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Air Plasma Processing of Poly(methyl methacrylate) Micro-beads: Surface Characterisations

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Abstract

This paper reports the surface processing of poly(methyl methacrylate) (PMMA) micro-beads by using a rotary air plasma reactor, and its effects on surface properties. The surface properties, including surface wettability, surface chemistry and textures of the PMMA beads, were characterized. It was observed that the air plasma processing can improve the surface wettability of the PMMA microbeads significantly. A 15 minutes plasma processing can reduce the surface water contact angle of PMMA beads to about 50° from its original value of 80.3° . This was accompanied by about 8% increase in surface oxygen concentration as confirmed by XPS analysis. The optical profilometry examination revealed the air plasma processing resulted in a rougher surface that has a “delicate” surface texture. It is concluded that the surface chemistry and texture, induced by air plasma processing, co-contributed to the surface wettability improvement of PMMA micro-beads.

Keywords: air plasma processing; poly(methyl methacrylate) beads; Wettability; surface texture.

1. Introduction

The synthetic polymeric microbeads such as poly(methyl methacrylate) (PMMA), polylactic acid (PLA), polyglycolic acid (PGA) and polystyrene (PS) beads, have been widely used in the field of regenerative medicine to facilitate growth of biological cells [1, 2] and for drug delivery [3-6]. In these applications, the surface properties such as chemistry and wettability need to be optimized in order to

control the protein adsorptions and biological interactions [7]. Most of biopolymer surfaces are hydrophobic nature, these are not necessarily appropriate substrates for protein adsorption and cell attachment [1, 2]. Usually, surface modifications are required before these synthetic polymer microbeads can be successfully used in regenerative medicine [8, 9].

The intrinsic interactions between biological environment and biomaterials mainly depend on surface properties such as chemical composition, surface texture and surface wettability of biomaterials [8, 10]. The surface properties of biomedical devices can be tailored to enhance their service functionality and performances through various surface processing approaches [11-14]. There are many methods for biopolymer surface modification such as plasma enhanced chemical vapour deposition (PECVD) [12, 15], UV induced ozone treatment, and wet chemical treatments [16-18]. Plasma modification techniques have advantages over other approaches in that it has the ability to uniformly modify the surface without affecting the bulk properties [12]. Plasma processing has been widely used in the field of tissue engineering and regenerative medicine for the pre-treatment of bio-polymers to improve their cellular performance [12, 19]. Previous studies by the author [20] have revealed that the surface properties such as surface chemistry and surface topography can be modified by different types of plasma processing techniques [14]. Even the hydrophobic PTFE surfaces can be converted to a more hydrophilic condition by plasma processing [19, 21, 22]. The functional groups introduced to the surfaces can be used for protein immobilization and control of cell attachment to the surfaces [7, 23-25]. Apart from the change in surface chemistry, researches have reported that changes in surface

texture to biomaterial surfaces can also be induced by plasma processing [26, 27]. It is known that apart from surface activation of the polymer, exposure to plasma could lead to the degradation of polymer surface, depending on the duration of exposure used [26].

Poly(methyl methacrylate) is less hydrophobic than polystyrene and is reported to have reduced nonspecific protein and peptide binding [28]. PMMA micropsheres have good biocompatibility which allows the particles to be used in many medical and biochemical applications. Although many studies have been performed to modify flat PMMA surfaces using various plasma systems, few studies report surface modification of PMMA powder surface [14, 29, 30]. This paper reports a study of the effect of air plasma processing on PMMA microbeads in a rotating fluidized bed air plasma reactor, particularly investigates into the effect of air plasma have on the surface wettability and, changes in surface chemistry and textures induced. The surface chemical composition of processed PMMA beads were characterized using X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS). The surface wettability was evaluated by means of “floating” water contact angle measurements, and change in surface texture was examined by optical profilometry. The effect of processing time on surface chemistry and surface wettability have been discussed.

2. Experimental details

2.1 Surface processing of poly(methyl methacrylate) microbeads

The material used in this study was high quality clear poly(methyl methacrylate) (PMMA) microbeads (un-pigmented) (Cospheric LLC, USA) which have a density of 1.19 g/ml, and particle sizes ranging from 100 ~ 150 μm .

The surface processing of the PMMA beads was carried out using a lab-scale rotary plasma reactor.

The radio frequency (RF) power at 13.56 MHz was coupled to the quartz chamber (20 mm diameter and 50 mm long) via a manual impedance matching network using an externally wound copper coil. A

Pirani gauge and digital controller monitored pressures. A base pressure of typically 1×10^{-3} mbar was achieved using a rotary vacuum pump fitted with a liquid nitrogen (LN_2) cooled trap. Dry air was

introduced into the plasma reactor through a fine control leak valve. An RF power of 50 W and a constant air flow rate of $20 \text{ cm}^3 \text{ min}^{-1}$ were used in all experiments. A rotary drum with open ends,

driven by a speed adjustable motor, was placed in the quartz plasma reactor. The PMMA beads are feed into this rotary drum and are fluidized by the action of agitating blade and rotation of the chamber.

In the present work, all the treatments described were carried out using parameters of 60 rpm for the rotation of the drum. After exposure to the air plasma, the samples were washed with double distilled water in an ultrasonic bath, dried in flow of nitrogen for 30 minutes before characterisations.

2.2 Surface chemistry examinations of PMMA beads

Surface chemistry of the PMMA micro-beads was examined by an x-ray photoelectron spectrometer (Kratos Analytical Ltd, UK) as previously reported [31]. A low energy electron flood gun was used to compensate for surface charging. The carbon C1s signal from each specimen was corrected for surface charging to the hydrocarbon signal at 285.0 eV. For analysis, the specimens were transferred into the XPS analysis chamber. The chamber then pumped down to 1×10^{-8} torr before analysis. The secondary ion mass spectra of PMMA beads before and after air plasma processing were determined by using a static secondary ion mass spectroscopy (SIMS) system (MC300 Mk2, Millbrook Instrument, UK). The obtained mass spectra were normalized against the most abundant species, then subtracting the spectrum of pristine PMMA from those spectra of treated samples to obtain the difference spectra.

2.3 Surface wettability analysis

The “floating” water contact angle was measured using a dynamic contact angle analyser (First Ten Ångströms, USA) in a “floating method” as described elsewhere [9]. In this method, the PMMA micro-beads were placed on the surface of water contained in a glass vessel which had been pre-cleaned by deionised water. Images of floating micro-beads were captured automatically by the camera. The captured images were analyzed to obtain water contact angle of PMMA beads [31]. At least six microbeads were randomly chosen for the measurements from each treated group and the control group, from which average values and standard deviations were calculated. Typical wetting behaviour of

pristine PMMA microbead and air plasma processed microbead were shown in **Figure 1** (a) and (b), respectively.

2.4 Surface topography and texture examinations

Commercially available PMMA film (50 μm thick) (Goodfellow Cambridge Ltd., UK) was used for the investigation of the effect of air plasma on the surface topography and texture changes. The PMMA film was cut into 2.0 x 4.0 cm, placed on a glass slide and exposure to plasma under the same operational condition for 15 minutes. The processed specimens were water washed in ultrasonic bath immediately after exposure, dried in flow nitrogen for 30 minutes. The surface of PMMA films, before and after air plasma processing, were examined by an optical profilometry system (WYKO NT800, UK). The surface roughness including arithmetic mean of the surface roughness (R_a), maximum height of the profile (R_t) and the root mean square roughness (R_q) were calculated.

3. Results and discussions

3.1 Surface composition of the PMMA micro-beads

When exposures to the air plasma, the reactive species in the plasma react with the surface of the PMMA beads, resulted in the changes of the surface chemistry. The nature of the oxidized components formed on PMMA bead surface was analyzed by XPS. The surface composition of the PMMA beads was determined from the relative intensities of the XPS carbon 1s ($\text{C}1s$) and oxygen 1s ($\text{O}1s$) peaks obtained from the survey scan spectra, and C/O were calculated. The XPS survey scan spectra of the

PMMA microbeads before and after air plasma processing are shown in Figure 2(a). It was observed that air plasma processing resulted in an increase in surface oxygen concentration, about 5% and 7.5% (mass%) increase (prior to washing) were revealed for 5 and 15 minutes processed samples, respectively. The washing procedure reduced the surface oxygen concentration substantially by removing the low molecular weight scission products resulting from the plasma processing, leaving surface oxygen concentration of 34% and 37% for 5 and 15 minutes processed samples, respectively. This corresponds to a 10% and 8% decrease in surface oxygen for 5 and 15 minutes processed samples respectively, as a result of washing (Table 1).

Figure 2(b) shows the variation of C/O ratio with the air plasma processing time. It demonstrates C/O ratio decrease with the air plasma processing time. It was observed that pristine PMMA beads has a C/O ratio of 2.06 (mass%), this was reduced drastically to 1.64 after exposure to plasma for 2 minutes. Further exposure leading to the C/O ratio decrease gradually and reaches 1.48 after 15 minutes plasma processing.

The change in surface chemistry resulting from the air plasma processing has been studied by analysis of the carbon 1s and oxygen 1s peaks. A typical XPS C1s and O1s spectra for pristine and air plasma processed PMMA beads are shown in Figure 3(a) and (b), respectively. It was observed that the C1s envelope of the specimens can be resolved into four peaks. The C1s peak at 285 eV corresponding to CH_x - and C-C units of the PMMA. The C1s peak at 285.7 eV is due to the quarternary carbon units of

the PMMA; the third C1s peak at 286.8 eV is due to -C-O- species, while C1s peak at 289.1 eV can be assigned to the carboxylic group (O-C=O). Broadening and a large degree of overlap of the peak areas observed in plasma processed PMMA bead samples in Figure 3(a) were due to the introduction of oxygen chemical functionalities to the surfaces. The O1s spectra can be resolved into two main peaks. The component at 532.8 eV can be assigned to carbonyl group (C=O), and the O1s peak at 533.8 eV is due to the methyl ester group (C-O-CH₃).

The variations of functional groups on the surface of PMMA beads before and after air plasma processing are listed in **Table 2**. As reported, the processed PMMA beads show loss of alkyl components (C_xH_y) significantly, with an increase in C-CO, C-O-CO and C-C=O carbon groups. The longer the processing time, the lower the proportion of C1s component 1 and 3, and the higher the concentration of component 4 is on the surfaces. This variation of the surface functional groups demonstrated the C-H bond in methyl group was cleaved by air plasma to produce activated radicals. The incorporation of oxygen to surface of PMMA results in the formation of oxygen-containing components groups such as alcohols group (C-O), ethers (C-O-C), ketones (C-CO-C), aldehydes (C-CHO), esters (C-CO-O-C) and carboxyl groups. The proportion of carbonyl groups continues to rise throughout the treatment times. This was confirmed by the evidence of sustained increase in O1s component 1 (carbonyl oxygen) with the air plasma processing time (Figure 3(b)). Loss of oxygen due to washing occurs, by removal of C-OR, C=O and O-C=O containing groups i.e. those which require

the most polymer chain scission. The loss of oxygen-containing groups upon washing explained the recovery of surface water contact angle, as reported in section 3.2.

The surface chemistry of PMMA beads before and after air plasma processing was further investigated by using static SIMS. The obtained spectra were normalised against the most abundant fragments, and the differential spectra were obtained by subtracting normalised spectrum of pristine PMMA beads. Figure 4 shows the positive and negative ion mass spectra of pristine PMMA beads and, differential spectra for 15 minutes air plasma processed PMMA beads. The positive spectrum of pristine PMMA (Figure 4(a)) reveals typical intense carbon hydrogen mass fragments such as C_2H_n^+ (27 amu) and C_3H_n^+ (41 amu). Oxygen-containing hydrocarbon fragments centred 57 amu ($\text{C}_3\text{H}_5\text{O}^+$), 59 amu (COOCH_3^+), 69 amu ($\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}\equiv\text{O}^+$) and 73 amu ($\text{CH}_2\text{COOCH}_3^+$) were also evidenced.

After air plasma exposure, in addition to the mass clusters centred at 41 amu and 57 amu, new clusters peaked at 44 amu ($\text{CO}_2^+ / \text{C}_3\text{H}_8^+ / \text{CH}_2=\text{CH}(\text{OH})^+$), 46 amu (CH_2O_2^+) and 74 amu ($\text{CH}_2=\text{C}(\text{OH})\text{OCH}_3^+$) were also identified from the differential spectra of air plasma processed specimen (PMMA-15 in Figure 4(a)). The presence of mass fragments CH_3^+ (15 amu), $\text{CO}^+ / \text{C}_2\text{H}_4^+$ (28 amu) and $\text{CO}_2^+ / \text{C}_3\text{H}_8^+ / \text{CH}_2=\text{CH}(\text{OH})^+$ (at 44 amu) in the differential spectra indicates the formation of oxygenated mass fragments as a consequence of air plasma exposure. This is in agreement with XPS examination that demonstrated the increasing of oxygen content and oxygen-containing functional groups as a result of the incorporation of oxygen to the PMMA bead surface, as reported in Figure 2 & Figure 3. Close

inspection of the positive mass spectra reveals significant H_2O^+ ion appears at 18 m/z on 15 minutes air plasma processed PMMA surface. However, this H_2O^+ ion peak reduced to original level after water wash. Similar variation was also revealed for CH^{3+} ion which appears at 15 m/z. This observation supports the assertion that water vapour was physically adsorbed to loosely bounded layer created by C-C chain scission, and this loosely bounded layer was easily be removed by washing.

The negative ion mass spectrum of pristine PMMA beads is shown in Figure 4(b). The spectrum shows typical mass fragments C^- (12 amu), CH^- (13 amu), CH_2^- (14 amu), O^- (16 amu), OH^- (17 amu), C_2^- (24 amu), C_2H^- (25 amu), CN^- (26 amu) and CH_3O^- (31 amu). It was demonstrated from the differential spectra of 15 minutes air plasma processed PMMA bead that mass fragments at 16 amu (O^-) and at 31 amu (CH_3O^-) were evidenced. This confirms the air plasma surface processing resulted in the incorporation of oxygen to the surface of PMMA beads. The OH^- ion appears at 17 amu supports the assertion that some reactive sites created by air plasma were terminated by hydrolysis by adsorbing water vapour upon exposure to air environment.

If only consider the chemical structure of the PMMA, an increased amount of C1s component 3 would be expected in associate with the increasing of O1s component 2. However, it was noted in this study that the C1s component 3 was not increase with the increase of O1s component 2 (Table 2). On the contrary, a slight reduced amount of C1s component 3 was observed on plasma processed PMMA surfaces. This discrepancy could be attributed to the physical absorbed oxygen and water vapour on

PMMA surface, as revealed by SIMS examination. The physically adsorbed oxygen is different from that oxygen in the C1s component 3. In this study, we are unable to differentiate the amount of physically adsorbed oxygen from chemically bounded oxygen in oxygen-containing functional groups due to the limitation of our XPS technique. While the physically adsorbed oxygen will be removed, together with polymer debris on PMMA surface upon water wash. The water wash may have less effect on the oxygen that bounded in the functional groups, thus the amount of C1s component 4 is not reduced accompanying the decrease of oxygen component.

3.2. Surface wettability changes as a result of air plasma processing

The surface wettability of the PMMA micro-beads was evaluated before and after air plasma processing in terms of surface water contact angle. To determine the effect of air plasma processing on the surface wettability, the water contact angles of PMMA beads were measured immediately without wash. The variation of surface water contact angle as a function of air plasma processing time is shown in Figure 5. It was observed that the surface water contact angle on PMMA beads is sensitive to the air plasma processing. The processing of PMMA microbeads resulted in decrease in surface water contact angle, as measured by “floating” method. The longer the processing time, the lower the water contact angle observed. The pristine PMMA bead has a contact angle of 80.3°, this was reduced to 72° after only 1 minute exposure. It is further reduced to about 50° after 15 minutes air plasma processing, as determined by “floating” method. The decrease in water contact angle after air plasma processing is an indication of increase in the surface energy as a result of surface oxidization by air plasma.

Detailed analysis of the relationship between water contact angle and air plasma processing time identified two stages. The initial stage was characterized by rapid decrease of contact angle upon exposure to the air plasma. This primary decrease stage continued for about four minutes, water contact angle decreased to 62° from its initial 80.3° for pristine PMMA beads. Beyond that the contact angle decrease gradually with the processing time and reaches 50° after 15 minutes processing.

Previous studies on PMMA surface modification by plasma techniques have observed the recovery of water contact angle after ultrasonic water wash, and attributed this to the removal of loosely bound low molecular weight polymer products produced in the plasma treatment process [26, 29]. The presence of these loosely bound polymer products may affect the biocompatibility of oxidised polymer materials by causing changes to ionic constitution of cell culture medium. Therefore, the removal of low molecular weight oxidised material (LMWOM) is an important process in the surface modification of biopolymers for biomedical applications, and to ensures consistency in the surfaces used for future studies. Ultrasonic wash in water for 10 minutes was performed to the PMMA beads to determine the effect of washing on the surface wettability. The water contact angle of PMMA beads after ultrasonic wash is shown in Figure 5. It can be seen that divergence of the water washed and unwashed curves. The washing procedure led to the recovery of surface water contact angle, by approximately 5° compared to the unwashed specimens at each processing time. This indicates that the ultrasonic water washing removes some components of the LMWOM from the PMMA beads, as reported in section 3.1.

3.3 Surface topography and textures

Previous study [30] on PMMA surface processing using dielectric barrier discharge (DBD) plasma technique revealed the activated species in plasma environment react with the PMMA surface and produce radicals on the surface layer of the PMMA. The radicals eventually cause the PMMA surface layer to be oxidized. XPS analysis on air plasma processed PMMA beads in this study confirmed the surface of PMMA micro-beads was functionally oxidized (Figure 2). The introduction of oxygen to the PMMA bead surface resulted in an increased concentration of oxygen-containing functional groups, especially carboxyl group. This resulted in the decrease of water contact angle, improve the surface wettability significantly.

Surface roughness, often shortened to roughness, is a measure of the texture of a surface. It is quantified by the vertical deviations of a real surface from its ideal form. The etching of the surface by plasma altered the surface texture, thus the surface roughness. The optical profilometry examinations revealed that pristine PMMA has a maximum height of the profile (R_t) of 1.7 μm , this increased to 2.7 μm after 15 minutes air plasma processing (Figure 6). As a result of plasma etching, PMMA surface became “rougher” (Figure 6). The pristine PMMA surface has an arithmetical mean roughness (R_a) of 58.4 nm, this increased to 84.9 nm for air plasma processed surface. This represents about 45% increase in R_a . Correspondingly, the root mean square roughness (R_q) also increased to 114.4 nm from its original value of 78 nm.

The power spectral density (PSD) is related to the average amplitude of sine waves of reciprocal wavelength required to reconstruct by summation of the surface height profile, and was expressed as function of spatial frequencies of the measured surface profile. The PSD analysis revealed the air-plasma treated PMMA surface has a higher power spectral density than that of pristine PMMA surface, as demonstrated in Figure 7. The increase of surface roughness and power spectral density of PMMA surface after air-plasma processing indicate the processed PMMA surface has a higher specific surface area. While upon washing, the PSD decreases as a result of removal of the low molecular weight oxidised debris from the PMMA surface to reveal the authentic plasma processed surface texture. Although PSD values for authentic plasma processed surface are lower than unwashed surface, they remain higher than that of pristine PMMA surface in the range of $1 - 250 \text{ mm}^{-1}$, as observed in Figure 7. This indicates plasma processing lead to a more “delicate” PMMA surface texture.

As reported previously, the plasma etching leading to the surface roughing. Figure 6 shows the optical profilometer examination of the PMMA surface. It was observed that the surface roughness increased about 45% after 15 minutes air plasma processing. According to Wenzel model on a rough surface, for a hydrophilic surface (as in the case of plasma processed PMMA surface) the rough surface has a lower water contact angle than smooth surface [24]. In other words, surface roughness has an influence on the apparent water contact angle. A rougher hydrophilic surface will exhibit a lower apparent water contact angle than smooth surface. The rougher the surface, the greater contribution of the surface

texture to the decrease in surface water contact angles [20]. Therefore, it could be assumed that apart from surface chemistry, the change in surface roughness induced by air plasma also contributed to the reduction of water contact angle, as reported in section 3.2. However, although the changes in surface chemistry and surface topography have been examined in this study, it is not possible to decouple the contribution of change in surface texture from that of surface chemistry. In considering the plasma processing introduced significant amount of oxygen-containing functional groups which have a higher surface free energy [9, 27] to the PMMA bead surface, it is reasonable to assume the changes in surface chemistry contributed more to the improvement in surface wettability.

4. Conclusions

In this study, the surface of PMMA micro-beads was processed by using a controllable rotary air plasma reactor. The surface wettability, surface chemical compositions and surface textures of the PMMA micro-beads before and after surface processing have been characterised by means of “floating” particle water contact angle measurement, XPS and SIMS, and optical profilometry, respectively. The study demonstrates that rotary air plasma is an appropriate technique for the processing of PMMA micro-beads. The surface wettability measurements revealed that fast surface activation of PMMA surfaces can be achieved, only a few minutes exposure to plasma are required to changing the surface wettability of the PMMA micro-beads. The measured floating water contact angle decreased to about 50° from an original value of 80.3° after 15 minutes air plasma processing. This was accompanied by significant increase in surface oxygen concentration, about 7.5% (mass%) higher

was measured in the processed specimen. Correlation between chemical analysis, surface texture analysis and contact angle measurements of the pre- and post-treated surfaces indicates the improved wettability of the PMMA micro-beads could be attributed most to surface oxidation; whileas surface roughing also contributed to the wettability improvement to some degree. However, decoupling the effect of surface chemistry from surface texture is unrealistic in this study. This observation is in agreement with the previous DBD plasma processing of PMMA films [14].

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Captions for Figures:

Figure 1: Water contact angles measurements by floating method. (a): hydrophobic pristine PMMA bead and (b) hydrophilic air plasma processed PMMA bead floating in water, respectively.

Figure 2: XPS spectra for PMMA beads before and after air plasma processing. (a) survey scan and (b) variation of C/O ration with air plasma processing time.

Figure 3: XPS narrow scan spectra for pristine and air plasma processed PMMA beads. (a) C1s spectra and (b) O1s spectra

Figure 4: Normalized secondary ion mass spectra of pristine PMMA beads and difference spectra of 15 minutes plasma processed samples. (a) positive spectra and (b) negative spectra.

Figure 5: Variation of surface water contact angle of PMMA beads with air plasma processing time

Figure 6: Optical profilometer examinations of pristine PMMA surface (a) and air plasma 15 minutes processed PMMA surface ($R_a=58.37\text{nm}$; $R_q=78.31\text{nm}$ and $R_t=1.70\mu\text{m}$.) (b). The etching of the air plasma resulted in “rough” PMMA surface compared to the pristine specimen ($R_a=84.91\text{nm}$; $R_q=114.42\text{nm}$ and $R_t=2.71\mu\text{m}$.). Image size: $475 \times 635 \mu\text{m}$.

Figure 7: Power spectral density (PSD) versus spatial frequency for pristine and 15 minutes air plasma processed PMMA surfaces.

Table 1: Surface chemical composition of PMMA powder as determined by XPS analysis

Material	atom%		mass%	
	C1s	O1s	C1s	O1s
PMMA00	73.26	26.74	67.2	32.7
PMMA-5	68.68	31.32	62.1	37.8
PMMA15	66.4	33.6	59.7	40.2
PMMA-5-Wash	72.09	27.95	65.9	34
PMMA-15-Wash	69.38	30.62	62.9	37

Table 2: XPS derived concentration of molecular functionalities for the investigated specimens (%)

Specimen	C1s				O1s	
	1	2	3	4	1	2
Pristine PMMA	28.9	14.8	15.3	12.5	14.4	14.1
PMMA-5	23.7	15.0	14.4	13.8	18.5	14.6
PMMA-15	18.8	14.9	13.1	15.4	21.6	16.2
PMMA-15-Washed	21.9	14.1	14.2	15.4	18.7	15.7

Figure1a
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Figure2a

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