Development of High-Strength Poly (Vinyl Alcohol) Fibers (II)
- Gelation and Coagulation Behavior of PVA/DMSO/water solutions -

Do Hyun Kim , Won Jun Song and Chang Seoul

Department of Textile Engineering, Inha University, Inchon, Korea

1. Introduction

The production of high modulus and high strength poly (vinyl alcohol) films and/or fibers has been widely investigated and good results have been obtained by drawing of dried gel films prepared by crystallization from semi-dilute solutions in water and dimethyl sulfoxide(DMSO) mixtures [1,2]. According to their reports, the drawability of PVA gels depends on the degree of polymerization of the PVA, concentration of the solutions, compositions of co-solvents, quenching temperatures and so on [3,4]. And high drawability can be achieved from the transparent(homogeneous) PVA gels. Thus spinning dope solution for high-strength PVA fibers should be prepared by an appropriate solvent composition and concentration that forms transparent PVA gels in coagulating bath. To obtain better understand for the phenomena occurring in the gel-spinning of PVA, we should first set up the phase diagram for the PVA-water-DMSO three components system. The DMSO/water mixture has one of the interesting characteristics that the solvent mixtures ranging from 50 to 70 vol% DMSO does not freeze even at $-100°C$ [5]. In this study, we investigate the solution properties under various conditions like solvent compositions, polymer concentrations and coagulation temperatures. We also measured the coagulating rate of PVA gels in methanol. The stress-strain curve of an amorphous PVA single chain was generated using the molecular simulation program Cerius2.

2. Experimental

2.1 Preparation of solutions

95% saponified at-PVA samples with degree of polymerization(Pn) of 5000(Unitika Chemical Co. Ltd) were used in this study. A given amount of at-PVA was dissolved in a mixture of DMSO/water at about 120°C. The test tubes(10mm of diameter and 150mm of depth) are kept at 90°C for homogenization of the solutions.

2.2 Determination of Sol-Gel

Test tubes containing solution are kept at each temperature for 24 hours, then tubes are tilted for checking whether the solutions is gelled or not. If the meniscus of solution changes, we judge the sample is not gelled.

2.3 UV-Visible spectrometer

Absorbance for the coagulating solution at various concentration was measured by UV-1601PC(Shimadzu Co. Ltd) . The asorbance at 500nm is used for comparison in coagulating behavior.

2.4 Molecular Simulation

The single PVA chain with degree of polymerization of 100 is made and simulated using Cerius2(MSI Co. Ltd). The DREIDING 2.21 force field is applied and charge is calculated by charge equilibrium method.

3. Results and Discussion

The Fig.1 and Fig.2 are the phase diagrams of PVA solutions having solvent mole ratio 1:1(DMSO/water) and 1:2, respectively. The solid circles mean gel and crosses mean sol at each temperature after 24 hours.
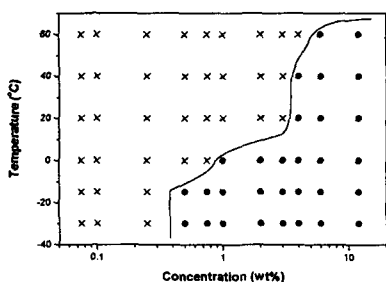

Fig. 1. Phase diagram at lower temperaures (DMSO:water=1:1).
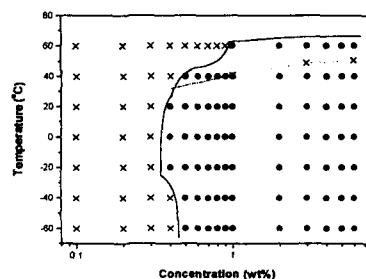
Fig. 2. Phase diagram at lower temperatures (DMSO:water=1:2).

An important difference between the two diagrams is existence of phase separation. PVA solution with 1:1 mole ratio solvent composition does not show phase separation and does not form gels under the critical concentration [6]. But PVA solution with 1:2 mole ratio solvent shows the phase separation and it leads to forming of gels under critical concentration.

Gelling times of each solution are measured by steel ball method and shown in Fig.3 and Fig.4. The critical concentrations for gelling are tabulated in table 1.

Coagulation time is measured by using the UV-Visible spectrometer. As PVA polymer are precipitating in the non-solvent bath, the beam blocked by the

coagulated PVA have a constant intensity. If the polymer coagulation process is finished, the apparent absorbance levels off and the time to this point can be thought as "the coagulation time". [7] Measured coagulation times are shown in Fig.5 and Fig.6. The coagulation times of solution of 6% and 12% are about 20 seconds and 40 seconds, respectively.

Table 1. The critical concentration obtained by above two experiments.

DMSO/water	$C^*_{t=\infty}$(wt%)	C^*(wt%)
1:1	0.42	~0.5
1:2	0.52	~0.5

Where $C^*_{t=\infty}$ is the value obtained from Fig.3 and Fig.4. C^* is the value obtained from Fig.1 and Fig.2.
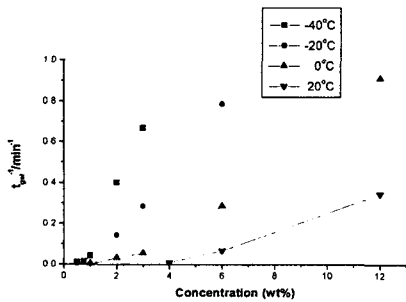

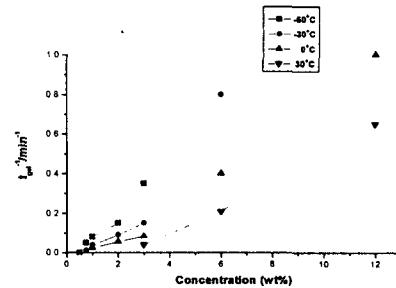Fig. 3. Reciprocal gelling time at various temperatures (DMSO:water=1:1)

Fig. 4. Reciprocal gelling time at various temperatures(DMSO:water=1:2).
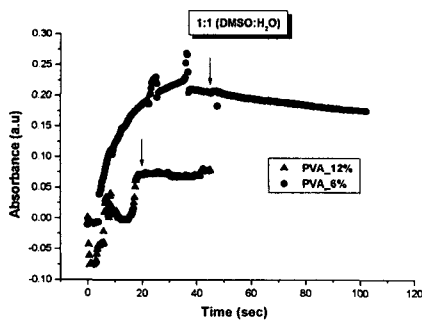

Fig. 5. Coagulation time for 6%,12% solution (DMSO:water=1:1) in methanol bath.
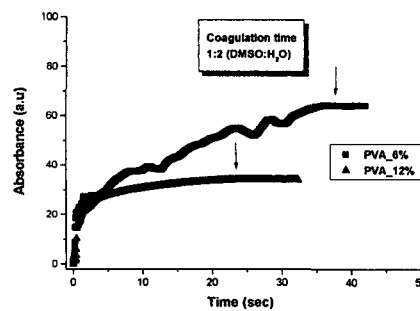

Fig. 6. Coagulation time for 6%,12% solution (DMSO:water=1:2) in methanol bath.

For molecular mechanics simulation, at-PVA with Pn of 100 was generated and 3D periodic boundary condition was applied. Then the structure was relaxed, and NVT ensemble molecular dynamics simulation at high temperature(1000 °K) is performed to avoid local minimum problem. To stabilize the cell, NPT ensemble molecular dynamics simulation at room temperature was implemented [8]. Finally reference state was saved by molecular mechanics simulation. Stepwise elongation was added to chain axis, and the system energy was minimized. The resulting stress-strain curve for amorphous PVA chain is shown in Fig. 7.
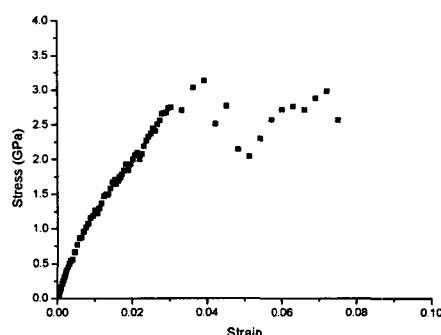
Fig. 7 Stress-strain curve obtained by
molecular mechanics

Reference

1) Cha. W. I., Hyon S. H. and Ikada, Y., *J. Polym. Sci. Part B: Polym. Phys.* 1994, 32, 297

2) M. Matsuo, Y. Sugiura, S. Takematsu, T. Ogita, T. Sakabe and R. Nakamura, *Polymer* Vol 38. No. 24, 5953-5967, 1997

3) Farrant J., *Nature*, 1965, 205, 1284

4) Friedberg F., Brown W., Henley D. and Ohman J., *Makromol. Chem.*, 1983, 66, 168

5) M. Watase and K. Nishinari, *Polym. J.*, Vol. 21, No. 7, pp 567-575, 1989

6) M. Ohkura, T. Kanaya and K. Kaji, *Polymer* Vol. 33, No. 17, 1992

7) M. Ohkura, T. Kanaya and K. Kaji, *Polymer* Vol. 33, No. 23, 1992

8) J. W. Kang, K. S. Choi, W. H. Jo and S. L. Hsu, *Polymer* Vol. 39 No. 26 pp 7079-7087, 1998