Carbohydrate Polymers **12** (1990) 329–335

Research Note

Rheology of a Xanthan Broth at Low Stresses and Strains

ABSTRACT

The structure of a concentrated (4·7 wt %) xanthan broth was probed by dynamic oscillatory, steady shear, and stress-relaxation tests on denatured, renatured, and native xanthan solutions. The range of the shear rates extended down to 10^{-5} s^{-1} to test for the existence of a yield stress. Though the viscosities at these very low shear rates were extremely high for polymer solutions (10^5 Pa. s), no evidence of a true yield stress was found. Long range order was indicated by a difference in complex and steady shear viscosity, presumably arising from inter-chain hydrogen bonding and liquid crystal formation. Differences in recoverable strain between the various samples arise from dissimilar structures and long range interactions in the solutions.

Xanthan gum, a high molecular weight polysaccharide secreted by the bacterium *Xanthomas campestris*, is used extensively as a viscosifier. The fermentation is carried out to xanthan concentrations of 3–4 wt % and the resulting viscous broth is sold directly as a product to the oil industry. Broth concentrates of 13 wt % xanthan, having paste-like consistencies, are also marketed. Much work has been done to understand the rheology of xanthan solutions (Rochefort & Middleman, 1987), but most work has focused on dilute solution properties. Few studies have reported properties of xanthan solutions in the concentration range encountered in the fermentation conditions.

Studies at higher xanthan concentrations include those of Whitcomb and Macosko (1978) on 1 wt % solutions, and Lim *et al.* (1984) on 0·1, 0·5, and 1 wt % solutions. Whitcomb and Macosko report an 'apparent yield stress' for xanthan. Lim *et al.*, showed that for 1% solutions, liquid crystalline regions exist which break and reform under shear; however, for 0·5% solutions and below, there exists weaker network structures, presumably due to hydrogen bonding interactions. Xanthan is known to undergo an order–disorder transition (helix-random coil) as a function of temperature. The effect of this transition on the viscosity and power law parameters of 0·05–0·5 wt % solutions has been studied by Rochefort

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and Middleman (1987) and in a more limited fashion by Rinaudo and Milas (1978) and Milas and Rinaudo (1979).

In this work, the results of dynamic oscillatory, steady shear, and steady stress experiments on native, denatured and renatured xanthan solutions are presented. The range of shear rates are extended down to 10^{-5} s^{-1} to test for the existence of true yield stresses in concentrated xanthan solutions.

A commercially available xanthan broth, Flocon 4800 (Pfizer) containing 4·7 wt % xanthan is employed and referred to as 'native' xanthan. 'Renatured' xanthan was made by heating the native xanthan to 90 °C for 20 min and allowing it to cool slowly (Jeannes *et al.*, 1961; Besio *et al.*, 1987). Denatured xanthan was obtained by adding 4 M urea to the heated xanthan before cooling (Jamieson *et al.*, 1982).

A Rheometrics System IV Rheometer with a sensitive fluids transducer was employed in dynamic oscillatory, steady shear viscosity and transient shear measurements. A Rheometrics Stress Rheometer was used to perform measurements at constant stress. The stress rheometer can impose much smaller stresses and measure much lower strain rates than the System IV.

In Fig. 1, steady shear viscosity, η, and complex viscosity, η^* for the three solutions are presented. The complex viscosity, determined from dynamic oscillatory experiments, is defined

$$\eta^* = [(G')^2 + (G'')^2]^{1/2}/\omega \qquad (1)$$

where ω = frequency; G', G'' = storage and loss moduli. The shear viscosities of all three solutions are similar over four orders of magnitude in shear rate. Complex viscosities are 4–6 times larger than steady shear viscosities. For simple polymer solutions, the steady shear viscosity as a function of shear rate is identical to the complex viscosity as a function of frequency — the Cox–Mertz rule (Cox & Mertz, 1958; Kulicke *et al.*, 1980; Booij *et al.*, 1983; Leblans *et al.*, 1985). However, for systems with long-range ordering and structure such as highly filled polymer melts and polymer gels, the complex viscosity is higher than the steady shear viscosity (Prud'homme, 1987). The complex viscosity of the native and renatured samples are essentially identical, whereas the complex viscosity of the denatured sample is higher. This indicates that the concentrated denatured sample has a more entangled and interacting structure than the other two samples. However, this interaction is weak since under steady shear it is disrupted and all three samples have similar shear viscosities. This distinct behavior of the denatured sample is also seen in its elastic properties, to be discussed below.

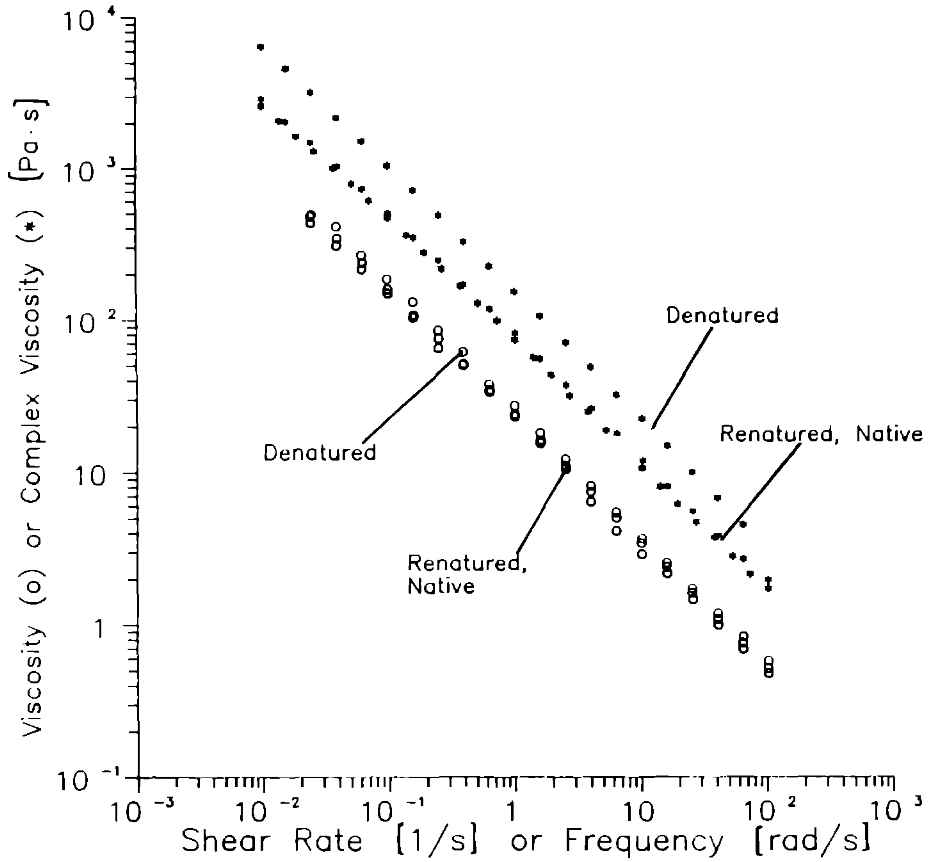

Fig. 1. Steady shear viscosity (o) and complex viscosity (*) of native, renatured, and denatured 4·7 wt % xanthan solutions. Complex viscosities measured at 5% strain. Ambient temperature 25 ± 1°C.

The steady shear data from the System IV rheometer were supplemented by viscosity data taken with the Rheometrics Stress Rheometer at 2 and 15 Pa stresses. In Fig. 2, viscosities determined from both instruments are plotted. The data show that the xanthan neither displays a true yield stress (i.e. the viscosity would diverge towards infinity as the yield stress was approached at low shear rates), nor does the solution show evidence of a zero shear viscosity, even at shear rates of 10^{-5} s^{-1}. The viscosity at 10^{-5} s^{-1} is in the range of 10^5 Pa.s, which is similar to the viscosity levels of polyolefin melts. The extra-low shear data are almost co-linear (within the data scatter) with the viscosities measured at higher shear rates. A power law correlation describes the steady shear

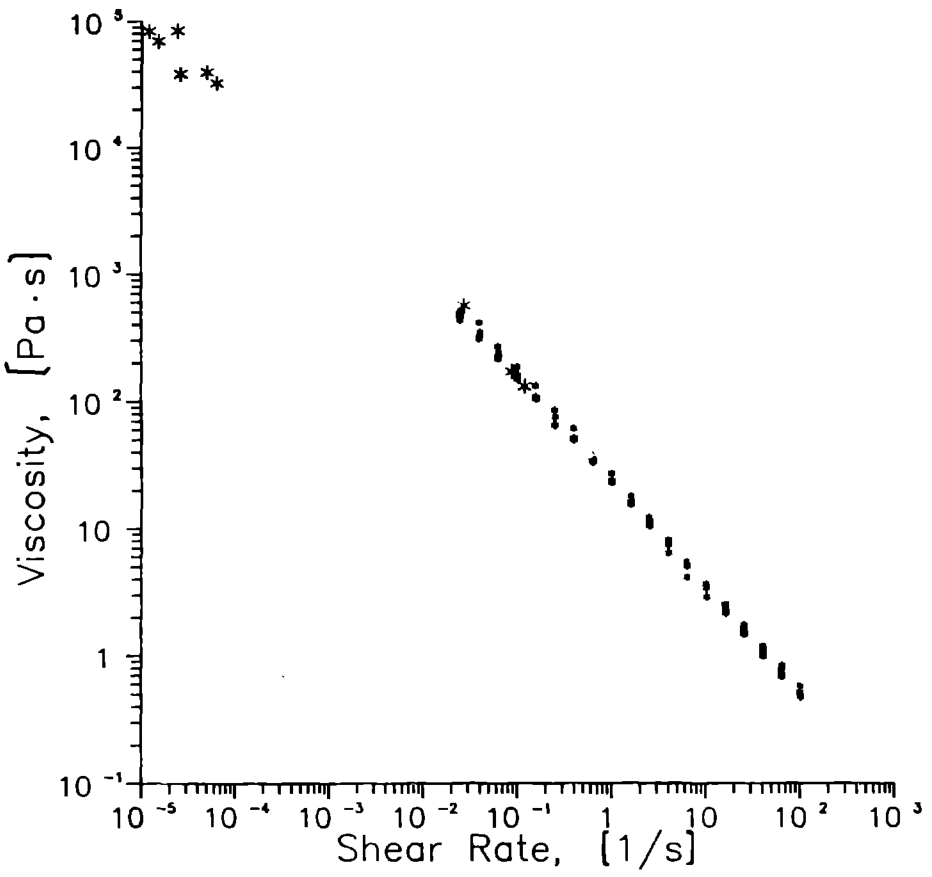

Fig. 2. Steady shear viscosity of native, renatured, and denatured 4·7 wt % xanthan solutions measured on the System IV Rheometer (*), and at lower stresses on the Rheometrics Stress Rheometer (large *) In steady shear, the viscosities of all three samples are comparable.

viscosity of all three xanthan solutions over the full range of strain rates from 10^{-5} to $10^2\ s^{-1}$.

$$\eta(\text{Pa.s}) = 21\ \dot{\gamma}(\text{s}^{-1})^{-0{\cdot}825} \tag{2}$$

Elastic recovery after the cessation of steady shear is a sensitive measure of the stored elastic energy in a system. Figure 3 shows the result of a recovery test at constant stress of 2·0 Pa. The material elastically deforms and flows during the 2400s when stress is imposed; and the material elastically recoils after the stress is removed. The recoverable strain (i.e. the strain during elastic recoil), following the removal of constant stress of 2·0 Pa imposed for 2400 s, for the native, denatured, and renatured samples is shown in Fig. 3. The total (i.e.

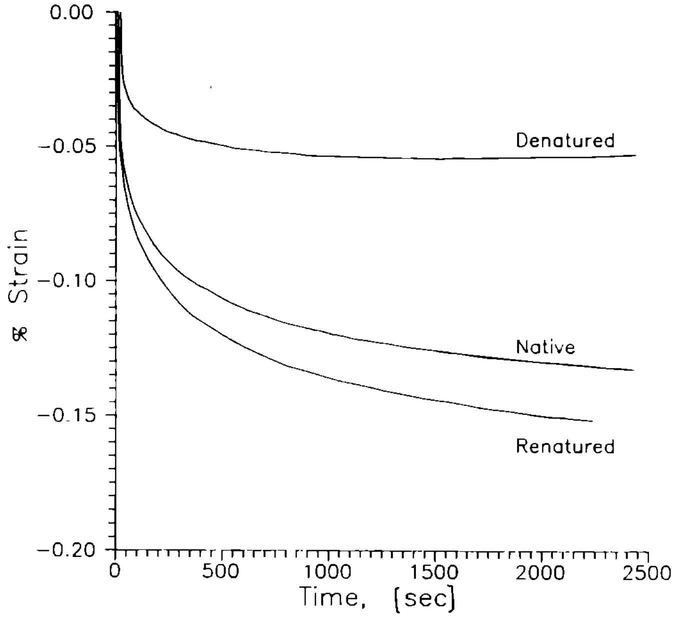

Fig. 3. Recovery of denatured, renatured, and native 4·7 wt % xanthan solutions after a stress of 2 Pa was imposed for 2400 s.

$t \rightarrow \infty$) recoverable strain divided by the imposed stress defines the recoverable compliance, J_{eR}, which is shown in Table 1. The denatured xanthan has the smallest recoverable strain; the native and renatured samples have roughly comparable values.

The difference in recoverable strain and complex viscosities arise from differences in interactions and long-range structure in the solutions. The two different tertiary structures are shown schematically in Fig. 4(a)–(d). The native and renatured samples consist of rigid helical rods (Sato *et al.*, 1984) that order into liquid crystal domains at high concentrations (Fig. 4(a)), (Lim *et al.*, 1984). This large domain structure leads to $\eta^* > \eta$ and a relatively large recoverable strain. In the denatured state, the secondary helical structure of the chains is disrupted, but interactions from inter-chain hydrogen bonding and hydrophobic bonding still occur. This highly entangled, interacting network (Fig. 4(c)) has high η^* values; but the recoverable strain is limited to the length scale of a chain rather than the longer length scale of a crystal domain. A simple experiment was conducted to demonstrate the importance of liquid crystal domains on the process of relaxation. A fluid sample was placed between cross polarizers separated by a 1 mm spacer plate. The top polarizer was rotated, shearing the sample and setting up a birefringence pattern (Lim *et al.*, 1984). Once shearing was stopped, the birefringence

TABLE 1
Low Shear Rate Viscosities from Stress Rheometer

Xanthan	*Stress [Pa]*	*Shear rate [s⁻¹]*	*Viscosity [Pa . s]*	J_{eR}
Native	2	$5{\cdot}0 \times 10^{-5}$	$3{\cdot}9 \times 10^{4}$	0·0068
	15	0·12	$1{\cdot}3 \times 10^{2}$	0·0065
Denatured	2	$2{\cdot}4 \times 10^{-5}$	$8{\cdot}4 \times 10^{4}$	0·0033
	15	$2{\cdot}7 \times 10^{-2}$	$5{\cdot}6 \times 10^{2}$	0·0043
Renatured	2	$6{\cdot}3 \times 10^{-5}$	$3{\cdot}2 \times 10^{4}$	0·0079
	15	$8{\cdot}7 \times 10^{-2}$	$1{\cdot}7 \times 10^{2}$	0·0058

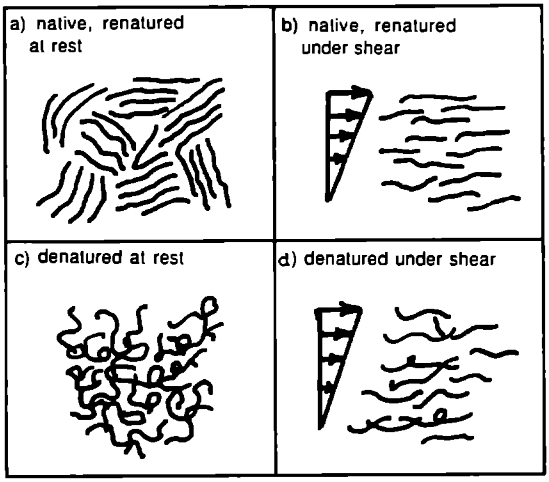

Fig. 4. Tertiary domain structures for xanthan solutions: (a) liquid crystal domain structure due to rigid rod secondary structure; (b) under shear the domains are broken apart; (c) denatured entangled structure; (d) under shear the entanglements are partially removed.

pattern decayed over approximately 20 min for the denatured sample, but did not relax over a period of 120 min for the native or renatured samples. Under steady shear at moderate rates, the domains are disrupted and all three samples behave similarly as shown in Figs 4(b) and 4(d).

CONCLUSIONS

Measurements at very low shear rates ($\sim 10^{-5}$ s^{-1}) show no evidence of yield behavior for 4·7 wt % xanthan solutions, however, the viscosity levels of 10^5 Pa.s at these low shear rates are exceedingly high for a polymer solution. The complex viscosities η^* of xanthan solutions measured using dynamic oscillatory tests are higher than the steady shear viscosities η. This lack of correspondence between η^* and η suggests the presence of long range order for these solutions arising from inter-chain hydrogen bonding and liquid crystal domain formation. The complex viscosities of xanthan solutions denatured with urea are higher than solutions of native or renatured xanthan, but the elastic recoverable strains are lower. This is interpreted in terms of differences in domain structures between the denatured sample and the other two samples.

ACKNOWLEDGMENT

This work was supported by National Science Foundation grants to M. M. Santore and R. K. Prud'homme (Presidential Young Investigator).

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(Revised version received 6 February 1989; accepted 11 February 1989)