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The Effects of MWD on the Rheological Properties of Shear-Induced Structural Formation for PVA Solutions in DMSO

Eun Jeoung Lee, Byoung Chul Kim*

Summary: The effects of molecular weight distribution (MWD) on the rheological responses of shear-induced structural formation in the general-purpose polyvinyl alcohol (PVA) solutions dissolved in dimethyl sulfoxide (DMSO) were investigated. On the whole, time-dependence of rheological properties was more influenced by the PVA solutions with broad MWD at the similar weight average molecular weight (M_w). The dynamic viscosity (η') of PVA/DMSO solution with broad MWD was lower than that with narrow MWD at the similar M_w until the second time sweep (T2) of PVA/DMSO solution. After the time-sweep experiment was repeated, the η' of PVA/DMSO solution with narrow MWD was lower than that of PVA/DMSO solution with broad MWD at the similar M_w. The G' until 5 min of relaxation of PVA/DMSO solution with broad MWD was lower than that of PVA/ DMSO solution with narrow MWD at the similar M_w. After the time-sweep experiment was repeated, the G' of PVA/DMSO solution with narrow MWD was lower than that of PVA/DMSO solution with broad MWD at the similar M_w. It could be interpreted as a consequence of the formation of three-dimensional gel structure through the polar interactions by hydroxyl groups whose strength was dependent on shearing conditions and MWD.

Keywords: atactic; relaxation; shear-induced structural formation; solution rheology; time-dependence

Introduction

PVA is a synthetic polymer[1] which comes in three types, i.e., isotactic, atactic, and syndiotactic. PVA has unique chemical and physical properties as well as utilized in various industrial applications because the polar hydroxyl groups existing as pendent group of PVA form hydrogen bonding and react with many kinds of functional groups.[2]

Lots of rheological studies have been made on PVA solutions in water,[3] water/DMSO, and other solvents.[4] It has been known from 1950's that the concentrated solution of PVA produces gel by gradual increase in viscosity when it is maintained below room temperature.[5] Some results on the rheological properties of syndiotactic PVA solutions have been reported.[6] One of the results for the s-PVA solutions is the solutions of s-PVA exhibited some characteristic rheological responses similar to lyotropic liquid crystalline polymer systems. However, only a few reports on the rheological properties of atactic PVA solutions in DMSO, ethylene glycol, glycerin, and N-methylpyrrolidone are available in spite of industrial importance for the PVA products.

The properties of polymers are dependent on the type of physical bonds across the polymer chains as well as the type of chemical bonds along the polymer chains. In the case of polymers with strong polar intermolecular interactions such as PVA,

Department of Molecular System Engineering/Fiber & Polymer Engineering, Hanyang University, Seoul, Korea
Fax: (+82)-2-2297- 4941
E-mail: ejle@unitel.co.kr

the molecular aggregation has a significant effect on the physical properties, which is greatly affected by conformation of polymer molecules.

Recently we reported that a-PVA exhibited very unusual rheological responses. For a-PVA solutions in DMSO, the 14 wt% PVA solutions exhibited very unusual rheological behavior, showing definite double sol-gel phase transitions with the shear rate.[7]

It is real important to control the processing conditions with consideration of rheological behaviors precisely, for the manufacturing of the PVA products such as fiber, film, medical substitute, adhesive, and sizing agent with excellent properties.[8] Important variables affecting practical polymer processing and performance are its syndiotactic dyad content, M_w, MWD, concentration of polymer, and the kind of solvent systems. 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.[9–13] We already reported the shear-dependent gelation behavior of PVA solutions in DMSO.[7,14]

This study investigated the effect of MWD on rheological responses of shear-induced structural formation in the general-purpose PVA solutions dissolved in DMSO to design the processability of PVA solution.

Experimental Part

PVA (Aldrich Chemical) with a degree of saponification greater than 99% was used. The PVA samples were coded according to their M_w; PVA-A [$M_w = 89{,}000$–$98{,}000$] and PVA-B [$M_w = 85{,}000$–$146{,}000$], and PVA-C [$M_w = 124{,}000$–$186{,}000$]. PVA-B and PVA-A6C3 had similar M_w, but different MWD, which was prepared by mixing PVA-A and PVA-C by 64:36 in weight percent.

The syndiotactic dyad 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 the 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 non-oscillatory 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 η' at low frequency region (2 rad/s) for 14 wt % PVA/DMSO solution system with the similar M_w, but different MWD. It is noted in Figure 1 that the η' until the T2 of PVA/DMSO solution with broad MWD is lower than that of PVA/DMSO solution with narrow MWD at the similar M_w. This agrees well with the theoretical prediction by Middleman.[15] However, the η' of PVA/DMSO solution with broad MWD is increased more after the 10 min of relaxation and the third time sweep (T3). Therefore, after the time-sweep experiment is repeated, the η' of PVA/DMSO solution with narrow MWD is lower than that of PVA/DMSO solution with broad MWD at the similar M_w. In all cases, viscosity is increased as the time-sweep experiment is repeated, resulting in shear-induced thickening over the period of the repeating

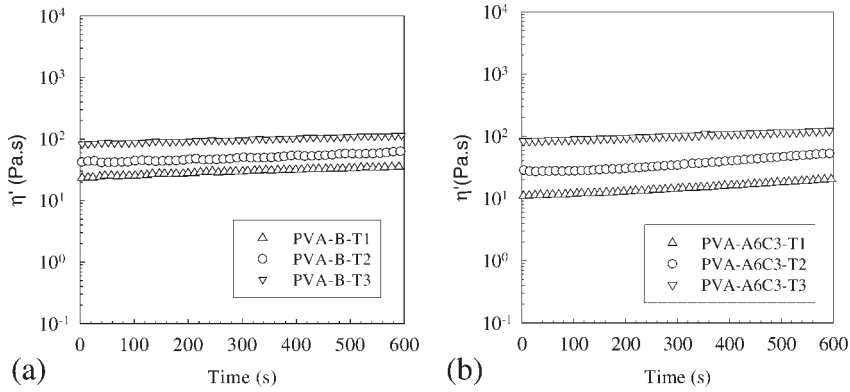

Figure 1.
Variation of dynamic viscosity with time at 30 °C: frequency = 2 rad/s, (A) PVA-B 14 wt %, (B) PVA-A6C3 14 wt %.

time sweep procedure. The time dependence is more noticeable with PVA/DMSO solution with broad MWD. This means that aggregate structure is more readily built up under shear probably due to greater freedom of PVA molecules with broad MWD in the solution. The less noticeable time dependence of the PVA/DMSO solution with narrow MWD results partly from the formation of stronger aggregates at the early stage of shearing due to more entanglement.

Figure 2 shows the variation of G′ with time at low shear rate region (2 rad/s) for 14 wt % PVA/DMSO solution system with the similar M_w, but different MWD. The G′ is increased as the time sweep process proceeds. During the repeating time sweep procedure, the increase of G′ is more noticeable with the PVA/DMSO solution with broad MWD for the same reasons discussed in the viscosity section. The effect of MWD on the elasticity of polymer is controversial, but it is reported that elasticity is increased with widen the MWD.[16–19] The G until 5 min of relaxation of PVA/DMSO solution with broad MWD is lower than that of PVA/ DMSO solution with narrow MWD at the similar M_w. However, the G of PVA/ DMSO solution with broad MWD is increased more as the time-sweep experiment is repeated. Therefore, after the time- sweep experiment is repeated, the G of PVA/ DMSO solution with narrow MWD is lower than that of PVA/DMSO solution with broad MWD at the similar M_w. This means that in case of PVA/DMSO solution with

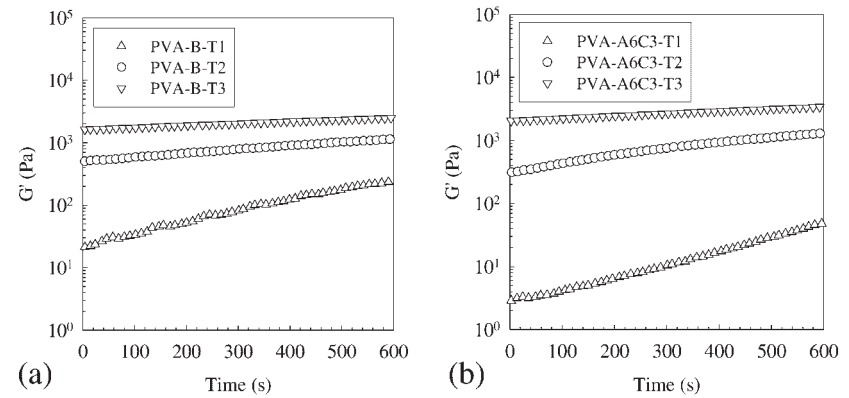

Figure 2.
Variation of storage modulus with time at 30 °C: frequency = 2 rad/s, (A) PVA-B 14 wt %, (B) PVA-A6C3 14 wt %.

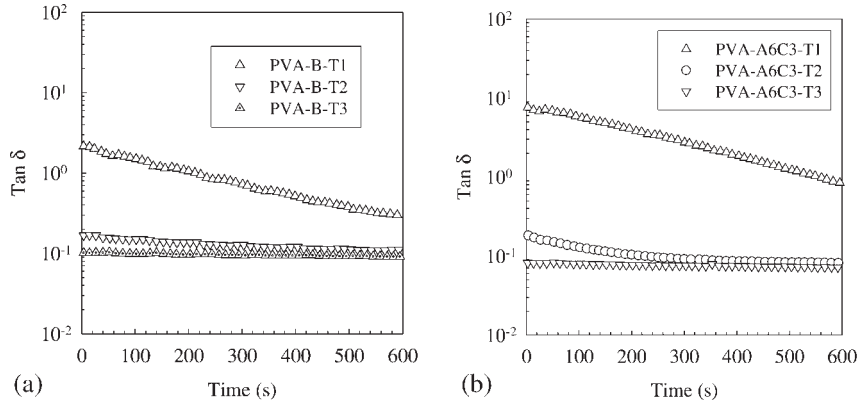

Figure 3.
Variation of loss tangent with time at 30 °C: frequency = 2 rad/s, (A) PVA-B 14 wt %, (B) PVA-A6C3 14 wt %.

broad MWD, the arrangement of polymer chain under shear rate makes more favorable conditions for intra- and intermolecular interactions, and then gives rise to more structure formation as the time-sweep experiment is repeated.

Figure 3 shows the variation of tan δ with time at low shear rate region (2 rad/s) for 14 wt % PVA/DMSO solution system with the similar M_w, but different MWD. The value of tan δ is a quantitative measure of a solid-like elastic body or liquid-like viscous fluid in a system. In principle, the fluid character is dominant when G″ is greater than G′, and the solid character is dominant when G′ is greater than G″. At the balance point of G′ and G″, gelation is defined by Winter and Chambon.[20] With respect to Winter's view on gelation, shear induced gelation is appeared at the first time-sweep (T1). PVA/DMSO solution with narrow MWD shows early shear induced gelation (at the T1 stage). The gel structure of PVA/DMSO solution becomes more and more stronger as the time-sweep experiment is repeated.

For polymeric systems in which some pseudo-structures are involved, the λ under dynamic shear can be calculated as follows:[21]

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

where J' and η^* are the compliance and complex viscosity, respectively. If there are

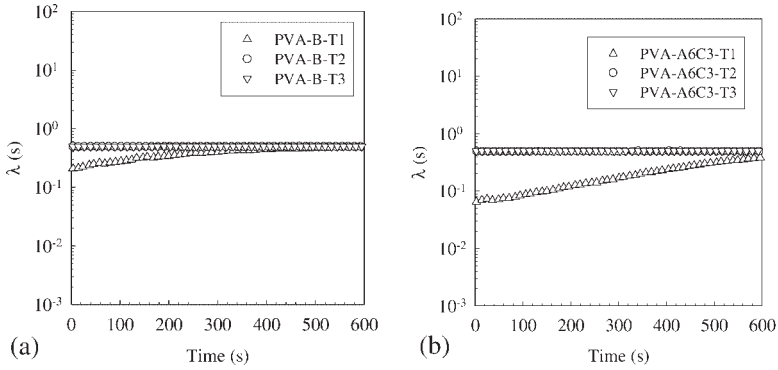

Figure 4.
Variation of relaxation time with time at 30 °C: frequency = 2 rad/s, (A) PVA-B 14 wt %, (B) PVA-A6C3 14 wt %.

some molecular orders or physical structures, a much longer λ is expected.[22]

Figure 4 shows the variation of λ with time at low shear rate region (2 rad/s) for 14 wt % PVA/DMSO solution system with the similar M_w, but different MWD. The λ of the PVA/DMSO solution system with the similar M_w, but different MWD shows the time dependence. The λ was increased with time, and then leveled off after prolonged shearing. The λ was more noticeably increased at the T1 for PVA/DMSO solution with broad MWD than those with narrow MWD. The increase of λ represents the gradual decrease of chain mobility of molecules resulting from the restriction between molecules by intermolecular interaction. This also suggests that some physical bonds through polar interactions are more effectively formed at broad MWD with the similar M_w.

Conclusions

The effect of MWD on rheological responses of shear-induced structural formation in the general-purpose PVA solutions dissolved in DMSO was more influenced for PVA/DMSO solutions with broad MWD at the similar M_w.

1. η' of PVA/DMSO solution with broad MWD was lower than that with narrow MWD at the similar M_w until the T2 of PVA/DMSO solution. After the time-sweep experiment was repeated, the η' of PVA/DMSO solution with narrow MWD was lower than that of PVA/DMSO solution with broad MWD at the similar M_w.
2. G' until 5 min of relaxation of PVA/DMSO solution with broad MWD was lower than that of PVA/ DMSO solution with narrow MWD at the similar M_w. After the time-sweep experiment was repeated, the G' of PVA/DMSO solution with narrow MWD was lower than that of PVA/DMSO solution with broad MWD at the similar M_w.
3. With respect to Winter's view on gelation, gelation was more affected by PVA solutions with broad MWD than by those with narrow MWD over the period of shearing.
4. λ was increased with time, and then leveled off after prolonged shearing. λ was more noticeably increased at the T1 for PVA solutions with broad MWD than those with narrow MWD.

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[1] I. Sakurada, "*Polyvinyl Alcohol Fibers*", M. Lewin, Ed., Marcel Dekker, New York 1985, p. 3.
[2] H. Kurokawa, M. Shibayama, T. Ishimaru, S. Nomura, *Polymer* **1992**, *33*, 2182.
[3] L. K. Koopal, *Colloid Polym. Sci.* **1981**, *259*, 490.
[4] D. Eagland, F. F. Vercauteren, T. G. Scholte, W. A. B. Donners, M. D. Lechner, R. Mattern, *Eur. Polym. J.* **1986**, *22*, 351.
[5] N. Hirai, *Nippon Kagaku Zasshi* **1954**, *75*, 697.
[6] B. C. Kim, W. S. Lyoo, W. S. Ha, *Polym. J.* **1998**, *30*(5), 424.
[7] E. J. Lee, N. H. Kim, K. S. Dan, B. C. Kim, *J. Polym. Sci. Part B: Polym. Phys.* **2004**, *42*, 1451.
[8] M. Shibayama, M. Adachi, F. Ikkai, H. Kurokawa, S. Sakurai, S. Nomura, *Macromolecules* **1993**, *26*, 623.
[9] F. Tanaka, S. F. Edwards, *Macromolecules* **1992**, *25*, 1516.
[10] G. Marucci, S. Bhargava, S. L. Cooper, *Macromolecules* **1993**, *26*, 6483.
[11] S. Q. Wang, *Macromolecules* **1992**, *25*, 7003.
[12] K. H. Ahn, K. Osaki, *J. Non-Newtonian Fluid Mech.* **1995**, *56*, 267.
[13] A. K. Lele, R. A. Mashelkar, *J. Non-Newtonian Fluid Mech.* **1998**, *75*, 99.
[14] S. I. Song, B. C. Kim, *Polymer* **2004**, *45*, 2381.
[15] S. Middleman, *J. Appl. Polym. Sci.* **1967**, Vol. II, 417.
[16] J. W. C. Adamse, H. Janeschitz-Kriegl, J. L. den Otter, J. L. S. Wales, *J. Polym. Sci. A-2* **1968**, *6*, 871.
[17] R. L. Combs, D. F. Slonaker, H. W. Coover, *J. Appl. Polym. Sci.* **1969**, *13*, 519.
[18] C. D. Han, T. C. Yu, K. U. Kim, *J. Appl. Polym. Sci.* **1971**, *15*, 1149.
[19] J. E. Guillet, R. L. Combs, D. F. Slonaker, D. A. Weems, H. W. Coover, *J. Appl. Polym. Sci.* **1965**, *9*, 757, ibid. **1965**, *9*, 767.
[20] H. H. WinterF. Chambon, *J. Rheol.* **1986**, *30*, 367.
[21] K. F. Wissburn, A. C. Griffin, *J. Polym. Sci. Polym. Phys. Ed.* **1982**, *20*, 1835.
[22] K. F. Wissbrun, A. C. Griffin, *J. Polym. Sci. Polym. Phys. Ed.* **1982**, *20*, 1985.

