

Effect of PEO on the Network Structure of PVA Hydrogels Prepared by Freezing/Thawing Method

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ABSTRACT: Poly(vinyl alcohol) (PVA)/poly(ethylene oxide) (PEO) hydrogels were prepared by freezing/thawing method for application as a wound dressing. The effect of PEO content on the network structure of PVA hydrogel was investigated in terms of crystalline and rheological properties. It was found that a low amount of PVA crystallites were present in PVA/PEO hydrogels. With increasing content of PEO, the crystallinity of PVA hydrogel decreased, but the apparent dimensions of crystallites increased. The shear storage modulus (G') decreased slightly with the increasing temperature within 30–50°C, probably resulting from the breaking of the hydrogen bonding; while it decreased sharply within 50–70°C, probably resulting from the melt of the crystallites of PVA hydrogel. The physical crosslinking density (D_{pc}) increased with decreasing PEO content, while decreased more dramatically with increasing temperature, indicating that hydrogen bonding was easier to be broken at high temperature. At very low strain amplitudes, the loss modulus (G'') of the hydrogel is lower than the storage modulus (G') and G' is independent of the strain amplitude, indicating that the deformation imposed on the network structure is entirely reversible. With increasing content of PEO, G' at low frequency decreased, and the mesh size (L_c) increased, indicating of the decrease of the physical crosslinking density of PVA/PEO hydrogels.

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INTRODUCTION

In recent years, hydrogels with high water content, mechanical strength, and elasticity prepared by aqueous solution of PVA have received increasing interest for their various pharmaceutical and biomedical applications. PVA hydrogels can be cross-linked by difunctional crosslinking agents, electron beam or γ -irradiation and freezing/thawing method, of which freezing/thawing method addresses toxicity issues because it does not require the presence of a crosslinking agent, and freeze/thawed gels have also demonstrated enhanced mechanical properties, particularly for biomedical applications.^{1,2}

Since the preparation of pure PVA hydrogels using freezing/thawing techniques was first reported by Peppas in 1975,³ a considerable amount of research has been conducted on the freezing/thawing process as well as on the characterization of such gels produced with these techniques. These previous works demonstrated that frozen/thawed PVA hydrogels can be considered as complex systems whose structure and macroscopic properties depend on several phenomena (crystallization, hydrogen bonding and, in some cases, phase separation) occurring

during gelation. The presence of crystals in frozen/thawed PVA hydrogels has been indicated by different authors employing several techniques as, for instance, solid-state ¹³C-NMR, DSC, X-ray diffraction, and wide-angle scattering techniques.^{4–6} NMR experiments performed on a-PVA hydrogels obtained by freeze/thaw cycles has indicated the presence of hydrogen bonds and enabled the estimation of the number of monomer units involved in zero, one, or two hydrogen bonds.^{7,8} Moreover, there has been a considerable amount of research investigate the addition of other components, notably other polymers, with PVA to create a material with desirable characteristics, for example, PVA/PAA IPN-hydrogels were proved to be PH-sensitive; PVA/glycerin hydrogels was highly absorbent and converts wound exudates to the hydrogel matrices that create a moist and clean environment in the wound healing process.^{1,9,10}

Poly(ethylene oxide) (PEO) is a water-soluble, biocompatible thermoplastic polymer, which has been widely applied in biomedical fields. Low molecular weight PEO can be used as plasticizer due to its excellent chain flexibility, while high molecular weight PEO exhibits high mechanical strength and toughness

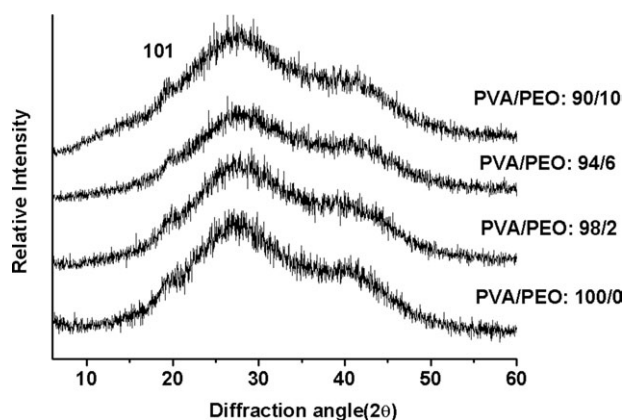


Figure 1. X-ray diffraction profiles of PVA/PEO hydrogels with different compositions.

and has been successfully applied as toughening agent of polymer materials. The system of PVA/PEO polymer blend is also of great interest. Iinamura et al. reported the presence of a liquid-liquid phase separation in the PVA/PEO/water system.¹¹ Yoshii et al. investigated the behavior of electron beam (EB) cross-linked PVA/PEO hydrogel.¹² PVA/PEO hydrogels with various compositions were also prepared by freezing/thawing method for application as a wound dressing in our previous work.¹³ It was found that both mechanical and swelling properties of PVA hydrogel increased with increasing content of PEO. In this work, the effect of PEO content on the crystalline and rheological properties of the PVA gel was investigated for the first time, and the network structure related with the crystallization and hydrogen bonding of the gel was demonstrated.

EXPERIMENTAL

Materials

PVA (polymerization degree of 1000, hydrolysis degree of 99%) used in this work is a commercial product and supplied by Sichuan Vinylon (China). PEO with an average molecular weight (M_n) of 5×10^5 g/mol was purchased from Shanghai Jichen Chemical (Shanghai, China). Other chemical agents were all of analytical purity and used as received.

Preparation of PVA/PEO Hydrogels

Aqueous solution of PVA/PEO was prepared by dissolving PVA and PEO in distilled water at 95°C. The PVA/PEO compositions were 100/0, 98/2, 96/4, 94/6, 92/8, and 90/10 by weight, respectively. The PVA aqueous solutions were poured into mold, and hydrogel films with 2 mm thick were formed by subjecting the polymer aqueous solutions to 5 repeated freezing/thawing cycles, consisting of a 12 h freezing step at -20°C followed by a 4 h thawing step at room temperature.

Measurements

Wide Angle X-Ray Diffraction (WAXD) Analysis. Wide-angle X-ray diffraction analysis of PVA/PEO hydrogels was performed with a Rigaku D/max IIIB X-ray diffractometer (Japan) at room temperature. The Cu K α irradiation source was operated with a step size of 0.02° from $2\theta = 5$ –60°, the scanning rate was 3°/min.

Rheological Property

The viscoelasticity properties of PVA/PEO hydrogels were performed on Rheometer System Gemini 200 of Malvern Instrument Co. (UK) with parallel plates 25 mm in diameter with a plate-to-plate distance of 1–2 mm. Both the strain and the frequency sweep experiments were performed at room temperature. In the frequency sweep experiments, the shear storage modulus G' and loss modulus G'' were measured in the linear viscoelastic regime, for frequencies ranging from 0.1 to 100 Hz, at a maximum strain, γ of 0.1%. This γ value was determined by preliminary strain sweep experiments, in which the storage and loss modulus were measured as a function of strain at a fixed frequency value of 1 Hz to check if the deformation imposed on the gel structure during the rheological experiment was entirely reversible. A strain value, γ of 0.1% at 1 Hz was found to be suitable for all the samples investigated. The temperature dependence of the rheological properties was investigated in the temperature range of 30–50°C at 1 Hz with a heating rate of 1 K/min.

RESULTS AND DISCUSSION

Crystalline Behavior of PVA/PEO Hydrogels

The X-ray diffraction profiles of the PVA/PEO hydrogel films with different compositions were reported in Figure 1. The diffraction profiles of the samples exhibit two halos centered at $2\theta \approx 28^\circ$ and 41° , forming from water in the hydrogel, and a weak peak in the 2θ range 18–21° which corresponds to the diffraction planes (101) of crystalline PVA. This result demonstrates the presence of a low amount of small crystalline PVA aggregates in the PVA/PEO hydrogels.

The degrees of crystallinity (X_c) of the PVA/PEO hydrogel samples were evaluated from Figure 1 as the ratio between the area of the crystalline reflection in the 2θ range 18–21° and the area subtending the whole diffraction profile of the gel sample. As shown in Table I, in all cases, X_c is very low, in the range 0.27–2.08%, and it decreases with increasing content of PEO.

Apparent crystalline dimensions along the diffraction planes (101) were calculated by measuring the half-width of the corresponding Bragg reflection and applying the Scherrer formula^{14,15}:

$$D_{hkl} = \frac{k \cdot \lambda}{\beta \cdot \cos \theta}$$

where D_{hkl} is the apparent crystalline dimension along a given lattice direction, k is a constant ($k = 0.89$ rad), λ is the wave

Table I. Degree of Crystallinity and Apparent Dimensions of Crystallites of PVA/PEO Hydrogels with Different Compositions

PVA/PEO (weight ratio)	2θ	Peak height (counts/s)	Crystallinity (X_c %)	Apparent dimensions of crystallites (Å)
100/0	19.177	72.32	2.08	40
98/2	19.444	72.93	1.28	51
94/6	19.630	75.03	0.93	61
90/10	19.017	70.85	0.27	93

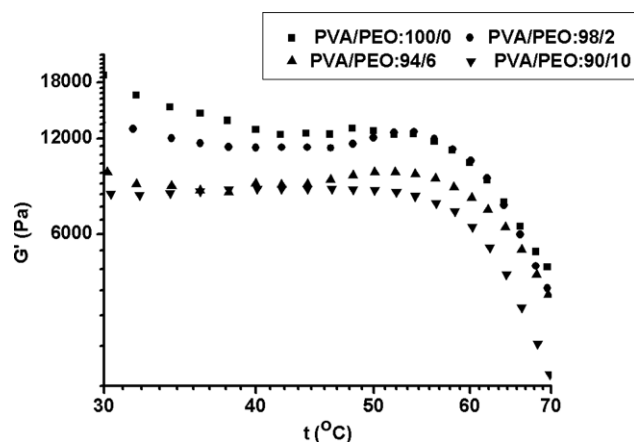


Figure 2. Storage modulus G' as a function of temperature for PVA/PEO hydrogels with different compositions.

length of the X-rays, β is the half-width (expressed in radians), and θ is the Bragg angle. As shown in Table I, the apparent dimensions of crystallites increases with increasing content of PEO, indicating the increase of the crystallite size of the PVA crystalline.

Physical Crosslinks in PVA/PEO Hydrogels

The temperature dependence of shear storage modulus G' is plotted in Figure 2 for hydrogel films with different PVA/PEO compositions. It can be seen that for all samples, G' decreased slightly with increasing temperature in the temperature range of 30–50°C, probably resulting from the breaking of the hydrogen bonding; while G' decreased sharply with increasing temperature in the temperature range of 50–70°C, probably resulting from the melt of the crystallites of PVA hydrogel. However, the more PEO content in PVA/PEO hydrogel film, the less the decreasing trend of G' .

According to Weisfeld etc., while the primary or covalent crosslinks are unaffected under normal conditions, secondary bonds, or physical crosslinks disappear with increasing temperature in a manner that may be estimated by the Arrhenius relationship^{16,17}:

$$D_{pc} \approx A \exp \left[\frac{-E_a}{RT} \right] \quad (1)$$

where D_{pc} is the secondary crosslink concentration, A a constant, R the general gas constant, T the absolute temperature, and E_a is the activation energy of bonding.

Since freeze/thawed hydrogels are formed by physical crosslinks, the measured modulus is the effective sum of secondary bonding effects, as shown as follows:

$$E = D_{pc}RT = ART \exp \left[\frac{-E_a}{RT} \right] \quad (2)$$

where E is elastic modulus. Another form of the equation can be written as:

$$\ln \left(\frac{E}{T} \right) = \ln(AR) - \frac{E_a}{RT} \quad (3)$$

E can also be obtained by

$$E = 2G'(1 + \mu) \quad (4)$$

where μ is Poisson ratio. As μ equals to 0.43–0.47 for hydrogel materials, we take average value 0.45 in calculation.

So eq. (5) can be written as:

$$\ln \left(\frac{G'}{T} \right) = \ln(AR) - \frac{E_a}{RT} - \ln[2(1 + \mu)] \quad (5)$$

Values of E_a thus obtained are in the order of 76–2096 J/mol. D_{pc} was therefore calculated according to eqs. (2) and (4). For the temperature range of 30–50°C, the plot of D_{pc} versus temperature was shown in Figure 3. It can be seen that for all samples of PVA hydrogel, D_{pc} decreased with increasing temperature, indicating of the breaking of hydrogen bonding. PVA hydrogel film with less PEO content has relatively high physical crosslink density, indicating of the increasing number of hydrogen bonds and degree of crystallinity of PVA hydrogel.

It can also be noted that for hydrogel film with less PEO content, D_{pc} decreased more dramatically with increasing temperature, indicating that large amount of weak hydrogen bonds per unit volume are easier to be broken at high temperature.

Network Structure of PVA/PEO Hydrogels

Figure 4 shows the strain dependence at the frequency of 1 Hz of the shear storage modulus, G' , and loss modulus, G'' for PVA/PEO hydrogels with different PVA/PEO composition. At very low strain amplitudes, the loss modulus of the hydrogel is lower than the storage modulus, which is consistent with the existence of a network structure. In addition, it can be noted (Figure 4) that, for small strain amplitudes, G' is independent of the strain amplitude, which indicates that the deformation imposed on the network structure is entirely reversible. At

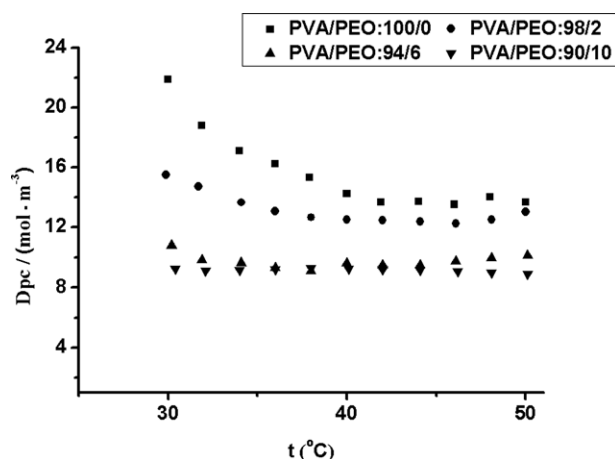


Figure 3. Physical crosslinking density of PVA/PEO hydrogels with different compositions.

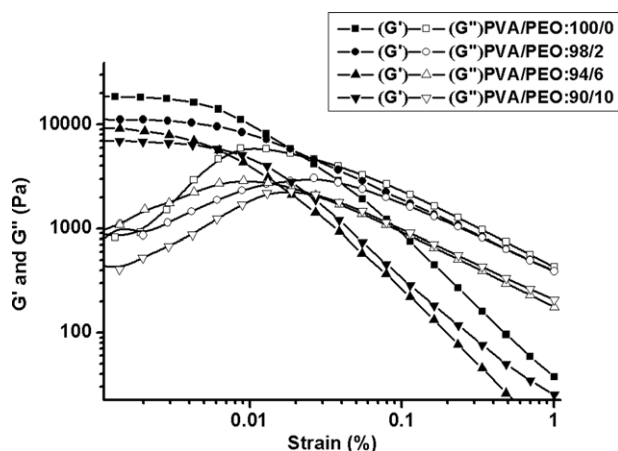


Figure 4. Storage modulus G' and loss modulus G'' at 1 Hz as a function of strain for PVA/PEO hydrogels with different compositions.

higher strain amplitudes, G' is a decreasing function of the strain amplitude and the deformation is no longer reversible.

The frequency dependence of G' is plotted in Figure 5 for hydrogel films with different PVA/PEO compositions. It can be seen that G' does not depend on the test frequency in the range between 0.1 and 100 Hz. With increasing content of PEO, G' decreased.

The relationships between the network structure of the PVA/PEO hydrogels and their rheological behavior can be better understood in Figure 6, where G' , the storage modulus values at 1 Hz, are plotted as a function of the degree of crystallinity, X_c , determined from X-ray diffraction analysis. It can be seen that the crystallinity of the hydrogel is the main factor that controls the G' values at low strain amplitude.

In the hypothesis that the hydrogels may be regarded as a classic network, in spite of the fact that they present a complex hierarchical structure, the storage modulus determined at low strain amplitude and low frequency of the hydrogels (i.e., in the fully elastic, reversible regime), G' may be related to the

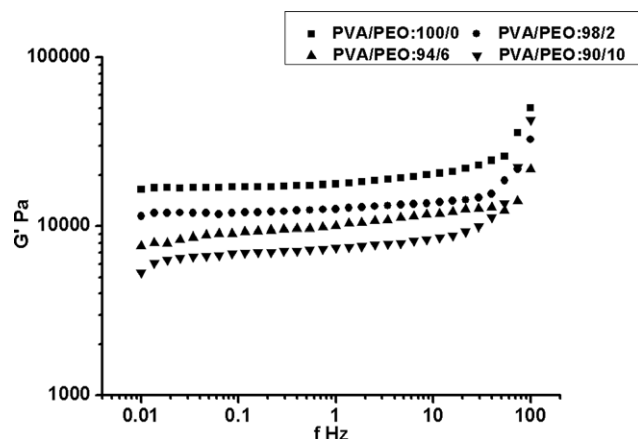


Figure 5. Shear modulus G' as a function of frequency for PVA/PEO hydrogels with different compositions.

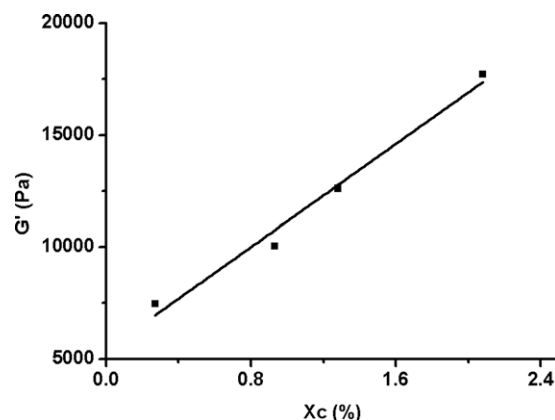


Figure 6. Shear modulus G' , at 1 Hz, as a function of the degree of crystallinity, X_c , for PVA/PEO hydrogels with different compositions.

average number of equivalent units in a “network strand,” N , connecting two “ideal” junctions and to the approximate, the average value of the network mesh size L_c by use of eqs. (6) and (7)^{5,10,14}:

$$G' = RT\Phi^{1/3}/N_{Av}a^3N \quad (6)$$

$$L_c = (\Phi)^{-1/3}(C_{\infty}N)^{1/2}a \quad (7)$$

In eq. (6) N_{Av} is the Avogadro number, G' is the shear modulus of PVA/PEO hydrogel samples, R is the gas constant, T is the absolute temperature, ϕ is the polymer volume fractions of gel in the swollen state, $N_{Av}a^3$ is the molar volume of the solvent, N is the average number of equivalent units with volume equal to the solvent volume (a^3), comprised between two junctions (in a “network strand”). In eq. (7) C_{∞} is the characteristic ratio of PVA, equal to 8.3.

As shown in Table II, values of L_c thus obtained are in the order of 47–87 nm. With increasing content of PEO, G' decreased, and L_c increased, indicating that addition of PEO reduced the physical crosslinking density. This result was consistent with the SEM result in our previous work.¹³ As shown in Figure 7, PVA/PEO hydrogel films represent a porous structure and the size of pores increased with increasing content of PEO.

In summary, in the PVA/PEO hydrogel network, the polymer chains interact through hydrogen bonding, which is responsible

Table II. Storage Modulus, G' at 1 Hz, Average Number of Equivalent Units in a Network Strand, N , and Average Length of Network Strands L_c , in PVA/PEO Hydrogels with Different Compositions

PVA/PEO (weight ratio)	G' (Pa)	N	L_c (nm)
100/0	17,720	5.60	47.05
98/2	12,610	8.20	59.41
94/6	10,040	10.81	71.62
90/10	7,481	14.99	87.14

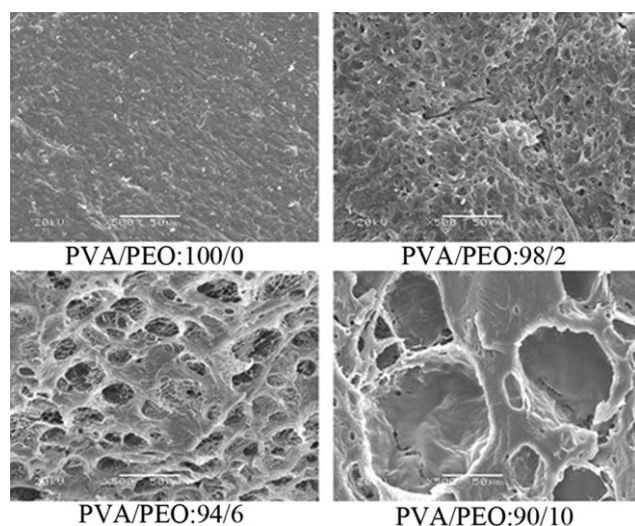


Figure 7. SEM of PVA/PEO hydrogel films with different compositions.

for the formation of crystalline region, and the crystallites act as physically cross-linking points. Addition of PEO to PVA/water system increased the distance between PVA molecules resulting in decrease of the number of hydroxyl groups in per unit volume, and thus the interaction of hydrogen bonding was weakened. Therefore, with the increasing content of PEO, the degree of crystallinity of PVA hydrogel decreased, and the physical crosslinking density decreased, resulting in the increase of the network mesh size and decrease of the storage modulus.

CONCLUSIONS

PVA/PEO hydrogels with various compositions were prepared by freezing/thawing method. The effect of PEO content on the network structure of the hydrogel was studied. The WAXD result showed that a low amount of small PVA crystalline aggregates were present in PVA/PEO hydrogels. With increasing content of PEO, the crystallinity of PVA hydrogel decreased, but the apparent dimensions of crystallites increased. The shear storage modulus (G') decreased slightly with increasing temperature within 30–50°C, probably resulting from the breaking of the hydrogen bonding; while G' decreased sharply with increasing temperature within 50–70°C, probably resulting from the melt of the crystallites of PVA hydrogel. The physical crosslinking density (D_{pc}) increased with decreasing PEO content, while it decreased more dramatically with increasing temperature, indicating that hydrogen bonding was easier to be broken at high temperature. At very low strain amplitudes, the loss modulus (G'') of the hydrogel is lower than the storage modulus (G')

and G' is independent of the strain amplitude, indicating that the deformation imposed on the network structure is entirely reversible. The crystallinity of the hydrogel is the main factor that controls the G' values. With increasing content of PEO, G' at low frequency decreased, the mesh size (L_c) increased, indicating of the decrease of the physical crosslinking density of PVA/PEO hydrogels.

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