Preparation and Characterization of Interpenetrating Polymer Network Silicone Hydrogels with High Oxygen Permeability

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ABSTRACT: In the current work, interpenetrating polymer network (IPN) silicone hydrogels are prepared by UV-initiated polymerization of acrylate monomers including siloxane macromer, methacryloxypropyl tris (trimethylsiloxy) silane (TRIS) and N,N-dimethylacrylamide (DMA)/N-vinyl-2-pyrrolidone (NVP) in the presence of free radical and cationic photoinitiators. The polymerization mechanism is investigated preliminarily by the formation of gel network. The morphology of the hydrogels is characterized by fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and transmission electron microscope (TEM). The results show that the IPN hydrogels exhibit a heterogeneous morphology. The surface wettability is examined by the contact angle goniometer. The result reveals that the IPN silicone hydrogels possess hydrophilic surfaces with the lowest water contact angle of 59°. Furthermore, the oxygen permeability of the hydrogels is measured by an oxygen transmission tester. The results indicate that the IPN silicone hydrogels have excellent oxygen permeability with the highest Dk of 226 barrer. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 2749–2757, 2010

Key words: interpenetrating polymer network; silicone hydrogel; photopolymerization; oxygen permeability

INTRODUCTION

Silicone hydrogels, combining softness and comfort of hydrogel and higher gas permeability of siloxane, have attracted much attention because of the applications in the areas of contact lenses. They are commonly prepared by the copolymerization of siloxane macromer, hydrophobic comonomer and hydrophilic comonomers, such as 2-hydroxyethyl methacrylate (HEMA), N,N-dimethylacrylamide (DMA) and N-vinyl pyrrolidone (NVP).[1] With DMA, low modulus can be achieved along with poor surface wettability.[2] The silicone hydrogels have to experience surface modification to improve the hydrophilicity for the application of contact lenses. While with NVP, good surface wettability can be realized but with high moduli.[2] Because of poor copolymerization of NVP and (meth)acrylate functional monomers,[3–7] the resulting materials often show inconsistent quality, such as poor mechanical properties and water content. Lai[3] studied the copolymerization of NVP and HEMA, finding that ethylene glycol dimethacrylate (EGDMA) is not an effective crosslinker for NVP. Methacryloxyethyl vinyl carbonate (HEMAVC) and allyl methacrylate (AMA) can incorporate both HEMA and NVP, but work for the copolymerization of a formulation containing less NVP.[3] Ethylidene-bis-3-(N-vinyl-2-pyrrolidone) (EBVP), containing two NVP units bounding together with an ethylidene linkage, can crosslink NVP sufficiently.[8]

Another approach to prepare silicone hydrogels is using the interpenetrating polymer networks (IPN) technique. From a synthetic standpoint, IPNs come 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, noninterfering routes. Abbasi et al.[9] prepared silicone rubber/poly(2-hydroxyethyl methacrylate) (PHEMA) IPNs by polymerizing HEMA in the presence of swollen silicone rubber. The obtained IPNs absorb water in the manner of hydrogels and exhibit mechanical properties superior to hydrogels. Liu and Sheardown[10] developed IPNs based on poly(dimethyl siloxane) (PDMS) and poly(N-isopropyl acrylamide) (PNIPAAM). The IPNs exhibit oxygen and glucose permeability as well as improved wettability compared to PDMS homopolymer and greater mechanical strength than that of PNIPAAM homopolymer. Recently Chekina et al.[11]

developed a silicone hydrogel based on sequential interpenetrating network synthesis. The silicone network is obtained by the interaction between two siloxane oligomers comprising hydride and vinyl functional groups, and the hydrophilic network is prepared by radical copolymerization of hydrophilic monomers. Silicone hydrogels prepared by the sequential technique may be out of shape during the preparing process. The simultaneous IPN can be prepared by synthesizing simultaneously two polymers through different polymerization mechanisms.[9–11] The primary advantage of simultaneous technique over sequential technique lies in the convenience, high efficiency and cost-saving. To the knowledge of authors, there is no report about the preparation of silicone hydrogels by the simultaneous IPN manner.

The primary interest of photopolymerization lies in the high polymerization rates, together with the advantage of a solvent-free formulation curable at ambient temperature. Free radical and cationic photopolymerizations each have unique advantages and limitations. Free radical photopolymerization is a very fast process and not inhibited by water or moisture. However, it may suffer from well-known oxygen inhibition effects. Photoinitiated cationic polymerization is practically nonterminating and not inhibited by oxygen, but has the disadvantage of water or moisture sensitivity. Hybrid free-radical/cationic photopolymerization has been suggested as a way to combine the advantages of these two classes of photopolymerization.[12–14] In our previous study, photopolymerization of HEMA and NVP in the presence of free radical and cationic initiators has been employed to prepare the hydrogels with high water content and antidehydration ability. The hybrid free-radical/cationic photopolymerization mechanism is proposed to explain the formation of HEMA/NVP simultaneous IPN hydrogels. During the photopolymerization process, HEMA and NVP copolymerize by free radical mechanism; meanwhile, the free radical initiator activates the cationic initiator to initiate the cationic polymerization of NVP in the presence of the crosslinker EBVP.

In this report, to combine the surface hydrophilicity and oxygen permeability, the IPN silicone hydrogels are prepared by UV-initiated hybrid photopolymerization of acrylate monomers including siloxane macromer, methacryloxypropyl tris (trimethylsiloxy) silane (TRIS) and N,N-dimethylacrylamide (DMA)/N-vinyl-2-pyrrolidone (NVP) in the presence of free radical and cationic photoinitiators. The polymerization mechanism is investigated preliminarily by the formation of gel network. The morphology of the hydrogels is examined by FTIR, DSC, and TEM. Furthermore, the surface hydrophilicity and oxygen permeability of the hydrogels are investigated by

contact angle goniometer and oxygen transmission tester.

EXPERIMENTAL

Materials and methods

Methacryloxypropyl tris (trimethylsiloxy) silane (TRIS), 2-hydroxyethyl methacrylate (HEMA), N-vinyl-2-pyrrolidone (NVP), and N,N-dimethylacrylamide (DMA) were purchased from Aldrich and purified by distillation under reduced pressure before use. Isophorone diisocyanate (IPDI) and polydimethylsiloxane with hydroxyl groups at both terminals (KF6002, Mn 3200) were used as received from Deguass and Shin-Etsu, respectively. Free radical photoinitiator Darocur 1173 and cationic photoinitiator 4, 4′-dimethyl diphenyl iodonium hexafluorophosphate were obtained from Ciba and Igm, respectively. Dibutyltin dilaurate (DBTDL), hydroquinone and n-hexanol were used as received from Shanghai Chemical Reagents. Ethylidene-bis-3-(N-vinyl-2-pyrrolidone) (EBVP) was prepared by the method as described in the literature.[8]

Preparation of siloxane macromer[15]

Preparation of siloxane macromer is carried out in two steps. A three necked flask equipped with a mechanical stirrer, a reflux condenser and a thermometer is immersed in an oil bath and charged with 1.60 g of IPDI and 0.14 g of DBTDL. 11.52 g of KF6002 is then added with vigorous stirring for 5 h at 40°C. In the second step, 0.94 g of HEMA and 0.07 g of hydroquinone are added, and the temperature of the reaction mixture is maintained at 80°C. Completion of the reaction is confirmed by the disappearance of the characteristic-NCO peak at 2275 cm^{-1} in the FTIR spectrum, which is recorded on a Bruker Vector 22 FTIR spectrometer in the range 4000–400 cm^{-1}. IR (KBr, cm^{-1}): 1700–1730 (C=O), 3349 (N—H), 1000–1100 (Si—O—Si), 798 (Si—CH$_3$). A representation of this reaction is shown in Scheme 1.

Preparation of hydrogels

Formulations for the preparation of hydrogels are shown in Table I, in which siloxane macromer and EBVP are used as crosslinkers, Darocur 1173 is used as free radical initiator, and 4,4′-dimethyl diphenyl iodonium hexafluorophosphate is used as cationic initiator. The mixture of each formulation is introduced between two glass plates (7.5 cm × 2.5 cm) and cured under a high-pressure mercury lamp emitting overwhelmingly light at 365 nm for 1 h. Film thickness is controlled by a Teflon gasket which gives a fairly consistent thickness of 0.25 mm. The
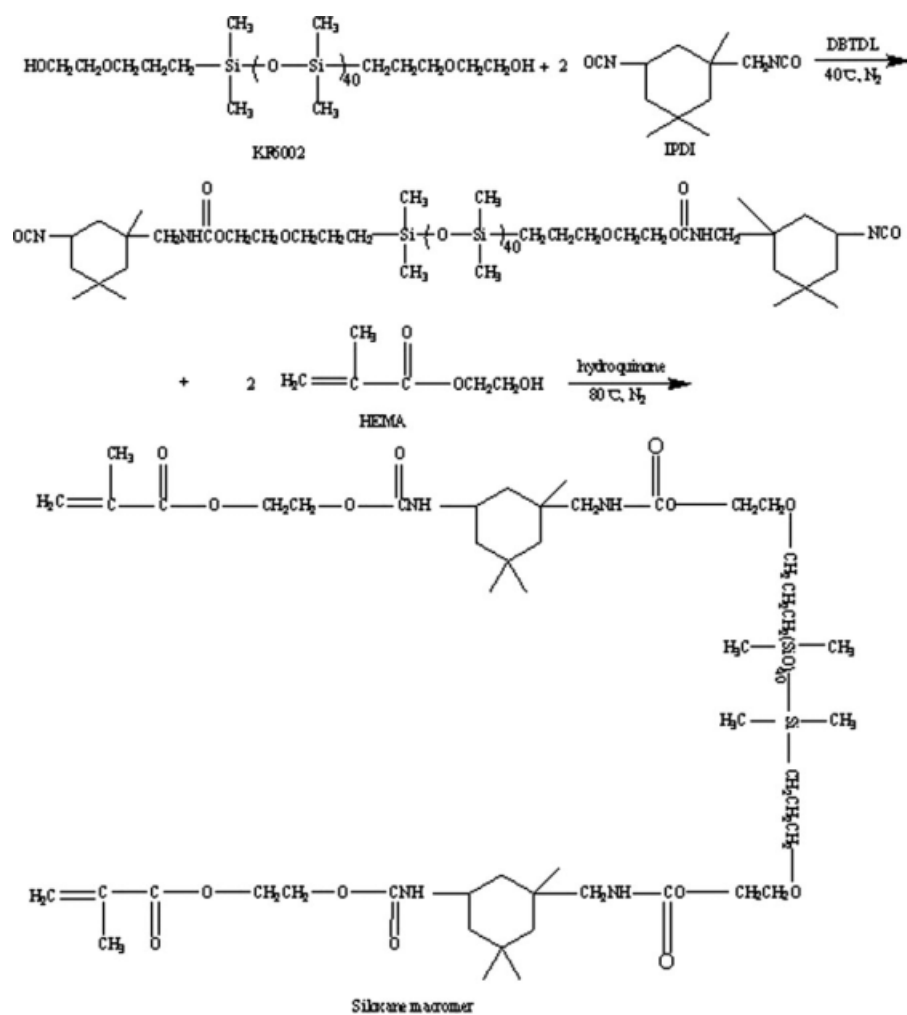
Scheme 1 Synthetic scheme for the siloxane macromer.

TABLE I
Formulations of Free Radical, Cationic and Hybrid Polymerizations and the Corresponding Gel Fractions

Formulation	Siloxane macromer	TRIS	DMA	NVP	EBVP	Darocur 1173	4,4'-dimethyl diphenyl iodonium hexafluorophosphate	Gel fraction (%)
				Feed (wt %)[a]				
1	43	43	14	0	0	0.5	0	88.46
2	0	0	0	100	0.3	0.5	0	0
3	0	0	0	100	0.3	0	0.5	0
4	0	0	0	100	0.3	0.5	0.5	97.59
5	30	30	10	30	0	0.5	0	82.60
6	30	30	10	30	0.3	0.5	0.5	93.48
7	30	30	10	30	0.3	0.5	0	82.46
8	30	30	10	30	0	0.5	0.5	84.30
9	21.5	21.5	7	50	0	0.5	0	74.48
10	21.5	21.5	7	50	0.3	0.5	0.5	95.82
11	13	13	4	70	0	0.5	0	65.50
12	13	13	4	70	0.3	0.5	0.5	96.40
13	39	39	12	10	0.3	0.5	0.5	90.52
14	34	34	12	20	0.3	0.5	0.5	91.75
15	26	26	8	40	0.3	0.5	0.5	94.47

[a] wt % of total monomers including siloxane macromer, TRIS, DMA, and NVP.

TABLE II
Formulation, Water Content and Contact Angle of the IPN Silicone Hydrogels

	Feed (wt %)[a]								
Formulation	Siloxane macromer	TRIS	DMA	NVP	EBVP	Darocur 1173	4,4'-dimethyl diphenyl iodonium hexafluorophosphate	Water content (%)	Contact angle (°)
1	50	30	10	10	0.3	0.5	0.5	22.22	90 ± 2.6
2	40	30	10	20	0.3	0.5	0.5	32.04	82 ± 1.7
3	30	30	10	30	0.3	0.5	0.5	42.44	76 ± 1.8
4	20	30	10	40	0.3	0.5	0.5	52.09	65 ± 1.0
5	10	30	10	50	0.3	0.5	0.5	63.00	57 ± 1.7

[a] wt % of total monomers including siloxane macromer, TRIS, DMA, and NVP.

films are extracted with ethanol and water for 24 h, respectively. Subsequently, the films are swollen to equilibrium in distilled water before characterization and the silicone hydrogels are obtained.

To investigate the water content and contact angle, mechanical properties and the oxygen permeability of silicone hydrogels, specific formulations are designed as listed in Tables II–IV. The preparation of hydrogels is carried out with the same method as described earlier.

Characterization of hydrogels

Gel fraction

The as prepared silicone hydrogels are dried to a constant weight in vacuum and weighed before and after extraction. Gel fraction (G, %) is calculated gravimetrically by the following formula:

$$G = \frac{W_g}{W_o} \times 100\%$$

where, W_o and W_g are the weights of films before and after extraction, respectively.

Fourier transform infrared spectroscopy (FTIR)

The as prepared silicone hydrogels are dried and crushed and made into potassium bromide pellets. FTIR spectra are recorded on a Bruker Vector 22 FTIR spectrometer in the range 4000–400 cm^{-1}.

Differential scanning calorimetry (DSC)

The silicone hydrogels at dry state are sealed in aluminum pans, and measurements are performed by TA Instruments Q10 differential scanning calorimeter under a high-purity continuous helium purge. The samples are subjected to the following thermal cycle: a first heating up to 250°C, then cooling, and a second heating at a scan rate of 10°C/min over a temperature range from −140 to 250°C or 25 to 250°C. The glass transition temperature (T_g) is taken as the onset of heat flow as the function of temperature.

Transmission electron microscope (TEM)

The silicone hydrogels at dry state are embedded in Epon 812 epoxy resin which then polymerized overnight at 60°C. Hundred nanometer ultrathin sections are cut using a Power Tome XL microtome and

TABLE III
Formulation, Modulus and Tensile Strength of the IPN Silicone Hydrogels

	Feed (wt %)[a]								
Formulation	Siloxane macromer	TRIS	DMA	NVP	EBVP	Darocur 1173	4,4'-dimethyl diphenyl iodonium hexafluorophosphate	Modulus (MPa)	Tensile strength (MPa)
1	10	50	10	30	0.3	0.5	0.5	0.95 ± 0.09	0.85 ± 0.06
2	20	40	10	30	0.3	0.5	0.5	1.16 ± 0.07	0.96 ± 0.08
3	30	30	10	30	0.3	0.5	0.5	1.35 ± 1.02	1.18 ± 0.05
4	40	20	10	30	0.3	0.5	0.5	1.43 ± 0.05	1.34 ± 1.04
5	50	10	10	30	0.3	0.5	0.5	1.78 ± 1.05	1.62 ± 0.09

[a] wt % of total monomers including siloxane macromer, TRIS, DMA, and NVP.

TABLE IV
Formulation and Oxygen Permeability of the IPN Silicone Hydrogels

| Formulation | Feed (wt %)[a] | | | | | | | Oxygen permeability, Dk (barrer) |
	Siloxane macromer	TRIS	DMA	NVP	EBVP	Darocur 1173	4,4′-dimethyl diphenyl iodonium hexafluorophosphate	
1	30	30	10	30	0.3	0.5	0.5	118.66
2	35	35	7.5	22.5	0.3	0.5	0.5	133.32
3	40	40	5	15	0.3	0.5	0.5	159.99
4	45	45	2.5	7.5	0.3	0.5	0.5	226.65
5	25	45	7.5	22.5	0.3	0.5	0.5	119.99
6	30	40	7.5	22.5	0.3	0.5	0.5	125.32
7	40	30	7.5	22.5	0.3	0.5	0.5	133.32
8	45	25	7.5	22.5	0.3	0.5	0.5	139.32

[a] wt % of total monomers including siloxane macromer, TRIS, DMA, and NVP.

placed on a 200 mesh formvar coated copper grid. Cross-sections of the films are observed and photographed using a Hitachi H-7650 transmission electron microscope with an 80 kV electron beam.

Water content

The equilibrium water content of the hydrated polymer film is calculated as follows:

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

where, W_s and W_d are the weights of films at hydrated state and dry state respectively.

Contact angle

The water contact angles of the silicone hydrogels are measured at ambient temperature by the sessile drop method, using the Shanghai Zhongchen Digital Technical JC2000C1 goniometer. The contact angle reported here is an averaged value of at least three measurements.

Mechanical test

Stress–strain measurements of hydrated UV-cured films are carried out using an Instron series IX materials testing system at room temperature. Dog-bone shaped samples are cut from the silicone hydrogels (5 mm wide at the narrowest point with a gage length of 15 mm). Thickness of the samples is measured with a digital micrometer having a precision of 1 μm. A crosshead speed of 10 mm/min is used and at least three samples are tested for each type of the samples.

Oxygen permeability

The oxygen permeabilities of the silicone hydrogels are measured by the two-chamber method[16] on a

Mocon OX-TRAN® model 2/21 oxygen transmission rate tester and are expressed as Dk in unit of barrer (1 barrer = 10^{-11} cm^2 mL O$_2$/s mL mmHg).

RESULTS AND DISCUSSION

Preparation of silicone hydrogels

Table I lists the formulations for the preparation of silicone hydrogels. The high pressure mercury lamp chosen in this study emits light at 365 nm, which can directly excite the decomposition of Darocur 1173. In the photopolymerization process of the silicone hydrogels, the free radical initiator Darocur 1173 not only serves to initiate the radical polymerization, but also activates the cationic polymerization.[17] For the formulation 2 containing free radical initiator and the formulation 3 containing only cationic initiator, no gel is detected as showed in Table I. The result reveals that NVP can not form crosslinked network using EBVP as a crosslinker in the presence of free radical initiator or cationic initiator lonely. While both of the free radical and cationic initiators are used for the formulation 4 in Table I, the gel fraction reaches up to 97.59%. It means that NVP can polymerize sufficiently initiated by a combination of free radical and cationic initiators. It is proposed that the copolymerization of NVP with EBVP is initiated by cationic initiator 4,4′-dimethyl diphenyl iodonium hexafluorophosphate which is activated by radical initiator Darocur 1173[14,18] and experiences cationic mechanism.[18]

For the polymerization system of DMA, TRIS and NVP in the presence of the crosslinker siloxane macromer and free radical initiator (formulation 5 in Table I), the gel fraction is 82.60%, signifying that the formulation 5 could undergo free radical polymerization. When another crosslinker EBVP (formulation 7 in Table I) is added into this formulation, the gel fraction shows no significant increase

indicating that the crosslinker EBVP can not improve polymerization of formulation 7. When the cationic initiator is incorporated into the formulation 5 as shown in formulation 8, there is little difference between the gel fractions of the obtained hydrogels. The results reveal that the formulation can not undergo cationic polymerization if the crosslinker EBVP is not added.

For the polymerization of formulation 1 in Table I, it is revealed that siloxane macromer, TRIS and DMA polymerize well in the presence of the radical initiator. For the polymerization of siloxane macromer, TRIS, DMA and NVP in the presence of the radical initiator (formulations 5, 9 and 11 in Table I), the gel fractions are 82.60%, 74.48%, and 65.50%, respectively. It means that the gel fraction decreases with the increase of the NVP content in the formulation, signifying poor copolymerization of acrylate monomers with NVP. For the polymerization of DMA, TRIS, and NVP using the crosslinkers of siloxane macromer and EBVP in the presence of the free radical and cationic initiators (formulations 6, 10, and 12 in Table I), the gel fractions reach up to more than 93%. The result reveals that Darocur 1173 not only initiates the radical copolymerization of acrylate monomers and NVP, but also activates the cationic initiator to initiate the cationic polymerization of NVP in the presence of EBVP. The obtained silicone hydrogel may consist of two IPNs. One is a copolymeric network of acrylate monomers and NVP formed by radical polymerization, and the other is a NVP-crosslinked homopolymer network formed by cationic mechanism. Figure 1 summarizes the hybrid polymerization mechanism of siloxane macromer, TRIS, DMA and NVP with the free radical initiator Darocur 1173 in conjunction with the cationic initiator.

FTIR analysis

FTIR spectra of NVP-crosslinked homopolymer network derived from formulation 4 in Table I, acrylate
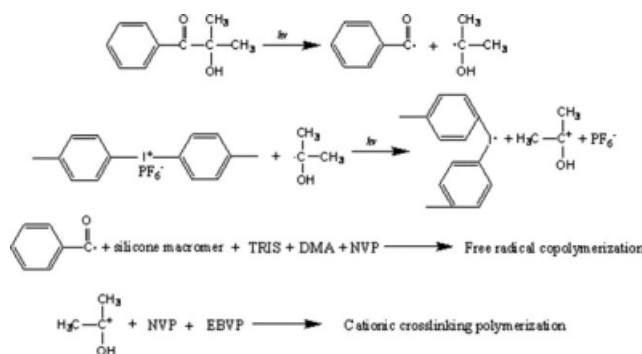

Figure 1 Free radical and free radical promoted cationic photopolymerizations.
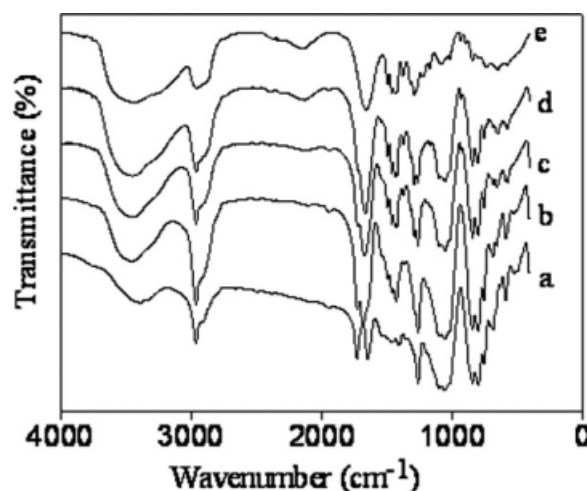
Figure 2 FTIR spectra of dried hydrogels derived from: (a) formulation 1, (b) formulation 8, (c) formulation 10, (d) formulation 12, (e) formulation 4 as cited in Table I.

network derived from formulation 1 in Table I and IPN silicone hydrogels derived from formulations 8, 10, and 12 in Table I are shown in Figure 2. The spectrum of NVP-crosslinked homopolymer network [Fig. 2(e)] has a peak centered at 1291 cm^{-1}, a characteristic absorption for C—N stretching. The absorption peak at 1656 cm^{-1} is associated with the C=O group. The acrylate network [Fig. 2(a)] has the characteristic bands at 1261 cm^{-1} and 1057 cm^{-1} assigned to Si—CH$_3$ stretching and Si—O stretching respectively. The peaks at 1647 cm^{-1} and 1728 cm^{-1} are due to the presence of hydrogen-bonded and nonhydrogen-bonded carbonyl groups respectively.[19,20] The spectra of IPN silicone hydrogels present the characteristic adsorption bands of the NVP-crosslinked homopolymer network and acrylate network as revealed in Figures 2(b–d). No new peak, which might indicate chemical crosslinking, appears. For the IPN silicone hydrogels, the intensities of Si—O and Si—CH$_3$ peaks increase with acrylate monomer content in the formulation, and the intensity of C—N peak increases with NVP content in the formulation. For the carbonyl peaks in the IPN silicone hydrogels derived from the formulation 10 in Table I containing 50 wt % NVP [Fig. 2(c)] and formulation 12 in Table I containing 70 wt % NVP [Fig. 2(d)], the dominant portion of hydrogen-bonded is informed from stronger peak at 1647 cm^{-1} rather than at 1728 cm^{-1}. The peak of nonhydrogen-bonded carbonyl group nearly disappears, signifying that hydrogen bonding is strengthened between the NVP-crosslinked homopolymer network and acrylate-NVP copolymeric network. Furthmore, comparing the peak of carbonyl group in the acrylate network with that of the IPN silicone hydrogel derived from the formulation 8 in Table I containing 30 wt % NVP [Fig. 2(b)], the frequency of the
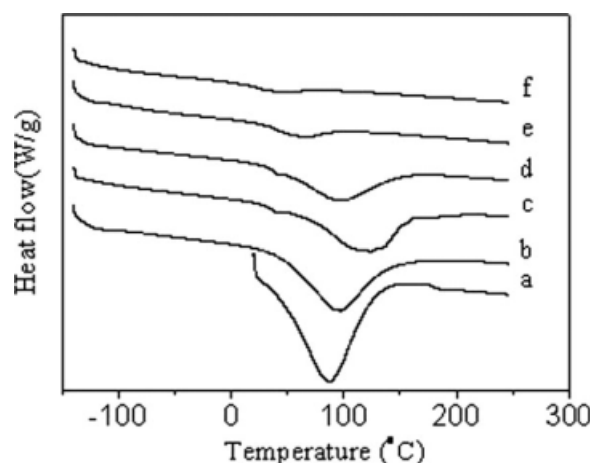
Figure 3 DSC curves of dried hydrogels derived from: (a) formulation 4, (b) formulation 12, (c) formulation 10, (d) formulation 8, (e) formulation 13, (f) formulation 1 as cited in Table I.

nonhydrogen-bonded carbonyl group shifts to the lower value, also indicating that the strength of the hydrogen bonding becomes stronger.[21]

Differential scanning calorimetry analysis

The DSC curves of acrylate network derived from formulation 1 in Table I, NVP-crosslinked homopolymer network derived from formulation 4 in Table I and IPN silicone hydrogels derived from formulations 8, 10, 12, and 13 in Table I as a function of temperature are plotted in Figure 3. The glass transition temperature (T_g) of the acrylate network is found to be 39°C [Fig. 3(f)], reflecting the easy mobility of the network,[21] and that of the NVP-crosslinked homopolymer network is 86°C [Fig. 3(a)] in agreement with the result reported in the literature.[22] For the IPN silicone hydrogels derived from the formulation 10 in Table I containing 50 wt % NVP [Fig. 3(c)] and the formulation 8 in Table I containing 30 wt % NVP [Fig. 3(d)], they both exhibit two T_gs, corresponding to those of acrylate-NVP copolymeric network and NVP-crosslinked homopolymer network. The result implies that the microphase separation occurs in the IPN silicone hydrogels. For the silicone hydrogels, the elevation of T_g for each network indicates that the molecular motion of one network in the IPN hydrogels is limited by the other network because of the interaction between the networks.[23] The disappearance of T_g for NVP-crosslinked homopolymer network and the shifting of T_g to higher temperature (64°C) for acrylate-NVP copolymeric network are observed for the IPN silicone hydrogel derived from the formulation 13 in Table I containing 10 wt % NVP [Fig. 3(e)]. In addition, the disappearance of T_g for acrylate-NVP copolymeric network and the shifting of T_g to higher temperature (96°C) for

NVP-crosslinked homopolymer network can be observed from the IPN hydrogel derived from the formulation 12 in Table I containing 70 wt % NVP [Fig. 3(b)]. The results can be explained that the molecular motions of one of the networks in the IPN hydrogels nearly inhibit the molecular motions of the other network due to the strong intermolecular interaction between the two networks in the IPN hydrogels.

Morphology of the IPN silicone hydrogels

Figure 4 shows the morphology of hydrogels observed by TEM. The images reveal the heterogeneous morphology with phase domain size ranging from less than 30 nm [Fig. 4(a,b)], 100 nm [Fig. 4(c)] to 400 nm [Fig. 4(d)]. Clearly, for the IPN silicone hydrogel derived from the formulation 13 in Table I containing 10 wt % NVP [Fig. 4(a)], the NVP-crosslinked homopolymer network as a dispersed phase are proportionally distributed well in the acrylate-NVP copolymeric network, which suggests a certain degree of miscibility between the two networks.[24] With the increase of the NVP content in the formulation, the bright domain is extended and dual-continuity phases are observed for the IPN silicone hydrogels derived from the formulation 8 in Table I containing 30 wt % NVP [Fig. 4(b)] and the formulation 10 in Table I containing 50 wt % NVP [Fig. 4(c)]. Furthermore, the images provide more direct evidence that the IPN silicone hydrogel derived from the formulation containing 30 wt % NVP has greater degree of interpenetration than that derived from the formulation containing 50 wt % NVP. The morphology of the dual-phase continuity of IPN silicone hydrogels derived from formulations containing 30 wt % and 50 wt % NVP determines two T_gs as revealed in Figure 3(c,d). For the IPN silicone hydrogel derived from the formulation 12 in Table I containing 70 wt % NVP [Fig. 4(d)], the phase inversion starts and the phase of the NVP-crosslinked homopolymer network becomes the more continuous due to the changes of component ratio.

Water content and contact angle

The water content and contact angle of IPN silicone hydrogels are listed in Table II. To remove the effect of DMA and TRIS on the water content and contact angle result, the two components in different formulations are set as the same content.

The water content increases with the NVP content in the formulations. It is assumed that the amount of water molecules diffusing into the silicone hydrogels increase with the NVP content due to the hydrophilicity of the monomer NVP. The contact angle of IPN silicone hydrogels decreases from 90° to 57°
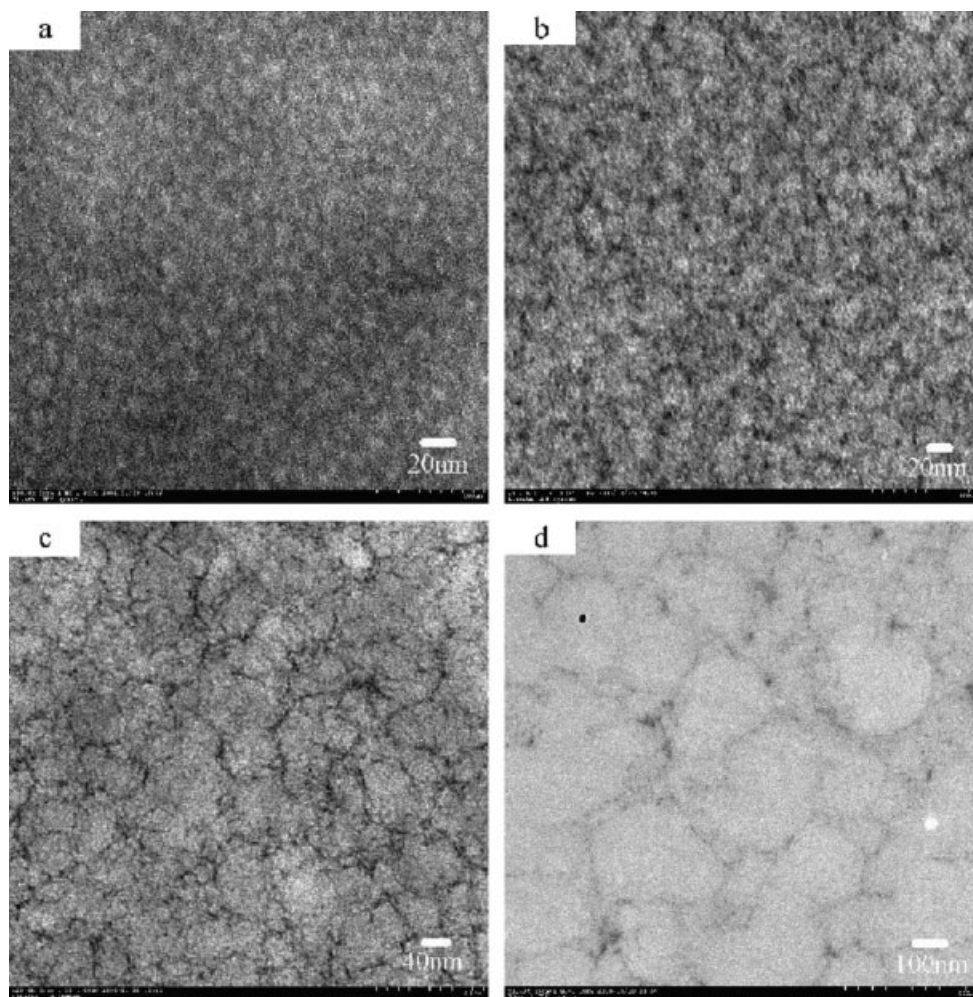
Figure 4 TEM images of dried hydrogels derived from: (a) formulation 13, (b) formulation 8, (c) formulation 10, (d) formulation 12 as cited in Table I.

when the NVP content in the formulation increases from 10 wt % to 50 wt %. This is probably because that when more amount of NVP is incorporated into the IPN silicone hydrogels, the amount of NVP-crosslinked homopolymer network enriched on the surface becomes larger.[10] Therefore, the surface wettability increases with the NVP content in the formulation.

Mechanical properties

The modulus and tensile strength of the IPN silicone hydrogels tested in the hydrated state are summarized in Table III. The hydrogels used for the mechanical property characterization are prepared with the same content of hydrophilic monomers DMA and NVP in different formulations. Both of the modulus and tensile strength decrease with the increase of the TRIS content in the formulations. The phenomenon may be explained that the overall crosslinking density of the hydrogels is reduced as the

amount of TRIS is increased. The silicone hydrogels possess excellent tensile strength and the maximum value reaches 1.62 MPa. These results reveal that the IPN silicone hydrogels may be good candidate of the contact lens materials.

Oxygen permeability

The oxygen permeability of the IPN silicone hydrogels derived from siloxane macromer, TRIS, DMA and NVP is shown in Table IV. The oxygen permeability of the IPN silicone hydrogels increases with the amount of silicon-containing monomers in the formulation. The oxygen permeability Dk is 118.66 barrer when 60 parts of the silicon-containing monomers are used, and increases up to 226.65 barrer when the content of silicon-containing monomers is 90 parts. The effect of siloxane macromer/TRIS ratio on oxygen permeability with their total amounts of 70 parts in the formulation is demonstrated from formulation 5 to formulation 8 in Table IV. The
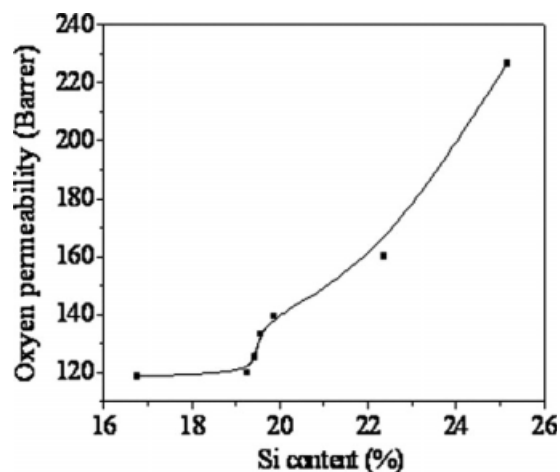
Figure 5 Relationship between oxygen permeability of IPN silicone hydrogels and Si content in the hydrogel.

oxygen permeability of the silicone hydrogels shows no significant change because the siloxane macromer and TRIS have almost the same Si content (29.4% for siloxane macromer and 26.5% for TRIS).[25,26]

Relationship between Si content in the hydrogel and oxygen permeability of the silicone hydrogels is shown in Figure 5. The Si content in the hydrogel is calculated as follows: first, the values of siloxane macromer and TRIS contents in the formulations are respectively multiplied by % Si content of siloxane macromer and TRIS. Then, both values are added to obtain the Si content in the hydrogel. The oxygen permeability bottoms out at 118.66 barrer with a Si content of 17% and reaches up to the maximum value of 226.65 barrer with the Si content of 25%. The results indicate that the oxygen permeability of silicone hydrogels depends on the Si content irrespective of whether it comes from monomer TRIS or siloxane macromer.[25,26]

CONCLUSION

The IPN silicone hydrogels are prepared by the hybrid photopolymerization of acrylate monomers including siloxane macromer, methacryloxypropyl tris (trimethylsiloxy) silane (TRIS) and *N,N*-dimethylacrylamide (DMA)/*N*-vinyl-2-pyrrolidone (NVP) in the presence of free radical and cationic photoinitiators. The obtained silicone hydrogels comprise two networks, one NVP-crosslinked homopolymer network and the other acrylate-NVP copolymeric network. The IPN hydrogels have the heterophase morphology and only physical entrapment between the networks. Furthermore, the silicone hydrogels possess hydrophilic surfaces and excellent mechanical properties. The tensile strength of the silicone hydrogels reaches as high as 1.62 MPa. The oxygen permeability increases with the Si content in the hydrogel and reaches up to the maximum value of 226.65 barrer with the Si content of 25%. The results indicate that the IPN silicone hydrogels have potential applications in the area of gas permeable contact lenses without surface modification.

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