Degradation of crosslinked resins in water and electrolyte solutions

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In addition to chemical processes such as the hydrolysis of ester groups, there are physical processes contributing to the hygrothermal degradation of crosslinked polyester resins. This paper discusses the interaction between physical and chemical processes and reports short and long term observations on the degradation of several resins of various compositions during immersion in aqueous liquids. Initial swelling is accompanied by weight changes which are the result of (i) absorption of water (ii) leaching of non-bound substances and (iii) leaching of hydrolysis products. Leached substances are identified qualitatively by n.m.r. spectroscopy and, in some cases, semi-quantitatively by gas-liquid chromatography (g.l.c.). Osmotic disc cracks greatly accelerate the hydrolysis process and appear to be caused mainly by the presence of residual or added glycol in the resins. (These cracks were almost entirely absent from a vinyl ester resin). Scanning and high resolution transmission electron micrographs demonstrate the nature and extent of surface physical damage by water.

Keywords Polyester; hydrolysis; leaching; osmosis; microscopy; degradation

INTRODUCTION

The absorption of water by crosslinked epoxide and polyester resins is recognized to be important in many technical applications and has received widespread attention. Consideration has been given to the applicability of Fick's Law[1-6], the relationship between equilibrium water uptake and temperature[7], the leaching of non-bound substances from the network[8-9], swelling stresses[10], the effect of stress on diffusivity[11], cracking[12], mechanical[13-14] and electrical[15] property changes and the reversibility of the above changes on drying[15].

An important observation, with support from other sources, was made by Dewimille *et al.*[15], who noticed that thermally activated diffusion appears to predominate in epoxide resins at moderate (<65°C) temperatures, for short immersion times, but that beyond these limits, irreversible damage occurs. It seems probable that a similar generalization can be made for crosslinked unsaturated polyesters, though the temperature and time limitations vary with each resin. Polyester resins in hot water are known to undergo chemical scission of the ester groups, but the factors determining the rate of hydrolysis (other than temperature) have not been reported, nor has the relative importance of this process among other possible causes of degradation been assessed. Other potential degradative processes include osmotic cracking (which is well known, but its origin has never been precisely explained and its impact on hydrolysis rates apparently not considered) and leaching. There does not appear to be any detailed description of the nature of the leached substances, or their relative abundance in aqueous extracts in the literature.

The investigation was therefore intended to determine more precisely the physicochemical changes occurring in crosslinked polyesters during water immersion.

EXPERIMENTAL

The resins used are listed in *Table 1*. Resins numbered 1 to 5 were isophthalic resins, produced commercially using the formulations given. Typically, isophthalic acid and maleic anhydride were reacted with a few mole % excess of glycols over the nominal quantities, to counteract losses during condensation. Acid values and heat distortion temperatures were measured by standard techniques [B.S.3532, (1962) and B.S.2782, section 102G, (1970) respectively].

Resin 6 was an orthophthalic resin of analogous formulation to that of 1 and 2. It was prepared in-house by condensing the given molar proportions of reagents at 190°–200°C until the desired acid value was reached. Five mole % of excess glycol was used, to counteract condenser losses.

Resin 7 was a commercial vinyl ester resin[16], essentially a conventional epoxide prepolymer with terminal unsaturation for crosslinking with styrene. This resin did not contain the conventional hydrolysable phthalate ester groups (see *Table 1*, footnote).

Curing conditions are given in *Table 2*. The cast sheets were then machined to form specimens of the following kinds:

(a) for resins 2, 3, 4, 5: 25 mm × 25 mm × 3 mm
(b) for resins 1 and 6: 80 mm × 20 mm × 3.5 mm.

Samples were immersed in tubes of distilled water in thermostatted baths. Periodically they were removed, wiped with an absorbent cloth, weighed, measured with a travelling microscope and returned to the baths. Some

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Table 1 Resins used

Resin no.	Molar proportions PA	MA	IPA	PG	DEG	Acid value (mg)	Heat distortion temperature (°C) (B.S. 2782, 502G)	Styrene content (% w/w)
1	–	1	1	1	1	27	79	41
2	–	1	1	1	1	18	75	41
3	–	1	1	2	0	11	100	38
4	–	1	2	0	3	18	28	32
5	–	3	1	4	0	25	130	38
6	1	1	–	1	1	30	60	31
7			see below*			8	100	47

MA = maleic anhydride
IPA = isophthalic acid
PG = 1,2 propylene glycol
DEG = diethylene glycol
PA = phthalic anhydride

* Resin 7 was of general structure:

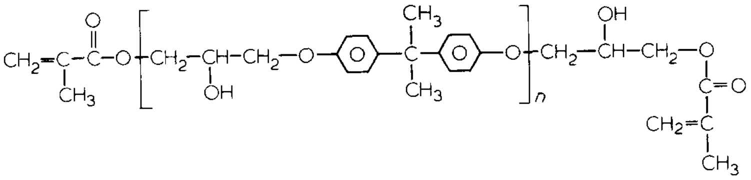


Table 2 Curing systems*

Resin no.	MEKP[1] (w/w %)	Cobalt[2] accelerator (w/w)	Dimethyl[2] aniline (w/w %)
1	1.5	0.08% of 9% (alsynate)	–
2	2.0	1.0% of 0.4% (octoate)	–
3	2.0	1.0% of 0.4% (octoate)	–
4	2.0	1.0% of 0.4% (octoate)	–
5	4.0	1.0% of 0.4% (octoate)	–
6	2.0	0.5% of 6% (octoate)	–
7	2.0	0.5% of 6% (octoate)	0.1

* Cure was at ambient temperature for 24 h with 3 h postcure at 80°C
Resin 7 was further postcured for 3 h at 100°C
Notes: 1. 50% methyl ethyl ketone peroxide diluted with a phthalate paste
2. In styrene solution

were dried to constant weight under vacuum at 50°C. Resin 1 was immersed in sulphuric acid and sodium chloride solutions. Resin 1 was immersed at 65°C and 30°C and the other resins at 50°C.

Powdered samples of resin 1 were separately extracted with hot water and the solutions examined by gas liquid chromatography. Other specimens were extracted with deuterium oxide, the solutions then evaporated to dryness and the residues redissolved in deuterochloroform for examination by 90 MHz proton n.m.r.

Resin sheets were normally cast between Melinex^{R} sheets supported by glass plates. There was no noticeable cure inhibition or styrene evaporation.

Samples of resin were first cut from the resin sheets, by means of razor blades, to form very small blocks. These blocks resembled pyramids from which each apex had been removed. The cutting was performed so that the surface to be examined by transmission electron microscopy formed the small flat top of the truncated pyramid; the area of this region was less than 1 mm^2. Then thin sections of resin were cut from the apex by means of a Huxley Mark II ultramicrotome, fitted with a glass knife, so as to produce slices 70 nanometres thick and approximately 0.2 mm square. These slices were handled by floating them onto distilled water and thus transferring them to grids covered with a carbon film. (This sectioning technique is widely used for biological materials embedded in a plastics matrix). The slices were examined by means of a Phillips EM 301 transmission electron microscope. Further samples were examined after immersion in water. Other sheets, cast in silicone rubber moulds, or cured with surfaces exposed to air during cure, frequently developed opacity on immersion in water. The opaque surfaces were examined by a Cambridge 600 scanning electron microscope.

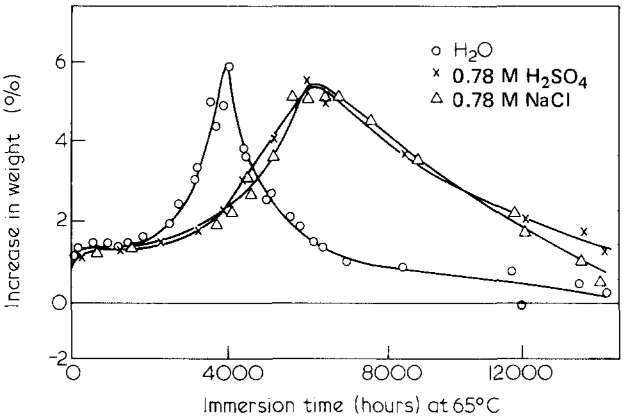


Figure 1 Observed net weight changes of resin 1 immersed in aqueous liquids at 65°C

RESULTS AND DISCUSSION

Internal crack development

The net weight increases observed after immersion at 65°C are shown for resin 1 in *Figure 1*. Samples immersed

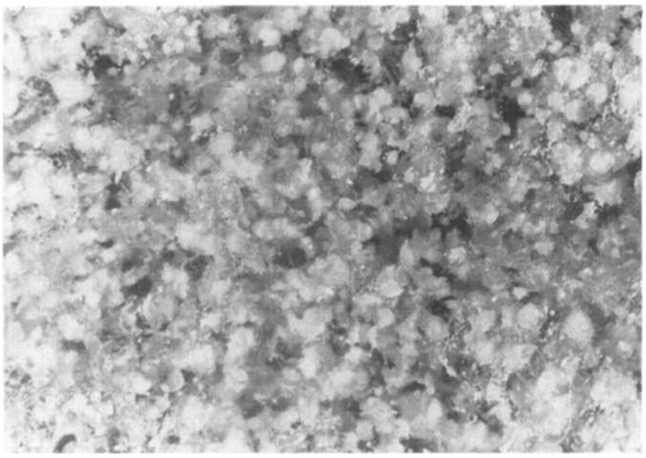


Figure 2 Osmotic cracks in resin 1 after 8000 h immersion in distilled H_2O at 65°C (x10.5)

in distilled water reached a peak weight increase of approximately 6%, followed by a sharp decline. Similar, but shifted, broader peaks were observed for samples immersed in 0.78M H_2SO_4 and 0.78M NaCl. The onset of a rapid increase in weight was in all three cases broadly simultaneous with the appearance of disc cracks (see *Figure 2*) of the kind previously reported without explanation by Steel[12], and attributed by Ashbee *et al.*, following a series of elegant and important experiments, to osmotic pressure arising from inorganic impurities[17,18]. It will be shown here that the chief impurity in polyesters is the glycol used to synthesize the resin.

The osmotic origin of these circular cracks is confirmed by the following observations:

(a) The time to onset of disc cracking and to subsequent peak weights was greater for samples immersed in aqueous solutions than for samples immersed in distilled water.

(b) The time to onset of disc cracking was greater in 6M than in 2M NaCl solution.

(c) The addition of an extra 5% w/w propylene glycol to the resin before crosslinking reduced the time of onset of the disc cracks from about 2000 h at 65°C in water to little more than 100 h.

(d) The addition of similar quantities of water-insoluble hydrocarbons did not affect the crack nucleation time.

(e) Subjection of the resin to vacuum treatment before crosslinking (to minimize residual free diol) delayed the onset of cracking.

The prime cause of the osmotic process is probably the phase-separated, unreacted glycol, which happens to be water-soluble. Some resin manufacturers take steps to remove residual glycol, but others do not, and some add small quantities of additional glycol after manufacture, so as to adjust various resin properties.

Extraction of powdered resin 1 with water, followed by gas liquid chromatographic analysis of the extract, indicated that the crosslinked resin contained initially about 1.7% of residual propylene glycol, but only a trace of diethylene glycol.

Sometimes disc cracks formed first within the body of the sample, but in other cases they were observed first near the surfaces. This seemed to be a function of water temperature and of the rate at which glycol could diffuse out of the surface regions, compared with the rate of entry of water.

When disc cracks formed within the body of the resin, they proliferated along specific paths, resulting in dendritic patterns, as if the position of each crack had been determined by the stress field around the previous one.

Cracks induced in resin 1 at 65°C were randomly orientated, except in the central core, where preferential orientation was induced because of swelling stresses.

Addition of 1% finely divided sodium chloride to the resin before crosslinking did not produce large disc cracks of the kind normally found. Some very much smaller ones were evident, but these reached only about 50 μm. Doubling the quantity of free radical inhibitor (100 ppm hydroquinone) had no obvious effect on crack nucleation time or size; nor did filtering out the existing inhibitor.

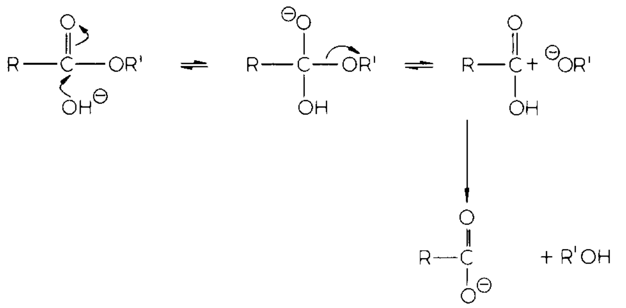
On thoroughly drying the resin the disc cracks often appeared to shrink and close up, but this tendency became less pronounced at long exposure times.

Osmotic cracks were observed most readily in resin 4. They were less obvious in the other resins and cracks in the vinyl ester resin formed only very slowly. This resin did not contain any free glycol but could contain minute traces of other water-soluble substances.

Hydrolysis (resin 1)

Hydrolysis of crosslinked polyesters is believed to leave the crosslinks unaffected, so the main constituent of the residue is a styrene–fumaric acid copolymer[19–21]. Consequently, little or no free fumaric acid should be released by hydrolysis.

At low pH, hydrolysis is to some extent reversible, and incomplete[21]. But the hydrolysis of esters is more rapid in alkali because of the formation of a resonance-stabilized carboxylate anion with little tendency to react with alcohol:



After long periods, white deposits collected at the edges of disc cracks, migrating to the specimen surfaces and collecting at the bottom of the glass immersion tubes. This white substance was dried and analysed. Its melting-point was 340°C and the n.m.r. and infrared spectra were consistent with those of isophthalic acid.

The formation of disc cracks increases the available surface area at which hydrolysis preferentially occurs. The sites of disc cracks are probably glycol-rich. When specimens were carefully dried to determine their dry weight, it was clear that the onset of disc crack formation was followed by very marked acceleration in weight loss (see *Figure 3*) coinciding with the peaks of *Figure 1*. However, the observed weight losses in H_2O, 0.78M NaCl and 0.78M H_2SO_4 never approached those seen in 0.78M NaOH (*Figure 4*). This reagent produced rapid visible changes, with surface layers being loosened and detached,

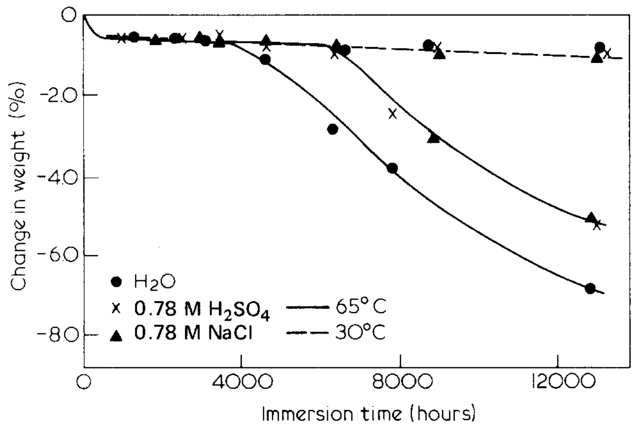


Figure 3 Change in weight of resin 1 after drying out from immersion in aqueous liquids at 30°C and 65°C

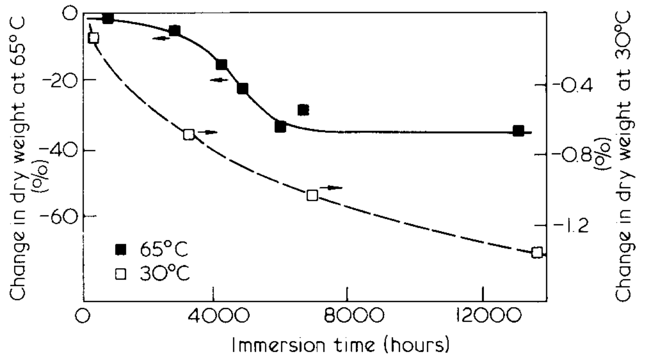


Figure 4 Change in weight of resin 1 after drying out from immersion in sodium hydroxide solution at 30° and 65°

regardless of any osmotic crack formation. The final residue was non-flammable, contained about 65% of the original mass and was much more easily and quickly dried to constant weight than the other residues.

Leaching

The reduction in weight on drying unimmersed samples of resin 1 was less than 1% and was caused by the drying process itself removing volatile, non-bound substances. The specimens dried out after the first few thousand hours immersion showed the same weight loss. Extraction of powdered, otherwise unimmersed resin with hot water followed by gas liquid chromatographic analysis showed 1.7% unreacted styrene present and 0.8% propane 1,2 diol, which is higher than expected from the drying experiments. (There was also a trace of diethylene glycol). This small discrepancy could possibly be explained by postulating postcure and further styrene reaction on devolatilizing under dry conditions, but it is also probable that trapped residuals are more easily and completely removed from water-plasticized resin than from dry resin.

After the formation of disc cracks, net weight losses increased, with formation of additonal leachable material.

N.m.r. spectra of the deuterium oxide extract from unimmersed resins 2, 3, 4 and 5 showed qualitatively that there was practically no leached fumaric acid, except in the case of resin 5, which was synthesized using 3 moles of unsaturated acid to one of isophthalic and therefore could easily have some unreacted unsaturation. Isophthalic acid could be detected in all cases and large quantities of free propylene glycol were found leached from resins 3 and 5. Resin 4 lacked free diethylene glycol and all leached substances contained glycol in bound form. The total quantity of leached material is given for a few illustrative cases in *Table 3*; solution concentration has a considerable effect.

Electron micrographs of resin surfaces

The surfaces of control samples appeared smooth when examined by transmission electron microscopy. Samples immersed in distilled water at 50°C for 3800 h contained numerous dark specks (*Figure 5*) of diameter around 15 nm. These specks were always within 400 nm of the water-exposed surface and are attributed to the formation of phthalic acid by hydrolysis, rather than to diffusion of substances from the distilled water into the resin.

Samples with defective surfaces, such as those cast in contact with air or silicone rubber, instead of glass or Melinex^R rapidly developed opacity in water. *Figure 6* shows a scanning electron micrograph of the foam-like surface layer, approximately 100 μm deep. Transmission electron micrographs showed extensive damage, and incipient cracks could be detected (*Figure 7*). Similar materials showed considerable void formation when examined at very high magnifications (×135000). Previous observations of opacity in water-immersed samples have been attributed by Rosen[22] to microfracture, and to clustering of water molecules about polar sites and microvoids. Pantony[23] attributed opacity

Table 3 Total quantity of leached substances from resins*

Resin no.	Immersion time (h)	Immersion liquid	Temperature (°C)	% Leached matter (w/w)
1	6000	2M NaCl	65	0.5
1	13000	2M NaCl	65	2.2
1	10000	6M H_2SO_4	65	0.9
1	8000	0.78M NaOH	65	32
2	750	H_2O	50	1.6
3	1000	H_2O	50	0.6
4	1000	H_2O	50	2.7
5	750	H_2O	50	2.1

* The geometry of the immersed samples is given in the Experimental section

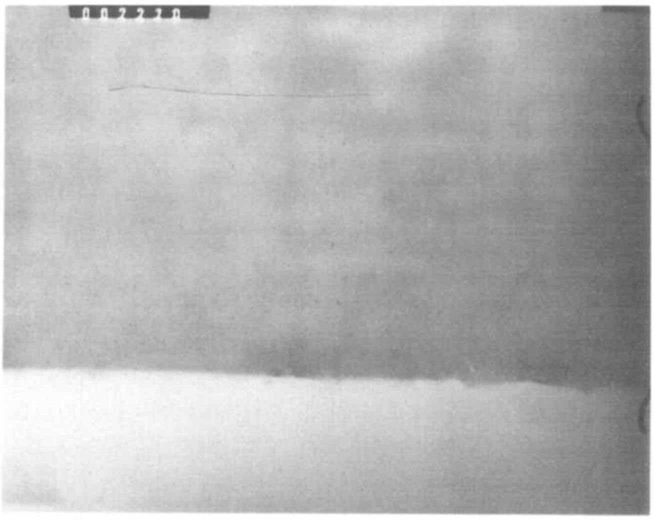


Figure 5 Transmission electron micrograph of surface of resin 6 after 3800 h immersion in water at 50°C (x135000)

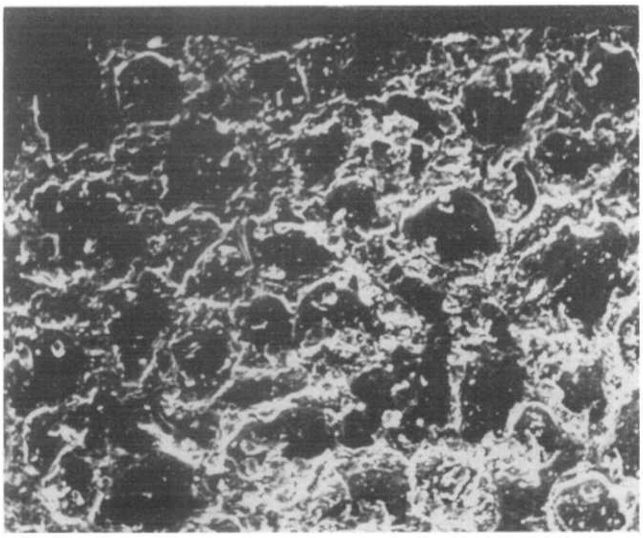


Figure 6 Scanning electron micrograph of surface of a resin showing water-induced opacity

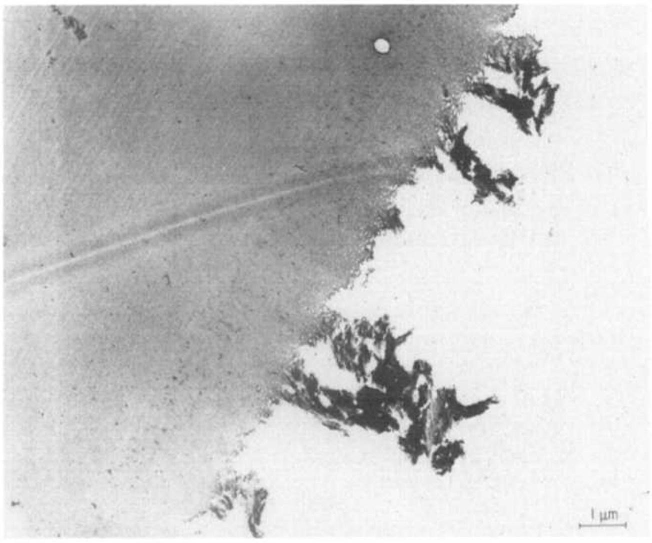


Figure 7 Transmission electron micrograph of damaged surface of resin 5 after immersion in water at 50°C for 8 days (x 17 100)

to hydrolysis. In our samples it disappeared on drying, except after prolonged immersion.

True water absorption values

Weight increases such as those shown in *Figure 1* are commonly reported in the literature. They are not true water absorption values but the resultant of true water uptake and weight loss processes. The true water absorption rate for resin 1 is given in *Figure 8* and was obtained by subtracting the weight of leached material from the observed net increase. There was still a peak, but the subsequent decline was arrested and followed by a plateau. When dilute H_2SO_4 or NaCl solutions were used, the peaks and plateaux became merged. Loss of specimen weight by leaching accelerated with time until the accessible hydrolysis sites became exhausted, leaving a swollen network in a pseudo-equilibrium state. NaOH caused much more extensive hydrolysis, with no peak apparent.

At 30°C, water uptake was very much slower, with no rapid change in appearance or weight (*Figure 9*).

Dimensional changes on water immersion closely paralleled the net weight increases observed in *Figure 1*. Hydrolysis and leaching eventually produced shrinkage. At high concentrations, swelling was negligible (*Figure 10*). Sodium hydroxide, however, produced continual swelling, with dimensional changes eventually exceeding 35%.

Table 4 gives the extent of recovery of dimensions on drying. Generally, recovery was substantially complete for short immersions, but resin 4 contracted a little.

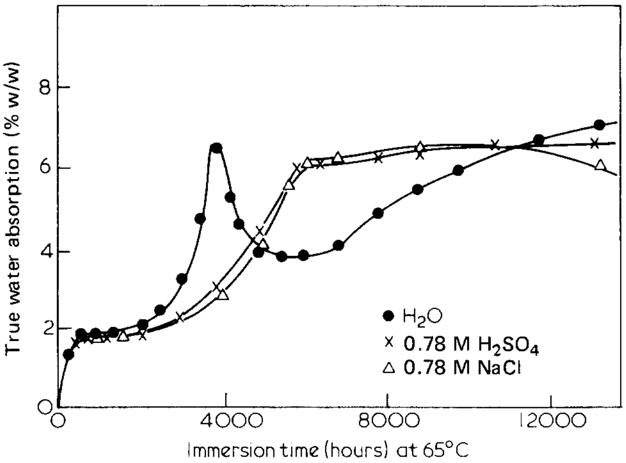


Figure 8 True water absorption (corrected for leaching losses) of resin 1 immersed in aqueous liquids at 65°C

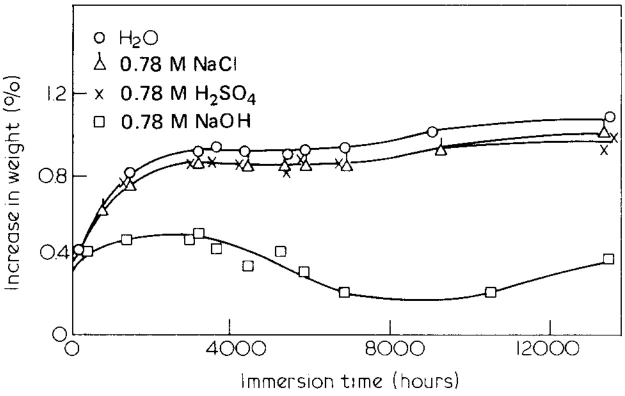


Figure 9 Observed net weight changes of resin 1 when immersed in aqueous liquids at 30°C

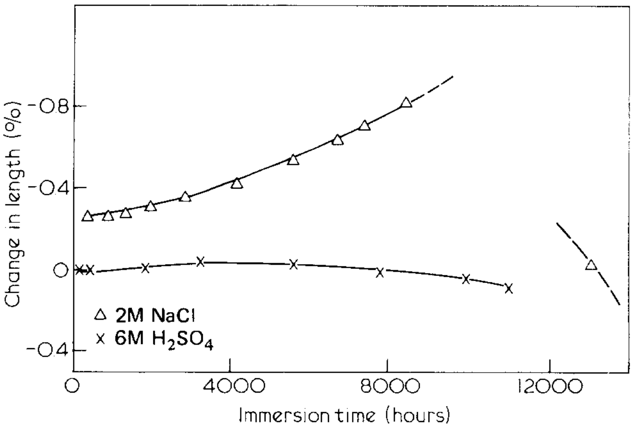


Figure 10 Change in dimensions of resin 1 in relatively concentrated solutions at 65°C

Table 4 % Dimensional increase

Immersion time (h)	Resin no. 2		Resin no. 3		Resin no. 4		Resin no. 5	
	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
168	0.83	0.07	0.30	*	0.57	−0.65	0.68	−0.14
336	0.75	0.47	−0.11	*	1.06	−0.08	1.02	0.25
840	1.05	0.08	−0.11	*	1.31	−0.24	0.68	−0.05
1176	1.29	0.03	−0.11	*	0.74	−0.66	1.12	0.14

* Negligible change

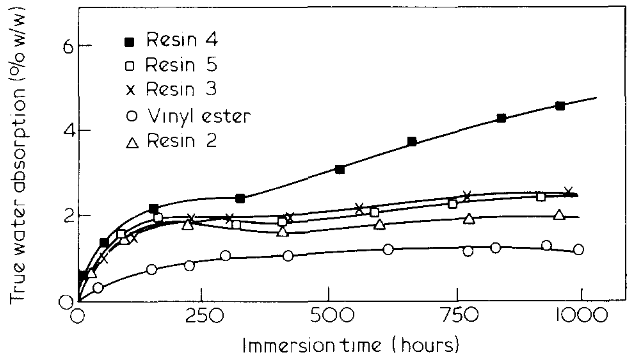


Figure 11 True water absorption (corrected for leaching losses) of isophthalic polyesters 2 to 5 and of the vinyl ester resin

Effects of resin formulation

Resin 4 showed ready osmotic crack development, high water absorption and a failure to achieve original dimensions on drying. This can be explained by the formulation; the glycol content was entirely diethylene, rather than partly propylene glycol; diethylene glycol units are hydrophilic. The low maleic:phthalic ratio also results in a resin with lower crosslink density than that of the other conventional polyesters used, and resin 4 was the only one immersed at a temperature above its heat distortion point, because diethylene segments enhance segmental mobility.

Resins 3 and 5 differed mainly in maleic:phthalic ratio, and therefore in crosslink density and aromatic content. Differences in true water uptake were very small (*Figure 11*) but the higher maleic:phthalic ratio of resin 5 produced less net weight change, and more short-time leaching (*Table 3*). The extent of short-term leaching depends on the quantity of non-bound extractable matter, and cannot easily be predicted from the formulation.

CONCLUSIONS

The degradation of cast polyester resins by hot water begins with water uptake, swelling and leaching of non-bound substances. Nevertheless hydrolysis is the main irreversible process and this would be much slower if it were not for osmotically induced cracks, which greatly accelerate it. The osmotic process depends on traces of water-soluble, phase-separated substances, particularly glycols. Of all the isophthalic polyester resins examined, that made from equal molar proportions of propylene glycol and diethylene glycol proved most resistant to water damage. However, other facturs such as molecular weight are also important.

Microscopic evidence suggests that water damage at air-inhibited resin surfaces can be very rapid, although the region affected is less than 100 μm thick.

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