

Rheology of complex fluids: associating polymers

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The rheological behavior of an associating polymer, a hydrophobically-modified alkali-soluble (HASE) copolymer, is presented. The molecular constitution of the polymer is similar to materials currently employed as rheology modifiers in water-borne coatings. Usually, rheology modifiers of the HASE type comprises blocks of monomers which include acrylic (or methacrylic) acid, acrylates (ethyl or butyl acrylate) and a proportion of an ethoxylate macromonomer attached to the polymeric backbone. Rheological tests include steady simple shear and small-amplitude oscillatory shear flow. In simple shear, evidences of shear-induced structuring are manifested as a shear-thickening region in the viscosity-shear-rate curve. A deviation from a Maxwell-like behavior in oscillatory shear indicates that the network dynamics of the polymer are no longer represented by a single characteristic time, in accordance with a broadening of the relaxation spectrum. This behavior arises from both hydrophobic associations and topological entanglements.

Keywords: Associating polymers; rheology modifiers; viscoelastic properties

En este trabajo se presenta el comportamiento reológico de un copolímero asociativo hidrofólicamente modificado soluble en medio alcalino. La constitución molecular del polímero es similar a la que tienen los materiales comúnmente utilizados como modificadores reológicos en recubrimientos base agua. Los modificadores reológicos de este tipo están formados por bloques de monómeros entre los que se incluyen al ácido acrílico (o metacrílico), acrilatos (etil o butilacrilato) y una determinada proporción de un macromonómero etoxilado enlazado a la cadena principal del polímero. Las pruebas reológicas realizadas incluyen flujo cortante simple y flujo oscilatorio de pequeña magnitud. En flujo cortante simple se produce una estructuración inducida por el mismo flujo la cual se manifiesta como un aumento de la viscosidad cuando la velocidad de corte se incrementa. Las desviaciones observadas del comportamiento Maxwelliano bajo flujo cortante oscilatorio indican que la dinámica de la red polimérica no puede ser representada por un solo tiempo característico, lo que manifiesta un ensanchamiento en el espectro de relajación. Este comportamiento se origina del doble efecto de las asociaciones hidrofólicas y de los entrelazamientos topológicos del polímero.

Descriptores: Polímeros asociativos; modificadores reológicos; propiedades viscoelásticas

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1. Introduction

Traditional latex coatings, such as vinyl acrylic emulsion paints, make use of a cellulosic rheology modifier, the hydroxyethyl cellulose (HEC) that is sensitive to bacterial activity. To improve paint rheology control and to avoid degradation by biological activity, new rheology modifiers have been synthesized during the last decade. Most of the rheology modifiers are associative polymers which contain a proportion of hydrophobic groups placed either randomly or in blocks along the polymer backbone or as terminal moieties. In aqueous solutions, the structuring of water essentially forces the hydrophobic groups together into clusters. The intermolecular or intramolecular clustering of hydrophobes results in the formation of a pseudo polymeric network, in which the hydrophobic clusters are the crosslink junctions. The macromolecular hydrophobic moieties may also associate with other hydrophobic surfaces such as latex particles. Thus, the over-

all association produces an increase in the viscosity of the latex system.

The latex-polymer system possesses high viscosity at low shear conditions because of the network structure. As the shear rate is increased, the hydrophobes detach from the latex particles reducing the network connectivity and decreasing the coating viscosity during the application. This mechanism produces shear-thinning. After coating application and removal of the shear field, there is a slow re-adsorption of the polymer hydrophobes onto the surfaces of the latex particles. This leads to improved flow and leveling for the latex systems thickened with associative polymers [1].

The purpose of the present investigation is to illustrate the rheological properties of aqueous solutions of associative polymers representative of current commercial products.

Interpretation of data is undertaken by comparison with theories which relate the microscopic lifetime of a junction formed by the hydrophobic groups of the polymer and the macroscopic stress relaxation time.

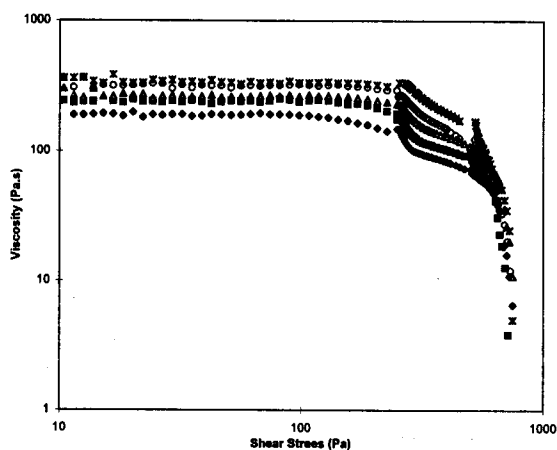


FIGURE 1. Variation of the shear viscosity of a HASE-type polymer (EP-1332) with the shear stress for five temperatures: (X) 5°C, (O) 10°C, (Δ) 15°C, (\blacksquare) 20°C, (\blacklozenge) 25°C. Polymer concentration in water is 2.5 wt%.

2. Experimental part

The polymers used were two HASE-type modifiers (Acrysol 935 from Rhom and Hass and EP-1332 from National Starch) which presented a plateau viscosity of the aqueous solution at pH = 9. The polymer was dissolved at several concentrations around 2 wt% and the pH level was adjusted using sodium hydroxide. Rheological tests were conducted in a Carri-med controlled stress rheometer CSL-500 with the cone and plate fixture, using the flow, creep and oscillatory modes.

3. Results and discussion

Figure 1 illustrates data of one of the HASE polymers, at 2.5wt% concentration, depicting the variation of the steady shear viscosity as a function of the applied shear stress for five different temperatures (5, 10, 15, 20 and 25°C). A region of almost constant viscosity is observed for stresses lower than approximately 100 Pa. For stresses above a critical value, an abrupt decrease in viscosity is observed. This drop in viscosity is manifested as a marked discontinuity in the viscosity-shear rate curve. In this region, the viscosity is found to decrease as a function of inverse shear rate. Note that the critical stress increases for the lower temperatures.

A weak shear thickening, manifested as a small increase in viscosity with stress, is also observed. This behavior has been attributed to shear-induced structuring through hydrophobic associations [2]. Indeed, a possible mechanism suggests that the increase in viscosity results from the formation of intermolecular associations in flow at the expense of intramolecular interactions present in the absence of an externally imposed deformation. Intermolecular associations of hydrophobic

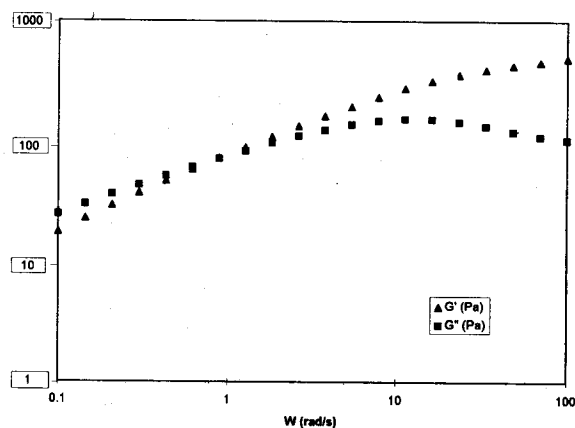


FIGURE 2. Variation of the elastic modulus (G') and viscous (or loss) modulus (G'') with frequency for the same system of Fig. 1. Temperature is 5°C.

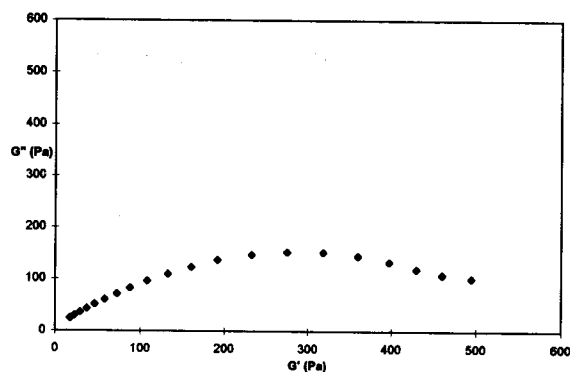


FIGURE 3. Cole-Cole plot (G'' versus G') of the same system of Fig. 1. Temperature is 5°C.

hobes promote an increased structuring manifested as higher resistance to flow. On the other hand, in the high shear regime, the imposed stress produces a depletion of the association network leading to pronounced shear thinning.

The frequency dependence of the storage (G') and loss (G'') moduli of the associative polymer at a temperature of 5°C is shown in Fig. 2. As observed, the frequency at which the moduli coincide is different to that of the maximum in G'' . This feature indicates a departure from a single relaxation time constant or Maxwellian behavior. This departure is apparent in Fig. 3, (Cole-Cole plot of G'' versus G') where deviations from a semicircle are large.

The variation of the moduli with frequency for this system, shows features similar to polymers interacting by topological entanglements. In fact, the limiting slopes of the moduli at low frequencies deviate substantially from the slopes of two and one for G' and G'' , respectively. This response presumably reflects a broadening of the terminal relaxation spectrum due to the combined effects of topological entanglements and hydrophobic associations. In a discussion by En-

glish *et al.* [2], on HASE systems, the terminal relaxation time or disengagement time of a single chain from the network is associated, on a molecular level, with the maximum observed in G'' (see Fig. 2). This time is much longer in comparison to the characteristic time of a single hydrophobe within a junction domain. Systems without entanglements but with hydrophobic associations, are the so-called hydrophobically-modified ethoxylated-urethane (HEUR) polymers. Because these polymers usually have low molecular weights with telechelic hydrophobic groups, their linear viscoelastic properties have been shown to be adequately described by the Maxwell model with a single characteristic time [3]. Stress relaxation in the HASE systems is then better explained in terms of a hindered reptation mechanism invoked in the model of Leibler *et al.* [4].

In the latter model, consideration is given to the dynamics of temporary networks which have tie points with relative weak binding energies, so that junctions break and reform frequently on the time scale of the experiments. A network with such reversible crosslinks exhibits enhanced viscoelasticity compared to polymers which do not have associating groups. One of the most striking features of truly reversible networks is the existence of two maxima in the loss modulus and an elastic modulus which has contributions of both crosslinks and entanglements. Although the second peak in G'' is not observable over the frequency range shown in Fig. 2, the high viscoelasticity and non-Maxwellian behavior of the HASE-polymers treated here suggest that their rheological behavior indeed arises from both hydrophobic associations and topological entanglements.

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