

Dynamic mechanical characterization of hydrogel blends of poly(vinyl alcohol-vinyl acetate) with poly(acrylic acid) or poly(vinyl pyrrolidone)

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Transparent hydrogels were prepared by blending solutions of poly(vinyl alcohol-vinyl acetate) with either poly(acrylic acid) or poly(vinyl pyrrolidone) in the presence of glutaraldehyde as a crosslinking agent. The network obtained from the poly(vinyl pyrrolidone) system was subjected to various thermal treatments, the effects of which have been studied. Dynamic mechanical analysis was used to characterize the hydrogels and to establish the suitability of these blends for use in biomedical applications. The swelling behaviour was followed under dynamic loads as well as by mass difference. Different frequencies were used to study the dynamic properties of the hydrogel blends which showed an increase in storage modulus with increasing frequency. A comparison of modulus values obtained dynamically were in agreement with data obtained mechanically in tension.

1. Introduction

The important contribution that hydrogels make to biomedical applications are based on their unique properties, such as minimal interfacial tension with surrounding biological fluids, permeation, diffusion of low molecular weight compounds and reduced mechanical and frictional irritation to tissues [1]. Traditional characterization methods for hydrogels involve parameters such as equilibrium water uptake, mesh size and degree of crosslinking. Some data related to mechanical properties in tension, compression and shear are reported, the mode being related to the intended application [2, 3]. The dynamic mechanical analysis (DMA) of hydrogels and soft tissues reported in the literature are rare. The importance of this technique cannot be overestimated, considering that many applications of hydrogels involve the material being subjected to cyclic loads of differing magnitudes. Furthermore, information related to the viscoelastic behaviour of hydrogels can also be gained through DMA. In situations involving swelling, it is also possible to measure dynamic properties as swelling occurs.

Dynamic mechanical characterization is routinely performed for plastics, composites and rubbers, however, little is reported for hydrogels [4, 5]. Wilson and Turner [6] prepared hydrogels from poly(hydroxy ethyl methacrylate) (PHEMA) with water contents

ranging between 40 and 43%, testing at 11 Hz from -160 to -20°C using an Autovibron apparatus. A reduction in the storage modulus at -136°C was observed which was attributed to "devitrification" of water. The storage modulus decreased to half its value after this transition. Reported values for the modulus were rather high since they pertain to frozen hydrogels, no data was available at room temperature. Watase and Nishinari [7] studied the rheological changes in poly(vinyl alcohol) (PVA) gels induced by immersion in water. The dynamic modulus was determined on cylinders of PVA using a freeze and thaw technique. It was observed that for samples not immersed in water, the dynamic modulus increased with the number of freeze-thaw cycles. When the temperature was varied from 15 to 55°C , an initial increase in modulus was observed which decreased above 35°C due to chain disentanglement and melting of crystallites. Hydrogels of PVA prepared from a 15% solution by repeated freeze-thawing [8] also showed that mechanical modulus was a function of the number of freeze-thaw cycles. No significant variation of the viscoelastic properties from 15 to 50°C was observed but an irreversible change occurred at 50°C . Hydrogels prepared by freeze-thaw methods seem to generally show variation in the modulus at certain temperatures.

The present paper presents a study of dynamic mechanical behaviour of poly(vinyl alcohol-vinyl acetate)/poly acrylic acid and poly(vinyl alcohol-vinyl acetate)/poly(vinyl pyrrolidone) blends. The blends were prepared from water soluble polymers and did not involve a freeze-thaw cycle. Temperature, frequency and time dependence of the modulus are reported for different equilibrium water content (EWC) values in the hydrogel. A comparison of the mechanical properties of the hydrogel blends in a tension test mode and a cyclic loading situation are also reported.

2. Experimental procedures

Poly(vinyl alcohol) (PVA), $M_w = 125\,000$, 88% hydrolysed (PVA) and poly(vinyl pyrrolidone) (PVP), $M_w = 44\,000$, supplied by BDH were used without further purification. Poly(acrylic acid) (PAA), $M_w = 1\,250\,000$, supplied by Aldrich was used as received. 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 were mixed in order to obtain a final concentration of 50% w/w of polymer pairs; PAA-PVA and PVP-PVA. After mixing, an acidified solution of the crosslinking agent, glutaraldehyde, was added and the mixture heated at 60 °C for one hour. Films of the resulting polymer blends were cast onto polystyrene Petri dishes and dried 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 gels prepared from PVP-PVA were either partly soluble or completely soluble in water [11], hence, in the case of this system, a 50% blend with glutaraldehyde has been studied.

Dynamic mechanical analysis (DMA) was performed in tension using a Perkin-Elmer DMA-7 fitted with a water bath. Five specimens for each of the blends were tested. Hydrogel strips of 15 × 3 × 0.1 mm in dimension were tested at different frequencies, applying sufficient force to produce a deformation less than 2%. The temperature and frequency dependence of the modulus was recorded from 20 to 60 °C and 0.1 to 50 Hz, respectively. The time-dependent behaviour of each hydrogel was studied at selected frequencies of 1.0 and 10 Hz. The swelling behaviour of each hydrogel was also determined by both DMA and mass loss measurements.

3. Results

3.1. Miscibility of polymer blends

Clear and transparent films were obtained immediately after casting the polymer blends, suggesting complete miscibility of these systems. Thermal treatment of the xerogels resulted in a slight yellowish coloration. Further investigations into the miscibility of the blends using DMA showed that both PAA-PVA and PVP-PVA systems were miscible in the whole range of composition, which is in agreement with previous findings [9,10]. The presence of a single alpha transition (T_g) was observed in the $\tan \delta$ versus tem-

perature curves for both systems as can be seen in Figs. 1 and 2. As expected, with increasing crosslink density, this transition was displaced toward higher temperatures with a corresponding reduction in the value of $\tan \delta$ (Figs. 1 and 2).

All blends of the PAA-PVA system studied exhibited a single decrease in the storage modulus during the glass-rubber transition, which is characteristic of miscible blends. Modulus measurements indicated an increase in value with increasing PAA content, reaching a maximum at 50% composition. The modulus of pure PAA could not be determined accurately due to its brittle nature. In the case of DMA, the effect of thermal treatment was studied only on the PVA-PAA (50%) blend due to its superior properties. When thermal treatment was gradually increased from 100 °C to 120 and 150 °C, the modulus decreased at 120 °C but increased again at 150 °C. This observation can be explained by anhydride formation [12] at higher temperatures (150 °C) whereas only double bonds and ether formation occurs at 120 °C [13]. The ring structure of the anhydride contributes significantly to the mechanical properties. When glutaraldehyde was used to induce crosslinking, a steady increase in modulus was observed for the xerogels with increase in thermal treatment as can be seen in Table I.

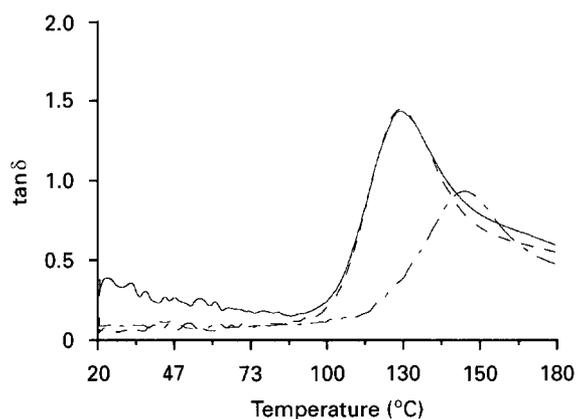


Figure 1 Effect of thermal treatment on the miscibility of 50/50 PAA-PVA blends: — 30 min, 100 °C; --- 0 min, 120 °C; -.- 0 min, 150 °C.

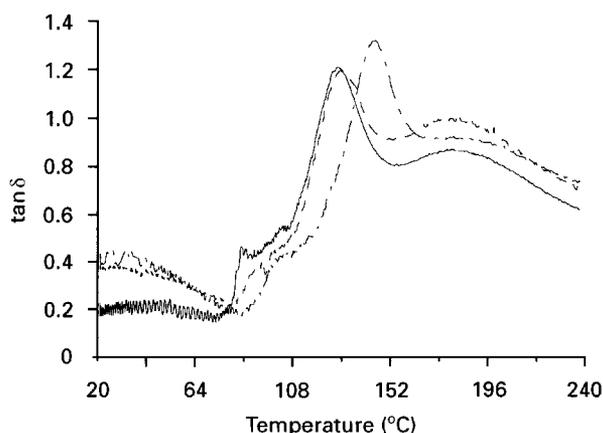


Figure 2 Effect of thermal treatment on the miscibility of 50/50 PVP-PVA blends: — 30 min, 100 °C; --- 0 min, 120 °C; -.- 0 min, 150 °C.

3.2. Swelling measurements

In each system studied, a two-stage swelling process was observed; the first stage involved softening followed by diffusion of water into the network. Hydrogels of higher water uptake were obtained with the PVP-PVA blend compared with the PAA-PVA blend. A reduction in the EWC value with thermal treatment confirmed the formation of a more highly crosslinked network. This increase in crosslink density also led to a reduction in extractable mass and an increase in the polymer volume fraction in the gel. These results are summarized in Table II.

The higher hydrophilicity of the PVP-PVA hydrogels was also evident from the swelling experiments under dynamic loads as can be seen in Figs. 3 and 4.

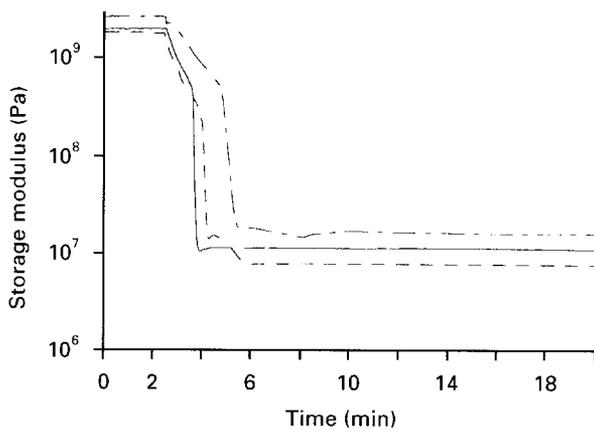


Figure 3 Modulus variation with time for 50/50 PAA-PVA blends after swelling: --- 30 min, 100 °C; — 0 min, 120 °C; - · - 0 min, 150 °C.

TABLE I Modulus variation in xerogels of PVA-PAA with thermal treatment with and without glutaraldehyde

Polymer blend	Thermal treatment (°C)	Storage modulus (Pa)
PVA-PAA (50%)	100	4.36×10^9
	120	1.31×10^9
	150	3.16×10^9
PVA-PAA (50%) + glutaraldehyde (5%)	100	9.39×10^8
	120	2.15×10^9
	150	2.50×10^9

TABLE II Swelling behaviour of hydrogels

Hydrogel	Thermal treatment (°C)	EWC (%)	Degree of swelling	Extractable mass (%)	Polymer volume fraction (v_2)
PVA-PAA (50 wt %) + 5% glutaraldehyde	120	32.6	0.48	6.40	0.67
PVA-PAA (50 wt %) + 5% glutaraldehyde	150	21.9	0.28	5.90	0.78
PVA-PVP (50 wt %) + 5% glutaraldehyde	120	86.7	6.30	41.8	0.13
PVA-PVP (50 wt %) + 5% glutaraldehyde	150	76.2	3.20	27.6	0.23

The time required to reach an equilibrium storage modulus was greater for the PAA-PVA hydrogels. Similarly, hydrogels thermally treated at 150 °C took a longer period of time to reach an equilibrium storage modulus than those prepared at 120 °C. The transition from a glassy xerogel to a rubbery hydrogel was indicated by a decrease in modulus; in the case of PAA-PVA hydrogels this was from an initial value of 10^9 Pa to a final value of 10^7 Pa whereas for the

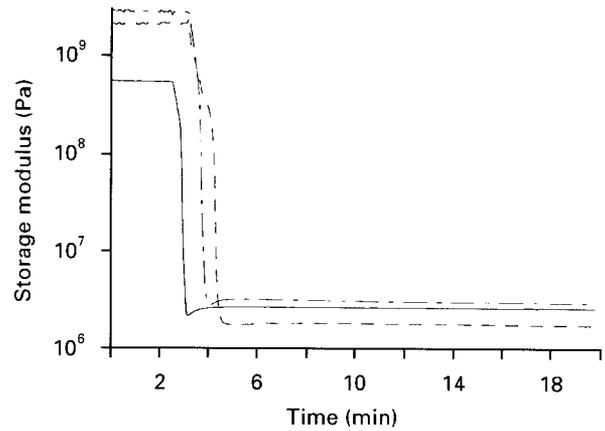


Figure 4 Modulus variation with time for 50/50 PVP-PVA blends after swelling: --- 30 min, 100 °C; — 0 min, 120 °C; - · - 0 min, 150 °C.

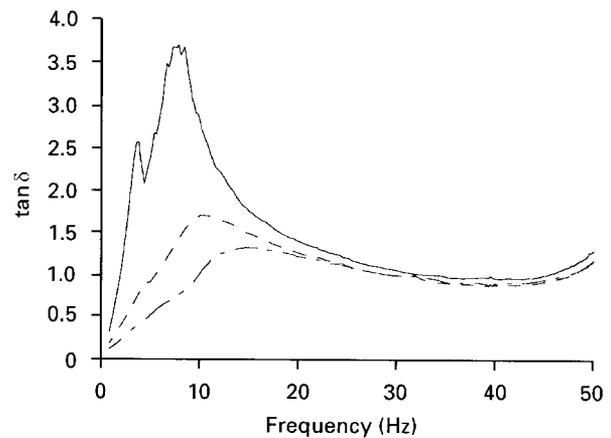


Figure 5 Frequency dependence of $\tan \delta$ for 50/50 PAA-PVA hydrogels: — 30 min, 100 °C; - · - 0 min, 120 °C; --- 0 min, 150 °C.

PVP-PVA hydrogels the decrease in modulus was from 10^9 to 10^6 Pa (Figs. 3 and 4).

When higher frequencies were used in the determination of dynamic properties of the hydrogels an increase in storage modulus was observed which remained constant with time. Furthermore, in the frequency range 0.1–50 Hz, a decay in the modulus was observed. Interestingly, when $\tan \delta$ was plotted against frequency, broad peaks were detected, the

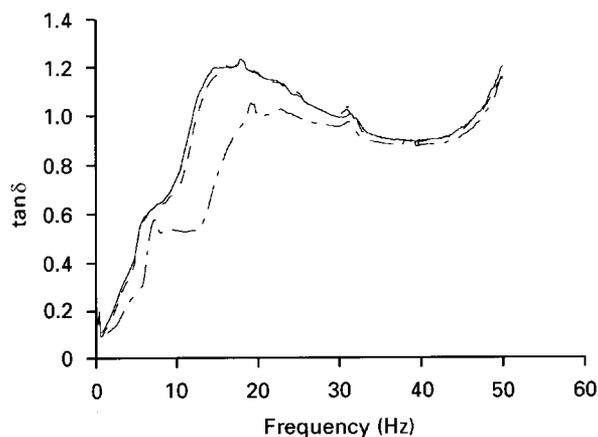


Figure 6 Frequency dependence of $\tan \delta$ for 50/50 PVP-PVA hydrogels: — 30 min, 100°C; --- 0 min, 120°C; - - - 0 min, 150°C.

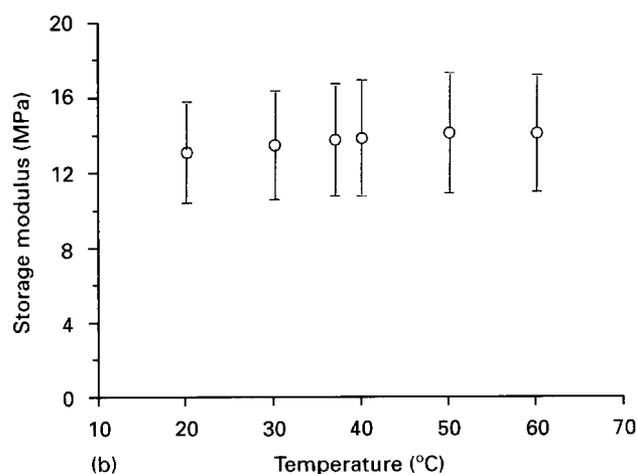
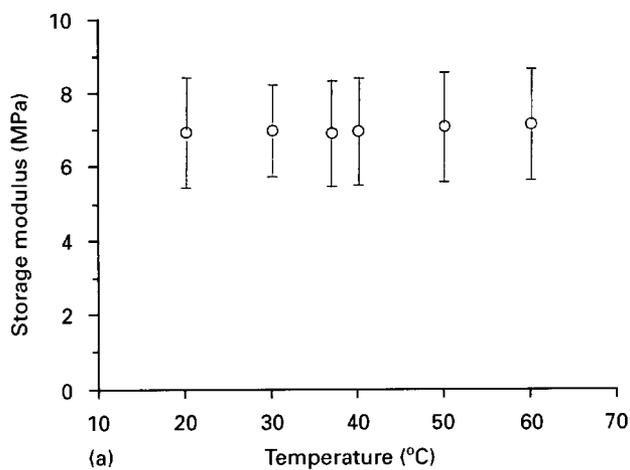


Figure 7 Temperature dependence of the storage modulus for 50/50 PAA-PVA hydrogels treated at (a) 120°C and (b) 150°C.

maxima being displaced towards higher frequencies with increasing crosslinking in the hydrogel network (Figs. 5 and 6). Dynamic properties were also determined for the hydrogel blends by varying the temperature between 20 and 60°C. The storage modulus of both PVA-PAA and PVA-PVP did not vary with temperature but the modulus increased with increasing thermal treatments for both PVA-PAA (Fig. 7) and PVA-PVP (Fig. 8).

DMA not only provided information related to the mechanical behaviour of these hydrogels but also

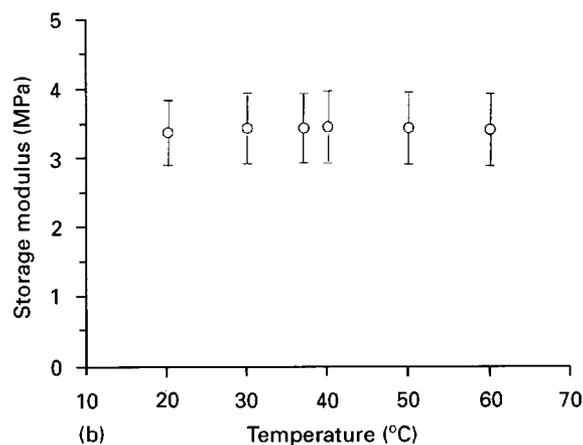
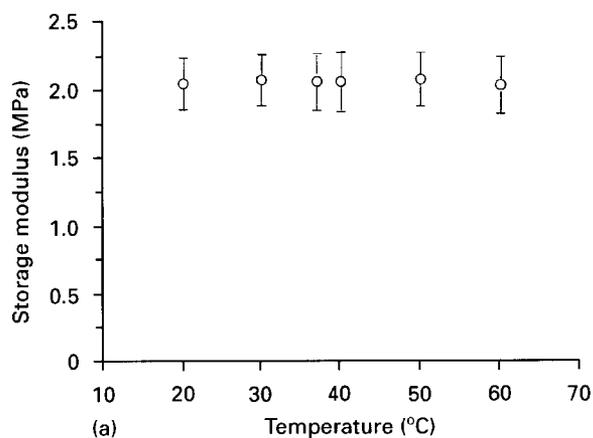


Figure 8 Temperature dependence of the storage modulus for 50/50 PVP-PVA hydrogels treated at (a) 120°C and (b) 150°C.

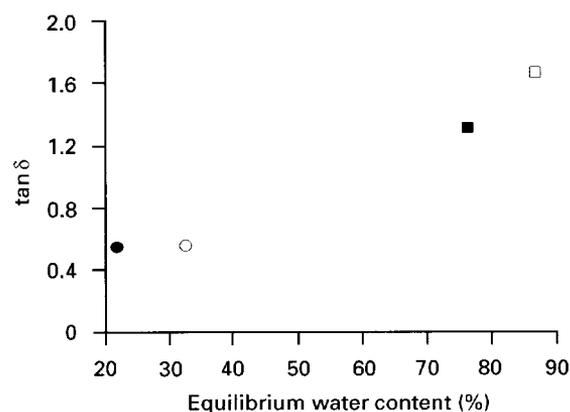


Figure 9 Dependence of $\tan \delta$ on EWC for PAA-PVA and PVP-PVA hydrogels. \circ PAA-PVA + GU, 120°C; \bullet PAA-PVA + GU, 150°C; \square PVP-PVA + GU, 120°C; \blacksquare PVP-PVA + GU, 150°C.

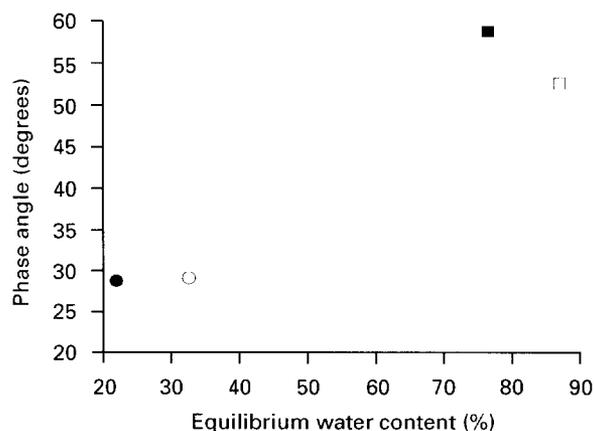


Figure 10 Dependence of the phase angle on EWC for PAA-PVA and PVP-PVA hydrogels. ○PAA-PVA + GU, 120 °C; ● PAA-PVA + GU, 150 °C; □ PVP-PVA + GU, 120 °C; ■ PVP-PVA + GU, 150 °C.

TABLE III Comparison of the storage modulus with Young's modulus for PVA-PVP (50%) and PVA-PVP (50%) blends

Hydrogel	Thermal treatment (°C)	Young's modulus (MPa)	Storage modulus (MPa)
PAA50-PVA50 + GU	120	20	17.2
PAA50-PVA50 + GU	150	20	32.9
PVP50-PVA50 + GU	120	0.61	1.80
PVP-PVA50 + GU	150	1.51	2.90

GU: Glutaraldehyde 5% by weight.

information on their viscoelastic behaviour. As can be seen in Fig. 9, hydrogels with higher water contents (PVP-PVA) exhibited higher $\tan \delta$ values. Correspondingly higher phase angles were also observed in the PVP-PVA hydrogel (Fig. 10).

Finally, a comparison of the modulus values obtained from DMA and mechanical tests on an Instron show good agreement, although the values are higher from DMA but are of the same magnitude (Table III). Also, the trends are in good agreement, which shows that modulus increases with thermal treatment in the case of hydrogels and PVA-PAA have higher modulus than PVA-PVP blends.

4. Conclusions

Isotropic hydrogels were obtained by crosslinking aqueous solution of PVA with either PAA or PVP. Higher water uptake was observed in the PVP-PVA

hydrogel due to the higher hydrophilicity of the PVP polymer. The superior mechanical properties of the PAA-PVA hydrogel are due to higher molecular weight and stronger hydrogen bonding. Dynamic mechanical analysis revealed important information relating to the swelling behaviour, modulus variation with crosslink density and transitions involved from xerogel to hydrogel. Increasing the crosslink density by thermal treatment increased the storage modulus. No significant change in modulus with temperature variation in the range 20–60 °C was observed indicating that these hydrogel blends have the thermal stability for application as an implant material. No change in the storage modulus was detected with time but a frequency dependency was observed.

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