COVER SHEET

METHACRYLOXYETHYL PHOSPHATE GRAFTED ePTFE MEMBRANES for BIOMEDICAL APPLICATIONS

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ABSTRACT: Expanded Poly (tetrafluoroethylene) (ePTFE) membranes were modified by graft copolymerization with methacryloxyethyl phosphate (MOEP) in methanol and 2-butanone (also known as methyl ethyl ketone MEK) at ambient temperature using gamma irradiation. The effect of dose rate (0.46 and 4.6 kGy/h), monomer concentration (1-40%) and solvent were studied and the modified membranes were characterised by weight increase, X-ray photoelectron spectroscopy (XPS), Fourier Transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). XPS was used to determine the % degree of surface coverage using the C-F (ePTFE membrane) and the C-C (MOEP graft-copolymer) peaks. Grafting yield as well as surface coverage were found to increase with increasing monomer concentration and were significantly higher for samples grafted in MEK than in methanol solution. SEM images showed distinctly different surface morphologies for the membranes grafted in methanol (smooth) and MEK (globular) indicating phase separation of the homopolymer in MEK. We propose that in our system, the non-solvent properties of MEK for the homopolymer play a more important role than solvent chain transfer reactions in determining grafting outcomes.

Key words: ePTFE, methacryloxyethyl phosphate (MOEP), fluoropolymers and irradiation grafting

INTRODUCTION

Fluoropolymers are one class of polymers that have found many applications varying from use as separation membranes and industrial coatings to biomaterials in the medical and dental field.[1] Their wide range of applications is due largely to their chemical and thermal inertness. However, although the bulk properties of a particular fluoropolymer might be suitable for a specific application, in some instances the surface properties prove less than ideal. In particular, the fact that like most industrial polymers fluoropolymers are hydrophobic, has meant a limited efficacy in some applications. One fluoropolymer, which because of its acceptable biocompatibility, has enjoyed widespread use in medical applications, especially for peripheral vascular surgery, is polytetrafluoroethylene (PTFE).[2-3] The expanded form of polytetrafluoroethylene (ePTFE) with its highly porous fibrillated structure is used in guided bone regeneration for both dental and maxillo-craniofacial applications.[4-6] In addition, it is currently one of the best non-resorbable, sub-cutaneous augmentation materials used in facial prostheses to restore a normal appearance in patients who have lost facial tissue through cancer, birth defects, or trauma. Studies have shown that the expanded form of PTFE performs well in animals [7] as well as in humans.[8] However, like many implant materials it does not form an ideal interface with bone and we are investigating the possibility of improving its bone bonding ability by making it more hydrophilic as well as introducing potential nucleation sites for the growth of hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$), the inorganic component of bone.

The surface modification of polymers using radiation-induced graft copolymerisation -in order to produce a wide range of materials with specific properties- has been a

successful strategy for many years. [9] A comprehensive and useful review by Dargeville *et al* on the high energy grafting of fluoropolymers covers much of the literature for a range of monomers and fluorinated polymers. [10] Control of the induced changes can be achieved through judicious choice of monomer as well as varying grafting method, dose rate and solvent. The surface properties of the grafted polymers can differ substantially from those of the parent polymers, a fact that can be advantageously exploited to produce graft-copolymers with specific properties.

It has been shown that the presence of negatively charged functional groups, in particular phosphate groups, on the surface of hydrophobic polymers has a significant effect on their bioactivity both *in vitro* and *in vivo*. Polymeric grafting with the phosphate containing monomer methacryloxyethyl phosphate (MOEP) (Figure 1), has been carried out on silk fabrics [11], poly(ethylene terephthalate) [12] and high density polyethylene (HDPE) [13, 14] as well as poly(acrylonitrile)[15, 16]. In one study the surface modification of materials used in orthopaedic applications involved the graft polymerisation of MOEP to HDPE and was aimed at producing an improved bone-bonding polymer surface.[14] Even at low graft densities of 0.8 – 3.0 $\mu g/cm^2$, the modified polymer showed improved carbonated hydroxyapatite growth *in vitro*, under so-called simulated body fluid (SBF) conditions. Subsequent *in vivo* evaluation of the modified polymer showed significant enhancement of bone growth at the material-bone interface to that of the unmodified polymer.[17] Clearly, a very low grafting yield of MOEP on HDPE is sufficient to improve the bioactivity of this material.

As part of an on-going study on the grafting of phosphate monomers onto commercially available fluoropolymers, we are investigating the grafting of monoacryloxyethyl phosphate (MAEP) and MOEP onto ePTFE with a view to producing a more bioactive surface on fluoropolymers used in cranio-facial applications.[18-20] When MAEP was grafted onto selected fluoropolymers [18] the increased surface bioactivity of the ePTFE membranes as evidenced by the growth of calcium phosphate minerals in SBF, was attributed to an increase in surface hydrophilicity and introduction of mineral nucleation sites.[19] Although a previous study showed that sometimes a low degree of grafting is sufficient to enhance surface biomineralization [17], in the case of the MAEP modified ePTFE materials an external surface coverage of 44% was required in order to induce calcium phosphate nucleation.[19] Based on these promising results and the continued widespread use of ePTFE membranes as biomaterials we have extended our surface modification studies to the gamma irradiation induced graft polymerisation of MOEP to ePTFE under varying reaction conditions. Hence, in this study our aim was to produce a range of MOEP modified ePTFE materials with varying degrees of grafting and surface coverage in order to investigate how these parameters influence on the bioactivity of the modified surface. The bioactivity results are reported separately.[20]

EXPERIMENTAL

Materials

Expanded poly (tetrafluoroethylene) (ePTFE) Sumitomo Poreflon® 020-80 membranes (thickness 70 μm) were from Sumitomo Electric, (Osaka, Japan). The melting peak at 329°C in the DSC trace of 18 J/g yielded a degree of crystallinity for the membrane of approximately 22% [21] when using a value for the heat of fusion of 82 kJ/kg.[22, 23] The SEM image of the unmodified PTFE membrane (Figure 2) shows the highly porous nature of this material.

Ethylene glycol methacrylate phosphate (MOEP) was supplied by Sigma, Australia. The monomer was used as purchased without removing the stabilizer (1000 ppm hydroquinone monomethyl ether). Analytical grade methanol and HPLC standard (99.7% pure) methyl ethyl ketone were purchased from Sigma and used as supplied. Ultrapure water from a Hi-Pure Water System, Permutit (Australia) was used. All solvents were purged with nitrogen for 30-60 minutes before use.

Graft Polymerization

ePTFE membrane pieces (diameter of 10 mm) were washed by Soxhlet extraction in methanol for 12 hours and subsequently dried under vacuum. Each polymer piece was placed in a glass test tube containing solvent and monomer and the tube was sealed with a Suba cap. Dissolved oxygen in the monomer solution containing the polymer substrate was removed by bubbling nitrogen gas for 15 minutes. Graft polymerization of MOEP onto the polymer membranes was achieved by gamma irradiation at ambient temperature under nitrogen using a ^{60}Co Nordian (Canada) gamma cell 220 for higher dose rates (4.6 kGy/h) and a 200 Nordian Gamma-cell (Canada) for low dose rates (0.46 kGy/h).

Following graft copolymerisation, membranes were placed into mesh containers and washed with methanol for 24 hours at 40-45^{o}C to remove any residual monomer and loose homopolymer occluded onto the membrane. The membranes were then dried to a constant weight.

Characterisation of grafted PTFE membranes

The degree of overall grafting was obtained gravimetrically as the percentage of weight increase of the ePTFE membrane using the following equation:

$$\text{Degree of Grafting (\%)} = \frac{w_g - w_o}{w_o} \times 100$$

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

X-ray Photoelectron Spectroscopy (XPS) analysis of the unmodified membrane and the grafted membranes (sample sets A, B and a) were recorded on a PHI Model 560 XPS/SAM/SIMSI Multi-technique Surface Analysis System with a Model 225-270AR Cylindrical Mirror Analyser (CMA). MgK_{α} radiation (1253.6 eV) was used for all spectra. The survey scans were taken in the range of 0-1000 eV at a pass energy of 100 eV with a resolution of 0.5 eV. The multiplex scans of selected elements (C 1s, F 1s, O 1s and P 1s regions) were collected at 50 eV with a resolution of 0.1 eV. The binding energy of the samples was calibrated using that of the F(1s) peak (688 eV) [24]. The peak areas for atomic concentrations were measured from the multiplex spectra.

XPS analysis of the grafted membranes (sample set b) were recorded using a Kratos, Axis Ultra XPS system, employing a 165 mm, 180 degree hemispherical analyser with 8 channeltrons (Kratos Analytical, Manchester, England). A AlK_{α} radiation (1486.6 eV) typically run at 150 W (15 kV, 10 ma) was used for all spectra. The survey scan range of 0-1200 eV with a pass energy of 160 eV and the multiplex scans with a pass energy of 20 eV were carried out.

Surface coverage of PMOEP was obtained by using the areas of the carbon peaks as follows:

$$\text{Degree of Surface Coverage (\%)} = \frac{A(C-others)}{A(C-others)+A(C-F)} \times 100$$

For representation, the carbon peak which is not C-F is written as C-others, since it contains carbons such as C=O and C-O.

Fourier Transform Infrared Attenuated Total Reflectance (FTIR-ATR) spectra were collected on a Nicolet Fourier Transform Infrared Spectroscopy equipped with a diamond ATR (64 scans over the region of 4000 – 525 cm^{-1}, resolution $4cm^{-1}$).

Scanning Electron Microscopy (SEM) analysis of the gold-coated grafted membranes was performed using a FEI Quanta 200 SEM (FEI Company Oregon, USA) operating in standard high vacuum mode and equipped with a Meeco Image Slave digital image acquisition system.

Results

Grafting conditions such as radiation dose rate, monomer concentration and solvent all play a crucial role in determining both the grafting rates and the extent and type of surface changes in the final grafted copolymer. Dose rate (0.46 and 4.6 kGy/h),

monomer concentration (1–40 %) and solvent (methanol and MEK) were investigated with respect to the overall grafting yield, the external surface coverage, and morphology of the graft-copolymer. Since the aim of the synthesis was to produce ePTFE membranes with hydrophilic functional groups on the surface but minimal bulk changes due to irradiation effects, we limited our study to one dose of 10 kGy.

The ePTFE substrate is a highly porous material (Figure 2) and grafting can therefore occur both on the external surface and inside the pores. In the following text, however, the term "surface coverage" refers only to the external surface of the material as analysed using XPS.

Characterisation of the graft-copolymers by XPS and ATR-FTIR

XPS and ATR-FTIR spectroscopy were used to verify the successful grafting of MOEP onto the ePTFE membranes. As seen from the XPS results in Figure 3a the unmodified ePTFE membrane shows the expected characteristics with a fluorine peak at 689.7 eV [F (1s)] and a single fluorocarbon peak at 292.5eV [C-F(1s)]. From the representative XPS scans for membranes with different degrees of grafting, the characteristic MOEP copolymer peaks, C-others peak [C(1s)] at 282.5 eV as well as an oxygen peak [O(1s)] at 531.7 eV and a smaller phosphorous peak [P(2p)] at 130.7 eV, can be seen to increase with increasing grafting. As seen in Figure 3b and 3c the characteristic [F(1s)] and [C-F(1s)] peaks are still visible for lower grafting yields, whereas in Figure 3d where the surface coverage is ~100% these peaks are no longer visible.

The FTIR ATR spectra for the 600-1900 cm^{-1} region for both ungrafted and grafted membranes are shown in Figure 4. Characteristic C-F stretching vibrations at 1201

and 1146 cm^{-1} can be seen in the spectrum for ungrafted ePTFE (Figure 4a). The PMOEP grafted samples show additional bands at 1721-1727 (C=O stretching), ~1060 (P-O-(C) stretching) and ~964 cm^{-1} (P-O-(H) stretching). Small bands in the region of 1490-1370 cm^{-1} correspond to the C-H bending. The intensity of these PMOEP peaks correlate with the surface grafting yields. [18]

Overall Grafting Yield and Surface Coverage

Grafting yield as a function of monomer concentration (1 – 40%) for the two dose rates as well as the two solvents studied is shown in Figure 5. For samples grafted in methanol solution a grafting yield was not detectable for monomer concentrations of 1 – 10%. At higher monomer concentrations an increase in grafting yield with concentration was observed, reaching a maximum yield of 45%. In contrast, for samples grafted in MEK an increase in grafting yield with monomer concentration was observed for the entire concentration range studied. In this system a maximum grafting yield of 97-100% was observed.

XPS multiplex scans ([C(1s)] insert in Figure 3) were used to obtain C-others/(C-others + C-F) atomic ratios to calculate a comparative measure of the degree of surface coverage of the grafted MOEP monomer and these results are shown in Figure 6. In MEK, high surface coverage at monomer concentrations higher than 1% was found for both dose rates (Figure 6). The surface coverage reaches nearly 100% at monomer concentrations as low as 5% in MEK for the low dose rate. However, for the samples grafted in methanol, the large PTFE membrane peaks of [F(1s)] and [C-F(1s)] are still present in the XPS spectrum (Figure 3) even after grafting with a monomer concentration of 40%. In methanol the maximum surface coverage obtained was 45% for monomer concentrations greater than 25%.

As can be seen from Figure 5, grafting yields were very similar irrespective of the dose rate used, although consistently slightly higher for the lower dose rate for the methanol samples. For the MEK systems there is a dose rate dependence on the surface coverage with the low dose rate yielding the higher surface coverage (Figure 6).

Important observations can be made by comparing overall grafting yield and surface coverage. For the samples grafted in methanol at monomer concentrations of 20-40%, the overall grafting yield continued to increase, whereas, the degree of surface coverage remains at 20-45%. For samples grafted in MEK, on the other hand, the grafting yield is similar for the two dose rates but the surface coverage reaches 100% for a 5% monomer concentration at low dose rate and for the 20% sample at high dose rate.

Surface morphology

SEM proved a useful and revealing technique in analyzing the graft-copolymers. The graft morphology of samples grafted in methanol solutions with monomer concentrations of 20% and above were smooth in appearance with the underlying fibrillar structure still apparent under the grafted layer (Figure 7a). As seen in the high magnification micrograph of the same sample in Figure 7b in addition to the surface graft layer, MOEP copolymer can be clearly seen within the fibrillated porous structure of the membrane.

Samples grafted in MEK showed similar smooth graft morphology for low monomer concentrations of 1 – 5% (Figure 7c), but at higher concentrations the graft morphology was much thicker and granular in appearance and none of the ePTFE

fibrillar structure was obvious (Figure 7d). This was observed for both dose rates investigated.

The samples shown in Figure 7a and 7c are produced in methanol (30% MOEP) and MEK (5% MOEP), respectively, and have very similar surface morphologies, however, the grafting yields are significantly different (40 and 18%, respectively). For samples produced in MEK (≥10% MOEP) with grafting yields at low as 32% a granular morphology is observed as seen in Figure 7d. Thus, the morphology observed is not an effect of monomer concentration or overall grafting yield but rather the outcome of specific solvent properties.

Homopolymer formation

The amount and morphology of homopolymer formed in the grafting reaction was investigated qualitatively. All MEK solutions turned turbid after gamma irradiation even at low monomer concentrations. This indicates formation of homopolymer and also that MEK is a non-solvent even for the shorter MOEP oligomers. As the monomer concentration increased larger amounts of precipitate formed. For monomer concentrations of 1-10% the methanol solutions remained clear. But for monomer concentrations of 20-40% the reaction mixtures were all viscous gels by the end of the irradiation process. The morphology of the homopolymer for methanol and MEK samples can be seen in Figure 7e and 7f (40 and 10% monomer, respectively). Clearly, the morphology of the homopolymer parallels that of the graft copolymer formed in these solvents (i.e. 7a and 7d, respectively).

Discussion

In order to study the effect of the charged phosphate groups on the *in vivo* bioactivity of the grafted copolymers we choose solvents which might be expected to give different grafting outcomes. Indeed we found that in our system the role of the solvent played an essential role not only on the grafting yield, but also on the surface coverage and graft-copolymer morphology.

As Chapiro has stated "the addition of a solvent to a monomer/substrate combination can enhance the yield in the radiation-induced grafting and determine the specific nature of the graft copolymer". [27] In our study solvent choice was limited because attempts at achieving higher grafting yields and surface coverage using solvents such as dichloromethane were limited by the lack of solubility of the monomer.

The chain of events in the grafting process involves solvent irradiation in the first instance. The initiation rate for the formation of solvent free radicals could be expected to be different for the solvents used. This is followed by monomer radical and PTFE surface radical formation. It is well established that the solvent plays a critical role in the competing processes which are occurring during the grafting process. Thus, the solvent may affect the diffusion of the monomer or homopolymer radicals, solubility of homopolymer, monomer solvation, and the electron donor and acceptor properties of the monomer. Thus, in addition to preferential solvation effects and monomer properties, kinetic effects such as chain transfer reactions and termination by highly mobile radicals formed from the solvent also greatly affect the grafting outcomes.

Effect of dose rate on grafting

Nasef has studied the effect of grafting conditions on the radiation-induced grafting of styrene onto different fluorinated polymers including PTFE. [25, 26] He attributed the high degree of grafting at a low dose rate to several effects including the formation of "efficient" radicals that react easily with the monomer molecules. Combined with low viscosity of the grafting solution and good monomer diffusion the result was a higher grafting rate. For our samples, in methanol we do not observe large differences either in the grafting yield or in the degree of surface coverage with the different dose rates. However, in MEK, although the grafting yield is unaffected by dose rate the surface coverage is significantly higher at the lower dose rate. In conclusion, good grafting yields can be achieved at a low dose rate in the simultaneous grafting of a phosphate monomer MOEP onto ePTFE.

Chain Transfer Properties of the Solvents

To the best of our knowledge, chain transfer constants (C_s) for MOEP are unavailable but those for methylmethacrylate (MMA) can give some indication of the expected trend. The C_s at 60^o for MMA in methanol and MEK are 0.20 and 0.45 respectively. Since Chapiro [28] demonstrated that in a solvent with a high C_s value the growing chain will be quickly terminated leading to lower grafting yields there have been numerous studies confirming this. Among these, Cardona *et al* [29]and Nasef [25-26] showed in their radiation induced grafting studies of styrene onto various fluorinated substrates that lower grafting occurs in methanol (C_s = 0.296) than in dichloromethane (C_s = 0.150). From the MMA C_s values and the fact that homopolymer is formed in both solvents, which are also (to different degrees) both non-solvents for the homopolymer, it could be predicted that greater grafting yields

would be obtained in methanol. However, this is not what we observe and unless the C_s values for our phosphomer are the reverse for MMA it appears that chain transfer effects are not dominant in our system.

Homopolymer Morphology

The studies by Cardona *et al* [29] and Nasef [25-26] concluded that both the formation and subsequent solubility of homopolymer contribute to the grafting outcomes. The SEM micrograph in Figure 7d for the MEK grafted sample and Figure 7f for the homopolymer shows that phase separation has caused a globular formation of the thick pMOEP grafted layer / homopolymer. This is in contrast to the copolymer morphology for the methanol grafted sample shown in Figure 7a and the homopolymer seen in 7e. Clearly the surface morphology is controlled by the homopolymer / graft copolymer solubility in the two solvents.

Solvent Effects on Grafting and Homopolymer Formation

In methanol there is almost negligible grafting and no visible homopolymer formation at monomer concentrations of 1-10% (Figure 5). The maximum surface coverage observed is 45% (Figure 6). Significant grafting is only observed at monomer concentrations of ca. 20% which is also when the homopolymer starts to form a gel.

For all concentrations in MEK, degree of grafting and surface coverage as well as homopolymer precipitation increase. The fact that MEK seems to be a non-solvent for even the shorter MOEP oligomers appears to have a less adverse effect on the

grafting process than gel formation in methanol where viscosity effects probably affect radical diffusion to the ePTFE surface.

There are no obvious inhibition effects in methanol and initially monomer diffusion is likely to be similar in the two solvents as the viscosity of methanol and MEK are similar and radical diffusion to the PTFE reaction sites cannot be limited by homopolymer induced viscosity. Since chain transfer effects cannot explain the trends observed we suggest that reactive radiation formed solvent radicals in methanol have a higher affinity for termination than those formed in MEK. Termination of substrate radicals in methanol can explain why a maximum of 45% surface coverage is observed.

Substrate Swelling

The inert nature of PTFE is well known and its swelling behaviour in solvents and monomers is considered negligible since significant swelling does not occur in most organic solvents [30] and only minimal swelling in chlorinated or fluorinated solvents not containing hydrogen is reported. [31] However, among the various groups that have studied the effect of solvents on the radiation-induced grafting of styrene onto different fluorinated membranes including PTFE [25-29] several have proposed that even small swelling differences in specific solvents can have a significant outcome on the grafting.

Early in the irradiation process and at low monomer concentrations the influence of the solvent is such that the monomer can still freely access the PTFE surface. The changing nature of the surface - even with only a very low number of PMOEP grafted chains - is such that some swelling of the surface must be occurring and diffusion

inside the pores is enhanced. This might explain why grafting occurs to a large extent within the pores of the substrates grafted in methanol.

Although the *grafting front mechanism* first proposed by Chapiro *et al* [28] in their seminal grafting paper has been shown to also occur when grafting to PTFE and other fluoropolymers and it has been used to explain the fact that for PTFE even at low radiation dose rates grafting can occur not only on the surface but also throughout the substrate, the porous nature of our substrate precludes the testing of this hypothesis.

Conclusion

Our results clearly demonstrate that a judicious choice of solvent and grafting conditions makes it possible to produce a range of modified ePTFE materials. It appears that for our system in addition to some membrane swelling and the termination by solvent radicals in methanol, the non-solvent properties of MEK play a more important role than the individual chain transfer properties in determining not only the rate of grafting but also degree of surface grafting and its morphology. In a separate study, we are currently extending this study to a series of mixed solvent systems.

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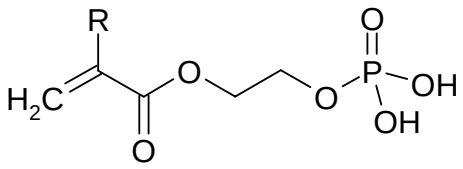
Figures

1. Chemical structures of the monomers methacryloyloxyethyl phosphate (MOEP) and monoacryloxyethyl phosphate (MAEP)
2. Scanning electron micrograph of untreated ePTFE membrane
3. XPS spectra of (a) untreated ePTFE, samples grafted at 4.6 kGy/h in (b) 30% MOEP in methanol, 29% surface coverage, (c) 10% MOEP in MEK, 76% surface coverage, (d) 40% MOEP in MEK, 100% surface coverage
4. ATR-FTIR spectra of (a) untreated ePTFE, samples grafted at 4.6 kGy/h in (b) 30% MOEP in methanol, 29% grafting yield, (c) 10% MOEP in MEK, 23% grafting yield, (d) 40% MOEP in MEK, 99% grafting yield
5. Grafting yield (%) vs. MOEP concentration(% w/v); ◇ solvent methanol, dose rate 4.6 kGy/h; ○ solvent methanol, dose rate 0.46 kGy/h; Δ solvent MEK, dose rate 4.6 kGy/h; □ solvent MEK, dose rate 0.46 kGy/h
6. Surface coverage (%) vs. MOEP concentration (% w/v); ◇ solvent methanol, dose rate 4.6 kGy/h; ○ solvent methanol, dose rate 0.46 kGy/h; Δ solvent MEK, dose rate 4.6 kGy/h; □ solvent MEK, dose rate 0.46 kGy/h
7. SEM images of ePTFE membranes modified by graft copolymerisation in (a) 30% MOEP in methanol (grafting yield 40%, surface coverage 33%); (b) high magnification of (a); (c) 5% MOEP in MEK (grafting yield 18%, surface coverage 99%); (d) 30% MOEP in MEK (grafting yield 65%, surface coverage 100%); homopolymer formed in (e) 30% MOEP in methanol; (f) 10% MOEP in MEK



R = H; Monoacryloxyethyl phosphate (MAEP)

R = CH_3; Methacryloyloxyethyl phosphate (MOEP)

Figure 1

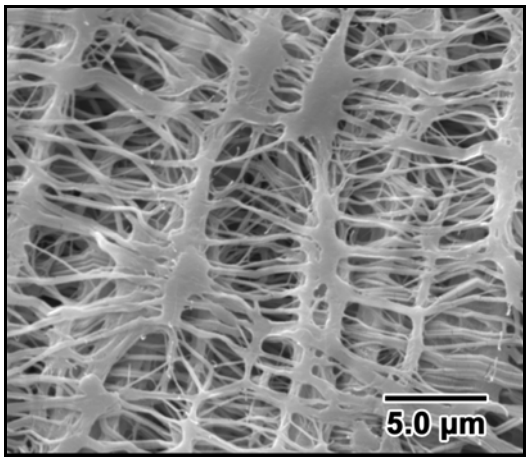
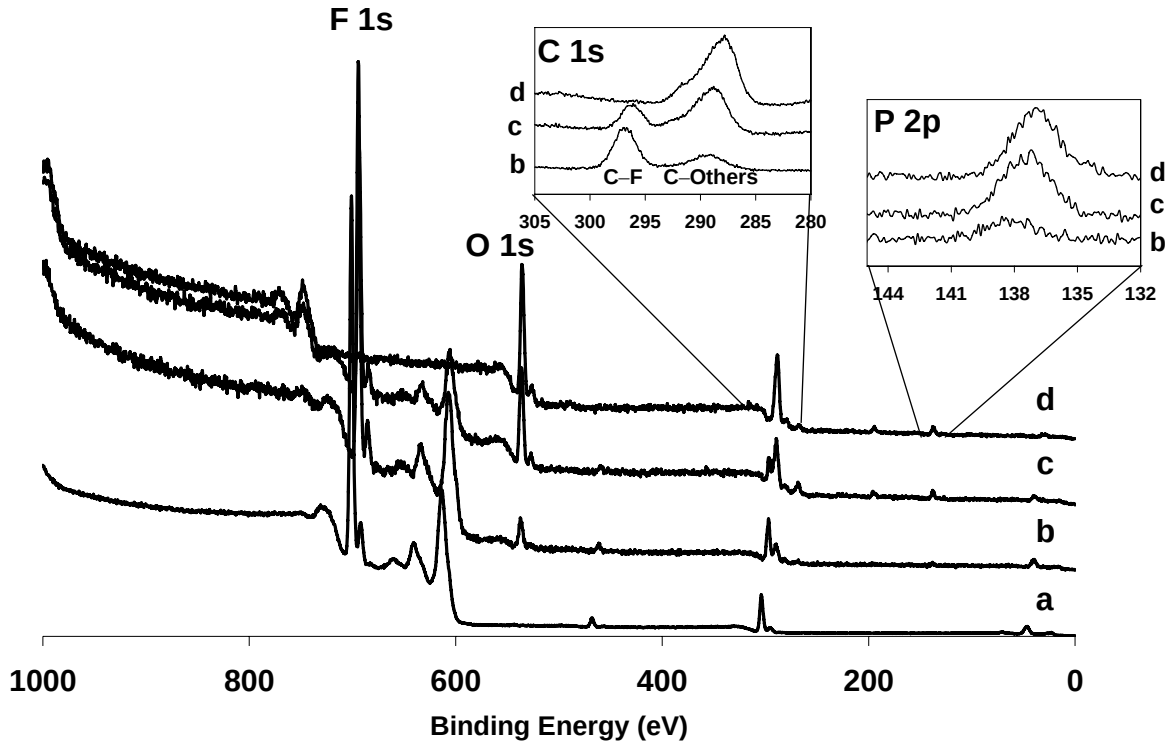


Figure 2


F 1s
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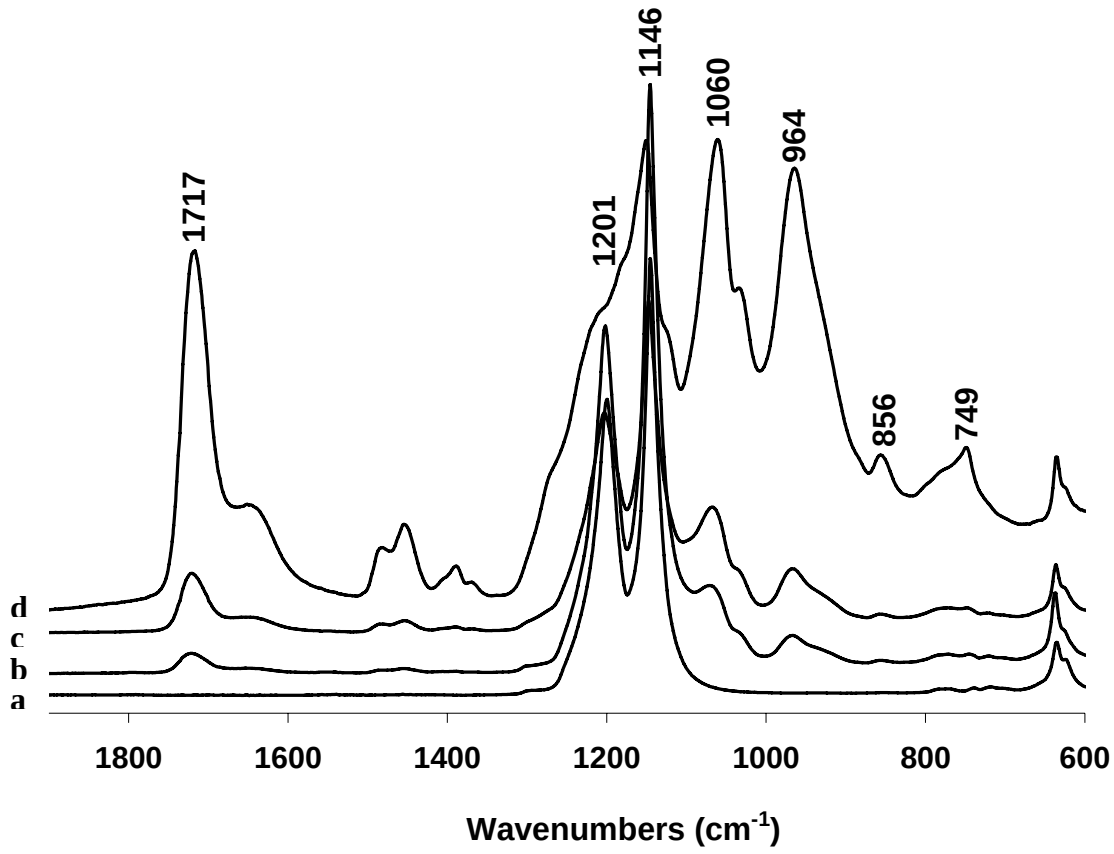
Binding Energy (eV)

Figure 3.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800
600
Wavenumbers (cm-1)

Figure 4

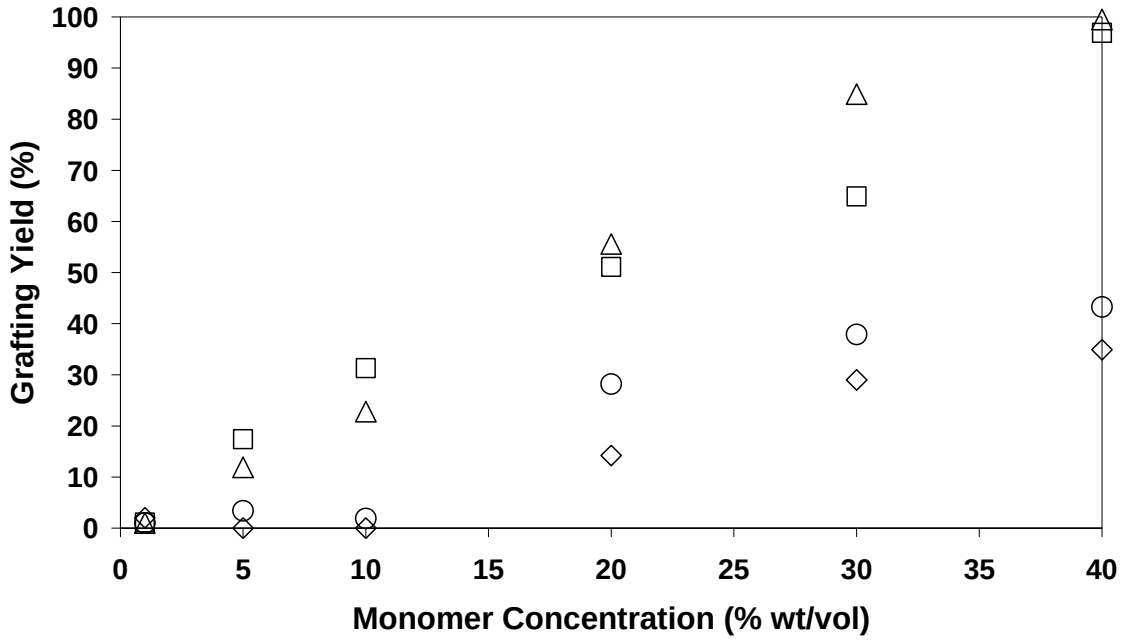
Grafting Yield (%)
100
90
80
70
60
50
40
30
20
10
0
0
5
10
15
20
25
30
35
40
Monomer Concentration (% wt/vol)

Figure 5.

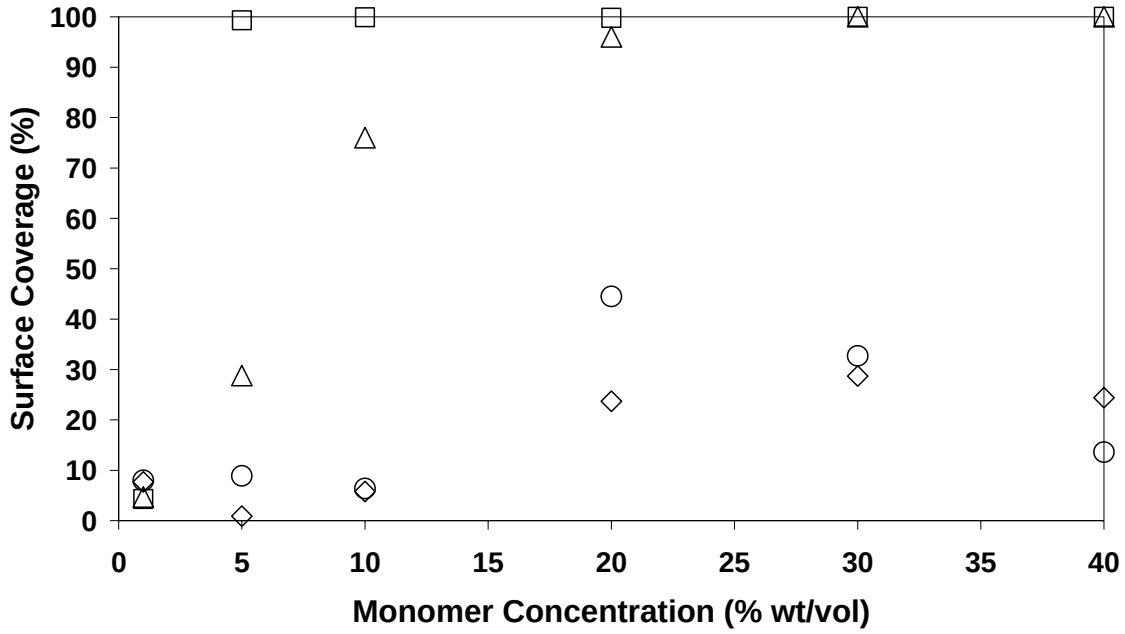
Surface Coverage (%)
100
90
80
70
60
50
40
30
20
10
0
0
5
10
15
20
25
30
35
40
Monomer Concentration (% wt/vol)

Figure 6.

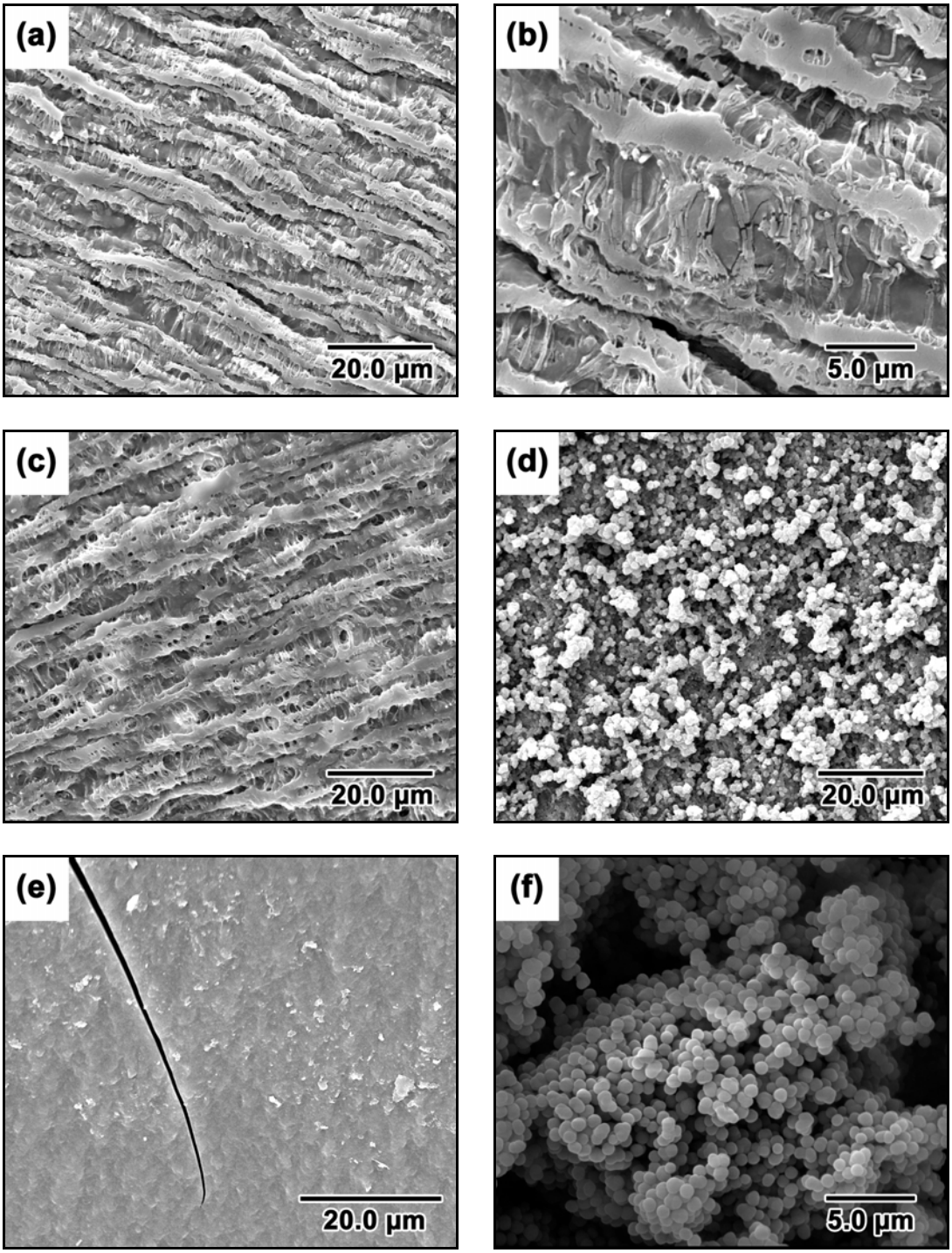

Figure 7

Published as:

Wentrup-Byrne, Edeline and Grøndahl, Lisbeth and Suzuki, Shuko (2005) Methacryloxyethyl phosphate-grafted expanded polytetrafluoroethylene membranes for biomedical applications.. *Polymer International* 54:pp. 1581-1588.