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Surface studies on acrylic bone cement

A. Bettencourt [a,*], A. Calado [a,b], J. Amaral [a,b], A. Alfaia [a,b], F.M. Vale [c], J. Monteiro [d], M.F. Montemor [e], M.G.S. Ferreira [e], M. Castro [a,f]

[a] *Faculdade de Farmácia, Universidade de Lisboa, Av. Prof. Gama Pinto, Lisbon 1649-003, Portugal*
[b] *Centro de Electroquímica e Cinética, Faculdade de Ciências, Universidade de Lisboa, Lisbon, Portugal*
[c] *Faculdade de Medicina de Lisboa, Universidade de Lisboa, Lisbon, Portugal*
[d] *Serviço de Ortopedia, Hospital de Santa Maria, Lisbon, Portugal*
[e] *Dep. Eng. Química, Instituto Superior Técnico, Universidade Técnica de Lisboa, Lisbon, Portugal*
[f] *Centro de Estudos de Ciências Farmacêuticas, Faculdade de Farmácia, Universidade de Lisboa, Lisbon, Portugal*

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Abstract

Poly(methyl methacrylate) (PMMA) is used to fill the gap between the prosthesis and the surrounding bone in cemented arthroplasties. Biocompatibility problems related to bone cement application limit the clinical success of these cemented arthroplasties. Being the cement surface in close connection with the living bone, it is reasonable to assume that surface properties such as, surface composition and surface energy, will play a role in the biomaterial performance. X-ray photoelectron spectroscopy (XPS) analysis and surface energy studies were carried out during 4 months, in order to assess a possible correlation between aging time and surface changes. The aging of PMMA, in a biological model fluid, strongly influences the composition and wettability of the cement surface. These changes may be explained through the hydrolysis of PMMA ester groups and the subsequent hydrogen bonding. Although our study does not exactly reproduce the in vivo environment surrounding a prosthesis, it suggests that the changes in the composition and wettability of the surface may modulate the host response towards the implant, thus contributing to its loosening.

Keywords: Poly(methyl methacrylate); Methyl methacrylate; Bone cement; Aging; Surface chemistry; Surface energy

1. Introduction

Poly(methyl methacrylate) (PMMA) is used to fill the gap between the prosthesis and the surrounding bone in cemented arthroplasties.

Despite its wide acceptance as a grouting material in orthopedic application, the cement is not without drawbacks. The main one is the role it has been postulated to play in the late aseptic loosening, and hence clinical life of the arthroplasty (Lewis, 1997).

The processes involved in aseptic loosening are not clearly understood (Hughes et al., 2003). Being the cement surface in close connection with the living bone it is reasonable to assume that the interaction between the biomaterial surface and bone will play a role in the biocompatibility problems related to bone cement application.

* Corresponding author. Tel.: +351-1-217946423; fax: +351-1-217946470.
E-mail address: asimao@ff.ul.pt (A. Bettencourt).

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In fact, the first step in the interaction between an implanted material and a host biological tissue consists of the formation of a proteinaceous layer adsorbed on to biomaterial surfaces that will influence cellular attachment and ultimately host response to biomaterial (Lopes et al., 1999). Therefore, surface properties—such as surface chemistry and surface energy—of the interface created when bone cement is placed within the body will influence the behaviour of both protein and cells towards the biomaterial and, therefore, its in vivo performance. On previous work, the authors (Bettencourt et al., 2002), found that the aging of PMMA for 1 month, in a biological model fluid (phosphate buffer saline solution: PBS) has changed its wettability behaviour.

In the present paper, we have extended the artificial aging of PMMA, in PBS, for a longer period of time (4 months), in order to assess a possible correlation between aging time and surface changes. The surface changes were evaluated by wettability studies and X-ray photoelectron spectroscopy (XPS) analysis. The wettability properties of bone cement were analysed through contact angle measurements and surface energy estimation. XPS analysis was carried out in order to obtain information on the changes of the chemical composition of the surface.

XPS is a surface analysis technique, the impact of which on materials characterisation has been two-fold: first, it is a non-destructive technique and analyses a material without any special sample preparation and, secondly, through its surface sensitivity XPS provides information on the atomic neighbour of a given atom existing on the surface. The technique is quantitative and detailed analysis of the ionisation peaks through peak fitting algorithms allows both identification and quantification of the different atomic valences (Briggs and Seah, 1990).

2. Materials and methods

2.1. Materials

CMW 1 Radiopaque, an orthopaedic bone cement, was obtained from DePuy CMW (DePuy International Ltd., England); PBS (without $CaCl_2$ and $MgCl_2$) was obtained from GibcoBRL (Life Technologies); 1,2-propanediol was reagent grade (Merck, Darmstadt, Germany); deionised water was obtained with the Milli Q-Water Purification System (Millipore).

2.2. Methods

2.2.1. Preparation of PMMA cylinders and plates

Polyethylene syringes were used for moulding bone cement in a cylinder form.

PMMA plates were prepared according to the procedure described in Bettencourt et al. (2002).

2.2.2. XPS analysis

The PMMA cylinders previously prepared were exposed to 25 ml of PBS (the medium was changed daily) for 4 months at 37 °C. The cylinders were subjected to XPS analysis every month.

The analytical experiments were made using a 310 F Microlab (VG Scientific) equipped with a non-monochromated Mg (K_α) X-ray source. Spectra were taken using a 15-keV source. Spectra were run in constant analyser energy mode (CAE = 30 eV); the energetic resolution being about 0.9 eV. The calibration of the analyser was made according to the following peak energies: Cu LMM at 918.62 eV, Ag MNN at 357.80 eV and Au NVV at 70.1 eV.

The XPS spectra are referred to C 1s at 285 eV. An error of 0.1 eV is assumed in peak positions.

2.2.3. Contact angle and surface energy determinations

PMMA plates were exposed to 25 ml of PBS and incubated for 4 months at 37 °C (the medium was changed daily). The plates were subjected to contact angle analysis and surface energy estimation every 2 weeks.

Contact angle measurements were performed with the aid of a Kruss K121 tensiometer (Kruss GMBH, Hamburg, Germany) using the Wilhelmy Plate method, by immersing the plates 4 mm into the test liquids (water and 1,2-propanediol) at a speed of 20 $\mu m\,s^{-1}$. Advancing contact angles were used for surface energy estimation. Three replicates were carried out for each plate (Bettencourt et al., 2002).

Equations for surface energy estimation were solved using the equation handling KRUSS-software program: contact angle measuring system K121 (version 2.049).

3. Results and discussion

Our study does not take into account all the complexity of the biological environment but it aims to decompose the overall problem into elementary steps. We have incubated PMMA in a biological model fluid under physiological pH and temperature conditions.

In the selected experimental conditions, the relation between aging time and surface changes was analysed through XPS analysis, contact angle and surface energy determinations.

3.1. XPS analysis

The modifications induced on the surface composition by aging were assessed by XPS. We began XPS studies with the original PMMA samples, before being submitted to incubation. For these samples (Fig. 1a) four peaks are clearly observed: the highest peak observed at 285 eV represents C–H (Fig. 2; carbon no. 1), the peak at 285.6 eV represents C–C=O (Fig. 2; carbon no. 2), the peak at 286.7 eV is characteristic of C–O–C (Fig. 2; carbon no. 3), and the one at higher binding energies (288.7 eV) corresponds to C=O (Fig. 2; carbon no. 4). This spectra is very close to that expected for PMMA (Briggs and Beamson, 1992), indicating that rearrangements of PMMA surface groups due to XPS procedure are negligible. On the contrary,

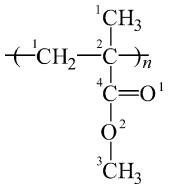

Fig. 2. Chemical structure of the repeating unit of PMMA polymer.

the aging time induces strong changes in the polymer surface (Fig. 1b). In Fig. 3, that represents the evolution of atomic % of each C 1s contribution with aging time, a strong decrease of C=O and –C–O–C can

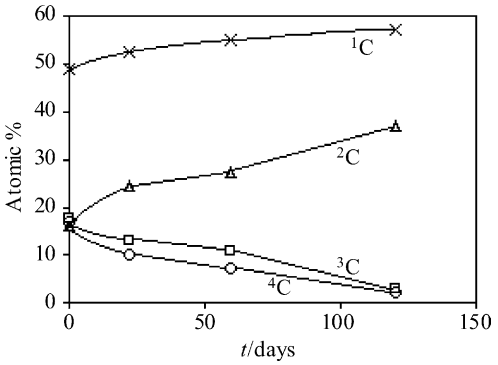

Fig. 3. Fitting results for the C 1s ionisation spectra after different aging times.

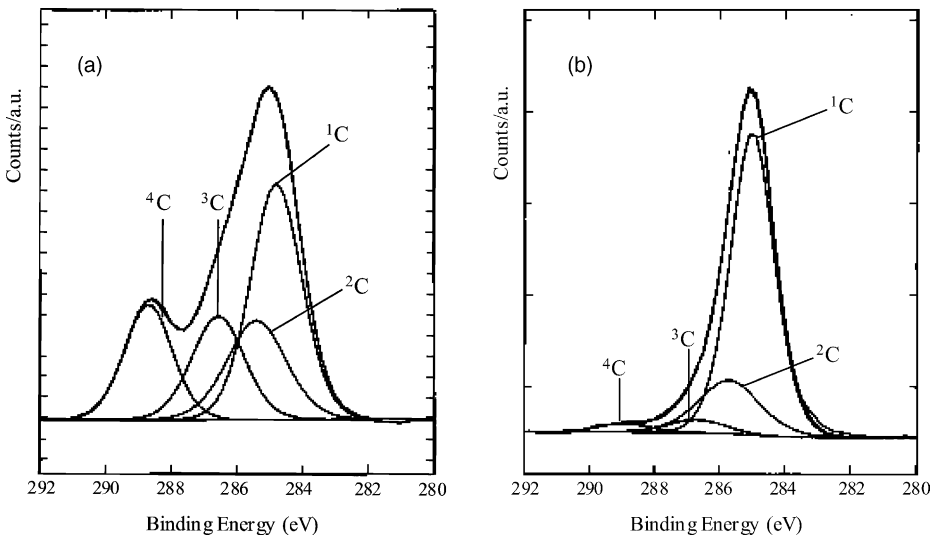

Fig. 1. XPS spectra for C 1s ionisation at $t = 0$ month (a) and after 4 months of aging (b).

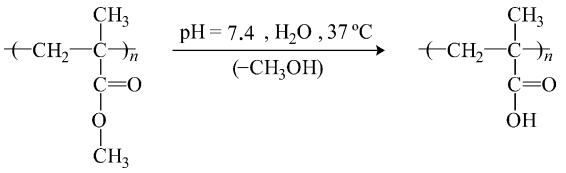

Fig. 4. Schematic representation of hydrolysis.

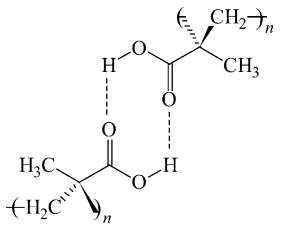

Fig. 5. Schematic representation of hydrogen bonding.

be seen, whereas an increase on the type of –C–C=O functional groups is observed. The amounts of C–H remain practically constant (Fig. 3) suggesting that the saturated chains of the polymer remain unchanged.

The changes observed on C=O and C–O–C account for important changes on the ester groups of the polymer. These changes can be explained attending to the aging process. Since the polymer is exposed to a solution of pH 7.4 ($t = 37\,^{\circ}C$) it may suffer hydrolysis, induced by water (Euranto, 1969). This hydrolysis will affect the ester group, according to the scheme shown in Fig. 4. A similar in vivo mechanism of degradation has already been proposed by Coury et al. (1996), but in acidic pH conditions combined with hydrolysing enzymes.

The proposed mechanism can thus explain the decrease of C–O–C, characteristic of the ester group. However, a decrease on the C=O was not expected, since this functional group, after the hydrolysis, remains in the polymer chain. Moreover, there is also an increase on the C–C=O functional groups. These facts suggest that a new type of bond is formed, superimposing the initial C–C=O.

This new type of bonds can be correlated with the formation of hydrogen bonds between the hydroxyl and carbonyl groups of adjacent PMMA chains (Fig. 5).

The effect is clearly confirmed through the observation of the O 1s ionisation spectra (Fig. 6).

The original PMMA (Fig. 6a) shows two contributions from oxygen: one at 531.9 eV expected for O=C (Fig. 2, oxygen no. 1) and another one at 533.4 eV accounting for O–C (Fig. 2, oxygen no. 2). After 4 months (Fig. 6b) of aging the spectra is strongly

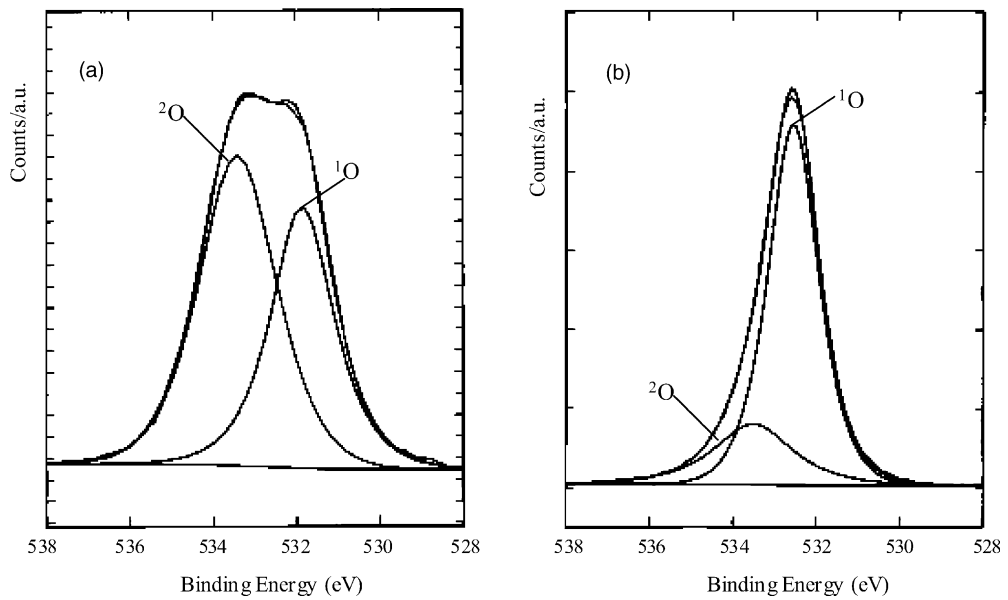

Fig. 6. XPS spectra for O 1s ionisation at $t = 0$ month (a) and after 4 months of aging (b).

different. The intensity of the peak at 533.4 eV decreases, being in accordance with the behaviour of the C–O–C evolution observed in the C 1s spectra. However, the O 1s peak at lower binding energies shifts to values around 532.6 eV, thus corresponding to a new type of oxygen. The binding energy of this new bound is more likely for O–H groups (Briggs and Beamson, 1992).

The hydrolysis and hydrogen bonding can thus explain the changes observed in the C 1s and O 1s ionisation spectra. The decrease of C–O–C can be explained by the formation of C–OH, which is in accordance with the decrease of O–C observed in O 1s spectra. The decrease of C–O in C 1s spectra may be explained due to its involvement in hydrogen bonding that is clearly identified in O 1s ionisation spectra.

3.2. Contact angle and surface energy determinations

Using the experimental values of contact angles measured with the reference liquids (water and 1,2-propanediol), it was possible to estimate the surface energy (γ) of PMMA plates and its dispersive (γ^{d}) and polar components (γ^{p}) based on the harmonic mean method proposed by Wu (1971). For further details see Bettencourt et al. (2002).

The time evolution of the dispersive and polar components of PMMA surface energy is presented in Fig. 7. These results are in accordance with our previous studies (Bettencourt et al., 2002), showing that in particular it is the polar component that changes with time. The increase in the polar component will correspond to an increase in hydrophilicity of the cement surface. These findings are in accordance with the proposed mechanism as ester groups will be replaced during aging by the more polar carboxylic groups.

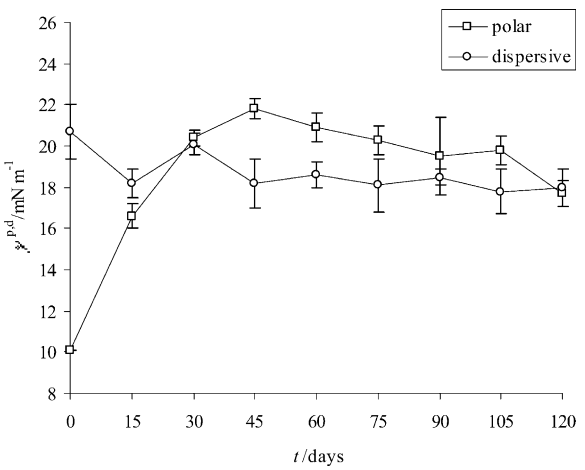

Fig. 7. Experimental polar ($\gamma^{p} \pm$ S.D.) and dispersive ($\gamma^{d} \pm$ S.D.) surface energy values of PMMA plates.

The way in which wettability influences biological response is controversial! In general, hydrophilic surfaces display a better affinity with cells and there are studies (Redey et al., 2000) suggesting that the enhancement of the polar component of the biomaterial may improve osteoblastic (bone forming cells) attachment. However, other studies (Redey et al., 1999; Zanchetta and Guezennec, 2001) suggest that osteoclast (bone resorbing cells) adhesion is enhanced by the polar component and that osteoblast due to their hydrophobic character specifically attaches onto hydrophobic surfaces.

XPS and wettability studies show that PMMA aging increases bone cement hydrophilicity. In our opinion, this fact may influence the cellular events taking place at the bone/biomaterial interface, contributing to the aseptic loosening of the implant.

4. Conclusions

The artificial aging of PMMA, strongly influences the composition and wettability of acrylic cement surface.

The XPS analysis suggests the formation of new bonds and the degradation of the initial ones, mainly those involving the ester group. The new bonds are clearly identified in the O 1s spectra, which show a response characteristic of the presence of OH groups. Wettability studies showed a significant increase in the surface energy polar component, corresponding to an aging increase of hydrophylicity.

The changes in the composition and wettability of the surface may be explained through the hydrolysis of PMMA ester groups and the subsequent formation of hydrogen bonds between the hydroxyl and the carbonyl groups of adjacent PMMA chains.

Although our study does not exactly reproduce the in vivo environment surrounding a prosthesis, it is a contribution for the understanding of bone cement surface changes that will modulate the host response towards the implant.

Acknowledgements

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