Plasma graft of poly(ethylene glycol) methyl ether methacrylate (PEGMA) on RGP lens surface for reducing protein adsorption

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Abstract
Poly(ethylene glycol) methyl ether methacrylate (PEGMA) was grafted on fluorosilicone acrylate rigid gas permissible contact lens surface by means of argon plasma induced polymerization to improve surface hydrophilicity and reduce protein adsorption. The surface properties were characterized by contact angle measurement, x-ray photoelectron spectroscopy (XPS) and atomic force microscopy respectively. The surface protein adsorption was evaluated by lysozyme solution immersion and XPS analysis. The results indicated that a thin layer of PEGMA was successfully grafted. The surface hydrophilicity was bettered and surface free energy increased. The lysozyme adsorption on the lens surface was reduced greatly.

Keywords: RGP contact lens, PEGMA, plasma graft polymerization, protein adsorption

(Some figures may appear in colour only in the online journal)

1. Introduction

As a compound of silicone and fluorocarbon, fluorosilicone acrylate (FSA) has a reputation of good gas permeability. For this reason, it is now the main material for manufacturing rigid gas permeable contact lenses. Unfortunately, the lens surface is hydrophobic for the existence of fluorocarbon. It is generally believed that protein adsorption is greater and stronger on hydrophobic than on hydrophilic surfaces because of the strong nonpolar interactions between hydrophobic groups of protein and those of the material surface [1]. The surface hydrophobicity of the RGP lens affects its susceptibility to protein and lipids adsorption from tear fluid when being worn [2–4]. So improving the surface hydrophilicity of RGP lens by means of surface modification is necessary. Many methods have been applied to modify the polymer surface for biomedical applications. Among them, low temperature plasma is widely applied [5, 6]. The reactions induced by plasma take place only on the very thin upper surface and have no effect on the substrate [7]. In the literature [8] it has been reported that poly(N-vinyl pyrrolidone) was covalently grafted onto the surface of poly(styrene-b-(ethylene-co-butylene)-b-styrene) (SEBS) elastomer via UV-induced graft polymerization combined with plasma pretreatment, and protein adsorption and platelet adhesion onto the PNVP-modified surface were significantly inhibited. Plasma surface treatment has also been used for surface modification of silicone hydrogel contact lenses [9].

As reported, the incorporation of a hydrophilic polyethylene oxide (PEO) molecules chain onto the polymer surface would decrease the adsorption of protein and platelet [10]; it is because the PEO on the surface displays minimum interfacial free energy and steric stabilization effects. The grafted chains had high surface mobility and large excluded volume, which helped to expel protein molecules in water [10, 11]. As the literature [12] reported, Poly(ethylene glycol) methyl ether methacrylate (PEGMA) was covalently grafted on the Poly(styrene-b-(ethylene-co-butylene)-b-styrene)
copolymer biomedical elastomer surface by photo-initiated graft polymerization. Compared with the control SEBS film, the PEGMA-modified SEBS film showed an enhanced surface wettability and excellent anti-protein adsorption. In this paper, we used argon plasma to graft PEGMA onto an oxygen plasma pretreated RGP contact lens to improve surface wettability and reduce protein adsorption. The surface properties were analyzed by x-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and CA measurements respectively. The surface protein adsorption was evaluated by lysozyme solution and XPS analysis.

2. Materials and procedures

2.1. Materials

FSA RGP lenses were first rinsed by abundant distilled water and then dried at room temperature prior to use. PEGMA (SR550) was purchased from Sartomer (Guangzhou) Chemicals Ltd. whose structure is shown in scheme 1.

2.2. Argon plasma induced graft polymerization of PEGMA

In this study we used a capacitively coupled plasma generator (DL-01, Suzhou Omega Machinery Electronic Technology Co., Ltd) for surface modification. The plasma frequency was 40 kHz. For plasma treatment, the treatment chamber was flushed with argon first and then evacuated to a vacuum of about 5 Pa. After that, oxygen was introduced to get about 30 Pa pressure and the plasma generator was turned on with determined power for a preset time. After oxygen plasma pretreatment, the lens samples were fetched out and air exposed at room temperature for one hour. The surface oxidized samples were then immersed in PEGMA/ethanol solution for about 10 s. After being dried for ten minutes under 50 °C, they were further treated by argon plasma to graft PEGMA on the surface. The process of argon plasma graft is similar to oxygen plasma treatment. After argon plasma induced graft polymerization, lens samples were flushed with water to get rid of the residual monomers and physically adsorbed homopolymers.

2.3. Characterization

Water and the diiodomethane contact angle (CA) on the lens surface were tested using the sessile drop method under room temperature with an OCA 40 Micro (DataPhysics, Germany). Wu’s [13] harmonic means method was applied to calculate the surface free energy. XPS (Axis Ultra DLD, Kratos Analytical Ltd, England) was tested with Al Kα X-ray (hv = 1486.6 eV) as the excitation source. Binding energy was calibrated by C 1 s of C–C (C–H) as 284.6 eV. The surface wettability was examined with AFM (SPI3800N, Seiko Instruments Inc, Japan).

Lysozyme for protein adsorption study was obtained from Sigma. The phosphate buffer saline (PBS) was self-prepared by dissolving 8.0 g NaCl, 0.2 g KCl, 1.44 g Na2HPO4 and 0.24 g KH2PO4 in 1 l deionized water and then adjusting the pH value with Na2HPO4 to 7.4. The concentration of the lysozyme PBS solution was 2 mg ml⁻¹. The lenses were first rehydrated by PBS and then immersed in the prepared lysozyme solution at 25 °C for 24 h. The lenses were then fetched out, gently rinsed by PBS and distilled water. After drying, the lenses were tested by XPS and N 1 s intensity was used to evaluate the protein absorption on the surface [14].

3. Results and discussion

This study included oxygen plasma oxidization and argon plasma graft polymerization. The oxygen plasma oxidization introduced peroxides and hydroperoxides on the FSA lens surface, which improved the surface wettability and made the following monomer coating more effective.

3.1. The surface oxidization of RGP lens by oxygen plasma

Plasma treatment imports polar groups on the polymer surface. The first process of this study was oxygen plasma oxidization. Figure 1 shows the effect of oxygen plasma treatment time (figure 1(a)) and power (figure 1(b)) on the RGP lens surface free energy. The lens surface free energy increased significantly after plasma treatment. The plasma treatment time and power have almost the same influence on the surface energy. The increase of surface energy was mostly contributed to its polar part, while the dispersive part almost remained unchanged. This can be explained by the introduction of the polar groups on the lens surface by plasma treatment and further oxidation in air [15]. These polar groups include peroxide and hydroperoxide, which could promote the following adsorption of PEGMA monomer on the surface. The formation of these polar groups was the result of the reactions between radicals formed by plasma treatment with air oxygen and water vapor. Thus, the exposure of samples to air after plasma treatment is very important for more polar groups’ formation on the surface. In order to avoid extensive surface etching under higher plasma power and longer exposure time, a moderate plasma power of 120 W with the exposure time of 60 s was sufficient for the surface oxidation, and this plasma condition was also applied for further argon plasma graft of PEGMA.

3.2. Argon plasma induced graft of PEGMA

After oxygen plasma oxidization and PEGMA monomer coating on the surface, the lenses were further treated with argon plasma polymerization. Figure 2 shows the XPS spectra...
of RGP lenses before and after plasma polymerization. PEGMA monomer concentration was 10%. The elements on the surface are F, O, N, C and Si. Their atomic percentages are listed in table 1. After PEGMA graft polymerization, the atomic concentration of O 1s increased greatly from 16.56% to 29.82%. F 1s and Si 2p peak decreased after the graft polymerization. It indicated that PEGMA was grafted successfully on the sample surface. However, the peaks of F 1s and Si 2p were not overwhelmed by the grafted PEGMA. This means that the thickness of the polymerized PEGMA layer did not exceed the XPS sampling depth for the polymer, which was normally thinner than 10 nm.

Figure 3 shows C1s spectra before and after modification confirmed the successful graft of PEGMA. The moderate increase of –O–C=O could be ascribed to PEGMA and the surface oxidation by argon plasma treatment. Meanwhile, the –CF2 component was submerged slightly by the grafted PEGMA layer.

Figure 1. The effect of O2 plasma treatment on surface energy, (a) plasma exposure time (120 W), (b) plasma power (60 s).

Figure 2. XPS of lens before (a) and after (b) PEGMA graft.

Plasma treatment could create active sites on the polymer material surface through bond scission [16]; this kind of bond scission will change the surface elements chemical state. As the thickness of the grafted PEGMA layer is very thin, so Ar plasma can also affect the chemical state of other elements on the substrate. The component ascribed to silicate (103.2 eV, –Si–O–) (figure 4(b)) increase sharply compared with the spectrum before modification. As indicated in figure 4(a), the Si element shows the form of –Si–CH3 (101.5 eV) totally for the untreated sample. After plasma treatment, silicone (–Si–CH3) was transformed mainly into silicate (–Si–O–). This was because Si–C bonds were broken under the reactions of plasma particles and the radicals formed reacted with oxygen to form –Si–O.

The graft ratio of PEGMA can be expressed briefly by the C–O relative percentage of C 1s. There will be more C–O on the surface with more PEGMA grafted. Figure 5 shows the influence of PEGMA concentration on C–O percentage and water CA. The figure shows that C–O percentage increased with the increase of PEGMA monomer concentration and reached a maximum value when PEGMA monomer concentration is 10%, while the water CA decreased. This result indicated the improvement of surface wettability with PEGMA graft polymerization. The water CA decreased from the original 104° to about 75° when the monomer concentration reached 10%. The change tendency of CA with monomer concentration consists well with that of C–O groups. It confirmed that the grafted PEGMA chain was the main factor responsible for surface hydrophilicity improvement. Our previous work demonstrated that plasma treatment could decrease the surface water CA of the RGP lens to below 40° [17], but the surface CA of the RGP lens after PEGMA has been grafted is greater than this value. It might be because the thickness of the grafted PEGMA layer on the lens surface is beyond the surface sensitivity of CA measurement [18].
Figure 6 shows the AFM photos of the RGP lens surface before and after PEGMA graft polymerization. It can be seen that the surface of the original RGP lens was smooth. After PEGMA grafting, the surface became rougher. Many small island-like protrusions appeared, which may be the grafted PEGMA chains. The surface roughness (Ra) calculated from AFM analysis increased from 2.54 nm for the original lens to 5.26 nm after PEGMA grafting. The surface roughness increase was the combination of plasma surface etching and the PEGMA graft polymerization. Both the grafted PEGMA chain and the increase of surface roughness together were responsible for the surface hydrophilicity improvement.

3.3. Protein adsorption on PEGMA grafted lens surface

The study was aimed to reduce the protein adsorption on the RGP lens surface by surface graft polymerization. In the

<table>
<thead>
<tr>
<th>Sample</th>
<th>F</th>
<th>O</th>
<th>N</th>
<th>C</th>
<th>Si</th>
<th>Relative percentage of C 1s components (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>12.98</td>
<td>16.56</td>
<td>1.38</td>
<td>57.58</td>
<td>11.49</td>
<td>-CH/-C-C</td>
</tr>
<tr>
<td>b</td>
<td>6.39</td>
<td>29.82</td>
<td>0.74</td>
<td>57.15</td>
<td>5.89</td>
<td>43.48</td>
</tr>
</tbody>
</table>

Table 1. The XPS quantitative results before (a) and after (b) surface modification.

![Figure 3. The C 1s XPS before (a) and after (b) PEGMA graft.](image)

![Figure 4. The Si 2p XPS before (a) and after (b) PEGMA graft.](image)

![Figure 5. The influence of monomer concentration on the graft ratio of PEGMA and surface hydrophilicity.](image)
study, we chose lysozyme as the model protein to characterize the surface protein adsorption as lysozyme is the common and main protein in tears. XPS survey spectra were applied for qualitative evaluation for protein adsorption. Figure 7 shows the XPS results of the lens surface after being immersed into the lysozyme solution. It showed that for the untreated sample (figure 7(b)), there is a strong N 1s peak, which comes from the protein adsorbed on the surface. The F 1s and Si 2p peak were submerged by the adsorbed protein layer. Figure 7(a) is the result of the PEGMA grafted sample. The N 1s peak ascribed to protein was weaker compared with the untreated sample. It demonstrates that the surface protein adsorption decreased. The widely accepted mechanism for the reduction of proteins adsorption on the PEG-grafted surface includes their low interfacial free energy in water and steric stabilization effects, as well as the unique solution properties and molecular conformation of the PEG chains in water [19], which all rejected the adsorption of protein on the surface.

4. Conclusion

In this paper, we successfully grafted PEGMA onto FSA RGP lens surface by means of argon plasma induced graft polymerization. A moderate plasma condition of 120 W power and 60 s exposure time was optimal for surface oxidation and graft polymerization. For PEGMA graft, the optimal monomer concentration was 10%. The thickness of the grafted PEGMA layer was as thin as several nanometers. After modification, the surface hydrophilicity was improved with the water CA being decreased from 104° to 75°. The lysozyme adsorption decreased significantly after surface modification.

Acknowledgments

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