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Photoinduced graft polymerization of 2-methacryloyloxyethyl phosphorylcholine on silicone hydrogels for reducing protein adsorption

Jing Jing Wang · Fang Liu

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Abstract The biomimetic synthetic methacrylate monomer containing a phosphorylcholine group, 2-methacryloyloxyethyl phosphorylcholine (MPC), has been widely used to improve the surface property of biomaterials. In the current report, both hydrophilic and antifouling surfaces were prepared on silicone hydrogels with MPC grafted by UV-induced free radical polymerization. The MPC-grafted silicone hydrogels were characterized by graft yield and static water contact angle (SCA) measurements. According to the results, the graft yield reached a maximum at 5 min of UV exposure time and 8 wt% MPC concentration. The modified silicone hydrogels possessed hydrophilic surfaces with the lowest water contact angle of 20°. The oxygen permeability of the MPC-grafted silicone hydrogels was as high as the unmodified silicone hydrogel. The mechanical property of silicone hydrogels was maintained at about 95% of the tensile strength and elastic modulus after the MPC grafting. The results of the in vitro single protein adsorption on the MPC-grafted silicone hydrogels were in agreement with the SCA measurements. The smaller the water contact angle, the greater was the protein repelling ability. The MPC-grafted silicone hydrogel is expected to be a novel biomaterial which possesses excellent surface hydrophilicity, antifouling property, oxygen permeability and mechanical property.

J. J. Wang (✉) · F. Liu
Department of Polymer Materials and Engineering,
School of Material Engineering, Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu Province,
Yancheng Institute of Technology, Yancheng 224051,
People's Republic of China
e-mail: jjwang3@hotmail.com

1 Introduction

Silicone hydrogels, combining comfort of hydrogels and excellent gas permeability of siloxanes, have attracted much attention because of the applications in the areas of contact lenses. However, the native hydrophobicity and biofouling tendency of silicone hydrogels have been one of the biggest limitations for biomaterial applications [1–3].

To modify the disadvantages of silicone hydrogel based materials, surface coating or grafting with hydrophilic polymers on silicone hydrogels is the most widespread technique to enhance the surface hydrophilicity. Surface graft polymerization is better than coating due to the chemical stability of its covalent bonding with a substrate and lower risk for deposition [2]. The conventional grafting polymerization technique requires chemically reactive groups on the surface. For this reason, a series of functionalization techniques, such as ultraviolet (UV) irradiation [4, 5], plasma [6, 7], ion beams [8], and chemical initiators [9–11], are necessary for covalent grafting. Among these techniques, the radiation grafting method is one of the most preferable methods because of the rapid generation of active radical sites without catalytic contamination on the surface of grafting materials.

UV radiation grafting methods, including preirradiation and simultaneous irradiation grafting, can introduce specific functional moieties to a polymeric substrate. For the former method, the polymeric substrate is irradiated first in vacuum, nitrogen or air, and then the monomer is grafted by peroxide radicals; for the latter method, the polymeric substrate is simultaneously irradiated in the presence of monomers. Consequently, when vinyl monomers are present, free radical graft polymerization occurs at these reactive sites, resulting in the formation of polymer chains that are covalently bonded to the surface of the substrate [4].

In order to obtain biomaterials with antifouling property, various types of polymers, such as poly(ethylene glycol) (PEG), poly(2-hydroxyethyl methacrylate), poly(acrylic acid), poly(acrylamide), and poly(*N*, *N*-dimethylacrylamide) could be grafted on surfaces [12]. Among these monomers, the PEG grafted surface has shown good antifouling characteristics. The use of biomimetic materials is another promising approach to enhance the antifouling ability. The biomimetic surface based on phosphorylcholine containing phospholipid polymers has shown an excellent resistivity of non-specific protein adsorption [4, 13–15]. These biomimetic polymers are included in 2-methacryloyloxyethyl phosphorylcholine (MPC), a methacrylate monomer having a zwitterionic phosphorylcholine headgroup in the side chain [4]. Poly(2-methacryloyloxyethyl phosphorylcholine) [poly(MPC)] is known to possess a large amount of free water fractions around the chain, which resists non-specific protein adsorption [16–24] and provides stabilization of biomolecules such as proteins, when the biomolecules are adsorbed on the surface. In the previous report, Willis et al. [18] prepared phosphorylcholine (PC)-coated silicone hydrogel contact lenses for use in extended wear. The PC coating was achieved by means of an in-mould coating (IMC) technique that produced a uniform and stable surface. The coating imparted higher wettability and lower protein adsorption compared to the uncoated lens. Recently, Shimizu et al. [19] prepared sequential interpenetrating polymer network (IPN) silicone hydrogels based on crosslinked poly(bis(trimethylsilyloxy) methylsilylpropyl glycerol methacrylate) (PSiMA) and poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC). The prepared silicone hydrogel, which possessed super-hydrophilic surface, excellent optical and mechanical properties, was suitable for use as a material for preparing contact lenses.

In the current work, silicone hydrogels were prepared by the copolymerization of methacrylated polydimethylsiloxane macromonomer, hydrophobic comonomer 3-methacryloxypropyl tris(trimethylsoloxy silane) (TRIS), and hydrophilic comonomer *N*, *N*-dimethyl acrylamide (DMA). Then the obtained silicone hydrogels were modified by grafting MPC initiated by UV light. The MPC-grafted silicone hydrogels were characterized by graft yield and static water contact angle (SCA) measurements. Eventually the oxygen permeability, mechanical properties and protein adsorption of the MPC-grafted silicone hydrogels were investigated.

2 Materials and methods

2.1 Materials

N, *N*-dimethylacrylamide (DMA) and 3-methacryloxypropyl tris (trimethylsiloxy) silane (TRIS) were purchased from Aldrich and purified by distillation under reduced pressure before use. Free radical photoinitiator Darocur 1173 was obtained from Ciba Co. and used as received. 2-methacryloyloxyethyl phosphorylcholine (MPC) was purchased from Nanjing Letian S &T Development Company. 1, 1-Diphenyl-2-picrylhydrazyl (DPPH) obtained from Aldrich was used for the quantification of peroxide concentration. Fibrinogen and lysozyme were purchased from Biozyme Company. The bifunctional methacrylated polydimethylsiloxanes macromer (MS) was prepared by the method as described in the literature [25].

2.2 Preparation of silicone hydrogels [2]

Bifunctional methacrylated polydimethylsiloxanes macromer (MS, 30 wt%), TRIS (30 wt%) and DMA (40 wt%), in a weight ratio chosen to total 100 parts, were mixed with 20 parts of n-hexanol and 0.5 part of photoinitiator Darocur 1173. The mixture was introduced between two glass plates (7.5 × 2.5 cm) and cured under a high-pressure mercury lamp emitting UV light with a mixed wavelength, where the main wavelengths were 305 and 365 nm. Film thickness was controlled by a Teflon gasket which gave a fairly consistent thickness of 0.25 mm. The films were respectively extracted with ethanol and water for 24 h. After immersing in fresh distilled water, transparent silicone hydrogel membranes were obtained with water content of 40 wt% measured by gravimetric assay.

2.3 Surface modification of silicone hydrogels by UV irradiation

The grafting experiment was carried out by a simultaneous irradiation grafting method. MPC/ethanol solution was purged with nitrogen for 2 h in order to minimize the presence of oxygen. Subsequently, the MPC/ethanol solution (2, 4, 6, 8, 10 and 12 wt%) was introduced into a slit constructed between a silicone hydrogel membrane and a photomask by utilizing cover glasses (150 μm thickness, Matsunami Glass) as spacers, and was then exposed through the photomask to UV light with a mixed wavelength, where the main wavelengths were 305 and 365 nm. The cover glasses were used as transparent photomasks, and the UV light was irradiated through the cover glasses in order to obtain completely grafted samples. After UV irradiation for a prescribed time, the silicone hydrogel membrane was rinsed with deionized water for 1 day to remove unreacted MPC and homopolymer of MPC. Finally MPC-grafted silicone hydrogels were obtained and stored in water [6, 26].

2.4 Determination of UV irradiation time

To obtain the optimal UV irradiation time, the amount of peroxide formed around the membrane after UV irradiation was quantified by the DPPH titration method [27]. The DPPH/toluene solution was degassed by a nitrogen gas purge for 30 min. The irradiated silicone hydrogel membrane was dipped into the DPPH/toluene solution at 65°C for 2 h in a shaking water bath to decompose the peroxides formed around the membrane. The amount of DPPH reacted with peroxides was measured with a JASCO V-560 UV/vis spectrophotometer at 520 nm. A calibration curve was obtained with five DPPH/toluene solutions of known concentration (0.0625, 0.125, 0.25, 0.5 and 1×10^{-4} mol/l). In order to obtain the optimal UV irradiation time, the relationship between irradiation time and peroxide concentration was investigated.

2.5 Characterization of MPC-grafted silicone hydrogels

The graft yield of samples was obtained gravimetrically by the following equation:

$$\text{Graft yield}\left(\text{mg/cm}^2\right) = (W_f - W_i) \div A$$

where A was the surface area of silicone hydrogel membrane, W_f and W_i were the final and initial weights of membrane before and after UV-induced grafting modification respectively.

The static water contact angle (SCA) of samples was measured at ambient humidity and temperature by the sessile drop method, using JC2000C1 goniometer of Zhongchen Digital Technical Co., China. The contact angle reported here was an averaged value of at least three measurements.

The oxygen permeability of samples was measured by the two-chamber method on a Mocon OX-TRAN® model 2/21 oxygen transmission rate tester and was expressed as Dk in unit of barrer (1 barrer = 10^{-11} cm^2 ml O_2/s ml mmHg) [28].

Thickness of samples was measured by ellipsometry. Measurements were taken on a Gaertner LSE single wavelength ellipsometer. The light source had an angle of incidence of 70° and was generated by a helium–neon laser. Nine measurements were taken per substrate and averaged to give the thickness grafted to the silicone hydrogel substrate. Averaging thickness of three substrates gave the average thickness reported for each sample.

Mechanical properties of samples were carried out using an Instron series IX materials testing system at room temperature. Dog-bone shaped samples were cut from the hydrogels (5 mm wide at the narrowest point with a gage length of 15 mm). Thickness of the samples was measured with a digital micrometer having a precision of 1 μm. A crosshead speed of 10 mm/min was used and at least triplicate was tested for each sample.

The surface elemental composition of samples at dry state was analyzed by X-ray photoelectron spectroscopy using a Shimadzu ESCA 750 spectrometer using MgKa radiation. The take-off angle of photoelectron was 45°.

In vitro single protein adsorption experiments were performed in phosphate-buffered saline (PBS, pH 7.4). Samples were immersed respectively in fibrinogen and lysozyme solutions at concentrations of 1.0 and 2.0 mg/ml. Modified and unmodified silicone hydrogel membranes were first immersed in PBS filled 24-well plate for 24 h in order to be fully hydrated. The sample was moved into wells containing the single protein solution, and the adsorption was allowed to proceed at 37°C for 12 h under gentle shaking. Each sample was then rinsed in the fresh PBS by 50 dippings. The samples were subsequently transferred into a well-plate filled in 1 ml of PBS solution containing 1 wt% of sodium dodecyl sulfate (SDS), and the adsorbed protein was completely desorbed by sonication for 5 h. The concentration of protein in the SDS solution was determined by the bicinchoninic acid assay method [5]. From the concentration of protein, the amount of protein adsorbed on the surface was calculated.

3 Results and discussion

3.1 Determination of UV irradiation time

The peroxides species can be used to initiate the surface free radical polymerization in a mechanism generally proposed for the UV-induced surface graft polymerization [12]. Free radicals generated in the original silicone hydrogel membrane without dipping into the MPC monomer solution after UV irradiation could be used to initiate the grafting reaction. The amount of peroxide was determined by measurement of the concentration of consumed DPPH molecules that reacted with free radicals generated after UV irradiation [29]. Therefore, the DPPH titration method was utilized to determine the optimal UV irradiation time. Figure 1 shows the effect of UV irradiation time on the radical concentration generated on the silicone hydrogel surface after UV irradiation. Seen from Fig. 1, the concentration of peroxides increased with the UV irradiation time and reached almost constant at 5 min. According to the results, an exposure time of 5 min was regarded as the optimal UV irradiation time for this study.

3.2 MPC graft polymerization on silicone hydrogels

The grafting experiment was carried out by a simultaneous irradiation grafting method. The effect of MPC

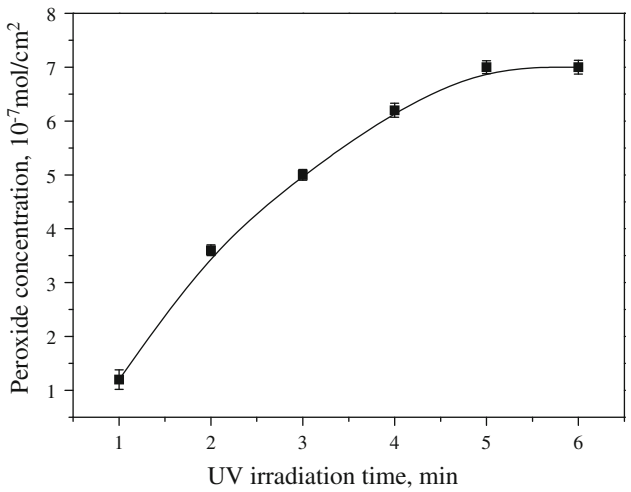

Fig. 1 Effect of UV irradiation time on the peroxide concentration generated on the silicone hydrogel surface after UV irradiation

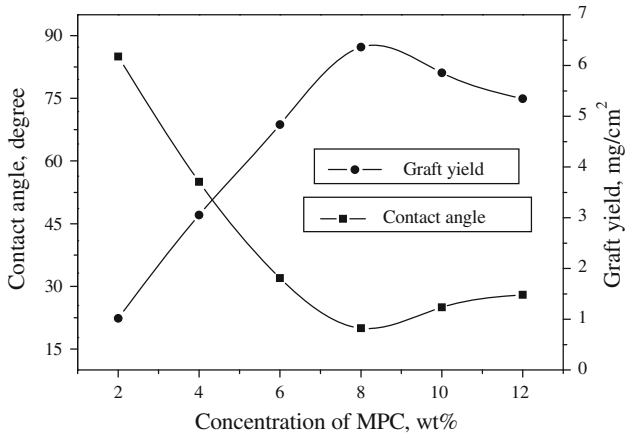

Fig. 2 Effect of the MPC concentration on the graft yield and wettability with irradiation time of 5 min

concentration on the graft yield and wettability was investigated with irradiation time of 5 min. As shown in Fig. 2, the static water contact angle (SCA) linearly decreased with an increase of MPC concentration due to the hydrophilicity of the grafted poly(MPC). Therefore, the decrease in the SCA clearly indicated the introduction of poly(MPC) chains on the surfaces of silicone hydrogels. However, above the concentration of 8 wt%, the SCA gradually increased. It was deduced that excessive use of the MPC monomer accelerated the formation of homopolymer of MPC, without reaction with the substrate of the silicone hydrogel. The MPC grafted silicone hydrogels abbreviated as Si-*g*-MPC 1–4 were obtained respectively by graft polymerization of MPC with concentrations of 2, 4, 6 and 8 wt%, fixing the irradiation time of 5 min. For comparison, Si-*g*-0 refers to the pristine unmodified silicone hydrogel.

3.3 Oxygen permeability

Oxygen permeability is an important factor for biomaterial applications, such as ophthalmologic biomaterials and artificial lungs. Therefore, the effect of the MPC grafting on the oxygen permeability was checked by directly measuring the Dk values of MPC-grafted silicone hydrogels.

Table 1 lists the graft layer thickness and Dk values of the MPC-grafted silicone hydrogels. The DK of the unmodified silicone hydrogel was 129.5 barrer, and that of the MPC-grafted silicone hydrogels was between 127.8 and 129.1 barrer. The MPC-grafted silicone hydrogels maintained over 98% of the oxygen permeability due to the considerably thinner graft layer thickness (less than 100 nm) compared to that of the unmodified silicone hydrogel membrane (0.25 mm).

The oxygen permeability was extensively discussed in the field of soft contact lens biomaterials. It was suggested that the oxygen transmittance, Dk/l (thickness of contact lens), for continuous wear soft contact lens should be 87–125 barrer/mm for a human cornea. Because the thickness of commercial soft contact lens was less than 100 μm, this oxygen transmission requirement was easily obtained for the MPC-grafted silicone hydrogels in the current research [4].

3.4 Mechanical properties

The UV-induced free radical graft polymerization methods may pose a problem concerning the bulk mechanical property for the silicone hydrogels. Tensile tests were performed on the MPC-grafted silicone hydrogels to determine the effect of grafting on the mechanical properties.

Table 2 shows the results of the tensile strength and elastic modulus for the unmodified and MPC-grafted silicone hydrogels. Both the tensile strength and elastic modulus of the MPC-grafted silicone hydrogels were lower than those of the unmodified silicone hydrogel by less than 5%. Seen from the results, although the deterioration of the silicone hydrogel bulk properties occurred, it seemed to be

Table 1 DK values and graft layer thickness of the MPC-grafted silicone hydrogels

Sample	DK, barrer	Graft layer thickness, nm
Si-*g*-0	129.5 ± 0.2	0
Si-*g*-MPC 1	129.1 ± 0.1	36 ± 1.5
Si-*g*-MPC 2	128.6 ± 0.1	58 ± 1.6
Si-*g*-MPC 3	128.1 ± 0.2	70 ± 1.1
Si-*g*-MPC 4	127.8 ± 0.1	78 ± 1.8

Table 2 Mechanical property of the MPC-grafted silicone hydrogels

Sample	Tensile strength, MPa	Elastic modulus, MPa
Si-*g*-0	1.49 ± 0.02	1.26 ± 0.02
Si-*g*-MPC 1	1.48 ± 0.01	1.25 ± 0.02
Si-*g*-MPC 2	1.45 ± 0.02	1.23 ± 0.01
Si-*g*-MPC 3	1.43 ± 0.01	1.21 ± 0.01
Si-*g*-MPC 4	1.42 ± 0.01	1.20 ± 0.01

too limited to affect the practical uses of silicone hydrogels.

3.5 XPS analysis

X-ray photoelectron spectroscopy (XPS) was used to characterize the surface of MPC modified and unmodified silicone hydrogels. The main reason for the use of XPS was the information depth of this analytical method (approximately 10 nm for polymeric materials) and the ability of this method to obtain comprehensive information about the elemental and chemical composition of samples in a single experiment [1, 2].

As listed in Table 3, there was no phosphorus on the surface of unmodified silicone hydrogel, while the phosphorus component in the phospholipid moiety was observed on the surfaces of MPC-grafted silicone hydrogels. The ratio of the peak area of phosphorus to that of carbon (P/C) was calculated and also summarized in Table 3. The P/C value of the silicone hydrogels was in the range of 0.0239–0.0570, and increased with the graft yield. These results clearly indicated that the phospholipid moiety was introduced onto the silicone hydrogel surface by the UV-induced graft polymerization.

3.6 In vitro protein adsorption

Proteins contained in the eye liquids in contact with the implanted lenses are expected to adsorb very rapidly onto the surface of the lenses. This nonspecific adsorption of proteins is uncontrolled and is thought to trigger

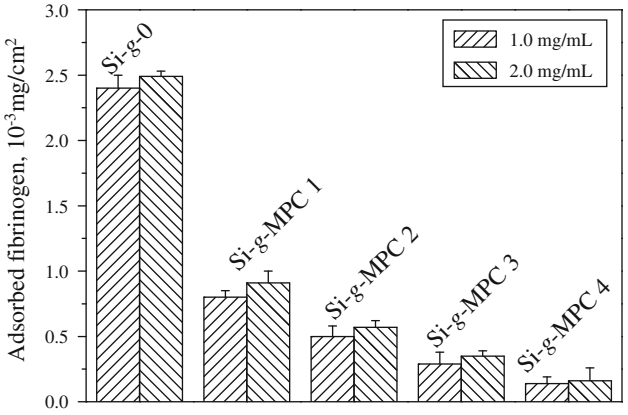

Fig. 3 Amount of fibrinogen adsorption on the unmodified and MPC-grafted silicone hydrogels

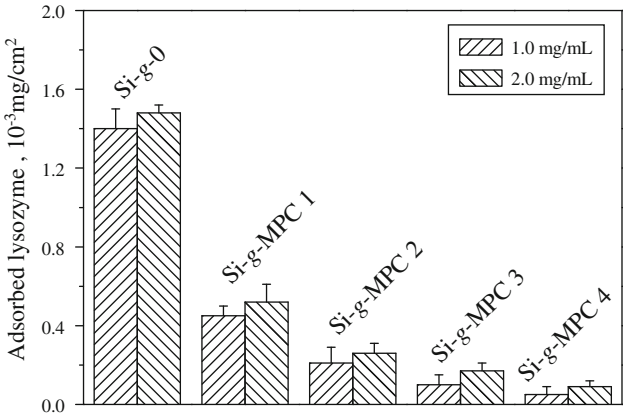

Fig. 4 Amount of lysozyme adsorption on the unmodified and MPC-grafted silicone hydrogels

deleterious reactions of the body, such as foreign body response and fibrous encapsulation. Therefore, in vitro protein adsorptions were tested to estimate the protein repellency properties of the grafted silicone hydrogels in relation with the graft yield [2, 4].

Figures 3 and 4 respectively show the amount of fibrinogen and lysozyme adsorptions on silicone hydrogel membranes at two concentrations. The amount of protein adsorptions from PBS buffer became larger when the

Table 3 Surface elemental compositions of the MPC-grafted silicone hydrogels determined by XPS at a 45° take off angle

Sample	C	O	N	Si	P	P/C
Si-*g*-0	58.7	26.0	2.5	12.8	0	0
Si-*g*-MPC 1	58.5	26.8	2.9	10.4	1.4	0.0239
Si-*g*-MPC 2	58.3	27.5	3.2	8.9	2.1	0.0360
Si-*g*-MPC 3	58.1	28.1	3.5	7.5	2.8	0.0482
Si-*g*-MPC 4	57.9	29.2	4.1	5.5	3.3	0.0570

higher concentration was used. Furthermore, it was found that fibrinogen and lysozyme adsorptions decreased effectively with increasing graft yield at both concentrations. The least amounts of fibrinogen and lysozyme adsorptions on the MPC-grafted silicone hydrogel surfaces from 1.0 mg/ml PBS buffer were 0.12 and 0.05 μg/cm^2, which were respectively about 94% and 96% reduction compared to the unmodified silicone hydrogel. The protein adsorption results were in agreement with the water contact angle measurements. The smaller the water contact angle, the greater was the protein repelling ability.

The mechanism of protein repulsion by an MPC-grafted surface was based on water interactions. It is well known that phosphorylcholine (PC) groups are highly hydrated. Ishihara et al. [30] observed that MPC-based polymers contained a large fraction of free water, and that adsorbed proteins assumed conformations similar to their native states, while MPC-free materials induced significant changes in the adsorbed protein conformations. The thick hydration layer was believed to repel proteins and made the protein conformations unchanged. The excellent performance in the protein adsorption resistivity of the poly(MPC)-modified surfaces appeared to be highly correlated to the thick hydration layer.

3.7 Storage stability of the grafted layer

The grafted silicone hydrogels were kept in water, and changes in contact angle examined as a function of time after the UV-induced graft polymerization are plotted in Fig. 5. It was found that the silicone hydrogels grafted with the hydrophilic monomer MPC exhibited almost the same contact angle during storage. These results indicated that covalently introduced poly(MPC) caused the stable surface hydrophilicity [2].

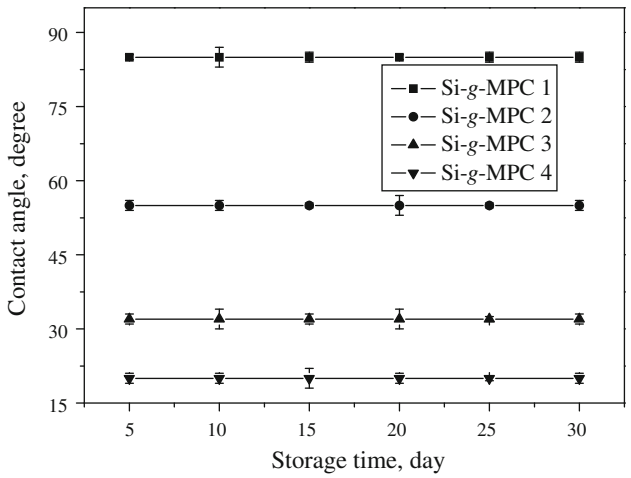

Fig. 5 Change of the water contact angles of MPC-grafted silicone hydrogels with time after being stored in water

4 Conclusion

In this report, 2-methacryloyloxyethyl phosphorylcholine (MPC) was grafted onto silicone hydrogels by UV-induced free radical polymerization, in order to enhance the surface hydrophilicity and antifouling property. The results indicated that the MPC-grafted silicone hydrogels possessed hydrophilic surfaces with the lowest water contact angle of 20°. The excellent oxygen permeability and mechanical property of the unmodified silicone hydrogel were maintained after the MPC grafting. The results of the in vitro single protein adsorption on the MPC-grafted silicone hydrogels were in agreement with the static water contact angle measurements. The smaller the water contact angle, the greater was the protein repelling ability. The MPC-grafted silicone hydrogel is attractive for biomedical materials especially contact lens.

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