Comparative Study of Unsaturated Halo and Nonhalo Polyesters and Inhibition of Double-Base Rocket Propellants

J. P. AGRAWAL* and K. S. KULKARNI

Explosives Research and Development Laboratory, Sutarwadi, Pune-411008, India

SYNOPSIS

Unsaturated halo and nonhalo polyesters, based on tetrachlorophthalic anhydride, tetrabromophthalic anhydride, and phthalic anhydride with diethylene glycol and maleic anhydride, have been synthesized, using a "2-step" polyesterification process. These were mixed with 35% styrene monomer and 0.02% hydroquinone. The structural aspects of halo and nonhalo polyesters have been studied by IR and NMR. Further, these polyesters have been characterized for various properties. A comparison of various properties suggests that tensile strength, bond strength, heat resistance, flame retardance, gel time, and oxygen index follow the order as BP-35 > CP-35 > NHP-35, whereas the order for other properties, such as exotherm peak temperature, thermal conductivity, % elongation, and nitroglycerine absorption, is BP-35 < CP-35 < NHP-35. Variation in the properties of cured halo and nonhalo polyesters has been discussed in terms of structural considerations. The nature of P-t profile of inhibited double-base (DB) rocket propellants on static evaluation suggests that CP-35 is a potential inhibitor for DB propellants. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

A wide range of unsaturated polyesters[1-3] and chloropolyesters[4-6] (rigid, semirigid, semiflexible, flexible, and very flexible) have been synthesized and characterized by us. Furthermore, double-base (DB) rocket propellants, inhibited with selected unsaturated polyesters and chloropolyesters, have been statically evaluated for functional test. It has been extensively reported in the literature that flame retardant characteristics improve considerably by introducing chloro and bromo groups into the glycol/di basic acid.[7-11] However, a literature survey shows that a comparative study of halo and nonhalo polyesters, based on diethylene glycol (DEG), maleic anhydride (MAn), tetrachlorophthalic anhydride (TCPAn)/tetrabromophthalic anhydride/phthalic anhydride (PAn), has not been reported as yet, particularly with reference to the inhibition of double-base rocket propellants.

The object of the present study is to formulate, to synthesize, and to characterize halo and nonhalo polyesters with regard to tensile strength, % elongation, gel time, exotherm peak temperature, bond strength with DB propellants, heat resistance, flame retardance, oxygen index, thermal conductivity, and nitroglycerine (NG) absorption. The probable structures for these halo and nonhalo polyesters have also been assigned with the help of IR and NMR and variation in the properties of these polyesters has been explained on the basis of their assigned structures.

EXPERIMENTAL

Materials

The specifications of the materials used for the present study are as follows:

- Phthalic anhydride: (F.W.) 148, (m.p.) 131–134°C.
- Tetrachlorophthalic anhydride: (F.W.) 286, (m.p.) 254–258°C, (% Chlorine) 48.5.

- Tetrabromophthalic anhydride: (F.W.) 464, (m.p.) 274–276°C, (% bromine) 68.92.
- Maleic anhydride: (m.p.) 53°C, (density at 20°C) 0.934.
- Diethylene glycol: (B.P.) 253°C, [Ash (max) %] 0.01, (density at 27°C) 1.114.
- Styrene monomer: (B.P.) 145 ± 2°C, (Specific gravity at 25°C) 0.9055.
- Cobalt (II) naphthenate as accelerator: (3% solution in methylene chloride).
- Methyl ethyl ketone peroxide as catalyst: (50% solution in diethyl phthalate).

These were commercial chemicals and were used without further purification.

- Double-base (DB) rocket propellants, having the following compositions, were prepared in our laboratory by the casting technique.

1. Casting powder (CP): {[Nitrocellulose] 90.5%, [Diethylphthalate] 4%, [Lead stearate] 3%, [2-Nitrodiphenylamine (2-NDPA)] 2%, [Potassium sulfate] 0.5%}.
2. Casting liquid (CL): [(Nitroglycerine) 80%, (Diethyl phthalate) 18%, (2-NDPA) 2%]. Ratio of CP : CL :: 65 : 35.

METHODS

Synthesis of Halo and Nonhalo Polyesters

The synthesis of halo and nonhalo polyesters was carried out by following a "2-step" polyesterification process.[12] Polyesterification was carried out in an electrically heated, 4-necked flask, fitted with stirrer, thermometer, and inert gas (nitrogen) and an up-

right water condensor. One mole of diethylene glycol (DEG) and 0.5 moles of phthalic anhydride (PAn) were charged into the flask and the temperature was raised to 160 ± 5°C. After 4 h, reflux condensor was replaced by a Dean and Starks' tube and water, produced by the reaction, was removed until the acid value dropped down to 50 ± 2. The reaction mixture was cooled, 0.5 mole of maleic anhydride (MAn) was added, and the mixture was refluxed for 2 h. The temperature then was gradually raised and the water produced by the reaction was distilled off, until the acid value dropped to 50 ± 2. The resultant polyester was cooled, vacuum was applied, and 0.02 hydroquinone was added as a stabilizer. This viscous liquid, that is, unsaturated polyester, was blended with 35% styrene monomer and was stored in an amber-colored bottle. This polyester was designated as NHP-35, that is, a nonhalo polyester containing 35% styrene monomer.

The halo polyesters, based on tetrachlorophthalic anhydride (TCPAn) and tetrabromophthalic anhydride (TBPAn), were also synthesized similarly. These halo polyesters were also viscous liquids, were blended with 35% styrene monomer and 0.02% hydroquinone as stabilizer, and were designated as CP-35 and BP-35, respectively. The details of the formulations and acid values of these polyesters are shown in Table I.

Characterization of Halo and Nonhalo Polyester

Halo and nonhalo polyesters were characterized with regard to:

- Infrared (IR) spectra, recorded with a Perkin-Elmer spectrophotometer, Model-457, by a smear method.

Table I Composition of Halo and Nonhalo Polyesters

Halo and Nonhalo Polyester	Molar Ratios of Ingredients					Acid Values	
	Phthalic Anhydride (PAn)	Tetra Chlorophthalic Anhydride (TCPAn)	Tetra Bromo Phthalic Anhydride (TBPAn)	Maleic Anhydride (MAn)	Diethylene Glycol (DEG)[a]	Before Addition of MAn	After Addition of MAn
Nonhalo polyester (NHP)	0.5	—	—	0.5	1.0	48.5	51.0
Chloro polyester (CP)	—	0.5	—	0.5	1.0	49.5	50.5
Bromo polyester (BP)	—	—	0.5	0.5	1.0	48.7	48.0

[a] DEG was taken 20% excess in order to compensate for glycol losses.

- The Nuclear Magnetic Resonance (NMR) spectra, recorded with an FT-80 NMR spectraphotometer, using $CDCl_3$ as a solvent and tetramethyl silane (TMS) as an internal standard.

- Gel time and exotherm peak temperature, determined as described earlier.[13]

The specimens for tensile strength and % elongation,[14] nitroglycerine absorption,[15] heat resistance,[16] flame retardance,[3] oxygen Index,[17] and thermal conductivity,[18] were cast and cured by 2% each of accelerator and catalyst at ambient temperature (+27°C). Bond strength, with double-base propellant, was determined using propellant pieces (5 cm length × 2 cm width × 1 cm thickness) having cleaned surfaces. All surfaces of the propellant pieces were covered with aluminum foil, except for one side (2 cm × 1 cm), where bonding with inhibitor was tested. The propellant pieces were kept in aluminum trays, spaced at a distance of 1 cm apart. The inhibitor, that is, the polyester resin with accelerator and catalyst, was poured into the gap of propellant pieces; bonded propellant pieces were removed after curing, that is, after ≈ 24 h. The propellant pieces, bonded with the inhibitor, were then tested for breaking load on an Instron machine and bond strength was calculated as

$$\text{Bond Strength} = \frac{\text{Breaking Load}}{\text{Cross Sectional Area}} \; (\text{kg/cm}^2)$$

Inhibition and Static Evaluation of DB Propellant[19]

The inhibition was performed by casting technique. The double-base propellant was machined before inhibition to 107–108 mm in diameter and 120–125 mm in length. The propellant sustainer was cleaned with trichloroethylene and was rubbed with emery paper. The sustainer propellant was then mounted on a base plate of mild steel. The inhibition mold, having dimensions of 113–114 mm at the inner diameter and a length of 140 mm, was assembled. The selected polyester, which was CP-35 with 2% each of accelerator and catalyst, was then poured without applying any barrier coat. The propellant was removed from the mold after completion of the curing process, that is, after 24 h. The inhibited propellant sustainer was machined to a diameter of 112–113 mm and a length of 140 mm. The sustainer was then

X-rayed on an X-ray machine supplied by M/s Philips, Germany. The X-ray screening was performed in two orientations, perpendicular to each other in order to ensure that the propellant and inhibitor were free from any defects, such as internal cracks and air pockets.

The static evaluation of double-base propellant was carried out at ambient temperature (+28°C). The chamber pressure, obtained experimentally, matched the pressure calculated on the basis of the equation shown below:

$$P_c = \left[\frac{apK_N}{C_D} \right]^{(1/(1-n))}$$

where (P_c) chamber pressure; (a) a constant; (p) density of propellant; (K_N) Ab/At, ratio of burning area to throat area; (C_D) discharge coefficient; (n) pressure index.

RESULTS AND DISCUSSION

Structural Aspects

First Step Reaction

In the first step reaction, the entire quantity of DEG has been reacted with PAn/TCPAn/TBPAn until an acid value of 50 ± 2 is achieved. The assignment of infrared bands of halo/and nonhalo prepolymers and their polyesters are shown in Table II. Furthermore, NMR spectra of these prepolymers are shown in Figure 1(A, B) and (C), and the assignment of chemical shifts of NHP is shown in Table III.

Halopolyesters have been synthesized by replacing PAn by TCPAn or TBPAn, respectively, that is, hydrogens of the aromatic ring of PAn have been replaced by chlorine or bromine while other ingredients, including their molar proportions, are the same. IR spectra of halo prepolymers show additional peaks in the region around 800–600 and 500–600 cm^{-1}, corresponding to C — Cl and C — Br bonds, respectively, while the other IR peaks are similar to the NHP prepolymer. On the other hand, the NMR spectra of these prepolymers [Fig. 1(B) and (C)] indicate the absence of aromatic protons (chemical shift at 7–8 δ). Based on this data, probable structures of NHP, CP, and BP prepolymers may be assigned as follows:

(PAn/TCPAn/TBPAn) (DEG)

−H₂O
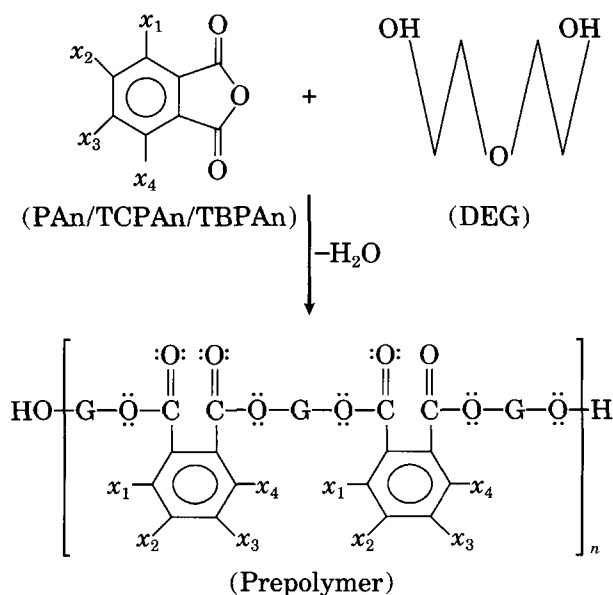
(Prepolymer)

where $(x) = H$ for nonhalo polyester, $(x) = Cl/Br$ for halo polyester, and $G = $ glycol, that is DEG.

Second Step Reaction

The initial step prepolymers are reacted with MAn in order to obtain nonhalo and halo polyesters. The IR bands of nonhalo and halo polyesters are shown in Table II and their NMR spectra are shown in Figure 2. The IR spectra of NHP, CP, and BP show an additional peak around 1640–1660 cm⁻¹ corresponding to a —C═C— in the polyester backbone resulting from the reaction with MAn, while other IR peaks are similar to earlier prepolymers. The NMR spectra of NHP, CP, and BP show chemical shifts at 6.7–6.9 δ and 6.2–6.3 δ, corresponding to the cis and trans stereoisomers, respectively. This is observed due to isomerization, which occurs during the polyesterification reaction, as previously reported in the case of unsaturated polyesters.[17] Based on this data, structures for halo and nonhalo polyesters may be assigned as follows:

1-Step Prepolymer +

(Maleic Anhydride)

−H₂O
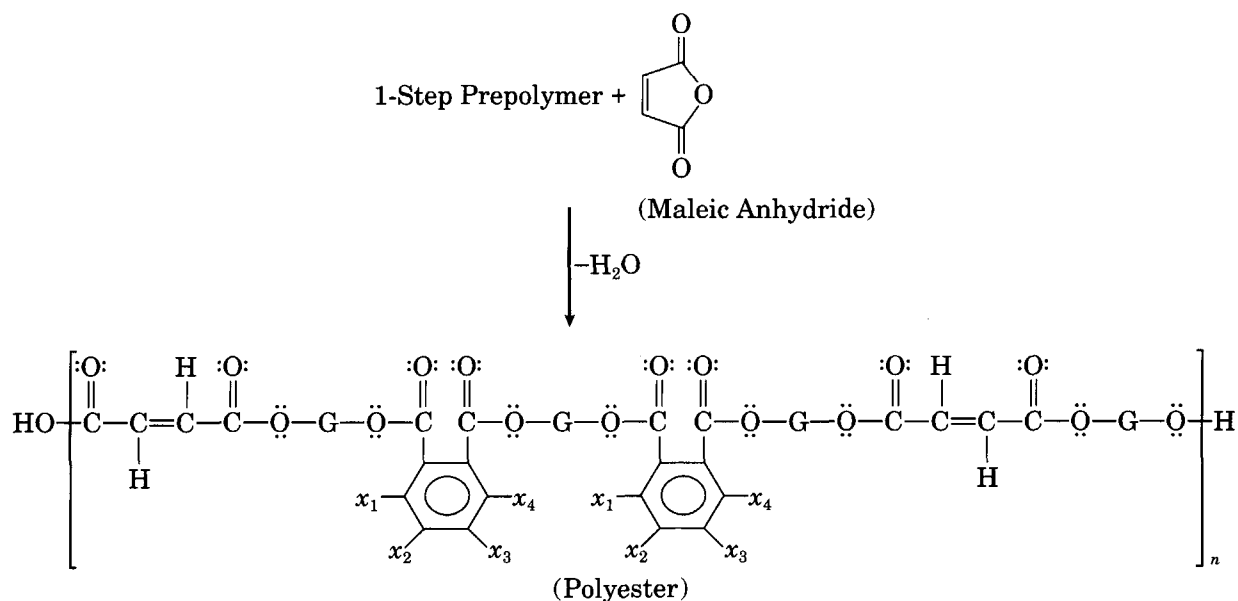
(Polyester)

where $x = H$ for nonhalo polyester, $x = Cl/Br$ for halo polyester, and $G = $ glycol, that is DEG.

Gel Time and Exotherm Peak Temperature

The gel time (G_t) and exotherm peak temperature (E_{PT}) data are given in Table IV and the variation of temperature vs. time during gelling is shown in Figure 3. It is shown in Table IV that the order for G_t is

BP-35 > CP-35 > NHP-35
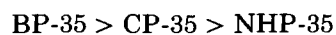
This order may be explained on the basis of the curing mechanism of polyesters. As reported in the literature,[22] curing of unsaturated polyesters is based on a free radical mechanism and involves principally three steps, that is, initiation, chain growth, and chain termination. The organic peroxides, such as methyl ethyl ketone (MEK) peroxide and cyclo-

Table II Assignment of Infrared Absorption Bands for Nonhalo and Halo Prepolymers and Polyesters[20,21]

IR Frequencies (cm^{-1})	Assignments			
	Nonhalo Prepolymer	Halo Prepolymer	Nonhalo Polyester (NHP)	Halo Polyester (HP)
3500 (broad)	—OH stretching group	—OH stretching group	—OH stretching group	—OH stretching group
2960 (weak)	—CH (stretching) methylenic	—CH (stretching) methylenic	—CH (stretching) methylenic	—CH (stretching) methylenic
1760 (strong and sharp)	C=O stretching of ester Carbonyl group	C=O stretching of ester Carbonyl group	C=O stretching of ester Carbonyl group	C=O stretching of ester Carbonyl group
1640–1660 (broad)	—	—	—C=C group due to maleic anhydride	—C=C group due to maleic anhydride
1550 (weak)	Aromatic ring	Aromatic ring	Aromatic ring	Aromatic ring
1100–1200 (weak)	C—O—C ester	C—O—C ester	C—O—C ester	C—O—C ester
800–600	—	C—Cl	—	C—Cl
500–600		C—Br		C—Br

hexanone (CH) peroxide, produce free radicals in the presence of cobalt naphthenate. The free radicals add to the double bonds of the styrene monomer, resulting in activated benzyl radicals, which, in turn, attack the double bonds of the polyester backbones. This continues until the entire sample is converted into a solid 3-dimensional interpenetrating network. This means that the time required for the gelling of the polyester, that is, G_t, depends upon

1. the accessibility of double bonds of polyester backbones to attack by the styryl radicals. Thus, in the case of NHP-35, there is no steric hindrance to the attack by the activated styryl radicals and G_t is lower. However, in the case of CP-35, when PAn is replaced by TCPAn, that is, C—H is replaced by C—Cl (chlorine is a somewhat larger group), accessibility of polyester backbones for the attack by the styryl radicals becomes difficult and, as a result, the G_t of CP-35 is longer than NHP-35. In case of BP-35, where C—Cl is replaced by C—Br (Br is a highly bulky substituent), the accessibility of the polyester backbones to the attack by the activated styryl radicals becomes more difficult and results in a higher G_t than CP-35. Therefore, G_t increases from NHP-35 to BP-35.

2. Hindered diffusion of the catalyst and the accelerator to halo and nonhalo polyesters increases from NHP-35 to BP-35. It is evident, from the viscosity data of these halo and nonhalo polyesters, that the viscosity increases from NHP-35 to BP-35 (Table IV). As viscosity increases from NHP-35 to BP-35, diffusion of the accelerator and the catalyst is hindered in the same direction and, accordingly, G_t increases in the same direction.

Regarding E_{PT}, it is reported[23] that the curing of unsaturated polyesters is an exothermic reaction and that heat is liberated by the conversion of —C=C— bonds to —C—C— bonds. Since the quantity of maleic anhydride incorporated is the same in NHP-35, CP-35, and BP-35, the same amount of heat is expected to be liberated and, therefore, E_{PT} should be comparable. However, the measured E_{PT} values for NHP-35, CP-35, and BP-35 are 151°, 127°, and 46°C, respectively. It is well known[24] that the E_{PT} is inversely related to G_t. If G_t is longer, a part of the heat librated during gelling is dissipated, leading to a decrease in E_{PT}. As G_t increases from NHP-35 to BP-35, a part of heat liberated during gelling is dissipated, leading to a decrease in E_{PT}. This could be one of the possible reasons for the trend observed in E_{PT}.
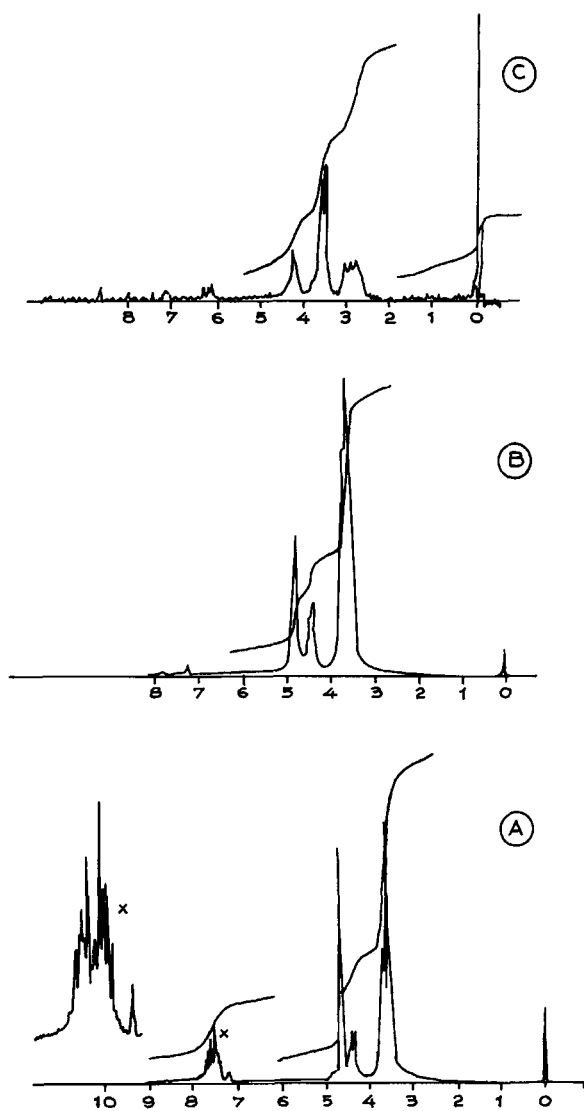
Figure 1 NMR Spectra of nonhalo and halo prepolymer (before addition of maleic anhydride). (A) Nonhalo prepolymer, (B) Chloro-prepolymer, and (C) Bromo-prepolymer.

TENSILE STRENGTH, % ELONGATION, AND BOND STRENGTH WITH DB PROPELLANTS

Tensile strength, % elongation, and bond strength data for the halo and nonhalo polyesters are presented in Table IV. It is evident that the relative order for % elongation, for the materials measured, is

NHP-35 > CP-35 > BP-35

Table III   Assignments of NMR Chemical Shifts of Prepolymer of Nonhalo Polyester[20,21]

Chemical Shift (ppm)	Assignments
7.69	X_1 and X_4 (aromatic protons)
7.48	X_2 and X_3 (aromatic protons)
4.35	$CH_2 — O — R$
3.50–3.60	$OH — CH_2 — CH_2 — O$ of ester

This order may be explained on the basis of data reported in the literature,[25] which suggest that polymers having bulky substituents have lower flexibility, because of steric hinderance to rotation. In the case of NHP-35, there is less steric hindrance, since there are no bulky substituents in PAn and this material would be expected to be more flexible than the halo polyesters. In the case of CP-35, the bulky
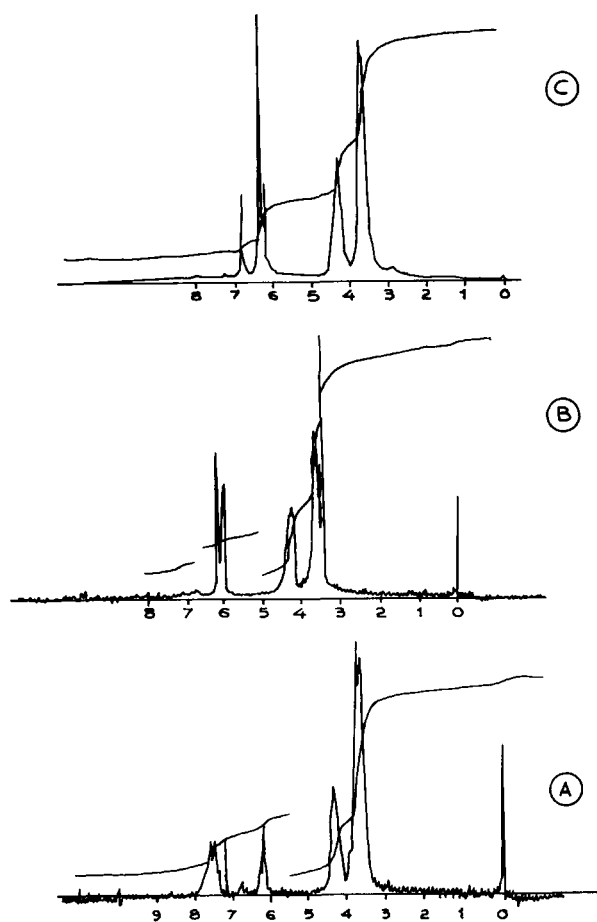

Figure 2 NMR spectra of nonhalo and halo polyesters (after addition of maleic anhydride). (A) Nonhalo polyester, (B) Chloropolyester, and (C) Bromopolyester.
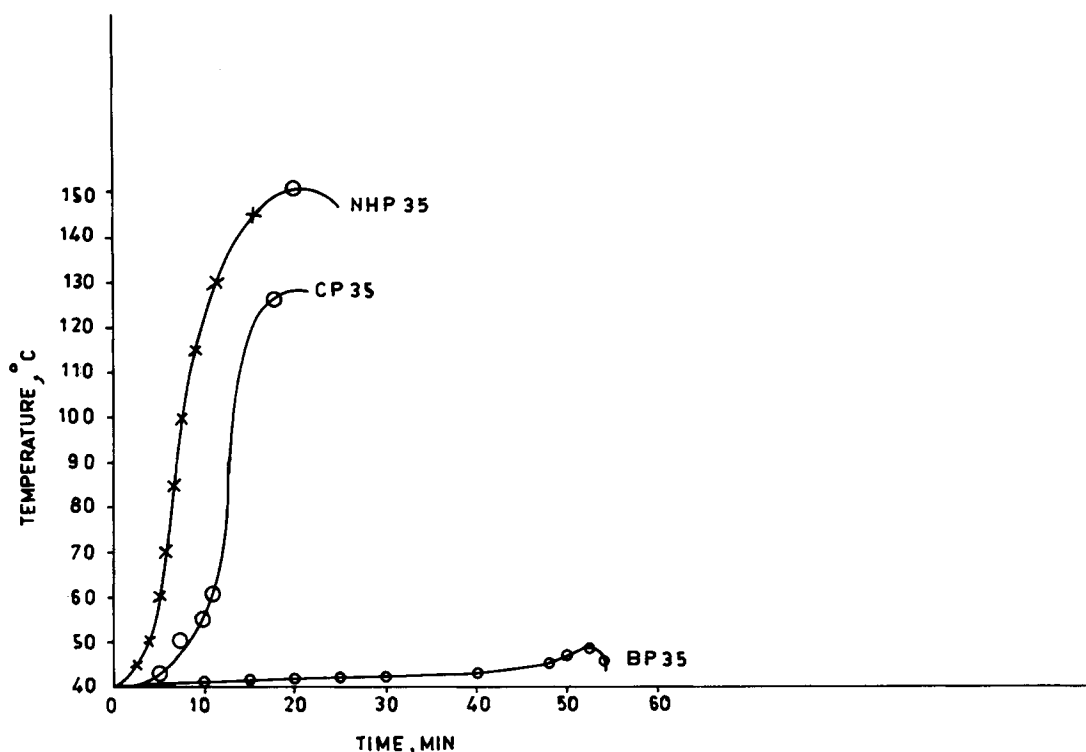
Figure 3   Exotherm curves for nonhalo and halo polyesters.

chlorine groups lower the polymer flexibility, resulting in a reduction in % elongation. The bulkiness further increases, in the case of BP-35, due to the presence of large bromo substituents, which leads to a further reduction in elongation, as compared with NHP-35 and CP-35.

The literature on the mechanical properties of thermosets suggests that % elongation and tensile strength of unsaturated polyesters are interrelated, that is, if the elongation decreases, the tensile strength increases, and vice versa.[26] Therefore, the tensile strength of the materials studied follows the order NHP-35 < CP-35 < BP-35. This result is in agreement with the findings of Nametz,[10] who has

reported that the molecular rigidity of polyesters increases upon the introduction of chlorine or bromine groups, which leads to a corresponding improvement in tensile strength.

As the flexibility (elongation) decreases in the order BP-35 < CP-35 < NHP-35, the bond strength is expected to increase in the opposite order. This is observed experimentally, and is in agreement with our findings, reported earlier, for unsaturated polyesters and chloropolyesters.[1-6]

Thermal Conductivity

The thermal conductivities (λ) for NHP-35, CP-35, and BP-35 are presented in Table IV. As reported

Table IV   Viscosity, Gel Time, Exotherm Peak Temperature, Tensile Strength, % Elongation, Bond Strength, and Thermal Conductivity of Halo and Nonhalo Polyesters

| Polyester	Viscosity at 25°C, C_{ps} (after addition of 35% styrene)	Gel Time, at 40°C (min)	Exotherm Peak Temperature (°C)	Tensile Strength (kg/cm²)	Elongation (%)	Bond Strength with DB Propellants (kg/cm²)	Thermal Conductivity (W/mK)
NHP-35	30	4.5	151	78	19	32	0.91
CP-35	40	11	127	123	15	52	0.87
BP-35	70	28	46	129	3	56	0.513

in the literature,[27] the thermal conductivity of polymers is related to the elongation and increases when the elongation increases. The order for % elongation for the polyesters in this study is BP-35 < CP-35 < NHP-35. It is, therefore, expected that the order for λ should also be BP-35 < CP-35 < NHP-35.

NITROGLYCERINE ABSORPTION

The variation of nitroglycerine (NG) absorption with time for NHP-35, CP-35, and BP-35 is displayed graphically in Figure 4. It is evident from Figure 4 that the order for NG absorption is

$$NHP\text{-}35 > CP\text{-}35 > BP\text{-}35$$

This order may be explained on the basis of structures of NG and unsaturated polyesters. The general structure of unsaturated polyester is described earlier, while the structure for NG is shown below:

(Nitroglycerine)
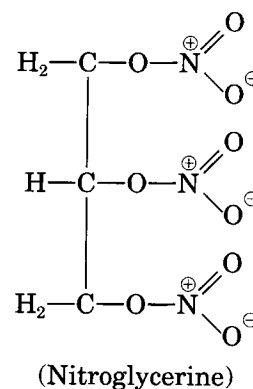
It is clear from the structures that an unsaturated polyester has several electron donor sites, whereas NG is a strong electron acceptor. As a result, the electrostatic force of attraction operates between NG and polyester and leads to the migration of NG from the propellant towards the polyester. This migration may be retarded by introducing electronegative groups, such as chlorine or bromine, into either the aliphatic/aromatic acid or the glycol.[4] If electron acceptor groups, such as chloro or bromo, are introduced into the aromatic acid, the structure of the resulting polyester is
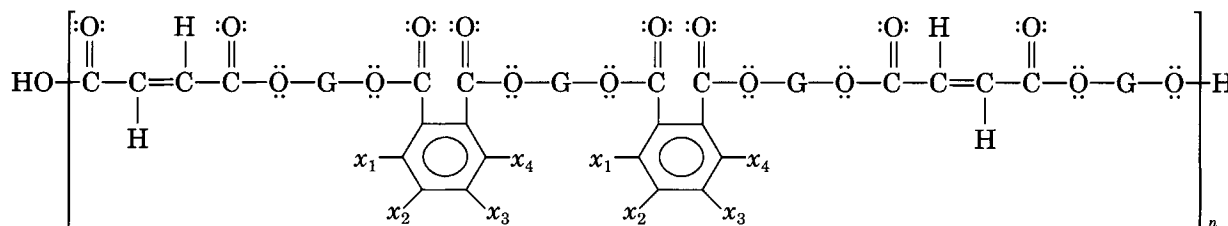

where x = Cl/Br; G = Glycol, that is, DEG.

Thus, the electrostatic force of attraction between NG and halo polyesters is reduced as compared to nonhalo polyesters, which leads to a reduction in NG absorption. It is evident from the data that BP-35 shows less NG absorption than CP-35, even though chlorine is more electronegative than bromine. This may be due to the bulkiness of the bromine group, as compared to chlorine, which retards the accessibility of bromopolyesters to NG molecules, resulting in lower NG absorption. This is also supported by the data on tensile strength, which is indicative of the extent of crosslinking and increases in this order.[4]

Heat Resistance

The heat resistance data, defined in terms of "loss of volatiles" for halo and nonhalo polyesters, is presented in Table V. From the data, the order for volatile losses is

$$NHP\text{-}35 > CP\text{-}35 > BP\text{-}35.$$
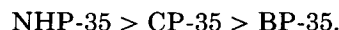
It may be recalled that the order for % elongation is

$$NHP\text{-}35 > CP\text{-}35 > BP\text{-}35$$

This order means that the extent of compactness for molecular structures increases from NHP-35 to BP-35 through CP-35, which retards the escape of volatile matter. As a result, the extent of "volatile losses" decreases from NHP-35 to BP-35 through CP-35. In other words, the order of heat resistance is

$$NHP\text{-}35 < CP\text{-}35 < BP\text{-}35$$

Flame Retardance

Flame retardance, defined in terms of the change in "burning rate" for NHP-35, CP-35, and BP-35, is presented in Table VI, along with theoretically cal-
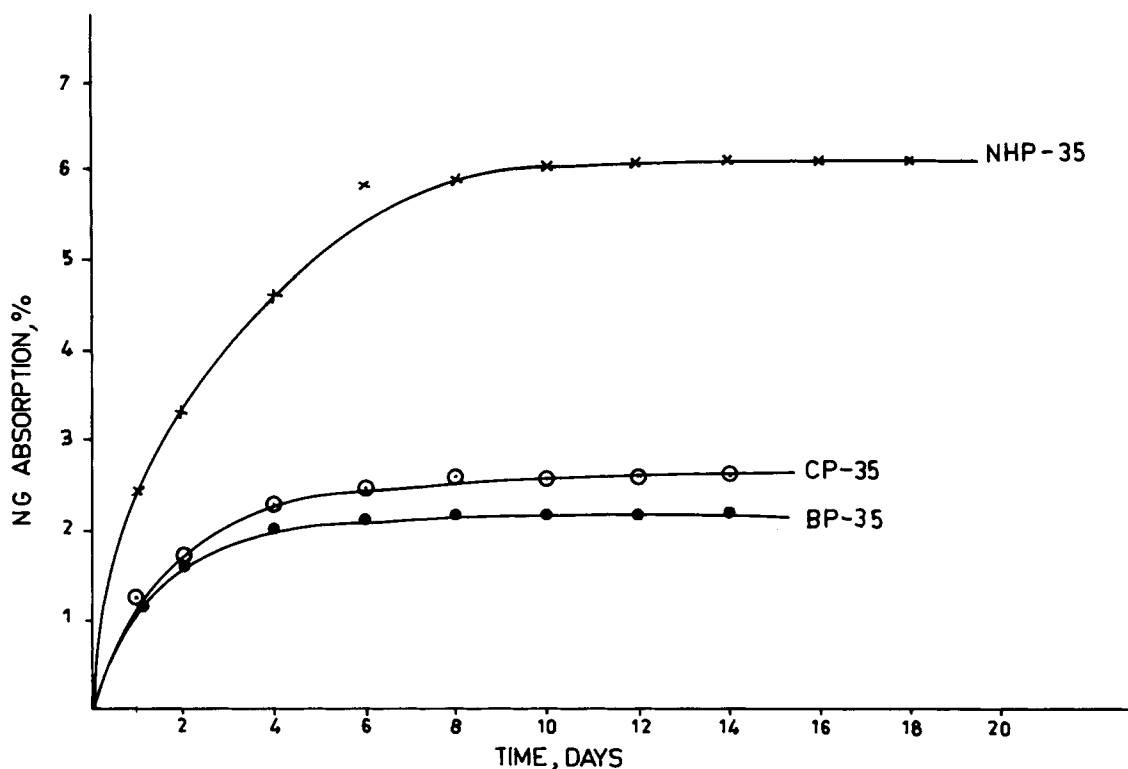
Figure 4   Effect of time on nitroglycerine absorption of nonhalo and halo polyesters.

culated % chlorine and bromine. It is evident that the burning rate of NHP-35 is 0.61 mm/sec, while those of CP-35 and BP-35 are 0.45 and 0.38 mm/sec, respectively. The lower burning rate for CP-35 and BP-35 may be explained on the basis of data reported by several researchers.[28,29] These researchers have established that halogen substituents impart flame retardant characteristics to polymers, due to the release of HCl or HBr, and also that HBr is liberated in higher concentrations at lower temperatures. Furthermore, bromopolymers are more flame resistant than chloropolymers because —C—Br bonds are weaker than —C—Cl bonds. This enables Br radicals to interfere with the flame propagation process during combustion. Therefore, bromopolyesters are more effective as flame retardants than they are as chloropolyesters, and the or-

der of flame resistance is BP-35 > CP-35 > NHP-35. Accordingly, the burning rate decreases from NHP-35 to BP-35.

Oxygen Index

"Oxygen index" is defined as the minimum concentration of oxygen in a mixture of oxygen and nitrogen that supports candlelike combustion. The oxygen number, n, was calculated using the formula

$$n(\%) = \frac{O_2}{O_2 + N_2} \times 100$$

where O_2 and N_2 are the volumetric flow in cc/sec. Oxygen Index (n) for the halo and nonhalo polyesters is presented in Table VI. The order for n is BP-35 > CP-35 > NHP-35, which means that BP-

Table V   Effect of Time on Volatile Losses for Halo and Nonhalo Polyesters

Polyester	Loss in Weight (%), Time (h)					
	1 h	2 h	3 h	4 h	5 h	6 h
NHP-35	0.51	0.92	1.15	1.28	1.39	1.42
CP-35	0.33	0.50	0.68	0.79	0.83	0.85
BP-35	0.29	0.46	0.58	0.67	0.70	0.72

Table VI   Flame Retardance and Oxygen Index of Halo and Nonhalo Polyesters

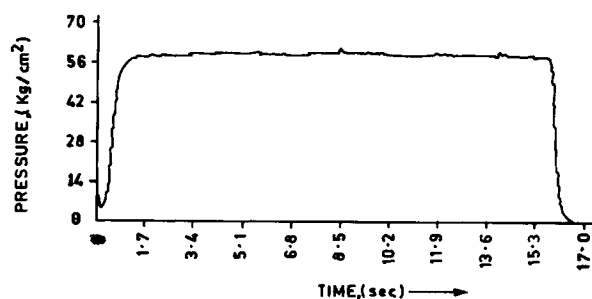| Polyester	Burning Rate (mm/sec)	Oxygen Index (%)	Theoretical Chlorine (%)	Theoretical Bromine (%)
NHP-35	0.61	16.52	—	—
CP-35	0.45	18.20	15.32	—
BP-35	0.38	19.54	—	26.5

Figure 5 Pressure–time profiles for double-base propellant inhibited with CP-35 at ambient temperature (+35°C).

35 requires more oxygen than CP-35 to sustain candlelike burning and, similarly, CP-35 requires more oxygen than NHP-35. In other words, BP-35 is a better flame retardant than CP-35 which, in turn, is better than NHP-35. This is in agreement with the data for burning rates and heat resistance for these polyesters (Table VI).

The tensile strength, % elongation, bond strength with propellant, NG absorption, and flame retardant characteristics are important properties for polymeric materials to have, in order to judge their suitability for the inhibition of rocket propellants. The elongation of BP-35 is only 3% and, therefore, is not be suitable for the inhibition of double-base rocket propellants. Furthermore, in comparison to the other properties of CP-35 and BP-35, for example, the cost of basic materials, that is, TCPAn and TBPAn, and the time required for the synthesis of CP-35 and BP-35, suggest the suitability of CP-35 for the inhibition of DB rocket propellants.

The inhibited, machined, and X-rayed DB propellant sustainers have been statically evaluated after conditioning at ambient temperature (+35°C). The pressure–time profile is shown in Figure 5. The P–t curve is neutral and flat throughout the duration of the combustion, indicating that CP-35 works satisfactorily as an inhibitor for DB propellants.

REFERENCES

1. J. P. Agrawal, M. P. Chouk, and V. M. Kate, *Indian J. Tech.*, **22**, 460 (1984).
2. J. P. Agrawal, M. P. Chouk, A. K. Singhal, K. S. Kulkarni, and P. S. Vasudevan, *Proc. Indian Nat. Sci. Acad.*, **52A**, 676 (1986).
3. J. P. Agrawal, M. P. Chouk, and R. S. Satpute, *Br. Polym. J.*, **14**, 29 (1982).
4. J. P. Agrawal and K. S. Kulkarni, *Def. Sci. J.*, **36**, 409 (1986).
5. J. P. Agrawal and K. S. Kulkarni, *J. Appl. Polym. Sci.*, **32**, 5203 (1986).
6. J. P. Agrawal, R. S. Satpute, K. S. Kulkarni, V. P. Bansod, M. P. Chouk, and A. R. Inamdar, *Composites*, **21**, 345 (1990).
7. M. Carrie-Mauriseer and J. Tranchant, *Fr. Demande*, 2,337,117, Societe Nationale des Pourdres at Explosifs, 29 July 1977; *Chem. Abstr.*, **89**, 27,030 (1978).
8. E. Behnke and H. Wulff, *Chemische Werke G.M.b.H.*, Ger. 1,109, 886; *Chem. Abstr.*, **56**, 1600h (1962).
9. R. C. Nametz, J. Di Pietro, and I. N. Einhorn, *Am. Chem. Soc. Div. Org. Coatings Plast. Chem.*, **28**(1), 204 (1968).
10. R. C. Nametz, *Ind. Eng. Chem.*, **59**, 99 (1967).
11. J. A. Schneider, R. G. Pews, and J. D. Herring, *Am. Chem. Soc. Div. Org. Coatings Plast. Chem.*, **29**, 382 (1969).
12. J. P. Agrawal and M. P. Chouk, *Res. and Ind.*, **27**, 19 (1982).
13. J. P. Agrawal, M. P. Chouk, R. S. Satpute, and V. C. Bhale, *J. Polym. Sci. Part A Polym. Chem.*, **27**, 409 (1989).
14. ASTM Standards on Plastics, ASTM D-638, American Society for Testing and Materials, Philadelphia, 1945.
15. J. P. Agrawal and R. D. Pokharkar, *J. Sci. Ind. Res.*, **39**, 633 (1981).
16. P. E. Robitschek and B. C. Thomas, *Ind. Eng. Chem.*, **46**, 1629 (1954).
17. *Annual Book on ASTM Standards Part 35*, ASTM D-2863 American Society for Testing and Materials, Philadelphia, 1975.
18. *Annual Book on ASTM Standards Part 35*, ASTM D-433 American Society for Testing and Materials, Philadelphia, 1975.
19. J. P. Agrawal and J. M. Vergnaud, *J. Sci. Ind. Res.*, **57**, 375 (1992).
20. K. Nakanishi, *Infrared Absorption Spectroscopy*, Holden–Day, San Francisco, 1962, p. 44.
21. V. O. Parikh, *Absorption Spectroscopy of Organic Molecules*, Addison Wesley, London, 1973.
22. J. P. Agrawal, K. S. Kulkarni, and R. S. Satpute, *Popular Plastics*, **30**, 31 (1985).
23. H. V. Boenig, *Unsaturated Polyester: Structure and Properties*, Elsevier, New York, 1964, p. 98.
24. J. P. Agrawal, *Eur. Polym. J.*, **24**, 33 (1988).
25. M. P. Stevens, *Polymer Chemistry—An Introduction*, Addison-Wesley, 1975, p. 63.
26. H. V. Boenig, *Unsaturated Polyesters: Structure and Properties*, Elsevier, New York, 1964, p. 143.
27. B. Seymour and C. E. Carraher, *Structure–Property Relationships in Polymers*, Plenum, New York, 1984, p. 89.
28. H. F. Mark, N. G. Gaylord, and N. M. Norbert, Eds., *Encyclopedea of Polymer Science and Technology, Vol. 7*, Interscience, Wiley, New York, 1967, p. 16.
29. J. Troitzsch, *International Plastics Flammability Handbook*, Hanser, Munich 86, 1983, p. 46.