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Time-Dependent Rheology of Concentrated Xanthan Gum Solutions

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ABSTRACT

The objective of the present study is to systematically elucidate the time-dependent rheological behavior of concentrated xanthan gum solutions in a wide variety of shear flow conditions. In order to analyze the time-dependent behavior, start-up, interrupted shear flow, step shear flow and cyclic shear flow experiments have been conducted in this work.

INTRODUCTION

Xanthan gum is a high molecular weight extracellular polysaccharide produced by the bacterium *Xanthomonas campestris.* Xanthan gum is a non-gelling biopolymer that exists in aqueous media with an ordered rigid chain conformation.[1] It is able to form highly viscous solutions even at low concentrations whose stability to temperature and pH is responsible for its great acceptance in many industries.[2-3] Due to its exceptional rheological properties, xanthan gum is widely used as an effective stabilizer or a suitable thickener for various kinds of water-based systems. Its numerous areas of application cover a broad range including food, pharmaceutical, cosmetic, agricultural, textile, ceramic, and petroleum industries.[4-6]

The knowledge of rheological properties of aqueous xanthan gum systems is of paramount importance and their correct measurements provide useful information for engineering applications, formulation of commercial production, design and process evaluation, quality control, and storage stability because rheological characteristics affect the flow behavior during processing as well as the usage of the final products. Because of such an industrial significance, a relatively substantial amount of literature has been published on the rheological properties of dilute and semi-dilute (or moderately concentrated) xanthan gum solutions prepared from aqueous media. However, only a little attention has been given to the rheology of highly concentrated solutions of xanthan gum, even though these systems are much more important from an industrial point of view. In particular, to the best of our knowledge, almost no studies have been reported concerning the systematic characterization of their time-dependent rheological behavior.

The objective of this study is to systematically elucidate the time-dependent rheological behavior of concentrated xanthan gum solutions through an interpretation of stress overshoot phenomenon and thixotropic behavior in various flow conditions.

In order to analyze the time-dependent rheological behavior of concentrated xanthan gum systems, start-up, interrupted shear flow, step shear flow and cyclic shear flow experiments have been performed in this work.

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To investigate the interrupted shear flow behavior, samples are initially subjected to start-up flow. After the stresses reach steady values, shearing is stopped for a period of specific time (rest time), and the flow is restarted at the same shear rate as before.

In step shear flow fields, during four steps, start-up tests of different shear rates are applied to concentrated xanthan gum solutions. The shear rates of start-up flow in each step are increased or decreased step by step.

In cyclic shear flow fields, samples were subjected to up-and-down flow conditions with different maximum shear rates for several pre-specified times. After the first cyclic flow was finished, the second cyclic up-and-down flow was immediately restarted. The hysteresis loop areas of the first and subsequent cycle flow fields can indicate the effect of the cyclic shearing time on thixotropic behavior.

To investigate the effect of the rest time, after the first cyclic flow was finished, shearing is stopped for a period of specific time (rest time), and the second cyclic flow was restarted. A comparison of the maximum stress value of the first cyclic flow with the maximum stress value of the subsequent cyclic flow can be an indication of the effect of rest time for structural recovery.

EXPERIMENTAL SECTION

Preparation of Xanthan Gum Solutions

The xanthan gum sample used in this study was a commercially available product supplied from the Sigma-Aldrich Corporation (USA).

In this experiment, aqueous xathan gum solutions were prepared by constant stirring using a magnetic bar for 24 hr at room temperature. Then, a propeller–type variable-speed homogenizer was used to provide a further necessary agitation of xanthan gum solutions. The agitation was continued for 3~5 hr with a rotational speed of 300 rpm until the polymer was perfectly dissolved and the solutions were lump-free. In order to complete the hydration of the polymer, the prepared solutions were kept at rest at room temperature for more than 12 hr prior to conducting the rheological measurements.

Rheological Measurements

The rheological properties of prepared xanthan gum solutions were measured using a strain-controlled rheometer [Advanced Rheometric Expansion System (ARES), Rheometric Scientific, USA] equipped with a parallel-plate fixture with a radius of 12.5 mm and a gap size of 2.0 mm. All measurements were performed at a fixed temperature of 20 ℃.

In order to investigate the interrupted shear flow behavior of concentrated xanthan gum solutions, different shear rates of $\dot{\gamma}$ = 1, 10, and 100 1/s were applied to sample solutions during the shearing times of 1, 5, 10, 15, and 20 minutes and then several rest times of 1, 5, 10, 15, 20, and 30 minutes were provided in each case. After then, a subsequent cycle identified with the first cycle was restarted.

In step shear flow fields, two kinds of experiments were performed. One is a reduction in step shear rate experiment in which the shear rate in the first step was fixed at 100 1/s. The second, third, and forth step tests were subsequently continued at shear rates of 10, 1, and 0.1 1/s, respectively. The other one is an incremental step shear rate experiment which steps a reverse course of a reduction in step shear rate experiment.

In cyclic shear flow fields, different maximum shear rates of $\dot{\gamma}$ = 1, 10, and 100 1/s were applied to sample solutions during the cyclic shearing times of 2, 10, 20, 30, 40 and 60 min. After then, a subsequent cyclic flow identified with the first cycle was immediately restarted.

In cyclic flow fields with a rest time, different maximum shear rates of $\dot{\gamma}$ = 1, 10, and 100 1/s were applied to sample solutions during the cyclic shearing times of 2, 10, 20, 30, 40 and 60 min and then several rest times of 1, 5, 10, 15, 20, and 30 min were provided in each case. After then, a subsequent cyclic flow identified with the first cycle was restarted.

Before the xanthan gum solutions were loaded, the two plates were covered with sandpaper in order to remove a wall slippage between the test material and the plates. In all measurements, a fresh sample solution was used and rested for 20 min after loading to allow material relaxation and temperature equilibration.

RESULTS AND DISCUSSION

Figure 1 shows the time-dependence of the interrupted shear stress for 3 wt% xanthan gum solution. Stress overshoot phenomenon is observed in both start-up cycles, but the maximum stress value ($=\sigma_{m1}$) during the first start-up cycle is not equivalent to that ($=\sigma_{m2}$) of the subsequent start-up cycle. In addition, the equilibrium stresses in two start-up cycles do not show an equal value. These results mean that the destroyed structure of this system during the first start-up cycle is not completely recovered during the rest time.

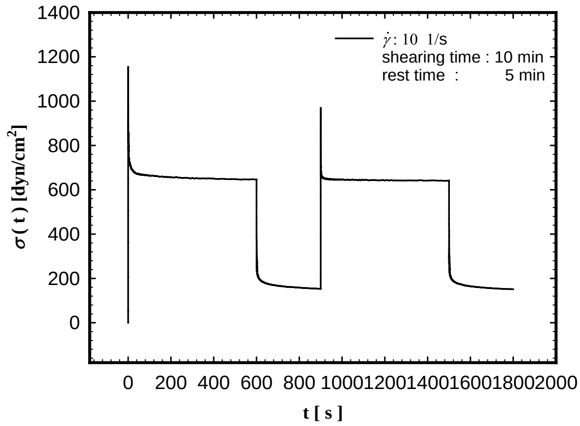

Figure 1. Interrupted shear flow behavior for 3 wt% xanthan gum solution at shear rate of 10 1/s with a rest time of 5 min.

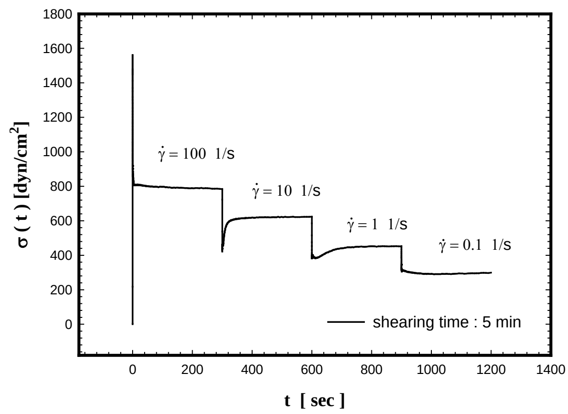

Figure 2. Variation of shear stress obtained from a reduction in step shear rate experiment for 3wt% xanthan gum solution. ($\dot{\gamma}$ = 100→10→1→0.1 1/s)

Figure 2 represents the variation of the shear stress obtained from the reduction in step shear rate experiment in which the shear rate was suddenly reduced from 100 1/s to 0.1 1/s with a four-step logarithmic scale after a pre-designed fixed shearing time of 5 min. When the shear rate is suddenly reduced, the shear stress shows firstly an undershoot behavior followed by a slow increase until reaching the equilibrium value, and the degree of an undershoot is larger for higher initial shear rates.

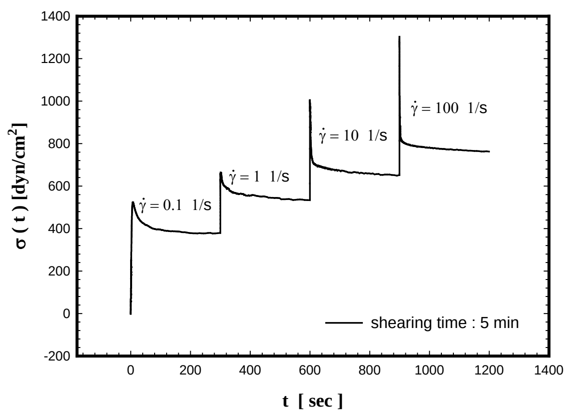

Figure 3. Variation of shear stress obtained from an incremental step shear rate experiment for 3wt% xanthan gum solution. ($\dot{\gamma}$ = 0.1→1→10→100 1/s)

Figure 3 illustrates the variation of the shear stress obtained from an incremental step shear rate experiment in which the four shear rates were set to proceed a reverse course of the reduction in step shear rate test reported in Figure 2. When the shear rate is suddenly increased, the shear stress exhibit firstly an overshoot behavior followed by a rapid decrease until reaching the equilibrium value, and the degree of an overshoot becomes larger for higher final shear rates.

Figure 4 demonstrates the thixotropic behavior for 3 wt% xanthan gum solution in cyclic flow conditions. Stress overshoot phenomenon is observed in the first cyclic flow, but this phenomenon disappears in the subsequent cyclic flow. Stress overshoot phenomenon observed in the first cyclic flow indicates a breakdown of initial structure by start-up, and imperfection of structural recovery causes no stress overshoot phenomenon in the subsequent cyclic flow. This breakdown of initial structure includes a destruction of hydrogen bond and a rupture of entanglement of xanthan gum macromolecules.

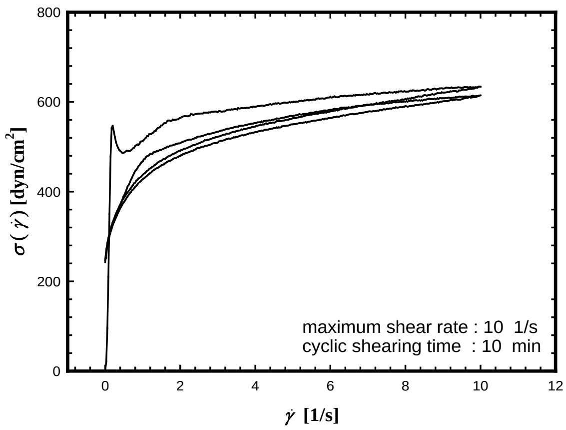

Figure 4. Shear stress versus shear rate obtained from a cyclic shear flow experiment for 3 wt% xanthan gum.

Figure 5 displays the thixotropic behavior in the cyclic flow with a rest time of 20 min for 3 wt% xanthan gum solution. Stress overshoot phenomena are observed in both cyclic flows, but the maximum stress value ($=\sigma_{m1}$) during the first cyclic flow is not equivalent to that ($=\sigma_{m2}$) during the subsequent cyclic flow. It means that some extent of structural recovery of xanthan gum occurred ; i.e., a little rebuilding of hydrogen bond and entanglement of xanthan gum took place during the rest time.

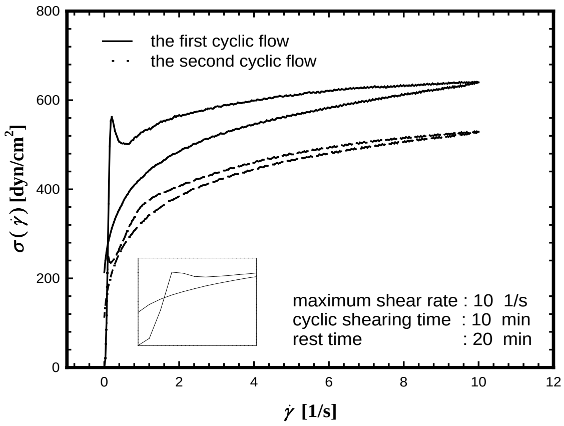

Figure 5. Shear stress versus shear rate obtained from a cyclic shear flow experiment with rest time for 3 wt% xanthan gum solution.

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