Colloids and Surfaces A: Physicochem. Eng. Aspects 364 (2010) 105–108

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Investigating the Uni-HEUR thickener performance considering hydrophilic segment length

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ARTICLE INFO

Article history:
Received 12 January 2010
Received in revised form 4 May 2010
Accepted 5 May 2010
Available online 12 May 2010

Keywords:
Uni-HEUR
Hydrophilic
Hydrophobic
Segment
Thickener

ABSTRACT

Hydrophobically modified ethoxylated urethane models were synthesized through hydrophobic modification of poly(ethylene glycol) (PEG) by octadecyl isocyanate. Their structure consisted of linear water-soluble PEG backbones of number average molecular weight 6000 and 10,000 which end capped by aliphatic C_{18} chains attributed to octadecyl isocyanate. The behavior of thickener models was studied in both DDI (double distilled water) and a water-based resin of vinyl acrylic copolymer emulsion. The steady and oscillatory shear viscosity of both aqueous and resin systems containing the thickener models were determined. The result for constant hydrophobic length (C_{18}) showed that the associative thickener with higher molecular weight of PEG or longer hydrophilic length presents superior rheological properties. The concentration of thickeners can influence the phase behavior of the systems in such a way that for smaller length of the thickener the interconnection among micelles and the emulsion particles exist at equilibrium (concentrations of 2–3 wt%). However, for the higher-length associative polymer, it disappears upon a concentration rise to 4 wt%.

1. Introduction

The rheological behavior of associative thickener is a topic of considerable interest to both industry and academia. In recent years, the hydrophobically modified ethoxylated urethanes (HEURs) have been widely studied [1–8]. The structure of HEUR associative thickeners consists of a hydrophilic segment such as poly(ethylene glycol) and the hydrophobic hydrocarbon groups located at the ends of hydrophilic segments. Polyurethane associative polymers can be divided, considering the synthesizing method or molecular weight distribution into two categories: S-G HEUR and Uni-HEUR [9]. The S-G HEUR has a distribution of molecular weights and is produced by a step growth polymerization technique. The isocyanate terminated prepolymer is prepared via reaction of poly(ethylene glycol) and a molar excess of an aliphatic diisocyanate. The S-G HEUR polymer is obtained by the reaction of an aliphatic alcohol or an alkyl amine with the isocyanate terminated prepolymer. The Uni-HEUR is synthesized by adding a mono-isocyanate, containing an aliphatic chain, to PEG. This could also be done by adding a large excess of diisocyanate to PEG followed by the reaction of an aliphatic alcohol and/or an alkyl amine. In this case, an associative polymer is obtained with a low molecular weight distribution proportional to molecular weight distribution of the PEG. The schematic structure of both S-G HEUR and Uni-HEUR are presented in Fig. 1.

The S-G HEUR associative thickeners have been studied thoroughly [10–18]. Topics include synthesis and characterization of thickeners, comparing the thickening efficiency of S-G and Uni-HEURs, studying the transient network theory or physical network formation. The effect of molecular weight and hydrophobic length has also been widely studied. Other studies include investigating the effect of internal groups due to the presence of diisocyanate and the influence of the molecular weight of the prepolymer on the properties of aqueous S-G HEUR solutions. There are many research reports on Uni-HEUR in the literature [19–28]. They have focused on shear flow behavior, degree of hydrophobic substitution, the binding behaviors of ionic and anionic surfactant with HEUR polymers and relationship between structure and rheological properties.

In this work, two Uni-HEUR thickeners were designed and synthesized with a constant hydrophobic length and various hydrophilic lengths attributed to the two different molecular weights of PEG. The rheological properties of thickener models were studied in the aqueous solution and in a water-based resin.

2. Materials and methods

In order to conduct the polymerization various chemicals are needed as they follow: poly(ethylene glycol) as polyol with the

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doi:10.1016/j.colsurfa.2010.05.002

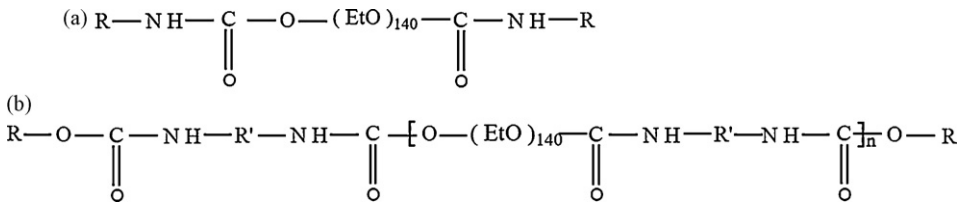

Fig. 1. The schematic structure of hydrophically modified ethoxylated urethane with hydrophilic backbone and hydrophobic end segments (R), (a) Uni-HEUR (b) S-G HEUR.

molecular weight 6000 and 10,000 which was purchased from Merck. Octadecyl isocyanate as the diisocyanate (CH_3-$(CH_2)_{17}$-NCO) was received from Sigma–Aldrich and was used as received. The catalyst of the reaction, dibutyltin dilurate was obtained from Fluka. Petroleum ether, a solvent with a low boiling point, was purchased from Pars chemie. Industrial grade THF, Toluene and acetone to be used as solvent were obtained and utilized. As latex, some industrial latex, briefly called VC-146, was kindly provided by an Iranian company: Simab Resin. Vc-146 is basically a vinyl acrylic copolymer produced by an emulsion polymerization procedure. The viscosity of resin versus shear rate has a slope of −1 where viscosity ranges from 10 to ca. 0.005 Pas and shear rate varies from 0.01 to 100 s^{-1}. The steady shear viscosity measurements were performed implementing a Paar Physica MCR 300 cone and plate rheometer. The cone angle and plate diameter were 2° and 50 mm, respectively. The temperature was set to 25 °C. The rheometer was utilized in two different modes, the steady state and the dynamic oscillatory modes. The time for the steady viscosity measurement was selected to ensure the steady state viscosity. The strain/stress for the dynamic test was chosen in such a way to produce data in the linear viscoelastic region for the applied frequencies. G′ and G″ were obtained and was converted to the complex viscosity. The dynamic and steady state viscosity were plotted in the same graph for the sake of comparison. The change in viscosity is also shown as bar-graph for different concentrations of the used associative polymer in water with and without the latex (acrylic) particles.

2.1. Synthesis procedure

In this work, Uni-HEUR was achieved from direct reaction of PEG with octadecyl isocyanate. Octadecyl isocyanate contains only one isocyanate functional group. If there is any trace of water in the reaction system, it can easily react with isocyanate group. This prevents the substitution of hydrophobic segment with PEG and results in reduction of the degree of substitution. Thus, it is necessary to dry all the raw materials and solvents, i.e. PEG, THF and toluene.

PEG was dried by the azeotropic distillation from toluene in a reaction flask. Octadecyl isocyanate was added to the mixture of PEG and the dried toluene. Then five droplets of dibutyltin dilurate in 50 cc of the dried THF were added to reaction system. The reaction vessel was a four-neck 500 ml round bottom flask. The flask was equipped with a magnetic stirrer and a reflux column equipped with the dried and pure nitrogen gas. They were located in an oil bath at 50 °C. The reaction mixture was then continuously stirred for approximately 1.5 h.

The reactor content was precipitated in petroleum ether (four volumes of petroleum ether and one volume of reaction mixture) collected on a sintered glass funnel and dried in a vacuum oven. Purification of the HEUR thickener models was performed by dissolution in warm acetone, filtering on a filter paper and further precipitation into petroleum ether. Final product was produced by collecting on a sintered glass followed by drying in a vacuum oven.

3. Results and discussion

The steady shear viscosity profiles as a function of shear rate for the aqueous solutions of three concentrations of 2, 3 and 4 wt% of thickener model in double distilled water are depicted in Fig. 2. All three solutions of Uni6M showed an initial reduction in viscosity. The rate of reduction is reduced by increasing the weight percent of thickener. The dissolution phenomena in aqueous solution are twofold. One is the micelle formation between individual thickener molecules and seconds is the interconnection of these micelles to form a two/three dimensional structure. The interaction among micelles affect the viscosity profile at low shear rates if they interconnected. Upon increase concentration, the interconnecting molecules form new micelles resulting in a loose network and viscosity becomes pseudo-Newtonian. So the phenomenon one proposes is the interplay between a new micelle formation and the existing micelles interconnection. For the most concentrated sample, the smallest slope of viscosity versus shear rate is observed which boosts the hypothesis of new micelle formation with less interaction. Fig. 3 shows the viscosity profile for dissolution of Uni6M in the VC-146 water-based resin. Here, unlike the behavior of Uni6M in water, an initial sharp drop in viscosity with shear rate is not observed. The dynamic viscosity for three concentrations remains the same and the steady viscosity profile shows the same trend. This indicates that the micelles do not interconnect with increasing the polymer concentration in the resin.

The thickening efficiency is determined from the low shear viscosity shown in Figs. 2 and 3 (ca. 0.01 s^{-1}) and depicted in Fig. 4. We see that the thickening efficiency was increased with rising Uni-HEUR concentration. There is no significant rise in thickening efficiency upon addition of 2 and 3 wt% of thickener while a considerable increase in thickening efficiency is observed once 4 wt% of Uni-HEUR model is added.

The profile of steady shear viscosity versus shear rate of samples with various concentration of Uni10M in water is observed in Fig. 5.

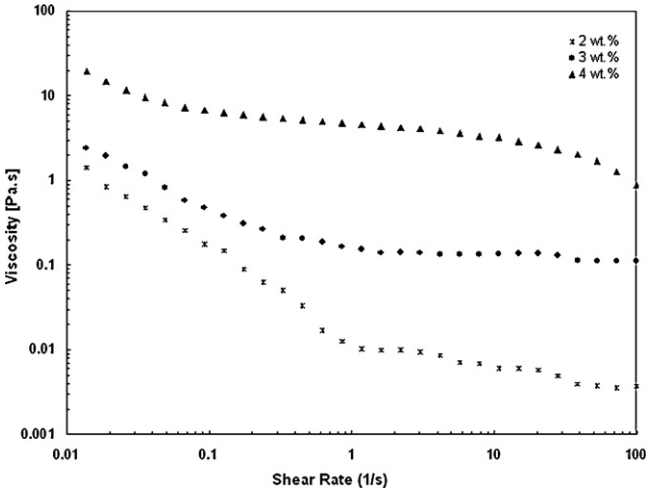

Fig. 2. Schematic shear viscosity profiles of Uni6M aqueous solution.