Colloid Polym Sci 278:1198–1204 (2000)

ORIGINAL CONTRIBUTION

J. H. Choi
W. S. Lyoo
H. D. Ghim
S.-W. Ko

High molecular weight syndiotacticity-rich poly(vinyl alcohol) gel in aging process

Received: 2 December 1999
Accepted: 12 July 2000

J. H. Choi · H. D. Ghim · S.-W. Ko (✉)
Department of Fiber and Polymer Science
College of Engineering
Seoul National University
Seoul 151–742, Korea
e-mail: sohkwonk@gong.snu.ac.kr

W. S. Lyoo
School of Textiles, Yeungnam University
Kyongsan 712–749, Korea

Abstract The properties of the aged gels of high molecular weight syndiotacticity-rich poly(vinyl alcohol)s (HMW S-PVAs) with different syndiotactic diad (*s*-diad) contents were investigated. HMW S-PVA gels with *s*-diad content of 61.5% and 58.2% showed the rapid increases of the syneresis and the turbidity from the early stage of aging time, which is ascribable to the phase separation, while that with *s*-diad content of 55.7% did not. From the morphological study, it was confirmed that the phase separation in HMW S-PVA gel with *s*-diad content of 61.5% occurred without the liquid-liquid phase separation in sol state, whereas both the liquid-liquid phase separation in sol state and the subsequent phase separation in gel state occurred in the case of HMW S-PVA gel with *s*-diad content of 58.2%. On the other hand, HMW S-PVA gel with *s*-diad content of 55.7% showed neither the liquid-liquid phase separation in sol state nor the phase separation in gel state in the long period of time. It was also confirmed from wide angle X-ray diffractogram that the crystallization was accompanied by the phase separation in gel state in the aging process of PVA gel. However, the crystallization was hindered by the fast network formation at the initial stage of time. Later the syndiotacticity promoted the crystallization. The tensile modulus of HMW S-PVA gel with higher syndiotacticity increased more significantly with time.

Key words Aging · Poly(vinyl alcohol) · Gel · Syndiotacticity · High molecular weight

Introduction

Poly(vinyl alcohol) (PVA) is a semicrystalline polymer having hydroxyl groups which give rise to inter- and intra-molecular hydrogen bondings. PVA is classified into three types, isotactic, atactic, and syndiotactic ones, according to the stereoregularity of hydroxyl groups. Syndiotacticity-rich PVA (S-PVA) has been known to have different properties compared with atactic PVA (A-PVA) due to the increased intermolecular hydrogen bondings between the adjacent chains. Also, molecular weight is another factor to affect the bulk and solution properties of PVA. Actually, high molecular weight (HMW) S-PVA fibers and films have superior mechanical properties to those of atactic ones [1–3]. Recently, HMW S-PVA of a well-oriented microfibrillar structure was synthesized [4–7]. HMW S-PVAs with lower syndiotactic diad (*s*-diad) contents have shapeless morphologies but those with *s*-diad content over 56% are fibrous with high degree of crystallinity and orientation of the crystallites [6].

Most PVA solutions including PVA/water solution are well known to form thermally reversible gels at low temperature. The stereoregularity of PVA affects its gel properties as well. Aqueous solutions of S-PVA form hard elastic gels more easily than those of A-PVA and the melting point of the S-PVA gel is remarkably higher than those of A-PVA gels [8–11]. In addition, the properties of PVA gel – like turbidity – depend on other factors such as concentration and solvent used [12–15].

Syneresis has been well known as a term of the gradual change in the structure of a gel accompanying shrinkage of its volume and exclusion of the solvent. It should be noted that this definition does not involve the shrinkage of a gel which is caused by evaporation of the solvent from the surface of a gel in an open system. Syneresis means the shrinkage caused by inner structural change, such as a very slowly occurring phase separation in gel network and/or crystallization, implying that the just formed gel is not in its equilibrium state. The syneresis of A-PVA and S-PVA gel in the aging process was reported in consideration of the initial polymer concentration [12] and the additives such as saccharose [13] and saccharide [14]. In addition, it was also reported that low molecular weight S-PVA solution became turbid with the progress of time [15–18], and this was greatly affected by the solvent composition of water and dimethyl sulfoxide (DMSO).

Aging of PVA gel is an interesting topic because the appearance and the properties of a gel change spontaneously as time goes by. In this paper, the study on an aged gel of HMW S-PVA was made from a standpoint of liquid-liquid separation and crystallization. The changes in morphology, polymer concentration, and transparency of the gel were investigated regarding phase separation and related to the syndiotacticity of the polymer. In addition, the contribution of crystallization to the properties of the aged gels was also investigated.

Materials and methods

Homopolymerization

Poly(vinyl pivalate) (PVPi) was synthesized by the bulk-polymerization of vinyl pivalate (VPi) at 30 °C using 2,2′-azobis(2,4-dimethylvaleronitrile) (ADMVN) as an initiator. HMW S-PVA with an *s*-diad content of 61.5% was prepared by saponifying PVPi. The number average degree of polymerization (P_n), the degree of saponification (*DS*), and *s*-diad content of HMW S-PVA were determined by the same method adopted in the previous papers [4–7] and listed in Table 1.

Copolymerization

VPi and vinyl acetate (VAc) in different mole ratios were copolymerized in bulk at 30 °C using ADMVN to produce P(VPi/VAc) copolymers having different syndiotacticities [6]. HMW S-PVAs with *s*-diad contents of 58.2% and 55.7% were prepared by saponifying copoly(VPi/VAc)s. The characteristics of these HMW S-PVAs are shown in Table 1.

Table 1 Polymerization conditions and molecular parameters of UHMW S-PVA

ADMVN conc. ($mol/mol_{monomer}$)	VPi mol % in feed	P_n	S-diad content (%)	*DS* (%)
3.0×10^{-4}	100	9,900	61.5	99.9
2.0×10^{-5}	60	10,400	58.2	99.9
1.0×10^{-5}	30	10,100	55.7	99.9

P_n is the degree of polymerization

Solution preparation

HMW S-PVA was hard to dissolve homogeneously in pure water and water-rich mixed solvent, so a mixture of DMSO/water with 80 vol.% DMSO was chosen as a solvent. HMW S-PVA was dissolved in the solvent at 120 °C for 2 h and was kept for 30 min to ensure homogenization. The homogeneous solution was quenched and kept at 0 °C to prepare HMW S-PVA/DMSO/water gel.

UV/VIS spectroscopy

The turbidity of HMW S-PVA gel was evaluated from the light transmission. The transmittances of the gel and the solution were measured at the wavelength of 600 nm with a Perkin Elmer 551S UV/VIS spectrophotometer.

Optical microscopy

The appearances of HMW S-PVA gel and solution were examined by optical microscopy. The gel and solution were placed between a slide glass and a cover glass and examined with an optical microscope.

Wide angle X-ray diffractometry

Wide angle X-ray diffractogram (WAXD) of HMW S-PVA gel was obtained by Rigaku D/Max-III X-ray diffractometer with Nickel-filtered CuKα radiation (1.54178 Å) at 40 kV and 30 mA. The scan speed was 4.0 degree/min.

Tensile test

The stress-strain curves were obtained using a universal tensile machine (UTM, LR10K, Lloyd). The extension speed was fixed to 10 mm/min. The initial gauge length of the specimen was 28 mm.

Results and discussion

In this work, the concentration of HMW S-PVA solution was fixed to 4.0 g/dl regardless of the syndiotacticity. All solutions having different syndiotacticities were gelled at 0 °C within 1 h. Figure 1 shows the change of the concentration of HMW S-PVA in gel. At the initial stage the phase separation took place in gel and thus the phase was divided into the polymer-rich phase and the polymer-poor phase. This is known as the generation of concentration fluctuation. The polymer-poor phase, i.e., the solvent-rich phase, was entrapped in the polymer rich phase. With the progress of time, the polymer-rich phase became richer and the polymer-poor phase became poorer. In the long run, the solvent-rich phase, which is almost "the solvent-only phase," was squeezed out of the gel surface and the concentration of polymer in the gel increased more and more. From the

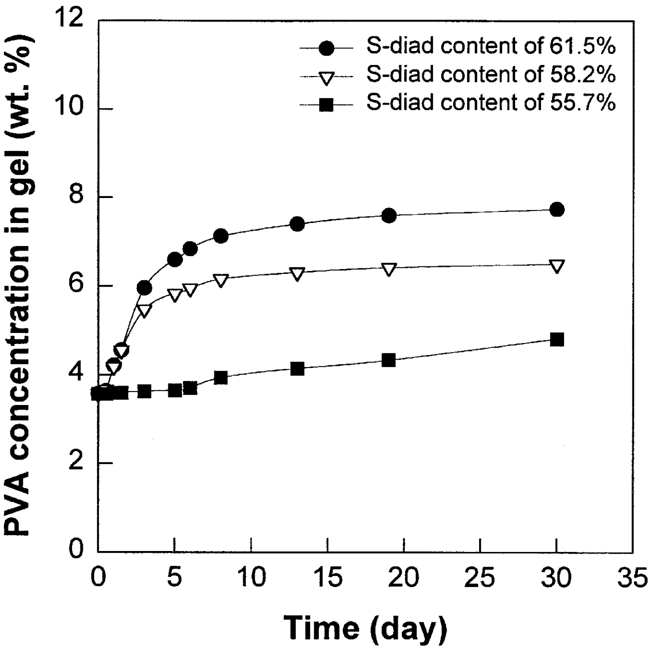

Fig. 1 Change of polymer concentration in UHMW S-PVA gel at 0 °C with time

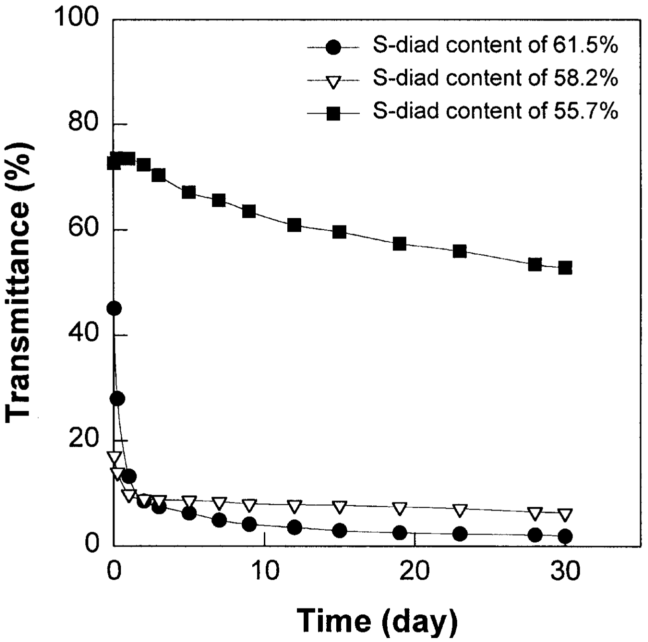

Fig. 2 Change in the light transmittance of UHMW S-PVA gel at 600 nm with time at 0 °C

initial stage, a great difference was found between the gels of HMW S-PVAs with *s*-diad content of 61.5% or 58.2% and that of HMW S-PVA with *s*-diad content of 55.7%. The syneresis of the gels of HMW S-PVAs with *s*-diad content of 61.5% or 58.2% was prominent as compared with that of HMW S-PVA with *s*-diad content of 55.7%. In other words, the phase separation in HMW S-PVA gel with *s*-diad content of 55.7% was less serious. After 3 days, the difference between the gels of HMW S-PVAs with *s*-diad content of 61.5% and 58.2% was also found. In addition, the phase separation in HMW S-PVA gels with *s*-diad content of 61.5% and 58.2% took place quickly and reached each maximum within a relatively short time interval, while that in HMW S-PVA gels with *s*-diad content of 55.7% occurred gradually. Accordingly, it is obvious that the syneresis of HMW S-PVA gel is greatly favored as the syndiotacticity increases.

As times passed by, PVA gel became translucent in some cases, which has been explained by the phase separation and the crystallization. Figure 2 shows the change of light transmittance of HMW S-PVA gel with aging. At the initial stage, HMW S-PVA gels with *s*-diad contents of 61.5% and 58.2% lost their clarity rapidly. After 2 days, the turbidity of these gels increased gradually with time. On the other hand, HMW S-PVA gel with *s*-diad content of 55.7% exhibited no significant increase of turbidity. This is perfectly analogous to the results from Fig. 1. It is evidently true that the phase separation plays an important role in the formation of the turbid gel. In the case of HMW S-PVA gel with *s*-diad content over 58.2%, phase separation in gel state occurred to a considerable extent to cause opacity of the gel.

The change of appearance of the gel with time is illustrated in Figs. 3–5. The as-cast gel of HMW S-PVA with *s*-diad content of 58.2% showed heterogeneous morphology, while those of HMW S-PVAs with *s*-diad content of 61.5% and 55.7% did not, as shown in Fig. 3. This is because 4.0 g/dl HMW S-PVA solution with *s*-diad content of 58.2% underwent liquid-liquid phase separation before gelation, whereas those of HMW S-PVAs with *s*-diad content of 61.5% and 55.7% did not, resulting in the lowest light transmittance of HMW S-PVA gel with *s*-diad content of 58.2% at the initial stage (Fig. 2). The turbidity of PVA gel depends on the rate of gelation and liquid-liquid phase separation in the sol state [19]. If the gelation rate is high enough to cause gelation prior to liquid-liquid phase separation, a homogeneous gel structure is developed. If the gelation rate is sufficiently low, liquid-liquid phase separation occurs before gelation and a gel becomes opaque even at an incipient state. The gelation of HMW S-PVA solution with *s*-diad content of 58.2% occurred more slowly than that of HMW S-PVA solution with *s*-diad content of 61.5%, so the liquid-liquid phase separation could be followed by gelation. On the other hand, the gelation rate of HMW S-PVA with *s*-diad content of 61.5% was so high that the solution was gelled prior to the liquid-liquid phase separation. In the case of HMW

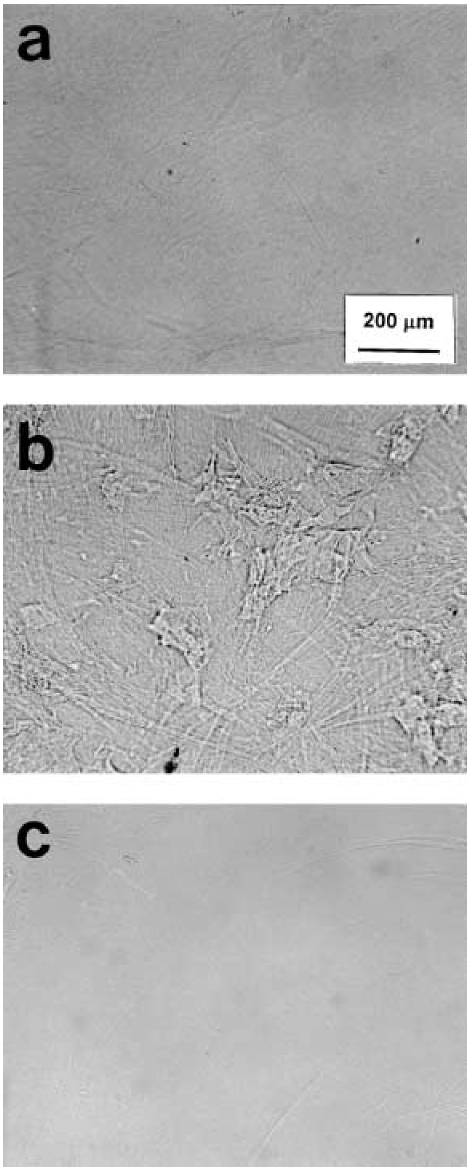

Fig. 3a–c Microphotograph of UHMW S-PVA gel aged for 1 h. S-diad contents: **a** 61.5%; **b** 58.2%; **c** 55.7%

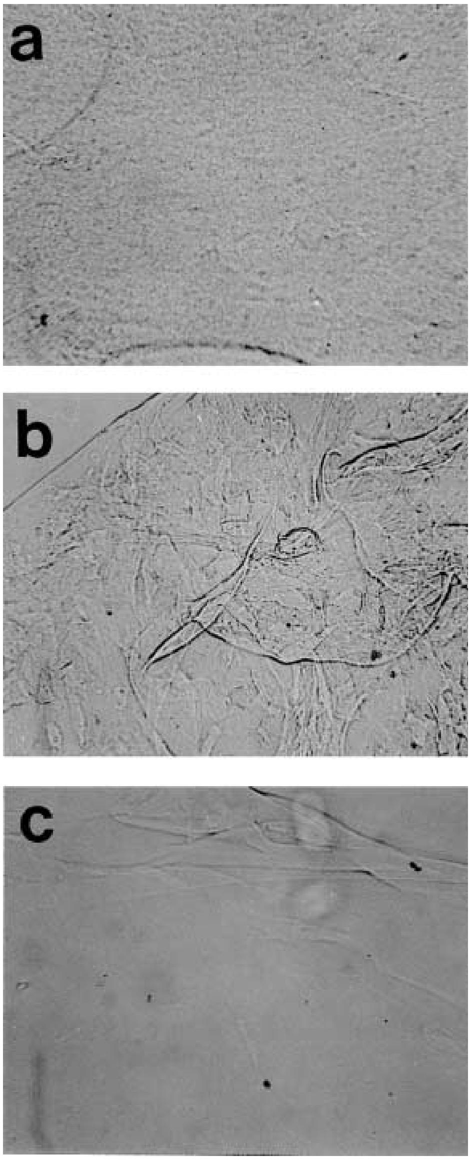

Fig. 4a–c Microphotograph of UHMW S-PVA gel aged for 3 h. S-diad contents: **a** 61.5%; **b** 58.2%; **c** 55.7%

S-PVA solution with *s*-diad content of 55.7%, the liquid-liquid phase separation was not favored although gelation took place slowly. However, some interesting changes were observed in successive aging of the gels. After 3 h, the spot-like heterogeneity was developed in HMW S-PVA gel with *s*-diad content of 61.5% (Fig. 4a), which is responsible for the subsequent decrease of the light transmittance. This is explained by the fact that the phase separation occurred in the gel phase without liquid-liquid phase separation, leading the reduction of the phase-separated domain size. The heterogeneous appearances of the gels of HMW S-PVAs with *s*-diad contents of 61.5% and 58.2% became more serious with aging. On the other hand, HMW S-PVA gel with *s*-diad content of 55.7% did not reveal the heterogeneous appearance at all even after 1 month, indicating phase separation in the gel state did not take place to any great extent as illustrated in Fig. 5c. The crumple formation in gel resulted from the volume shrinkage attributed to syneresis. This quite coincides with the results found in Figs. 1 and 2.

For examination of crystallization in the aging process, a WAXD of the HMW S-PVA gel was obtained (Fig. 6). The intensities of the peaks corresponding to the 100 plane at 10° and the 101 plane at 20° increased with aging irrespective of the syndiotacticity of the

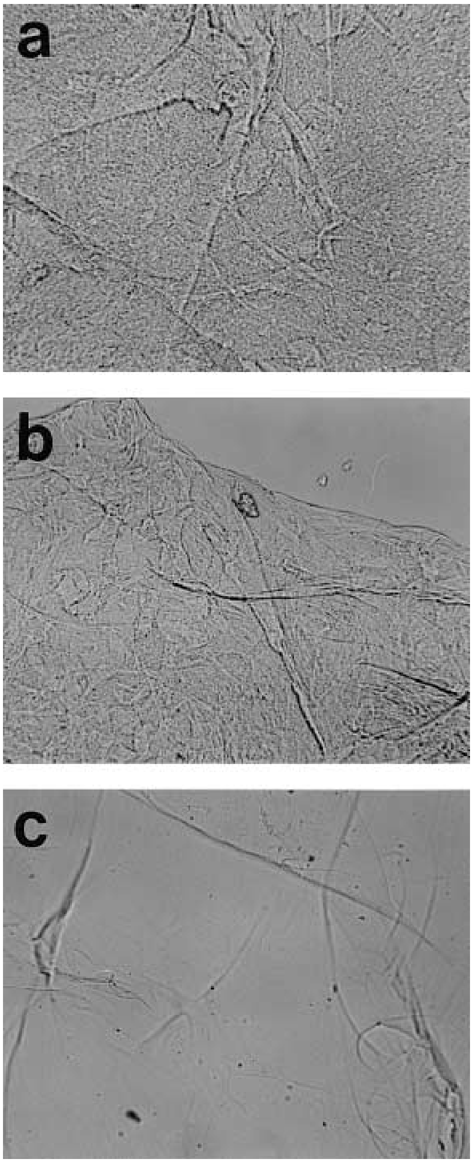

Fig. 5a–c Microphotograph of UHMW S-PVA gel aged for 4 weeks. S-diad contents: **a** 61.5%; **b** 58.2%; **c** 55.7%

samples, indicating that the crystallization had been accompanied commonly in the aging process of HMW S-PVA gels. Based on the results of small angle neutron scattering measurement, it is reported [20] that the correlation length increased rapidly with time in the early stage of gelation, which is assigned to the characteristic length of the concentration fluctuations during the induction period of the crystallization of PVA. After reaching a maximum, it decreased to about 180 Å, which is the average distance between the nearest-neighboring crystallites. Hence, the crystallization of PVA gel is a characteristic feature when it is aged. A difference was found at the peaks of 100 plane with respect to the syndiotacticity. At the initial stage, the crystals in the 100 plane of HMW S-PVA gel with *s*-diad content of 55.7% were developed ascendingly among the sample as depicted in Fig. 6c. However, with

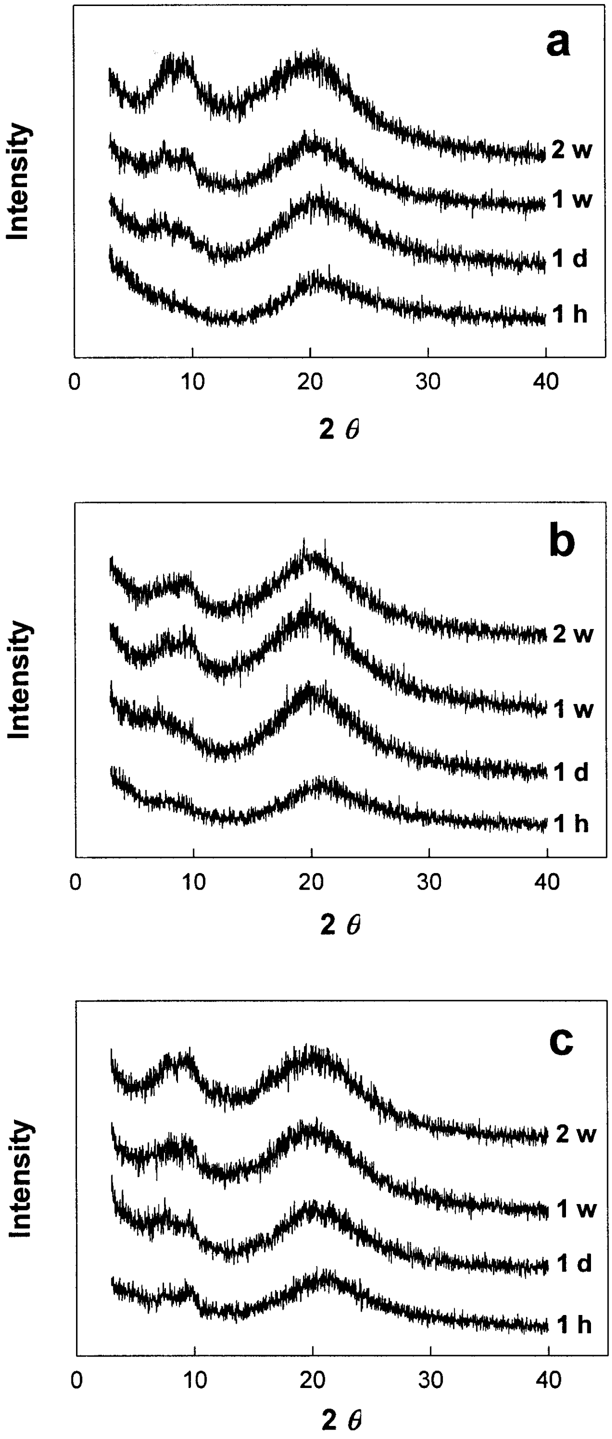

Fig. 6a–c WAXD of UHMW S-PVA gel with aging time. S-diad content: **a** 61.5%; **b** 58.2%; **c** 55.7%

the passage of time, the crystals in the 100 plane of HMW S-PVA gel with *s*-diad content of 61.5% were developed preferentially. This can be explained by the relationship between the gelation rate and the crystallization. The critical gelation temperatures of 4.0 g/dl solutions of HMW S-PVAs with *s*-diad content of 61.5%, 58.2%, and 55.7% were 65 °C, 35 °C, and 0 °C, respectively. In this study, the gelation was carried out by standing the solutions at 0 °C regardless of the syndiotacticity of PVA. So, the gelation rate of HMW S-PVA with *s*-diad content of 61.5% was the highest among them. The fast network formation of HMW S-PVA with *s*-diad content of 61.5% hindered the crystallization at the initial stage i.e., 1 h. Thus, the crystallization of HMW S-PVA gel with *s*-diad content of 55.7% was dominant due to the slowest network formation. With the passage of time, the syndiotacticity would promote the crystallization. Hence, the most developed crystal structure was found in HMW S-PVA gel with *s*-diad content of 61.5% after 2 weeks.

Figure 7 shows the change in Young's modulus (*E*) of HMW S-PVA gel obtained from stress-strain curves. The gel with higher syndiotacticity had higher *E* from the initial stage. With the passage of time, *E* was enhanced to a large scale. This is mainly due to the syneresis of the gel. The increase of the polymer concentration due to the extensive phase separation in the gel during the aging process causes an increase of crosslinking density. Hence, the enhancement of *E* is directly related with the degree of syneresis. Actually, high strength and high modulus PVA gel film was obtained by the gel aging method [21]. The difference between the moduli of HMW S-PVA gels with *s*-diad content over 58% and those with *s*-diad content of 55.7% became larger because the syndiotacticity of PVA promoted the phase separating ability of the gel.

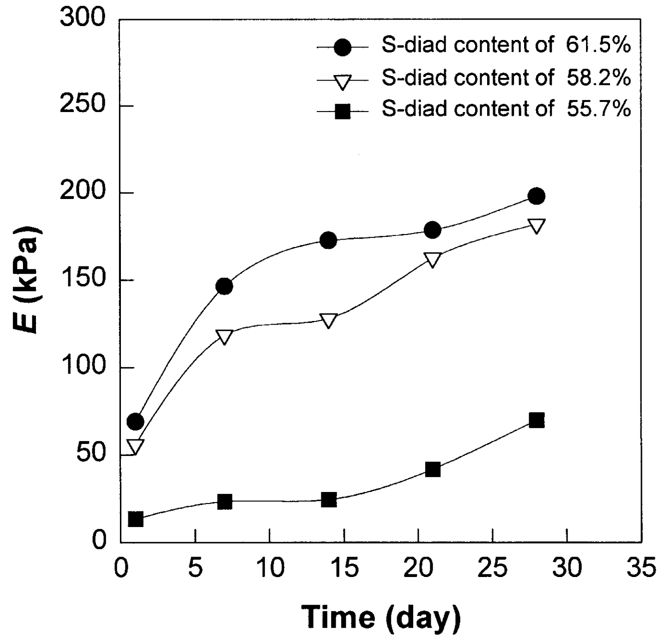

Fig. 7 Change in Young's modulus of UHMW S-PVA gel aged at 0 °C with time

Conclusion

In the aging process of HMW S-PVA gel, the syneresis due to phase separation was found. From the early stages of aging, the syneresis of HMW S-PVA gel with *s*-diad content over 58.2% was prominent as compared with that of HMW S-PVA with *s*-diad content of 55.7%. The significant increase in turbidity of HMW S-PVA gel with *s*-diad content over 58.2% is evident from the liquid-liquid phase separation before gelation or the phase separation after gelation, which was confirmed by the heterogeneous appearance. Taking these results into consideration, it is suggested that the syndiotacticity of HMW S-PVA accelerates the phase separation in gel, especially at the initial stages. The crystallization of HMW S-PVA gel was hindered by the fast network formation early on. However, in the later stages, the syndiotacticity promoted the crystallization rather than phase separation. The *E* of HMW S-PVA gel with higher syndiotacticity increased more significantly with time due to a higher degree of phase separation. Through the series of experiments, it is concluded that the syndiotacticity is the one of the important factors governing the phase separation and the crystallization of HMW S-PVA aged gel. Also, there is a profound difference in the characteristics between the aged gels with *s*-diad contents of 55.7% and *s*-diad content over 58.2%.

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