Contribution of carboxyl end-groups to the hydrolytic instability of crosslinked polyesters

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INTRODUCTION

Commercial unsaturated polyester resins consist of unsaturated polyesters dissolved in styrene; curing gives three-dimensional crosslinked interpolymer. Since polystyrene is resistant to chemical attack, this leaves the polyester as the component responsible for breakdown. Ester linkages are the most logical reactive groups to be involved and this assumption is supported by the fact that good agreement has been observed between ester content and corrosion[1].

Hydrolysis of ester groups results in formation of carboxyl groups and in urethane elastomers it has been shown that this leads to an autocatalytic acceleration of further decomposition, unless the carboxyl groups so formed are rendered ineffective[2–4]. In fact, the presence of carboxyl group scavengers in urethane elastomers has resulted in a very reasonable improvement of the hydrolytic stability. This autocatalytic action of carboxyl groups in polyester-based polyurethanes led to the suggestion that a similar mechanism might be followed in unsaturated polyesters. Polyester chains are terminated in hydroxyl or carboxyl groups; it seemed to be worthwhile to determine the effect of decreasing the carboxyl content on the hydrolytic resistance of an unsaturated polyester, as part of a general programme studying the technology of these materials.

As carboxyl group scavengers, a carbodiimide and glycidyl methacrylate have been used. All the modification reactions have been examined on a terephthalate-based unsaturated polyester 'Impolex'* T 400 (*Figure 1*) in the absence of any solvent.

Carbodiimides used in this work were the mono- or polycarbodimides with structures given in *Figure 2*; results for the latter only are quoted in *Tables 1* and *2*, since this appeared to have the better compatibility in the final product.

Carbodiimides are characterized by the highly unsaturated group –N=C=N– which reacts with the carboxyl group resulting in *O*-acylisoureas[5,6] (equation 1)

O-acylisoureas are unstable compounds and they react further by two competing paths, to produce either an N-acylurea (rearrangement) (equation 2) or a urea and the anhydride of the acid (equation 3).

On the other hand, in a system with a polyester alkyd and an epoxide such as glycidyl methacrylate, a number of reactions can take place, the most important of which are equations (4), (5) and (6)

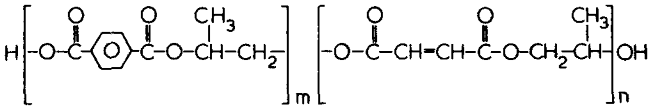


Figure 1 'Impolex T400' polyester alkyd (terephthalic acid/maleic anhydride/propylene glycol copolymer) – model structure

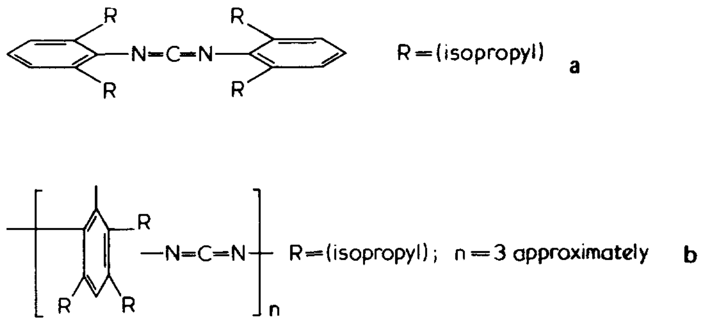
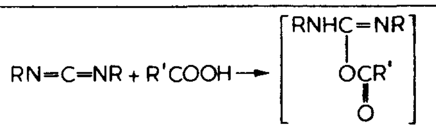
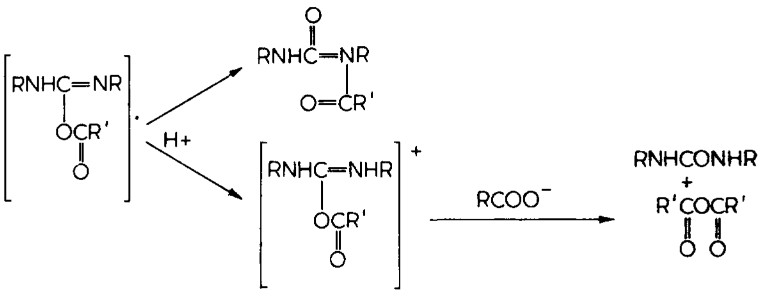


Figure 2 (a) Monocarbodiimide; (b) polycarbodiimide

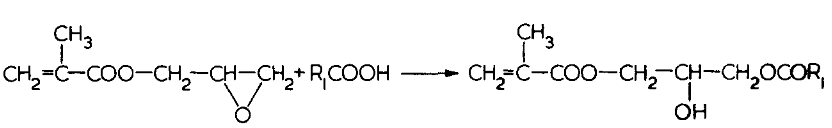


$$RN{=}C{=}NR + R'COOH \longrightarrow \left[\begin{array}{c} RNHC{=}NR \\ | \\ OCR' \\ \| \\ O \end{array}\right]$$ (1)

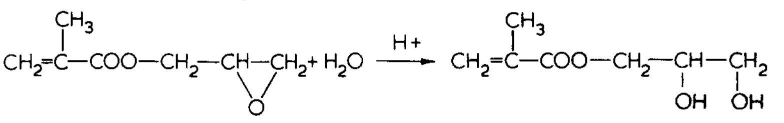


(2)

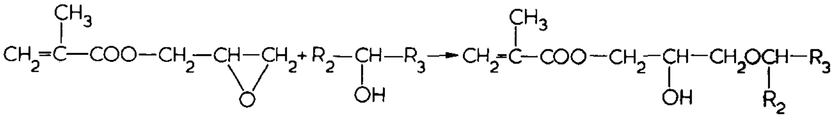
(3)



$$CH_2{=}C(CH_3){-}COO{-}CH_2{-}\underset{O}{CH{-}CH_2} + R_1COOH \longrightarrow CH_2{=}C(CH_3){-}COO{-}CH_2{-}CH(OH){-}CH_2OCOR_1$$ (4)



$$CH_2{=}C(CH_3){-}COO{-}CH_2{-}\underset{O}{CH{-}CH_2} + H_2O \xrightarrow{H+} CH_2{=}C(CH_3){-}COO{-}CH_2{-}CH(OH){-}CH_2(OH)$$ (5)



$$CH_2{=}C(CH_3){-}COO{-}CH_2{-}\underset{O}{CH{-}CH_2} + R_2{-}CH(OH){-}R_3 \longrightarrow CH_2{=}C(CH_3){-}COO{-}CH_2{-}CH(OH){-}CH_2OCH(R_2){-}R_3$$ (6)

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* Trade name of Imperial Chemical Industries Ltd. 'T400' refers strictly to the polyester–styrene solution; the base polyester was used in this work

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Table 1 Flexural strength and modulus retention of end-group-modified samples after 10 days storage at 100° C

			Flexural strength			Flexural modulus		
No	Modification to unsaturated polyester	Acid number (mg KOH/g)	Control* specimens (MN/m^2)	Tested* specimens (MN/m^2)	Retention (%)	Control specimens (GN/m^2)	Tested specimens (GN/m^2)	Retention (%)
1	Unmodified	9.57	114.2	106.2	93.0	2.89	2.93	101.4
2	Heated	9.50	112.8	104.1	92.3	2.98	2.95	99.0
3	Carbodiimide	2.54	118.5	107.2	90.5	3.08	2.99	97.1
4	Glycidyl methacrylate	1.63	109.6	106.6	97.3	2.95	2.91	99.0
5	'Impolex T400' resin	~7	115.4	107.4	93.1	2.77	2.90	104.7

* Control: specimens stored at 25° C; tested: specimens stored at 100° C

Table 2 Flexural strength and modulus retention of end-group-modified samples after 10 days immersion in boiling water

			Flexural strength			Flexural modulus		
No	Modification to unsaturated polyester	Acid number (mg KOH/g)	Control* specimens (MN/m^2)	Tested* specimens (MN/m^2)	Retention (%)	Control specimens (GN/m^2)	Tested specimens (GN/m^2)	Retention (%)
1	Unmodified	9.57	114.2	96.4	84.4	2.89	2.83	97.9
2	Heated	9.50	112.8	89.8	79.6	2.98	2.67	89.6
3	Carbodiimide	2.54	118.5	94.1	79.4	3.08	2.90	94.2
4	Glycidyl methacrylate	1.63	109.6	93.9	85.7	2.94	2.72	92.5
5	'Impolex T400' resin	~7	115.4	104.7	90.7	2.77	2.77	100.0

* Control: specimens stored at 25° C; tested: specimens immersed in boiling water

If the amount of water present in the reacting system is much lower than the concentration of epoxides, then reaction (5) is suppressed. Reactions of hydroxyl groups to form hydroxyethers (6) occur to some extent, but with base catalysts the reaction with carboxyl groups is more selective[7].

TESTING PROGRAMME

The polyester which forms the basis of 'Impolex T400' was reacted with the carbodiimide or glycidyl methacrylate. The polyester was treated at 120°C with carbodiimide (10% in excess of the quantity required to react with all the carboxyl groups) for 2 h. With similar temperature and time a 50% excess of glycidyl methacrylate was employed; it was also important to include 0.1% hydroquinone as inhibitor to protect the methacrylate unsaturation, otherwise extensive crosslinking occurred. As all the modification reactions were run at elevated temperatures, the unmodified polyester, heated at the same conditions, was also included in the tests in order to determine the effect of the heating treatment on hydrolysis resistance.

All the treated and untreated polyesters were dissolved in styrene to form 50% (w/w) solutions of the polyesters. It was important to powder the resin before dissolution in the styrene; a laboratory type grinder was used for this purpose, and to minimize loss of styrene, the process was carried out at room temperature. To the stirred monomer containing 250 ppm t-butyl catechol (to increase gel time in the final crosslinking reaction), powdered resin was added slowly to avoid the formation of agglomerates, the total dissolution cycle taking 2–2.5 h. Finally the syrup was filtered through glass wool and preferably cast into sheet the same day. Methyl ethyl ketone peroxide and cobalt octoate, each at 1% (w/w), were used as initiator and accelerator respectively and were mixed well prior to casting.

The mould comprised a metal frame to define the thickness (3 mm) on a glass plate with oriented poly(ethylene terephthalate) film as release agent. Excess of catalysed resin was poured into the mould which was covered by polyester film after allowing air bubbles to come to the surface. Excess resin was removed by rolling over the surface of the upper film and finally the assembly was covered with another glass plate, thus avoiding distortion of the sheet and air inhibition of the upper surface during curing. Mouldings were cured for 24 h at room temperature followed by post-cure for 3 h at 80°C and 3 h at 120°C. Specimens cut from each casting were divided into three sets of at least five specimens. Specimens of the first set were kept at room temperature. Specimens of the second set were immersed in boiling water and specimens of the third set were kept in an oven at 100°C. After 10 days, the flexural strengths and moduli of all the specimens were determined. The test of storage at 100°C was included in the testing programme in order to see how elevated temperatures contribute to the deterioration of the material during hydrolytic attack.

RESULTS AND DISCUSSION

Data developed on flexural strength and modulus retention after 10 days storage at 100°C or immersion in boiling water are quoted in *Tables 1* and *2*. The following conclusions are reached:

Storage for 10 days at 100°C causes a slight deterioration in the flexural strength of all the resins tested. However, the glycidyl methacrylate treated resins perform better than the control resin, whereas no difference is noticed between the latter and the heated or carbodiimide-treated resins. On the other hand no significant deterioration of the flexural modulus is obtained. Commercially available 'Impolex T 400' resin shows a behaviour similar to that of the control system.

According to the test of 10 days' immersion in boiling water, reduction of the carboxyl content of the resins does not appear to improve hydrolysis resistance. In fact, modification with glycidyl methacrylate does not affect the hydrolytic stability, whereas utilization of carbodiimide deteriorates it. Furthermore, all the modified resins show a lower retention of flexural modulus compared with the control, possibly due to the heating stage which appears to cause deterioration of hydrolysis resistance. Commercial 'Impolex T400' resin gives excellent results as a high retention of flexural strength is obtained: flexural modulus also remains unchanged. One reason for this may be a rather higher styrene content in the commercial product.

In agreement with the literature[7], these results suggest that elimination of the carboxyl groups of unsaturated polyester resins does not necessarily improve the hydrolytic stability. For a reduction in the carboxyl content of a polyester to improve the corrosion hydrolysis resistance appreciably may require a resin of low intrinsic resistance: 'Impolex T400' resins are, however, recommended for use under corrosive service conditions. The autocatalytic action of free carboxyl groups in hydrolysis does not seem to be inhibited by the elimination of the carboxyl endgroups, the concentration of which is already low (about 7 mg KOH/g for commercial 'Impolex T400'). In fact, during hydrolytic attack new carboxyl groups are formed and possibly it is these that cause the autocatalytic acceleration of the decomposition. The practice in polyester based polyurethanes is to incorporate carbodiimides for continuous elimination of these new carboxyl groups[2,3]. However, long-term tests seem to be necessary to establish a better correlation between acid value and hydrolytic stability as short-term data at elevated temperatures are usually characterized by a large experimental error[7].

REFERENCES

1 Updegraff, H., Doyle, M. J. and Kerle, E.J. *Proc. Ann. Conf. Reinf. Plast./Compos. Inst., Soc. Plast. Ind.*, 1969, **24**, 9A

2 Neymann, W., Peter, J., Holtschmidt, H. and Kallert, W. *Proc. Rubber Technol. Conf., 4th,* London, 1962, 59

3 Magnus, G., Dunleavy, R. A. and Critchfield, F. E. *Rubber Chem. Technol.*, 1966, **39**(4), 1328–37

4 Ossefort, Z. T. and Testroet, F. B. *Rubber Chem. Technol.* 1966, **39**, 1308

5 Saunders, J. H. and Frisch, K. G. in 'Polyurethanes Chemistry and Technology. Part 1. Chemistry', Interscience, 1962, p 116–118

6 Smith, P. 'The chemistry of open-chain organic nitrogen compounds', W. A. Benjamin, 1965, Vol 1, 250–256

7 Seifert, W. K., Stevens, M. P., Gardner, J. D. and Percival, D. F. *J. Appl. Polym. Sci.* 1965, **9**, 1681