

IMPROVED OXYGEN PERMEABILITY AND MECHANICAL STRENGTH OF SILICONE HYDROGELS WITH INTERPENETRATING NETWORK STRUCTURE*

Jing-jing Wang and Xin-song Li**

*Biomaterials and Drug Delivery Laboratories, School of Chemistry and Chemical Engineering,
Southeast University, Nanjing 211189, China*

Abstract The interpenetrating polymer network (IPN) silicone hydrogels with improved oxygen permeability and mechanical strength were prepared by UV-initiated polymerization of monomers including methacryloxypropyl tris(trimethylsiloxy)silane (TRIS), 2-hydroxyethylmethacrylate (HEMA) and *N*-vinyl pyrrolidone (NVP) in the presence of free radical photoinitiator and cationic photoinitiator. The polymerization mechanism was investigated by the formation of gel network. The structure of IPN hydrogels was characterized by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and transmission electron microscopy (TEM). The results showed that the IPN hydrogels exhibited a heterogeneous morphology. The mechanical properties, surface wettability and oxygen permeability were examined by using a tensile tester, a contact angle goniometer and an oxygen transmission tester, respectively. The equilibrium water content of the hydrogels was measured by the gravimetric method. The results revealed that the IPN hydrogels possessed hydrophilic surface and high water content. They exhibited improved oxygen permeability and mechanical strength because of the incorporation of TRIS.

Keywords: Interpenetrating polymer network; Silicone hydrogel; Photopolymerization; Oxygen permeability; Mechanical strength.

INTRODUCTION

Hydrogels are crosslinked hydrophilic polymers that can absorb substantial amounts of water while maintaining a distinct three-dimensional structure^[1–3]. They have widely been used in the areas of contact lenses. Conventional hydrogel contact lenses are commonly prepared by copolymerization of various monomers such as 2-hydroxyethylmethacrylate (HEMA), *N*-vinyl pyrrolidone (NVP) and methacrylic acid (MAA)^[4]. Because of poor copolymerization of NVP and (meth)acrylate functional monomers^[5–7], the resulting materials often show inconsistent quality, such as poor mechanical properties and water content. Lai^[5] studied the copolymerization of NVP and HEMA, finding that ethylene glycol dimethacrylate (EGDMA) was 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. Ethylidene-bis-3-(*N*-vinyl-2-pyrrolidone) (EBVP), containing two NVP units bounding together with an ethylidene linkage, can crosslink NVP sufficiently^[8].

The conventional hydrogel contact lenses usually show low oxygen permeability, which is directly proportional to their water contents, falling in the range of 8–40 barrer^[9]. Because of the relatively insufficient oxygen permeability of these hydrogel lenses, and of the physical and physiological limitation of highly

* This work was financially supported by the National Natural Science Foundation of China (Nos. 50573011 and 50673019).

** Corresponding author: Xin-song Li (李新松), E-mail: lixs@seu.edu.cn

Received October 9, 2009; Revised December 7, 2009; Accepted December 16, 2009

doi: 10.1007/s10118-010-9142-6

hydrated hydrogel contact lenses, the available conventional hydrogel lenses do not transmit the minimum oxygen requirement of the cornea under the closed eyelid conditions. Therefore, all the individuals who use the conventional hydrogel lenses under extended wear conditions will cause corneal edema^[10]. In the past decade, silicone hydrogel contact lenses, combining softness and comfort of hydrogel and higher oxygen permeability of siloxane, have been developed for the extended wearing of one month. They are prepared by the copolymerization of siloxane macromer, hydrophobic comonomer and hydrophilic comonomer. The silicone hydrogels have to experience surface modification to improve the hydrophilicity for the application of contact lenses. However, extra steps, specialized equipment and complicated procedures can increase overall manufacturing costs.

An alternative approach to prepare hydrogels is using the interpenetrating polymer networks (IPN) technique. It can combine the properties of several polymeric materials into a new material with the improvement of the mechanical properties^[11]. Polymerization of monomers which experience different mechanisms, *e.g.* radical and cationic types, is a strategy for the preparation of IPN. Actually, hybrid free-radical/cationic photopolymerization is an effective way, which can combine the advantages of these two classes of photopolymerization^[12–14]. In our previous report^[15], hybrid free-radical/cationic photopolymerization of HEMA and NVP in the presence of free radical and cationic initiators has been employed to prepare IPN hydrogels. During the photopolymerization process, HEMA and NVP copolymerized by free radical mechanism; meanwhile, the free radical initiator activated the cationic initiator to initiate the cationic polymerization of NVP in the presence of the crosslinker EBVP. The IPN hydrogels possessed high-water-content and anti-dehydration ability because of the incorporation of poly(*N*-vinyl pyrrolidone) (PVP) network^[15].

The oxygen permeability and mechanical strength are key performance characteristics for hydrogel contact lenses. Methacryloxypropyl tris(trimethylsiloxy)silane (TRIS) has been used extensively in the development of rigid gas permeable lens materials with good oxygen permeability^[9]. In this report, the interpenetrating polymer network (IPN) silicone hydrogels are prepared by UV-initiated hybrid photopolymerization of monomers including TRIS and HEMA/NVP in the presence of free radical photoinitiator and cationic photoinitiator in order to improve the oxygen permeability and mechanical strength. The IPN hydrogels are examined by FTIR, DSC and TEM. Mechanical property, oxygen permeability and surface wettability of the IPN hydrogels are further investigated.

EXPERIMENTAL

Materials

N-vinyl-2-pyrrolidone (NVP) and 2-hydroxyethyl methacrylate (HEMA) were purchased from Aldrich chemical Co. and purified by distillation under reduced pressure before use. Methacryloxypropyl tris(trimethylsiloxy)silane (TRIS) and ethylene glycol dimethacrylate (EGDMA) were purchased from Aldrich chemical Co. and used without further purification. Free radical photoinitiator Darocur 1173 and cationic photoinitiator 4,4'-dimethyl diphenyl iodonium hexafluorophosphate were obtained from Ciba Co. and Igm Inc. respectively. Ethylidene-bis-3-(*N*-vinyl-2-pyrrolidone) (EBVP) was prepared by the method as described in the literature^[8].

Preparation of Hydrogels

The hydrogels are prepared with the formulations as shown in Table 1 with EGDMA and EBVP as crosslinkers, Darocur 1173 as free radical initiator, and 4,4'-dimethyl diphenyl iodonium hexafluorophosphate 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 UV light at 365 nm for 1 h, and polymer film is obtained. The film thickness is controlled by a Teflon gasket which gives a fairly consistent thickness of 0.25 mm. The films are weighed (W_0), and then extracted with ethanol for 48 h. The obtained IPN hydrogels are washed and kept in distilled water for further characterization with Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and transmission electron microscopy (TEM).

Table 1. Formulations of free radical, cationic and hybrid photopolymerizations and their gel fractions

Sample	Feed (wt%)*						4,4'-Dimethyl diphenyl iodonium hexafluorophosphate	Gel fraction, G (%)
	TRIS	HEMA	NVP	EGDMA	EBVP	Darocur 1173		
1	66.5	33.5	0	0.3	0	0.5	0	95.29
2	0	0	100	0	0.3	0.5	0	0
3	0	0	100	0	0.3	0	0.5	0
4	0	0	100	0	0.3	0.5	0.5	97.72
5	46.5	23.5	30	0.3	0	0.5	0	87.66
6	46.5	23.5	30	0.3	0.3	0.5	0.5	99.44
7	33.5	16.5	50	0.3	0	0.5	0	81.11
8	33.5	16.5	50	0.3	0.3	0.5	0.5	98.74
9	20.0	10.0	70	0.3	0	0.5	0	61.93
10	20.0	10.0	70	0.3	0.3	0.5	0.5	98.30

* Weight per cent of total monomers including TRIS, HEMA and NVP

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

$$G = \frac{W_g}{W_0} \times 100\%$$

where, W_0 and W_g are the weights of film before and after extraction, respectively.

In order to confirm the presence of the NVP homopolymer network in the IPN hydrogels, the degradation experiment is carried out as follows. The IPN hydrogel derived from formulation 8, NVP homopolymer hydrogel crosslinked by EBVP derived from formulation 4 and copolymeric hydrogel of HEMA, TRIS and NVP derived from formulation 7 in Table 1 are treated in 5 mol/L NaOH aqueous solutions at 70°C for 6 h, and then extracted in water thoroughly. Then the residues after extraction are characterized by FTIR.

Table 2. The formulations for the preparation of IPN hydrogels and poly(HEMA-co-NVP) hydrogels

Sample	Feed (wt%)*						4,4'-Dimethyl diphenyl iodonium hexafluorophosphate	Gel fraction, G (%)
	TRIS	HEMA	NVP	EGDMA	EBVP	Darocur 1173		
IPN hydrogel 1	10	18	72	0.3	0.3	0.5	0.5	98.15
IPN hydrogel 2	15	17	68	0.3	0.3	0.5	0.5	98.32
IPN hydrogel 3	20	16	64	0.3	0.3	0.5	0.5	98.51
IPN hydrogel 4	25	15	60	0.3	0.3	0.5	0.5	98.60
IPN hydrogel 5	30	14	56	0.3	0.3	0.5	0.5	98.69
Poly(HEMA-co-NVP) hydrogel 1	0	28	72	0.3	0	0.5	0	60.82
Poly(HEMA-co-NVP) hydrogel 2	0	32	68	0.3	0	0.5	0	64.29
Poly(HEMA-co-NVP) hydrogel 3	0	36	64	0.3	0	0.5	0	71.36
Poly(HEMA-co-NVP) hydrogel 4	0	40	60	0.3	0	0.5	0	75.48
Poly(HEMA-co-NVP) hydrogel 5	0	44	56	0.3	0	0.5	0	80.04

* Weight per cent of total monomers including TRIS, HEMA and NVP

In order to investigate the effect of TRIS on the water content, mechanical properties and surface wettability of hydrogels, special formulations are designed as listed from formulations 1 to 5 in Table 2. The preparation of hydrogels is carried out with the same method as described above. For comparison, poly(HEMA-

co-NVP) hydrogels are prepared with the formulations as listed from formulations 6 to 10 in Table 2, in which EGDMA is used as the crosslinker, Darocur 1173 is used as the free radical initiator. The gel fractions are measured as shown in Table 2.

Characterization of Hydrogels

Fourier transform infrared spectroscopy (FTIR)

The IPN hydrogels derived from the formulations as cited in Table 1 are dried and crushed and made into potassium bromide pellets. FTIR spectra are recorded on a Bruker Vector 22 FTIR spectrometer in the range of 4000–400 cm^{-1} .

Differential scanning calorimetry (DSC)

The IPN hydrogels derived from the formulations as cited in Table 1 at dry state are sealed in aluminum pans, and measurements are performed by a 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 K/min over a temperature range from 20°C to 180°C. The glass transition temperature (T_g) is taken as the onset temperature of heat flow change with increasing temperature.

Transmission electron microscopy (TEM)

The IPN hydrogels derived from the formulations as cited in Table 1 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 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.

Mechanical test

Stress-strain measurements of hydrogels derived from the formulations as cited in Table 2 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.

Contact angle

The water contact angles of the hydrogels derived from the formulations as cited in Table 2 are measured at ambient temperature by the sessile drop method, using a JC2000C1 goniometer (Shanghai Zhongchen Digital Technical Co.). The contact angle reported here is an averaged value of at least three measurements.

Oxygen permeability

The oxygen permeability of the hydrogels derived from the formulations as cited in Table 2 is measured by the two-chamber method^[16] on a permeometer model 201T (Rheder Development Co.) and is expressed as Dk in unit of barrer (1 barrer = $7.5 \times 10^{-14} \text{ m}^2 \text{ mL O}_2/(\text{s mL Pa})$).

RESULTS AND DISCUSSION

Preparation of IPN Silicone Hydrogels by Hybrid Photopolymerization

The IPN silicone hydrogels are prepared by UV-initiated hybrid photopolymerization of monomers including TRIS and HEMA/NVP in the presence of free radical photoinitiator and cationic photoinitiator. In order to have an insight into the mechanism of the hybrid photopolymerization of HEMA, TRIS and NVP, several formulations are designed and listed in Table 1. Their corresponding gel fractions are also summarized in Table 1.

Darocur 1173 can be used as the effective free radical photoinitiator to initiate the radical polymerization^[17–21], which is confirmed by the gel fraction of the polymerization of HEMA and TRIS using

EGDMA as the crosslinker in the presence of Darocur 1173 (formulation 1).

Formulations 2, 3 and 4 in Table 1 are designed to confirm that NVP can photopolymerize by the cationic mechanism. For the polymerization of NVP using EBVP as the crosslinker in the presence of only free radical initiator (formulation 2) or cationic initiator (formulation 3), no gel is detected. The result demonstrates that NVP can not polymerize efficiently using EBVP as the crosslinker in the presence of only free radical initiator or only cationic initiator. While both of the free radical and cationic initiators are used together (formulation 4), the gel fraction of the photopolymerization of NVP reaches up to 97.77%. It suggests that NVP can polymerize sufficiently using EBVP as the crosslinker initiated by a combination of free radical and cationic initiators. The results could be explained as follows. Although the cationic photoinitiator 4,4'-dimethyl diphenyl iodonium hexafluorophosphate itself could only absorb the UV light below 300 nm, the hydroxy benzyl radicals photochemically generated from the free radical initiator Darocur 1173 reduce the cationic photoinitiator to yield corresponding carbocations capable of initiating cationic polymerization of NVP^[14, 22–24]. In fact, the polymerization of NVP by the cationic mechanism has been confirmed by the previous studies^[25–30]. Therefore the free radical initiator Darocur 1173 not only serves to initiate the radical polymerization, but also activates the cationic polymerization.

For the copolymerization of HEMA, TRIS and NVP using EGDMA as the crosslinker in the presence of free radical initiator Darocur 1173 (formulations 5, 7 and 9 in Table 1), the gel fractions are 87.66%, 81.11% and 61.93% respectively. Obviously, the gel fraction decreases with the increase of NVP content in the formulation due to the poor copolymerization of (meth)acrylate functional monomers and NVP. However, for the polymerization systems of HEMA, TRIS and NVP using EGDMA and EBVP as crosslinkers in the presence of the free radical and cationic initiators (formulations 6, 8 and 10 in Table 1), the gel fraction reaches up to more than 98%. The results indicate that Darocur 1173 not only initiates the radical copolymerization of HEMA, TRIS and NVP, but also activates the cationic initiator to initiate the cationic polymerization of NVP in the presence of EBVP^[14, 22–24]. The hybrid photopolymerization mechanism of HEMA, TRIS and NVP with the free radical initiator Darocur 1173 in conjunction with the cationic initiator is summarized in Fig. 1. As discussed above, the hydrogels prepared by hybrid photopolymerization of HEMA, TRIS and NVP consist of two interpenetrating polymer networks (IPNs). One is a copolymeric network of HEMA, TRIS and NVP formed by radical polymerization, and the other is a NVP homopolymer network formed by cationic mechanism.

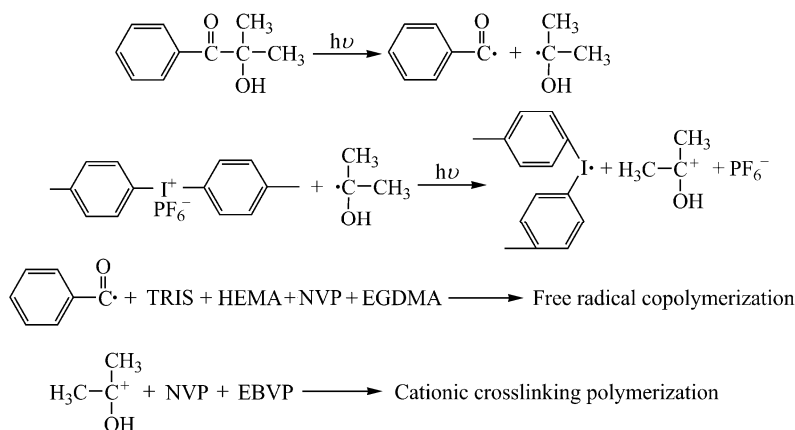


Fig. 1 Free radical and free radical promoted cationic photopolymerizations

In order to provide more evidence of the NVP homopolymer network in the IPN hydrogels, further degradation experiment is carried out^[31]. It is found that the copolymeric network derived from formulation 7 using the crosslinker EGDMA degrades totally. The IPN hydrogels derived from formulation 8 have a dry

residue of 25% after degradation and extraction. The NVP homopolymer network derived from formulation 4 after degradation has a dry residue of 100%. Figure 2 shows the spectra of the residues. No difference among the spectra of the residues, but clear distinction between the spectra of the IPN hydrogel derived from formulation 8 before and after extraction is observed as revealed in Fig. 2. The characteristic band at 1259 cm^{-1} assigned to the $\text{Si}-\text{CH}_3$ stretching disappears for the IPN hydrogel after extraction. It's assumed that the degradation has no significant effect on the NVP homopolymer network in the IPN hydrogels. Due to the degradation of the crosslinker EGDMA in the NaOH solution, the copolymeric network of HEMA, TRIS and NVP crosslinked by EGDMA is extracted from the IPN hydrogel. Therefore, the residue of the IPN hydrogel after extraction probably is the NVP homopolymer network.

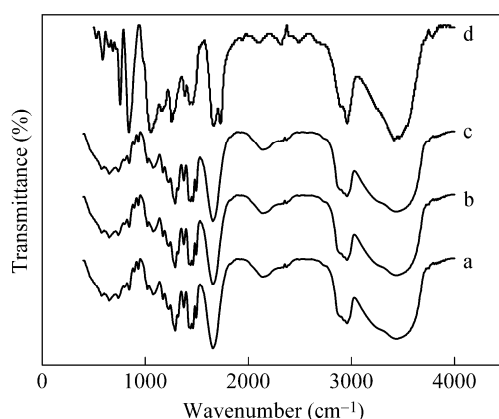


Fig. 2 FTIR spectra for dried samples of hydrogels derived from (a) formulation 4 in Table 1 without degradation, (b) formulation 4 in Table 1 after degradation, (c) formulation 8 in Table 1 after degradation and (d) formulation 8 in Table 1 without degradation

FTIR Analysis

FTIR spectra of four dried hydrogels are shown in Fig. 3. The spectrum of NVP-crosslinked homopolymer network derived from the formulation 4 in Table 1 (Fig. 3a) shows a peak at 1286 cm^{-1} , a characteristic peak for the $\text{C}-\text{N}$ stretching. The absorption peak at 1646 cm^{-1} is associated with the $\text{C}=\text{O}$ group. The acrylate network derived from the formulation 1 in Table 1 (Fig. 3d) has the characteristic band at 1259 cm^{-1} assigned to the $\text{Si}-\text{CH}_3$ stretching. The peak at 1731 cm^{-1} is due to the presence of the carbonyl group, as reported elsewhere. The spectra of IPN hydrogels derived from the formulations 6 and 10 in Table 1 present the characteristic adsorption bands of the NVP-crosslinked homopolymer network and the acrylate network as revealed in Figs. 3(b) and 3(c). No new peak, which might indicate chemical crosslinking, appears. For the IPN hydrogels, the intensity of $\text{Si}-\text{CH}_3$ peak increases with the content of acrylate monomers in the formulations, and intensity of $\text{C}-\text{N}$ peak increases with content of NVP in the formulations. The IPN hydrogels derived from the formulation 6 in Table 1 containing 30 wt% NVP (Fig. 3c) and the formulation 10 in Table 1 containing 50 wt% NVP (Fig. 3b) have the peaks centered at 1646 cm^{-1} and 1731 cm^{-1} , which might be due to the presence of hydrogen-bonded and nonhydrogen-bonded carbonyl groups respectively as reported in the literature^[32, 33]. The peak at 1731 cm^{-1} becomes weaker with the increase of NVP content in the formulations signifying weakened hydrogen bonding between polymer networks.

Differential Scanning Calorimetry Analysis

The DSC curves of dried hydrogels as a function of temperature are plotted in Fig. 4. The glass transition temperature (T_g) of the pure acrylate network derived from the formulation 1 in Table 1 is found to be 40°C (Fig. 4a), reflecting the easy mobility of the network^[34], and that of NVP-crosslinked homopolymer network derived from the formulation 4 in Table 1 is 83°C (Fig. 4e) in agreement with the result reported in the literature^[35]. Although the IPN hydrogels derived from the formulations 6, 8 and 10 in Table 1 consist of two

different polymer networks which possess different T_g s, it is notable that a single T_g , indicating the excellent compatibility of the polymer chains, is observed for these IPN hydrogels in the region from 50°C to 200°C as indicated in Fig. 4. The IPN hydrogels have the T_g value higher than that of the acrylate network and NVP-crosslinked homopolymer network, which is ascribed to interactions between the networks which act as hydrogen bonding and physical entrapment, thus reducing the mobility of polymer chains.

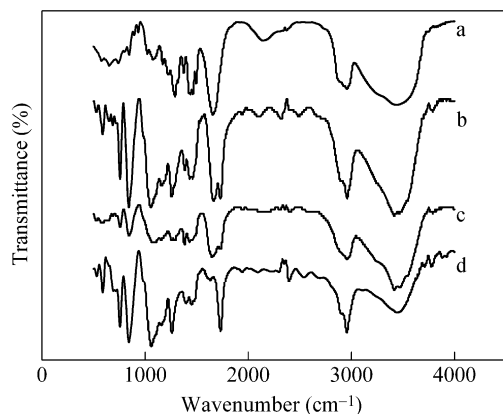


Fig. 3 FTIR spectra of dried hydrogels derived from (a) formulation 4, (b) formulation 8, (c) formulation 6 and (d) formulation 1 as cited in Table 1

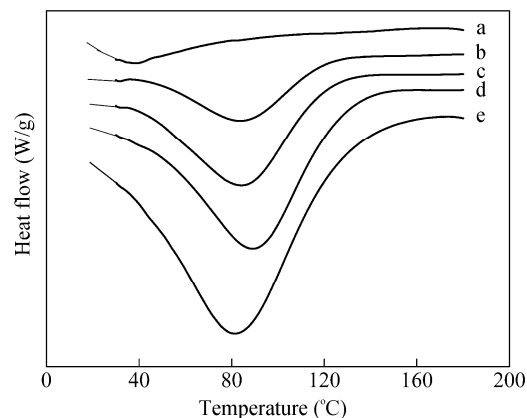


Fig. 4 DSC curves of dried hydrogels derived from (a) formulation 1, (b) formulation 6, (c) formulation 8, (d) formulation 10 and (e) formulation 4 as cited in Table 1

TEM Analysis

Figure 5 shows the morphology of IPN hydrogels observed by TEM. The hydrogels are heterogeneous with phase domain sizes less than 20 nm. It is assumed that interpenetrating process between the NVP-crosslinked homopolymer network and acrylate-NVP copolymeric network improves their compatibility^[36]. Furthermore, the hydrogel derived from formulation 6 has smaller phase domain size than that derived from formulation 8 in Table 1, which suggests the higher degree of compatibility between the two networks in the IPN hydrogel.

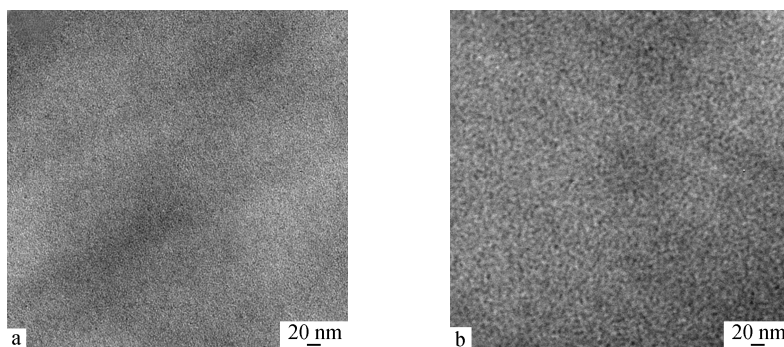


Fig. 5 TEM images of dried hydrogels derived from (a) formulation 6 and (b) formulation 8 as cited in Table 1

Water Content and Contact Angle Measurements

In order to compare the properties of the IPN hydrogels with those of the poly(HEMA-*co*-NVP) hydrogels, special formulations are designed as listed in Table 2. As shown in Table 2, the gel fractions of IPN hydrogels 1–5 are more than 98%, signifying the monomers could polymerize efficiently. For the poly(HEMA-*co*-NVP) hydrogels 1–5, the gel fractions are less than 81%. The result confirms the poor copolymerization between acrylate monomers (HEMA and TRIS) and NVP.

The water content and contact angle of the IPN hydrogels 1–5 and poly(HEMA-*co*-NVP) hydrogels 1–5 are listed in Table 3. There is no significant difference of the water content and contact angle values between the

two series of hydrogels. The results indicate the IPN hydrogels possess hydrophilic surfaces and high water content after incorporation of TRIS into the hydrogels. This is attributed to the fact that NVP used in the preparation of IPN hydrogels polymerizes more sufficiently.

Table 3. Water content, mechanical properties, surface wettability and oxygen permeability of the IPN hydrogels and poly(HEMA-co-NVP) hydrogels

Sample	Water content (%)	Contact angle (°)	Modulus (MPa)	Tensile strength (MPa)	Oxygen permeability (barrer)
IPN hydrogel 1	68.53	26.0 ± 2.6	1.36	1.75	32.6
IPN hydrogel 2	73.44	30.0 ± 2.6	1.14	1.64	43.5
IPN hydrogel 3	77.51	35.0 ± 1.0	0.92	1.49	52.4
IPN hydrogel 4	82.66	38.0 ± 1.7	0.83	1.24	60.0
IPN hydrogel 5	88.51	43.0 ± 1.7	0.76	1.08	72.3
Poly(HEMA-co-NVP) hydrogel 1	71.32	22.0 ± 1.0	1.25	1.02	28.8
Poly(HEMA-co-NVP) hydrogel 2	75.48	25.0 ± 2.6	1.05	0.90	24.5
Poly(HEMA-co-NVP) hydrogel 3	78.90	29.0 ± 1.7	0.86	0.71	20.4
Poly(HEMA-co-NVP) hydrogel 4	83.38	33.0 ± 2.6	0.75	0.58	16.7
Poly(HEMA-co-NVP) hydrogel 5	86.76	36.0 ± 1.7	0.68	0.43	10.6

Mechanical Properties

The modulus and tensile strength of the IPN hydrogels and the poly(HEMA-co-NVP) hydrogels are measured and listed in Table 3. As revealed in Table 3, the two series of hydrogels have similar modulus. However, the tensile strength of the IPN hydrogels is higher than that of the poly(HEMA-co-NVP) hydrogels when the same amount of NVP is used in the formulation. For the IPN hydrogels, physical entrapment between the NVP-crosslinked homopolymer network and the acrylate-NVP copolymeric network results in an effective transfer of stress between the two networks, thus leading to an enhancement in the tensile strength. The poly(HEMA-co-NVP) hydrogels show poor tensile strength because of the poor copolymerization of NVP and (meth) acrylate functional monomers as reported previously^[5–7].

Oxygen Permeability Measurements

Table 3 lists the oxygen permeability of the IPN hydrogels and the poly(HEMA-co-NVP) hydrogels. With TRIS incorporated, the oxygen permeability of the IPN hydrogels is dramatically enhanced, ranging from 32.6 barrer to 72.3 barrer. The oxygen permeability of poly(HEMA-co-NVP) hydrogels depends exclusively on water content, falling in the range of 10.6–28.8 barrer. With the incorporation of TRIS, the IPN hydrogels derived from TRIS, HEMA and NVP exhibited improved oxygen permeability by virtue of the bulkiness of the siloxane group ($-\text{Si}(\text{CH}_3)_2-\text{O}-$) and chain mobility that characterize such materials and which is responsible for the high diffusivity of oxygen through siloxane-containing materials^[37]. The result is in agreement with the previous report, in which TRIS was incorporated into the hydrogel materials based on the polyurethane prepolymer and hydrophilic monomer to obtain hydrogels with improved oxygen permeability^[38].

CONCLUSIONS

The interpenetrating polymer network (IPN) silicone hydrogels with improved oxygen permeability and mechanical strength are prepared by UV-initiated polymerization of monomers including TRIS, HEMA and NVP in the presence of free radical and cationic photoinitiators. FTIR, DSC and TEM characterization of the IPN hydrogels suggest the heterophase morphology and only physical entrapment between the networks. After TRIS incorporation, the IPN hydrogels still possess hydrophilic surfaces and high water content, and they have greatly improved tensile strength and oxygen permeability compared with those of poly(HEMA-co-NVP) hydrogels.

ACKNOWLEDGEMENTS The authors thank Hydron Co. Ltd.

REFERENCES

- 1 Han, Y.A., Lee, E.M. and Ji, B.C., *Chinese J. Polym. Sci.*, 2009, 27(3): 359
- 2 Huang, J., Huang, Z.M., Bao, Y.Z. and Weng Z.X., *Chinese J. Polym. Sci.*, 2006, 24(2): 195
- 3 Mina, M.F. and Alam, M.M., *Chinese J. Polym. Sci.*, 2005, 23(3): 269
- 4 Garrett, Q., Laycock, B. and Garrett, R.W., *Investig. Ophthalmol. Vis. Sci.*, 2000, 41: 1687
- 5 Lai, Y.C., *J. Appl. Polym. Sci.*, 1997, 66: 1475
- 6 Lai, Y.C., *J. Polym. Sci. Part A: Polym. Chem.*, 1997, 35: 1039
- 7 Gallardo, A., Fernández, F., Bermejo, P., Rebuelta, M., Cifuentes, A., Díez-Masa, J.C. and Román, J.S., *Biomaterials*, 2000, 21: 915
- 8 Haaf, F., Sanner, A. and Straub, F., *Polym. J.*, 1985, 17: 143
- 9 Lai, Y.C., *J. Appl. Polym. Sci.*, 1996, 60: 1193
- 10 Compañ, V., Andrio, A., López-Aleman, A., Riande, E. and Refojo, M.F., *Biomaterials*, 2002, 23: 2767
- 11 Tang, Q.W., Sun, X.M., Li, Q.H., Wu, J.H. and Lin, J.M., *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 2009, 346: 91
- 12 Oxman, J.D., Jacobs, D.W., Trom, M.C., Sipani, V., Ficek, B. and Scranton, A.B., *J. Polym. Sci. Part A: Polym. Chem.*, 2005, 43: 1747
- 13 Cho, J.D. and Hong, J.W., *J. Appl. Polym. Sci.*, 2004, 93: 1473
- 14 Decker, C., Nguyen Thi Viet, T., Decker, D. and Weber-Koehl, E., *Polymer*, 2001, 42: 5531
- 15 Wang, J.J., Sun, F.Q. and Li, X.S., *J. Appl. Polym. Sci.*, 2010, 117: 1851
- 16 Compañ, V., Andrio, A., López-Aleman, A. and Riande, E., *Polymer*, 1999, 40: 1153
- 17 Decker, C., *Macromol. Rapid. Commun.*, 2002, 23: 1067
- 18 Dendukuri, D., Panda, P., Haghoie, R., Kim, J.M., Hatton, T.A. and Doyle, P.S., *Macromolecules*, 2008, 41: 8547
- 19 Zhang, X.H., Yang, J.W., Zeng, Z.H., Wu, Y.W., Huang, L., Chen, Y.L. and Wang, H.H., *Polym. Eng. Sci.*, 2007, 47: 1082
- 20 Lecamp, L., Youssef, B., Bunel, C. and Lebaudy, P., *Polymer*, 1999, 40: 6313
- 21 Zhou, J., Collard, D.M., Park, J.O. and Srinivasarao, M., *J. Phys. Chem. B*, 2005, 109: 8838
- 22 Degirmenci, M., Hepuzer, Y. and Yagci, Y., *J. Appl. Polym. Sci.*, 2002, 85: 2389
- 23 Decker, C., *Nucl. Instrum. Meth. B*, 1999, 151: 22
- 24 Cho, J.D. and Hong, J.W., *J. Appl. Polym. Sci.*, 2004, 93: 1473
- 25 Meghabar, R., Megherbi, A. and Belbachir, M., *Polymer*, 2003, 44: 4097
- 26 Doneux, C. and Caudano, R., *Langmuir*, 1997, 13: 4898
- 27 Léonard-Stibbe, E., Lécayon, G., Deniau, G., Viel, P., Defranceschi, M., Leceay, G. and Delhalle, J., *J. Polym. Sci. Part A: Polym. Chem.*, 1994, 32: 1551
- 28 Tsubokawa, N. and Yoshihara, T., *Polym. J.*, 1991, 23: 177
- 29 Tsubokawa, N., Maruyama, H. and Sone, Y.J., *J. Macromol. Sci. A*, 1988, 25: 171
- 30 Tsubokawa, N., Inagaki, M., Kubota, H. and Endo, T., *J. Polym. Sci. Part A: Polym. Chem.*, 2003, 31: 3193
- 31 Rodrigues, S.M. and Vale, P., *Toxicon*, 2009, 53: 806
- 32 Begum, M. and Siddaramaiah, J. *Mater. Sci.*, 2004, 39: 4615
- 33 Zeng, M., Zhang, L.N. and Kennedy, J.F., *Carbohydr. Polym.*, 2005, 60: 399
- 34 Fornasiero, F., Ung, M., Radke, C.J. and Prausnitz, J.M., *Polymer*, 2005, 46: 4845
- 35 Ramya, C.S., Selvasekarapandian, S., Savitha, T., Hirankuma, G., Baskaran, R., Bhuvaneswari, M.S. and Angelo, P.C., *Eur. Polym. J.*, 2005, 42: 2672
- 36 Qin, C.L., Cai, W.M., Cai, J., Tang, D.Y., Zhang, J.S. and Qin, M., *Mater. Chem. Phys.*, 2004, 85: 402
- 37 Nicolson, P.C. and Vogt, J., *Biomaterials*, 2001, 22: 3273
- 38 Lai, Y.C. and Baccei, L.J., *J. Appl. Polym. Sci.*, 1991, 42: 2039