

UV-curing of simultaneous interpenetrating network silicone hydrogels with hydrophilic surface

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Abstract Simultaneous interpenetrating polymer network silicone hydrogels have been prepared by UV-initiated free radical/cationic hybrid photopolymerization of a mixture of methacrylate macromonomer polyethylene glycol diacrylate (PEGDA) and vinyl ether terminated polydimethylsiloxane macromonomer (VESi). The consumption of each macromonomer upon UV-irradiation was monitored in situ by real-time infrared spectroscopy. The analysis of transmission electron microscope indicated that the silicone hydrogels exhibited a heterogeneous morphology. The physicochemical properties of the silicone hydrogels, such as water content, ion permeability, oxygen permeability, and contact angle were investigated. The results showed that water content and ion permeability increased with the PEGDA content in the formulation, and the silicone hydrogels exhibited excellent oxygen permeability with the highest D_k of 248 barrer. The results of contact angle measurements indicated that the silicone hydrogels possessed hydrophilic surfaces with the lowest water contact angle of 32° . The study of the protein resistance revealed that the amount of protein adsorbed was significantly reduced with the PEGDA content in the formulation.

Keywords Silicone hydrogel · Interpenetrating polymer network (IPN) · Hybrid photopolymerization · Oxygen permeability

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Introduction

Silicone hydrogels have been widely used as various biomedical devices, especially as contact lens [1]. If a material to be used as contact lens, various properties including transparency, mechanical strength, oxygen permeability, permeability to ions as well as surface hydrophilicity, and anti-biofouling properties, must be satisfied all together. Therefore the selection of the optimum material is very 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: sequential IPN and simultaneous IPN. Previously, the possibility of obtaining silicone hydrogels using the sequential IPN synthesis was demonstrated. The process included the following successive stages: the synthesis of silicone network, its saturation with hydrophilic monomers (2-hydroxyethyl methacrylate [4], *N*-isopropyl acrylamide [5], methacrylic acid [6], and 2-methacryloyloxyethyl phosphorylcholine [7]), and preparation of the hydrophilic polymer network using ethylene glycol dimethacrylate as a crosslinker. A drawback of this approach was a relatively rough structure of the obtained silicone hydrogels, as indicated by the material opacity under the unhydrated state. In addition, the primary advantage of simultaneous technique over sequential technique lies in the convenience, high efficiency and cost-saving [8, 9]. 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/cationic hybrid photopolymerization has been suggested as a way to combine the advantages of free radical and cationic photopolymerizations [10–12].

The ability to resist protein adsorption is of great importance for a biomaterial, especially for a contact lens [13, 14]. On the eye, the contact lens is immersed in the tear film, which is largely comprised of proteins, lipids, and various electrolytes. Adsorption of proteins from the tear fluid onto the lens is a common problem and depends on a number of factors, including the nature of the materials from which the lens is made. This fouling can lead to dehydration of the lens and instability of the tear film, resulting in discomfort, and lack of tolerance in the wearer [15, 16]. Poly(ethylene glycol) (PEG) is a synthetic polymer that is very effective at preventing protein adsorption as a result of its hydrophilicity, high surface mobility, and low interfacial free energy with water. The covalent grafting of PEG by plasma and chemical initiators onto a variety of substrates, including silicon [17], polyurethane [18], polysulfone membranes [19], and poly(2-hydroxyethyl methacrylate) hydrogels [20] has been reported along with a quite satisfactory protein-repellent effect. It may be anticipated that the protein-repellent properties of PEG would prevent an extracellular matrix from being formed and, thus, cells from adhering [21]. In addition to these antifouling properties, PEG is optically transparent when hydrated, which is of the utmost importance for materials to be used as optical devices [22].

In the current report, silicone hydrogels were prepared by free radical/cationic hybrid photopolymerization of PEGDA and bifunctional vinyl ether terminated

polydimethylsiloxane macromonomer (VESi). The consumption of each macromonomer upon UV-irradiation was studied using real-time infrared (RTIR) spectroscopy as an analytical tool, which allows to monitor in situ the polymerization of each macromonomer of the mixture and to record directly the conversion versus time profiles. Finally the physicochemical properties of the prepared silicone hydrogels were evaluated.

Experimental section

Materials

Free radical photoinitiator (Darocur 1173 from Ciba Specialty Chemicals) was used to generate the free radicals that were to initiate the polymerization of the methacrylate monomer. A diaryliodonium hexafluorophosphate salt (DAI from Ciba Specialty Chemicals) was used to generate the protonic acid, which would initiate the cationic polymerization of the vinyl ether terminated macromonomer. The macromonomer polymerizing by free radical mechanism was polyethylene glycol diacrylate (PEGDA from Aldrich Chemicals). The macromonomer polymerizing by cationic mechanism was bifunctional vinyl ether terminated polydimethylsiloxane macromonomer (VESi), which was prepared by the method as described in the literature [23]. BCA Protein Assay Reagent Kit K3000 was purchased from Shanghai Biocolor BioScience & Technology Company.

Kinetic analysis of the photopolymerization

A mixture of PEGDA and VESi containing 2 wt% of each free radical and cationic photoinitiators was applied onto a silicon wafer, at a typical thickness of 24 nm. 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/cm², 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 real-time infrared (RTIR) spectroscopy. 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: 1,638 cm⁻¹ for the methacrylate double bond [24] and 3,116 cm⁻¹ for the vinyl ether double bond [25]. 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 macromonomers PEGDA and VESi were first dissolved in ethanol; subsequently 2 wt% of each free radical and cationic photoinitiators were added. The mixture of each formulation was introduced between two glass plates (7.5 × 2.5 cm²) 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 silicone hydrogels were obtained.

Characterization of silicone hydrogels

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 ultrathin 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 transmission electron microscope with an 80 kV electron beam.

The equilibrium water content (EWC) of the silicone hydrogels was measured in buffer solution (pH 7.4) at 37 °C, and was calculated as follows:

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

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 at 37 °C 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 buffer solution of NaCl with 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]:

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

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

Stress–strain measurements 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 oxygen permeability was measured by the two-chamber method [26] 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).

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 MgK α 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 Co., 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). Samples were immersed in 4.5 mg/mL of bovine serum albumin, 0.3 mg/mL of fibrinogen from bovine serum, and 2.0 mg/mL of lysozyme from chicken egg white solutions, respectively. Silicone hydrogel membranes were first immersed in PBS filled 24-well plate for 24 h in order to be fully hydrated. The samples were moved into wells containing single protein solutions, and adsorptions were 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 [17]. From the concentration of protein, the amount of protein adsorbed on the surface was calculated.

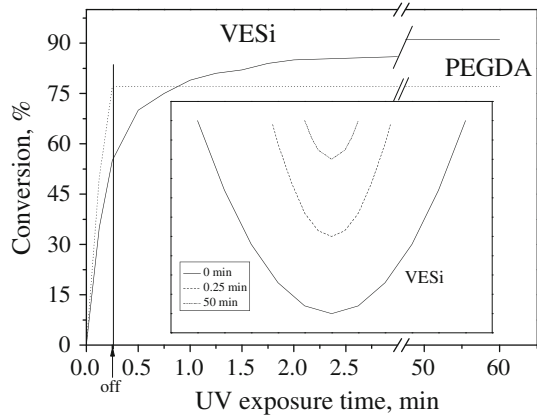
Results and discussion

Photopolymerization of the PEGDA/VESi system

In this research, a hydroxyphenylketone (Darocur 1173) was used to generate the free radicals which would initiate the polymerization of polyethylene glycol diacrylate (PEGDA). A diaryliodonium hexafluorophosphate salt (DAI) was used to generate the protonic acid, which would initiate the cationic polymerization of bifunctional vinyl ether terminated polydimethylsiloxane macromonomer (VESi). A distinct characteristic of cationic-type polymerization is that the propagating polymer cations are not reacting among themselves, unlike the propagating polymer radicals. Once initiated, the cationic polymerization will therefore continue to proceed after the UV exposure upon storage of the sample in the dark [10, 12]. This post-polymerization reaction can be easily visualized by RTIR spectroscopy, simply by continuing to record the decay of the vinyl ether IR band after the UV-irradiation.

Figure 1 shows the typical polymerization profiles recorded for the mixture of PEGDA and VESi (PEGDA/VESi = 1/1 by weight) exposed to UV-radiation for only 15 s. The adsorption peak for VESi in IR band at 0, 0.25, and 50 min has also been shown in Fig. 1. It can be seen that the vinyl ether macromonomer VESi continued to polymerize slowly after the light had been switched off (from 55 to 79 % within the first 1 min), while the conversion of PEGDA stayed constant at 77 %. In spite of the short UV exposure, a complete reaction of the vinyl ether

Fig. 1 Dark polymerization after 15 s UV exposure of the PEGDA/VESi system. PEGDA/VESi = 1/1 by weight; photoinitiator: [Darocur 1173] = 2 wt%; [DAI] = 2 wt%



groups was achieved after storing the sample for 40 min in the dark. This behavior can be explained by the incomplete polymerization of PEGDA which leaved a greater molecular mobility to the vinyl ether macromonomer VESi within the IPN formed [12].

Transmission electron microscope (TEM) analysis

The morphology of the silicone hydrogels observed by TEM is shown in Fig. 2. The silicone hydrogels were heterogeneous with phase domain sizes less than 10 nm. It was assumed that interpenetrating process between the crosslinked PEGDA and VESi networks improved their compatibility. Furthermore, the silicone hydrogel prepared with PEGDA content of 40 % had smaller phase domain size than that prepared with PEGDA content of 20 % 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 40 % in the formulation [8].

Water content

Figure 3 illustrates the relationship between water content of the silicone hydrogels and PEGDA content in the formulation. It was shown that the water content of the silicone hydrogels correlated significantly with the PEGDA content. The linear regression ($R = 0.9978$) was positive, which indicated that increasing PEGDA content would result in an increase in water content due to the excellent hydrophilicity of PEGDA. Presumably the hydrogel domains in the silicone hydrogel formed by the crosslinked PEGDA network were connected together so that water molecules could easily diffuse to the hydrogel domains.

Ion permeability

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

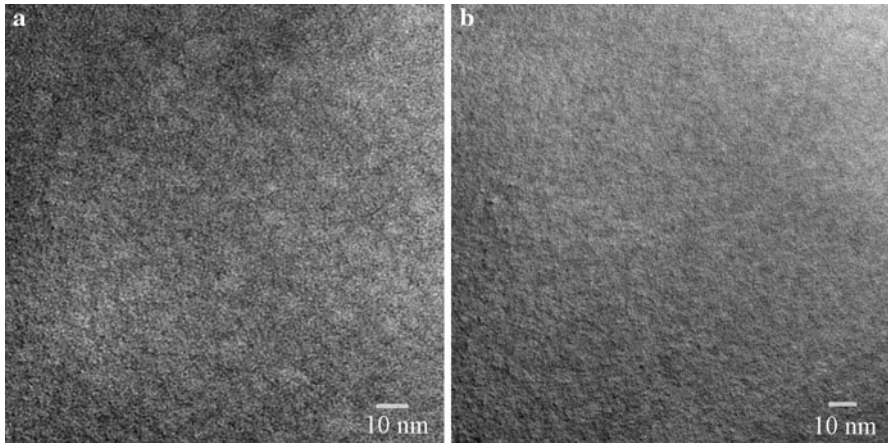
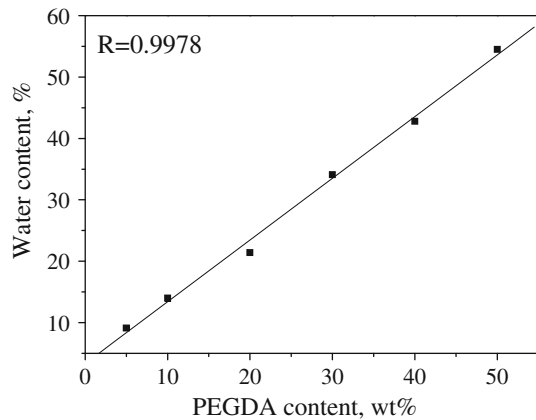


Fig. 2 TEM images of dried silicone hydrogels prepared with PEGDA content of **a** 20 %, **b** 40 % in the formulation, respectively

Fig. 3 Dependence of water content of silicone hydrogels on PEGDA content in the formulation



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 Fig. 4. Kim et al. [27] reported that a D value $>6.0 \times 10^{-6} \text{ mm}^2/\text{min}$ was required to insure adequate transport of ions to the cornea. As shown in Fig. 4, all of the silicone hydrogels had sufficient values of D , i.e., contact lenses made of these silicone hydrogels would transfer enough ions to the cornea to satisfy the needs of metabolism. The D value increased with the PEGDA content in the formulation, which was reasonable because the ions were expected to move through the hydrogel phase.

Mechanical property

The mechanical strength of the PEGDA/VESi hydrogels is shown in Fig. 5. It is well known that the tensile strength of a hydrogel is associated with hydrogen

Fig. 4 Change of the D values for the silicone hydrogels with the PEGDA content in the formulation

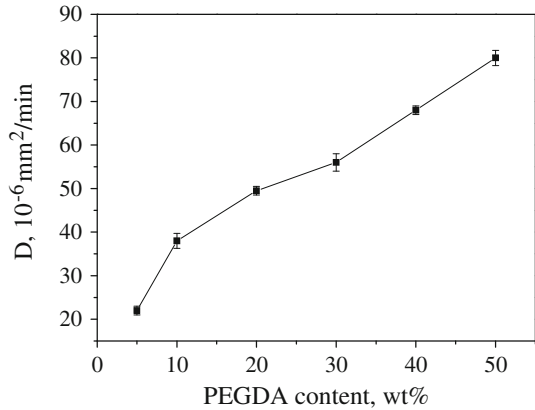
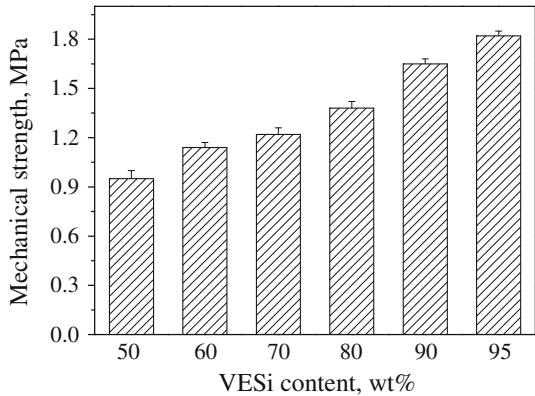


Fig. 5 Relationship between mechanical strength of silicone hydrogels and VESi content in the formulation

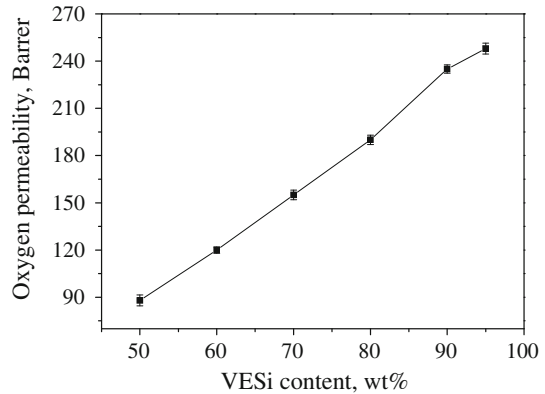


bonds, Van der Waals forces and chemical crosslinking in the hydrogel network. At a lower swelling ratio, the polymer chains are close to each other, and the network density is tight. The interaction between polymer chains in hydrogels is reinforced, and the hydrogel exhibited good mechanical strength. On the contrary, at a higher swelling ratio, the hydrogel network is diluted and the Van der Waals forces are weakened, which leads to the decrease of the tensile strength of hydrogels. Owing to the higher hydrophilicity of PEGDA than VESi, the swelling ratio decreased with the increase of the VESi content in the formulation. Therefore, the mechanical strength of PEGDA/VESi hydrogels increased with the VESi content.

Oxygen permeability

Oxygen permeability is an important factor for silicone hydrogels if used as biomaterials, such as contact lenses and artificial lungs. Figure 6 shows the oxygen permeability of the silicone hydrogels, which was evaluated by directly measuring the D_k values. The expression D_k , which is the product of the oxygen diffusion coefficient (D) and the oxygen solubility coefficient in the material (k), has become

Fig. 6 Relationship between oxygen permeability of silicone hydrogels and VESi content in the formulation



universally accepted, as the term referring to the intrinsic property of a material to transport oxygen through its bulk.

Seen from Fig. 6, with the increase of the VESi content in the formulation, the oxygen permeability gradually increased, ranging from 88 to 248 barrer. The silicone hydrogels exhibited excellent oxygen permeability by virtue of the bulkiness and chain mobility of the siloxane group ($-\text{Si}(\text{CH}_3)_2-\text{O}-$), which characterized such materials and was responsible for the high diffusivity of oxygen through silicone-containing materials [8].

Analysis of the elemental surface compositions

X-ray photoelectron spectroscopy (XPS) was used to characterize the surface of 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.

The elemental surface compositions of the silicone hydrogels determined by XPS are summarized in Table 1. With the increase of the PEGDA content in the formulation, the compositions of C and O increased, while the composition of Si decreased. The C/O ratios of the silicone hydrogel surfaces were close to the theoretical 2/1 ratio calculated from the repeat unit ($\text{CH}_2\text{CH}_2\text{O}$) of PEGDA and $(\text{CH}_3)_2\text{SiO}$ of VESi, indicating that both of PEGDA and VESi were present on the silicone hydrogel surfaces, although the amount of the latter decreased as the PEGDA content in the formulation increased [17].

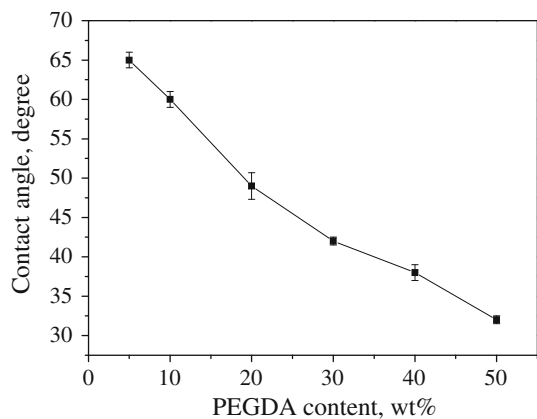
Contact angle

The water contact angles of the silicone hydrogels are summarized in Fig. 7. It was clear that when the PEGDA content in the formulation increased, the contact angle was reduced from 65° to 32° . The results revealed that the silicone hydrogels possessed highly hydrophilic surfaces due to the excellent hydrophilicity of PEGDA. These contact angle data agreed with the results of XPS. As determined by

Table 1 Surface elemental compositions of the silicone hydrogels determined by XPS at a 45° take off angle

Sample	C	O	N	Si	C/O
Silicone hydrogel 1	62.1	28.1	1.8	8.0	2.2100
Silicone hydrogel 2	63.5	28.9	1.2	6.4	2.1972
Silicone hydrogel 3	64.9	29.5	0.9	4.7	2.2000
Silicone hydrogel 4	65.8	30.0	0.7	3.5	2.1933
Silicone hydrogel 5	66.9	30.6	0.5	2.0	2.1863
Silicone hydrogel 6	67.6	31.0	0.4	1.0	2.1806

Silicone hydrogels 1, 2, 3, 4, 5, and 6 were prepared with PEGDA content of 5, 10, 20, 30, 40, and 50 wt% in the formulation, respectively

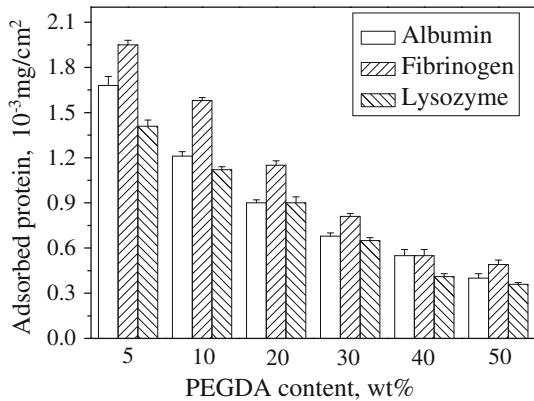
Fig. 7 Effect of PEGDA content in the formulation on the contact angle of silicone hydrogels

XPS, when the amount of PEGDA in the formulation increased, the amount of crosslinked PEGDA network on the surface would increase. Therefore, surface hydrophilicity of the silicone hydrogels increased with the PEGDA content in the formulation.

Protein adsorption resistance

Figure 8 shows the amounts of albumin, fibrinogen, and lysozyme adsorption on the silicone hydrogel membranes. It was found that the amount of protein adsorptions decreased effectively with increasing PEGDA content in the formulation. The least amounts of albumin, fibrinogen, and lysozyme adsorptions on the silicone hydrogel surfaces were, respectively, 0.4, 0.49, and 0.36 $\mu\text{g}/\text{cm}^2$. 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. The reduction in protein adsorption to the silicone hydrogel surface must be due to the hydrated chains from PEGDA which were enriched on the silicone hydrogel surface. The hydrated chains may prevent protein molecules from their direct contact with the silicone hydrogel surface owing to their steric hindrance effect [20, 22].

Fig. 8 Influence of PEGDA content in the formulation on the amount of protein adsorption on silicone hydrogels



Conclusions

Simultaneous interpenetrating polymer network (IPN) silicone hydrogels with hydrophilic surface were prepared by free radical/cationic hybrid photopolymerization of a mixture of methacrylate macromonomer polyethylene glycol diacrylate (PEGDA) and vinyl ether terminated polydimethylsiloxane macromonomer (VESi). In the case of the hybrid photopolymerization of PEGDA and VESi, the living character of the cationic polymerization of VESi was beneficial because it allowed the unreacted vinyl ether groups to further polymerize upon storage of the sample in the dark, thus leading to a fully cured IPN polymer. The IPN silicone hydrogels had heterophase morphology and the interpenetrating process between the two networks in the IPN improved their compatibility. The water content of the silicone hydrogels correlated significantly with the PEGDA content in the formulation, and the silicone hydrogels had excellent oxygen permeability with the highest D_k of 248 barrer. The contact angle measurements indicated that the silicone hydrogels possessed hydrophilic surfaces with the lowest water contact angle of 32° . 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.

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References

1. Chekina NA, Pavlyuchenko VN, Danilichev VF, Ushakov NA, Novikov SA, Ivanchev SS (2006) A new polymeric silicone hydrogel for medical applications: synthesis and properties. *Polym Adv Technol* 17:872–877
2. Willis SL, Court JL, Redman RP, Wang JH, Leppard SW, Byrne VJO', Small SA, Lewis AL, Jones SA, Stratford PW (2001) A novel phosphorylcholine-coated contact lens for extended wear use. *Biomaterials* 22:3261–3272
3. Chen J, Liu M, Chen S (2009) Synthesis and characterization of thermo- and pH-sensitive kappa-carrageenan-g-poly(methacrylic acid)/poly(*N,N*-diethylacrylamide) semi-IPN hydrogel. *Mater Chem Phys* 115:339–346

4. Abbasi F, Mirzadeh H (2003) Properties of poly(dimethylsiloxane)/hydrogel multicomponent systems. *J Polym Sci B Polym Phys* 41:2145–2156
5. Liu L, Sheardown H (2005) Glucose permeable poly (dimethyl siloxane) poly (*N*-isopropyl acrylamide) interpenetrating networks as ophthalmic biomaterials. *Biomaterials* 26:233–244
6. Turner JS, Cheng YL (2003) Morphology of PDMS-PMAA IPN membranes. *Macromolecules* 36:1962–1966
7. Shimizu T, Goda T, Minoura N, Takai M, Ishihara K (2010) Super-hydrophilic silicone hydrogels with interpenetrating poly(2-methacryloyloxyethyl phosphorylcholine) networks. *Biomaterials* 31:3274–3280
8. Wang JJ, Li XS (2010) Preparation and characterization of interpenetrating polymer network silicone hydrogels with high oxygen permeability. *J Appl Polym Sci* 116:2749–2757
9. Cano FB, Visconte LLY (1998) UV-polymerization of 2-ethylhexyl acrylate in interpenetrating polymer networks-some mechanical properties. *Polym Bull* 40:83–87
10. Oxman JD, Jacobs DW, Trom MC, Sipani V, Ficek B, Scranton AB (2005) Evaluation of initiator systems for controlled and sequentially curable free-radical/cationic hybrid photopolymerizations. *J Polym Sci, Part A* 43:1747–1756
11. Cho JD, Hong JW (2004) UV-initiated free radical and cationic photopolymerizations of acrylate/epoxide and acrylate/vinyl ether hybrid systems with and without photosensitizer. *J Appl Polym Sci* 93:1473–1483
12. Decker C, Nguyen Thi Viet T, Decker D, Weber-Koehl E (2001) UV-radiation curing of acrylate/epoxide systems. *Polymer* 42:5531–5541
13. Yao K, Huang XD, Huang XJ, Xu ZK (2006) Improvement of the surface biocompatibility of silicone intraocular lens by the plasma-induced tethering of phospholipid moieties. *J Biomed Mater Res* 78A:684–692
14. Santos L, Rodrigues D, Lira M, Real Oliveira ME, Oliveira R, Vilar EY, Azeredo J (2007) The influence of surface treatment on hydrophobicity, protein adsorption and microbial colonisation of silicone hydrogel contact lenses. *Cont Lens Anterior Eye* 30:183–188
15. Taddei P, Balducci F, Simoni R, Monti P (2005) Raman, IR and thermal study of a new highly biocompatible phosphorylcholine-based contact lens. *J Mol Struct* 744–747:507–514
16. Mann AM, Tighe BJ (2007) Tear analysis and lens-tear interactions Part I. Protein fingerprinting with microfluidic technology. *Cont Lens Anterior Eye* 30:163–173
17. Sugiura S, Edahiro JI, Sumaru K, Kanamori T (2008) Surface modification of polydimethylsiloxane with photo-grafted poly(ethylene glycol) for micropatterned protein adsorption and cell adhesion. *Colloids Surf B Biointerfaces* 63:301–305
18. Archambault JG, Brash JL (2004) Protein repellent polyurethane-urea surfaces by chemical grafting of hydroxyl-terminated poly(ethylene oxide): effects of protein size and charge. *Colloids Surf B Biointerfaces* 33:111–120
19. Thom V, Jankova K, Ulbricht M, Kops J, Jonsson G (1998) Synthesis of photoreactive α -azidobenzoyl ω -methoxy poly(ethylene glycol)s and their end-on photo-grafting onto polysulfone ultrafiltration membranes. *Macromol Chem Phys* 199:2723–2729
20. Bozukova D, Pagnouille C, De Pauw-Gillet MC, Ruth N, Jérôme R, Jérôme C (2008) Imparting antifouling properties of poly(2-hydroxyethyl methacrylate) hydrogels by grafting poly(oligoethylene glycol methyl ether acrylate). *Langmuir* 24:6649–6658
21. Zhang F, Kang ET, Neoh KG, Wang P, Tan KL (2001) Modification of Si(100) surface by the grafting of poly(ethylene glycol) for reduction in protein adsorption and platelet adhesion. *J Biomed Mater Res* 56:324–332
22. Bozukova D, Pagnouille C, De Pauw-Gillet MC, Desbief S, Lazzaroni R, Ruth N, Jérôme R, Jérôme C (2007) Improved performances of intraocular lenses by poly(ethylene glycol) chemical coatings. *Biomacromolecules* 8:2379–2387
23. Kayaman-Apohan N, Demirci R, Cakir M, Gungor A (2005) UV-curable interpenetrating polymer networks based on acrylate/vinylether functionalized urethane oligomers. *Radiat Phys Chem* 73:254–262
24. Lecamp L, Pavillon C, Lebaudy P, Bunel C (2005) Influence of temperature and nature of photo-initiator on the formation kinetics of an interpenetrating network photocured from an epoxide/methacrylate system. *Euro Polym J* 41:169–176
25. Wei H, Li Q, Ojelade M, Madbouly S, Otaigbe JU, Hoyle CE (2007) Thiol-Ene free-radical and vinyl ether cationic hybrid photopolymerization. *Macromolecules* 40:8788–8793

26. Erdodi G, Kennedy JP (2005) Water-swollen highly oxygen permeable membranes: analytical technique and syntheses. *J Polym Sci, Part A* 43:3491–3501
27. Kim J, Conway A, Chauhan A (2008) Extended delivery of ophthalmic drugs by silicone hydrogel contact lenses. *Biomaterials* 29:2259–2269