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States of water in poly(vinyl alcohol)/ poly(sodium L-glutamate) blend hydrogels

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Tough and rubber-like physically crosslinked hydrogels were prepared by blending of concentrated aqueous solutions of poly(vinyl alcohol) (PVA) and poly(sodium L-glutamate) (PSLG) in an autoclave under 2 atm pressure at 120°C. There are three types of water in every blend hydrogel, i.e. free water, unfrozen water (namely bound water), and frozen bound water. Unfrozen water content increases with increasing PSLG content because of the increase in the number of the ionic –COONa group, which has many bonding sites with the water molecular. Heat of thawing per unit weight of water, i.e. free and frozen bound waters, not containing unfrozen water (ΔH_w), estimated for hydrogels having various water contents, was obtained by dehydration and was smaller than that of free water. Spin lattice relaxation time (T_1), obtained by pulsed nuclear magnetic resonance measurement, decreases with increasing PSLG content. These results for ΔH_w and T_1 are caused by the interaction between water and ionic –COONa groups of the PSLG molecules.
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INTRODUCTION

Recently, we obtained hydrogels, which had a high Young's modulus even in the state of relatively high water content, from a concentrated aqueous solution of poly(vinyl alcohol) (PVA) and another hydrophilic polymer such as poly(sodium L-glutamate) (PSLG)[1,2] or poly(allyl amine) HCl salt[3], by using an autoclave at elevated temperature and pressure.

The water contents of these hydrogels were higher than that of the PVA hydrogel, which was cast from a 15 wt% aqueous solution of PVA and then swollen in water, and were similar to that of a PVA hydrogel prepared by repeated freezing and thawing[4]. Young's moduli of the blend hydrogels were lower than those of hydrogel prepared from a concentrated aqueous solution of PVA by casting. These moduli were twice as large as that of PVA hydrogel prepared by repeated freezing and thawing, and increased with increasing content of another blended hydrophilic polymer although physical crosslinks formed by PVA crystallites decreased. These results mean that the increase in Young's modulus is mainly caused by the physical crosslinks of a polymer–polymer complex between PVA and the hydrophilic polymer.

Furthermore, the time dependence of the streaming potential across the hydrogel membranes was analysed as the relaxation of the polymer chains dissolved in the liquid phase of the membrane[5]. The relaxation time decreased with increasing PSLG content; it is thus clear that the crosslinks formed with the complex increase with increasing blend content.

Since it is well known that hydrophilic polymers generally have three types of absorbed water, i.e. free, frozen bound, and unfrozen water[6–8], it may be expected that the blend hydrogels obtained also have similar states of water. Many investigators have studied the state of water in chemically crosslinked PVA gels[9,10] and concluded that in these gels also three types of water exist. However, the detailed properties of the frozen bound water in the hydrogels have not yet been clarified.

In this paper, we study mainly the state of frozen bound and unfrozen water in physically crosslinked PVA hydrogels prepared by blending PVA with anionic poly(sodium L-glutamate).

EXPERIMENTAL

Chips of poly(γ methyl L-glutamate) (PMLG) (degree of polymerization 280) were placed in 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 separated by filtration, washed with methanol, and dried *in vacuo*[11].

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 made by agitation at room temperature. Mixtures of PVA with PSLG of five different weight contents, with pH values about 6, were prepared in the autoclave under 2 atm at

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