



# The comparison of rheological properties of aqueous welan gum and xanthan gum solutions

Long Xu, Guiying Xu\*, Teng Liu, Yijian Chen, Houjian Gong

Key Laboratory of Colloid and Interface Chemistry, Shandong University, Ministry of Education, Shandong University, Jinan 250100, PR China

## ARTICLE INFO

### Article history:

Received 29 July 2012

Received in revised form

26 September 2012

Accepted 27 September 2012

Available online 13 October 2012

### Keywords:

Welan gum

Xanthan gum

Rheological behavior

Double helix

Gel

## ABSTRACT

Rheological properties of welan gum and xanthan gum solutions have been characterized systematically at various concentrations, temperatures and salinities. It is found that the viscoelasticity of welan gum is higher than that of xanthan gum at the same condition though the molecular weight of welan gum is lower. In view of this, welan gum will make a good performance in enhanced oil recovery, especially in high temperature and high salinity reservoirs. Network structure can be formed in solutions of welan gum and xanthan gum for the dynamic modulus has exponential relationship with the concentration. Moreover, the molecular aggregates of welan gum adopt a different arrangement with that of xanthan gum, adjacent double helices of welan gum arrange in parallel as the zipper model. The structure formed by zipper model is still stable in high temperature and high salinity.

© 2012 Elsevier Ltd. All rights reserved.

## 1. Introduction

Water-soluble polymers have been used for polymer flooding in enhanced oil recovery (EOR) (Kjønksen, Beheshti, Kotlar, Zhu, & Nyström, 2008; Long, Li, Xu, & Masliyah, 2011; Sabhapondit, Borthakur, & Haque, 2003; Taylor & Nasr El Din, 1998; Zhang, Dong, & Zhao, 2010). They can control mobility and reduce the formation permeability in the reservoir by increasing the viscosity of the injected water. The increased viscosity of the polymer solution can increase the residual resistance factor and improve sweep efficiency. So an important feature for a potential polymer to be used for polymer flooding in EOR is that the solution of water-soluble polymer has the favorable rheological behaviors, increasing the swept volume of displacement fluids (Kang & Dong, 1997, chap. 1; Rao et al., 2011).

Xanthan gum is a high molecular extracellular polysaccharide produced by bacterium *Xanthomonas campestris*. At present, xanthan gum is one of the two commonly water-soluble polymers used for polymer flooding, and makes a more excellent performance in salt resistance than that of hydrolyzed polyacrylamide (HPAM) in EOR. But the aqueous solution is deficient in elasticity. At lower temperature xanthan gum molecules exist as a double helix, but get converted into disordered coil at higher temperature (Bejenariu, Popa, Picton, & Le Cerf, 2010). The application of xanthan gum is

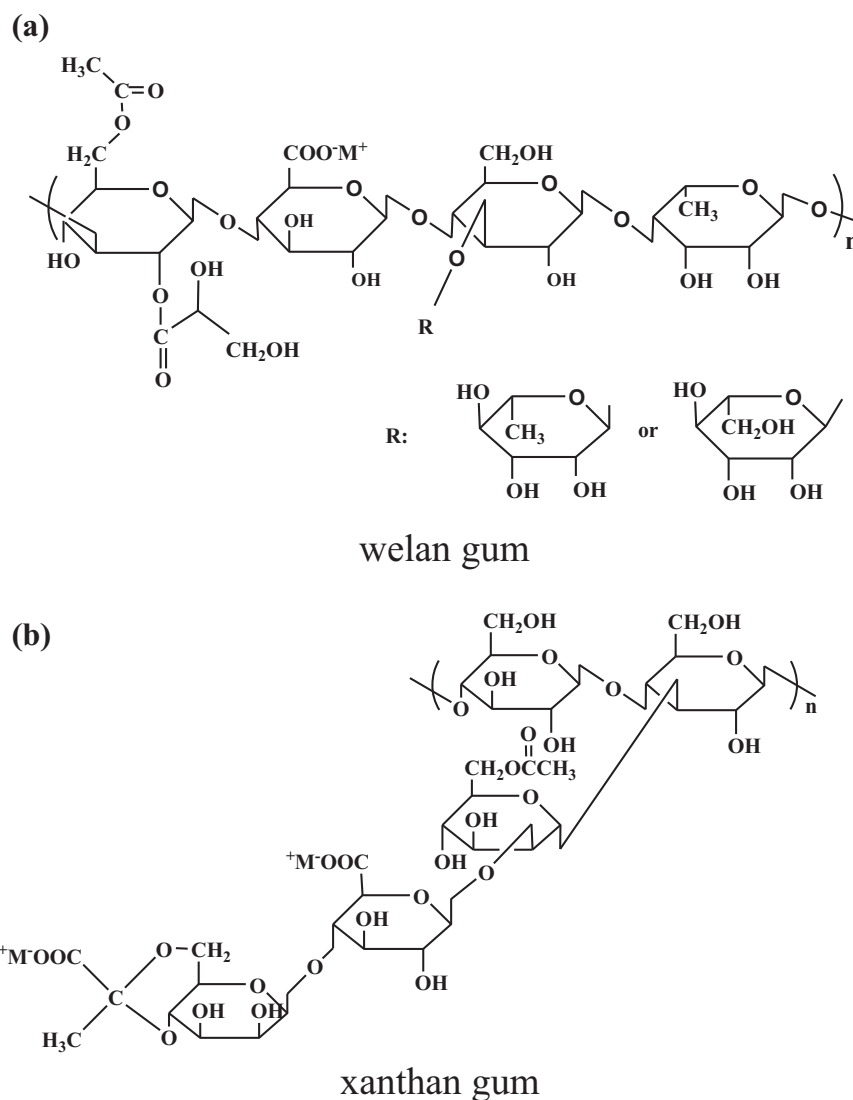
limited in the high temperature reservoirs for its defect in thermal stability.

Welan gum is a new microbial polysaccharide produced by *Alcaligenes* sp. It has potential industrial applications in food, concrete, petroleum, ink and other industries (Mohammed, 2006; Ogugbue and Shah, 2009; Plank, Lummer, & Dugonjic-Bilic, 2010; Sonebi & Malinov, 2011). Especially in the oil industry, welan gum is expected to become a novel oil recovery agent for its excellent rheological properties (Colby, 2010; Masakuni & Masahiro, 1990). Recently, we have found that when welan gum was injected the oil recovery is markedly higher than that of xanthan gum at the same condition (Xu, 2012, chap. 2).

The rheological properties of macromolecular solutions are important for many industrial fields, and the microstructure or interaction between macromolecule and solvent in solutions may be illustrated via them (Rashidi, Blokhus, & Skauge, 2010; Saadatabadi, Nourani, & Emadi, 2010; Xin, Xu, Gong, Bai, & Tan, 2008; Xin, Xu, Wu, Li, & Cao, 2007; Yu, Zhou, & Zhou, 2010). For example, the rheological behaviors of injected fluids play an important role in modifying oil-displacing efficiency in EOR, which attracts considerable attention in controlling viscoelastic properties of injected fluids (Wang, Xia, Liu, & Yang, 2001). The rheological behavior of welan gum solutions has rarely been reported so far (Masakuni & Masahiro, 1990). In this paper, we have systematically investigated the influence of the concentration, temperature and salinity on the rheological properties of welan gum solutions, comparing with that of xanthan gum at the same time, in order to provide basic data for the application of welan gum in EOR.

\* Corresponding author. Fax: +86 531 88564750.

E-mail address: [xuguiying@sdu.edu.cn](mailto:xuguiying@sdu.edu.cn) (G. Xu).



**Fig. 1.** (a) The structure of welan gum. Welan gum consists of pentasaccharide repeating unit,  $\beta$ -1,3-D-glucopyranosyl,  $\beta$ -1,4-D-glucuronopyranosyl,  $\beta$ -1,4-D-glucopyranosyl and  $\alpha$ -1,4-L-rhamnopyranosyl, and a single monosaccharide side-chain at O-3 of the 4-linked glucopyranosyl. The monosaccharide may be either L-rhamnopyranosyl or L-mannopyranosyl in the approximate ratio 2:1, and about half of the repeat units or more have acetyl and glyceryl substituents (Rinaudo, 2004; Tako, Teruya, Tamaki, & Konishi, 2009). (b) The structure of xanthan gum. Xanthan gum has a cellulosic backbone consisting of five monosaccharides to give a pentasaccharide repeating unit. The cellulosic backbone is substituted at C-3 on alternate  $\beta$ -1,4-D-glucopyranosyl residues with a trisaccharide side chains of  $\beta$ -D-rhamnopyranosyl,  $\beta$ -1,4-D-glucuronopyranosyl and  $\alpha$ -1,2-D-mannopyranosyl with various amounts of acetyl and pyruvate substituents (De Jong & Van de Velde, 2007; Mukherjee, Sarkar, & Moulik, 2010; Rodd, Dunstan, & Boger, 2000).

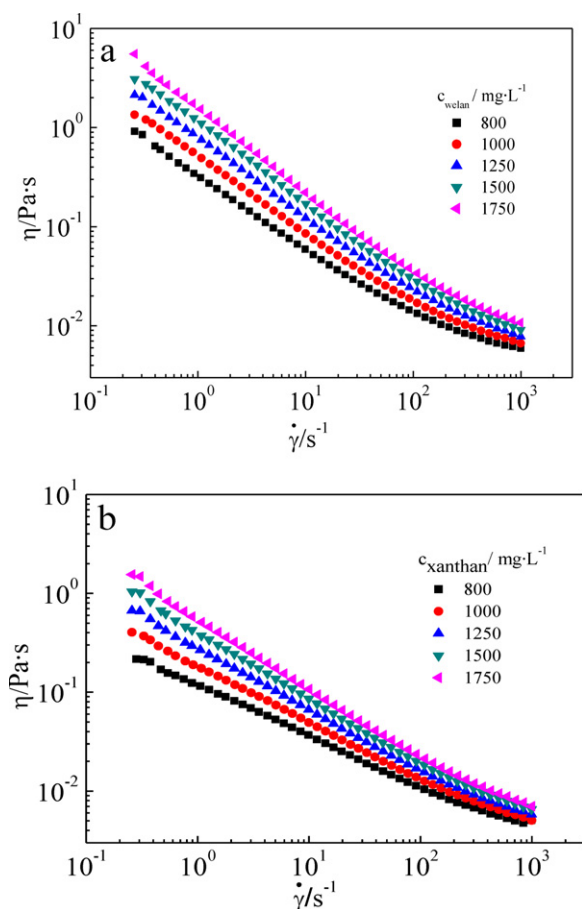
## 2. Experimental

### 2.1. Materials

Welan gum was supplied by Food Fermentation Industry Research Institute of Shandong Province, China. The molecular weight is about  $6.6 \times 10^5 \text{ g mol}^{-1}$ , and the intrinsic viscosity is  $4479 \text{ mL g}^{-1}$ . Xanthan gum (FUFENG 80) was produced by Inner Mongolia Fufeng Biotechnology Co., Ltd. The molecular weight is about  $2.0 \times 10^6 \text{ g mol}^{-1}$ , and the intrinsic viscosity is  $7627 \text{ mL g}^{-1}$ . The structures of welan gum and xanthan gum are displayed in Fig. 1a and b. Water used in the experiment was triply distilled by a quartz water purification system. Salinity of three mineralized water used in the experiment is  $3908 \text{ mg L}^{-1}$ ,  $6664 \text{ mg L}^{-1}$  and  $9374 \text{ mg L}^{-1}$ , respectively, which is based upon the formation water in three oil fields.

### 2.2. Rheology

The concentrated solutions of welan gum and xanthan gum were prepared by mechanical stirring at room temperature, and then were diluted to the required concentrations. The rheological measurements were carried out on a Haake RS75 Rheometer (Germany) with a coaxial cylinder sensor system Z41-Ti. The maximum allowable temperature deviation was  $\pm 0.1^\circ \text{C}$ . Samples were kept stationary more than 24 h before measuring to guarantee that no bubbles present in them. Samples were remained 5 min before measuring. Rate control mode, CR, was chosen in the steady-state shearing experiment, the range of shear rates was from  $0.01 \text{ s}^{-1}$  to  $1000 \text{ s}^{-1}$ . The stress sweep was carried out with the stress range from 0.01 Pa to 20.00 Pa at the fixed frequency 1.00 Hz. Then the oscillatory frequency sweep measurements were carried out at a frequency of 0.01–10.00 Hz in the oscillation mode, OSC.



**Fig. 2.** (a) The apparent viscosity of welan gum as a function of shear rate at different concentrations,  $T = 298$  K. (b) The apparent viscosity of xanthan gum as a function of shear rate at different concentrations,  $T = 298$  K.

### 3. Results and discussion

#### 3.1. The concentration dependence of rheological properties of polysaccharides

Fig. 2a presents the steady-state shearing curves of welan gum solutions at different shear rates. Obviously, the apparent viscosity of welan gum is heightened with increasing the concentration. The typical behavior of pseudoplastic fluid is observed for all samples as the increasing of the shear rate, namely, the apparent viscosity of welan gum solution decreases gradually with the increase of shear rate, while the shear stress increases continuously, which can be seen in Fig. S1. The marked rheology of welan gum solutions comes from its large molecular weight. The entanglements of macromolecular chains increase at high concentration, the apparent viscosity increases correspondingly. Similar rheological properties are observed in xanthan gum, as shown in Figs. 2b and S1. The phenomenon of shear thinning behavior is related to the orientation of macromolecules along the stream line of the flow (Chagas, Machado, Haag, de Souza, & Lucas, 2004). In the low shear rate, the stretching polysaccharide molecules intertwined to form aggregates, the high viscosity is due to the large fluids flow resistance. Increasing shear rate destroys aggregates and dispersing molecules arrange along the flow direction, as well as fluids' flow resistance declines, resulting in the decrease of apparent viscosity (Oh, So, & Yang, 1999).

The relation between apparent viscosity and shear rate can be fitted by the following power law equation (1) and

**Table 1**

The rheological parameters obtained by power law and cross-empirical equation for welan gum and xanthan gum at different concentrations. The correlation coefficients are all more than 0.99.

	$\eta_0$ (Pa s)	$\eta_\infty$ (Pa s)	$\dot{\gamma}_b$	$m$	$k$	$n$
$c_{\text{welan}}$ (mg L <sup>-1</sup> )						
800	1.31	0.013	0.40	1.17	0.35	0.30
1000	1.77	0.022	0.51	1.22	0.55	0.24
1250	2.83	0.030	0.49	1.24	1.15	0.13
1500	4.04	0.039	0.51	1.25	1.99	0.08
1750	8.51	0.058	0.30	1.23	2.36	0.09
$c_{\text{xanthan}}$ (mg L <sup>-1</sup> )						
800	0.31	0.006	0.56	0.81	0.12	0.49
1000	0.65	0.009	0.35	0.85	0.19	0.42
1250	1.13	0.014	0.37	0.97	0.28	0.35
1500	1.57	0.021	0.38	1.06	0.41	0.29
1750	2.30	0.029	0.37	1.14	0.55	0.23

cross-empirical equation (2) (Mu & Li, 2001; Mu, Li, Jia, Wang, & Zhang, 2002):

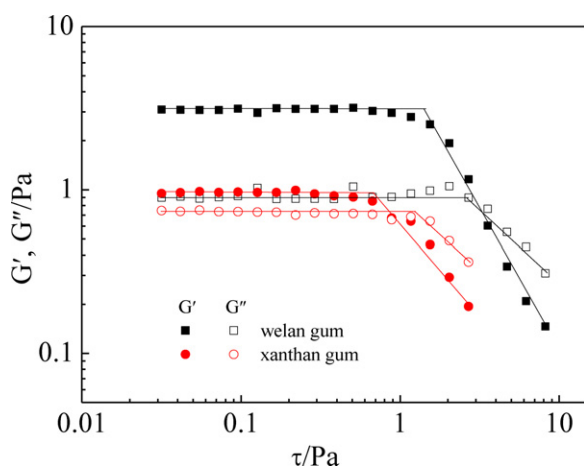
$$\eta = k(\dot{\gamma})^{n-1} \quad (1)$$

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (\dot{\gamma}/\dot{\gamma}_b)^m} \quad (2)$$

$k$  and  $n$  in Eq. (1) are consistency index and flow behavior index, respectively.  $\eta_0$ ,  $\eta_\infty$ ,  $\dot{\gamma}_b$  and  $m$  in Eq. (2) represent the zero-shear viscosity, the infinite-shear viscosity, the critical shear rate and the shear rate factor, respectively. The value of  $\dot{\gamma}_b$  indicates the magnitude that structure can be supported to the shear, and  $m$  mainly reflects the changes of structure caused by the increase of shear rate. From fitting results, we can distinguish the type of fluids, and obtain some information on the structure (Xin et al., 2008).

The rheological parameters for the welan gum and xanthan gum solutions are shown in Table 1. All samples exhibit a good fit to power law equation and cross-empirical equation. With increasing the concentration, the zero-shear viscosity and the infinite-shear viscosity increase simultaneously, and both are higher in welan gum than those in xanthan gum at the same concentration. The value of  $k$  is directly proportional to the concentration, while the relationship of  $n$  and concentration is just opposite. All values of  $n$  are less than 1, indicating that all samples belong to pseudo-plastic fluids. At the same concentration, the values of  $k$  of welan gum are higher than those of xanthan gum, while the values of  $n$  of welan gum are lower than those of xanthan gum. The molecular weight of welan gum is lower than that of xanthan gum, but the apparent viscosity of welan gum is higher than that of xanthan gum, demonstrating that the tacking ability of welan gum is more prominent.

The high plateau where complex modulus is independent of the shear stress is considered to be the linear viscoelastic region. Generally, samples are always ensured that they are within the linear viscoelastic region before carrying out the frequency oscillatory measurement. As shown in Fig. S2, both welan gum and xanthan gum show the linear viscoelastic region. The complex modulus ( $G^*$ ) remains nearly constant with the increase of stress ( $\tau$ ) until the critical stress value ( $\tau_c$ , the stress at the inflection point) is reached. The range of linear viscoelastic region is dependent on the concentration of polysaccharide, and  $\tau_c$  shows a directly proportional relationship with the concentration. The value of  $\tau_c$  reflects the shear resistance of molecular aggregates, when  $\tau > \tau_c$ , the initial molecular aggregates are disrupted. With the increase of concentration, molecular chains overlap and entangle with each other, which can withstand greater shear stress. Meanwhile, the rise of the critical complex modulus ( $G_c^*$ , the complex modulus at the inflection point) indicates that increasing concentration can enhance the viscoelasticity.



**Fig. 3.** The storage modulus ( $G'$ , solid) and loss modulus ( $G''$ , hollow) as a function of shear stress for welan gum and xanthan gum,  $c_{\text{gum}} = 1750 \text{ mg L}^{-1}$ , and  $T = 298 \text{ K}$ .

Take  $1750 \text{ mg L}^{-1}$ , for example, it can be seen from Fig. 3 that storage modulus ( $G'$ ) is higher than loss modulus ( $G''$ ) for welan gum in the linear viscoelastic region. This phenomenon indicates that the elastic component occupies a larger proportion of the solution compared to viscosity component at the low applied stress. Then, the value of the dynamic modulus decreases sharply when the applied stress exceeds  $\tau_c$ , and slopes of both curves are not equal.  $G'$  is lower than  $G''$  when the applied stress beyond the cross-point of curves, which indicates that system is more viscous than elastic at high applied stress. It can also be found that  $\tau_c$  of  $G''$  is higher than that of  $G'$ , revealing that the elasticity of welan gum is easier to be changed by applied stress. Xanthan gum exhibits the same situation, the plateau value of  $G'$  ( $0.94 \text{ Pa}$ ) is higher than that of  $G''$  ( $0.70 \text{ Pa}$ ). Compared with xanthan gum, the viscoelasticity of welan gum is more prominent. In addition,  $\tau_c$  of the dynamic modulus of welan gum is higher than that of xanthan gum, revealing that welan gum can bear larger stress.

Fig. S3 shows that the dynamic modulus of welan gum increases with increasing the concentration.  $G'$  of welan gum is higher than  $G''$  in the range of experimental frequency, indicating that the elastic component is dominant in the viscoelasticity, it can be concluded that a gel structure may be formed (Nitta, Takahashi, & Nishinari, 2009; Oh et al., 1999). The solution of xanthan gum at low concentration shows the typical nature of disordered structure that  $G''$  is higher than  $G'$  and strong dependence of modulus on the frequency, the overlapping frequency reduces with increasing concentration, and at high concentration the solution exhibits the gel-like nature. So, increasing concentration results in the xanthan gum solution transforms from the viscous fluid to the elastomer gradually.

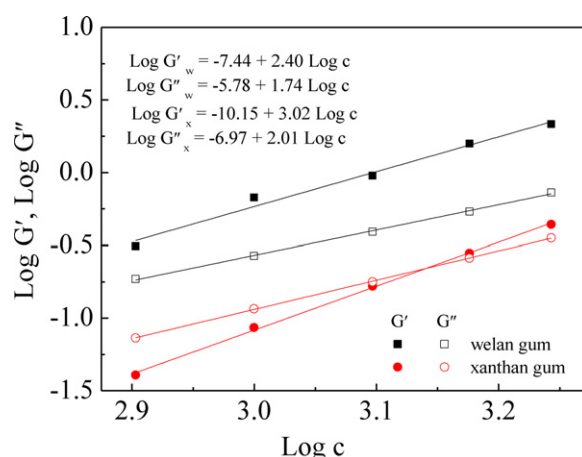
According to the theory proposed by MacKintosh, Käs, and Janmey (1995), the storage modulus and the loss modulus have exponential relationship with the concentration for solutions with gel-like structure. When logarithm is taken on both sides of exponential equation, linear equations are obtained as Eqs. (3) and (4).

$$G' = p \cdot c^a \rightarrow \log G' = \log p + a \log c \quad (3)$$

$$G'' = q \cdot c^b \rightarrow \log G'' = \log q + b \log c \quad (4)$$

where  $a$  and  $b$  are power law index of  $G'$  and  $G''$ , respectively. They reflect the concentration dependence of  $G'$  and  $G''$ . The symbols  $p$  and  $q$  are elastic coefficient and viscous coefficient, respectively. They reflect the magnitude of elasticity and viscosity of gel. The concentration dependence of  $G'$  and  $G''$  is fitted by Eqs. (3) and (4).

Data met the linear relation well, as shown in Fig. 4, indicating firmly that cross-linking gel or network structure is formed. From fitting equations we can see that  $p$  of welan gum is higher than that



**Fig. 4.**  $\log G'$  (solid) and  $\log G''$  (hollow) as a function of  $\log c$  for welan gum and xanthan gum,  $\tau = 0.1 \text{ Pa}$ ,  $f = 0.1 \text{ Hz}$ , and  $T = 298 \text{ K}$ . Straight lines are fitting curves. The results obtained by fitting are shown in figure. The correlation coefficients are all more than 0.99.

of xanthan gum, indicating that the solution of welan gum is more elastic. The value  $a$  of welan gum is lower than that of xanthan gum, indicating that elasticity of xanthan gum is more dependent on the concentration. Likewise, the solution of welan gum is more viscous than that of xanthan gum, while viscosity of xanthan gum is more dependent on the concentration.

### 3.2. The temperature dependence of the rheological properties of polysaccharides

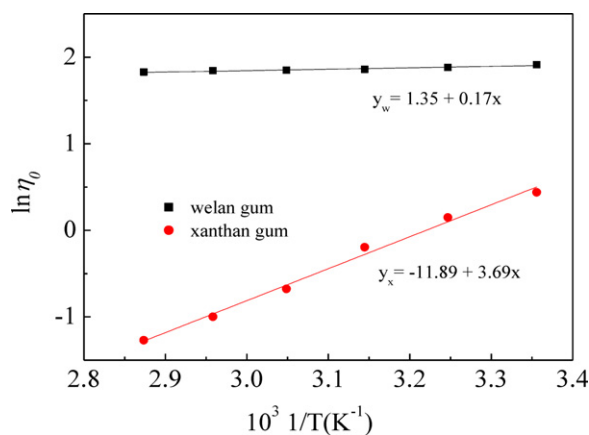
The temperature has little effect on the apparent viscosity of welan gum solution, especially in the low shear rate, and the apparent viscosity just declines slightly at the high temperature in the high shear rate, as seen in Fig. S4. Welan gum shows a good thermal stability with the change of temperature. Nevertheless, the temperature has a great impact on xanthan gum. Especially in the low shear rate ( $< 20 \text{ s}^{-1}$ ), the apparent viscosity of xanthan gum reduces obviously with increasing temperature. The phenomenon illustrates that the microstructure of xanthan gum solution makes a poor temperature resistance. When the shear rate is higher, the change of apparent viscosity at different temperatures is consistent. The viscosity retention rate ( $\phi$ , ratio of the viscosity at different temperatures and the initial viscosity at  $298 \text{ K}$ ) at different temperatures and  $7 \text{ s}^{-1}$  is given in Fig. S5. The  $\phi$  values of both polysaccharides decrease with increasing temperature. The  $\phi$  values of welan gum are higher than those of xanthan gum. The  $\phi$  value of xanthan gum is merely 50% when the temperature reaches  $75^\circ \text{C}$ , while the  $\phi$  value of welan gum is 72%. The viscosity loss of welan gum solution is obviously less than that of xanthan gum. The molecular aggregation of xanthan gum is more sensitive to the temperature change, while the welan gum solution is able to maintain high viscosity at high temperature. This is in agreement with the result reported by Morris, Gothard, Hember, Manning, and Robinson (1996).

The zero-shear viscosity of the solutions reduces with increasing temperature, indicating that the microstructure has changed. For polysaccharides welan gum and xanthan gum, the network structure is destroyed gradually by heating. The influence of the temperature on the zero-shear viscosity can be described by Arrhenius equation (5) (Schulte, Enders, & Quitzsch, 1999):

$$\ln \eta_0 = \ln A + \frac{Ea}{RT} \quad (5)$$

where  $A$  is the exponential factor,  $Ea$  is the shear activation energy and  $R$  is the thermodynamic constant.  $Ea$  reflects the influence





**Fig. 5.** The relationship between  $\ln \eta_0$  and  $1/T$  for welan gum and xanthan gum. Straight lines are fitting curves. The results obtained by fitting are shown in figure. The correlation coefficients are all more than 0.99.

extent of the temperature on the zero-shear viscosity, the high  $Ea$  indicate that the solution is more sensitive to the temperature, and the microstructure is more prone to change. The relationship between  $\ln \eta_0$  and  $1/T$  in solutions of welan gum and xanthan gum is shown in Fig. 5. Values of  $Ea$  are obtained from the slope of lines. The results show that  $Ea$  ( $30.69 \text{ J mol}^{-1}$ ) of xanthan gum is much higher than that of welan gum ( $1.37 \text{ J mol}^{-1}$ ). The microstructure of xanthan gum is more sensitive to the temperature, and thermal stability is worse than that of welan gum.

All samples of welan gum and xanthan gum exist in the linear viscoelastic region at the range of experimental temperatures. The temperature plays little effect on the critical complex modulus and critical stress of welan gum, and these parameters of welan gum are higher than those of xanthan gum at the same temperature. The frequency dependence of  $G'$  and  $G''$  for welan gum and xanthan gum at different temperatures indicates that there is little variation in the dynamic modulus of welan gum when the temperature increases (see Fig. S6), and the elasticity component is the dominating factor in the range of sweep frequency, while the xanthan gum solution is more elastic than viscous at low temperature and more viscous than elastic at high temperature. The viscoelasticity of welan gum solution is larger than that of xanthan gum, indicating that the temperature resistance of welan gum is superior to that of xanthan gum.

### 3.3. The effect of salinity on rheological properties of polysaccharides

Table 2 shows that all rheological parameters of both polysaccharides solutions decline in the presence of inorganic salts. This phenomenon is normal in polyelectrolyte solutions. The electrostatic repulsion between charged groups of macromolecules is screened by inorganic cations, making macromolecules to adopt a more compact conformation. In addition, inorganic ions which

**Table 2**

The apparent viscosity ( $\eta$ ), storage modulus ( $G'$ ) and loss modulus ( $G''$ ) of welan gum (w) and xanthan gum (x) solutions at different salinities:  $c_{\text{gum}} = 1750 \text{ mg L}^{-1}$ ,  $T = 298 \text{ K}$ ,  $\dot{\gamma} = 7 \text{ s}^{-1}$  and  $f = 0.1 \text{ Hz}$ .

Salinity ( $\text{mg L}^{-1}$ )	The steady-state shear		The dynamic viscoelasticity			
	$\eta_w$ (Pa s)	$\eta_x$ (Pa s)	$G'_w$ (Pa)	$G'_x$ (Pa)	$G''_w$ (Pa)	$G''_x$ (Pa)
0	0.40	0.14	2.16	0.73	0.44	0.36
3908	0.18	0.12	1.04	0.49	0.28	0.27
6664	0.17	0.12	0.97	0.45	0.29	0.27
9374	0.16	0.11	0.82	0.42	0.28	0.25

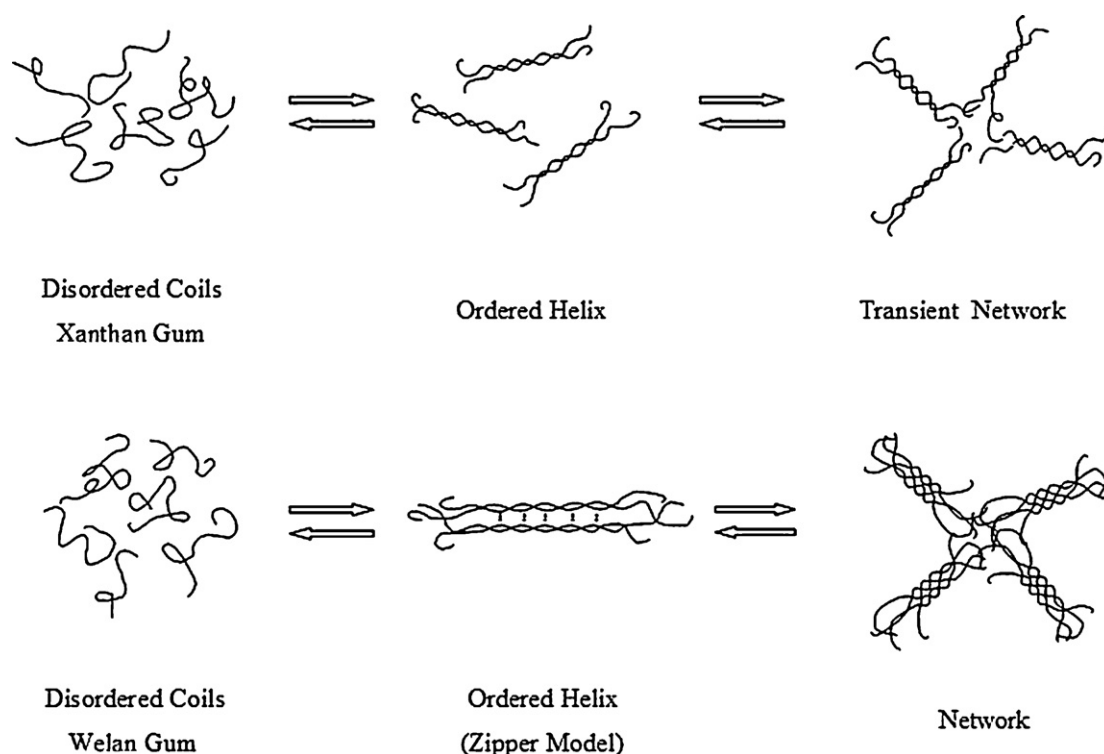
have a strong hydration can also compact the hydrated layer around polysaccharide molecules, the viscosity decreases as a result. However, as the salinity increases further, the apparent viscosities of welan gum and xanthan gum solutions change little, showing a good performance in salt resistance.

The addition of salts to polysaccharides solutions leads to an apparent reduction in dynamic modulus (see Fig. S7). The dynamic modulus of welan gum reduces with the increase of salinity, but the elasticity component is also the dominating factor in the mineralized water. The dynamic modulus of xanthan gum is almost not altered by further increase of salinity, which is in accordance with the result obtained by Wang, Wang, and Sun (2002). Though the dynamic modulus of welan gum decreases with the increase of salinity, it is still higher than that of xanthan gum which can be seen clearly in Table 2 (the dynamic viscoelasticity). The above-mentioned results show that the dynamic viscoelasticity and the apparent viscosity of welan gum solutions are higher than those of xanthan gum solutions.

### 4. Tacking mechanism

An order–disorder transition exists which responds to changes in concentration, temperature and ionic strength within the xanthan gum solutions. High concentration and addition of salts are in favor of the ordered structure, and high temperature favors the disordered structure (Choppe, Puaud, Nicolai, & Benyahia, 2010; Dario, Hortencio, Sierakowski, Queiroz Neto, & Petri, 2011). Our experimental results are consistent with these conclusions, and the similar transition occurs on welan gum. It has found that welan gum can form perfect double helices in the previous research, acetyl and glyceryl groups of welan gum can promote the association between backbones, and play an active role in the formation of the double helix (Matsukawa & Watanabe, 2007; Member & Morris, 1995). Acetyl groups located on the periphery of the helix can stabilize the double helix, and glyceryl substituents located in the core of the helix can modify its geometry. But acetyl groups in xanthan gum locate on side chains of molecules, consequently, long side chains make molecules difficult to form regular double helices due to the steric effect. Moreover, the electrostatic repulsion of xanthan gum also increases the difficulty of molecular aggregation due to the charge of xanthan gum is more than that of welan gum (De Jong & Van de Velde, 2007; Wyatt, Gunther, & Liberatore, 2011).

The storage modulus of xanthan gum is higher than the loss modulus at high concentration, low temperature and high vibration frequency, showing the properties of the weak gel. So we infer that its aggregation structure may be just a transient network which is sustained through the entanglement of soft segments of molecular chains, or by chain cross-linking with a finite time as shown in Scheme 1, and will be destroyed easily by the outside disturbance. The molecular weight of welan gum is lower than that of xanthan gum, but it shows higher viscoelasticity on the same shear, temperature and salinity. This is mainly because the molecular aggregation of welan gum adopts another distribution pattern, as illustrated in Scheme 1. Acyl and glyceryl substituents in welan gum can increase the flexibility of molecular bundles, and lower the charge density (Noda et al., 2008; Ogawa, Matsuzawa, & Iwahashi, 2002; Rinaudo, 2004; Yoneda et al., 2008), promoting inter-helical association. The intermolecular association of welan gum may take place between the methyl group of the L-rhamnosyl residue and the counter hemiacetal oxygen atom of the L-rhamnosyl residue on different molecules via Van der Waals force, and between side and backbone chains of different molecules by hydrogen bond. Adjacent double helices of welan gum arrange in parallel as the zipper model (Nakajima, Ikehara, & Nishi, 1996), which makes double



**Scheme 1.** The schematic representation of proposed mechanism for the structural transition of welan gum and xanthan gum.

helices great entanglement. The character of gel is shown so that the storage modulus of the solution is higher than the loss modulus. The movement of molecules is limited partially due to the zipper model arrangement of double helices, so the network structure of welan gum is not sensitive to the temperature. When the molecular charge is shielded by inorganic cations, the electrostatic interaction weakens. But the hydrogen bond and Van der Waals force between molecules still play a positive role in keeping the viscoelasticity of the solutions.

## 5. Conclusions

Rheological properties of solutions of welan gum and xanthan gum have been investigated at different concentrations, temperatures and salinities. The aqueous solutions of welan gum show a higher viscoelasticity at the same condition though the molecular weight of welan gum is lower than that of xanthan gum. The storage modulus and the loss modulus have exponential relationship with the concentration. Network structure can be formed in solutions of welan gum and xanthan gum. Moreover, the molecular aggregation of welan gum adopts a different arrangement with that of xanthan gum. Adjacent double helices of welan gum arrange possibly in parallel as the zipper model. The network structure formed by zipper model is more stable than that of xanthan gum which is just a transient one, and can resist higher shear, temperature and salinity.

## Acknowledgements

We gratefully acknowledge the financial support from the Natural Science Foundation of China (Grant No. 20833010) and the Special Program for Major Research of the Science and Technology, China (Grant No. 2011ZX05024-004-08).

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.carbpol.2012.09.082>.

## References

- Bejenariu, A., Popa, M., Picton, L., & Le Cerf, D. (2010). Effect of concentration, pH and temperature on xanthan conformation: A preliminary study before crosslinking. *Revue Roumaine de Chimie*, 55, 147–152.
- Chagas, B. S., Machado, D. L. P., Haag, R. B., de Souza, C. R., & Lucas, E. F. (2004). Evaluation of hydrophobically associated polyacrylamide-containing aqueous fluids and their potential use in petroleum recovery. *Journal of Applied Polymer Science*, 91, 3686–3692.
- Choppe, E., Puaud, F., Nicolai, T., & Benyahia, L. (2010). Rheology of xanthan solutions as a function of temperature, concentration and ionic strength. *Carbohydrate Polymers*, 82, 1228–1235.
- Colby, R. (2010). Structure and linear viscoelasticity of flexible polymer solutions: Comparison of polyelectrolyte and neutral polymer solutions. *Rheologica Acta*, 49, 425–442.
- Dario, A. F., Hortencio, L. M. A., Sierakowski, M. R., Queiroz Neto, J. C., & Petri, D. F. S. (2011). The effect of calcium salts on the viscosity and adsorption behavior of xanthan. *Carbohydrate Polymers*, 84, 669–676.
- De Jong, S., & Van de Velde, F. (2007). Charge density of polysaccharide controls microstructure and large deformation properties of mixed gels. *Food Hydrocolloids*, 21, 1172–1187.
- Kang, W., & Dong, X. (Eds.). (1997). *Tertiary oil recovery chemical principles*. Beijing, China: Chemical Industry Press.
- Kjønikesen, A. L., Beheshti, N., Kotlar, H. K., Zhu, K., & Nyström, B. (2008). Modified polysaccharides for use in enhanced oil recovery applications. *European Polymer Journal*, 44, 959–967.
- Long, J., Li, H., Xu, Z., & Masliyah, J. H. (2011). Improving oil sands processability using a temperature-sensitive polymer. *Energy and Fuels*, 25, 701–707.
- MacKintosh, F. C., Käs, J., & Janmey, P. A. (1995). Elasticity of semiflexible biopolymer networks. *Physical Review Letters*, 75, 4425–4428.
- Masakuni, T., & Masahiro, K. (1990). Rheological properties of welan gumin aqueous media. *Agricultural and Biological Chemistry*, 54, 3079–3084.
- Matsukawa, S., & Watanabe, T. (2007). Gelation mechanism and network structure of mixed solution of low- and high-acyl gellan studied by dynamic viscoelasticity, CD and NMR measurements. *Food Hydrocolloids*, 21, 1355–1361.

- Member, M. W. N., & Morris, E. R. (1995). Solubility, solution rheology and salt-induced gelation of welan polysaccharide in organic solvents. *Carbohydrate Polymers*, 27, 23–36.
- Mohammed, S. (2006). Rheological properties of grouts with viscosity modifying agents as diutan gum and welan gum incorporating pulverised fly ash. *Cement and Concrete Research*, 36, 1609–1618.
- Morris, E. R., Gothard, M. G. E., Hember, M. W. N., Manning, C. E., & Robinson, G. (1996). Conformational and rheological transitions of welan, rhamosan and acylated gellan. *Carbohydrate Polymers*, 30, 165–175.
- Mu, J., & Li, G. (2001). Rheology of viscoelastic anionic micellar solutions in the presence of a multivalent counterions. *Colloid and Polymer Science*, 279, 872–878.
- Mu, J., Li, G., Jia, X., Wang, H., & Zhang, G. (2002). Rheological properties and microstructures of anionic micellar solutions in the presence of different inorganic salts. *Journal of Physical Chemistry B*, 106, 11685–11693.
- Mukherjee, I., Sarkar, D., & Moulik, S. P. (2010). Interaction of gums (guar, carboxymethylhydroxypropyl guar, diutan, and xanthan) with surfactants (DTAB, CTAB, and TX-100) in aqueous medium. *Langmuir*, 26, 17906–17912.
- Nakajima, K., Ikehara, T., & Nishi, T. (1996). Observation of gellan gum by scanning tunneling microscopy. *Carbohydrate Polymers*, 30, 77–81.
- Nitta, Y., Takahashi, R., & Nishinari, K. (2009). Viscoelasticity and phase separation of aqueous Na-type gellan solution. *Biomacromolecules*, 11, 187–191.
- Noda, S., Funami, T., Nakauma, M., Asai, I., Takahashi, R., Al-Assaf, S., et al. (2008). Molecular structures of gellan gum imaged with atomic force microscopy in relation to the rheological behavior in aqueous systems. 1. Gellan gum with various acyl contents in the presence and absence of potassium. *Food Hydrocolloids*, 22, 1148–1159.
- Ogawa, E., Matsuzawa, H., & Iwahashi, M. (2002). Conformational transition of gellan gum of sodium, lithium, and potassium types in aqueous solutions. *Food Hydrocolloids*, 16, 1–9.
- Ogugbue, C. C., & Shah, S. N. (2009). Friction pressure correlations for oilfield polymeric solutions in eccentric annulus. In *Amer Soc Mechanical Engineers (ASME)* New York.
- Oh, M. H., So, J. H., & Yang, S. M. (1999). Rheological evidence for the silica-mediated gelation of xanthan gum. *Journal of Colloid and Interface Science*, 216, 320–328.
- Plank, J., Lummer, N. R., & Dugonjic-Bilic, F. (2010). Competitive adsorption between an AMPS (R)-based fluid loss polymer and welan gum biopolymer in oil well cement. *Journal of Applied Polymer Science*, 116, 2913–2919.
- Rao, L., Xue, Y., Zhou, C., Tao, J., Li, G., Lu, J. R., et al. (2011). A thermostable esterase from *Thermoanaerobacter tengcongensis* opening up a new family of bacterial lipolytic enzymes. *Biochimica et Biophysica Acta*, 1814, 1695–1702.
- Rashidi, M., Blokhuis, A. M., & Skaug, A. (2010). Viscosity study of salt tolerant polymers. *Journal of Applied Polymer Science*, 117, 1551–1557.
- Rinaudo, M. (2004). Role of substituents on the properties of some polysaccharides. *Biomacromolecules*, 5, 1155–1165.
- Rodd, A. B., Dunstan, D. E., & Boger, D. V. (2000). Characterisation of xanthan gum solutions using dynamic light scattering and rheology. *Carbohydrate Polymers*, 42, 159–174.
- Saadatabadi, A. R., Nourani, M., & Emadi, M. A. (2010). Rheological behaviour and hydrodynamic diameter of high molecular weight, partially hydrolyzed poly(acrylamide) in high salinity and temperature conditions. *Iranian Polymer Journal*, 19, 105–113.
- Sabhapondit, A., Borthakur, A., & Haque, I. (2003). Water soluble acrylamidomethyl propane sulfonate (AMPS) copolymer as an enhanced oil recovery chemical. *Energy and Fuels*, 17, 683–688.
- Schulte, J., Enders, S., & Quitzsch, K. (1999). Rheological studies of aqueous alkylpolyglucoside surfactant solutions. *Colloid and Polymer Science*, 277, 827–836.
- Sonebi, M., & Malinov, S. (2011). Neural network modeling of rheological parameters of grouts containing viscosity-modifying agent. *ACI Materials Journal*, 108, 316–326.
- Tako, M., Teruya, T., Tamaki, Y., & Konishi, T. (2009). Molecular origin for rheological characteristics of native gellan gum. *Colloid and Polymer Science*, 287, 1445–1454.
- Taylor, K. C., & Nasr El Din, H. A. (1998). Water-soluble hydrophobically associating polymers for improved oil recovery: A literature review. *Journal of Petroleum Science and Technology*, 19, 265–280.
- Wang, D., Xia, H., Liu, Z., & Yang, Q. (Eds.). (2001). *Study of the mechanism of polymer solution with visco-elastic behavior increasing microscopic oil displacement efficiency and the forming of steady "oil thread" flow channels*. Jakarta, Indonesia: SPE.
- Wang, F., Wang, Y. J., & Sun, Z. (2002). Conformational role of xanthan in its interaction with locust bean gum. *Journal of Food Science*, 67, 2609–2614.
- Wyatt, N. B., Gunther, C. M., & Liberatore, M. W. (2011). Increasing viscosity in entangled polyelectrolyte solutions by the addition of salt. *Polymer*, 52, 2437–2444.
- Xin, X., Xu, G., Gong, H., Bai, Y., & Tan, Y. (2008). Interaction between sodium oleate and partially hydrolyzed polyacrylamide: A rheological study. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 326, 1–9.
- Xin, X., Xu, G., Wu, D., Li, Y., & Cao, X. (2007). The effect of CaCl<sub>2</sub> on the interaction between hydrolyzed polyacrylamide and sodium stearate: Rheological property study. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 305, 138–144.
- Xu, L. (2012). The interaction between welan gum and sodium fatty alcohol polyoxyethylene ether sulfate. Master thesis. Jinan, China: Shandong University, p. 98.
- Yoneda, Y., Mereiter, K., Jaeger, C., Brecker, L., Kosma, P., Rosenau, T., et al. (2008). van der Waals versus hydrogen-bonding forces in a crystalline analog of cellobiose: Cyclohexyl 4'-O-cyclohexyl β-D-cellobioside cyclohexane solvate. *Journal of the American Chemical Society*, 130, 16678–16690.
- Yu, W., Zhou, W., & Zhou, C. (2010). Linear viscoelasticity of polymer blends with co-continuous morphology. *Polymer*, 51, 2091–2098.
- Zhang, H., Dong, M., & Zhao, S. (2010). Which one is more important in chemical flooding for enhanced oil recovery, lowering interfacial tension or reducing water mobility? *Energy and Fuels*, 24, 1829–1836.