

# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index  
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?  
Contact [book.department@intechopen.com](mailto:book.department@intechopen.com)

Numbers displayed above are based on latest data collected.  
For more information visit [www.intechopen.com](http://www.intechopen.com)



---

# Degradation of Polyesters in Medical Applications

---

Mashiur Rahman

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/47765>

---

## 1. Introduction

The foundations of polyesters were laid by Carothers and Hill at the beginning of the 1930s [1]. Carothers and Hill synthesized polyesters with low melting temperatures (m.t.) and hydrolytically sensitive, such as the polyester produced from propylene glycol and hexadecanedicarboxylic acid, m.t. 75°C, *w*-hydroxydecanoic acid, m.t. 65°C, *w*-hydroxypentadecanoic acid, m.t. 95°C [2]. In the early 1940s, Whinfield and Dickson [3] in the United Kingdom, and Schlack [2] in Germany used terephthalic acid to develop polyesters with higher melting points. Poly(ethylene terephthalate) or PET, was first commercially produced by Imperial Chemical Industries (ICI) and DuPont and has become the most important man-made fibre in apparel and non-apparel applications.

The use of textiles in medical applications has a long history starting as early as 1952 with the first porous plastic arterial prosthesis Vinyon “N” fabric. It was made from 41 dtex yarn (yarn linear density) with a fabric count of 144×90 per square inch [4]. However, its use was discontinued due to the loss of more than 50% tensile strength within a year. Grafts from Ivalon, Orlon and Teflon textile fibers were also made, but discarded due to dilatation and loss in mechanical properties before anticipated lifetime [5]. Polyesters, because of their high strength, high modulus, low creep and biocompatibility, are being widely used for various medical applications as non-implantable and implantable materials, such as artificial tendon, artificial ligament, vascular grafts, artificial kidney, aortofemoral grafts, and many extra-anatomic bypass grafts (Table 1) [6]. However, the long term durability of polyester for implantable applications is in question because of slow degradation or aging of polyesters that occur in physiological conditions by physical and chemical processes that are synergistic in character. Both *in vivo* and *in vitro* studies showed that the cumulative effects of such slow degradation processes will ultimately lead implant failure via mechanical breakdown. The numerous occurrences of such failures of PET grafts were reported

Application	Polyester	Long term durability
Orthopaedic bandage	Polyester woven, polyester non-woven	Not applicable
Plasters	Polyester woven, non-woven, knitted	Not applicable
Non-biodegradable sutures	Polyester monofilament, braided	Applicable
Artificial tendon	Polyester woven, braided	Applicable
Artificial ligament	Polyester braided	Applicable
Vascular grafts	Polyester woven, knitted	Applicable
Heart valves	Polyester woven, knitted	Applicable
Artificial kidney	Polyester hollow fibre	Applicable
Surgical gowns	Polyester woven, non-woven	Not applicable
Surgical masks	Polyester non-woven	Not applicable
Surgical drapes, cloths	Polyester woven, non-woven	Not applicable
Surgical hosiery	Polyester knitted	Not applicable
Hospital blankets	Polyester woven, knitted	Not applicable
Uniforms	Polyester woven	Not applicable
Protective clothing	Polyester nonwoven	Not applicable

**Table 1.** Use of polyesters in different medical applications [6].

[7,8,9,10,11]. Table 2 shows the clinical data on patients who developed complications, some of whom died due to failure of PET Dacron grafts [7]; however, numerous Dacron graft failures were unpublished due to the fear of litigation [12,13]. The average time for graft failure was reported to range from 5.8 years and 7.4 years depending on the textile construction of the graft [7]. Of the five deaths reported (Table 2), two patients died just after 2 years following implantation due to the failure of a knitted PET graft and an unspecified PET graft. *In vivo* failure of the PET graft was mainly due to the breakdown of the PET fibers [5], which might have occurred because of manufacturing defects, residual stress and physiological environments [7]. Therefore, the objective of this chapter is to compare the *in vivo* polyester implant failures with the *in vitro* data in order to establish the failure mechanism.

## 2. Structure and properties of polyester for implant application

The polyester used for medical textile purposes, where long term durability is required, is different from the polyester used for apparel uses in respect of strength and fine structure. For implant applications, high strength, high modulus and low elongation are required (Table 3). Developments in polymer technology, spinning techniques, drawing techniques and machines were required to produce such high tenacity fibre [14].

Location	Failure time (y)	Type of graft	Defect/causes of failure	Outcome
Aortobifemoral	2	Knitted	Aortic tear, dilation & 3 cm rent	Hematuria, dead
Iliofemoral	2	Unspecified	Inguinal tear, developed a 2cm slit	Replaced, alive
Aortobifemoral	3.5	Weavenit	Bifurcation tear, 1 cm tear along the guide line	Replaced, alive
Aortic tube	10	Knitted	Aortic rupture, 96.9% loss in tensile strength	Dead
Aortobifemoral	5	Knitted Dacron	Bifurcation tear Surface cracks	Dead
Aortobifemoral	8	Weavenit	Inguinal tear, Disintegration, holes, split etc.	Replaced, alive
Aortobifemoral	8	Tetoran woven	Aorti-ureter, cracks	Hematuria, dead
Aortoiliac/femoral	6	Cooley double velour	Right femoral aneurysm, broken graft fibres	Replaced, alive
Aortobifemoral	5	Double velour	Inguinal tear,	Replaced, alive
Aorto right femoral	7	Knitted double velour	Right femoral aneurysm, manufacturing faults	Replaced, alive
Aortobifemoral	7	Unspecified	Left femoral aneurysm, structural deficiencies	Replaced, alive
Aorta-femorals	5	Woven	Suture tear (polyester)	Dead
*Axillo-femoro-femoral	4	weavenit	Thrombosis	Dead
*Ilio-femoral (transversal)	10	weavenit	Thrombosis	Dead
*Aorot-femoral (bilateral)	25	weavenit	Thrombosis	Dead

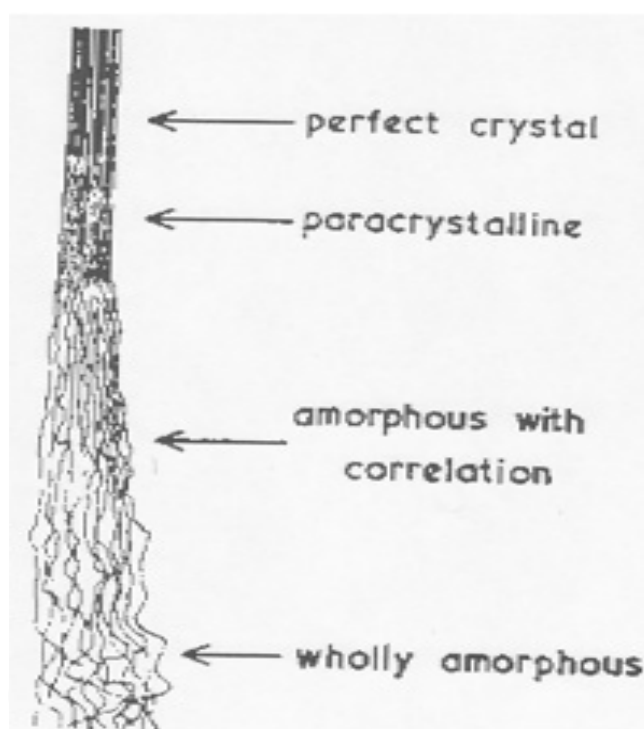
**Table 2.** Clinical data on patients who developed primary Dacron graft failure [7]. \*[7a]

The production of standard polyester involves the extrusion of the polymer melt by pumping it through narrow capillaries where it obtains fibrous geometry. The fibre modulus and strength increase and then decrease as the spinning speed is increased but elongation decreases continuously as the spinning speeds are increased. PET fibres melt spun at a take up velocity of around 1000m/min have an amorphous structure and are called low orientations yarns. A take up velocity of around 3000m/min gives the partially oriented yarns (POY) and above 4000m/min gives fully oriented yarns (FOY) [16]. The main structural changes occur during the drawing process as the molecules acquired a more

ordered structure (Figure 1), conformational changes take place where disordered gauche conformations of the ethylene glycol unit are changed into the ordered trans conformations [17].

Polyester type	Breaking tenacity (g/d)	Tensile strength (psi)	Breaking elongation (%)	Elastic recovery (%)	Stiffness (g/d)	Toughness (g/d)	Intrinsic viscosity (dl/g)
Apparel grade Polyester	2.0-2.5	33,000-42,000	18-60	67-86 at 2%	7-31	0.28-1.5	0.6-0.7
Medical grade polyester	7.2-8.2	118,000-140,000	*7-10	99 at 1%	54-77	0.35-0.55	0.90-1.0

**Table 3.** Mechanical properties of apparel and medical grade PET [15]. \*Trevira high tenacity, type 703.



**Figure 1.** Range of molecular order in polymer packing [18].

For implant applications, higher molecular weight polymer is essential to obtain higher strength fibre. The molecular weight is usually determined from the intrinsic viscosity (IV) or the limiting viscosity number of the fibre in a given solvent at a stated temperature; then the relationship is used between limiting viscosity number and molecular weight based upon the Mark-Houwink relationship:  $[\eta] = KM^a$ , where 'K' and 'a' are constants which have been determined for the given solvent in relation to either number average or weight average molecular weights. The intrinsic viscosity of apparel grade polyester of tenacity: 2.0-2.5 g/d is about 0.60 to 0.70 g/dl in *o*-chlorophenol at 30°C [19] but to obtain high tenacity

(8.0-10.0 g/d) PET fibres, the intrinsic viscosity should be about 0.9dl/g and for a tenacity of up to 16.0-20.0 g/d this value should be 2.6dl/g [14,20].

Yarns for implant applications require more complex drawing and heat treatment in order to produce the required tenacity, elongation, thermal shrinkage, orientation of the molecules, and crystallinity of the fibres. In this process, machines with a larger number of godets than usual are used, where between the first pair of godets the yarns received some pre-orientation so that they could run smoothly in the later stages of processing [14]. The latest method to produce industrial yarn such as tyre cord consists of producing the yarns at speeds in excess of 3,000 m/min to produce high modulus, low shrinkage yarn through subsequent drawing and heat treatment in several stages with heated godets and steam. This requires winding speeds of more than 6,000 m/min, depending on the viscosity of the melt and the yarn denier [21].

### 3. Degrading agents of polyesters

#### 3.1. *In vivo* degradative agents

The degrading agents for implant applications can be physical (pulsaile force, high blood pressure), chemical (blood and physiological fluids), biological (thrombosis, infection), and thermal (body temperature: normal and elevated due to fever). Table 4 summarizes various degradative agents in physiological condition with their effects and possible unfortunate outcomes.

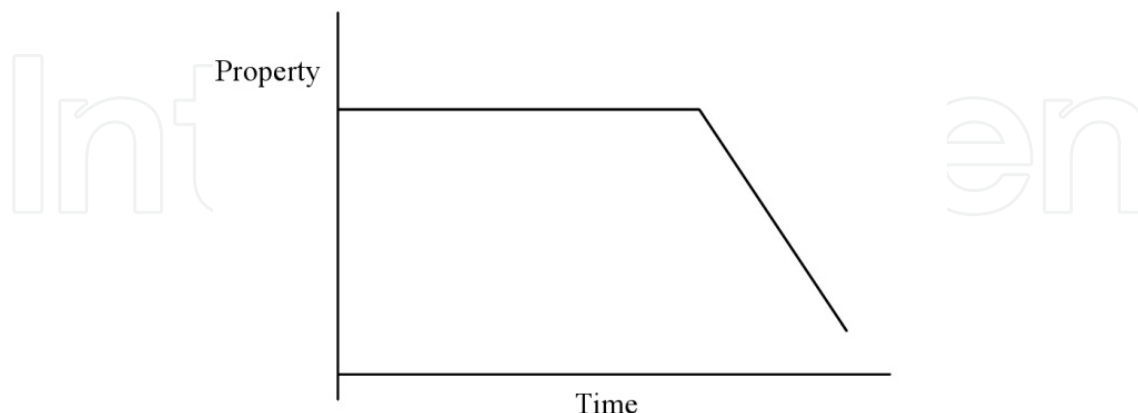
Agent	Source	Effect/outcome
Pulsatile force	Physiological stress, hypersensitiveness	Dilation, reduction in strength, death, cost of replacement
Residual stress	Textile processing, Physiological stress	Strength loss/rupture, death, cost of replacement
Physiological fluids	Patients body	Strength loss/rupture, death, cost of replacement
Thrombosis	Biological	Loss of implants' function (smooth blood flow), cost of repair, ongoing monitoring
Infection	Biological	Loss in physiological function, death, cost of replacement, ongoing monitoring
Temperature	Physiological	Loss in mechanical properties, premature rupture, death, cost of replacement
Defects	Textile processing	Rupture, strength loss, death, cost of replacement

**Table 4.** Various degrading sources of polyester in medical applications

#### 3.2. The effect of stress on polyester durability

When polyester is used for implant applications, it would be expected to be under stress. Depending on the physiological location, two types of stresses that are encountered by polyesters *in vivo*, such as intermittent and continuous stress. However, in some location within the human body, the stresses encountered usually consist of several components acting simultaneously.

In general, oriented fibre forming polymers like polyesters when exposed to environmentally hostile conditions, show slow but negligible strength loss and slow loss in other properties over considerable lengths of time prior to sudden catastrophic failure [22], as shown in Figure 2.



**Figure 2.** Changes of properties of polymers with time [22].

In case of polyester, it is reported that the yarn stressed to 70, 75, 80 and 85% of ultimate stress will have expected times-to-failure of  $1 \times 10^5$ ,  $5 \times 10^3$ , 100 and 10 hours respectively [23]. The accelerated effect of stress and pigments on HDPE (High Density Polyethylene) for outdoor applications in the presence of various pigments and stabilizers, stress induced oxidation of polypropylene [24] and the accelerated effect of chemicals on HDPE geomembrane liners under load was reported [25]. Among the other industrially used polymers, the effect of stress during exposure to an  $\text{NO}_x$  environment for Nylon [26] and the effect of load on Kevlar fibres of poly(p-phenylene terephthalamide) was investigated [27]. For medical application, polyurethane fibres lost strength when treated under stress with water, ethanol and bovine serum after three months contact but under relaxed conditions there was no detectable strength loss [28].

Degradative agents	Short term resistance	Long term resistance
Dilute acid	Good resistance	Passable resistance
Concentrated acid	Moderate resistance	No resistance
Dilute alkali	Good resistance	Moderate resistance
Concentrated alkali	Moderate resistance	No resistance
Salt (brine)	Good resistance	Good resistance
Mineral oil	Good resistance	Good resistance
UV	Good resistance	Moderate resistance
UV (Stabilized)	Good resistance	Passable resistance
Heat (dry), 100°C	Good resistance	Good resistance
Steam, 100°C	Moderate resistance	No resistance
Moisture absorption	Good resistance	Good resistance
Creep tendency	Good resistance	Good resistance

**Table 5.** Resistance of polyester to common chemicals



### 3.3. Effect of chemicals on the degradation of PET

Despite the use of high tenacity PET in recent years, the main problems associated with polyesters are the hydrolysis in acid and alkaline media (Tables 5 and 6) and it was found that polyester is not suitable for use at even low alkaline pH (pH=9) [38].

Chemical compound	pH	Percentage strength retained after 1 year (20°C)
Sodium hydroxide, 0.1%	12.1	94
Sodium hydroxide, 2%	12.8	Severely degraded
Ammonium hydroxide	8-10	88
Ammonium hydroxide, 2%	11.4	Severely degraded
Calcium hydroxide, 15%	12.4	Severely degraded
Diethylamine	3.5	Severely degraded
Hydrazine, 2%	10.6	76
Hydrazine, 5%	10.8	Severely degraded
Potassium hydroxide, 0.1%	12.5	90
Potassium hydroxide, 2.0%	13.4	Severely degraded

**Table 6.** Alkali resistance of PET [31]

### 3.4. The hydrolysis of polyesters

Hydrolysis basically is the reverse reaction of the synthesis of PET. In hydrolysis the long chain linear molecule is split by a water molecule because of the scission of an ester bond. There are mainly three types of hydrolysis which may occur with polyesters during implant application:

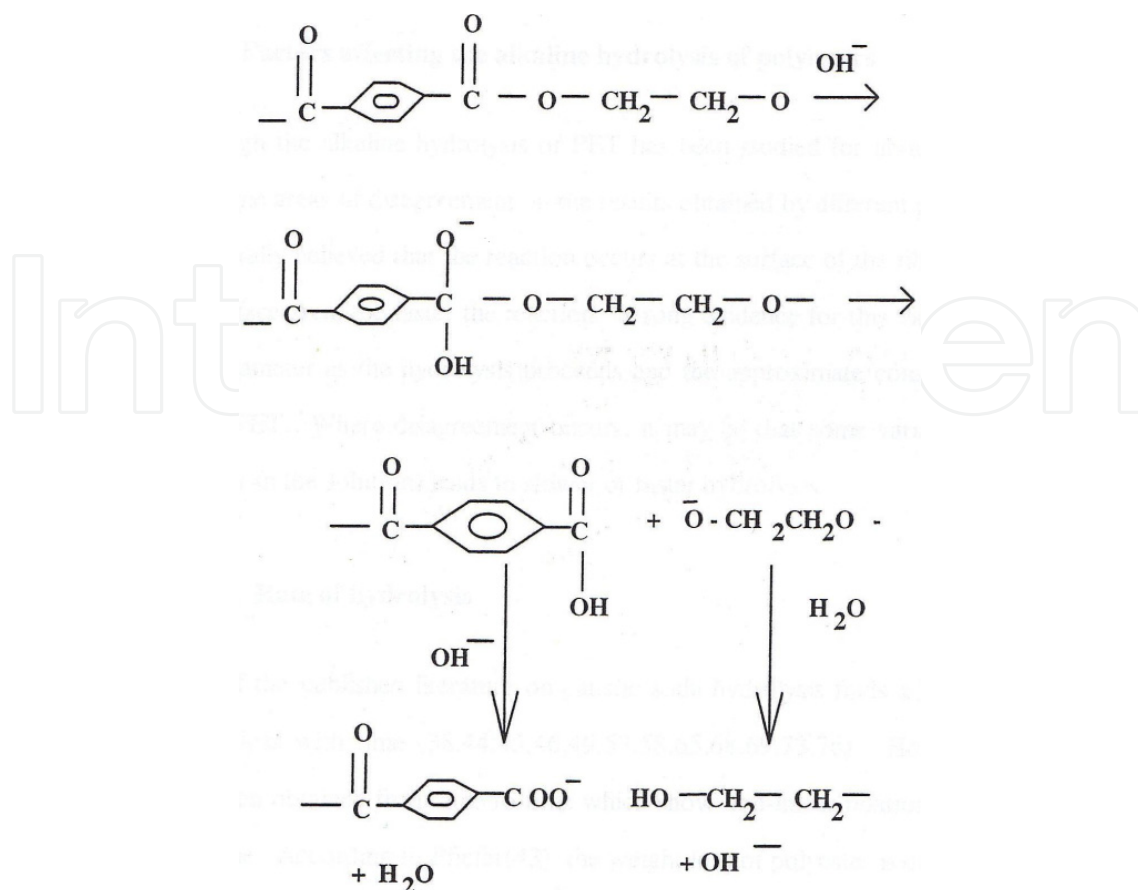
- Acid hydrolysis;
- Hydrolysis in water;
- Alkaline hydrolysis;

### 3.5. Acid hydrolysis of polyesters

In the acid hydrolysis, protonation of the in-chain oxygen atom of the ester group, followed by reaction with water produces one hydroxyl and one carboxyl end group, as shown in Figure 3.

It was found that 30% HCl halved the tenacity of the apparel polyester after 3 days of treatment at 70°C, whereas under these conditions 30% NaOH would destroy a yarn of any commercial diameter [33]. Further, in 50% nitric acid after 72 hours of treatment, the apparel grade fibres lost 14.5% strength at 40°C, but in 30% HCl at 40°C after 72 hours of treatment, no apparent loss of strength was found; at 60°C, for the same time, no significant strength loss was noticed in sulphuric acid of 70% concentration [32]. For industrial grade geotextile yarn, at 21°C after one year in 20% HCl (pH=0.1) the fibre is completely degraded whereas in 38% H<sub>2</sub>SO<sub>4</sub> (pH=0.1) for the same conditions the strength of the fibres was almost





**Figure 3.** Reaction mechanism of the acid hydrolysis of polyesters [33].

unchanged [34]. Regardless of polyester types, usually, the reactivity of inorganic acids at equivalent concentration in aqueous media was in the order  $\text{HCl} > \text{HNO}_3 > \text{H}_2\text{SO}_4 > \text{H}_3\text{PO}_4$  and attributed this order to the ability of the acid to diffuse into and dissolve in the PET [33].

Acid-catalyzed hydrolysis of esters is much slower at a given temperature than alkali-catalyzed hydrolysis if both are carried out homogeneously and in the heterogeneous hydrolysis that occurs in dilute solutions of strong acid and alkali; the surface attack on polyester fibres by acids is much slower than by alkali [33]. For implant application, generally the implants do not come into contact with the acid environment and therefore, further discussion on acid degradation will be very limited.

### 3.6. Hydrolysis of polyesters in water alone and other environments

PET is attacked by water or steam which causes hydrolysis of the chain. Reaction with water is very slow at lower temperatures, but the rate of attack increases with increasing temperature. For example, when treated with water at  $70^\circ\text{C}$  for four weeks there is no apparent effect on PET but 60% tenacity loss was observed after three weeks at  $100^\circ\text{C}$  and 64% after 10 hours of treatment in saturated steam at  $150^\circ\text{C}$  [39]. During the treatment with water the fibres do not lose any significant weight.

As well as other hydrolysis in the human body, bacterial attack may occur though after 17 years of micro-organisms environment *in vitro*, no effects was noticed [29]. Sato [35], however, reported an effect of a crude enzyme solution of *Cladosporium cladosporioides* FERM J-8, prepared from the fungus. The tensile strength, extension behavior, and relative viscosity were remarkably reduced at 30°C at the given pH values used (5.5, 7.0 and 8.0) after two weeks of treatment and these changes were believed to be due to the hydrolysis with esterase of *Cladosporium cladosporioides*. Such experimental conditions are likely to be obtained in the physiological environment, particularly the temperature and the alkaline pH, but it is not known if polyester implants will encounter such bacteria *in vivo*.

Generally, polyester implants encounter only alkaline condition *in vivo* which is much more severe than hydrolysis in acid and other hydrolysis conditions [33]. Considering the impact of alkaline chemicals (blood) and physiological stress, the chapter is devoted on the factors which impact alkaline hydrolysis and the synergistic effects of alkali and stress.

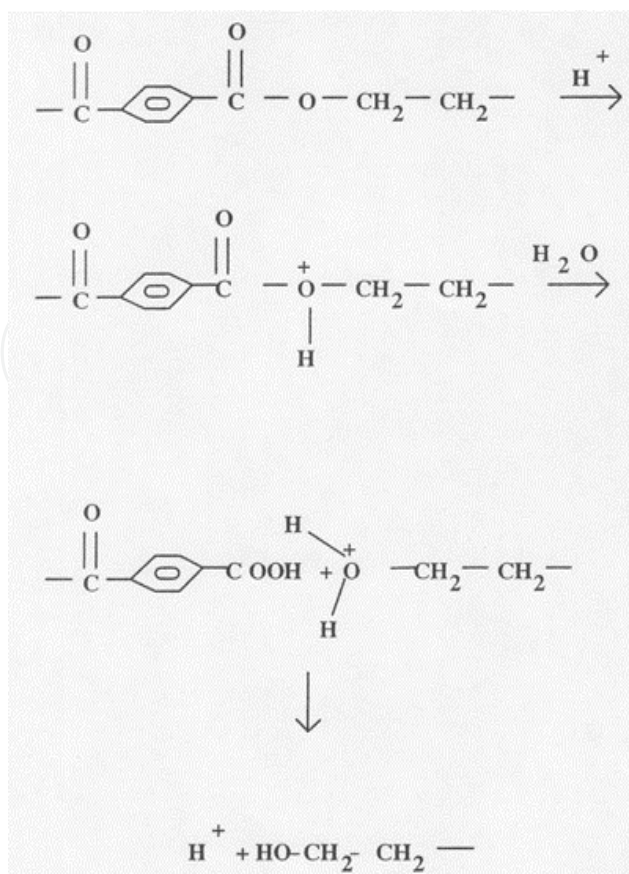
### 3.7. Alkaline hydrolysis

In 1952 Hall and Whinfield [36] reported that the effect of alkali on PET was to improve the handle of textiles; since then numerous attempts have been made to understand this subject. This alkaline hydrolysis has several advantages in the apparel industry, in that it produces light weight materials without using light weight yarns which reduces the cost of production and it also gives surface modification of the fibres. Such alkaline sensitivity of polyesters is also useful in countering the problem of cyclic trimer deposition during the high pressure dyeing of the fibres by using a small amount of alkali in the dye bath which hydrolyses this trimer [33].

The alkaline hydrolysis of PET can be expressed in the following way:

The hydroxide ions attack the electron-deficient carbonyl carbons of the polyesters to form an intermediate anion. Further reaction breaks the macromolecular chain and produces –COOH and O<sup>-</sup>-CH<sub>2</sub>-CH<sub>2</sub>- as shown in Figure 4. The final products of the hydrolysis are hydroxyl groups and carboxylate anion groups.

Although the alkaline degradation routes for polyesters have been studied for about 60 years for apparel polyesters, there are still some areas of disagreement in the results obtained by different groups of workers. For example, during alkaline hydrolysis, it is generally believed that the reaction occurs at the surface of the fibres so that the greater the surface area, the faster the reaction. Strong evidence for this view is the reduction in fibre diameter as the hydrolysis proceeds and the approximate constancy of the tenacity of the fibre. Where disagreement occurs, it may be that some variables in the polyesters, for example, types of polyesters, spin finish, fibre, yarn and fabric geometry, thermal history, comonomers, surface properties, delustring agents and solution type which lead to slower or faster hydrolysis. This variability in the rate is also applicable to medical polyester as recently as 2009, a lifetime between 156 months to 240 months for polyester implants (Aorto and Axillo bifemorale) was recorded [37].



**Figure 4.** Reaction mechanism of alkaline hydrolysis [37].

### 3.7.1. Factors affecting alkaline hydrolysis

Most of the published literature on alkaline hydrolysis finds a linear relationship of weight loss with time [39,40,41,42,43,44,45,46,47,48,49,50]. However, other results have been obtained from time to time which show non-linear relationships of weight loss with time [40,51,52,53]. The non-linear relationship occurred due to the stoichiometric quantity of alkali, solution type (alcoholic or aqueous), and other factors (e.g. solvent, stress). If the hydrolysis is confined to the fibre surface and no other factors involved, then the tenacity, elongation, modulus, density and molecular weight of the hydrolyzed fibres should not be changed. But a tenacity loss is frequently reported in the literature [39-44,46,48,53-55], as well as a reduction in breaking elongation [44,48,53-55], modulus [53] and molecular weight for explanted polyester implant [37] and apparel polyester [46,56] of the hydrolyzed fibres.

#### 3.7.1.1. Effect of yarn geometry on alkaline hydrolysis

The hydrolysis of polyester fabric is dependent on the nature of the component yarns in the fabric and their construction details [42]. The authors ranked the fibres on the extent of weight reduction as follows: Bright/Textured > Rotaset bright/Textured > Rotaset/Crimped > Rototextured/Textured > Rotaset/Textured. Similarly, fabrics made from mixtures of spun yarn and filament yarn were degraded more rapidly than the wholly filament fabric [31]. Also, Regular textured yarn [54] and polyester implant made from textured yarn [37]

degraded faster than the original flat yarn. For geotextile polyesters, PET needled non-woven (heavy weight) degraded more rapidly than the PET heat set non-woven fabric which was itself more rapidly degraded than the PET needled non-woven light weight fabric [57-58]. The authors attributed the differences to different molecular weight, crystallinity, and processing history of each type of polyester; other factors such as different fibre decitex were not considered.

#### 3.7.1.2. *Effect of heat setting temperature on alkaline hydrolysis*

Medical grade polyester filament yarn requires more complex drawing and heat treatment. Generally the heat treatment is carried out after the drawing process to stabilize the yarn against thermal shrinkage during further processing and end use. The amount of shrinkage increases as the stretching in the yarn is increased. To remove the internal stresses, heat setting is carried out at about 140-220°C using heated draw rollers to give dimensional stability to the yarn which is most important for medical applications. However, to achieve the slowest rate of degradation *in vivo*, heat setting must be carried out at about 140-200°C under stressing condition [59-60] and heat setting temperatures above and below this temperature range increase the rate of degradation [39,42]. In contrast, heat setting of PET fibres at 120°C or higher prior to alkali treatment caused an increase in fibre density and increased the weight loss [61]. No explanation for these changes was offered and there is no clear unambiguous conclusion that follows from these studies. However, some of these discrepancies might be due to different heat setting procedures (free to relax or fixed dimensions) or different heat setting times.

#### 3.7.1.3. *Effect of filament cross-section*

All so called first generation (up to 1970s) polyester implants were made from trilobal PET and later changed to circular cross-section as alkaline hydrolysis depends on the shape of the filament used [62]. For instance, fibres of bright round cross section are more resistant to hydrolysis than the delustrated multi-lobal cross section fibres [43]; however, this does not distinguish between the two effects of cross-section shape and delustrant content. Investigation on the effect of different shapes of filament such as round, trilobal, pentalobal and octalobal on the rate of alkaline hydrolysis showed that the weight loss (%) was highest for the octalobal fibres and lowest for round cross-section fibres [63]. But differences in yarn decitex and delustrant content made the interpretation of these results difficult. It was already known that delustrated fibres are attacked more rapidly than bright fibres [60,64], so the effect of cross-section shape remains unclear. Given the greater surface area of the trilobal, pentalobal and octalobal fibres, a higher rate of hydrolysis would be expected and for implant application, in order to reduce the degradation rate, the cross-section of fibre should be circular.

#### 3.7.1.4. *Effect of additives*

There are many types of materials which can be added to a yarn during and after the manufacturing period such as delustring agents, antistatic agents, spin finish, etc. The rate of alkaline hydrolysis of dull fibres which contains TiO<sub>2</sub> was greater than for equivalent

bright fibres [60,64]. The surface pitting occurs due to the presence of  $\text{TiO}_2$  [44,53,54] which eventually reduces the strength of the fibres.

The traditional definition of spin finish is a material which provides surface lubricity to the yarn so that smooth, high speed transfer over various metallic guides can take place with the minimum amount of fibre breakage [65]. A hydrophilic type spin finish can be used for apparel polyester processing and a hydrophobic type spin finish is used for industrial polyester. For example, to produce polyester tire cord yarns a mixture of polyoxyethylated-polyoxypropylated compounds of molecular weights of about 300 to 1,000 is very effective [66]. Another type of spin finish based on a polyalkylene glycol of molecular weight of at least about 300 is applied to tire yarns and subsequently the yarn is heated for 10 to 160 seconds at a temperature of  $215^\circ\text{C}$  to  $230^\circ\text{C}$  which improved the compression-extension durability of the fibres in rubber [67]. It may be that the manufacturers may use a special spin finish for the processing of medical textile yarns but no information on this is given in the literature.

#### *3.7.1.6. Effect of comonomers in the polyester*

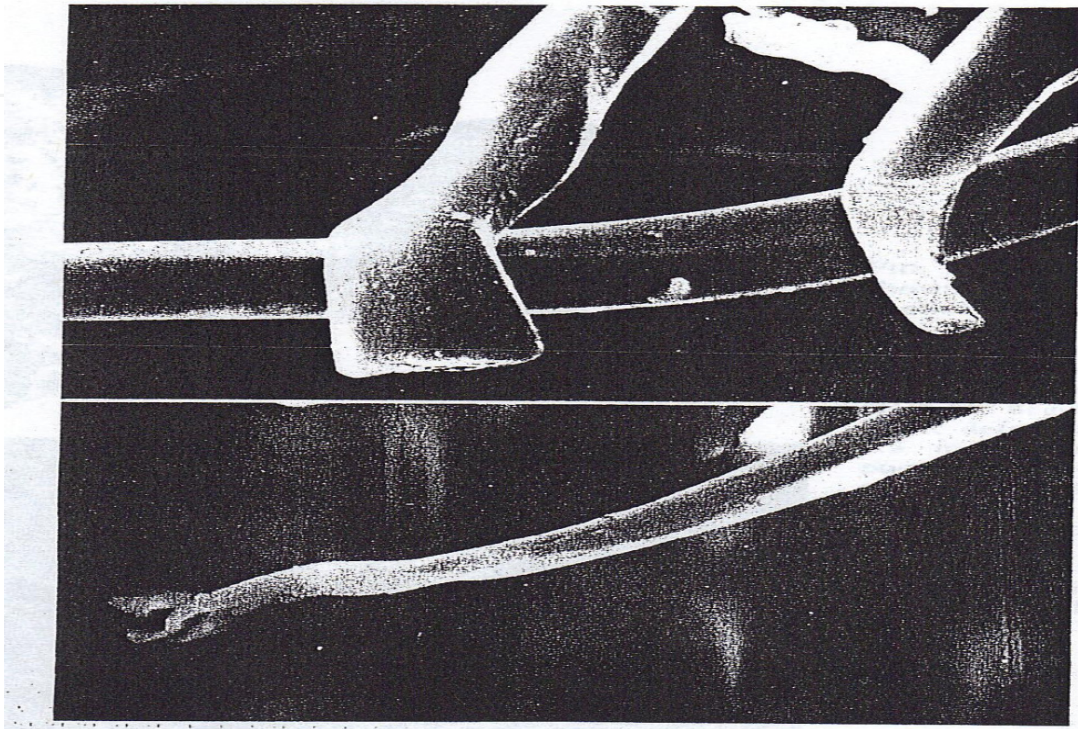
The rate of alkaline degradation of polyesters is dependent on the chemical composition and structure of polymer. The cationic dyeable polyesters hydrolyze more rapidly than ordinary polyester, because such polyesters contain the strongly electron-attracting sulphonate group [68,69,70]. The most used chemical unit is the sodium salt of the 5-sulphoisophthaloyl group, incorporated as the corresponding dimethyl or bis(hydroxyethyl) ester into the polymer manufacturing process, and it is incorporated as the repeat unit at 2-2.5 mol% concentration. The electron density on the carbonyl groups is reduced and the electrostatic interaction between hydroxyl ion and carbonyl group is increased. So the hydrolysis of modified polyester containing this suphonate group is expected to be easier than for the ordinary polyester. Other copolymers such as adipate copolymers and the block copolymers containing polyether blocks also have higher hydrolysis rates, but on the other hand copolymerization with butane-1,4-diol units reduces the hydrolysis rates [33].

Hydrolysis of aromatic ester homologues made from  $\beta$ -hydroxy-ethyl aromatic acids have higher alkali resistance compared to that of PET [45] and aliphatic polyesters with substantial hydrocarbon:ester ratios have hydrolytic stability similar to PET but with higher ester group content and with esters derived from strong acids, very rapid hydrolysis can occur [33]. Such polyesters are polyglycolide, polydioxanone etc. can be used as absorbable sutures but some aliphatic polyester, such as polypivalolactone are less rapidly hydrolyzed than PET and can be used for implant application. Partially aromatic polyesters such as, poly(4-oxyethoxybenzoate), poly(ethylene diphenoxyethane-4,4'-dicarboxylate), poly(ethylene naphthalene-2,6-dicarboxylate) and poly(tetramethylene terephthalate) have higher hydrolytic stability than PET, whereas some liquid crystalline polymers such as that formed from 1,4-oxybenzoate, 1,4-dioxyphenylene and isophthaloyl units have a hydrolytic stability similar to that of PET [33].

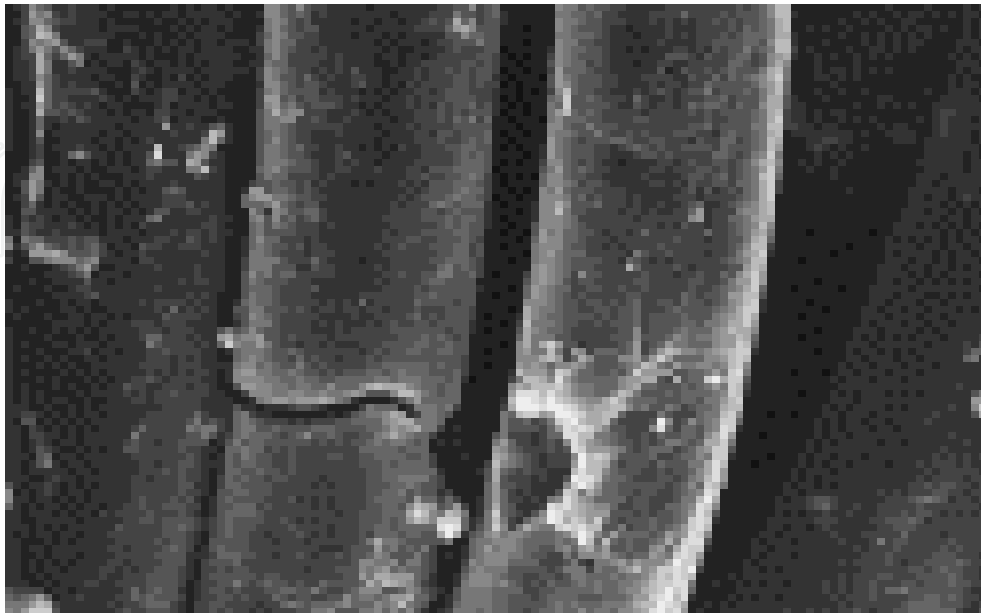


#### 4. *In vivo* rupture of polyesters

The failure of a polyester implant is defined as the inability of the implant fabrics such as woven, knitted and braided to retain its structural integrity after implantation for the anticipated lifetime. Scanning electron microscopic (SEM) examination of ruptured polyester implants revealed fibre thinning (reduction in diameter), transverse cracks, fractures and complete breakage of fibres, Figure 5 [5]. Further, scanning electron micrographs

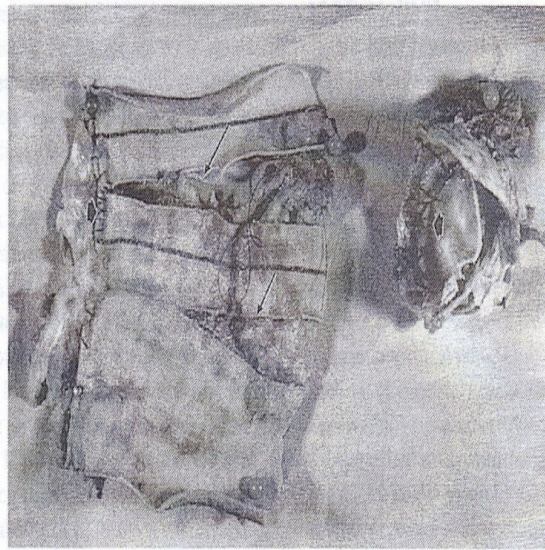


**Figure 5.** Broken, abruptly ruptured thinned out polyester filament [5].

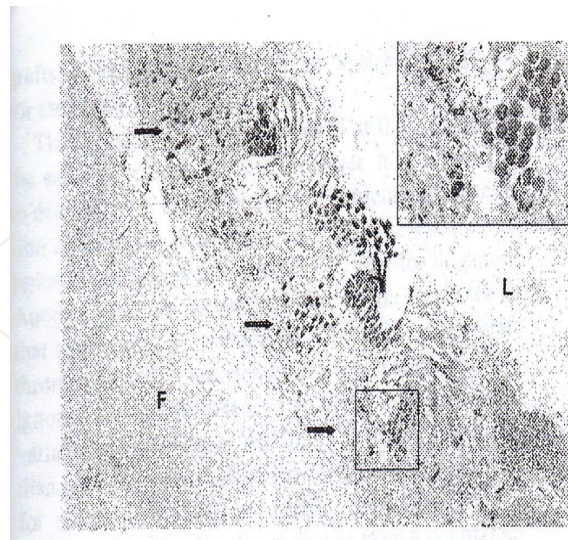


**Figure 6.** Cracks and holes in the explanted graft [62].

show fibre break down with resultant tears and full circumference transverse cracks as shown in Figure 6 [62], longitudinal splits, Figure 7 [71], and broken filaments, Figure 8 [8]. It is believed that the residual stress from manufacturing processes (for example, winding, warping, sizing, weaving/knitting and wet processing) and continuous hydrodynamic strain due to pulsatile blood flow, results in progressive stretching and thinning of the filament yarns, which causes cracking and gradual rupture of some filaments[5,72]. The entire load is then transferred to the remaining neighbouring filaments of the yarn, which were finally snapped (Figures 5 & 9).



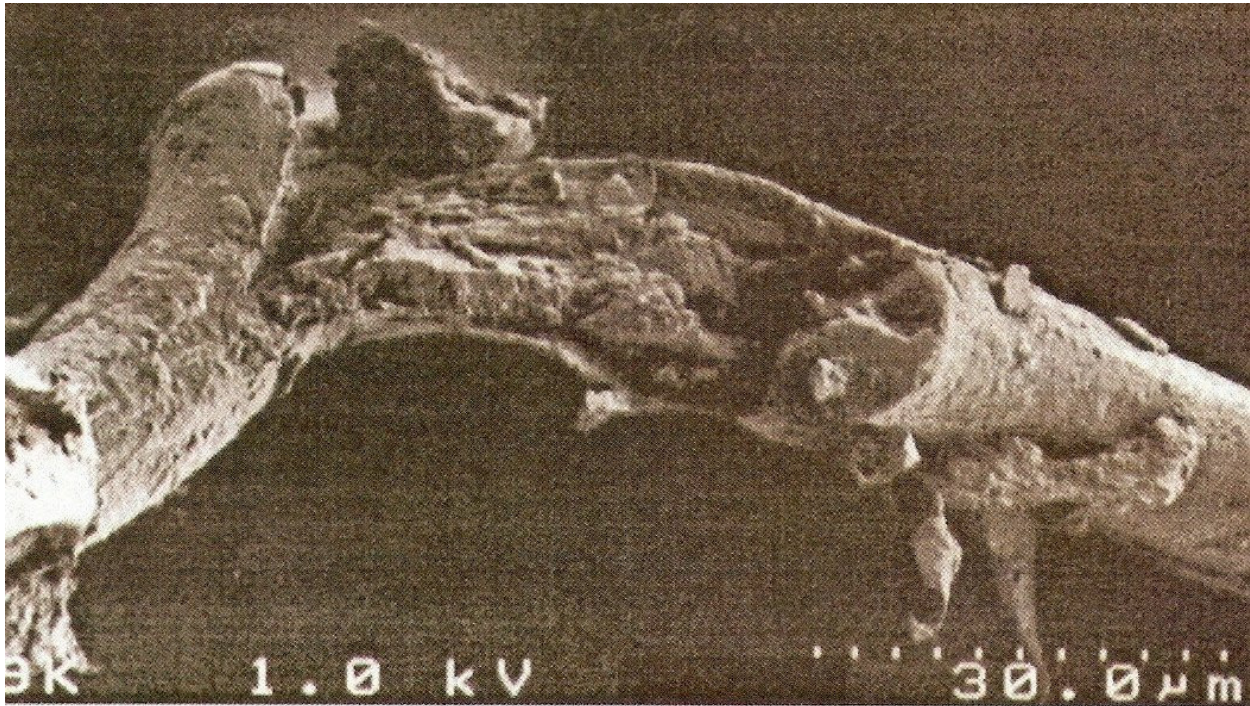
**Figure 7.** Ruptured PET graft, explanted after 15 years [71]



**Figure 8.** Broken filaments in the explanted polyester graft [8].

Other in vivo degradative phenomena reported were (Table 7) loss in bursting strength [73,74], yarn shifting [75], loss in cover factor [76], polymer degradation [12], dilation [13,62], loss in tensile strength [77], decreases in molecular weight and increases in end groups [37].





**Figure 9.** Filament of a 13-year-old vascular graft showing a fracture in the centre and the relatively smooth surface of the filament on the right side [73].

Changes in PET property	Duration (year)	Reference
Loss (25%) in Busting strength	13.5	[74]
Loss (55%) in Busting strength	5	[73]
Yarn shifting (2mm)	2.5	[75]
Cover factor (increase permeability)	5.5	[76]
Polymer degradation	16.0	[12]
Dilatation	9.0	[13]
Dilatation	--	[62]
Loss on tensile strength (40%)	14	[77]
Stiffness	14	[77]
Decrease in molecular weight (50%)	17	[37]
Increase in end groups, OH (100%) and COOH (170%)	17	[37]

**Table 7.** *In vivo* changes due to degradation and structural damage of polyester implant.

## 5. *In vitro* hydrolysis studies of implants:

*In vivo* ruptured (Section 4) PET showed numerous transverse cracks, reduction in diameter, loss in molecular weight and increase in end groups (Table 7). This is due to the internal degradation of PET in alkaline conditions (blood pH=7.4) under stressing environment (pulsatile force and force due to hypertension). During *in vitro* studies, we investigated the effect of applied stress and residual stress on PET implants at 40°C in the aqueous alkaline solution [78]. The temperature, chemical environment (alkaline pH), applied stress, and

residual stress were chosen to mimic the physiological condition of the human body. To accelerate the process, the pH chosen was much higher ( $\text{pH} > 13$ ) than the pH of the human blood and extracellular fluid ( $\text{pH} = 7.4$ ), [79,80]. The *in vitro* results produced with applied stress and residual stress in the alkaline chemical environment showed transverse cracks on the surface of the PET implants. This evidence also confirmed the findings of transverse cracks on PET prosthetic grafts removed from human bodies because of failures.

## 5.1. Effect of applied stress in alkaline environment

### 5.1.1. Weight loss (%) and mechanical properties

Time (hour)	Applied load (MPa/kg)	Weight loss (%)		Loss in breaking load (%)		Loss in breaking strain (%)		% loss in work of rupture	
		<sup>a</sup> PET1	<sup>b</sup> PET2	<sup>a</sup> PET1	<sup>b</sup> PET2	<sup>a</sup> PET1	<sup>b</sup> PET2	<sup>a</sup> PET1	<sup>b</sup> PET2
24	0	3.4	5.6	6.4	4.0	5.0	4.3	30.6	10.4
	12.3/0.1kg	--	--	--	--	--	--	--	--
	61.5/0.5kg	3.5	5.4	14.9	8.1	19.9	12.9	36.2	26.2
	123/1 kg	3.4	4.8	18.2	10.2	21.6	18.2	39.2	30.7
	246/2 kg	4.5	5.4	18.4	22.8	25.5	30.5	43.6	51.5
48	0	8.0	11.0	16.0	10.9	7.5	4.5	27.9	18.0
	12.3/0.1kg	--	--	--	--	--	--	--	--
	61.5/0.5kg	8.2	10.8	19.0	17.9	23.2	19.1	42.2	37.6
	123/1kg	8.3	11.6	24.6	19.0	22.3	23.9	43.6	42.5
	246/2kg	8.5	10.5	32.1	44.4	36.6	44.3	62.7	72.5
96	0	15.3	18.5	23.0	22.7	12.9	12.0	35.8	32.3
	12.3/0.1kg	18.7	--	28.7	--	20.0	--	46.9	--
	61.5/0.5kg	16.5	17.6	28.9	26.2	25.6	19.6	53.8	45.8
	123/1kg	18.9	20.6	34.6	32.6	27.4	29.3	56.0	56.3
	246/2kg	20.2	25.2	58.6	73.1	51.5	65.6	82.0	86.7

**Table 8.** (%) loss in weight and mechanical properties of applied stressed polyester fibres in alkaline environment (10% NaOH), at 40°C [78].<sup>a</sup>PET1: Trevira (Hoechst) high tenacity PET; <sup>b</sup>PET2: Tergel Tech (Rhône Poulenc) high tenacity PET;

The weight loss (%) data of PET1 and PET2, are shown in Table 8. This table tracks the results of up to 96-h treatment period, in which relaxed and different stressing conditions were observed at 40°C. The weight loss (%) was approximately linear with time at a rate of 0.16% per hour for PET1 and 0.22% for PET2 for the relaxed ('0' load) and lower loaded PET samples (12.3–123 MPa). However, after 96 hour of treatment, weight loss was significantly higher for the highest loaded samples (246 MPa) than the relaxed and lower loaded samples.

The weight losses of PET2 samples were higher than the weight losses of the equivalent PET1 samples, even though PET1 is a slightly finer fiber (5.5 dtex) compared to PET2 (5.7 dtex). It must be realized that part of the weight loss for both samples is due to finish dissolving, although PET1 has the higher amount of finish (1.3%) than PET2 (1.0%).

The reason for the increased weight loss (%) due to highest applied stress is unknown. No *in vivo* weight loss data is available although thinning was reported in the ruptured polyester implant [5]. One suggestion is that the weight loss of the polyesters is related to the surface area of the fibre [45,69]. The increased surface area of the PET1 fibers which was found to be only  $\approx 2.0\%$ , by taking the extension of  $5.0\%$  due to the 2000 g (246 MPa) applied load from the load-elongation curve. Therefore, the slight increase in surface area for PET1 ( $\approx 2.0\%$ ) does not account for the greater discrepancy in the amount of weight loss for the relaxed and highest loaded samples of PET1 and PET2. Another factor that might have contributed to the higher weight losses was the fact that there were broken filaments similar to *in vivo* broken filaments as shown Figures 5 and 9 [5,73] in the hydrolysis bath of the highest loaded samples.

For both PET1 and PET2 samples, the breaking load decreased with an increase in treatment time as well as with increase in stressing on the fibers (Table 8). The breaking load loss of the stressed samples is higher than that of the relaxed samples and the most significant losses occurred at the highest loading conditions. For example, after 96 h of treatment, the PET1 samples which were under 246 MPa load, lost 58.6% of breaking load compared to only 23% for relaxed samples, under the same experimental conditions; PET2 samples lost 73 and 22.6%, respectively. It should also be noted that very similar loss in tenacity was observed for both PET samples.

Alkaline hydrolysis takes place only at the surface of the fibers resulting in thinner fiber, which was also reported in the *in vivo* ruptured implants; hence the percentage weight loss should be proportional to the percentage breaking load. However, a nonlinear relationship between weight loss and breaking load loss was reported due to the presence of solvents in the alkaline bath, titanium dioxide in the fiber, and crimp in the fiber [55,64,39]. The highest loaded samples (246 MPa) of both PET1 and PET2, in all treatment conditions, showed percentage loss in breaking load approximately three to four times than the percentage loss in weight. It is reported that in relaxed condition, the loss in breaking load for filament yarn can be between one and two times the percentage loss in weight [39,43,54], which the present *in vitro* study also confirms. For the highest loaded samples (246 MPa) the loss in breaking load and the loss in tenacity are very similar, therefore, the hydrolysis under applied loading conditions is no longer restricted to the surface. It is hypothesized that under higher loading conditions, the hydroxyl ions are able to penetrate deeper inside the PET fiber and causes internal hydrolysis. The scanning electron micrographs, shown later, display the formation of the deeper surface cracks under the heaviest loads.

The breaking strain (Table 8) and work of rupture (Table 8) decrease with the increasing treatment time and increasing loading condition, and the loss was most significant at the highest loading condition. For both PET1 and PET2, the modulus of the fibers decreased ( $\sim 20\%$ ) significantly after 96 hour of treatment. However, the decrease in modulus was not significant between the samples of relaxed condition and lower loading conditions. For all PET fibers, loss of mechanical properties during alkaline hydrolysis, both in relaxed and loading conditions decreased in the following order: modulus < breaking strain < breaking load < work of rupture; with work of rupture being the highest losing property. The data



shown in the present study were obtained at 10% NaOH concentration which is unrealistic for medical applications; however, we have established that similar results could be found for more diluted concentrations of NaOH under stressing conditions [81].

Since the properties of the fibers decreased significantly when exposed to alkali and load, the PET samples were treated with water alone under loading conditions to understand the hydrolysis mechanism, and whether the loss of properties under such conditions was partly due to water hydrolysis under load. At room temperature, there were no significant changes in properties; however at 40°C, with the highest load of 246 MPa, PET1 samples shows a slight decrease (10%) in breaking load and tenacity, and a slight increase in modulus. A more significant decrease was observed in the breaking strain (20%) and work of rupture (30%). However, once again more significant decrease was observed for the breaking strain (20%) and work of rupture (30%) under highest loading conditions.

When treated with water and loading conditions, the physical appearances of the fibers did not change. The fibers retained their original luster after treatment in water for all loading conditions and at all temperatures. The handling properties of both relaxed and loaded samples in water were the same as the original fibers; whereas, alkaline-treated samples with higher loads tended to have a stiffer handle.

### 5.1.2. Effect of residual stress (pre-loaded samples) in alkaline environment

Weight loss (%) and Mechanical properties:

Treatment conditions	Time (hour)	Weight loss (%)	Breaking load (cN)	Breaking load (%)
PET1/NaOH/zero load	72	11.5	40.7±3.2	14.9
PET1/NaOH/zero load	72	13.6	44.9±1.8	14.3
PET1/NaOH/zero load	96	15.3	36.8±1.3	23.0
PET1/NaOH/zero load	96	18.5	40.5±1.6	22.7
PET1/NaOH/ 246MPa pre-load	48	7.9	33.8±2.3	29.3
PET1/NaOH/246 MPa pre-load	72	13.5	26.9±3.4	43.7
PET1/NaOH/246 MPa preload	96	19.4	22.2±2.1	53.6
PET2/NaOH/246 MPa pre-load	96	23.3	15.9±1.1	66.8

**Table 9.** Effect of residual stress (pre-loaded samples) in alkaline environment on PET weight loss (%), breaking load loss (%), and surface characteristics [82].

The weight loss (%), breaking load (cN) and breaking load (%) along with surface characteristics of PET1 and PET2 samples treated in aqueous NaOH in pre-loading conditions are given in Table 9. The weight loss (%) for both PET samples treated in aqueous NaOH in relaxed condition (no applied or pre-load) is increased with increasing treatment time. Similar trend in weight loss (%) increase with treatment time was observed for pre-

loading (Table 9) conditions. However, like applied loaded samples in alkaline (NaOH) environment, the weight loss (%) of the preloaded samples was higher than the relaxed samples for the similar treatment conditions. For example, after 96 hours of treatment in aqueous NaOH, the relaxed PET1 samples (PET1/NaOH/zero load) lost 15.3% weight, whereas the pre-loaded samples (PET1/NaOH/246 MPa pre-load) lost 19.4% weight. The breaking load loss (%) for the relaxed samples treated in aqueous NaOH was similar to corresponding weight loss (%) except for 96 hours treated samples. The 96 hours treated samples in relaxed condition (PET1/NaOH/zero load) produced higher breaking load (%) than the corresponding weight loss (%). The breaking load loss (%) for the pre-loaded samples (PET1/NaOH/246 MPa pre-load; PET2/NaOH/246 MPa pre-load) was much higher than the corresponding weight loss (%).

### 5.1.3. Effect of residual stress (pre-loaded samples) in acid environment and other alkaline (NH<sub>4</sub>OH) environment

The weight loss (%), breaking load (cN) and breaking load loss (%) for PET1 samples treated with H<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>OH is given in Tables 10 and 11 respectively. The weight loss (%) was negligible for sulphuric acid treated samples in relaxed and applied loading conditions; however, the breaking load loss (%) was significantly higher and increased with increasing treatment time. For example, sample (PET-A/H<sub>2</sub>SO<sub>4</sub>/246 MPa applied-load) treated with 5% H<sub>2</sub>SO<sub>4</sub> for 96 hours lost 70% of breaking load. Similar trend was observed with the NH<sub>4</sub>OH treated samples (Table 11). The degree of attack on the mechanical properties of PET by the aqueous solution of NH<sub>4</sub>OH is dependent on solution concentration and stressing conditions. While the weight loss (%) of NH<sub>4</sub>OH treated samples was unchanged, the breaking load loss (%) was increased with the increasing applied loading conditions and concentration of NH<sub>4</sub>OH. For example, at 2% NH<sub>4</sub>OH and 246 MPa applied-load, the breaking load loss was 23.5% compare to 69.1% for 5% NH<sub>4</sub>OH under similar treatment condition (Table 11). The weight loss (%) data agree with the data published in the literature as no weight loss (%) was obtained when PET was treated in aqueous ammonia at 30°C for 10 days [19] and n-butylamine at 21°C for 72 hours [39]. However, a small amount of weight loss (3.3%) was reported when polyester was treated with 10% (w/w) aqueous solution of ethanolamine for 6 hour at 100°C [39].

Treatment conditions	Time (hour)	Weight loss (%)	Breaking load (cN)	Breaking load (%)
PET1/H <sub>2</sub> SO <sub>4</sub> /246 MPa applied-load	24	**NS	37.7±1.4	21.2
PET1/H <sub>2</sub> SO <sub>4</sub> /246 MPa applied-load	48	**NS	30.8±1.8	35.6
PET1/H <sub>2</sub> SO <sub>4</sub> /246 MPa applied-load	72	**NS	21.8±2.2	54.3
PET1/H <sub>2</sub> SO <sub>4</sub> /246 MPa applied-load	96	**NS	14.2±1.7	70.2

**Table 10.** Weight loss (%), breaking load loss (%), and surface characteristics of the H<sub>2</sub>SO<sub>4</sub> treated samples in applied loading condition [82]. \*\*NS: Not significant

Treatment conditions	Time (h)	Breaking load (cN)	Weight loss (%)	<sup>c</sup> Breaking load (%)
Control filament	0	45.9±2.8	0.0	0.0
<sup>a</sup> PET-A/NH <sub>4</sub> OH /zero load)	120	43.5±4.2	0.5	5.2
<sup>a</sup> PET1/NH <sub>4</sub> OH /123 MPa applied-load)	120	42.2±3.7	+2.6	8.1
<sup>a</sup> PET1/NH <sub>4</sub> OH /246 MPa applied-load	120	35.1±3.1	+2.3	23.5
<sup>b</sup> PET1/NH <sub>4</sub> OH /zero load)	120	31.3±2.5	0.7	31.8
<sup>b</sup> PET1/NH <sub>4</sub> OH/123 MPa applied-load	120	24.2±2.8	+1.4	47.3
<sup>b</sup> PET1/NH <sub>4</sub> OH/246 MPa applied-load	120	14.2±2.7	+1.8	69.1

**Table 11.** Weight loss (%), breaking load loss (%), and surface characteristics of the NH<sub>4</sub>OH treated samples in relaxed and applied loading condition [82] <sup>a</sup>:concentration of NH<sub>4</sub>OH:2%; <sup>b</sup>: concentration of NH<sub>4</sub>OH:5%; treatment time:120 days. <sup>c</sup>:breaking load value in cN.

## 5.2. Scanning Electron Microscopy (SEM):

A remarkable phenomenon was observed when polyester fibers were hydrolyzed in alkali under stressing (applied and pre-stressing) conditions. After treatment with applied and pre-loads of 1.5 kg (184 MPa) and 2.0 kg (246 MPa), it was noticed that the fibers had lost their brightness, an effect obvious even to the naked eye. The delustrated appearance was noticed at the loads of 184 MPa and 246 MPa and appeared to increase with increasing reaction time. Such a change in appearance was not observed when the samples were treated with alkalis alone, in either relaxed condition or lower level of loads ( $\leq 123$  MPa), nor for the samples which were treated with the highest load of 2.0 kg in water alone. This delustring effect in the alkaline-treated samples is thought to be due to the presence of voids which are generated within the fibers, caused by exposure to both alkali and load.

The SEM micrographs of original PET1 (Figure 10) and PET2 (Figure 11) are cylindrical in shape and the surface of the fibers is smooth. Minor spots were seen on both PET samples which could be due to the particulate impurities during manufacturing of the fibers. When treated in relaxed condition with the alkali, the fiber surface remains quite smooth with a few defects detectable along the length of the fiber (Figure 12). These defects appear to be short, elongated pitting, parallel to the fiber axis. The presence of TiO<sub>2</sub> is responsible for this type of pitting on the surface as reported in the literature [60,64,83].

Figures 13-15 show the SEM microphotographs of PET1 treated with aqueous NaOH under 246 MPa stressing conditions at 40°C for different treatment times. The surface of these samples shows deeply penetrating and acutely elongated cracks which increased with treatment time. The fiber edge seen in the samples treated for 48 h (Figure 13) is smooth and unpitted. The same fiber at 72 h (Figure 14) shows more pitting. After 96 h of treatment, the sample had a weight loss of 20.2% and corresponding loss in work of rupture of 82.0%, and has also lost smooth linear edge of the fiber (Figure 15). The surface showed deep cracking and irregularities. Similar cracks and surface irregularities were observed in the sample treated with alkaline with a load of 184 MPa (Figure 16). By contrast, only shallow pitting on the surface (Figure 17) of the fibers was observed with the lower loaded samples ( $\leq 123$

MPa). SEM microphotographs of PET2 samples which were treated for 48 h (Figure 18) and 96 h (Figure 19) respectively, with 246 MPa load also showed the same pattern of increased cracking and loss of smooth linear edge over time. The appearance of cracks on the room temperature treated samples is quite different than the appearance of cracks generated at 40°C. The cracks are rather 'dull' and 'unpronounced' at room temperature [81]; whereas, at 40°C, the heavily degraded samples of PET1 and PET2, the cracks are deeper and more acute, resembling a jagged 'corallite structures' (Figures 15 & 19).

Both PET1 and PET2 samples show the formation of large cracks of varying length and width across the surface of the fiber. Yet there are differences in the formation of cracks between PET1 and PET2 samples. In PET1 samples cracks are produced in two directions (Figure 15), longitudinal and transverse, with most of the cracks being transverse, at right angle to the direction of applied load. In the PET2 fibers (Figure 19) the cracks are transverse only, at right angles to the applied load. The cracks in the PET2 samples were also wider and longer. For example, the longest transverse crack in the PET1 sample was found to be about 6.7  $\mu\text{m}$  (Figure 15), while in the PET2 it was about 7.5  $\mu\text{m}$  (Figure 19). It is likely that the greater length of the cracks in the PET2 samples is responsible for the larger loss in mechanical properties. The differences between these two PET samples may reflect differences in processing history and in particular differences in the draw ratio and thermal history.

As the surface cracks formed only in the most heavily loaded samples, it was suspected that the load alone might have been responsible for the formation of cracks. However, SEM microphotographs of PET1 and PET2 samples which were treated with only water and 246 MPa load at 40°C temperature for 96 h show no cracks, nor any longitudinal marks such as are seen in alkaline-treated samples treated under relaxed conditions. PET sample treated with water and highest load are very similar to the original PET sample.

Since it is evident that the surface defects can be detected by treating PET with NaOH in relaxed and applied loading conditions, further investigations were carried out to find out whether residual stressing condition, which can exist in the implant while in the human body, could be responsible for the formation of cracks. The residual stressing condition is created in the polyester by 'pre-loading' the PET samples [82] and then treating with alkaline solution in relaxed condition. This pre-loading condition creates residual stress in the samples. The residual stress in the textile structure is generated in two ways: (a) during textile transformation (spinning/winding/warping/weaving) and (b) during normal functioning in the human body due to intermittent pulsatile forces. It is reported that the residual stress in the textile structure is responsible for premature rupture of small caliber straight tubes (bifurcated grafts, femoro-popliteal grafts and axillo-femoral grafts) [84]. Figure 20 shows the scanning electron micrograph obtained from the pre-stressed sample of PET1 (PET1/NaOH/246 MPa pre-load) treated in 10% alkaline solution at 40°C. Both transverse and axial cracks can be seen in this micrograph. In contrast, only transverse cracks are present in the PET2 pre-stressed (PET2/NaOH/246 MPa pre-load) sample. The axial cracks in the pre-stressed sample (Figure 20) are much wider and deeper than the relaxed sample (Figure 12), however, both axial and transverse cracks are much less



prominent than those of the 246 MPa applied-loaded sample (Figures 15 & 19). The axial cracks in the pre-stressed sample is much prominent than the transverse cracks. It seems that the axial cracks in all three alkaline treated PET1 samples (relaxed-Figure 12, applied-loaded-Figure 15 and pre-loaded-Figure 20) are parallel to each other and the angle between the axial cracks and filament axis is approximately about  $2^{\circ}$  to  $5^{\circ}$ . Similar axial pits and craters have been observed in the explanted Vanguard stent grafts [85].

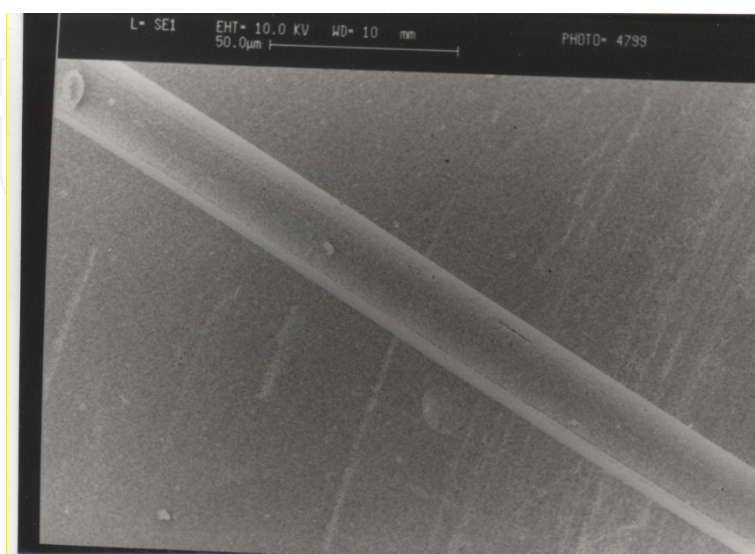
No surface cracks were observed when the PET1 samples were treated with 5% sulphuric acid in relaxed condition and in stressing condition (Figures 21; PET1/H<sub>2</sub>SO<sub>4</sub>/246 MPa applied-load). Similar surface characteristics were observed when the PET1 samples treated with 2% and 5% NH<sub>4</sub>OH in relaxed (PET1/NH<sub>4</sub>OH/zero load; Figure 22), 123 MPa loading (PET1/NH<sub>4</sub>OH/123 MPa applied-load; Figure 23) and 246 MPa loading (PET1/NH<sub>4</sub>OH/246 MPa applied-load; Figure 24) conditions. The smooth appearance of the acid and ammonium hydroxide treated micrographs with 246 MPa loading conditions was surprising as both samples (PET1/H<sub>2</sub>SO<sub>4</sub>/246 MPa applied-load; PET1/NH<sub>4</sub>OH/246 MPa applied-load) lost about 70% breaking load (Tables 10 & 11). The results suggest that the reaction of H<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>OH in relaxed and stressed conditions (below and above yield loads) takes place throughout the actual substance of the fibres with a gradual chemical degradation of PET and splitting of linkages in the long chain polyester molecules. No cracks have been observed when polyester was treated with neat n-butylamine at 21°C for 72 hours [46]; however, formation of spiral, helical, transverse and axial cracks on various amine treated polyesters have been reported [46,86].

The implications of the *in vitro* study become significant and applicable when compared to PET prosthetic grafts removed from the deceased human bodies. In these cases, where PET failures resulted in deaths [5,7,37,72], similar transverse cracks and irregularities in fiber edge were observed. This *in vitro* study confirms that transverse cracks formed on the PET prosthetic grafts when the applied load exceeded the yield load in an alkaline environment. The yield load was measured using 'The Slope Threshold Method [87] which was found to be  $1.22 \pm 0.05$  kg for PET1 and  $1.24 \pm 0.08$  kg for PET2 which is lower than the applied load of 1.5 kg (184 MPa) and 2.0 kg (246 MPa). In certain parts of the human body, the PET prosthetic grafts remain under stressing conditions which is greater than critical level of load [72]. Also, due to the hypersensitiveness in some patients, PET implants encounter higher level of loads. Where the environment is similar to the alkaline condition (blood pH =7.4) and above yield loads, deep transverse cracks formed, which eventually cause failure in the PET prosthetic grafts, resulting in death. We speculate that the higher temperature (40°C) is responsible for an increased mobility of the OH<sup>-</sup> ions, thus producing deeper penetration in PET fibers through the highly stressed ester bonds and resulting in the 'corallite structures' observed [78].

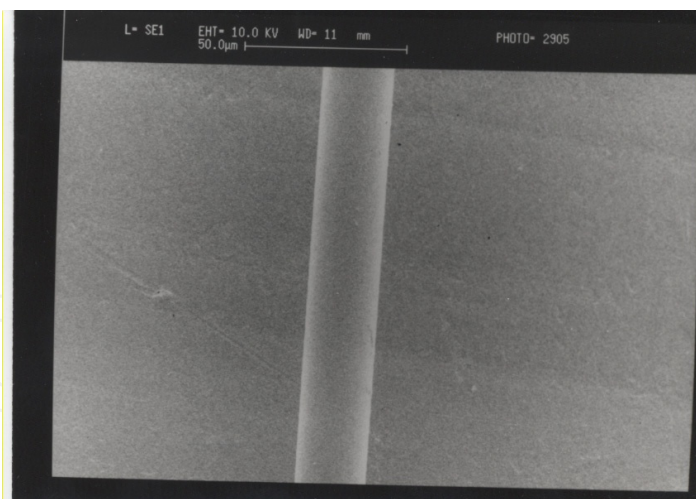
The surface characteristics of PET are different for different loading conditions and PET types. When the applied load was below yield load (12.3-123 MPa) of PET, only longitudinal cracks were observed in the PET1 samples and no visible cracks in either directions were observed in the PET2 samples except the 96 hours treated PET1 samples with 123 MPa

applied loading condition (Figure 17) which shows the onset of crack formation. However, when the applied load was above the yield load which was 2000 g or 246 MPa applied-load and pre-load, severe longitudinal and axial cracks were generated in the PET1 samples (Figures 13-16, 20) and axial cracks were seen in the PET2 sample (Figures 18-19). The length and width of the cracks were increased with the severity of the hydrolysis. The longitudinal cracks were more prominent in the stressed and pre-stressed PET1 sample (Figures 13-16, 20) than the relaxed PET1 sample (Figure 12) for the similar hydrolysis conditions. The axial crack patterns (crack length, width and frequency) are different for PET1 and PET2 for the similar treatment condition. The difference in dimensions of crack size in PET1 and PET2 is due to the presence of different size crystals which depends on the processing and thermal history. The size and amount of crystals formation is dependent of the rate of nucleation rate. It is known that smaller and numerous crystals are formed with high nucleation rate while larger and few crystals are formed with slow nucleation rate [33]. Further, the differences in crack dimensions (width and length) in a particular PET are dependent on the fibrillar dimensions as well as stress in-homogeneity. For PET, the fibrillar transverse dimension was found to be between 150-1000 Å and the fibrillar length was 500-10,000 Å [88].

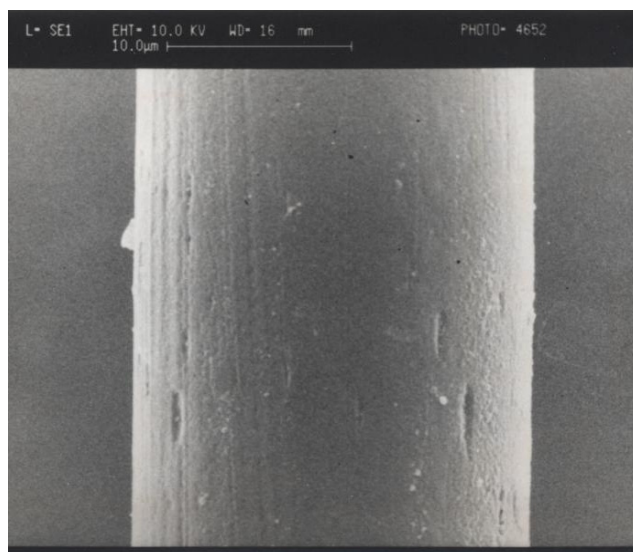
The transverse and longitudinal cracks in the stressed and pre-stressed PET samples are similar to those observed in the ruptured PET implants *in vivo* that resulted in numerous human deaths [5,72,85]. The longitudinal cracks in the PET1 sample might have been originated from the surface defects or due to the presence of TiO<sub>2</sub> as the sample is bright and contained about 0.1% TiO<sub>2</sub>. Although TiO<sub>2</sub> should not be used in medical grade PET as it damages cell membranes [89] and increases the rate of degradation [60,64]. The scanning electron micrographs of titanium dioxide induced longitudinal cracks formation have been published for medical (Figure 25) and apparel grade polyesters [64,90]. Alternatively, the PET1 sample might have manufacturing defects, possibly from the heat setting treatments.



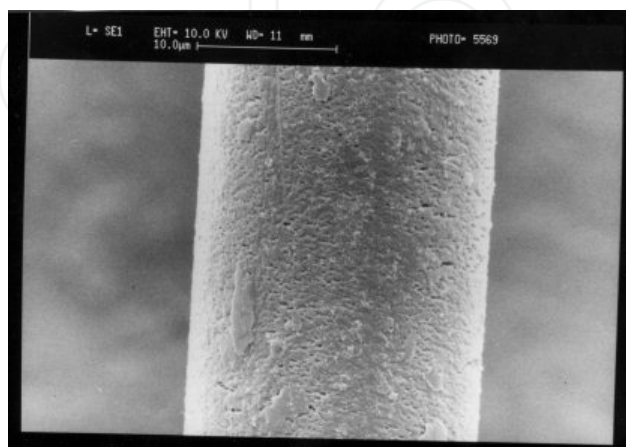
**Figure 10.** SEM micrograph of virgin PET1 [91].



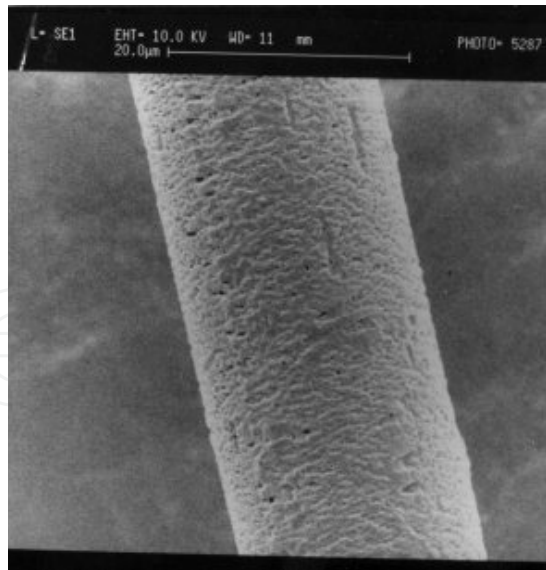
**Figure 11.** SEM micrograph of virgin PET2 [91].



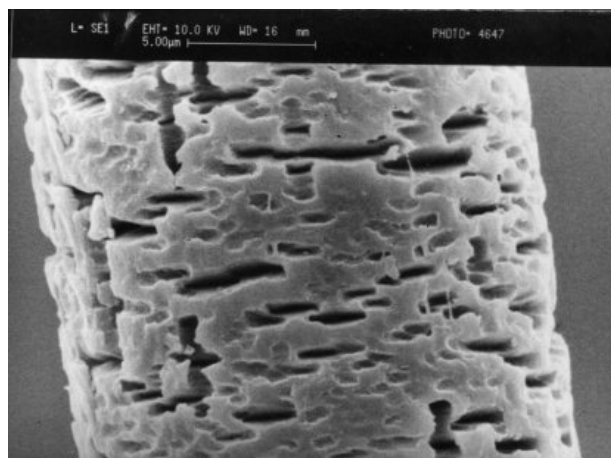
**Figure 12.** Scanning electron micrograph of PET1 treated in relaxed state with 10% NaOH, 96 hours/40°C [91].



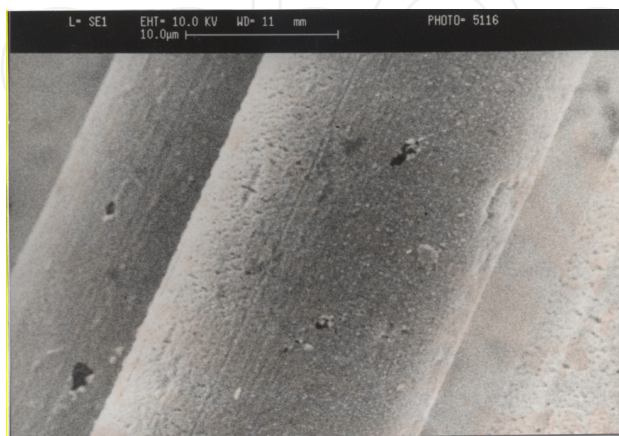
**Figure 13.** SEM micrograph of PET1 sample treated with 9.81% NaOH/48 h/40 ° C temperature/2 kg loads [78]



**Figure 14.** SEM micrograph of PET1 sample treated with 9.81% NaOH/72 h/40°C temperature/2 kg load [78].

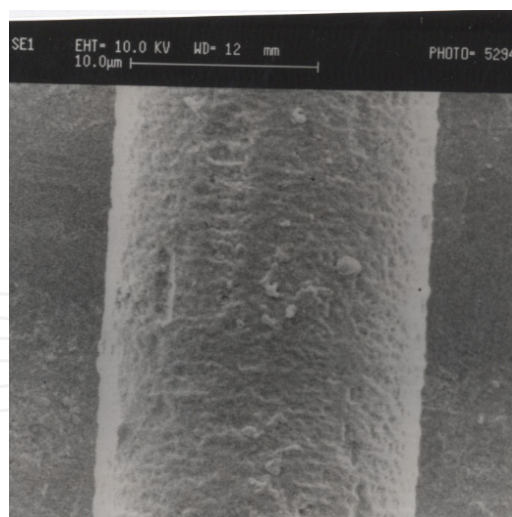


**Figure 15.** SEM micrograph of PET1 sample, treated with 9.81% NaOH/96 h/40°C temperature/2 kg load (246 MPa) [78].

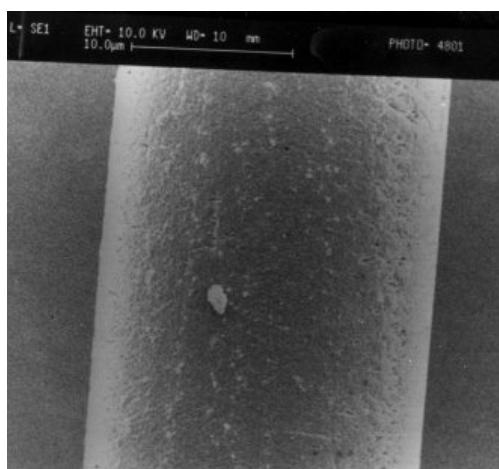


**Figure 16.** Scanning electron micrograph of PET1 treated at room temperature for 20days under 1500g (184 MPa) stressing condition in 10% NaOH [91].

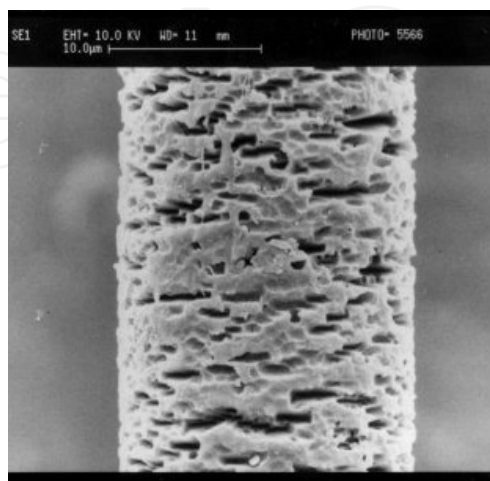




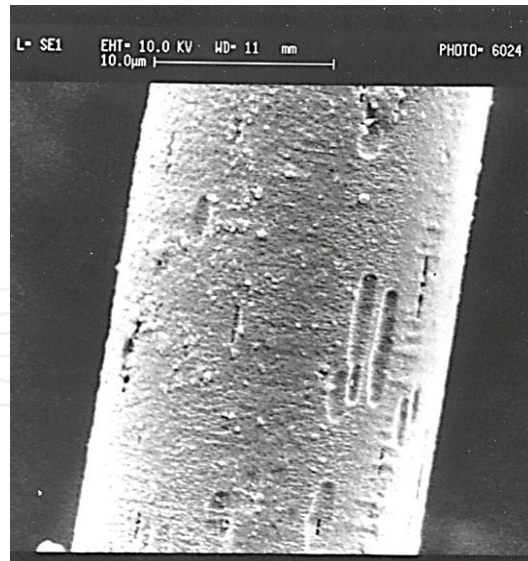
**Figure 17.** Scanning electron micrograph of PET1 treated at room temperature for 20days under 1000g (123 MPa) stressing condition in 10% NaOH [81].



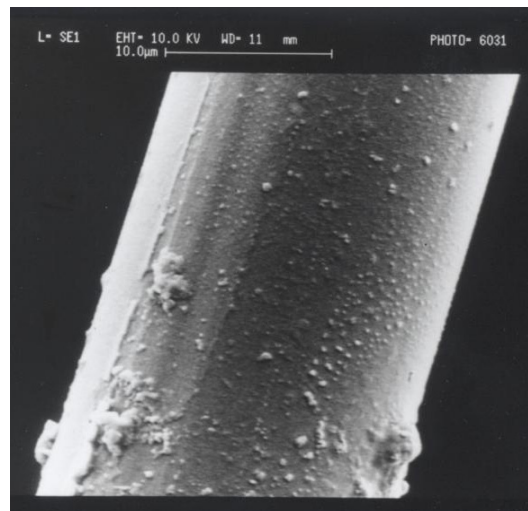
**Figure 18.** SEM micrograph of PET2 sample, treated with 10.06% NaOH/48 h/40°C temperature/246 MPa [78].



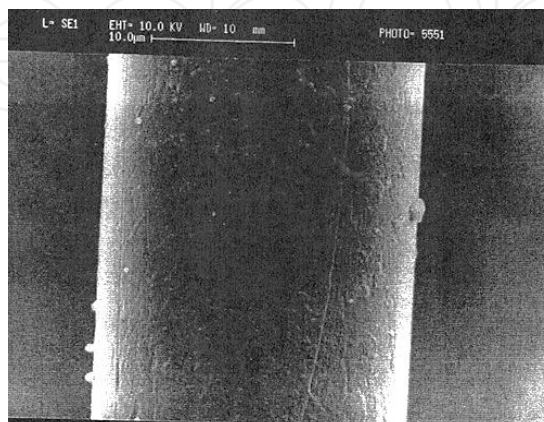
**Figure 19.** SEM micrograph of PET2 sample, treated with 10.06% NaOH/96 h/40°C temperature/246 MPa [78].



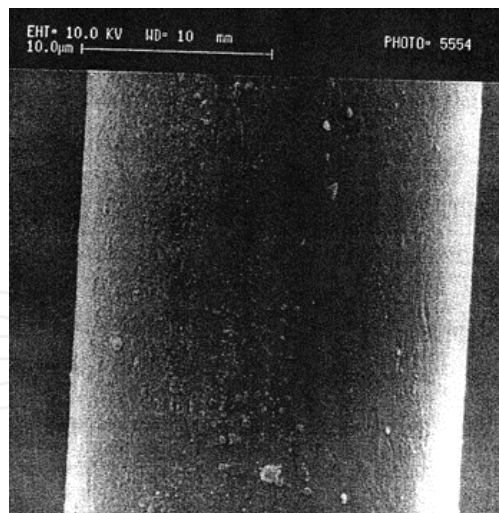
**Figure 20.** Micrograph of pre-stressed sample (pre-stressed for 48 hours) treated with 10% NaOH in relaxed condition, 40°C for 96 hours [82].



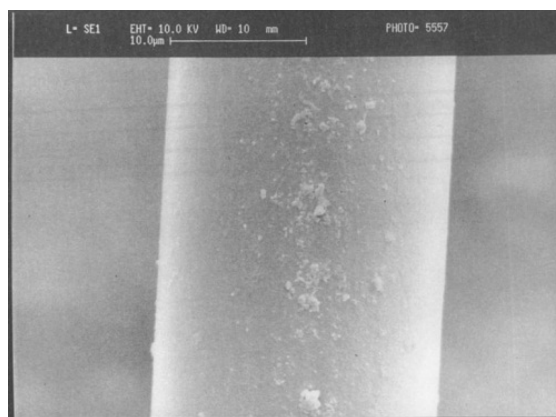
**Figure 21.** Micrograph of 2000g stressed sample treated with 5%  $\text{H}_2\text{SO}_4$ , 40°C/48 hours [82].



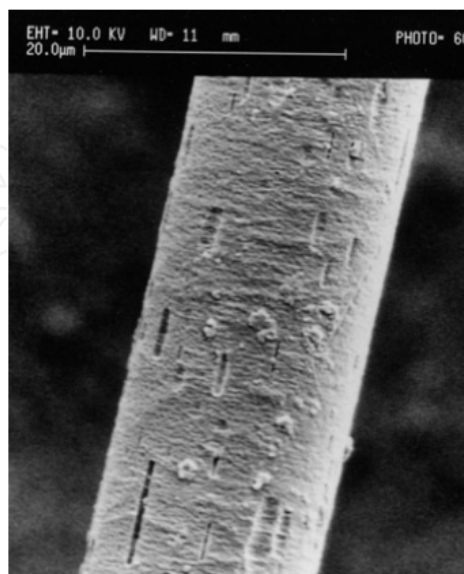
**Figure 22.** SEM micrograph of PET sample treated with 5% ammonium hydroxide, at room temperature, 120 days, under relax condition [91].



**Figure 23.** SEM micrograph of PET1 treated with 5% ammonium hydroxide, at room temperature, 120 days, under 1kg load [91].



**Figure 24.** Micrograph of 2000g stressed sample treated with 5%  $\text{NH}_4\text{OH}$ , room temp./120 days [91].



**Figure 25.** SEM micrograph of PET1 sample, treated with 4.0%  $\text{NaOH}$ , 4h at  $100^\circ\text{C}$ . (Titanium dioxide content: 0.1%) [90]



## 6. Accelerated degradation tests and lifetime prediction:

Due to the physical and chemical variability within the PET, it is very difficult to estimate how long PET implants will last in the physiological conditions. One suggestion is that when using PET medical devices for human spare parts, the surgeons must be committed to a follow-up of such a patient for his/her remaining life. Only by this means will the safety and effectiveness of the spare part become known. Others plea for reporting all graft failures, preferably with identifying details of material and construction and an attempt to evaluate factors responsible for failure.

Previously it was reported that the weight loss (%) of medical grade PET roughly fits the ICI formula [91] given in Equation (1). An empirical equation was also reported relating to loss in breaking load with treatment time and applied load for a specific NaOH concentration and treatment temperature [78]. The generic empirical equation is given in Equation (2) and the Equations (3) and (4) were computed by Statistical Package for Social Science (SPSS) 'Enter Method' for PET1 and PET2 respectively at 40°C and 10% NaOH concentration using breaking load (cN) data. The breaking load data for PET1 and PET2 is given in Table 8.

$$\text{Weight loss}(\%) = \frac{0.47t(x^2 + 6x)}{1.082^{100-T} \sqrt{d}} \quad (1);$$

Where  $t$  = time in hour,  $x$  = concentration of NaOH (%);  $T$  = temperature in °C;  $d$  = decitex of fibre.

$$Y = \beta_0 + \beta_1 T + \beta_2 L^2 \quad (2)$$

where  $Y$  = predicted breaking load (cN);  $T$  = Treatment time (day);  $L$  = applied load (g);

$$Y = 47.1 - 3.44 T - 2.26 * 10^{-6} L^2 \quad (3)$$

$(R^2 = 0.85, S = 2.88, 95\% \text{ confidence lim} = \pm 6.27)$

$$Y = 56.4 - 4.79 T - 4.36 * 10^{-6} L^2 \quad (4)$$

$(R^2 = 0.90, S = 3.56, 95\% \text{ confidence lim} = \pm 7.77)$

In the Equations (3) and (4),  $R^2$  is the coefficient of determination,  $S$  is the standard deviation about regression and 95% confidence limits for the predicted breaking load  $Y$  are given by  $\pm t_{0.025} S$ , where  $t_{0.025}$  is obtained from probability points of the  $t$  distribution table using  $n-2$ (=12) degrees of freedom.

Using the Equation (3) for PET1, the lifetime for 50% loss in breaking load for 'zero applied loading' condition would be only  $\approx 7$  days in 10% NaOH at 40°C. Since the dependence of NaOH concentration with the weight loss (%) is  $(x^2+6x)$  according to Equation (1), assuming the rate of weight loss is proportional to breaking load loss, we can calculate the lifetime using lower concentration of alkali which is likely to encounter by PET implants. Hence, for 0.01% or 0.0025M NaOH (pH<11), the lifetime would be about 50 years in zero loading condition.

Similarly for PET2 sample, using the Equation (4) and taking the dependence of NaOH ( $x^2 + 6x$ ), the life time would be about 45 years in 0.0025 M NaOH at 40°C. The calculated lifetime for PET varies between 16.5 years to 214 years depending on the exposure conditions (Table 12). Since the pH of blood is only 7.4, physiological fluids alone cannot be responsible for pre-mature rupture of PET implants as reported in the numerous medical literatures (Table 2). However, where the pre-mature rupture occurred, perhaps the main contributing factor was the site specific physiological loads that exceed the polyester yield load. Another reason for pre-mature rupture of PET implants was the use of apparel grade PET materials [10] as it was found that the retrieved PET implants in Hospital Saint-Joseph, Marseille, France, was manufactured from semi-dull, round cross-section, textured multifilament, Type 56T Dacron. This specific type of polyester was apparel grade and not to be used for implants. The textured and semi-dull polyesters degrade faster than the clear (bright) and flat filament polyester yarns [46].

Predicted life-time (yeas)	Types of PET	Conditioned considered	Reference
27	Bottled PET	Wet soil	[92]
214	High tenacity filament, 1100 detex, 200f	pH = 10 (Na <sup>+</sup> ), 25°C	[24]
16.5	High tenacity filament, 1100 detex, 200f	Ca <sup>++</sup> , 25°C	[24]
100	High tenacity filament	Saturated soil, pH=2-10	[24]

**Table 12.** Life-time predictions for PET.

## 7. Conclusions

In order to predict a realistic lifetime of a PET implant, a far greater studies are required than the present one and any previous studies. The polyesters must be carefully selected before their implantation considering the exposure conditions and fibre physical and fine structures. Use of apparel grade polyesters to manufacture implants must be forbidden as changes in polymerization techniques, additives, and processing treatments all enhance the long term durability of polyesters. The textile properties of implants must be recorded before their implantation as it would be easier to compare with the ruptured explanted samples. There is a clear lack of communications between surgeons and textile scientists as most of the ruptured explanted samples analyzed without using any textile standards.

Thus far, the durability of polyester implants is still in questionable because of pre-mature ruptures. In an attempt to address the longevity issue, ‘lifetime’ of medical grade polyester has been calculated from empirical equations. However, to avoid short-term accelerated tests for long term physiological durability, it is recommended to test polyester in animal models.

## Author details

Mashiur Rahman

*Department of Textile Sciences, Faculty of Human Ecology, University of Manitoba, Winnipeg, Manitoba, Canada*

## 8. References

- [1] Carothers W H, Hill J W [1952] Studies of polymerization and ring formation XV: Artificial fibres from synthetic linear condensation super polymers. *J. Amer. Chem. Soc.* 54:1579-1587.
- [2] Ludwig H (1971). *Polyester Fibres Chemistry and Technology*, Wiley Interscience, London, 1p.
- [3] Whinfield J R, Dickson J T (1947). *Brit. Pat.* 578,079.
- [4] Voorhees A B Jr, Laretzki A, Blakemore A H (1952) The Use of Tubes Constructed from Vinyon "N" Cloth in Bridging Arterial Defects (a Preliminary Report). *Ann. Surg.* 135:332– 336.
- [5] Berger K, Sauvage L (1981) Late Fiber Deterioration in Dacron Arterial Grafts. *Anna. Surg.* 193:477-491.
- [6] Rajendran S, Anand S C (2002) Development in Medical Textiles, *Textil. Progr.* 32:1–37.
- [7] Wilson S E, Krug R, Mueller G, Wilson L (1997) Late Disruption of Dacron Aortic Grafts. *Ann. Vasc. Surg.* 11:383-386. 7a. Maarek JM, Guidoin R, Aubin M, Prud'homme RE, (1984) Molecular weight characterization of virgin and explanted polyester arterial prostheses. *J. Biomed. Res.* 18:881-894.
- [8] Van Damme H, Depre M, Creemers E, Limet R (2005) Intrinsic Structural Failure of Polyester (Dacron) Vascular Grafts. A General Review. *Acta. Chir. Belg.* 105:249-255.
- [9] Tomizawa Y (2003) Vascular Grafts: Basic Research and Clinical Applications. In: Tura A, editor. *Vascular Grafts Experimenting and Modelling, Advances in Fluid Mechanisms*, Vol: 34, WIT Press, Southampton, pp. 1–39.
- [10] King M W, Zhang Z, Guidoin R (2001) Microstructural Changes in Polyester Biotextiles During Implantation in Humans. *J. Textil. Apparel. Technol. Manag.* 1:1–8.
- [11] Ottinger L W, Darling R C, Wirthlin L S, Linton R R (1976). Failure of Ultra light weight Knitted Dacron Grafts in Arterial Reconstruction. *Arch. Surg.* 111:146–149.
- [12] Chakfe N, Riepe G, Dieval F et al. (2001) Longitudinal ruptures of polyester knitted vascular prostheses. *J. Vasc. Surg.* 33:1015-1022.
- [13] Trippstad A (1985). Late Rupture of knitted Dacron Double Velour arterial Prostheses, *Acta. Chir. Scand.* 151:391-395.
- [14] Falkai B V (1996) ), Developments in the production of industrial PET filaments. *Asian Text. Res.* 5:26-38.
- [15] Adanur S (1995) Fibre Properties and Technology. In: Adanur S. editor. *Wellington Sears Handbook of Industrial Textiles*, Lancaster, USA: Technomic Publishing Co. Inc. pp 555-607.
- [16] Shimizu J, Kikutani T (1993) *Polyesters 50 Years of Achievement*, The Textile Institute, Manchester, UK, 166p.
- [17] Ward I, Cansfield D O, Carr P (1993). *Polyesters 50 Years of Achievement*, The Textile Institute, Manchester, UK. pp 192-195.
- [18] Hearle J W S, Greer R (1970) Fibre Structure. *Text. Prog.* 2:1-18.
- [19] Zeronian S H, Collins M J (1988). *Text. Chem. Colour.* 20:25-28.
- [20] Ziabicki A (1996). *Text. Res. J.* 66:705-712.

- [21] Baur K H (1993). Polyesters 50 Years of Achievement, The Textile Institute, Manchester, UK.
- [22] Tamblyn J W, Newland G C (1965). Induction period in the aging of polypropylene. *J. Appl. Polym. Sci.* 9:2261-2260.
- [23] Voskamp W, Risseuw P (1987) Method to establish the maximum allowable load under working conditions of polyester reinforcing fabrics. *Geotext. Geomembr.* 6:173-184.
- [24] Horrocks A R, D'Souza J A (1992). Degradation of Polymers in Geotextiles and Geomembranes. In: Hamid S, Amin M, Maadhah A, editors. *Handbook of Polymer Degradation*, (Eds). New York: Marcel Dekker Inc, PP433-505.
- [25] Stessel R I, Hodge J S (1995) Chemical resistance testing of geomembrane liners. *J. Hazard. Mater.* 42:265-267
- [26] Smith L V, Devires K L (1993). Mechanical properties of polymeric fibres exposed to stress in a NO<sub>x</sub> environment. *Polymer*, 34:546-550.
- [27] Morgan R J, Pruenda C O, Buller N et al. (1984). 29<sup>th</sup> SAMPE Symposium, April 3-5, 891.
- [28] Ely J L (1984) Polyurethane in Biomedical Engineering, Planck H, Egbers G, Syre L. editors. Elsevier Science, Amsterdam, 1-15.
- [29] Lecrecq B, Schaeffner M, Delmas ph et al. (1990). Proc. 4<sup>th</sup> Int. Conf. on Geotextiles, Geommebranes and Related Products, Hoedt, G. D. (Edt), The Hague, Balkema, Rotterdam, pp 679-684.
- [30] Van Zantem R V(1986) Geotextiles and Geomembranes in Civil Engineering, Balkema, Rotterdam, pp 213-241.
- [31] Davis G W (1989) Aging and durability of polyester geotextiles. In: Koerner R. M. editor. *Durability and Aging of Geosyntheticd*. New York: Elsevier Applied Science. p65.
- [32] Korshak V V, Vinogradova S V (1965) Polyesters, Pergamon Press, Oxford, England.
- [33] McIntyre J E (1998 Polyester Fibres, In: Lewin M, Pearce E M, editor. *Handbook of Fibre Science and Technology: Fibre Chemistry*, Volume IV. NY: M. Dekker, NY, pp 1-73.
- [34] Sprague C J, Davis G W (1991) High-Tech Fibrous Materials, Chapter-20. ACS-Series-457, pp 304-319.
- [35] Sato M (1983). Sen-i Gakkaishi, 39, T209-219.
- [36] Hall J, Whinfield J R (1952). U.S. Pat., 2,590,402.
- [37] Chaouch W, Dieval F, Le Nouen, D, Defoin A, Chakfe N, Durand B(2009) <sup>1</sup>H-NMR spectroscopic study of the effect of aging vascular prostheses made of poly(ethylene terephthalate) on the macromolecular weight. *J. Biomed. Mater. Res.: Part A*, 91A, 939-952.
- [38] Goedt G D (1990). Discussuin of polyester durability, Proc. 4<sup>th</sup> Int. Conference on Geotextiles, Geomembranes and Related Products, The Hague, Balkema, Rotterdam, 1171.
- [39] ICI (UK), Chemical Properties of Terylene, The Effects of Alkalis, Industrial Fibre Manual, 1978; Section A1/3.
- [40] Gawish S M, Ambroise G(1986) Amer Dyestuff Reporter. 5:30-32.
- [41] Dave J, Kumar R, Srivastava H C (1987) Studies on modification of polyester fabrics I: Alkaline hydrolysis. *J. Appl. Polym. Sci.* 33:455-477.
- [42] Teli M, Purkaystha A (1993) Amer. Dyestuff. Reporter. 82:34-40.
- [43] Houser K D (1983) Text. Chemists Colourists. 15:70/37-72/39.
- [44] Ellison M S, Fisher L D, Zeronian S H (1982) *J. Appl. Polym. Sci.* Physical properties of polyester fibers degraded by aminolysis and by alkanol hydrolysis. 27:247-257.

- [45] Yamamoto Y, Sangen O, Nakano H (1984). *Sen-i Gakkaishi*, 40:T122-124.
- [46] Zeronian S H, Collins M J (1989) Surface Modification of Polyester by Alkaline Treatments. *Text. Prog.* 20:1-26
- [47] Namboori C G G, Haith M S (1968) Steric effects in the basic hydrolysis of poly(ethylene terephthalate). *J. Appl. Polym. Sci.* 12:1999–2005.
- [48] Namboori C G G (1969). *Text. Chem. Colourists*, 1:50/24-51/25.
- [49] Olson L M, Wentz M (1984). *Text Chem Colourists*, 16:48/35-54/41.
- [50] Cho H, Huh M W, Furuhashi K, Sakamoto M (1992). *Sen-i Gakkaishi*, 48:T610-618.
- [51] Grancaric A M, Kallay N (1993) Kinetics of polyester fiber alkaline hydrolysis: Effect of temperature and cationic surfactants. *J App. Polym. Sci.* 49:175–181.
- [52] Shenai V A, Lokre D B (1978). *Text. Dyer Printer*, 11:27-28.
- [53] Sanders E M, Zeronian S H (1982) An analysis of the moisture-related properties of hydrolyzed polyester. *J. Appl. Polym. Sci.* 27:4477–4491.
- [54] Maillo J, Gacen J, Naik A (1993). *Melliand Textilber.* 74: E291-293.
- [55] Jan S S, Uen J L, Shyu G A, Wu C L, Chen C C (1992). *Amer. Dyest. Rep.* 81:32-37&40.
- [56] Mathur A, Netravali A N, O'Rourke T D (1994). *Geotext. Geomemb.* 13:591-626.
- [57] Halse Y, Koerner R M, Lord A E, (1987a) Effect of high levels of alkalinity on geotextiles. Part I:  $\text{Ca}(\text{OH})_2$  solutions. *Geotext. Geomemb* 5:261-282.
- [58] Halse Y, Koerner R M, Lord A E (1987b) Effect of high levels of alkalinity on geotextiles. Part II:  $\text{NaOH}$  solutions. *Geotext. Geomemb*, 6: 295-305.
- [59] Niu S, Wakida T (1993) Effect of Heat-Setting Temperature on Alkali Hydrolysis of Poly (Ethylene Terephthalate) Fibers. *Text. Res. J.* 63:346-350.
- [60] Collins M J, Zeronian S H, Meyer M S (1991) The use of aqueous alkaline hydrolysis to reveal the fine structure of poly(ethylene terephthalate) fibers. *J. Appl. Polym. Sci.* 42:2149–2162.
- [61] Hashimoto T (1959). *Sen-i Gakkaishi*, 15:794.
- [62] Nunn D B (1999) Structural Failure of Dacron Grafts. *Semin. Vasc. Surg.* 12: 83-91.
- [63] Tsuji W, Nakao T, Doyama Y et al. (1984). *Sen-i Gakkaishi*, 40:T350-358.
- [64] Solbrig C M, Obendorf S K (1991) Alkaline Hydrolysis of Titanium Dioxide Delustered Poly(ethylene Terephthalate) Yarns. *Text. Res. J.* 61:177-181.
- [65] Postman W (1980). *Text. Res. J.* 50:444-453.
- [66] Marshal R M, Dardoufas K C (1977). US Patent, 4,019,990.
- [67] Marshal R M, Dardoufas K C (1976). US Patent, 3,962,516.
- [68] Latta B (1984) Improved Tactile and Sorption Properties of Polyester Fabrics Through Caustic Treatment, *Text. Res. J.* 54:766-775.
- [69] Guang L, Lixia G, Tong S (1993) *J. China Text. Univ.* 10:34.
- [70] McIntyre J E (1985) *In: Handbook of Fibre Science and Technology, Vol. 4: Fibre Chemistry.*
- [71] Berman S S, Hunter G C, Smyth S H et al. (1995) Application of computed tomography for surveillance of aortic grafts. *Surgery*, 118: 8-15.
- [72] Yashar J J, Richman M H, Dyckman J, Witoszka M, Burnard R J, Weyman A K, Yashar J (1978) *Surgery*, 84: 659.



- [73] Riepe G, Loos J, Imig H, Schroder A, Schneider E, Petermann J, Rogge A, Ludwig M, Schenke A, Nassutt R, Chakfe N, Morlock M (1997) Long-term in vivo Alterations of polyester Vascular Grafts in Humans. *Eur. J. Vasc. Endovasc. Surg.* 13:540-548.
- [74] Rao T J, Pan C, Guidon R, Marceau D et al. (1991) Soft Filamentous Woven Polyester Arterial Prostheses from China. *Biomaterials*,12:335-344.
- [75] Guidoin R, Marois Y, Douville Y, et al. (2000) First-Generation Aortic Endografts: Analysis of Explanted Stentor Devices from the EUROSTAR Registry. *J. Endovasc. Ther.* 7:105-122.
- [76] Riepe G, Heintz C, Kaiser E et al. (2002) What can we Learn from Explanted Endovascular Devices. *Eur. J. Vasc. Endovasc. Surg*, 24:117-122.
- [77] Ambrad-Chalela E, Shi Q, Berman A et al. (2001) Favorable Histologic Findings and Tensile Strength at 14 Years in Knitted Polyester Aortofemoral and Femoropopliteal Grafts in the Same Patient. *Ann. Vasc. Surg.* 15:578-581.
- [78] Rahman M, East G (2006) Effect of applied stress on the alkaline hydrolysis of poly(ethylene terephthalate) at 40°C: Relevance to medical textiles. *J. Appl. Polym. Sci.* 102:4814-4822.
- [79] Marieb E P (2000) *Essentials of Human Anatomy and Physiology*, 6th ed. San Francisco, USA: Addison Wesley Longman. 80p.
- [80] Chan J C (1983) *Adv. Pediatr.* 30:401.
- [81] East G, Rahman M (1999) Effect of applied stress on the alkaline hydrolysis of geotextile poly(ethylene terephthalate). Part 1: room temperature, *Polymer*, 40:2281-2288.
- [82] Rahman, M, East G (2012). *In Vitro* Study of Poly(ethylene terephthalate) Implants for Long-term Durability. *Text. Res. J.* accepted for publication.
- [83] Fujimoto K, Iohara K, Ohwaki S, Murase Y J (1991) *J. Appl. Polym. Sci.* 42:1509.
- [84] Damme H, Depre M, Creemers E, Limet R (2005) Intrinsic Structural Failure of Polyester (Dacron) Vascular Grafts. A General Review. *Acta. Chir. Belg.* 105:249-255.
- [85] Chuter T A M (2009) Durability of Endovascular Infrarenal Aneurysm Repair: When Does Late Failure Occur and Why? *Semin. Vasc. Surg.* 22:102-110.
- [86] Holmes S A (1996). Surface Defect Geometry/Tensile Failure Relationships of Aminolyzed Poly(ethylene terephthalate) *Text. Res. J.* 66:214-218.
- [87] *INSTRON Series IX* (1992), *Automated Materials Testing System, Version-5, D12-14*.
- [88] Tucker P, George W (1972) Microfibres Within Fibres: A Review, *Pol. Eng. Sci.* 12: 364-377.
- [89] Valant J, Drobne D, Novak S. (2011) Effect of ingested titanium dioxide nanoparticles on the digestive gland cell membrane of terrestrial isopods. *Chemosphere*, 87:19-25.
- [90] Rahman M, East G (2009) Titanium Dioxide Particle-induced Alkaline Degradation of Poly(ethylene Terephthalate): Application to Medical Textiles. *Text. Res. J.* 79:728-736.
- [91] Rahman M (1997). *The Alkaline Degradation of Poly(ethylene terephthalate) Geotextiles*, University of Leeds, UK.
- [92] Allen N S, Mohammad M, Edge M, Jones K. (1991) Environmental Degradation of Poly(ethylene Terephthalate). *Text. Res. J.* 61:690-696.