Intermolecular interactions in a blend of poly(vinyl alcohol) and poly(sodium-L-glutamate)

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Tough and rubber-like hydrogels were prepared by blending concentrated aqueous solutions of poly(vinyl alcohol) (PVA) and poly(sodium-L-glutamate) (PSLG) in an autoclave under a pressure of $\sim 2 \times 10^5$ Pa at 120°C. The structure and interactions between PVA and PSLG in blends in the dry state were investigated. It is suggested that the blends consist of rigid segments of PVA chains which interact with PSLG side chains, small PVA crystallites which act as crosslink points and amorphous chain sequences of PVA and PSLG.

(Keywords: blend; hydrogel; poly(vinyl alcohol); poly(sodium-L-glutamate); molecular interaction; hydrogen bond; polymer complex)

INTRODUCTION

Hydrogels of poly(vinyl alcohol) (PVA) prepared by repeated freezing and melting[1] are rubber-like[2], and even with relatively higher water contents have a high modulus. Thus, they are useful as biomaterials[3]. We studied the reason for the high modulus[4,5] and concluded that it was due to the formation of crosslinks by multiply bonded water molecules in the crystalline and amorphous regions.

Recently other materials useful as tough and rubber-like high modulus hydrogels have been prepared from mixtures of water-soluble polymers such as PVA and poly(sodium-L-glutamate) (PSLG) in an autoclave at a slightly elevated pressure and temperature without repeated freezing and melting[6].

In studies by Kuhn *et al.*[7–9] the water-soluble non-ionic PVA has been shown to form rubber-like hydrogels having chemical crosslink points with a polyelectrolyte poly(acrylic acid). These materials are of great interest for the direct conversion of chemical to mechanical energy. Smith *et al.*[10] obtained a gelatinous precipitate by blending poly(ethylene glycol) with poly(acrylic acid), and prepared a clear, flexible and homogeneous film by heating and pressing after drying. They studied the stiffness, the glass transition temperature (T_g) and the heat stability of the film, and concluded that the unique properties of the complex resulted from hydrogen bonding between two polymers. Later, Ohno *et al.*[11–13] found in the system poly(methacrylic acid)/poly(*N*-vinyl-2-pyrrolidone) that by increasing the initial polymer concentration a homogeneous solution, precipitate and gel formed. Their study concentrated mainly on the formation mechanism of the blend in a dilute solution. They also proved the existence of hydrogen bonds by using calorimetry[14], as did Becturov *et al.*[15]. According to Kawakami *et al.*[16], a hydrogel was obtained by blending PVA with poly(sodium acrylate) in a relatively concentrated solution at $\sim 1 \times 10^5$ Pa, below 100°C and in low pH conditions.

In this paper, investigations are reported on the structure and interactions between PVA and PSLG in the dry state of the material obtained by blending concentrated aqueous solutions of these polymers in an autoclave at a slightly elevated pressure and temperature.

EXPERIMENTAL

Chips of poly(γ-methyl-L-glutamate) (PMLG) (degree of polymerization 280) were placed into a methanol/water (75/25 w/w) mixture containing 1.8 wt% sodium hydroxide, and allowed to saponify for 3 h under agitation. The resulting sodium salt of PMLG, namely poly(sodium-L-glutamate) (PSLG) was filtered, washed with methanol and dried *in vacuo*.

The PVA was supplied by Kurarey Co. Ltd as POVAL-120 (degree of polymerization 1700, degree of saponification 98.5 mol%). It was dissolved in water at a concentration of 12.5 wt% using an autoclave at 120°C with stirring. The PSLG (12.5 wt%) solution was obtained at room temperature using agitation. Mixtures of PVA with PSLG in three different ratios, with pH ~ 6, were prepared in an autoclave under $\sim 2 \times 10^5$ Pa at 120°C. After storage at room temperature for 1 day, the solution separated into two phases, one of which was a solution, while the other was a rubber-like coagulated high modulus hydrogel. No such high modulus hydrogels were prepared from mixtures at normal atmospheric pressure. However, they were formed from a concentrated aqueous solution of PVA in the autoclave at a slightly elevated pressure and temperature in the same pH conditions of the mixtures. The coagulated hydrogels obtained were then dried at 70°C *in vacuo* for 6 days and were used as samples in further studies.

To determine the true PSLG content in the blends, ^{1}H nuclear magnetic resonance (n.m.r.) spectra were obtained using a Varian 200 MHz spectrometer with a

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solid content of ~10% in D_2O solution. The true PSLG contents were calculated from the ratio of the peak areas of -CH and -NH groups for PSLG against the total areas.

Differential scanning calorimetry (d.s.c.) experiments were performed on a Perkin Elmer DSC-II in the temperature range −30 to 250°C at a heating rate of 20°C min^{-1}.

Loss tangent (tan δ) curves were obtained by using a Rheovibron-IIC (Toyo Boldwin Co. Ltd) at a frequency of 11 Hz and a heating rate of 1.5°C min^{-1}.

Fourier transform infra-red (*FT*i.r.) spectra were obtained using a model AQS-20 spectrometer (Analect Service Engineer Co. Ltd) using KBr disks (32 scans were used).

Wide angle X-ray scattering experiments were performed using a diffractometer (Rigaku-Denki 2028) at a scanning rate of 1° min^{-1}.

RESULTS AND DISCUSSION

Figure 1 shows the effect of PSLG content of the initial mixture on the PSLG content of the blends. The PSLG content in the hydrogels is smaller than that of the initial solution. Since phase separation was observed as described above, part of the PSLG from the original solution must have remained in the supernatant liquid.

Figure 2 shows d.s.c. thermograms. The onset of the glass transition and the melting of PVA are observed clearly at ~70 and 210°C. There are two jumps in the d.s.c. curve of PSLG which begin at −10 and 150°C, respectively. PSLG is the sodium salt of poly(L-glutamic acid) (PGA) whose side chain length is similar to that of PMLG. PMLG exhibits two dispersions, one is at room temperature, while the other is at ~140°C on the tan δ curve. They have been ascribed to the segmental motions of the long side chain and of the main chain[17,18] in PMLG, respectively. It is suggested that, in the case of PSLG, the two discontinuities correspond to the same processes. The T_g of the PGA main chain was observed at 130°C by d.s.c.[19]. Since the corresponding process in PSLG occurs at a temperature higher by ~20°C than in PGA, it seems reasonable that the segmental mobility of the PSLG main chain is reduced by the presence of sodium ions, and is thus shifted towards higher temperatures than that of PGA.

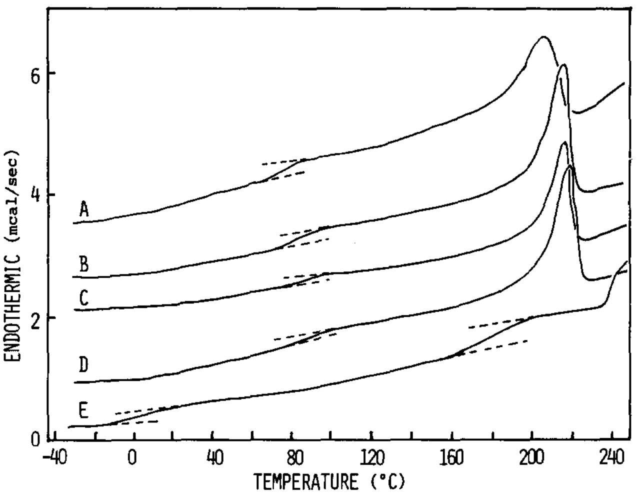

Figure 2 D.s.c. thermograms of pure PVA(A) and the blends PVA/PSLG = 7/3(B), 5/5(C) and 3/7(D) and pure PSLG(E)

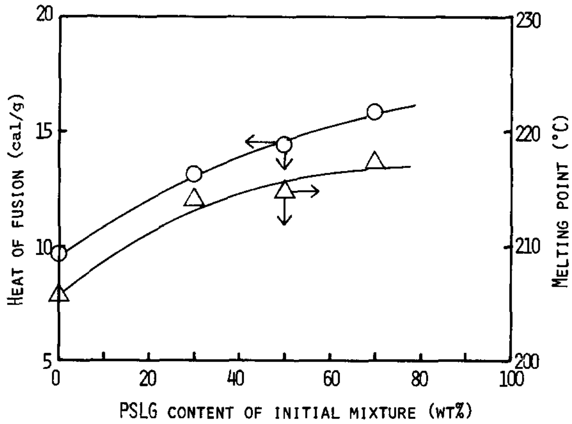

Figure 3 Heat of fusion (○) and melting point (△) as a function of PSLG content

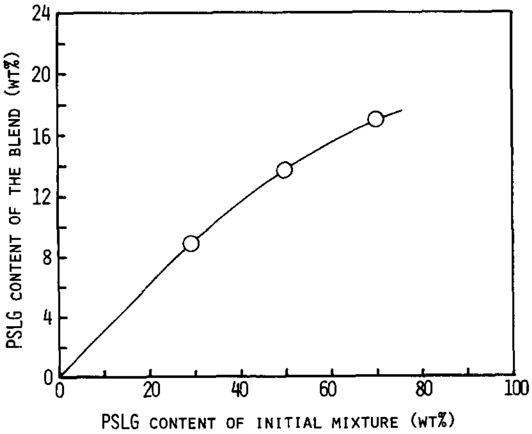

Figure 1 Relation between the PSLG content in the initial solution and the PSLG content of the hydrogel

In the case of the blends, the low temperature discontinuity ascribed to side chain motion is not observed in the d.s.c. curve. Because of the strong interaction between the ionic groups in the PSLG and the hydroxyl groups in the PVA, the PSLG side chains are surrounded in the blends by material which is very different from that in the homopolymer. There is only one discontinuity due to the glass transition, which becomes less intense with increasing PSLG content. Thus, it is reasonable to conclude that the PVA chains interact with the PSLG side chains and become more rigid segments. Also, it can be seen that the T_g of PSLG is shifted slightly towards higher temperatures than that of PVA. This also suggests that the interaction decreases the segmental mobility of the remaining amorphous PVA which does not interact with the PSLG side chains. Above 230°C, both PVA and PSLG are subject to degradation, as seen in the upswing increasing slope of the d.s.c. curve. This feature is not seen in the blends, which may suggest increased stability of the systems. Since both PVA and PSLG are amorphous above ~220°C, it is clearly seen that blending increases the thermal stability of the materials.

Melting of PVA crystallites is observed above 165°C in the blends. *Figure 3* shows the dependence of the heats of fusion (ΔH_m) and the melting temperatures (T_m) of the PVA on the PSLG content. Both ΔH_m and T_m increase with increasing PSLG content, although usually these values for a crystalline polymer decrease on blending[20]. On the other hand, as will be seen later from the *FT*i.r. results, the crystallinity decreases with increasing PSLG content. These results are very unusual and the discrepancy suggests that the crystallites of PVA are more highly organized in the blends than in the pure PVA homopolymer, i.e. there is an increase in crystallite size and a difference in density between the crystalline and amorphous regions.

The crystallite size was calculated from Sherrer's equation by using a 1 0 1 plane:

$$\text{crystallite size}_{hkl} = \frac{K\lambda}{\beta_0 \cos\theta} \qquad (1)$$

where $h\ k\ l$ is the index of the plane, $K = 1$, $\lambda = 1.54$ Å, and β_0 is the half width of the 1 0 1 plane. The crystallite size of PVA increases with increasing PSLG content, as shown in *Figure 4*. This result supports the above discussion.

Figures 5 and *6* show the temperature dependences of the loss tangent (tan δ) and storage modulus (E'), respectively. The T_g of PVA is observed[21] as a shoulder at 86°C (arrow) which is higher by ~15°C than the T_g measured by d.s.c. This discrepancy may be due to the different frequencies of the experiments. Molecular motions in the disordered crystalline regions of PVA are observed[21,22] as a broad peak at 115°C; this molecular motion was not observed in the d.s.c. curve. The E' value of PVA decreases in a manner reported by other investigators[19]. The drop in the modulus is associated with the molecular motions both in the non-crystalline regions as well as in the imperfectly formed crystallites. The tan δ curve for PSLG was not observed because the PSLG used was of a very low degree of polymerization and the film cast from aqueous solution was very brittle.

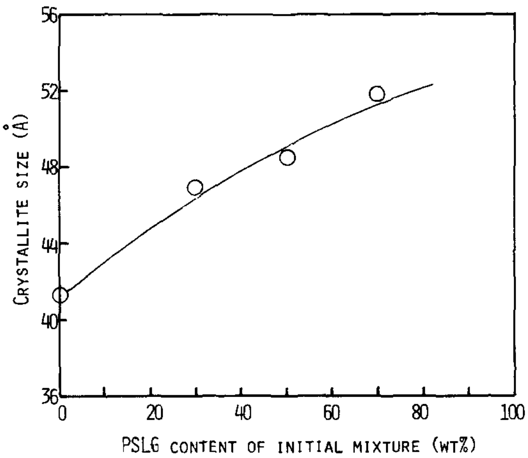

Figure 4 Crystallite size of PVA as a function of PSLG content

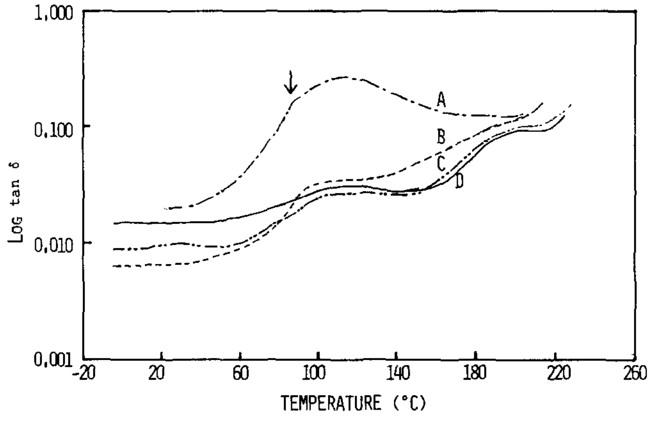

Figure 5 Temperature dependence of tan δ of pure PVA(A) and the blends PVA/PSLG = 7/3(B), 5/5(C) and 3/7(D)

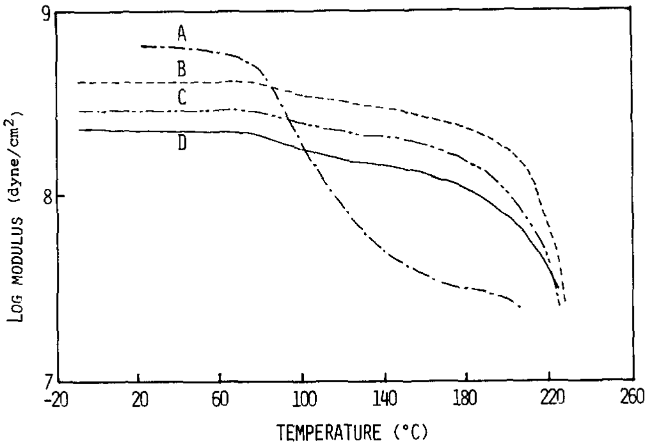

Figure 6 Temperature dependence of storage modulus of pure PVA(A) and the blends PVA/PSLG = 7/3(B), 5/5(C) and 3/7(D)

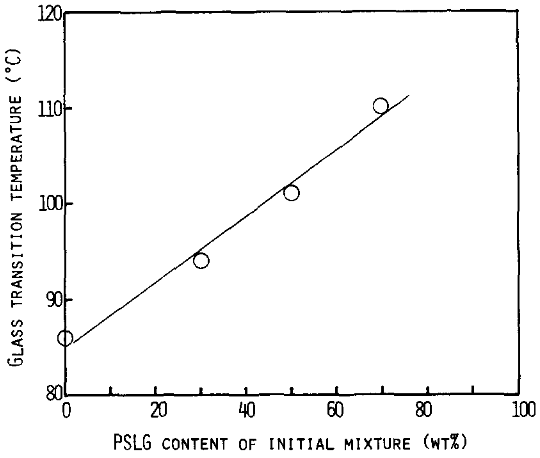

Figure 7 Dependence of T_g on PSLG content

In the case of the blends, motions due to PSLG side chains are not observed in any of the tan δ or d.s.c. curves. This result is consistent with the suggestion that the ionic groups in the PSLG side chains interact strongly with the hydroxyl groups in the PVA, and that they are surrounded in the blends by a material which is very different from that in the homopolymer. The intensity of the shoulder due to the glass transition of PVA decreases drastically. This also suggests that some of the amorphous PVA chains are involved in the polymer complexes. With increasing PGLS content, the T_g is shifted slightly towards higher temperatures, as shown in *Figure 7*, where T_g was decided by fitting the observed curve with two Gaussian curves. This also supports the suggestion, as mentioned above, that the interaction decreases the segmental mobility of the remaining PVA chains which do not interact with the PSLG side chains.

The intensity of the peak due to the disordered crystalline regions also decreases drastically. This means that the amount of PVA in these regions decreases in favour of the rigid PVA segments in the blends. There is a shoulder at ~195°C due to the glass transition of the PSLG main chain, although this transition is not observed on the d.s.c. curve, because of overlap with the large endothermic melting peak of the remaining PVA crystallites. The intensity of this shoulder decreases initially with increasing PSLG content. This indicates that the PSLG main chains are more restricted as a result of interactions with -OH groups of PVA. The value of E' starts decreasing slowly at ~80°C. The rate of decrease of the modulus is very much slower than in the pure PVA, because the PVA chains are complexed with the PSLG chains.

Figure 8 shows *FT*i.r. spectra of pure PVA and PSLG, as well as their blends. The spectra of the blends are similar to the spectra of PVA. However, there are two weak bands at 1570 and 1670 cm^{-1}, corresponding to the amide I and II regions of PSLG.

To investigate the interaction mechanism in the polymer blends, the subtraction of the *FT*i.r. spectra of one of the pure polymers from those of the blend is very useful because of the high sensitivity[23] of this approach. *Figure 9* shows the results of the subtractions of the spectrum of pure PSLG from those of the blends at 4400–2400 and 1750–750 cm^{-1}. These subtraction spectra correspond to the spectra of PVA as modified by the interaction of PVA with PSLG. The hydrogen bonded -OH band at 3340 cm^{-1} is clearly shifted towards lower wavenumbers by blending, which indicates the formation of a strong hydrogen bond. By contrast, the -C-O- band for the PVA, appearing at 1094 cm^{-1}, is shifted very slightly towards higher wavenumbers. For this slight shift of the -C-O- band towards higher wavenumbers, the explanation of Ping *et al.*[24] is invoked: in pure PVA, since the -OH groups form hydrogen bonds as described above, the -C-O- stretching wavenumber is lower than that of a free -C-O-H group. When strong interactions are present between the -OH in the PVA and the COO$^-$ and Na$^+$ ions in the PSLG side chain as a result of blending, the strength of the interaction between the PVA hydrogen and the carboxylate oxygen is stronger than the strength of the PVA hydroxyl groups with each other.

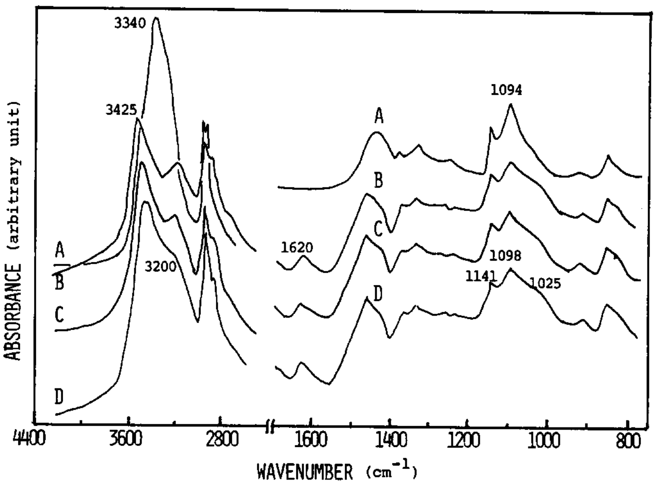

Figure 9 *FT*i.r. spectra of pure PVA(A) and subtraction of spectra of pure PSLG from the spectra of blends PVA/PSLG = 7/3(B), 5/5(C) and 3/7(D) in the range 4400–2400 and 1700–750 cm^{-1}

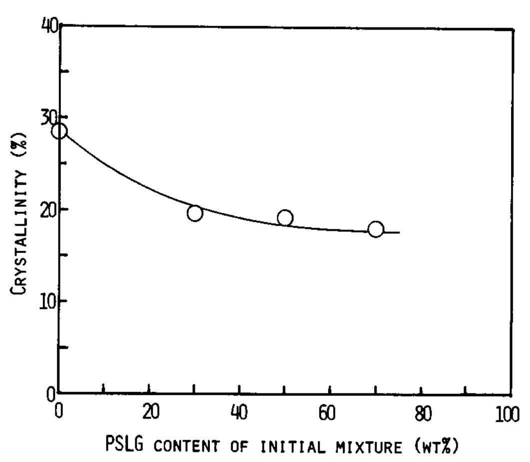

Figure 10 Dependence of crystallinity on PSLG content

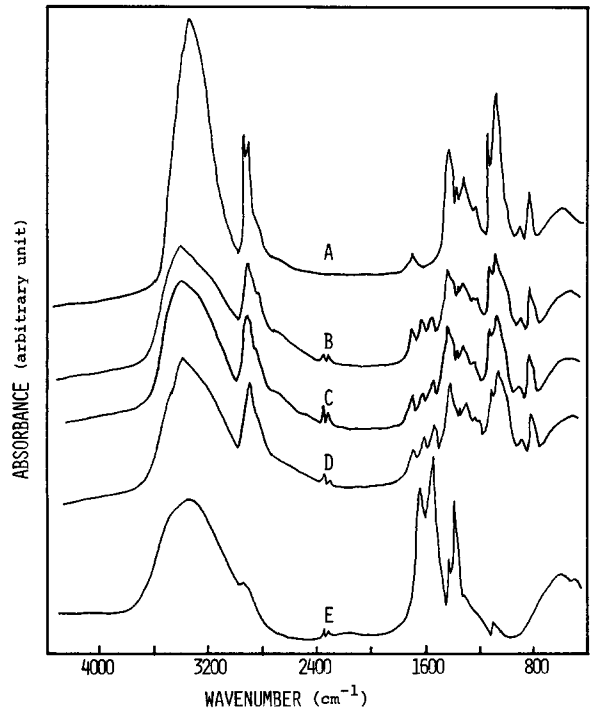

Figure 8 *FT*i.r. spectra of pure PVA(A) and the blends PVA/PSLG = 7/3(B), 5/5(C) and 3/7(D) and pure PSLG(E)

According to Kawakami *et al.*[16], the hydrogels of PVA with poly(acrylic acid) were obtained by the formation of hydrogen bonds in low pH conditions. On the other hand, intermolecular hydrogen bonds are formed in the dry state of the hydrogels at pH ~6. These differences are caused by both polymers (PVA and PSLG) diffusing easily at slightly elevated pressure and temperature and they then interact in the blend.

There are two new peaks at ~3425 and 1620 cm^{-1} in the spectra of the blends, which are not found in pure PVA or PSLG. The 3425 cm^{-1} band appears near the NH stretching band and the 1620 cm^{-1} band appears near the amide I band. These are probably also due to interactions between the -OH groups of PVA and the -NH and -C=O groups of the PSLG backbone, and are consistent with the result that the intensity of the shoulder at 195°C on the tan δ curve decreases by blending.

Furthermore, there is a crystalline band at 1141 cm^{-1} and an amorphous band at 1025 cm^{-1} in the spectra[25]. The degree of crystallinity (χ) can be calculated from equation (2). It is found that χ decreases initially with increasing PSLG content (*Figure 10*):

$$\chi = \frac{\text{peak area of crystalline band} \times 100}{\text{addition of peak areas of crystalline and amorphous bands}} \quad (2)$$

The decrease in crystallinity was discussed earlier in connection with the d.s.c. and tan δ data, and is due to the formation of rigid PVA segments by the interaction of PVA chains with PSLG side chains.

The toughness and rubber-like properties of the blend hydrogels can be explained by the interactions of PVA chains with side chains of PSLG, resulting in the formation of a polymer complex, as well as by the presence of PVA crystallites.

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