Simultaneous Interpenetrating Network Silicone Hydrogels Prepared by Free Radical/Cationic Hybrid Polymerization

Jing Jing Wang, Fang 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

Correspondence to: J. J. Wang (E-mail: jjwang1@hotmail.com)

ABSTRACT: Simultaneous interpenetrating polymer network silicone hydrogels have been prepared by UV-initiated polymerization of a mixture of methacrylate monomer 2-methacryloyloxyethyl phosphorylcholine (MPC) and vinyl ether terminated polydimethylsiloxane (VESi) macromonomer. The consumption of each (macro)monomer upon UV-irradiation was monitored *in situ* by real-time infrared spectroscopy. The methacrylate monomer MPC was shown to polymerize faster and more extensively than the vinyl ether terminated macromonomer VESi. Curing experiments performed in the presence of air and under air diffusion-free conditions indicated that the free radical polymerization of MPC was affected by the oxygen inhibition effect, while the cationic polymerization of VESi was influenced by the atmosphere humidity. The results of the transmission electron microscope studies indicated that the silicone hydrogels were heterogeneous with phase domain sizes less than 10 nm. The physicochemical properties of the silicone hydrogels, such as water content, ion permeability, oxygen permeability, and contact angle were also investigated. The results showed that water content and ion permeability increased with the MPC content in the formulation, and the silicone hydrogels exhibited excellent oxygen permeability with the highest Dk of 255 barrer. The contact angle measurements indicated that the silicone hydrogels possessed hydrophilic surfaces with the lowest water contact angle of 20°. The result of the protein resistance revealed that the amount of protein adsorbed was significantly reduced with the MPC content in the formulation. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Silicone hydrogels, which are composed of separate siloxane phases and hydrogel phases, have been widely used as various biomedical devices, especially as contact lens.[1] It has been recognized that the multiplicity of properties required from a material to be used as the basis for contact lens, including transparency, mechanical strength, oxygen permeability, permeability to ions, and other nutrient molecules as well as surface hydrophilicity and antibiofouling properties, makes the selection of the optimum material challenging.[2]

An interpenetrating polymer network (IPN) comprising two or more networks that are interlaced on a molecular scale but not covalently bonded to each other may combine networks with different properties and structures.[3] From a synthetic standpoint, IPN comes in two varieties: (a) sequential IPN, in which one network is swollen and polymerized in the presence of the other, and (b) simultaneous IPN, in which both of the networks

are synthesized at the same time by independent and noninterfering routes. IPN silicone hydrogels composed of silicones and hydrogels, including poly(2-hydroxyethyl methacrylate),[4] poly(*N*-isopropyl acrylamide),[5] poly(vinyl alcohol),[6] poly(methacrylic acid),[7,8] copolymer of *N*,*N*-dimethylacrylamide and *N*-vinylpyrrolidone,[9] and poly(2-methacryloyloxyethyl phosphorylcholine)[10] have been developed. Chekina et al. developed a silicone hydrogel based on sequential interpenetrating network synthesis. The silicone network was obtained by the interaction between two siloxane oligomers comprising hydride and vinyl functional groups, and the hydrogel network was prepared by radical copolymerization of hydrophilic monomers.[9] Recently Shimizu et al. prepared sequential IPN silicone hydrogels based on cross-linked poly(bis(trimethylsilyloxy) methylsilylpropyl glycerol methacrylate) and 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.[10]
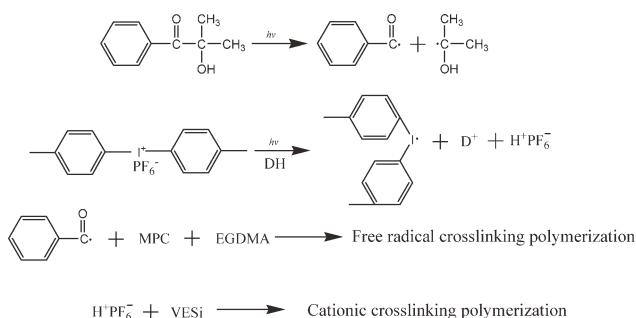
Figure 1. The mechanism of the free radical/cationic hybrid photopolymerization.

Silicone hydrogels prepared by the sequential technique may be out of shape during the preparing process. The primary advantage of simultaneous technique over sequential technique lies in the convenience, high efficiency and cost-saving.[11,12] Most of the time, blends of methacrylate monomers, which polymerize by a radical mechanism, and vinyl ether functionalized monomers, which polymerize by a cationic mechanism, were irradiated to produce simultaneous IPN. Free radical photopolymerization is a very fast process and not inhibited by water or moisture. However, it easily suffers from well-known oxygen inhibition effects. Photoinitiated cationic polymerization, conversely, is practically nonterminating and not inhibited by oxygen, but has the disadvantage of water or nucleophile sensitivity. Free radical/cationic hybrid photopolymerization has been suggested as a way to combine the advantages of these two classes of photopolymerization.[13–15]

In the previous studies, cross-linked PMPC hydrogels were synthesized and characterized for use as soft contact lens materials. The PMPC hydrogels exhibited excellent protein resistance and surface wettability but poor oxygen permeability.[16,17] In the current report, silicone hydrogels were prepared by free radical/cationic hybrid photopolymerization of 2-methacryloyloxyethyl phosphorylcholine (MPC) and bifunctional vinyl ether terminated polydimethylsiloxane (VESi) macromonomer. The consumption of each (macro)monomer upon UV-irradiation was studied using real-time infrared (RTIR) spectroscopy as analytical tool, which allowed to monitor in situ the polymerization of each (macro)monomer of the mixture and to record directly the conversion versus time profiles. Finally, the physicochemical properties of the prepared silicone hydrogels were evaluated.

EXPERIMENTAL

Materials

BCA Protein Assay Reagent Kit K3000 was purchased from Shanghai Biocolor BioScience & Technology Company. Free radical photoinitiator (Darocur 1173 from Ciba Specilty Chemicals) was used to generate the free radicals that were to initiate the polymerization of the methacrylate monomer. A diaryliodonium hexauorophosphate salt (DAI from Ciba Specialty Chemicals) in the presence of a hydrogen donor molecule (DH) was used to generate the protonic acid, which would initiate the cationic polymerization of the vinyl ether terminated macromonomer. The monomer polymerizing by radical mechanism was

MPC (from Nanjing Letian S&T Development Company). The macromonomer polymerizing by cationic mechanism was bifunctional VESi macromonomer (Mn 3800 as measured by gel permeation chromatography), which was prepared by the method as described in the literature.[18] Ethylene glycol dimethacrylate (EGDMA) used as the crosslinker was obtained from Aldrich chemical Company. The mechanism of the free radical/cationic hybrid photopolymerization is summarized in Figure 1.

Kinetic Analysis of the Photopolymerization

A mixture of MPC and VESi containing 1 wt % of crosslinker EGDMA and 2 wt % of each free radical and cationic photoinitiators was applied onto a silicon wafer, at a typical thickness of 24 mm [Figure 2(a)]. In some experiments a 15-mm thick transparent polypropylene film was laminated on top of the mixture to prevent the diffusion of air [Figure 2(b)]. The sample was placed in the compartment of an infrared (IR) spectrophotometer where it was exposed to the UV radiation of a medium pressure mercury lamp. The light intensity at the sample position was fixed at 60 mW/cm^2, as measured by radiometry (IL-390 radiometer). The polymerization of the sample exposed to both the UV beam and the analysis IR beam was followed in situ by RTIR spectroscopy, as shown in Figure 3, depicting the instrumental set-up. The disappearance of each one of the two functional groups was monitored continuously by setting the wave number of the IR detection at the proper value: 1638 cm^{-1} for the methacrylate double bond[19] and 3116 cm^{-1} for the vinyl ether double bond.[20] By operating the IR-spectrophotometer in the absorbance mode, conversion versus time curves were recorded. The amount of unreacted functionalities in the UV-cured polymer was determined from the value of the final conversion reached at the end of the UV exposure.

Preparation of Silicone Hydrogels

The (macro)monomer MPC and VESi were first dissolved in ethanol; subsequently 1 wt % of crosslinker EGDMA and 2 wt % of each free radical and cationic photoinitiators were added. The mixture of each formulation was introduced between two quartz slides (7.5 × 2.5 cm^2) and cured under a high-pressure mercury lamp emitting overwhelmingly light at 365 nm for 1 h. Film thickness was controlled by a Teflon gasket which gave a fairly consistent thickness of 0.25 mm. The films were extracted with ethanol and water for 24 h, respectively. Subsequently, the films were swollen to equilibrium in distilled water before characterization and the rectangular silicone hydrogels (7.0 × 2.0 cm^2) were obtained.
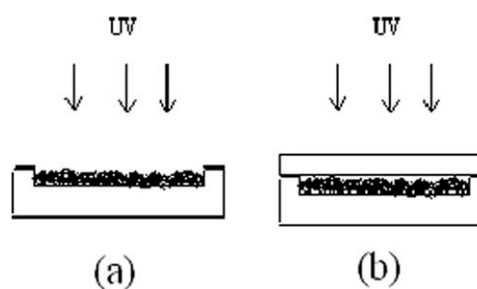

Figure 2. The schematic illustration of the tested sample for the photopolymerization.
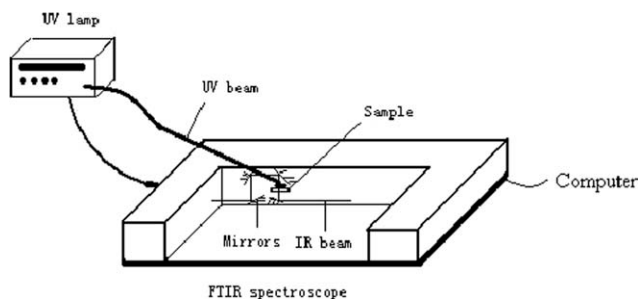
Figure 3. Instrumental set up for RTIR spectroscopy analysis of the photopolymerizations.

Characterization of Silicone Hydrogels

Fourier transform infrared spectroscopy (FTIR) spectra of the silicone hydrogels at dry state were recorded on a Bruker Vector 22 spectrometer in the range 4000–500 cm^{-1}.

The morphology of the silicone hydrogels was characterized by transmission electron microscope (TEM). The silicone hydrogels at dry state were embedded in Epon 812 epoxy resin which then polymerized overnight at 60°C. Hundred nanometer ultra-thin sections were cut using a Power Tome XL microtome and placed on a 200 mesh formvar coated copper grid. Cross-sections of the films were observed and photographed using a Hitachi H-7650 TEM with an 80 kV electron beam.

The equilibrium water content of the silicone hydrogels was calculated as follows:

$$EWC(\%) = \frac{W_s - W_d}{W_s} \times 100\% \qquad (1)$$

where, W_s and W_d were the weights of hydrogels at hydrated state and dry state, respectively.

The ion permeability of the silicone hydrogels was determined using a basic experimental set-up that involved the use of a cell with both a "donating" and a "receiving" reservoir, separated by the silicone hydrogel under study. Ion permeability was established by measurement of the flow of ions from the donor reservoir (loaded with a solution of NaCl of known ionic concentration), across the silicone hydrogel and into the receiver (loaded with pure water) by a conductivity electrode and meter. The diffusion coefficient (D, mm^2/min) for ion transport could then be calculated using the gradient of the resulting graph to provide the rate of ion transport (n', mol/min) and substituting into the following formula[2]:

$$D = \frac{n'}{A \times (dc/dx)} \qquad (2)$$

where, A was the area of ion transport (mm^2), dc was the concentration difference (mol/mm^3) and dx was the thickness of silicone hydrogel film (mm).

The oxygen permeability was measured by the two-chamber method[21] 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). Figure 4 shows the

scheme of the equipment developed for determining the oxygen permeability. The equipment consisted of two chambers: the receiver chamber where the oxygen concentration was monitored, and the donor chamber where oxygen concentration was constant. The two chambers were separated by the sample held in place by soft rubber gaskets. The testing pressure and the flow rate of oxygen were, respectively, determined to be at 0.3 MPa and 20 mL/min.

The surface elemental composition of the silicone hydrogels 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°.

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

In vitro single protein adsorption experiments were performed in phosphate-buffered saline (PBS, pH 7.4). The silicone hydrogels were immersed in PBS overnight prior to immersing in bovine serum albumin (BSA) and lysozyme solutions both at concentrations of 5.0 mg/mL for 12 hr at 37°C and then rinsed with 500 mL of fresh PBS twice by stirring method (300 rpm for 5 min). The adsorbed protein was detached in sodium dodecyl sulfate (SDS) 1 wt % in water by sonication for 5 h and the concentration of protein in the SDS solution was determined by the bicinchoninic acid assay method.[22] From the concentration of protein, the amount of protein adsorbed on the surface was calculated.

RESULTS AND DISCUSSION

Photopolymerization of the Methacrylate and Vinyl Ether (Macro)Monomers

The photoinitiated polymerization of each (macro)monomer alone has first been examined, before studying the photopolymerization of the (macro)monomer mixture, which generated the IPN. In particular, the influence of atmospheric oxygen on the polymerization kinetics of each (macro)monomer was examined.

The methacrylate monomer MPC polymerized readily when it was exposed to UV radiation in the presence of the radical
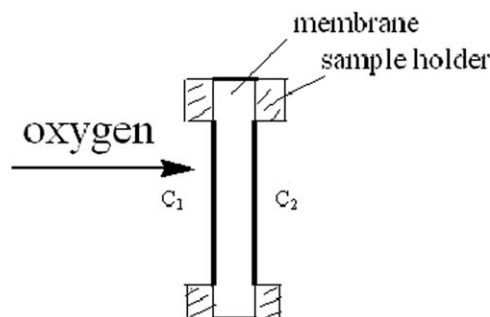

Figure 4. Illustration of the measurement chamber of the oxygen transmission rate tester. The concentration (*C*) of dissolved oxygen in contact with the two sides of the membrane was different (C1 > C2).
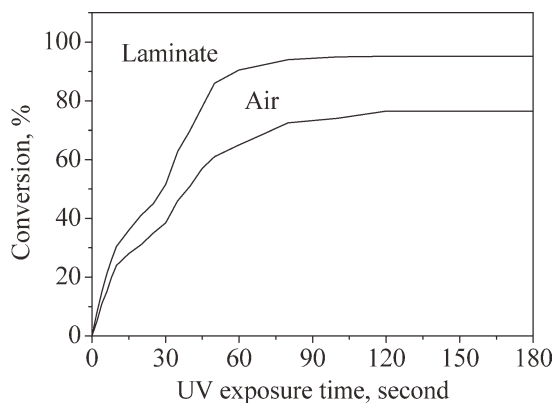
Figure 5. Photoinitiated radical polymerization of MPC. Photoinitiator: [Darocur 1173] = 2 wt %; Crosslinker: [EGDMA] = 1 wt %.

photoinitiator under air diffusion-free conditions (laminate) and reached 90.5% conversion within 60 s, as shown in Figure 5. The great reactivity of free radicals toward the methacrylate double bond was considered to be mainly responsible for the higher initiation efficiency of this type of photoinitiator. The radical photoinitiator had the advantage of absorbing in the near UV region, where the mercury lamp had their strongest emission, and was thus particularly well suited for the UV-curing of MPC.[23] This value hardly changed upon further exposure because of the severe mobility restrictions brought upon by the build-up of the glassy polymer network.

In the presence of air, the polymerization of MPC proceeded initially less rapidly and was progressively slowing down because of the inhibitory effect of atmospheric oxygen on this radical-induced polymerization (Figure 5). The conversion value leveled off at 76.5% after a 2-min exposure, so that the polymer network cured in the presence of air contained a significant amount of unreacted methacrylate double bonds (23.5% of the original amount).

Figure 6 indicated that the vinyl ether terminated silicone-containing macromonomer VESi underwent polymerization at a slower pace than the methacrylate monomer MPC.[14,15,23] The reason for the slower UV-curing of VESi lied in a poorly effi-
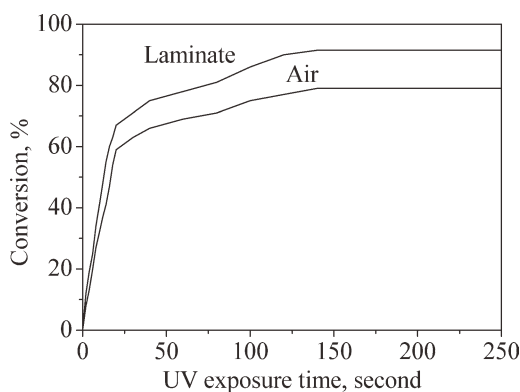
cient initiation process, which was partly due to the low UV absorbance of aryliodonium salts. A distinct characteristic of cationically initiated polymerization is that the propagating oxonium ions are not reacting among themselves. Consequently, once initiated, cationic polymerization will continue to proceed itself.

It was also seen that the cationic polymerization proceeded slowly and less extensively for the sample in contact with air than in the laminated condition. This was probably attributed to the effect of humidity in the air on the polymerization by nucleophilic attack on the oxonium cation.[20]

Photopolymerization of the Methacrylate/Vinyl Ether System
When the methacrylate/vinyl ether (macro)monomer mixture (MPC/VESi = 1/1 by weight) was exposed to UV radiation in the presence of the free radical and cationic initiators under air-free conditions (laminate), the polymerization of both (macro)-monomer occurred simultaneously, as shown in Figure 7. As expected, VESi polymerized less rapidly and less extensively, the conversion versus time curve being very similar to the one recorded upon UV-irradiation of the neat macromonomer (Figure 6).
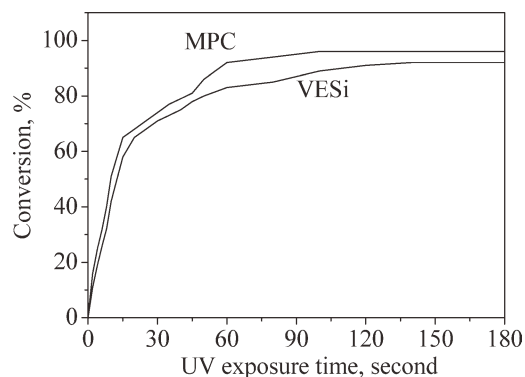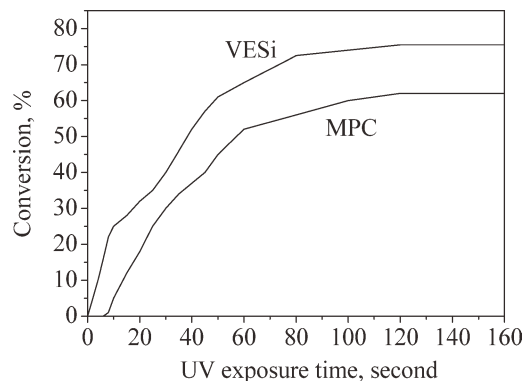

Figure 7. Photoinitiated polymerization of MPC/VESi hybrid system under laminate conditions. MPC/VESi = 1/1 by weight; photoinitiator: [Darocur 1173] = 2 wt %; [DAI] = 2 wt %; Crosslinker: [EGDMA] = 1 wt %.

Figure 6. Photoinitiated cationic polymerization of VESi. Photoinitiator: [DAI] = 2 wt %.

Figure 8. Photoinitiated polymerization of MPC/VESi hybrid system in the presence of air. MPC/VESi = 1/1 by weight; photoinitiator: [Darocur 1173] = 2 wt %; [DAI] = 2 wt %; Crosslinker: [EGDMA] = 1 wt %.
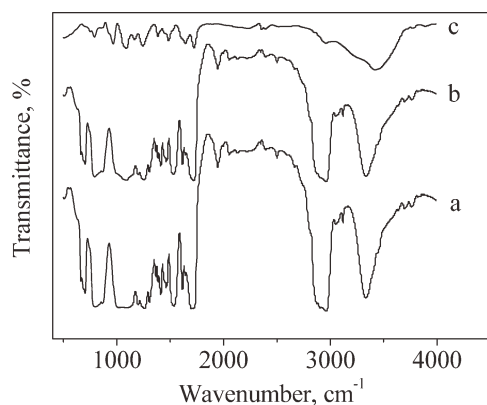
Figure 9. FTIR spectra of (a) poly(VESi); (b) silicone hydrogel derived from MPC content of 25% in the formulation; (c) PMPC.

A quite different behavior was observed by performing the same experiment in the presence of air, as shown in Figure 8. The polymerization of VESi was found to be more fast and complete than MPC. The methacrylate monomer MPC started to polymerize only after 6 s of UV exposure, to reach hardly 62% conversion after 2 min. Such a drastic effect was attributed to the inhibitory effect of atmospheric oxygen on radical-initiated polymerization on one hand. The free radicals, produced by photolysis of the initiator during the induction period, served to consume the oxygen dissolved in the system, which would become chemically bonded to the polymer in the form of hydroperoxides. Polymerization of the methacrylate double bond would only start once the concentration of the dissolved oxygen had decreased sufficiently (by at least two orders of magnitude) to allow the monomer MPC to compete successfully with oxygen for the scavenging of the initiating radicals[15]. Conversely, the build-up of the crosslinked VESi network and the resulting increase in viscosity slowed down the polymerization of MPC. Therefore, MPC started to polymerize in the hybrid system after a certain induction period.

Bulk Characterization

FTIR spectra of the polymerized MPC (PMPC), polymerized VESi [poly(VESi)], and the silicone hydrogel are shown in Figure 9. The characteristic bands of the poly(VESi) [Figure 9(a)] at 1265 and 1060 cm^{-1} were assigned to Si—CH$_3$ stretching and Si—O stretching. The peaks at 1630 and 1734 cm^{-1} were due to the presence of hydrogen-bonded and nonhydrogen-bonded carbonyl groups, respectively, as reported elsewhere.[24] The spectrum of PMPC [Figure 9(c)] showed a characteristic peak for —POCH$_2$ group at 1244 and 1088 cm^{-1}. The absorption peak centered at 1723 cm^{-1} was associated with the C=O group. The peak at 966 cm^{-1} was due to the —N$^+$(CH$_3$) stretching. The spectra of the silicone hydrogel [Figure 9(b)] presented the characteristic adsorption bands of poly(VESi) and PMPC. For the absorption of the silicone hydrogel, intensities of Si—O and Si—CH$_3$ peaks increased with the VESi content, while intensity of —POCH$_2$ peak increased with MPC content in the formulation. For the carbonyl peaks in the silicone hydrogel, the dominant portion of nonhydrogen bonded was identified from a stronger peak at 1730 cm^{-1} rather than at 1645 cm^{-1}.

The morphology of the silicone hydrogels observed by TEM is shown in Figure 10. The silicone hydrogels were heterogeneous with phase domain sizes less than 10 nm. It was assumed that interpenetrating process between the crosslinked MPC and VESi networks improved their compatibility. Furthermore, the silicone hydrogel prepared with MPC content of 25% [Figure 10(b)] had smaller phase domain size than that prepared with MPC content of 15% [Figure 10(a)] in the formulation, which suggested the higher degree of interpenetrating between the two networks in the IPN for the silicone hydrogel derived from PEGDA content of 25% in the formulation.[11]

Figure 11 illustrates the relationship between water content of the silicone hydrogels and MPC content in the formulation. The results showed that the water content of the silicone hydrogels correlated significantly with the MPC content. The linear regression ($R = 0.9981$) was positive, which indicated that increasing MPC content would result in an increase in water content due to the excellent hydrophilicity of the monomer MPC. Presumably the hydrogel domains in the silicone hydrogel formed by the crosslinked MPC network (PMPC) were connected together so that water molecules could easily diffused to the hydrogel domains.
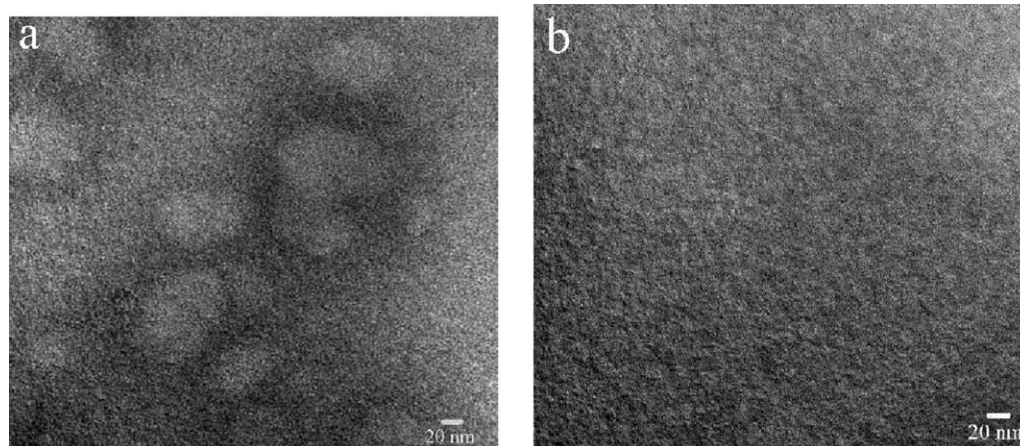

Figure 10. TEM images of silicone hydrogels derived from MPC content of (a) 15%, (b) 25% in the formulation.
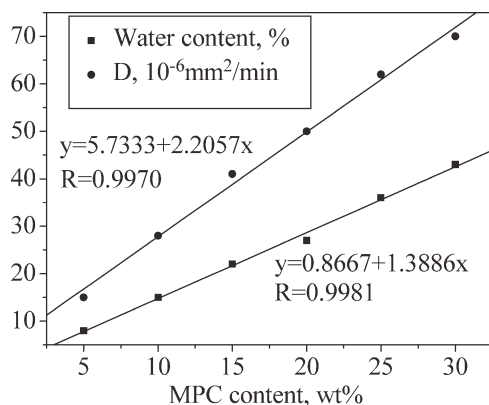
Figure 11. Dependence of water content and *D* values of silicone hydrogels on MPC content in the formulation.

Figure 12. Change of oxygen permeability and contact angle of silicone hydrogels with MPC content in the formulation.

Another property that is considered to be of great importance for silicone hydrogels if used as contact lenses is the ability to allow transport of ions and other nutrients through the lens to the cornea. One measure of the lens' ability to perform this function is the ion diffusion coefficient (*D*). The *D* values for the silicone hydrogels are shown in Figure 11. Kim et al.[25] reported that a *D* value greater than 6.0×10^{-6} mm^2/min was required to ensure adequate transport of ions to the cornea. As shown in Figure 11, all of the silicone hydrogels had sufficient values of *D*, that was contact lenses made of these silicone hydrogels would transfer enough ions to the cornea to satisfy the needs of metabolism.

The linear regression (*R* = 0.9970) was positive, indicating that the *D* value increased with the MPC content in the formulation, which was reasonable because the ions were expected to move through the hydrogel phase (PMPC network). Similar results were obtained in the previous report, in which the *D* value of the silicone hydrogels prepared by the sequential technique increased with the PMPC content in the IPN. Therefore, it was concluded that ion permeability was primarily relative to the hydrogel phase in the silicone hydrogels.

Oxygen permeability is an important factor for biomaterial applications, such as ophthalmologic biomaterials and artificial lungs. Figure 12 shows the oxygen permeability of the silicone hydrogels, which was evaluated by directly measuring the *Dk* values. The expression *Dk*, which is the product of the oxygen diffusion coeffi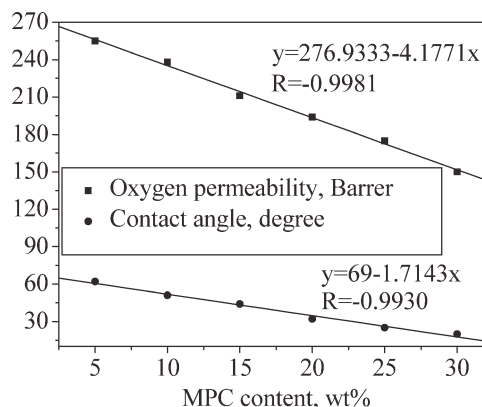cient (*D*) and the oxygen solubility coefficient in the material (*k*), has become universally accepted, as the term referring to the intrinsic property of a material to transport oxygen through its bulk.

Seen from Figure 12, with the increase of the MPC content in the formulation, the oxygen permeability gradually decreased. That was to say, the oxygen permeability of the silicone hydrogels increased with the VESi content, ranging from 150 to 255 barrer. The silicone hydrogels exhibited excellent oxygen permeability by virtue of the bulkiness and chain mobility of the siloxane group ($-Si(CH_3)_2-O-$), which characterized such materials and was responsible for the high diffusivity of oxygen through silicone-containing materials. The result was in agreement with the previous reports, in which silicone-containing (macro)monomers was incorporated into the IPN hydrogels to enhance the oxygen permeability.[11,26]

Surface Characterization
The elemental surface compositions of the silicone hydrogels determined by XPS are summarized in Table I. The results showed that the amount of phosphorus on the surfaces of silicone hydrogels increased with the MPC content in the formulation. The ratio of the peak area of phosphorus to that of carbon (P_{2p}/C_{1s}) was calculated and summarized in Table I. The P_{2p}/C_{1s} value of the silicone hydrogels was in the range from 0.0025 to 0.0277, and increased with the MPC content in the formulation. The results indicated that the content of PMPC enriched on the surface increased with the MPC content in the formulation.

Table I. The Elemental Surface Composition of Silicone Hydrogels from XPS Measurement

Sample[a]	MPC content (wt %)	C_{1s}	O_{1s}	N_{1s}	Si_{2p}	P_{2p}	P_{2p}/C_{1s}
Silicone hydrogel 1	5	59.14	30.01	2.87	7.83	0.15	0.0025
Silicone hydrogel 2	10	60.50	27.45	3.15	8.55	0.35	0.0058
Silicone hydrogel 3	15	58.95	28.11	3.04	9.32	0.58	0.0098
Silicone hydrogel 4	20	59.83	28.24	2.93	8.16	0.84	0.0140
Silicone hydrogel 5	25	58.58	28.50	2.76	9.04	1.12	0.0191
Silicone hydrogel 6	30	58.42	27.23	2.55	10.18	1.62	0.0277

[a]Silicone hydrogels 1, 2, 3, 4, 5, and 6 were prepared with MPC content of 5, 10, 15, 20, 25, and 30 wt %, respectively, in the formulation.
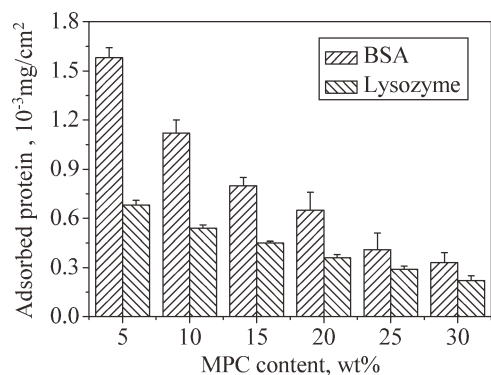
Figure 13. Effect of MPC content in the formulation on the amount of protein adsorption on silicone hydrogels.

The water contact angles of the silicone hydrogels are summarized in Figure 12. The linear regression ($R = -0.9930$) was negative, indicating that the contact angles decreased when the MPC content increased in the formulation. As MPC was incorporated, the contact angle was reduced from 62° to 20°. The results revealed that the silicone hydrogels possessed highly hydrophilic surfaces due to the excellent hydrophilicity of MPC. In the previous reports, Wang and Shimizu[10,12] have demonstrated that silicone hydrogels prepared by the sequential interpenetrating technique also possessed hydrophilic surface. These findings supported well our experimental data. These contact angle data agreed with the results of XPS in the current research. As determined by XPS, when the amount of MPC in the formulation increased, the amount of PMPC on the surface would increase. Therefore, surface hydrophilicity of the silicone hydrogels increased with the MPC content in the formulation. In the previous report,[11] the contact angle of the simultaneous IPN silicone hydrogels decreased when the content of the hydrophilic monomer N-vinyl-2-pyrrolidone (NVP) in the formulation increased, ranging from 90° to 57°. The silicone hydrogels in the current research exhibited better surface hydrophilicity because of the stronger hydrophilicity of MPC than NVP.

Protein Adsorption Resistance

Figure 13 shows the amount of BSA and lysozyme adsorption on the silicone hydrogel membranes. It was found that the amount of BSA and lysozyme adsorptions decreased effectively with increasing MPC content in the formulation. The least amounts of BSA and lysozyme adsorptions on the silicone hydrogel surfaces from 5.0 mg/mL PBS buffer were 0.33 and 0.22 μg/cm^2. 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. In the previous report,[12] the BSA adsorption on the silicone hydrogels prepared by the sequential IPN technique also decreased with increasing MPC content in the formulation. The silicone hydrogels in the current research exhibited better protein repelling ability due to the smaller water contact angle.

The mechanism of protein repulsion by a PMPC enriched surface was based on water interactions. It is well known that

phosphorylcholine (PC) groups are highly hydrated. Ishihara et al.[27] 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 make the protein conformations unchanged. The excellent performance in the protein adsorption resistivity of the PMPC enriched surfaces appeared to be highly correlated to the thick hydration layer.

CONCLUSION

Simultaneous IPN silicone hydrogels were prepared by free radical/cationic hybrid photopolymerization of a mixture of methacrylate and vinyl ether (macro)monomers. The methacrylate monomer MPC was shown to polymerize faster and more extensively than the vinyl ether terminated silicone-containing macromonomer VESi. Curing experiments performed in the presence of air and under air diffusion-free conditions indicated that the radical polymerization of MPC was affected by the oxygen inhibition effect, whereas the cationic polymerization of VESi was influenced by the atmosphere humidity. The silicone hydrogels exhibited heterogeneous morphology with phase domain sizes less than 10 nm. The water content of the silicone hydrogels correlated significantly with the MPC content in the formulation, and the silicone hydrogels had excellent oxygen permeability with the highest Dk of 255 barrer. The contact angle measurements indicated that the silicone hydrogels possessed hydrophilic surfaces with the lowest water contact angle of 20°. 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.

REFERENCES

1. Nicolson, P. C.; Vogt, J. *J. Biomater.* **2001,** *22,* 3273.

2. Willis, S. L.; Court, J. L.; Redman, R. P.; Wang, J. H.; Leppard, S. W.O'Byrne, V. J.; Small, S. A.; Lewis, A. L.; Jones, S. A.; Stratford, P. W. *Biomaterials* **2001,** *22,* 3261.

3. Chen, J.; Liu, M.; Chen, S. *Mater. Chem. Phys.* **2009,** *115,* 339.

4. Abbasi, F.; Mirzadeh, H. *J. Polym. Sci. B: Polym. Phys.* **2003,** *41,* 2145.

5. Liu, L.; Sheardown, H. *Biomaterials* **2005,** *26,* 233.

6. Shin, M. S.; Kim, S. J.; Kim, I. Y.; Kim, N. G.; Song, C. G.; Kim, S. I. *J. Appl. Polym. Sci.* **2002,** *85,* 957.

7. Turner, J. S.; Cheng, Y. L. *Macromolecules* **2003,** *36,* 1962.

8. Turner, J. S.; Cheng, Y. L. *Macromolecules* **2000,** *33,* 3714.

Applied Polymer

9. Chekina, N. A.; Pavlyuchenko, V. N.; Danilichev, V. F.; Ushakov, N. A.; Novikov, S. A.; Ivanchev, S. S. *Polym. Adv. Technol.* **2006,** *17,* 872.

10. Shimizu, T.; Goda, T.; Minoura, N.; Takai, M.; Ishihara, K. *Biomaterials* **2010,** *31* 3274.

11. Wang, J. J.; Li, X. S. *J. Appl. Polym. Sci.* **2010,** *116,* 2749.

12. Wang, J. J.; Li, X. S. *Polym. Adv. Technol.* **2011,** *22,* 2091.

13. Oxman, J. D.; Jacobs, D. W.; Trom, M. C.; Sipani, V.; Ficek, B.; Scranton, A. B. *J. Polym. Sci. Part A: Polym. Chem.* **2005,** *43,* 1747.

14. Cho, J. D.; Hong, J. W. *J. Appl. Polym. Sci.* **2004,** *93,* 1473.

15. Decker, C.; Nguyen Thi Viet, T.; Decker, D.; Weber-Koehl, E. *Polymer* **2001,** *42,* 5531.

16. Kiritoshi, Y.; Ishihara, K. *Polymer* **2004,** *45,* 7499.

17. Goda, T.; Watanabe, J.; Takai, M.; Ishihara, K. *Polymer* **2006,** *47,* 1390.

18. Kayaman-Apohan, N.; Demirci, R.; Cakir, M.; Gungor, A. *Radiat. Phys. Chem.* **2005,** *73,* 254.

19. Lecamp, L.; Pavillon, C.; Lebaudy, P.; Bunel, C. *Eur. Polym. J.* **2005,** *41,* 169.

20. Wei, H.; Li, Q.; Ojelade, M.; Madbouly, S.; Otaigbe, J. U.; Hoyle, C. E. *Macromolecules* **2007,** *40,* 8788.

21. Erdodi, G.; Kennedy, J. P. *J. Polym. Sci. Part A: Polym. Chem.* **2005,** *43,* 3491.

22. Sibarani, J.; Takai, M.; Ishihara, K. *Colloids Surf. B* **2007,** *54,* 88.

23. Decker, C.; Zahouily, K.; Valet, A. *Macromol. Mater. Eng.* **2001,** *286,* 5.

24. Zeng, M.; Zhang, L. N.; Kennedy, J. F. *Carbohydr. Polym.* **2005,** *60,* 399.

25. Kim, J.; Conway, A.; Chauhan, A. *Biomaterials* **2008,** *29,* 2259.

26. Wang, J. J.; Li, X. S. *Chin. J. Polym. Sci.* **2010,** *28,* 849.

27. Ishihara, K.; Nomura, H.; Mihara, T.; Kurita, K.; Iwasaki, Y.; Nakabayashi, N. *J. Biomed. Mater. Res.* **1998,** *39,* 323.