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Effect of applied stress on the alkaline hydrolysis of geotextile poly(ethylene terephthalate). Part 1: room temperature

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Abstract

A study has been made of the effect of an imposed tensile stress on the rate of hydrolysis of geotextile grade polyester in aqueous sodium hydroxide solution at room temperature. Weight losses of samples stressed with loads up to the yield point were virtually the same as for relaxed samples. For stresses which exceeded the yield point, significantly larger weight losses were obtained, particularly at longer reaction times. The mechanical properties of the filaments, particularly tenacity, breaking strain and work of rupture, were reduced as the imposed stress increased, and very severe losses in properties were observed when the stress exceeded the yield stress. Scanning electron microscopy revealed that, at the highest stresses studied, surface cracking occurred, which became progressively more severe as the time of treatment increased. An empirical equation was obtained which showed that the breaking load of the filaments decreased proportionally with time and with the square of the imposed stress.

Keywords: Geotextile; Polyester; Hydrolysis

1. Introduction

The alkaline hydrolysis of poly(ethylene terephthalate) [PET] yarns was first described by Waters [1] in 1950. Since then, numerous studies have been reported and reviews of the topic have appeared [2,3]. It is generally agreed that aqueous sodium hydroxide solutions only attack the surface of PET fibres so that the fibre diameter decreases as the hydrolysis proceeds. Whilst the breaking load of the fibre falls as the cross-section area decreases, the tenacity of the fibres is generally maintained. Use has been made of this reaction in textiles to produce lightweight fabrics and to modify the surface of the fibres [4–10].

The use of PET in geotextile applications has raised the question of the effect of alkali on the long term durability of PET [11–13], and some have recommended that PET geotextiles should not be used where the ground has a pH ≥ 9 [14]. The present study was undertaken to investigate the susceptibility of geotextile grade PET to aqueous alkaline attack and, in particular, to determine the effect of an applied stress on the rate of surface hydrolysis. Similar studies on the rate of oxidation of polypropylene [15] and the rate of oxidation of nylon [16] have been reported, and in each case, the effect of applied stress has been to accelerate the rate of breakdown. As we completed our study, we found that there was, in fact, recently published work showing that the alkaline hydrolysis of PET was also accelerated by an applied stress [17]. Our results confirm this earlier report and give more details of the magnitude of the effect.

2. Experimental

2.1. Materials

Two different PET yarns were investigated: Trevira type 730, 1100dtex f 200 with a tenacity of 74 cN/tex, coded as PET1; and a Tergal type 156, 1100dtex f 192 with a tenacity of 80 cN/tex, coded as PET2. The yarns were used as supplied. Solutions of sodium hydroxide (AR grade) were made up in distilled water and stored in plastic bottles; concentrations were determined by titration with potassium hydrogen phthalate.

2.2. Hydrolysis procedure

Two-metre lengths of yarn were wound around a hollow stainless steel tube (16 cm long, 1 cm diameter); at one end of the tube the yarn was tied, through a hole, while the other end of the yarn was attached to various loads (100, 500,

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Table 1
Weight loss data for hydrolysis in 10.1% NaOH at room temperature

Load on fibre g (MPa)	Weight loss%[a]					
	10 day		20 day		30 day	
	PET1	PET2	PET1	PET2	PET1	PET2
0	11.4	10.1	22.0	21.9	31.6	33.3
100(12.3)	12.2	10.2	25.4	23.2	35.9	34.1
500(61.5)	11.2	10.1	21.1	23.0	34.1	34.4
1000(123)	11.4	11.1	22.0	23.7	34.3	33.0
1500(184)	12.9	—	—	—	—	—
2000(246)	13.9	12.8	20.2	26.7	45.9	54.4

[a] Duplicate values vary by ± 1.7%

1000, 1500 and 2000 g). The yarn, whilst under the applied load, was then carefully wound onto the tube; the yarn sample was then secured by wrapping several turns around a screw which was then tightened in a hole at the other end of the tube, to maintain the applied stress. Such samples were then immersed in 85 ml samples of the alkali in polypropylene dyeing tubes and shaken periodically. Room temperature was monitored and varied between 20 and 23°C. This procedure gave initial stresses of 12.3, 61.5, 123, 184 and 246 MPa, respectively, which would reduce during the experiment as some degree of stress relaxation would occur. For PET1, the corresponding percentages of the ultimate stress were 1.2, 6.0, 12.0, 18.0 and 24.1, respectively.

After hydrolysis, samples were soaked in water for 5 min and then immersed in 100 ml of 0.1% HCl for 10 min; final washing in water was continued until the pH was neutral. Treated yarns were allowed to dry at room temperature for 48 h and then weight losses were measured.

2.3. Mechanical measurements

The mechanical properties of individual filaments taken from treated yarns were determined on an Instron 1026 universal tester with the series ÌX test method. The crosshead speed was 50 mm/min, the 500 g load cell was used and full scale load was 100 g. Fibre samples were first glued on cardboard squares with an inner dimension of 20 mm and then the framed fibres were clamped in the tester at a 20 mm gauge length. Prior to testing, all fibres were conditioned at 20 ± 2°C and 65 ± 2% relative humidity for at least 48 h; at least 20 specimens of each sample were tested, and their average values and standard deviations were obtained. Breaking load, tenacity, breaking strain, work of rupture and Young's modulus were all measured.

The breaking load of the yarns was also measured on the Textechno Statimat, using a gauge length of 100 mm, a 100 N load cell and a test speed of 50 mm/min.

2.4. Scanning electron microscopy

Samples were examined on a Cambridge Sterioscan S360 connected to a Quantimet 570 Image Analyser. Samples were coated with gold before examination.

3. Results and discussion

3.1. Weight loss measurements

Table 1 shows the weight loss data for both PET samples, subjected to hydrolysis in 10.1% aqueous sodium hydroxide

Table 2
Breaking load data of PET1 treated at room temperature at different stress levels, 10.1% NaOH

Load on fibre g (MPa)	Treatment time (day)					
	10		20		30	
	Breaking load (cN)	Breaking load loss (%)	Breaking load (cN)	Breaking load loss (%)	Breaking load (cN)	Breaking load loss (%)
Control filament	48.6(± 3.2)	—	48.6(± 3.2)	—	48.6(± 3.2)	—
0(0.00)	40.9(± 2.4)	16.4	35.9(± 4.1)	26.1	30.2(± 2.5)	37.9
100(12.3)	38.2(± 3.1)	21.4	27.6(± 3.4)	43.3	27.4(± 1.9)	43.7
500(61.5)	37.8(± 4.2)	22.1	28.3(± 3.5)	41.8	24.9(± 4.1)	48.7
1000(123)	33.8(± 3.6)	30.4	29.1(± 3.1)	40.1	21.7(± 3.9)	55.4
1500(184)	26.9(± 6.7)	44.6	—	—	—	—
2000(246)	16.7(± 5.2)	65.7	7.3(± 2.7)	85.0	*D	*D

*D = degraded sample
Standard deviations in parentheses

Table 3
Breaking strain data of PET1 treated at room temperature at different stress levels, 10.1% NaOH

Load on fibre g (MPa)	Treatment time (day)					
	10		20		30	
	Breaking strain(%)	(%) Loss in breaking strain	Breaking strain(%)	(%) Loss in breaking strain	Breaking strain(%)	(%) Loss in breaking strain
Control filament	21.1(± 1.1)	—	21.1(± 1.1)	—	21.1(± 1.1)	—
0(0.00)	18.4(± 1.3)	12.8	17.7(± 1.0)	16.2	16.2(± 1.8)	23.1
100(12.3)	16.5(± 1.5)	21.9	13.5(± 0.8)	36.0	15.4(± 0.7)	26.8
500(61.5)	15.0(± 1.1)	28.9	13.3(± 1.2)	36.6	13.3(± 1.0)	36.8
1000(123)	13.5(± 2.2)	36.1	13.4(± 1.5)	36.3	11.7(± 1.7)	44.3
1500(184)	11.4(± 2.0)	45.8	—	—	—	—
2000(246)	8.7(± 2.0)	58.5	5.7(± 1.5)	73.2	*D	*D

*D = degraded sample
Standard deviation in parentheses

for up to 30 days at room temperature under the different loads applied. Very similar results were observed for both yarns and the weight loss was approximately linear with time at a rate of 1% day^{-1} for the relaxed yarns and those with a stress of up to 123 MPa (equivalent to 1 kg load). For the highest stressed samples (246 MPa), greater weight losses were observed, which were particularly significant after 30 days. The linear weight loss–time behaviour is commonly seen in studies of the alkaline hydrolysis of PET and is not remarkable [2]. The higher weight losses at the highest applied stress suggested that the rate of attack of the aqueous sodium hydroxide on the surface of the PET must be accelerated by the applied stress, as was the appearance of these samples after the 30 day treatment. There were many broken filaments in the samples which had also delustred; the significance of this latter observation became apparent when SEM studies were carried out.

3.2. Mechanical properties

Table 2 shows the changes in breaking load as a function of time of hydrolysis and applied load (expressed as both load in grams and applied stress) for PET1. Very similar data, not reported here, were observed with PET2 and will be reported elsewhere [18]. For the unstressed samples, the decrease in breaking load was approximately linear with time. The effect of an applied stress is to increase the loss in breaking load in all cases. At low stress levels (up to 123 MPa), the effect of increasing the applied stress was small; between 123 and 246 MPa, the loss in breaking load was doubled for the 10 and 20 day samples. Given the magnitude of this effect, it is not surprising that the highest stressed samples failed to survive 30 days hydrolysis; no measurements were made of these samples in view of the large number of broken filaments.

The percentage loss in the breaking load of PET fibres in aqueous sodium hydroxide is usually equal to the percentage weight loss or, at most, up to twice this value [19]. The data for the PET1 samples show percentage losses in breaking load of no more than about twice the percentage loss in weight, except for the two most heavily stressed samples, those at 184 and 246 MPa. It seemed that, for the most heavily loaded samples, the alkaline hydrolysis reaction could no longer be viewed as a surface reaction; under these stressed conditions, some internal hydrolysis must have been occurring. Calculation of the tenacity changes (not given) from the breaking load and the weight loss

Table 4
Work of rupture data of PET1 treated at room temperature at different stress levels, 10.1% NaOH

Load on fibre g (MPa)	Treatment time (day)					
	10		20		30	
	Work of rupture (N.cm)	(%) Loss in work of rupture	Work of rupture (N.cm)	(%) Loss in work of rupture	Work of rupture (N.cm)	(%) Loss in work of rupture
Control filament	10.9(± 1.3)	—	10.9(± 1.3)	—	10.9(± 1.3)	—
0(0.00)	7.6(± 1.0)	30.2	6.2(± 1.1)	43.1	4.7(± 0.6)	56.4
100(12.3)	5.9(± 1.1)	46.3	3.1(± 0.6)	71.1	3.7(± 0.5)	66.1
500(61.5)	5.1(± 0.9)	53.3	3.3(± 0.8)	69.9	2.9(± 0.7)	73.8
1000(123)	4.2(± 1.5)	61.6	3.5(± 0.8)	68.1	2.3(± 0.7)	79.0
1500(184)	2.9(± 1.3)	73.3	—	—	—	—
2000(246)	1.3(± 0.6)	87.9	0.4(± 0.3)	96.2	*D	*D

*D = degraded sample
Standard deviation in parentheses

Table 5
Modulus data of PET1 treated at room temperature at different stress levels, 10.1% NaOH

Load on fibre g (MPa)	Treatment time (day)					
	10		20		30	
	Modulus (cN/tex)	(%) Loss in modulus	Modulus (cN/tex)	(%) Loss in modulus	Modulus (cN/tex)	(%) Loss in modulus
Control filament	758(± 48.5)	—	759(± 48.5)	—	759(± 48.5)	—
0(0.00)	800(± 32.1)	− 5.5	779(± 70.5)	− 2.8	763(± 62.1)	− 0.6
100(12.3)	754(± 55.4)	0.7	731(± 68.9)	3.6	743.8(± 39.7)	1.9
500(61.5)	780(± 68.9)	− 2.9	741(± 47.2)	2.4	735(± 83.3)	3.1
1000(123)	755(± 58.9)	0.5	741(± 36.8)	2.3	718(± 53.7)	5.4
2000(246)	582(± 78.5)	23.3	550(± 116.6)	27.5	*D	*D

*D = degraded samples
Standard deviations in parentheses

data show percentage reductions smaller than the reductions in breaking load for the relaxed and least stressed samples. Strictly speaking, if the attack of sodium hydroxide was restricted to the surface of the filaments, the tenacity should remain constant; in practice, small reductions of 5–10% in tenacity are commonly observed [2,4,5,20,21]. But for the highest loaded samples, the percentage changes in both tenacity and breaking load are very similar, and are no longer compatible with the concept of a surface hydrolysis process. Indeed, as will be shown later, surface cracks occur on the fibres under the heaviest loads.

Table 3 shows the changes in breaking strain. Again, the pattern of behaviour is similar to that observed with the breaking load, i.e. increasing the applied stress increases the percentage loss in breaking strain with the largest effect being noted at the highest stress used. The breaking strain of the filaments falls to 25% of the original after 20 days hydrolysis at 246 MPa. Much the same effects are seen in the work of rupture data given in Table 4, where the magnitude of the losses in work of rupture are greater than in the earlier tables due to the combined effect of reductions in both tenacity and extension at break.

By contrast, there are no significant changes in filament modulus except for the highest stressed samples, as Table 5 shows. All the data so far shown were obtained with 10.1% aqueous sodium hydroxide; such a high concentration is clearly unrealistic for a geotextile situation. Accordingly, some experiments were carried out using more dilute sodium hydroxide, 1.0%, to see if the effect of load could still be detected. The weight losses observed and the changes in mechanical properties are shown in Tables 6 and 7 for samples treated in 1.0% aqueous sodium hydroxide for 120 days at room temperature. Under relaxed conditions, the reduction in breaking load was essentially negligible, while the breaking strain and work of rupture actually increased by about 10%. Under the heaviest loading, the tenacity of the PET fell by almost 25% and the work of rupture by 40%. The effect of applied stress is very clearly significant in more dilute sodium hydroxide solution, with a similar pattern of behaviour to that seen earlier.

3.3. Scanning electron microscopy

On SEM examination, the original PET filaments show a smooth, featureless surface typical of a melt spun yarn. Visual observation of the degraded samples indicated that the most heavily stressed samples (at 184 and 246 MPa) became progressively delustred as the time of hydrolysis increased, in contrast to the other samples which remained more or less lustrous. SEM examination showed the reasons for this, as shown in Figs 1 and 2. The first figure shows the surface of PET1 after 10 days hydrolysis in 10.1% alkali under a 2 kg load, corresponding to a weight loss of about 14% and a breaking load reduction of about 66%. The surface of the fibre is a mass of cracks of varying lengths and widths. The reason for the delustring of the fibres and the large fall in breaking load was now apparent.

Table 6
Weight loss, breaking load and tenacity data of PET1 treated at room temperature, 120 days treatment at different stress levels, 1.0% NaOH

Load on fibre g (MPa)	Property changes				
	Weight loss(%)	Breaking load (cN)	Breaking load loss(%)	Tenacity(cN/tex)	Tenacity loss(%)
Control filament	—	45.9(± 2.8)	—	83.5(± 5.1)	—
0(0.00)	3.75	44.4(± 1.8)	3.3	84.0(± 3.3)	− 0.6
1000(123)	3.81	39.6(± 1.9)	13.8	74.8(± 3.5)	10.4
1500(184)	4.06	37.3(± 2.5)	18.7	70.8(± 4.6)	15.2
2000(246)	4.41	33.7(± 2.7)	26.6	64.2(± 5.0)	23.1

Standard deviation in parentheses

Table 7
Breaking strain, work of rupture and modulus data of PET1 treated at room temperature, 120 days treatment at different stress levels, 1.0% NaOH

Load on fibreg (MPa)	Property changes					
	Breaking strain(%)	Breaking strain loss(%)	Work of rupture N.cm	Work of rupture loss(%)	Modulus(cN/tex)	Modulus loss(%)
Control filament	19.1(± 1.8)	—	9.2(± 1.5)	—	741(± 56)	—
0(0.00)	20.9(± 0.8)	−9.4	10.1(± 0.8)	−9.8	696(± 30)	6.1
1000(123)	18.0(± 1.3)	5.8	7.3(± 0.9)	20.7	648(± 36)	12.5
1500(184)	16.1(± 1.2)	15.1	6.2(± 1.2)	32.6	647(± 58)	12.9
2000(246)	15.8(± 1.0)	17.3	5.4(± 0.9)	41.3	628(± 77)	15.3

Fig. 2 shows the fibre surface after 20 days attack in 10.1% aqueous sodium hydroxide under the same loading; the weight loss was about 26% and the breaking load loss was about 85%. The surface is now so grossly irregular that the filament edge no longer appears linear, and it appears that preferential attack has occurred leaving raised ‘blocks’ of PET. Fig. 3, by contrast, shows the surface of PET1 treated for 30 days in 10.1% aqueous sodium hydroxide under a load of only 1 kg, i.e. at 123 MPa. This fibre shows some shallow pitting but nothing as severe as in Figs 1 and 2; there was a weight loss of 34% and a breaking load loss of 55% and little loss of lustre. Fig. 4 shows the surface of PET1 after treatment in the more dilute sodium hydroxide solution (1%) after 120 days and a 2 kg load; here the weight loss was only 4% but the breaking load loss was 26%. A fine pitting of the surface is present together with some cracking, both causing a delustring effect.

To check that the high stress alone was not causing the fibre surface cracking, samples of PET1 were subjected to a 2 kg load in water at room temperature for 90 days. No surface deterioration could be detected by SEM nor were there any significant changes in the mechanical properties of the filaments. The results clearly indicate that the surface cracks only appeared when the filaments were treated in aqueous sodium hydroxide at the two highest loads used; no cracks appeared on treatment with the alkali alone nor with applied load alone. The yield load of the PET1 yarn was measured and found to be 1.22 ± 0.05 kg, so that the cracking only occurred on samples where the applied load exceeded the yield load. Similar results were obtained with PET2, suggesting that the cracking of the surface may be a characteristic feature of polyester when stressed beyond its yield point in aqueous alkali.

We can only speculate at present on the mechanism of the crack formation. It is known that PET fibres can show pitting when treated with aqueous sodium hydroxide, an effect enhanced when the fibres are delustred with TiO_2 [2,21,22]. Examination of the surface of PET1 after sodium hydroxide treatment under relaxed conditions showed no pitting of the type normally associated with the presence of TiO_2 ; only a few small shallow depressions (1–2 μm long, 0.2 μm wide) and some faint grooves parallel to the fibre axis could be

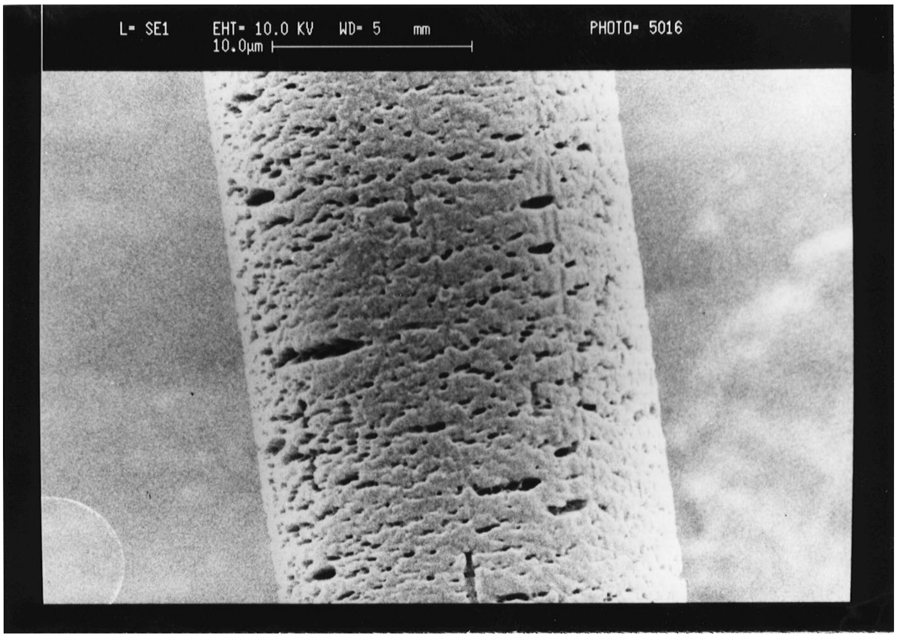

Fig. 1. SEM micrograph of PET1 sample, treated with 10.1% NaOH/10 days/room temp./2 kg load.

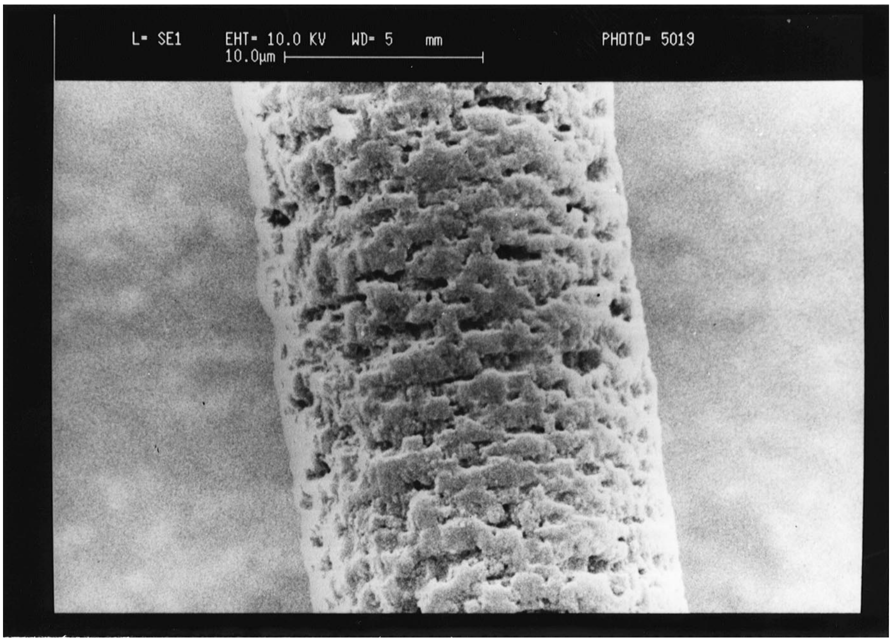

Fig. 2. SEM micrograph of PET1 sample, treated with 10.1% NaOH/20 days/room temp./2 kg load.

seen. The yarns studied were described as bright so that the effect of delustrant can be discounted. It is known that conformational changes occur during the extension of PET yarns and films [23,24], and that beyond the yield point structural rearrangements occur, giving a more oriented structure. It may be that these rearrangements modify the fibre surface, allowing diffusion of the aqueous alkali into the fibre. The highly stressed ester bonds within the structure may then undergo rapid hydrolysis. The smallest areas of attack seen on the surface look like pores about 0.2 μm in diameter, often created close to each other (see Fig. 1). These pores then seem to coalesce to give the cracks. Presumably, as the PET chains undergo hydrolysis, some release of the stress on the chains will occur so that some areas may be slower to react than others. This might be a factor leading to the irregular surface shown in Fig. 2. Cracks on the surface of PET fibres are characteristically seen in many

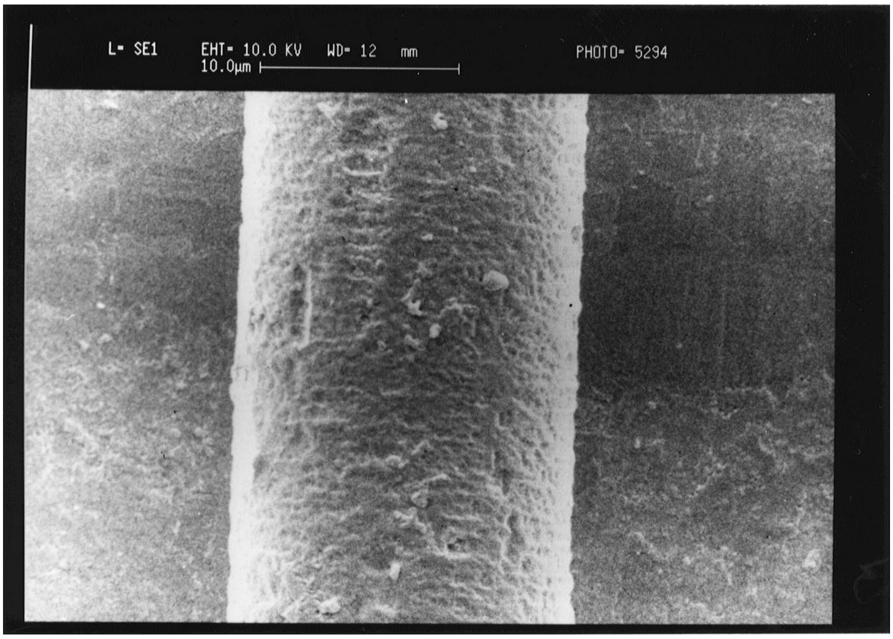

Fig. 3. SEM micrograph of PET1 sample, treated with 10.1% NaOH/30 days/room temp./1 kg load.

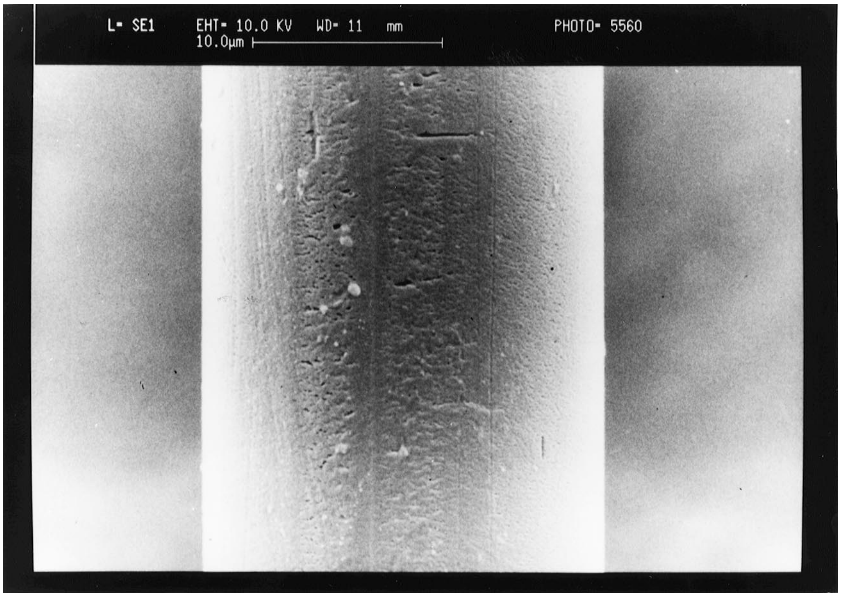

Fig. 4. SEM micrograph of PET1 sample, treated with 1.0% NaOH/120 days/room temp./2 kg load.

aminolysis reactions [2]. However, these are usually continuous transverse cracks which lead ultimately to disc-like residues and are quite distinct from those observed in the present work.

4. Empirical equation

The variation of breaking load with applied load and time was analysed using the SPSS linear regression package, and

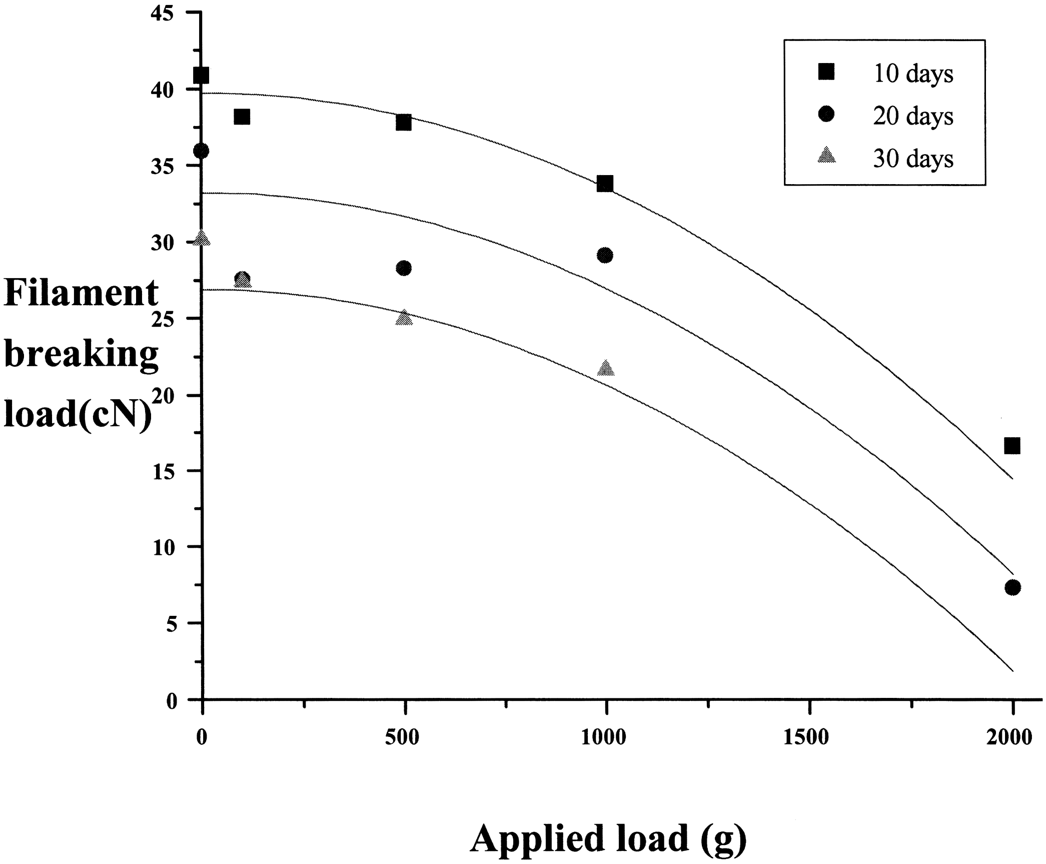

Fig. 5. Relation between applied load and filament-breaking load [curves calculated from equation (1), points experimental], PET1.

a good fit was obtained with Eq. (1), which gives:

$$Y = A - \beta_0 t - \beta_1 L^2 \qquad (1)$$

where $Y =$ filament breaking load (cN); $t =$ treatment time (days); $L =$ applied load (g).

Fig. 5 shows the experimental data and the curves calculated for $A = 45.9$ cN, $\beta_0 = 0.63$ cN day^{-1}, $\beta_1 = 6.26 \times 10^{-6}$ cN g^{-2}. The coefficient of determination R^2 was 0.96 and the standard deviation about the regression was 2.63.

The form of this equation highlights why the filament breaking load is so sensitive to the applied load. It must be emphasized that this equation is purely empirical; however, similar equations were also found to fit the behaviour of PET2 at room temperature and 40°C, and PET1 at 40°C [25]. These data will be reported elsewhere.

5. Conclusions

The present study has revealed that the reaction of aqueous sodium hydroxide with geotextile polyester yarns stretched beyond the yield point leads to surface cracks which significantly reduce the strength of the fibre. The effect of stress on the alkaline hydrolysis thus parallels the effect of stress already observed on the oxidation of both polypropylene [15] and nylon [16]. We had believed that the present study was the first to show the effect of applied stress on the attack of aqueous sodium hydroxide on polyester, until we noted the recent work of Netravali et al. [17]. They also found an accelerated rate of attack when polyester was subjected to alkaline hydrolysis under an applied load, but made no comments regarding surface crack formation. It is difficult to compare their results with those obtained in the present study, as the rate of attack in the unstressed state was much greater than we observed. The present study supports the view that caution should be exercised when polyester geotextiles are being considered for applications where the conditions of use may be alkaline.

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