Rheological Characterization of Shear-Induced Structural Formation in the Solutions of Poly(vinyl alcohol) in Dimethyl Sulfoxide

Eun Jeoung Lee,[1] Kyung Sik Dan,[2] Byoung Chul Kim[3]

[1]*The Research Institute of Industrial Sciences, Hanyang University, Seoul, Korea*
[2]*SKC Co., Ltd., Advanced Technology R&D Center, Suwon, Korea*
[3]*Division of Applied Chemical Engineering, Hanyang University, Seoul, Korea*

ABSTRACT: Gelation behavior of the solutions of poly(vinyl alcohol) (PVA), whose syndiotactic diad content was 52% and weight-average molecular weight of PVA ranged from 89,000 to 186,000, in dimethyl sulfoxide (DMSO) was investigated in terms of shear rate, concentration, and molecular weight of the polymer. To trace time-dependent gelation behavior, a programmed time sweep experiment was carried out by repeating the following procedure 3 times; 10 min of measurement followed by 5 min relaxation. All of the PVA solutions in DMSO exhibited time-dependent rheological responses, particularly under low shear rate of 2 rad/s, indicative of the formation of physical structures. At high shear rate of 200 rad/s the rheological responses were independent of time. Referring to Winter's view on gelation, a weak shear produced a soft gel structure whereas a strong shear produced an irreversible strong gel. Gelation was more affected by molecular weight than by concentration over the period of shearing. At low frequency, relaxation time was increased with time, and then leveled off after prolonged shearing. At high frequency, however, little change of relaxation time was noticed. They can be interpreted as a consequence of formation of three-dimensional gel structure through the polar interactions by hydroxyl groups whose strength was dependent on shearing conditions. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 465–471, 2006

Key words: shear-induced structural formation; time-dependence; solution rheology; relaxation

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a linear, flexible-chain polymer, in which polar hydroxyl groups existing as pendent group form strong and influential inter- and intramolecular hydrogen bonding. According to the stereoregularity of hydroxyl groups, PVA is classified to three types: atactic (a-PVA), isotactic, and syndiotactic (s-PVA). PVA has good linearity, flat zigzag conformation, high crystallinity, alkali resistance, and adhesive property. These advantageous properties find a wide range of applications such as reinforcement of cement, concrete, and plastic, substitute of asbestos, tire cord, and film.[1,2]

Some results on the rheological properties of a-PVA gel[3–5] and s-PVA gel[6,7] have been reported; s-PVA exhibits completely different rheological properties[8–10] from a-PVA in addition to higher crystallinity and better mechanical properties. High cost of monomer, vinyl pivalate, and drastic process conditions have prevented s-PVA from commercialization. Consequently, a-PVA was successfully commercialized and is being used as a general-purpose resin. Recently we reported that a-PVA exhibited very unusual rheological responses. For a-PVA solutions in dimethyl sulfoxide (DMSO), the 14 wt % PVA solutions exhibited very unusual rheological behavior, showing definite double sol–gel phase transitions with the shear rate.[11] Hence it is necessary to understand the rheological characteristics of these systems precisely to design processing conditions for the manufacturing of the PVA products with desired properties.[3] Since the secondary physical bonding is sensitive to the processing conditions, the PVA solutions in DMSO show time and shear-dependent rheological responses. For example, it is possible to induce gelation under an external stimulus.[12–16] In spite of its real importance, few reports have been disclosed on this aspect.

A polymer gel is a continuous network of chains crosslinked by chemical or physical junctions. Physical junctions in polymer gels may be classified into at least four types[17,18]: crystallites for crystalline polymers, double helical structure for biological polymers, nodules for block copolymers, and polymer–solvent complexes.[19]

It is expected that PVA/DMSO solution systems show the shear induced gelation because the intermo-
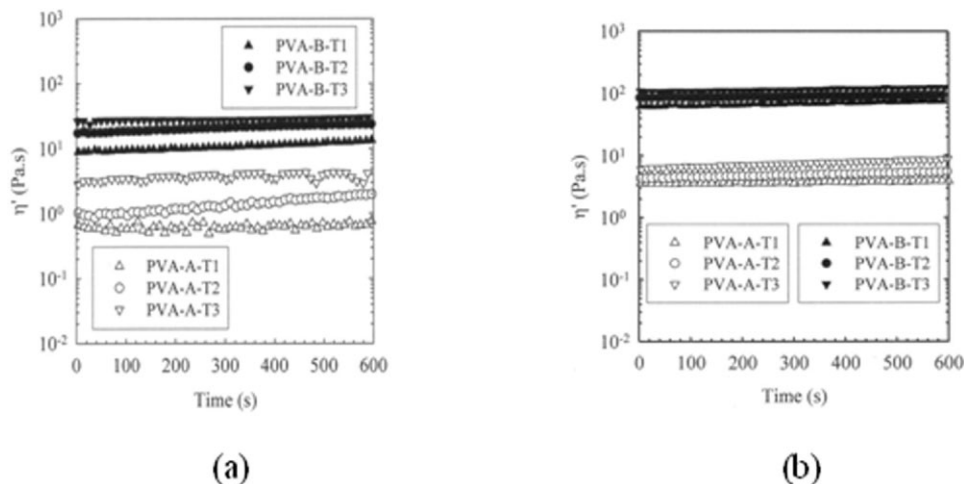
Figure 1 Variation of dynamic viscosity with time at 30°C; frequency = 2 rad/s; (a)10 wt % (b) 14 wt %.

lecular physical bonding shows the continuous change on an external stimulus such as shear rate. Gelation under shear conditions may provide us with important information that can be crucial in explaining the mechanisms and factors governing the building up of structures of physical gels.[20–24] We already reported shear-dependent gelation behavior of PVA solutions in DMSO.[11,25] This study investigated the time-dependent gelation behavior of the solutions at two distinctive shear rates, that is, 2 and 200 rad/s, at which the solutions exhibited shear-insensitive and shear-sensitive viscosity behaviors, respectively.

EXPERIMENTAL

PVA (Aldrich Chemical) with a degree of saponification greater than 99% was used. The PVA samples were coded according to their molecular weight; PVA-A [weight-average molecular weight (M_w) = 89,000 ~ 98,000] and PVA-B (M_w = 124,000–186,000). The syndiotactic diad content determined by 300 MHz ^{1}H NMR (Varian Gemini) was 52%. DMSO (Aldrich Chemical) was used without further purification. Since the method of preparing solutions has significant effects on the rheological properties, PVA was dissolved in DMSO at 90°C under the same dissolving procedure; stirred for first 2 h and then placed still for 3 h. To exclude the possibility of incomplete dissolution of the polymer in the solvent, the solution was optically examined.

The rheological properties were measured with an advanced rheometric expansion system (Rheometric Scientific) at 30°C. Parallel-plates were adopted whose diameter and gap were 50 and 1 mm, respectively. After being loaded between parallel plates, the solution specimen was fully relaxed for 20 min. Frequency sweep experiment was carried out from 0.05 to 500 rad/s and time sweep experiment was performed at 2

and 200 rad/s by repeating the following procedure 3 times; 10 min of measurement followed by 5 min of relaxation. The relaxation is truly a nonoscillatory time period. The experimental results indicated in many cases the development of structure/gelation during this time period.

RESULTS AND DISCUSSION

Figure 1 shows the time dependence of viscosity at 30°C and at low shear rate (2 rad/s) for 10 and 14 wt % PVA/DMSO solutions. In all cases viscosity is increased as the time-sweep experiment is repeated, bringing about a shear-induced thickening over the period of the repeating time sweep procedure. The time dependence is more noticeable with decreasing concentration and molecular weight of the polymer. This means that aggregate structure is more readily built up under shear probably due to greater freedom of PVA molecules in the solution. As one knows, shearing leads to a local orientation of molecular chains as depicted in Scheme 1.[25] At rest, PVA chains are expected to have a coiled conformation, as shown in Scheme 1(a). However, shearing produces some
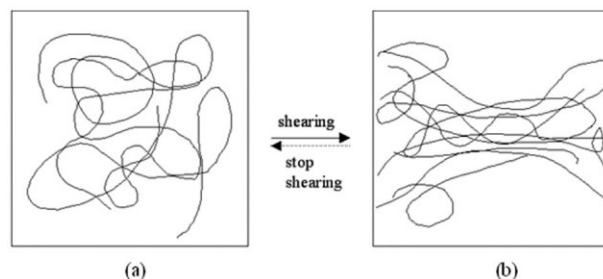

Scheme 1 (a) Unsheared and (b) sheared structures of PVA molecules of the solutions of atactic PVA in DMSO.
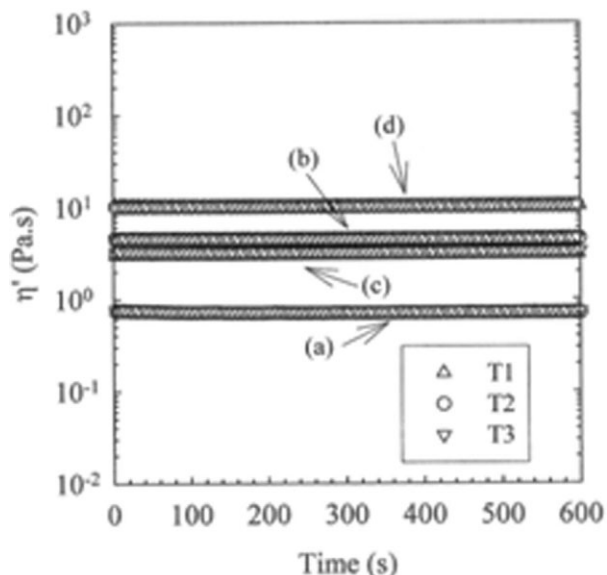
Figure 2 Variation of dynamic viscosity with time at 30°C; frequency = 200 rad/s; (a) PVA-A 10 wt %, (b) PVA-B 10 wt %, (c) PVA-A 14 wt %, and (d) PVA-B 14 wt %.

local orientation and stretching of the PVA chains as shown in Scheme 1(b). In the oriented region, lateral approach of the PVA chains gets easier, which makes the resultant aggregates stronger by more effective polar interactions. Thus, orientation by stretching of the chains gives the greater number of effective polar interactions, producing a stronger physical gel. In consequence, viscosity increase is the most noticeable with the polymer with lower molecular weight, PVA-A. The less noticeable time dependence of the solutions of higher molecular weight and higher concentration results partly from formation of stronger aggregates at the early stage of shearing due to longer molecular chain and more entanglement and partly from poor relaxation of molecular chains orientated by shear.

Figure 2 shows the time dependence of viscosity at high shear rate of 200 rad/s for 10 and 14 wt % PVA/DMSO solutions. Unlike at 2 rad/s viscosity shows little time dependence, giving rise to almost a master curve for T1, T2, and T3. This can be elucidated
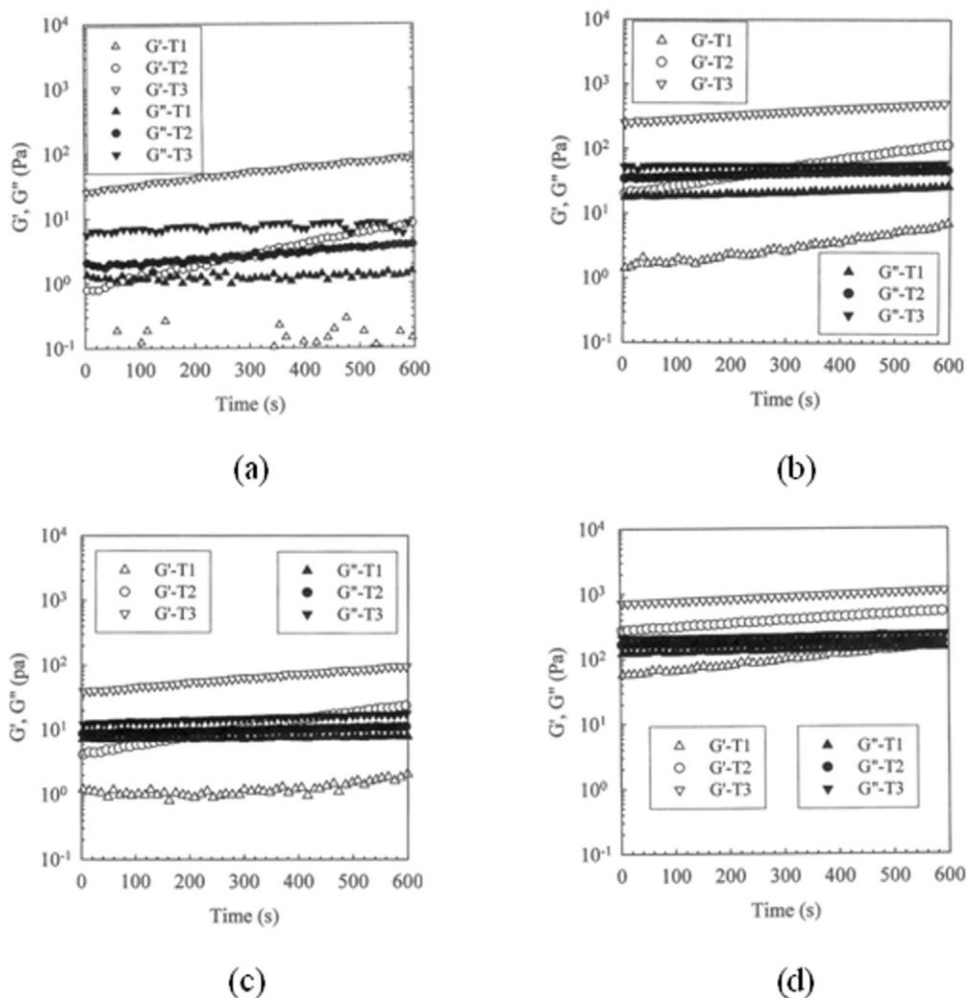
Figure 3 Variation of G' and G'' with time at 30°C; frequency = 2 rad/s. (a) PVA-A 10 wt %, (b) PVA-B 10 wt %, (c) PVA-A 14 wt %, and (d) PVA-B 14 wt %.
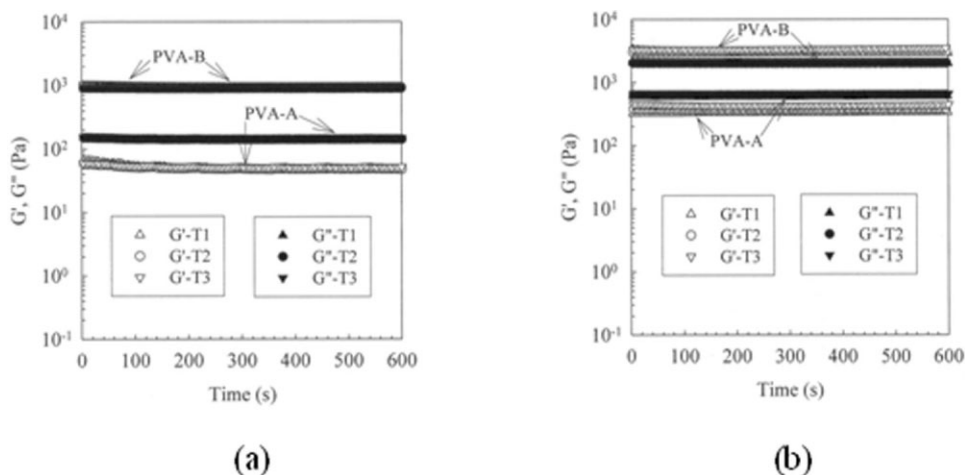
Figure 4 Variation of G' and G'' with time at 30°C; frequency = 200 rad/s; (a) 10 wt % and (b) 14 wt %.

by the fact that the strong shear let the polymer chains instantaneously be oriented on shearing which offers very favorable conditions for effective hydrogen bonding. Thus, most hydrogen bonds are formed at the starting point of shearing. Consequently, the shear-induced thickening effect is negligible. This suggests that a strong shear can have a drastic impact on the buildup of aggregated structures in highly polar polymer solution systems.

Figure 3 shows the variation of the storage (G') and loss modulus (G'') at low shear rate (2 rad/s) for 10 and 14 wt % PVA/DMSO solution at 30°C. The G', a measure of field strength, is increased as the time sweep process proceeds whereas the G'' exhibits only a slight increase with shearing time. During the repeating time sweep procedure, increase of G' and G'' is more noticeable with solutions of lower molecular weight and lower concentration for the same reasons discussed in the viscosity section.

Figure 4 shows the variation of G' and G'' with time at high shear rate of 200 rad/s, for the same solutions. Less time dependence of G' and G'' appears.

Gelation behavior with the variation of rheological properties can be more obviously considered by the introduction of the concept of loss tangent (tan δ) in dynamic rheology.[26] Figure 5 shows the variation of tan δ with time at low shear rate of 2 rad/s for 10 and 14 wt % PVA/DMSO solutions. In principle, viscous liquid character is dominant when G'' is greater than G' (tan δ > 1), and elastic solid character is dominant when G' is greater than G'' (tan δ < 1). Winter and Chambon[26] defined a gelation point, at which G' and G'' (tan δ = 1) are balanced. For the case of PVA-A 10 wt %, PVA-B 10 wt %, and PVA-A 14 wt %, liquid-like viscous fluid characteristics is shown at first time-sweep (T1) and shear induced gelation takes place at the second time-sweep (T2). PVA-B 14 wt % solution with higher molecular weight and higher concentra-

tion shows early shear induced gelation (at the T1 stage).

In an oscillatory shear experiment, the strength of networks (S) at gel point can be expressed by eq. (1).[26]

$$S = G_c'[\pi\omega_0/2]^{-1/2} \tag{1}$$

In which, ω_0 is the angular frequency of the experiment. The Gc' is G' at the time of its intersection with G''. The value of S calculated is given in Table I. The order of the magnitude of network strength is PVA-B 14 wt %, PVA-B 10 wt %, PVA-A 14 wt %, and PVA-A 10 wt %, suggesting that the strength of the physical aggregates is stronger at higher molecular weight and at higher concentration.

At high shear rate (200 rad/s) the solutions exhibit little time dependence of tan δ as shown in Figure 6. This means that the structure is deformed on initial shearing under high shear rate and additional deformation of structure little proceeds over the period of repeating time sweep. The time-independent nature must be due to inhibition of aggregates.

PVA-B 14 wt % and PVA-B 10 wt % are characterized as a solid-like elastic body but PVA-A 10 wt % and PVA-A 14 wt % as a liquid-like viscous fluid. In particular, gelation behavior at high shear rate is more influenced by molecular weight rather than by concentration over the period of repeating time sweep procedure.

For polymeric systems in which some pseudostructures are involved, relaxation time (λ) under dynamic shear can be calculated by eq. (2).[27]

$$J' = G'/(|\eta^*|\omega)^2 = \lambda/|\eta^*| \tag{2}$$

In which, J' and η^* are the compliance and complex viscosity, respectively. If there is some molecular order or physical structure, a much longer relaxation
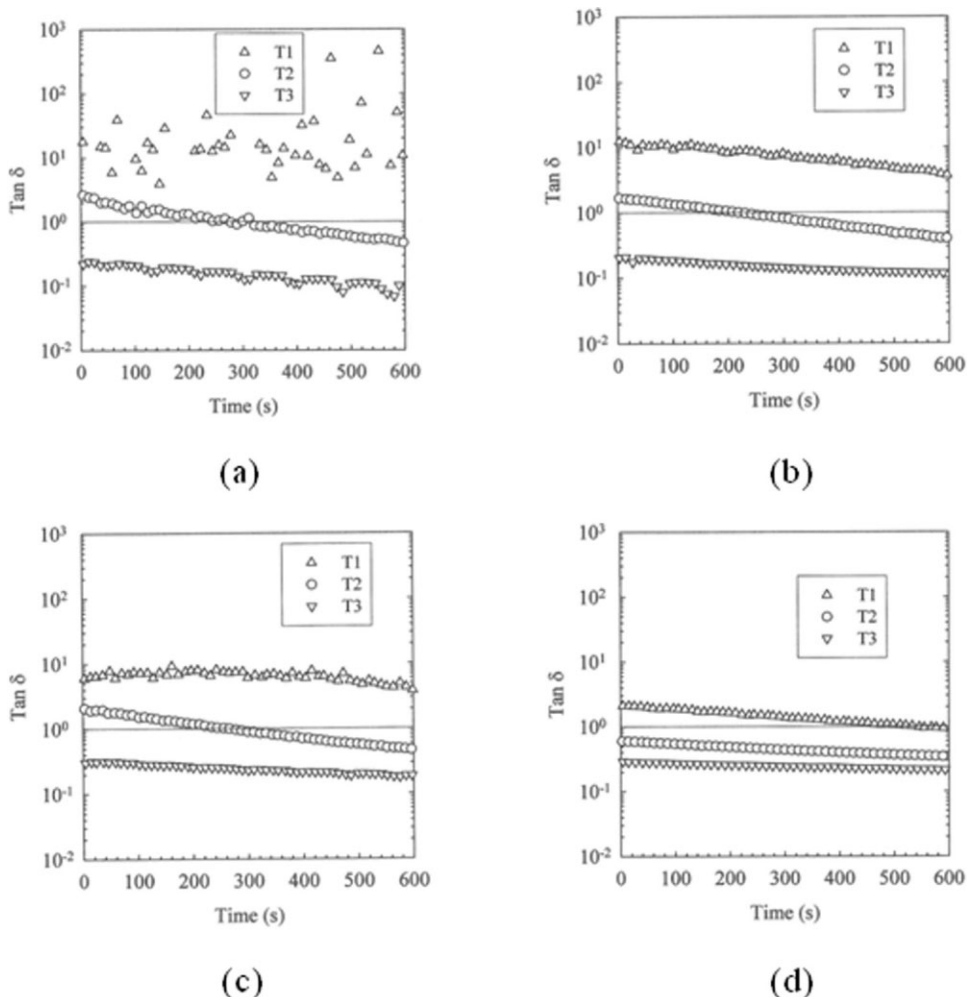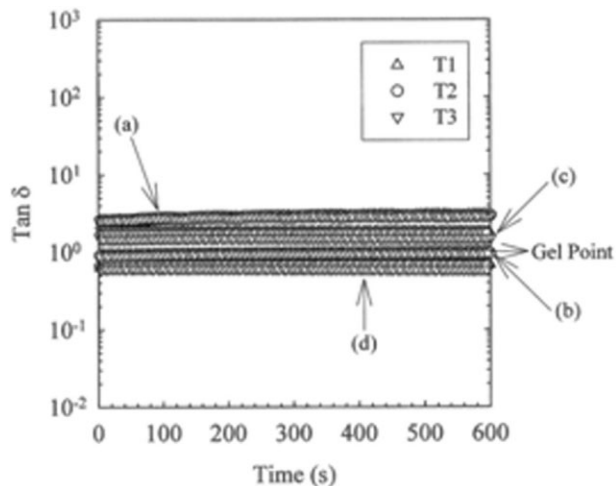
Figure 5 Variation of tan δ with time at 30°C; frequency = 2 rad/s; (a) PVA-A 10 wt %, (b) PVA-B 10 wt %, (c) PVA-A 14 wt %, and (d) PVA-B 14 wt %.

time is expected. Figure 7 shows the variation of time at low shear rate (2 rad/s) for 10 and 14 wt % PVA/DMSO solutions. In general, λ is longer than relaxation time of general solution system, and λ for PVA/DMSO solution system shows time dependence. The increase of λ represents the gradual decrease of chain mobility of molecules resulting from restriction between molecules by intermolecular interaction. At high shear rate of 200 rad/s the λ shows little time

TABLE I
Strength of the Network at Gel Point
(Frequency, 2 rad/s)

PVA	Concentration (wt %)	Strength of the network at gel point (Pa s$^{1/2}$)
A	10	3.14
A	14	13.9
B	10	57.6
B	14	207

Figure 6 Variation of tan δ with time at 30°C; frequency = 200 rad/s; (a) PVA-A 10 wt %, (b) PVA-B 10 wt %, (c) PVA-A 14 wt %, and (d) PVA-B 14 wt %.
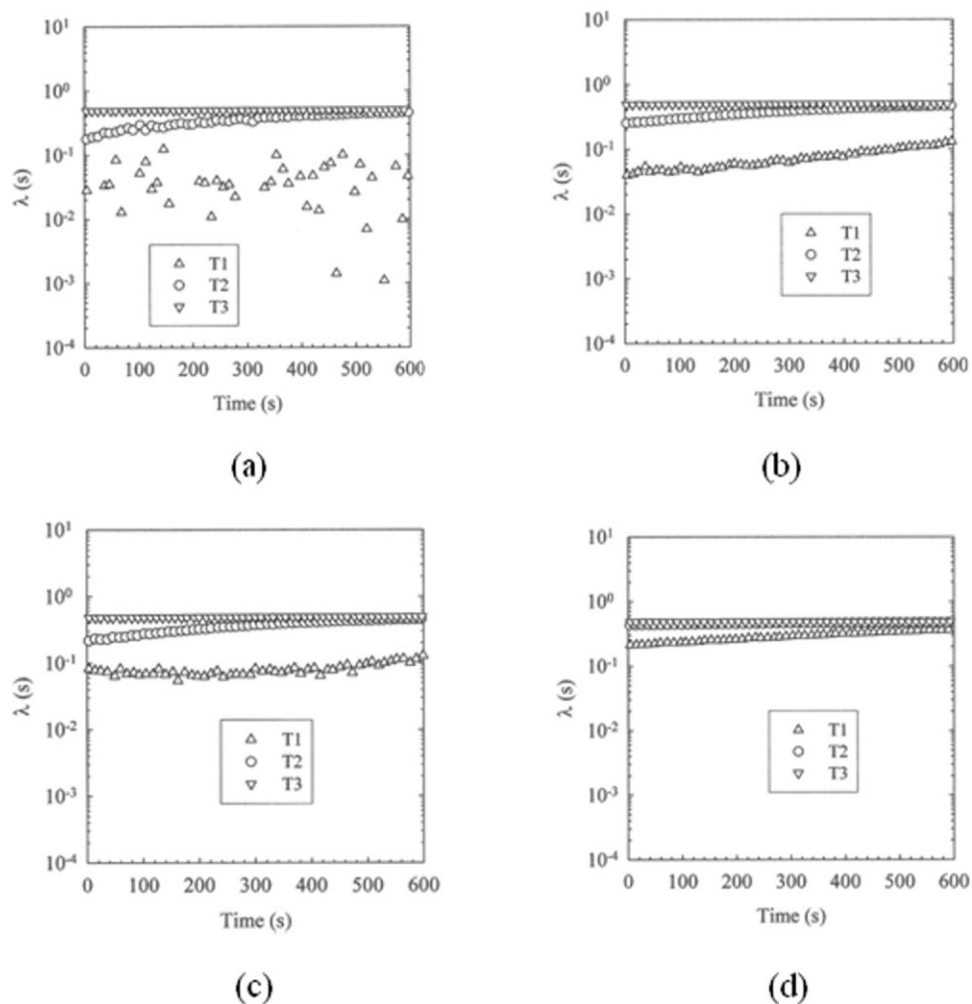
Figure 7 Variation of λ with time at 30°C; frequency = 2 rad/s; (a) PVA-A 10 wt %, (b) PVA-B 10 wt %, (c) PVA-A 14 wt %, and (d) PVA-B 14 wt %.

dependence and has almost constant value as shown in Figure 8. These phenomena further reconfirm the shear induced gelation previously discussed.

CONCLUSIONS

For PVA solutions in DMSO, the time-dependent rheological responses were noticeably influenced by shear rate, molecular weight, and concentration of polymer. At low frequency of 2 rad/s, the shear-induced gelation showed time-dependence over the period of repeating the time sweep procedure. At high frequency of 200 rad/s, however, the solutions showed little time dependent gelation behavior. This indicated that shear rate had a paramount effect on the gelation behavior at given conditions. If a strong gel was once formed by a strong shear, no additional gelation or additional deformation of the gel proceeded further even by prolonged shearing.
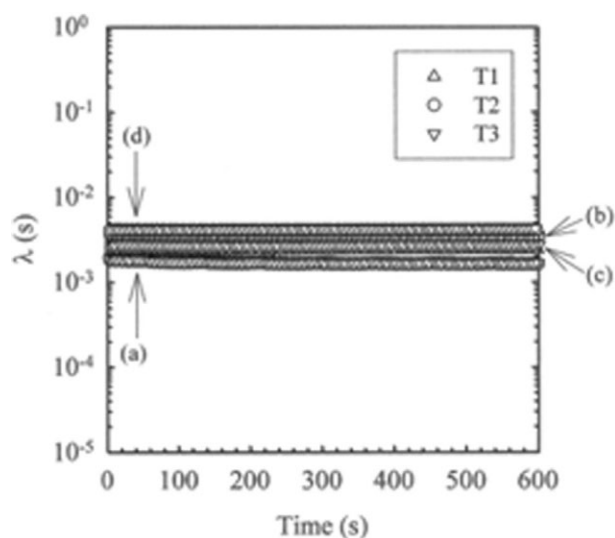
Figure 8 Variation of λ at 30°C; frequency = 200 rad/s; (a) PVA-A 10 wt %, (b) PVA-B 10 wt %, (c) PVA-A 14 wt %, and (d) PVA-B 14 wt %.

References

1. Ohmori, A.; Sano, H.; Yoshimochi, H.; Sano, T.; Naramura, S. U.S. Pat. 5,229,057 (1993).
2. Narukawa, H.; Mizobe, A.; Nakahara, F.; Kubotsu, A.; Akiyama, A.; Nishiyama, M.; Nagamatu, K.; Miyazaki, H. U.S. Pat. 5,110,678 (1992).
3. Shibayama, M.; Adachi, M.; Ikkai, F.; Kurokawa, H.; Sakurai, S.; Nomura, S. Macromolecules 1993, 26, 623.
4. Watase, M.; Nishinari, K. Polym J 1989, 21, 567.
5. Tanigami, T.; Murase, K.; Yamaura, K.; Matsuzawa, S. Polymer 1994, 35, 2573.
6. Choi, J. H.; Lyoo, W. S.; Ghim, H. D.; Ko, S. W. Colloid Polym Sci 2000, 278, 1198.
7. Choi, J. H.; Ko, S. W.; Kim, B. C.; Blackwell, J.; Lyoo, W. S. Macromolecules 2001, 34, 2964.
8. Lyoo, W. S.; Kim, B. C.; Ha, W. S. Polym Eng Sci 1997, 37, 1259.
9. Lyoo, W. S.; Kim, B. C.; Ha, W. S. Polym J 1998, 30, 424.
10. Lyoo, W. S.; Choi, J. H.; Kim, B. C.; Blackwell, J. Macromolecules 2001, 34, 3982.
11. Lee, E. J.; Kim, N. H.; Dan, K. S.; Kim, B. C. J Polym Sci Part B: Polym Phys 2004, 42, 1451.
12. Maerker, J. M.; Sinton, S. W.; J Rheol 1986, 30, 77.
13. Odell, J. A.; Muller, A. J.; Keller, A. Polymer 1988, 29, 1179.
14. Tirtaatmadja, V.; Tam, K. C.; Jenkins, R. D. Macromolecules 1997, 30, 1426.
15. Wolf, B.; Scirocco, R.; Frith, W. J.; Norton, I. T. Food Hydrocolloids 2000, 14, 217.
16. Kujawa, P.; Rosiak, J. M.; Selb, J.; Candau, F. Macromol Chem Phys 2001, 202, 1384.
17. De Gennes, P.G. Scaling Concepts in Polymer Physics; Cornell University Press: Ithaca, 1979.
18. Francois, J.; Gan, Y. S.; Sarazin, D.; Guenet, J. M. Polymer 1988, 29, 898.
19. Ohkura, M.; Kanaya, T.; Kaji, K. Polymer 1992, 33, 3686.
20. Tanaka, F.; Edwards, S. F. Macromolecules 1992, 25, 1516.
21. Marucci, G.; Bhargava, S.; Cooper, S. L. Macromolecules 1993, 26, 6483.
22. Wang, S. Q. Macromolecules 1992, 25, 7003.
23. Ahn, K. H.; Osaki, K. J Non-Newtonian Fluid Mech 1995, 56, 267.
24. Lele, A. K.; Mashelkar, R. A. J Non-Newtonian Fluid Mech 1998, 75, 99.
25. Song, S. I.; Kim, B. C. Polymer 2004, 45, 2381.
26. Winter, H. H.; Chambon, F. J Rheol 1986, 30, 367.
27. Wissburn, K. F.; Griffin, A. C. J Polym Sci Polym Phys Ed 1982, 20, 1835.