Graft Copolymerization of Methoxyacrylethyl Phosphate onto Expanded Poly(tetrafluoroethylene) Facial Membranes

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ABSTRACT: Expanded poly(tetrafluoroethylene) (ePTFE) membranes were modified by graft copolymerization with methoxyacrylethyl phosphate (MOEP) in methyl ethyl ketone (MEK) solutions at ambient temperature using gamma irradiation. The effect of monomer concentration (3–30%) was studied and the modified membranes were characterized by weight increase, x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), contact angle measurements, and differential scanning calorimetry (DSC). Results show that the ePTFE membrane had a degree of crystallinity of 59% and that this did not significantly change after grafting indicating that grafting occurs in the amorphous regions. SEM images showed a globular surface morphology for the grafted membranes. XPS was used to evaluate the chemical structure of the graft copolymer and to determine the XPS grafting extent using the C-F (ePTFE membrane) and the C-C (MOEP graft copolymer) peaks. The graft yield as well as grafting extent was found to increase with increasing monomer concentration. Concomitantly, the contact angle was found to decrease with increasing monomer concentration. No direct correlation was found between XPS grafting extent and the advancing water contact angle illustrating that the former does not adequately give an indication of the copolymer surface coverage of the first molecular layer. J Appl Polym Sci 117: 3331–3339, 2010

Key words: polytetrafluoroethylene (PTFE); x-ray photo electron spectroscopy (XPS); thermal properties; biomimetic; graft copolymer

INTRODUCTION

Poly(tetrafluoroethylene) (PTFE) has been used in medicine since the middle of the last century. In some applications, however, it proved less than ideal with its excellent properties proving insufficient in the harsh *in vivo* environment. Over the ensuing decades initially fibrillar and then the expanded forms of PTFE (ePTFE), were developed.[1] ePTFE proved more favorable than the non-expanded version because it is not only bio-stable but it also has an antithrombotic surface.[2] Furthermore, it is more conveniently processed into continual lengths, tubes, sheets, and can also be shaped into three-dimensional forms.[1] This opens up applications where it can be used in sutures and vascular grafts for high flow vessels,[3] and in dentistry and cranio-maxillo-facial surgery as both a hard and soft tissue replacement material.[4] One problem that can occur upon implantation of a biomaterial if the surface properties are not optimal is the formation of a fibrous connective tissue layer around the implant which prevents integration and can cause pain, loosening of the implant, damage to the local tissue, and the need for revision surgery. One requirement of the ePTFE membranes used as soft tissue replacements in facial reconstruction is the need to interface with the surrounding bone. However, due to its hydrophobic surface, ePTFE lacks this capability. Hence, we have been investigating the surface modification of ePTFE membranes[5–9] with the view to improve its interaction with osseous tissue.

Surface modification of polymers can be used to selectively change the surface properties of a material already possessing good mechanical properties. Because of their versatility, grafting techniques have been receiving increasing attention in the area of biomaterials science. However, some methods of grafting can cause adverse biological effects, such as those that cause leaching of chemicals or additives, and hence, are not recommended for materials intended for clinical use. The most common techniques used for the production of materials for clinical

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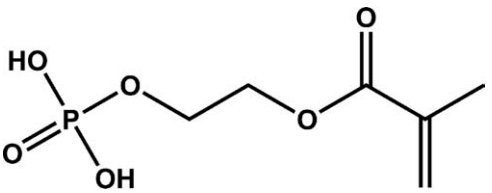

Figure 1 Chemical structure of methoxyacrylethyl phosphate.

applications are radiation activation, radiation copolymerization, plasma activation, and plasma polymerization.[10] A range of these techniques has been used for grafting onto PTFE substrates: plasma activation using different carrier gasses such as H_2O,[11,12] N_2,[11] O_2,[13] and Ar[14–17]; plasma polymerization[18]; and radiation grafting by electron beam pre-irradiation,[19] proton beam irradiation,[20,21] ^{60}Co gamma pre-irradiation,[14,20,22–25] as well as simultaneous ^{60}Co gamma irradiation.[26–31]

Improved "bone bonding ability" (often referred to as bioactivity) can be achieved by grafting judiciously-chosen functional groups that can induce hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] nucleation and growth. The growth rate of apatite formation has been shown to decrease with the functional group in the order $PO_4H_2 > COOH >> CONH_2 \cong OH > NH_2 >> CH_3 \cong 0$.[32] In our previous study on the grafting of methoxyacrylethyl phosphate (MOEP, Fig. 1) onto an ePTFE implant analog (from Sumitomo®) using methyl ethyl ketone (MEK) and methanol as solvents, we found grafted samples showed improved calcium phosphate growth in simulated body fluid (SBF), improved serum protein adsorption, as well as attachment of human osteoblast-like SaOS-2 cells.[9] Although samples grafted in either solvent showed the same number of attached cells, significantly more cells on the membrane grafted with MOEP in MEK displayed a spreading morphology. This suggests that this grafting system is the one preferred by cells, at least *in vitro*.

In the present study, a medical implant material, the ePTFE subcutaneous augmentation implant material (SAM from Gore and Associates) was surface modified by gamma-induced polymerization using MOEP in MEK at various monomer concentrations. The aim of the study was to evaluate grafting outcomes on this medical implant to investigate how our previous surface modification approach would affect this morphologically heterogeneous and much thicker membrane. It is important to fully characterize any commercial product subsequent to modification to assess not only the nature of that modification, but also to ensure that the substrate is not compromised. As has been shown in previous work, multiple techniques are required to get a complete analysis of the surface properties. Therefore, in this study, the resulting grafted membranes were assessed in terms of surface chemistry and morphology, wettability, and thermal properties.

MATERIALS AND METHODS

Materials

Expanded poly(tetrafluorethylene) (ePTFE), was obtained from W. L. Gore & Associates (Newark, Delaware) under the trade name Gore-Tex® (thickness 1.0 mm). The membranes were pre-treated by washing in methanol (40°C, 12 h) and subsequently dried in a vacuum oven to constant weight (40°C, 80 kPa) resulting in contraction of the membranes by $\sim$ 20%. Methoxyacrylethyl phosphate (MOEP) was supplied by Sigma-Aldrich and was used as supplied without removing the monomethylether hydroquinone [MEHQ (1000 ppm)] inhibitor. 2-Butanone (methyl ethyl ketone, MEK) was from Riedel-de-Hahn. All reagents were analytical grade and deionized water (Milli-Q®) was used throughout. All solvents were purged with nitrogen for 10 min before use.

Graft polymerization

Graft polymerization of MOEP onto the ePTFE membranes was achieved by simultaneous gamma irradiation at a radiation dose of 8 kGy using a ^{60}Co Nordian Gamma-cell 220 (Ontario, Canada) at a dose rate of 3.4 kGy/h. All grafting and preparation was done in the absence of light to minimize possible peroxide formation in the MEK solutions. The ePTFE membranes ($\sim 1 \times 1$ cm^2) were weighted by nickel-chromium wire before being placed in the monomer solution (2 mL). Dissolved oxygen was removed by one of two methods; either using nitrogen degassing or by applying vacuum. In the case of nitrogen degassing, the nitrogen gas was streamed through the solution both before and after sample addition for 10 min each. The vacuum method of degassing used is known as the freeze-pump-thaw method and involves freezing the monomer solution, evacuating the tube, followed by subsequent thawing of the monomer solution. This process was repeated three times at a vacuum of 10^{-3} torr. After gamma irradiation, samples were washed three times in methanol (5 min), followed by stirring overnight at ambient temperature in methanol. Finally, the samples were stirred for about 2 weeks in Milli-Q® water with daily water changes until constant wet weight was achieved. The samples are named in terms of monomer concentration/graft condition using graft condition abbreviations "N" and "V" for grafting under nitrogen and grafting

under vacuum, respectively. For example, the designation 30-N refers to the ePTFE sample grafted in contact with a solution of monomer concentration 30 w/v % under nitrogen.

Characterization

The graft yield was obtained gravimetrically as the percentage of weight increase of the ePTFE membrane using the following equation:

$$\text{Graft Yield } (\%) = \frac{w_g - w_o}{w_o} \times 100\%$$

w_g and w_o are the weights of grafted and original ePTFE membranes, respectively.

Differential scanning calorimetry (DSC) traces were recorded using a Perkin-Elmer DSC-7 equipped with PYRIS Version 3.5 Thermal Software. The instrument was calibrated using T_m of indium (156.6°C) and zinc (419.6°C) and their heats of fusion (28.42 J/g and 107.46 J/g, respectively). Melting transitions were determined using heating and cooling rates of 10°C/min for the temperature range of 200–400°C for samples of $\sim$ 10 mg.

Thermal gravimetric analysis (TGA) was completed on samples of 10 mg over the temperature range from 25°C to 400°C in a nitrogen atmosphere using a Shimadzu TGA, fitted with a TGA-50 detector. The flow rate was 80 mL/min, the heating rate 10°C/min, the holding time 3 min at 400°C.

X-ray Photoelectron Spectroscopy (XPS) analysis was performed on a Kratos Axis Ultra X-ray photoelectron spectrometer using monochromated Al Ka (1486.6 eV) at 15 kV and 10 mA (150 W), the slot size of 0.7 × 0.3 mm^2 gives a sampling area of 1.4 × 0.6 mm^2. The sampling depth was up to 10 nm with 63% of the collected signal being from the top 3 nm. Data was collected in a fixed analyser transmission mode (FAT): survey scans at 1200–0 eV with 1.0 eV steps at a pass energy of 160 eV; narrow scans at 0.1 eV steps at a pass energy of 20 eV. Vision 2 software was used for curve fitting as well as for data acquisition and processing. All binding energies were referenced by setting the highest component of the C 1s peak to 292.48 eV; this component corresponds to carbon in a fluorocarbon environment.[33] Component energies, number of peaks, and peak widths (FWHM of 1.2, 1.3, 1.0, and 1.3 for all F 1s, O 1s, C 1s, and P 2p, respectively) were fixed initially and refinement was carried out only for peak heights. In a final refinement cycle, component energies and peak widths were also refined and these changed by less than 1.0%. Spectral assignments were based on previously published data.[33,34] The XPS grafting extent of the graft copolymer was determined from the curve fitted high resolution C 1s scan and calculated using:

$$\text{XPS Grafting Extent } (\%) = \frac{\text{Carbon}_{\text{All}} - \text{Carbon}_{\text{C–F}}}{\text{Carbon}_{\text{All}}} \times 100\%$$

where $\text{Carbon}_{\text{All}}$ is the atom percent of all C 1s and $\text{Carbon}_{\text{C–F}}$ is the carbon–fluorine component of the C 1s region. Cryo-XPS of the MOEP monomer was performed by cooling to $<$ 150 K in a gold-plated recessed sample stub using a Kratos WX-524 Load Lock Cooling Device under vacuum ($\sim$ 20 min). The Load Lock turbo pump was backed up using a diaphragm pump to ensure that no oil vapors were present that might condense on the cold sample surface. The Kratos Axis Ultra modified standard XYZ theta sample stage was concomitantly cooled using liquid nitrogen. A temperature of $<$ 150 K was maintained throughout analysis.

Scanning Electron Microscopy (SEM) analysis of platinum-coated samples was performed using a JOEL 6400F scanning electron microscope at 7 kV (×1500) for pure ePTFE and 15 kV (×1000) for grafted samples.

Sessile water contact angle measurements were performed on a custom built apparatus comprising a combined stage and lens assembly fitted with a CCD camera. Images were processed using Scion Image software. Contact angle measurements were performed by placing the sample on the backlit Teflon stage; 5 μL aliquots of Milli-Q® were syringed onto the sample surface to a volume of 20 μL using a 50 μL glass syringe fitted with a stainless steel needle. The needle tip remained in the droplet during the experiment to eliminate vibrations caused by removal of the needle. The effect of the surface free energy of the needle was calculated and found to be within the standard deviation of the contact angle values. Receding measurements were made by subsequent syringing 5 μL aliquots away from the droplet, with the needle remaining in the droplet. The contact angle was calculated using:

$$\tan\frac{\theta}{2} = \frac{2h}{d}$$

where h is the height and d is the diameter of the drop. Six areas on each sample were examined (three positions on each side of the sample) and errors calculated as the standard deviation of the mean. To obtain the advancing contact angle, the average of the 5, 10, and 15 μL drops were used, while the receding contact angle values were obtained from the 5 μL drop only.

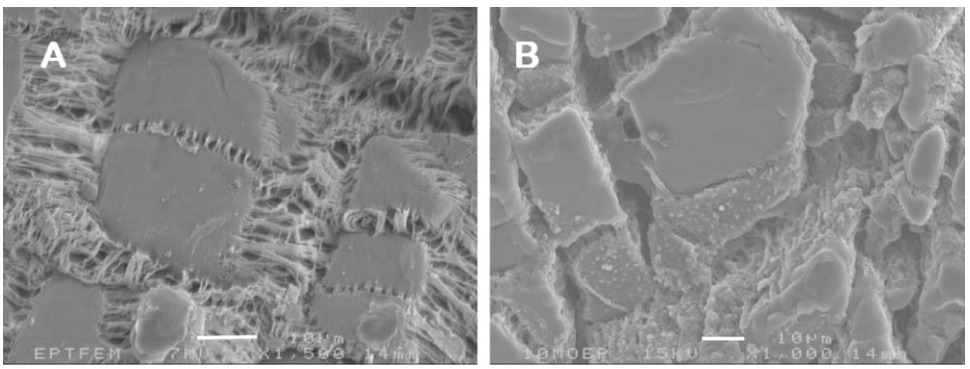

Figure 2 Scanning electron micrographs of (A) untreated ePTFE membrane and (B) MOEP-*g*-ePTFE (10-N). Scale bar represents 10 μm.

RESULTS AND DISCUSSION

The ePTFE substrate used in the current study differs from the Sumitomo® analog membrane, which we previously successfully optimized for bone bioactivity.[9] The Gore SAM used in this study is thicker than the Sumitomo® membrane by a factor of about 10 (1 mm and 0.07 mm, respectively). The gross structural morphology of the Gore ePTFE is also significantly different to that of the Sumitomo® membrane which has much smaller nodal regions. In addition, the crystallinity values of the two materials were significantly different (see below) with the Gore product having higher crystallinity. Because of these differences, it is important to assess the grafting outcomes of Gore SAM and assess how they differ from the analog test material. Moreover, since this project aims at improving a commercial implant material very detailed characterization is needed and multiple analytical techniques are required to achieve a complete picture of the modified material.

Morphology and thermal properties of ePTFE and MOEP-*g*-ePTFE

The gross morphology of the ePTFE membranes studied can be described as islands or "nodes" interconnected by fibrils. The nodal diameter is on average 10–20 μm with a similar internodal distance, as illustrated in the SEM image shown in Figure 2(A). Although, in general, this morphology is uniform, regions with nodal or fibril congestion do sometimes occur. The membrane porosity is reported to be greater than 70%[35] and the membrane thickness is 1 mm. A thick and granular morphology of the graft copolymer was observed for samples prepared by grafting MOEP in MEK [Fig. 2(B)]. This globular morphology has been observed for both graft copolymers and homopolymers in our previous studies where MOEP was grafted onto a Sumitomo® ePTFE membrane[8] and was attributed to the poor solubility of the graft copolymer in MEK.

The first (irreversible) and second (reversible) melting temperatures, T_m, for ePTFE were found to be 343 and 326°C, respectively. This is in agreement with the literature values.[36] From the first melting peak a value for ΔH of 49 J/g was obtained, yielding a degree of crystallinity of $\sim$ 59% when using a value for the heat of fusion of 82 J/g.[36,37] One high graft yield sample (30-N) was also investigated by DSC. Although the first melting temperature differed from that of the untreated substrate (T_m = 335°C) it was still within the range reported previously for PTFE.[37] The value for the second T_m was found to be similar to that measured for ePTFE. Although the grafted sample showed an additional exothermic peak at $\sim$ 300°C in the first T_m curve, this was absent in the second T_m curve. This suggests the evolution of a decomposition product most likely related to the graft copolymer. This was verified by TGA where a significant mass loss corresponding to half the mass of the graft copolymer was observed in the temperature range 280–330°C. TGA of the corresponding homopolymer formed concomitantly displayed a similar 50% mass loss within the same temperature range. The crystallinity of PTFE in the grafted 30-N sample was found not to differ significantly from that of the untreated ePTFE substrate. This indicates that grafting does not interfere with the crystalline domains and strongly indicates that grafting occurs predominantly onto the amorphous regions of the polymer. Similar substrate crystallinity effects have previously been observed.[38,39]

Characterization of MOEP-*g*-ePTFE by XPS

Figure 3(A,B) show XPS multiplex scans of both untreated ePTFE (methanol washed) and grafted ePTFE samples (20-N). In the untreated sample, as expected, only fluorine and carbon peaks are present. In sample 20-N the fluorine and carbon peaks from the substrate are still present. However, the fluorine peak is diminished in intensity and the

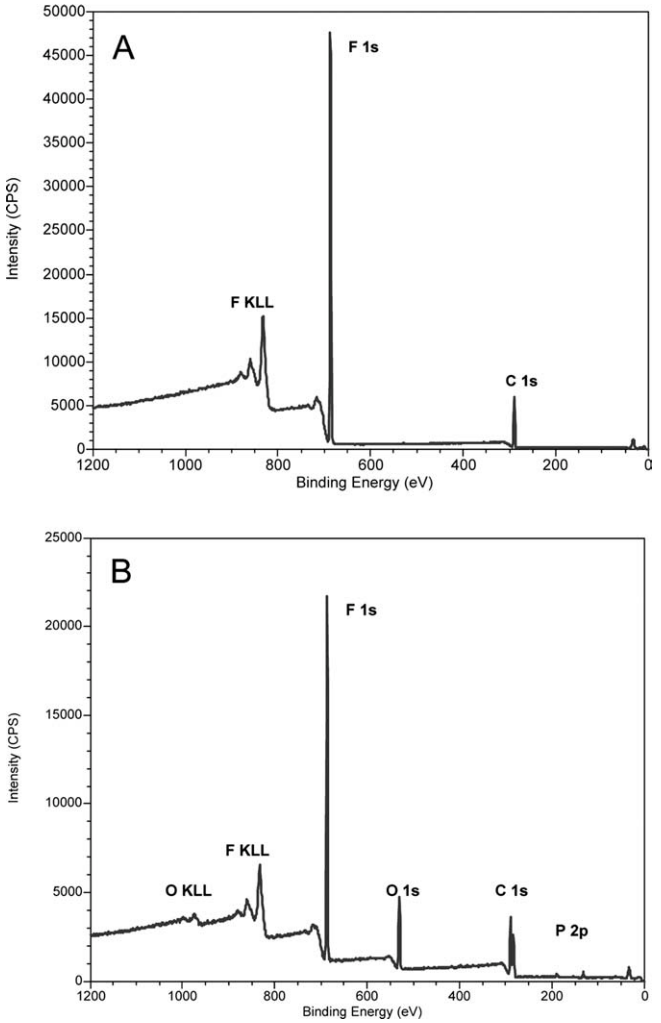

Figure 3 XPS survey spectra of (A) ePTFE (methanol washed) and (B) ePTFE grafted sample 20-N.

carbon peak is now a doublet peak. In addition, oxygen and phosphorous peaks are now observed. Notably, no silicone contaminations are observed in these samples. The high resolution scan of the C 1s region of the grafted 20-N sample displays a complex profile (Fig. 4). Curve fitting into peaks corresponding to different carbon environments is in good agreement with the chemical structure of the graft copolymer (Fig. 4). The peak at 292.5 eV corresponds to carbon in a fluorine environment, and therefore, to the substrate carbons. All other carbons in the 285–289 eV region correspond to the carbons of the graft copolymer. Since the C1s peaks for each of the two components are well separated it is easy to assess the chemical structure of the grafted polymer.

The curve fit of the graft copolymer region displays a peak (g) at a binding energy of 285.0 eV corresponding to carbon–carbon and carbon–hydrogen bonded carbons, as well as the adventitious carbon. The peak (f) at 285.7 eV is assigned to the carbon bound to the carbonyl ester group (C—COO). The peaks at 286.8 eV (e) and 287.3 eV (d) are assigned to carbon singly-bonded to an oxygen atom (C—O) with the higher energy peak assumed to be due to the carbon closest to the carboxylic ester. The high energy peak at 289.1 eV (c) corresponds to the carbon of the ester moiety (O—C=O). The ratios between the peaks (g: f: e: d: c = 2: 1.2: 0.9: 0.8: 0.8) are in good agreement with the expected ratios based on the chemical structure. Carbon singly-bonded to a fluorine atom (C—F) and carbon connected to the carbon singly-bonded to fluorine (C—C—F) occur at the binding energies of 287.2 eV and 285.2 eV, respectively.[33] However, these species are expected to contribute only to a very small extent to the overall spectrum, and therefore, no attempt has been made to include them in the curve fit. The former overlaps with peak (d) and the latter with peak (g) (Fig. 4).

Table I lists a comparison of the atomic ratios of the monomer and for both the grafted polymer and homopolymer formed in the solution for sample 20-N. This sample is representative for all the graft copolymers and has a sufficiently high graft yield and XPS grafting extent to give accurate values for the analysis. From the data it can be seen that the atomic ratios of the monomer are close to the theoretical values but that those for the grafted polymer

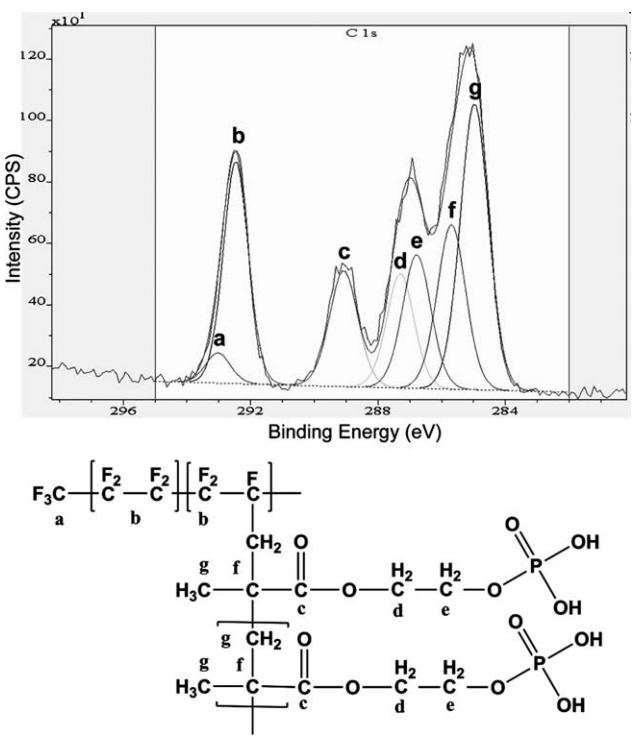

Figure 4 XPS high resolution spectrum of the C 1s region of sample 20-N indicating the fitted peaks. (a): C—F_3, (b): C—F_2, (c): O—C=O, (d): C—O(C=O), (e): C—O, (f): C—COO, (g): C—C, CH_3.

TABLE I
Atomic Ratios Obtained from the XPS Survey and Curve Fitted XPS C 1s Narrow Scan for a Selection of Samples

Sample	C/P[a]	C/O[a]	C—O/C=O[b]
Monomer	7.7	1.0	2.4
Homopolymer	16.1	1.8	1.5
20-N	19.5 ± 0.6	1.7 ± 0.2	2.1 ± 0.2
Theoretical monomer	6	1	2
Theoretical diene	12	1.5	2

[a] The atomic concentration of C is obtained from the curve fitted C 1s narrow scan (peaks c–g, Fig. 4), while the atomic concentrations for P and O are obtained from the multiplex spectrum.
[b] The atomic concentration of C—O is obtained from peaks d and e while the atomic concentration of C=O is obtained from peak c (Fig. 4).

and the homopolymer, while generally similar to each other, are significantly different to the theoretical values. In our previous study, we demonstrated that the monomer in fact contains a large amount of diene impurity (25%) as well as a similar amount of phosphoric acid.[40] The chemical structures of the impurities and the fact that they are present in very similar amounts results in elemental compositions, observed in the XPS spectrum, that coincidentally correspond to the theoretical values. Furthermore, the presence of this significant amount of diene impurity clearly has implications for the chemical structures of the polymers being formed. In the present study, however, the statistical incorporation of this diene impurity cannot explain the atomic ratios obtained for either the homopolymer or the grafted copolymer. Using NMR we have previously shown that the PMOEP synthesized using reversible addition-fragmentation chain transfer (RAFT) is hydrolytically unstable with respect to cleavage at the phosphate ester bond.[40] In the present study, where the graft copolymer was prepared by gamma radiation-induced grafting in MEK, we come to a similar conclusion: although the C/P ratio is very high, the value of the C—O/C=O ratio is identical to the theoretical value. This implies that minimal cleavage has occurred at the carbon ester and that only the phosphate ester has undergone cleavage (Table I). It can be concluded therefore that in these grafted samples, the grafted polymer possesses a complex chemistry containing both hydroxyl and phosphate functional groups. In addition, it is expected that the structure has a high degree of crosslinking. This is a result of both diene incorporation and also a result of hydrogen abstraction from the polymer backbone during gamma irradiation.

Graft yield and grafting extent

In the concentration range studied (3–30%), it was observed that the graft yield increased with increasing monomer concentration as shown in Table II. No significant differences in the grafting yields were observed between samples prepared using the different degassing techniques: the result is a linear relationship between grafting yield and MOEP concentration (Fig. 5). The grafting yields obtained in the current study (a maximum of 34%) are lower than those reported previously by Wentrup-Byrne et al.[8] for grafting MOEP onto the Sumitomo® membrane (a maximum of ~ 100%). This difference is most likely due to the differences in crystallinity of these two ePTFE substrates: GORE-TEX® 59%, Sumitomo® 22%.[8] However, it is possible that differences in porosity and/or sample thickness also affect the grafting outcome.

From the C 1s region of the high resolution XPS spectra, the grafting extent was determined as the percent carbon from the grafted polymer. The terms "degree of surface coverage,"[6,8] "external surface coverage,"[7] and "surface grafting yield"[9] were previously used to denote what from now on will be termed XPS grafting extent. As will be clarified in this article and what has become apparent during

TABLE II
Properties of Grafted ePTFE Samples Irradiated in MEK at 8 kGy at a Dose Rate of 3.4 kGy/h

Sample	[MOEP] (w/v%)	Condition	Graft yield (%)	Grafting extent (%)	θ_A (°)	θ_R (°)
U	–	–	–	–	135 ± 6	136 ± 6
3-V	3	Vacuum[a]	1.9	10	135 ± 7	97 ± 14
3-N	3	Nitrogen[b]	2.4	31	129 ± 3	84 ± 14
6-V	6	Vacuum	4.0	62	118 ± 5	53 ± 5
6-N	6	Nitrogen	5.7	64	108 ± 6	38 ± 8
10-V	10	Vacuum	8.0	91	105 ± 12	36 ± 10
10-N	10	Nitrogen	10.8	79	100 ± 14	37 ± 12
20-V	20	Vacuum	19.2	55	87 ± 8	29 ± 13
20-N	20	Nitrogen	28.1	92	52 ± 15	0 ± 0
30-V	30	Vacuum	34.4	65	73 ± 10	3 ± 3
30-N	30	Nitrogen	28.5	78	67 ± 12	4 ± 10

[a] Vacuum refers to grafting under vacuum using the freeze-pump-thaw technique.
[b] Nitrogen refers to grafting under a nitrogen atmosphere.

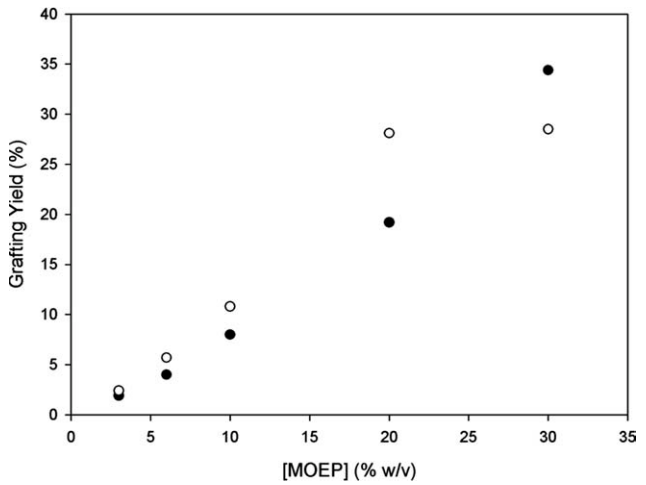

Figure 5 Grafting yield as a function of MOEP concentration in MEK, using two preparation methods. ●, Grafted under vacuum; ○, Grafted under nitrogen.

the evolution of these extended studies, is that these earlier descriptions are not ideal terms. The XPS grafting extent was found to be similar for both degassing techniques displaying a linear relationship for samples produced up to 10% MOEP after which limiting conditions were observed (Fig. 6). A maximum XPS grafting extent of 90% was achieved at 10% w/v MOEP concentration. At higher monomer concentrations, the values decreased irrespective of the preparation technique. Similar observations were made for the grafting of MOEP onto the Sumitomo® membrane, although for these samples, 100% was obtained for the high monomer concentration.[8] It is important to note that the fact that the grafting extent levels off at 10% w/v MOEP but does not reach 100%, whereas the graft yield continues to increase, suggests that the graft copolymer formed at higher monomer concentrations is in fact grafted to a large extent inside the pores or into the bulk of the substrate. Since these differences between the grafting extents of the Sumitomo® and GORE-TEX® membranes are most likely related to their differences in crystallinity, it is thus possible that the theoretical 100% grafting extent cannot be obtained for the more crystalline GORE-TEX® samples at the dose applied. It can be safely concluded that due to the fact that grafting is predominantly taking place in the amorphous regions the crystalline domains which are ungrafted remain exposed on the surface to XPS analysis.

Contact angle measurements

Untreated ePTFE is extremely hydrophobic and has a contact angle of 135°. This is somewhat higher than that reported for solid PTFE[36] and is most likely due to its porous nature. The hydrophobicity (advancing contact angle) of the grafted samples is found to decrease with increasing monomer concentration (Table II). For a few samples, (prepared by nitrogen degassing), a hydrophilic surface ($\theta_A < 65°$)[41] resulted after grafting. The receding measurements for the grafted samples likewise decrease with increasing monomer concentration. None of the grafted substrates demonstrated an advancing contact angle value expected for pure homopolymer. This can be attributed to the fact that the conformation of the polymer in the dry state exposes its hydrophobic backbone to the outmost surface. This is confirmed by the receding contact angles which in some samples are very low. The contact angle hysteresis is very large (up to 75°) indicating that the grafted samples have either increased roughness and/or are chemically heterogeneous or as described earlier, underwent conformational changes during the contact angle measurement experiment.[42] No significant differences in the contact angle values are observed for samples prepared using the different preparation techniques.

There is an apparent correlation between both advancing and receding contact angle values and the average graft yield for both sample sets (N and V in Table II). A decreased hydrophobicity with increased grafting yield is observed as expected when a hydrophilic monomer is used. It is surprising that there is a lack of correlation between advancing and receding contact angle values and the average XPS grafting extent (Table II) since both techniques probe the material surface. Thus, for samples 10-N and 30-N very similar values for grafting extent (79% and 78%, respectively) are observed but their contact angles differ significantly (100 ± 14 and 69 ± 12, respectively). Likewise, although samples 6-V and 30-V display similar grafting extents

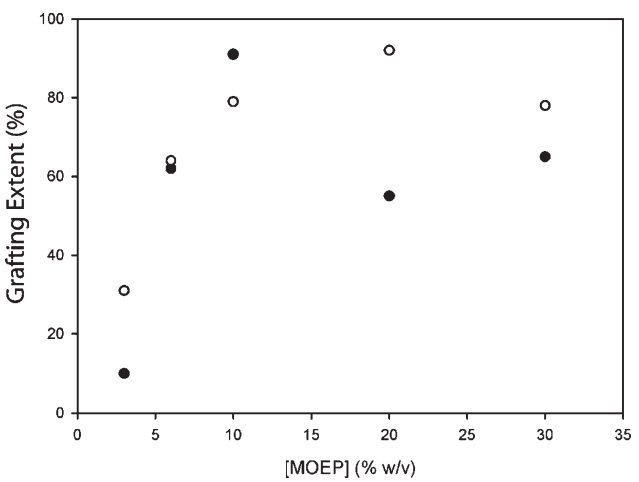

Figure 6 Grafting extent as a function of MOEP concentration in MEK, using two preparation methods. ●, Grafted under vacuum; ○, Grafted under nitrogen.

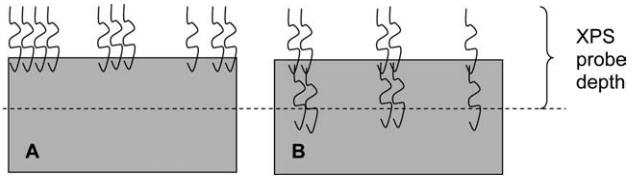

Figure 7 Illustration of two samples displaying the same XPS grafting extent but different actual surface coverage of the graft copolymer as assessed by contact angle measurements. Sample A is more hydrophilic than sample B.

(62% and 65%, respectively), their advancing and receding contact angles differ significantly (Table II). In both cases, the samples prepared at the lower monomer concentration are clearly more hydrophobic than those produced with the higher monomer concentration. This discrepancy can be explained in terms of the different probing depths of the two techniques. Thus, water contact angle measurements probe the top molecular layer whereas XPS probes up to 10 molecular layers. Water contact angle measurement, is therefore a better tool, for evaluating the actual surface coverage of the graft copolymer. These observations also highlight that the XPS grafting extent is not a true measure of surface coverage. Figure 7 illustrates how different degrees of actual surface coverage evaluated using contact angle measurements can lead to the same value for the XPS grafting extent. These results clearly illustrate the importance of using multiple techniques to correctly characterize grafted materials.

One important conclusion that can be drawn from the combined observations of this study is that a higher monomer concentration does not necessarily result in higher surface coverage as analyzed by water contact angle measurements. A comparison of samples 20-N and 30-N, which display similar wettabilities, strongly suggests that an increase in monomer concentration which leads to an increase in the observed graft yield is the result of grafting into the pores and/or the bulk of the membrane rather than across the surface. To obtain a complete picture of the distribution of the graft copolymer, it is necessary to comprehensively evaluate all the data (graft yield, grafting extent, and water contact angle). It is thus possible to obtain a good picture of the distribution of the graft copolymer within the ePTFE membrane. A more thorough investigation of the distribution of the graft copolymer will require the use of more sophisticated analytical techniques and such studies are currently underway.

CONCLUSION

It was found that for the highly porous ePTFE membrane studied, grafting occurred preferentially in the amorphous regions of the substrate. Detailed XPS analysis showed that the grafted samples displayed a more complex chemistry than expected due to the instability of the phosphate ester bonds in the graft copolymer. Although there was no significant difference in the grafting outcome for the different sample preparation techniques, it was clear that the graft yield, grafting extent, and contact angles were greatly dependent on the monomer concentration. A simple correlation was found between graft yield and water contact angle. However, the grafting extent, as evaluated by XPS, did not display a corresponding simple relationship. This highlights the need for multiple analytical techniques for an in-depth characterization. In addition, by comparing data from the three techniques used, it is possible to determine whether grafting has preferentially occurred on the surface or in the bulk.

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