

Interactions of methylated β -cyclodextrin and hydrophobically modified alkali-soluble emulsion (HASE) polymers: a rheological study

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ABSTRACT

The interactions between methylated β -cyclodextrin (CD) and hydrophobically modified alkali-soluble associative polymers (HASE) were examined by a rheological technique. The effect of "capping" of hydrophobes by methylated β -cyclodextrin on the viscosity and modulus was evaluated. Model HASE polymers with C₁ to C₂₀ alkyl hydrophobic groups ethoxylated with ~ 10 moles of ethylene-oxide (EO10) and at concentrations up to 3 wt% were examined. With the addition of methylated β -CD, the steady shear viscosity profiles shift from a Newtonian profile to one that display a shear-thinning characteristic. Significant "capping" of the hydrophobes occurs for HASE polymers with C₁₂, C₁₆ and C₂₀ hydrophobes as reflected by the large reduction in the viscosity. However, the steady shear viscosity remains constant when the concentration of β -CD exceeds 1 wt%, suggesting that β -CD is not able to fully encapsulate the hydrophobes of the HASE polymer. The temperature variation plots indicate that the activation energy of the HASE-EO10-C₂₀ system and β -CD is dependent on the magnitude of the applied shear stress. These results further reinforce the hypothesis that β -CD is not able to completely remove all the hydrophobic associations.

Keywords : methylated β -cyclodextrin, associative polymers, rheology, hydrophobicity.

1. Introduction

Aqueous coating systems typically employ thickeners to achieve the desired rheological properties needed for a given application. Associative thickeners, [Li (1995), Tam and Tiu (1996)] which thicken by hydrophobic associations, are becoming more popular. Various types of associative thickeners such as hydrophobically modified polyurethane (HEUR), hydrophobically modified alkali soluble emulsions (HASE), hydrophobically modified cellulosic system, and hydrophobically modified polyacrylamides have been reported in the literature [Jenkins (1990), Annable and co-workers (1993), Aubry and Moan (1994), Hulden (1994)]. Some of these associative thickeners contain organic co-solvents. The function of organic co-solvents is to suppress the viscosity of the aqueous solution containing the associative thickener, which is necessary for handling purposes. While these organic co-solvents perform their intended function, they pose potential environmental, safety and health concerns. Viscosity suppression may also be accomplished by the use of surfactants. While,

this presents no specific health/environmental hazard, it complicates the formulation and alters the performance of paints.

A method, which uses a cyclic polysaccharide molecule (β -cyclodextrin in this case) to suppress the viscosity of the aqueous solution containing the thickener was recently patented by Eisenhart and co-workers (1992), and Lau and Shah (1994). This procedure is very effective in reducing the viscosity of the thickener solutions. Lau & Shah (1994) disclosed that methyl β -cyclodextrin is effective in suppressing the viscosity of the aqueous solutions of hydrophobically modified thickeners. Both Eisenhart and co-workers (1992) and Lau and Shah (1994) disclosed that modified version of cyclodextrin are preferred to the unmodified versions of cyclodextrin. Recently Islam & co-workers (2000) studied the interaction of methylated β -cyclodextrin on HASE solutions using static and dynamic light scattering techniques. Their study showed that β -cyclodextrin may be able to fully encapsulate the hydrophobes. However, the implication of such interactions on the rheological behavior has not been reported. The present study is aimed at developing a better understanding on the interaction between the methylated β -cyclodextrin and HASE polymers. This paper examines the interactions of

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β -cyclodextrin and a series of model HASE polymers with different hydrophobic moieties and its effects on the rheological properties.

2. Experimental Section

2.1. Materials and Sample Preparation.

The materials used in this study are model HASE polymers prepared by Union Carbide. Details on the polymerization technique and dialysis have been reported by Jenkins and co-workers (1996), and Tam and co-workers (1997). The chemical structure of the HASE polymer is shown in Fig. 1, where $x:y:z=49:50:1$; x, y, z represents the mole fraction of each segments of the polymer chain. P is the length of PEO chains and R is the hydrophobic alkyl group. Details of the chemical composition of HASE model polymers used in this study are shown in Table 1. Randomly methylated- β -cyclodextrin was obtained from Cyclodextrin Technologies Development Inc and its properties are described in details by Shieh and Hedges (1996) and Szejtli (1998). Fig. 2 gives a pictorial representation of the top and side views of a β -cyclodextrin (β -CD) molecule. Structurally β -CD consists of 7 D-glucopyranosyl units connected by alpha-(1,4) glycosidic linkages. The most stable three dimensional molecular

configuration for these non-reducing cyclic oligosaccharides takes the form of a toroid with the upper (larger) and lower (smaller) opening of the toroid presenting secondary and primary hydroxyl groups, respectively, to the solvent environment. The interior of the toroid is hydrophobic as a result of the electron rich environment provided in large part by the glycosidic oxygen atoms. The hydrophobic

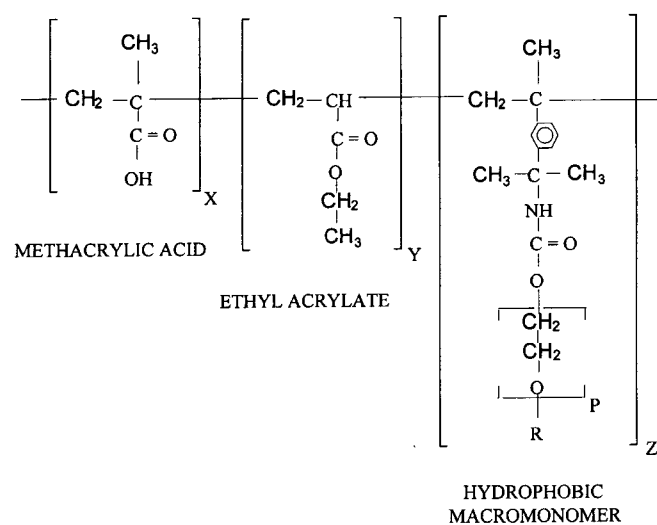
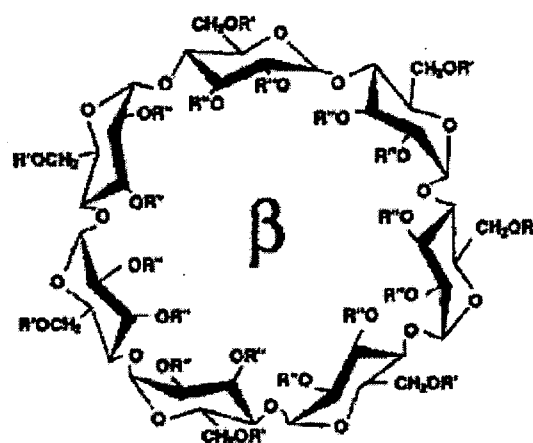
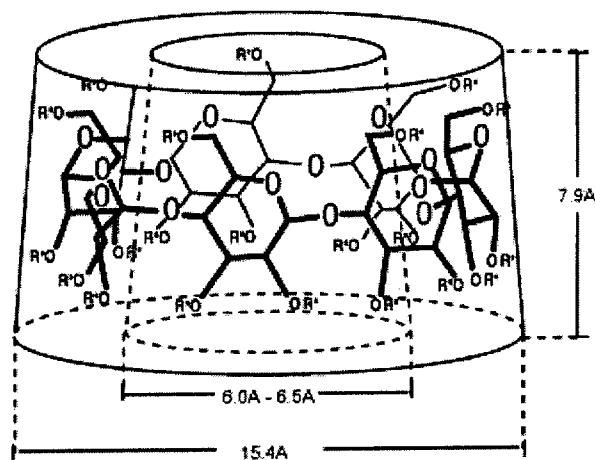


Fig. 1. Chemical structure of model HASE polymer.



(a) Top view



(b) Side view

Fig. 2. Pictorial representation of β -cyclodextrin molecule (a) top view, (b) side view (obtained from Cyclodextrin Technologies Development, Inc.).

Table 1. Chemical compositions of model HASE-EO10 polymers

Polymer designation	Carbon Number of Hydrophobe	Target EO	Actual EO	Hydrophobe formula
HASE-EO10-C1	1	10	10.2	CH ₃
HASE-EO10-C4	4	10	10.0	C ₄ H ₉
HASE-EO10-C8	8	10	10.3	C ₈ H ₁₇
HASE-EO10-C12	12	10	9.2	C ₁₂ H ₂₅
HASE-EO10-C16	16	10	10.3	C ₁₆ H ₃₃
HASE-EO10-C20	20	10	10.5	C ₂₀ H ₄₁

cavity is ~ 6 -7 Angstroms in diameter. We hope to utilise the hydrophobic cavity to encapsulate the hydrophobic moiety of the associative polymer.

A 3 wt% stock solution of model HASE emulsion polymer was prepared in 1×10^{-4} M KCl. From the 3 wt% stock solution, various weight concentrations of HASE samples were prepared by diluting with 1×10^{-4} M KCl. 2-amino-2-methyl-1-propanol (AMP) was added to neutralize the polymer to the desired pH of ~ 9 . It has been shown by Tam and co-workers (1998) that there is no significant change in the viscosity when the pH is greater than 9.

2.2. Preparation of methyl β -CD solutions.

Since the maximum solubility of pure β -CD is approximately 18 grams per 100 grams of 10^{-4} M KCl [Shieh and Hedges (1996)], 10 grams of pure β -CD was used instead. The pure β -CD powder was mixed with 10^{-4} M KCl solution using the ultrasonic bath (Branson 1210) until no powder was observed at the bottom of the container. The container was then sealed. The HASE and β -CD solution of the desired concentration was prepared and the pH value of the mixture adjusted to pH of ~ 9.0 to 9.5. This final solution was mixed thoroughly using a magnetic stirrer for 24 hrs at 60°C and rheological tests were conducted.

A Contraves Low shear (LS 40) and Rheometric Scientific ARES fluid rheometers were used for rheological measurements. The LS 40 is a controlled rate rotational rheometer and is fitted with the MS 41S/1S concentric cylinder measuring system consisting of a cup with the diameter of 12 mm and a bob with the diameter of 11 mm and length of 8 mm. Rheometric Scientific ARES fluids rheometer with double wall Couette cylinder geometry (Cup OD = 34 mm, Cup ID = 27.95 mm, Bob OD = 32 mm, Bob ID = 29.5 mm) was also used for rheological measurements. Both the rheometers are equipped with a circulating water bath to control the temperature to within $\pm 0.1^\circ\text{C}$. Experiments were carried out at various temperatures ranging from 10 - 45°C .

3. Results and Discussion

3.1. Effect of Carbon Number on the Flow Properties of HASE-EO10Cn Polymers

In this study, the hydrophobe in the HASE-EO10-Cn series is varied from C_7H_{15} to $\text{C}_{20}\text{H}_{41}$ alkyl chains. The hydrophobicity of the macromonomer increases with the length of hydrophobe or carbon content of the alkyl chain. The nature of the hydrophobes controls the strength of the intermolecular associative junctions, which is directly related to the strength of the network structure [Guo (1997)]. The thickening efficiency of the model associative polymer is dependent on the length of the alkyl chain of the hydrophobe.

Fig. 3(a) to 3(d) show the steady shear viscosity profiles of 0.5 to 2.0 wt% model HASE systems respectively. At a lower concentration of 0.5wt%, essentially Newtonian viscosity profiles are observed. However, at higher concentrations, shear-thinning behavior becomes evident and the extent of shear thinning behavior is more pronounced for C_{16} & C_{20} solutions. As the hydrophobe length increases the extent of shear thinning is delayed i.e. for C_{16} & C_{20} solution, shear thinning occurs at higher shear rates. The Newtonian region corresponds to the net balance in the destruction and creation of hydrophobic junctions. The shear thinning at high shear rates is related to the disruption of increasing proportion of active junctions.

Fig. 4 shows the influence of length of alkyl chain on the viscosity of different polymer concentrations of HASE solutions neutralized to pH of 9.0. For the 0.1wt% solutions, the viscosity decreases with increasing length of alkyl chains. At low concentration, fewer hydrophobes are present in the solution and these hydrophobes tend to form predominantly intra-molecular hydrophobic clusters. Such interaction decreases the hydrodynamic volume, resulting in the decrease in the viscosity of the system. For all the concentrations greater than 0.1 wt%, the viscosity decreases as the carbon number of the hydrophobes increases from 1 to 8, which is attributed to the increase in the intra-molecular interaction. At polymer concentrations of less than 1.5 wt%, the viscosity of the solution increases when carbon number increases from 8 to 16 and then decreases when the carbon number approaches 20. This trend can be correlated to the onset of the development of the associative polymer network. The balance in the formation of intra-molecular and intermolecular junctions is responsible for the trend observed in Fig. 4. The size of individual cluster comprising of 3 to 5 polymer chains decreases with increasing hydrophobicity of the macromonomer [Dai *et al.* (2000)]. The decrease is related to the increase in the aggregation number as the carbon content increases. The increase in the viscosity between the C_8 and C_{16} hydrophobe is related to development of increasing proportion of inter-molecular network junctions. This is attributed to the existence of a critical network concentration at between 1.0 to 1.5 wt%. At the critical network concentration, the associative network structure becomes developed. However, when the concentration exceeds 1.5 wt%, the viscosity of the solution increases with the carbon number. Above the critical network concentration, there are temporary cross-links between aggregates, which reinforce the structure of the polymer, and possess a higher resistance to shear deformation. This leads to an increase in the viscosity.

Previous rheological studies [Seng *et al.* (1998)] on HASE-EO35 polymers in low salt solution (i.e. 10^{-4} M KCl) revealed that the carbon number of the macromonomer did not have any significant effect on the

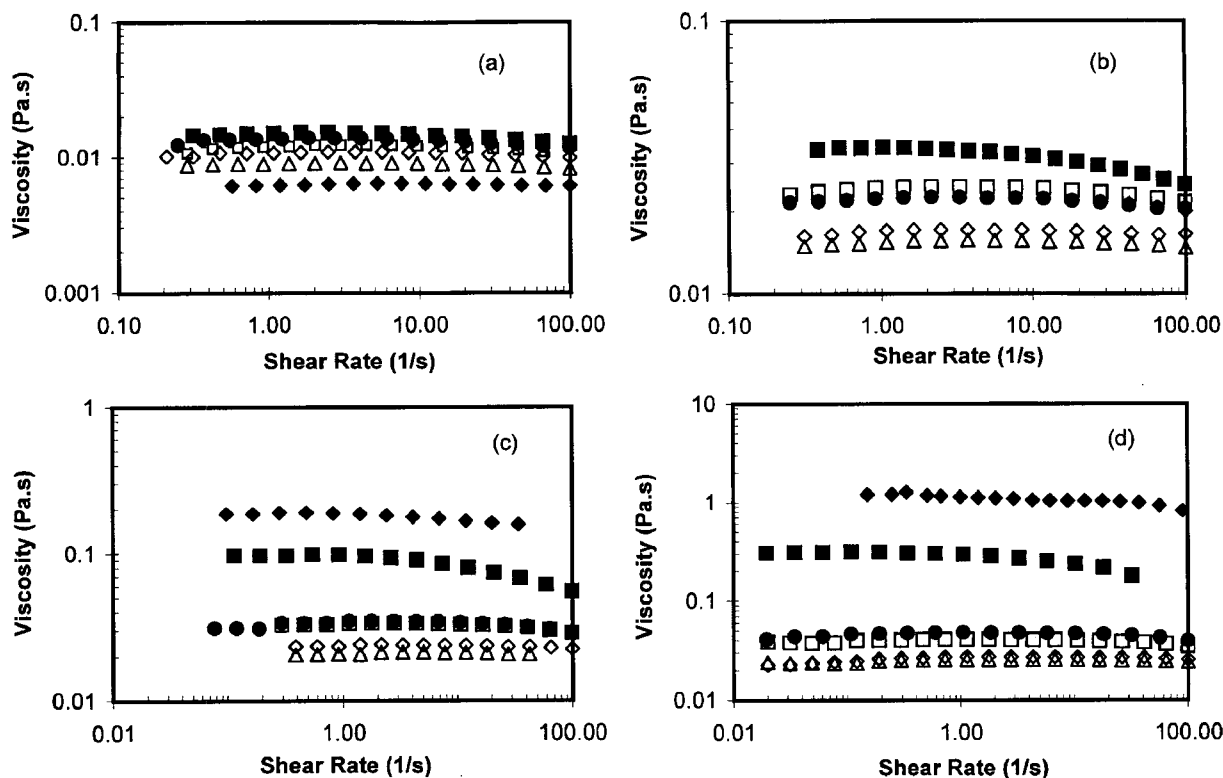


Fig. 3. Dependence of viscosity on the shear rate for (a) 0.5 wt%, (b) 1.0 wt%, (c) 1.5 wt% and (d) 2 wt% of the model polymer systems. Legends: \square HASE-EO10-C1; \diamond HASE-EO10-C4; \triangle HASE-EO10-C8; \bullet HASE-EO10-C12; \blacksquare HASE-EO10-C16; \blacklozenge HASE-EO10-C20.

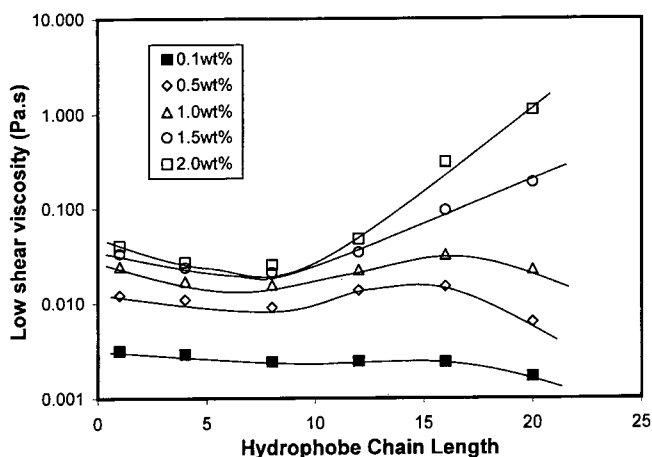


Fig. 4. Influence of carbon number on the viscosity of HASE-EO10 series at various concentrations at pH of 9.0.

solution viscosity when carbon number is less than eight. However, at carbon number greater than eight, the viscosity of the HASE solutions increased as the carbon number increased. This behavior is almost similar to that of HASE-EO10 polymers examined here. Due to the different critical network concentration, there may be a change in the rheological properties of the HASE-EO10 polymers at concentration greater than 1.5 wt%.

3.2. Effect of Adding Randomly Methylated β -Cyclodextrin into model HASE-EO10 Series.

Cyclodextrin has an internal hydrophobic cavity that is able to associate with the hydrophobes of HASE polymer. After “capping” the hydrophobe, the hydrophilic exterior of the cyclodextrin would favor interactions with water. Hence, viscosity changes can be detected. We examined effect of using different concentrations of methylated β -cyclodextrin on the flow characteristics of the HASE-EO10 polymer series. The carbon number was varied from C₁ to C₂₀ and the concentration of β -CD was varied from 1 wt% to 3 wt%. The concentration of HASE-EO10 series was kept constant at 2 wt%. The effects of β -CD concentrations on the viscosity profile of different HASE solutions are shown in Fig. 5 (a) to 5 (d) for HASE-EO10-C₁ HASE-EO10-C₁₂, HASE-EO10-C₁₆ and HASE-EO10-C₂₀ respectively.

The viscosity of β -CD/HASE-EO10 polymer solutions decreases with increasing β -CD concentrations. This suggests that the structure of the associative network is being disrupted by the addition of β -CD. This behavior is most significant in the HASE-EO10-C₁₆ and HASE-EO10-C₂₀ mixed with β -CD (Fig. 5(c) and 5(d)). It can also be concluded that the amount of “capping” by β -CD is dependent on the hydrophobicity of the HASE polymer.

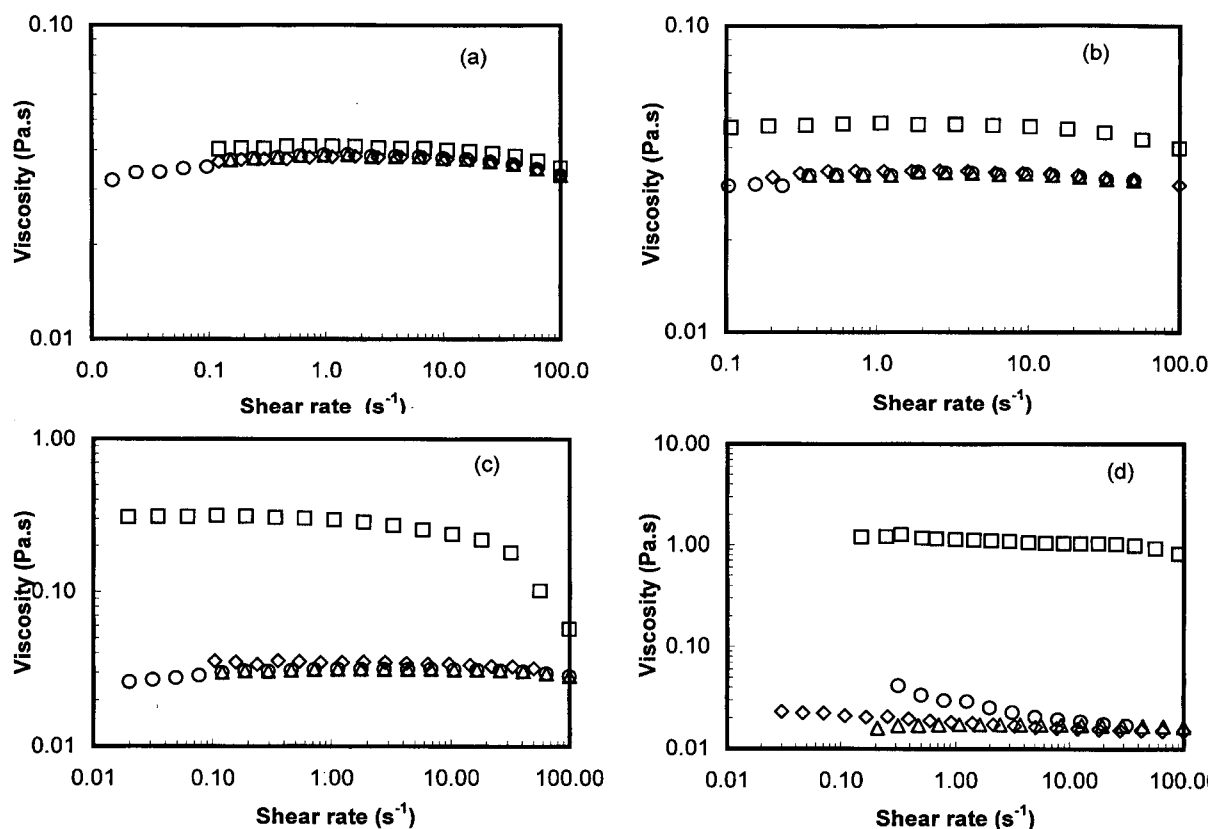


Fig. 5. Effect of different concentrations of methylated β -CD on shear viscosity for (a) HASE-EO10-C1, (b) HASE-EO10-C12, (c) HASE-EO10-C16 and (d) HASE-EO10-C20 model polymer system.
 Legends: \square 0.0 wt%; \diamond 1.0 wt%; \triangle 2.0 wt%; \circ 3.0 wt%.

A control experiment was also carried out with HASE polymer without hydrophobic macromonomer (designated as HASE 107) attached to the polymer backbone. The addition of 0.5 to 3 wt% of β -CD to the HASE 107 does not significantly change the viscosity of the solution. In fact, the HASE 107 mixed with β -CD exhibits a Newtonian viscosity profile, since HASE 107 possesses a structure consisting of blocky EA groups, which associate with one another along the polymer backbone. The present result suggests that the association cannot be affected by the addition of β -CD. However, β -CD may interact with CH_3 or CH_2 groups along the backbone of the HASE 107 system. Islam *et al.* (2000) studied similar polymer in the presence of β -CD using static and dynamic light scattering and observed that the size of the cluster does not change. They also performed light scattering experiments on HASE-EO31-C₂₀ and a large drop in the particle size was observed when the molar ratio of β -CD to the hydrophobes is larger than 200. However, when the molar ratio is less than 200, there is no significant decrease in the particle size.

Adding 0.5 wt% to 3 wt% of β -CD into HASE-EO10-C₁, HASE-EO10-C₄ and HASE-EO10-C₈ does not alter the viscosity of the solution (Fig. 6). This could be due to the

length of the hydrophobe, which forms individual clusters with the hydrophobic backbone that acts as an artificial barrier that prevent β -CD polymers from penetrating into the cluster. Thus, β -CD is unable to remove these associations by “capping” the hydrophobes.

On the other hand, adding 0.5 wt% to 3 wt% of β -CD into HASE-EO10-C₁₂, HASE-EO10-C₁₆ and HASE-EO10-C₂₀ significantly changes the viscosity of the solution. From Fig. 6, it is clear that the relative viscosity of the solution after adding β -CD shows a sharp decrease after a small amounts of β -CD is added into the solution. Thus, β -CD have the potential to bind to the hydrophobic moiety of the HASE polymer and reduce the tendency of HASE polymer to associate and form cross-links between the polyelectrolyte chains. Evidently, the interaction between the β -CD and HASE polymer is strong enough to disrupt the polymer network structure. This indicates that β -CDs have capped the hydrophobes thereby partially destroying the polymer network structure. It can be seen that the viscosity of the β -CD/HASE solutions does not decrease further after the addition of 1 wt% of β -CD. That is, the β -CD could not fully cap all the hydrophobes. This is a clear demonstration of the ability of CDs to partially cap the hydrophobes. Tsianou and Alexandridis (1999), while

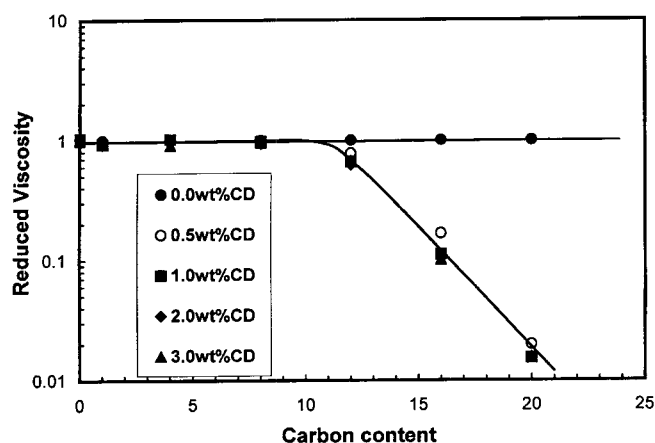


Fig. 6. Effect of addition of methylated β -CD on the reduced viscosity of HASE-EO10 model polymer system.

examining both β -CD and β -CD (having different cavity diameter and different capacity for accommodating hydrophobic species), at different surfactant (SDS) concentration demonstrated the ability of the cyclodextrins to control (and completely reverse) the viscosity enhancement effected by surfactant mixed with oppositely charged polyelectrolyte. Similar findings were reported by Lau and Shah (1994).

3.3. Effect of temperature on 2 wt% of HASE HASE-EO10-C₂₀ polymer at different concentrations of Methylated β -Cyclodextrin.

One of the techniques used to probe the polymer associative mechanism is by studying the polymer response when subjected to different temperatures. Since HASE-EO10-C₂₀ is the most hydrophobic among the HASE-EO10 polymer series, it was chosen for the study on temperature effects in the presence of β -CDs. The viscosity profile of 2 wt% HASE-EO10-C₂₀ exhibits a shear thinning behavior upon the addition of β -CD for concentration of between 1 to 5 wt%. Fig. 7a shows the viscosity profile of 3 wt% β -CD in 2 wt% HASE-EO10-C₂₀ HASE polymer system. It is clear that the network structures are broken down continuously when the shear stress is increased. This indicates that β -CD has fragmented the hydrophobic associations between the hydrophobes of HASE-EO10-C₂₀.

It can be seen that the viscosity profiles of HASE-EO10-C₂₀/ β -CD solutions (Fig. 7a) shift downwards as the temperature increases. The viscosity-temperature dependence follows the typical Arrhenius expression as indicated in Fig. 7b for a 2 wt% HASE-EO10-C₂₀ in 1 wt% β -CD solution. With increasing temperatures, the polymer hydrophobes become more hydrophobic and thus, the aggregation number of the junction increases resulting in a corresponding decrease in the number of junctions. As a result, the viscosity of the polymer decreases. At low shear

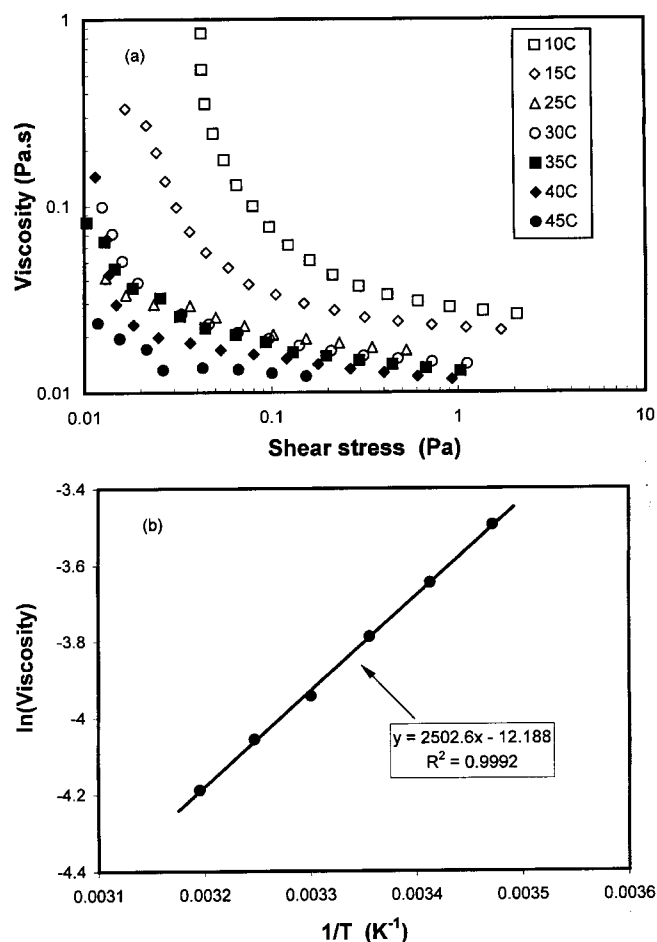


Fig. 7. (a) Influence of temperature on the viscosity of 3 wt% methylated β -CD & 2 wt% HASE-EO10-C₂₀ solution; (b) Arrhenius dependence of viscosity on temperature for 2 wt% HASE-EO10-C₂₀ in 1 wt% β -CD.

rates, the structure of the HASE-EO10-C₂₀ & β -CD combined system is not totally destroyed. Moreover, the recovery rate of the HASE-EO10-C₂₀ & β -CD solution is very fast (< 10 sec) and the recovery rate could be faster than the rate of deformation. Therefore, the hydrophobes associate with one another at a faster rate than the destruction of the junctions. The addition of β -CD up to 1 wt% causes the activation energy to decrease from 53 to 20-23 kJ/mol at moderate shear stress of 0.1 Pa, indicating that the overall strength of the junctions is reduced due to the disruption of the active junctions by β -CD molecules. It is also possible that there is more than one β -CD molecule associating with the HASE-EO10-C₂₀ hydrophobes at one time. This is due to the fact that the length of the HASE-EO10-C₂₀ hydrophobe (~ 31 angstroms) is much longer than the height of the β -CD cavity (~8 angstroms). Therefore, several β -CDs can string onto one HASE-EO10-C₂₀ hydrophobe. The schematic diagram is shown in Fig. 8.

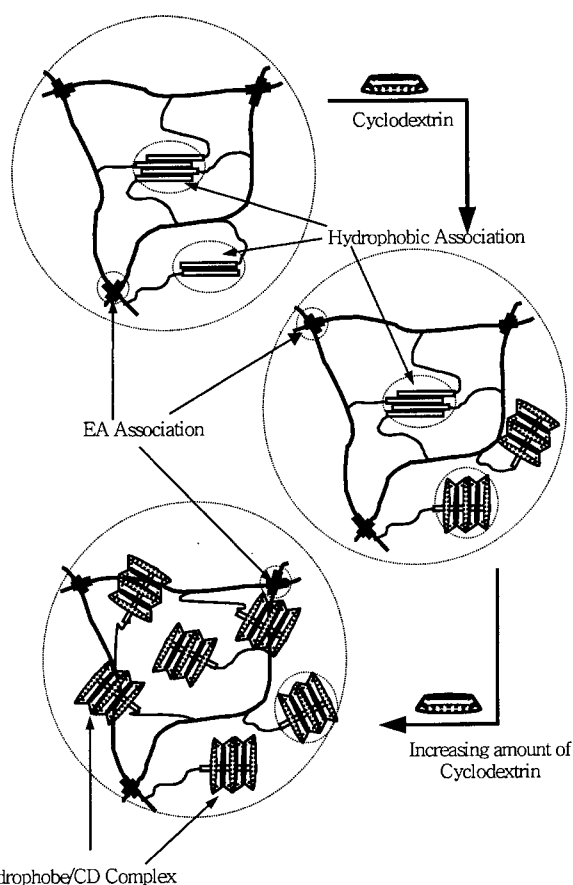


Fig. 8. Schematic diagram of more than one methylated β -CD polymer associating with the HASE-EO10-C20 hydrophobes.

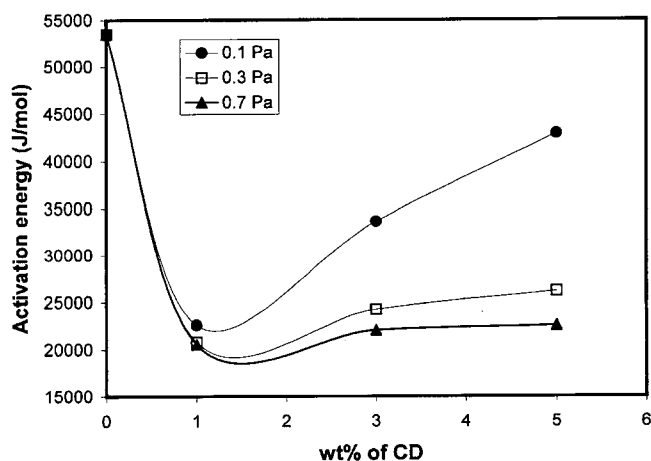


Fig. 9. Influence of different concentration of methylated β -CD on the activation energy of 2 wt% HASE-EO10-C20 at different shear stress.

From Fig. 9, it is observed that the magnitude of activation energy at three shear stresses differs significantly when the amount of β -CD exceeds 1 wt%. The largest activation energy is observed at a low shear stress of 0.1

Pa. The polymer/ β -CD complexes are extremely shear-sensitive and the strength decreases sharply, for example E_a of 2 wt% HASE in 5 wt% β -CD decreases from 42 to 23 kJ/mol when the applied stress increases from 0.1 to 0.7 Pa. The disruption of inter-molecular junctions by β -CD is responsible for the weakening of the network, which renders it to be more sensitive to deformation. However, the activation energy of the HASE-EO10-C₂₀ & β -CD solution increases at β -CD greater than 1 wt% for all shear stresses. Since, an increase in the activation energy corresponds to an increase in the strength of the junctions, we can infer that this may be due to the formation of β -CD complexes consisting of a fewer number of alkyl hydrophobic moieties from different backbone and β -CDs. These complexes are however extremely shear-sensitive. Since the alkyl group is linear, and the internal diameter of the β -CD cavity is much larger than the diameter of HASE-EO10-C₂₀ hydrophobe, more than one HASE-EO10-C₂₀ hydrophobes can fit into the β -CD molecule when the number of β -CD molecules is high.

We would like to point out that the rheological data are “macroscopic” property and thus may not provide all the microstructural information on the polymer-cyclodextrin interactions at a molecular level. Other experimental techniques, such as fluorescence [Winnik and Regismond (1996)], titration calorimetry [Bloor and co-workers (1995)] or light scattering [Tsianou and co-workers (1999)] may prove beneficial to this end. These techniques are currently being utilised to obtain detailed microstructural information of the complexes. Nevertheless, on the basis of analysis described above, we can extract useful information on the HASE-CD interactions. Despite its limitations, rheological techniques provide useful and direct information on the impact of adding additives on the rheological behaviour of a given formulation.

4. Conclusions

Our study has shown that HASE polymers interact with methylated β -CD. In the presence of methylated β -CD, the steady shear viscosity profiles display a shear-thinning behavior. There is significant “capping” of the hydrophobes in the HASE-EO10-C₁₂, HASE-EO10-C₁₆ and HASE-EO10-C₂₀ since the viscosity of these model systems in methylated β -CD decreases significantly. Further addition of methylated β -CD does not change the steady shear viscosity, suggesting that methylated β -CD is unable to “fully cap” the hydrophobes of the HASE polymer. The temperature variation plots indicate that the activation energy of the HASE-EO10-C₂₀/methylated β -CD complex is dependent on the magnitude of the applied shear stresses. These results further support the hypothesis that methylated β -CD and HASE polymers form complexes that are extremely shear-sensitive.

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