

Shear-induced structure and dynamics of hydrophobically modified hydroxy ethyl cellulose (hmHEC) in the presence of SDS

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(Received December 12, 2001; final revision received October 11, 2002)

Abstract

The interaction between hydrophobically modified hydroxyethyl cellulose (hmHEC), containing approximately 1 wt% side-alkyl chains of C₁₆, and an anionic sodium dodecyl sulphate (SDS) surfactant was investigated. For a semi-dilute solution of 0.5 wt% hmHEC, the previously observed behaviour of a maximum in solution viscosity at intermediate SDS concentrations, followed by a drop at higher SDS concentrations, until above the *cmc* of surfactant when the solution resembles that of the unsubstituted polymer, was confirmed. Additionally, a two-phase region containing a hydrogel phase and a water-like supernatant was found at low SDS concentrations up to 0.2 wt%, a concentration which is akin to the critical association concentration, *cac*, of SDS in the presence of hmHEC. Above this concentration, SDS molecules bind strongly to form mixed micellar aggregates with the polymer alkyl side-chains, thus strengthening the network junctions, resulting in the observed increase in viscosity and elastic modulus of the solution. The shear behaviour of this polymer-surfactant complex during steady and step stress experiments was examined in great detail. Between SDS concentrations of 0.2 and 0.25 wt%, the shear viscosity of the hmHEC-polymer complex network undergoes shear-induced thickening, followed by a two-stage shear-induced fracture or break-up of the network. The thickening is thought to be due to structural rearrangement, causing the network of flexible polymers to expand, enabling some polymer hydrophobic groups to be converted from intra- to inter-chain associations. At higher applied stress, a partial local break-up of the network occurs, while at even higher stress, above the critical or network yield stress, a complete fracture of the network into small microgel-like units, is believed to occur. This second network rupture is progressive with time of shear and no steady state in viscosity was observed even after 300 s. The structure which was reformed after the cessation of shear is found to be significantly different from the original state.

Keywords : hydrophobically modified polymer, SDS, polymer-surfactant interactions, shear-induced thickening, critical yield stress

1. Introduction

Hydrophobically associating polymers are a class of water-soluble polymers which consist of a long backbone, grafted to which are a small number of hydrophobic side-chains or terminal groups of alkyl chains consisting of 8–40 carbon atoms (Tanaka *et al.*, 1992). Several hydrophobically modified cellulosic polymers have been investigated in recent times, including hydroxy-ethyl cellulose (HEC) and ethyl-hydroxy ethyl cellulose (EHEC). Above the overlap concentrations, hydrophobically-modified polymers have been shown to display higher solution viscosity than their unmodified analogues at the same polymer concentration and molecular weight, due to hydrophobic asso-

ciation of the side chains. The increase in viscosity of the modified polymers is dependent on both the alkyl chain length and degree of substitution (Sau and Landoll, 1989; Tanaka *et al.*, 1992; Panmai *et al.* 1999). At the same degree of substitution, the level of viscosity increases as the length of the alkyl chains grafted on the backbone increases (Panmai *et al.*, 1999), and as the level of substitution of the alkyl chains increases, the viscosity first increases until it reaches a maximum, followed by a sharp decrease with further increase in the alkyl chain content. Beyond a certain limit of hydrophobic substitution or alkyl chain length, the hydrophobically-modified polymers are rendered insoluble, forming water-swollen polymer globules which then precipitate out of the solution (Kumar and Steiner, 1999).

From fluorescence studies, it was found that the ratio of the intensities of the two pyrene emission bands, I_3/I_1 ,

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increased significantly with polymer concentration (Sivadasan and Somasundaran, 1990; Evertsson and Nilsson, 1999), indicating the formation of polymer hydrophobic aggregates in solution with increasing degree of hydrophobicity. This increase in the pyrene emission bands was found to be less rapid above a certain critical concentration, c^* , which coincided with the critical overlap concentration of the polymer where a change in slope of the reduced specific viscosity versus polymer concentration occurred (Evertsson and Nilsson, 1999). Below c^* the hydrophobic associations are mostly intramolecular in nature, but as polymer concentration increases (below c^*), the aggregation number also increases significantly. Above c^* , polymer chains are in close proximity with one another such that overlap occurs and inter-chain associations of the polymer alkyl groups become prevalent. The hydrophobic aggregates form pseudo-crosslinks, joining together several polymer chains into a connected polymer network which, depending on the extent of the association, can span the entire solution volume. It is the formation of this polymer network which results in a substantial enhancement in the viscosity and elastic modulus of the hydrophobically modified polymer solution.

The interactions of hydrophobically-modified polymers with surfactants have been observed in a number of investigations, including fluorescence and surface tension (Sivadasan and Somasundaran, 1990; Evertsson and Nilsson, 1999), thermodynamic property (Thuresson *et al.*, 1995), light scattering (Nyström *et al.*, 1995; Kjoniksen *et al.*, 2000), as well as rheological property measurements (Sau and Landoll, 1989; Tanaka *et al.*, 1992; Kastner *et al.*, 1996; Thuresson *et al.*, 1997; Kulicke *et al.*, 1998; Nilsson *et al.*, 1998; Panmai *et al.*, 1999; Kjoniksen *et al.*, 2000). Large increase in the pyrene emission ratio of the hydrophobically-modified polymer in the presence of surfactant well below its *cmc* has been observed (Sivadasan and Somasundaran, 1990; Evertsson and Nilsson, 1999), suggesting that surfactant hydrophobic tails incorporate with polymer hydrophobic side groups to form mixed surfactant-polymer hydrophobe micellar complexes. An increase in the viscous and elastic properties of several semi-dilute hydrophobically-modified polymer solutions upon addition of both ionic and non-ionic surfactants has been reported (Sau and Landoll, 1989; Tanaka *et al.*, 1992; Nyström *et al.*, 1995; Thuresson *et al.*, 1997; Panmai *et al.*, 1999). For the neutral cellulosic-based polymers such as HEC and EHEC, large increase in both viscosity and elastic modulus with the addition anionic surfactants such as SDS has been found; this can be up to two to three orders of magnitude above that of the polymer without surfactant. This increase is found to be a function of the degree of hydrophobic substitution and polymer alkyl chain length (Sau and Landoll, 1989; Panmai *et al.*, 1999), as well as surfactant hydrophobic tail length (Tanaka *et al.*, 1992; Panmai *et al.*,

1999).

With increasing surfactant concentration, the zero-shear-rate viscosity of the hydrophobically-modified polymer solutions generally increases until it reaches a maximum, followed by a decrease with further increase in the surfactant concentration. At low surfactant concentrations, the free surfactant molecules are incorporated into the polymer hydrophobic junctions, forming mixed micellar aggregates. This results in an increase in the number of the mixed aggregates, and a gradual reorganisation of polymer hydrophobes from intra- to inter-chain associations (Annable *et al.*, 1993), as surfactant concentration increases. Such reorganisation is believed to enable previously unassociated or intra-molecularly associated polymer hydrophobes to take part in the bridging network (Tanaka *et al.*, 1992), thereby increasing the number of polymer chains involved in active junctions. The overall effect of this cooperative association of the surfactant with the hydrophobic aggregates or network bridges is an increase in the structural strength of the polymer network, as confirmed by an increase in the activation energy of the hmEHEC-SDS systems with increasing surfactant concentration (Thuresson *et al.*, 1997), that is, a decrease in the free energy of the system or a higher energy is required by the polymer alkyl groups to exit the hydrophobic domain, resulting in an increase in both the viscosity and elastic modulus of the solution.

The decrease in viscosity of the hydrophobically modified polymer-surfactant systems after the viscosity maximum is due to polymer hydrophobes or alkyl chains becoming "solubilized" by further addition of surfactant; this causes a decrease in the average number of hydrophobes per aggregate and hence the number of effective network bridges. Nilsson *et al.* (1998), using fluorescence quenching technique, found a reduction in the number of polymer hydrophobes, but a significant increase in the number of surfactants, in the mixed micellar aggregates of the hmHEC-SDS system at surfactant concentration above the maximum viscosity, as well as a 5 to 6-fold increase in the micellar aggregate concentration. It is generally believed that it is the reduction in the number of polymer hydrophobes per aggregate or network bridges that results in a weakening of the network structure, with the consequence of a decrease in both viscosity and elastic modulus with increasing surfactant concentration above the optimum value.

Finally, at a sufficiently high surfactant concentration, each polymer hydrophobe becomes totally solubilised or encapsulated within a small, spherical surfactant micelle and is thus prevented from further association. This results in a total disruption of the polymer network and the viscosity of the hydrophobically-modified polymer solution at high surfactant concentrations is thus reduced to that of the unmodified polymer (Tanaka *et al.*, 1992; Panmai *et al.*, 1999; Kulicke *et al.*, 1998). However, there are instances,

such as the hydrophobically modified, alkali-soluble emulsion (HASE) polymers in the presence of a non-ionic surfactant (Tirtaatmadja *et al.* 1998), or hmHEC in the presence of CTAB and NaSal (Panmai *et al.*, 1999), whereby the solution viscosity and elastic property keep on increasing as surfactant concentration increases. This is due to the surfactant molecules forming vesicles or rod-like micelles, which continue to grow in size with increasing surfactant concentration, and no disruption of the polymer network occurs.

Results of Kulicke *et al.* (1998) for the hydrophobically modified hydroxypropyl-methylcellulose (HPMC) and anionic SDS also show a similar increase in the viscosity to a maximum with increasing surfactant concentration, followed by a drop at higher surfactant concentrations to below the value for pure solution. Moreover, solutions of their more hydrophobic HPMC with moderate SDS concentration show shear-thickening viscosity behaviour, followed by shear-thinning. The shear-thickening behaviour has also been found for a class of associative thickeners, known as HEUR (Hydrophobically-modified Ethoxylated Urethane) polymers (Tam *et al.*, 1998; Annable *et al.*, 1993), and some surfactant-benzyl additive salt systems (Hu *et al.*, 1998). The HEUR polymer is a type of tri-block polymers, of polyethylene oxide chain end-capped with hydrophobic groups, which form closed and mainly intra-chain associations of identically sized, flower-like micelles of the end-capped hydrophobes, as well as inter-micelle cross-links joining the structure into a network at high concentration. Using a shear-imposed oscillation technique to examine the state of the network structure at different applied stress conditions, Tam *et al.* (1998) found that the plateau modulus in the shear-thickening region was higher than in the Newtonian region. This suggests that shear-thickening is a result of structural rearrangement which induces an increase in the number of active chains linking the micelles within the network. With further shearing at higher stress, a catastrophic break-down of the "flower" network occurs whereby a drastic drop in viscosity was observed.

Considering the brief summary given above of previous work in the area of hydrophobically modified polymer-surfactant interactions, much of the investigations have concentrated on dynamic oscillatory experiments in order to determine structure function relationships for these complex network systems at or close to equilibrium states. In the case of the hmHEC-SDS system, this is certainly the case. In this work, we extend the understanding of the dynamics of this particular polymer-surfactant system by probing the non-equilibrium behaviour through the imposition of steady shear flow and step-stress jumps to the developed equilibrium network. We investigate the interactions between the hydrophobically-modified hydroxy ethyl cellulose and anionic SDS, in the range of surfactant

concentrations which allow the formation of a one-phase solution. The resultant shear-induced rheological properties of this complex, transient network obtained in steady shear and step-stress experiments will be shown together with their dynamic results, and the structure elucidated based on the rheological results obtained.

2. Experiments

The hydrophobically modified hydroxy ethyl cellulose (hmHEC) used in this study was a commercial sample of Natrosol Plus-330PA from Hercules Chemical. According to the manufacturer, the molecular weight of the unmodified polymer is approximately 250,000-300,000 g/mol and the hmHEC polymer contains approximately 1 wt% grafted alkyl chains of length C_{16} . The anionic surfactant used was SDS (Sodium dodecyl sulphate) from Fluka Chemicals Co. Solutions of 0.5 wt% hmHEC with a range of SDS concentrations from 0 to 0.5 wt% were prepared from stock solutions of 2 wt% hmHEC and 2 wt% SDS in milli-Q water. The solutions were mixed by rolling gently overnight and left to equilibrate for 24 hours before testing. Both the steady shear and dynamic oscillatory measurements were carried out within two weeks of preparation of the samples.

Shear properties of the solutions were carried out in two stress-controlled rheometers: Rheologica Stresstech and Rheometrics SR5, using both a cone-and-plate geometry and a Couette geometry. Both steady and dynamic oscillatory shear measurements were carried out. For the dynamic experiments, all frequency sweep measurements were performed in the linear viscoelastic region, obtained *a priori* using the stress sweep measurements. All measurements were carried out at 21°C.

3. Results

3.1. Effect of SDS concentration on solution zero-shear-rate viscosity

For the unmodified HEC of molecular weight 250,000 to 300,000 g/mol, the overlap concentration c^* has been found to be 0.2 wt% (Panmai *et al.*, 1999). The solutions of 0.5 wt% hmHEC used in this study (of similar molecular weight to that of Panmai *et al.*, 1999) are therefore in the semi-dilute concentration region where overlap of the of the polymer chains are prevalent. Fig. 1 shows the zero-shear-rate viscosity of hmHEC solutions as a function of SDS concentration. This is very similar to the results given in Panmai *et al.* (1999) for the same hmHEC. The zero-shear-rate viscosity of the solutions of hydrophobically-modified polymer was found to be about an order of magnitude above that of the unmodified polymer of the same molecular weight and concentration (Panmai *et al.*, 1999), indicating that significant inter-chain associations of poly-

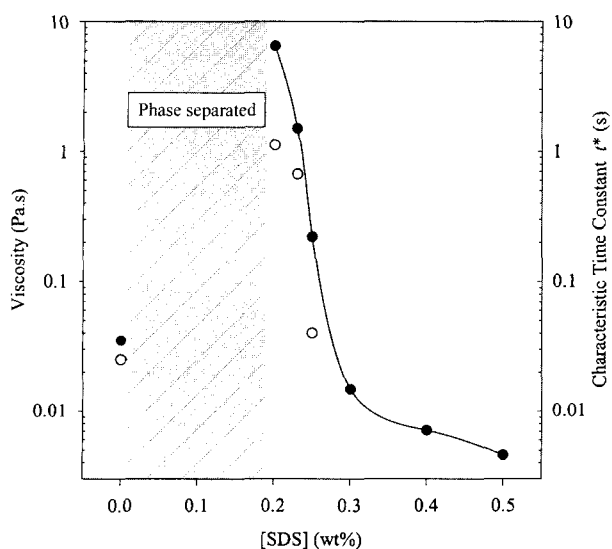


Fig. 1. Zero shear viscosity (filled symbols) and characteristic time constant t^* (unfilled symbols) against SDS concentration for the solutions of 0.5 wt% hmHEC, with the shaded area indicating the two-phase region.

mer hydrophobic groups are present in solution in addition to entanglements of the HEC polymer backbone.

With the addition of small quantities of SDS between 0.025 to 0.18 wt%, the hmHEC solutions studied phase-separated into a gel phase and a supernatant phase of mainly surfactant and water. This is shown in Fig. 1 as a cross-hatched region. This phase separation has also been found for hmHEC in the presence of SDS and other anionic surfactants by others (Panmai *et al.*, 1999, Dualeh and Steiner, 1991; Kumar and Steiner, 1999). Kumar and Steiner (1999) suggested that SDS surfactant acted on the polymer backbone and side alkyl chains in opposite ways, with SDS driving the HEC backbone to collapse, but enhancing the solubility of the hydrocarbon side chains. Which one of these two effects dominates will depend on both polymer concentration and factors affecting polymer structure, such as alkyl chain length, degree of substitution, degree of polymerisation, and the stiffness of the backbone. Nilsson *et al.* (1998) and Tanaka *et al.* (1992) found no such phase separation when studying the same hmHEC as used in this work, but at higher polymer concentrations of 1 and 2 wt% respectively.

For the hmHEC of 0.5 wt% used in this study and with the addition of a small amount of SDS < 0.20 wt%, the surfactant molecules must have bound strongly to the limited number of existing, mainly inter-chain hydrophobic aggregates, causing a rearrangement of the aggregates to such an extent that the aggregation number of polymer hydrophobes involved in each aggregate is significantly enhanced. The number of polymer chains per aggregate is vastly increased, with the consequence that the polymers

are drawn closer together to form a percolated network which occupies a confined volume smaller than that of the entire solution. The remaining excess volume then forms the supernatant phase of mainly water and minute amount of surfactant. Dualeh and Steiner (1991) studied the polymer-rich hydrogel formed from hmHEC interacting with SDS below its *cmc* and found that the volume of the gel phase formed increased and the gel strength, measured in terms of their plateau modulus, decreased with increasing surfactant concentration. From fluorescence quenching studies these authors found that as the surfactant concentration increased, the number of surfactant per micellar aggregate also increased while the number of polymer hydrophobic groups per aggregate decreased. So with fewer alkyl chains associated within each aggregate, the network of surfactant-polymer complex becomes more loosely bound, and this results in hydrogel which is larger in volume, but becoming weaker in strength.

The results found by Dualeh and Steiner (1991) are in agreement with our findings that as more SDS is added to the hmHEC solution, a state is reached when the polymer network becomes so expanded that it occupies the entire solution volume and a single continuous phase is now present. This occurs at SDS concentration of approximately 0.2 wt% in our work, which is below the *cmc* of the surfactant (i.e. 8mM or 0.23 wt%), in good agreement with the results of Panmai *et al.* (1999) at the same hmHEC concentration. Sivadasan and Somasundaran (1990) and Evertsson and Nilsson (1999) studied hm-HEC and hm-EHEC below their overlap concentrations, and found an increase in the pyrene emission ratio, I_3/I_1 , above the value for the pure polymer when low concentrations of SDS up to 5 mM were added, above which this ratio increased rapidly up to the value for pure SDS above its *cmc*. From equilibrium dialysis results, Evertsson and Nilsson (1999) found a very low degree of binding of SDS on to the hmHEC polymer occurred below 5 mM, a result confirmed also by the low SDS aggregation number obtained from fluorescence quenching studies (Nilsson *et al.*, 1998). While above 5 mM SDS, a rapid increase in the degree of binding of SDS and a constant rise in the SDS aggregation number in the presence of a hydrophobically-modified polymer suggested a critical association concentration *cac* of SDS in the presence of the polymer at approximately 5 mM. Below this, *cac*, there is a non-cooperative binding of SDS on to the polymer hydrophobic aggregates, while above 5 mM SDS the surfactant molecules associate strongly or cooperatively with polymer alkyl groups to form mixed micellar aggregates. In our system, a similar situation is believed to take place with extra surfactant-polymer micellar complexes formed above 0.2 wt% SDS (equivalent to 5.3 mM), which helps liberate polymer hydrophobes from the tightly bound aggregates found in the gel phase at lower surfactant concentrations. As the

As SDS concentration increases there is also an increase in the number of mixed aggregates, each with fewer polymer alkyl chains associated, such that the polymer network is sufficiently expanded to occupy the whole solution volume and a single phase is now present. The SDS concentration at which the two-phase system becomes a single-phase solution in our study can thus be thought of as the critical association concentration, *cac*, of SDS in a solution of 0.5 wt% hmHEC.

Above the *cac*, i.e. ca. 0.2 wt% SDS concentration, the binding of surfactant to form mixed aggregates clearly contributes to strengthening of the polymer network compared to the pure polymer (with no added surfactant), as can be seen from the solution zero-shear-rate viscosity being significantly higher (about 200 times) than that of the solution of pure polymer. The zero-shear-rate viscosity of these one-phase solutions is a maximum at SDS concentration of 0.2 wt%. Above this concentration, the viscosity starts to decrease until at 0.3 wt%, which is above the *cmc* of SDS (i.e. 8 mM or 0.23 wt%), the viscosity is below that of the pure polymer. With further increase in surfactant concentration beyond 0.3 wt%, the solution viscosity continues to drop until it reaches the viscosity of the unmodified polymer, as found by others (Nyström *et al.*, 1995; Panmai *et al.*, 1999). The maximum in solution viscosity found at SDS concentration of 0.2 wt% must entail an optimum combination of both the number of alkyl groups in the mixed micellar aggregates and the total number of such aggregates.

Up to this point, the results obtained are in agreement with those found by previous workers for the hmHEC-SDS system. However, none of the previous work has investigated the effect of shear on the network structure of the polymer-surfactant complex formed. The results shown in the following sections and ensuing discussion will thus concentrate on providing some insight into the effect of shear on the structural changes in these solutions, i.e. the creation of shear-induced network states.

3.2. Non-linear shear experiments: steady shear and large amplitude oscillatory shear

The steady shear viscosity curves as a function of shear rate of all the hmHEC solutions studied are shown in Fig. 2. For the solution of hmHEC with no added surfactant, a zero-shear-rate viscosity of 0.03 Pa.s is observed below shear rates of 20 s⁻¹, while at higher rates the viscosity shows slight shear-thinning behaviour. For the solutions with 0.2 to 0.25 wt% SDS, the viscosity curves show distinct shear-induced thickening behaviour at intermediate shear rates, followed by shear-thinning at higher rates. At SDS concentrations of 0.3 wt%, the viscosity drops to below that of the pure hmHEC solution and shows a very slight shear-thinning behaviour over most of the shear-rate range measured. At higher SDS concentrations, the vis-

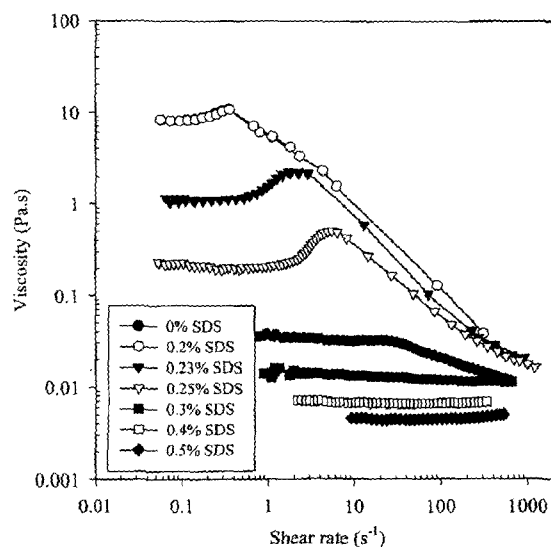


Fig. 2. Steady shear viscosity against shear rate for solutions of 0.5 wt% hmHEC at various SDS concentrations.

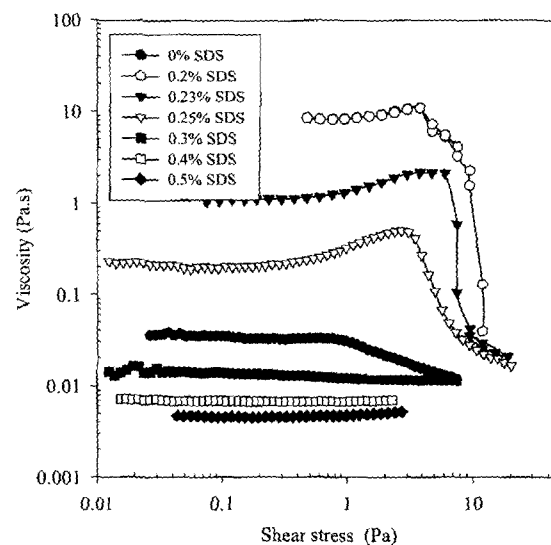


Fig. 3. Steady shear viscosity against shear stress for solutions of 0.5 wt% hmHEC at various SDS concentrations.

cosity is even lower and the solutions are now totally Newtonian over the entire range of shear rates investigated. The enhancement and subsequent reduction of the zero-shear-rate viscosity at intermediate and high SDS concentrations, respectively, has already been discussed.

However, the most interesting shear-induced behaviour is shown by the solutions at moderate SDS concentrations between 0.2 and 0.25 wt%. These solutions show distinct shear-thickening followed by a shear-thinning region at higher shear rates. The drastic drop in viscosity at high shear rates is better observed with the viscosity data plotted as a function of shear stress, as shown in Fig. 3. From the work of Tam *et al.* (1998) for the HEUR system and

Kulicke *et al.* (1998) for HMPC with SDS, it is believed that the shear-thickening behaviour observed for the hmHEC-SDS solutions is also due to shear-induced restructuring of the polymer network. When subject to certain shear stress, the polymer is able to expand causing some intra-chain associations to be converted to inter-chain associations. However, it is not clear at this stage if this restructuring of the network would result in an increase in the number of mixed polymer-surfactant aggregates or merely an increase in the number of polymer hydrophobes per aggregate. Although the stress-imposed oscillation studies of Tam *et al.* (1998) for their HEUR system suggested an increase in the plateau modulus, and hence the effective elastic junction density, in the shear-thickening region and a decrease in the values of the plateau modulus in the shear-thinning region, it is not clear at this stage if the same applies to our case of mixed aggregate involving both polymer hydrophobic groups and surfactant tails. Alternatively, the shear thickening behaviour could also result from simple expansion of the network, made possible by the stretching of the flexible HEC backbones which are connected to the hydrophobic aggregates. Further work utilising light scattering techniques is required to determine the exact nature of this anomaly.

As seen in Fig. 3, the stress at the onset of shear-induced thickening behaviour is related to the viscosity of the solution and hence the strength of the network structure, with the 0.2 wt% SDS solution showing the highest onset stress and the 0.25% SDS solution the lowest. The extent of the maximum increase in viscosity in the shear-thickening region is, however, higher for the 0.25 wt% compared to the 0.2 wt% SDS solutions, with the 0.25 wt% solution showing a 200% rise compared to an increase of approximately 50% for the 0.2 wt% solution. As the SDS concentration is increased, the number of polymer alkyl groups in the mixed micellar aggregates is expected to decrease, but these aggregates will still contain a significant number of intra-chain associations which when sheared are amenable to conversion to inter-chain associations. The larger viscosity increase upon shearing in the higher SDS solution may be related to the fact that as the number of polymer alkyl chains in the aggregates decreases with increasing SDS concentration, the activation energy for hydrophobic chain disengagement from the junction also decreases (Thuresson *et al.*, 1997), paving the way to ease of hydrophobic chain pull-out for the conversion from intra- to inter-chain associations to occur when the network is subject to an applied shear stress.

This shear-induced thickening and subsequent thinning (or abrupt loss of structure) is also observed, for the three solutions of 0.2 to 0.25 wt% SDS, in the oscillatory stress sweep measurements beyond the linear viscoelastic regime. Thickening behaviour can be seen in both storage and loss moduli, G' and G'' , and the onset stresses are

found to be dependent on the structural strength of the solution (in terms of viscosity or shear modulus), and to some extent on the oscillation frequency tested. Although in the non-linear viscoelastic region or Large Amplitude Oscillatory Shear (LAOS) experiments, the exact magnitudes of G' and G'' obtained from the rheometers used will not be quantitatively correct (as the software available only provides a single frequency of best fit to the dynamic response curves, which are usually skewed and thus contain a number of harmonics), the values should at least be qualitative for comparison purposes. A typical set of oscillatory stress sweep results are shown in Fig. 4(a) and (b) for the 0.2 wt% SDS solution at 6.3 and 0.63 rad./s respectively. At a frequency of 6.3 rad./s, the loss modulus shows a distinctly higher level of thickening behaviour compared to the storage modulus, but once shear-thinning occurs, the decrease in the storage modulus is more drastic, a behaviour found also in the lower oscillation frequency of 0.63 rad./s, although not as distinct. This leads us to conclude that the thickening may be due more to structural rearrangement which brings about an increase in the effective

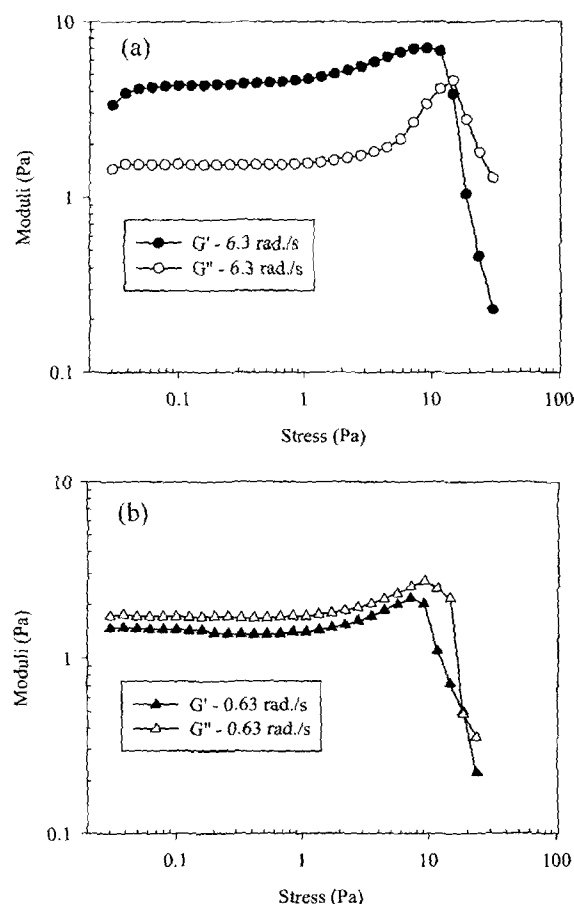


Fig. 4. Oscillatory stress sweep curves for the solution of 0.5 wt% hmHEC and 0.2 wt% SDS at: (a) 6.3 rad./s and (b) 0.63 rad./s.

volume of the network and hence the viscosity, rather than a significant increase in the number of bridges or alkyl chains per aggregate, which should result in a larger increase in the storage than in loss modulus values. But the number of aggregates drops significantly when break-down of the structure occurs at higher applied (oscillatory) stress, thus the cause of the drastic drop in the G' values.

Further, in the LAOS experiments, the effective or mean stress felt by the sample is simply $\tau_0/\sqrt{2}$, where τ_0 is the magnitude of the oscillatory stress. We can use this relationship to shift the dynamic data in Fig. 4 along the stress axis by a factor of $1/\sqrt{2}$ and compare them with the steady shear results in Fig. 3, both as a function of stress. These results, although not plotted together, can be seen to show good correspondence in terms of the stress at the onset of thickening and at the maximum viscosity/modulus. Such a treatment indicates that although the actual stresses for onset of thickening and thinning are not identical in the steady-shear and oscillatory situations, they are in fact very similar; this applies equally well to the other two solutions (i.e. 0.23 and 0.25 wt% SDS). This leads to the suggestion that any solution will require a stress commensurate to its network strength, as indicated by its relative viscosity or shear modulus, for any structural rearrangement or onset of shear-induced thickening to occur. However such thickening is not observed in the complex viscosity curve from oscillatory frequency sweeps, shown in Fig. 5, since these are conducted using small stress in the linear viscoelastic region. In all three solutions, the shear rate at onset of shear-induced thickening in the steady-shear viscosity curve approximately coincides with the angular frequency at which shear-thinning is observed in the dynamic vis-

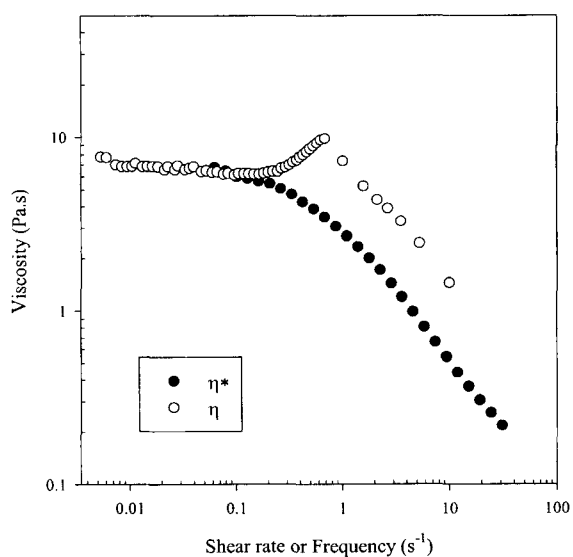


Fig. 5. Comparison of steady shear and dynamic complex viscosity curves for the solution of 0.5 wt% hmHEC and 0.2 wt% SDS.

cosity curve; this adds credence to the notion that the longest relaxation mode is an important indicator of the shear rate at which rearrangement occurs under applied stress fields.

For the three solutions with SDS concentrations of 0.2, 0.23 and 0.25 wt%, the shear-induced thickening is followed by a drastic drop in viscosity at higher applied stress. For the 0.2 wt% SDS, the shear-thinning appears to occur in two stages, one just after the maximum in viscosity above the stress of between 4 and 5 Pa, and the second and more drastic drop in viscosity occurs at higher stresses in excess of 6 Pa. The first viscosity decrease may be due to some structural rearrangement causing fewer alkyl chains to remain in the aggregates, while the second signals a catastrophic breakdown of the mixed surfactant-polymer aggregates or a large-scale pull-out of the alkyl groups from the mainly surfactant micelles, causing a break-up of the bridges joining together the network, and hence the network structure as a whole. The stress at which this break-up of the network occurs can thus be taken as an *effective structure yield stress* or *critical stress*.

3.3. Step-stress experiments

It is interesting to note that, in obtaining the viscosity curves shown in Figs. 2 and 3 for all solutions with shear-induced thickening characteristics, after the maximum viscosity, the measurement has not reached steady state within the 120 s of set measurement time using the Stresstech rheometer. We thus proceed to investigate this behaviour more closely. Results of step-stress experiments are shown in the viscosity-time plot in Fig. 6 for the 0.2 wt% SDS solution. It is seen that for the 0.2 wt% SDS solution up to the maximum in shear viscosity, i.e. at applied stress below approx-

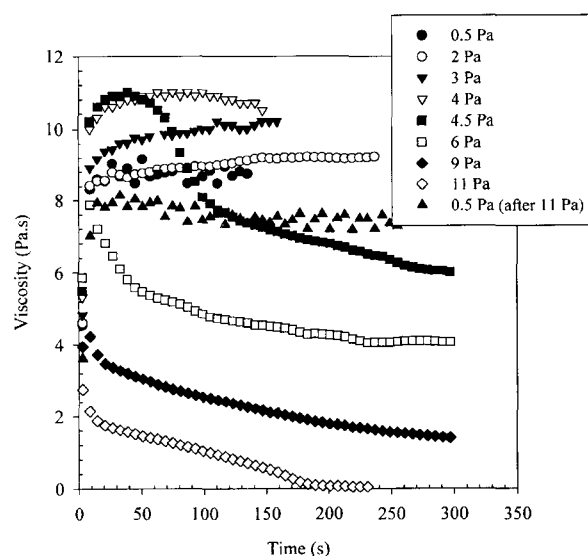


Fig. 6. Viscosity time sweep curves for the solution of 0.5 wt% hmHEC and 0.2 wt% SDS at various applied stresses.

imately 4.5 Pa, the viscosity data attain steady state within about 120 to 150 s from commencement of shearing. In the first shear-thinning region between stresses of 4.5 and 6 Pa, the viscosity decreases with time of shear, but still reaches a more or less steady state some time after about 200 s. At stresses above 6 Pa, i.e. 9 and 11 Pa, the structural breakdown of the network seems to proceed continually with shearing time, with the viscosity not approaching steady state even after 300 s (the maximum time measured), further confirming that once the *critical* stress has been reached, the destruction or break-up of the mixed aggregates can proceed with time until possibly a complete breakdown of the network is reached. Note that the zero-shear-rate viscosity obtained after the solution has been sheared at the highest stress of 11 Pa is now lower than the original measured value, i.e. 7 Pa.s compared to 9 Pa.s. This two-stage shear-thinning behaviour is not initially obvious in the other two solutions, but something similar to this two-stage thinning behaviour can be detected in the 0.25 wt% SDS solution, in the form of a hysteresis found in the viscosity curves once the solution has been subjected

to the *critical* stress, as will be discussed later.

At this point of the discussion we must recognise that such behaviour may be interpreted as slip at the surfaces of the cone and plate, as has been noted by Sadeghy and James (2000) for HEUR polymers. We have performed preliminary experiments using parallel plates with varying gaps, as performed by Sadeghy and James (2000), on our system with interesting results (not shown). For the 0.5% hmHEC + 0.2% SDS, firstly at the critical stress value after the maximum viscosity, there is a slight gap dependence, with decreasing gap showing a decrease in viscosity, with all data approaching that achieved by the cone and plate geometry (where the shear rate/stress is constant throughout). One might assume that slip indeed exists. However, at higher stresses post this critical stress, the trend in viscosity is reversed. The viscosity of the smaller gap parallel plate is now higher than that of the larger gap parallel plate and that of the cone and plate geometry. We thus believe that the noted decrease in viscosity with decreasing gap in the parallel plate is due to a shear-induced state at the outer radius of the plates (i.e. where the shear rate is largest). The

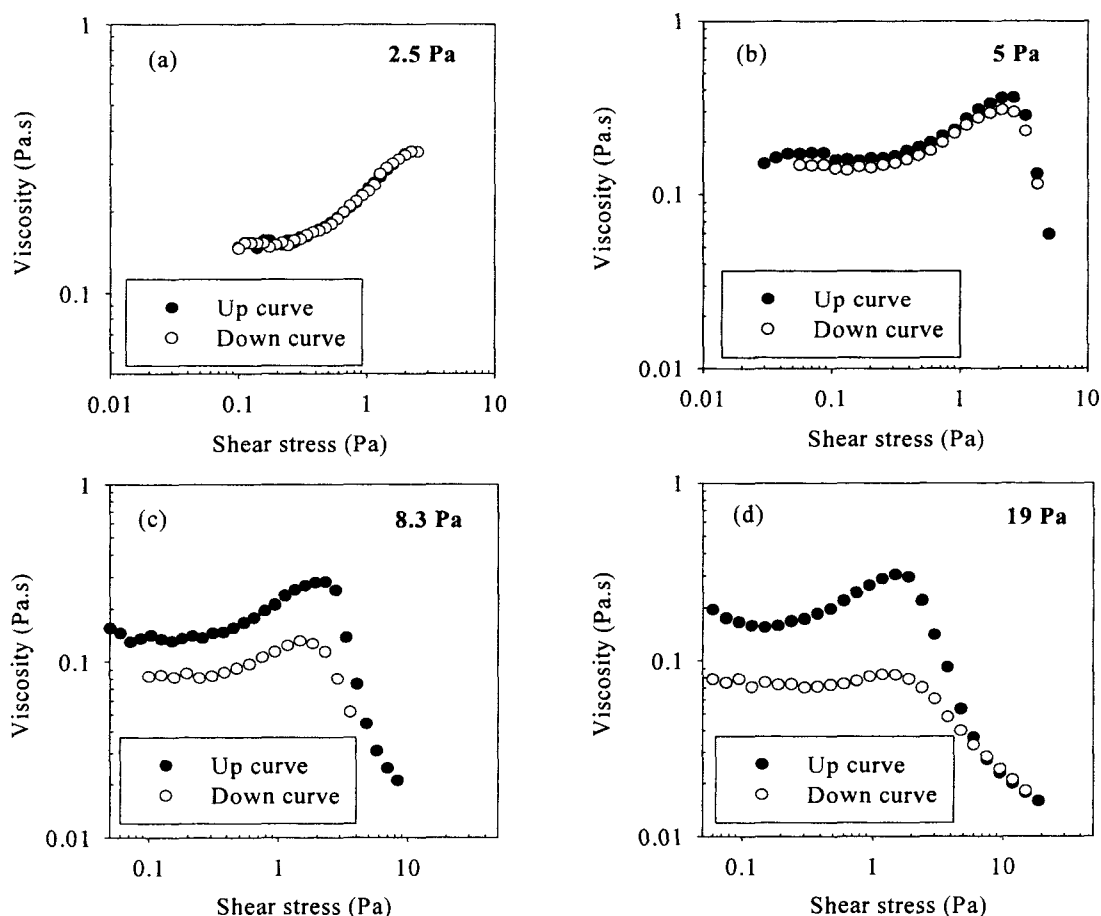


Fig. 7. Steady shear viscosity curves for the solution of 0.5 wt% hmHEC and 0.25 wt% SDS, for applied stress up to: (a) 2.5 Pa, (b) 5 Pa, (c) 8.3 Pa, and (d) 19 Pa.

material on the inside of the plate is unaffected. As the gap decreases, that shear rate at the outer edge approaches the shear rate achieved in the cone and plate geometry. As the shear rate increases, the situation obviously gets far more complex. We are intending to investigate this phenomenon further, but for the sake of this paper we believe that wall slip is not the cause of the noted decrease in viscosity and further work is underway.

In further support of this statement, prior to reaching this critical stress, the shear viscosity curve can be reproduced, as shown for the 0.25 wt% SDS solution in Figs. 7(a) and 7(b) for maximum applied stresses up to of 2.5 and 5 Pa. However, after the critical stress (between 6 and 8 Pa), we see that the data cannot be reproduced when the solution is tested again at low rates. This is shown in Figs. 7(c) and 7(d) for the solution which has been subjected to maximum stresses of 8.3 and 19 Pa respectively. The zero-shear-rate viscosity of the solution measured after the maximum stress has been applied is now significantly lower, and although the shear-thickening is still present for the 8.3 Pa case, it is almost non-existent after the stress of 19 Pa has been applied to the solution. Note that each data point within these curves has achieved what is termed steady state within the Stresstech software, i.e. the shear rates measured vary less than $\pm 1\%$ about a mean value for a given period of time. The only exceptions are the data above a stress of ~ 2.5 Pa, i.e. after the maximum viscosity, which were taken at time of 120 seconds after the start of the measurements, as no steady state has been reached within this timeframe. That is, the system displays a similar behaviour as shown for the 0.2 wt% SDS in Fig. 6. Hence, we propose that after the structural break-down of the network, the reformation process must have brought about a somewhat weaker network structure compared to the original, with either fewer polymer hydrophobes binding to the aggregates or more intra-chain hydrophobes present per junction. Alternatively, higher stresses may have induced an effective conversion of the network to a solution of small aggregated bundles of hmHEC around a number of SDS micelles, i.e. akin to small hydrogel particles.

3.4. Dynamic oscillatory experiments

The dynamic oscillatory results for the pure hmHEC solution and solutions with added 0.2, 0.23 and 0.25 wt% SDS are shown in Fig. 8. The data were all measured using small strain within the linear viscoelastic region. For these solutions, the storage and loss modulus curves intercept each other within the experimental frequency range, of 50 rad./s. From the point of interception, we can determine the crossover modulus G_c and crossover frequency ω^* ; these values are given in Table 1 for the four solutions. The longest relaxation time of the network of polymer-surfactant complex t^* can be estimated from the inverse of the frequency at the point of intercept of the G' and G'' curves, i.e.

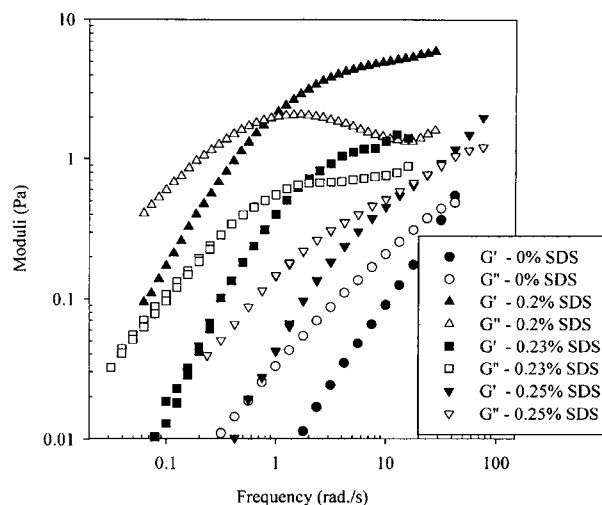


Fig. 8. Dynamic storage and loss modulus curves for solutions of 0.5 wt% hmHEC at various SDS concentrations.

Table 1. Crossover modulus and frequency for solutions of 0.5 wt% hmHEC at various SDS concentrations

[SDS] (wt%)	G_c (Pa)	ω^* (rad./s)	$t^*=1/\omega^*$ (s)	Me (g/mol.)	Me/M_w
0	0.5	40	0.025	1.2×10^7	41
0.2	2.0	0.9	1.1	3×10^6	10
0.23	0.7	1.5	0.67	8.7×10^6	29
0.25	0.77	24	0.04	7.9×10^6	26

$t^* = 1/\omega^*$. The estimated values of t^* are also included in Fig. 1 as a function of SDS concentration, showing good self-consistency between the viscosity data obtained via steady shear measurements and elastic property, in the form of relaxation time, obtained from small amplitude oscillatory experiments.

From the dynamic storage modulus results shown in Figure 8, it is apparent that the plateau modulus G_N^0 is clearly not observable for the solutions of 0 and 0.25 wt% SDS. We may use the result of a single-mode network model that at crossover, $G' = G'' = G_c = G_N^0/2$ to estimate G_N^0 . The value of G_N^0 may be utilised to provide an estimate of the apparent molecular weight between elastically effective aggregates of polymer hydrophobes and surfactant, Me , using the general result from rubber elasticity network theory, that is, $Me = cRT/G_N^0$ (Ferry, 1980). The values of Me for the three solutions containing polymer-surfactant complex, plus the solution of pure polymer, are also given in Table 1 and range from 3×10^6 to 1.2×10^7 g/mol. These numbers are much larger than the molecular weight of the polymer, indicating that the polymer or polymer-surfactant network may consist of independent micro-structures or clusters, each containing between 10 to 40 polymer chains (of molecular weight 300,000 g/mol), i.e. equivalent to the

ratio M_e/M_w . Interestingly, the pure hmHEC is found to contain the largest number of about 40 polymer chains in the cluster, while the 0.2 wt% SDS solution contains the minimum number. These micro-structures or clusters then form hydrophobic associations with other such clusters via the hydrophobic side-chains on the outer surface of these clusters. With the addition of 0.20 wt% SDS the hydrophobic junctions between the clusters are reinforced by the binding of surfactant to form polymer-surfactant complex micellar junctions, as discussed previously. The minimum number of polymer chains per cluster found for the 0.2 wt% SDS solution also corresponds to the largest number of aggregates present in the network. This, together with the creation of surfactant enhanced micellar junctions, results in a greatly increased network strength, as manifested in the highest shear viscosity and elastic modulus. With further addition of SDS, the distance between elastically effective junctions or the number of polymer per cluster increases, hence the total number of clusters decreases, approaching that of the pure hmHEC solution, hence the drop in the network strength and corresponding decrease in the viscosity and moduli values with increasing SDS concentration. Interestingly, Nishikawa *et al.* (1998) reported from fluorescence studies on an identical polymer-surfactant system, that even though the number of polymer hydrophobes in each mixed micellar junction is low due to the stiff polymer backbone, larger polymer aggregates existed throughout solution. Unfortunately, no actual numbers of polymers involved in the clusters were detailed.

As more SDS is added (above 0.25 wt%), the distance between aggregate junctions obviously increases beyond that of the pure hmHEC solution, as such a length scale (i.e. longest relaxation time or value of G_c) is no longer accessible utilising our equipment (i.e. we cannot observe a crossover region).

Following the above discussion we thus propose that these viscoelastic hmHEC solutions do not represent a traditional percolative network of interconnected individual chains. Instead they are a large fractal network, of some defined fractal dimension d_f , composed of interconnected clusters of aggregated hmHEC chains of similar, and in fact most likely equal, d_f , akin to a concentrated solution of hairy spheres. Once surfactant is added, such hydrophobic junctions between the microclusters are strengthened and the number initially increased due to the strong driving force for formation of the surfactant-polymer micellar complex, as discussed previously. This results in the phase separation observed at low surfactant concentration and an obvious, significant reduction in the molecular weight between elastically effective junctions due to an increased junction density throughout all regions of the solution (Duahleh and Steiner, 1991). As the concentration of SDS is increased beyond the point where the network fills the entire solution volume forming again a one-phase system,

the aggregated number of polymer chains between junction points is continually increasing, until it finally returns back to that of the pure system. This does not mean that the size of the base microcluster is changing, just that the number of external junction points associated with these clusters is decreasing. However, we must recognise that the use of such a relationship to calculate the value of M_e for such a complex system (especially in the absence of true G_N^0 values) is purely for comparative purposes at this stage, and although there is a definite decrease in the moduli value as the surfactant concentration increases from 0.2 to 0.23 and 0.25 wt%, the number of polymer chains in the cluster given above is an indication only.

It is also apparent from the dynamic data that there is a definite decrease in the longest relaxation time of the systems as surfactant concentration increases, indicating a faster dissipation of stress. This is consistent with the assertion that the network junctions of mixed micelles have fewer polymer hydrophobic side-chains involved as surfactant concentration increases, resulting overall in a reduced number of effective junctions across (and possibly within) the microclusters.

3.5. Proposed shear-induced structures of hmHEC-SDS complexes

Considering the above discussion, and again drawing on the previously described mechanistic interpretations provided by Annable *et al.* (1993) and Tam *et al.* (1998), and on the recent models provided by Marrucci *et al.* (1993) and Vaccaro and Marrucci (2000) describing non-linear extensibility of linked chains between flower-like micelle clusters in associating telechelic HEUR polymer systems, we propose here a mechanistic model for the observed shear-induced thickening, thinning and final rupture of a network of hydrophobically modified HEC and SDS. We must recognise that the hmHEC + SDS system is inherently very different to HEUR and HASE systems, with the stiff cellulose backbone removing much of the conformational freedom allowed to the HASE and HEUR systems, not to mention the site specific nature of the hydrophobic groups in the well designed HASE or HEUR systems. This inherent chain rigidity will ultimately affect the solution morphology by increasing the probability of macroaggregates in solution, rather than smaller aggregates favoured in HEUR and HASE systems.

Fig. 9 provides a schematic of how these observed rheological phenomena may occur at the nominated stress transition levels. In this figure the spheres represent microclusters of 10 to 40 hmHEC polymer chains, as discussed previously. At low stresses the perturbed network of hmHEC microclusters is capable of relaxing back to the equilibrium state in the given time-frame associated with the invoked perturbation to the network. At higher stresses (labelled τ_{vis} in Fig. 9), expansion of the network occurs,

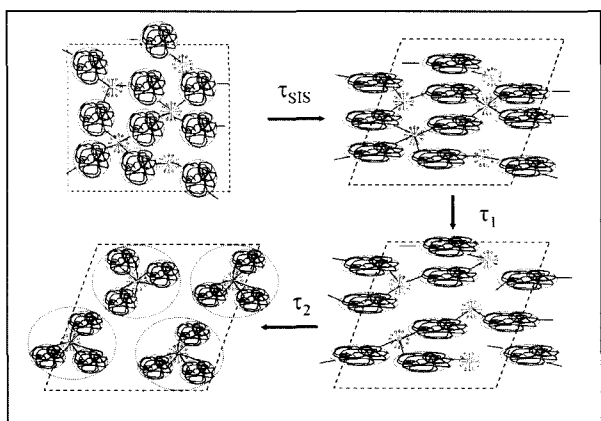


Fig. 9. Schematic diagrams of the proposed structures of polymer-surfactant complexes for the solutions showing shear-induced thickening, followed by structural break-up at higher stresses.

allowing structural rearrangement via the transient conversion of intra-chain hydrophobic associations between side branches (on the surface of the clusters) into inter-chain mixed micellar junctions. This transient exchange may increase the overall number of junctions, in line with the suggestions of Marrucci *et al.* (1993) and Vaccaro and Marrucci (2000), and/or the number of polymer hydrophobic groups per junctions may also increase, and hence increase the shear viscosity of the solution. At the lower *critical* stress, (labelled τ_1 in Fig. 9), the network undergoes partial, localised fracture as a result of a loss of active chain junctions on the surface of the microclusters throughout the volume, but is able to recover quickly these lost structural joints (as shown by the resilience of the 0.25 wt% SDS solution) as the generic fractal structure of the network has not been substantially changed. At and beyond the upper *critical* stress (labelled τ_2 in Fig. 9), the network is completely fractured across the whole sample volume as the fraction of active chain junctions at the surface of these microclusters approaches zero and a major structural change occurs, encouraged by the established flow. The final state of the sample is believed to be a loosely connected network of microgel-like clusters of similar fractal dimension as existed previously in the unperturbed network, with each cluster consisting of several polymer chains (~10 to 40) as found from the crossover modulus value at equilibrium states discussed in the previous section. Each of these collections of clusters is envisaged to be fairly self-contained and have few loose polymer alkyl side-chains, such that association with others to form a percolated network is significantly curtailed under flow, hence the drastic change in solution properties when sheared beyond this upper *critical* stress. That is, the imposition of shear simply brings the solution to a state where the smallest aggregated fractal cluster dominates the rheology of the

solution, in the absence of network ties to other such aggregates. This stage-wise network rupture is thus proposed to be representative of a significant morphological change within the solution due to the imposed stress or flow field, from an expanded network consisting of microclusters of hydrophobic junctions between flexible polymer chains, to a fractured network of larger aggregates, to finally a loosely connected microgel particle network. Note that at all stresses, the base unit is still the 10 to 40 hmHEC polymer chains forming the microcluster. High shear stress simply reduces the system back to the basic building blocks of the spanning network.

Attempts have been made to utilise Small Angle Neutron Scattering (SANS) to provide more detailed insight into the origin of these obvious structural transitions. Unfortunately, SANS data showed little difference in the system at each shear stress where a notable rheological transition occurred, suggesting that the appropriate length scales are beyond SANS resolution. Pedley *et al.* (1989) reported a similar outcome of SANS experiments for sodium sulfonated polystyrene ionomers, showing interestingly that shear-thickening was not accompanied by appreciable chain stretching (at least that which is detectable by SANS) in the direction of shear. The authors suggested that larger structural units, consisting of aggregates of many chains, must therefore exist in such associative polymer solutions. Marrucci *et al.* (1993) provided support for the mechanism proposed by Pedley *et al.* (1989) and suggested that if such large aggregates were attached to one another by a few chains to form a continuous network, as we have suggested to be the case for hmHEC and SDS, such an outcome (or lack of one as the case may be) for SANS investigations could be rationalised by considering that the proportion of the unstretched chains in the aggregates would, in effect, smother the small number of chains undergoing stretching at the surface of the aggregates. This chain stretching would thus be undetectable by neutron scattering even though chain stretching (at the surface of these aggregates) would still result in the prevailing contribution to the stress tensor in their model (Marrucci *et al.*, 1993). Further insight may be provided via static and dynamic light scattering or birefringence techniques to determine the actual or prevalent size domain at each sheared region. Preliminary static light scattering measurements (not shown here) performed in our group under quiescent conditions at all SDS concentrations show a correlation between added SDS and the characteristic length scale of the dominant species in solution, eluding to the fact that indeed there are aggregates of the size postulated in this paper which are dependent on the SDS concentration. Further static and dynamic light scattering experiments are underway. Other techniques such as fluorescence quenching, similar to those provided by Nishikawa *et al.* (1998), may also be necessary to provide further insight.

4. Conclusion

At 0.5 wt% in aqueous solution, hydrophobically modified HEC forms a two-phase system in the presence of low concentrations of SDS (< 0.2 wt%), consisting of a dense hydrogel and a supernatant. At higher SDS concentrations equal to and above 0.2 wt%, a one-phase system was formed. The viscosity of the hmHEC solution is greatly enhanced due to the cooperative binding of the surfactant onto the polymer alkyl (hydrophobic) aggregates. With further increases in SDS concentration, the solution viscosity decreases until above 0.3 wt% SDS, it is reduced to below that of the hmHEC polymer with no added surfactant. Prior to this SDS concentration, the hmHEC-SDS solutions show shear-induced thickening behaviour when sheared at low stresses, partial (recoverable) fracture of the network at moderate stresses and total network fracture at high stresses. From the effective molecular weight between elastic junctions estimated from the crossover modulus, G_c , we proposed that the hmHEC network consists of a basic unit of microstructures or clusters of 10 to 40 hmHEC polymer chains. These clusters are hydrophobically linked with others via the hydrophobic chains on the surface of the clusters, and the junctions are enhanced by the mixed hydrophobic aggregates formed in the presence of SDS. Shear-induced thickening is thus believed to be due to structural rearrangement of these clusters, resulting in an increase in the effective number of bridges formed between them by polymer alkyl side-chains. Further increase in the stress causes a partial fracture of the microgel network, and thus a decrease in the viscosity. This partially fractured network quickly recovers once this level of stress is removed. However, beyond an upper critical stress, the system is proposed to be reduced to the basic microgel-like structures, with minimum numbers of particle-particle junctions existing throughout the solution. At such high stresses, these microgel particles are expected to be in a modified state with fewer side branches persisting at the surface of the particles than at lower stress levels due to the imposed flow. Such particle-particle associations, previously made possible by surface hydrophobe groups, are thus curtailed, producing the observed lower viscosity of the hmHEC-SDS solutions when remeasured.

Acknowledgements

The authors would like to thank Dr Johannes Zipfel (ILL, Grenoble) for the SANS tests and analysis. The authors are also very grateful for the support provided by the Particulate Fluids Processing Centre, the University of Melbourne, and to the reviewers for their constructive comments.

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