Characterization of Associating Hydrogels of Poly(vinyl alcohol) and Poly(vinyl pyrrolidone)

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ABSTRACT: In this study, hydrogels were prepared from blends of poly(vinyl alcohol) (PVA) and poly(vinyl pyrrolidone) (PVP). The miscibility of the polymers was confirmed with differential scanning calorimetry with the appearance of a single glass-transition temperature. Additionally, a negative Flory–Huggins interaction parameter further verified the interaction between PVA and PVP. We evaluated the stability of the hydrogels by swelling the gels in phosphate-buffered saline solutions at pH 7.4. With attenuated total reflectance-Fourier transform infrared spectroscopy, it was determined that, during swelling, PVP dissolved out of the gel over time and the equilibrium gel content of PVP was nearly identical in all of the samples investigated. After the dissolution of PVP, the equilibrium water content of the gels ranged from 64 to 76 wt %. Additionally, rubber elasticity studies were performed to elucidate information about the physically crosslinked network structure. As determined from rubber elasticity experiments, the mesh size of the physically crosslinked hydrogels ranged from 90 to 230 Å. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 541–549, 2009

Key words: blends; hydrogels; infrared spectroscopy; miscibility

INTRODUCTION

The blending of polymers provides a powerful way to produce new materials with exciting new properties that arise from the combination. This strategy tends to be less expensive and time-consuming than the development of new monomers and/or new polymerization routes.[1] Additionally, one can obtain a wide range of material properties by merely changing the blend composition. However, not every pair of polymers can form homogeneous blends. Homogeneous miscibility in polymer blends requires a negative free energy of mixing:

$$\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T \cdot \Delta S_{\mathrm{mix}} \quad (1)$$

where ΔG is the free energy change of mixing, ΔH is the enthalpy change of mixing, T is the temperature, and ΔS is the enthropy change of mixing.

For the case of blending two high-molecular-weight polymers, the entropy change is negligible; therefore, a negative enthalpy change upon mixing is required for miscibility; that is, it must be an exothermic process. As such, the blending process requires specific interactions between the polymers, including hydrogen bonding and the formation of ion–dipole, dipole–dipole, or n–π complexes. The most commonly used criterion for verifying the homogeneity of two polymers is the existence of a single glass-transition temperature for the blend that falls between the glass-transition temperatures of the original polymers.[1–5]

A particularly interesting blend can be formed with the hydrophilic polymers poly(vinyl alcohol) (PVA) and poly(vinyl pyrrolidone) (PVP). These two polymers exhibit miscibility because of hydrogen bonding between the PVA hydroxyl group and the PVP carbonyl group.[2–8] The melting temperature of the pure semicrystalline polymer PVA (T_m^0) is about 230°C, and PVA has a glass-transition temperature at approximately 80°C.[2] PVP is a highly amorphous polymer with a glass-transition temperature around 150°C. For blends of PVA and PVP, several groups have reported a single glass transition on the basis of differential scanning calorimetry (DSC) data.[2,3,5,7,8]

For the case of blends prepared from a semicrystalline polymer and an amorphous polymer, T_m^0 and the degree of crystallinity will be depressed because of the presence of the amorphous polymer.[9,10] Nishio et al.[7] found that T_m^0 was depressed systematically with an increase in PVP content as determined with DSC, and the Flory–Huggins interaction

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parameter (χ_{12}) was found to be -0.35 (230°C). The presence of crystallites was detected with wide-angle X-ray diffraction, and it was determined that the crystallinity of PVA decreased rapidly with increasing PVP with no crystallite formation in blends containing more than 60 wt % PVP. Li et al.[8] observed a melting peak in PVA/PVP blends containing more than 50 wt % PVA. Additionally, they reported that the melting temperature decreased with increasing PVP content, and χ_{12} for the blends was calculated to be -0.52 at 230°C. Zhang and Yin[5] studied the crystalline structures of PVA/PVP blends with small-angle X-ray scattering, also showing that the degree of crystallinity decreased with increasing PVP content.

As mentioned previously, blend formation between PVA and PVP is driven by hydrogen bonding between the carbonyl group of PVP and the hydroxyl group of PVA.[5,7,8] The IR peak of the PVP carbonyl group has been observed to shift to lower wave numbers in Fourier transform infrared (FTIR) spectroscopy and has been used as evidence of the presence of hydrogen bonds.[8,11] High-resolution solid-state ^{13}C-NMR was also used to detect the presence of intermolecular hydrogen bonds between the carbonyl group of PVP and the hydroxyl group of PVA.[12]

PVA and PVP have both been shown to be biocompatible and have been used in a wide range of biomedical applications.[12–14] The clinical implications of the use of PVA hydrogels as artificial articular cartilages and the resulting mechanical properties have been discussed by several groups.[13,15] Peppas and coworkers[12,16,17] investigated the application of PVA as a drug-delivery carrier for the controlled release of therapeutic agents. Freichel and Lippold[18] developed an oral-erosion-controlled drug-release system based on PVA. PVP was used extensively as a blood plasma substitute in Germany during World War II and is still used as a blood plasma substitute and stockpiled for emergency use in some countries.[19] Because of its pharmacologically inert and nontoxic properties, PVP has been used as solid dispersion to enhance the dissolution rates of hydrophobic drugs, including sulfonamides, hypoglycemics, steroids, and antimicrobials.[20–23] Because of its hydrophilic properties, PVP has also been used to modify the surfaces of catheter materials to reduce bacterial adhesion and encrustation.[24–26]

Although significant work has been done to understand the miscibility of PVA and PVP blends, no work has focused on the swelling behaviors or the stabilities of the physically crosslinked hydrogels based on PVA/PVP blends. The purpose of this study was to synthesize hydrogels from PVA/PVP blends that contained physical crosslinks consisting of PVA crystallites and PVA/PVP hydrogen bonds. Additionally, we intended to study the structure and properties of the swollen networks *in vitro*. As PVA and PVP are both biocompatible, these new hydrogels may have promising characteristics that would make them candidates for biomedical applications, such as drug delivery, joint resurfacing, or nucleus pulposus replacement in the intervertebral disc.[27–30]

EXPERIMENTAL

Preparation of the polymer blends

PVA (elvanol grade 71-30, average molecular weight = 143,000, degree of hydrolysis = 99.0–99.8%) was obtained from du Pont de Nemours & Co. (Wilmington, DE). PVP (average molecular weight = 10,000) was obtained from Aldrich Chemical Co., Inc. (St. Louis, MO). Solutions of PVA and PVP were prepared by the dissolution of various ratios of the polymers in deionized water at 90°C overnight. The solutions, which contained 10 wt % polymer, were homogenized for 30 min with sonication. The ensuing solutions were cast into Plexiglas trays and dried at 37°C for 72 h. The nominal compositions of the dried blends were 5, 10, 25, and 50 wt % PVP.

Miscibility analysis

The thermal transitions of the blends were determined with DSC (model 2010, TA Instruments, Inc., Wilmington, DE). In these experiments, 4–6 mg of a dried sample was placed in an aluminum pan and heated at a ramp rate of 5°C/min up to 250°C with nitrogen as the purging gas. The glass-transition temperature, melting temperature, and melting enthalpy were determined for each of the samples.

Dissolution analysis

The dissolution behavior of the gels was examined with swelling studies and attenuated total reflectance (ATR)-FTIR spectroscopy (Nicolet Magna-IR 560 spectrometer, Madison, WI). For the studies, thin, flat strips of dried polymer films were mounted on a zinc–selenium ATR crystal, and the IR spectra were obtained with 2048 scans at a resolution of 2 cm^{-1}. These samples were then weighed in air and heptane and placed in phosphate-buffered saline (PBS) solutions at pH 7.4 and 37°C. At set times after immersion (1, 4, 8, 12, and 24 h), the strips were removed from solution and weighed. These strips were then dried *in vacuo* between flat plates for 72 h, and the weights were recorded.

After this, the strips were mounted again to the ATR crystal, and the IR spectra were obtained as described previously. We performed quantitative analysis of the blend composition before and after swelling by comparing the change in the ratio of the

PVP carbonyl stretching peak (1654 cm^{-1}) and the PVA carboxyl stretching peak (1086 cm^{-1}).

Swelling studies

Discs with diameters of 6.0 mm were cut from the blended films and dried *in vacuo* for 48 h. The weights of the dry discs were measured in air and heptane to determine the dry polymer volume and density. The discs were then swollen in PBS solution (pH 7.4) in a shaker bath at 37°C. The mass of the hydrogels were measured after 30 min, 1 h, 4 h, 8 h, and 24 h of swelling and then daily for the 1st week and weekly up to 8 weeks (56 days). The PBS solutions were changed daily for the 1st 2 weeks and then weekly. The mass swelling ratio for the gels (q) was calculated as the ratio of the gel weight to the dry weight of the discs. The equilibrium volume swelling ratio (Q) and the equilibrium polymer volume fraction in the swollen state ($\upsilon_{2,s}$) were calculated as follows:

$$Q = v_{2,s}^{-1} = \frac{\rho_p}{\rho_w}(q-1)+1 \qquad (2)$$

where ρ_p is the density of the dry polymer blend and ρ_w is the density of the swelling media. After 8 weeks, the swollen discs were removed from solution, and the dry weights were measured in air and heptane.

Structural analysis

The mechanical properties of the gels were determined with an automated material testing system (Instron model 4442, Canton, MA) with a 50-N load cell. The swollen PVA/PVP gels were cut into strips 5 mm wide by 0.6 mm thick. The samples were placed in the grips of the tester and elongated at a constant extension rate of 5 mm/min up to a maximum elongation of 20%. The stress–strain behavior was observed and used in the evaluation of the crosslinked structure of the networks with rubber elasticity theory.

RESULTS AND DISCUSSION

The preparation of PVA/PVP mixtures in aqueous solution is a convenient and efficient way to synthesize blends from these two polymers. PVA and PVP are both water soluble because of the interactions of their polar side groups with water. The carbonyl group of PVP forms strong hydrogen bonds with water and ensures that PVP readily dissolves in water at room temperature. PVA has a lower water solubility and requires a higher temperature (85–100°C) for rapid, homogeneous dissolution. In this study, PVA and PVP powders were added to deionized water and heated to 90°C as a more precise way to get the desired PVA/PVP ratios in blends than some previously reported methods, in which PVA/PVP solutions were prepared by the mixture of PVA solutions and PVP solutions.[2,3,5,7,8,31] This physical method is a viable means of hydrogel preparation without concerns of the leaching of toxic agents, such as residual monomers, initiators, and crosslinking agents, which is inevitable in most typical chemical crosslinking processes.

Miscibility of the PVA/PVP blends

The presence of a single glass-transition temperature has been widely accepted as a demonstration of the miscibility of polymer blends.[1,3–5] From DSC studies, single glass-transition temperatures were observed for each blend sample (Fig. 1), which indicated that PVA and PVP were miscible in the range of compositions tested in this study.

The pure PVA samples yielded a relatively sharp endothermic peak with a melting temperature at approximately 227°C (Fig. 1). However, the PVA melting peak shifted to a lower temperature with increasing PVP content in the blend. The area of the melting peak was also found to decrease accordingly. The smaller peak indicated a reduced enthalpy of melting because of a decrease in the amount of PVA crystals. The degree of crystallinity of the PVA/PVP blends was calculated by the comparison of the melting enthalpy of the samples to the enthalpy required to melt 100% crystalline PVA (~ 138.6 J/g).[32–34] The melting enthalpy was obtained by integration of the area under the melting peak of PVA (Universal Analysis-NT, Version 2.5H, TA Instruments). On the basis of the decreasing enthalpy of melting, the degree of crystallinity of the PVA/PVP blends was found to decrease with increasing PVP composition in the blending systems (Fig. 2).

A depression of the melting temperature is typically observed when a semicrystalline polymer and an amorphous polymer are blended.[9,35] Even though the two polymers were miscible in the amorphous regions of the blends, the presence of the amorphous polymer hindered the crystallite formation of the semicrystalline polymer. In this case, the bulky pyrrolidone ring of PVP hindered the formation of PVA crystallites, which resulted in the depression of the PVA melting peak and the degree of crystallinity. This depression phenomenon could be used to determine χ_{12}, which is related to the enthalpy of mixing. When two polymers are mixed together, the entropy of mixing becomes negligible because of their combined high molecular weight. Therefore, the equilibrium melting temperature depression (ΔT_m) can be expressed by the following equation:[7,8,35]

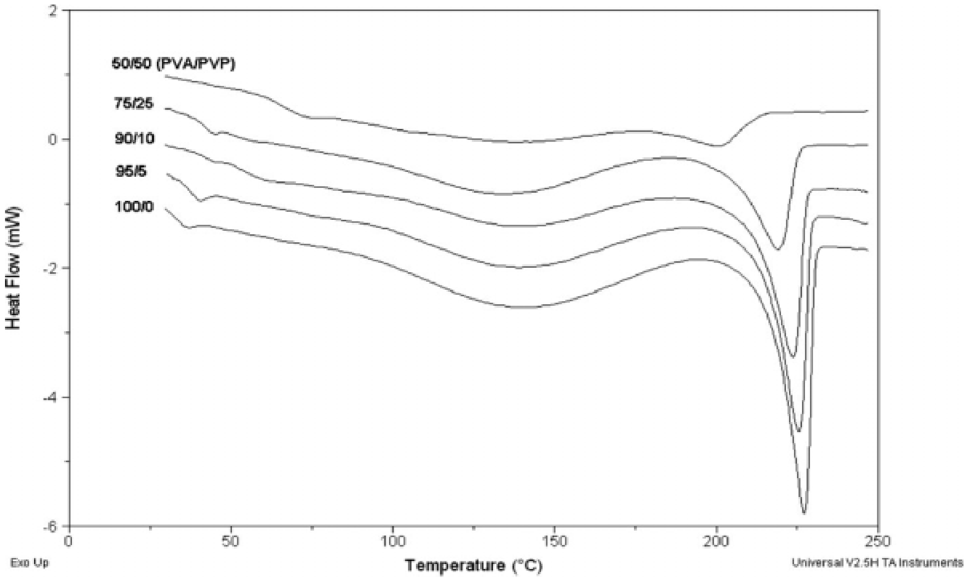

Figure 1 DSC thermograms of the PVA/PVP blends ramped at 5°C/min to 250°C with nitrogen as the purging gas.

$$\Delta T_m = -T_m^0\left(\frac{V_2 B}{\Delta H_2}\right)\phi_1^2 \tag{3}$$

where the subscripts 1 and 2 are used to designate the amorphous (PVP) and semicrystalline (PVA) components, respectively; V_2 is the molar volume of the repeating unit of PVA; ΔH_2 is the molar enthalpy of fusion of the repeating unit of PVA; and ϕ_1 is the volume fraction of PVP. The term B refers to the interaction energy density of the two polymers and is related to χ_{12} by the following equation:

$$\chi_{12} = \frac{BV_1}{RT_m} \tag{4}$$

where R is the gas constant, V_1 is the molar volume of the repeating unit of component 1, and T_m is the melting temperature of the blend. With $T_m^0 = 227°\text{C}$ for the pure PVA film, $V_1 = 92.0$ cm^3/mol, $V_2 = 32.8$ cm^3/mol, and $\Delta H_2 = 6.7$ KJ/mol, the term B was calculated from the slope of ΔT_m versus ϕ_1^2 plot (Fig. 3).

The value of χ_{12} was calculated for the different blend compositions examined in this study. The results ranged from −0.77 to −0.81 and are shown in Table I. The negative values for χ_{12} indicated that the mixing of the two polymers was exothermic, which means that the polymer pair formed thermodynamically stable compatible blends. The magnitudes of the χ_{12} values calculated in this study were comparable to those reported in the literature: −0.65[7] and −0.52[8] at 230°C. However, the values of χ_{12} that we obtained were more negative, which indicated stronger intermolecular interactions between the two polymers. On the basis of these strong intermolecular associations, these systems

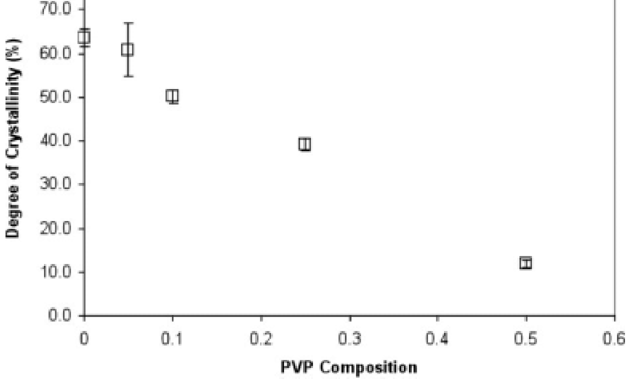

Figure 2 Degree of crystallinity of the PVA/PVP blends.

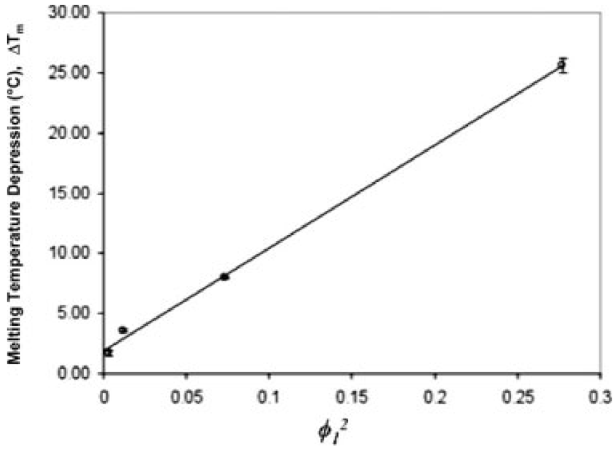

Figure 3 ΔT_m as a function of ϕ_1^2 for the calculation of χ_{12} ($n = 3$).

TABLE I
χ_{12} Values for the PVA/PVP Blends

	PVA/PVP			
	95/5	90/10	75/25	50/50
T_m (°C)	225.5 ± 0.1	223.6 ± 0.2	219.2 ± 0.1	201.6 ± 0.7
χ_{12}	−0.77	−0.78	−0.78	−0.81

were proposed for use as physically crosslinked, swellable hydrogels.

Stability of the PVA/PVP hydrogels

The main purpose of this research was to develop a hydrogel system that could be used in biomedical applications, such as controlled drug delivery, tissue engineering, or orthopedic applications. Understanding the stability of the PVA/PVP hydrogels following immersion in aqueous media is critical to understanding the ability of the hydrogels to function in biomaterials applications. In this study, the chemical composition changes of the gels during swelling were elucidated with FTIR spectroscopy. The FTIR spectra were first collected for the vacuum-dried PVA/PVP thin films after preparation but before swelling (Fig. 4). The characteristic peaks representing distinct absorbances on the two polymers were the secondary alcohol —C—C—O stretch peak at 1086 cm^{-1} for PVA[36] and a mixed mode of carbonyl group stretch and —N—C stretch at 1654 cm^{-1} for PVP.[37] The height of the PVP 1654-cm^{-1} peak increased with increasing PVP composition, whereas the height of PVA 1086-cm^{-1} peak decreased. The initial ratios established from the prepared films of known PVA/PVP ratios were used to develop a calibration curve.

The weights of the dry polymer films were first recorded, and then, the samples were immersed in PBS solution at pH 7.4 and 37°C to mimic physiological conditions. At set times of 1, 4, 8, 12, and 24 h, the swollen films were taken out of PBS and dried *in vacuo* for 72 h between two glass slides to avoid deformation. The dried samples were weighed, and FTIR spectra were collected for each with the same number of scans and resolution as the original dry films. For all of the samples analyzed, the height of the carbonyl peak decreased over time, which indicated that the concentration of carbonyl groups decreased after immersion in PBS solution. Representative spectra of the films with an initial 50/50 PVA/PVP ratio are shown in Figure 5 to demonstrate this observation. The reduction of carbonyl groups in the hydrogel blends was due to the dissolution of PVP from the gels during the swelling process. The greatest decrease occurred in the 1st hour of swelling, regardless of the starting PVP composition, which indicated that most PVP dissolved out of the hydrogel network after only a short period of immersion in the buffered solution.

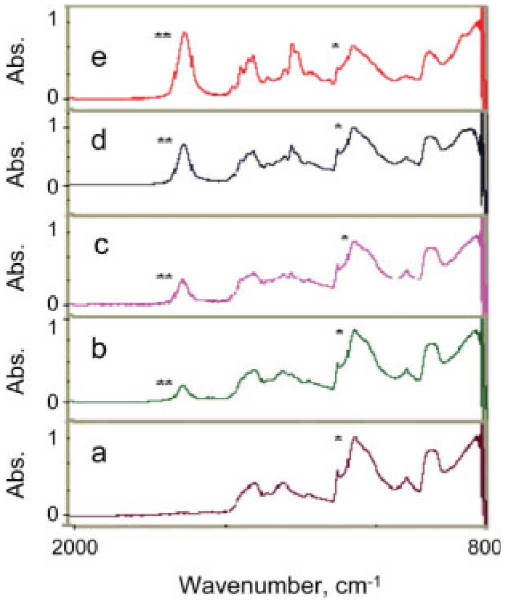

Figure 4 ATR-FTIR spectra of the PVA/PVP dry films before swelling: (a) 100/0, (b) 95/5, (c) 90/10, (d) 75/25, and (e) 50/50 PVA/PVP. * = —C—C—O stretch peak of PVA; ** = carbonyl group stretch peak of PVP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

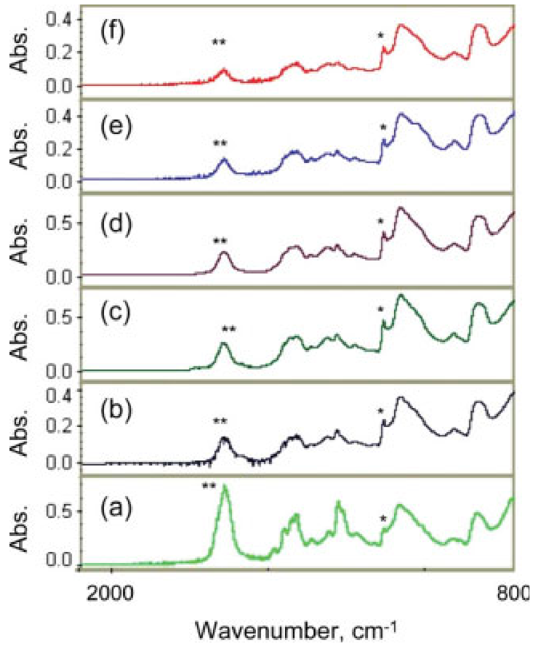

Figure 5 ATR-FTIR spectra of the original 50/50 PVA/PVP hydrogels: (a) before swelling, (b) after 1 h of swelling, (c) after 4 h of swelling, (d) after 8 h of swelling, (e) after 12 h of swelling, and (f) after 24 h of swelling. * = —C—C—O stretch peak of PVA; ** = carbonyl group stretch peak of PVP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

To evaluate the composition changes of the blends, quantitative analysis was performed with Beer's Law. A linear relation between the peak height ratio (the 1086-cm^{-1} peak of PVA and the 1654-cm^{-1} peak of PVP) was obtained with the hydrogel blends prepared with 0.5, 1, 2, 5, 10, 25, and 50 wt % PVP. Quantitative analysis allowed for the determination of the final compositions of PVA and PVP after immersion in PBS solution. Combining the results from the quantitative IR analysis and the weight measurement, we calculated the percentage of PVP that dissolved out of the blend network from a simple mass balance equation:

$$\% \text{ PVP dissolution} = \frac{W_0 \cdot x_{\text{PVP},0} - W_t \cdot x_{\text{PVP},t}}{W_0 \cdot x_{\text{PVP},0}} \times 100\% \tag{5}$$

where W_t is the dry weight of the polymer film after immersion at time t, W_0 is the original dry weight before immersion, and $x_{\text{PVP},t}$ and $x_{\text{PVP},0}$ are the compositions of PVP at time t and time 0, respectively.

The percentage PVP dissolution behaviors of the 95/5, 90/10, 75/25, and 50/50 PVA/PVP blends are shown in Figure 6. By the end of 24 h of swelling in PBS, more than 80% of PVP dissolved from all four hydrogel formulations, despite the initial PVA/PVP contents. The PVP dissolution rate in the 1st hour increased with higher initial PVP content. This rapid dissolution of PVP was attributed to the relatively high affinity of PVP for water and to the bulky nature of the PVP. The carbonyl groups in PVP are strong proton acceptors, which can form hydrogen bonds with both PVA and water molecules. Therefore, water provides competition for hydrogen bonding, and increased amounts of water will lead to the dissolution of hydrogen bonds between PVP and PVA. Furthermore, the bulky pyrrolidone groups would hinder the formation of PVA crystallites and, thus, have a significant impact on the hydrogel network structure. Even though more hydrogen bonds could form in the amorphous regions of the blends with higher PVP contents, the hindrance of PVP on the formation of PVA crystallites led to a lower degree of crosslinking of hydrogel networks. These more loosely crosslinked systems took up water more quickly, which resulted in a faster dissolution of PVP from the network.

The dissolution of PVA upon hydrogel swelling was also calculated in the same way. For the original 5 and 10 wt % PVP blends, no significant loss of PVA was observed; whereas for the 25 and 50% PVP blends, about 3.5 and 6% of the PVA dissolved out after 24 h of immersion in PBS. The dissolution of PVA was also a result of the less crosslinked networks, which resulted from increased concentrations of pyrrolidone groups in the blend system.

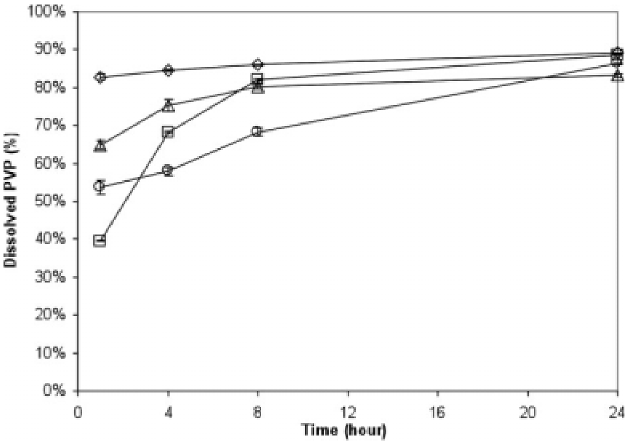

Figure 6 PVP dissolution from the PVA/PVP network. Initial PVA/PVP ratio: (□) 95/5, (○) 90/10, (△) 75/25, and (◇) 50/50 ($n = 5$).

Equilibrium swelling behavior

As shown in the DSC results (Fig. 2), the degree of crystallinity of PVA decreased with increasing PVP content in the blend system, which indicated that fewer crystallites were formed with higher initial PVP content. However, after immersion in water, the components of the blends, mainly PVP, dissolved out of the hydrogel network. To understand the true swelling behavior of the ensuing hydrogels after the dissolution of PVP, the blend films were cut into discs 6.4 mm in diameter and immersed in PBS for 1 week to let the system reach equilibrium. The discs were dried *in vacuo* for 72 h. The swelling study was then performed on the dry discs in PBS (pH 7.4) in a shaking bath at 37°C for 8 weeks to mimic long-term physiological exposure. The masses of the gels were measured after 0.5, 1, 4, 8, and 24 h of swelling and then daily for the 1st week and weekly for 8 weeks (56 days). The PBS solutions were changed daily for the 1st 2 weeks and then weekly. q was calculated as the ratio of the gel weight to the dry weight of the discs at each set time. After 8 weeks, the swollen discs were removed from the solution, and the dry weights were measured. No significant difference in dry mass was observed for the samples, as the compositions of PVA and PVP had already reached equilibrium during the 1-week preswelling process. Therefore, the density of each dried film was assumed to remain the same throughout the duration of the study. With this assumption, Q was calculated with eq. (2).

The hydrogels with more PVP initially present in the blends had higher Q's (Fig. 7), which indicated that the network was less physically crosslinked, which was in agreement with the DSC results. The networks with high PVP content were more expandable in water and, therefore, capable of absorbing more water. The water content of each hydrogel at the end of 56 days of swelling was calculated with the assumption that the weight of polymer did not change over time:

$$\%\ \text{Water content} = \frac{W_{\text{gel}} - W_p}{W_{\text{gel}}} \times 100\% \tag{6}$$

where W_{gel} is the hydrogel weight at the end of 56 days of swelling and W_p is the dry weight of the sample before swelling.

The water content ranged from 65% for the pure PVA films to 76% for the original 50/50 blends (Fig. 8). The crystallites of PVA acted as crosslinking points to hold the hydrogel network together, which resulted in a three-dimensional structure that did not dissolve in water. Fewer crystallites, or fewer crosslinks, present in the network resulted in a more flexible structure that was able to absorb more water. Therefore, the water-absorbing ability was related to the network structure and offered some information about the degree of crosslinking for a given network.

Structural analysis

The structures of the hydrogels were evaluated and characterized with rubber elasticity theory on the basis of swelling studies and mechanical analysis. The shear modulus (G) was related to the degree of swelling and was calculated as follows[38]:

$$\frac{\tau}{\alpha - 1/\alpha^2} = G v_{2,s}^{-1/3} \tag{7}$$

where τ is the shear stress, α is the elongation, and $\upsilon_{2,s}$ is the equilibrium polymer volume fraction in the swollen state, which was obtained from the swelling studies.

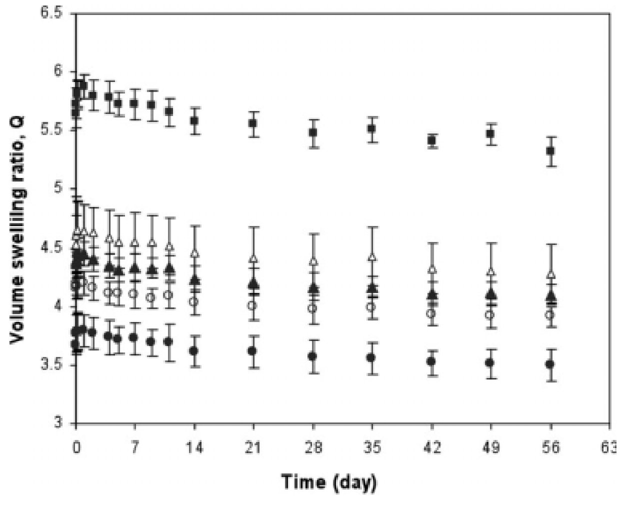

Figure 7 Q of PVA/PVP after 1 week of predissolution. Initial PVA/PVP ratio: (●) 100/0, (○) 95/5, (▲) 90/10, (△) 75/25, and (■) 50/50 (n = 5).

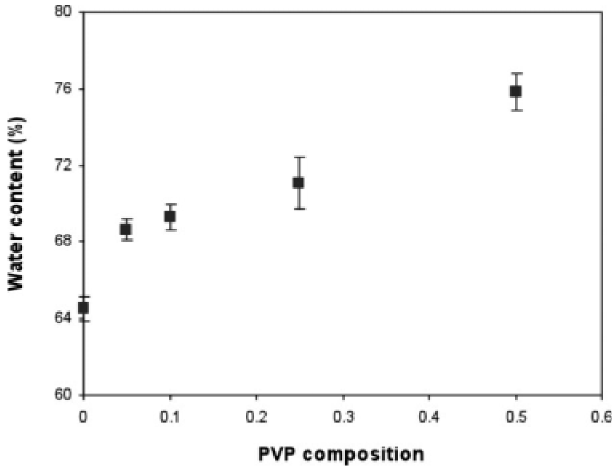

Figure 8 Water content of the PVA/PVP hydrogels after 56 days of swelling (n = 5).

For hydrogel networks in the presence of a solvent, the following expression was developed by Peppas and Merrill[34]:

$$\frac{\tau}{\alpha - 1/\alpha^2} = RT_{\rho_{2,r}}\left(\frac{1}{\overline{M_c}} - \frac{2}{M_n}\right)\left(\frac{v_{2,s}}{v_{2,r}}\right)^{1/3} \tag{8}$$

where $\rho_{2,r}$ is the density of the polymer in the relaxed state, immediately after crosslinking but before swelling, and was calculated as the weighted average of the densities for our physically blended gels. $\upsilon_{2,r}$ is the polymer volume fraction in the relaxed state, $\overline{M_c}$ is the average molecular weight between crosslinks, and M_n is the number-average molecular weight of the polymer blend chains.

As noted earlier, most PVP dissolved out of the hydrogel network in the buffered solution, despite the starting PVP composition. M_n could be treated as the M_n of PVA alone (M_n = 77,000) with the assumption that all of the PVP dissolved out of the hydrogel network by the end of the swelling studies. Combining eqs. (7) and (8), we calculated $\overline{M_c}$ for the hydrogels that were swollen for 56 days (Fig. 9). The values of $\overline{M_c}$ increased for the hydrogels with more PVP initially blended in the system, which indicated that fewer crosslinks were present.

The hydrogel average mesh size (ξ) is the linear distance between junction crosslinks and was calculated as follows[32,39,40]:

$$\xi = \left(\frac{2C_n\overline{M_c}}{M_0}\right)^{1/2} l v_{2,s}^{-1/3} \tag{9}$$

where C_n is the characteristic ratio, M_0 is the molecular weight of the average repeating unit calculated, and l is the carbon–carbon bond length for vinyl polymer chains (l = 1.54 Å).

As it was assumed that all PVP had dissolved out by the end of 56 days, the values of PVA used were for $C_{n,\ \mathrm{PVA}} = 8.3^6$ and $M_0 = 44$ g/mol. The ξ values of the hydrogels ranged from 90 to 230 Å and increased with increasing PVP content in the blends (Fig. 10). ξ is the average end-to-end distance between the crosslinks in the polymer networks. Hydrogels with bigger ξ values have fewer crosslinks and are more swellable in aqueous solutions. The dissolution studies showed that most of the blended PVP dissolved out of the hydrogel network during the swelling process, whereas most of PVA remained in the system, which indicated that the crystallites of PVA were the main source of physical crosslinks present in the hydrogels. The initial presence of PVP in the blends hindered the formation of PVA crystallites, which led to fewer crosslinked hydrogel networks. As a result, the calculated ξ for the network increased with increasing initial PVP content in the blends.

CONCLUSIONS

The PVA/PVP blends were miscible over the composition range tested in this study, as confirmed by DSC thermograms with the appearance of a single glass-transition temperature. The negative value of χ_{12}, obtained from ΔT_m, also verified the homogeneous miscibility of the two polymers.

The stability of the PVA/PVP blends was studied in PBS at physiological temperature and pH, and PVP was found to dissolve out of the hydrogel networks with ATR-FTIR spectrometry. The percentage of PVP dissolution was shown to approach an equilibrium value regardless the starting PVP content, which indicated that the formation of hydrogen bonds between PVA and PVP in the presence of water was a dynamic equilibrium process. Additionally, the crystallites of PVA were found to be the dominating source of physical crosslinking in the hydrogel network. Hydrogels with various structures, that is, ξ's, swelling behaviors, and mechanical properties, were obtained after the dissolution of PVP reached equilibrium.

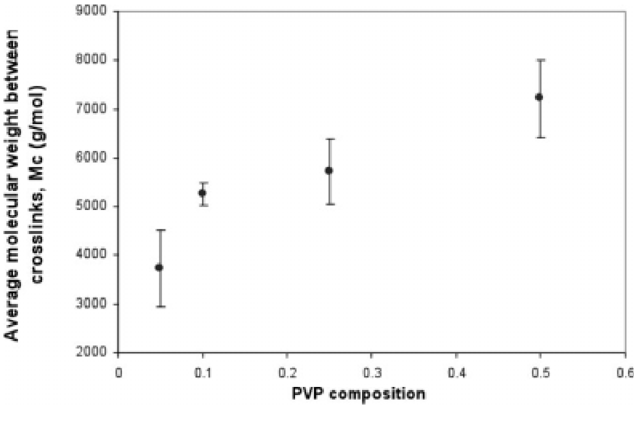

Figure 9 $\overline{M_C}$ after 56 days of swelling ($n = 5$).

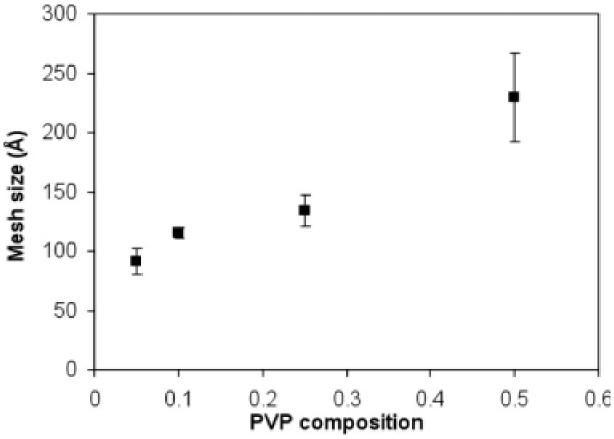

Figure 10 ξ of hydrogels with different PVP contents after 56 days of swelling ($n = 5$)

Overall, the blending of PVA and PVP offered a competitive way to synthesize biocompatible hydrogels with desired structures and mechanical properties by the mere adjustment of the composition of PVP in the system.

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