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Associating and rheological behaviors of fluorinated cationic guar gum in aqueous solutions

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ABSTRACT

The fluorinated cationic guar gum (FCGG) was prepared with cationic guar gum (CGG) and fluorinated reactive monomer (FAM). FAM was synthesized from isophorone diisocyanate and 2,2,3,4,4,4-hexafluoro-1-butanol. The molecular structure, associating and rheological behaviors of FCGG were studied by the FT-IR, ^{19}F NMR, X-ray diffraction, dynamic rheometer and fluorescence spectroscopy, respectively. The results show that FAM is successfully incorporated into CGG. With the increased degree of substitution (DS), the crystallinity is reduced from 3.01 to 0.67% and the characteristic relaxation time is changed significantly from 0.10 to 3.3 s. At low shear rates (<20 s^{-1}), the viscosity of FCGG solution increases with the increase of shear rates. The bigger the DS, the higher the apparent viscosity. The viscosity retention factor of FCGG can reach 126.97% at 30 °C and 51.33% at 60 °C, respectively. The data indicate that FCGG has much better heat resistance.

1. Introduction

Guar gum (GG) is a non-ionic, water-soluble, biodegradable and biocompatible heteropolysaccharide composed of a linear backbone of β-1,4-linked D-mannose units (M) and is solubilized by the presence of randomly attached α-1,6-linked galactose units (G) as side chains. The ratio of mannose to galactose unit (M/G) ranges from 1.5:1 to 2:1 apparently due to climate variations (Abdel-Halim & Al-Deyab, 2011a, 2011b). In order to enhance the application scope of guar gum, its modification has been reported by several researchers through grafting (Abdel-Halim & Al-Deyab, 2011a,b), derivatization (Trivedi, Kalia, Patel, & Trivedi, 2005) and cross-linking (Barbucci, Pasqui, Favalorob, & Panariello, 2008). Its derivatives with various functional groups hold important potential applications in numerous industries, such as food, paints and pigments, oil field, mining, paper-making, water treatment, personal care, pharmaceutical and agriculture (Ma & Pawlik, 2007; Wang, Ellis, & Ross-Murphy, 2006). Cationic guar gum (CGG) is a kind of modified guar gum in which partial hydroxyl groups are replaced by quaternary ammonium groups. The introduction of quaternary ammonium groups impart cationic characteristics to the gum. It is one of the most used derivatives. Compared with native guar gum, the CGG has better solubility and thermal stability in solution and the content of water insoluble substrate is obviously lower than that of native guar gum (Singh, Tiwary, & Kaur, 2010).

Hydrophobically associating polymer or polysaccharides (HAP) is defined as a kind of polymer which contains a major part of hydrophilic polymer backbone and a small part of hydrophobic groups (Charpentier-Valenza, Merle, Mocanu, Picton, & Muller, 2005; Zhang, Wu, Li, & Wang, 2005). The minor amount of hydrophobic groups can associate together assembly and then form a dynamic physical cross-linking network which makes the hydrodynamics volume increase (Feng, Billon, Grassl, Khoukh, & François, 2002). As a result, the substantially enhanced solution viscosity and even special rheological behavior of the aqueous solutions can be obtained. At present, most studies are concentrated on the modification of GG with the hydrocarbon hydrophobic chain and obtain good association effects (Charpentier-Valenza et al., 2005; Lapasin, Lorenzi, Pricl, & Torriano, 1995). Whereas fluorocarbon chains possess the lower surface energy and the stronger associative effect compared with hydrocarbon chains (Zhang, Da, Butler, & Hogen-Esch, 1992). Therefore, the fluorinated monomers used as hydrophobic groups will provide the solutions with better hydrophobically associating properties. It is noteworthy that hydrophobic modification is adverse to the solubility of the modified polymers.

In order to obtain a novel guar gum derivative with excellent solubility and special rheological behavior, we have studied the modification of CGG with fluorinated groups and the solution properties of the derivatives. In this work, fluorinated reactive monomer (FAM) was prepared with isophorone diisocyanate and

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2,2,3,4,4,4-hexafluoro-1-butanol. Then a novel guar gum derivative containing fluorinated groups (FCGG) was synthesized from FAM and CGG. There are fewer studies that reported previously about this work. The molecular structure of the product was characterized through FT-IR, ^{19}F NMR and XRD. Then, the associating and rheological behaviors were reported by means of the dynamic rheometer and fluorescence spectroscopy.

2. Materials and methods

2.1. Materials

The cationic guar gum (CGG) was purchased from Pekin Jiade Biochemistry Co. Ltd. (the weight average molecular weight M_w was approximately 1.0×10^5). Isophorone diisocyanate (IPDI) was purchased from Tianjin Kermel Chemical Reagent Co. Ltd. (Tianjin, China). 2,2,3,4,4,4-Hexafluoro-1-butanol (FH) was purchased from Harbin Xeogia Group Co. Ltd. (Harbin, China). Dibutyltion dilaurate (T-12) was purchased from Tianjing Hongyan Chemical Reagent Co. Ltd. (Tianjin, China). Acetone, tetrahydrofuran and petroleum ether were from Zhonghai Chemical Industry (Shandong, China). Distilled water was used for all experiments.

2.2. Synthesis of FCGG

Firstly, the fluorinated reactive monomer (FAM) based on IPDI and FH was synthesized through solution polymerization. 0.11 mol of IPDI and 50 ml of acetone were charged into a dry vessel fitted with a reflux condenser, a mechanical stirrer, a digital thermometer and a nitrogen gas inlet. The solution of 20 ml of acetone with 0.1 mol of FH was added dropwise into the vessel for 1.0 h. Then the T-12 (0.02 wt% based on the total reactant mass) was added and the content was stirred for 6.0 h under the state of circulation reflux. After the acetone was removed by distillation, the viscous liquid was obtained and FAM was finally obtained by washing the viscous liquid with petroleum ether three times (100 ml every time).

The CGG was dried to the constant weight in a vacuum at 105 °C for 24 h to remove the free water completely. 8.0 g of the dried CGG and 230 ml of tetrahydrofuran were charged into a dry vessel fitted with the same equipments as shown in the first step. The solution of 20 ml of tetrahydrofuran with different amounts of FAM was added dropwise into the vessel for 1.0 h. Then the T-12 (0.02 wt% based on the total reactant mass) was added and the content was stirred for another 12.0 h under the state of circulation reflux. The product was extracted from acetone for about 24 h and dried in a vacuum. The degree of substitution (DS) was determined by nitrogen analysis.

2.3. FT-IR

FT-IR spectroscopy of CGG and FCGGs were studied on FT-IR spectrometer (Model V70, Bruker) in the dry air at room temperature. The gum samples were pressed directly on to attenuated reflectance KBr crystal as the sampling unit.

2.4. ^{19}F NMR

^{19}F NMRs of CGG and FCGGs were analyzed by a NMR spectroscopy (DPX-400 spectrometer, Bruker) at 376.3 MHz. The digital resolution was ±0.01 ppm, with 0.1% in D_2O as solvent.

2.5. XRD

X-ray (XRD) diffraction patterns of CGG and FCGGs were analyzed by X-ray diffractometer (Model D/Max-2400, Rigaku, Japan) with Cu K_α radiation at a voltage of 40 kV and 100 mA current. The scattered radiation (2θ) was detected in the range of 2–60° with a step size of 0.02°.

2.6. Rheological study

The apparent viscosity and rheological behaviors of CGG and FCGGs at different concentrations from 0.05 to 0.60 g dl^{-1} were performed with the Haake rheometer (RS150L, Therm Haake Co., Germany) equipped with a cone and plate measuring unit. The dynamic measurements were conducted in the range of frequency from 0.01to 100 Hz or the temperature range from 15 to 75 °C, respectively. All the measurements were made within the linear viscoelastic region and the solution concentrations was 0.50 g dl^{-1} unless otherwise specified.

2.7. Fluorescence spectroscopy (FS)

The fluorescence spectroscopy (FS) of CGG and FCGGs at different concentrations from 0.05 to 0.60 g dl^{-1} were performed through Fluorophotometer (Cary Eclipse, Agilent) at 25 °C with excitation at 338 nm and with a bandpass slit width of 3.0 nm in a scanning range of 350–550 nm. Polarity parameter (I_1/I_3) of pyrene equal to the ratio of the first to the third emission peak intensities (I_1 = 371 nm, I_3 = 383 nm) was measured. Pyrene was used as fluorescent probe. The solutions for fluorescence measurements were prepared by first pipetting 0.012 ml of pyrene stock solutions (2.0×10^{-4} mol/l in ethanol). Then, 3.0 ml of polymer solution with a given concentration was added to the flask and also treated by ultrasound for 0.5 h before the FS measurements were carried out.

2.8. Degree of substitution (DS)

The degree of substitution (expressed as DS, which is defined as the number of the substituted hydroxyl groups per sugar unit of guar gum) was determined from the contents of nitrogen. The nitrogen contents of the products (N wt%) was measured by an elemental analyzer (EA, Heraeus Co., Germany). And DS′ (quaternary ammonium groups) of CGG was calculated according to the following equation (Huang, Yu, & Xiao, 2007):

$$\mathrm{DS}' = \frac{162.2 \times N\ \mathrm{wt\%}}{1401 - 151.6 \times N\,\mathrm{wt\%}} \quad (1)$$

The DS′ value of the purchased CGG was found to be 0.20. DS (FAM) was calculated by Eqs. (2) and (3).

$$\mathrm{DS}' = \frac{(162.2 - 2DS + M \times 2DS)N\ \mathrm{wt\%}}{1401 - 151.6 \times N\,\mathrm{wt\%}} \quad (2)$$

$$\mathrm{DS} = \frac{280.2 - 192.5N\,\mathrm{wt\%}}{806.8 \times N\,\mathrm{wt\%}} \quad (3)$$

where DS′ = 0.20 and M was the molecular weight of FAM.

3. Results and discussion

3.1. FT-IR and ^{19}F NMR

The FAM is successfully incorporated into FCGG and this can be obtained by FT-IR and ^{19}F NMR (Fig. 1).

Fig. 1a presents the FI-IR spectra of FAM, CGG and FCGG, respectively. There is a strong absorption peak of ν_{C-F} (1250 cm^{-1}) and the characteristic absorption bands of carbamate (ν_{N-H}: 3342 cm^{-1}, 1529 cm^{-1}; $\nu_{C=O}$ = 1727 cm^{-1}; ν_{C-O} = 1118 cm^{-1}) in the spectrum of FAM (Pretsch, Bühlmann, Bu̧hlmann, & Badertscher, 2009). The carbimide group (2268 cm^{-1}) and —CH_3 (1371 cm^{-1}) still appear, which indicates that FAM is synthesized successfully. Compared with FT-IR spectrum of CGG, the characteristic absorption peaks of

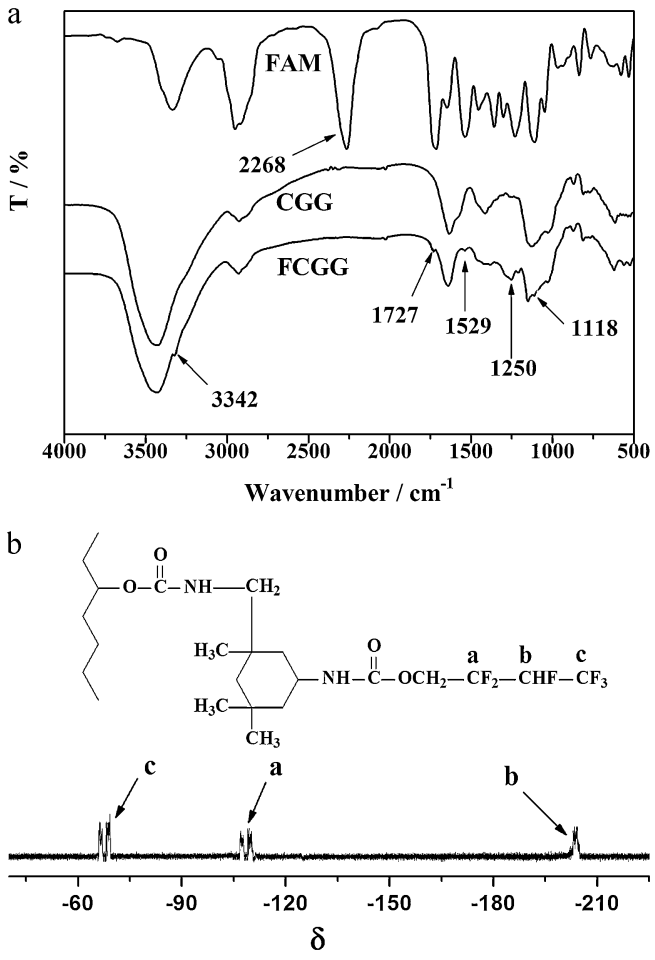

Fig. 1. Characterization of CGG and FCGG. (a) FT-IR and (b) ^{19}F NMR.

FAM show up in the FCGG spectrum. At the same time, the characteristic absorption of the said —NCO is vanished. These data depict that the FAM is incorporated into FCGG.

As shown in ^{19}F NMR spectrum (Fig. 1b), it is known that there are three different chemical environments of fluorine atoms in FCGG molecules. Due to the effects of Van der Waals force and coupling effect, the double peaks of $-CF_3$ groups appear in the low-field range (near −68.02 ppm) and peaks of $-CF_2$ group appear at near −109.21 ppm. Peaks of —CHF appear in the high-field range (−205.12 ppm) without effect of van der Waals force (Schorn, Naumann, Scherer, & Hahn, 2001). The results of ^{19}F NMR confirm that the FAM is effectively introduced into FCGG.

3.2. X-ray diffraction analysis

The wide angle XRD patterns of CGG and FCGG are presented in Fig. 2. From the curve of CGG, it is obvious that the shape of the peak becomes a wide peak known as "bun-like peak" and the peak line was not smooth, which is thus caused by the amorphous phase in CGG. However, the sharp peak (x = 20.38°) on the "bun-like peak" indicates that CGG exhibits a very small crystallinity (the degree of crystallinity is 3.01%). Similar phenomenon has been reported in the literature (Pal, Mal, & Singh, 2007). After fluoridation, remarkable reductions in crystallinity are observed (Fig. 2b–d). The higher the DS, the lower the crystallinity. These losses of crystallinity may be attributed to the effect of the replacement of the hydroxyl groups by the fluorinated groups. Hydrogen bonds will have been able to maintain the stability of guar gum crystal and the crystallinity is reduced when they are broken (Gong, Liu, Chen, Han, Gao, & Zhang, 2012). Moreover, the molecular structure becomes more complex because of the incorporation of the fluorinated hydrophobic groups. The irregular degree of the macromolecular chain segment increases and degree of crystallinity decreases, correspondingly.

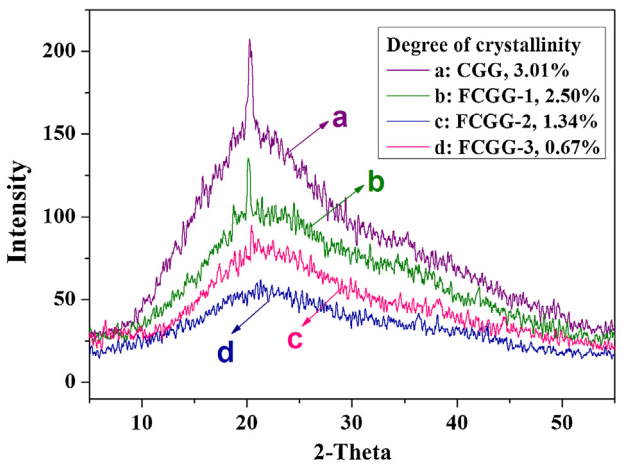

Fig. 2. XRD patterns of CGG and FCGG with different DS.

3.3. Associating behaviors

Fig. 3 shows significantly the special and unique associating behaviors of FCGG with different FAM contents from both macroscopic and microscopic aspects. The data of the CGG are shown in the comparison. The change in the apparent viscosity of sample solutions is the macroscopic behavior of their hydrophobic associative property, which presents the special thickening effect of FCGG.

The relationship between FCGG concentration and the apparent viscosity is shown in Fig. 3a. When FCGG concentration increases, apparent viscosities of all the three kinds of FCGGs are on the rise correspondingly. It is worth mentioning that there is a sudden increase on the apparent viscosity. However, this abrupt augment is not shown in the viscosity-concentration curve of CGG. The resultant trend indicates that FAM is successfully introduced into CGG and endows the special increasing pattern of apparent viscosity. At the same time, the higher the content of FAM is, the lower concentration the sudden increase takes place. This non-linear sudden increase of apparent viscosity of FCGG is the macroscopical expression of the transformation from intra-molecular aggregates to inter-molecular ones. The transformation makes the macromolecular chains cross-link and then the hydrodynamics volume enhances.

The fluorometry can reveal the hydrophobic associative property of FCGG on a molecule level. The values of I_1/I_3 in fluorescence spectra, which is equal to the ratio of the first emission peak (I_1 = 371 nm) intensity to the third emission peak (I_3 = 383 nm) intensity of pyrene, are measured. This value is the so-called polarity parameter and strongly dependent on the polarity around pyrene probe. The stronger the polarity of the microenvironment around pyrene probe, the higher the value of I_1/I_3 (Beghein et al., 2007; Ren, Gao, Lu, Liu, & Zhen, 2006). For example, the value of I_1/I_3 is 1.87 and 0.58 when the pyrene is in the pure water and in the non-polar cyclohexane, respectively.

As seen from Fig. 3b, the value of I_1/I_3 of FCGG declines slightly from the beginning because there are a small amount of intra-molecular hydrophobic micro domains in the FCGG aqueous solution. With the increased FCGG concentration, lots of the hydrophobic micro domains appear and the polarity of microenvironment surrounding pyrene drastically weakens. Then the value

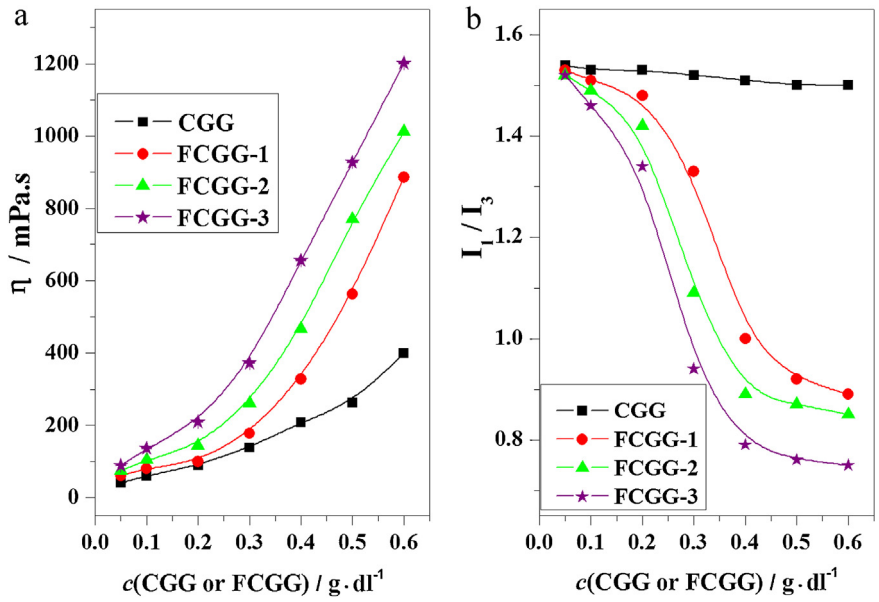

Fig. 3. Associating behaviors of solutions of CGG and FCGG. (a) The change of viscosity via concentration (shear rate: 15.0 s^{-1}). (b) The change of I_1/I_3 via concentration.

of I_1/I_3 diminishes abruptly. Due to the limited solubilization of pyrene in the solutions (Shashkina et al., 2003), the value of I_1/I_3 keeps unchanged after a certain concentration. The value of I_1/I_3 in CGG solution keep balance as CGG concentration increases. It vividly displays that there are no hydrophobic micro domains and associating effects in the CGG solutions. These conclusions confirm again and supplement the foregoing results of the thickening effects by the measurement of apparent viscosity.

3.4. Rheological behavior

3.4.1. Power-law model

Power-law model can preferably reflect rheological properties of the solution. The $\sigma \sim \gamma$ curves of the sample aqueous solutions are fitted by Ostwald–Dewael model and Herschel–Bulkley model, respectively. Ostwald–Dewael model (Li, Hou, & Li, 2012) is described by Eq. (4).

$$\sigma = k\lambda^n \tag{4}$$

Herschel–Bulkley model is described by Eq. (5).

$$\sigma = \sigma_0 + K\lambda^N \tag{5}$$

where σ is the shear stress, σ_0 is the yield stress, γ is the shear stress, n or N is the liquidity index, the k or K is the consistency coefficient. n or N is 1.0 for the Newtonian fluid and is <1.0 for non-Newtonian fluid. n (or N) and k (or K) values can be obtained through $\sigma \sim \gamma$ curves in Fig. 4.

For the samples, all the fitting results of Eqs. (4) and (5) are listed in Table 1. From the regression coefficients (R^2) values, it can be concluded that the flow curves of FCGG-2 and FCGG-3 may be fitted better by Herschel–Bulkley model than by Ostwald–Dewael model. The value of σ_0 is 5.36 Pa for FCGG-2 and 13.26 Pa for FCGG-3, respectively. The solution presents gel-like behaviors when the σ_0 value is higher. It is depicted that the more hydrophobically fluorinated groups in the cationic guar gum molecules, the easier the associations in the solutions. This kind of hydrophobic self-assembly behavior makes the apparent viscosity increase and the networking structures enhance.

It is thought that the curves can be fitted very well for the samples CGG and FCGG-1 by Ostwald–Dewael model because all the R^2 values reach 0.9996. There is no yield stress existing in the samples solutions. The CGG and the FCGG-1 solutions are viscous but not gel-like. The results indicate that the relative low contents of hydrophobically fluorinated groups in FCGG cannot be enough to associate and form gel at the same concentration.

3.4.2. Dynamic moduli

It can be seen that the modification of CGG with FAM gives rise to a strong viscosity enhancement of the FCGG solutions. Similarly, the viscoelastic behaviors will be strongly influenced by the so-called self-assemble behaviors. The measurements of dynamic moduli have been performed in the linear viscoelastic region.

Fig. 5 describes the storage moduli (G') and the loss moduli (G'') of the FCGG with different DS. With the increase of DS, both moduli are enhanced and the relaxation spectra shift to relative lower frequencies (Nga, Tama, & Jenkins, 2001). For the FCGG-2 and the FCGG-3 solutions, G' becomes larger than G'' at a certain

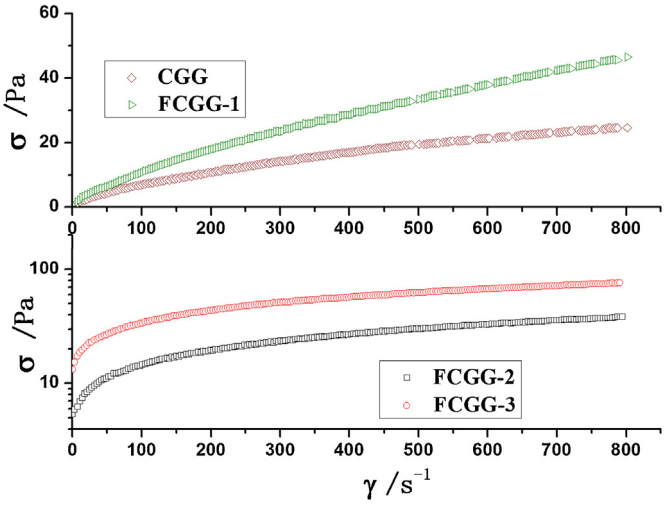

Fig. 4. The relationship of $\sigma \sim \gamma$ of CGG and FCGG with different DS.

Table 1
Some properties of CGG and FCGG aqueous solutions.

Models	Samples	DS	σ_0	N or n	K or k (mPa s^n)	R^2	τ_c (s)
A[a]	CGG	0	0	0.627	0.389	0.9996	0.02
	FCGG-1	0.0025	0	0.701	0.427	0.9996	0.10
	FCGG-2	0.0065	0	0.414	2.238	0.9912	0.67
	FCGG-3	0.0100	0	0.349	7.211	0.9913	3.33
B[b]	FCGG-2	0.0065	5.36	0.503	1.862	0.9995	0.67
	FCGG-3	0.0100	13.26	0.519	2.290	0.9998	3.33

[a] Ostwald–Dewael model.
[b] Herschel–Bulkley model.

frequency, which illustrates the importance of elastic part formed in the solutions. The higher the DS, the lower the frequency at which G' surpasses G''.

In the case of maxwellian behavior, a characteristic relaxation time τ_c can be estimated from the frequency (ω_c) corresponding to the crossing point G_c ($G'(\omega) = G''(\omega)$; $\tau_c = 1/\omega_c$). The results are showed in Table 1. The τ_c of CGG is 0.02 s and increases remarkably when the FAM is incorporated into CGG. When the DS increases from 0.0025 to 0.0100, the τ_c is changed significantly from 0.10 to 3.3 s. This obvious increased τ_c indicates that the higher DS of FCGG can produce more physically cross-linking net structures, which can build viscoelasticity up (Volpert, Selb, & Candau, 1998). The observed enhancement of the relaxation time indicates an augmentation of the association life-time between macromolecules via hydrophobically fluorinated groups.

3.4.3. Effects of shear rate

Effects of shear rate on the apparent viscosity of the CGG and the FCGG solutions are shown in Fig. 6. The apparent viscosities of all the FCGG samples are higher than that of the CGG. It is somewhat surprising that, at low shear rates (<20 s^{-1}), the viscosity of FCGG increases with the increased shear rate. At the same time, the bigger the DS, the higher the apparent viscosity. It is noteworthy that FCGG-1 sample exhibits good thickening properties even the DS only reached 0.0025. This result shows the strong efficiency of FAM as the hydrophobe. The increased FAM amounts are more effective for the associative properties. It can be interpreted by the change from intra- to inter-molecular interactions under the low shear force (Volpert et al., 1998). At higher shear rates, all samples display the shear thinning property and the viscosities of FCGGs are still higher than that of the CGG. This means that a complete rupture of the hydrophobic associations occurs in the above-mentioned accessible shear rate range.

3.4.4. Effects of temperature

Heat resistance of GG is an important factor for evaluating the practical applicability in several industrial fields. Fig. 7a shows the effects of the temperature on the apparent viscosities of the CGG and the FCGG solutions.

The apparent viscosity of CGG decreases from the beginning and the declining rate of the apparent viscosity accelerates when the temperature is higher than 40 °C. Along with the increase of the temperature, the molecular energy of thermal motion increases and the cavity in solution augments and inflates. As a result, the flow resistance decreases and then the apparent viscosity reduces. The apparent viscosities of FCGG solutions show the different change tendency. The apparent viscosities decline after the temperature increases to some extent. The higher the DS, the more considerable the increasing degree. The maximum value of the apparent viscosity of FCGG-1, FCGG-2 and FCGG-3 appears at 32 °C, 40 °C and 45 °C, respectively.

The viscosity retention factor (R_v), which is the ratio of equilibrious viscosity to the starting viscosity, is used to represent the heat resistance performance. For example, the R_v of FCGG-2 and FCGG-3 can reach 118.52% and 126.97% at 30 °C and 47.88% and 51.33% at 60 °C, respectively. When the temperature augments to some extent, the intra-molecular association is weakened and the expansion of the macromolecular coils takes place. The stretching coils are favorable toward inter-molecular association and then the apparent viscosity increases. But when the temperature continually increases, the thermal-motion of molecules is intensified and the inter-molecular association effects are weakened. Hence, the apparent viscosity reduces. The results indicate that the relative high temperature can help the self-assembly behavior through the hydrophobically associating effects to improve the heat resistance of FCGG solutions.

The loss factor ($\tan\delta = G''/G'$) is an important parameter for representing the viscoelasticity of solution. The system of the solution

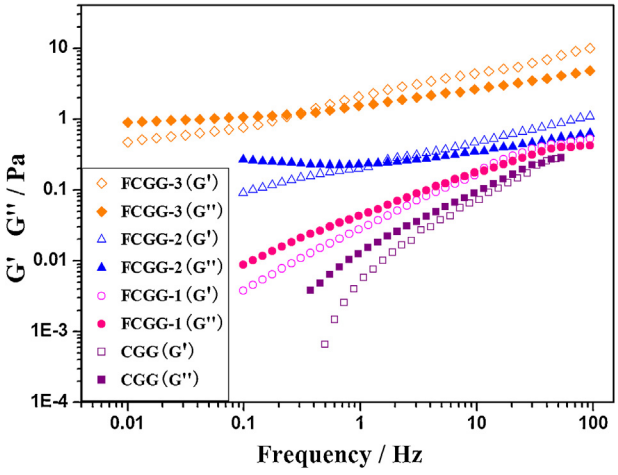

Fig. 5. Storage modulus (G') and loss modulus (G'') via frequency.

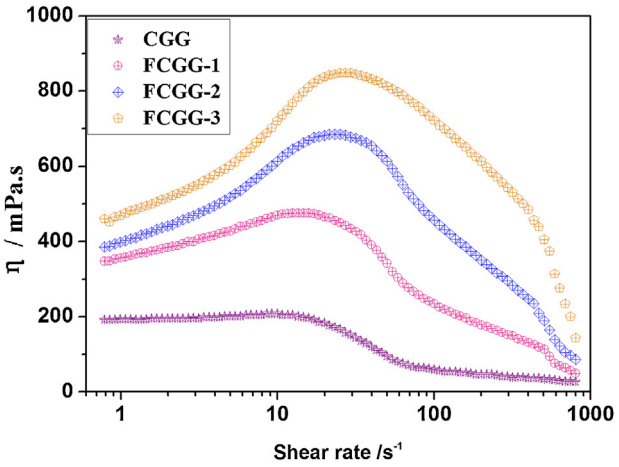

Fig. 6. Effects of shear rates on the solution viscosity (shear rate: 15.9 s^{-1}).

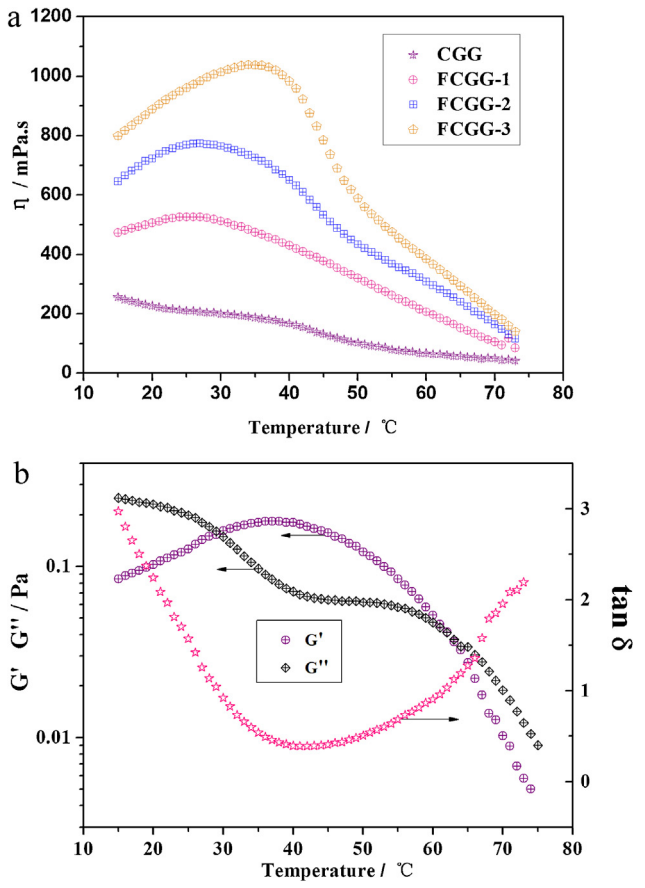

Fig. 7. Effects of temperature on the solution rheological behaviors. (a) The solution viscosity (shear rate: 15.6 s^{-1}). (b) The moduli (G',G'') and loss factor (tan δ) of FCGG-2.

appears viscidity when the value of tan δ is >1 and elasticity when the value of tan δ is <1. The moduli (G',G'') and loss factor (tan δ) of FCGG-2 are clearly shown in Fig. 7b.

The value of tan δ appears the minimum at 40 °C. From the beginning, FCGG-2 solution presents viscidity due to tan δ > 1. When temperature is 30 °C (tan δ = 1), the system of FCGG-2 solution starts to show up the elasticity performance and enhance till 40 °C. Subsequently, the system still appears elasticity, but the elasticity performance declines and viscidity performance increases. The system resumes showing viscidity until 60 °C (tan δ = 1). These may be attributed to the reason that the moderate temperature may prompt the stretching of the macromolecular chains and the hydrophobic groups are associated together assembly to form "physical cross-linking network structures", which can built up the elasticity of solution system.

4. Conclusion

In order to obtain a novel guar gum derivative (FCGG) with excellent solubility and special rheological behavior, the fluorinated reactive monomer (FAM) based on isophorone diisocyanate (IPDI) and 2,2,3,4,4,4-hexafluoro-1-butanol (FH) was successfully synthesized and incorporated in the backbone of cationic guar gum (CGG). When the DS of FAM in FCGG increases from 0 to 0.010, the degree of crystallinity of FCGG reduces from 3.01 to 0.67% because the regular arrangement of CGG molecular is disturbed by the incorporation of FAM. At the same time, there exists intra- and inter-molecular hydrophobic micro domains in the FCGG aqueous solution. As a result, FCGG solution has the unique associating and rheological behaviors. The characteristic relaxation time (τ_c) is changed significantly from 0.10 to 3.3 s. At low shear rates (<20 s^{-1}), the viscosity of FCGG increases with the increased shear rate. The bigger the DS, the higher the apparent viscosity. The viscosity retention factor (R_V) of FCGG with DS = 0.010 could reach 126.97% at 30 °C and 51.33% at 60 °C, respectively. The data indicate that the modified guar gum has much better heat resistance.

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