

Endgroup Modification of Unsaturated Polyesters. Effect on Chemical Resistance

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Synopsis

Endgroups of unsaturated polyesters formulated with mole ratios of 2/1/3 and 1/1/2 isophthalic acid/maleic anhydride/propylene glycol were modified. Carboxylic acid content was effectively reduced by esterification with alcohols or epoxides, amidation with phenyl isocyanate, or neutralization with amines. Hydroxyl content was reduced by esterification with acids or anhydrides and urethane formation with phenyl isocyanate. Chemical resistance was determined by measuring the decrease in flexural strength and modulus with exposure to 10% solutions of sodium hydroxide and sulfuric acid at 82°C. A 2-week test using the medium chemical-resistant 2/1/3 polyester indicated that any modification which decreased the carboxylic acid content improved chemical resistance. Modifications which increased or decreased the hydroxyl content had no significant effect in the 2-week tests; however, decrease of hydroxyl content appeared important in 6-month exposure tests. The 1/1/2 resins which have high initial chemical resistance had poorer chemical resistance after endgroup modification than the unmodified 1/1/2 resin, with the exception of the phenyl isocyanate-modified product which was equal to the unmodified resin. Water (0.8%) and xylene (0.1%) had no effect on chemical resistance. However, larger amounts of residual solvent were disadvantageous.

INTRODUCTION

There has been considerable interest in recent years in polymers for applications requiring corrosion resistance.¹ Unsaturated polyesters, because of their low cost, versatility, and ease of application, are widely used for this purpose.¹⁻³ Polyesters manufactured specifically for corrosion resistance are usually formulated with 2,2-bis[*p*-(2-hydroxy-*n*-propoxy)-phenyl]propane (Dow-565),^{2,7} 2,2-bis(4-hydroxycyclohexyl)propane (hydrogenated Bisphenol A),⁸ or isophthalic acid.^{3,6}

There are several approaches one can take to modify polyesters for improved chemical resistance. For example, one can vary the crosslinking monomer,⁹ glycol,⁹ or dibasic acid¹⁰ to increase the hydrophobic character of the resin or increase the steric hindrance about the ester linkages. Alternatively, one can decrease the number of ester groups per unit chain length as in the modified bisphenol type.^{2,7} This paper is concerned with the effect on resistance to acid and base of increasing the hydrophobic character of the endgroups of isophthalic acid-type polyesters. Methods used may be

summarized as follows: (1) esterification of carboxyl and hydroxyl groups with alcohol and acid or anhydride, respectively; (2) reaction of carboxyl and hydroxyl groups with phenyl isocyanate to give amide and urethane endgroups, respectively; (3) reaction of carboxyl and hydroxyl groups with epoxide to give hydroxyester and hydroxyether endgroups, respectively; (4) neutralization of carboxyl groups with amine.

Initially, our approach was to modify the endgroups of a resin having relatively medium chemical resistance so that improvements would show up in a rapid screening test. For this purpose we chose a resin formulated with a mole ratio of 2/1/3 isophthalic acid/maleic anhydride/propylene glycol. Best modifications were then applied to the more chemically resistant 1/1/2 isophthalic acid/maleic anhydride/propylene glycol resin for long-range testing. In addition, some of the 2/1/3 resins were included in the long-range test. Major emphasis was placed on reducing the carboxyl content of the polyesters since, as shown below, carboxyl groups appeared to affect chemical resistance to a greater extent than did the hydroxyl groups.

EXPERIMENTAL

Polyesters for Modification

The 2/1/3 and 1/1/2 isophthalic/maleic/propylene glycol polyesters were prepared on a pilot-plant scale by the two-step process.¹¹ For the sake of uniformity, all modifications were run on these two control batches of resin. The former was used for screening out the best modifications.

For this work, we have reported the endgroup concentrations as milliequivalents of carboxyl or hydroxyl per 1000 g. of resin solids rather than as the more conventional acid number or hydroxyl number. The 2/1/3 resin had 211 and 265 meq. of carboxyl and hydroxyl per 1000 g., respectively; the 1/1/2 resin had 241 and 263 meq., respectively. Acid number and hydroxyl number are obtained by multiplying these values by 0.0561.

Carboxyl content was determined in the conventional way by dissolving a weighed sample of resin in a 3:1 toluene-isopropyl alcohol solution and titrating to a phenolphthalein endpoint with methanolic potassium hydroxide. Hydroxyl content was determined by a method analogous to that reported¹² for polyether alcohols by acetylating the hydroxyl groups of a 7-g. sample (containing about 0.3 meq. of hydroxyl groups/g. of resin) dissolved in 5 ml. of ethyl acetate with 5 ml. of a solution of acetic anhydride (2*M*) and *p*-toluenesulfonic acid (0.3*M*) in ethyl acetate (reaction time, 15 min. at 50°C.), hydrolyzing the excess acetic anhydride, and back-titrating to a cresyl red-thymol blue endpoint with methanolic potassium hydroxide. If the polyester is colored, the first color change is the endpoint. In order to correct for carboxyl groups, a solution of the polyester in ethyl acetate mixed with hydrolysis reagent is titrated with 0.1*N* base. Titration of the acetylating agent is very accurate, and the overall experi-

mental error is $\pm 3\%$. With decreasing hydroxyl content, more polyester, more solvent, and longer reaction times were used.

Modifications were usually run on 1000-g. batches of molten resin solids or resin solutions in 2-liter, four-necked flasks equipped with stirrer, condenser, nitrogen inlet, and thermometer. Reaction times are shown in the accompanying tables. All modifiers were obtained commercially and used without further purification.

Esterification of Endgroups

Hydroxyl groups of the 2/1/3 resin were esterified by reacting resin solids with an equivalent amount of lauric acid (based on hydroxyl) at 210°C. or by reacting a xylene solution of resin with 20% excess (on hydroxyl) acetic anhydride at 138°C. In the latter reaction, excess acetic anhydride and acetic acid were removed by azeotroping with *n*-octane and xylene, respectively, followed by sparging with nitrogen to remove hydrocarbon. In the former reaction, small amounts of xylene were added, and water of esterification was azeotroped out through a Dean-Stark trap. Solvent was always removed at the end of the reaction by blowing with nitrogen (2 hr. at 30 l./hr. at 200–210°C.).

Hydroxyl groups were also esterified with acrylic anhydride to form an unsaturated endgroup that would copolymerize with styrene on curing. This was accomplished by using large amounts of inhibitor to avoid premature gelation.

Carboxyl groups of the 2/1/3 resin were esterified with equivalent amounts (on carboxyl) of benzyl alcohol or 1,4-dimethylolcyclohexane at 208–226°C., xylene being used to azeotrope out water. For long-range testing, the carboxyl groups of the 1/1/2 resin were esterified with a large excess of *n*-butyl alcohol at 210°C. This procedure was lengthy because the alcohol modifier exchanged with the ester groups of the polyester chain, and transesterification with removal of butyl alcohol was necessary to build up the original viscosity.

Modification with Phenyl Isocyanate

The 2/1/3 resin in xylene solution was first dried by azeotroping out water, then reacted with varying amounts of phenyl isocyanate at 143°C. The 1/1/2 resin solids were dried by sparging with nitrogen, then reacted with phenyl isocyanate at 182–188°C.

Modifications with Epoxide

Epoxide modifications were run on dried resin (azeotroping or sparging) at 149–188°C. in the presence of benzyldimethylamine or sodium carbonate (in the case of propylene oxide) catalyst. Saturated epoxides studied were cyclohexene oxide and propylene oxide; unsaturated epoxides were vinylcyclohexene oxide, glycidyl acrylate, and allyl glycidyl ether. Because of the tendency for these unsaturated epoxides to copolymerize with the maleic double bond, initial products for screening of chemical resistance were heav-

ily inhibited. Later processing studies to prepare products for long-range testing showed that very high inhibitor levels were unnecessary. No inhibitor at all was used with the glycidyl acrylate modification of the 1/1/2 resin.

In the presence of the amine or carbonate catalysts, epoxides reacted quite selectively with carboxyl groups, as shown by measurements of epoxide uptake, acid number decrease, and unreacted epoxide remaining in the resin. Reactions were generally rapid; however, in the case of propylene oxide, that modifier's low solubility at the reaction temperature caused somewhat longer reaction times. In addition, the rapid reflux of the propylene oxide (a Dry Ice condenser was used for this modification) caused cooling and thickening at the resin surface, giving rather unsatisfactory stirring.

Neutralization with Amine

Neutralization of carboxyl groups with amine was the simplest modification, requiring only dropwise addition of an equivalent amount of amine based on carboxyl to a stirred styrene solution of polyester at room temperature. A variety of amines was screened for effect on chemical resistance, including unsaturated amines for copolymerization with styrene and tertiary amines to provide steric blocking for the endgroup.

Analysis of Residual Modifier, Solvent, and Water

All analyses were done by gas chromatography; the following columns were used: (A) 12-ft. \times 0.25-in. O.D., GE Silicone SF-96 on Fluoropak; (B) 7-ft. \times 0.25-in. O.D., mixture of 60 parts of 13% Carbowax 400 on Fluoropak and 40 parts of 7% GE Silicone SF-96 on Fluoropak.

Trace amounts of xylene and benzene were determined on column A at 140°C. with a helium flow rate of 42 ml./min. by injecting acetophenone solutions of the resin (30–40% resin). Retention times were as follows: water, 1.3 min.; benzene, 2.7 min.; xylene, 5.6 min.; phenyl isocyanate, 7.5 min.; acetophenone, 13.0–14.0 min. With acetophenone as internal standard, solvent analyses were accurate to $\pm 0.05\%$ of the true value.

Impurity peaks in the acetophenone interfered with water analyses on column A. More accurate determinations of water ($\pm 0.03\%$ absolute) were obtained on column B at 150°C., and a helium flow rate of 16 ml./min. by injecting styrene solutions of polyester and using styrene as internal standard. Retention times were as follows: benzene, 6.1 min.; water, 7.6 min.; xylene, 11.0 min.; styrene, 17.2 min.

Modifiers were analyzed in similar fashion by use of both columns and various solvents. For example, propylene oxide was analyzed on column B in acetone solvent; allyl glycidyl ether was analyzed on column A in acetophenone solvent.

Product Testing

All physical testing of polyesters was done with $1/8$ -in. clear castings according to standard ASTM methods.¹³ Styrene solutions were inhibited

with 250 ppm *tert*-butylcatechol prior to preparation of castings. Castings were cured with 1% benzoyl peroxide, 0.55% methyl ethyl ketone peroxide, and 0.15% cobalt naphthenate (6% Co) for 4 hr. at 38°C. and 1 hr. each at 60, 80, and 135°C. Some of the amine-modified resins were catalyzed with 1% cumene hydroperoxide and 0.16% cobalt naphthenate to prolong the gel time and facilitate preparation of bubble-free castings, because in some cases the amine promoted the decomposition of benzoyl peroxide.

Chemical resistance was determined by immersing test specimens in 10% solutions of sodium hydroxide and sulfuric acid at 82°C. for appropriate time intervals, then measuring the decrease in flexural strength and modulus from the initial values. For screening purposes, samples were immersed for 2 weeks. In the long-range test, samples were tested after immersion times of 1 month, 3 months, and 6 months.

RESULTS AND DISCUSSION

Two Weeks' Exposure

In order to study the effect of endgroups on chemical resistance, a 2/1/3 isophthalic/maleic/propylene glycol polyester was chosen as control resin. Clear castings of this polyester showed an average (of five separately cured samples) of 64 and 77% retention of initial flexural strength after immersion in 10% sodium hydroxide and 10% sulfuric acid, respectively, for 2 weeks at 82°C. Thus, improvements achieved by modifying the carboxyl and hydroxyl groups could be detected in the 2-week screening test, even though the experimental error ($\pm 7\%$) was large.

For screening purposes, the improvement of product properties was emphasized over a study of process variables, hence large amounts of inhibitor were often added to prevent premature gelation. These had no apparent effect on chemical resistance, however, and later products prepared for long-range testing contained minimal amounts of inhibitor. In addition to endgroup modification, the effect of residual water and solvent was also studied to ensure that poor resistance was not caused by these variables.

Table I lists control runs (products 1-4) and those modifications which caused little improvement in chemical resistance in the 2-week test. Tables II and III describe product properties and processing details of modified resins having improved resistance to acid and base in the 2-week test. Amine modifications are excluded from Table III, since this only involved adding amine to styrene solutions of polyester at room temperature.

Effect of Residual Solvent, Water, and Modifier

Product 4, Table I, shows that 0.75% xylene in the resin decreased the resistance to acid and base. Xylene or other fairly volatile solvents could be removed to 0.1% by sparging a 1000-g. batch of resin for about 2 hr. at 200°C. at a nitrogen flow rate of 30 l./hr. These traces of solvent did not affect chemical resistance (Table II), and all modifications using solvent were similarly treated.

TABLE I
Modified 2/1/3 Isophthalic/Maleic Propylene Glycol Polyesters with Partially Improved Chemical Resistance after 2 Weeks' Exposure

No.	Modification	Endgroups, meq./1000 g.		Solvent, % ^a	H ₂ O % ^a	Resid- ual modi- fier, % ^a	Im- pact strength ft.-lb./ temp., °C. ^c	Heat distor- tion in. ^b	Viscosity, poise ^d	Flexural strength ^e		Flexural modulus ^e			
		COOH	OH							Initial, Retention, % ^f	Initial, Retention, % ^f				
1	Unmodified (control run)	211	265	0	0.37	0	4.1	87	15.3	21	77	64	5.5	98	91
2	Dried resin (control run)	211	265	0	0.09	0	5.0	86	15.3	22	82	55	5.5	100	91
3	Added water (control run)	211	265	0	0.77	0	3.5	87	15.3	20	83	63	5.4	102	93
4	Added xylene (control run)	211	265	0.75	0.40	0	3.8	86	15.3	20	62	54	5.7	80	85
5	Lauric acid	260	86	0.02	0.25	—	4.2	80	16.5	19	59	77	5.5	84	99
6	Acetic anhydride	208	16	0	0.30	0	4.4	88	16.5	20	61	74	5.7	94	88
7	Acrylic anhydride	146	115	0.10	—	0	4.2	90	148	20	90	62	5.5	99	94
8	Glycidyl acrylate	28	448 ^g	0	—	0.7	1.8	88	46	17	82	78	5.0	103	100
9	<i>n</i> -Propylamine	0	265	0	0.4	—	3.5	91	14.1	15	87	73	5.4	100	96
10	Diethylamine	0	265	0	0.4	—	3.4	89	18.9	17	88	47	5.5	95	85
11	Pyridine	0	265	0	0.4	—	3.4	87	15.25	19	84	58	5.3	77	85
12	Triallylamine	0	265	0	0.4	—	3.5	91	15.25	19	84	58	5.4	94	94

^a Based on resin solids.

^b Izod unnotched, ASTM D256-56; average of 10 samples.

^c ASTM D648-56.

^d 60:40 Polyester-xylene solution; determined by comparison with Gardner-Holdt standards.

^e ASTM D790-59T; average of 7 samples.

^f Two weeks' exposure to 10% solutions at 82°C.

^g Calculated value, assuming each COOH is converted to OH.

The control polyester was found to contain about 0.4% water. It was therefore of interest whether water would have an effect on chemical resistance. Product 2, Table I, containing 0.09% water, was obtained by preparing a 50:50 styrene-polyester solution and azeotroping off the water on a rotary evaporator at reduced pressure until the styrene content was 40%. This product was compared with control resin (product 1) containing 0.37% water and the control resin containing 0.4% added water (product 3). Within experimental error, these three products showed no difference in chemical resistance. The impact strength of the resins appeared to decrease with increasing amounts of water, however; this has since been confirmed with other polyesters.¹⁴

Residual amounts of modifier up to 0.3% had no apparent negative effect on chemical resistance during the 2-week test, although it is possible that improvements caused by endgroup modification could mask out such an effect.

Esterification

Esterification of carboxyl endgroups with benzyl alcohol or 1,4-dimethylolcyclohexane (products 13 and 15, Table II) improved the base resistance of the polyester significantly. Esterification of the hydroxyl groups with lauric acid or acetic anhydride (products 5 and 6, Table I) improved base resistance only slightly but lowered the acid resistance. When, however, the acetic anhydride-modified polyester (product 6) was further esterified with benzyl alcohol, the twice-modified polyester (product 14, Table II) showed improved acid and base resistance. Carboxyl groups have, therefore, a greater effect on resistance to acid and base than hydroxyl groups, and decreasing the carboxyl content increases chemical resistance. A serious disadvantage to esterification with alcohols is the long reaction time (up to 16¹/₂ hr.).

Hydroxyl groups were esterified with acrylic anhydride to introduce an unsaturated endgroup that would be copolymerizable with styrene and hence sterically blocked by the crosslinking reaction. This modification was difficult, because premature copolymerization of the acrylic double bonds with the maleic double bonds of the polyester occurred. Initial gelation problems were overcome by using large amounts of strong inhibitors such as copper and diphenylquinone.¹⁵ The products were very viscous but showed improved resistance to acid (product 7, Table I). Unsaturated endgroups were introduced more effectively with simultaneous removal of carboxyl groups by using epoxides and amines (see below).

Phenyl Isocyanate

Conversion of almost all carboxyl groups to amide groups and of about 70% of the hydroxyl groups to urethane groups resulted in a product (product 20, Table II) which had essentially quantitative retention of flexural properties after 2 weeks' exposure to acid and base. If smaller amounts of

TABLE II
Modified 2/1/3 Isophthalic/Maleic/Propylene Glycol Polyesters with Improved Chemical Resistance after 2 Weeks' Exposure

No.	Modification	Endgroups, meq./1000 g.		Solvent, % ^a	H ₂ O, % ^a	Residual Modifier % ^a	Im- pact strength, ft.-lb./ in. ^b	Heat distortion temp., °C. ^c	Viscosity, poise ^d	Flexural strength ^e		Flexural modulus			
		COOH	OH							Initial Retention, % ^f	Initial Retention, % ^f	Initial Retention, % ^f	Initial Retention, % ^f		
1	Unmodified (control run)	211	265	0	0.37	0	4.1	87	15.3	21	77	64	5.5	98	91
13	Benzyl alcohol	69	292	0.06	0.20	0	4.4	89	15.3	21	67	83	5.7	96	98
14	Benzyl alcohol on no. 6	89	130	<0.10	—	0	3.2	84	11.8	18	87	96	5.6	98	98
15	1,4-Dimethylol-cyclohexane	49	416	0.01	0.30	0	4.8	86	27	18	104	100	5.6	101	97
16	Propylene oxide	47	429 ^g	0	0	0.3	4.5	86	54	18	85	91	5.3	101	94
17	Cyclohexene oxide	8	468 ^g	0	0	<0.1	3.7	79	41	18	98	97	5.3	98	98
18	Vinylcyclohexene oxide	25	451 ^g	0	0	0.20	3.7	81	41	18	96	91	5.4	96	91
19	Allyl glycidyl ether	37	429 ^g	0	0	0.25	3.7	79	81	18	104	86	5.3	101	91
20	Phenyl isocyanate	6	84	0	0.40	0	2.4	72	27	16	95	99	5.2	100	100

21	Phenyl iso- cyanate	41	101	0.02	0.20	0	4.7	86	17.6	19	87	85	5.7	95	90
22	Phenyl iso- cyanate	108	146	0.17	0.20	0	4.3	87	22.7	20	79	88	5.6	100	94
23	Allylamine	0	265	0	0.4	—	3.4	88	6.27	17	90	90	5.2	92	85
24	Diallylamine	0	265	0	0.4	—	3.4	91	17.6	20	88	90	5.4	96	87
25	Triethylamine	0	265	0	0.4	—	3.9	92	—	17	88	100	5.4	94	82
26	<i>N,N</i> -Dimethyl- aniline	0	265	0	0.4	—	3.4	87	17.25	19	84	90	5.3	100	94

^a Based on resin solids.

^b Izod unnotched, ASTM D256-56; average of 10 samples.

^c ASTM D648-56.

^d 60:40 Polyester-xylene solution; determined by comparison with Gardner-Holdt standards.

^e ASTM D790-59T; average of 7 samples.

^f Two weeks' exposure to 10% solutions at 82°C.

^g Calculated value, assuming each COOH is converted to OH.

TABLE III
Processing of Polyesters Having Improved Chemical Resistance after 2 Weeks' Exposure

No.	Modification	Catalyst		Based on, moles	Modifier, moles/mole endgroup	Inhibitor and concn., ppm ^e	Time, hr.	Temp., °C.
		Type and concn., % ^a						
13	Benzyl alcohol	None		—	1 ^b	DPQ, 800	11 ¹ / ₂	225
14	Benzyl alcohol on no. 6	None		—	1 ^b	None	16 ¹ / ₂	210
15	1,4-Dimethylolcyclohexane	None		—	1 ^b	HQ, 500	15 ¹ / ₂	210
16	Propylene oxide	None		—	7 ^b	DPQ, 500	9 ¹ / ₄	176
17	Cyclohexene oxide	BDMA, 10		COOH + OH	1 ^c	DPQ, 500	2	160
18	Vinylcyclohexene oxide	BDMA, 10		COOH	1.2 ^b	DPQ, 1000 Cu, 300	1	149
19	Allyl glycidyl ether	BDMA, 10		COOH	1.2 ^b	DPQ, 1000 Cu, 300	1/2	160-182
20	Phenyl isocyanate	DMEA, 4		C ₆ H ₅ NCO	2 ^c	BQ, 500 DPQ, 300	24	143
21	Phenyl isocyanate	DaBCO, 4		C ₆ H ₅ NCO	1 ^c	—	13	143
22	Phenyl isocyanate	DaBCO, 5		C ₆ H ₅ NCO	1 ^d	—	8	143

^aBDMA = Benzyl dimethylamine, DaBCO = 1,4-diazabicyclo[2.2.2]octane, DMEA = dimethylethanolamine.

^bBased on COOH.

^cBased on COOH + OH.

^dBased on OH.

^eDPQ = Diphenylquinone, BQ = benzoquinone, HQ = hydroquinone, Cu = copper as copper naphthenate.

endgroups were converted, the products were less improved (products 21 and 22).

All modifications of the 2/1/3 resin for screening were run in xylene solution at reflux temperature. Resins were initially dried by azeotroping out water. Later modifications for long-range testing were run without solvent at higher temperatures and consequently much shorter reaction times.

Observations arising from this modification study are as follows.

(1) The following order of activity of catalysts was observed for reaction of carboxyl groups: *N,N*-dimethylethanolamine \geq 1,4-diazabicyclo-[2.2.2]-octane (Dabco) \gg di-*n*-butyltin dilaurate (Niax D-22).

(2) With dimethylethanolamine, the carboxyl groups reacted faster with phenyl isocyanate than the hydroxyl groups; with Dabco, both endgroups reacted with phenyl isocyanate at about the same rate.

(3) With no catalyst, the carboxyl groups did not react, while 40% of the hydroxyl groups reacted in 13 hr. at 82–160°C.

(4) When excess phenyl isocyanate based on total endgroups was used, the quality of the product was lowered, as shown by lower initial flexural and impact strengths. This may be due to the formation of dimers and polymers of phenyl isocyanate itself.

Epoxides

With the exception of glycidyl acrylate, epoxides improved the acid-base resistance of the polyesters (products 16–19, Table II). Since carboxyls react with epoxide to form hydroxyesters, this indicated again the importance of carboxyl groups over hydroxyl groups in influencing chemical resistance. Reactions of hydroxyl groups to form hydroxyethers occurred to some extent, but with base catalysts the reaction with carboxyl groups was more selective. This modification provided a rapid and convenient method of introducing both saturated and unsaturated endgroups while decreasing the acid number. Although one might expect products having copolymerizable endgroups to be most resistant, no difference was observed between saturated and unsaturated epoxides. Glycidyl acrylate (product 8, Table I) caused only a medium increase in base resistance; this was unexpected in view of the results obtained with other epoxides.

Other observations arising from epoxide modification are as follows.

(1) A larger excess of glycidyl acrylate (50% on carboxyl) was required to reduce the carboxyl content of the 1/1/2 resin than of the 2/1/3 resin (10% excess on carboxyl). Analysis of carboxyl content and residual epoxide indicated that about 42% of the glycidyl acrylate reacted with hydroxyl groups of the 1/1/2 resin while practically none reacted with hydroxyl groups of the 2/1/3 resin. This might arise from the proportionately large amount of maleic carboxyl having a relatively lower nucleophilicity for attack on epoxide carbon. An alternate possibility is that initial nucleophilic attack on epoxide carbon is via the amine catalyst, and a relatively more stable amine salt is formed with the resin having the higher maleic content.

Either possibility would increase the chance of competing nucleophilic attack by hydroxyl groups of the polyester.

(2) Only about 5% of the allyl glycidyl ether reacted with hydroxyl groups of the 1/1/2 resin, compared with about 42% for glycidyl acrylate. This may reflect the lower electronegativity of the allyl ether group of allyl glycidyl ether, making its epoxide carbons less susceptible to nucleophilic attack.

(3) With the allyl glycidyl ether modification, inhibitor was necessary to prevent the viscosity from increasing to an unmanageable level. Much of the viscosity increase appeared, however, to be independent of inhibitor level.

Amines

Neutralization of carboxyl groups with amine appeared to improve chemical resistance in some cases but not in others. No structural correlations with chemical resistance were evident. For example, allyl- and diallylamine (products 24 and 25, Table II) caused improvement, while triallylamine (product 12, Table I) had no effect within experimental error. In addition, the tertiary amines triethylamine and dimethylaniline (products 25 and 26, Table II) improved chemical resistance, while pyridine and triethylamine (products 11 and 12, Table I) did not.

Six Months' Exposure

The encouraging results obtained in the 2-week screening test prompted us to investigate chemical resistance of some low carboxyl number products over a 6-month period. Modifications of the 2/1/3 isophthalic/maleic/propylene glycol resin with phenyl isocyanate, allyl glycidyl ether, cyclohexene oxide, and allylamine were included. (These products were prepared and cured at a different time from those in the 2-week test; hence, their initial properties are slightly different.) The more chemically resistant 1/1/2 isophthalic/maleic/propylene glycol resin was modified with *n*-butyl alcohol, phenyl isocyanate, glycidyl acrylate, allyl glycidyl ether, propylene oxide, cyclohexene oxide, allylamine, and triethylamine for inclusion in the 6-month test. Initial properties of all products for long-range testing are shown in Table IV. Per cent water is not listed because, as shown in the screening test, it has no apparent effect on chemical resistance. Residual modifier was reduced to less than 0.5% in all cases. Modifications for the 6-month test differed from those for the 2-week test in the following manner.

(1) All processing was done on fused resin rather than in solvent (apart from amine modification).

(2) Inhibitor added during reaction was kept to a minimum. The allyl glycidyl ether resin used 100 ppm diphenylquinone and 10 ppm copper; the propylene oxide resin used 500 ppm diphenylquinone. Other products contained none. All products were inhibited with *tert*-butylcatechol before copolymerizing with styrene (see Experimental Section).

TABLE IV
Initial Properties of Endgroup-Modified Polyesters After 6 Months' Exposure

No.	Modification	Endgroups, meq./1000 g.		Viscosity, poise	Styrene, %	Flexural strength, psi × 10 ^{-3a}	Flexural modulus, psi × 10 ^{-5a}	Impact strength, ft.-lb./in. ^b	Heat distortion temp., °C. ^c
		COOH	OH						
2/1/3 Resin									
27	Unmodified (control run)	211	265	15.25	40	20	5.2	4.9	92
28	Phenyl isocyanate	10	136	15.25	40	18	5.2	2.9	86
29	Allyl glycidyl ether	11	465 ^d	20.2	40	20	5.3	4.4	86
30	Cyclohexene oxide	30	446 ^d	12.9	40	21	5.4	4.5	86
31	Allylamine	0	265	6.27	40	17	5.2	3.4	88
1/1/2 Resin									
32	Unmodified (control run)	241	263	20.2	40	17	4.9	2.9	114
33	<i>n</i> -Butyl alcohol	9	263	22.7	40	17	5.3	1.5	78
34	Phenyl isocyanate	59	66	38.7	40	16	5.5	2.3	107
35	Glycidyl acrylate	9	495 ^d	17.6	40	19	5.5	1.9	103
36	Allyl glycidyl ether	50	454 ^d	27	40	19	5.6	2.0	104
36A	Allyl glycidyl ether	50	454 ^d	5.25	50	18	5.6	2.3	102
37	Propylene oxide	7	497 ^d	39	40	16	5.3	1.7	101
37A	Propylene oxide	7	497 ^d	5.0	50	16	5.4	2.7	107
38	Cyclohexene oxide	2	502 ^d	20.2	40	16	5.6	2.3	103
39	Allylamine	0	263	36.2	40	17	5.2	—	—
40	Triethylamine	0	263	—	40	17	5.5	—	—

^a ASTM 790-59T.

^b Izod unnotched, ASTM D256-56.

^c ASTM D648-56.

^d Calculated value, assuming each COOH is converted to OH.

(3) Propylene oxide modification was catalyzed with sodium carbonate according to a previously described method.¹⁶

(4) Products of allyl glycidyl ether and propylene oxide modification of the 1/1/2 resin were tested at both 40% and 50% styrene. This was to check some of the higher viscosity products at a more workable viscosity.

Products were tested after immersion times of 1 month, 3 months, and 6 months.

2/1/3 Resin

Figures 1 and 2 show the drop in flexural strength of the 2/1/3 resins during 6 months of exposure to base and acid. In base (Fig. 1), the improve-

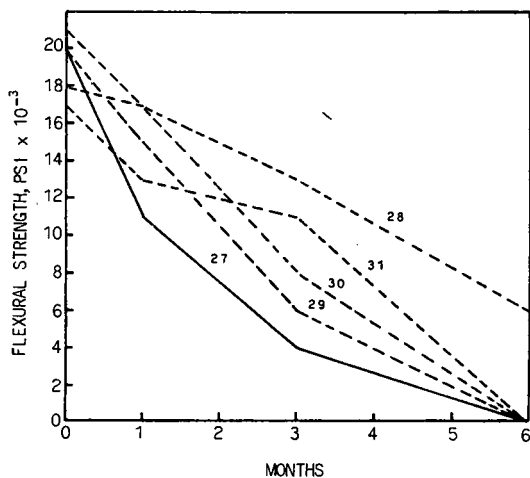


Fig. 1. Flexural strength of 2/1/3 resins immersed in 10% NaOH: (27) unmodified; (28) phenyl isocyanate; (29) allyl glycidyl ether; (30) cyclohexene oxide; (31) allylamine.

ment in chemical resistance can be clearly seen, even though all but the phenyl isocyanate product failed at 6 months. In acid (Fig. 2), the allylamine product deteriorated more rapidly initially but leveled off with the control resin at 6 months. The other modifications, particularly phenyl isocyanate, gave superior products at 6 months, although 1- and 3-month data are less clear-cut. It is interesting that best overall improvement was obtained with phenyl isocyanate, the only modification that reduced both carboxyl and hydroxyl number. This suggests that for long-term exposure, hydroxyl groups are also important.

1/1/2 Resin

Figures 3-6 show the drop in flexural strength of the 1/1/2 resins during 6 months of exposure to acid and base. Results here were unexpected. Figures 3 and 4 show that *n*-butyl alcohol and amines had a detrimental effect on chemical resistance. Phenyl isocyanate was equal to the control resin at

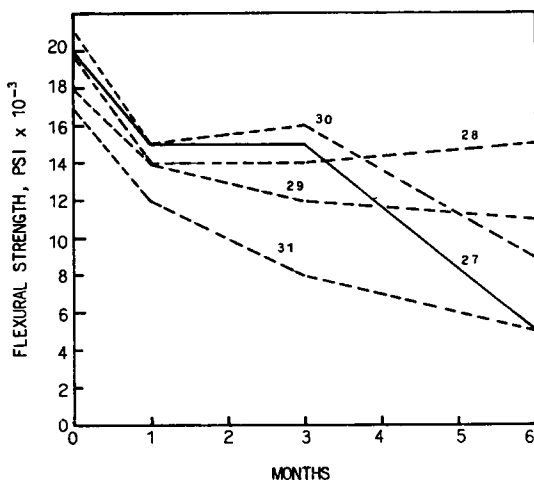


Fig. 2. Flexural strength of 2/1/3 resins immersed in 10% H_2SO_4 : (27) unmodified; (28) phenyl isocyanate; (29) allyl glycidyl ether; (30) cyclohexene oxide; (31) allylamine.

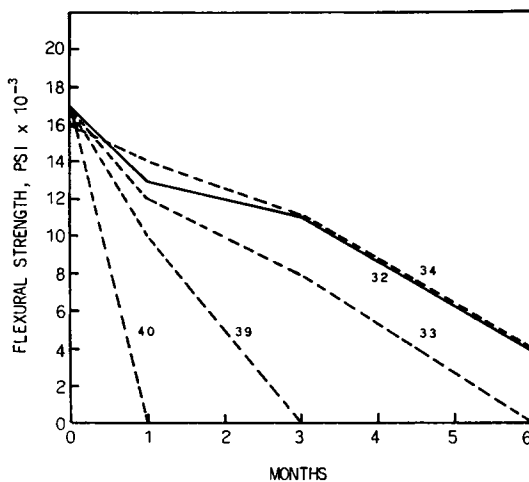


Fig. 3. Flexural strength of isocyanate-, alcohol-, and amine-modified 1/1/2 resins in 10% $NaOH$: (32) unmodified (40% styrene); (33) *n*-butyl alcohol; (34) phenyl isocyanate; (39) allylamine; (40) triethylamine.

equal styrene levels. Epoxide modification (Figs. 5 and 6) also lowered the chemical resistance of the 1/1/2 resin. Only the propylene oxide-modified product containing 50% styrene did not fail in 6 months. In cases where styrene level was varied, higher styrene contents gave better chemical resistance, although the allyl glycidyl ether product failed in 6 months at both styrene levels. Effect of styrene concentration was not investigated any further, since Leitheiser and Dalluge⁴ and Schmidt¹⁷ had already reported on this variable, and our results were in agreement with their conclusions.

Per cent retention of flexural modulus of all products in the long-range test after 6 months' immersion are summarized in Figure 7. Modulus data can be misleading, because products close to failure may show high modulus values because of embrittlement during exposure to the corrosive chemicals.

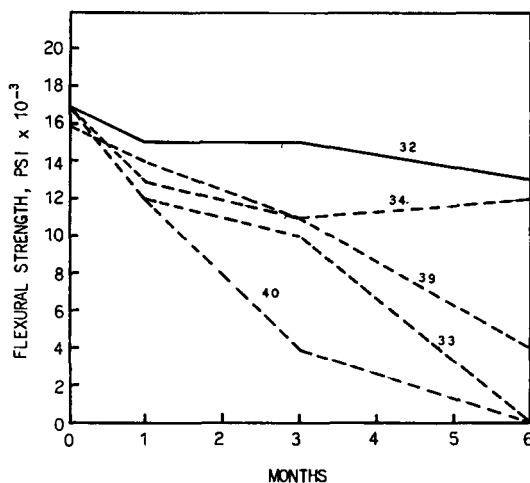


Fig. 4. Flexural strength of isocyanate-, alcohol-, and amine-modified 1/1/2 resins in 10% H_2SO_4 : (32) unmodified (40% styrene); (33) *n*-butyl alcohol; (34) phenyl isocyanate; (39) allylamine; (40) triethylamine.

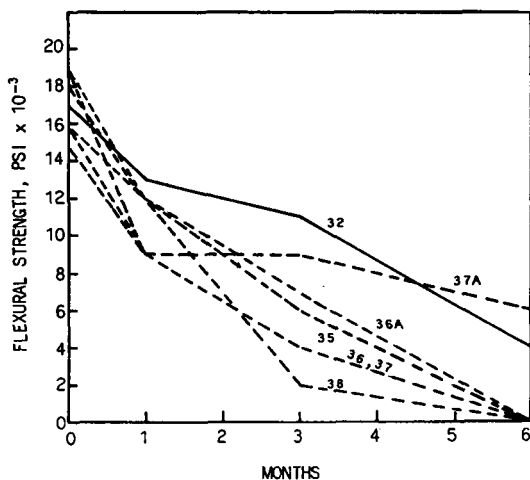


Fig. 5. Flexural strength of epoxide-modified 1/1/2 resins in 10% $NaOH$: (32) unmodified (40% styrene); (35) glycidyl acrylate; (36) allyl glycidyl ether (40% styrene); (36A) allyl glycidyl ether (50% styrene); (37) propylene oxide (40% styrene); (37A) propylene oxide (50% styrene); (38) cyclohexene oxide.

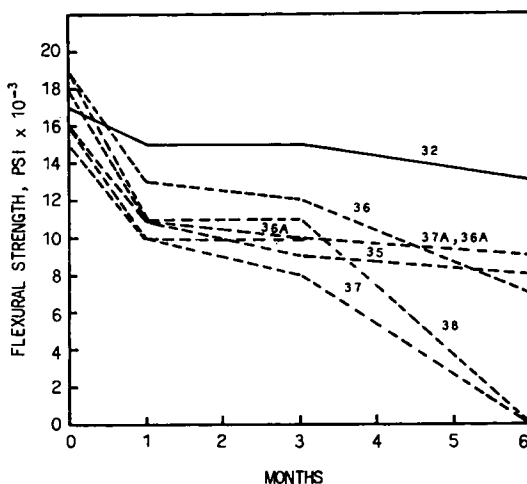


Fig. 6. Flexural strength of epoxide-modified 1/1/2 resins in 10% H_2SO_4 : (32) unmodified (40% styrene); (35) glycidyl acrylate; (36) allyl glycidyl ether (40% styrene); (38A) allyl glycidyl ether (50% styrene); (37) propylene oxide (40% styrene); (37A) propylene oxide (50% styrene); (38) cyclohexene oxide.

CONCLUSIONS

Endgroups of polyesters were modified in fusion or solvent reactions with phenyl isocyanate, epoxides, alcohols, acids, anhydrides, and amines. Premature gelation was prevented by inhibitors, and rates of reaction and selectivity for hydroxyl or carboxyl groups were controlled by the type and amount of catalysts.

The fact that endgroup modification can, in principle, improve the chemical resistance of a polyester to 10% solutions of sodium hydroxide and sulfuric acid at 82°C. was shown by testing a modified medium resistant 2/1/3 isophthalic acid/maleic anhydride/propylene glycol polyester for 2 weeks. In this test, improvements in chemical resistance were observed with any modification that decreased the carboxyl content of the polyester; decreasing or increasing the hydroxyl content had no significant effect. Extended exposure of these resins showed that a modified resin deteriorated (lost flexural strength) at a lower rate than the unmodified resin and indicated that decreasing hydroxyl groups is also important for long-range chemical resistance. When testing was continued for 6 months, the phenyl isocyanate-modified polyester maintained the improvement, while other resins failed together with the unmodified resin. A polyester which has very good initial chemical resistance (1/1/2 isophthalic acid/maleic anhydride/propylene glycol) was not improved by endgroup modification. The chemical resistance was unchanged when modified with phenyl isocyanate and was lowered with other reagents. These results suggest that chemical resistance is markedly dependent on formulation and that modifications which improve one type of polyester may not necessarily improve another. Re-

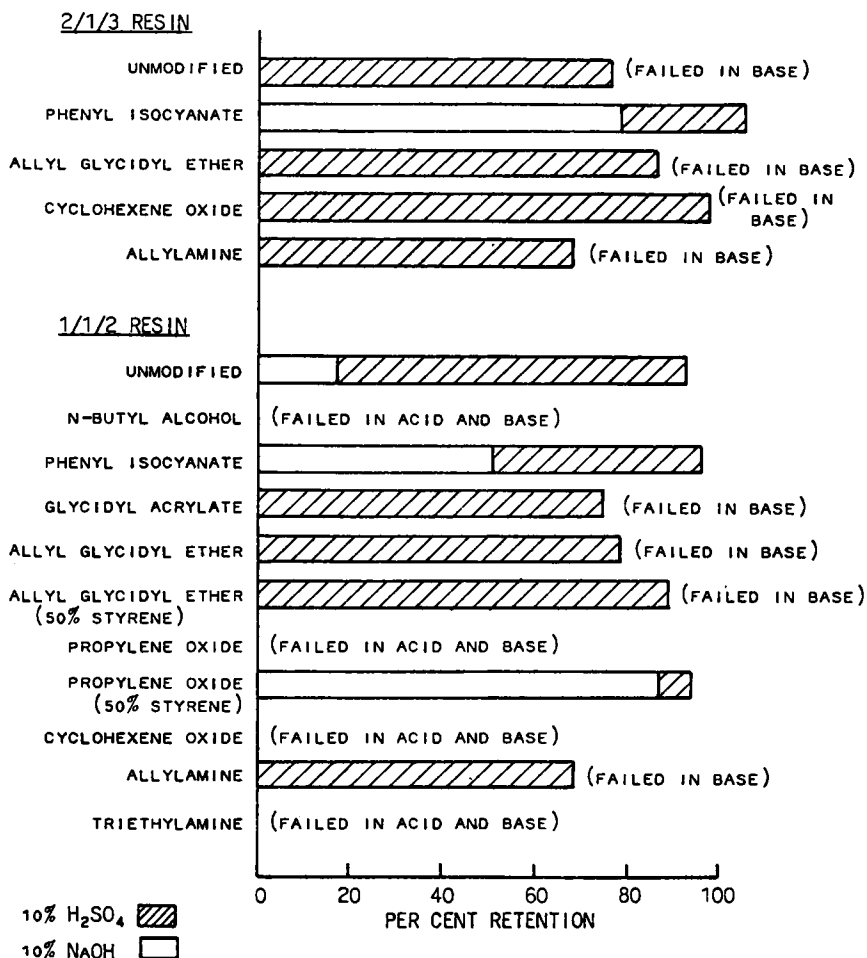


Fig. 7. Flexural modulus retention of endgroup-modified resins after 6 months' immersion in acid and base.

ducing both carboxyl and hydroxyl content of a polyester (as with phenyl isocyanate) improves chemical resistance, but it appears to require a resin of low intrinsic resistance for the effect to be noticeable in a test involving high temperature exposure. Water in the amount of 0.8% was found to have no effect on chemical resistance. However, xylene in about the same amount was disadvantageous. Small amounts (0.1%) of solvent had no effect.

Reasons for the difference in behavior between two such similar polyester formulations are not obvious. One explanation may be that decreasing the hydrophilic character of the endgroups causes an initial improvement in resistance to aqueous acid and base that is masked out by the superior intrinsic chemical resistance of the 1/1/2 resin. This superior initial resistance is to be expected since the cured resin is more highly crosslinked. The initial

improvement might then be followed by some effect resulting from certain endgroup modifications (such as epoxide) which catalyzes further hydrolysis of ester groups in the polyester chains, causing more rapid deterioration of the modified resin with time. Whether or not this phenomenon is caused by the modification catalyst, by the introduction of ether groups by reaction with epoxide, or some other variable, is difficult to determine. It is also not clear why such a catalytic effect should be more pronounced with the 1/1/2 resin.

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Résumé

On a modifié les groupements terminaux de polyesters insaturés possédant des rapports molaires 2/1/3 et 1/1/2 en acide isophtalique/anhydride maléique/propylène glycol. On a pu réduire la teneur en acide carboxylique, par estérification avec des alcools ou

avec des époxydes, par amidification avec l'isocyanate de phényle, ou par neutralisation avec des amines. La teneur en hydroxyle est réduite par estérification avec des acides ou des anhydrides, et par formation d'uréthane avec l'isocyanate de phényle. La résistance chimique est déterminée en mesurant la diminution de la force à la flexion et du module après un traitement avec des solutions à 10% de soude caustique et d'acide sulphurique à 82°C. Un test de 2 semaines, sur le polyester à résistance chimique moyenne 2/1/3, indique que n'importe quelle modification qui diminue la teneur en acide carboxylique, améliore la résistance chimique. Les modifications qui diminuent ou augmentent la teneur en hydroxyle n'avaient pas d'effet marqué pendant le test de 2 semaines; cependant des changements importants apparaissent dans les tests de six mois. Les résines 1/1/2, qui possèdent une résistance chimique initiale élevée, possèdent une résistance chimique moins élevée après modification de leurs fonctions terminales que la résine 1/1/2 inchangée à l'exception du produit modifié avec l'isocyanate de phényle, qui possède les mêmes propriétés que la résine non modifiée. L'eau (0.8%) et le xylène (0.1%) n'avaient pas d'effet sur la résistance chimique. Cependant des quantités de solvant résiduel plus importantes sont désavantageuses.

Zusammenfassung

Die Endgruppen von ungesättigten Polyestern aus Ansätzen mit dem Molverhältnis 2/1/3 und 1/1/2 Isophthalsäure/Maleinsäureanhydrid/Propylenglykol wurden modifiziert. Der Gehalt an Karboxylgruppen konnte durch Veresterung mit Alkoholen und Epoxyden, durch Amidierung mit Phenylisocyanat oder durch Neutralisierung mit Aminen wirksam herabgesetzt werden. Der Hydroxylgruppengehalt wurde durch Veresterung mit Säuren oder Anhydriden und durch Urethanbildung mit Phenylisocyanat reduziert. Die chemische Beständigkeit wurde durch Messung der Abnahme der Biegefestigkeit und des Moduls bei der Einwirkung 10% iger Natriumhydroxyd- und Schwefelsäurelösungen bei 82°C bestimmt. Ein 2-Wochen-Test an dem 2/1/3-Polyester von mittlerer chemischer Beständigkeit zeigte, dass jede Modifizierung, welche zu einer Abnahme des Karboxylgruppengehaltes führt, die chemische Beständigkeit verbessert. Modifizierungen, welche zu einer Zunahme oder Abnahme des Hydroxylgruppengehaltes führten, hatten bei dem 2-Wochen-Test keinen bemerkenswerten Einfluss; sie scheinen jedoch für Tests mit 6-monatiger Einwirkung wichtig zu sein. Die 1/1/2-Harze, welche anfangs hohe chemische Beständigkeit besitzen, zeigten nach der Endgruppenmodifizierung eine geringere chemische Beständigkeit als das nicht modifizierte 1/1/2-Harz, mit der Ausnahme des phenylisocyanatmodifizierten Produkts, welches dem nicht modifizierten Harz gleichwertig war. Wasser (0,8%) und Xylol (0,1%) hatten keinen Einfluss auf die chemische Beständigkeit. Grössere Mengen an Lösungsmittelrückständen waren jedoch unvorteilhaft.

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