

# On the hydrolytic stability of polyester yarns

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**Abstract** The relationships between strength, molecular weight and the rate of hydrolytic attack are determined for two polyester fibres which differ in their carboxyl end group concentration. Chemical and physical tests are described briefly and predictions are made of the rates of hydrolysis at ambient and other temperatures. It is concluded that the fibres are suitable for use in environments likely to be found in civil engineering applications, when lifetimes of many hundreds of years can be expected at ambient temperature.

## Introduction

Polyester yarns are quite widely used for industrial purposes. The combination of strength, stiffness and low creep makes them suitable for a number of applications where steel would be either too heavy or too susceptible to corrosion, and the cost of fibres such as aramids cannot be justified.

Many of these applications are in the form of ropes, such as standing or running rigging in ships; mooring lines for ships or floating facilities; stays for radio antennae, or as strips for reinforcing soil.

In many of these cases, the ropes are in water, or in situations where they may occasionally get wet. In the

case of ground water, this may be mildly acidic or alkali. Some rope constructions, such as the parallel lay ropes used to achieve maximum stiffness, will surround the fibres with a sheath that primarily serves to give the rope some coherence, but will also restrict access of water to the fibre core. For the purposes of this exercise, however we assume a worst-case scenario where water will be in permanent contact with the fibre.

It is known that polyester fibres will hydrolyse, with  $H^+$  ions attacking the ester linkage and breaking the chain. This reduces the polymer chain length, with direct consequences for the strength of the fibre. The most comprehensive study of polyester hydrolysis, by McMahon et al. [1], indicated that rates of hydrolysis were low, but in the context of the lifetime of civil engineering applications, were not negligible. However, McMahon's tests were carried out 45 years ago; since then, many changes have taken place in fibre technology. His fibres were produced for the textile industry; they had lower degrees of polymerisation, with molecular weights approximately half of those available today; they were not so highly drawn, and the carboxyl end group concentration (CEG) was probably higher than the industrial polyesters produced today.

It was thus deemed necessary to obtain data, and to model the hydrolysis process, using polyester yarns as used in modern rope construction. The modelling process had to make use of parameters that could be measured; these were taken to be the strength of the yarns and the molecular weight, both obtained after immersion in water at different temperatures and for different durations. Standard physical chemistry test procedures, such as Gel permeation chromatography (GPC) and Intrinsic Viscosity (IV) tests, had to be employed.

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## Principles of analysis

The object of the analysis is to determine the rate at which strength is lost with time as hydrolysis proceeds. The fundamental reaction is chain scission, which results in a reduction of polymer chain length, and hence a lower molecular weight. The rate of chain scission will be a function of temperature, so it will be necessary to determine the activation energy of the reaction. It will also be necessary to determine the relationship between molecular weight and strength, which can be expected to exist but whose form is, *ab initio*, unknown.

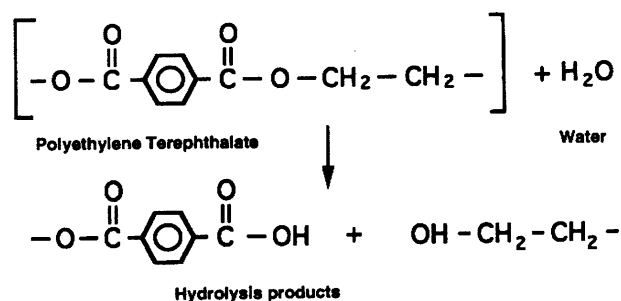
Thus, several stages of the analysis are needed

- Relationships have to be established between the intrinsic viscosity, the number average molecular weight  $M_n$  and the weight average molecular weight  $M_w$ .
- The change in molecular weight can then be used to determine the number of chain scissions after different times and at different temperatures.
- The rate of the hydrolysis reaction can be calculated at different temperatures from the number of chain scissions.
- The activation energy of the chain scission reaction can then be found.
- A relationship will be established between molecular weight and strength.
- The various results will be combined to give the required relationship between strength, time and temperature.
- Plots of retained strength against time and temperature will be produced which will be of use to engineers designing applications of polyester ropes.

## Hydrolysis mechanisms

### Neutral hydrolysis

The neutral hydrolysis reaction for polyester can be written [2] as



which clearly results in a reduction in the length of the molecular chain and consequently a reduction in molecular weight. Polyester fibres depend on molecular orientation and chain length for their strength, so hydrolysis will result in a reduction of the tensile properties. Eventually, more and more ester links will be destroyed until the fibre disintegrates.

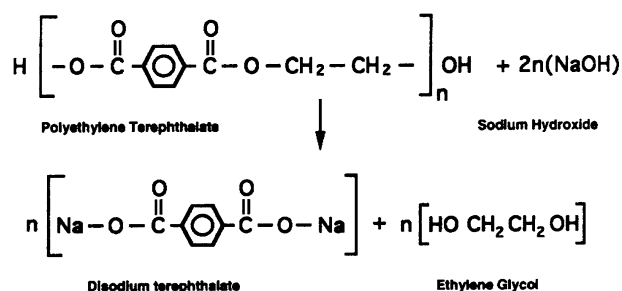
Ravens and Ward [3] showed that the rate of hydrolysis is proportional to the square root of the carboxyl end group concentration, and they also found the activation energy of the hydrolysis mechanism to be 112.5 kJ/mol.

### Acid hydrolysis

The mechanism of acid hydrolysis is the same as neutral hydrolysis, since in both cases the  $\text{H}^+$  ion is involved. But the acid attack should occur more rapidly, since the ions are present at higher concentrations. However, it is known [4, 5] that there are big differences in the effects of different acids, which may be attributed to different rates of diffusion into the polyester.

### Alkali hydrolysis

The mode of attack by alkaline species is different, since it involves attack by the  $\text{OH}^-$  ion [6], and takes place by removing material from the surface of the fibre. The alkali randomly attacks the ester groups of the polymer molecule and removes short chains, which are then hydrolysed. Overall, the reaction can be written as



### Fibres tested

Two fibres were tested in the present study. Both were candidate yarns for use in ropes, and also in strips, which are used in the civil engineering industry for reinforcing soils, and thus are often buried in the ground. They are, in many circumstances, below the water table, and the water conditions can be expected to vary, in exceptional cases, from mildly acidic (pH5) to mildly alkali (pH9). More extreme cases are not normally encountered, and if they were, variations to

the design or remedial measures would be undertaken. For the purposes of this study, however, a range from pH4 to pH11 has been considered.

The two fibres that have been studied will be denoted here simply as PET1 and PET2. They have comparable physical properties, but PET1 has a lower CEG concentration (15 M eq/g) than PET2 (30 M eq/g). Untwisted yarn samples of 1,100 decitex were used for all tests; the short-term strengths were measured as 85.5 N (PET1) and 82.3 N (PET2).

### Design of tests

In planning the tests, certain criteria were adopted.

- It was recognised that hydrolysis would be slow, so test programmes over extended periods of time should be allowed for.
- Testing could be speeded up by raising the temperature, but not to the extent where the  $T_g$  of the yarns (approx 75 °C) was exceeded to any great degree, as this could introduce additional mechanisms.
- It was expected that the strength would be related to the molecular weight in some way, so both strength and the molecular weights should be measured. It was possible that the strength–molecular weight relationship obtained during initial polymerisation might differ from that obtained when molecular weight was being reduced as a result of hydrolysis.
- There might be some effect due to fibres being under load; glass fibres, for example, are known to stress-corrode. It could be argued that load could provide some energy that would assist in breaking the molecular bonds; on the other hand, it could be argued that stress tends to straighten the chains, thus improving the orientation of the molecules, which is known to improve strength.
- Both acids and alkalis might affect the strength of the fibres; acids increase the  $H^+$  concentration, which would increase the rate of attack, and alkalis introduce another mechanism of attack which affects the outer surface of the fibres.

Tests were planned which would cover all these aspects.

### Sample environment

Fibres of both types of polyester were stored in water and other solutions, which were held at constant temperature by electric heating elements.

- Relaxed samples, wrapped loosely on stainless steel I-frames, were placed in de-ionised water at pH7. Samples were maintained at three temperatures:
  - 50 °C
  - 70 °C
  - 85 °C.
- Relaxed samples, wrapped around smaller glass frames at 70 °C, were placed in beakers containing the following solutions held at 70 °C:
  - $H_2SO_4$  at pH4
  - $Ca(OH)_2$  or NaOH nominally at pH11.
- Loaded samples were placed over multiple pulleys with weights suspended from the ends, to maintain a significant tension in the yarns, in deionised water at 70°. Samples were held at 3 different tensions:
  - 20% of break load
  - 30% of break load
  - 40% of break load

The use of long yarns over pulleys meant that it was not possible to measure the extension reliably, so creep rate could not be measured as part of the procedure.

- Some yarns were coiled loosely in a beaker of deionised water at ambient laboratory temperature (approx 20 °C).

### Yarn handling

Considerable care was exercised in the handling of the yarns during the tests [7]. It was found that allowing the yarns to dry after hydrolysing but before strength testing caused a significant reduction in the absolute strength and an increase in variability. This was due to the build-up of static charge on the yarns, which allowed the individual filaments of the yarn to separate, followed by damage when the yarns were handled. It is not expected that such a reduction in strength would occur in a rope where the filaments could not separate.

The procedure adopted, for both control and hydrolysed samples, was thus to remove the test frames from the tanks; after allowing the yarns to cool, they were unwound from the frames, and then tested immediately. Samples that had been in chemical solutions were rinsed in distilled water prior to testing.

### Test procedures

Tensile strength tests were carried out on all samples. Thirty samples were tested from each batch of the

unloaded or chemically treated yarns, with 10 samples for each batch of the loaded yarns.

Two chemical tests were carried out on the yarn samples by ICI Wilton Laboratories. The first was the GPC test, which has the potential to determine the full molecular weight distribution, but for the present project only the number average and weight average molecular weights were reported. The other test was the IV test, which can be related to the molecular weights by empirical relationships.

### Test results for relaxed samples

Tables 1 and 2 give summaries of the test results on relaxed samples in water at different temperatures. (UBL = ultimate breaking load of control specimens.)

In addition to the tests carried out in this programme, additional test data was available from ICI (private communication) relating IV to molecular weight; this had been obtained from a different batch of fibre but it was believed that the relationship between IV and MW was applicable to all polyesters. This data is presented in Table 3.

### Analysis of results

Relationship between IV,  $M_n$  and  $M_w$

The IV can be related empirically to the molecular weight by the Mark–Houwink equation [8]. This takes the form:

$$[\eta] = aM^z \quad (1)$$

**Table 1** Results for PET1

Temperature (°C)	Time days	IV [ $\eta$ ] (dl/g)	(From GPC tests)		Tensile strength		Elongation	
			$M_n$	$M_w$	Average %UBL <sup>a</sup>	CoV (%)	Average (%)	CoV (%)
Control	0	0.860	30,700	113,000	100	2.9	10.23	5.8
	582	–	–	–	100.6	2.8	10.40	5.2
50	91	–	32,700	109,000	99.76	2.7	11.55	3.2
	132	0.804	30,500	108,000	97.02	2.1	11.14	3.1
	270	0.865	35,500	107,000	97.85	2.9	11.64	3.1
70	65	0.823	27,900	101,000	93.56	2.2	14.36	3.4
	130	0.785	26,500	99,300	93.19	2.6	13.95	2.7
	190	0.747	22,000	93,600	92.36	1.8	13.70	2.6
	337	0.658	24,800	77,000	88.54	2.4	13.87	2.5
85	20	0.780	36,700	97,900	94.87	2.3	16.34	1.8
	84	0.662	21,600	69,100	82.10	2.6	16.34	2.5
	130	0.445	15,800	44,400	68.25	3.6	15.02	2.6

<sup>a</sup> Average of 30 tests. UBL = 85.5 N

**Table 2** Results for PET2

Temperature (°C)	Time days	IV [ $\eta$ ] (dl/g)	(From GPC tests)		Tensile strength		Elongation	
			$M_n$	$M_w$	Average %UBL <sup>a</sup>	CoV (%)	Average (%)	CoV (%)
Control	0	0.866	39,500	109,000	100	3.4	11.32	4.5
	582	–	–	–	101.8	2.6	11.74	3.5
50	91	0.837	30,300	106,000	99.70	2.6	12.41	4.1
	132	0.835	42,700	110,000	98.06	3.3	12.74	3.7
	270	0.820	29,600	101,000	97.21	2.8	12.07	2.7
70	65	0.676	22,000	88,600	89.70	2.3	14.99	2.8
	130	0.683	28,700	88,100	85.54	2.1	15.24	2.3
	190	0.629	29,600	81,900	85.90	2	15.32	2.2
	337	0.502	18,600	54,300	69.74	4.5	13.49	3.7
85	20	–	–	–	92.10	1.6	18.07	2.3
	84	0.458	15,000	44,400	67.68	2.3	15.90	4.6
	130	0.326	10,700	27,000	48.85	4.5	13.66	2.3

<sup>a</sup> Average of 30 tests. UBL = 82.3 N

**Table 3** ICI test data

IV $[\eta]$ (dl/g)	$M_n$	$M_w$
0.585	23,900	64,700
0.650	27,900	77,000
0.668	29,000	82,400
0.689	25,600	74,700
0.758	28,500	89,200
0.746	32,500	91,000
0.730	35,200	92,900
1.074	47,300	13,5000
0.796	31,500	90,500
0.796	31,200	92,500
0.796	32,300	91,900
0.911	42,400	112,000
0.873	33,800	111,000
0.925	37,700	116,000
1.000	42,000	126,000
0.887	36,100	97,200
0.899	41,100	112,000
0.913	41,000	115,000
0.902	39,100	108,000
0.899	37,400	101,000
0.872	36,700	98,700
0.878	41,800	113,000

where  $a$  and  $\alpha$  are determined experimentally, and  $M$  can represent either  $M_n$  or  $M_w$  ( $a$  and  $\alpha$  will differ in each case). Figures 1 and 2 show the available data, together with regression lines which give the following relationships:

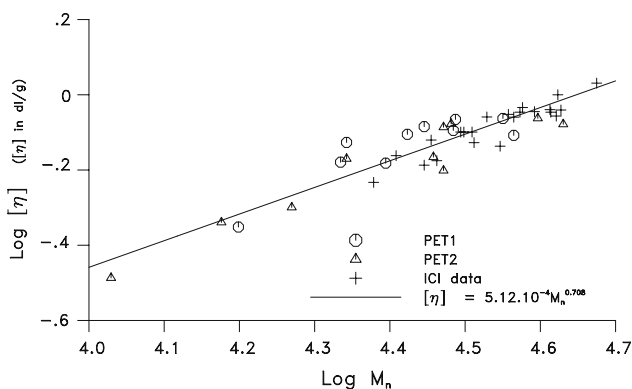
$$[\eta] = 5.12 \cdot 10^{-4} \cdot M_n^{0.708} \text{ (dl/g)} \tag{2}$$

$$[\eta] = 1.64 \cdot 10^{-4} \cdot M_w^{0.74} \text{ (dl/g)} \tag{3}$$

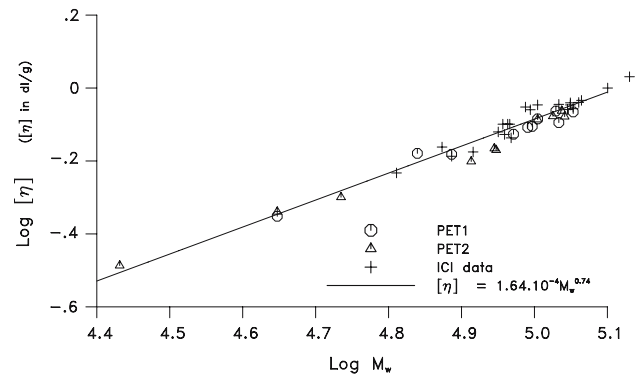
The first of these will be used to determine the rate of chain scission from the IV relationship.

A relationship is also needed between  $M_n$  and  $M_w$ . Combining Eqs. 2 and 3 gives

$$M_w = 4.66M_n^{0.96} \tag{4}$$



**Fig. 1** Relationship between  $[\eta]$  and  $M_n$



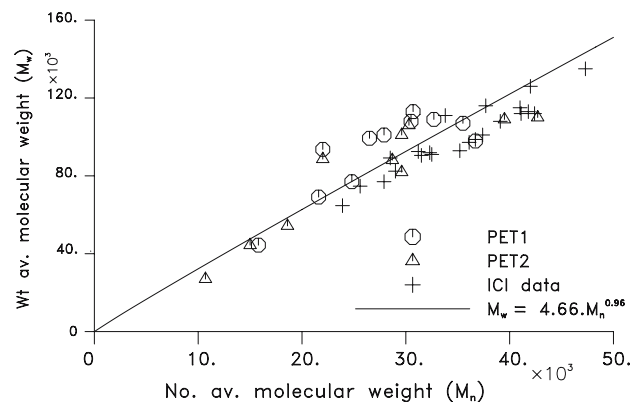
**Fig. 2** Relationship between  $[\eta]$  and  $M_w$

This is very close to a linear relationship, and plotting this equation with the test data on Fig. 3, shows that the degree of non-linearity of the relationship is small by comparison with the scatter in the data. Thus, it will be assumed that  $M_w$  is a linear function of  $M_n$  over the range of results available. It will turn out not to be necessary to establish the exact slope of this relationship, merely its form. The results also show that the ICI data, although on a different polyester, falls within the same spread as the data obtained in these tests, so will be included in the subsequent analysis.

**Rate of reaction**

The extent of hydrolysis can be related to the number average molecular weight. A polymer unit, initially  $n$  units long with a molecular weight  $M_0$ , reacts with  $x$  molecules of water. The same weight of polymer is now shared between  $x+1$  pieces, so the number average molecular weight ( $M_t$ ) after time  $t$  is now  $M_0/(x+1)$ . Thus,

$$x = \frac{M_0}{M_t} - 1 \tag{5}$$



**Fig. 3** Relationship between  $M_n$  and  $M_w$

This can be rewritten in terms of the IV, using Eq. (2), to give

$$x = \left[ \frac{[\eta]_0}{[\eta]_t} \right]^{1/\alpha} - 1 \quad (6)$$

where  $\alpha$  is taken as 0.708 from Eq. (2). The rate of reaction can be determined either from the  $M_n$  data, obtained from GPC testing (using Eq. (5)), or from the intrinsic viscosity (using Eq. (6)). The first method might seem more direct but there is much more scatter in the GPC results, so the IV results are used in preference.

Chain scission acts on the ester links in the polymer. There are two ester links in each unit of the polymer, except for the end groups where there is only one. Thus, in a chain initially  $n$  units long, there are  $2(n-1)$  ester links. After hydrolysis, there will be  $2(n-1)-x$  ester links.

The rate of hydrolysis at a given temperature can be expressed [1] as:

$$\frac{dx}{dt} = k \cdot [\text{ester}] \cdot [\text{H}_2\text{O}] \quad (7)$$

or

$$\frac{dx}{dt} = k(A-x)(B-x) \quad (8)$$

where  $k$  is the reaction coefficient for that temperature; [ester] and  $[\text{H}_2\text{O}]$  are the concentrations of ester links and water, respectively.  $A$  and  $B$  are the initial concentrations of ester links and water, respectively.

The concentration of water was very much larger than that of polymer, and can be regarded as being available in unlimited quantities. Thus,  $[\text{H}_2\text{O}]$  remains sensibly constant, so a simplified relationship can be used

$$\frac{dx}{dt} = k_1(A-x) \quad (9)$$

where  $k_1$  is a new constant. This expression can be integrated to give

$$\log \frac{A}{A-x} = k_1 \cdot t \quad (10)$$

It should be noted that  $\log \frac{A}{A-x} \approx \frac{x}{A}$  when  $x \ll A$ , so Eq. (10) represents the proportion of ester links that have been attacked.

The IV of the control specimens was 0.86 dl/g, whence  $M_0$  is 36,120 from Eq. (2). The molecular weight of one monomer unit is 192, which gives the

initial degree of polymerisation ( $n$ ) as 189, and the initial concentration of ester links ( $A$ ) as 376.

It is now possible to determine the rate of the reactions. From the IV results in Tables 1 and 2, the value of  $x$  can be determined using Eq. (6). This allows  $\log \frac{A}{A-x}$  to be plotted against time, which is done for both polymers in Figs. 4 and 5. The results are reasonably close to a straight line in all cases, and this allows the value of  $k_1$  to be calculated. These values are given in Table 4.

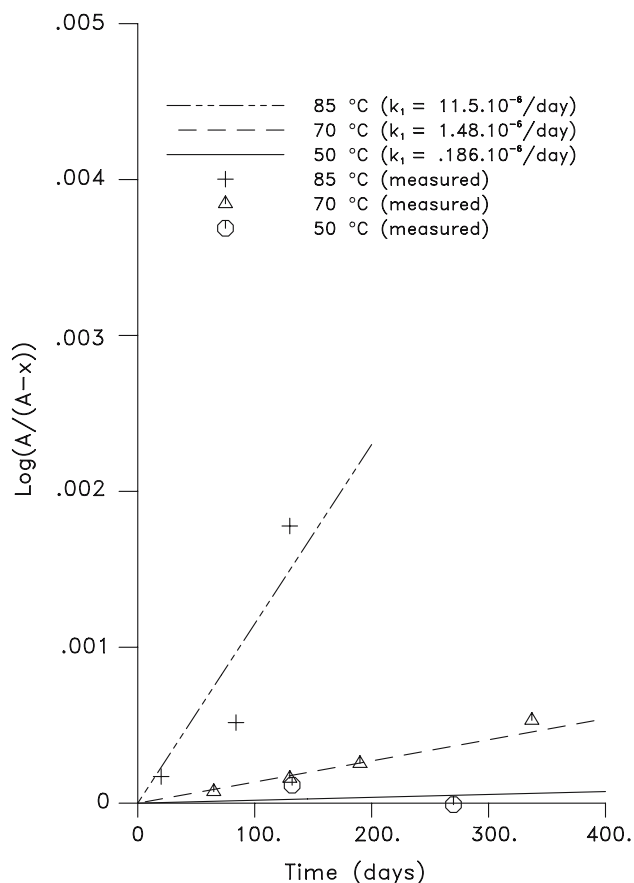
#### Effect of temperature

The rate of reaction can be expected to follow the Arrhenius equation, which is expressed in terms of the activation energy  $E_a$  and the absolute temperature ( $T$ ).

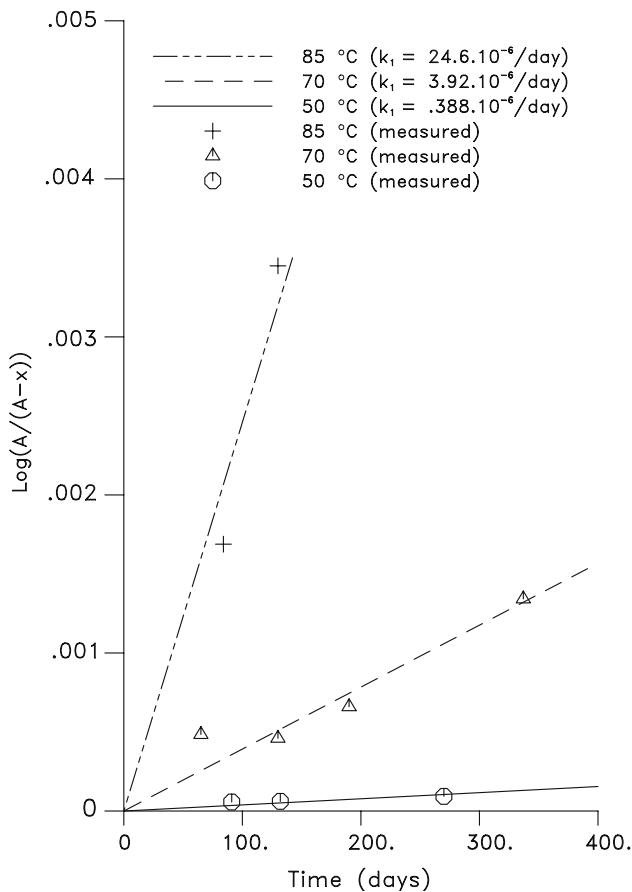
$$k_1 = C \cdot e^{-\frac{E_a}{RT}} \quad (11)$$

where  $R$  is the gas constant (8.314 J/mol K). This can be rearranged to give

$$\log(k_1) = \log C - \frac{E_a}{2.303RT} \quad (12)$$



**Fig. 4** Rate of chain scission for PET1



**Fig. 5** Rate of chain scission for PET2

Figure 6 shows a plot of  $\log(k_1)$  against  $1/T$  for both polyesters, from which the following relationships can be obtained.

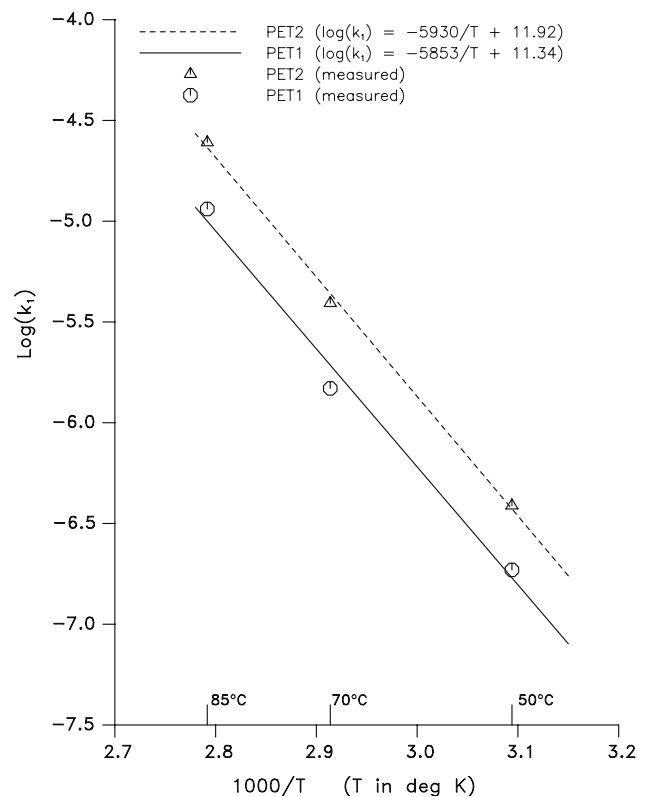
$$\log(k_1) = -\frac{5853}{T} + 11.34 \quad (\text{for PET1}) \quad (13)$$

$$\log(k_1) = -\frac{5930}{T} + 11.92 \quad (\text{for PET2}) \quad (14)$$

These equations correspond to activation energies of 112.7 kJ/mol for PET1 and 113.3kJ/mol for PET2. These values compare well with values of 109 kJ/mol quoted by McMahon et al. [1] and 113 kJ/mole quoted by Davies et al. [9].

**Table 4** Rates of reaction

Temperature (°C)	$k_1$ for PET1 (1/day) $\times 10^{-6}$	$k_1$ for PET2 (1/day) $\times 10^{-6}$
50	0.186	0.388
70	1.480	3.920
85	11.50	24.60



**Fig. 6** Effect of temperature on hydrolysis of polyester

It should be noted that the results at 85 °C, which is above the glass transition temperature for polyester, appear to be consistent with the values obtained at lower temperatures.

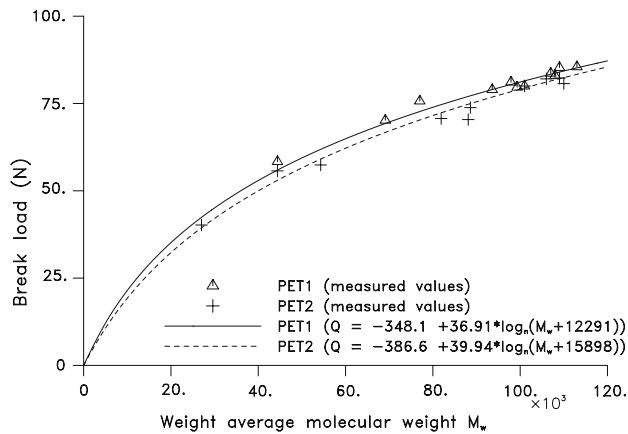
#### Relationship between strength and molecular weight

The data in Tables 1 and 2 were used to prepare a plot of strength ( $Q$ ) versus  $M_n$  and  $M_w$ . There was considerably more scatter on the plot involving  $M_n$  than on that involving  $M_w$ . Various non-linear regression analyses were carried out on both plots for both materials, and it was finally concluded that the best fit was obtained when a logarithmic expression was used on  $M_w$ , with separate functions for the two materials.

The relatively small amount of data for low molecular weights caused some problems, so an additional data point giving zero strength at zero  $M_w$  was added, and additional weight was given to the control tests, for which more test data was available. The extra data point at  $M_w = 0$  could be removed later if more test data becomes available at low  $M_w$ .

The test data and the best fit curves are shown on Fig. 7; the equations for the best fit lines are





**Fig. 7** Break load and  $M_w$

$$Q = -348.065 + 36.910 \cdot \log_n(M_w + 12291) \quad (\text{PET1}) \tag{15}$$

$$Q = -386.647 + 39.943 \cdot \log_n(M_w + 15898) \quad (\text{PET2}) \tag{16}$$

These data are in Newtons for a 1,100 decitex yarn.

**Prediction of strength for given time and temperature**

It is now possible to combine these various results to give a method of predicting strength under different circumstances. One further observation is however needed.

The progress of the reaction is measured by the number of ester links broken ( $x$ ), which is defined by Eq. (5) in terms of the number average molecular weight. However, the relationship between strength and molecular weight is between  $Q$  and  $M_w$ . Thus, it is necessary to rewrite Eq. (5) in terms of  $M_w$ . It was observed above that  $M_w$  and  $M_n$  can be considered to be linearly related, at least to the extent that can be reasonably deduced from the scatter.

Thus, it is reasonable to write

$$x = \frac{M_{w0}}{M_{wt}} - 1 \tag{17}$$

Such an observation has corollaries for the way chain scission takes place, since it implies that the chain scission preserves the relative proportions of light and heavy species within the sample, rather than preferentially cutting off individual units from the end of the chain. Hydrolytic attack is located randomly. This is confirmed by observing Fig. 3, in which the values of  $M_n$  and  $M_w$  obtained by GPC testing are in an approximately constant ratio.

The steps needed to determine  $Q$ , given  $t$  and  $T$  are given in the Table 5. Each of these steps is separately invertible, so the same principles can be used to determine any one of  $Q$ ,  $t$  or  $T$  if the other two are known.

Figures 8 and 9 show test results for PET1 and PET2, together with the predictions of this method, for all three temperatures tested. Confidence intervals are shown for the test results at the 95% level. There is reasonable, but not exact, agreement; the method does seem to give results which are sufficiently accurate for sensible predictions about lifetimes to be made.

**Predictions of strength loss with time**

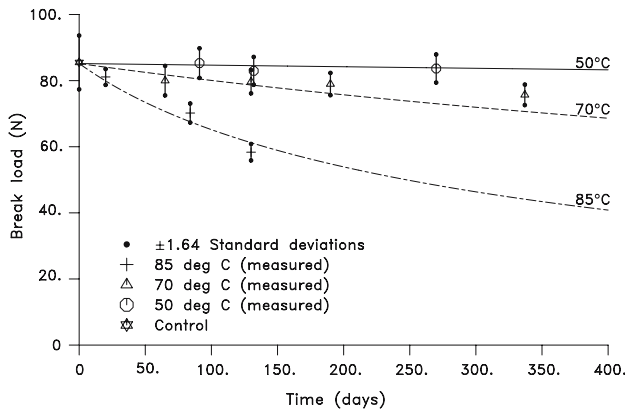
The method given in the preceding section has been used to predict loss of strength with time at various temperatures. Figures 10 and 11 show the time for the strength to drop to a given proportion of the short-term strength for the two materials at different temperatures. It can be seen that there is a large difference between the fairly rapid loss of strength at high temperature, and the much lower loss at ambient temperature. The lines have the same slope because the activation energies for the two polyesters are similar, but the PET1 curves are higher because the rate of hydrolysis is lower. The curves do not guarantee that the fibres will have very long lifetimes in all circumstances, but they do show that deterioration due to hydrolysis is unlikely to be a problem.

Table 6 presents the same results for two chosen temperatures. The value of 20°C represents a reasonable figure for an average temperature in temperate latitudes, and it is clear that no significant hydrolysis

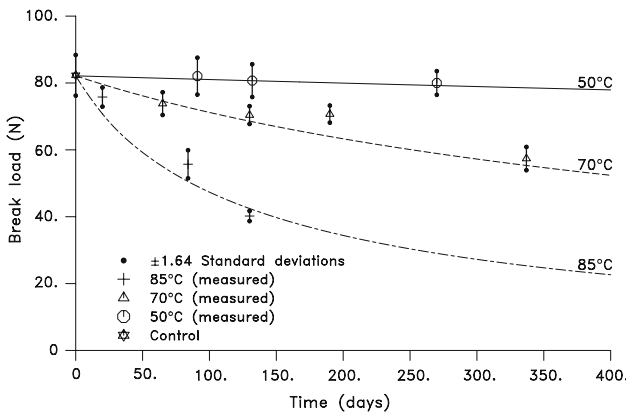
**Table 5** Calculation of residual strength given time and temperature

Step	PET1	PET2
Calculate rate $k_1$	$k_1 = 10^{(11.34-5853/T)}$	$k_1 = 10^{(11.92-5930/T)}$
Calculate No. of scissions	$x = A \left( 1 - \frac{1}{10^{k_1 t}} \right)$ ( $A = 376$ )	
Calculate $M_w$	$M_w = \frac{113000}{(x+1)}$	$M_w = \frac{109000}{(x+1)}$
Calculate break load	$Q = -348.1 + 36.91 \times \ln(M_w + 12291)$	$Q = -386.6 + 39.94 \times \ln(M_w + 15898)$



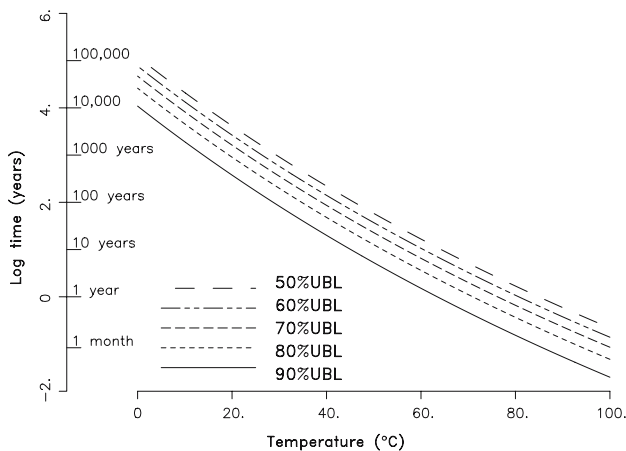


**Fig. 8** Break load for PET1

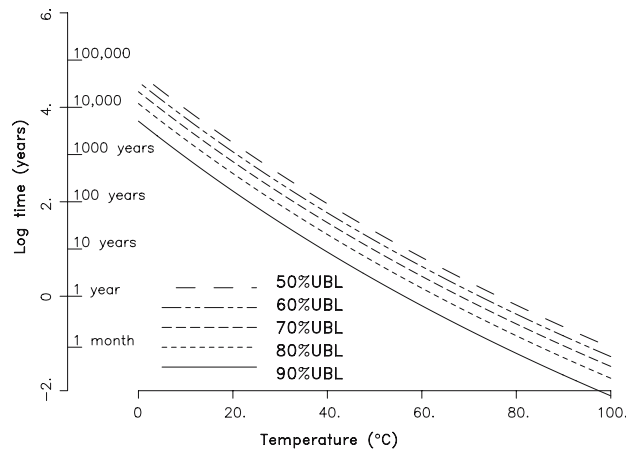


**Fig. 9** Break load for PET2

will occur for either fibre during reasonably foreseeable lifetimes. However, it must be remembered that temperatures quoted in weather reports are shade temperatures, and significantly higher temperatures will occur in the tropics, especially when ropes are exposed. The figures for 40 °C show that for long-



**Fig. 10** Residual strength of PET1



**Fig. 11** Residual strength of PET2

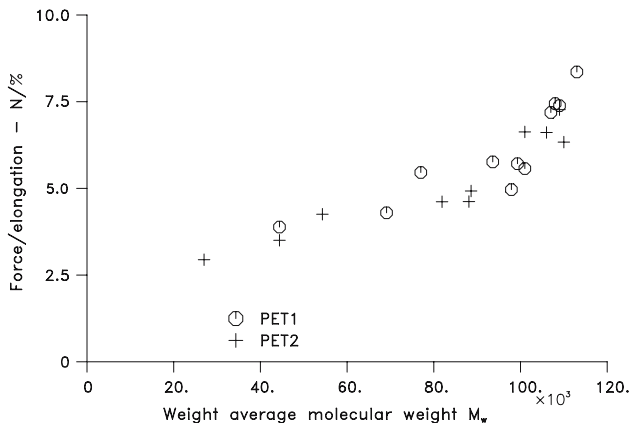
term applications in exposed locations, there is a significant advantage from a fibre with lower CEG, such as PET1.

**Change in modulus**

The elongation at failure was measured in all strength tests. They clearly show (Tables 1 and 2), that the elongation increases as hydrolysis occurs. It is reasonable to suppose that the loss of stiffness is related to the molecular weight, as is the strength. Figure 12 shows the strength divided by elongation at failure, which can be regarded as an equivalent elastic modulus, against the molecular weight. The modulus reduces non-linearly as hydrolysis takes place, with similar results for both PET1 and PET2. This diagram takes no account of any change in shape of the load deflection curve which was not recorded in the tests, and it should be pointed out that many other factors can affect the stiffness of the fibres, such as temperature and

**Table 6** Retained strength at 20 and 40 °C

Temperature (°C)	Strength %UBL	Time (years)	
		PET1	PET2
20	90	390.6	188.2
	80	933.7	429.0
	70	1,681	756.6
	60	2,738	1,216
	50	4,297	1,889
40	90	20.67	9.58
	80	49.40	21.8
	70	88.90	38.5
	60	144.9	61.9
	50	227.3	96.2



**Fig. 12** Stiffness versus molecular weight

moisture uptake, which were not altered in the present study.

The reduction in apparent modulus may well be accounted for by other factors, such as changes in fibre properties which are known to take place. These include relaxation due to dry heat or changes in length due to moisture uptake. A more comprehensive study of these effects, which would require monitoring the change in length through the different processes, is required before a complete description of the phenomena can be given.

**Loaded samples in water**

Tables 7 and 8 give the results of tensile strength tests carried out on specimens that had been held under load at 70°C. Chemical tests have not been carried out on these specimens. These results are plotted on Figs. 13 and 14, together with the data for relaxed samples.

**Table 7** Retained strength of loaded samples of PET1 at 70 °C

Load level %UBL	Time days	Tensile strength		Elongation	
		Average %UBL <sup>a</sup>	CoV (%)	Average (%)	CoV (%)
Control	–	100.00	1.4	10.63	5.6
20	36	98.42	4.4	9.16	4.4
	146	95.07	2.9	8.42	5.5
30	75	92.90	2.9	9.66	2.2
	139	91.46	3.4	8.91	4.2
	198	90.49	3.4	9.32	5.0
	350	86.28	2.5	6.60	3.5
40	90	96.63	3.5	9.00	3.2
	272	91.45	2.4	7.42	2.8

<sup>a</sup> Average of 10 tests. UBL = 83.1 N

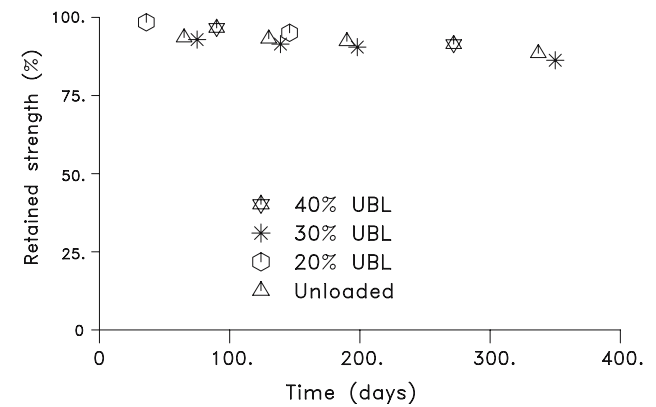
**Table 8** Retained strength of loaded samples of PET2 at 70 °C

Temperature (°C)	Time days	Tensile strength		Elongation	
		Average %UBL <sup>a</sup>	CoV (%)	Average (%)	CoV (%)
Control	–	100.00	3.4	11.55	4.1
20	36	98.52	2.4	9.83	3.2
	146	86.10	5.2	8.00	6.8
30	126	82.78	4.0	9.08	7.2
	191	80.78	3.7	8.96	5.4
40	250	77.86	5.9	7.74	6.5
	90	90.04	4.9	9.49	4.7
	272	78.72	4.6	5.91	6.0

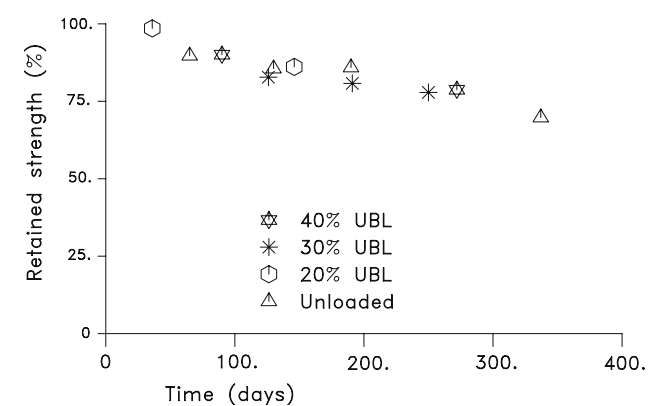
<sup>a</sup> Average of 10 tests. UBL = 81.3 N

There is a marginal increase in strength of the loaded samples over the unloaded ones, but there is significant scatter, and for practical purposes it does not appear as though the rate of hydrolysis is affected by the loading.

The significant difference between the loaded and the unloaded samples occurs in the elongation at break. This is lower for the loaded samples, which may



**Fig. 13** Retained strength of loaded PET1 at 70 °C



**Fig. 14** Retained strength of loaded PET2 at 70 °C

be attributed to the fact that some extension has already occurred due to polymer chain realignment while the samples were under load, although this was not measured in the tests.

The process being observed here may be analogous to that of hot stretching yarns, which has the effect of increasing the length of the yarns, while decreasing the elongation at break for subsequent loading. As with the unloaded samples, this is an aspect that needs further study.

**Samples in chemical solutions**

Tables 9 and 10 give the results of tensile strength tests on the polyesters after they have been held in various chemical solutions at 70 °C. The Ca(OH)<sub>2</sub> solution was not entirely sealed against the air, and it is believed that it largely converted to CaCO<sub>3</sub>. The pH could not be raised above 9, despite the presence of undissolved

**Table 9** Retained strength of PET1 in chemical solutions at 70 °C

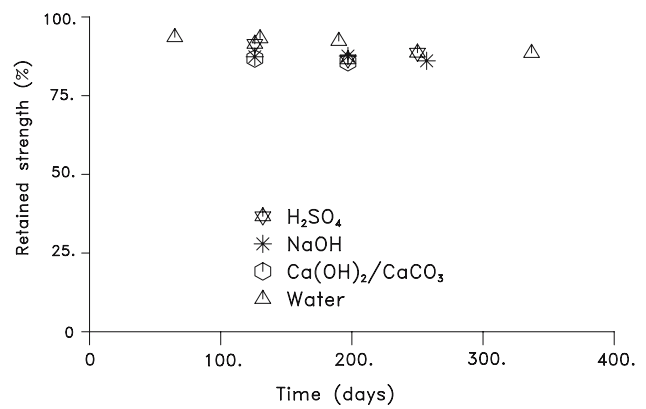
Temperature (°C)	Time days	Tensile strength		Elongation	
		Average %UBL <sup>a</sup>	CoV (%)	Average (%)	CoV (%)
Control	–	100.00	2.93	10.36	5.90
Ca(OH) <sub>2</sub> and CaCO <sub>3</sub>	126	86.77	5.12	14.04	4.56
	197	85.60	2.87	13.31	2.76
NaOH	126	87.35	8.71	13.84	6.10
	197	87.58	3.88	13.89	4.56
	257	86.06	4.49	13.83	4.04
H <sub>2</sub> SO <sub>4</sub>	126	91.45	2.56	14.23	3.11
	197	86.53	4.06	13.87	4.23
	250	88.64	3.70	14.19	3.50

<sup>a</sup> Average of 30 tests. UBL = 85.4 N

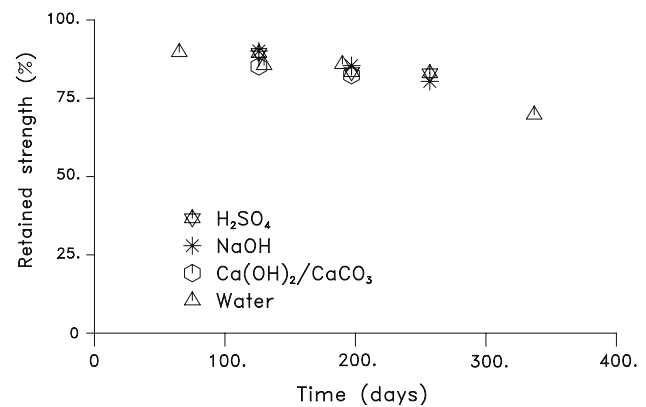
**Table 10** Retained strength of PET2 in chemical solutions at 70 °C

Temperature (°C)	Time days	Tensile strength		Elongation	
		Average %UBL <sup>a</sup>	CoV (%)	Average (%)	CoV (%)
Control	–	100.00	2.93	11.16	4.57
Ca(OH) <sub>2</sub> and CaCO <sub>3</sub>	126	85.17	2.30	15.49	3.26
	197	82.35	8.33	14.42	6.44
NaOH	126	90.07	2.31	14.68	2.88
	197	85.42	2.15	14.98	2.87
	257	80.39	1.98	14.52	2.72
H <sub>2</sub> SO <sub>4</sub>	126	89.46	2.33	15.49	1.79
	197	83.33	3.53	14.53	3.96
	257	82.97	2.07	15.06	2.57

<sup>a</sup> Average of 30 tests. UBL = 81.6 N



**Fig. 15** Retained strength of PET1 in solution at 70 °C



**Fig. 16** Retained strength of PET2 in solution at 70 °C

crystals. This will mirror the behaviour in the ground where Ca(OH)<sub>2</sub> is almost never present due to its high reactivity with CO<sub>2</sub> and salts present in the ground.

The NaOH solution was held at pH11, and the H<sub>2</sub>SO<sub>4</sub> solution was held at pH4. There were no difficulties in maintaining these chemical solutions.

Figures 15 and 16 show these results together with the corresponding results of relaxed samples in water. There is no significant difference between the strength of fibres in water and those in chemical solutions. The strain capacities were also very similar to those of the unloaded samples.

**Discussion**

The results of the hydrolysis tests on polyester samples show measurable rates of change in strength at temperatures of 85, 70 and 50 °C. These results have been combined with the results of chemical tests to give a consistent method of predicting loss of strength after immersion in water at different temperatures for different lengths of time.

At ambient temperature, there will be little loss of strength for several centuries. PET1 polymer is seen to be about twice as resistant to hydrolysis as PET2. Both fibres show similar activation energies, which implies that the same mechanism occurs, but the rate of reaction appears to vary with the CEG concentration.

The application of tensile force to the specimens does not appear to have a measurable effect on the strength, nor does replacing water with mild solutions of acid or alkali.

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## References

1. McMahon W, Birdsall HA, Johnson GR, Camilli CT (1959) *J Chem Eng Data* 4(1):57
2. Risseuw P, Schmidt HM (1990) Hydrolysis of HT polyester yarns in water at moderate temperature. In: Proceedings of the 4th international Conference on Geotextiles, Geomembranes and related products, Balkema, vol 2, The Hague, Netherlands, pp 691–696
3. Ravens DAS, Ward I (1961) *Trans Faraday Soc* 57:150
4. Furrer E (1958) *Text-Rundsch* 13:129
5. Ludewing H (1964) *Polyester fibres, chemistry and technology*, Wiley Interscience
6. Chapatawala MN (1988) *Colourage* 33(26):26
7. Merii AL (1992) Durability of polyester and aramid yarns in aqueous solutions. PhD Thesis, University of London
8. Miller M (1968) *The structure of polymers*, Reinhold
9. Davies T, Goldsmith Pt, Ravens DAS, Ward IM (1962) *J Phys Chem* 66:175