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Thickening Mechanism of Associative Polymers

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Summary: Steady state viscosity and viscoelasticity of HMHEC solutions were studied. Viscosity increases with concentration due to a reinforcement of the micellar network. High shear rate viscosities are independent of temperature. Two relaxation processes were observed, the long one related to the lifetime of the hydrophobic junction and the short related to rapid Rouse-like relaxations of the free chains. When SDS is added, mixed micelles form that reinforce the network up to an optimum [SDS]/[HMHEC] ratio. Above this ratio, the micelles in excess isolate the polymer chains, the long relaxation process disappears and Rouse-like relaxations occur, corresponding to rapid movements of free chains.

Keywords: rheology; viscoelastic properties; HMHEC; associative polymers; thickener

Introduction

When a latex paint is formulated, a careful adjustment of the final rheology is needed. The high-shear-rate viscosity must be high enough to give sufficient film build and hiding but low enough to avoid extreme brush or roller drag. Viscosity at low shear rates must be high enough to prevent settling during storage and sagging after application, but has to allow the leveling of the film. It implies that a shear-thinning behavior is generally required. Latex coatings require the addition of thickeners to achieve the proper rheology. Water-soluble polymers modified through the addition of hydrophobic groups are used as viscosity modifiers in a variety of water-borne technologies including paints, inks, and cosmetics[1-5]. These copolymers typically consist of a hydrophilic backbone with a small number of hydrophobic groups either randomly distributed along the polymer chain or present as terminal groups. These polymers are termed associating polymers (AP) because they thicken the aqueous medium due to the aggregation of hydrophobes into surfactant-like micelles. The hydrophobes of the same chain can be joined to the same micelle, forming a loop[6], but they can also be joined to different micelles. If micelles are formed by hydrophobes of different molecules and molecules have hydrophobes in different micelles, hydrophilic backbones act as bridges between micelles. Then a three-dimensional network is extended and viscoelastic properties of the solution are enhanced. A full formulated

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paint has a big quantity of components that can interact with the thickener and modify the rheology. So, for a good understanding of the thickening mechanism it is necessary to study simpler systems, as water solutions of APs. The effect of the addition of other components, as surfactants, can be then studied.

APs commonly used are hydrophobically modified ethoxylated urethanes (HEUR), hydrophobically modified cellulose derivatives, for example the hydrophobically modified hydroxyethyl cellulose (HMHEC), and hydrophobically modified alkali swellable polymers (HASE). Their water solutions have been described to be shear-thinning and viscoelastic[7-11]. Viscoelasticity of HEURs end-capped with alkyl groups has been widely studied. A single Maxwell model can describe linear viscoelasticity of their solutions. The relaxation time has been identified as the disengagement time of a hydrophobe from the micelle[8]. Unlike what happens with end-capped HEURs, a single Maxwell model cannot describe HMHEC linear viscoelastic behavior, and a generalized Maxwell model with a relaxation time spectra has to be used to fit viscoelasticity[12], through the equations

$$G' = \int_{-\infty}^{+\infty} H(\ln \lambda) \frac{(\omega\lambda)^2}{1+(\omega\lambda)^2} d\ln\lambda \tag{1}$$

$$G'' = \int_{-\infty}^{+\infty} H(\ln \lambda) \frac{\omega\lambda}{1+(\omega\lambda)^2} d\ln\lambda \tag{2}$$

where G’ and G” are storage and loss moduli, ω is the frequency and $H(\ln\lambda)$ is the spectra of relaxation times λ.

Rheology of AP solutions can be drastically modified through the addition of surfactants, because they interact with the hydrophobic groups of the polymer. This effect is strongly dependent upon the ratio surfactant/AP[13]. In some cases there is a range of surfactant concentrations where a phase separation occurs into a non-viscous supernatant and a viscoelastic hydrogel precipitate[4,14-15]. In other cases, an increase on viscoelasticity is observed up to an optimum surfactant concentration, followed by a hard decrease at higher surfactant concentrations[4-5,15-16]. This behavior has been attributed to the formation of surfactant-polymer mixed micelles. As a result, a higher number density of micelles exists and they are closer together. This permits the conversion of looping chains to bridging chains in such a way that the network reinforces and viscoelasticity increases, up to an optimum surfactant concentration. Over this concentration, the increased number of surfactant micelles progressively lowers the probability of more than one hydrophobe from different polymer chains in a given micelle, in such a way that bridges break, micelles become isolated and the network dissipates. Once the network is disintegrated the AP responds to surfactant in a manner essentially identical to that of a water-soluble polymer.

In this communication, viscoelasticity and shear-thinning behavior of HMHEC water solutions are presented and related with the thickening mechanism. Then, the influence of the addition of an anionic surfactant, the sodium dodecyl sulfate (SDS), is studied.

Materials and methods

HMHEC (molecular weight $M_W = 560000$; hydrophobes = hexadecyl) and SDS were supplied by Aldrich. Solutions were prepared with Millipore MilliQ water. Oscillatory measurements were carried out with a Haake RS100 Rheometer in the control shear stress mode. Previous stress sweep were developed to find the linear range. Shear-thinning experiments were performed with a RS150 Rheometer in the controlled shear rate mode. Various double cone and cone and plate sensors were used depending on the viscosity range of the samples.

Results and discussion

HMHEC water solutions

Figures 1 a) and b) show the steady state viscosity of HMHEC solutions at several concentrations and temperatures. A shear-thinning behavior is observed for all cases, except at the lower concentration, were a slight shear-thickening is observed, that is attributed to loop-to-bridge shear-induced transitions as molecules elongate under shear[9]. At higher concentrations shear-thickening is not observed probably because when micelles are close enough the number of bridges is not limited by the distance between them and elongation of chains does not favors the formation of new bridges.

Figure 1 a) shows that concentration increases viscosity in all the range of shear rates, as expected, since a higher number of micelle-like aggregates favors the formation of bridges and enhances the network. It can be observed in Figure 2 b) that viscosity at low shear rates decreases with temperature T, and tends to be independent of T at high shear rates. While at low shear -in the Newtonian range- the association structure and, as a consequence, the viscosity, depends on Brownian motion and, consequently, on temperature, at higher shear rates Brownian motion can be neglected in front of shear. Therefore, viscosity tends to be independent of temperature.

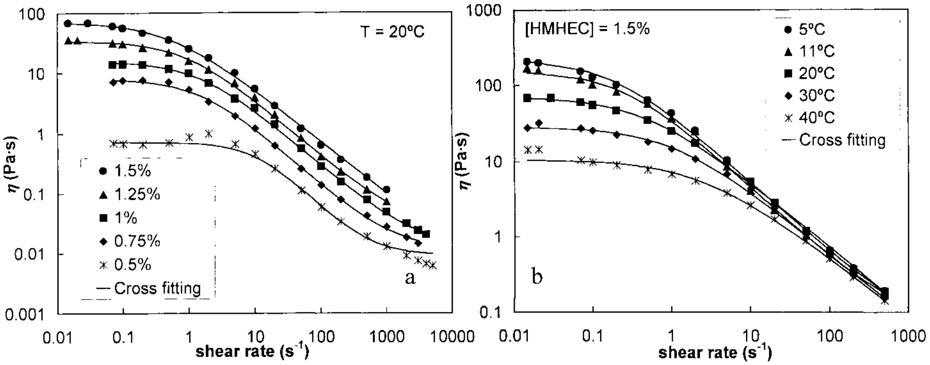

Figure 1. Steady state curves of HMHEC aqueous solutions a) at T = 20°C and several concentrations; b) at [HMHEC] = 1.5% and several temperatures.

Experimental data shown in Figure 1 have been fitted through the Cross model (Equation 3), where η_0 and η_∞ are the low and high shear viscosities, subindex c indicates the shear rate at which equilibrium viscosity is in the middle of η_0 and η_∞ and the exponent m is around 0.9. As it can be seen, the fitting is quite good, except at 0.5%, because the shear-thickening behavior cannot be described by the Cross model.

$$\eta(\dot{\gamma}) = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1+\left(\frac{\dot{\gamma}}{\dot{\gamma}_c}\right)^m} \qquad (3)$$

Viscoelasticity of HMHEC solutions cannot be fitted through a single Maxwell model. Figure 4 shows that two differentiated relaxation processes occur, one at intermediate (long relaxation process) and the other at high frequencies (short relaxation process). It can be seen in this Figure that oscillatory results can be fitted through the generalized Maxwell model if $H(ln\lambda)$ is supposed to have the shape of a logarithmic distribution around a mean relaxation time[12], which is identified with the inverse of the exit rate of an hydrophobe from its micelle[8]. This corresponds to the long relaxation process. An addend which is proportional to the frequency has to be used in Equation 2 to fit loss modulus at the higher frequencies. It has been related to rapid Rouse-like relaxations of the free chains[12].

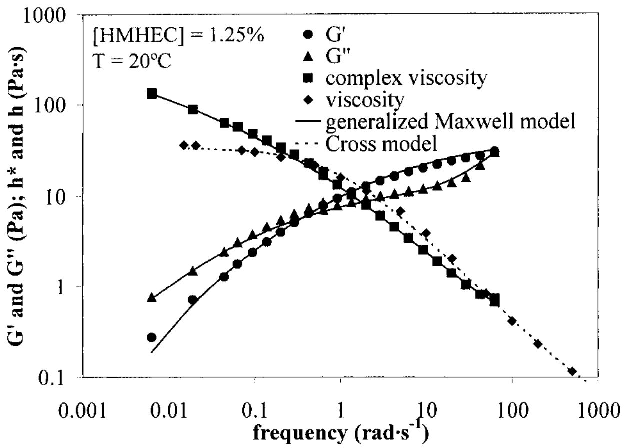

Figure 2. Frequency sweep and steady state curves of 1.5% HMHEC aqueous solution at T = 20°C.

The steady-shear viscosity has been added to the figure for comparison with the oscillatory complex viscosity, η^*. It can be seen that the Cox-Mertz rule, that describes the case in which the magnitude of the complex viscosity and the steady shear viscosity superimpose when shown in the same graph, is not satisfied, a common occurrence for associating polymers[17]. Moreover, zero shear and zero frequency viscosities do not coincide. Higher differences are obtained at lower concentrations.

HMHEC-SDS water solutions

When SDS, an anionic surfactant, is added to the solution, phase separation occurs in a range of [SDS]/[HMHEC] ratio at HMHEC concentrations below 1.2%. Above this concentration, a high enhancement of viscoelasticity functions is observed for the same ratio of surfactant/AP. Addition of more SDS above this optimum ratio produces the disappearance of the two phases existing for HMHEC concentrations below 1.2% and a progressive decrease of viscoelasticity functions for all the cases. Figure 3 shows the increase of the complex viscosity curve η^* at a concentration of SDS that corresponds to the optimum ratio, and the subsequent decrease when more surfactant is added, for a solution of 1.25% HMHEC.

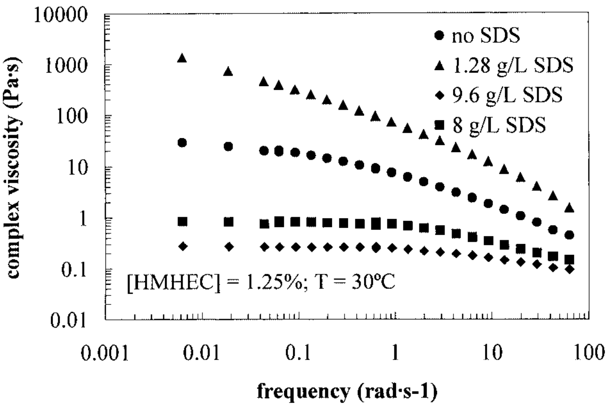

Figure 3. complex viscosity curves η* for HMHEC = 1.25% without and with several quantities of SDS.

Zero frequency viscosity has been calculated through extrapolation of empirical fittings of the oscillatory viscosity, for solutions where no phase separation occurs. Results are shown in Figure 4 as the reduced viscosity $\eta_0/\eta_{0(\text{no SDS})}$ *vs.* [SDS]/[HMHEC] for several concentrations of HMHEC. It can be seen that curves superimpose independently of the concentration of the polymer. The maximum is reached around [SDS]/[HMHEC] = 0.08.

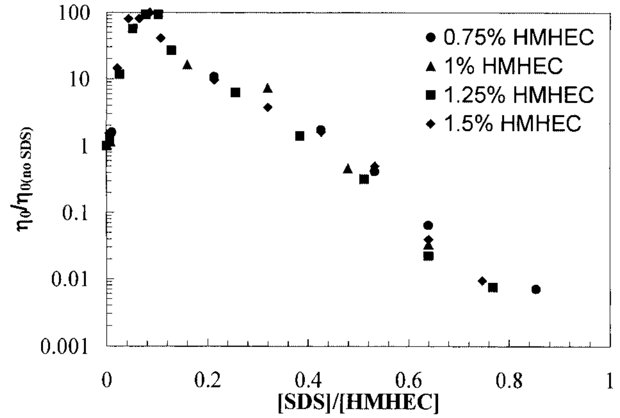

Figure 4. Low frequency reduced viscosity $\eta_0/\eta_{0\ (no\ SDS)}$ *vs.* [SDS] / [HMHEC] ratio for all concentrations of HMHEC tested.

It is well established[8-9,18] that associating polymers thicken the medium because of hydrophobic associations into micelle-like aggregates that are bridged through hydrophilic backbones forming a three-dimensional network. Hydrophobic groups of the same molecule can associate to the same micelle, forming a loop that does not participate in the network, or can be joined to different neighboring micelles, bridging them and enhancing the network. At relatively low concentration of micelles, distances between them are long and for this reason few bridges can exist, and many hydrophobic groups are forming loops. When SDS is added, it associates with the hydrophobes of the polymer and forms mixed micelles. The formation of mixed micelles releases hydrophobes to form additional micelles and, as a result, the average separation between them decreases and looping chains can change into bridging ones. This contributes to the enhancement of the network and the increase of viscoelasticity. The phase separation observed for HMHEC solutions below 1.2% is attributed to the strong enhancement of interpolymer association. The big forces between micelles tend to bring them close, and then the more diluted solutions expel the excess of water into a supernatant fluid. When HMHEC concentration is increased, the volume of the watery supernatant fluid progressively decreases, up to 1.2% HMHEC, where there is no more water excess.

Above the optimum ratio, an increasing amount of surfactant molecules causes the formation of more mixed micelles in which the average number of involved polymer side chains progressively decreases, and as a result the number of bridges between them diminishes, until a situation is reached at which every side chain is covered by its own SDS micelle. Then, the solutions respond in a manner essentially identical to that of a water-soluble polymer. Figure 5 shows that at the higher [SDS]/[HMHEC] ratios tested the long relaxation process has disappeared, indicating that no more interpolymer associations occur. Storage and loss modulus, G' and G", superimpose at high frequencies with a slope of 0.5 or run parallel with a slope around 2/3. The shape of this curves indicates that solutions relax through a Rouse-like[19] or a Zimm-like[20] model, corresponding to short relaxation processes related to rapid movements of free polymer chains into the solvent.

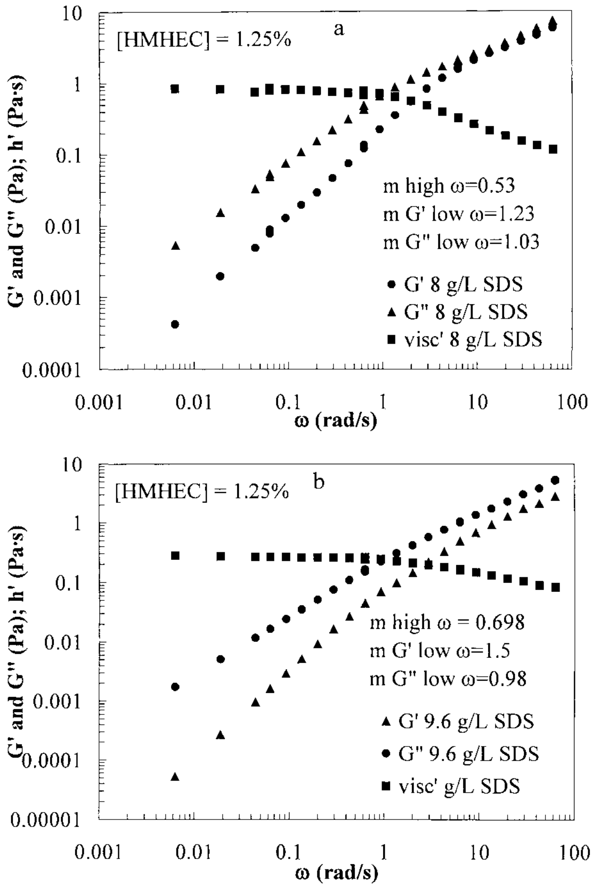

Figure 5. Frequency sweeps of HMHEC-SDS water solutions at high ratios of [SDS]/[HMHEC].

Conclusions

HMHEC water solutions present a shear-thinning behavior that can be fitted to the Cross model. The steady state viscosity increases with the concentration in all the range of shear rates, because of the reinforcement of the micellar three-dimensional network. Only the viscosity at low and intermediate shear rates is affected by temperature, decreasing with it due to an increase of Brownian motion. At higher shear rates, Brownian motion can be neglected compared with the effect of shear and temperature does not affect viscosity.

These solutions present two relaxation processes. The long one can be fitted through the generalized Maxwell model if the spectra of relaxation times is supposed to have the shape of a logarithmic distribution of relaxation times around a mean relaxation time that can be identified with the exit rate of an hydrophobe from its micelle.

When SDS is added, a phase separation or an increasing of viscoelastic parameters occur up to an optimum [SDS]/[HMHEC] ratio, due to the enhancement of interactions produced by the formation of mixed micelles. At higher ratios, the excess of micelles produces the breakdown of the network because micelles become progressively poorer in HMHEC hydrophobes, up to the total isolation of polymer chains, when each hydrophobic group is joined to a different SDS micelle. Then, HMHEC molecules can move freely around the solution, in such a way that Rouse and Zimm behaviors are observed.

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