Preparation and Antidehydration of Interpenetrating Polymer Network Hydrogels Based on 2-hydroxyethyl Methacrylate and *N*-vinyl-2-pyrrolidone

Jingjing Wang, Fuqian Sun, Xinsong Li

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

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ABSTRACT: This work reports the preparation of 2-hydroxyethyl methacrylate (HEMA)/*N*-vinyl-2-pyrrolidone (NVP) interpenetrating polymer network (IPN) hydrogels by UV-initiated polymerization in the presence of free radical photoinitiator Darocur 1173 and cationic photoinitiator 4,4′-dimethyl diphenyl iodonium hexafluorophosphate. The polymerization mechanism was investigated by the formation of gel network. The structure and morphology of the HEMA/NVP IPN hydrogels were characterized by fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM). The results showed that the IPN gels exhibited homogeneous morphology. The dehydration rates of HEMA/NVP IPN hydrogels were examined by the gravimetric method. The results revealed that the hydrogels had a significant improvement of antidehydration ability in comparison with poly(2-hydroxyethyl methacrylate) (PHEMA) hydrogel embedded physically with poly(*N*-vinyl-2-pyrrolidone)(PVP). © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1851–1858, 2010

Key words: interpenetrating polymer network; hydrogel; UV-initiated polymerization; antidehydration

INTRODUCTION

Hydrogels are water-swollen macromolecular matrices consisting of polymeric chains crosslinked together either covalently or noncovalently and insoluble in water at physiological temperature, pH, and ionic strength. In the past several decades, they have been used to develop medical devices including drug delivery systems, tissue engineering scaffolds, biosensors, etc. because of the excellent biocompatibility.[1–3] One of the significant applications of hydrogels is used as soft contact lens materials due to their wearing comfort.[4] There are many types of hydrogel contact lens materials commercially available based on crosslinked combinations of various monomers including, 2-hydroxyethylmethacrylate (HEMA), *N*-vinyl pyrrolidone (NVP), methacrylic acid (MAA), methyl methacrylate (MMA), cyclohexyl methacrylate, and substituted acrylamides.[5]

Soft contact lens materials with high-water content and antidehydration ability usually have superior wearing comfort. High-water content contact lens is commonly prepared by the copolymerization of moderately hydrophilic HEMA with highly hydrophilic, nonionic monomers such as NVP, or with highly hydrophilic, ionic monomers such as MAA. Due to poor copolymerization of methacrylate monomers and NVP, the resultant hydrogels often show inconsistent quality, such as poor control of dimension, modulus, and water content.[6] Lai[7] studied the copolymerization of NVP and HEMA, finding that ethylene glycol dimethacrylate (EGDMA) is not an effective crosslinker for NVP. The reactivity ratios for the copolymerization of MMA (as monomer 1) and NVP (as monomer 2)[8] are $r_1 = 5$ and $r_2 = 0.02$. Contact lens with antidehydration ability can be prepared by embedding poly(*N*-vinyl-2-pyrrolidone) (PVP) physically into hydrogel contact lens network, which shows a slow dehydration rate.[9] However, loss of the linear PVP is observed during the extraction purification process of the hydrogel.[10]

Hydrogel contact lens can be prepared by photo initiated curing or heat curing. The primary advantage of photopolymerization over heat polymerization lies in its high polymerization rates, which can be reached under intense illumination, together with the advantage of a solvent-free formulation curable at ambient temperature. Photo initiated polymerization can be conducted by both radical and cationic means. 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, on the

Correspondence to: X. Li (lixs@seu.edu.cn).
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TABLE I
Formulations of Free Radical, Cationic and Hybrid Polymerizations and their Gel Fractions

Formulation	Feed (wt %)[a]						Gel fraction (%)
	HEMA	EGDMA	NVP	EBVP	Darocur 1173	4,4′-dimethyl diphenyl iodonium hexafluorophosphate	
1	100	0.3	0	0	0.5	0	96.64
2	0	0	100	0.3	0.5	0	0
3	0	0	100	0.3	0	0.5	0
4	0	0	100	0.3	0.5	0.5	97.77
5	70	0.3	30	0	0.5	0	89.90
6	70	0.3	30	0.3	0.5	0.5	98.85
7	50	0.3	50	0	0.5	0	81.75
8	50	0.3	50	0.3	0.5	0.5	98.25
9	30	0.3	70	0	0.5	0	62.51
10	30	0.3	70	0.3	0.5	0.5	98.12

[a] wt % of total monomers including HEMA and NVP.

other hand, is practically nonterminating and not inhibited by oxygen, but have 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.[11–13]

In this article, the HEMA/NVP IPN hydrogels with antidehydration ability were prepared by UV-induced hybrid free radical/cationic photopolymerization using crosslinkers of EGDMA and ethylidene-bis-3-(*N*-vinyl-2-pyrrolidone) (EBVP). The latter containing two NVP units bounding together with an ethylidene linkage can crosslink NVP sufficiently.[14] The hybrid photopolymerization was investigated by the formation of gel network. The resultant IPN hydrogels were characterized by fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and mechanical tester. Furthermore, the equilibrium water content and dehydration rate of HEMA/NVP IPN hydrogels were examined by the gravimetric method.

EXPERIMENTAL

Materials

2-Hydroxyethyl methacrylate (HEMA) and *N*-vinyl-2-pyrrolidone (NVP) were purchased from Aldrich chemical Co. and purified by distillation under reduced pressure before use. Ethylene glycol dimethacrylate (EGDMA), free radical photoinitiator Darocur 1173 and cationic photoinitiator 4,4′-dimethyl diphenyl iodonium hexafluorophosphate were used as received from Aldrich chemical Co., Ciba Co. and Igm, respectively. Sodium hydroxide (NaOH) was purchased from Shanghai Lingfeng Chemical Reagent (China). Ethylidene-bis-3-(*N*-vinyl-2-pyrrolidone) (EBVP) was prepared by the method as described in the literature.[14]

Preparation of hydrogels

Formulations for the preparation of the hydrogels based on HEMA and NVP are listed in Table I, in which EGDMA and EBVP were used as crosslinkers, Darocur 1173 and 4,4′-dimethyl diphenyl iodonium hexafluorophosphate were used as free radical initiator and cationic initiator respectively. The mixture of each formulation was introduced between two glass plates (7.5 cm × 2.5 cm) and cured under a high-pressure mercury lamp (Spectronics co., USA), emitting UV light from 320 to 400 nm for 1 h, and polymer film was obtained. The film thickness was controlled by a Teflon gasket, which gave a fairly consistent thickness of 0.25 mm. The polymer films were extracted with boiling water for 48 h, and then were kept in distilled water for further characterization.

The prepared polymer films were dried to a constant weight in vacuum and weighed before and after extraction in boiling water. The gel fraction (G) was calculated gravimetrically by the following formula:

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

where, W_o and W_g were the weights of films at dry state before and after extraction, respectively. The results were showed in Table I.

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

TABLE II
Formulations of HEMA/NVP and HEMA/PVP Hydrogels and the Corresponding Values of RPD_5

	Feed (wt%)[a]							
Formulation	HEMA	EGDMA	NVP	EBVP	DAROCR 1173	4,4′-dimethyl diphenyl iodonium hexafluorophosphate	PVP	RPD_5
1	100	0.3	0	0	0.5	0	0	38.94
2	95	0.3	5	0.3	0.5	0.5	0	30.19
3	90	0.3	10	0.3	0.5	0.5	0	26.73
4	80	0.3	20	0.3	0.5	0.5	0	21.37
5	70	0.3	30	0.3	0.5	0.5	0	18.63
6	60	0.3	40	0.3	0.5	0.5	0	10.17
7	50	0.3	50	0.3	0.5	0.5	0	9.43
8	95	0.3	0	0	0.5	0	5	36.73
9	90	0.3	0	0	0.5	0	10	31.83
10	85	0.3	0	0	0.5	0	15	26.46
11[b]	90	0.3	0	0	0.5	0	10	32.60
12[b]	90	0.3	0	0	0.5	0	10	34.94

[a] Note: wt % of total monomers including HEMA and NVP or HEMA and PVP.
[b] 11 and 12 meant the hydrogels derived from formulation 9 were extracted in water for 12 and 48 h before test.

To investigate the dehydration behavior of hydrogels, special formulations for the preparation of poly (HEMA-*co*-NVP) hydrogels and PHEMA hydrogels with PVP embedded physically are listed in Table II, in which EGDMA was used as the crosslinker, Darocur 1173 was used as the free radical initiator. The hydrogels were prepared following the same procedure as above.

Characterization

FTIR were recorded on a Bruker Vector 22 FT spectrometer in the range 4000–400 cm^{-1}.

SEM measurement of the films was made to assess the morphology of the samples. Films for SEM measurement were frozen in liquid nitrogen and then fractured and sputter coated with gold to view the cross section. SEM micrographs of the surfaces were performed on the film surfaces using a Hitachi S-3400N scanning electron microscope.

Stress–strain measurements of the hydrated polymer films were carried out using an Instron series IX materials testing system at room temperature. Dog-bone shaped samples were cut from the films (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. Each sample was tested in triplicate using a crosshead speed of 10 mm/min.

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

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

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

Relative percentage dehydration (RPD) was measured to assess the dehydration rate of the hydrogels. The amount of water loss from the hydrated polymer film under the humidity of 60% at 25°C was recorded by a TA instruments Q600 thermogravimetric analyzer. To control the humidity accurately, a hygrometer and a short water column were included in the TGA's air-intake line.[12] The testing procedure was as follows: A given hydrated hydrogel polymer film was first placed in distilled water for 10 min, then removed and gently blotted using pieces of filter paper to remove the water on the surface of the film. Subsequently, the film was immediately placed into the sample chamber and the weight of the film was recorded for a period of time. The percentage of water loss was calculated according to the following equation:[15]

$$\mathrm{RPD_t} = \frac{\mathrm{EWC_o} - \mathrm{EWC_t}}{\mathrm{EWC_o}} \times 100$$

where, RPD_t was the relative percentage dehydration at time t, EWC_t was the water content at time t and EWC_o was the initial water content of the hydrated polymer film.

RESULTS AND DISCUSSION

Hybrid photopolymerization of HEMA and NVP

The IPN hydrogels are prepared by UV-initiated hybrid photopolymerization of monomers including HEMA and NVP in the presence of free radical photoinitiator and cationic photoinitiator. To have an insight into the mechanism of the hybrid photopolymerization of HEMA and NVP, several formulations are designed and their corresponding gel fractions are listed in Table I.

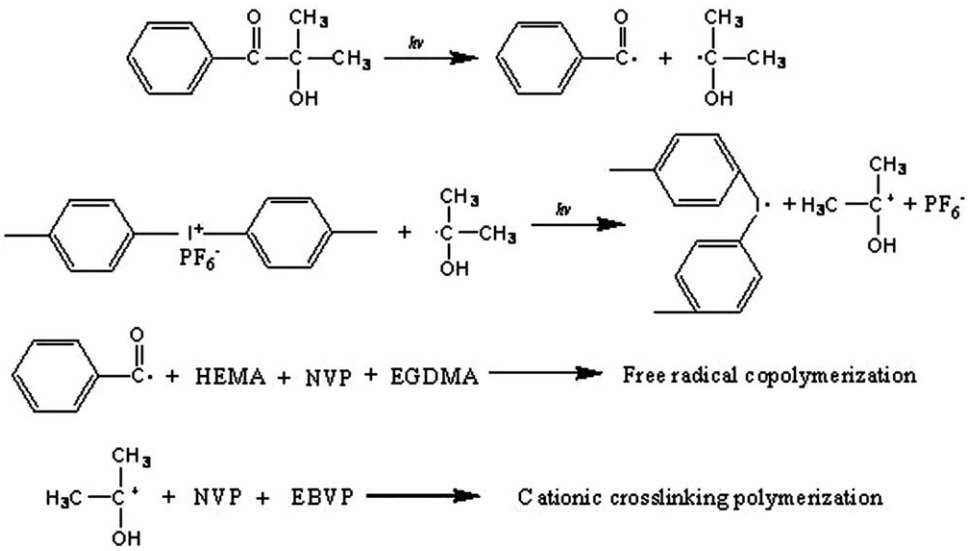

Figure 1 Free radical and free radical promoted cationic photopolymerizations.

It's found that the polymerization of HEMA using EGDMA as the crosslinker in the presence of Darocur 1173 gives high gel fraction as illustrated in the formulation 1 of Table I. The result confirmed that Darocur 1173 could be used as an effective free radical initiator to initiate the radical polymerization of HEMA.[16–20]

For the polymerization system of NVP using EBVP as the crosslinker in the presence of only free radical initiator (formulation 2) or cationic initiator (formulation 3), no gel was detected. The result demonstrated that NVP could 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 were used together (formulation 4), the gel fraction of the photopolymerization of NVP reached up to 97.77%. It's revealed that NVP could polymerize sufficiently using EBVP as the crosslinker initiated by a combination of free radical and cationic initiators. The results may be explained by photoinitiated radical polymerization and cationic polymerization mechanism as reported in the previous work.[21,22] 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 reduced the cationic photoinitiator to yield corresponding carbocations capable of initiating cationic polymerization of NVP.[12,13,23,24] In fact, the polymerization of NVP by the cationic mechanism has been confirmed in the literature.[25–30] Therefore the free radical initiator Darocur 1173 not only served to initiate the radical polymerization, but also activated the cationic polymerization.

For the copolymerization of HEMA and NVP using EGDMA as the crosslinker in the presence of free radical initiator Darocur 1173 (formulations 5, 7, and 9), the gel fractions were 89.90, 81.75, and 62.51% respectively. Obviously, the gel fraction decreased with the increase of NVP content in the formulation due to the poor copolymerization of HEMA and NVP. However, for the polymerization systems of HEMA 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 I), the gel fractions reached up to more than 98%. The results indicated that Darocur 1173 not only initiated the radical copolymerization of HEMA and NVP, but also activated the cationic initiator to initiate the cationic polymerization of NVP in the presence of EBVP.[12,13,23,24] The hybrid photopolymerization mechanism of HEMA and NVP with the free radical initiator Darocur 1173 in conjunction with the cationic initiator may be summarized in Figure 1.[23] As discussed above, the hydrogels prepared by hybrid photopolymerization of HEMA and NVP consisted of two interpenetrating polymer networks (IPNs). One was a copolymeric network of HEMA and NVP formed by radical polymerization, and the other was a NVP homopolymer network formed by cationic mechanism.

To provide more evidence of the NVP homopolymer network in the IPN hydrogels, further degradation experiment was carried out.[22,31] We found that the copolymeric network derived from formulation 7 using the crosslinker EGDMA degraded totally. The IPN hydrogel derived from formulation 8 had a dry residue of 27% after degradation and extraction. The NVP homopolymer network derived from formulation 4 after degradation had a dry residue of 100%.

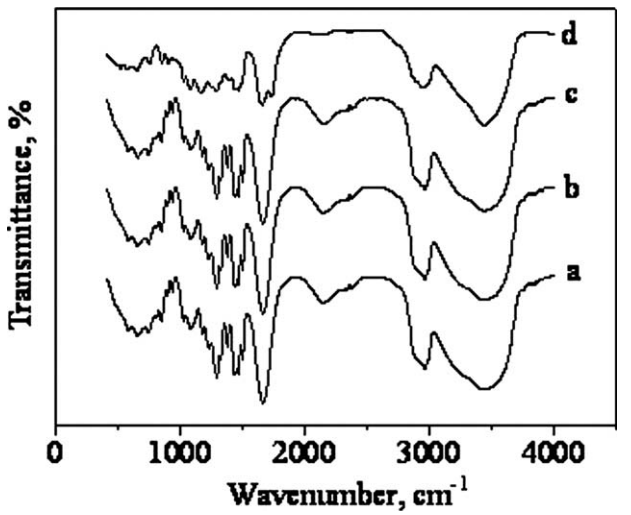

Figure 2 FTIR spectra for dried samples of hydrogels derived from (a) formulation 4 in Table I without degradation; (b) formulation 4 in Table I after degradation; (c) formulation 8 in Table I after degradation; (d) formulation 8 in Table I without degradation.

Figure 2 shows the spectra of the residues. There was no obvious difference among the spectra of these residues. It was assumed that the degradation had no significant effect on the NVP homopolymer network in the IPN hydrogels. But clear distinction between the spectra of the IPN hydrogel derived from formulation 8 before and after extraction was observed as revealed in Figure 2. The peak centered at 1654 cm^{-1} for the IPN hydrogel, which might be due to the presence of hydrogen-bonded carbonyl groups, disappeared after extraction.[32,33] Because of the degradation of the crosslinker EGDMA in the NaOH solution, the copolymeric network of HEMA and NVP-crosslinked by EGDMA was extracted from the IPN hydrogel. Therefore, the residue of the IPN hydrogel after extraction probably was the NVP homopolymer network.

Characterization of hydrogels

FTIR spectra of crosslinked PVP derived from formulation 4, crosslinked PHEMA derived from formulation 1, and HEMA/NVP IPN hydrogels derived from formulations 6, 8, and 10 in Table I are shown in Figure 3. The spectrum of crosslinked PVP [Fig. 3(e)] showed a characteristic peak for C—N stretching at 1291 cm^{-1} and a peak centered at 1639 cm^{-1} associated with the C=O group. The characteristic band of crosslinked PHEMA [Fig. 3(a)] was assigned to the C–O stretching centered at 1261 cm^{-1}. The peaks at 1730 cm^{-1} and 3447 cm^{-1} were due to C=O, and O—H stretching of PHEMA, respectively. The IR spectra of HEMA/NVP IPN hydrogel [Fig. 3(b–d)] contained the characteristic adsorption bands of PVP and PHEMA as indicated in Figure 3. No new peak, which might indicate chemical crosslinking, appeared.[34] For the IPN hydrogel, the intensities of C—O and C—N peaks increased with the contents of HEMA and NVP in the formulation. The IPN hydrogels derived from formulations containing 30 wt %, 50 wt %, and 70 wt % of HEMA had the peaks centered at 1654 and 1725 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 adsorption intensity of the peak at 1654 cm^{-1} became stronger with the increase of HEMA content signifying strengthened hydrogen bonding in the hydrogels.

The morphology of the HEMA/NVP IPN hydrogels was investigated by SEM. The representative SEM images of the HEMA/NVP IPN gels are shown in Figure 4. The images revealed the homogeneous and compact morphologies of the IPN hydrogels indicating good compatibility of the copolymeric network of HEMA and NVP with NVP-crosslinked homopolymer network. This may be attributed to the strong hydrogen bonding interaction in the IPN hydrogels.

Figure 5 shows the relationship between water content of the HEMA/NVP IPN hydrogels and the content of NVP. As the NVP content increased from 10 to 50 wt %, the water content of the IPN hydrogel increased from 50.1 to 84.58%. The result may be attributed to the ability to take up water of sufficiently polymerized NVP in the hydrogels.

Figure 6 shows the relationship of modulus and tensile strength of the HEMA/NVP IPN hydrogels with NVP content in the formulation. Both of modulus and tensile strength decreased with the increase of NVP content as shown in Figure 6. The phenomena

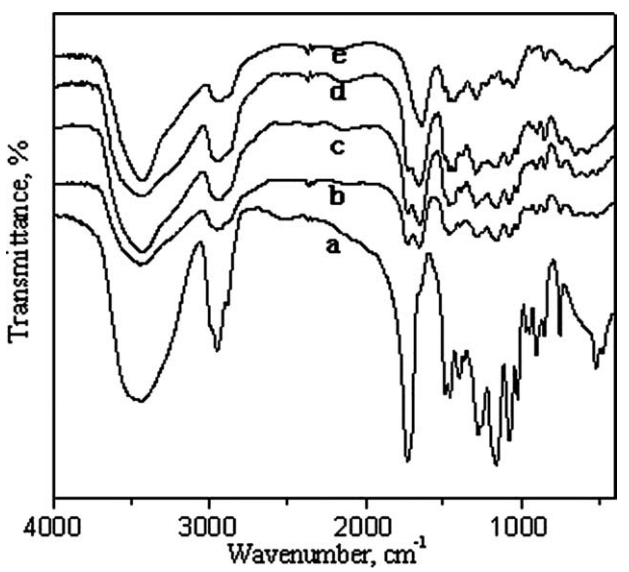

Figure 3 FTIR spectra of dried hydrogels derived from formulation (a) 1; (b) 6; (c) 10; (d) 12; (e) 4 as cited in Table I.

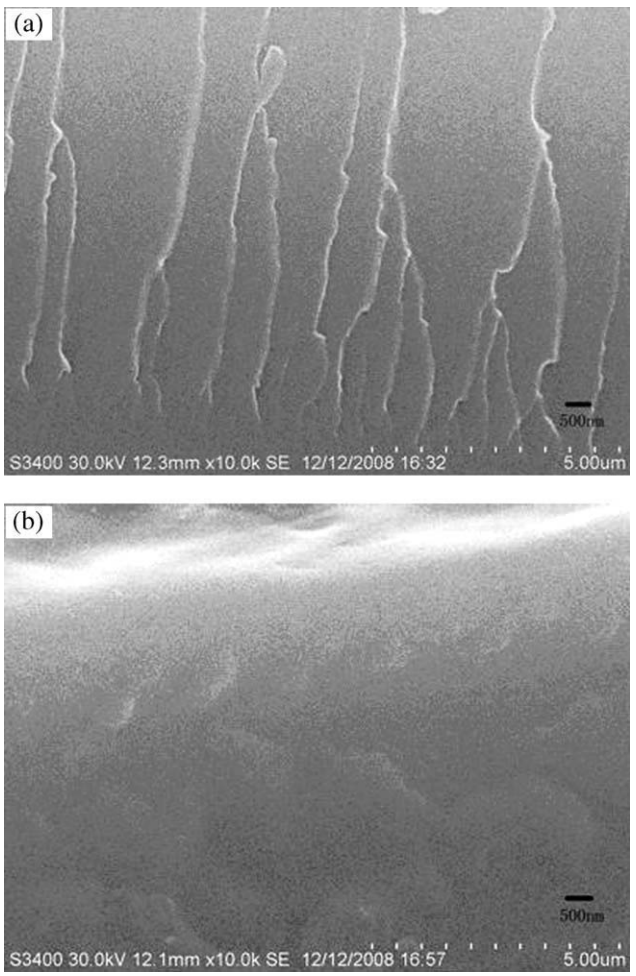

Figure 4 Scanning electron microscope images of fracture surface of dried hydrogel derived from formulation (a) 6; (b) 10 as cited in Table I.

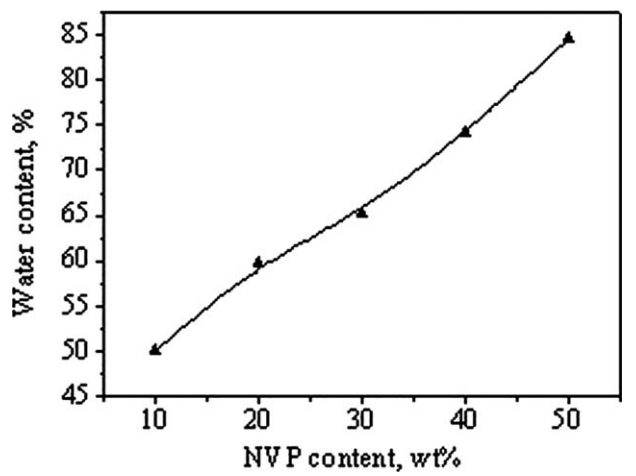

Figure 5 The relationship between the water content of HEMA/NVP IPN hydrogels and the content of NVP in the formulation with the total content of HEMA and NVP 100 wt %, EGDMA 0.3 wt %, EBVP 0.3 wt %, Darocur-1173 0.5 wt % and 4, 4′-dimethyl diphenyl iodonium hexafluorophosphate 0.5 wt%.

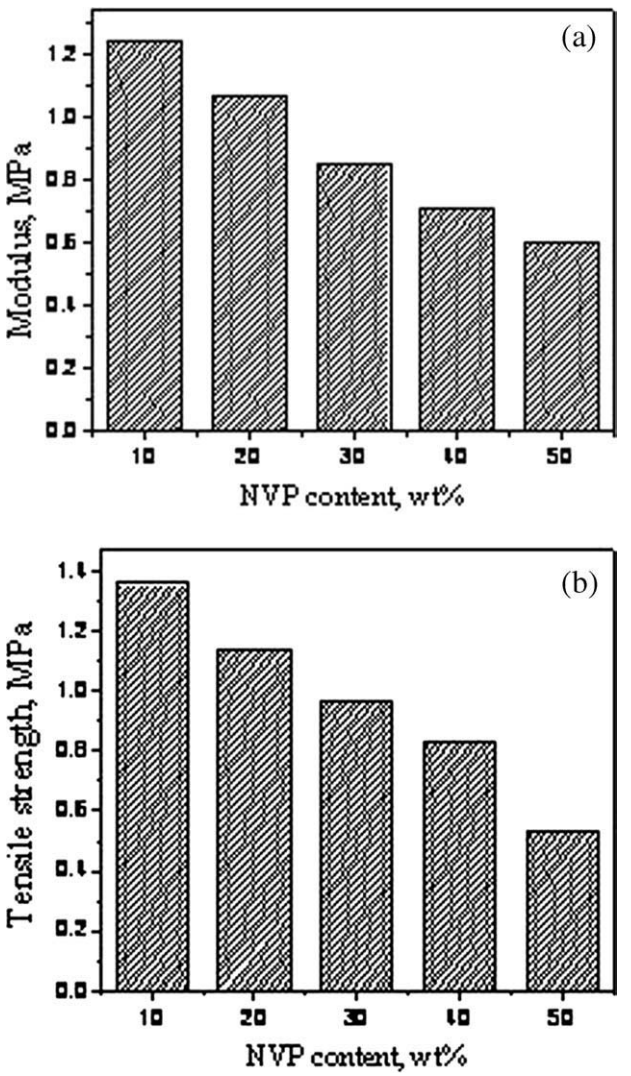

Figure 6 The relationship between hydrogel modulus (a), tensile strength (b), and NVP content in the formulation with total content of HEMA and NVP 100 wt %, EGDMA 0.3 wt %, EBVP 0.3 wt %, Darocur-1173 0.5 wt %, and 4,4′-dimethyl diphenyl iodonium hexafluorophosphate 0.5 wt %.

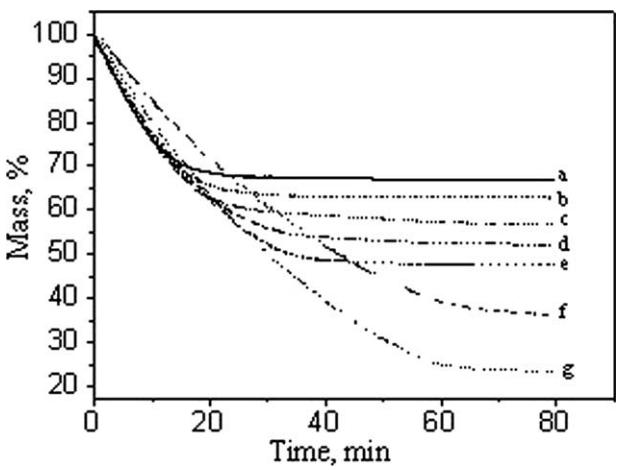

Figure 7 Dehydration profiles of the hydrogels derived from formulation (a) 1; (b) 2; (c) 3; (d) 4; (e) 5; (f) 6; (g) 7 as cited in Table II.

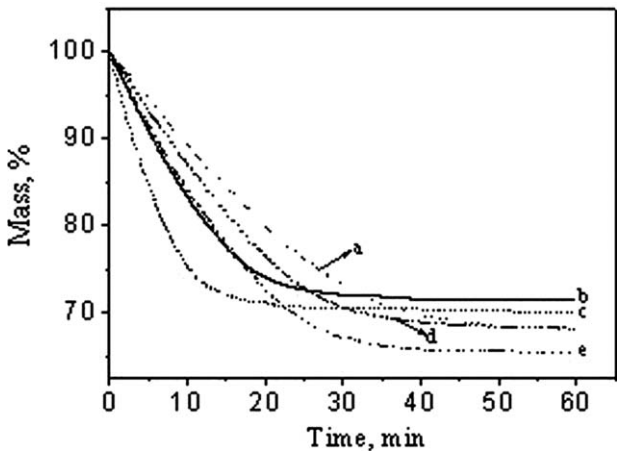

Figure 8 Dehydration profiles of the hydrogels derived from formulation (a) 10; (b) 11; (c) 8; (d) 12; (e) 9 as cited in Table II.

could be explained that the increase of water content of the IPN hydrogels caused by the increase of NVP content (as shown in Fig. 5), induced the decrease of the modulus and tensile strength.

Dehydration behavior

dehydration profiles show a relatively linear loss during the first several minutes, followed by a plateau as indicated in Figures 7 and 8. To investigate the dehydration rate of the HEMA/NVP IPN hydrogels, several formulations were designed and listed in Table II with a comparison of PHEMA hydrogels with PVP embedded physically. The dehydration rate of the hydrogels was assessed by the relative percentage dehydration at fifth minute (RPD_5).[9] The results are shown in Table II. Obviously both the PHEMA hydrogels with PVP embedded physically (formulations 8–12 in Table II) and the HEMA/NVP IPN hydrogels (formulations 2–7 in Table II) showed smaller RPD_5 value compared to that of PHEMA hydrogel derived from formulation 1. Furthermore, by comparing the RPD_5 value of the hydrogel derived from formulation 2 with that of the hydrogel of formulation 8, and the RPD_5 value of the hydrogel derived from formulation 3 with that of the hydrogel derived from formulation 9, it was found that the HEMA/NVP IPN hydrogels showed fairly smaller RPD_5 value than that of the PHEMA hydrogels with PVP incorporated. The results indicated that for the HEMA/NVP IPN hydrogels, crosslinked PVP network in the hydrogels behaved as the water retention agent, resulting in the slow dehydration rate. Furthermore, the antidehydration ability of the crosslinked PVP network was better than that of the linear PVP. In addition, the PHEMA hydrogels with PVP embedded physically extracted in water (formulations 11 and 12 in Table II) showed faster dehydration rate than that of the hydrogel without extraction (formulation 9 in Table II). This may be attributed to the loss of part linear PVP embedded physically in the PHEMA hydrogel.

CONCLUSION

UV-initiated 2-hydroxyethyl methacrylate (HEMA)/*N*-vinyl-2-pyrrolidone (NVP) hybrid photopolymerization was employed to prepare HEMA/NVP IPN hydrogels with antidehydration ability. The IPN hydrogels may consist of two networks, copolymeric network of HEMA and NVP and NVP-crosslinked homopolymer network. The homogeneous morphology of the prepared IPN hydrogels was confirmed by the FTIR and SEM. The HEMA/NVP IPN hydrogels showed stronger anti-dehydration ability than that of PHEMA hydrogels with PVP embedded physically. The results indicated that the HEMA/NVP IPN hydrogels may have potential application as novel contact lenses.

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