

Investigation of the Interpolymer Association Between Poly(vinyl alcohol) and Poly(sodium styrene sulfonate) in Aqueous Solution

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Received 13 June 2008; accepted 12 November 2008

DOI 10.1002/app.29705

Published online 6 March 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A viscosimetric method has been used to study the interpolymer association between poly(vinyl alcohol) (PVA) and poly(sodium styrene sulfonate) (PSSNa) in aqueous solution. At constant molecular weight of PSSNa, it was found that, the PVA and PSSNa associations were improved with the decrease of molecular weight of PVA and the decrease of its hydrolysis degree. The measurement of intrinsic viscosity $[\eta]$ and the determination of Huggins associative coefficient K_H of different PVA samples were used to select the most appropriate PVA sample, which leads to homogeneous polymer–polymer mixtures (PVA with hydrolysis degree

87–89%, molecular weight 124,000–186,000 g/mol, intrinsic viscosity $[\eta] = 1.02$ dL/g, and Huggins associative coefficient $K_{H,ass} = 0.76$). The obtained results show that the interpolymer association between PVA and PSSNa, in aqueous solution, is mainly due to intermolecular hydrogen bonds between hydroxyl groups of PVA and sulfonate groups of PSSNa. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3395–3401, 2009

Key words: polymer miscibility; interpolymer associations; viscosity; hydrogen bonds; poly(vinyl alcohol); poly(sodium styrenesulfonate); Huggins coefficient

INTRODUCTION

The fabrication of new polymeric materials endowed with new properties plays an important role in many processes of industrial innovation. The polymer–polymer compatibility remains an attractive field of polymeric research. It aims to prepare new materials endowed with better properties rather than their original individual components. It also allows preparing equivalent material properties with lower production cost.^{1–3}

In literature, the compatibility of two polymers was interpreted, in a part, by the formation of specific interactions such as hydrogen bonds, the Van der Waals forces, and/or electrostatic interactions. In the case of PVA, the miscibility with another polymer is mainly due to the cross-hydrogen bond interactions. Such interactions are especially important between completely or partially associative polymers.^{4,5}

Because of its simplicity and inexpensive equipment, the viscosimetric method has been extensively used to study the compatibility of polymers. The simplest test for polymer noncompatibility is their

separation into two phases when the polymers are dissolved in the same solvent. The viscosimetric method makes it possible to further characterize the mixtures of macromolecules in the disperse state. In the solution, the establishment of attractive intermolecular interactions induces an increase in the system viscosity.^{6–13} However, the interactions as characterized by a relative increase in the solution's viscosity may be insufficient to induce polymer compatibility in the solid state. The solvent's molecules that dissolve the chains of both polymers may screen out the eventual repulsive interactions between some parts of the two polymer chains. After solvent removal, and parts brought into short distances, the repulsive interactions between the hetero-chains and the attractive ones between homo-chains will lead to a phase separation.

Based on the fact that within liquid medium the attractive interactions causes expansion of polymer chains while the repulsive interactions lead to the shrinkage of polymer coils, several models were proposed to investigate the polymer–polymer compatibility.^{5,11,14–16}

Krigbaum and Wall¹⁶ model permits the estimation of polymer compatibility by the comparison of the experimental and theoretical values of polymer–polymer interaction parameter. According to this model, two polymers, A and B, were considered

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compatible when the value of their experimental interaction parameter, k_{AB} is higher than the value of the theoretical one, otherwise, they will be considered incompatible.

Based on Krigbaum and Wall model, several attempts were proposed to describe the polymer-polymer compatibility.⁹⁻¹¹ However, because of the small difference between small numbers (values of interaction parameters or intrinsic viscosities); an erroneous conclusion could be committed. Such feature remains the main drawback of the attempts based on polymer-polymer interactions parameters and intrinsic viscosity value differences.⁹⁻¹¹

To overcome these drawbacks, we used the Staikos and Tsitsilianis, Staikos and Bokias^{12,13} as a model to study the PVA and PSSNa compatibility in aqueous solutions. This simple model which is deduced from the model of the additivity of polymer viscosities is adapted to characterize the interactions between nonionic and ionic polymer in dilute aqueous solution. At constant total concentration C , the theoretical reduced viscosity $(\eta_{sp}/C)_{theo}$ of the polymer mixtures and without polymer interactions, can be calculated from the following equation:

$$(\eta_{sp}/C)_{theo} = W_1(\eta_{sp1}/C_1) + W_2(\eta_{sp2}/C)$$

Thus $(\eta_{sp}/C)_{theo}$ is the theoretical reduced viscosity of the polymers mixture.

W_1 and W_2 are the weight fractions of the ionic and nonionic polymers in solution, respectively. (η_{sp1}/C_1) is the reduced viscosity of ionic polymer at the different concentrations C_1 at which it exists in the different compositions of the mixture and (η_{sp2}/C) is the reduced viscosity of the nonionic polymer at concentration C .

Using this formula, two polymers are considered compatible when their experimental reduced viscosity is larger than their theoretical one and incompatible in the opposite case. The ratio of experimental to theoretical reduced viscosities $\tau = (\eta_{sp}/C)_{exp}/(\eta_{sp}/C)_{theo}$ is usually used to determine polymer compatibility. Interpolymer associative interactions would be considered dominating when the ratio value is larger than one.

Otherwise, the intrinsic viscosity and Huggins coefficient give useful information about the chain hydrodynamic volume and the intrachain interactions, respectively. Theoretically, the increase of the value of Huggins coefficient was interpreted as the result of the increase in intramolecular interactions which induces shrinkage of polymer chains and reducing the system homogeneity. Whereas, the decrease of the Huggins coefficient value was considered as a sign of the intermolecular interactions increase that favors the polymer compatibility. Moreover, it is well established that a Huggins coef-

ficient between 0.3 and 0.5 characterizes a good solvent. In the case of associative polymers, the value of Huggins coefficient can reach extreme values those outside the range [0.3-0.5].¹⁷⁻²¹

To calculate the value of polymer intrinsic viscosity and the Huggins associative coefficient ($K_{H,ass}$) the following equation was used:

$$\eta_{sp}/C = [\eta] + bC$$

where η_{sp}/C is the reduced viscosity, $[\eta]$ is the intrinsic viscosity of polymer, and b is a constant which is used to calculate the Huggins coefficient: $K_{H,ass} = b/[\eta]^2$.

The final objective of the present work was to prospect the possibility of using PVA-PSSNa blend to prepare ion-exchange membranes. In the first part, the interactions in solution of the polymers were prospected. The stronger the interactions between the two polymers, the more stable the solid membranes with interpenetrating polymer networks like-structure. As ion-exchange membranes are used in aqueous media, strong interactions between the polymers are needed to prevent a loss of PSSNa chains into the external phase. Crosslinking of PVA into a semi-interpenetrating polymer network could further improve the blend structure.²² To select the best polymer components for ion-exchange membrane preparation, the dependence of the polymer compatibility on the molecular weight and the hydrolysis degree of PVA is taken as an example. A particular attention was also paid to the study of PVA behavior in aqueous solution: determination of intrinsic viscosity and Huggins associative coefficient. The total concentration of PVA and PSSNa mixture was maintained at 2 g/dL to reduce the polyelectrolyte behavior at low PAA concentration (increase of viscosity), and to anticipate the behavior of the polymer blend in the solid state (interpenetrating polymer networks).

EXPERIMENTAL PROCEDURES

Samples of PVA and PSSNa were supplied by Aldrich company. The polymer properties are summarized in Table I. The samples were used without further purification. PVA and PSSNa solutions were prepared separately by dissolving polymer in deionized water and heating under reflux, with stirring, at 90°C for 1 h (2 g/dL). Afterwards, the PVA and PSSNa solutions were cooled at room temperature and clarified through 1.2 and 0.45 μ m Millipore filter, respectively. The two solutions were mixed in defined proportions to obtain a value of 2 g/dL as the total polymer concentration.

For the viscosimetric measurements of PVA and PSSNa mixtures, a Couette-type viscosimeter was

TABLE I
Symbols and Properties of PVA and PSSNa Samples as Given by the Supplier

Symbol sample	DH (—OH) (%)	Acetate (%)	Supplied M_w
PVA98/31	98–99	2–1	31,000–50,000
PVA98/85	98–99	2–1	85,000–146,000
PVA98/124	98–99	2–1	124,000–186,000
PVA87/124	87–89	13–11	124,000–186,000
PSSNa	–	–	70,000

used (“low shear rheometer 30” from Contraves) at two shear rates, 3.23 s^{-1} and 5.96 s^{-1} . The apparent reduced viscosity at the two shear rates were the same. The measurements were done at 25°C .

RESULTS AND DISCUSSION

Before the viscosity study of PVA and PSSNa mixtures, the PVA intrinsic viscosity and Huggins associative coefficient were determined, in view, to understand the behavior of PVA chains in aqueous solution and to anticipate the nature of interactions in ternary systems.^{9,17}

PVA intrinsic viscosity and Huggins associative constant

The reduced viscosity of PVA samples was reported as a function of its concentration and thus illustrated in Figure 1. The results are summarized in Table II.

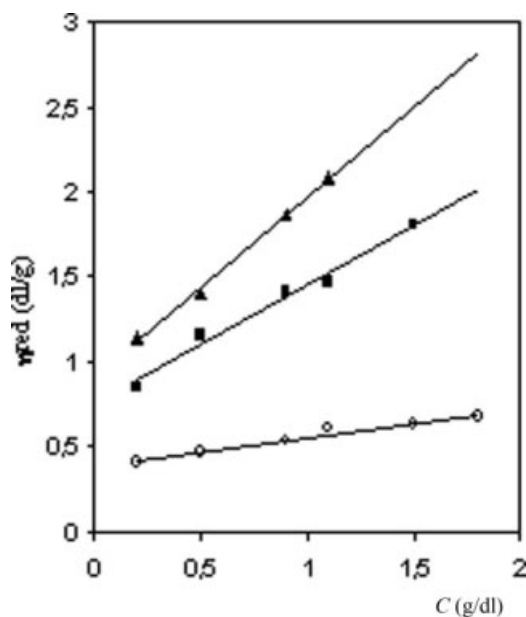


Figure 1 The reduced viscosity of PVA solutions as a function of concentration C (g/dL) at three molecular weights: (\blacktriangle) PVA98/124, (\blacksquare) PVA98/85 and (\circ) PVA98/31 solutions.

TABLE II
Intrinsic Viscosity and Huggins Associative Constant Values of PVA Samples at Different Molecular Weight

PVA sample	PVA98/31	PVA98/85	PVA98/124
$[\eta]$ (dL/g)	0.38	0.75	0.90
$K_{H, \text{ ass.}}$	1.17	1.27	1.31

It shows the intrinsic viscosity and Huggins associative coefficient increase with respect to the increase of PVA molecular weight. The variation of the Huggins coefficient proves that intramolecular interactions are more important within the chains with the highest molecular weight. Obviously, these interactions are due to hydrogen bonds between hydroxyl groups belonging to the PVA chains.

The intrinsic viscosity and the Huggins coefficient were calculated for two PVA samples with different hydrolysis degree (HD: molar % of hydroxyl group content). As shown in Figure 2 and summarized in Table III, the reduction of HD (or increase in the content of acetate groups) provokes an increase in intrinsic viscosity and a decrease in intramolecular interactions. These two results are in agreement because the presence of hydrophobic groups (acetate groups) weakens the intramolecular interactions and enhance the expansion of polymer chains which leads to an increase in the intrinsic viscosity.²³

Influence of PVA molecular weight on polymer compatibility

Figure 3 shows the ratio of experimental to theoretical reduced viscosities ($\tau = (\eta_{sp}/C)_{m \text{ exp}} / (\eta_{sp}/C)_{m \text{ theo}}$) of polymer mixtures as a function of PSSNa fraction. The increase of this ratio with decreasing PVA molecular weight suggests an increase in the polymer

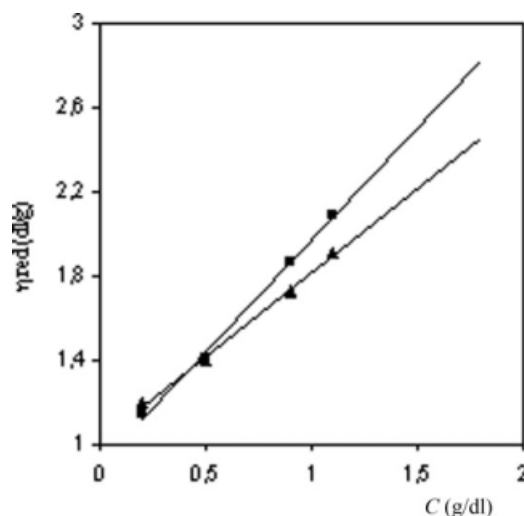


Figure 2 The reduced viscosity of PVA solutions as a function of concentration C (g/dL) at two hydrolysis degrees: (\blacksquare) PVA98/124 and (\blacktriangle) PVA87/124 samples.

TABLE III
Intrinsic Viscosity and Huggins Associative Constant
Values of PVA Samples At Different HD

PVA sample	PVA98/124	PVA87/124
$[\eta]$ (dL/g)	0.90	1.02
$K_{H, ass.}$	1.31	0.79

hetero-association with the decrease in molecular weight. Such behavior would result from a decrease in intramolecular interactions within PVA chains as expected from the PVA chain length reduction. Otherwise, it is well recognized that a decrease in the component molecular weight favors thermodynamically polymer compatibility via an entropy increase.^{5,6}

In spite of the apparent compatibility deterioration which is presumably due to formation of a compact interpolymer complex structure within PVA98/85/PSSNa and PVA98/124/PSSNa mixtures ($\tau < 1$), no sign of precipitation or increase in solution turbidity were noticed after long storage (7 days). (N.B The appearance of precipitate or the increase of mixture turbidity were considered by many authors^{24,25} as a sign of compatibility deterioration).

Influence of hydrolysis degree (HD) of PVA sample on polymer compatibility

The variation of the ratio from experimental to theoretical, represented by Figure 4 shows that PVA87/124 is more compatible with PSSNa than PVA98/

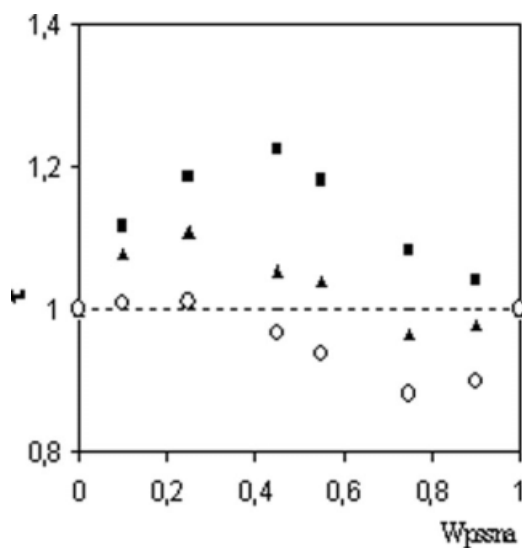


Figure 3 Ratio of experimental to theoretical reduced viscosity of PVA/PSSNa mixtures, as a function of PSSNa fraction, at $C = 2$ g/dL, for three PVA samples with different molecular weight. $\tau = (\eta_{sp}/C)_{m \cdot exp} / (\eta_{sp}/C)_{m \cdot theo}$. (■): PVA98/31/PSSNa mixture $M_w = 31,000$ g/mol. (▲): PVA98/85/PSSNa mixture, $M_w = 85,000$ – $146,000$ g/mol. (○): PVA98/124/PSSNa mixture, $124,000$ – $186,000$ g/mol.

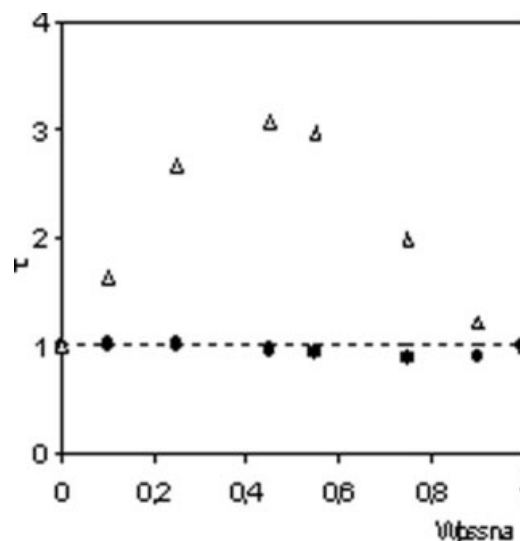


Figure 4 Ratio of experimental to theoretical reduced viscosity of PVA/PSSNa mixtures. ($\tau = (\eta_{sp}/C)_{m \cdot exp} / (\eta_{sp}/C)_{m \cdot theo}$) as a function of PSSNa fraction, at $C = 2$ g/dL, for two PVA samples with different hydrolysis degree. (△): PVA87/124/PSSNa mixture, HD = 87–89%. (●): PVA98/124/PSSNa mixture, HD = 98–99%.

124. This behavior was interpreted in the literature²⁶ as a consequence of the lower intrachain hydrogen bonding potential in the former PVA sample. The increase in acetate content in PVA87/124 reduces the intrachain interactions (low $K_{H, ass} = 0.76$) and improves the expansion of polymer coils (high $[\eta] = 1.02$ dL/g). More hydroxyl groups are then available as hydrogen bond-donors to develop more inter-chain interactions with the sulfonate acceptor group in PSSNa; and thus, the presence of a moderate amount of acetate groups in PVA appears to be important to obtain PVA/PSSNa compatibility. This result confirms the early hypothesis which assumed that the compatibility of PVA and PSSNa is due to the formation of hydrogen bonds between the hydroxyl groups of PVA and the sulfonate groups of PSSNa.²⁷

Influence of the acid or salt form of the polystyrene ionic derivative on polymer compatibility

As shown in Figure 5, the deviation of the ratio from experimental to theoretical reduced viscosity of PVA/PSSH is widely positive in comparison with that of PVA/PSSNa (slightly positive for $W_{PSSNa} < 0.6$ and negative afterwards). Of course, the difference between two curves is due to the nature of counter-ion of the polystyrene ionic derivative. The high PVA/PSSH compatibility is due to the protonated form of sulfonate groups. In this form, the PSSH would develop strong hydrogen bonds with the hydroxyl groups within PVA chains. However,

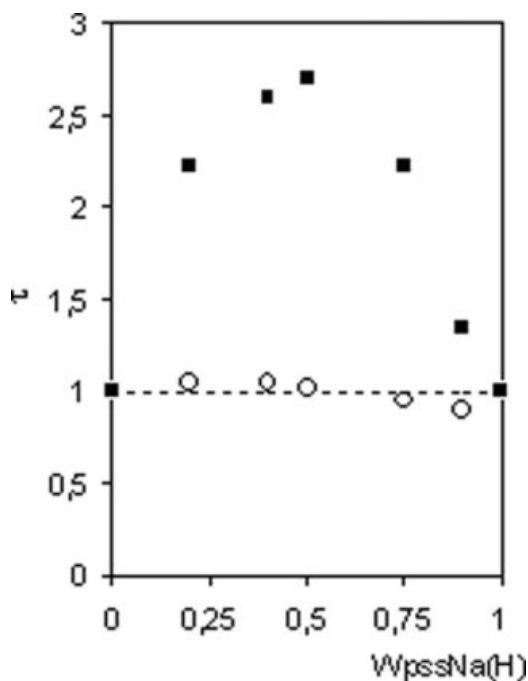


Figure 5 Ratio of experimental to theoretical reduced viscosity as a function of PSSNa fraction for PVA87/85/PSSNa and PVA87/85/PSSH mixtures at total concentration $C = 1\text{ g/dL}$. (○): PVA87/85/PSSNa curve. (■): PVA87/85/PSSH curve.

the highest compatibility between PVA and PSSH at about W_{PSSH} (0.5 and the existence of the largest amount of interacting groups (OH within PVA and $-\text{SO}_3\text{H}$ within PSSH) can be assigned to the weakness of intrachain hydrogen bonds along PVA chains. Therefore, the hydrogen bonding between the hydroxyl groups (strong donor) and the sulfonate group (hydrogen bond acceptor or Lewis base) promotes the compatibility between PVA and PSSNa. This result is consistent with that in the literature, concerning the high compatibility between poly Lewis-acid and poly Lewis-base. Indeed, homopolymers' compatibility is generally promoted by specific intermolecular interactions.²⁸ As showed in earlier studies, some compatible polymer blends, like PVA, polyvinylpyrrolidone,²⁹ PSSNa, and poly(acrylic acid),³⁰ were promoted by strong Lewis acid/Lewis base interactions. Polycarbonate and poly(butylene terephthalate) compatibility was also reported due to similar interactions.³¹ The free energy gain by interactions between the electron pair donors and acceptors must be high enough to drive the blend to compatibility. This would be the case of our system in a certain range of PSSNa in its blends with PVA, as the latter contains a high density of/Lewis acid group/OH, when compared with the density of the electron accepting groups in PSSNa.

Influence of the total polymer concentration on polymer compatibility

First, it may be noted that the reduced viscosity increased with the total polymer concentration from 1.85 dL/g for 1 g/dL to 5.4 dL/g for $C = 4\text{ g/dL}$.

Second, the results presented in Figure 6 mainly show that, with increasing polymer concentration, the formation of a compact interpolymer structure compared with a gel-like interpolymer structure is favored in the low WPSSNa composition region.

It is well known that the dissolution of PVA in water is mainly due to the hydration of PVA chain by hydrogen bonding between OH groups of polymer and water molecules. Experimentally, we observed that with the increase of the hydrolysis degree, the PVA dissolution required higher heating temperature to break-up stronger interactions in pure-PVA solid. In fact, PVA in solid state is a semi-crystalline polymer with two domains, well organized chain-domains or "crystallites" and random-chain domains which is "amorphous." Such a repartition may also exist in aqueous solution where the PVA chains form paracrystalline domains and amorphous domains as reported by Lewandowska et al.²⁰ The dissolution of PVA starts with the interactions between OH groups in amorphous zone and the water molecules. Then, the thermal weakening of hydrogen bonds in crystallites makes the

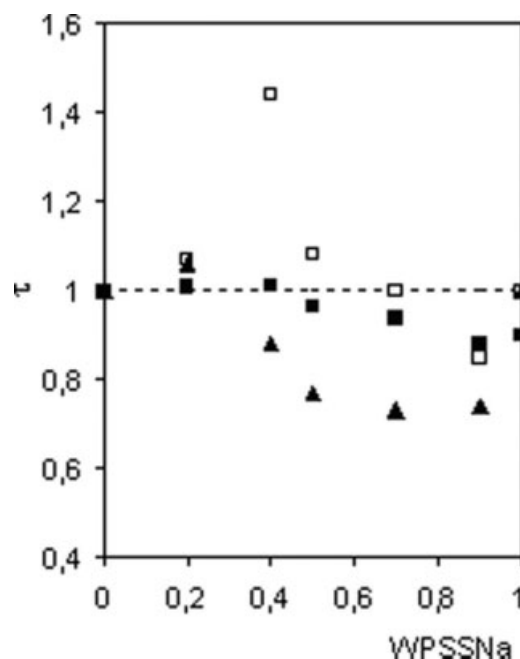


Figure 6 Ratio of experimental to theoretical reduced viscosity of PVA/PSSNa mixtures, as a function of PSSNa fraction at different total concentrations of PVA/PSSNa mixtures. (□) PVA98/124/PSSNa mixture, $C = 1\text{ g/dL}$. (■) PVA98/124/PSSNa mixture, $C = 2\text{ g/dL}$. (▲) PVA98/124/PSSNa mixture, $C = 4\text{ g/dL}$.

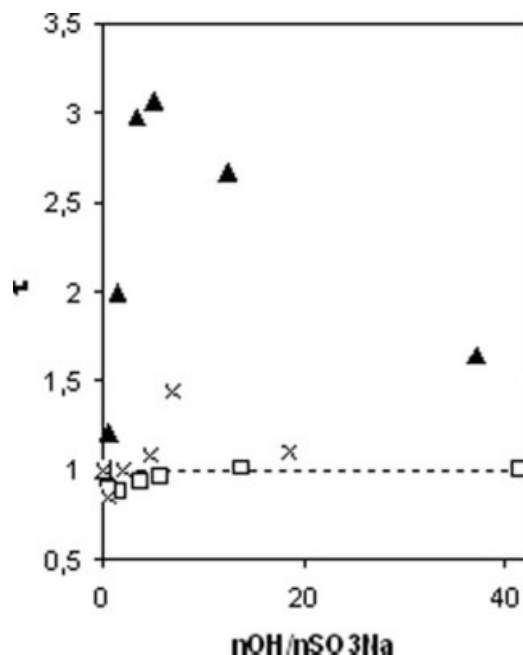


Figure 7 Ratio of experimental to theoretical reduced viscosity as a function of the ratio of hydroxyl groups to sulfonate in PVA/PSSNa mixtures at different total concentrations and hydrolysis degree of PVA. (▲) PVA87/124/PSSNa mixture, $C = 2$ g/dL. (□) PVA98/124/PSSNa mixture, $C = 2$ g/dL. (×) PVA98/124/PSSNa mixture, $C = 1$ g/dL.

interactions of water with OH groups in those crystallites possible, leading to a complete chain hydration.

With the increase in the polymer concentration, the chains tend to be more organized in a denser medium with chains closer in space, and thus less involved in intermolecular interactions with PSSNa. Moreover, a higher polymer compatibility at moderate polymer fraction ($W_{\text{PSSNa}} = 0.4$) means an OH groups playing the main role in intermolecular interactions. One may conclude that the intrachain interactions are dominating and the PVA chains tend to form paracrystalline domains at high PVA fractions, whereas the reverse situation occurs at low PVA fractions.

To understand the relationship between hydroxyl and sulfonate groups, the numbers of hydroxyl groups and sulfonate groups were calculated for each mixture from the mass fraction of each polymer in the mixtures taking into consideration the hydrolysis degree of the PVA sample. The weight of repeating unit used was 206 g/mol for PSSNa and 44 g/mol for PVA.

Figure 7 shows the variation of the ratio of experimental to theoretical reduced viscosity as a function of the ratio of total hydroxyl to sulfonate groups.

The calculations of the number of hydroxyl and of sulfonate groups within polymer chains makes pos-

sible the evaluation of the groups' number involved into polymer interactions mainly if the homo-interactions are neglected. The higher polymer-polymer compatibility observed at low hydrolysis degree, the lower the total polymer concentration are mainly governed by the content in hydroxyl groups within PVA. At high concentration and hydrolysis degree, these groups are preferentially involved in intramolecular interactions (homo-interactions) along PVA chains.

As a conclusion, it seems that the highest ratio, (i.e., the highest intermolecular interactions between PVA and PSSNa which corresponds to the best polymer-polymer compatibility), is observed when the total number of hydroxyl groups is 8–10 times that of sulfonate groups. Nevertheless, it must be noted that the hydroxyl groups within PVA are not totally available for PVA-PSSNa interactions. One part of these groups would be involved in the paracrystalline domains especially at a high hydrolysis degree and concentration.

CONCLUSIONS

The viscosity results showed that the associative interactions between PVA and PSSNa were improved with the decrease of hydrolysis degree (HD) of PVA and the decrease of its molecular weight (M_w). The good interpolymer association between PVA and PSSNa was attributed to the establishment of intermolecular hydrogen bonds between the PVA hydroxyl groups and the PSSNa sulfonate groups as previously proven by the total compatibility of PVA and PSSNa.

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