

Nonlinear rheology of aqueous solutions of hydrophobically modified hydroxyethyl cellulose with nonionic surfactant

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Abstract

Shear thickening and strain hardening behavior of hydrophobically modified hydroxyethyl cellulose (HMHEC) aqueous solutions was experimentally examined. We focused on the effects of polymer concentration, temperature, and addition of nonionic surfactant. It is found that HMHEC shows stronger shear thickening at intermediate shear rates in a certain concentration range. In this range, the zero-shear viscosity scales with polymer concentration as $\eta_0 \sim c^{5.7}$, showing a stronger concentration dependence than for more concentrated solutions. The critical shear stress for complete disruption of the transient network follows $\tau_c \sim c^{1.62}$ in the concentrated regime. Dynamic tests of the transient network on addition of surfactants show that the enhanced zero-shear viscosity is due to an increase in network junction strength, rather than their number, which in fact decreases. The reduction in the junction number could partly explain the weak variation of strain hardening extent for low surfactant concentrations, because of longer and looser bridging chain segments, and hence lesser nonlinear chain stretching.

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1. Introduction

Water-soluble polymers are receiving much attention in industry for safety and environmental concerns. They are used to modify the rheological properties of various water-based formulations, such as latex paints, drilling mud, and cosmetics. To improve the thickening efficiency, the polymer is hydrophobically modified to become amphiphilic by grafting alkyl short chains either randomly along its backbone (comblike) or to its two ends (telechelic) as hydrophobes. Such a modification results in additional interactions among species, thereby leading to more versatile flow behavior. The objective of this paper is to examine the rheological behavior of a comblike, hydrophobically modified polymer (HMP) in aqueous solution and the effects of temperature and added nonionic surfactant.

It has been known that shear thickening can occur at moderate shear rates for aqueous solutions of hydrophobically modified ethoxylated urethanes (HEUR, an end-capped PEO) [1].

The proposed mechanisms to account for the shear thickening are: (1) flow-induced loop-to-bridge transition [2–5], (2) cooperative effect of non-Gaussian chain stretching [6], and (3) network reorganization [7]. The three mechanisms may coexist, and their relative importance depends on the polymer molecular weight, concentration, and hydrophobe size. Studying HEUR polymer ($M_n = 51,000$, $M_w/M_n \sim 1.7$), Tam et al. [2] were the first to report the occurrence of a flow-induced loop-to-bridge transition, inferred from an increased plateau modulus in the experiments with superposition of a small oscillation on a steady shear flow. However, the above transition argument appears inappropriate for cases with high enough concentrations. Moreover, Ma and Cooper [8] experimentally found no discernible shear thickening for unimodal polydisperse HEUR polymer. They justified this observation by a cooperative effect of non-Gaussian chain stretching, which can take place at certain critical shear rates only for a sample with low enough polydispersity.

Relatively weak shear thickening was observed for hydrophobically modified alkali-soluble emulsion (HASE) polymer solutions at intermediate shear stresses and low concentrations [9]. This polymer is a hydrophobically modified

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carboxylic acid containing copolymer, i.e., a comblike polyelectrolyte with hydrophobes randomly distributed along its backbone. The shear thickening and strain hardening behavior [9–11] is attributed to shear-induced structuring through hydrophobic association, which is inferred again from the aforementioned flow-superposition experiments. The shear thickening of HASE polymer is weaker than that observed for HEUR, primarily due to the competing effects between topological disentanglement and induced hydrophobic association at moderate shear rates [9].

Another commercially available comblike polymer, hydrophobically modified hydroxyethyl cellulose (HMHEC), by contrast, has received little attention and is less well understood regarding the shear thickening and strain hardening behavior. Maestro et al. [12] observed weak shear thickening only for the HMHEC solution at 0.5 wt%, which was the lowest concentration investigated in their study. They attributed the shear thickening to flow-enhanced interchain association of hydrophobes. However, no systematic studies on the shear thickening were carried out in their paper. Our recent study [13] on the viscosity of HMHEC found that this polymer did show a shear thickening behavior at moderate shear rates for 0.35, 0.4, and 0.5 wt%, beyond which only typical shear thinning was observed.

On the basis of telechelic polymers, rudimentary theoretical models for physical gels were developed [1,6,14–17], which could qualitatively capture the signature of nonlinear rheological behavior of HEUR [16]. Very recently, Tripathi et al. [18] modified the network models to a sophisticated theoretical formulation, capable of quantitative prediction of the shear thickening of two model HEUR systems. However, it is questionable whether these models can also apply to comblike HM polymers in view of structural difference.

The flow properties of HM polymers can be further complicated by addition of surfactant, because of interactions between the two species. Ma and Cooper [19] observed shear thickening for HEUR polymer solutions at 0.05 M sodium dodecyl sulfate (SDS, an ionic surfactant). At lower SDS concentrations, the solution behavior became unclear because of the onset of flow instabilities. The incipient shear thickening occurs at the same reduced shear rate as in the corresponding solution without SDS (see Fig. 10 of their paper). This finding supported the free path model of non-Gaussian chain stretching [6], predicting that the critical reduced shear rate depends only on the polymer molecular weight. One can also find from that figure that the degree of shear thickening was hardly changed on the addition of 0.05 M SDS, although it was not pointed out by the authors. For comblike HMP, Talwar et al. recently examined the low-shear flow behavior of HASE + nonylphenol ethoxylate surfactant (NPe series, nonionic), and reported that the presence of surfactant affected the relaxation time and plateau modulus [20]. For HMHEC, however, Maestro et al. found that the addition of C₁₂E₄ (polydispersed Brij30) affected only the relaxation time [21]. To date, there exists no study on how nonionic surfactants can affect the nonlinear flow behavior of HMHEC.

In this paper, we experimentally investigate the shear thickening and strain hardening behavior of HMHEC, focusing on the effects of concentration, temperature, and added nonionic

Table 1
Specifications of nonionic surfactants

Surfactant	Molecular formula	M_w^a (g/mol)	CMC ^a (ppm)	Manufacturer
C ₁₂ E ₅	CH ₃ (CH ₂) ₁₁ (OCH ₂ CH ₂) ₅ OH	406.5	27.6	Fluka
C ₁₂ E ₉	CH ₃ (CH ₂) ₁₁ (OCH ₂ CH ₂) ₉ OH	582.8	46.6	Sigma

^a Provided by supplier.

surfactant on the nonlinear rheology. It is aimed at seeking a better understanding of flow behavior of comblike HMP.

2. Experimental

2.1. Materials

2-Hydroxyethyl cellulose hydrophobically modified with hexadecyl groups from Aldrich was used as supplied. According to the manufacturer, the polymer has an average molecular weight $M_w = 560,000$ g/mol with the molar substitution (MS) and degree of substitution (DS) for hydroxyethyl groups being 2.7–3.4 and 2.0, respectively. The degree of polymerization is estimated to be ~ 1880 . DS is defined as the average number of hydroxyl groups, which have been replaced by hydroxyethyl groups, for an anhydrous glucose repeating unit, so it can range from 0 to a maximum 3. MS is the average number of hydroxyethyl groups per anhydrous glucose repeating unit, and thus can be any value greater than zero. Our H¹ NMR result found that each polymer molecule has on average 10 hydrophobes randomly distributed along its backbone. The nonionic surfactants used are C₁₂E₅ (pentaethylene glycol monododecyl ether) and C₁₂E₉ (polyoxyethylene 9 lauryl ether). Table 1 shows their specifications. The surfactant species are highly monodisperse, according to the manufacturer, and were used without further purification. A stock solution of HMHEC was prepared by dissolving the dry powder in deionized water that had been further purified through a Millipore MilliQ purification system. The solution was magnetically stirred for at least 2 h at 40 °C, and then cooled down to room temperature. A homogeneous clear solution was obtained. The stock solution was stored under nitrogen gas in a fridge at 4 °C. A similar procedure was used to prepare surfactant stock solutions. Subsequent dilution was done to prepare HMHEC solutions at desired lower concentrations. The mixture solutions were then obtained by adding correct amounts of the surfactant stock solution to achieve the desired compositions. Samples were stored in the refrigerator for at least 24 h in order to complete hydration and interactions.

2.2. Rheometry

The rheological properties of the solutions were measured using a Haake RS75 rheometer with a DC50 temperature controller (water circulating bath). A double concentric-cylinder (DG41) geometry or a cone-and-plate (C60/4, cone diameter and angle are 60 mm and 4°) fixture was used to carry out the measurements, depending on the solution viscosity and shear rate range. Both controlled stress (CS) and controlled rate (CR)

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