), 1.3 δ ($-C=C-CH_2$ in the side chain), 2.3 δ ($Ar-CH_2$), 5.2 δ ($-CH=CH-$ open chain), and 6.7 and 6.9 δ ($Ar-H$). Based on the molecular weight, IR and NMR data, the following structure is proposed for the prepolymer:



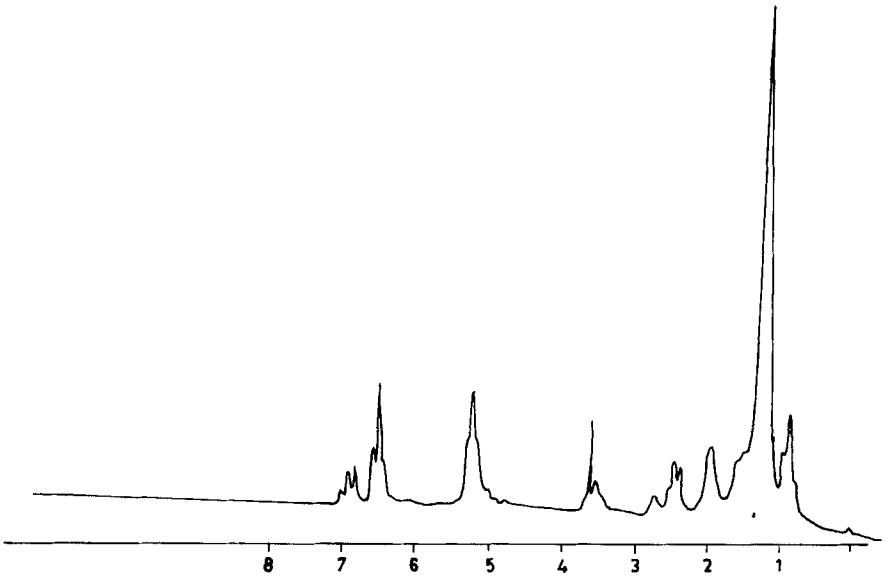


FIG. 2a. NMR of cardanol-glycol(ethylene glycol) prepolymer.

As described in the Synthesis Section, this was reacted with ECH in order to get an epoxy flexibilizer (Flexibilizer 1). The IR spectra of Flexibilizer 1 indicates additional peaks at 910 and 1050 cm^{-1} (corresponding to a terminal epoxy group and the alkyl ether bond of an epoxy ring) in addition to peaks in the prepolymer [6]. The NMR spectra of Flexibilizer 1 is shown in Fig. 2b where a chemical shift is also observed at a 2.3 δ multiplet ($Ar-O-CH_2-$) in addition to the chemical shifts observed in the prepolymer.

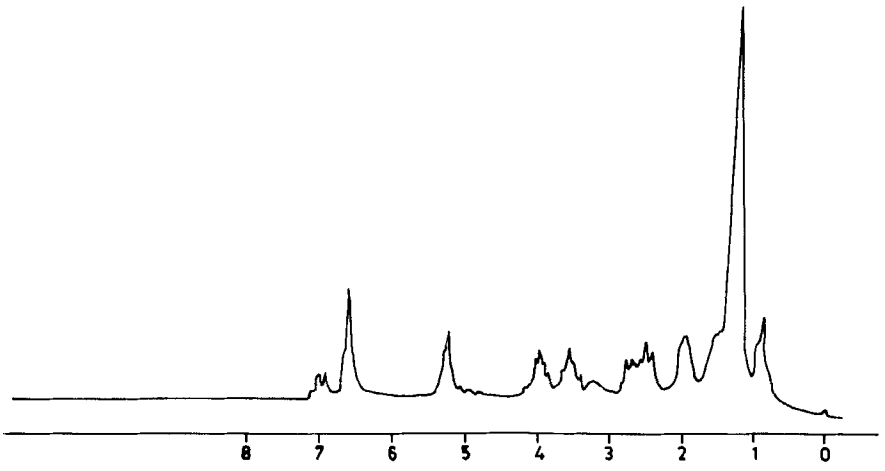
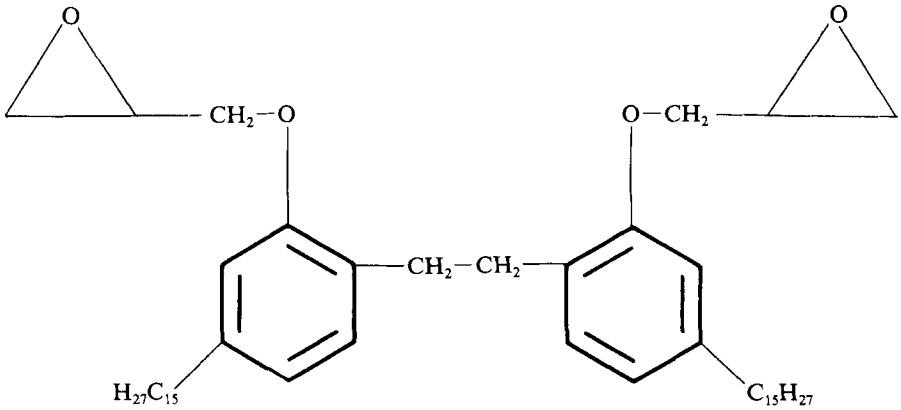


FIG. 2b. NMR of epoxy flexibilizer based on EG.

TABLE 4. Viscosity, Epoxide Equivalent, and Number-Average Molecular Weight Data for Various Flexibilizers

Flexibilizer	Viscosity, cP at 27°C	Epoxide equivalent, mg KOH/g flexibilizer	Number-average molecular weight, $\overline{M}_n$
1	500	475	736
2	365	630	740
3	360	850	880
4	540	600	760
5	210	695	790

The epoxide equivalent and number-average molecular weight of Flexibilizer 1 are 475 and 750, respectively. The data on IR, NMR, epoxide equivalent, and $\overline{M}_n$ suggest the following structure for Flexibilizer 1:



Various flexibilizers based on glycols-DEG, PEG-200, PG, and DPG were also synthesized. Flexibilizers 2, 3, and 5 (based on DEG, PEG-200, and DPG, respectively) and their prepolymers show additional ether linkage peaks in the IR spectra (1100–1200 cm^{-1}) in addition to other peaks observed in Flexibilizer 1 and its prepolymer. Similarly, in the NMR spectra, an additional chemical shift at 3.6 δ ($-CH_2-O-CH_2-$) corresponds to ether linkages in these prepolymers as well as in the flexibilizers. The viscosity, epoxide equivalent, and number-average molecular weight ($\overline{M}_n$) values for different flexibilizers based on various glycols are given in Table 4. Based on IR, NMR, $\overline{M}_n$, and epoxide equivalent data, the general structure of these flexibilizers may be as shown in Fig. 3.

Characterization of Cured Dobeckot E-4 Flexibilizer Formulations

Various formulations of Dobeckot E-4 and Flexibilizers 1, 2, 3, 4, and 5 (in different proportions) are given in Table 2, and the effect of their addition is discussed here.

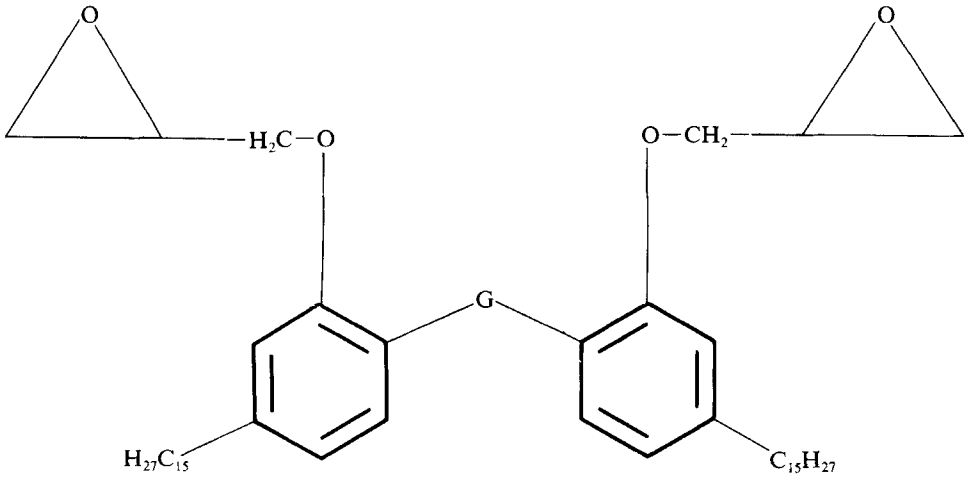


FIG. 3. General structure of flexibilizers, where —G— is a glycol moiety, i.e.,

EG = $-CH_2-CH_2-$

DEG = $-CH_2-CH_2-O-CH_2-CH_2-$

PG = $-\underset{\displaystyle CH_3}{CH}-CH_2-$

DPG = $-CH_2-\underset{\displaystyle CH_3}{CH}-O-CH_2-\underset{\displaystyle CH_3}{CH}-$

PEG = $+CH_2 \cdot CH_2O+_n$

Elongation and Tensile Strength

Tensile strength and percent elongation for these formulations are given in Table 5.

The structures of these flexibilizers are shown in Fig. 3, and it is seen that the chain length increases from Flexibilizer 1 to 3 and 4 to 5 as glycol (EG) is replaced by DEG and PEG-200 and PG to DPG, respectively. As the chain length of flexibilizer backbone increases, the addition of flexibilizer is expected to increase percent elongation, which is observed experimentally (Table 5). This is also supported by the elongation data of the formulations when the proportion of flexibilizers is reduced by 50%. (Compare the elongations of Formulations 2 and 7, 3 and 8, 4 and 9, 5 and 10, and 6 and 11.)

It is reported in the literature [8] that elongation and tensile strength are interrelated; if elongation increases, tensile strength decreases in most of the thermosets and vice versa. Since elongation increases from Formulations 2 to 4 and 5 to 6, the tensile strength is expected to decrease in this order, i.e., Formulations 2 to 4 and 5 to 6.

Brittle Temperature, Thermal Conductivity, and Shore Hardness

The data for these properties are given in Table 5. It is well known that elongation is interrelated with brittle temperature (B.T.) and Shore hardness, and if elongation increases, B.T. and Shore hardness decrease. The elongation increases

TABLE 5. Mechanical Properties of Various Epoxy-Flexibilizer Formulations

Formulation	Tensile strength, kg/cm^2	Elogation, %	Thermal conductivity, W/mK	Brittle temperature, °C	Shore hardness	Oxygen Index (*n*)
1	285	5.0	0.79	24.5	72 (D Scale)	18.9
2	22	42	0.92	18.5	85 (A Scale)	18.5
3	17	50	0.97	17.0	79 (A Scale)	17.1
4	10.5	54	1.35	16.5	58 (A Scale)	15.3
5	18	45	0.91	18.0	80 (A Scale)	16.8
6	14	48	1.27	17.0	60 (A Scale)	17.2
7	50	36	0.64	20.5	93 (A Scale)	18.01
8	46	44	0.89	20.0	83 (A Scale)	18.10
9	23.8	47	1.23	18.5	79 (A Scale)	16.10
10	30	40	0.81	21.0	88 (A Scale)	18.60
11	30	44	1.21	20.0	86 (A Scale)	18.80

from Formulations 2 to 4 and 5 to 6 (Table 5), and therefore B.T. and Shore hardness decrease in this order.

It is reported in the literature [9] that an increase in chain length (indicated by elongation) facilitates the transmission of heat, i.e., results in higher thermal conductivity. As elongation increases from Formulation 2 to 4 and 5 to 6, thermal conductivity also increases accordingly (Table 5).

Plasticizer (Emolein) Absorption

Graphical presentation of emolein absorption for these formulations is shown in Figs. 4a and 4b. It is seen that the emolein absorption increases from Formulations 2 to 4 and 5 to 6 as the chain length of glycol increases.

The tensile strength decreases from Formulations 2 to 4 and 5 to 6. Because the tensile strength is indicative of crosslinking density, crosslinking density decreases in this order. This means that the compactness of the structure gradually decreases in this order and, accordingly, emolein absorption increases from Formulations 2 to 4 and 5 to 6. This is supported by the data of Parker and Moffett [10] and Agrawal et al. [11, 12] in the case of unsaturated polyesters.

Heat Resistance and Oxygen Index

Graphical presentation of heat resistance data is shown in Figs. 5a and 5b, and Oxygen Index (*n*) data for these formulations are given in Table 5.

It is seen that the loss in weight increases on incorporation of Flexibilizers 1 to 5. It is also seen that the loss in weight increases from Formulation 2 to 4 and 5 to 6 which contain Flexibilizers 1 to 3 and Flexibilizers 4 to 5, where the chain length of glycol gradually increases. It also increases with the time of exposure, which is in accordance with the data for unsaturated polyesters and chloropolyesters [13, 14].

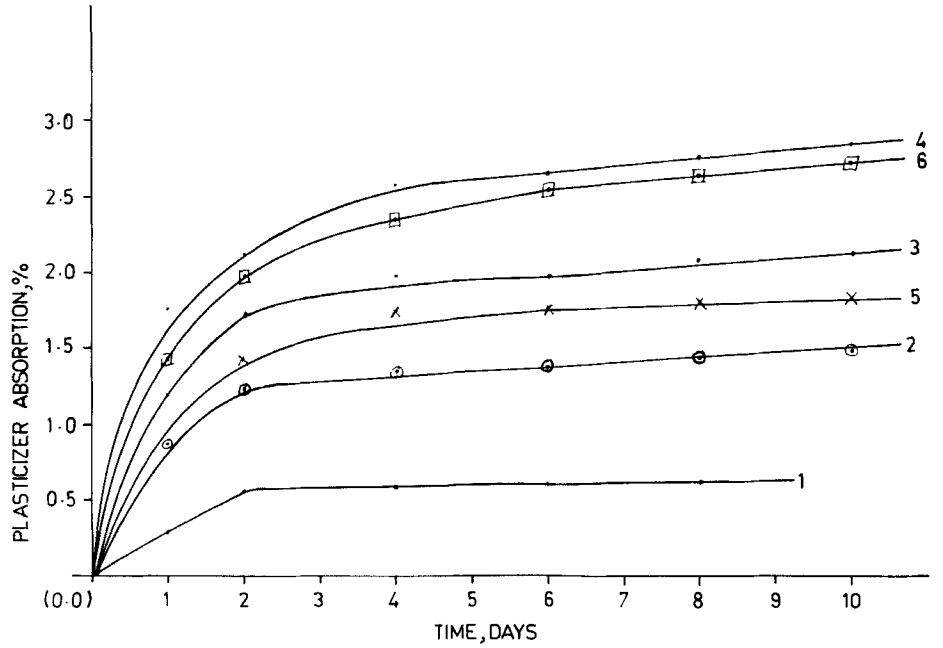


FIG. 4a. Effect of time on plasticizer absorption of Formulations 1 to 6.

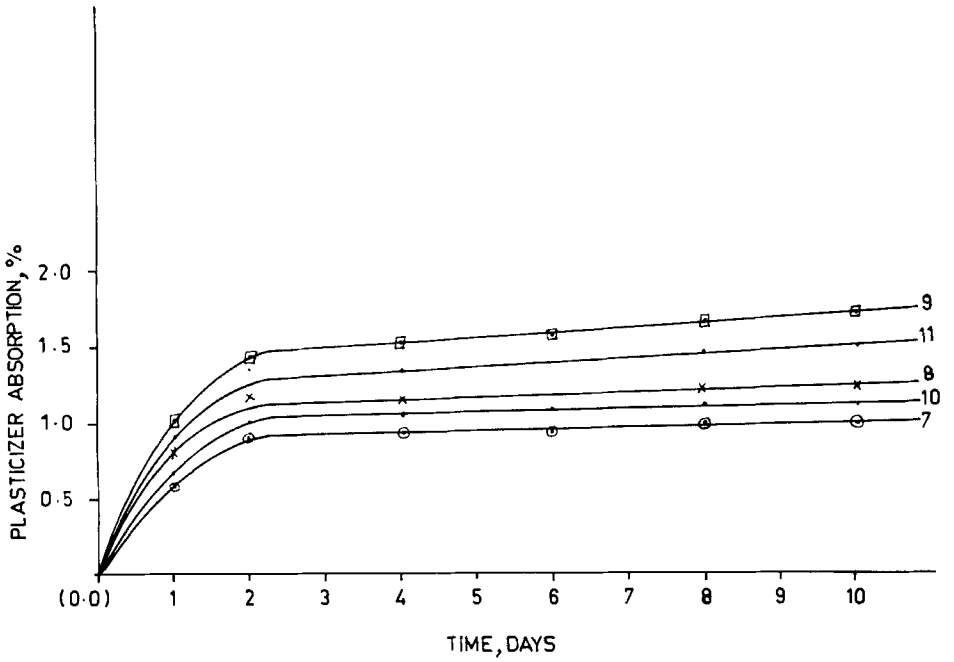


FIG. 4b. Effect of time on plasticizer absorption of Formulations 7 to 11.

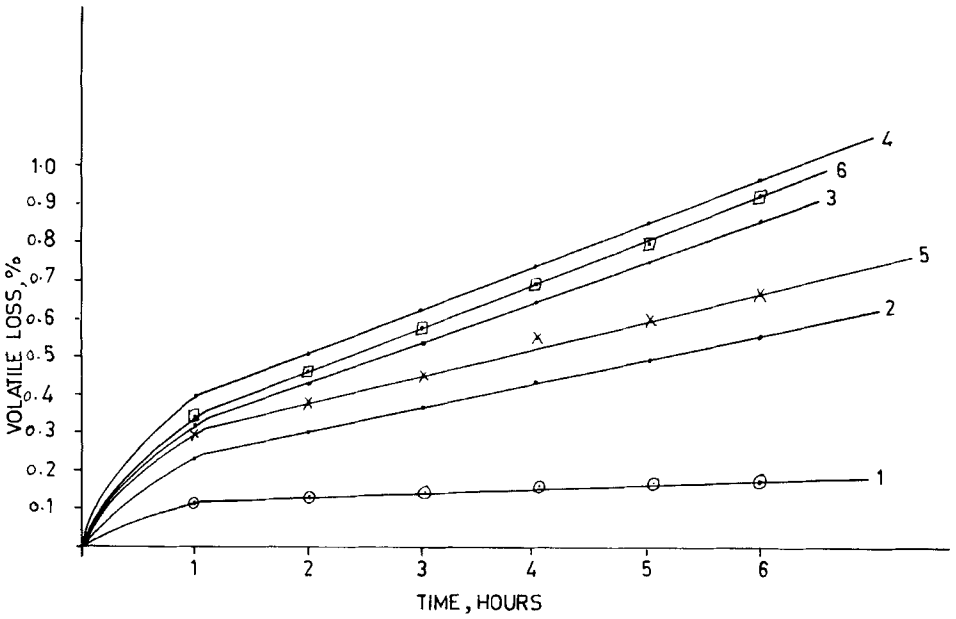


FIG. 5a. Volatile losses versus exposure at 150°C for Formulations 1 to 6.

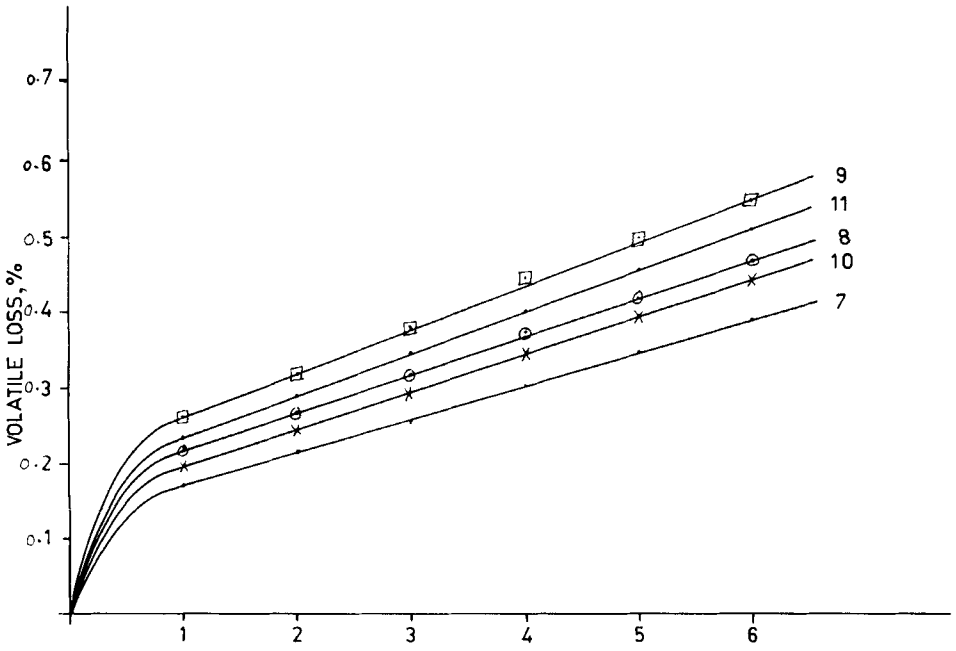


FIG. 5b. Volatile losses versus exposure at 150°C for Formulations 7 to 11.

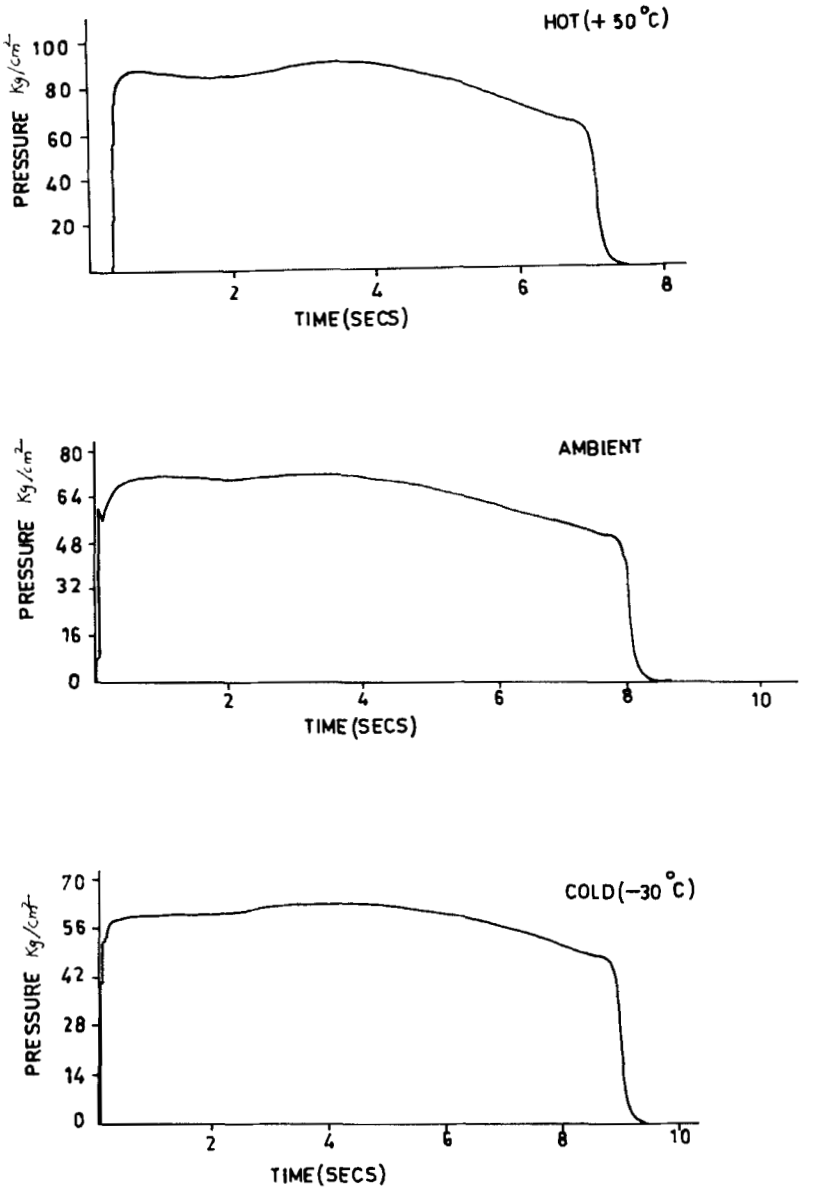


FIG. 6. Pressure-time profiles of composite propellant inhibited with Formulation 7.

As brought out in the Plasticizer Absorption Section, compactness of structures decreases as we proceed from Formulation 2 to 4 and 5 to 6 and 7 to 9 and 10 to 11. This facilitates the loss of volatile matter and, accordingly, the loss in weight increases in this direction, i.e., it increases from 2 to 4 and 5 to 6 and 7 to 9 and 10 to 11.

The Oxygen Index (n) data show that it varies from 15 to 18%, and there is no significant variation in terms of combustion behavior due to varying the flexibilizer. This is likely because of reported experimental error in the determination of n is 3 to 5%. However, in view of theoretical considerations, n is expected to decrease with the addition of flexibilizers because their incorporation enhances the oxygen content of structural networks and leads to a reduction in the oxygen necessary for candle-like combustion.

Based on the data generated for various properties, Formulation 7 containing Flexibilizer 1 was selected to study the effect of the well-known antimony trioxide filler as a flame retardant. The data indicate that 30% antimony trioxide gives the necessary flame retardance to the resulting product.

Formulation 7 with 30% filler has been selected for the inhibition of composite propellants. The composite propellants inhibited with this formulation have been statically evaluated after conditioning at ambient, hot (+50°C for 16 h), and cold (−30°C for 20 h); the p–t profiles are given in Fig. 6.

The p–t profiles closely match the theoretically calculated p–t profiles. This infers that the bonding of the inhibitor to the propellant was intact at the time of combustion and that no additional surface was exposed to flame. This implies that this inhibitor/inhibition system is working satisfactorily for the inhibition of composite propellants from +50 to −30°C.

SUMMARY

Five epoxy flexibilizers based on cardanol, ECH, and several glycols have been synthesized, and their structures have been established. The effect of these flexibilizers on the properties of Dobeckot E-4 has also been studied in terms of tensile strength, percent elongation, nonexplosive plasticizer (emolein) absorption, heat resistance, Oxygen Index, brittle temperature, thermal conductivity, etc. Data on various characteristics of these formulations suggest that Formulation 7 is a potential formulation for the inhibition of composite rocket propellants. This is confirmed by static evaluation of composite rocket propellants inhibited with Formulation 7 with 30% Sb_2O_3 at ambient, hot, and cold temperatures.

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