Effect of Stereoregularity and Molecular Weight on the Mechanical Properties of Poly(vinyl alcohol) Hydrogel

Ryohei Fukae,[1] Miki Yoshimura,[1] Tohei Yamamoto,[2] Katsuyoshi Nishinari[3]

[1]School of Human Science and Environment, University of Hyogo, Himeji 670-0092, Japan
[2]Faculty of Engineering, University of Hyogo, Himeji 671-2201, Japan
[3]Department of Food and Human Health Sciences, Osaka City University, Osaka 558-8585, Japan

ABSTRACT: The effect of the stereoregularity and molecular weight of poly(vinyl alcohol) (PVA) on the mechanical properties of hydrogel was investigated. Compressive strength, creep behavior, and dynamic viscoelasticity were measured on hydrogels of syndiotacticity-rich PVA derived from poly(vinyl pivalate) (D_p = 1690 diad-syndiotacticity = 61%, D_p = 8020 diad-syndiotacticity = 62%) and atactic PVA (D_p = 1750 diad-syndiotacticity = 54%, D_p = 7780 diad-syndiotacticity = 54%). Increasing the molecular weight of molecular chains constituting the gel improved the compressive strength of atactic PVA hydrogel. The stereoregularity of PVA had a greater effect than molecular weight on the strength of the hydrogel. Gel prepared from 8.8 g/dL syndiotacticity-rich PVA had a high compressive modulus of 10 kPa, and the compressive modulus of the gel prepared from 3.3 g/dL was comparable with that of atactic PVA hydrogel prepared with more than 6 g/dL. The dynamic storage modulus of the gel derived from syndiotacticity-rich PVA was remarkably higher than that of the atactic PVA gel and remained constant up to 60°C. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 573–578, 2011

Key words: poly(vinyl alcohol); hydrogel; mechanical property; syndiotacticity; molecular weight

INTRODUCTION

Poly(vinyl alcohol) (PVA) hydrogel has attracted much attention as a soft material that can be used as an actuator, biosensor, and in biomedical applications.[1,2] The gel, prepared by freezing and thawing a PVA solution, is known for its high water content but generally shows poor mechanical properties and low thermal stability.[3–7]

We produced PVA with high syndiotacticity by the polymerization of vinyl pivalate (VPi), followed by saponification of the resulting polymer.[8,9] PVA with high syndiotacticity and high molecular weight was also obtained from the photo-emulsion polymerization of VPi.[10] The hydrogel of syndiotacticity-rich PVA derived from poly(vinyl pivalate) (PVPi) had a higher melting temperature than the hydrogel of atactic PVA derived from poly(vinyl acetate) (PVAc). The apparent enthalpy of the junction fusion in the hydrogel of syndiotacticity-rich PVA was estimated to be 102 kJ/mol, 2.6-fold higher than that of atactic PVA.[11,12] The high thermal stability of the gel is attributed to the enhanced formability of crystallite in the longer stereoregulated sequences of syndiotacticity-rich PVA.[13–16]

Several studies of the mechanical properties of gel prepared from PVA with high syndiotacticity have been reported, but these studies have been almost exclusively performed with gels using dimethyl sulfoxide (DMSO), ethylene glycol, or a mixture of DMSO and water (DMSO/water) as the dispersion medium.[17–19] The gel of PVA with high syndiotacticity is easy to prepare using DMSO or DMSO/water. The PVA is soluble in DMSO or DMSO/water but difficult to dissolve homogeneously in pure water.

Choi et al. reported that the syndiotacticity of PVA promotes an increase in the dynamic storage modulus of DMSO/water gels.[18] High syndiotacticity clearly improves the mechanical properties of the PVA gel. It has not yet been sufficiently established, however, that high syndiotacticity has the same effect on a hydrogel as it does on a DMSO/water gel. The gelation rate of a PVA-DMSO/water solution reportedly depends on the ratio of DMSO and water in commercially atactic PVA.[20] The solvent composition in gelation consequently has a great effect on the structure of the resulting gel. The stereoregularity and molecular weight of PVA are likely to affect hydrogel and DMSO/water gel differentially with regard to the mechanical properties.

One of the most desirable application of PVA gel is its biomedical use, such as for drug delivery

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systems,[2,6] tissue engineering scaffolds,[21,22] artificial corneas,[23,24] and so forth. A hydrogel is preferred over an organic gel for these applications in terms of biocompatibility. For a PVA hydrogel to be utilized effectively, the effects of syndiotacticity and molecular weight of PVA on the mechanical properties must be elucidated. Even with regard to PVA-DMSO/water gels, there has been no adequate discussion of the individual effects of the stereoregularity and molecular weight of PVA on the mechanical properties.[18]

This study was performed to clarify the effect of the stereoregularity and molecular weight of PVA on the mechanical properties of the hydrogel. Two pairs of syndiotacticity-rich PVA and atactic PVA were prepared. One pair had nearly the same high molecular weight and the other had nearly the same low molecular weight. For the practical use of high water content gel, compressive stress–strain behavior and dynamic viscoelastic behavior were evaluated in PVA hydrogels with a polymer concentration of less than 10 g/dL. Creep behavior was also examined to estimate dimensional stability.

EXPERIMENTAL

Preparation of PVA samples

Syndiotacticity-rich PVA was derived from PVPi that was prepared by solution polymerization of VPi at 60°C with methanol as the solvent.[8,9] Syndiotacticity-rich PVA with a high molecular weight was derived from PVPi prepared by photo-emulsion polymerization of VPi at 0°C.[10] Atactic PVA with a high molecular weight (at-H) was derived from PVAc prepared by photo-emulsion polymerization of vinyl acetate at 0°C.[25] Commercially available atactic PVA (at-L) was obtained from Kuraray. Syndiotacticity-rich PVA samples (st-L, st-H) with nearly the same molecular weights as at-L and at-H, respectively, were selected for gel preparation.

The degree of polymerization (D_p), degree of diad-syndiotacticity, and degree of saponification of the PVA samples used in this study are listed in Table I. The D_p was estimated from the intrinsic viscosity of the acetylated sample. The degree of diad-syndiotacticity and the degree of saponification were determined from the ^{1}H-NMR spectrum of PVA.

Gel preparation

An aqueous solution of PVA was prepared by dissolving the PVA in a sealed tube at ~ 130°C. Hydrogel was obtained by allowing the solution to stand at −38°C for 72 h. The polymer concentration of the prepared gel was corrected to take into account the amount of water squeezed out during gelation. The

TABLE I
PVA Samples Used for Gel Preparation

PVA Sample	Degree of polymerization[a]	Diad-syndiotacticity[b] (%)	Degree of saponification[b] (%)
at-L	1,750	53.9	99.9
at-H	7,780	53.7	99.9
st-L	1,690	61.2	99.9
st-H	8,020	61.9	99.9

[a] Estimated from the intrinsic viscosity of acetylated sample.
[b] Determined from ^{1}H-NMR spectrum.

degree of syneresis is expressed as the weight ratio of the squeezed water to the solution before gelation.

Measurements

A compressive stress–strain test was performed on a cylindrical gel specimen (10 mm in diameter × 10 mm in length) at a compressive speed of 10 mm/min and at room temperature using a Rheometer RX-1600 (Iio Electric). To observe creep behavior, the deformation value under a constant stress of 700 Pa was recorded as a function of time. The dynamic storage modulus and mechanical loss tangent were measured at 0.5 Hz and at a heating rate of 1°C/min in silicon oil with a thermomechanical analyzer TMA/SS6100 (Seiko Instruments). A cylindrical specimen (8 mm in diameter × 10 mm in length) was used, and its bases were fixed with α-cyanoacrylate adhesive.[26] The data listed in tables are obtained through the measurement of more than four samples. The compressive stress–strain behaviors, creep behaviors, and dynamic viscoelastic behaviors also verify their repeatability through measurement of several samples prepared under the same condition.

RESULTS AND DISCUSSION

Gelation and syneresis of PVA solution

Aqueous at-L solution with a polymer concentration of more than 4 g/dL turned to gel when left to stand at −38°C for 72 h. Under the same condition, each of the at-H, st-L, and st-H solutions with a lower polymer concentration (~ 2 g/dL) yielded a hydrogel.

Syneresis is exhibited in the gelation of PVA solution through a freezing and thawing procedure, because of the increased growth of the crystallites in the gel.[1,27] Table II shows the degree of syneresis in the gelation of aqueous PVA solutions with various polymer concentrations. The syneresis intensified properly in solutions with a lower concentration of

TABLE II
Syneresis of PVA Aqueous Solution in Gelation[a]

PVA sample	Polymer conc. before gelation (g/dL)	Polymer conc. after gelation (g/dL)	Degree of syneresis[b] (%)
at-L	4.0	4.3	7.2
	6.0	6.1	1.6
	8.0	8.0	0.4
	8.8	8.8	0
at-H	2.0	2.9	31.4
	3.5	4.2	16.1
	6.0	6.6	9.3
st-L	2.3	3.3	30.6
	4.8	6.4	24.6
	6.9	8.8	21.4
st-H	2.0	2.7	25.9

[a] By freezing PVA aqueous solution at −38°C for 72 h.
[b] Weight ratio of the squeezed water to the solution before gelation.

any kind of PVA, and each of the at-H, st-L, and st-H solutions exhibited fairly high syneresis compared with at-L. The st-L solution with 2.3 g/dL showed 31% syneresis and even an st-L solution with 6.9 g/dL showed 21% syneresis.

Gel samples are hereafter indicated by the PVA sample name with the value of the polymer concentration after syneresis. There was only one st-H gel sample because of its low water solubility.

Compressive stress–strain behavior

Compressive stress–strain behaviors of at-L and at-H hydrogels are shown in Figure 1, and those of st-L and st-H hydrogels are shown in Figure 2. In both
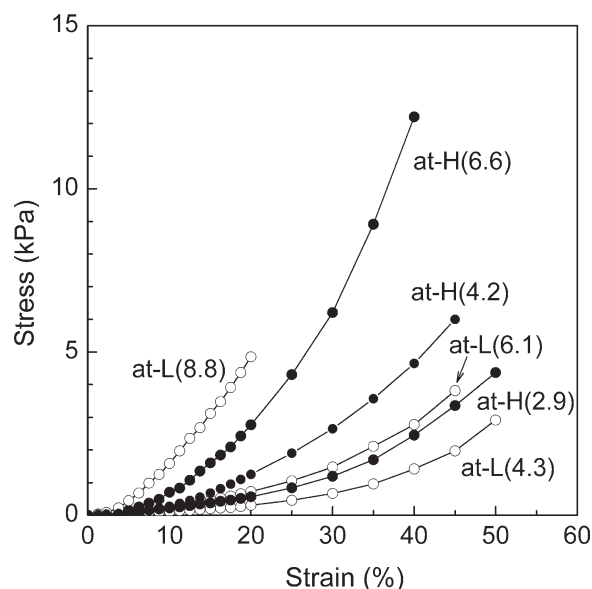
Figure 1 Compressive stress–strain behaviors of at-L and at-H hydrogels. The value in bracket is the polymer concentration of gel sample.
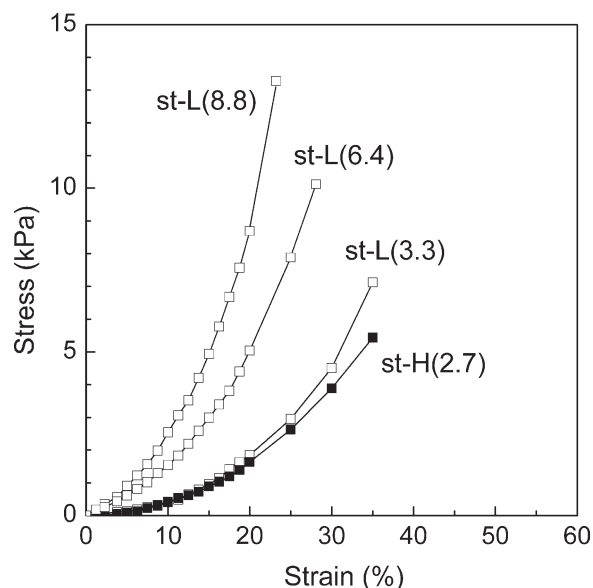
Figure 2 Compressive stress–strain behaviors of st-L and st-H hydrogels. The value in bracket is the polymer concentration of gel sample.

at-L and at-H gels, the compressive strength increased with an increase in the polymer concentration, and the compressive strain at break decreased with an increase in the concentration. The degree of the increase in compressive strength of at-H gel, however, was higher than that of at-L gel. The compressive strength of at-H gel was also greater than that of at-L at similar concentrations.

On the other hand, the st-L gel showed a considerably high compressive strength compared with at-L gel, despite having the same molecular weight as at-L. The compressive strength of the st-L gel with a polymer concentration of 8.8 g/dL was approximately threefold higher than that of the at-L gel.

The compressive moduli of the PVA gels evaluated by the stress–strain curves are listed in Table III. The compressive moduli of the st-L gels were

TABLE III
Compressive Modulus of PVA Hydrogels[a]

Gel sample	Polymer conc. of gel (g/dL)	Compressive modulus (kPa)
at-L	4.3	1.2 ± 0.3
	6.1	2.8 ± 0.5
	8.0	4.0 ± 0.3
	8.8	6.0 ± 0.8
at-H	2.9	1.2 ± 0.4
	4.2	2.6 ± 0.5
	6.6	4.3 ± 0.4
st-L	3.3	3.4 ± 0.6
	6.4	7.1 ± 0.4
	8.8	10.4 ± 0.7
st-H	2.7	1.6 ± 0.3

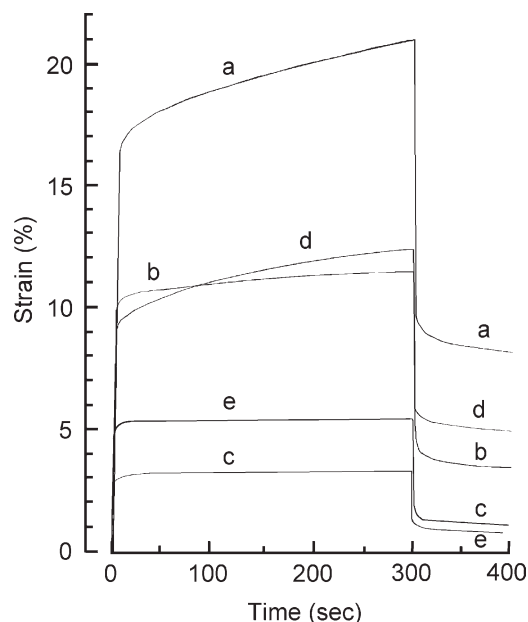[a] Evaluated by the compressive stress–strain curve.

Figure 3 Creep behaviors of at-L and at-H hydrogels under a load of 700 Pa for 300 s: (a) at-L(4.3); (b) at-L(6.1); (c) at-L(8.8); (d) at-H(2.9); (e) at-H(6.6).

considerably higher than those of the other types of gels. The st-L gel with a polymer concentration of 8.8 g/dL had a high compressive modulus of 10 kPa, and the compressive modulus of the st-L gel with a polymer concentration of 3.3 g/dL was comparable with that of the at-L gel with a polymer concentration of more than 6 g/dL.

We previously reported that a hydrogel comprising syndiotacticity-rich PVA has a higher peak intensity at 19.5° (2θ) than does atactic PVA on wide-angle X-ray diffraction trace.[11,12] The peak is assigned to the reflection of the (101) plane caused by crystallites in the PVA hydrogel.[7,28] There is a large amount of crystallite in hydrogels composed of syndiotacticity-rich PVA. The crystallites appear to function as pseudo-crosslinks, thereby improving the mechanical strength of the hydrogel.[16,29]

Creep behavior

Creep behaviors of at-L and at-H hydrogels under a load for 300 s are shown in Figure 3, and those of st-L and st-H hydrogels are shown in Figure 4. The amount of deformation of any gels reflects their compressive strength. The stereoregularity of PVA constituting gel had a marked effect on the creep behavior. As for the effect of molecular weight, the at-H gel showed less deformation than the at-L gel.

Table IV lists the values of instantaneous elastic strain (εH), retarded elastic strain (εV), and equilibrium viscous flow (εN), calculated from the creep curves in Figure 3 and Figure 4. εH is the deformation based on the entropic elasticity of the molecular
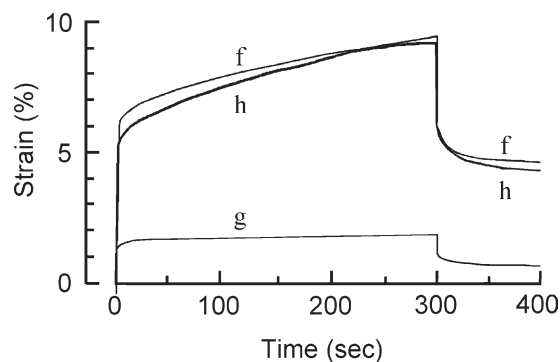
Figure 4 Creep behaviors of st-L and st-H hydrogels under a load of 700 Pa for 300 s: (a) st-L(3.3); (b) st-L(8.8); (c) st-H(2.7).

chains between pseudo-crosslinkings, and εV is the deformation, which involves the removal of the crosslinking junction. εN is based on the flow of the gel itself and cleavage of the crosslinking.

The value of εH in the st-L gel was lower in comparison with the at-L gel, despite their having the same polymer concentration. The gel of syndiotacticity-rich PVA had high entropy elasticity, even in the low polymer concentration.

The influence of the stereoregularity of PVA on εV was not clear, but there was an effect of molecular weight between at-L gel with 6.1 g/dL and at-H gel with 6.6 g/dL. Entanglement of the longer molecular chains of at-H restricted the fluidity of the crosslinking junction itself. The values of εN in at-H, st-L, and st-H gel were relatively lower than that of at-L gel, especially in gels with a low polymer concentration. Gel flow was restricted by increasing the molecular weight and stereoregularity of molecular chains constituting the gel.

Dynamic viscoelastic behavior

There are few reports on the dynamic viscoelastic behavior of PVA hydrogel, and even fewer reports

TABLE IV
Creep Strain Results of PVA Hydrogel[a]

PVA sample	Polymer conc. of gel (g/dL)	εH^{b} (%)	εV^{b} (%)	εN^{b} (%)
at-L	4.4	16.3	1.9	2.8
	6.1	9.0	1.8	0.5
	8.8	2.8	0.3	0.1
	12.0	1.9	0.1	0.1
at-H	2.9	9.1	1.5	1.6
	6.6	4.5	0.5	0.2
st-L	3.3	6.5	1.5	1.8
	8.8	1.5	0.3	0.1
st-H	2.6	5.3	2.1	1.7

[a] Under a constant stress of 700 Pa for 300 sec.
[b] εH, instantaneous elastic strain; εV, retarded elastic strain; εN, equilibrium viscous flow.
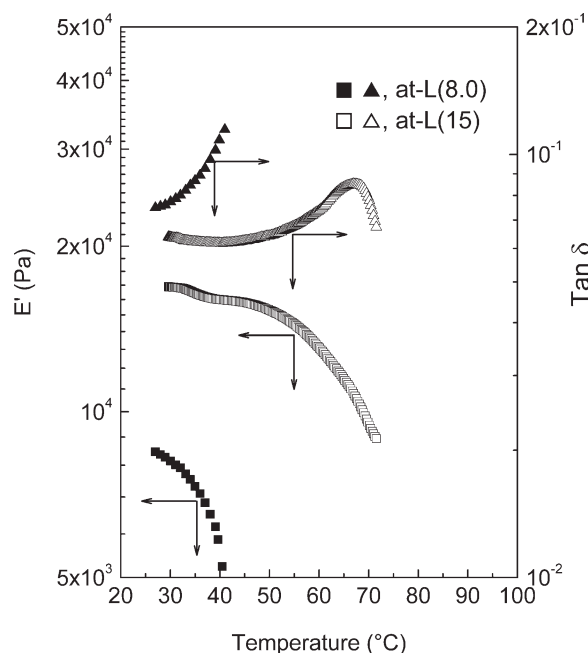
Figure 5 Temperature dependencies of the E' and the tan δ of at-L(8.0) and at-L(15).

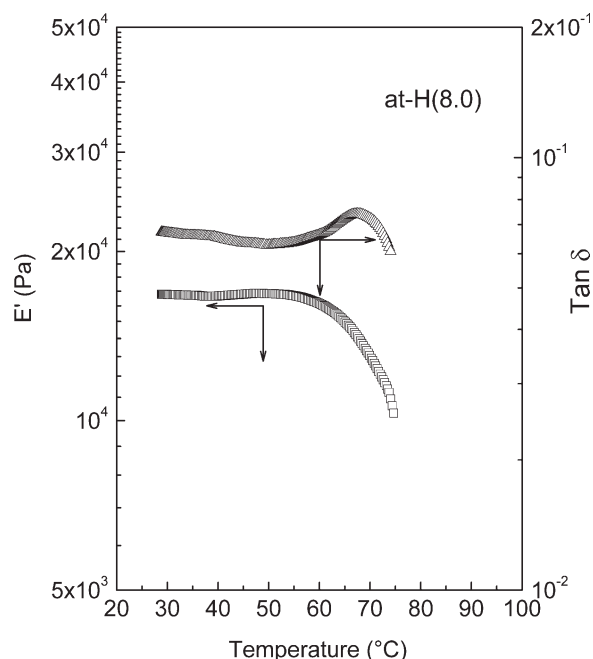**Figure 6** Temperature dependencies of the E' and the tan δ of at-H(8.0).

of hydrogels composed from PVA with a high molecular weight and/or stereoregularity. Watase et al. reported the behavior of hydrogels prepared by freezing at −40°C for 40 h using atactic PVA with a D_p of 2400.[3,5] The gel with a 10 wt % polymer concentration showed a dynamic storage modulus (E') of 1.2×10^4 Pa, and the gel with 15 wt % showed an E' of 1.8×10^4 Pa at 30°C. The storage modulus of these gels decreased rapidly at 45–50°C.

Temperature dependencies of the E' and the mechanical loss tangent (tan δ) of at-L hydrogels with polymer concentrations of 8.0 and 15 g/dL are shown in Figure 5, that of at-H hydrogel with 8.0 g/dL is shown in Figure 6 and that of st-L hydrogel with 8.0 g/dL in Figure 7. The storage modulus of the at-L gel with 8.0 g/dL was 8.1×10^3 Pa at 30°C. The storage modulus of the at-L gel with 15 g/dL was 1.7×10^4 Pa at 30°C and began to decrease with an increasing in temperature. The peak tan δ was observed near 67°C. These results are consistent with those reported by Watase et al.[3,5]

The storage modulus of the at-H gel with 8.0 g/dL was 1.7×10^4 Pa at 30°C. This E' was remarkably higher than that of the at-L gel with the same polymer concentration. The storage modulus did not decrease up to temperature of 55°C but then rapidly decreased. Although the peak tan δ was observed at nearly the same temperature as that of the at-L gel with 15 g/dL, the peak was broad and the peak intensity was lower than that of the at-L gel. Entanglement of the longer molecular chain constituting the gel probably reduced the removal of the crosslinking junction.

The storage modulus of the st-L gel with 8.0 g/dL was high (3.6×10^4 Pa at 30°C). The E' was substantially maintained up to 60°C and decreased at around 65°C. The temperature range in which E' was maintained was remarkably wide. The peak tan δ was observed at 69°C, which was slightly higher than that of the at-L and at-H gels, and broad compared with the at-L and at-H gels. The st-L gel had
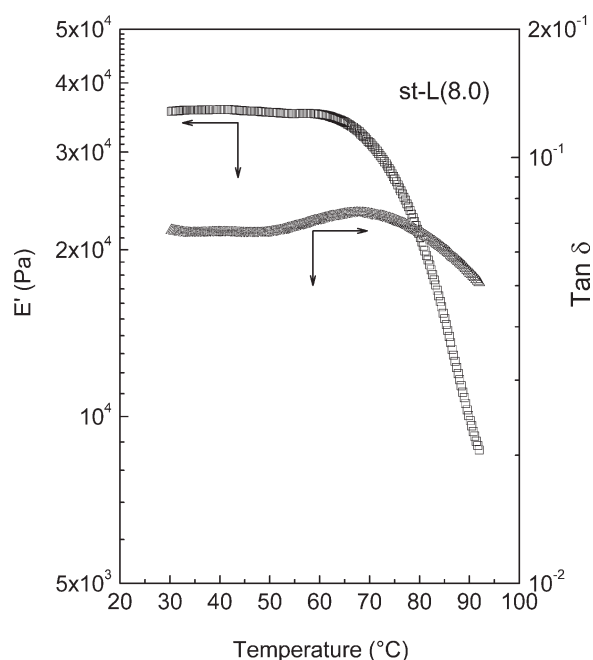

Figure 7 Temperature dependencies of the E' and the tan δ of st-L(8.0).

considerably different viscoelastic behavior than the at-L gel, although the molecules constituting the gel had nearly the same molecular weight as those constituting the at-L gel, likely because of the formation of large amounts of pseudo-crosslinking and the strong restraint of the molecular motion brought on by the stereoregulated sequences of the syndiotacticity-rich PVA.[11,12,18,29] Unfortunately, we were unable to obtain a st-H gel sample that was strong enough to measure its dynamic viscoelastic behavior because of the extremely low water solubility of st-H. It is likely that the thermal stability of gel strength is influenced more by the stereoregularity of the PVA than by the molecular weight.

CONCLUSIONS

The findings of this study indicate that increasing the molecular weight of PVA improves the mechanical strength and shape-stability of the hydrogel. Moreover, the gel properties were more affected by the stereoregularity of the PVA than the molecular weight. The compressive strength of syndiotacticity-rich PVA gel was approximately threefold higher than that of atactic PVA gel, despite their having the same polymer concentration. The dynamic storage modulus of the gel with 8 g/dL syndiotacticity-rich PVA was greater than that of atactic PVA gel with a polymer concentration of 15 g/dL and remained fairly constant up to 60°C. Entanglement of the long molecular chain and the large amounts of crossliking improve the mechanical of PVA hydrogels.

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