Chinese Journal of Chemical Engineering 23 (2015) 1440–1446

Contents lists available at ScienceDirect

Chinese Journal of Chemical Engineering

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

Fluid Dynamics and Transport Phenomena

Rheological and drag reduction properties of hydroxypropyl xanthan gum solutions☆

Meng Tian [1], Bo Fang [1],*, Leiping Jin [1], Yongjun Lu [2], Xiaohui Qiu [2], Hao Jin [1], Kejing Li [1]

[1] *Shanghai Key Laboratory of Mutiphase Materials Chemical Engineering, Lab of Chemical Engineering Rheology, Research Center of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China*
[2] *Langfang Filial of Research Institute of Petroleum Exploration and Development, PetroChina, Langfang 065007, China*

ARTICLE INFO

Article history:
Received 18 September 2014
Received in revised form 14 January 2015
Accepted 27 March 2015
Available online 10 April 2015

Keywords:
Hydroxypropyl xanthan gum
Rheological properties
Drag reduction
Cryo-FESEM

ABSTRACT

Hydroxypropyl xanthan gum (HXG) was prepared from xanthan gum (XG) and propylene oxide under alkaline condition. Rheological and drag reduction properties of different concentrations of aqueous HXG and XG solution were studied. The micro-structure network of HXG and XG solutions was investigated by Cryo-FESEM. The results showed that HXG and XG solutions could exhibit shear thinning property. The apparent viscosity of 6 $g\cdot L^{-1}$ HXG solution was 1.25 times more than that of 6 $g\cdot L^{-1}$ XG solution. The storage modulus G' and the loss modulus G'' of HXG solutions were greater than those of XG solutions, and thixotropic and viscoelastic properties were more significant in HXG solutions. The HXG and XG solutions reduced the pressure drop of straight pipe, and the maximum drag reduction of 1 $g\cdot L^{-1}$ HXG and XG in smooth tube reached 72.8% and 68.1%, respectively. Drag reduction rate was increased as the concentration increased. The HXG solution may become a new polymeric drag reducer.

1. Introduction

Xanthan gum (XG) is a kind of natural polysaccharides with high molecular weight [1,2], which comes from aerobic fermentation process of *Xanthomonas campestris* [3–5]. Since Kelco applied XG into industrial production at early 1960s, it has been widely used in food, medicine, textile, cosmetics, fire and oil fields [6]. Due to the characteristics of high viscosity, high resistance to acid, alkali and salt [7], xanthan gum possesses good prospects in the field of petroleum recovering. In order to improve its dissolution rate, XG was modified with formaldehyde by Su *et al.* [8]. XG derivatives were also obtained by reaction with an unsaturated organic acid (acrylic acid) or with acidic reactive derivatives (acryloyl chloride, maleic anhydride) [9–11]. But the modification processes of XG were complicated, and the reaction conditions need stringent control. To the authors' best knowledge, the hydroxypropyl modification of the xanthan gum has not been reported yet.

Liquids are mostly transported through pipes [12–14]. Addition of a small amount of polymer to the Newtonian fluid could significantly reduce the friction coefficient in pipe flow. This phenomenon was known as the drag reduction effect [15–17], which was discovered in 1949. Since then, drag reduction has been documented in a variety of systems with different results [18–23]. Lumly [24] believed that the key to drag reduction was the increase in apparent viscosity of the molecular extension of polymers in the flow outside the viscous sublayer effect. Virk and Wagger [25,26] also proposed that polymer molecules elongated (in a rod or an extended thread) may lead to effective drag reduction.

In this work, hydroxypropyl xanthan gum (HXG) was prepared by the reaction of hydroxyl of XG with propylene oxide under alkaline condition. Rheological and drag reduction properties of aqueous HXG and XG solutions were studied. HXG solutions exhibited higher apparent viscosity, more obvious thixotropy, much stronger viscoelasticity and better drag reduction than XG solutions did at the same concentration. HXG can be a new drag reducer polysaccharide for use in shale gas and petroleum fracturing fluid fields.

2. Materials and Methods

2.1. Material

Xanthan gum was food grade and purchased from Runchuang Food Company (Shanghai). 1,2-propylene oxide was the etherified reagent and purchased from Shanghai Lingfeng Chemical Reagent Ltd. The reaction solvent was ethanol, chemical pure, from Sinopharm Chemical Reagent Co. The pH adjusting agents were NaOH and acetic acid, all analytical pure (AR).

2.2. Experimental methods

2.2.1. Preparation of hydroxypropyl xanthan gum (HXG)

To remove moisture, the XG powder was previously dried at 45 °C for 8 h. The syntheses were performed in ethanol–water solution

---

☆ Supported by the National High Technology Research and Development Program of China (2013AA064801).

* Corresponding author.
E-mail address: fangbo@ecust.edu.cn (B. Fang).

http://dx.doi.org/10.1016/j.cjche.2015.04.003
1004-9541/

(70wt%), in the presence of etherification agent, 1,2-propylene oxide. XG (20 g) was dispersed in 28 g ethanol (AR) and 12 g 0.5 mol·L^{-1} NaOH solution in a three-neck flask under constant stirring to alkalize XG for 1 h at 25 °C. Then the system was adjusted to pH 9–10 by diluting acetic acid. Heated up to 75 °C with reflux under stirring, 8 ml of 1,2-propylene oxide was added to the system by drop wise, and the reaction lasted for 4 h. Finally, the obtained suspension was filtered, rinsed 4 times with ethanol/water mixtures (50wt%, 80wt%, 90wt% ethanol solution) (40 ml) and finally with ethanol (AR, 50 ml). The final HXG product was light yellow powder with particle size in 0.149-0.178 mm (80–100 mesh) after drying at 50 °C for 12 h and grounding. The yield was 92%.

2.2.2. Measurement of hydroxypropyl molar substitution degree

The content of hydroxypropyl in HXG was measured by ultraviolet visible light spectrophotometer (UV762, Shanghai Lengguang Technology Co., China) at 595 nm, referring to the standard Q/SH 0050-2007 [27]. The average hydroxypropyl weight fraction of HXG was 4.38% over three measurements.

2.2.3. Preparation of HXG and XG solutions

Aqueous HXG and XG solutions with different concentrations ranging from 1 to 10 g·L^{-1} were prepared by dissolving the dry biopolymer (XG and HXG) in deionized water with agitation. Additionally, the aqueous solutions were fully swelled for 6 h before rheological measurements.

For drag reduction tests as noted below, 40 L solutions of different concentrations ranging from 0.4 to 1.0 g·L^{-1} were prepared in tap-water.

2.2.4. Rheological measurements

The rheological measurements were performed in a rotational rheometer (Physica MCR 101, Anton Parr, Austria), using a cone and plate geometry (CP25-1-SN10665, cone angle 1.001°, diameter 24.955 mm, plate distance 0.05 mm) and a Peltier-based temperature control. The steady shear viscosity was measured at a constant shear rate of 170 s^{-1}. In the shear-thinning measurements, the viscosity was recorded in the range of shear rate from 0.01 to 1000 s^{-1}. In oscillatory measurements, a strain sweep was performed from 0.01% to 100% at a given frequency 1.0 rad·s^{-1} to fix the upper limit of the linear viscoelastic zone at a strain value of 30.0% and the storage modulus G' and the loss modulus G'' were determined through small amplitude oscillatory shear at frequencies ranging from 1 to 100 rad·s^{-1}. In thixotropy measurements, the shear rate increased from 0.01 to 170 s^{-1} in 40 s, and then decreased from 100 to 0.01 s^{-1} in the same time. All measurements were performed at 30.0 °C ± 0.1 °C.

The shear resistance and heat resistance of solutions were measured on a high temperature rheometer (RS6000, Haake, Germany), using a parallel plate (PZ38, plate diameter 38 mm). The temperature was raised from 30 °C to set temperature (80 °C or 100 °C) within 30 min, then the viscosity of solution was recorded with time at constant temperature and constant shear rate 170 s^{-1} for 90 min.

2.2.5. Drag reduction measurement

The experimental facility of drag reduction was a circulation pipeline testing system, composed of a liquid storage tank, a centrifugal pump, a turbine flow meter, a pressure sensor and a stainless steel pipe. The pipe flow chart was given in Fig. 1. The test section was a smooth tube (length 2.0 m; inner diameter 20.5 mm). Tap water was used in equipment calibration. The tube length is about 3.3 m before the entrance of test section, which is long enough for full development of tubular turbulent flow. In addition, this is supported by the fact that the curve of water friction coefficient with Reynolds number is coincided with the Prandtl–Karman curve in Section 3.3.

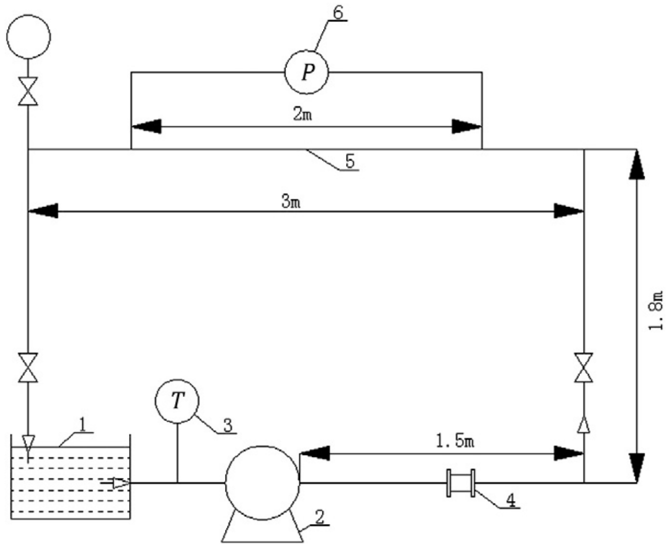

Fig. 1. The experimental flow chart. 1 — liquid storage tank; 2 — centrifugal pump; 3 — thermometer; 4 — flowmeter; 5 — smooth pipe; 6 — pressure sensor.

According to the rheological measurements, the drag reducing solutions showed the shear thinning behavior which could match with the power law. The generalized Reynolds number Re_G [28] and the Fanning friction factor f of the power fluid are given by Eqs. (1) and (2), respectively:

$$Re_G = \frac{\rho v^{2-n} d^n}{8^{n-1} K}\left(\frac{4n}{3n+1}\right)^n \tag{1}$$

$$f = \frac{\Delta P \pi^2 d^5}{32 l q_v^2 \rho} \tag{2}$$

where q_v is the volume flow rate (m^3·s^{-1}); v is the flow velocity (m·s^{-1}); ΔP is the pressure drop in straight pipe (kPa); l is the length of testing section (m); ρ is the density of the fluid (kg·m^{-3}); d is the inner diameter of the testing pipe (m).

The two asymptotic regimes [25,29] describe the turbulent drag reducing performance. One is the Prandtl–Karman regime for Newtonian turbulent flow. The curve of water friction coefficient f with Re_G in smooth tube was coincided with the Prandtl–Karman regime under the same conditions in this experiment:

$$f^{-1/2} = 4.0\,\lg\left(Re f^{1/2}\right) - 0.4. \tag{3}$$

The other one is the Virk regime for maximum possible drag reduction of polymer solution, which is given by

$$f^{-1/2} = 19.0\,\lg\left(Re f^{1/2}\right) - 32.4 \tag{4}$$

The drag reduction rate $R\%$ could be computed as

$$R\% = \frac{f_1 - f_2}{f_1} \times 100 \tag{5}$$

where f_1 is the friction factor of water and f_2 that of HXG or XG solution.

2.2.6. Cryo-FESEM

Sample solutions for cryogenic field emission scanning electron microscopy (Cryo-FESEM) were loaded into copper gauze and plunged frozen in liquid nitrogen at its boiling point. Then the samples were transferred into the cryo chamber of the microscope, which was held at a temperature of −130 °C. The samples were then sublimed at −130 °C for approximately 30 min. Once coated the samples were viewed at −130 °C. Images of the treated samples were obtained with