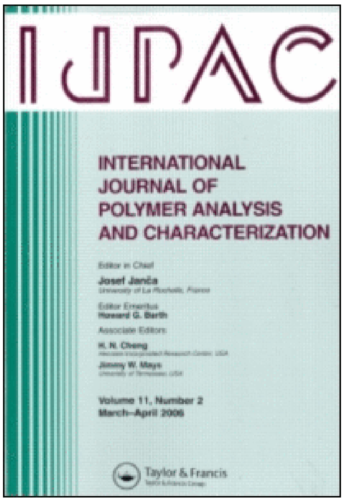

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Characterization of Some Modified Unsaturated Polyesters for Inhibition of Double-base Rocket Propellants

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Properties of a flexible unsaturated polyester (EP4), consisting of poly(ethylene glycol), isophthalic acid, maleic anhydride, and styrene, and a less flexible unsaturated polyester (FUP-9), consisting of poly(ethylene glycol), diethylene glycol, isophthalic acid, maleic anhydride, and styrene, have been studied with varying styrene monomer ratios and partial replacement aliphatic/aromatic cross-linking monomers. The effect of the addition of fillers, in terms of gel time, exothermic peak temperature, tensile strength, % elongation, Shore hardness, nitroglycerine absorption, water absorption, 'loss in weight', *i.e.*, heat resistance, oxygen index, and smoke density has also been studied. The data indicate that a composition of 60% EP-4 (50), styrene (25), and methyl methacrylate (25) with 40% alumina trihydrate holds potential for inhibition of double-base rocket/missile propellants, where signature related problems in missiles are of prime importance.

Keywords: Characterization; Unsaturated polyester; Inhibition; Double-base rocket propellants

INTRODUCTION

Major ingredients of double-base (DB) and composite modified double-base (CMDB) propellants are nitrocellulose (NC) and nitroglycerine (NG), in addition to other minor ingredients, such as stabilizers, opacifiers and burn-rate modifiers. Polyesters that bond

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strongly with double-base (DB) and composite modified double-base (CMDB) propellants are used for inhibition.[1-3] Elastopolyester-4 (EP-4, a very flexible unsaturated polyester based on poly(ethylene glycol) (200 MW) isophthalic acid and maleic anhydride with styrene monomer) and flexible unsaturated Polyester-9 (FUP-9, an unsaturated polyester based on a blend of poly(ethylene glycol) (200 MW) diethylene glycol, isophthalic acid and maleic anhydride and mixed with styrene monomer) have proved their potential for inhibition of DB and CMDB propellants,[1-5] encapsulation of Explosive Reactive Armour (ERA), fabrication of composite materials, *etc.* Modification of these polyesters may be done by adding various cross-linking monomers in varying proportions and by incorporating different fillers.

The object of this paper is to modify EP-4 and FUP-9 by varying proportions of styrene monomer and its partial replacement with other cross-linking monomers, such as diallyl phthalate (DAP), methyl methacrylate (MMA), and ethyl acrylate (EA), and by incorporating fillers like alumina trihydrate (ATH), antimony trioxide, melamine, and zinc borate in selected modified unsaturated polyester compositions, followed by characterization for various properties. Further, based on various properties, a modified polyester composition has been selected for inhibition of DB propellants and static evaluation.

MATERIALS AND METHODS

Materials

Materials used for this work and their specifications are diethylene glycol (DEG) (conforming to Indian Standard 7918-1975), poly (ethylene glycol) (200 MW, PEG-200) conforming to Indian Standard 12277-1968, isophthalic acid (IPA) (mp 340°C and purity not less than 98%), maleic anhydride, technical (MAn) (mp 54 ± 2°C and purity 98.5% minimum), styrene monomer (bp 145 ± 2°C and 0.9055 specific gravity at 25°C), *p*-toluene sulfonic acid (mp 100 – 105°C and purity 98% minimum), diallyl phthalate (LR grade, ester content 99%, and 1.20 – 1.25, specific gravity at 20°C), methyl methacrylate (LR grade, bp 101°C, and 0.904 g/cc density at 25°C), ethyl acrylate (LR grade, bp 99.4°C, and 0.9230 g/cc density at 20°C), cobalt naphthenate (3% solution in methylene chloride) as accelerator, methyl ethyl ketone peroxide (50% solution in diethyl phthalate) as catalyst, alumina trihydrate (purity 99.5% minimum, passing through 400 British standard sieves), antimony trioxide (purity 99.8% minimum, passing through 200 British standard sieves), melamine (purity 99.8%, mp 345°C, passing through 400 British standard sieves), and zinc borate (purity 99.8% minimum, passing through 200 British standard sieves).

Methods

EP-4 and FUP-9 polyesters were prepared by a 'two-step polyesterification process' as described in the literature.[6] For EP-4, in first step reaction, PEG-200 (1 mol) was mixed with isophthalic acid (0.6 mol) at 50° – 60°C with constant stirring in an inert atmosphere. One millimole of *p*-toluene sulfonic acid (based on the weight of isopthalic acid) was also added as an esterification catalyst. The temperature was raised to 160° – 180°C slowly in order to start the condensation reaction. After collecting approximately the calculated quantity of water, the acid value was checked periodically. The acid value at the end of first step was 20 ± 1 and as soon as this acid value was achieved, heating was stopped but stirring continued. The product was allowed to cool to 50° – 60°C. In the second step, maleic anhydride (0.3 mol) was added slowly in the reaction mass with constant stirring and in an inert atmosphere. The temperature was raised to 180° – 200°C. Slowly, the acid value was determined periodically again and water was collected. When the acid value reached 29 ± 1, the reaction was stopped and the product was cooled to 70°C with stirring on. Hydroquinone (0.02% based on the resin weight) was then added and mixed with the resin homogeneously. The product was removed, cooled and mixed with styrene monomer. FUP-9 was made in a similar manner: In the first-step reaction, diethylene glycol and poly(ethylene glycol) were mixed at a molar ratio 0.9 and 0.1, respectively followed by the addition of isophthalic acid (0.33 mol) and condensation. The acid value of the first step reaction was 50 ± 1. In the second step, maleic anhydride (0.66 mol) was added and the condensation continued until an acid value of 40 ± 1 was achieved. Then hydroquinone was added and the resin removed after cooling and mixed with styrene monomer.

Various formulations were characterized for the following properties: gel time and exotherm peak temperature,[7] Brookfield viscosity, mechanical properties, *i.e.*, tensile strength, %, elongation[8] and Shore hardness[9] (done with five specimens and their mean reported), chemical resistance in terms of nitroglycerine absorption[10] and water absorption,[11] heat resistance,[12] oxygen index[13] and smoke density,[14] and inhibition and static evaluation of inhibited double-base propellants.

The inhibition of double-base propellant sustainer was done by the casting technique.[2] The propellants were machined to 108-mm diameter and 100–102-mm length. The propellant was fixed to the bottom plate and wetted with the resin containing 2% each of accelerator and catalyst. The assembly was then made and the resin, containing accelerator and catalyst, was poured around the propellant and the inhibitor was allowed to cure. The propellant was extracted the next day and machined to 116-mm diameter. The propellant was also X-rayed to ensure that the propellant, as well as inhibitor, are free from internal defects, such as voids, cracks, and air bubbles, *etc.* Similarly, six propellants were inhibited, machined, X-rayed and statically evaluated: two each after conditioning at ambient temperature (27°C) for 24 h; in the cold (−40°C) for 24 h; and at elevated temperature (50°C) for 24 h.

RESULTS AND DISCUSSION

Effect of Variation of Styrene Monomer

Various compositions of EP-4 and FUP-9 have been made by varying the styrene monomer concentration (30 to 60%). Properties such as gel time, exotherm peak temperature, viscosity (before curing), and tensile strength, % elongation, Shore hardness, nitroglycerine absorption and water absorption (after curing) have been determined.

Gel Time, Exotherm Peak Temperature and Viscosity

The magnitudes of gel time and exotherm peak temperature for polymeric materials constitute an important criteria in connection with civil as well as military applications. For civil applications, longer gel time makes materials suitable for the manufacture of large-sized articles with lower internal stresses due to lower exothermal effect. For military applications, especially for the inhibition of DB rocket propellants, a compromise between gel time and exotherm peak temperature is required.[15]

At 40°C, viscosity of the virgin EP-4 and FUP-9 are 9266 cP and 12500 cP, respectively and that of styrene monomer is very low. It is seen from the data (Tabs. I and II) that viscosity decreases as the percentage of styrene monomer increases, which is due to the dilution effect of added styrene monomer and is obvious from the viscosity data of EP-4, FUP-9 and styrene monomer.

The gel time (G_t) and exotherm peak temperature (E_{PT}) of composition 3 (EP-4 containing 50% styrene monomer) is 21.3 min and 63°C, whereas for composition 6 (FUP-9 containing 40% styrene monomer) 15.1 min and 111°C, respectively. The G_t of FUP-9 is less as compared to EP-4 because of the fact that FUP-9 is based on mixed glycols, *i.e.*, PEG-200 (a long-chain glycol) and DEG (a short-chain glycol), whereas EP-4 is completely based on a long-chain glycol, *i.e.*, PEG-200. G_t and E_{PT} are inversely related to each other and therefore, as G_t decreases, E_{PT} is expected to increase as observed experimentally.

Tensile Strength, Percentage Elongation, and Shore Hardness

The effect of variation of styrene monomer concentration on tensile strength (TS) and % elongation of EP-4 and FUP-9 is shown in Tables I and II respectively. For the EP-4+styrene monomer system, TS increases as the percentage of styrene monomer increases from 30 to 60%, whereas there is no trend in the % elongation. The percentage elongation of EP-4 with 30% styrene monomer is 52% which becomes 84% when styrene monomer is 40% and decreases to 76% and 61% with 50% and 60% styrene monomer, respectively. Similar to tensile strength, Shore hardness also increases from 30 to 50% styrene.

In the case of FUP-9+styrene monomer system, TS and Shore hardness increase with an increase in concentration of styrene monomer. Contrary to TS, % elongation regularly decreases from

TABLE I Effect of styrene monomer on the properties of EP-4

Composition	*EP-4 : Styrene %*	*Viscosity cP*	*Gel time min*	*E_{PT}°C*	*Tensile strength Kg/cm^2*	*Elongation %*	*Shore hardness ('A' scale)*	*NG absorption (after 10 days) %*	*Water absorption (after 7 days) %*
1	70 : 30	137	–	–	10	52	55	63.06	8.59
2	60 : 40	60	–	–	32	84	60	60.15	8.13
3	50 : 50	32	21.3	63.0	62	76	62	53.82	7.11
4	40 : 60	24	–	–	101	61	71	51.17	6.11

TABLE II Effect of styrene monomer on the properties of FUP-9

Composition	*FUP-9 : Styrene %*	*Viscosity cP*	*Gel time, min*	E_{PT},°*C*	*Tensile strength Kg/cm*^{2}	*Elongation %*	*Shore hardness* (‘*A*’ *scale*)	*NG absorption* (*after* 10 *days*) %	*Water absorption* (*after* 7 *days*) %
5	70 : 30	110	–	–	60	19	45	12.96	5.94
6	60 : 40	60	15.1	111.0	148	13	50	10.00	5.38
7	50 : 50	36	11.7	153.0	185	10	55	9.30	4.32
8	40 : 60	27	–	–	210	10	57	8.38	3.75

30 to 60% styrene monomer. This is in agreement with the data reported recently by Agrawal *et al.*[16]

Chemical Resistance

The chemical resistance of these systems has been measured by determining nitroglycerine (NG) absorption and water absorption. The data for NG absorption and water absorption is given in Table I for the EP-4+styrene monomer system and in Table II for the FUP-9+styrene monomer system.

It is evident that NG absorption and water absorption decrease in both systems as the styrene level increases in the polyester systems. The NG absorption of cured products is usually less, at higher styrene content.[17, 18] The chemical resistance of cured polyesters depends upon the styrene content of the resin.[19] In general, highly cross-linked polyester that contains the theoretical amount of styrene for each cross-link appears to have greater resistance both to chemical attack and to penetration of solvent. Also, highly cross-linked polyester systems containing no styrene or a lower amount of styrene are easily attacked.

The nitroglycerine and water absorption for FUP-9+styrene monomer system is less due to increased compactness in the molecular structure of the FUP-9 as a result of the replacement of PEG-200 (a long-chain glycol) by DEG (a short-chain glycol). It is supported by the tensile strength which is more for FUP-9 and indicates more compactness of molecular structure in FUP-9 as compared to EP-4. The data reported by Parker and Moffett,[17] who studied water absorption of propylene–fumarate–phthalate, diethylene–fumarate–phthalate and propylene–maleate–adipate resins, is similar to our findings.

Tensile strength, percent elongation and NG absorption are important properties of polymeric materials and a compromise among these properties is needed while selecting a polymer for inhibition of rocket propellants to ensure successful performance during static evaluation at ambient and extreme temperatures.[6] As a result, EP-4 containing 50% styrene monomer (composition 3) and FUP-9 containing 40% styrene monomer (composition 6) have been selected for further study. The styrene monomer was partially replaced by aromatic cross-linking monomers, such as diallyl phthalate (DAP), and aliphatic cross-linking monomers, such as methyl methacrylate (MMA) and ethyl acrylate (EA), and characterization was done for various properties.

Effect of Replacement of Styrene Monomer by Different Cross-linking Monomers

Gel Time, Exotherm Peak Temperature and Viscosity

The data on gel time (G_t), exotherm peak temperature (E_{PT}) and viscosity for the EP-4 + styrene and FUP-9 + styrene systems are given in Tables III and IV, respectively. It is seen that the viscosity is nearly same for all aliphatic monomers on partial replacement of styrene because there is not much difference in their viscosities at 40°C. However, the viscosity increases on the addition of diallyl phthalate, which is mainly due to its high viscosity (140 cP at 40°C).

The presence of MMA retards curing of polyesters because of the extension of chains which is evident on partial replacement of styrene by MMA in EP-4, as well as in the FUP-9 system. As the G_t and E_{PT} are inversely related [15] and G_t increases as a result of partial replacement of styrene by MMA, E_{PT} is expected to decrease, as observed experimentally.

DAP, which contain two allyl groups that are sterically hindered unsaturated groups, copolymerizes less rapidly than vinyl monomers [20] if used alone. But in combination with styrene, it is observed that there is not much difference in G_t as compared to styrene alone, implying that the reactivity of the system dose not differ significantly. However, in the case of the FUP-9 system, there is no specific trend. In the case of EP-4, E_{PT} first decreases and then increases but for FUP-9, it regularly decreases as the percentage of DAP monomer increases. The decrease in exotherm peak temperature is due to the DAP having sterically hindered unsaturated groups. It may, therefore be employed where high exotherm peak temperature is undesirable.

EA can be used alone or in combination with styrene for modifying properties of polyesters, but the final products are generally too soft and flexible to be of much use. It is suitable for rigid polyesters based

TABLE III Effect of partial replacement of styrene by MMA and DAP monomer on properties of composition 3

Composition	*Styrene monomer replacement*	*Replacement %*	*Gel time min*	E_{PT} °C	*Viscosity cP*	*Tensile strength Kg/cm²*	*Elongation %*	*Shore hardness 'A' scale*	*NG absorption (after 10 days) %*	*Water absorption (after 7 days) %*
3	–	0	21.3	63	32	62	76	62	53.82	7.11
9	MMA	25	51.0	47	28	50	80	48	77.03	4.61
10		50	63.0	42	31	22	115	40	107.67	6.06
11	DAP	25	23.0	48	50	21	82	60	62.38	7.89
12		50	20.0	58	91	8	51	68	47.61	7.08

TABLE IV Effect of partial replacement of styrene by MMA, DAP and EA monomer on properties of composition 6

Composition	*Styrene monomer replacement*	*Replacement %*	*Gel time min*	E_{PT} °*C*	*Viscosity cP*	*Tensile strength* Kg/cm^2	*Elongation %*	*Shore hardness 'A' scale*	*NG absorption (after 10 days) %*	*Water absorption (after 7 days) %*
6	–	0	15.1	111	60	148	13	50	10.08	5.38
13	MMA	25	17.2	107	85	155	14	63	5.12	1.43
14		50	26.1	100	54	39	32	58	10.18	2.27
15	DAP	25	7.3	105	290	113	24	72	2.98	2.41
16		50	11.4	75	335	131	10	80	2.68	1.81
17	EA	25	18.0	125	60	64	26	71	6.88	1.74
18		50	21.0	122	43	15	22	78	16.19	2.90

on propylene glycol, isophthalic acid and maleic anhydride (in different proportions) and mixed with styrene monomer like rigid Polyester-3 (PR-3) and rigid Polyester-4 (PR-4) [4] and to some extent, for FUP-9. The data on gel time indicate that it increases as the percentage of EA increases. This is perhaps due to extension of chain length resulting in less reactivity and thus increase in gel time. The E_{PT} first increases and then slightly decreases as EA percentage increases.

Tensile Strength, % Elongation and Shore Hardness

The data is given in Tables III and IV for EP-4 and FUP-9 systems, respectively. In the case of MMA, TS and Shore hardness decrease, whereas % elongation increases for EP-4. The decrease in TS and Shore hardness is due to the chain length extension [21] introduced by cross-linking of the MMA and consequently, increase in % elongation. For FUP-9, the tensile strength and Shore hardness first slightly increase followed by a decrease. The elongation, however, regularly increases. The addition of DAP monomer with styrene monomer shows that the TS decreases in the EP-4 as the concentration of DAP increases. However, there is no specific trend in FUP-9. For EA, TS decreases as the percentage of EA increases in FUP-9. This increase in % elongation in case of EA is due to chain length extension [21] introduced by EA cross-linking.

Chemical Resistance

The nitroglycerine and water absorption data for EP-4 and FUP-9 is given in Tables III and IV, respectively. The nitroglycerine and water absorption data for EP-4 with styrene in conjunction with DAP does not have any specific trend, *i.e.*, where 25% styrene is replaced by DAP, nitroglycerine and water absorption increase. This trend is, however, reversed when 50% styrene is substituted by DAP. When MMA and EA are added in conjunction with styrene monomer [21] in the polyesters, nitroglycerin absorption increases because of an increase in the chain length. The increase in chain length is supported by the elongation data.

Effect of Fillers on Selected Compositions

The use of unsaturated polyesters for inhibition of double-base rocket propellants has become popular in recent years [1–3, 7, 22] and a variety of techniques have been employed in an attempt to confer flame retardant characteristics to polyester resins. These are the addition of inorganic additives, organic additives or a combination of both. Also, by introducing the flame retardant element in the polymer itself. The use of inorganic fillers, such as antimony trioxide, alumina trihydrate, zinc borate, *etc.*, to impart flame retardant[23] appears to be very interesting as these are usually inexpensive and in many cases, help to improve mechanical properties.[24–26]

Based on the properties of various compositions studied, composition 10, composition 11 and composition 14, which possess a combination of different properties, were selected for studying the effect of some fillers.

Gel Time, Exotherm Peak Temperature and Viscosity

When fillers are used in thermosetting resins, the filler has a direct influence on the curing parameters, like gel time and exotherm peak temperature. The complexity of such an effect largely depends on how much the fillers[27, 28] absorb or adsorb the resin and their surface area, as well as their physico-chemical interactions with the polymeric matrices. Rao and Ramaswamy,[29] while studying the curing behavior of filled polyesters reported that, in the case of nonabsorbing or nonadsorbing type of fillers, the surface area plays an important role. The effect of alumina trihydrate, antimony trioxide, melamine, and zinc borate has been studied at levels of 10, 20, 30 and 40%. The effect of fillers on composition 10, composition 11 and composition 14 in terms of gel time, exotherm peak temperature and viscosity is shown in Tables V to VII.

As the percentage of fillers increases from 0 to 40%, the exotherm peak temperature decreases as the quantity of resin, which is the only source of heat liberation during polymerization because of conversion of —C=C— to —C—C— bonds,[30] decreases, thereby resulting in a decrease in exotherm peak temperature. Similarly, it is evident that increasing the amount of filler introduced into the polyester resins

TABLE V Effect of fillers on various properties of composition 10

Composition	*Filler*	%	*Gel time min*	E_{PT} °*C*	*Viscosity cP*	*Tensile strength Kg/cm^2*	*Elongation %*	*Shore hardness 'A' scale*	*Water absorption (after 7 days) %*	*Loss in wt. (after 6 h) %*	*Oxygen index n*	*Smoke density %*
10	0	0	63.0	42	31	22	115	40	6.06	2.19	21.8	34
19	Alumina trihydrate	10	59.3	41	40	25	112	42	4.35	2.09	23.1	20
20		20	58.3	–	48	28	110	43	–	1.51	23.8	18
21		30	57.2	–	78	41	109	47	3.88	1.89	24.1	12
22		40	57.0	40	110	57	72	51	3.07	1.68	24.4	8
23	Antimony trioxide	10	58.0	41	36	16	83	62	4.26	2.16	23.1	28
24		20	55.3	–	40	17	73	68	3.92	2.09	23.8	–
25		30	54.1	–	52	29	38	71	3.91	1.98	24.2	18
26		40	53.5	40	80	–	50	78	3.30	1.90	24.4	16
27	Melamine	10	53.1	41	46	27	87	62	4.33	2.08	21.8	28
28		20	49.3	–	56	29	86	64	4.28	1.99	23.1	22
29		30	42.0	–	77	28	57	70	3.18	1.97	23.9	20
30		40	41.0	40	120	–	32	72	2.85	1.87	24.0	60
31	Zinc borate	10	61.5	41	32	21	46	62	3.31	1.90	22.3	26
32		20	60.0	–	42	23	41	65	3.00	1.84	22.7	22
33		30	58.3	–	62	34	35	68	2.75	1.54	23.0	18
34		40	55.0	40	78	23	20	70	2.64	1.51	23.4	17

TABLE VI Effect of fillers on various properties of composition 11

Composition	*Filler*	%	*Gel time min*	E_{PT} °*C*	*Viscosity cP*	*Tensile strength Kg/cm*^{2}	*Elongation* %	*Shore hardness 'A' scale*	*Water absorption (after 7 days)* %	*Loss in wt. (after 6 h)* %	*Oxygen index n*	*Smoke density* %
11	0	0	23.0	48	50	21	82	60	7.89	4.51	21.7	58
35	Alumina trihydrate	10	22.8	46	58	23	74	62	7.62	4.20	22.6	32
36		20	21.7	–	69	26	67	64	6.21	4.08	23.1	28
37		30	21.0	–	92	33	63	68	5.18	3.68	24.0	23
38		40	20.0	45	100	39	48	2	4.05	3.56	25.7	20
39	Antimony trioxide	10	21.0	47	51	18	72	62	7.17	4.10	23.8	41
40		20	19.8	46	58	–	54	68	5.98	4.05	24.0	36
41		30	19.0	43	64	21	42	72	5.43	4.02	24.4	32
42		40	18.2	41	68	23	32	78	4.67	3.58	25.5	30
43	Melamine	10	18.0	47	61	29	80	64	7.21	4.48	23.8	31
44		20	17.3	46	78	31	75	68	7.17	3.62	24.3	29
45		30	17.1	45	110	–	62	71	6.58	3.58	25.1	25
46		40	15.0	43	150	34	57	73	3.89	1.89	26.0	17
47	Zinc borate	10	18.0	43	53	34	67	62	6.36	3.24	21.8	44
48		20	17.6	42	62	36	59	65	6.05	2.85	22.3	38
49		30	17.0	–	70	37	52	68	5.33	2.04	22.6	35
50		40	16.1	41	78	–	29	70	3.21	1.90	23.8	32

TABLE VII Effect of filler on various properties of composition 14

Composition	*Filler*	%	*Gel time min*	E_{PT} °*C*	*Viscosity cP*	*Tensile strength Kg/cm*^{2}	*Elongation %*	*Shore hardness 'A' scale*	*Water absorption (after 7 days) %*	*Loss in wt. (after 6 h) %*	*Oxygen index n*	*Smoke density %*
14	0	0	26.1	100	54	39	32	58	2.27	2.71	21.8	26
51	Alumina trihydrate	10	19.2	92	89	52	30	63	1.54	1.78	24.0	18
52		20	18.7	90	120	86	16	65	1.32	1.55	24.4	15
53		30	16.3	89	142	19	9	78	1.24	1.35	25.1	12
54		40	14.5	87	172	97	6	73	1.10	0.84	26.0	10
55	Antimony trioxide	10	15.5	95	78	35	25	61	1.61	1.56	25.7	20
56		20	14.3	92	84	36	15	62	1.60	1.29	26.0	18
57		30	13.0	91	112	43	8	65	1.52	1.20	27.0	17
58		40	11.0	89	143	48	5	69	1.41	1.14	27.1	12
59	Melamine	10	18.2	96	85	39	30	60	1.32	1.30	23.8	18
60		20	17.1	95	138	76	19	69	1.26	1.23	24.3	15
61		30	14.3	94	158	93	3	72	1.10	1.14	24.1	12
62		40	12.0	90	179	–	2	78	1.08	0.80	25.4	10
63	Zinc borate	10	19.1	97	74	65	29	70	2.01	2.49	23.5	22
64		20	18.3	95	78	–	17	72	2.01	1.86	24.3	18
65		30	18.0	93	112	94	6	78	1.98	1.77	24.6	16
66		40	17.9	90	120	115	3	80	1.93	1.54	25.0	12

decreases gel time. As these fillers are nonabsorbing types of fillers, gel time is reduced. This is in agreement with the data reported by Shukla and Rao[31] and Agrawal *et al.*,[32] in the case of a semiflexible unsaturated polyester resin-4+alumina trihydrate system. Shukla and Rao [31] suggests that the ratio of surface area of filler and the amount of polyester present are factors that control gel-time decrease. This observation can be further explored by analyzing the data reported by Oprea and Weiner.[33]

The data on viscosity indicate that viscosity of the system increases on addition of fillers when the amount of filler or its volumetric fraction increases, which is quite obvious. However, the changes in viscosity are not linear. Similar observations have been reported by Statt *et al.* [34]

Tensile Strength, % Elongation and Shore Hardness

Tables V to VII depict the data of tensile strength, % elongation and Shore hardness with different percentage of various fillers. In the case of alumina trihydrate, antimony trioxide, melamine and zinc borate systems, tensile strength increases with an increase in the percentage of filler, but percent elongation decreases. This is attributed to the reinforcement of resin matrix on addition of these fillers.[32, 35, 36] This is a shared general characteristic of polyesters and most other cross-linked polymers.[37] It is well known that the TS and % E are interrelated and if TS increases, elongation decreases and *vice versa.*[19] As TS increases with the addition of 10–40% filler, % E decreases in this order, as obtained experimentally.

It is also evident that the hardness of compositions containing filler increases with filler addition and hardness increases parallel to the filler load.[38]

Chemical Resistance

These compositions have also been studied for their chemical resistance in terms of water absorption. Tables V to VII show the variation of water absorption of filled unsaturated polyesters. It is clear that water absorption decreases as the quantity of fillers increases. This is due to fact that the percentage of resin, which is mainly responsible for water absorption, decreases as percentage of filler increases. Similar observation has already been reported by Feketa and McNally [39] in the case of water absorption of a polyester filled system, by Voo *et al.*,[40] with respect to a magnesium oxide-polyester system, and Agrawal *et al.*,[32, 35, 36] for unsaturated polyester-filler and chloropolyester-filler systems. Unsaturated polyesters are cellular in structure. Water molecules can easily seep into the cellular structure of the polyesters. The migration of water is prevented by physically blocking the pores by adding fillers.[41] Water absorption is directly proportional to the quantity of the resin and decreases with an increase in filler concentration.

Heat Resistance, Oxygen Index and Smoke Density

The heat resistance of filled systems has been measured in terms of loss in weight at 150 °C. Tables V to VII show the effect of heat on different filled compositions. The extent of weight loss increases as the heating is continued for a longer time. As the percentage of fillers increases, loss in weight decreases. This is based on the fact that the amount of resin, which is responsible for weight loss, decreases. This aspect has also been studied by us,[32, 35, 36] and Feketa and McNally [39] and the data are in close agreement.

The data on oxygen index (OI) and smoke density is presented in Tables V to VII. The OI data shows that it increases or, in other words, flame retardance increases as filler percentage increases.

The smoke density data show that it decreases as the filler concentration increases. This is because of the fact that the percent of resin decreases as the filler percent increases. This is in accordance with the fact that the addition of fillers reduces flammability, as well as smoke-generating tendency.[23, 42–45]

Under the influence of heat, polymers pyrolyze, and pyrolysis products can be spontaneously ignited, which further increases polymer temperature. Substances that can interfere at any stage of these reactions are termed flame-proofing agents.[46] The interference can be due to physical or chemical means – characteristic of the mechanism of the action of a flame-proofing agent. The fillers under study are inert and these fillers added to these polyesters act like a diluent by decreasing the fraction of burnable material. They inhibit smoke formation relative to their loads. There may be some exceptions to this role, mainly in the case of fillers that are able to react with pyrolysis products during combustion.

Nitroglycerine (NG) Migration Study

The rocket propellants for tactical missiles/rockets require use of inhibition systems that do not produce smoke at the time of combustion of inhibited propellants. For such applications, smoke density, in addition to tensile strength and elongation, becomes very important and therefore, composition 19 to composition 22 have been selected for NG migration study, which is also one of the important tests required for inhibitors. The data on NG migration is shown in Figure 1. The trend for NG absorption data is similar to water absorption

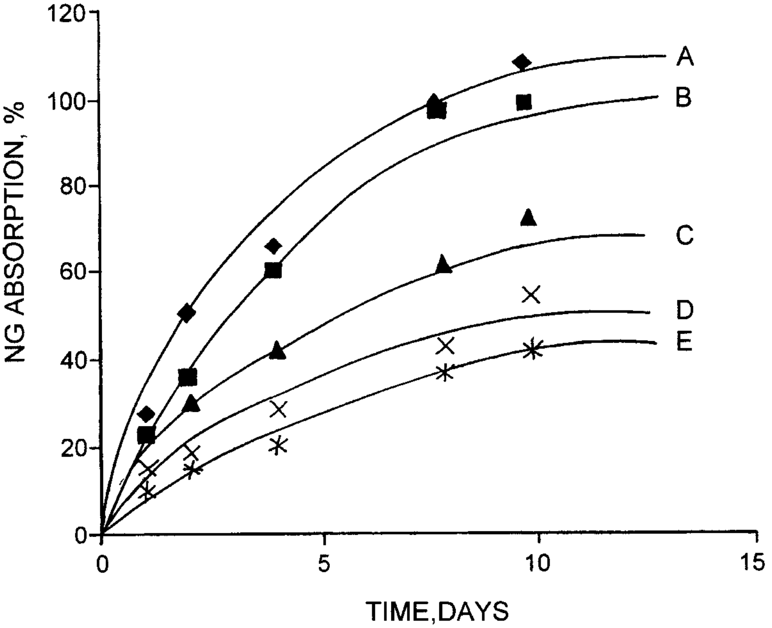

FIGURE 1 Variation of nitroglycerine absorption with time for composition 10+alumina trihydrate. A: composition 10 (composition 10+alumina trihydrate 0%); B: composition 11 (composition 10+alumina trihydrate 10%); C: composition 20 (composition 10+alumina trihydrate 20%); D: composition 21 (composition 10+alumina trihydrate 30%); E: composition 22 (composition 10+alumina trihydrate 40%).

data, *i.e.*, it decreases with increase in filler content. However, it increases with time.

Six double-base propellant solid cylinders (usually called double-base propellant sustainers) were inhibited with composition 22, using the casting technique. Two double-base propellant sustainers were conditioned at ambient temperature (27°C for 24 h), Two double-base propellant sustainers at elevated temperature (50°C for 24 h) and two double-base propellant sustainers at cold temperature (−40°C for 24 h) and statically evaluated. Pressure-time (P-t) profiles are shown in Figure 2.

Figure 2 shows that the *P-t* profiles are smooth and flat in all cases. This infers that composition 22, *i.e.*, composition 10, 60% (EP-4: 50+styrene: 25+MMA: 25) and 40% alumina trihydrate inhibition system works satisfactorily at ambient, hot (50°C) and at cold (−40°C) temperatures. Since, the smoke density is also low in this system, it holds great potential for inhibition of propellants, where smoke level at the time of flight of missiles is considered of prime importance.

The inhibitor for rocket propellants with low/reduced smoke at the time of combustion is of special interest for guided missiles and therefore, composition 22 has potential for inhibition of double-base rocket propellants for use in such missiles.

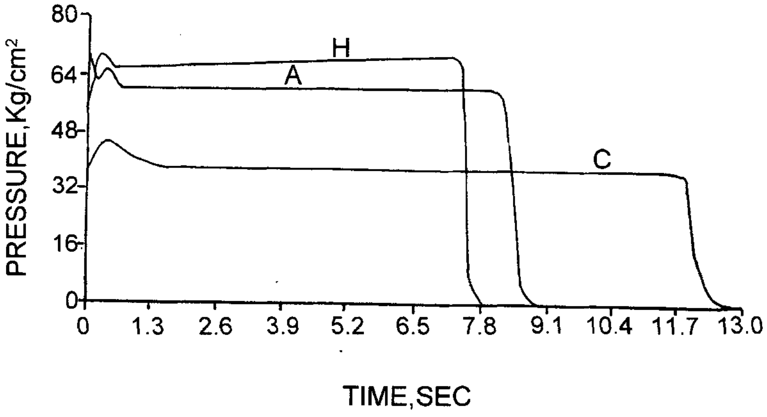

FIGURE 2 *P-t* profiles of double-base propellant sustainers inhibited with composition 22 at hot, ambient and cold temperatures. H: hot 50°C; A: ambient 27°C; C: cold −40°C.

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