Preparation and Viscosity Behavior of Hydrophobically Modified Poly(vinyl alcohol) (PVA)

G. O. YAHYA,[1] SK. ASROF ALI,[2] M. A. AL-NAAFA,[1] and E. Z. HAMAD[1,*]

Departments of [1]Chemical Engineering and [2]Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

SYNOPSIS

In this study, a novel series of water-soluble hydrophobically modified poly(vinyl alcohol) (PVA) is prepared by chemical modification of PVA, with the objective of investigating the polymer's rheological behavior for enhanced oil recovery applications. The solution viscosity of the polymer obtained is studied with respect to the polymer concentration, temperature, salinity, polymer modification, aging, shear rate, and polymer molecular weight. The solution viscosity of the PVA is greatly enhanced by the modification. The modified PVA exhibits a relatively high salt tolerance, typical of nonionic polymers, in the range of 0–7.0 wt % NaCl concentrations, and the viscosity of the polymer solution is relatively invariant with NaCl above 3.0 wt % NaCl concentration. Below 3 wt %, the viscosity shows a maximum then a minimum, an unusual behavior. Generally, the polymer exhibits an almost constant viscosity at high shear rates and a typical shear thinning behavior at low shear rates. In addition, increasing polymer concentration and molecular weight leads to an increase in the polymer solution viscosity. Moreover, the polymer exhibits smaller solution viscosity at a high temperature, and a slight decrease in viscosity is also exhibited by the modified polymer with aging. Comparison of the viscosities of 18 polymer modifications indicates that the larger the numbers of hydrophobic groups (side chains) in the polymer structure, the smaller the viscosity. Moreover, the longer the hydrophobic groups (side chains) in the polymer structure, the greater the viscosity, if their number is small.

INTRODUCTION

For the past several years, there has been substantial interest in water-soluble hydrophobic association polymers. Research in this area has concentrated on the synthesis and solution properties of hydrophobically associating polymers, which are characterized with hydrophobic moieties and can increase viscosity in aqueous solutions.[1-4] Such polymers are of interest in a number of important commercial applications such as enhanced oil recovery operations, drag reduction, flocculation, super absorbency, latex paints, and hydraulic fluids.

Hydrophobically associating polymers are water-soluble polymers containing a small number of hydrophobic groups that promotes association in aqueous solutions. As a consequence, these polymers exhibit thickening properties equivalent to those observed for higher molecular weight polymers. Moreover, because of the antipolyelectrolyte nature of some of these polymers, aqueous solutions of these hydrophobically associating polymers are less salt sensitive.[1-4] Under increasing shear, the physical links between chains are disrupted but reform with decreasing shear.[4] This way, it is possible to avoid the irreversible mechanical degradation that occurs for very high molecular weight polymers when subjected to high shear stresses.[5] The reversible association/dissociation process gives rise to particular rheological behaviors as a function of shear rate or shearing time. Such shear thinning and thixotropic properties are of great technological importance, especially in applications on water-based systems that involve a viscosity control.[6]

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 57, 343–352 (1995)
 CCC 0021-8995/95/030343-10

The preparation of water-soluble hydrophobic associative polymers can be carried out either by chemical modification of a preformed reactive polymer or by copolymerization of the appropriate monomers and macromonomers or by a combination of both methods. The former synthesis route has mainly been applied to cellulose derivatives, poly(oxyethylene), which leads to the so-called HEUR thickeners,[7] i.e., hydrophobically modified ethoxylated urethane polymers and, more recently, to poly(acrylic acid),[1] and to the grafting of poly(ethylene glycol) monomethyl ethers (MPEG) on to acrylic and methacrylic ester copolymers by transesterification reactions.[8] The latter synthesis route has also been applied to copolymerize maleic anhydride with 1-alkene.[9]

The chemical modification route of a preformed reactive polymer can be applied to modify poly(vinyl alcohol) (PVA), especially because it contains the hydroxyl functional groups. Hydrophobically modified PVA can be obtained by reacting acid chlorides of long chain fatty acids (hydrophobic moieties) with PVA to form ester linkage. Some reactions of acid chlorides of long chain acids and of other derivatives with PVA have been investigated,[10,11] but mainly with the objective of producing materials of potential utility in surface coatings and, in some cases, for substrate materials for photographic systems.

Hydrophobically modified PVA can exhibit enhanced viscosification as a result of intermolecular hydrophobic interaction that occurs in the polymer aqueous solution, thus leading to the formation of polymolecular associations and, hence, increases hydrodynamic volume. Furthermore, as a result of the polymer amphiphilic structure, i.e., consisting of hydrophilic groups (hydroxyl and urethane groups) and hydrophobic moieties (long chain fatty acid groups), the polymer is expected to exhibit high surface and interfacial activities. In view of these expected behaviors of the polymers, we became interested in preparing the polymer and, consequently, investigating the aqueous solution properties of the polymer for enhanced oil recovery applications. The polymer is expected to simultaneously provide aqueous solution with both high viscosity for mobility control and low interfacial tension between water and oil in the petroleum reservoirs for enhanced microscopic displacement efficiency in enhanced oil recovery operations. In addition, no work has been done on optimizing the polymer structure to simultaneously provide high solution viscosity and high surface activity. Moreover, very little work is available on the liquid–liquid interfacial tension of polymers in general. However, in the present article only viscosity behavior of the polymer is reported. The surface and interfacial activities of the polymer will be reported in a future publication. Detailed viscosity behavior and surface and interfacial activities of the hydrophobically modified polymers for enhanced oil recovery applications have not been investigated, at least to our knowledge, although viscosity and surface tension behaviors of aqueous solution of unmodified PVA have been reported.[12]

In the present study, chemical modification of PVA by urethanization and esterification of PVA by reacting different combinations of long chain fatty acid chlorides, decanoic acid chloride, docosanoic acid chloride, and stearic acid chloride, with the polymer was carried out with the objective of investigating the modified polymer's viscosity behavior, surface, and interfacial activities. The modification reaction was carried out on the urethanized PVA, because it has been established that partly urethanized PVA is more stable and more soluble in solvents, such as water, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO).[13] The long chain fatty acid chlorides were obtained from the reaction of fatty acid and thionyl chloride. The acid chlorides react readily with the hydroxyl groups to form esters. The viscosity behavior of the polymer has been investigated with respect to the polymer concentration, temperature, NaCl concentration, polymer modification, aging, shear rate, and polymer molecular weight. The hydrophobically modified PVA obtained in this work exhibits enhanced viscosification at moderate polymer concentration and also displays moderate salt tolerance.

EXPERIMENTAL SECTION

Materials

The polyvinylalcohol (PVA), with molecular weight of 72,000 and 100,000, was suppl ed by Fluka Chemie AG and used as received. The three fatty acids, docosanoic acid, stearic acid, and decanoic acid, were also supplied by Fluka Chemie AG and used as received. Thionyl chloride ($SOCl_2$), sodium hydroxide (NaOH), urea, and the solvents used in this work, such as methanol and dimethylformamide (DMF) were supplied by Fluka Chemie AG and also used as received.

Preparation of Partly Urethanized PVA

Polyvinyl alcohol (PVA), with its free hydroxyl groups, offers considerable latitude for chemical

transformations such as esterification, etherification, and acetalization. Partly urethanized PVA was prepared[13] by adding urea to PVA having a degree of polymerization of 1,600 and molecular weight of 72,000, and with degree of hydrolyzation of 97.5–99.5 mol % in distilled DMF at about 150°C. In a three-necked, 100 mL flask, equipped with a stirrer, a condenser, a thermometer, and a magnetic stirrer, 10 g of the PVA, 50 g of distilled DMF, and 13.65 g (1 mol urea to 1 base mol PVA monomer) of urea were placed. The flask was maintained at a temperature of 148–152°C, under N_2 gas to stop O_2 free radicals degradation in the reaction mixture. The reaction mixture became homogeneous within a few minutes and proceeded, accompanied by evolution of gas. The reaction was left for 2-$\frac{1}{2}$ h, after which the resulting polymer was precipitated into methanol, purified twice in excess methanol, then dried *in vacuo* at 70°C until a constant weight was obtained.

The same procedure was similarly applied to urethanize the PVA with a degree of polymerization of 2,000, a molecular weight of 100,000 and a degree of hydrolyzation of 86–89 mol %. Before the urethanization was carried out for this polymer, it was further hydrolyzed. The method of Bravar[14] was applied to hydrolyze the polymer. As an example, 10 g of the PVA was mixed with 200 mL of distilled water and then stirred with a magnetic stirrer at room temperature. Then, 2 mL of 40% NaOH was added dropwise with continuous stirring. The reaction mixture was left in this condition for 24 h, after which the resulting polymer was precipitated in 500 mL methanol, purified twice in excess methanol, then dried *in vacuo* at 70°C until a constant weight of about 7.55 g was obtained.

Preparation of Fatty Acid Chlorides

Three fatty acid chlorides, docosanoic acid chloride ($CH_3(CH_2)_{20}COCl$), stearic acid chloride ($CH_3(CH_2)_{16}COCl$), and decanoic acid chloride ($CH_3(CH_2)_8COCl$), were prepared from the reaction of the fatty acid with thionyl chloride ($SOCl_2$).

Preparation of Hydrophobically Modified PVA

Different combinations and ratios of the three acid chlorides were reacted with the urethanized PVA,

Table I The Solution Viscosity, Surface Tension, and Solubility Data of the Modified PVA with Different Combinations of Hydrophobic Groups

Series	Degree of Substitution C22 mol %	C18 mol %	C10 mol %	Polymer Concentration wt %	Viscosity (cps)	Surface Tension mN/*M*	Solubility in Water
1	0	0	0	5.0	120	43.89	Soluble
2	0	0	5.0	5.0	16	31.90	Cloudy
3	0	1.0	0	3.8	149	53.74	Cloudy
4	0	2.0	0	5.0	165.1	52.00	Cloudy
5	0.5	0.5	1.0	0.5	30.1	48.85	Soluble
6	0.5	1.5	1.0	0.5	25.0	52.61	Soluble
7	1.5	0.5	1.0	0.5	20.0	49.63	Soluble
8	1.5	1.5	1.0	0.5	15.0	50.13	Soluble
9	1.0	1.0	2.0	0.5	25.0	57.65	Soluble
10	0.5	0.5	3.0	0.5	30.1	55.58	Soluble
11	1.5	1.5	3.0	0.5	30.1	54.28	Cloudy
12	1.5	0.5	3.0	0.5	35.1	52.08	Cloudy
13	0.5	1.5	3.0	0.5	40.1	53.46	Cloudy
14	2.0	0.5	0.5	0.5	50.1	52.51	Cloudy
15	0.5	0.5	0.5	0.5	****	****	Insoluble
16	0.5	1.5	0.5	0.5	****	****	Insoluble
17	0	2.0	1.0	5.0	2740	28.05	Soluble
18	0	2.0	2.0	5.0	1085	24.15	Cloudy
19	0	0.5	1.0	5.0	34.1	38.43	Soluble
20	2.0	0	0.5	0.5	20.1	54.44	Soluble

C22 = Docosanoic acid hydrophobic group; C18 = Stearic acid hydrophobic group; C10 = Decanoic acid hydrophobic group; Shear rate = 8.0 s^{-1}; Temperature = 30°C; **** = Inaccurate; cps = centipoise.

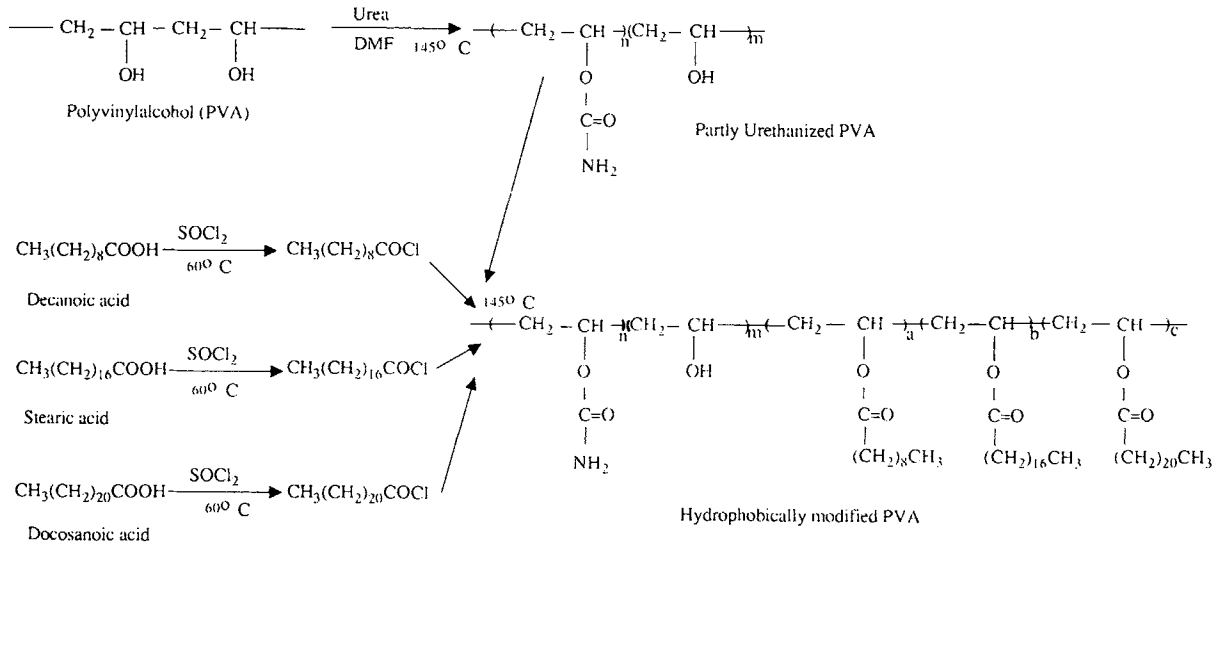

Figure 1 Reaction scheme and molecular structure of hydrophobically modified PVA.

for both PVA of degree of polymerization of 1,600 and 2,000. Some of the modified polymers obtained were found insoluble in water even after heating to an elevated temperature (i.e., 70°C), for several hours. However, most of the modified polymers were soluble in water at the ambient temperature. The different combinations of the hydrophobic side chains of the urethanized polymers obtained and the polymers solution properties, solubility in water, viscosity, and surface tension, are given in Table I.

An example of one of the modification reactions is as follows: 4 g of the urethanized PVA, having a degree of polymerization of 1,600 and molecular weight of 72,000, was mixed with 40 mL distilled DMF and heated to 140°C. It was maintained at this temperature until a clear homogeneous solution was obtained, after which the three combination of the acid chlorides i.e., 0.148 g (0.5 mol % docosanoic acid chloride substitution), 0.125 g (0.5 mol % stearic acid chloride substitution), and 0.157 g (1.0 mol % decanoic acid chloride substitution), already mixed in a small test tube, was introduced dropwise into the reaction mixture maintained at 140°C and stirred vigorously. The reaction was carried out under N_2 gas to stop O_2 free radicals degradation. After 2 min of the reaction time, the resulting polymer was precipitated into methanol, purified twice in excess methanol, and then dried *in vacuo* at 70°C.

The same procedure was similarly applied with the same combination of the three acid chlorides to the urethanized PVA having a degree of polymerization of 2,000 (molecular weight of 100,000). Hydrophobically modified PVA was then obtained for this combination and other different combinations using the same procedure. The detailed reaction scheme and structure of the hydrophobically modified PVA are given in Figure 1. The degree of urethanization for these kinds of polymers have been reported in an earlier publication.[13]

Experimental Measurement and Instruments

The solution viscosity behavior of the hydrophobically modified PVA was investigated with respect to polymer concentration, polymer molecular weight, temperature, salinity, aging, and effect of the modification for a moderate range of shear rates. In this study, concentrated stock solutions were prepared at least 24 h before use. Final solutions of the desired composition were obtained by dilution of the appropriate stock solution with water and, if necessary, addition of appropriate amount of solid NaCl. Most of the dissolution processes took 2–3 days. The viscosity and surface tensions of all the modified polymers obtained in this work are displayed in Table I. The solution viscosity of the hydrophobically modified polyvinyl alcohol (PVA) was determined using a digital Brookfield rotational viscometer with UL adapter accessories or a SC4-18 spindle accessory, whichever was appropriate, at shear rate rang-

ing from 0.4 to 79.4 s^{-1}. All viscosities for the polymer concentration ranging from 0.5 wt % to 5.0 wt % were measured at a temperature of 30–70°C.

RESULTS AND DISCUSSION

The viscosity behavior of the hydrophobically modified PVA is reported at different conditions as a part of a continuing research program to study the relationship between polymer structures and their solution viscosities behavior, and air–liquid surface and liquid–liquid interfacial activities with the objective of designing polymers with optimized structure for high solution viscosity and, simultaneously, high surface activity for applications in areas such as enhanced oil recovery. The surface and interfacial activities of the polymer will be reported in a future publication. In order to achieve this objective, the viscosity behavior of the hydrophobically modified PVA with combinations of 0.5 mol % C22, 0.5 mol % C18, 1.0 mol % C10 (series 5), and 2.0 mol % C18 1.0 mol % C10 (series 17) degree of substitutions were studied under various conditions of salinity, polymer concentration, temperature, aging, shear rates, and molecular weight. These two combinations, i.e., No. 5 and 17 in Table I, have been chosen from the other combinations displayed in Table I for detailed studies because they have been found to exhibit promising properties that conform with the objective of this research, unlike other combinations, such as series 2 and 3 in Table I, which have been found cloudy in solution. These combinations, i.e., 2 and 3, were not studied because they were incompletely soluble in water. The series 1 is unmodified PVA and, as such, its behavior was not studied, as the objective was to study the behavior of hydrophobically modified PVA. Although series 6 to 10 are soluble in water, their viscosities behavior and surface activity are simultaneously not as promising as series 5 and 17. Series 11 to 16 were also not studied because all have either been found cloudy or insoluble in water. Comparing the properties of series 18 to 20 with 17, one can see that series 17 has more promising properties than series 18 to 20. As such, with all these explanations, the choice of combinations 5 and 17 for detailed studies is justified. Moreover, an established procedural pattern has been followed in the choice of a mixture of the three long chain fatty acids, i.e., C10, C18, and C22, for the hydrophobic modification.

Figures 2–8 show the effects of polymer concentration, temperature, NaCl salt concentration, polymer modification, aging, shear rate, and molecular weight on the viscosity of the hydrophobically modified PVA with hydrophobic substitution of 0.5 mol % C22, 0.5 mol % C18, and 1.0 mol % C10.

As shown in Figure 2, the hydrophobically modified PVA exhibits a greater viscosity than the unmodified PVA i.e., original and urethanized PVA. The incorporation of the hydrophobic groups is the primary factor causing the enhancement of the viscosity by promoting intermolecular hydrophobic association. As a result of this interchain interactions, which leads to an increase in hydrodynamic volume and, consequently, causes increase in the viscosity of the modified polymer, this then indicates that hydrophobic interactions occur between chains, which leads to polymolecular structures with a large hydrodynamic radius. The enhanced viscosity obtained for the hydrophobically modified PVA is consistent with studies reported in the literature for hydrophobically associating polymers.[1,15–19] On the other hand, unmodified PVA is observed to decrease in viscosity after urethanization.

For the modified PVA under investigation, an almost shear rate independent viscosity is observed at high shear rate, as shown in Figures 2, 3, and 7. However, at low shear rates, a typical shear thinning behavior appears as depicted in the same figures for both polymers of molecular weights of 72,000 and 100,000. The shear thinning behavior exhibited by the polymer is probably due to the disorientation and disentanglement of the macromolecular chains under shear. The decrease in viscosity with increasing shear rate, i.e., shear thinning behavior, corre-

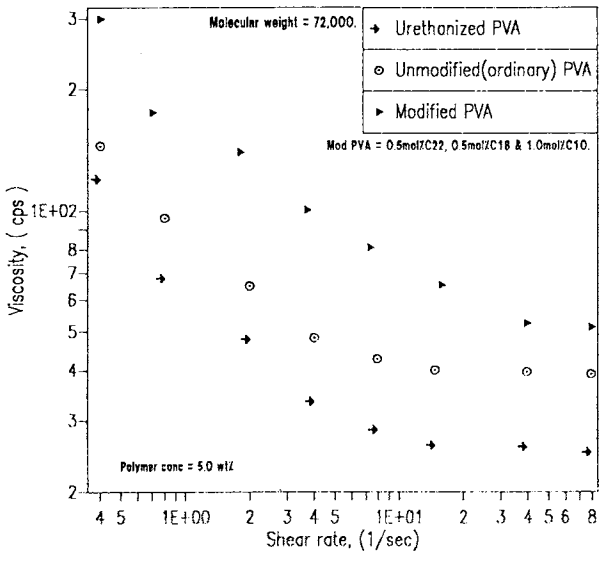

Figure 2 Variations of viscosity with shear rate for modified, urethanized and ordinary PVA at 30°C.

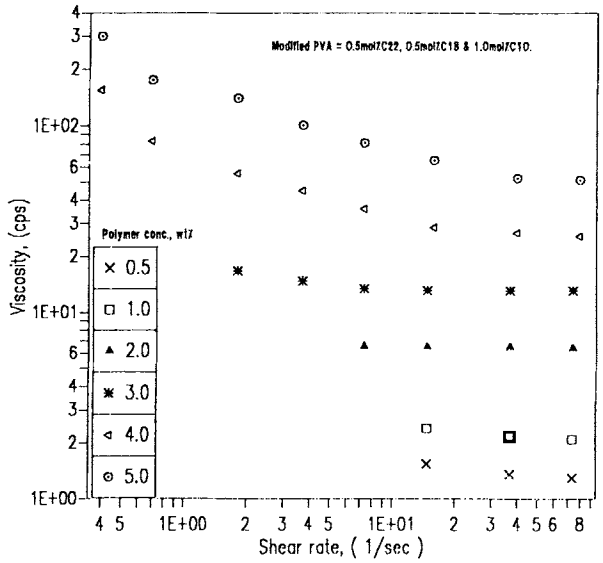

Figure 3 Variations of viscosity with shear rate and polymer concentration for modified PVA with a molecular weight of 72,000 at 30°C.

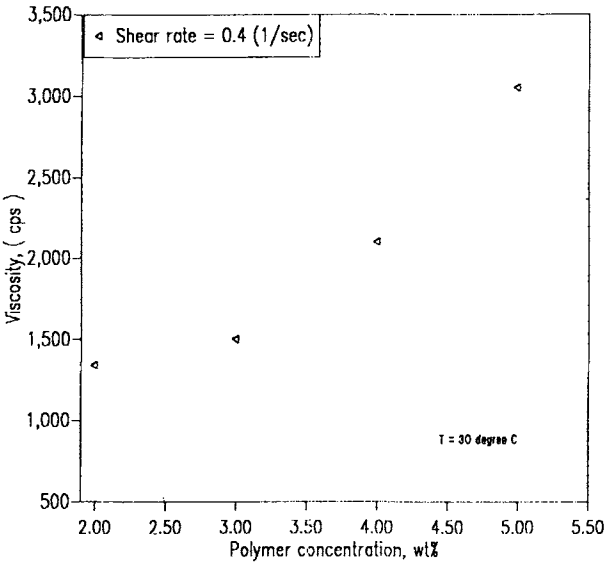

Figure 4 Effect of polymer concentration on the viscosity of modified PVA (0.5 mol % C22, 0.5 mol % C18, and 1.0 mol % C10) with a molecular weight of 100,000.

sponds to the progressive rupture of the intermolecular associations upon increasing the shear rate. A similar trend was observed by Kaczmarski et al.,[7] and Hill et al.,[3] in their studies.

The hydrophobically modified PVA also exhibits a sharp increase in viscosity with increasing polymer concentration for all the shear rates considered and for both polymers of molecular weights of 72,000 and 100,000 at 30°C. This behavior is displayed in Figures 4 and 5. The behavior is due to the formation of large aggregates as the polymer concentration is increased. This behavior is expected, because at low polymer concentration, the hydrophobic chains have little chance of interacting with each other, thus leading to the formation of small aggregates with a small hydrodynamic radius. However, as the polymer concentration is increased, hydrophobic intermolecular interactions are more probable, leading to the formation of large polymolecular aggregates with large hydrodynamic volumes and, consequently, high solution viscosity.[1,3,7,17,18]

The development of viscosity behavior for associative polymers like the one under investigation relies on an increase in the apparent macromolecular weight due to cooperative intermolecular aggregation among hydrophobic groups or moieties with increasing polymer concentration. Under high shear condition, the hydrophobic interactions can be disrupted, resulting in a decrease in the apparent molecular weight; hence, a decrease in solution viscosity. However, under low shear conditions the hydrophobic interchain associations will reform, restoring the high solution viscosity.[20,21]

Figure 5 shows the effect of temperature on the solution viscosity of the modified polymer. As expected, a sharp decrease in solution viscosity is observed with increasing temperature.

Figure 6 shows the effect of NaCl concentration on the solution viscosity of the modified polymer with a molecular weight of 72,000. The polymer was

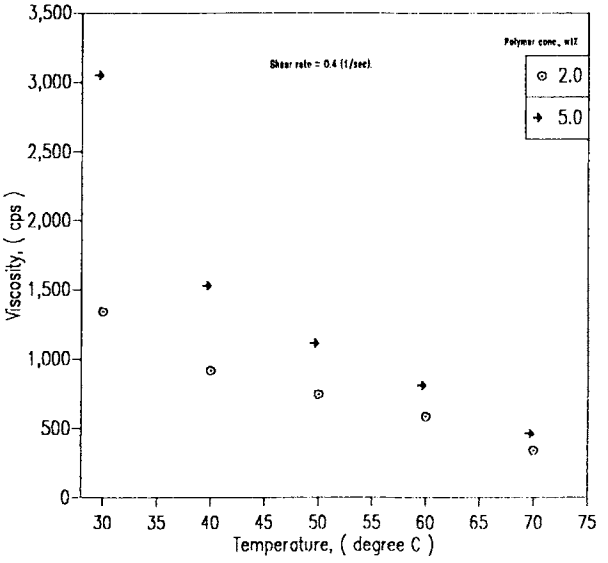

Figure 5 Plots of viscosity vs. temperature for modified PVA (0.5 mol % C22, 0.5 mol % C18, and 1.0 mol % C10) with a molecular weight of 100,000.

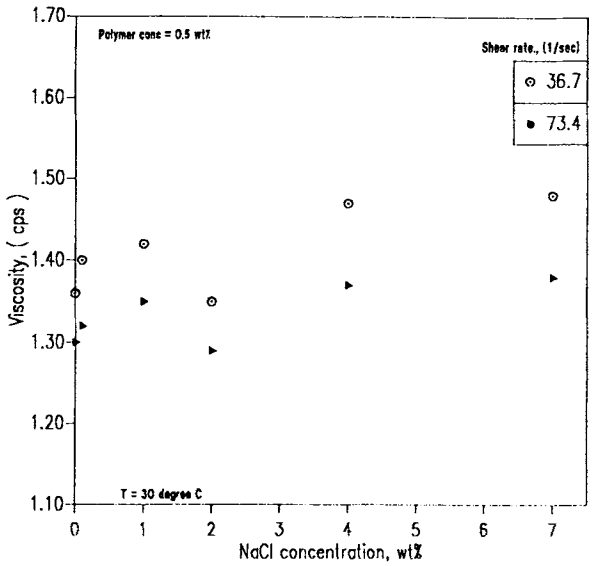

Figure 6 Effect of NaCl on the viscosity of modified PVA (0.5 mol % C22, 0.5 mol % C18, and 1.0 mol % C10) with a molecular weight of 72,000.

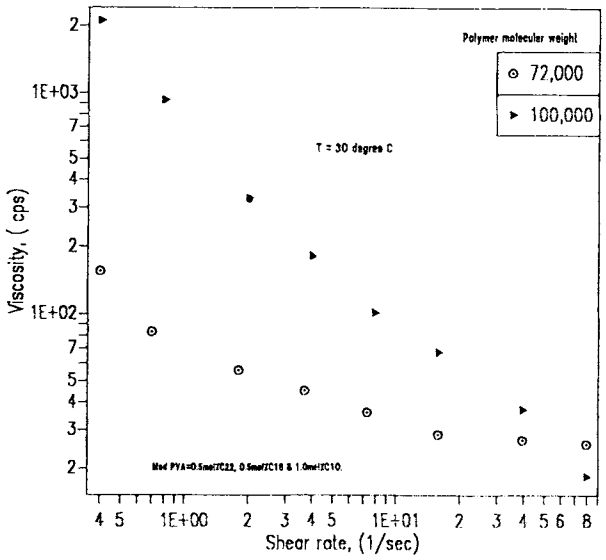

Figure 7 Variations of viscosity with shear rate and a molecular weight for modified PVA of polymer concentration of 4.0 wt %.

found salt tolerant up to 7.0 wt % of NaCl concentration. Beyond this concentration, a precipitate was observed. Within this range, i.e., 0–7.0 wt % NaCl concentration and for shear rate of 36.7 and 73.4 s^{-1}, an insignificant change in viscosity with an increasing NaCl concentration is observed. A maximum is observed at about 1.0 wt % NaCl concentration, and a minimum at about 2.0 wt % NaCl concentration. Above 2 wt % NaCl concentration, an increase in viscosity is observed up to about 4.0 wt % NaCl concentration and then levels off as the NaCl concentration is increased further. This maximum–minimum curve obtained in Figure 6 is unusual, especially for nonionic polymers like the one under investigation. What is usually expected for nonionic polymers is invariance of viscosity with increasing NaCl salt concentration. As such, further studies are underway to investigate this unusual behavior of the polymer with NaCl salt concentration. However, the relative invariance of viscosity to changes in salt concentration above 3.0 wt % NaCl concentration, as depicted in Figure 6, is one of the attractive feature of this hydrophobically modified polymer. Adding salt to the modified polymer is probably promoting an intermolecular association among the hydrophobic groups in the polymer structure, thus enhancing the viscosification ability of the polymer.

Figure 7 depicts the effect of polymer molecular weight on the viscosity of the modified polymer. A sharp increase in solution viscosity is actually observed as the molecular weight of the polymer is increased from 72,000 to 100,000 for the same polymer concentration of 4.0 wt % and for all the shear rates considered. This behavior is actually expected, and could be attributed to the increase in size of the polymer molecules as the molecular weight is increased, which leads to a higher hydrodynamic volume and, consequently, to viscosity enhancement.

Figure 8 depicts the effect of aging on the solution viscosity of the modified PVA with molecular weight

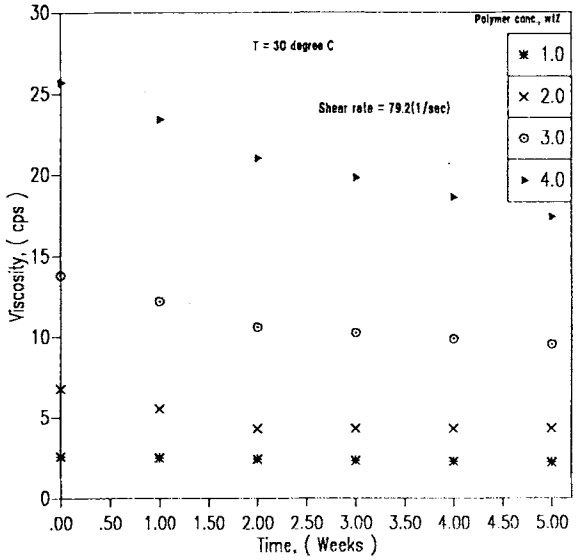

Figure 8 Effect of aging on the viscosity of modified PVA (0.5 mol % C22, 0.5 mol % C18, and 1.0 mol % C10) with a molecular weight of 72,000.

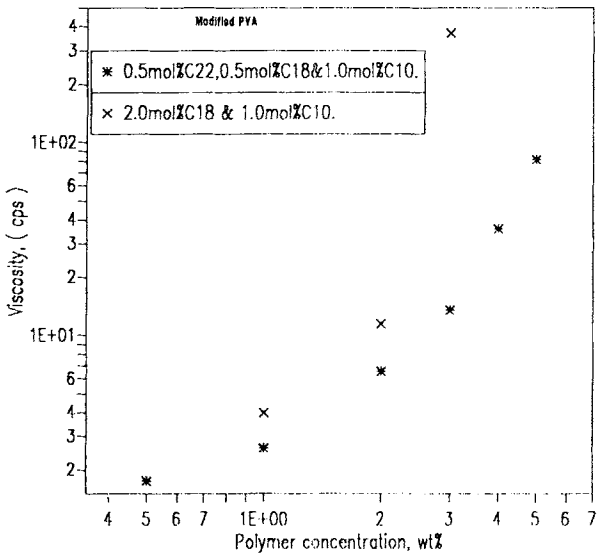

Figure 9 Effects of polymer concentration and modification on the viscosity of modified PVA with a molecular weight of 72,000 at 30°C.

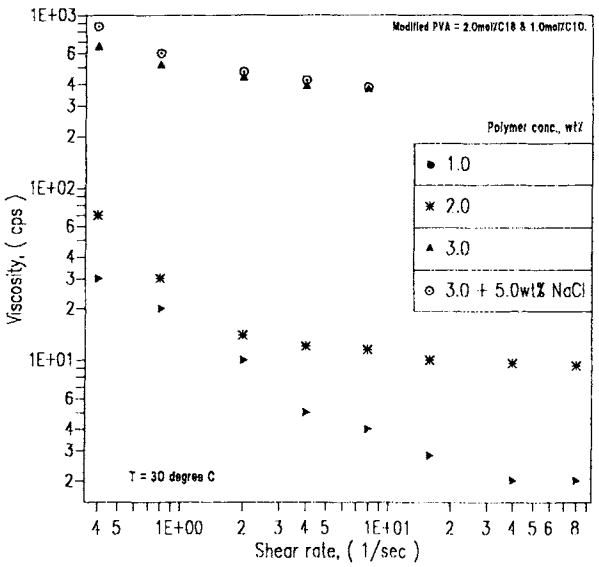

Figure 10 Variations of viscosity with shear rate and polymer and NaCl concentrations for modified PVA of a molecular weight of 72,000.

of 72,000. This was performed by measuring viscosity of the polymer at a week interval for about 5 weeks. The polymer solution viscosity was measured at 30°C. The viscosity of the polymer was observed to decrease slightly with time. This could be attributed to the hydrolysis of the ester linkage in the polymer structure.

Figures 9–11 display the effects of polymer concentration, polymer modification, shear rate, and NaCl concentration on the solution viscosity of the modified PVA with a molecular weight of 72,000 and with side chain combinations of 2.0 mol % C18 and 1.0 mol % C10. As displayed in Figure 9, the modified PVA with hydrophobic groups combination of 2.0 mol % C18 and 1.0 mol % C10 is observed to exhibit greater viscosity enhancement than the one studied earlier, i.e., 0.5 mol % C22, 0.5 mol % C18, and 1.0 mol % C10. The viscosity of the former is observed to increase more drastic with increasing polymer concentration than the latter. This behavior is probably due to the presence of more of the longer hydrophobic groups, i.e., 2.0 mol % C18 in the modified PVA with a hydrophobic combination of 2.0 mol % C18 and 1.0 mol % C10 than that of the other polymer studied earlier. The increase in the longer hydrophobic groups is probably causing more interchain hydrophobic interaction, which leads to a larger aggregate formation that results in large hydrodynamic radius and, consequently, causes the increase in viscosity.

Figures 9 and 10 also show the effect of polymer concentration on the viscosity of the modified PVA, i.e., 2.0 mol % C18 and 1.0 mol % C10. As expected, the viscosity of the polymer increases with increasing polymer concentration for all the shear rates considered. Figure 10 displays the effect of shear rate on the viscosity of the polymer. An almost constant viscosity is observed at high shear rate for all the polymer concentrations considered. However, at low shear rate, a typical shear thinning appears. Similar behavior is also observed for the modified

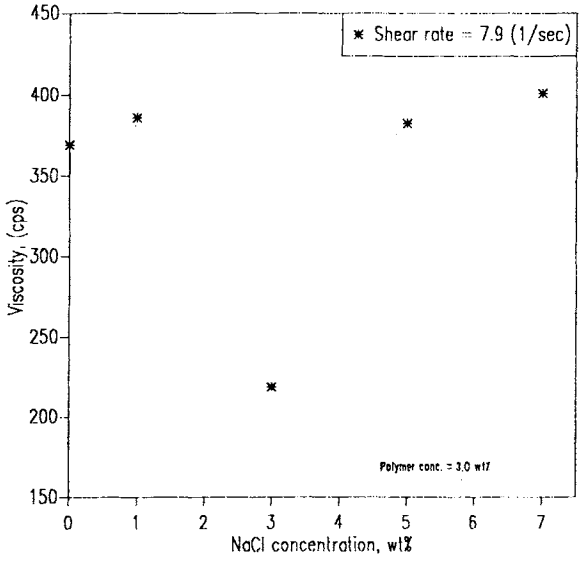

Figure 11 Effect of NaCl concentration on the viscosity of modified PVA (2.0 mol % C18 and 1.0 mol % C10) with a molecular weight of 72,000 at 30°C.

PVA studied previously and, thus, the same explanation for the behavior can be given for this case as well. Figures 10 and 11 depict the effect of NaCl salt on the viscosity of the polymer. A similar behavior observed for the previous polymer is also observed for this polymer. A maximum viscosity is observed at about 1.0 wt % NaCl concentration. From this NaCl concentration, i.e., 1 wt %, the viscosity decreases up to about 3.0 wt % NaCl concentration. Above 3.0 wt %, viscosity increases sharply up to the last point. As stated previously, further work is underway to investigate this unusual behavior of the polymer with NaCl salt.

CONCLUSION

A novel series of water-soluble hydrophobically modified PVA has been prepared by chemical modification of PVA via urethanization–esterification reaction of different combinations and ratios of long chain fatty acid chlorides. Because of the unique structure features of this hydrophobic-associating polymer, which is characterized with hydrophobic moieties (amphiphilic), that promotes intermolecular association among hydrophobic groups in the polymer structure, the polymer has been found to exhibit a high thickening ability such as a high solution viscosity that can be compared to what is usually required in enhanced oil recovery applications, although at moderate polymer concentrations. Furthermore, a relatively high salt tolerance, typical of nonionic polymers, is exhibited by the hydrophobically modified PVA in the range of 0–7.0 wt % NaCl concentrations. The relative invariance of viscosity to changes in NaCl concentration above 3.0 wt % NaCl concentration is one of the attractive features of this polymer. In this study, addition of NaCl is promoting an intermolecular hydrophobic association among hydrophobic groups in the polymer structures. Incorporation of hydrophobic groups onto the backbone of the modified polymer gives the polymer a greater thickening ability. This also indicates the occurrence of a hydrophobic association in the polymer structure. As expected, the polymer exhibits a greater viscosity enhancement for higher molecular weight than for lower molecular weight polymer. A slight reduction in viscosity is displayed by the polymer with aging. Evidence of instability in the ester linkage is indicated.

Generally, the viscosity–shear rate relationship for the polymer exhibits a nearly constant viscosity at high shear rates and a typical shear thinning behavior at low shear rates. The shear thinning characteristics of the polymer would actually be an advantage in polymer flooding. In the high shear region around the injection well bore the effective viscosity of the injected polymers would be relatively low, thus requiring low power to move. However, it would increase with decreasing shear as the polymer solution penetrates more deeply into the formation. In addition, increasing polymer concentration leads to an increase in the polymer solution viscosity. Moreover, the polymer exhibits a reduction in solution viscosity with increasing temperature, as expected. It can also be deduced from this work that the larger the amount of long hydrophobic groups in the polymer structure, the greater is the viscosity. Comparison of the viscosities of 18 polymer modifications indicates that the larger the numbers of hydrophobic groups (side chains) in the polymer structure, the smaller the viscosity. The large number of side chains promotes intramolecular association at the expense of intermolecular association. Moreover, the longer the hydrophobic groups (side chains) in the polymer structure, the greater the viscosity, if their number is small. The greater viscosity is due to the promotion of large number and stronger intermolecular associations.

The authors wish to acknowledge the support provided by King Fahd University of Petroleum and Minerals. The authors also gratefully acknowledge the stimulating discussions and comments provided by Shafkat A. Beg.

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Received October 25, 1994
Accepted January 19, 1995