The Hydrolytic Stability of PET Yarns under Medium Alkaline Conditions

H. M. Schmidt & F. W. T. te Pas
Akzo Nobel Central research, Arnhem, The Netherlands
P. Risseeuw & W. Voskamp
Akzo Nobel Geosynthetics bv, Arnhem, The Netherlands

ABSTRACT: Treatments of PET materials with a saturated solution of calcium hydroxide ($pH \approx 12.5$) have shown the great sensitivity of PET to alkalis under extreme conditions. In nature, however, a soil having a pH higher than 10 is rarely found. Therefore, it is more important for geotextile applications to know the resistance of PET at $pH = 10$ instead of the resistance at $pH = 12$. In an extensive program we have treated PET yarns (Diolen 164 S, Akzo) with a solution of $Ca(OH)_2$ at $pH = 10$ at 50, 70, and 90°C. The rate of hydrolysis was directly compared with the rate of degradation of PET at $pH = 7$ as a reference.

From the experiments the conclusion can be drawn that at a moderate temperature ($T \leq 50°C$) and a $pH \leq 10$ the hydrolysis of PET yarns is brought about by the reaction of PET with water molecules and not by a reaction with OH^- ions. Below 50°C the hydrolysis is not dependent on the pH in the region $7 < pH < 10$.

With the help of the Arrhenius equation a prediction of the time required for a strength reduction of 5% at 10 to 20°C is given.

1. INTRODUCTION

The polymer chains of polyethylene terephthalate (PET) contain ester groups, which can be split by hydrolysis. Two hydrolysis reactions can be distinguished: the reaction with H_2O molecules and the reaction with OH^- ions. Both reactions are totally different. In multifilament PET yarns the reaction with H_2O molecules takes place homogeneously throughout the filament (internal hydrolysis). The reaction is not controlled by the diffusion rate of the H_2O molecules in the PET matrix, but by the kinetics of the hydrolysis reaction. The reaction with OH^- ions takes place only at the filament surface (external hydrolysis). The charge of the ions prevents them from penetrating in the filament.

In the literature the sensitivity of PET materials to media with a high pH ($pH > 11$) is often mentioned[1][2]. However, for geotextiles of PET in natural soils, it is more relevant to know the resistance of the polymer to a pH of 9-10, because in nature, soils with a $pH > 10$ are rarely found[3]. The hydrolytic stability of PET geotextiles at $pH = 9-10$ has been investigated much less profoundly. Jailloux[4] is one of the few authors who gives results of tests at $pH = 9$ and 10, but only at 95°C. He finds that the degradation at $pH = 10$ is not higher than at $pH = 7$.

In an extensive program we have treated high-oriented PET yarn with a solution of $Ca(OH)_2$ at $pH = 10$ and at temperatures of 50, 70 and 90°C. The rate of hydrolysis was directly compared with the degradation rate of the yarn at $pH = 7$, which is used as a reference. Also experiments at $pH = 7$ and 10 with the addition of extra Ca^{++}-ions in the form of $CaSO_4$ were carried out in order to investigate the possible catalytic effect of Ca^{++} ions.

In the tests the length of the yarn samples was kept constant. Thus, the free shrinkage of the samples can be avoided. Shrinkage leads to a change in the physical structure of the yarn, which in turn influences the rate of hydrolysis.

2. YARN USED IN THIS STUDY

The tests were carried out on Diolen® 164 S (Akzo). This is a high-oriented PET yarn used for industrial and geotextile applications. The properties are listed in Table 1.

3. TEST PROCEDURES

3.1. Preparation of samples

The hydrolysis tests were carried out on yarn samples wound on glass spools (spool length 100 mm, outer diameter 60 mm). See Fig 1. Approximately 12 m of yarn was wound from a bobbin onto the glass spool at a low pretension of 150 cN (which corresponds to about 2% of the breaking strength). The wraps on the spool did not overlap. The ends of the yarn sample were attached to knobs on the spool.

The finish was largely removed from the yarn sample by immersing the spool in light petroleum ether for about 1 minute (boiling point 40-60°C). The spools were subsequently dried to the air.
All the tests were carried out with samples from the same bobbin in order to minimize the variation in the results.

Table 1. Properties of Diolen 164 S

Polymer	PET
Diethylene glycol content (%)	0.79
Relative viscosity (1 g/100 g m-cresol, 25°C)	1.77
Mn (number average molecular weight)	25,300
Carboxyl end-group content (meq/kg)	24
Linear density (nominal)	1100 dtex f 210
Twist	Z 130
Tenacity (mN/dtex)	72
Elongation at break (%)	11.6
Hot air shrinkage 4 min. 160°C (%)	2.2
Birefringence	0.1898
Density (kg/m^3)	1401

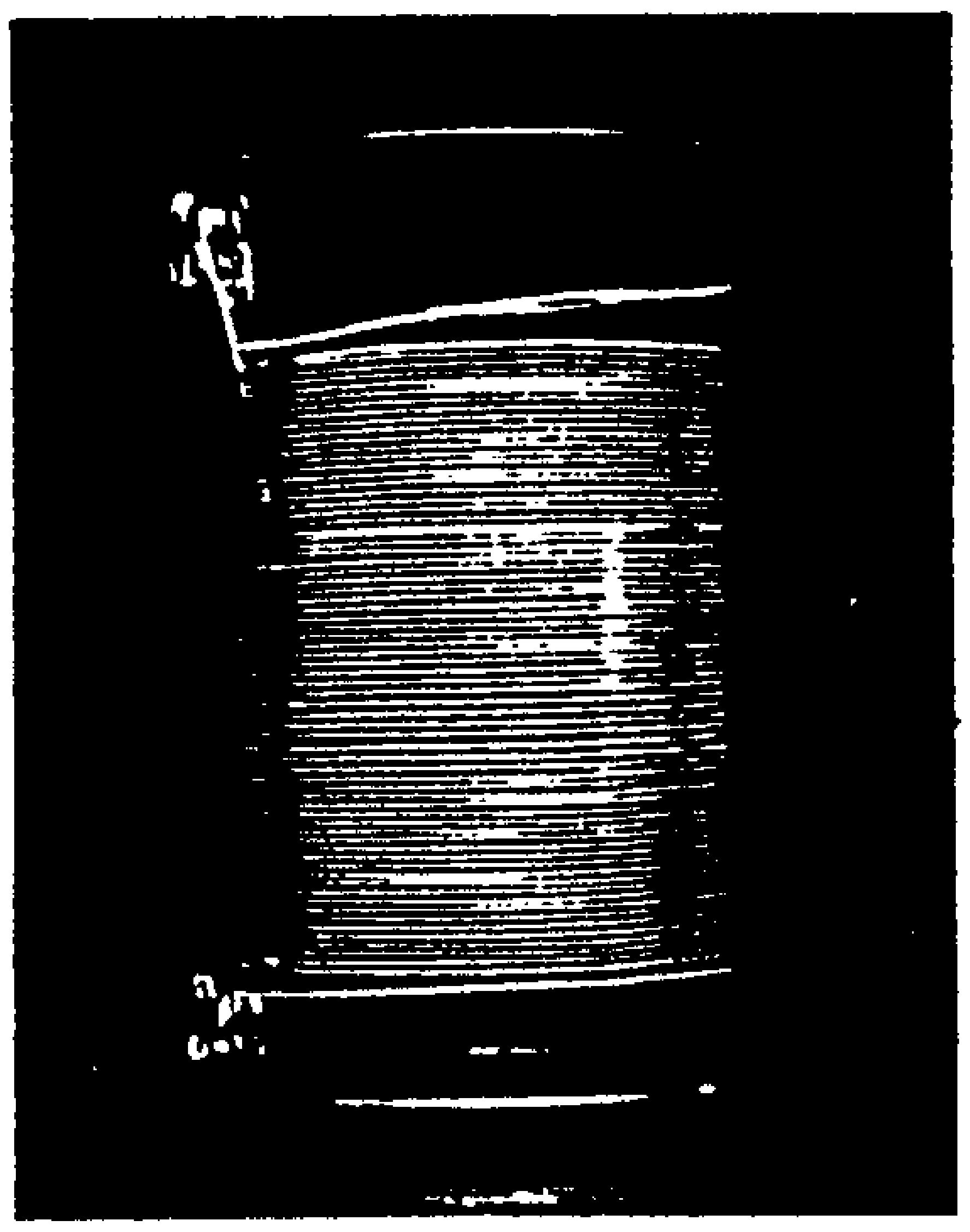

Figure 1. Yarn sample for hydrolysis tests

3.2. Hydrolysis tests

The hydrolysis tests > 100°C were carried out with saturated steam in a 75-litre commercial sterilization autoclave (Varioklav®, type 400 E, vertical).

The hydrolysis tests in water were carried out in small, double-walled 1.7-litre glass vessels. Water or glycol was circulated through the jacket coming from a thermostatically controlled bath. Nitrogen was passed over the liquid in the vessel for the removal of CO_2. The liquid in the vessel was agitated with a magnetic stirrer. Evaporation of water from the vessel was prevented by discharging the N_2 through a reflux condenser.

The water used in the tests was boiled (O_2 removal), demineralized water (Milli-q-water of Millipore). The hydrolysis liquids for the tests at a pH value > 7 were prepared by the addition of a saturated CaO solution (CaO A.R.-Baker) to demineralized water, in an amount such that the desired pH value was reached.

The pH values mentioned apply at room temperature. They were measured every 2 to 3 days and re-set to 10.00 or 11.00 ± 0.02 by adding a calculated amount of a saturated CaO solution. Table 2 lists the average pH values in the vessels in the various tests.

Table 2. Average of pH values

Temperature	Set value	Average actual value
90°C	10.00	9.85
90°C	11.00	10.85
70°C	10.00	9.94
50°C	10.00	9.97

4. MEASUREMENTS

After the prescribed hydrolysis time the glass spool was taken out of the glass vessel or, removed from the autoclave, rinsed with demineralized water and dried by overnight exposure to the air.

4.1. The breaking strength and the elongation at break were determined at 21°C, 65% relative humidity. All the samples were subjected to 5 tensile tests on an Instron Dynamometer (Type 2714-004) with curved clamps and the average strength and elongation as well as standard deviations were calculated. Length between clamps: 500 mm; Rate of specimen extension: 500 mm/min; Pre-tension: 5 mN/tex.

4.2. The linear density of the yarn samples was measured by determining the weight of 1 m of conditioned yarn. The values mentioned are the average results of 3 measurements.

4.3. For measuring the relative viscosity of the PET yarn samples, use was made of m-cresol as solvent or a mixture of trichlorophenol and phenol (TCF/F) 70:100 (parts by weight). Polymer concentration: 1 g PET in 100 g m-cresol or in 125 g TCF/F.

4.4. The distribution of the molecular weight was measured by size exclusion chromatography (SEC). The way this technique is carried out, will be published by our Analytical Department in the Journal of Chromatography.

4.5. For the SEM photomicrographs (Scanning Electron Microscopy) the yarns were prepared in the usual manner. The scans were made with a Philips 505 Scanner Electron Microscope.

5. RESULTS

Table 3 gives an overview of the different hydrolysis tests performed and contains also the measurement results of breaking strength, linear density and relative viscosity of the samples after the hydrolysis tests. Because of the long duration of some tests, the measurements were carried out over a long period. Therefore, in practically each series of measurements, an untreated yarn sample, as a reference, was included. The results of the measurements on the untreated yarn samples are given in Table 4.

Table 3. Properties of Diolen 164 S yarn samples after hydrolysis (> 100°C in saturated steam; < 100°C in water)

Test and sample code	Temp. °C/pH*	Time (days)	Linear density (dtex)	Breaking strength with st. deviation (N)	Rel. visc.	Residual strength (%)
05-A	134/7	2	-	45.5 (0.6)	1.29	55.6
06-A	120/7	3	1128	69.9 (0.8)	1.53	85.3
06-B	•	6	1133	47.0 (0.7)	1.33	57.4
06-C	•	9	1123	26.6 (0.7)	1.21	32.5
07-A	105/7	7	1130	74.4 (0.5)	1.63	92.1
07-B	•	14	1133	62.8 (1.7)	1.48	77.7
07-C	•	21	1117	48.3 (1.2)	1.35	59.8
08-A	90/7	14	1130	77.7 (0.3)	1.70	97.2
08-B	•	28	1142	74.9 (0.3)	1.64	93.7
09-A	90/10	14	1131	77.3 (0.7)	1.68	95.1
09-B	•	28	1101	70.8 (0.9)	1.60	87.6
10-A	90/11	14	1080	72.2 (0.8)	1.69	89.1
10-B	•	28	1140**	62.1 (0.2)	1.62	76.7
11-A	70/7	84	-	78.5 (0.4)	1.72	96.3
11-B	•	252	1133	73.6 (0.8)	1.61	88.7
11-C	•	420	1130	65.8 (0.5)	1.52	81.0
12-A	70/10	84	-	76.9 (0.5)	1.72	94.4
12-B	•	252	1104	71.1 (0.2)	1.61	86.4
12-C	•	420	1026	60.5 (0.7)	1.52	74.5
13-A	50/7	210	1126	79.8 (0.5)	1.75	98.3
13-B	•	420	1122	78.0 (1.6)	1.74	96.1
14-A	50/10	182	1141	80.6 (0.3)	1.76	98.4
14-B	•	420	1126	79.4 (1.6)	1.73	97.8
15-A***	90/7	14	1134	78.2 (0.4)	1.71	96.8
15-B	•	28	1141	75.9 (0.3)	1.63	93.9
16-A***	90/10	14	1134	77.0 (0.4)	1.70	92.8
16-B	•	28	1078	71.2 (0.7)	1.65	85.8
17-A	90/7	28	1126	76.4 (0.5)	1.64	93.7
17-B	•	56	1120	69.2 (0.7)	1.52	84.9
17-C	•	84	1139	57.2 (1.0)	1.41	70.2
17-D	•	112	1134	43.8 (0.9)	1.31	53.7

* For the average pH values during the tests, see Table 2

** Here a higher linear density is found as a result of deposits on the yarn.

*** Treated with water + 250 mg Ca^{++}/l

Table 4. Measured properties of untreated Diolen 164 S yarn samples used as reference

Reference of yarn sample	Linear density (dtex)	Breaking strength with st. deviation (N)	Elongation at break with st. deviation (%)	Relative viscosity
05-A	1120	81.9 (0.6)	12.7 (0.3)	1.76
06-A,B,C	1136	81.9 (0.6)	12.4 (0.4)	1.78
07-A,B,C	1130	80.8 (0.6)	12.1 (0.2)	1.79
08-A,B	1130	79.9 (0.7)	12.1 (0.3)	1.78
09-A	1118	81.3 (0.7)	12.2 (0.5)	1.77
09-B	1118	80.8 (1.0)	12.5 (0.3)	1.77
10-A,B	1140	81.0 (0.6)	12.4 (0.5)	1.78
11-A	-	81.5 (0.6)	12.3 (0.4)	1.78
11-B	1142	83.0 (0.9)	12.7 (0.4)	1.78
11-C**	-	81.2	12.4	1.78
12-A	-	81.5 (0.6)	12.3 (0.4)	1.78
12-B	1123	82.3 (0.3)	13.3 (0.1)	1.78
12-C**	-	81.2	12.4	1.78
13-A	1136	81.2 (0.7)	12.4 (0.3)	1.79
13-B**	-	81.2	12.4	1.78
14-A	1132	81.9 (0.2)	12.7 (0.2)	1.78
14-B**	-	81.2	12.4	1.78
15-A,B	1130	80.8 (0.6)	12.1 (0.2)	1.79
16-A,B	1142	83.0 (0.9)	12.7 (0.4)	1.78
17-A,B,C,D	1148	81.5 (2.3)	12.2 (0.8)	1.78

* For the average pH values during the tests, see Table 2

** Here the average values of all measurements have been taken, because starting yarn from the same spool was not available any more.

6. DISCUSSION

6.1. Influence of the pH on rate and type of hydrolysis

Fig. 2 shows the residual strength of Diolen 164 S as a function of time after hydrolysis at 3 different pH values, namely pH = 7, 10 and 11, at the same temperature (90°C). The effect of the pH on the rate of hydrolysis increases strongly above pH = 10.

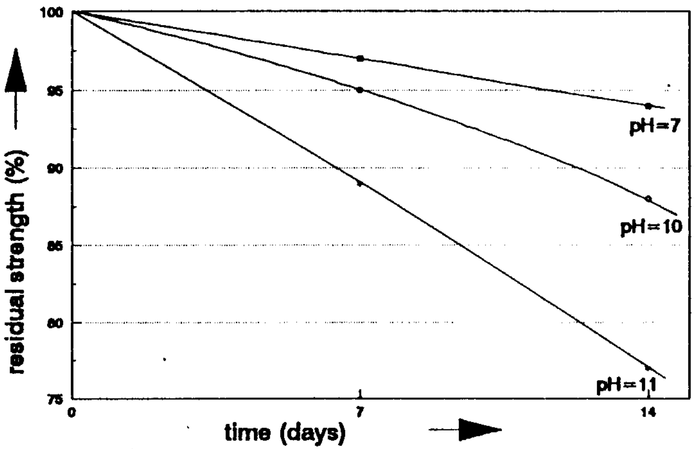

Fig. 2. Residual strength of Diolen 164 S after hydrolysis at different pH values at 90°C

In Fig. 3 the residual strength of Diolen 164 S is plotted against time after hydrolysis at pH = 7 and pH = 10 at 50, 70 and 90°C. The difference in loss of strength between pH = 7 and pH = 10 decreases with decreasing temperature (from 90 to 50°C). At 50°C a higher loss of strength at pH = 10 than at pH = 7, as is observed at 70° and 90°C, is not found any more.

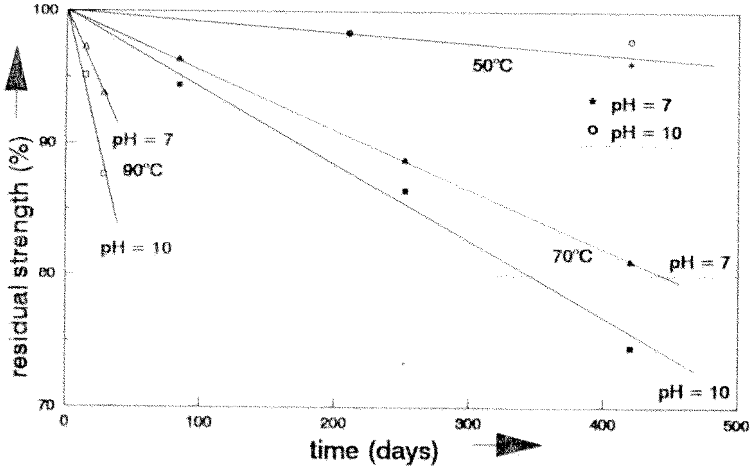

Fig. 3. Residual strength of Diolen 164 S after hydrolysis at pH = 7 and pH = 10

The following explanation is proposed for the above results. The internal and the external hydrolysis are two different independent reactions. The internal hydrolysis does not depend on the pH and proceeds as fast at pH = 10 or 11 as at pH = 7. At pH = 7 no external hydrolysis takes place. When the pH rises, the external hydrolysis starts at a definite value. This external hydrolysis takes place then in addition to the internal hydrolysis. So, when the loss of strength of PET yarn is higher at pH = 10 than at pH = 7, the extra loss of strength at pH = 10 is due to external hydrolysis.

At 50°C the loss of strength at pH = 10 is not higher than at pH = 7. This means that ≤ 50°C and pH ≤ 10 the contribution of the external hydrolysis to the loss of strength of PET yarns can be neglected with regard to the internal hydrolysis.

This conclusion is confirmed by SEM photomicrographs made of the filament surface of the samples before and after the tests. Fig. 4 gives a SEM photomicrograph of the yarn sample treated for 420 days at 50°C and pH = 10 (sample 14-B of Table 3) and Fig. 5 that of the sample treated for 420 days at 70°C and pH = 10 (sample 12-C of Table 3). Unlike the sample treated at 70°C and pH = 10, the sample treated at 50°C and pH = 10 does not show any significant "corrosion" of the filament surface brought about by external hydrolysis.

Also by comparing the linear densities of the samples, it can be concluded that at 50°C and pH = 10 no external hydrolysis has occured. See Table 5.

The weight of the yarn sample treated at 50°C and pH = 10 for 420 days does not differ from that of the yarn sample treated at 50°C and pH = 7 for 420 days.

As mentioned, the reactions of the external and internal hydrolysis proceed independently. This is also very nicely illustrated by the molecular weight distribution curves of:

- the sample treated at pH = 11 and 90°C for 28 days (sample 10-B)
- and the sample treated at pH = 7 and 90°C for 28 days (sample 08-B).

These curves practically coincide, see Fig. 6.

Table 5. Linear densities of Diolen 164 S before and after hydrolysis

Sample No.	Temp. °C	pH	Time (days)	Linear density (dtex)
untreated	-	-	-	1132*
11-C	70	7	420	1130
12-C	70	10	420	1026
13-B	50	7	420	1122
14-B	50	10	420	1126

* average value of the measurements in Table 4.

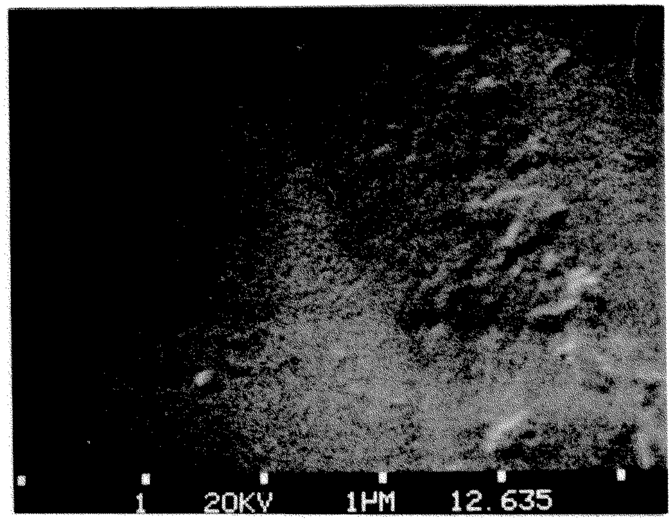

Figure 4. Diolen 164 S treated for 420 days at 50°C and pH = 10; 20000x

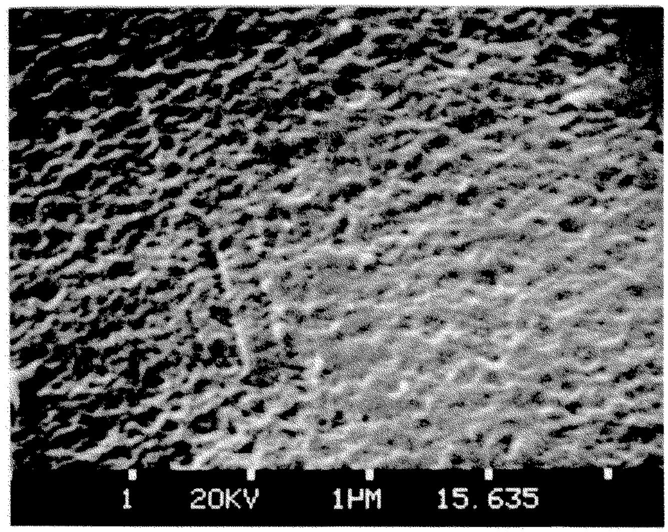

Figure 5. Diolen 164 S treated for 420 days at 70°C and pH = 10; 20000 x

Both diagrams give the MWD of the PET polymer present after internal hydrolysis. The effect of the external hydrolysis on sample 10-B, i.e. removal of a thin layer of the filament surface, is hardly perceptible in the MWD or solution viscosity, because this layer has almost completely disappeared. For the solution viscosities, see Table 3. The effect of the external hydrolysis manifests itself only in an extra reduction of the yarn strenght and a decrease of the linear density.

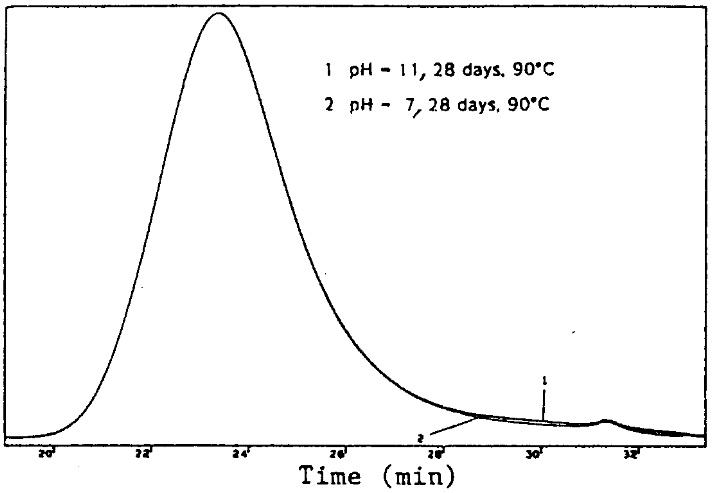

Fig. 6 Molecular weight distribution of the yarn sample treated at 90°C for 28 days at pH = 7 and pH = 11, respectively

6.2. Measurement of molecular weight and solution viscosity in support of the results of the strength determination

The rate of hydrolysis is shown in Figs. 2 and 3 by giving the residual strength as a function of time. The rate of internal hydrolysis can also be determined by measuring the molecular weight or by measuring the solution viscosity of the yarn samples. In fact, these measurements are still more direct, because the loss of strength is a result of the decrease in molecular weight.

The results of the measurements of the molecular weight and solution viscosity can be used to find out whether a measurement result of the yarn strength is on the high or on the low side, due to the variation in the strength determination. This can be derived from the plots of the residual strength of all yarn samples treated at pH = 7 against their molecular weight M_w and solution viscosity, respectively. See Figs. 7 and 8.

Both curves display the same path: a slight increase of the slope when going to a lower molecular weight or solution viscosity. As can be observed in both plots, the residual strength of 96.1%, found for sample 13-B, treated at 50°C and pH = 7 for 420 days, is on the low side. On the basis of the measured molecular weight and solution viscosity, this value should be at least 97%. A corrected value is used in section 6.4 for the estimation of the life-time of PET yarns at 10 to 20°C with the help of the Arrhenius equation.

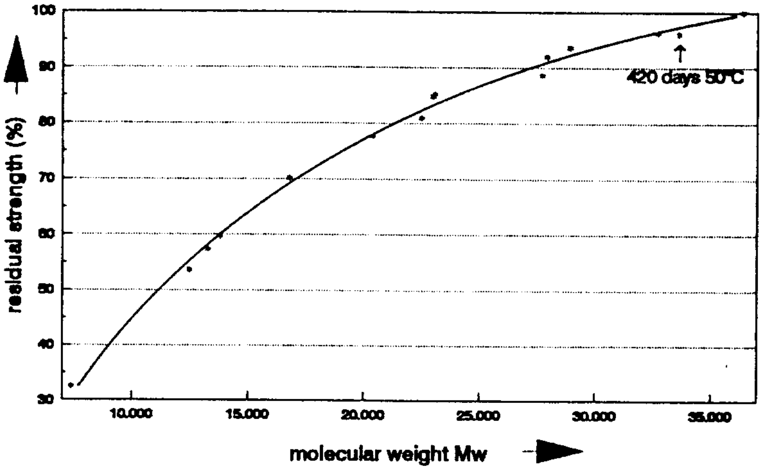

Fig. 7. Relation between residual strength and molecular weight (Mw) of the Diolen 164 S samples after hydrolysis at pH = 7

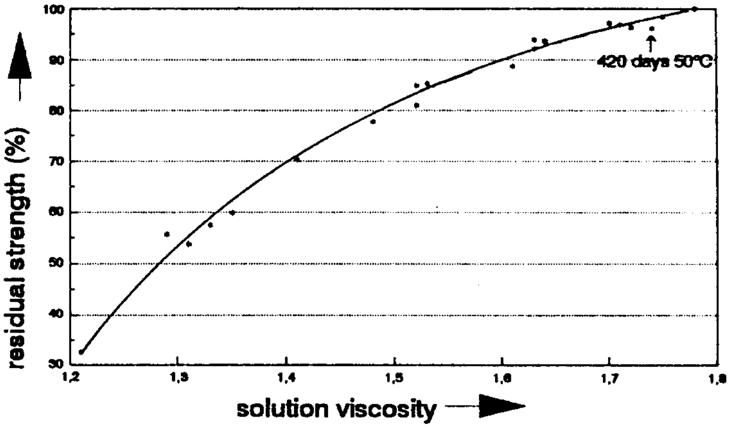

Fig. 8. Relation between residual strength and solution viscosity of the Diolen 164 S samples after hydrolysis at pH = 7

6.3. Influence of the addition of extra Ca^{++}

In soils which are rich in limestone and/or gypsum, the Ca^{++} concentration is higher than in a solution of Ca(OH)$_2$ with a pH-value of 10. It has been suggested that a high Ca^{++} concentration may have a catalytic effect on the hydrolysis[2].

Tests carried out at pH = 7 as well as at pH = 10 with the addition of 250 mg extra Ca^{++} (in the form of CaSO$_4$), do not point to such a catalytic effect. See Fig. 9 and Table 3.

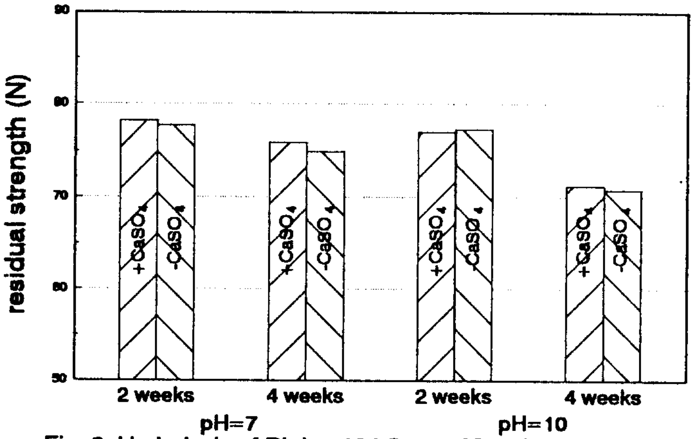

Fig. 9. Hydrolysis of Diolen 164 S at 90°C with and without 250 mg Ca/l (pCa = 2.2) added as CaSO$_4$

So, at pH = 10 a higher loss of strength caused by a high Ca^{++} concentration is not found.

6.4. The rate of internal hydrolysis in relation to the temperature

As mentioned before, natural soils seldom have a pH value > 10. It has been rendered plausible in section 6.1. that below 50°C and pH = 10 only internal hydrolysis plays a role. So, the rate of hydrolysis of PET yarn in the soil has to be derived from the data of the internal hydrolysis in Table 3.

By plotting the residual strength against the time for the different temperatures the $t_{95\%}$ value can be estimated at each test temperature. The $t_{95\%}$ is the time required to reach a residual strength of 95%.

The $t_{95\%}$ values for all test temperature are provided in Table 6.

Table 6. Time in which a residual strength of 95% ($t_{95\%}$) is reached

Code of hydrolysis test (see Table IV)	Temp. (°C)	$t_{95\%}$ (days)
05	134	0.26
06	120	1.25
07	105	4.20
08 and 17	90	24.04
11	70	107
13	50	525
13 after correction*	50	775

* see 6.5

An Arrhenius plot[5] can be made of these $t_{95\%}$ values. See Fig. 10.

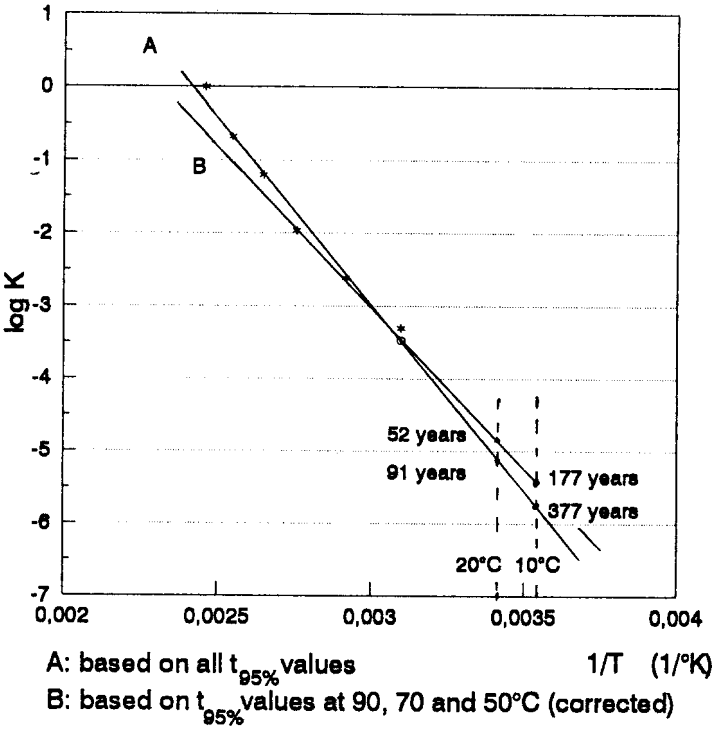

Fig. 10. Arrhenius plots based on $t_{95\%}$ values

The time in which at 20°C a residual strength of 95% is reached, calculated with the help of the Arrhenius equation, amounts to 91 years. When the Arrhenius equation is only applied to the $t_{95\%}$ values at 90, 70 and 50°C (at 50°C a corrected value of 775 days has been used now, see 6.5), instead of to all $t_{95\%}$ values, a lower value of $t_{95\%}$ at 20°C is obtained, namely 52 years. The difference between the two results is brought about by a change in the slope of the Arrhenius plot. At 10°C the $t_{95\%}$ values of 377 and 177 years are found, respectively.

The extrapolation with the Arrhenius equation leads only to correct results when the mechanism of the hydrolysis reaction does not change in the temperature range of the extrapolation. It might be that this is not exactly the case. However, the $t_{95\%}$ values at 10 to 20°C are of such an order of magnitude that a very long lifetime can be predicted for high-oriented PET yarns in soil.

6.5. For $t_{95\%}$ at 50°C a value of 525 days has been found. See Table 6. This value is based on the residual strength of 96.1% found after 420 days. There are several indications that this value of 96.1% is on the low side. These indications are:

- at pH = 10 and 50°C a residual strength of 97.8% has been found after 420 days (see Table 3);
- on the basis of the measurement of the solution viscosity the residual strength should to be 98.1% (see Fig. 8);
- on the basis of the measurement of M_w the residual strength has to be 97.1% (see Fig. 7).

The average residual strength of the 4 values is 97.3%. This gives a corrected $t_{95\%}$ at 50°C of 775 days (linear extrapolation).

CONCLUSIONS

The results are in agreement with the conception that the hydrolysis of PET by H_2O molecules and by OH^- ions are two independent reactions. At moderate conditions (T ≤ 50°C, pH ≤ 10) the hydrolysis of high-oriented PET yarn is only brought about by the reaction with H_2O molecules. At pH = 10 the reaction with OH^- ions starts only above 50°C.

The results lead to the conclusion that also in natural soils the loss of strength of high-oriented PET yarns is brought about by hydrolysis through H_2O molecules. The reaction with OH^- ions can be neglected < pH = 10. On the basis of the measurement results of the reaction with H_2O molecules it is predicted that high-oriented PET yarns are stable in soil for many decades. High Ca^{++} concentrations (250 mg/l has been investigated) have no accelerating effect on the hydrolysis ≤ pH = 10.

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