PROPERTIES OF SOME CHLORINE CONTAINING POLYESTERS

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Four different types of unsaturated polyesters, made by varying the molar ratios of chlorendic acid to isophthalic acid, were copolymerised with styrene. Thermal stability, self extinguishing property, red heat resistance and chemical resistance of all these types were determined and compared with red heat resistance of 'ATLAC' and thermal stability of highly rigid phthalate and isophthalate polyesters. It was noted that the heat, flame and chemical resistance can be enhanced by more density of cross linking, absence of free homopolymer of the cross linking monomer (styrene), avoidance of phthalate ester group, and incorporation of halogen containing compounds like chlorendic acid.

High strength to weight ratio, low pressure mouldability, easy handling, low cost of fabrication, easy maintenance and cleanliness of glass reinforced polyester articles have made polyester a unique and versatile material. Low thermal stability and inflammable nature of most of the polyesters have limited the scope of their applications. In the case of high speed aircrafts, guided missiles, rockets, heavy electrical and chemical industries[1], there is a great demand for high temperature stable plastics. Therefore attempts were made by various workers [2—5] to make polyester heat and flame resistant. Some of the commercialised products of this type are Hetron Resin—92 by Hooker Chemical Corporation, ATLAC resin, FRB-05A by Atlas Chemical Industries, and Laminac by American Cyanamid Co. Ltd. The information is all of a patented nature[6—10]. The object of the present studies is to develop a suitable polyester with enhanced flame resistance, thermal stability, transparency and chemical resistance and to correlate chemical structure with the above mentioned properties.

EXPERIMENTAL PROCEDURES

Four different formulations were made by varying the molar ratios of chlorendic acid* to isophthalic acid and following data were collected in respect of these and other commercial formulations like ATLAC**, highly rigid phthalate and rigid isophthalate polyesters, on (*i*) chemical resistance[11] (*ii*) red heat resistance[12], (*iii*) self extinguishing property[13] and (*iv*) thermal stability[14].

Preparation of resins

The four resins based on maleic anhydride, isophthalic acid, chlorendic acid and 1·2-propylene glycol were prepared according to method developed in our laboratories[15]. Isophthalic acid was partially replaced by chlorendic acid. Different resins with varying amounts of halogen content were prepared. The general type highly rigid and general type rigid isophthalic resin were also made according to the above method. All the resulting base resins were mixed with minimum amount of styrene required. The characteristics of the resins are given in Table 1.

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*Chlorendic acid is Hexachloro-endomethylene tetra hydro phthalic acid and is written as Het acid.

**Sample was provided by Atlas Chemical Industries, Wilmington, under the name ATLAC 382-FRB-05A.

TABLE 1

COMPOSITION OF HET. ISOPHTHALATE AND GENERAL TYPE POLYESTERS AND THEIR PROPERTIES

Polyester Nos.	Molar ratio					Resin properties			
	Diol 1·2-propylene glycol	Maleic anhydride	Isophthalic acid	Chlorendic acid	Phthalic anhydride	Acid value	Molar ratio of styrene to unsaturation in base polyesters	Viscosity of solution at 25°C	SPI GEL time at 180°C
1	2·2	1	0·8	0·2	—	29·2	1·7	800	6′5″
2	2·2	1	0·6	0·4	—	27·8	1·9	1000	5′30″
3	2·2	1	0·4	0·6	—	21·2	2·1	1100	5′25″
4	2·2	1	0·2	0·8	—	24·3	2·3	1300	5′5″
5	2·2	1	1·0	—	—	20·0	1·58	1200	5′3″
6	4·4	3	—	—	1	40·0	1·0	900	4′30″

Preparation of test specimen for thermal stability and chemical resistance

The specimens were cut from polyester glass laminates (chopped strand mat of low alkali content E-glass, manufactured by the Fibre Glass Industries, Inc., Amsterdan, N. Y. was used). The glass mat to resin ratio in the laminate was 3/7.

For the preparation of glass reinforced polyester test pieces, 6″×6″×1/8″ chromium plated mold was used. A thin film of PVA was applied from solution on the mould to act as mould releasing agent. A resin mix of predetermined pot life containing the polyester, M.E.K.P. as initiator and cobalt octate as accelerator was applied to the glass mat which was cut into suitable size and placed in position. The glass mat was impregnated with the resin by vertical strokes of a stout brush. After the impregnation sometime was allowed for the air bubbles to rise to the surface. The laminate was covered with clean cellophane film and air along with excess resin was squeezed out by means of a roller. The laminate was allowed to cure. Test pieces of size 2″×2″×1/8″ and size 3″×2″×1/8″ were cut from the laminate.

Preparation of test specimen for testing self extinguishing property and red heat resistance

The resin mix, containing polyester resin, initiator and accelerator was poured into suitable s.s. moulds (5″×0·5″×0·5″, 3×15×120 mm.) and allowed to cure at room temperature and later post cured at 100°C by infra-red lamps for 30 minutes. The specimen (5″×0·5″×0·5″) was marked with two lines for lengths of 1″ and 4″ from one end of the specimen.

TESTING OF SPECIMENS

Thermal stability test

The resistance to heat (i.e., thermal stability) was evaluated according to method of Eliot [14].

The loss in weight and appearance of the test specimen after keeping the specimen at 260°C in a constant temperature oven for a definite period of time were noted. The data collected are shown in Table 2.

TABLE 2

STUDY OF STABILITY OF POLYESTERS AT 260°C.

Polyester No. (See Table1)	Losses in weight after (in percent)					Remarks
	1 hour	2 hours	3 hours	4 hours	5 hours	
1	4·7	6·4	7·5	8·0	9·4	No distortion
2	4·45	5·4	7·35	9·25	10·5	—do—
3	3·05	3·9	4·37	5·49	6·55	Colour change is marked
4	4·85	7·1	7·85	9·7	12·9	—do—
5	4·35	4·9	6·9	6·6	7·5	No distortion
6	5·65	7·0	8·9	11·4	12·5	Distortion

Self extinguishing property test

The flammability tests were carried out according to A.S.T.M. standards [13].

The specimen ($5'' \times \frac{1}{2}'' \times \frac{1}{2}''$) was clamped at one end in support with longitudinal axis horizontal and its transverse axis inclined at 45° to the horizontal. Under the test specimen a piece of 20 mesh Bunsen burner gauze about 4 in. square was clamped in horizontal position 3/8″ below the edge of the specimen so that about ½″ of specimen was extended beyond the edge of the gauze. A pan of water was placed on the floor of the hood in position to catch any burning particles which might drop during the test. The specimen was ignited for 30 seconds by placing the blue flame 1″ high of a standard 3/8″ diameter Bunsen burner in contact with the end of the specimen. In case, the specimen continued burning, the burner was placed 18″ away. If the specimen got extinguished then another ignition was applied for 30 seconds and the burner was extinguished. The extent of burning was measured along the lower edge of the specimen. The results are presented in Table 3.

Red heat resistance test

A cast polyester test specimen 3×15×120 mm. was brought into contact with a glow bar (Apparatus IGI [1]) electrically heated to 950°C and loss of weight after 3 min. was determined in mg. and extension of flames in cm. The product of loss in weight (%) and

TABLE 3

STUDY OF FLAMMABILITY OF RIGID POLYESTERS

Polyester No. (See Table (1)	Length burnt (in.)	Rate of burning (in. /sec.)	No. of ignitions applied	No. of specimens tested	Remarks
1	$1\frac{3}{4}$	·0033	1	4	Self extinguishing
2	$\frac{3}{4}$	—	2	—do.—	Self extinguishing non-burning
3	$\frac{1}{2}$	—	—do—	6	—do—
4	0·8	—	—do—	4	—do—
5	$1\frac{1}{2}$	·0037	1	—do—	Self extinguishing
6	5	·0084	—do—	—do—	Highly combustible

TABLE 4

RED HEAT RESISTANCE OF RESINS

Polyester No. (See Table 1)	Loss in weight (mg.)	Extension of the flame (cm. approx.)	Red heat resistance (mg. cm.)	Remarks
1	2503	3	7509	Very poor resistance to heat, combustible.
2	1508	2	3160	Poor resistance to heat, but self extinguishing.
3	560	1	560	Self extinguishing and good resistant to heat.
4	1253	1·5	1879·5	Poor resistance.
Atlac*	1065	1	1069	Self extinguishing and tolerably good resistance to heat.

the flame extension in cm. is the quality measure for the resistance to red heat. The results are shown in Table 4.

Testing of laminated specimens against chemicals

The resistance to chemicals was evaluated according to A.S.T.M. standards on plastics[11]. The samples were immersed in chemical reagents. They were removed at different intervals of time for the check of weight and appearance. The loss in weight and delamination were noted. The results are given in Table 5.

RESULTS AND DISCUSSION

The acid numbers of the unsaturated polyesters prepared (Table 1) were comparable to most of the commercial products. However, their solubility in styrene varied depending on the percentage of chlorendic acid in the polymers. It was observed that molar proportion of styrene to unsaturation in polyesters give a solution of suitable viscosity range (800-1200 cps) increased with chlorendic acid content. This may be due to non-similar structure of base polyester containing chemically combined chlorendic acid with that of styrene[16]. Polyester No. 3 seems to have the minimum loss in weight (6·5%) after aging at 260°C for 5 hrs. (see Table 2). It can be due to incorporation of chlorendic acid[7] and cross linking by the optimum amount of styrene[17]. According to Funke & Hamann[17], there is an optimum molar ratio of unsaturated monomer to unsaturation in polyester for optimum crosslinking and the resultant cured products have high hydrolytic and thermal stability. It is usually near about two. We have found that in case of chlorendic acid based polyesters optimum molar ratio of styrene to unsaturation in polyesters was 2·1 to give maximum thermal stability, high self extinguishing property and maximum red heat resistance as can be judged from the properties of polyester No. 3 (Table 1, 3 & 4). This was further confirmed by chemical resistance test which gave minimum loss or gain in weight (Table 5) in various solvents acids and alkalies in the case of Polyester No. 3. This minimum loss in weight in chemicals is attributed to the least possibility of solvation of polymer due to maximum possible net work structure [17]. From red heat resistance point of view the above resin was better than even commercial resin ATLAC (Table 4).

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*Atlac is the name of a commercial resin manufactured by Atlas Chemical Industries.

TABLE 5

CHEMICAL RESISTANCE OF HET ISOPHTHALATE POLYESTERS MENTIONED IN TABLE NO. 1

Chemicals	% loss or gain in weight after 68 hours				% loss or gain in weight after 116 hrs				Remarks
	Polyester Nos.				Polyester Nos.				
	1	2	3	4	1	2	3	4	
Ortho phosphoric acid	+0·26	+0·135	+0·09	—0·175	+1·08	+0·241	+0·2	—0·175	Polyester No. 1 got damaged; other were fairly good.
Xylene	+4·6	+3·58	—0·2	+8·5	+[illegible]·2	+4·5	—0·4	+7·0	Polyester No. 3 is not damaged; fibres were visible in others.
Dioxane	—9·2	+1·1	—0·02	—0·156	—11·2	+2·34	—0·04	+4·95	All were damaged;. fibres were visible
Chloroform	—0·92	+2·85	+7·0	—3·8	—3·0	+4·6	+9·0	—8·15	—do—
Ethylene dichloride	—4·6	—3·02	+2·5	—2·58	—5·1	—6·2	+5·0	—2·63	All were damaged; fibres were visible.
Carbon tetra-chloride	7·3	+0·0815	—0·02	—4·65	9·5	+0·345	—0·04	+4·52	No change in physical appearance.
1% sodium hydroxide	—6·97	+0·62	—0·01	0·46	—6·67	+0·82	—0·01	—0·685	Fibres visible in all except in No. 3 black in colour.
10% sodium chloride	+0·314	+0·406	+0·3	+0·22	+1·38	+0·625	+0·2	+0·212	All remained uneffected.
10% sodium hydroxide	—17·0	—3·95	—1·2	—2·33	—17·4	—5·3	—1·5	—3·365	All specimen turned black. Fibres visible.
10% hydrochloric acid	0·525	+0·862	+0·01	+0·328	0·7	+0·44	+0·2	+0·355	Satisfactory in physical appearance.
30% sulphuric acid	+1·036	+0·61	+0·313	+0·368	+1·148	+0·63	+0·2	+0·79	No change in physical appearance.
3% sulphuric acid	+0·82	+0·55	+0·10	+0·446	+0·02	+0·70	+0·02	+0·51	No marked change in appearance.
Soluble phenol	+41·5	+23	+8·0	+19·9	+54	+25	+10·4	+10	Brown in colour. Swelled fibres visible.
Alcohol (95%)	+4·47	+2·48	—	+1·81	+3·56	+3·6	0·03	+1·89	No change in physical appearance.
Alcohol 50%	+5·7	+1·48	—0·01	+0·595	+5·35	+1·6	—0·03	+0·78	—do—
Distilled water	+0·366	+0·61	+0·03	+0·180	+2·0	+0·84	+0·08	+0·306	—do—

The high loss in weight of polyester No. 1 & 2 of Table 1 (9·5% and 10·5%) after aging at 260°C for 5 hrs. (Table 2) may be due to less cross linking because of insufficient amount of styrene and low chlorine content compared to polyester No. 3. This is further supported by the poorer chemical resistance (Table 5), red heat resistance (Table 4), and self extinguishing property (Table 3) of polyester No. 1 & 2 than polyester No. 3.

However in resin No. 4 (Table 1) inspite of higher chlorine content, the high loss in weight (12·9 %) after aging at 260°C for 5 hrs. may be attributed to homopolymer of styrene[18] in the cured resin as the styrene was more than optimum amount required for complete cross linking. The homopolymer of styrene is more susceptible to degradation[19] at high temperature than cross linked polyester. In this case as well, the poor chemical resistance (Table 5) and self extinguishing property (Table 3) show further the possibility of presence of polystyrene in this cured product.

High loss in weight (12·5 %) and distortion in the resin No. 6, which is a general purpose unsaturated phthalate polyester and low loss in weight (7·5 %) in resin No. 5 which is unsaturated isophthalate polyester, can be explained according to studies of Bender *et al* [20]. Bender mentions that phthalate polyester degrades easily to give volatile phthalic anhydride at high temperature whereas isophthalate polyester does not do so. The effect is due to vicinal carboxylic groups. On these very lines the self extinguishing property of resin No. 5 over inflammable nature (Table 3) of resin 6 is also justified.

CONCLUSION

On the basis of results discussed above, it was noted that apart from the incorporation of highly chlorinated chlorendic acid, high cross linking density, absence of components likely to form discrete molecules on heating like phthalic anhydride and absence of homopolymer like polystyrene play a vital role in imparting thermal stability and flame resistance to the polyester. Further work is in progress to compile extensive data to verify the above correlation of thermal stability of polyester with halogen content by means of differential thermal analysis and measurement of dielectric properties and then to correlate structures against properties of polyesters.

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