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Characteristic rheological features of PVA solutions in water-containing solvents with different hydration states

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Abstract

Two organic solvent systems containing equimolar ratio of water but different association strenght, 8/2 by wt mixture of dimethyl sulfoxide (DMSO) and water and 86.7/13.3 by wt mixture of *N*-methyl morpholine *N*-oxide and water (NMMO monohydrate), were chosen and the rheological properties of polyvinyl alcohol (PVA) solutions in the solvents were investigated and compared. The associated state of water in the solvent systems had a significant effect on the rheological properties of the solutions. In dilute concentration regime, NMMO monohydrate gave higher intrinsic viscosity than DMSO/water although two solvents gave similar values of the Mark–Houwink exponent. More noticeable difference was observed on the viscosity curve in high concentration regime. DMSO/water exhibited near a Bingham behavior and gave much lower power-law index than NMMO monohydrate. On the logarithmic plot of storage modulus (G') against loss modulus (G''), both solutions exhibited slight decrease in slope with increasing concentration. Of two solvent systems DMSO/water gave lower values of slope than NMMO monohydrate. In addition, NMMO monohydrate gave tan δ greater than one at low frequency whereas DMSO/water gave tan δ much less than one over the entire frequency range examined. Further, the frequency to cause gelation was decreased with increasing concentration in the case of NMMO monohydrate. This indicates that PVA/DMSO/water system is more heterogeneous because weakly bonded water molecules produce hydrogel structure.

Keywords: PVA solution; Rheology; Shear-induced gelation

1. Introduction

Polymer systems are made up of chemical bonds along the polymer chains and physical bonds across the polymer chains. The former includes covalent bonds and the latter results from hydrogen bonding, dipolar bonding, or van der Waals forces. The type of physical bonding has huge effects on the physical properties of polymers. Particularly with the systems in which hydrogen bonding has a dominant effect, the physical properties are strongly dependent not only on the molecular weight and concentration of polymer but also the kind of solvent systems.

Polyvinyl alcohol (PVA) is a semicrystalline polymer whose hydroxyl groups produce inter- and intra-molecular hydrogen bonding [1,2]. The extent of hydrogen bonding is greatly affected by stereoregularity of hydroxyl groups [3]. Specially designed syndiotactic-rich PVA exhibits rheological responses unbelievably different from general-purpose PVA due to more effective hydrogen bonding between adjacent chains as we already reported [3–5]. Thus, hydrogen bonding has a profound effect on the rheological and mechanical properties of the polymer, which is largely determined by the density and spatial arrangement of hydroxyl groups. Moreover, inter- or intra-molecular hydrogen bonding by hydroxyl groups may bring about complicated phenomena such as phase separation and gelation [4–7], which means the solution properties exhibit time-dependence. Thus, processing conditions (solvent, concentration, dissolving temperature, salt, etc.) should be carefully adjusted in spinning or film casting to obtain desired properties [8–11].

In PVA solutions in water-containing solvents such as DMSO/water mixture and NMMO hydrate, very complicated and strong physical interactions between solvent and polymer would be present. Consequently, the rheological properties of the PVA solutions are affected by effectiveness of the physical bonding. Particularly with water-containing

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solvent systems the physical state of water is very important to rheological responses because free water forms hydrogel structure. DMSO/water systems are expected to release water because of very weak hydration. On the other hand, NMMO hydrates would not release free water except at very elevated temperature because NMMO and water are firmly hydrated [12,13]. We investigated and compared the characteristic rheological responses of PVA solutions in these two solvent systems.

2. Experimental

2.1. Materials

The degree of saponification of PVA (Aldrich Co.) was 99% and the weight-average degree of polymerization (DP) was 5000. PVA resins with DP 1700 and 3300 were also used to calculate the Mark–Houwink exponent (α). The resins were vacuum dried at 80 °C for 24 h before use. EP grade DMSO (Aldrich Co.) was used without further purification. NMMO monohydrate was prepared by condensing a commercially available 49.6/50.4 (by wt) NMMO/H_2O mixture (BASF Co). To make the mole ratio of water to the solvent identical, 80/20 by wt DMSO/H_2O and 86.7/13.3 by wt NMMO/H_2O systems were prepared.

2.2. Preparation of solutions

Specific viscosity (η_{sp}) and intrinsic viscosity ($[\eta]$) were measured at 90 °C by Ubbelohde viscometer (Schoett Co.) over the concentration range 0.1–0.9 g/dL for DMSO/water and 0.1 – 0.5 g/dL for NMMO monohydrate.

$$\eta_{sp} = \eta/\eta_0 - 1 \tag{1}$$

in which, η and η_0 are the viscosity of polymer solution and pure solvent, respectively.

2.3. Rheological measurements

The rheological properties of concentrated solutions were measured by Advanced Rheometric Expansion System (ARES, Rheometric Scientific Co.) at 90 °C over the concentration range 8–12 wt%. Parallel plate geometry was adopted whose diameter and gap were 50 and 1 mm, respectively. Frequency ranged from 0.1 to 500 rad/s. PVA was dissolved in the solvents by stirring at 90 °C for 2 h. Since the dissolving conditions may affect the rheological responses, the dissolution conditions such as temperature and shear rate was strictly controlled to be constant for each sample to obtain good reproducibility of results. 0.5 wt% *n*-propyl gallate was added to avoid thermal degradation of NMMO monohydrate at elevated temperature.

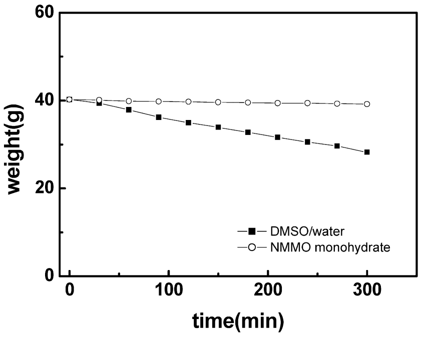


Fig. 1. Variation of weight with time for DMSO/water and NMMO monohydrate at 90 °C.

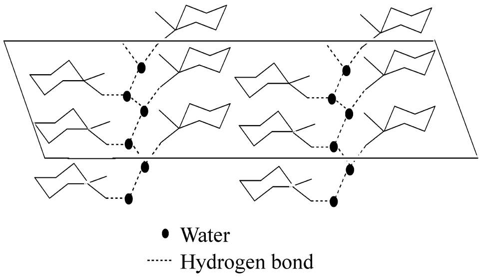
3. Results and discussion

3.1. Hydration state of solvents

To estimate the state of water in DMSO and NMMO during rheological measurement, weight loss of DMSO/-water and NMMO monohydrate with time at 90 °C was measured and presented in Fig. 1. NMMO monohydrate does not give any weight loss whereas the weight of DMSO/water is continuously decreased with time. This diagram offers an indirect estimation of the association state of water to solvent molecules. The hydration state of DMSO/water system is so weak that it readily deliberates water molecules. On the other hand, little water release from NMMO monohydrate is indicative of strong hydration, which agrees with the suggestion of Maia et al. [14,15]; the water molecules are arranged in a polymer-like self-structure through an extensive hydrogen bonding in NMMO monohydrate as shown in Scheme 1. Consequently, there is little weight loss at 90 °C even after 6 h. This implies that free water would be generated from DMSO but little water would escape from NMMO during rheological measurement.

3.2. Dilute solution

Fig. 2 presents the logarithmic plot of $[\eta]$ against molecular weight (Mw) at 90 °C for PVA solutions in DMSO/water and NMMO monohydrate, respectively. NMMO monohydrate gives greater values of $[\eta]$ than



Scheme 1. Physical structure of NMMO monohydrate suggested by Maia et al. [14].

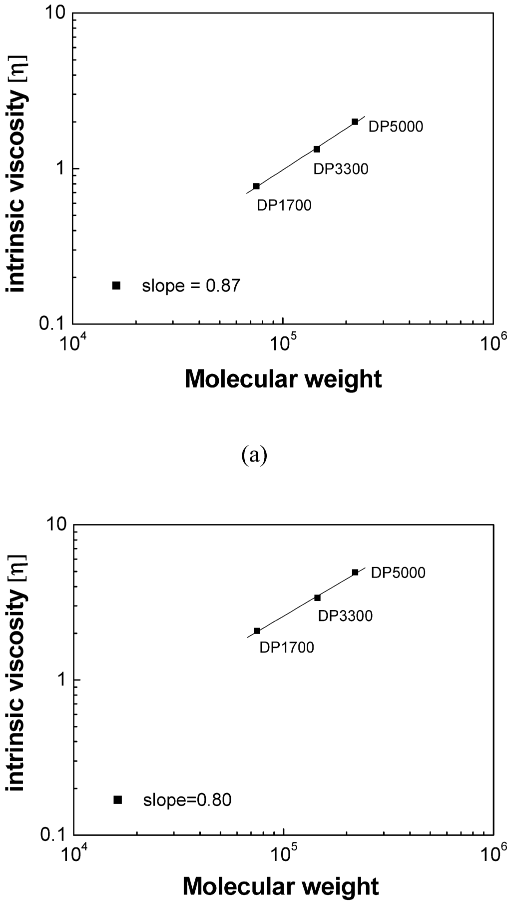
DMSO/water over the range of molecular weight examined, indicating that NMMO monohydrate leads to greater coiled chain expansion. This means that NMMO monohydrate plays as a better solvent for PVA than DMSO/water.

The Mark–Houwink exponent (α), determined by Eq. (2), may offer information of conformation of polymer molecules in the solution with molecular weight.

$$[\eta] = KM^{\alpha} \tag{2}$$

in which, K is constant and M is molecular weight of monodisperse polymer. Although this equation was firstly devised for monodisperse polymers it is applicable to polymers with narrow molecular weight distribution as well. The determined values of α are 0.87 in DMSO/water and 0.80 in NMMO monohydrate [16]. Only a little difference in the values of α for two solvent systems indicates that PVA molecules undergo almost the same conformational change in the solutions with molecular weight.

According to Frish and Simha [17] polymer solutions exhibit three distinct regions on the logarithmic plot of η_{sp} vs. $[\eta]C$, where C is concentration; (1) the dilute regime where $[\eta]C < 1$, (2) the semi-dilute unentangled regime where $1 < [\eta]C < 4$, and (3) the semi-dilute entangled regime where $[\eta]C > 4$. Fig. 3 shows the log–log plot of η_{sp} vs. $[\eta]C$ for the PVA solutions. NMMO monohydrate gives smaller values of η_{sp} than DMSO/water. Further, both solutions exhibit an inflection point in the semi-dilute unentangled regime, where only the polymer–polymer intermolecular interaction is allowed to influence the polymer motion [18]. NMMO monohydrate gives rise to the inflection point at lower concentration than DMSO/water. These facts are well consistent with the result in Fig. 2.



(a)

(b)

Fig. 2. Plot of intrinsic viscosity against molecular weight at 90 °C: (a) PVA/DMSO/water and (b) PVA/NMMO monohydrate.

3.3. Rheological properties of PVA solution systems

Fig. 4 shows dynamic viscosity (η') curve of PVA solutions in DMSO/water and NMMO monohydrate at 90 °C at several different concentrations, respectively. Both systems exhibit non-Newtonian flow behavior. It should also be mentioned that PVA/DMSO/water system gives lower values of power-law index but greater low-frequency viscosity than PVA/NMMO monohydrate system. As mentioned in Fig. 1, DMSO/water releases free water and some micro-scale phase separation may take place through the formation of hydrogels in the system. Scheme 2 schematically represents the formation mechanism of hydrogels in the PVA/DMSO/water systems. The great dependence of viscosity in the case of PVA/DMSO/water system results from the heterogeneity associated with localized gel formation. That is, the hydrogels formed at rest are so soft that to be easily destructed and deformed even by low shear. Hence, the viscosity decreases from low frequency. The less dependence of viscosity on concentration for PVA/DMSO/water system can also be accounted for on the same reason.

Except for the low frequency range in which aforementioned hydrogel structures still remain, NMMO monohydrate exhibits greater viscosity and more noticeable increase of the extent of viscosity increase with increasing concentration. This agrees with the prediction for the dilute solutions in Fig. 2 that NMMO monohydrate has greater solvating power to PVA molecules than DMSO/water.

According to molecular theories, the perfectly homogeneous and isotropic melts and solutions of polymers give

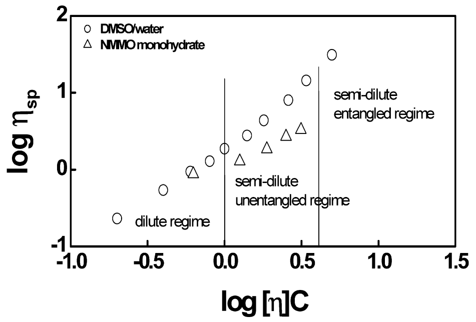
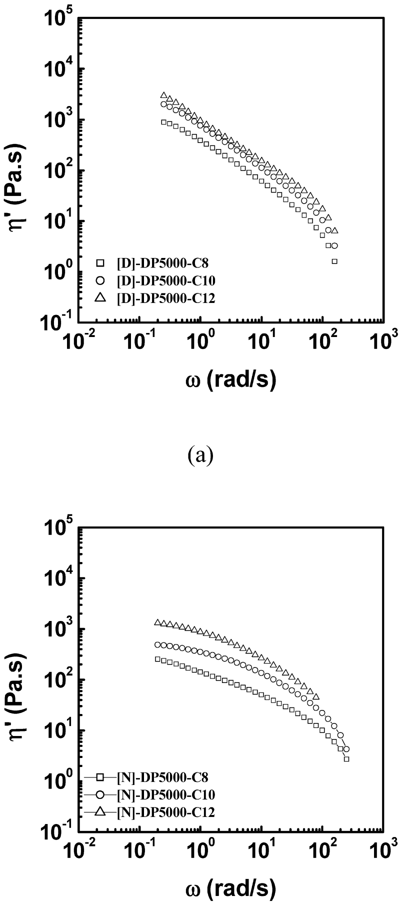


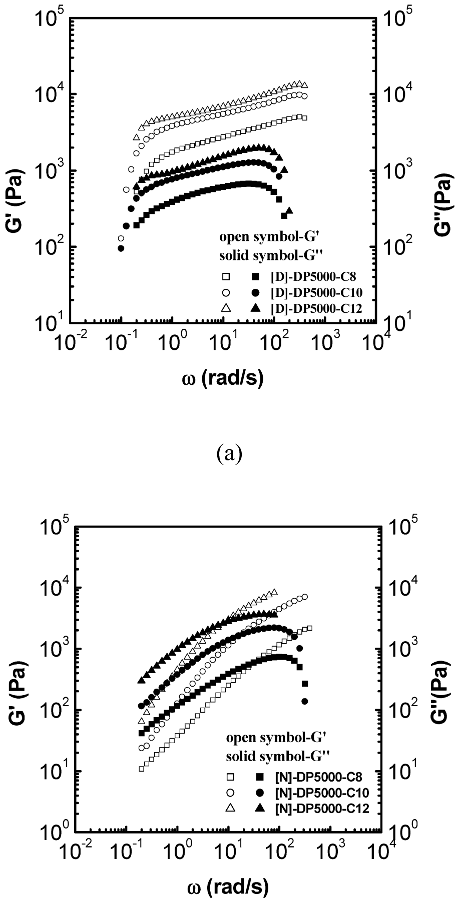
Fig. 3. Plot of log η_{sp} against log $[\eta]C$ for PVA solutions at 90 °C.



(a)

(b)

Fig. 4. Viscosity curve of PVA solution systems at 90 °C at several concentrations: (a) in DMSO/water and (b) in NMMO monohydrate.

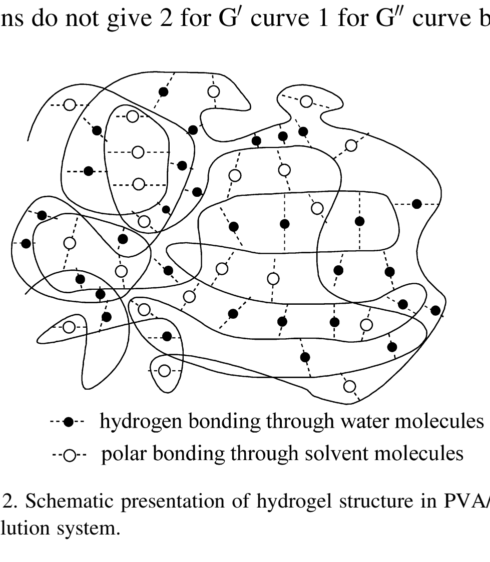


(a)

(b)

Fig. 5. Storage modulus (G') and loss modulus (G'') vs. frequency (ω) for PVA solution systems at 90 °C at several concentrations: in DMSO/water and (b) in NMMO monohydrate.

slope of 2 on the logarithmic plot of storage modulus (G') against frequency and slope of 1 on logarithmic plot of loss modulus (G'') against frequency in the terminal zone [19]. The logarithmic plot for the PVA solution systems is shown in Fig. 5. It is worth mentioning in the figure that the solutions do not give 2 for G' curve 1 for G'' curve but give values less than predicted. PVA/NMMO monohydrate system gives a crossover point of G' and G'' curves but PVA/DMSO/water system does not give it. In addition, the latter gives much greater G' than the former. Hydrogelation is responsible for this. That is, the ever-present hydrogels may play the role of crosslinking domains in the solution systems. On the same background, the logarithmic plot of G' against G'', for homogeneous polymer melts and polymer solutions produces a single master curve whose slope in the terminal zone is 2. However, PVA solution systems do not give a single master curve at 90 °C and the slope becomes less than 2 in the terminal zone as shown in Fig. 6, which also ascertains heterogeneity of the systems.



Scheme 2. Schematic presentation of hydrogel structure in PVA/DMSO/-water solution system.

Plot of loss tangent (tan δ) against frequency may give an important clue to elucidating the phase change with shear because tan δ is a quantitative measure of solid-like elastic body or liquid-like viscous fluid of a system. In principle, fluid character is dominant when the loss tangent value is greater than 1 and solid character is dominant when the value is smaller than 1. Hence, a gelation point can be evaluated from the curve, at which G' is equivalent to G''

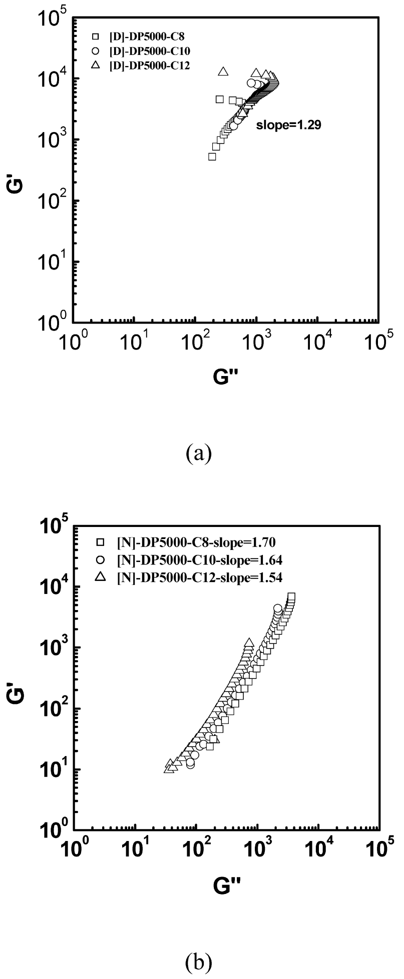


Fig. 6. Modified Cole–Cole plot for PVA solution systems at 90 °C at several concentrations: (a) in DMSO/water and (b) in NMMO monohydrate.

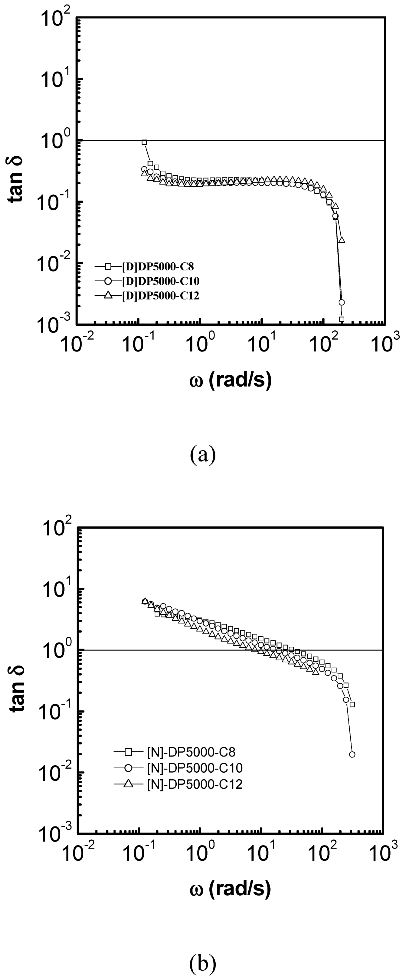
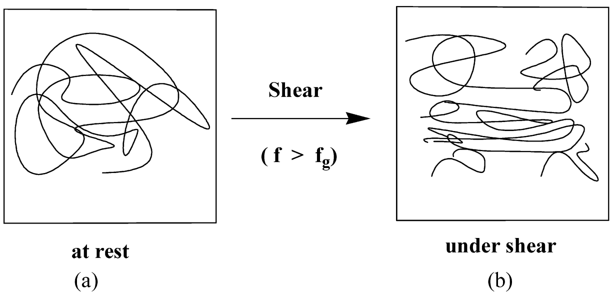


Fig. 7. Variation of $\tan\delta$ with frequency (ω) for PVA solution systems at 90 °C at several concentrations: (a) in DMSO/water and (b) in NMMO monohydrate.

[20]. Fig. 7 plots $\tan\delta$ of PVA solution systems against frequency at 90 °C. PVA/DMSO/water systems give $\tan\delta$ much less than 1 over the entire frequency range examined. Further, the value of $\tan\delta$ remains almost constant over 3 decades of frequency. This also verifies the presence of hydrogel in PVA/DMSO/water systems.

On the other hand, PVA/NMMO monohydrate systems shown in Fig. 7(b) shows sol-to-gel phase transition with increasing shear rate. Scheme 3 depicts the transformation of polymer molecules by shear. At rest (frequency = 0 rad/s), PVA chains are expected to be randomly coiled by Brownian motion as shown in Scheme 3(a). However, the motion is restricted by physical bonding through polar interactions and consequently PVA solution systems may have some 3-dimensional order at the molecular level. Under shear, however, some local orientation of the polymer molecules is attained as shown in Scheme 3(b), whose degree is dependent of the rate of shear. In the oriented region lateral approach of polymer molecules makes physical bonding through hydroxyl groups stronger. Consequently some oriented gel structure would be developed above a critical shear rate. Agreeing with this conjecture the PVA solution systems reveal onset frequency giving rise to gelation (f_g) which is generally decreased with increasing concentration because higher concentration offers greater intermolecular interactions. The onset frequency is shifted from 9 to 40 rad/s with decreasing concentration from 12 to 8 wt%.

The presence of pseudostructure by physical aggregation affects the relaxation behavior as well. For the polymeric



Scheme 3. Schematic presentation of PVA molecules in the solutions: (a) at rest and (b) under shear.

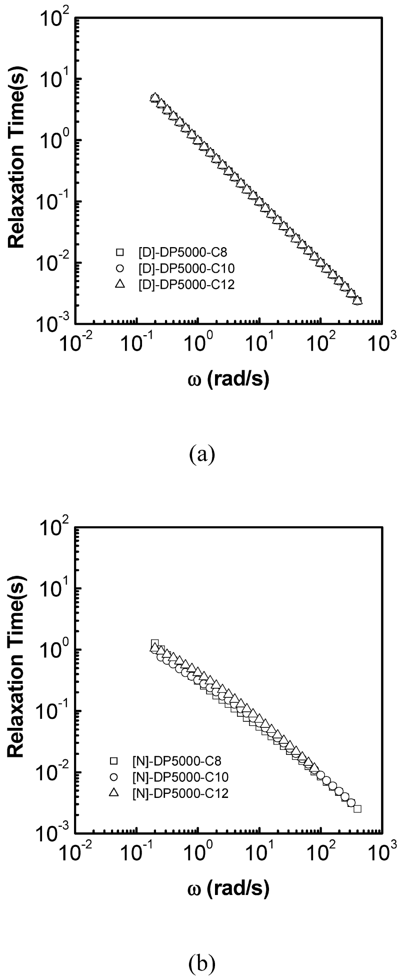


Fig. 8. Variation of relaxation time (λ) with frequency (ω) for PVA solution systems at 90 °C at several concentrations: (a) in DMSO/water and (b) in NMMO monohydrate.

systems in which some pseudostructures are involved, relaxation time (λ) under dynamic shear can be calculated by Eq. (3) [21].

$$J' = G'/([\eta^*]\omega)^2 = \lambda/[\eta^*] \tag{3}$$

in which, J' and η^* are compliance and complex viscosity, respectively. If there are some molecular order or physical structure, much longer relaxation time is expected [22]. Relaxation time of PVA solutions at 90 °C at several concentrations is plotted against frequency in Fig. 8. In case of PVA/NMMO monohydrate systems, relaxation time is increased with increasing concentration because of the increased number of entangling points. On the other hand, PVA/DMSO/water systems exhibit concentration independent relaxation time because the effects of hydrogels rule over the individual molecular motions. On similar speculation of the presence of hydrogels, PVA/DMSO/water systems give greater relaxation time than PVA/NMMO monohydrate systems.

4. Conclusion

The absence or presence of free water in the mixed solvent systems had a significant effect on the rheological behavior of PVA solutions. Thus, the associated state of water in the solvent systems had a significant effect on the physical properties of PVA solutions such as rheological responses and molecular relaxation behavior. These results may be effectively applied to the fabrication processes of PVA solutions such as filming and fiber spinning, in which precise control of rheological properties is important.

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