

Characterization of hydrogel blends of poly(vinyl pyrrolidone) and poly(vinyl alcohol–vinyl acetate)

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Hydrogel blends were prepared from water-soluble polymers of poly(vinyl alcohol–vinyl acetate) and poly(vinyl pyrrolidone). The method of preparation was optimized and different compositions of blends were characterized. The effect of thermal treatment and the introduction of an aldehydic crosslinking agent in the blend was also studied. The swelling characteristics of the various compositions, their thermal behaviour and the state of water was examined. Mechanical properties of the hydrogels were determined and it was observed that blends containing glutaraldehyde produced materials with good mechanical integrity and high water contents.

1. Introduction

The use of polymeric hydrogels as biomaterials is rapidly gaining importance due to their unique and interesting properties. The network structure present in hydrogels allows the retention of substantial amounts of water without dissolution of the polymer itself. The ability to retain water or other fluids imparts to the hydrogel low interfacial tension. Hydrogels also allow the permeation of low molecular weight moieties which is an advantage, especially in drug delivery applications.

Hydrogels are generally characterized by their hydrophilicity which is primarily due to the presence of hydrophilic groups in the matrix. The most important feature of a hydrogel is the amount of water it is able to absorb, defined as the equilibrium water content (EWC). Although a high water content is an attractive attribute, there are several disadvantages, the most important of which is poor mechanical strength which decreases with increasing water content.

Synthetic and natural polymers have been widely used as hydrogels. Poly(vinyl alcohol) (PVA) is an extensively studied polymer in relation to its use as a biomaterial [1] and from the point of view of the relative ease with which it can be crosslinked [2]. The majority of methods used to form hydrogels from PVA utilize a repeat freeze–thaw cycle of aqueous solutions, generating hydrogels with high water content. This repeated freeze–thawing process leads to the formation of crystallites which serve as the crosslinking bridges between chains [3, 4]. Peppas *et al.* [5] have reported the preparation of hydrogels from copolymers of N-2 vinyl pyrrolidone and vinyl acetate, using this method, resulting in materials with good mechanical properties.

In the present study hydrogel blends prepared from water-soluble polymers of PVA and poly(vinyl pyrrolidone) PVP are described and their characterization reported. PVP is a rigid polymer which possesses a bulky polar side group having a proton acceptor resulting in a relatively high glass transition temperature ($T_g = 158^\circ\text{C}$). The proton accepting group has the ability to interact with hydroxyl groups. PVA, on the other hand, is a ductile polymer and has available hydroxyl groups which may be able to provide a site for H-bonding. These combined features form the basis for blending the two components into a hydrogel.

The thermal behaviour of a number of such blends in both the xerogel and hydrated states has been studied. An assessment, by calorimetric measurement, of the state of water in the gels is also reported. The swelling characteristics and mechanical properties of these blends have been evaluated.

2. Experimental procedures

Poly(vinyl alcohol) (PVA), $M_w = 125\,000$, 88% hydrolysed (PVA) and poly(vinyl pyrrolidone) (PVP) $M_w = 44\,000$ were supplied by BDH and used without further purification. Glutaraldehyde (BDH) (50% aqueous solution) was used as a crosslinking agent at 5% w/w in the presence of lactic acid as catalyst.

1% aqueous solutions of individual polymers of PVA and PVP were prepared separately and mixed in order to obtain a final concentration of 25, 50 and 75% w/w of PVP. After mixing, the crosslinking agent was added in the presence of lactic acid and the mixture heated at 60°C for 1 h. Films were cast onto polystyrene Petri dishes, followed by drying at 60°C . Further crosslinking was introduced by thermal

treatment of the films at 120 °C and 150 °C after 30 min drying at 100 °C. The equilibrium water content (EWC) and related parameters were calculated as follows:

$$EWC = [(W_s - W_d)/W_s] \times 100$$

$$\text{Degree of swelling (DS)} = (W_s - W_d)/W_d$$

$$\text{Extractable mass (EM)} = [(W_i - W_d)/W_i] \times 100$$

where W_s is the weight of the swollen gel, W_d is the weight of the dry gel after swelling and W_i is the initial weight of the gel prior to swelling.

Calorimetric analyses were performed on a Perkin-Elmer DSC-7. DSC measurements on xerogels were carried out over the full range of compositions studied. Each of the xerogels were subjected to two heating and cooling cycles between 20 and 180 °C at a heating rate of 10 °C per minute in a nitrogen atmosphere. Hydrogels were tested by using fully hydrated gels at a heating rate of 2.5 °C per minute.

In order to assess the state of water in the hydrogels, gels were allowed to hydrate for 24 h and 10 mg of the hydrogel was sealed in an aluminium pan. The samples were then cooled to -50 °C and subsequently heated to 10 °C at a rate of 2.5 °C per minute.

For tensile tests, dumbbell specimens of 3 mm neck were thermally treated as previously stated and then swollen in distilled water for 24 h. Sample dimensions were measured before and after swelling using a micrometer. The hydrogels were tested using an Instron 4464 with a load cell of 2.5 N at a crosshead speed of 5 mm/min, keeping the samples wet by spraying constantly with water.

3. Results and discussion

The miscibility of polymer blends was studied using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The DSC thermograms (Figs 1 and 2) show the presence of a significant amount of water in the blends during the first cycle of heating even after the samples had been dried at 100 °C for a period of 30 min, a procedure which generally is an effective method to eliminate water.

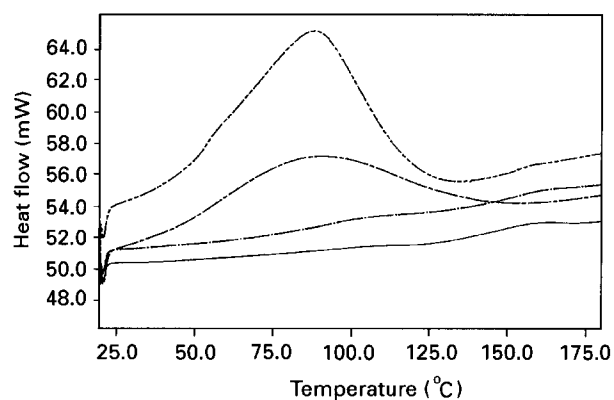


Figure 1 DSC thermograms for the first heating cycle of PVA:PVP blends of different compositions, PVP content: ----- 100%; -.-.- 75%; —·— 50%; ——— 25%.

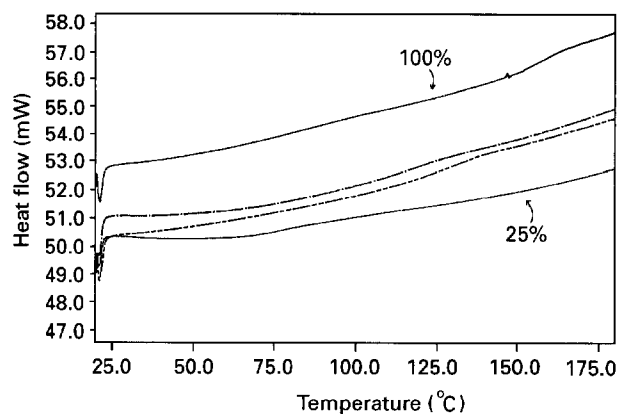


Figure 2 DSC thermograms for the second heating cycle of PVA:PVP blends of different compositions. PVP content: ----- 100%; -.-.- 75%; —·— 50%; ——— 25%.

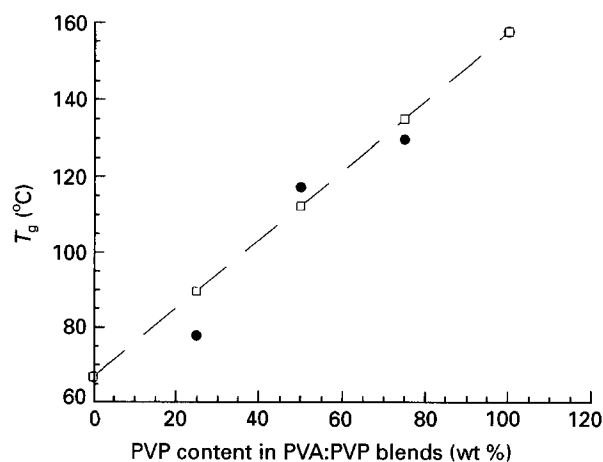


Figure 3 Comparison of calculated (□) and observed (●) values for T_g of PVA:PVP blends of different composition.

The water content was higher with higher concentrations of poly(vinyl pyrrolidone) in the blend. Two transition temperatures were observed for the 25% (PVP) and 50% (PVP) composition and no definite transition was observed for the 75% PVP blend due to water masking. Pure poly(vinyl pyrrolidone) which also showed retention of water, showed a transition at 158 °C in the second heating cycle. An analysis of each composition separately for the PVA25:PVP75 blend revealed no detectable transition in the first heating cycle due to masking by water but the second heating cycle showed a single T_g . This observation can be explained on the basis of the expulsion of water during the course of the scan and the formation of a network during the heating cycle. The PVA50:PVP50 blend showed phase separation more clearly in the first heating cycle, although a single T_g was observed in the second cycle. Finally the PVA75:PVP25 composition also showed two transitions in the first cycle, with the appearance of a single T_g in the second cycle. The appearance of a single T_g for all compositions in the second cycle confirmed the formation of a network during the heating cycle. A comparison of the T_g as observed in the second cycle of the different blends (Fig. 3) indicated an increase in value with increasing concentration of PVP. The experimentally determined

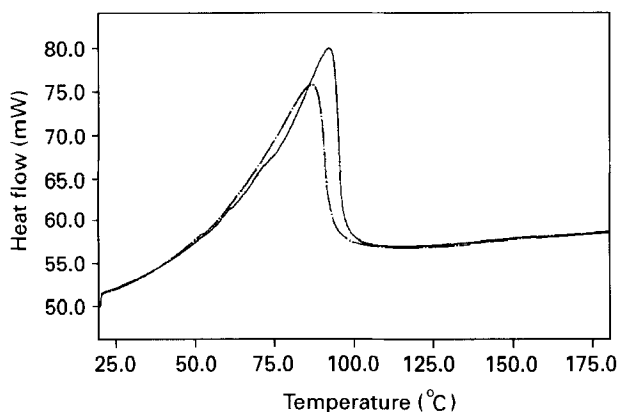


Figure 4 DSC thermograms of hydrogels of PVA50:PVP50 in the presence of glutaraldehyde, thermally treated at 120 (—) and 150 °C (---).

T_g values were in good agreement with the theoretically calculated values as shown in Fig. 3. The higher observed value of T_g for the 50% PVP:PVA blend compared to the calculated value indicates the existence of stronger interactions in comparison with the 25 and 75% PVP blends. The miscibility of the blends was further studied by dynamic analysis which again confirmed a single phase by the appearance of a single $\tan \delta$ peak for all compositions and a similar trend of increased values of T_g with increasing concentrations of PVP [6].

The xerogel blends of PVA50:PVP50 containing glutaraldehyde when further crosslinked by thermal treatment showed an increase in T_g with increasing crosslinking density which was further confirmed by DMA analysis [6]. Hydrogels based on PVA50:PVP50 in the presence of glutaraldehyde when heated from 20 to 180 °C showed a broad endothermic peak (Fig. 4) with two main features. Hydrogels with higher water content (thermal treatment at 120 °C) exhibited broader peaks than hydrogels with a lower water content (thermal treatment at 150 °C). Secondly, the maximum of the peak was found to be displaced towards higher temperatures but still remained below the normal boiling point of water, with an increase in water content.

The state of water molecules within the hydrogels was probed by DSC. Water molecules can be classified as free or bound water. This classification is based on cooling experiments where free water crystallizes at a higher temperature than bound water [8,9]. Two types of water were identified for the hydrogels in this study. Free water was associated with a sharp endothermic peak due to melting during the heating cycle and the bound water was observed as a broad peak with some overlap with the free water peak (Fig. 5). The melting point of free water was found to appear below 0 °C due to the presence of polymer chains in the solution.

PVA:PVP blends obtained by drying at 60 °C and those obtained after thermal treatment at 100, 120 and 150 °C were totally or partially soluble in water. Crosslinking was thus attempted on the 50% blend using glutaraldehyde (5 wt %) in the presence of lactic

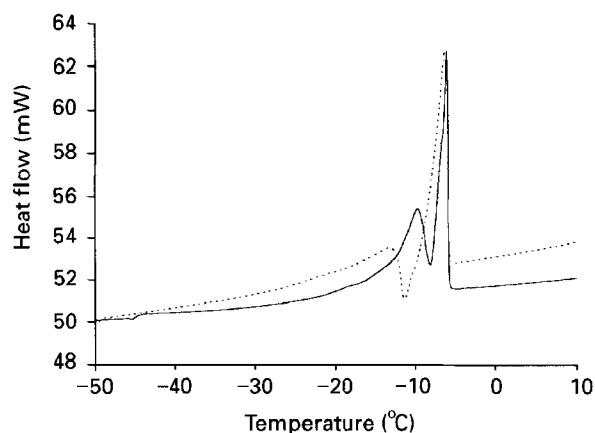


Figure 5 DSC thermogram indicating the state of water in a PVP:PVA (50%) hydrogel: — 120 °C; --- 150 °C.

TABLE I Swelling behaviour of PVA:PVP (50%) blends in presence of glutaraldehyde

Thermal treatment (°C)	Degree of swelling (%)	Equilibrium water content (%)	Extractable mass (%)
100	8.6	89.2	51.2
120	6.3	86.7	41.8
150	3.2	76.2	27.6

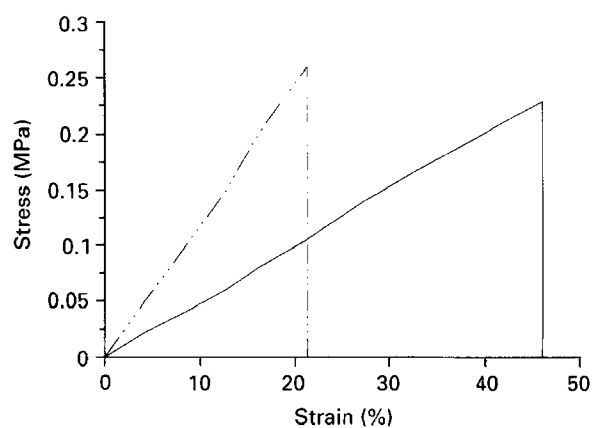


Figure 6 Stress-strain curve for a PVA:PVP (50%) hydrogel: — 120 °C; --- 150 °C.

acid as catalyst. This chemical crosslinking and subsequent thermal treatment produced hydrogels with high water uptake. The swelling behaviour of hydrogels is shown in Table I. It was observed that an increase in the temperature of the thermal treatment was followed by a decrease in the equilibrium water content, degree of swelling and extractable mass indicating a more highly crosslinked system.

The mechanical properties of hydrogels were determined for the PVA:PVP blends. From the stress-strain curve (Fig. 6) it can be seen that elastic hydrogels were obtained. It is evident that the presence of water in the hydrogels not only plasticizes the polymer network but increases the elasticity of the resulting gel. By increasing the crosslink density (thermal treatment at 150 °C), less water is allowed into the

TABLE II Mechanical properties of PVA:PVP (50%) blends in presence of glutaraldehyde

Thermal treatment (°C)	Ultimate tensile strength (MPa)	Young's Modulus (MPa)	Strain to failure (%)
100	0.10 ± 0.02	0.15 ± 0.07	70.0 ± 17.0
120	0.23 ± 0.10	0.61 ± 0.45	46.0 ± 27.0
150	0.26 ± 0.27	1.51 ± 1.00	21.0 ± 17.0

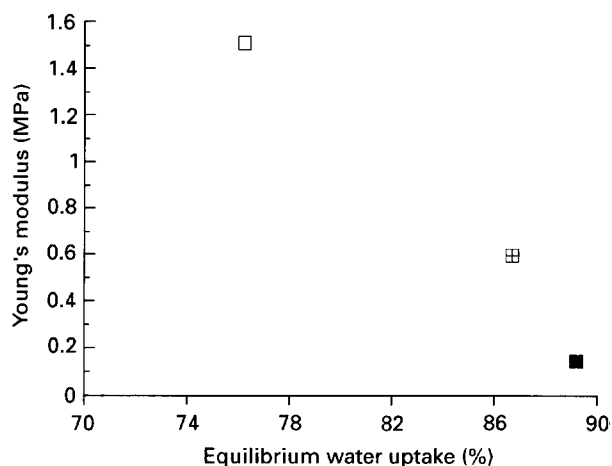


Figure 7 Variation of the Young's modulus with equilibrium water content of a PVA:PVP (50%) hydrogel thermally treated at 100 (■), 120 (□) and 150 °C (⊠).

hydrogel and a more brittle behaviour is observed. The mechanical properties of these hydrogels are presented in Table II. It can be seen that as thermal treatment is given at higher temperatures, the tensile strength and modulus increases whereas strain to failure is found to decrease. The variation of the Young's modulus with equilibrium water uptake is shown in Fig. 7. A comparison of these hydrogels with blends prepared from PVA with polyacrylic acid under the same conditions [6] show that PAA:PVA possess superior mechanical strength. However, the ring structure in the poly vinyl pyrrolidone group does not seem to contribute to the mechanical properties as much as might be expected but the hydrophilicity appears to be influenced by a greater degree. Epichlorohydrin cross-linked PVA hydrogels prepared by Bo [7] exhibited lower Young's modulus than the hydrogels studied here, suggesting that glutaraldehyde may be a more effective crosslinking agent and that the presence of

a second polymer is producing a reinforcing effect. These observations suggest that the mechanical behaviour of these types of hydrogels are not controlled by the chemical structure of the polymer used in their preparation but mainly by the amount of water present.

4. Conclusions

The present study shows that it is possible to prepare hydrogels by blending poly(vinyl alcohol-vinyl acetate) and poly(vinyl pyrrolidone) and subsequent crosslinking at 120 and 150 °C in the presence of glutaraldehyde. It was not possible to obtain hydrogels of PVA:PVP in the absence of a crosslinking agent by thermal treatment alone. The hydrogels exhibited a range of properties depending on the thermal treatment given and it was observed that an increase in the temperature of the thermal treatment provided a lower water content and subsequently an increase in ultimate tensile strength and Young's modulus. Hydrogels prepared by this method also showed the existence of both free and bound water.

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