Solvent Composition and Rheology of Starch–DMSO–Water Solutions

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ABSTRACT: The rheology of starch–DMSO–water solutions was studied as a function of water content and temperature. A correlation between flow regime, temperature, and water content was presented so as to characterize amylose conformation change in a novel way. Rheological behavior was characterized using an empirical equation to classify fluids under study as Newtonian, pseudoplastic, or dilatant. The temperature effect was analyzed through the determination of the apparent activation energy and preexponential constant. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1285–1290, 2001

Key words: starch; amylose; helix-coil transition; rheology; Arrhenius equation

INTRODUCTION

Starch is one of the most abundant sources of energy for life. This biological material, which consists of a mixture of amylose and amylopectin and whose composition depends on the vegetable source, has mainly been used in the food industry, although one can find in the literature radically different alternatives of use for this versatile biomaterial: from the substitution of albumin in plasma exchange,[1] to flocculation in wastewater treatment as well as mineral beneficiation,[2] to the reinforcement of thermoplastics.[3]

Specifically regarding its use in the food industry, chiefly as a rheological modifier, the process of gelatinization is one of the most important applications of this material in the form of aqueous dispersions.[4] Because amylose is a very

weakly branched polymer of D-glucose, of which amylopectin is its branched analog (the latter being much more soluble in water than the former), it has been shown that starch granular structure and morphology influence its rheological behavior through particle–particle interactions, playing a very important role in gelatinization.[5]

Regarding the rheology of biopolymer solutions, Flory was one of the pioneers in the study of helix-to-coil transitions in natural polymers, and found, in the specific case of collagen, that the process could be characterized through viscometry and polarimetry.[6] This sort of conformational transition has been characterized for xanthan,[7] carragens,[8] and many other natural polymers.[9] Nuessli et al. showed that decanal and (−)fenchone led to the formation of α-helices and induced the gelation of low-concentration starch systems.[10]

In the case of starch, helix–coil transition in amylose is highly involved in the process of gelation,[11] the mathematical description of which is quite complex, even if one works with the simulation of these macromolecules in vacuum.[12] When in solution, new variables are added to the

problem: the competition between polymer–polymer and polymer–solvent interactions becomes increasingly important. As Cheetham et al. showed in the case of solutions of amylose in DMSO/water mixtures, these conformational transitions are characterized as a function of solvent composition using specific rotation, limiting viscosity number, and ^{13}C–NMR chemical shifts.[13] These investigators also found, in accordance with what was previously widely reported in the literature, that amylose helix-to-coil conformational transition occurs at a DMSO : water ratio of 67 : 33. For lower contents of water, conformation is predominantly helical; for higher water contents the helical conformation is increasingly destroyed in favor of the random-coiled conformation.

The aim of this work is to relate changes in the rheology of starch–DMSO–water solutions to already mentioned changes in conformation of amylose. To do this, we will show that experimental data (τ, the shear stress, and $\dot{\gamma}$, the shear rate) obtained from experiments performed in a rheometer, can be adjusted to the following empirical equation:

$$\tau = \eta \dot{\gamma} + \alpha \dot{\gamma}^2 \tag{1}$$

where η is the Newtonian viscosity of the fluid (as $\dot{\gamma} \to 0$) and α is a constant that indicates the type of fluid with which we are dealing, according to the following values:

$$\begin{cases} \alpha < 0 & \text{pseudoplastic fluid} \\ \alpha = 0 & \text{Newtonian fluid} \\ \alpha > 0 & \text{dilatant fluid} \end{cases} \tag{2}$$

We will also show that the apparent energy of activation E_A can be obtained through the fitting of η, previously obtained from eq. (1), to the temperature, according to eq. (3)[14]:

$$\ln \eta = \ln \eta_0 + \frac{E_A}{RT} \tag{3}$$

Finally, it will be shown that the values of α, E_A, and the preexponential factor η_0 can be used to characterize the conformational transition of the amylose present in starch.

EXPERIMENTAL

A given solution was prepared by heating potato starch (Reagen, A.C.S. grade, weighed on a dry basis), water, and DMSO (Reagen, P.A., Brazil) at a given DMSO/water mass ratio under effective stirring at 80°C for 30 min. Stirring was continued for 24 h, at room temperature, before the analysis was carried out. For each DMSO/water weight composition, viscosity was monitored for 5 days. A constant value indicated that complete solubilization was achieved. All solutions were filtered, using a glass porous filter (#G4), prior to experiments in the rheometer. Mass/volume concentration of the solutions was 0.045 g/mL. In a previous work we showed that these starch–DMSO–water solutions had a critical concentration c^*, related to a transition from the dilute regime to the semidilute regime,[15] of 0.03 g/mL,[16] so that we assumed that we worked with solutions that were in the semidilute regime.

Viscosity measurements were carried out in a cone-plate–type Brookfield rheometer (Model DV-III), using spindle CP41. All measurements were performed within a torque range from 10 to 90% of its full scale. The experimental error involved in the torque measurement was 1% of its full scale, regardless of the measured torque, which was given in terms of percentage of full scale ($\%_{fs}$). Because shear stress is directly proportional to torque, experimental errors were calculated according to eq. (4):

$$\frac{\Delta \tau}{\tau} = \frac{\Delta \%_{fs}}{\%_{fs}} = \frac{1}{\%_{fs}} \tag{4}$$

RESULTS AND DISCUSSION

Figure 1 shows data obtained from the experiments performed in the rheometer. At first sight, one cannot see a great difference between the curves, apart from a slight tendency to a pseudoplastic behavior at higher temperatures and lower water contents. However, when plotting α as a function of temperature and water content, as shown in Figure 2, a more comprehensive observation can be made: it seems that at lower temperatures, and water contents up to 30%, the solutions behave as slightly dilatant fluids. One can find in the literature that there is a critical shear rate ($\dot{\gamma}_c$) above which there is the development of physical crosslinks in starch–DMSO–water solutions (DMSO : water = 90 : 10), which are in the semidilute flow regime (at 25°C this value was around 50 s^{-1} for a particular starch solu-
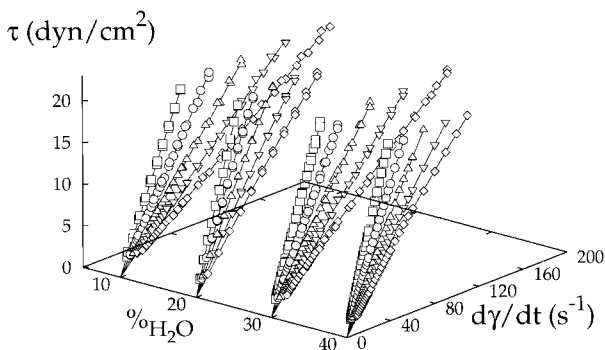
Figure 1   Shear stress versus shear rate for starch–DMSO–water solutions with different water contents: 5°C (squares), 15°C (circles), 25°C (up-triangles), 35°C (down-triangles), 45°C (diamonds). The continuous lines represent eq. (1).

tion).[17] The same author found that when working with two types of starch, waxy maze and normal maze, the former provided this sort of shear-induced physical crosslinking, in contrast with the latter, which was correlated to a possible higher occurrence of helically structured amylose in normal maze starch.

We observed a completely different behavior in our study: at DMSO : water ratios higher than 70 : 30 (where we do have amylose predominantly in its helical form) the solutions had a discrete dilatant behavior; at DMSO : water ratios lower than 70 : 30 (amylose in its random coil conformation) we had a clearly pseudoplastic behavior. We thus reasoned that, perhaps, what was thought to be shear-induced physical crosslinking, in our case was an effect in great part the result of solvent–solvent interactions, which would have influence in the type of flow experienced by the fluid: laminar or turbulent.[18] In laminar flow we have the fluid represented by layers of infinitesimal thicknesses; viscosity is related to shear between different layers, without mass transfer between them. If we continue to increase the shear rate, we get into the region of turbulent flow: energy is also dissipated in the transfer of mass from what should be one layer to what should be another one. If one has in mind that the Newtonian viscosity coefficient is also correlated to the energy dissipation rate per volume ($\dot{\omega}$) as[19]:

$$\omega = \eta \dot{\gamma}^2 \qquad (6)$$

one could hypothesize that perhaps what was thought to be dilatant fluid behavior, caused by

shear-induced physical crosslinking, could simply be the development of turbulence, which would dissipate more energy, resulting in an overestimated apparent viscosity. If this is true, one should observe the same behavior for the solvent system without any polymer. In Figure 3, which shows the shear rate–shear stress relationship for a 90 : 10 DMSO : water system, the same sort of dilatant behavior is shown. An interesting point is that, as we increased the water content, this effect decreased: one hypothesis is that DMSO acts as a hydrogen bond breaker,[20] making it easier to disorganize a layer, to transfer solvent molecules to another one. Now analyzing macromolecules and solvent molecules as a whole (as we have the polymer molecules in a helical form), it is observed that they occupy a smaller volume: solvent–solvent interactions are privileged, leading to a macroscopically classified turbulent flow; as we have randomly coiled polymer molecules within the solution, they occupy a bigger volume, leading to an increase in the probability of polymer–polymer interactions, resulting in a pseudoplastic behavior.

E_A and $\ln \eta_0$ were obtained for different solutions through plots of the logarithm of viscosity
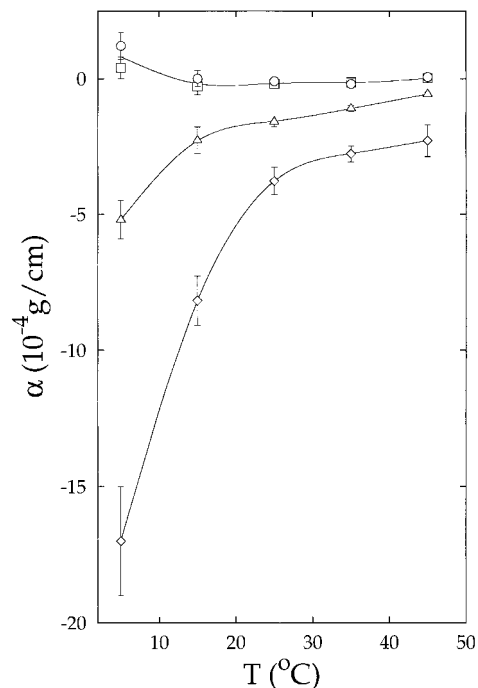

Figure 2 α as a function of temperature for starch–DMSO–water solutions with different water contents: 10% (squares), 20% (circles), 30% (triangles), 40% (diamonds).
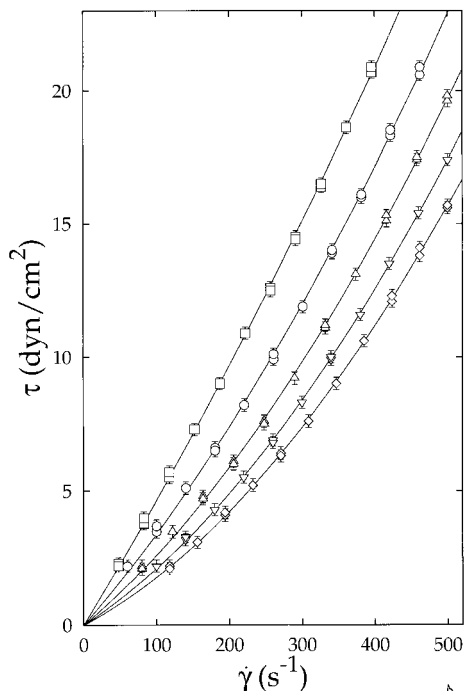
Figure 3 Shear stress as a function of shear rate for DMSO : water = 90 : 10. 5°C (squares), 15°C (circles), 25°C (up-triangles), 35°C (down-triangles), 45°C (diamonds).
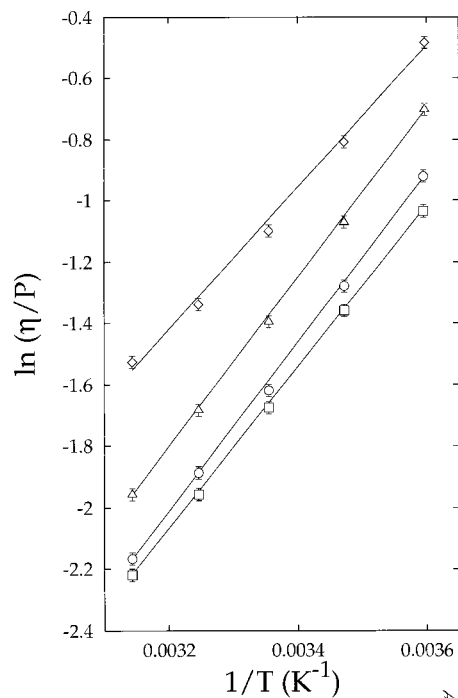

Figure 4 Logarithm of viscosity as a function of reciprocal absolute temperature for starch–DMSO–water solutions with different water contents: 10% (squares), 20% (circles), 30% (triangles), 40% (diamonds).

versus reciprocal absolute temperature, as shown in Figure 4. Figure 5, which shows the values of E_A as a function of water content, can now be used to strengthen our analysis. When in the dilute regime, at a constant temperature, viscosity follows the well-known Flory–Huggins equation[21]:

$$\frac{\eta_{sp}}{c} = \frac{\eta(c) - \eta(0)}{c\eta(0)} = \frac{\eta_0(c)e^{-E_A(c)/RT} - \eta_0(0)e^{-E_A(0)/RT}}{c\eta_0(0)e^{-E_A(0)/RT}}$$

$$= [\eta] - k_H[\eta]^2 c \quad (7)$$

where η_{sp} is the specific viscosity, c is the concentration, $[\eta]$ is the intrinsic viscosity, and k_H is the Huggins constant. In a previous work we showed that substituting eq. (7) into eq. (3) we have that, for solutions in the dilute regime[16]:

$$\eta_0(c) = [1 + [\eta]c + k_H([\eta]c)^2]\eta_0$$

$$E_A(c) = E_A(0) \quad (8)$$

We also showed that in the semidilute regime (which is the case of our solutions), E_A continuously rises with concentration (or, more exactly,
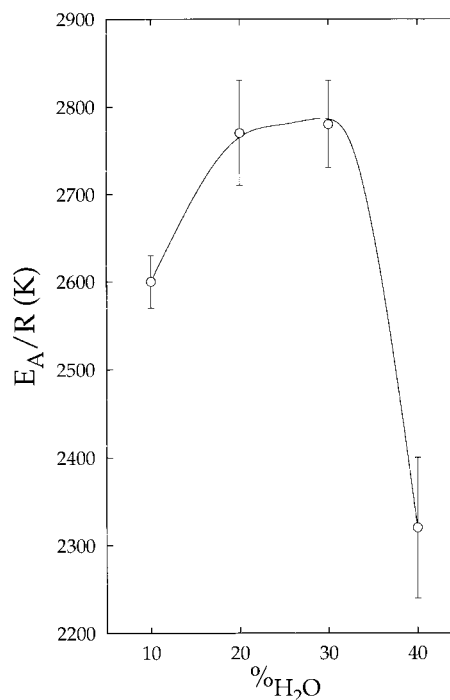

Figure 5 E_A/R as a function of water content for starch–DMSO–water solutions.
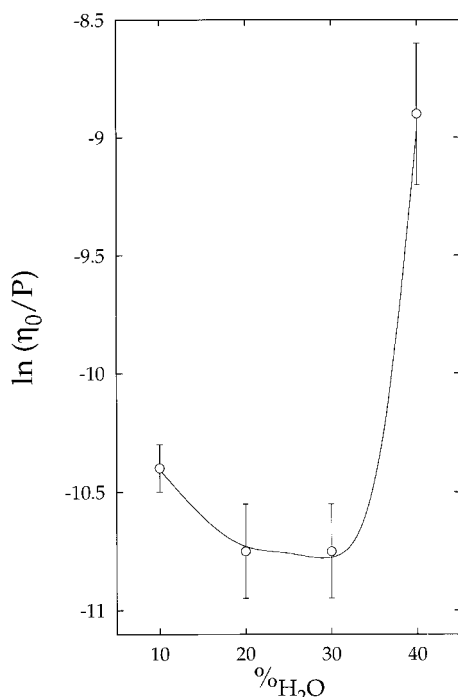
Figure 6 Ln η_0 as a function of water content for starch–DMSO–water solutions.

with occupied volume by macromolecules). So, if there is a change in conformation in the amylose from coil to helix, the decrease in occupied volume would be characterized by a sharp decrease in the apparent energy of activation.

The same sort of behavior is seen in Figure 6, which depicts the relationship between solution water content and the logarithm of the preexponential constant ln η_0. There is a sharp increase in the preexponential factor at a water content, again, between 30 and 40%. Gupta and Yaseen have determined these constants for different dilute solutions of PVC in cyclohexane : xylene blends and related them to $\Delta S^{\ddagger}$, the flow activation entropy[14]:

$$\eta_0 = \frac{N_0 h}{\bar{V}} \, e^{-\Delta S^{\ddagger}/R} \tag{9}$$

where N_0 is the Avogrado number, h is the Planck constant, R is the gas constant, and $\bar{V}$ is the liquid molar volume. The authors assumed that poorer solvent would increase the stiffness of the polymer chains, thus increasing $\Delta S^{\ddagger}$; as a consequence, η_0 would decrease. In our case, the opposite effect was observed: as amylose chains as-

sumed helical conformation, η_0 increased. If we bear in mind that, when in this conformation, the helix is closely packed, there is also the hypothesis that part of the activation entropy related to changes in conformation could be zero, in that amylose would flow as a whole without changing its conformation; then we would have a smaller $\Delta S^{\ddagger}$, resulting in a higher value of η_0.

CONCLUSIONS

The change in amylose conformation could be characterized through the calculation of the apparent energy of activation and preexponential constant from the application of the Arrhenius equation to measurements of viscosity at different temperatures. A possible change in flow from laminar to turbulent was also considered as another indication.

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