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Synthesis and characterization of carboxymethyl guar gum and rheological properties of its solutions

Honghong Gong, Mingzhu Liu*, Jiucun Chen, Fei Han, Chunmei Gao, Bing Zhang

Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, State Key Laboratory of Applied Organic Chemistry and Department of Chemistry, Lanzhou University, Lanzhou 730000, PR China

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ABSTRACT

Carboxymethyl guar gum was synthesized with a simple dry and multi-step method for the first time as a product of the reaction of guar gum and monochloroacetic acid in the presence of sodium hydroxide. The influences of a variety of reaction parameters for degree of substitution were evaluated. The product was characterized by a variety of material characterization techniques. FTIR showed new bonds at 1618, 1424 and 1325 cm^{-1} after carboxymethylation. SEM showed that the surface of guar gum particles was mostly ruptured. XRD revealed that guar gum crystallinity was reduced. The rheological properties of product pastes were studied using a rotational viscometer. The viscosity of products' solution decreased with increasing temperature and increased with increasing concentration. With the increase of storage time, the viscosity increased at first, and then decreased. In addition, a shear thinning pseudoplastic behavior was observed at all concentrations, temperatures and storage times.

1. Introduction

Guar gum (GG) is a naturally occurring polymer extracted from the seeds of *Cyamopsis tetragonalobus* plant and is commercially cultivated in parts of the Asian subcontinent as well as in North Africa and South America. It consists 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. Guar gum is widely used in a variety of industrial applications because of its low cost and its ability to produce a highly viscous solution even at low concentrations. The high viscosity of guar gum solutions arises from the high molecular weight of guar gum and from the presence of extensive intermolecular association (entanglement) through hydrogen bonding. Guar gum and its derivatives have thus spawned a variety of commercial and industrial uses in water treatment (Nayak & Singh, 2001; Picout, Ross-Murphy, Errington, & Harding, 2001; Singh, Singh, Pandey, & Sanghi, 2011), mining (Pawlik & Laskowski, 2006; Tripathy, Mishra, Srivastava, Mishra, & Behari, 2008), pharmaceutical (Sen, Mishra, Jha, & Pal, 2010; Thakur, Chauhan, & Ahn, 2009), oilfield (Caenn & Chillingar, 1996) and textiles (Schneider & Šostar-Turk, 2003; Šostar & Schneider, 1998; Thimma & Tammishetti, 2001).

However, incomplete hydration of guar gum at room temperature, poor clarity of the solution and the desire for products with modified or particular properties have led to the development of a variety of commercial ether derivatives (Risica, Barbetta, Vischetti, Cametti, & Dentini, 2010). Hence it is always reasonable to modify it to suit specific industrial process. Chemical modification of guar gum involves reaction of the hydroxyl groups on the anhydroglucose units (AGU) and these have been used to produce guar gum derivatives based on carboxymethylation (Pal, 2009), oxidation (Klein-Koerkamp et al., 2009), grafting (Pawlik & Laskowski, 2006; Singh et al., 2011; Tripathy et al., 2008) and crosslinking (Huang, Yu, & Xiao, 2006; Šostar & Schneider, 1998). Among the guar gum derivatives, carboxymethyl guar gum (CMGG) is very important because it covers a wide range of industrial applications.

Carboxymethyl guar gum is obtained by reacting guar gum with monochloroacetic acid or its sodium salt (SMCA) following activation of the guar gum with aqueous NaOH in slurry of an aqueous organic solvent. The carboxymethylation reaction on guar gum proceeds in two steps. The first step is an alkalization where the hydroxyl groups of the guar gum molecules are activated and changed into the more reactive alkoxide form (GG–ONa).

$$\text{GG–OH} + \text{NaOH} \rightarrow \text{GG–ONa} + H_2O \quad (1)$$

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* Corresponding author. Tel.: +86 931 8912387; fax: +86 931 8912582.
E-mail addresses: gonghh09@lzu.edu.cn (H. Gong), mzliu@lzu.edu.cn (M. Liu).

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The carboxymethyl groups are formed in a S_N2 reaction between the guar gum alkoxide and the SMCA. This main reaction is given by

$$\text{GG–ONa} + \text{Cl–CH}_2\text{–CO–ONa} \rightarrow \text{GG–O–CH}_2\text{–COONa} + \text{NaCl} \qquad (2)$$

Previous work showed preference for reaction at C6 during acetylation of starch using microwave heating. The greater rate of reaction at the primary hydroxyl at C6 is likely due to lesser steric hindrance than at secondary hydroxyls of C2 and C3 (Shogren & Biswas, 2006). Guar gum has the similar property.

A side reaction also occurs which competes with the production process of carboxymethyl guar gum. In this side reaction, sodium gylocate is produced at the expense of the guar gum derivative.

$$\text{NaOH} + \text{ClCH}_2\text{COONa} \rightarrow \text{HOCH}_2\text{COONa} + \text{NaCl} \qquad (3)$$

But this side reaction is significantly slower than the main reaction, for the conditions applied in this study the side reaction can be neglected.

Knowledge about solution properties is necessary to understand the polysaccharides' behavior in different applications. The main factors affecting the solution properties of polysaccharides are the molecular structures of the polysaccharides, such as the content of side galactose units and degree of substitution, molar mass, and temperature, pH, and ionic strength circumstances (Xu, Willför, Holmlund, & Holmbom, 2009). Carboxymethyl guar gum is now available in large amounts, and thus it is important to study its physicochemical properties to provide basic information for its applications.

In the present work, a simple dry carboxymethylated method was used considering the principle of green chemistry and green process technology, which aims to constantly decrease pollution, unnecessary energy, raw material consumption as well as the side reaction. In addition, the rheological properties of carboxymethyl guar gum solutions were investigated. The influences of concentration, temperature as well as storage time on rheological properties were studied.

2. Material and methods

2.1. Material

Guar gum (GG, viscosity 13,400 mPa s in 1% (w/v) aqueous solution at 25 °C) was kindly supplied by Beijing Guar Science & Trading Ltd. (Food Grade quality). Sodium hydroxide and monochloroacetic acid (MCA) were provided by Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China. Urea was purchased from Tianjin Chemical Reagent NO. 6 Factory, Tianjin, China. Sodium bicarbonate, sodium carbonate and other chemicals were analytical grade and used as received.

2.2. Preparation of carboxymethyl guar gum

Carboxymethyl reaction of guar gum was carried out with a simple dry method. The reactions were conducted in a 1 L jacketed stainless steel reactor vessel equipped with motor driven stirrer. Powdered sodium hydroxide of different quantities was mixed with native guar gum (25 g) completely and transferred to the reactor vessel. A small amount of aqueous-organic liquid medium (15 mL 95% C_2H_5OH) was added to the reactor vessel and the temperature was adjusted to 30 °C through the temperature of the circulating water in the jacket. The mixture was constantly stirred for 20 min. Then, MCA (16.04 g) was added into the reactor vessel and the reaction progressed for another 20 min. The intermediate was transferred into a sealed tin and the second step reaction progressed for 10 h at 60 °C oven. After reaction, the resultant product was dried at room temperature, milled, sieved and stored for further use.

2.3. Determination of degree of substitution (DS)

The degree of substitution of carboxymethyl guar gum was determined using titrimetry according to a previously reported method in the literature (Stojanović, Jeremić, Jovanović, & Lechner 2005). Carboxymethyl guar gum (1.5 g) was dispersed in 50 mL of 2 M HCl (used 70% methanol as solvent), and the suspension was under magnetic stirring continuously for 2 h. During this process, the carboxymethyl guar gum which was in sodium form (Na-CMGG) was converted to the hydrogen form (H-CMGG). H-CMGG was washed with 95% (V/V) ethanol until free of chlorine (tested by 0.1 M silver nitrate solution). The dispersion was filtered, and dried in an oven at 60 °C for 2 h. Dried H-CMGG (0.5 g) was dissolved in 50 mL of standardized 0.1 M NaOH solution and stirred for 2 h. Then the excess of NaOH was back titrated with standardized 0.1 M HCl solution using phenolphthalein as the indicator. The DS was determined using the following calculation:

$$w_A = \frac{C_{\text{NaOH}}V_{\text{NaOH}} - C_{\text{HCl}}V_{\text{HCl}}}{m} \qquad (4)$$

$$\text{DS} = \frac{162w_A}{5900 - 58w_A} \qquad (5)$$

where C_{NaOH} and C_{HCl} are the molar concentration of standard NaOH and HCl solutions, w_A is the mass fraction of $-CH_2COOH$ (acetyl group), 59 (g/mol) is the molar mass of $-CH_2COOH$, V_{NaOH} is the volume of NaOH (50.00 mL) and V_{HCl} is the volume of HCl used for the titration of the excess of NaOH, m (g) is the weight of polymer taken, 162 g/mol is the molar mass of the anhydroglucose unit.

2.4. Fourier transform infrared spectroscopy

Guar gum and carboxymethyl guar gum were characterized by Fourier transform infrared (FTIR) spectrophotometer (American Nicolet Corp. Model 170-SX). The samples were blended with solid KBr powder and about 40 mg of the blend was made into a pellet. The KBr pellet was dried and subjected to FTIR spectrophotometry. Transmittances were recorded at wave numbers between 4000 and 400 cm^{-1}.

2.5. Scanning electron microscopy

The granule morphology of guar gum and carboxymethyl guar gum samples was observed by JSM-6701F scanning electron microscopy (SEM) instrument (JEOL, Ltd. Japan) after coated with gold film.

2.6. X-ray diffraction analysis

X-ray diffraction patterns (XRD) of guar gum and carboxymethyl guar gum were analyzed using Rigaku D/Max-2400 X-ray power diffractometer (Rigaku, Tokyo, Japan) with Nickel filtered Cu K_α radiation (λ = 1.54056 Å) at a voltage of 40 kV and current of 100 mA. The scattered radiation was detected in the angular range of 2–80° (2θ), with a step size of 0.02° (2θ).

2.7. Differential scanning calorimetry

The glass transition temperature (T_g) of guar gum and carboxymethyl guar gum was measured on Sapphire differential scanning calorimetry (DSC) (Perkin-Elmer Corp., Wilton, CT) at a scanning rate of 20 °C/min under a dry nitrogen atmosphere. The weight of the samples ranged from 5 to 8 mg.

2.8. Pasting properties

Carboxymethyl guar gum is widely used in a variety of industrial applications such as oil recovery, food systems, paints, mineral industry, personal care and textile and so on. In most applications, several additives such as cosolvents or salts are also present in solution, besides gum and water. The presence of these additives can dramatically change the viscoelastic and structural properties of gum solutions, since they affect the quality of the solvent and thus both the chain conformation and the degree of intermolecular associations. To fully control the properties of gum solutions in applications it is therefore essential to characterize the change of solution's viscosity induced by the different additives and to correlate them to the modification of the rheological behavior. In the present study, the influences of different concentration, temperature dependence as well as storage time were studied.

The viscosity of a series of carboxymethyl guar gum solution was measured by a NDJ-1 rotational viscometer (Shanghai Shangtian Science Instruments, China) using the spindle No. 4 at 6, 12, 30 and 60 rotations per minute (rpm). Measurements were performed in duplicate with 30 s intervals and the date was averaged.

2.9. Preparation of the printing paste and the printing process

The thickener, auxiliaries and distilled water were well stirred in a mixer and allowed to stand 24 h at room temperature to attain full swelling. To prepare the printing colored paste, all stock pastes were adjusted to a viscosity in the range of 5000–8000 mPa s at a speed of 6 rmp, then 5% (w/w) dye was added to each stock paste and stirred for 10 min. The printing process is a sequence of several operations in order to obtain the penetration and the fixation of the dye molecule in the fibre. During the first step, the printing paste is deposited on the fabric through a 100-mesh plat screen. Then the printed textiles were dried for 5 min at 105 °C and fixed color for 10 min in saturated steam. Then the printed textiles were soaped for 5 min at 100 °C and washed in cold tap water, then dried and ironed.

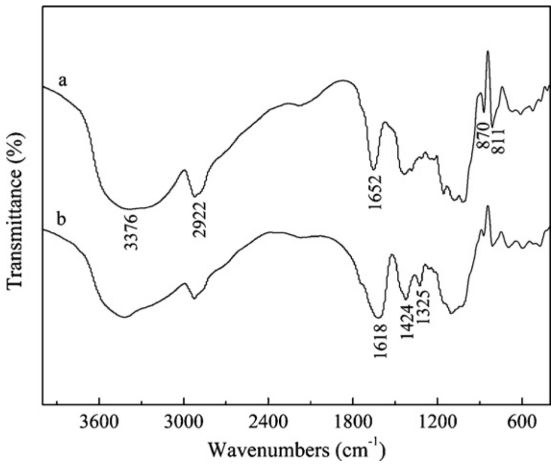

Fig. 1. FTIR spectra of GG (a) and CMGG (b, DS = 0.670).

3. Results and discussion

3.1. FTIR

The infrared spectra of native guar gum and a representative carboxymethyl guar gum (CMGG, DS = 0.67) are presented in Fig. 1. The broad band around 3376 cm^{-1} is attributed to O—H stretching vibration. We can also observe the —CH$_2$— symmetrical stretching vibrations at 2922 cm^{-1}. In native guar gum, the band at 1652 cm^{-1} is assigned to scissoring of two O—H bonds of absorbed water

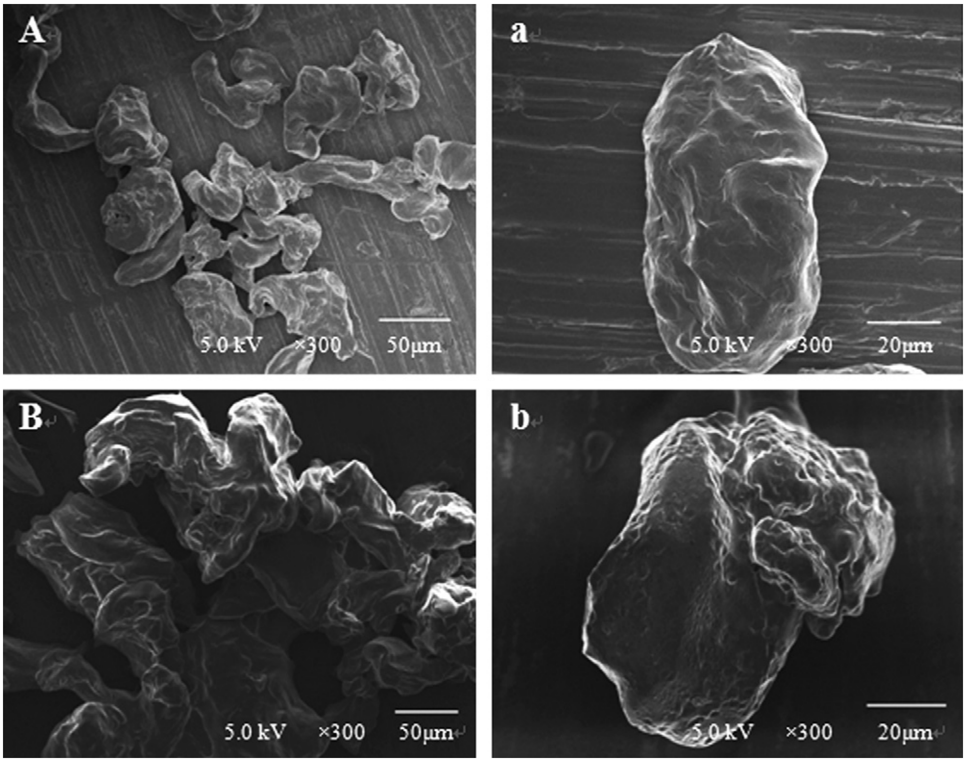

Fig. 2. SEM pictures of GG (A) and CMGG (B, DS = 0.670) and pictures of individual granules of GG (a) and CMGG (b, DS = 0.670).

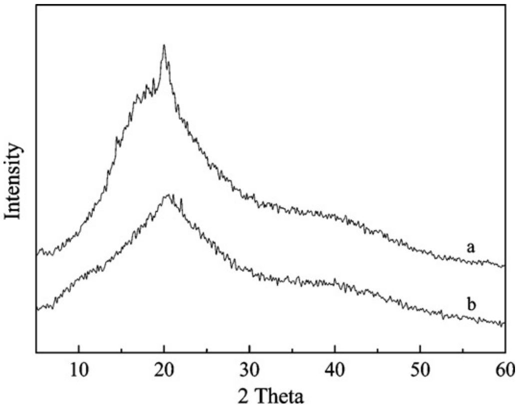

Fig. 3. XRD pattern of GG (a) and a representative CMGG (b, DS = 0.670).

molecules and the bands at 870 and 811 cm^{-1} are due to skeletal stretching vibrations of guar gum. The carboxymethyl guar gum shows new bands at 1618, 1424 and 1325 cm^{-1}. The characteristic peaks at 1618 cm^{-1} correspond to the —COO^{-} asymmetric stretching vibration. 1424 and 1325 cm^{-1} are the —COO^{-} symmetric stretching vibration. The new bands are assigned to carboxymethyl moieties and this indicates that the hydroxyl groups of guar gum molecules were carboxymethylated (Huang et al., 2006).

3.2. SEM

Scanning electron microscopy is used to investigate the granule morphology of the native guar gum and carboxymethyl guar gum (Fig. 2). Fig. 2A reveals that the native guar gum has discrete, elongated, irregular granular structure separated from each other. This observation is consistent with previous report on shape of guar gum (Trivedi, Kalia, Patel, & Trivedi, 2005). As observed, the conditions of modifications significantly alter the granular structure of the carboxymethyl guar gum. The morphology of carboxymethyl guar gum is shown in Fig. 2B, wherein the topology of the carboxymethyl guar gum is changed and some of the granules get attached by adhering themselves. The granules of native guar gum have an irregular but smooth surface and are basically with no defects (Fig. 2a). On the surface of carboxymethyl guar gum granules, there are lots of small alveolate holes, which looked like surface corrosion (Fig. 2b). The alkaline environment during the carboxymethylation process accounts for the structural changes (Wang, Pan, Hu, Miao, & Xu, 2010). Similar observations have been reported for potato carboxymethyl starch in the literature (Bi, Liu, Wu, & Cui, 2008). This result also suggests that guar gum crystallinity was altered and thus allowing the etherifying agents to have more access to the guar gum molecules for the carboxymethylation process.

3.3. XRD

The wide angle X-ray diffractogram of native guar gum and a representative carboxymethyl guar gum is presented in Fig. 3. From Fig. 3a, it is obvious that native guar gum exhibits a very small crystallinity. Similar appearance has been reported for native guar gum in the literature (Pal, Mal, & Singh, 2007). After carboxymethylation, a pronounced reduction in crystallinity is observed (Fig. 3b). This loss in crystallinity could be attributed to the effect of the replacement of the hydroxyl groups by the carboxymethyl groups. Hydrogen bonds maintain the stability of guar gum crystal, when they are broken, it could lead to reducing the crystallinity. This phenomenon corroborates the changes in the granule morphology revealed by the SEM.

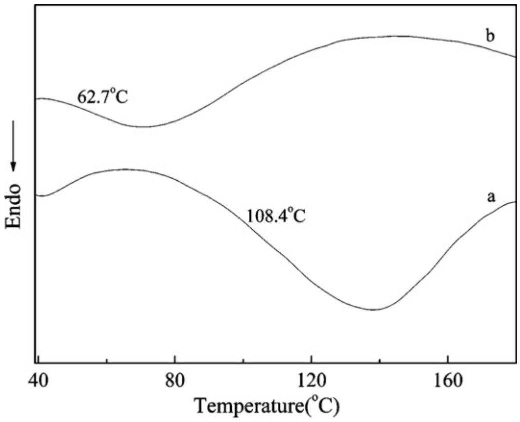

Fig. 4. DSC thermograms of GG (a) and CMGG (b, DS = 0.670).

3.4. DSC

Differential scanning calorimetry analysis is performed in order to understand the thermal behavior of galactomannan and how can it be influenced by polysaccharide structure and it is used for studying thermal transitions occurring in the course of heating under an inert atmosphere. DSC thermograms of native guar gum and carboxymethyl guar gum are presented in Fig. 4. The thermograms of native guar gum and carboxymethyl guar gum show a broad endothermic at 108.4 and 62.7 °C, respectively (Gliko-Kabir, Penhasi, & Rubinstein, 1999; Huang, Lu, & Xiao, 2007). The endothermic peak in the DSC thermograms can be attributable to the glass transition of guar gum and carboxymethyl guar gum. The glass transitions of polysaccharides are very dependent on the thermal history of the material and also on their structural features (Xu et al., 2009). As can be seen from Fig. 4, the glass transition temperature (T_g) of carboxymethyl guar gum is lower than native guar gum, which is attributed to the carboxymethylation process. The intermolecular and intramolecular hydrogen bonds are broken because of the carboxymethylation, which cause the movement of chain segments to become easier and the decrease of T_g. This result is consistent with XRD.

3.5. Effect of reaction parameters on DS value of CMGG

In the reaction of carboxymethyl guar gum synthesis, the main factors affecting the DS value were investigated, which included the molar ratio of NaOH to MAC (n_{NaOH}/n_{MCA}), the volume of 95% C_2H_5OH (V/V), reaction temperature and time of the first step and second step reaction.

The n_{NaOH}/n_{MCA} ratio would influence noticeably the reaction rate and the DS of carboxymethyl guar gum. For a proper comparison, the n_{MCA}/n_{NaOH} ratios were varied with the amount of NaOH at a constant and MCA intake. As shown in Table 1, the influence of various molar ratios of MCA to NaOH on the DS is presented. The DS increases to the maximal value of 0.67 with increment of n_{MCA}/n_{NaOH}. However, the DS decreases when the ratio added more than 0.55. This is because the increasing n_{MCA}/n_{NaOH} ratio would lead to consumption of NaOH, while under the reaction condition, the NaOH dosage is changeless (Gao, Lin, Lin, Ding, Huang, & Wu, 2011). During the carboxymethylation process, the NaOH provides the alkaline environment for the reaction as well as serves as the swelling agent to facilitate diffusion and penetration of the etherifying agent to the guar gum granular structure. The more the MCA is, the less the NaOH can react with guar gum, so higher n_{MCA}/n_{NaOH} ratio led to lower DS (Wang, Gao, & Li, 2009).

The effect of solvent medium on the extent of reaction is related to the miscibility, the ability to solubilized the etherifying agents

Table 1
Reaction conditions used for the carboxymethylation of guar gum.

Sample	$n_{\mathrm{MCA}}/n_{\mathrm{NaOH}}$[a]	$V_{95\%\ \mathrm{EtOH}}$[b]	T_1 (°C)[c]	t_1 (min)[d]	t_2 (min)[d]	T_2 (°C)[c]	DS[e]
CMGG-1	0.40	15	30	40	10	60	0.263
CMGG-2	0.45	15	30	40	10	60	0.483
CMGG-3	0.50	15	30	40	10	60	0.661
CMGG-4	0.55	15	30	40	10	60	0.670
CMGG-5	0.60	15	30	40	10	60	0.630
CMGG-6	0.55	13	30	40	10	60	0.431
CMGG-7	0.55	14	30	40	10	60	0.494
CMGG-8	0.55	16	30	40	10	60	0.439
CMGG-9	0.55	17	30	40	10	60	0.408
CMGG-10	0.55	15	20	40	10	60	0.491
CMGG-11	0.55	15	40	40	10	60	0.459
CMGG-12	0.55	15	50	40	10	60	0.401
CMGG-13	0.55	15	30	30	10	60	0.573
CMGG-14	0.55	15	30	35	10	60	0.483
CMGG-15	0.55	15	30	45	10	60	0.519
CMGG-16	0.55	15	30	50	10	60	0.451
CMGG-17	0.55	15	30	40	2	60	0.396
CMGG-18	0.55	15	30	40	6	60	0.463
CMGG-19	0.55	15	30	40	14	60	0.400
CMGG-20	0.55	15	30	40	18	60	0.392
CMGG-21	0.55	15	30	40	10	45	0.331
CMGG-22	0.55	15	30	40	10	50	0.410
CMGG-23	0.55	15	30	40	10	55	0.421
CMGG-24	0.55	15	30	40	10	65	0.544
CMGG-25	0.55	15	30	40	10	70	0.459

[a] $n_{\mathrm{MCA}}/n_{\mathrm{NaOH}}$ is the molar ratio of NaOH to MAC.
[b] $V_{95\%\ \mathrm{EtOH}}$ is the volume of 95% ethanol.
[c] T_1 and T_2 are the reaction temperature of the first step and second step, respectively.
[d] t_1 and t_2 are the reaction time of the first step and second step, respectively.
[e] DS is the degree of substitution of carboxymethylated guar gum.

and to swell the biopolymer and create an environment that favors carboxymethylation rather than glycolate formation Eq. (3). For dry method reaction, solvent content is a more important parameter than wet method reaction. In this work, 95% ethanol is used as reaction media for the guar gum carboxymethylation process. Table 1 shows that DS increase as the volume of 95% ethanol increased from 12 to 15 mL after that a sharp decline was observed. Diffusion of etherifying reagents and absorption of the reagents are dependent on solvent content. In addition, swelling of guar gum is also dependent on solvent and this would increase the surface area for reaction. These factors are responsible for the initial increase in the DS. But agglomeration occurred at a high solvent content, these phenomena reduced contact of etherifying agent with guar gum molecules, which leaded to the decrease of DS.

Carboxymethylated reaction of guar gum was performed at different temperatures. As shown in Table 1, whether the first step or the second step, it is observed that DS increases prominently as the reaction temperature increases and then decreases. An increase in temperature enhanced solubility of the etherifying agents and it also facilitated both the swelling of the guar gum molecules and the diffusion of the reactants (Lawal, Lechner, & Kulicke, 2008). The proportion of molecules which has higher energy than the activation energy is increased with the temperature rising, consequently the rate of reaction and the DS increase (Wang et al., 2010). However, the DS decreases when the temperature is higher than 30 °C. This is because of the volatilization of reaction medium.

The effect of reaction time of the first and second step on DS was investigated. The DS increases with the increase in reaction time and reaches a maximum and a significant decrease is observed on prolonging the time (Table 1). The enhancement of DS by prolonging the duration of reaction is a direct consequence of the favorable effect of time on swelling of guar gum as well as the diffusion and adsorption of the reactants with the ultimate effect of better contacts between the etherifying agents and guar gum. Similar observations were made earlier by different workers (Goyal, Kumar, & Sharma, 2007; Wang et al., 2010). However, longer time resulted in no further increase in DS. Some researchers speculated that the accessibility of etherifying agents have a maximum value no matter how long it takes (Wang et al., 2010).

3.6. Rheological properties of CMGG solutions

3.6.1. Influence of concentration on rheological properties

We examine the steady shear properties of carboxymethyl guar gum solution at different concentrations. Fig. 5 represents the steady shear viscosity curves measured at different concentrations ranging from 3% to 8% (w/w). Over the rotation rate range investigated, each of the concentrations exhibits shear thinning behavior and the non-Newtonian pseudoplastic behavior becomes more remarkable with the increase of the solution concentration. For dilute solution, the non-Newtonian regime is relatively small when the shear rate increases and is due to alignment and deformation

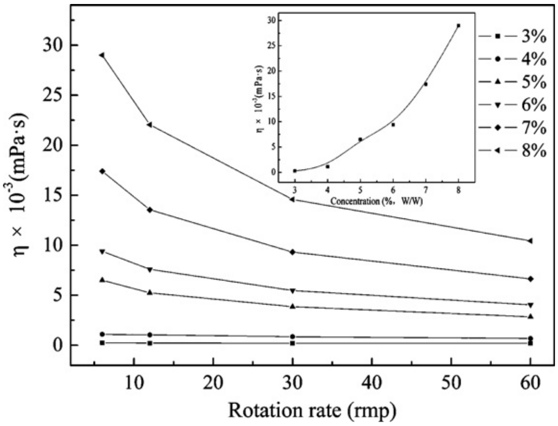

Fig. 5. Flow curves of CMGG polymers aqueous solution as a function of the rotation rate in different concentrations and apparent viscosity as a function of the polymer concentration.

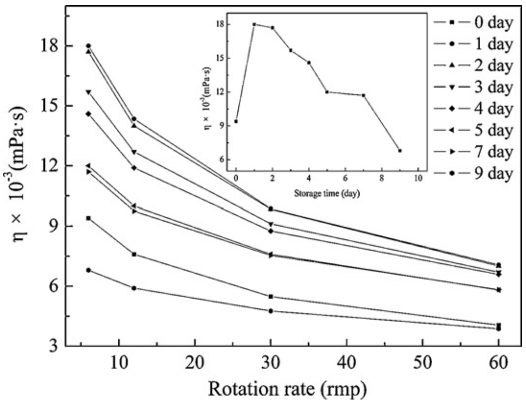

Fig. 6. Steady shear flow curves for aqueous systems of 6% CMGG solution and 25 °C at different storage days and apparent viscosity as a function of the storage time.

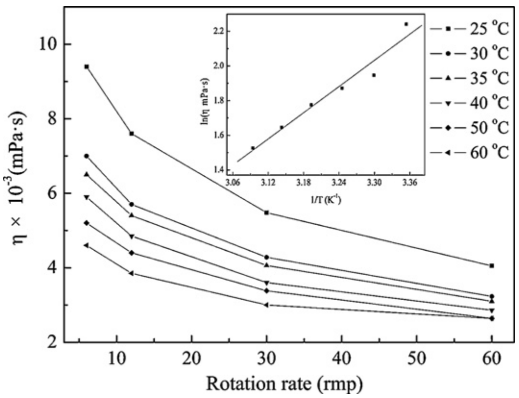

Fig. 7. Effect of rotation rate on apparent viscosity at temperature from 25 to 60 °C for 6% CMGG solutions.

of transiently elongated chains in the flow direction. At low or high shear rates, the disruption of entanglements by the imposed deformation is replaced by new interactions between different partners with no net change in the entanglement density and thus no reduction in the viscosity is observed. This situation corresponds to the horizontal "Newtonian plateau" in viscosity shear rate plots (Chan et al., 2007; Risica et al., 2010; Xiu, Zhou, Zhu, Wang, & Zhang, 2011; Xu et al., 2009). For more concentrated solutions, shear thinning is much more dramatic and arises from an additional mechanism involving entanglements. The shear thinning occurs when the rate of externally imposed movements becomes greater than the rate of formation of new entanglements and thus the cross-link density of the network is depleted and the viscosity consequently reduced (Risica et al., 2010). Looking at the carboxymethyl guar gum solutions (Fig. 5, inset), an appreciable increase in the viscosity of almost two orders of magnitude is observed passing from 3% to 8% polymer concentration. Increasing the polymer concentration leads to not only strengthening the topological constraints posed to each individual chain by the temporary polymer network but also enhancing the role of hydroxyl groups and the resulting hydrogen-bond intermolecular interactions, the viscosity consequently increases (Fijan, Šostar-Turk, & Lapasin, 2007; Nickzare, Zohuriaan-Mehr, Yousefi, & Ershad-Langroudi, 2009).

3.6.2. Stability to storage

Storage time has been considered in rheology studies as an important factor for the evaluation of flow properties and physicochemical stability. The optimum formulation (6%, w/w) was prepared and the properties of solution were evaluated during storage at 25 °C. Solution stability was determined by monitoring changes in viscosity of carboxymethyl guar gum solution with different storage time. Experimental steady shear flow curves are shown in Fig. 6. As can be shown from Fig. 6 that the sample's solution exhibits shear thinning behavior at any storage time and the non-Newtonian pseudoplastic behavior becomes less remarkable with the increasing storage time. The shear thinning behavior is attributed to the orientation of molecules in the direction of flow in the same way. And the reason is same to the above Section 3.6.1. The result also shows increase in the apparent viscosity as the storage time increased one day, and then a decline was observed on increasing the storage time (Fig. 6, inset). Because of the entanglements of molecule chains reaching maximum extent, the apparent viscosity of solution reaches maximum value in one day. Thereafter, the apparent viscosity decreases with the storage time increasing. This behavior can be interpreted by the creation during storage of more persistent entanglements are necessary to align the macromolecules (Chenlo, Moreira, & Silva, 2010) as well as the hydrolysis of glycosidic bonds of sample.

3.6.3. Influence of temperature on rheological properties

The flow behavior of carboxymethyl guar gum solutions has been investigated over the temperature range from 25 to 60 °C at a fixed concentration of 6% (Fig. 7). Fig. 7 shows the temperature dependence of the apparent viscosity for carboxymethyl guar gum sample. The viscosity of carboxymethyl guar gum solution decreased with the temperature increasing at any rotation rate. The reduction of viscosity may originate from changes in solvent power of water for the carboxymethyl guar gum molecules, which results in the chain collapse and a less entangled system. Furthermore, chain conformations due to higher levels of energy available may be changed at higher temperature, so that a less entangled structure is preferred (Farhoosh & Riazi, 2007; Nickzare et al., 2009).

The temperature effect on the viscous flow can be described by the Arrhenius relationship:

$$\eta = \eta_\infty \ \exp\left(\frac{E_a}{RT}\right) \tag{6}$$

where E_a is the activation energy of viscous flow (J/mol) and can be interpreted as the energy barrier that must overcome before an elementary flow process can occur, R is the universal gas constant and T is temperature (K). By rearranging Eq. (6), a $(\ln \eta)$ vs. $(1/T)$ graph can be generated from which the value of E_a can be estimated from the slope of fitting line (Chan et al., 2007; Marcotte, Taherian, Trigui, & Ramaswamy, 2001). The calculated E_a value for the shear flow of 6% carboxymethyl guar gum sample was 20.9 kJ/mol (Fig. 7, inset). As a general rule, the higher the activation energy turns, the more temperature dependent the flow becomes. E_a value of the sample is lower than the other polysaccharide (Chan et al., 2007; Choi & Yoo, 2008), indicating that its viscosity properties are less temperature-dependent.

3.7. Test of printing

The digital photos of printed cellulosic textile are shown in Fig. 8. To determine the effect of different thickeners on the quality of printed textile, the kind and usage of the other textile auxiliary remained unchanged in the process of printing. Obviously, the printing pattern of the paste of CMGG (Fig. 8a) and SA (Fig. 8b) is successive. It illustrates that the paste of CMGG could be used as a thickener in reactive dye printing. The fabric handle achieved using the paste of CMGG is same to SA, which implies that the paste of CMGG is a good alternative of SA used in reactive dye printing. However, compared with paste of SA (Fig. 8b), the color yield of paste of CMGG (Fig. 8a) is worse, which reveals that there is much

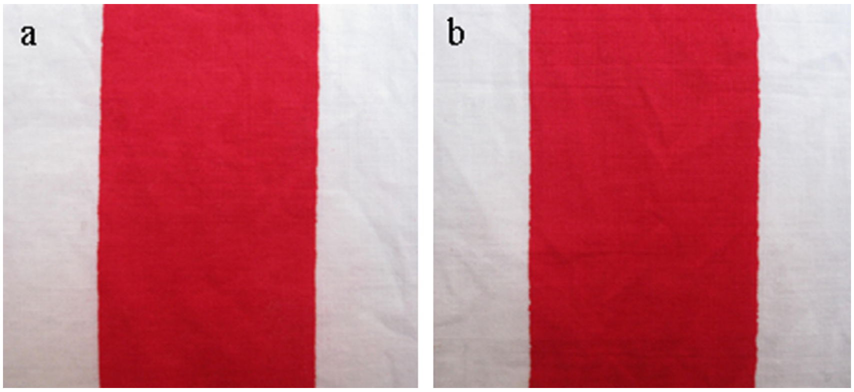

Fig. 8. Digital photos of printed textile (a, CMGG; b, SA).

work to do to improve the printing quality of the mixed paste. And we are still doing the work on this aspect.

4. Conclusions

In this work, we have developed a new way for the chemical modification of guar gum with a clean, cheap and dry method. We expounded on the factors influencing the synthesis such as the ratio of monochloroacetic acid to sodium hydroxide, the volume of 95% ethanol as well as the influence of reaction temperature and time. All these are with a view to optimizing the synthesis conditions for high degree of substitution. Optimal DS of 0.67 was achieved after 10.4 h in 15 mL 95% ethanol when $n_{\mathrm{MCA}}/n_{\mathrm{NaOH}}$ was 0.55 at the reaction temperature of the first and second step was 30 and 60 °C, respectively. According to the measure of sample viscosity, a clearly shear thinning pseudoplastic behavior was observed at all concentrations and temperatures for every sample solutions. Both an increase in concentration and a decrease in temperature were accompanied with an increase in pseudoplasticity. The viscosity of solution increased first and then decreased with the prolongation of storage time. CMGG was used in reactive printing and afforded print of successive printing pattern and good fabric handle. The results illustrated that the paste was a good alternative of SA in reactive dye printing. What's more, the synthesis process of carboxymethyl guar gum in convenient, low cost and eco-friendly, which might be expected to have wide applications in lots of industries.

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