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Properties modification of PET vascular prostheses

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Aging mechanisms have been investigated on polyethylene terephthalate (PET) fibres extracted from various vascular prostheses in order to identify the different modifications of the material's degradation. NMR spectroscopy provides a comprehensive view of chemical structures of macromolecules. Examination of a series of PET fibres showed significant chemical differences between the virgin prostheses and the explants, especially for diethylene glycol (DEG) and cyclic oligomeric groups. These analyses revealed that PET failures in vascular prostheses are susceptible to hydrolysis during *in vivo* stay. We also extended this ^{1}H NMR technique to determine the hydroxyl and carboxyl end-group concentrations. In order to validate the ^{1}H NMR results, complementary techniques – chemical titration and classical viscosimetry – were used. The obtained results showed an increase in end-group concentrations and a decrease of the viscosity averaged macromolecular weight (M_v) for the explants. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: chemical aging; ^{1}H NMR spectroscopy; polyethylene terephthalate; vascular prosthesis

INTRODUCTION

Arteries are blood vessels that carry oxygen and nutrients from the heart to the rest of the body. Healthy arteries are flexible, strong, and elastic. Over time, too much pressure in the arteries can make the thick walls stiff, sometimes restricting blood flow to the organs and tissues (Fig. 1 a,b).

Cardiovascular diseases are often treated by replacing the dysfunctional blood vessel with vascular prosthesis. Fabric materials were first used as vascular prostheses in the 1950s, when Voorhees *et al.*[1] implanted a polymeric vascular graft manufactured from vinyl chloride and acrylonitrile. Since then, a number of polymers have been used to fabricate vascular prostheses. Ideally, the prostheses should have the same properties as the healthy arteries so as not to tire the heart. Polyethylene terephthalate (PET) remains a primary choice for vascular prostheses because it is mechanically compatible with the host artery. In spite of this success, the lifespan of the textile prostheses is limited in time and many complications can occur following *in vivo* stay due to an age-related effect (Fig. 1 c–e). Failures may be related to the lesions that occur during the implantation and *in vivo* physicochemical degradation of materials.[2–4]

Therefore, it is important to understand in detail what happens throughout the textile structural deformation in order to improve the quality of the *in vivo* behavior of arterial prostheses and to avoid ruptures in the future. Previous studies have investigated the nature of morphological changes induced by aging on PET fibres extracted from explanted prostheses.[5–7]. Although these results found in the literature are very interesting, the other modifications such as chemical aging that depend directly on the stay in the biological environment have not been assessed.[2–7] Therefore, these previous studies are considered insufficient and unable to give a total description of aging. To know the type of modification that could arise in the polymer, complete physicochemical studies of explants have to be undertaken.

Although there are only a few publications in the literature that discuss the chemical aging of vascular prostheses (explants are difficult to obtain and only a few laboratories have the possibility to do so), the chemical degradation of classical PET has been studied extensively.[8–12] A systematic study of the chemical degradation of PET, realized by Pohl[9] in 1954, revealed that the hydrolytic scission of polyester chains can be investigated by end-group concentrations using classical titration. Further to this, several techniques to obtain chemical and structural information about molecules have been described. In addition to chemical methods for end-groups' analyses such as titration and viscometry method[13–15] various physical methods have been employed. These include optical spectroscopy, Fourier transform infrared (FTIR)[16] and UV methods.[17]

In the case of PET yarns extracted from different prostheses, all of the methods described to date suffer from some limitations with respect to sensitivity and/or versatility. Some of the associated problems are listed below.

- Large sample size requirement (for two methods: viscosimetry and titration). The sample size is a major problem for us, because of availability of the prostheses is insufficient. Typically, we should be able to work with a mass <5 mg to have conclusive results.

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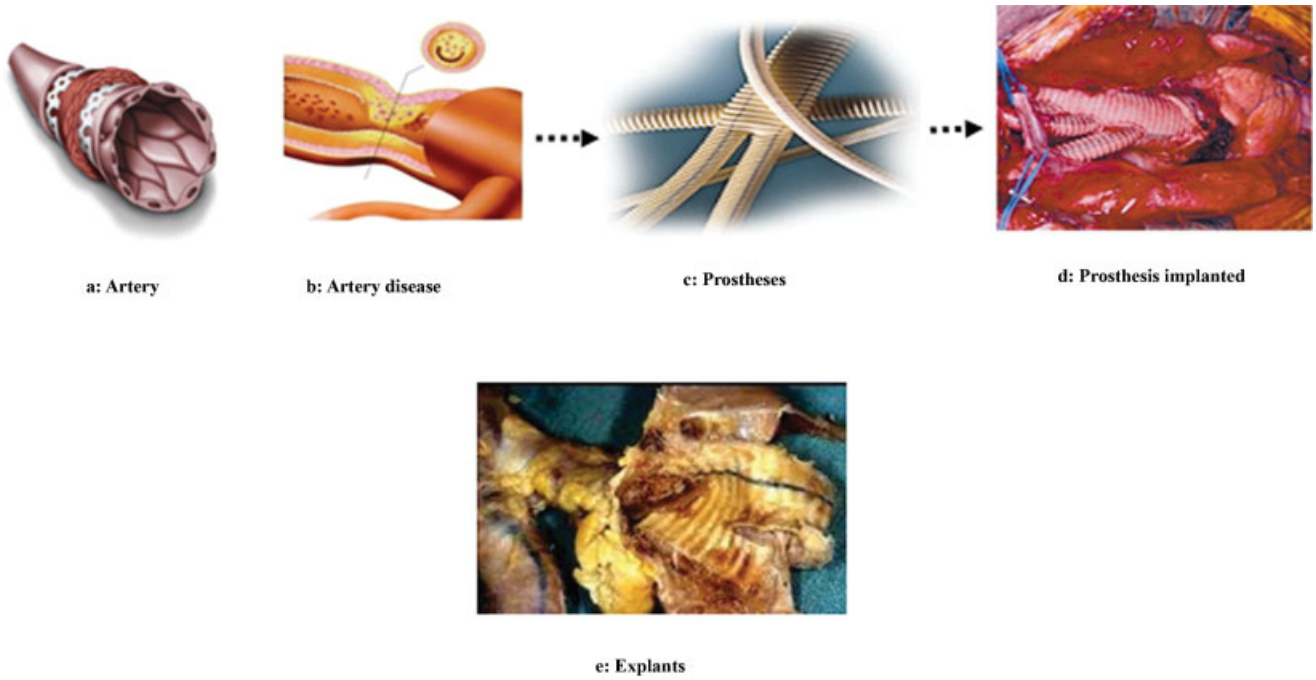

Figure 1. Dysfunctions of arteries and prostheses.

- In the case of infrared method, the quantitative analyses are very difficult. For example, bands of the PET end-groups are broad and they are poorly integrated.[16–19]

Need for development of another technique has been emphasized. NMR based techniques can offer the advantage of small sample requirement and enable quick (we find all information about end-groups and other PET groups in the same spectrum) and reliable study of the chemical aging.[20–22]

EXPERIMENTAL

Sample preparation

Cooley Double Velour (CDV) prostheses (virgin and explanted prostheses; Fig. 2), fabricated by Meadox Medical (Oakland, NJ,

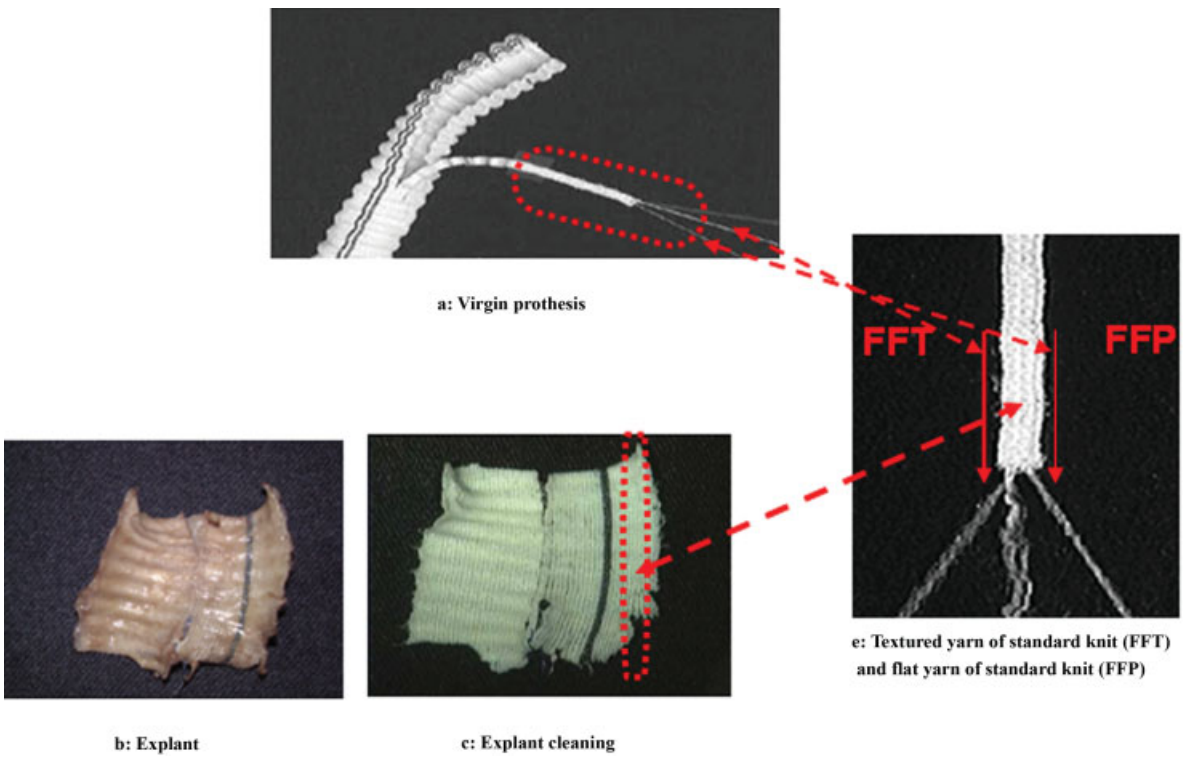

Figure 2. Sample preparation.

Table 1. Lifetime and localization of different prostheses

No	Reference	Implantation date	End of implantation	Lifetime (month)	Location of implantation
1	A	1982	1999	204	Aorto bifemorale
2	B	1978	1998	240	Aorto bifemorale
3	C	1981	1995	168	Axillo bifemorale
4	D	1978	1998	240	Aorto bifemorale
5	E	1980	1993	156	Axillo bifemorale
6	F	1979	1997	204	Axillo bifemorale
7	G	1979	1992	156	Axillo bifemorale

The different prostheses are Cooley Double Velours (CDV). The cause of degradation is mainly asymptomatic false aneurysm.

USA) were tested in this study. Explanted specimens were collected from 1992 to 1999 through the collaboration of several hospitals in Europe. We had the largest stock of various prosthetic explants in Europe but due to their *in vivo* degradation, the quantity of the obtained explants was not sufficient.

For these prostheses, three different zones are distinguished. The first one corresponds to the columns made of black yarns, used by the surgeon to correctly place prostheses. These columns are named Guide Lines (GL). The second zone corresponds to Remeshing Lines (RL) made of yarns forming the junction between the two parts of the basic knitting. The rest of the prosthesis forms the Standard Knit (SK). For GL and SK, there are two types of yarns: flat (FFP) and textured (FFT) yarns. Explanted grafts had *in vivo* residency times ranging from 156 to 240 months. The different prostheses used in this study are listed in Table 1.

The explanted prostheses were cleaned using a non-deleterious specific treatment for PET fibers in order to undertake chemical investigations (Fig. 2c). For this treatment, the explants were immersed in a 10% sodium hypochlorite solution agitating softly for about 3 h, followed by rinsing with distilled water. Hypochlorite remnants were neutralized using a 0.5% hydrogen peroxide solution. These prostheses were rinsed again with distilled water, dried, and stored.

After washing, the macroscopic examination of explanted prosthesis showed no abnormal deposits, no holes, and no tears on the surface.[2–7] This examination was performing using a Scanning Electron Microscope (SEM Hitachi S-2360N, Elexience, Verrières le Buisson, France), without metalization, under partial vacuum conditions (0.01–0.2 Torr).

Virgin prosthesis was used as a reference. So, in order to study only the effect of the chemical aging on the PET properties, this virgin prosthesis was sterilized and then it was cleaned with the same treatment as for the explants.

In this study, FFP and FFT filaments of SK (FFP and FFT, respectively. Fig. 2e) were analyzed. The filaments were taken by de-knitting the prostheses.

Nuclear magnetic resonance spectroscopy (NMR spectroscopy)

NMR experiments were recorded at 400 MHz on a Bruker Avance Spectrometer equipped with a QNP Z-gradient probe. All the ^{1}H NMR spectra were acquired with a 30° pulse corresponding to a pulse width of 3.1 μs. The delay time between each pulse was 8 s. ^{1}H NMR spectra were recorded during 4000 scans (number of acquired transients) for the adequate signal-to-noise ratio. The total acquisition time was approximately 14 h.

The experimental protocol is the same as the one reported previously in literature.[18,23] Solutions were prepared by dissolving the PET samples in tetrachloroethane-d2 (Deuterated tetrachloroethane 99.9% atomic deuterium) at 140° C (typically 2–4 mg) directly in an NMR tube and waiting for about 90 s to ensure a complete dissolution of the polymer. The mixture was cooled to ambient temperature. For these analyses, Topspin 1.3 software was used to treat the spectra and ^{1}D NMR processor 11.0 (ACD Labs) software was used to determine the peak integrals. Prior to signal integration, a linear baseline correction was applied between 2 and 12 ppm. The tetrachloroethane solvent ($(CDCl_2)_2$ at $\delta \sim 6$ ppm) was used as a reference for the chemical shift scale.

Determination of the end-group using the chemical titration method

Concentrations of carboxyl end-groups

For the rapid determination of carboxyl end-groups in PET we used the method described by Pohl.[9] This method entails dissolving the polymer in benzyl alcohol (0.5 g/5 ml) rapidly at a high temperature (180 °C), then quickly mixing the solution with chloroform, and titrating with sodium hydroxide and Phenol red indicator.

The obtained values must be corrected for the amount of carboxyl groups which are formed during the dissolution at this high temperature. The solvent used – benzyl alcohol – must be of high purity and free of water, lest hydrolysis at the high temperature during dissolution should take place.[10–12] Then, the concentration of carboxyl end-groups [COOH] was calculated by the following formula:[9]

$$[\mathrm{COOH}] = \frac{(V_t - V_b) \times 10^6 \times C_{tir}}{m} - [\mathrm{COOH}]_{CORR} \qquad (1)$$

where

[COOH] is the concentration of carboxyl end-groups (meq/kg), V_b the titer value for a blank of the heated benzyl alcohol with chloroform (μl), V_t the total titer value for the sample titration (μl), $[\mathrm{COOH}]_{CORR}$ the correction factor, C_{tir} the molar concentration of reagent blank and m the sample weight (g).

Concentrations of hydroxyl end-groups

Kern *et al.*[24] have reported a detailed study of the conversion of hydroxyl end-groups into carboxyl end-groups by reacting aliphatic polyesters after acylation with succinic anhydride. This

offers the possibility to determine the total number of carboxyl end-groups of PET by Pohl's titration methods.[8,9]

This method entails dissolving the polymer (0.1 g) in of 2 ml α-methyl naphthalene at 240 °C. Temperature is then reduced to 175 °C and a quantity of 0.1 g succinic anhydride is added. Heating is maintained for 4 h at 175 °C to ensure the total conversion of hydroxyl end-groups into carboxyl end-groups. Subsequently, the mixture is poured into an excess of ethanol.

Determination of carboxyl end-groups (by eqn (1)) before and after reaction with succinic anhydride identifies the hydroxyl end-groups.[8,24]

Viscosimetric method

In this method 200 mg of PET sample was dissolved in 20 ml of *m*-cresol at 100 °C for 30 min. Then the sample was cooled to ambient temperature. Afterwards, this solution was diluted ($C_1 = 10^{-2}$ g/mol) with pure solvent (*m*-cresol) to obtain different concentrations ($C_2 = 2 \times 10^{-3}$ g/mol, $C_3 = 4 \times 10^{-3}$ g/mol and $C_4 = 6 \times 10^{-3}$ g/mol). Intrinsic viscosity $[\eta]$ (the intrinsic viscosity is the hypothetical viscosity at "zero concentration") was determined to calculate the macromolecular weight with a simple equation (Mark–Houwink equation):

$$[\eta] = K(Mv)^a$$

Mv is the viscosity average macromolecular weight and "*K*" and "*a*" are the Mark–Houwink constants. There is a specific set of Mark–Houwink constants for every polymer–solvent combination. So we have to know these for our polymer–solvent combination in order to obtain an accurate measurement of the macromolecular weight.

For the used polymer–solvent combination,[23] $K = 0.77 \times$ ml/g and $a = 0.95$. So,

$$[\eta] = 0.77 \times 10^{-3} \ (Mv)^{0.95} \text{ and } Mv = \left(\frac{[\eta]}{0.77} \times 10^3\right)^{\frac{1}{0.95}} \quad (2)$$

RESULTS AND DISCUSSIONS

A typical NMR spectrum of PET at room temperature is shown in Fig. 3. Several main signals of ^{1}H NMR spectra were detected (Fig. 3). The chemical shifts of the PET spectra were 8.13 ppm (H_1) assigned to aromatic protons of terephthalate units and 4.69 ppm (H_2) assigned to methylene protons. The signals at 3.98 ppm (H_3) and 4.47 ppm (H_4) correspond to the protons in α and β positions of the hydroxyl end-groups, respectively.[20,21] The H_6 and H_5 signals at 3.88 and 4.5 ppm, respectively (CH_2 in α and β position of ether, respectively) were attributed to diethylene glycol (DEG) insertion into the PET chain, as shown by Kenwright *et al.*[25] Also, the ^{1}H NMR spectrum shows a very fine peak at 8.08 ppm (H_7) attributed to the cyclic oligomers of PET.[11,26]

Carboxyl and hydroxyl are the two major end-groups in PET.[16,19,25] Unfortunately, the signal attributed to the carboxyl end-groups is not identified using ^{1}H NMR after dissolution in deuterated tetrachloroethane, since this end-group concentration is very low for high molecular weight PET.[22,27] Derivatization methods are often employed to simplify the characterization of functional groups and to overcome these problems with direct NMR analysis.

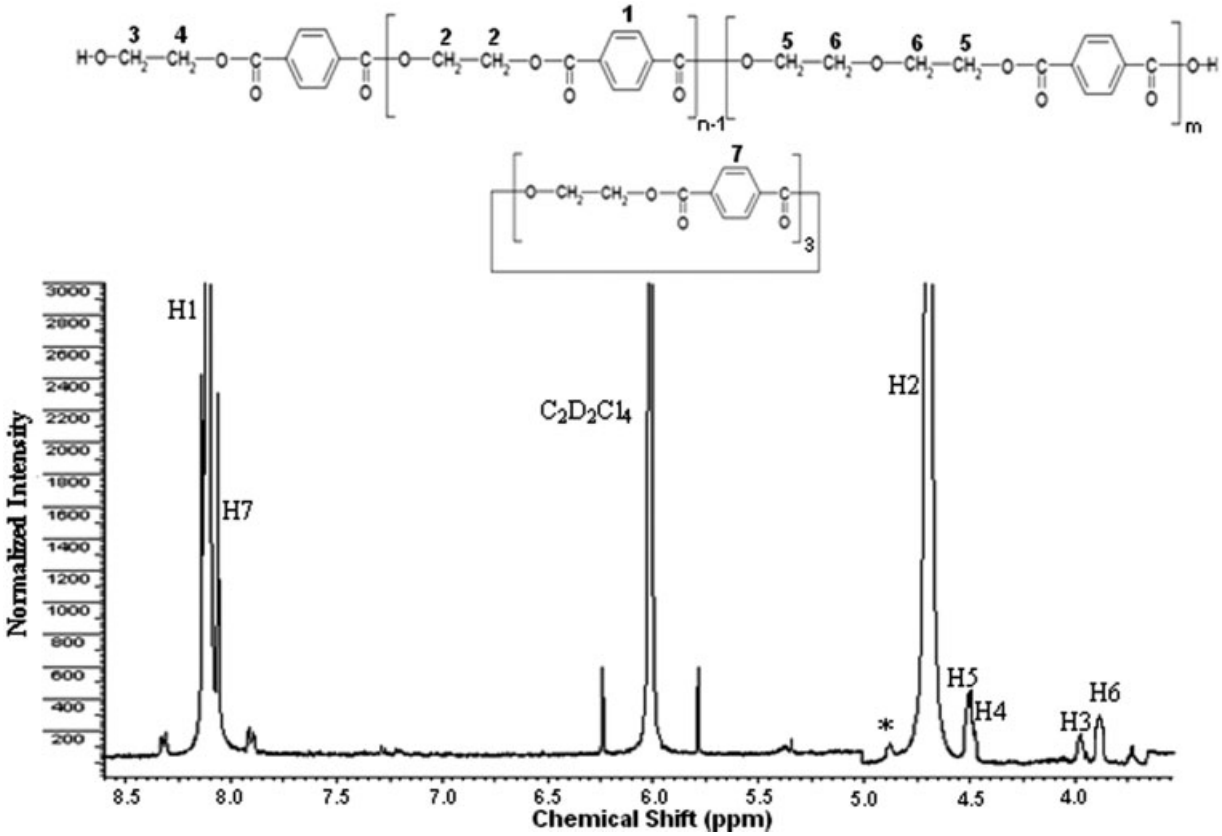

Figure 3. ^{1}H NMR spectrum of PET (400 MHz, $(CDCl_2)_2$, reference $(CDCl_2)_2$, δ $(CHCl_2)_2 = 6$ ppm) *, ^{13}C satellite peak

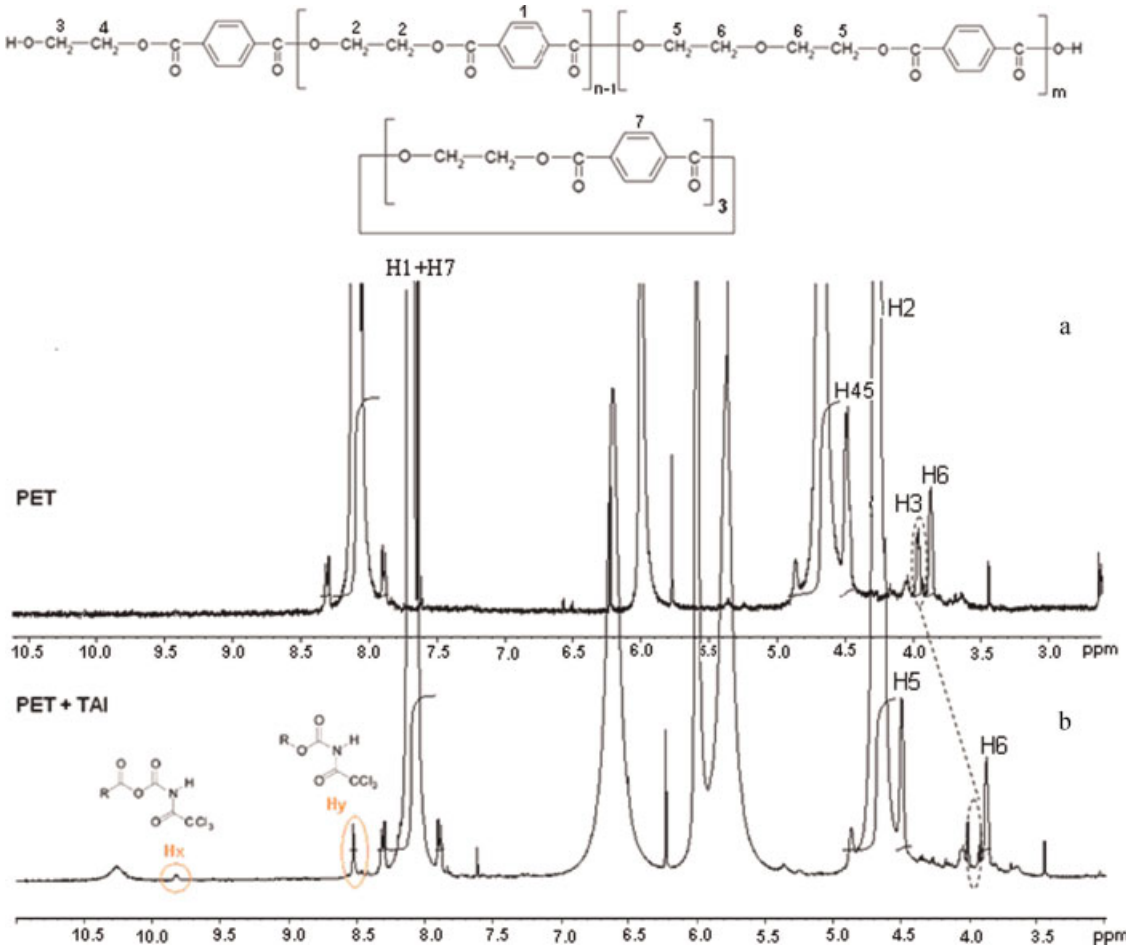

Figure 4. ^{1}H NMR spectra of the PET polymer (a) before and (b) after reaction with TAI. This figure is available in color online at www.interscience.wiley.com/journal/poc

End-groups determination

Liquid phase ^{1}H NMR is a very suitable method to quantify the hydroxyl and carboxyl end-group concentrations of PET after the reaction between the trichloroacetyl isocyanate (TAI) and PET end-groups.[22] Thus, an excess of TAI (4 μl) was added after dissolving the PET samples in tetrachloroethane-d2 (deuterated tetrachloroethane) with 99.9% atomic deuterium).[22]

Figure 4 shows a comparison between two ^{1}H NMR spectra ($(CDCl_2)_2$, 400 MHz, 4000 scans) of PET: PET before reaction with TAI (Fig. 4a) and PET after reaction with TAI (Fig. 4b). It can be seen (Fig. 4) that there are a number of changes in these two spectra. Upon reaction with TAI several signals disappear completely and are replaced with other new signals. Two peaks centered at 3.98 and 4.47 ppm – assigned to the protons in α (H_4) and β (H_3) position of hydroxyl end-groups, respectively, disappeared after reaction with TAI. A new peak appearing at 8.53 ppm (Hy), is attributable to the imidic hydrogen (NH) resonances from the reaction between hydroxyl end-groups and TAI ($\delta \sim 8$–9 for O—C(O)—NH—C(O)CCl_3: TAI derivatization of hydroxyl end-groups).[22,27]

Theoretically, the hydroxyl end-groups may be quantified by ^{1}H NMR.

$$2\, I_y = I_3 \qquad (3)$$

where I_y is the peak area of TAI derivatization of hydroxyl end-groups at 8.53 ppm (there is only one proton in this group). I_3 is the peak area of the H_3 signal before derivatization (there are two protons in this group). This is in agreement with the experimental results because we have found (Fig. 4):

Before reaction of TAI

$$I_3 = 0.49$$

After reaction with TAI, I_3 disappeared and I_y appeared

$$I_y = 0.245 = \frac{I_3}{2}$$

Thus, TAI has reacted quantitatively with all of the OH end-groups. The method has been successfully applied to quantitative determination of the hydroxyl end-groups.

We also note (Fig. 4) that there are a number of changes in the region of 9.5–10.5 ppm. According to Richard,[22] TAI capped carboxyl end-groups give rise to characteristic imidic NH resonances in a normally clear region of the ^{1}H NMR spectrum ($\delta \sim 9.5$–10 for C(O)–O–C(O)–NH–C(O)CCl_3: TAI derivatization of carboxyl end-groups). Figure 4 shows two peaks in this region at 9.85 and 10.3 ppm. We performed a blank solvent spectrum (spectrum of solvent tetrachloroethane $(CDCl_2)_2$ with TAI) to verify the origin of these peaks and consequently we note the existence of a signal at 10.3 ppm which is proportional to the quantity of the added solvent. The signal at 10.3 ppm was attributed to residual reaction between the solvent and TAI. In the same spectrum, no peak appears at 9.85 ppm. Consequently, the

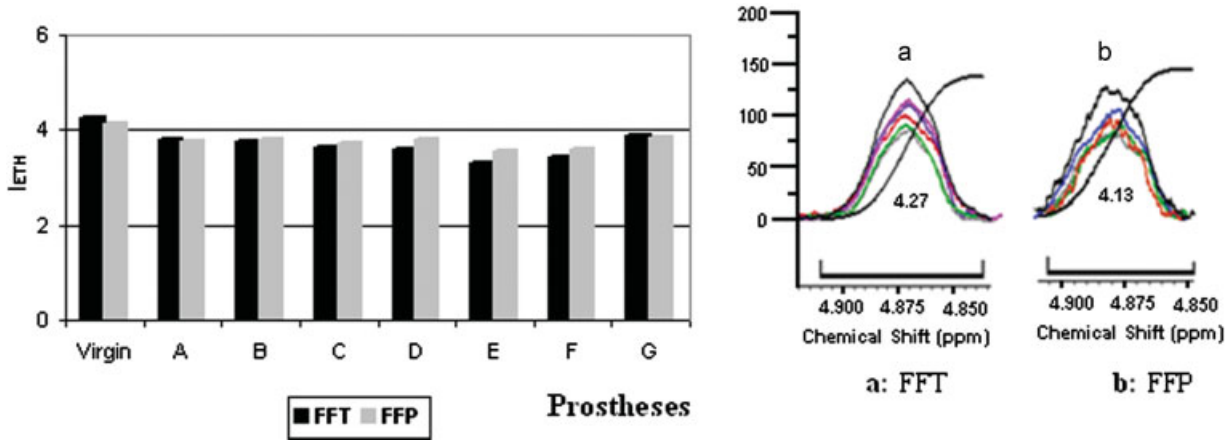

Figure 5. Variation of the ethylene groups for different prostheses. IETH is the integral value of the ethylene group peak; FFT, textured yarn of standard knit, FFP, flat yarn of standard knit.

peak at $\delta \sim 9.85$ ppm is attributed to the imidic NH signal from the reaction between carboxyl end-group of PET and TAI. The rest of these two spectra show similar signals intensities.

Comparison of various samples

Many types of information can be obtained from a ^{1}H NMR spectrum, especially quantification of the number and type of chemical entities in a macromolecule. In order to monitor the changes that occur in the PET polymer during *in vivo* stay, the signal at 8.35 ppm corresponding to ^{13}C satellite of aromatic protons (H_1) was used to the normalize all spectra.

Ethylene groups

Ethylene terephthalate repeating unit comprising the PET macromolecular chain is generally the first and most important attribute of a PET polymer. To compare the ethylene groups, the signal at 4.87 ppm corresponding to the ^{13}C satellite of these groups (H_2) was used.

Figure 5 shows a slight reduction in ethylene quantity for all explants compared to virgin prosthesis. This reduction can be explained by the rupture of macromolecular chains in an ethylene repeating unit during *in vivo* stay. Much work on the degradation of PET has been carried out and it has been considered that the degradation of PET proceeds by a random scission of ester linkages.[14,28]

Structural anomalies

The study of polymers starts by understanding the methods to synthesize the materials. Polymer synthesis is a complex procedure and can take place in a variety of ways.

Certain secondary reactions can occur during the synthesis of the PET, leading to non-conforming groups such as the formation of DEG and PET cyclic oligomer.

Diethylene glycol

The DEG groups are formed by secondary reaction during PET synthesis (Fig. 6).[29] DEG is known to be a weak point in the thermal degradation of PET.[28] Lecomte and Liggat[30] confirm that there is a degradation specific to DEG units, which occurs at 100 K below the degradation temperature of PET. The DEG groups provide some degree of flexibility to a relatively stiff PET backbone, which slows down its crystallization.[17]

Cyclic oligomer

In the process of producing linear polymers by condensation, cyclic oligomers are inevitably formed and their formation considerably affects the macromolecular weight distribution even though the total amount formed is less than 5%.[31] The dominant oligomeric species in PET is a cyclic trimer, which accounts for more than 77% of cyclic oligomers. The presence of the cyclic oligomers significantly affects the properties of the polymeric product. For example, cyclic (PET) oligomers tend to migrate to the surface of spun fibres and, under certain conditions, crystallize to produce a surface "bloom" which interferes with subsequent dyeing.[32]

Figures 7 and 8 show a remarkable reduction in the diethylene groups and PET cyclic oligomers for all explants compared to the virgin prosthesis. These results are in agreement with several previous studies,[8,30,33] which indicated that the increase in DEG content promotes hydrolysis and thermal and oxidative degradation. Holland and Hay[28] proved that DEG chain ends were more prone to degradation than the rest of the PET chain, leading to the formation of dioxane and carboxylic acid chain ends. Similarly, according to a few other studies,[30,31] the cyclic oligomers are released early during the degradation, and correspond to the first mass-loss step observed for PET.

This ^{1}H NMR method is described as the most effective because the technique allows us to extract information and deduce the existence of structural anomalies (DEG and PET cyclic oligomer), which are very sensitive to degradation. These results confirm

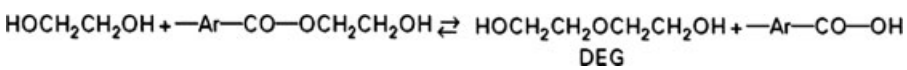

Figure 6. Formation of diethylene glycol (DEG)[29]

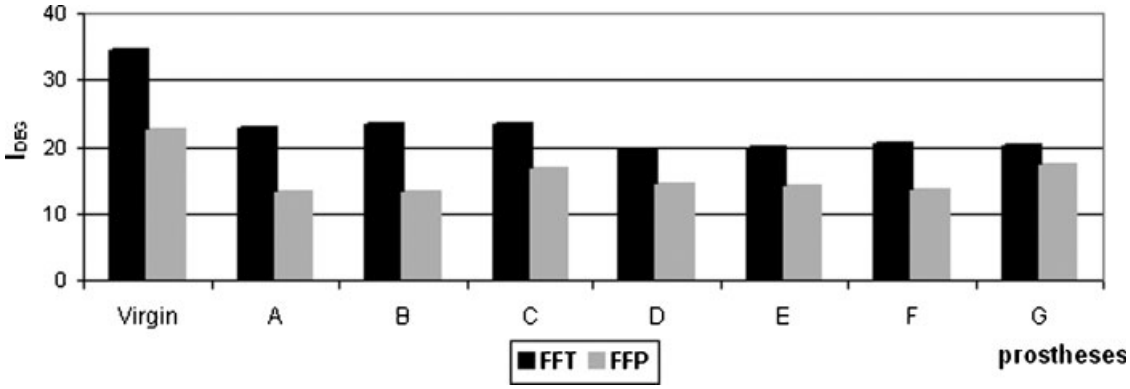

Figure 7. Variation of the diethylene glycol (DEG) groups. IDEG is the integral value of DEG group peak

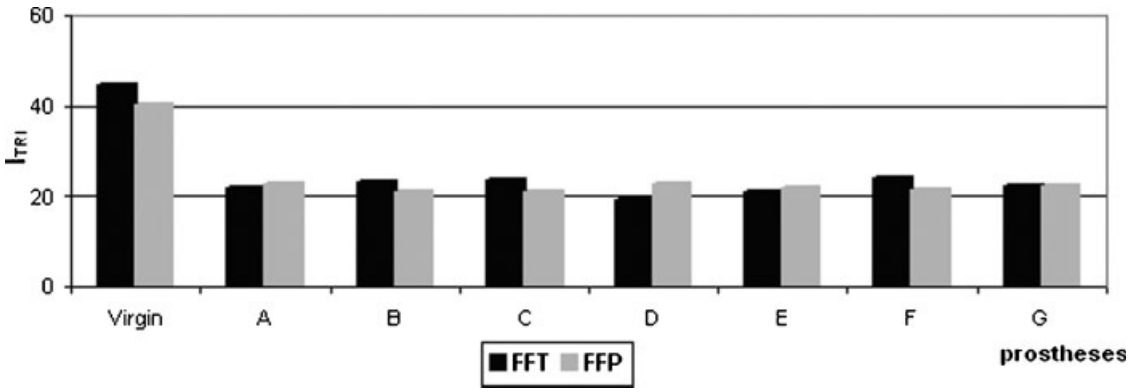

Figure 8. Variation of the cyclic oligomers. ITRI is the integral value of the cyclic oligomer group peak

that the ruptures in macromolecular chain can occur during *in vivo* stay. Subsequently, it is interesting to study the impact of this degradation on the evolution of end-groups and the macromolecular weight of PET polymer.

Determination of hydroxyl and carboxyl end-groups

Using ^1H NMR spectroscopy

The end-group signals appear in a clear region of the NMR spectrum at δ 7.5–11 ppm. The signal (Hy) of TAI derivatization of hydroxyl end-groups is observed at 8.53 ppm. The signal of TAI derivatization of carboxyl end-groups resonates at around 9.85 ppm.

Figures 9 and 10 show the evolution of hydroxyl and carboxyl end groups, respectively, for different explants. From these figures we can conclude that the chemical aging induced an increase of carboxyl and hydroxyl end-groups, mainly for FFT.

Chemical titration method

This titration requires a high amount of sample (20 mg), thus only the textured yarn of SK (FFT) extracted from the explanted prostheses was tested.

The contents of carboxyl and hydroxyl end-groups of PET vascular prostheses were then measured by the titration method. As shown in Figs 9–11, similar trends of the obtained end-group concentrations were deduced, using both methods: ^1H NMR and chemical titration. These results prove that the ruptures in macromolecular chain can occur during implantation. Thus, the end-group contents of PET can be used for the characterization of

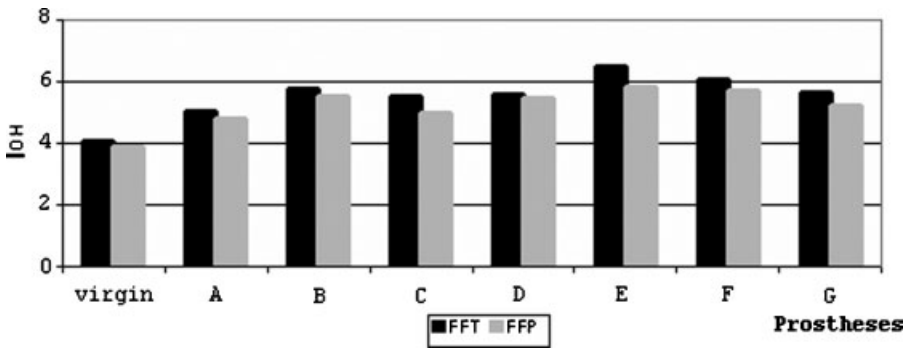

Figure 9. Comparison of the integral value of the hydroxyl end-groups after reaction with TAI. IOH is the integral value of the hydroxyl end-group peak

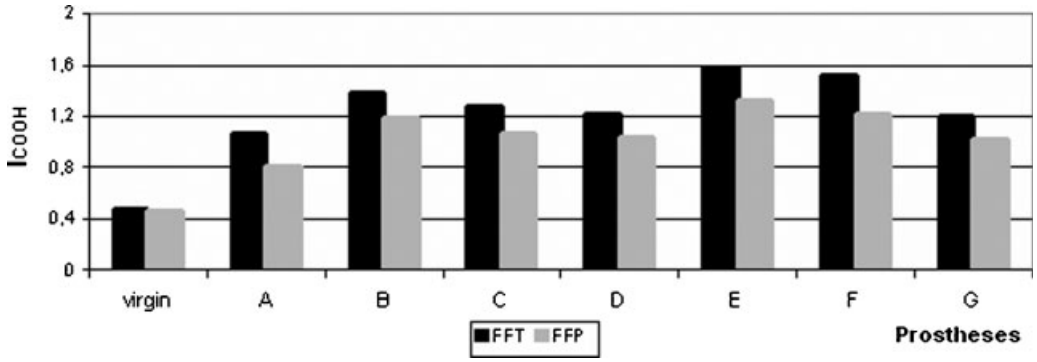

Figure 10. Comparison of the integral value of the carboxyl end-groups after reaction with TAI. ICOOH is the integral value of the carboxyl end-group peak

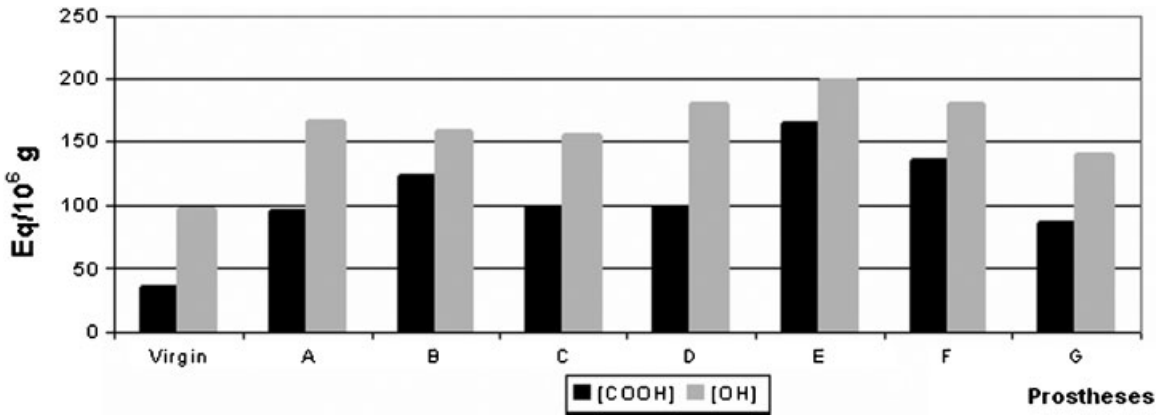

Figure 11. End-group concentrations (OH and COOH) for different explanted prostheses using the titration method

this polymer[34] and also to describe the chemical aging of the vascular prostheses during *in vivo* stays.

Determination of macromolecular weight using viscosimetric method

The viscosity average macromolecular weight ($M\nu$) was determined to verify the end-groups' evolution for explanted prostheses.

This viscosimetric method requires a high amount of sample (200 mg), thus only the textured yarns (FFT) were tested for some prostheses as virgin, A, C, E, and F (Fig. 12). $M\nu$\ values for various prostheses calculated using viscosimetric method, are summarized in Table 2.

Table 2 shows a significant reduction of $M\nu$ for the explanted prostheses. In addition, the lowest and the highest $M\nu$ value were found for prosthesis E and prosthesis A, respectively. These results are in good agreement with the ^{1}H NMR results, because the comparison of these two methods shows the same level of degradation.

These obtained results prove that the application of chemical constraints after implantation modifies the structure of the polymer and creates a significant degradation of PET proceeded by a random scission (Fig. 13). This is often due to the hydrolysis of the bonds connecting the polymer chain which in turn leads to an increase in the end-groups' concentrations and therefore a decrease in the macromolecular weight of the polymer.[14,35]

While the results show that the macromolecular weight values are significantly influenced by aging following implantation, the

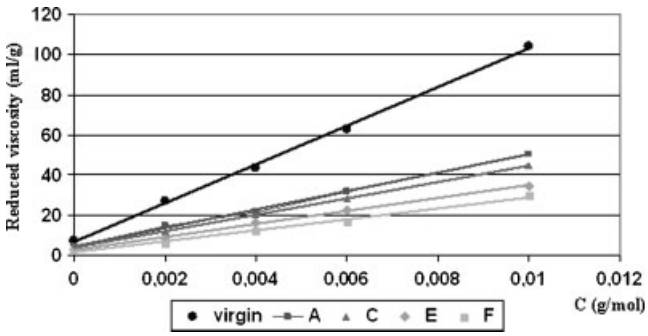

Figure 12. Reduced viscosity of different prostheses.

Table 2. $M\nu$ values using viscosimetric method

Samples (FFT)	$M\nu$
Virgin	15056
A	8910
C	7935
E	5584
F	6355

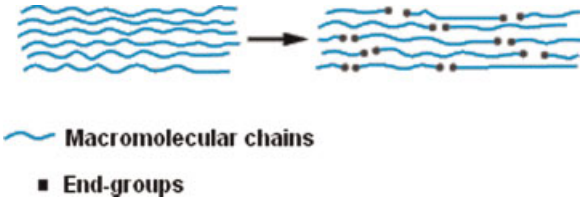

Figure 13. Chain scission in macromolecules. This figure is available in color online at www.interscience.wiley.com/journal/poc

impact of the duration of *in vivo* stay on the chemical degradation was difficult to evaluate (for example the prostheses A and F have the same lifespan (204 months) but they do not have the same degradation). Therefore, even if time clearly influences the level of degradation, the results highlight other mechanisms of the degradation that are probably related to human metabolism; these results are in agreement with the literature.[36]

CONCLUSIONS

^{1}H NMR technique was used to evaluate the state of chemical degradation and to illustrate the mechanisms of structural degradation of PET fibres extracted from explanted prostheses. Examination of a series of ^{1}H NMR spectra proves that implantation involves a transformation of the original structure of fibres found in prostheses. Although the influence of aging on ethylene glycol (EG) content was not significant, a remarkable reduction in the diethylene groups (DEG) and PET cyclic oligomers for the explanted prostheses was noted. In order to fully characterize the polymers, it is important to have a precise knowledge of the end-groups. The method of TAI derivatization facilitates analysis of hydroxyl and carboxyl end-groups. An increase in the end-group quantities at different aging times compared to those obtained for the virgin was found. This study revealed that the chemical aging process causes the chain scission in macromolecules, especially for texturized yarns. The viscosity average macromolecular weight $M\nu$ confirms the ^{1}H NMR results.

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