

Tetrachloro Phthalic Anhydride Based Chloropolyesters for Inhibition of Double Base Rocket Propellants

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Abstract. The choice of inhibiting materials for double base and composite modified double base rocket propellants has always been a difficult problem because of the presence of nitroglycerine in these propellants and its subsequent migration from the propellant towards the inhibitor. The inhibition of double base rocket propellants with unsaturated polyesters has become popular in recent years, but they usually suffer from the drawback of high nitroglycerine absorption. This may be considerably lowered by exploiting the concept of introduction of electron acceptance sites in one of the components used for the synthesis of unsaturated polyesters. Chloropolyester-1 (CP-1) based on tetrachlorophthalic anhydride (TCPAn), propylene glycol (PG) and maleic anhydride (MAN) and chloropolyester-2 (CP-2) based on TCPAn, polyethylene glycol mol. wt. 200 (PEG-200) and MAN have been synthesised and characterised for gel time, exotherm peak temperature, tensile strength, % elongation, bond strength, water absorption, nitroglycerine absorption, heat resistance and flame retardance. The blends of CP-1 and CP-2 designated as CPB-2 (CP-1 : CP-2 :: 20 : 80), CPB-4, CPB-6 and CPB-8 have also been formulated and characterised for these properties. Based on the data for various characteristics, CPB-4 has been selected for inhibition and static evaluation of rocket propellants. The double base rocket propellant sustainers containing 2-NDPA have been inhibited with CPB-4 without the application of any barrier coat and statically fired at ambient, cold (-40°C) and hot (+50°C) temperatures after conditioning. The pressure-time profiles were found to be smooth and flat in all cases, inferring that the CPB-4 inhibition system (without application of any barrier coat) is working satisfactorily.

1. Introduction

The inhibition of double base rocket propellants with unsaturated polyesters has become popular in recent years¹⁻⁴. But they usually suffer from the drawback of high nitroglycerine (NG) absorption^{5,6}. High NG migration from the propellant to

unsaturated polyesters may be considerably reduced by exploiting the concept of introduction of electron acceptance sites in one of the ingredients used for their synthesis'. A literature survey reveals that chloropolyesters based on tetrachloro phthalic anhydride have not been used for the inhibition of double base rocket propellants. The object of the present study is to synthesize chloropolyesters based on tetrachloro phthalic anhydride (TCPAn), their characterization and static evaluation of double base (DB) propellant using these chloropolyesters as inhibitors for them.

2. Materials and Methods

The materials required for the work, tetrachloro phthalic anhydride (**m.p. 255-258°C** and chlorine content 48.5 per cent), propylene glycol (BDH, L.R.), polyethylene glycol (mol. wt. 200, BDH, L.R.), maleic anhydride, technical (m.p. $51 \pm 2^\circ\text{C}$ and purity 98.5 per cent min.), styrene monomer (b.p. $145 \pm 2^\circ\text{C}$ and specific gravity 0.9055 at **25°C**), were procured from trade and used as such without further purification.

2.1 Preparation of Chloropolyesters

Polyesterification was carried out in an electrically heated 4 necked flask fitted with stirrer, thermometer and inert gas inlet leading to the bottom of reaction mixture, and an upright water cooled condenser. 1.5 mole of propylene glycol and 0.5 mole of TCPAn were charged into the flask and temperature was raised to 160°C. After 4 hour's condensation, condenser was replaced by Dean & Starks' tube and water produced was removed till the acid value comes to 60. The reaction mixture was cooled and 0.5 mole of maleic anhydride was added and it was refluxed for two hours. Now the temperature was raised and water produced by the reaction was distilled off till acid value of 60 is achieved. The chloropolyester was cooled, applied **vaccum** and then 0.02 per cent of hydroquinone (based on the weight of resin) was added. The finished chloropolyester was partially cooled and blended with 25 per cent styrene and cooled to room temperature. This chloropolyester was designated as CP-I.

CP-2 based on polyethylene glycol mol. wt. 200 (PEG-200, 1.2 mole), TCPAn (0.5 mole) and **MA**n (0.5 mole) was also made by **two**-step process similarly. The acid values before and after adding **MA**n were 35 and **35** respectively.

The blends of CP-1 and CP-2 in different proportions were prepared by mixing CP-1 and CP-2 and designated as CPB-2 (CP-1 : CP-2 : : 20 : SO), CPB-4, CPB-6 and CPB-8 were allowed to achieve equilibrium before determining their characteristics. The details are given in Table 1. It is reported in the literature that blends are better than mixed glycols based polyesters which have crystallizing tendency during storage*.

Table 1. Composition of chloropolyesters and their blends (CPB)

Designation	Molar Ratios of Ingredients				Acid Values		Composition of Blends	
	Longer Chain Glycol, Polyethylene Glycol Mol. wt. 200 (PEG-200)	Short Chain Glycol, Propylene Glycol (PG)	Tetrachloro Phtialic Anhydride (TCPAn)	Maleic Anhydride (MAAn)	Before Addition of MAAn	After Addition of MAAn	CP-2	CP-1
CP-2	1.2	0.0	0.5	0.5	35	35	—	—
CPB-2	—	—	—	—	—	—	80	20
CPB-4	—	—	—	—	—	—	60	40
CPB-6	—	—	—	—	—	—	40	60
CPB-8	—	—	—	—	—	—	20	80
CP-1	0.0	1.5	0.5	0.5	60	60	—	—

2.2 Gel Time and Exotherm Peak Temperature

Gel time and exotherm peak temperature were determined by the method reported earlier⁷.

2.3 Tensile Strength and Percent Elongation

Tensile strength and per cent elongation was determined by ASTM method⁹.

2.4 Water Absorption

Water absorption was also measured by ASTM method¹⁰.

2.5 Bond Strength

Bond strength with the propellant containing 2-NDPA was determined by the method reported earlier¹¹.

2.6 Nitroglycerine Absorption

Nitroglycerine absorption was measured by Liquid Absorption Method¹².

2.7 Heat Resistance

Heat resistance was measured by the method reported earlier¹².

2.8 Flame Retardance

Flame retardance was also measured by ASTM test method, D635-63, with some minor modifications as described in our earlier communication?

2.9 Inhibition and Static Evaluation of Double Base Rocket Propellants

The cast double base propellant sustainer containing 2-NDPA (as stabilizer) was machined to the dimensions 110 mm diameter and 150-160 mm length and was inhibited with CPB-4 by casting **technique**¹¹. It was extracted next day, machined to the dimensions 115 mm diameter, length 160-170 mm and X-rayed. Three propellant sustainers were similarly inhibited, machined and X-rayed and one each was statically evaluated after conditioning for 8 hrs at $+50^{\circ}\text{C}$, (hot) 18 hrs at -40°C , (cold) and at ambient, temperatures.

3. Results and Discussions

3.1 Gel Time and Exotherm Peak Temperature

The gel time and exotherm peak temperature data for CP-1 and CP-2 and their blends are given in Table 2 and time versus temperature curves (exotherms) are shown in

Table 2. Gel time and exotherm peak temperature for chloropolyesters and their blends (CPB)

Chloropolyesters and their blends	Gel time, (min.) ± 1 min.	Exotherm peak temperature, ($^{\circ}\text{C}$) $\pm 5^{\circ}\text{C}$
CP-2	40	44.5
CPB-2	30	66.0
CPB4	16	98.0
CPB-6	12	106.0
CPB-8	9	126.0
CP-1	7	148.0

Fig. 1. The gel time for CP-1, based on short chain glycol, PG, is 7 minutes and that of CP-2, which is based on PEG-200, is 40 minutes. CP-1, based on PG, consists of short chloropolyester chains, and that based on PEG-200, consists of longer chloropolyester chains. Since the longer chain molecules are less reactive than that of short chain molecules, it is expected that CP-2 will have longer gel time than CP-1 which is observed experimentally. It is also seen that as the proportion of CP-1 is increased, the gel time decreases. It is because of the fact that the proportion

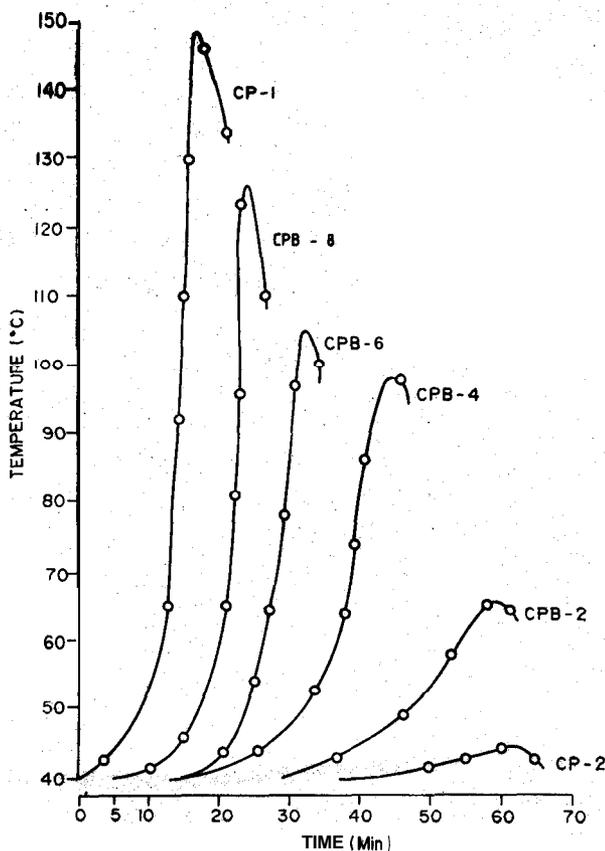


Figure 1. **Exotherm** curves for chloro-polyesters and their blends(CPB).

of CP-I whose gel time is less, increases from CPB-2 to CPB-8 and thus correspondingly gel time decreases.

The exotherm peak temperature of CP-2 is 44.5°C and that of CP-1 is 148°C . This may be explained on the basis of number of chloropolyester chains and bond energies of carbon-carbon single (C-C) bonds and carbon-carbon double (C = C) bonds. As explained above, CP-2 consists of longer chloropolyester chains and CP-I consists of shorter chloropolyester chains and therefore total number of chloropolyester chains for the same weight will be less in case of CP-2 than CP-I. It is also reported that the bond energy of carbon-carbon double (C = C) bond is 100 Kcals/mole and that of carbon-carbon single (C-C) bond is 58.8 Kcals/mole . On polymerization/curing/crosslinking, various chloropolyester chains are linked to one another through the conversion of double bonds into single bonds and as a result, 17.2 Kcals/mole ($2 \times 58.6 - 100 = 17.2$) energy is liberated. Since the number of chloropolyester chains for the same weight is less in case of CP-2 than CP-I, the exotherm peak

temperature will also be less in case of **CP-2** than CP- I which is experimentally obtained. As already explained, the number of chloropolyester chains based on PG, **increases** with the increase in the proportion of CP-I, it is therefore expected that the amount of heat liberated during **curing/polymerization** will also increase from CPB-2 to CPB-8 and CP-1. In other words, the exotherm peak temperature will increase from CPB-2 to CPB-8 and **CP-1**.

3.2 Tensile Strength, Per Cent Elongation and Bond Strength

The tensile strength, per cent elongation and bond strength data are given in Table 3. It is observed that the tensile strength increases as the proportion of CP-1 in chloropolyester blends increases and order is,

$$\text{CP-2} < \text{CPB-2} < \text{CPB-4} < \text{CPB-6} < \text{CPB-8} < \text{CP-1}.$$

Table 3. Tensile strength, percentage elongation and bond strength for chloropolyesters and their blends (CPB)

Chloropolyesters and their blends	Tensile strength (kg/cm ²)	Elongation %	Bond strength (kg/cm ²)
CP-2	5.40	17.00	5.0
CPB-2	13.75	23.00	19.5
CPB-4	58.20	19.00	47.3
CPB-6	155.00	11.00	64.3
CPB-8	298.00	3.00	80.3
CP-1	340.00	1.66	86.0

It may be explained on the basis of fact that as the proportion of CP-1 increases, the number of chloropolyester chains increases leading to increase in cross-linking density which results into increase in tensile strength from CP-2 to CPB-8 and CP-1. It is reported that tensile strength and per cent elongation are closely related' and as tensile strength increases, per cent elongation **decreases**¹³. This is a general characteristic of both unsaturated polyesters and most other crosslinked polymers and that is why, per cent elongation decreases as the tensile strength increases from CPB-2 to CPB-8.

The bond strength also increases from CP-2 to CPB-8 and CP-1. The reason is that the gel time decreases with increase in the proportion of CP-I in chloropolyester blends in the following order

$$\text{CP-2} > \text{CPB-2} > \text{CPB-4} > \text{CPB-6} > \text{CPB-8} > \text{CP-1}.$$

As the gel time decreases, the time for migration of nitro bodies from the propellant to the chloropolyester resin decreases and therefore the extent of interference by nitro bodies on curing/cross-linking/polymerization decreases in this order. The migration of nitro bodies from the propellant to the inhibitor results into incomplete curing and weak bonds if polyester is not fast curing^{14,15}. Since the gel time decreases with the replacement of CP-2 by CP-I, it is, therefore, expected that the bond strength will increase in the same manner and order will be as follows

$$CP-2 < CPB-2 < CPB-4 < CPB-6 < CPB-8 < CP-I.$$

3.3 Nitroglycerine and Water Absorption

The nitroglycerine and water absorption data are shown in Table 4 and Table 5 respectively.

Table 4. Effect of time on nitroglycerine absorption of chloropolyesters and their blends (CPB)

Chloro- polyesters and their blends	Nitroglycerine absorption, (%)							
	Days							
	1	2	4	6	8	10	12	14
CP-2	7.14	9.88	—	Specimen shattered in to pieces				—
CPB-2	3.55	4.33	5.26	5.65	5.98	6.18	6.21	6.30
CPB-4	1.98	2.61	3.23	3.77	4.25	4.60	4.74	4.15
CPE-6	1.08	1.30	1.55	1.67	1.72	1.73	1.75	1.78
CPB-8	0.60	0.75	0.88	0.97	0.98	1.01	1.04	1.06
CP-1	0.45	0.7	0.8	0.85	0.85	0.86	0.86	0.98

Table 5. Effect of time on water absorption of chloropolyesters and their blends (CPB)

Chloro- polyesters and their blends	Water absorption, (%)					
	Days					
	1	2	3	4	5	a
CP-2	6.43	9.41	11.02	11.57	11.89	12.04
CPB-2	4.68	7.62	8.79	9.45	9.85	9.96
CPB-4	1.89	2.61	3.02	3.20	3.34	3.42
CPB-6	0.66	1.15	1.36	1.49	1.56	1.62
CPB-8	0.29	0.43	0.51	0.60	0.66	0.71
CP-1	0.14	0.22	0.27	0.30	0.34	0.34

and the electrostatic force of attraction between the propellant and chloro/bromo polyester used as inhibitor, is reduced resulting into considerable reduction in the migration/absorption of nitroglycerine from the propellant to **chloro/bromo** polyester (Inhibitor).

Similar phenomenon is also observed in case of water absorption which also decreases in this order. These observations are similar to those reported by us on semiflexible unsaturated polyester **resins**².

3.4 Heat Resistance

The results of 'heat resistance' in terms of volatile losses for chloropolyesters and their blends are given in Table 6. Similar to other data, volatile losses also decrease from CP-2 to CPB-8 and CP-1 and at the same time increase with the time

Table 6. Volatile losses data of **chloropolyesters** and their blends (**CPB**)

Chloropolyesters and their blends	Loss in weight, % (hr)					
	1	2	3	4	5	6
CP-2	0.71	1.25	1.50	1.60	1.65	1.68
CPB-2	0.54	1.10	1.13	1.21	1.30	1.35
CPB-4	0.42	0.76	0.90	0.97	1.03	1.06
CPB-6	0.37	0.64	0.77	0.82	0.91	0.95
CPB-8	0.30	0.45	0.52	0.57	0.59	0.60
CP-1	0.17	0.30	0.36	0.37	0.40	0.40

of exposure. The tensile strength data indicate that cross-linking density increases in this manner,

$$\text{CP-2} < \text{CPB-2} < \text{CPB-4} < \text{CPB-6} < \text{CPB-8} < \text{CP-1}$$

and consequently volatile losses will decrease in the order.

$$\text{CP-2} > \text{CPB-2} > \text{CPB-4} > \text{CPB-6} > \text{CPB-8} > \text{CP-1}.$$

The graphical presentation of volatile losses verses time at 150°C for **chloropoly**-ester blend-4 (CPB-4) and **semiflexible** unsaturated polyester resin-4 is shown in Fig 2. The traces show **that** the fire retardant resin i.e. CPB-4 losses weight slowly during the heating cycle. This is probably due to the release of halogen or hydrogen halide which in a fire situation contributes to flame **extinction**¹⁸.

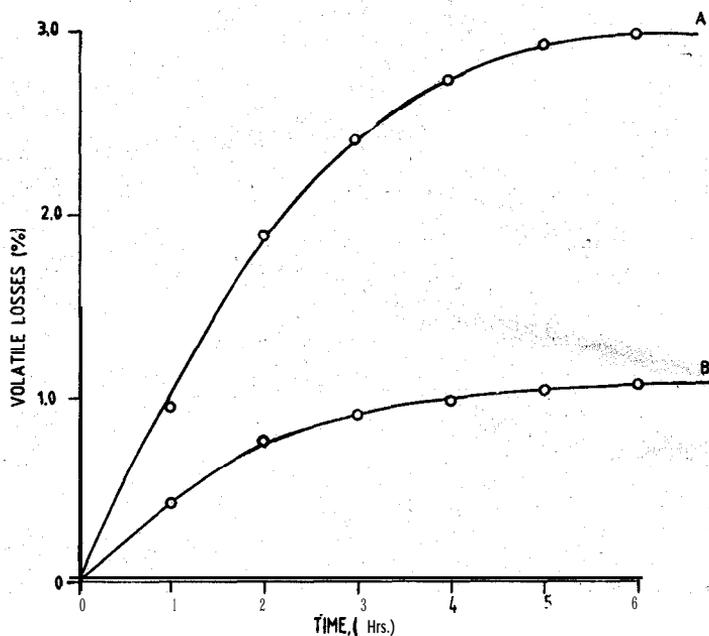


Figure 2. Volatile losses vs exposure at 150°C for
A-Semiflexible unsaturated polyester resin-4.
B-Chloropolyester blend4.

3.5 Flame Retardance

The data of flame retardance obtained as burning rate of chloropolyesters and their blends are given in the Table 7, along with the theoretically calculated chlorine percentage. It is seen that as the per cent of chlorine increases, the burning rate decreases. The burning rate varies from 0.58 **mm/sec** to 0.31 **mm/sec**. The burning rate data for semi-flexible unsaturated polyester resins has been reported by us² in the

Table 7. Flame retardance of chloropolyesters and their blends (CPB)

Chloropolyesters and their blends (CPB)	Theoretical chlorine, %	Burning rate, mm/sec.
CP-2	12.86	0.5824
CPB-2	13.988	0.4361
CPB-4	15.116	0.3983
CPB-6	16.244	0.3594
CPB-8	17.372	0.3350
CP-1	18.500	0.3132

range from 0.28 to 0.30 mm/sec. The reason is not clearly understood and experiments are in progress to pin point the exact reasons for higher burning rates in chloropolyesters and their blends.

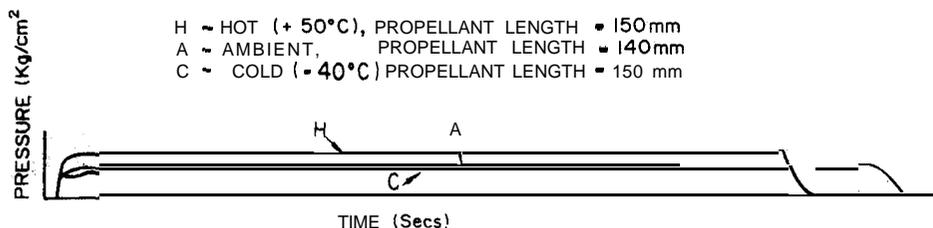


Figure 3. Pressure-time profiles for propellant inhibited with CPB-4.

Based on gel time, exotherm peak temperature, tensile strength, per cent elongation, bond strength, nitroglycerine and water absorption, heat resistance and flame retardance, CPB-4 has been found to be suitable for inhibition and static evaluation trials were conducted as, 1 number at ambient temperature; 2 numbers after conditioning at cold (-40°C) for 18 hrs and 2 numbers after conditioning at hot (+50°C) for 8 hrs. The pressure-time profiles, as shown in Fig. 3, are flat and pressure level is practically constant throughout the combustion duration. The constant pressure level indicates that burning surface is constant throughout the firing, which in other words, indicates the successful performance of chloropolyester blend CPB-4 inhibition system without the application of any barrier coat.

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