

Rheological Behaviors of PVA/H₂O Solutions of High-Polymer Concentration

Han-Wen Gao, Rong-Jie Yang, Ji-Yu He, Lei Yang

School of Materials Science, Beijing Institute of Technology, Beijing 100081, People's Republic of China

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ABSTRACT: The dynamic viscoelastic properties of poly(vinyl alcohol) (PVA)/H₂O solutions with concentrations of 10 to 25 wt % have been characterized by controlled-stress rheometry at 30°C. Parameters relating to the linear and nonlinear viscoelasticities include complex viscosity (η^*), storage modulus (G'), loss tangent ($\tan \delta$), relaxation time (λ), thixotropy, and creep. Change curves of η^* , G' , $\tan \delta$, and λ with frequency (ω) have been obtained for the PVA/H₂O solutions. Creep and recovery testing yielded compliance (J') curves with loading and unloading. Shear stress versus rate profiles of the PVA solutions have been obtained through thixotropic measurements. The PVA concentration has been found to have a profound influence on the rheological properties of the aqueous solutions. Four aqueous solutions of 10, 15, 20, and 25 wt % PVA at 30°C exhibited shear-thinning and showed different transition behaviors of η^* and G' with frequency, and different degrees of creep under constant stress to recovery with

time. The 10 wt % PVA solution was viscous and displayed the lowest η^* and G' ; the 25 wt % PVA solution was viscoelastic and displayed the highest η^* and G' ; the 15 and 20 wt % PVA solutions showed η^* and G' values and creep to recovery behaviors intermediate between those of the 10 wt % and 25 wt % PVA solutions. The different rheological properties of these PVA/H₂O solutions are considered to correlate with interchain hydrogen bonds and shear-induced orientation in the solutions. Shearing is able to break the intrachain and interchain hydrogen bonds, and, at the same time, the orientation creates new interchain hydrogen bonding. The reorganization of hydrogen-bonding mode contributes to the transitions of the macroscopic viscoelasticity with frequency. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1459–1466, 2010

Key words: PVA solutions; rheology; creep; hydrogen bonding

INTRODUCTION

Poly(vinyl alcohol) (PVA) was one of the first synthetic polymers to be produced on a large scale commercially and has been developed and utilized in various applications, including as a hydrogel for biomaterials, fibers for clothes and industries, films, membranes, materials for drug delivery systems, and cancer cell-killing embolic materials.^{1–4} Moreover, PVA hydrogel has received much attention for its good biocompatibility and usability in various biomedical applications.^{5–8}

Because of the large number of hydroxyl groups in PVA, hydrogen bonding has a pronounced effect on the bulk properties of PVA materials. Because of the presence of hydrogen bonding, PVA has a high-melting temperature, and, depending on the pattern of hydrogen bonding, it adopts different crystal structures.⁹ Although there have been many studies of hydrogen bonding in the crystal structure of PVA,¹⁰ there have been only a few studies on the

hydrogen bonding of PVA in aqueous solution. In particular, concentration is a fundamental factor affecting the physical properties of PVA solutions and products.

To adopt PVA/water solutions for industrial applications, it is important to characterize their rheological properties so as to be able to manufacture various products, such as hydrogels, fibers, and films, with excellent properties.¹¹ Rheology has also opened a way to the direct measurement of the mechanical properties of individual polymers with sensitivity and accuracy. PVA solutions show various rheological behaviors with respect to concentration, molecular weight, temperature, degree of saponification, and so on.

Lyoo et al.¹² studied the rheological properties of PVA solutions of 7.5, 10.0, and 12.5 g/dL with degrees of polymerization of 4000 and 1700 in dimethyl sulfoxide (DMSO)/H₂O mixtures. They found that PVA solutions with high molecular weights and high polymer concentrations develop molecular orientation more easily by shear. Lee et al.¹³ found that PVA solutions in DMSO were rheologically heterogeneous, although they were optically transparent. A 14 wt % PVA solution was found to exhibit very unusual rheological behavior,

Correspondence to: R.-J. Yang (yrj@bit.edu.cn).

with definite double sol–gel phase transitions with the shear rate. Choi et al.¹⁴ studied the rheological behavior of dilute and semidilute solutions of PVA of high molecular weight. The gelation process of this PVA solution could be divided into two types according to the concentration. The first type was the gelation that took place directly from the sol state to gel states with a clear gel point, which was seen in the concentration regime higher than the critical concentration. The second type of gelation occurred gradually, accompanying the evolution of gel-like properties in the sol state without a definite gel point, which was seen in the lower concentration regime. Lee et al.¹⁵ investigated the time-dependent rheological responses of PVA solutions in DMSO. They found that shear rate had a paramount effect on the gelation behavior. If a strong gel was first formed by a strong shear, then no additional gelation or deformation of the gel occurred, even upon prolonged shearing. However, research about the rheological properties of aqueous solutions of high PVA concentrations up to 25 wt % is still lacking, in spite of the practical importance. Moreover, much less is known about the creep-recovery and thixotropic behavior of PVA solutions compared with their linear viscoelasticity. In this study, we have investigated the dynamic rheological properties of PVA/H₂O solutions of concentrations from 10 to 25 wt %, including both their linear and nonlinear viscoelasticities.

EXPERIMENTAL

Materials

PVA powder (Beijing East Oil Chemical Company, Beijing, China) with an average degree of polymerization of 1700 and a degree of saponification of 99% was used. To obtain reproducible results, the powder was dried in a vacuum oven at 70°C for 24 h before use. The water used for all procedures was deionized.

Preparation of solutions

PVA was dissolved in water at 110°C for 3 h with stirring and the solution was kept for 2 h to ensure homogenization. As the dissolution conditions may affect the rheological properties, the temperature and shear rate were strictly controlled to be constant for each sample to obtain good reproducibility of results. The concentrations of the PVA solutions were set at 10 to 25 wt %. The samples were coded as PVA-X, where X is the concentration of PVA. For example, PVA-15 represents a solution of 15 wt % PVA.

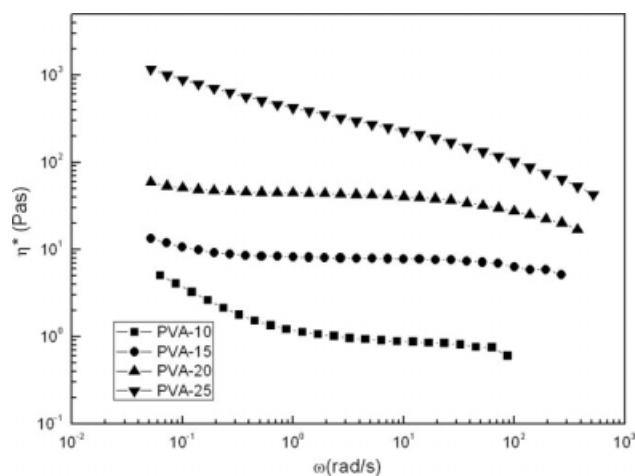


Figure 1 η^* curves of PVA/H₂O solutions at 30°C.

Rheological measurements

The rheological properties of the PVA solutions were measured by means of an RS300 controlled-stress rheometer (Thermo Haake) at 30°C. Parallel plate geometry was adopted, with a diameter of 35 mm and a gap of 1 mm. The rheometer was equipped with a temperature control unit (TC 501) that was calibrated to give the required temperature in the sample chamber. Before testing, the specimens were held at this temperature for 15 min to eliminate their thermal and shear histories. Frequency sweep tests were carried out in an oscillatory mode over the range from 0.05 to 500 rad/s. The strain level was determined by a strain sweep test so that all measurements were carried out within the linear viscoelastic regime.

The creep and recovery behaviors of the solutions were investigated. A constant stress of 5 Pa was applied, maintained for 50 s, and then suddenly removed. A hysteresis loop test was used to study the thixotropy of the samples. The shear rate was uniformly increased from 0.5 to 100 s⁻¹ over 1 min and was then decreased back to 0.5 s⁻¹ over 1 min. The thixotropic loop area was calculated with the aid of the software supplied with the RS300. Each measurement was repeated at least two or three times.

RESULTS AND DISCUSSION

In aqueous PVA solutions, there exist strong hydrogen-bonding interactions. These include intrachain and interchain as well as PVA to H₂O hydrogen bonds. Thus, the rheological properties of the solutions are mainly determined by the strength and number of hydrogen bonds.¹⁶

Figure 1 shows the complex viscosities (η^*) of the PVA/water solutions with different concentrations.

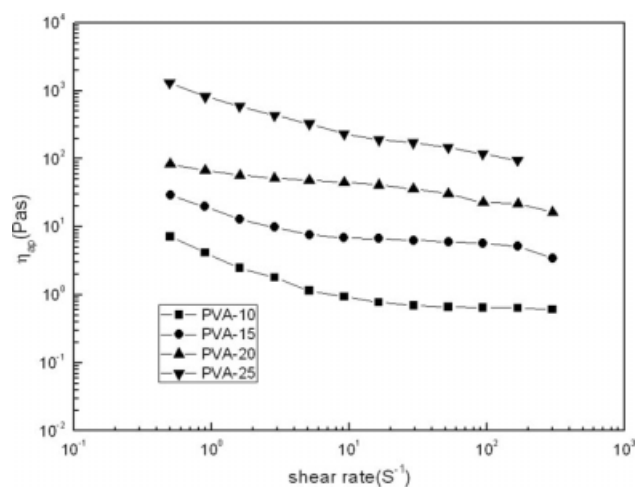


Figure 2 η_{ap} curves of PVA/H₂O solutions at 30°C.

It can be noted that all of the specimens showed non-Newtonian flow behavior, that is, a decrease in η^* with increasing ω , but three distinct cases may be distinguished. First, the PVA-10 solution showed distinct shear thinning at low frequencies, and then showed a transition to little dependence on the frequency. Second, the PVA-15 and PVA-20 solutions were insensitive to shear, and these showed an inconspicuous transition of η^* with ω . Third, PVA-25 showed shear thinning over the whole range from low to high shear. The increase in shear-thinning behavior of PVA-25 also indicates the presence of stronger polymer chain associations at rest.

Apparent shear viscosities (η_{ap}) of the PVA/water solutions were also measured, and the viscosity curves are shown in Figure 2. It can be seen that results similar to those in Figure 1 were obtained owing to the non-Newtonian character of the solutions. The non-Newtonian behavior might be

explained by the fact that orientation of molecular segments by the flow field occurs together with phase separation. However, the shear viscosity for the PVA-15 and PVA-20 solutions showed stronger thinning than the complex viscosity, such that the transitions of η_{ap} with shear rate became conspicuous for these solutions. Moreover, it seemed that η^* , rather than η_{ap} , could better uncover the differences in the rheological properties of the respective solutions. From this viscosity behavior, we could conclude that the concentration has a significant influence on the viscoelastic properties of PVA/water solutions.

Figure 3 shows the changes in the storage moduli (G') and the loss moduli (G'') of the PVA/H₂O solutions with ω . PVA solutions of higher concentration showed greater G' and G'' values. This may be due to the fact that the internal structures in a PVA/water solution of higher concentration are much tighter. All of the solutions showed increasing values of G' and G'' with ω . The absence of G' values for PVA-10 at high frequencies in Figure 3(a) is due to the low viscosity of the solutions, since the slippage of the solution from the bottom plate limits the effective frequency range for obtaining G' . From Figure 3(a), it can be seen that the 15 and 20 wt % PVA solutions displayed evident transitions of G' with ω , which are similar to what was observed for η^* and η_{ap} in Figures 1 and 2; for the 10 wt % PVA solution, the logarithmic G' versus ω plot was linear until 10 rad/s, whereas $\log G'$ of the 25% PVA solution increased almost linearly with $\log \omega$ from 10^{-1} to 10^3 rad/s. In addition, it should be noted that at the same ω , the value of G' increased with the concentration; moreover, an abrupt increase was observed on going from 20 to 25 wt % PVA. Figure 3(b) shows similar G'' versus ω plots for all of

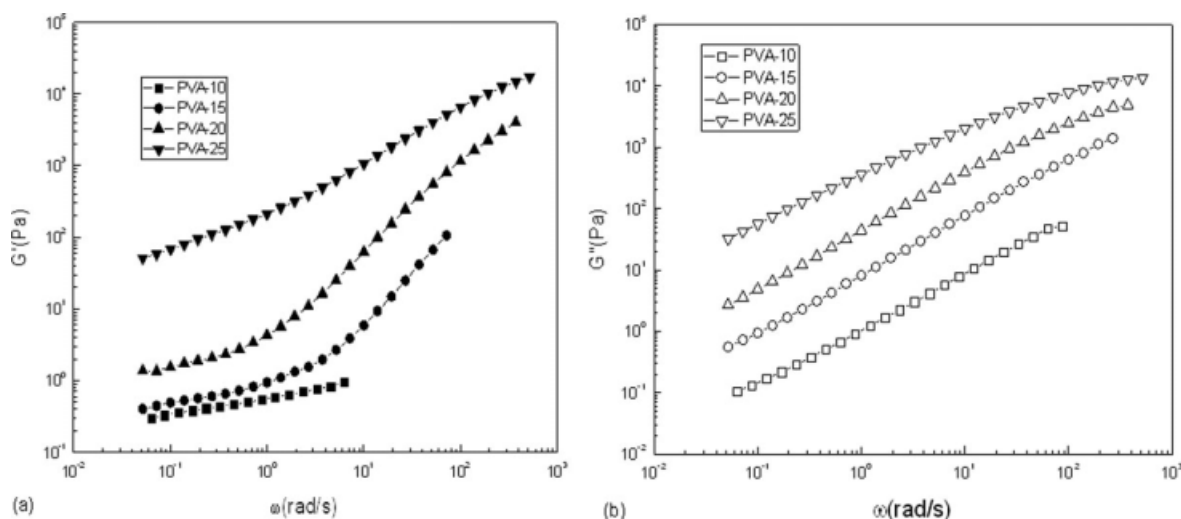


Figure 3 Storage (a) and loss (b) modulus of PVA solutions at 30°C.

the solutions. The value of G'' rises proportionally with concentration at the same ω .

According to Figures 1–3, the four PVA/H₂O solutions showed three kinds of rheological characteristics, which we assume to correlate with the properties of the intrachain and interchain hydrogen bonding of PVA. For the specimen of PVA-10, it is likely that there was only a limited number of interchain hydrogen bonds, and so it showed thinning due to the bonds breaking under low shear. That is, the hydrogels formed at rest are so soft that they can be easily destroyed and deformed, even by a low shear. Hence, the viscosity begins to decrease from low frequency. Under high shear, the induced orientation presumably created new interchain hydrogen bonds, which made the complex viscosity apparently constant with frequency, and therefore, a transition of the viscosity with frequency was observed.

In preparing the concentrated PVA/H₂O solution, it was noted that dissolution of a PVA content higher than 25 wt % was difficult to achieve because of macroscopic physical gelling at room temperature. Therefore, it was considered that in the PVA-25 solution, the neighboring PVA chains formed local chain associations through a number of interchain hydrogen bonds, and that these association regimes served as physical crosslinking points contributing to the gelling of the system. Such a solution was microscopically heterogeneous. The shear-thinning behavior of the PVA-25 solution might be attributed to breakage of the local association regimes by shearing; moreover, the shear-induced orientation could not compensate for the decrease in the number of interchain hydrogen bonds.

The 15 and 20 wt % PVA solutions can be considered as showing intermediate behavior between the PVA-10 and PVA-25 solutions. With strengthening shear, the decrease in their interchain hydrogen bonds could be nearly equal to the increase in the orientation-induced H...O bonds. This would account for the fact that they showed weak shear-thinning behavior over the wide range of frequencies applied. The change in the mode of the hydrogen-bonding interactions was not apparent from the viscosity curves in Figures 1 and 2, but in Figure 3(a), the transition of the storage modulus (G') with frequency clearly indicated that the shear-induced intermolecular hydrogen bonding became an important factor. In other words, as regards the dynamic viscoelasticity of the PVA solutions, the viscosity largely correlates with the number of hydrogen bonds, whereas the storage modulus further depends on the mode of the hydrogen-bonding interactions.

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

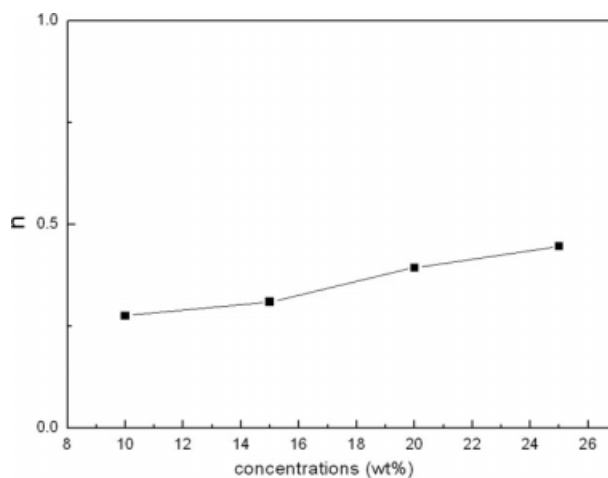


Figure 4 Viscoelastic exponent (n) of PVA solutions at 30°C.

polymers give curves with slopes of 2 and 1 in the terminal zone in logarithmic plots of G' and G'' , respectively, against frequency.¹⁶ As a rule, the deviation of the slope from the norm established for a perfectly homogeneous solution is an indication of the heterogeneity of the solution system. The slope of a logarithmic plot of G' against ω has been termed the viscoelastic exponent (n).^{17–19} The value of n has been reported to decrease with increasing entanglement density in entangled polymer solution systems; however, in nonentangled systems, such as incipient gelatin, the concentration rarely influences n .^{20,21}

As shown in Figure 4, the n values of the PVA solutions at 30°C varied with concentration in the range 0.28 to 0.45 and were not in accordance with the theoretically predicted values; moreover, the concentration had only a minor impact on the value of n . The low values of n clearly indicated that the PVA chains were significantly entangled. However, the low dependence of n on the concentration suggested that there were also microunentangled structures, like the liquid–liquid phase-separation structure, that is, a physically crosslinked hydrogel formed by interchain hydrogen bonds.

Plots of loss tangent ($\tan \delta$) against frequency may give important information for elucidating the phase change with shear because $\tan \delta$ is a quantitative measure of the solid-like elastic body or liquid-like viscous fluid of a system. In principle, fluid character is dominant when $\tan \delta > 1$ and solid character is dominant when $\tan \delta < 1$. Hence, a gelling point at which G' is equivalent to G'' can be evaluated from the curve of $\tan \delta$ with respect to ω .²² Figure 5 shows plots of $\tan \delta$ of the PVA solutions versus frequency.

The PVA-10, -15, and -20 solutions showed $\tan \delta > 1$, that is, liquid-like viscous fluid characteristics over the entire frequency range examined. The

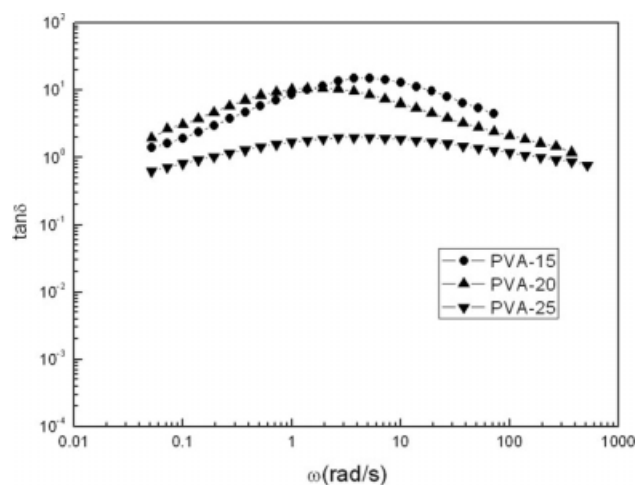


Figure 5 Tan δ with the frequency (ω) of PVA solutions at 30°C.

PVA-25 solution showed a smaller tan δ value than the others; when $\omega < 0.18$ rad/s, tan $\delta < 1$, which implies a solid-like property.

Figure 5 shows that there are peak values of tan δ versus ω for the PVA-15 and -20 solutions. The peaks correspond to the transitions of G' with ω in Figure 3. The peak of the PVA-20 solution is shifted to lower frequency compared with that of the PVA-15 solution. This means that in a concentrated solution, low shearing could be sufficient to cause the local orientation to favor an increase in the hydrogen bonding through approach of the PVA chains. As a result, the PVA solution of high concentration showed early shear-induced gelling.

In addition, for the PVA-25 solution, an inconspicuous peak was seen in the plot of tan δ versus ω , a kind of transition in the hydrogen-bonding mode. The results also implied that the local associations contributing to gelling of the solution at rest differed from the shear-induced orientation of the whole chain.

The presence of a pseudostructure due to physical aggregation in a polymer system affects the relaxation behavior. If there is some molecular order or physical structure, a much longer relaxation time is to be expected. For such polymeric systems, the relaxation time (λ) under dynamic shear can be calculated by eq. (1)²³ as follows:

$$J' = G'/([\eta^*]\omega)^2 = \lambda/[\eta^*] \quad (1)$$

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

Relaxation times of the PVA solutions at 30°C at several concentrations are plotted against frequency in Figure 6. The λ values for all of the PVA solutions decreased with increasing ω . At the low and high

ends of the frequency range, the λ of the PVA solutions showed only weak correlation with concentration.

It is worthy of consideration that transitions of the relaxation time with frequency are evident in Figure 6. These are similar to what was observed in Figures 1–5. In particular, for the PVA-20 solution at high frequency, λ tended toward that of the PVA-25 solution, and the PVA-15 solution also seemed to show such a tendency. These features can be easily understood because the shear-induced hydrogen-bonding structures are likely to be the same in solutions of distinct PVA concentrations under high frequency, and therefore, they have uniform relaxation times. The PVA solutions of high polymer concentration develop the reorganized hydrogel structure more rapidly upon shearing.

Creep and recovery testing is a good test method for viscoelasticity, since it allows one to differentiate well between the viscous and elastic responses of a test specimen. During the creep test of viscoelastic fluids, the stress applied will cause a transient response that includes the elastic and viscous contributions. An advantage of the following recovery phase after the release of the applied stress is that it separates the percentages of the total strain into the permanently maintained viscous part and the recovered elastic part.^{24,25}

In a creep test, a constant stress (τ) is applied and the time-related strain (γ) is measured. These are mathematically interrelated by the expression²⁶ as follows:

$$\gamma(t) = J(t) \cdot \tau \quad (2)$$

where $J(t)$ is the time-related compliance. It is a material constant similar to the viscosity in steady-state flow. The higher the compliance, the more

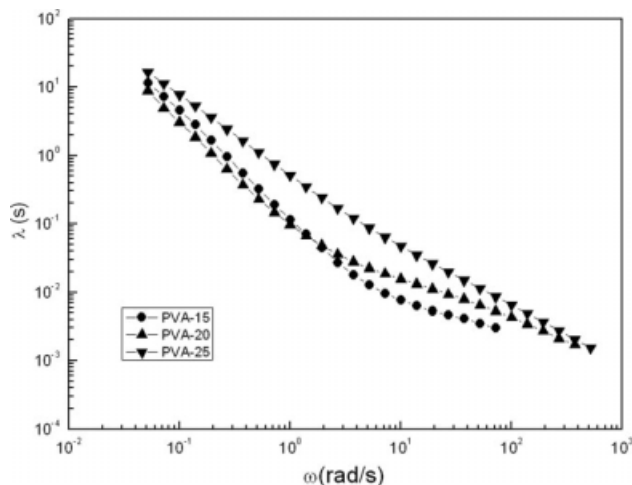


Figure 6 Variation of relaxation time with frequency for PVA solutions at 30°C.

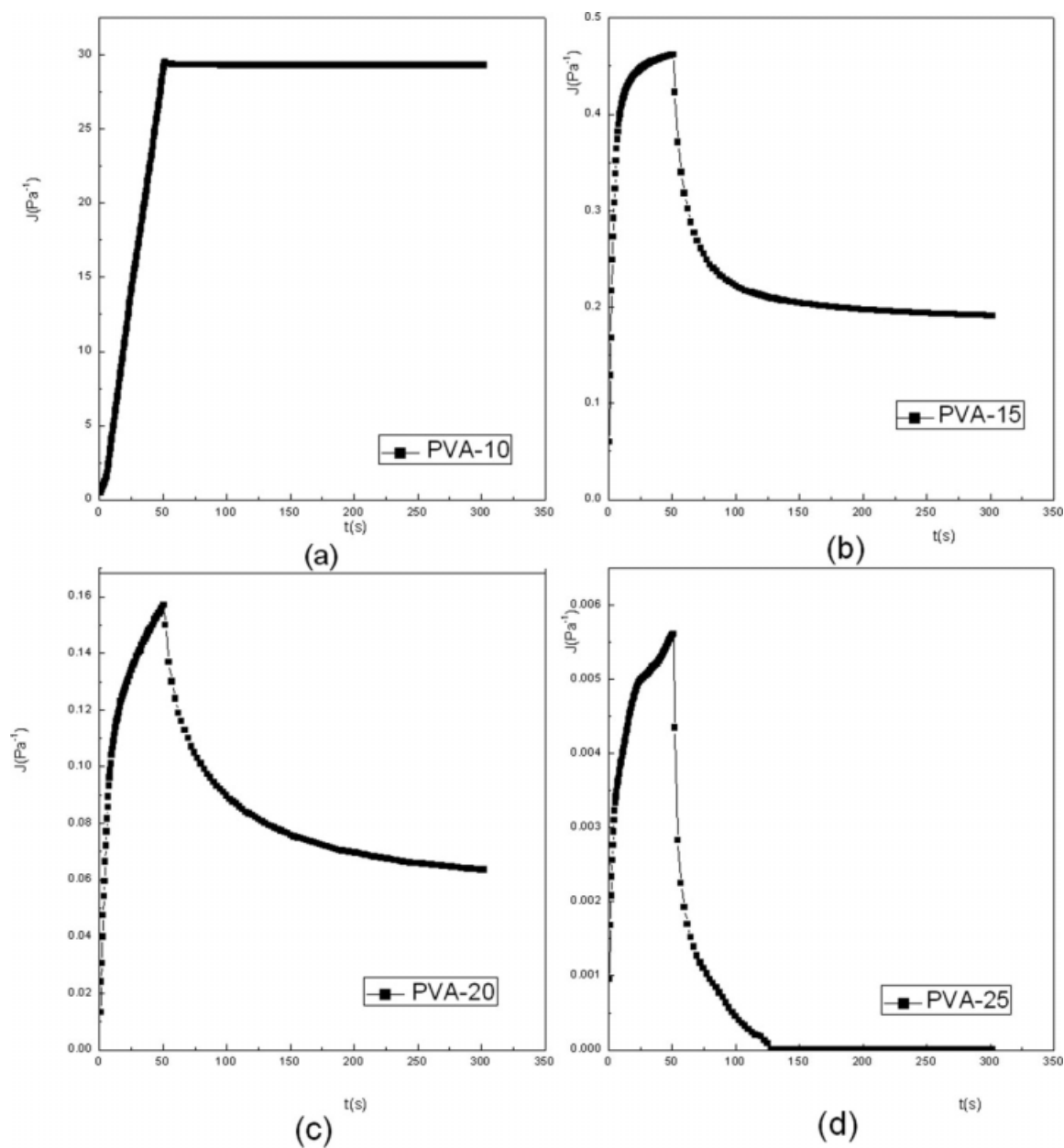


Figure 7 Creep and recovery curves of PVA solutions at 30°C.

easily the sample can be deformed by a given stress. Figure 7 shows creep and recovery curves for the PVA solutions. The values of the creep parameters for the PVA solutions are shown in Table I.

From Figure 7, it can be seen that the PVA-10 solution behaved as a viscous fluid and showed the highest compliance (29.52 Pa^{-1}); its strain could not be recovered. The PVA-25 solution showed the lowest compliance (0.0056 Pa^{-1}) and 100% recovery. Both the PVA-15 and PVA-20 solutions showed a permanent deformation of around 40% and an elastic recovery of around 60%.

The creep-recovery behaviors of the aforementioned PVA solutions evidenced that the PVA-10 solution was fully viscous, the PVA-25 solution was

nearly entirely gelled, whereas the PVA-15 and -20 solutions showed intermediate properties.

The thixotropic profiles of the PVA solutions are shown in Figure 8. We could not obtain the thixotropic profile of the PVA-25 solution under the present experimental conditions, since its high viscosity precluded accurate testing. The PVA-10, -15, and -20 solutions exhibited Bingham plastic behavior, that is, thixotropic shear-thinning character. The yield stress values for the onset of flow were obtained by extrapolation of the linear portions of the curves to zero shear rate, which is the critical stress that must be exceeded before the material starts flowing.^{27,28} As indicated in Table II, both the yield stresses and thixotropic loop areas of the solutions substantially

TABLE I
The Creep Behavior of Aqueous PVA Solutions

Samples	Total compliance after 50 s of loading (Pa ⁻¹)	Recoverable compliance after 200 s of unloading (Pa ⁻¹)	Total compliance after 50 s of loading followed by 200 s of unloading (Pa ⁻¹)	Compliance recovery percentage after 200 s of unloading (%)
PVA-10	29.520	0.200	29.320	0.71
PVA-15	0.462	0.268	0.194	58.0
PVA-20	0.157	0.091	0.066	58.0
PVA-25	0.0056	0.0056	0	100

increased with increasing PVA concentration. The results indicated that the more concentrated the PVA solutions, the denser the physical network structure.

CONCLUSIONS

The dynamic rheological properties of aqueous solutions of 10, 15, 20, and 25 wt % PVA have been investigated through controlled-stress rheometry. The respective solutions showed different shear-thinning behaviors, which were dependent on the PVA concentration. The 10 wt % PVA solution was found

to be viscous and showed the lowest η^* and G' values; the 25 wt % PVA solution was viscoelastic and showed the highest η^* and G' values; the 15 and 20 wt % PVA solutions showed intermediate properties.

As regards complex viscosity (η^*), the 10 wt % PVA solution showed fast shear-thinning at low frequency, and then from $\omega = 1$ rad/s, its viscosity showed a transition to become insensitive to frequency; the 15 and 20 wt % PVA solutions showed weak shear-thinning and an inconspicuous transition of viscosity with respect to frequency; the 25 wt % PVA solution showed fast shear-thinning over the

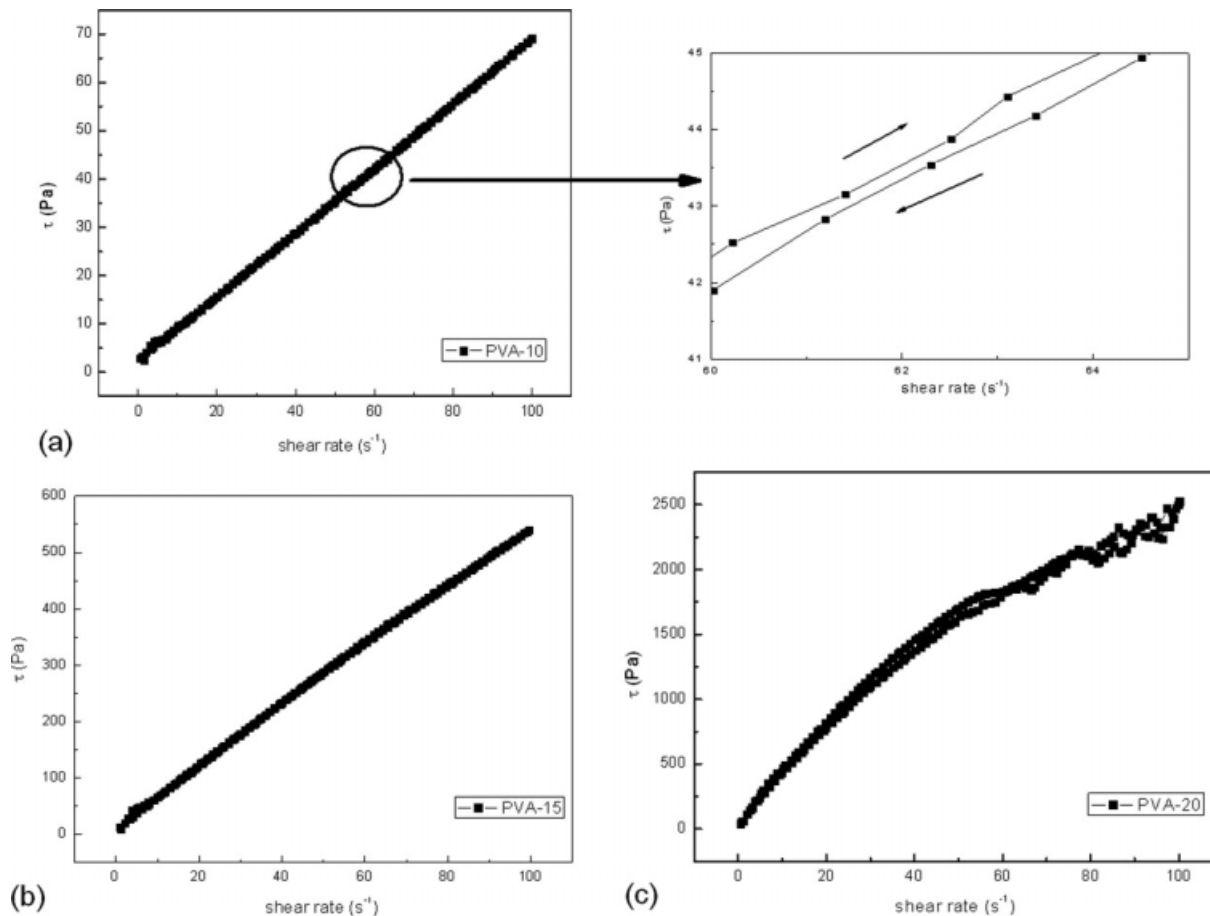


Figure 8 Thixotropy loops of PVA solutions at 30°C.

TABLE II
Thixotropic Behavior of PVA Solutions

Samples	Thixotropic area (Pa s ⁻¹)	Yield stress (Pa)
PVA-10	55	2.3
PVA-15	386	17.4
PVA-20	7079	110

tested frequency range. In terms of storage modulus (G'), the 15 and 20 wt % PVA solutions showed G' becoming strongly dependent on frequency in the range $\omega = 4\text{--}5$ rad/s; G' of the 25 wt % PVA solution increased linearly with frequency; for the 10 wt % PVA solution, G' could not be determined at high frequency. In addition, the relaxation times calculated from η^* and G' for the 15, 20, and 25 wt % PVA solutions tended to become very similar at high frequency.

In tests of creep to recovery, the strain of the 10 wt % PVA solution could not be recovered; the 15 and 20 wt % PVA solutions showed 60% recovery, whereas the 25 wt % PVA solution showed 100% elastic recovery. As regards thixotropic behavior, from 10 to 20 wt % PVA, the yield stress rises sharply. The yield stress of the 25 wt % PVA solution could not be measured.

The different rheological properties of these PVA/H₂O solutions at 30°C are considered to correlate with interchain hydrogen bonds and shear-induced orientation in the solutions. In the 10 wt % PVA solution, there is only a limited number of interchain hydrogen bonds, whereas in the 25 wt % PVA solution, the neighboring PVA chains form local association regimes through a large number of interchain hydrogen bonds. The cases of the 15 and 20 wt % PVA solutions are intermediate between those of the PVA-10 and PVA-25 systems.

Shearing is able to break the intrachain and interchain hydrogen bonds, whereas at the same time, the orientation creates new interchain hydrogen bonding. The reorganization in hydrogen-bonding mode contributes to the transitions of the macroscopic viscoelasticity with frequency. At high shearing rates, the orientation of the whole chains induces similar hydrogen-bonding structures in the systems of different PVA concentrations, and hence, their

dynamic mechanical performances tend to be uniform.

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