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MICROSTRUCTURAL CHANGES IN POLYESTER BIOTEXTILES DURING IMPLANTATION IN HUMANS

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ABSTRACT

We have previously reported that polyester arterial prostheses experience losses in strength and molecular weight while implanted in humans over extended periods. This study used thermal analysis, FTIR spectroscopy and vapor phase dyeing techniques to characterize changes in the microstructure of poly(ethylene terephthalate) biotextiles retrieved from patients after 2 to 16 years in vivo. It found that polyester fibers become increasingly more crystalline due to hydrolytic biodegradation near the surface, which results in a loss of amorphous material, and through a slow annealing effect of the body, which at 37 ºC causes the larger crystalline domains to grow at the expense of the smaller ones.

KEYWORDS: biotextile, biodegradation, crystallinity, implant retrieval, infrared spectroscopy, polyester, thermal analysis, vapor phase dyeing

INTRODUCTION

Biotextile structures, woven, knitted, felted and braided from poly(ethylene terephthalate) (polyester) fibers are currently implanted in humans during various types of surgical operations. Because of their superior tensile and bending properties, these polyester fibers and the structures made from them are considered mechanically suitable and biocompatible for use as sutures, internal patches, pledgets, ligamentous prostheses, hernia repair meshes, heart valve sewing cuffs, and endovascular stent grafts (Figures 1-5).

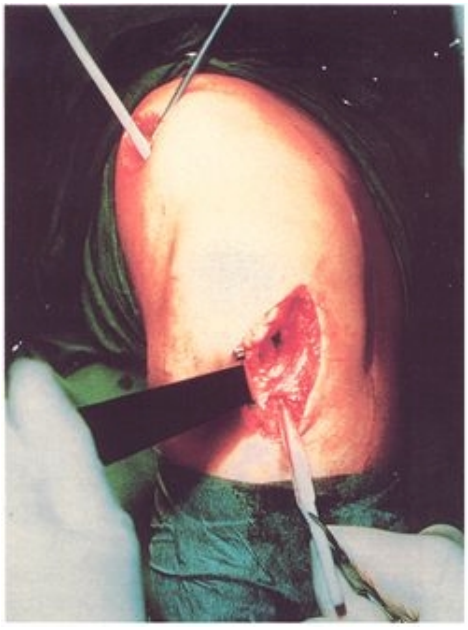

Figure 1: A replacement braided polyester anterior cruciate ligament prosthesis being implanted in a 25 year old football player following an injury in order to stabilize the left knee.

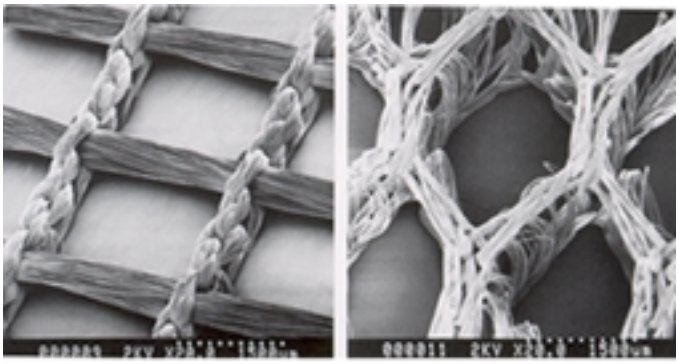

Figure 2: Scanning electron photomicrographs of two and three dimensional warp-knitted mesh fabrics for hernia repair knitted from polyester multifilament yarns.

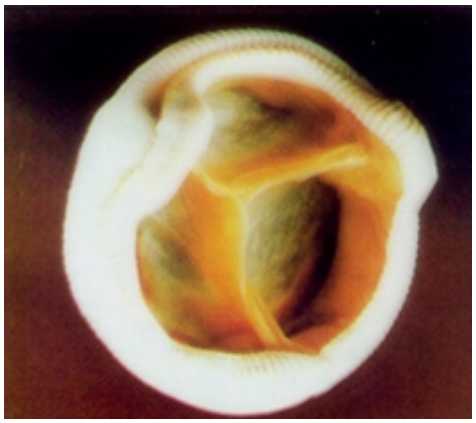

Figure 3: Bioprosthetic heart valve constructed from cross-linked porcine heart leaflets mounted in a sewing ring with a weft-knitted polyester sewing cuff.

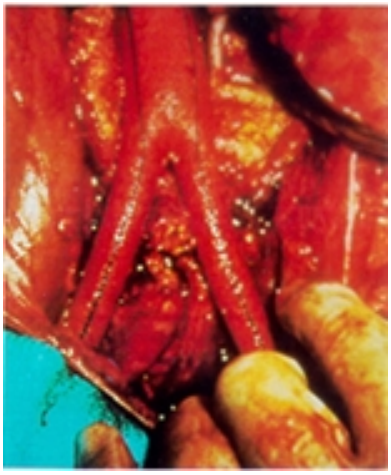

Figure 4: Bifurcated tubular arterial prosthesis warp-knitted from polyester multifilament yarns being installed in the aorto-biiliac position to replace the artherosclerotic vessels of an elderly patient.

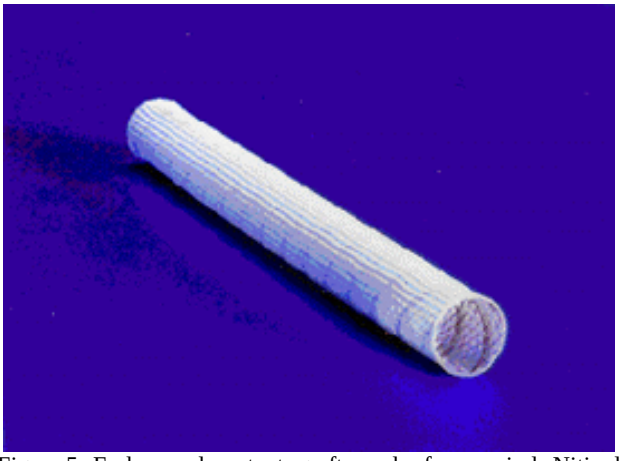

Figure 5: Endovascular stent graft made from spiral Nitinol stent and seamless woven tubular polyester graft for use in the repair of abdominal aortic aneurysms.

Over the years through the collaboration of surgeons and pathologists in Canada and Europe, our research group has been able to retrieve from autopsies and reoperations many hundreds of specimens and to evaluate their biological stability by comparing their properties to those of unused control specimens either supplied by manufacturers or harvested previously in the operating room at the time of original surgery. While the amount of control we have over the biological environment in such studies is limited, nevertheless, with a sufficiently large enough number of specimens we believe our findings are valid and reliable.

For instance we and other investigators previously reported visual evidence of mechanical damage, surface abrasion and chemical degradation of polyester fibers due to implantation as arterial prostheses or endovascular stent grafts (Figures 6-8)(1-3). In addition, we have shown that this deterioration is accompanied by a progressive decline in the bursting strength of the prosthesis with increasing time of implantation (2), and we have shown that this decline is associated both with permanent deformation and creep of the textile structure as well as a loss in the average molecular weight of the polyester polymer (4). Through the use of mass spectroscopy we have demonstrated that once implanted, the fibers swell and absorb a

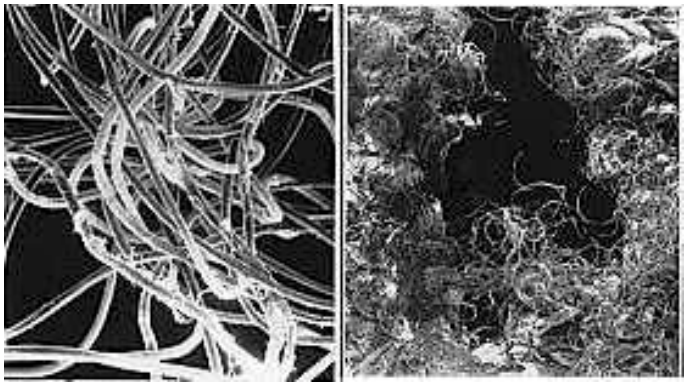

Figure 6: Scanning election photomicrograph of retrieved knitted polyester arterial prosthesis after 10 years *in vivo* showing evidence of mechanical damage to the polyester fibers

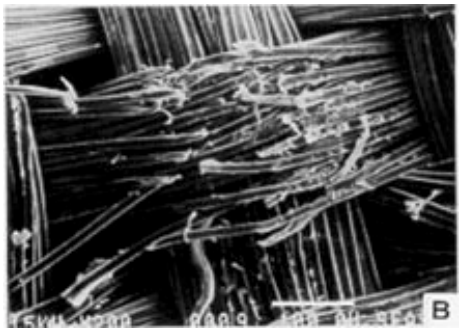

Figure 7: Scanning election photomicrograph of retrieved woven polyester arterial prosthesis showing evidence of surface abrasion between the metallic stent and the polyester fibers.

Figure 8: Scanning electron photomicrograph of retrieved knitted polyester arterial prosthesis after 4 years in vivo showing evidence of chemical degradation of the polyester fibers.

variety of biological species in addition to producing various monomer and oligomer fragments (5).

What is of particular interest is whether this swelling behavior significantly changes the mircostructure of the fibers, and if it does, whether the changes are confined to the surface of the fibers or occur throughout their diameter. This paper examines the microstructural changes that occur to polyester fibers when implanted as arterial prostheses in humans for periods of up to 16 years.

EXPERIMENTAL

Materials: The retrieved arterial prostheses used in this study were supplied by Dr. Robert Courbier, Hôpital Saint-Joseph, Marseille, France. Although the sample included different models of arterial prostheses, they were all manufactured by one company, C.R. Bard, Inc. Murray Hill, NJ, USA, from semi-dull, round cross-section, textured multifilament, Type 56T Dacron polyester yarns. The following specimens were selected by random stratified sampling to ensure a wide range of implantation times was included. The retrieval protocol has been described previously (2). On arrival at our laboratory each explant was photographed and a pathological examination of the luminal surface and surrounding tissue was undertaken by routine histology and scanning electron microscopy. As can be seen in Figures 9 and 10, there was evidence of occluding thrombus, atheroma (plaque) adhering to the luminal surface, as well as false aneurysm formation. Then the adhering tissue, thrombus and atheroma were removed by hand, and the device was cleaned by enzyme digestion at room temperature, exhaustive washing with distilled water and air drying (6). Note that the unused control specimens experienced the same cleaning, washing, and drying procedures.

Table 1: Information about the six Retrieved Polyester Arterial Prostheses Included in this Study

Period of Implantation (months)	Age of Patient at Implantation (years)	Site of Surgery	Cause of Implantation	Type of Prosthesis	Cause of Reoperation
24	68	aortobiiliac	Claud. 2	Knitted Vasculour D	Thrombosis
48	67	axillofem.	Claud. 3	Knitted DeBakey ULW	False Aneurysm
76	52	aortobifem.	Thrombosis	Knitted DeBakey Std.	False Aneurysm
96	53	fem. Pop.	Claud. 2	Knitted DeBakey ULW	Thrombosis
120	46	aortobifem.	Claud. 2	Knitted DeBakey Std.	False Aneurysm
192	28	aortobifem.	Claud. 2	Woven DeBakey	Thrombosis

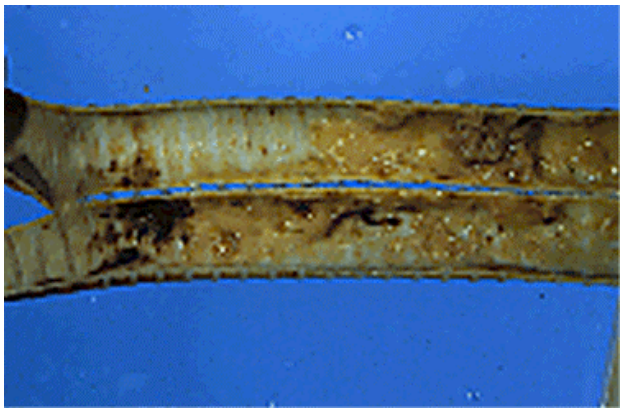

Figure 9

Figure 10

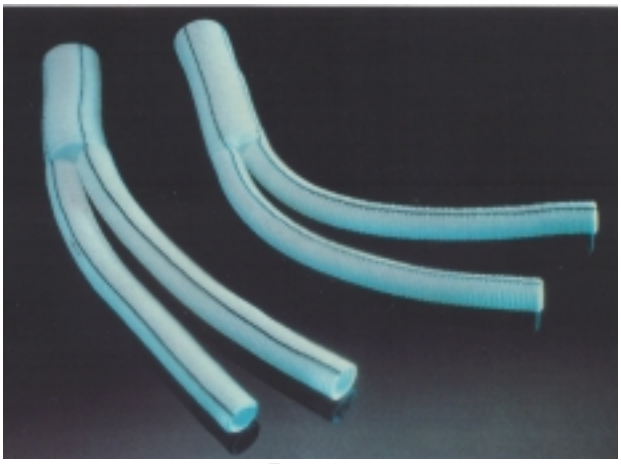

Figure 11

Figure 9: Retrieved polyester arterial prosthesis after 2 years *in vivo* cut open longitudinally and showing the presence of atheroma (plaque) and thrombus adhering to the luminal surface.

Figure 10: Cross-sectional view of retrieved polyester arterial prosthesis after 8 years *in vivo* showing a collapsed shape and the deposition of extensive thrombus occluding the lumen.

Figure 11: Two examples of new bifurcated tubular arterial prosthesis made from textured multifilament polyester yarns similar to those included as unused controls in this study.

Methods: The following three techniques were used to examine the microstructure of the polyester fibers in the retrieved and unused control prostheses (Figure 11).

a) Thermal Analysis

A Perkin Elmer Model DSC-5 differential scanning calorimeter was used. 10 mg specimens were heated under nitrogen

from room temperature to 300°C at a scan speed of 10°C/minute, and the thermographs were calibrated from the scans of known weights of indium and tin (7).

b) Fourier Transformed Infrared Spectrophotometry of Fiber Surface

A Bomem Model M-100 FTIR spectrophotometer with a Wilks ATR attachment was used to characterize the surface chemistry of the polyester fibers. This technique allows one to determine the proportion of the trans and gauche rotational isomers within the ethylene glycol residues of the polyester polymer (8). The trans and gauche conformer concentrations were determined by measuring the heights of the 969 cm^{-1} and 898 cm^{-1} absorption bands respectively and normalizing them against the thickness band at 870 cm^{-1}. The trans content of PET has been shown to correlate closely with the fiber's crystallinity (9).

c) Vapor Phase Dyeing

This technique was originally developed to dye acetate fibers with disperse shades at low temperatures (10). After immersing the unused and retrieved polyester specimens in a solution containing 20 g/1 Celliton Blue FFR and 20 g/1 Celliton Scarlet B (BASF Canada, Montreal, Québec) at room temperature, excess dye was removed with a padder and the dyeing was achieved by exposure to vapors of trichloroethylene and methyl salicylate (20:1) for one minute at 82°C. After rinsing, scouring and drying, the depth of shade of each specimen was measured in terms of lightness value on the modified CIE-L*a*b* scale with a Model D-25 Hunterlab Color Difference Meter. The darker the shade, the smaller the lightness value and vice versa.

RESULTS & DISCUSSION

a) Thermal Analysis

Table 2 lists the heats of fusion, ΔH, derived from the DSC thermographs, which are presented in Figure 12. The values for heat of fusion represent the area under each melt endotherm peak since no separate pre-melt endotherm peaks were observed. The crystallinity index was calculated using the value of 140 J/g for the heat of fusion, ΔH_o , of perfectly crystalline poly(ethylene terephthalate) (11).

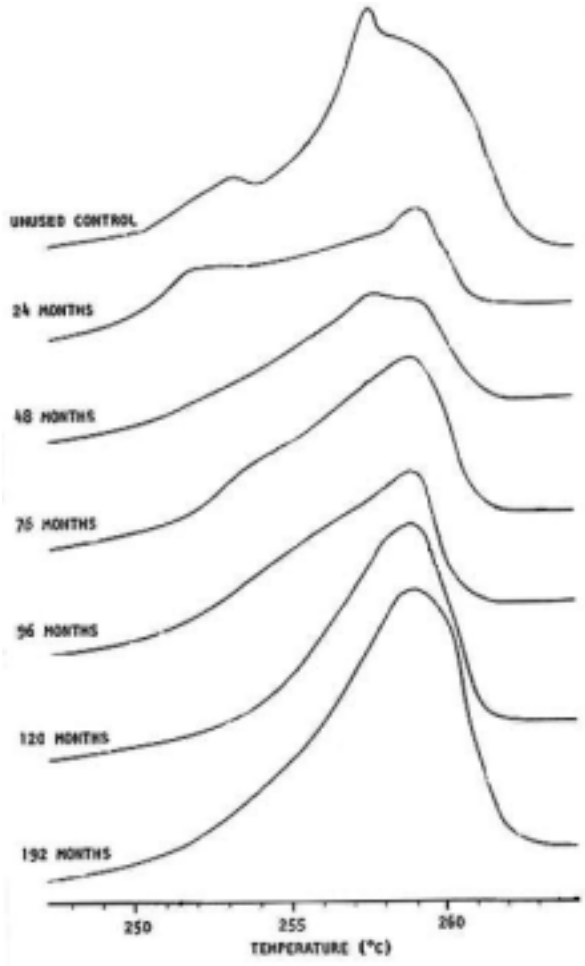

Figure 12: Melt endotherm peaks of control and retrieved polyester arterial prostheses after different periods of implantation.

Table 2: Results of Heat of Fusion and Crystallinity Index on Control and Retrieved Polyester Prostheses Obtained from DSC Analysis.

Period of Implantation (months)	Heat of Fusion,ΔH (J/g)	Crystallinity Index ($\Delta H/\Delta H_o$)
Unused control	44.9	0.32
24	42.4	0.30
48	43.1	0.31
76	44.0	0.31
96	41.9	0.30
120	45.8	0.33
192	48.3	0.34

The changes during implantation do not appear to be large, suggesting that the overall degree of crystallinity throughout the thickness of the polyester fibers does not alter significantly *in vivo*. At the same time changes in the shape of the melt endotherms, shown in Figure 12, do indicate that some structural changes are occurring during implantation. The double melt peaks move apart, with the lower 254° peak falling to 252° after 24 months, becoming a shoulder and eventually disappearing after 96 months of implantation. The main 258° peak appears to move to 259° where it becomes the dominant endotherm after 76 months. These observations point to a reorganization of the crystalline material during implantation with the proportion of larger crystalline regions increasing at the expense of the smaller ones.

b) FTIR of Fiber Surface

The ATR technique provided high quality spectra of the surface of explanted polyester fibers from which the trans, gauche and thickness bands could be identified and quantified. Figure 13 clearly shows that with longer implantation times, the trans concentration increases while the gauche concentration decreases. This provides strong evidence that the level of crystallinity near the fiber surface increases *in vivo*.

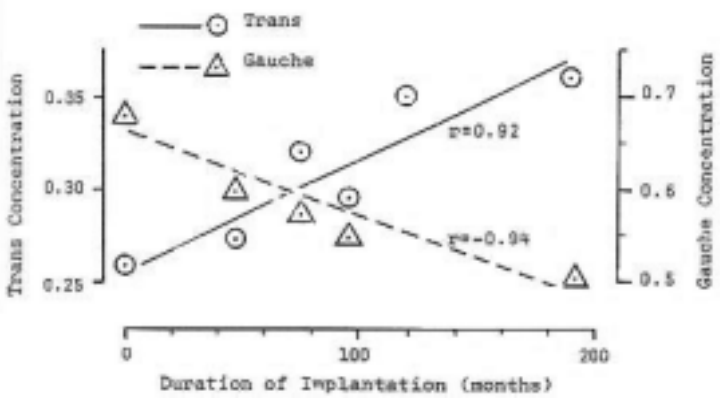

Figure 13: Changes in concentrations of trans and gauche conformers in the surface infrared spectra of control and retrieved polyester fibers after different periods of implantation.

c) Vapor Phase Dyeing

Figure 14 shows a plot of the lightness values of the control and retrieved polyester biotextiles after dyeing. There is a strong positive relationship with implantation time, indicating that the surface of polyester fibers becomes less and less accessible to the dyestuffs with longer and longer implantation times. These observations support the previous FTIR results and confirm that the fiber surface becomes increasingly more crystalline during implantation.

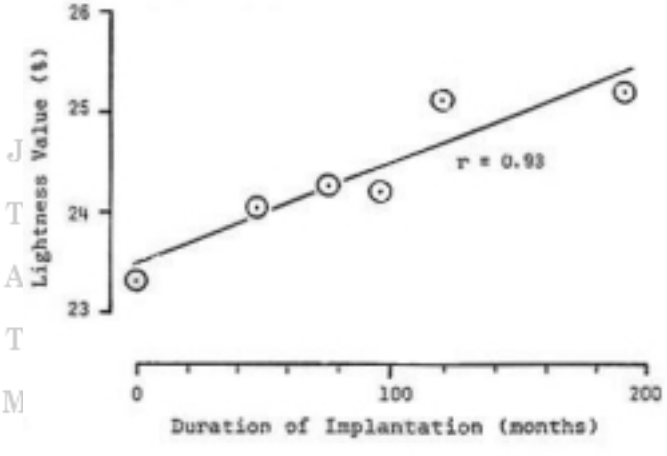

Figure 14: Lightness values of control and retrieved polyester arterial prostheses after vapor phase dyeing.

CONCLUSIONS

Our earlier work has shown that the loss of strength of polyester biotextile structures *in vivo* is accompanied by fiber swelling and a loss in average molecular weight of the polyester polymer (2). This has provided us with a somewhat simplistic model of the biodegradation process. The additional finding from the current study points to a more complex model, in which the slow biodegradation of polyester fibers *in vivo* is a multi-step process. After fiber swelling and molecular chain scission has commenced, an increasing proportion of the amorphous material near the fiber's surface appears to be lost. The microcrystalline structure can then be reorganized through the growth of larger crystalline regions at the expense of the smaller ones and amorphous regions. The

resulting "annealed" structure will likely offer improved resistance to further degradation and explain why the kinetics of the chain scission reaction reported previously are not linear but follow a logarithmic decay model (4).

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DISCLAIMER

The opinions expressed herein are solely those of the authors, and do not necessarily represent existing or forthcoming policies of the affiliated or sponsoring agencies.

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