Carbohydrate Polymers 82 (2010) 167–172

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Effect of degree of acetylation on thermoplastic and melt rheological properties of acetylated konjac glucomannan

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ARTICLE INFO

Article history:
Received 5 February 2010
Received in revised form 20 April 2010
Accepted 20 April 2010
Available online 29 April 2010

Keywords:
Konjac glucomannan
Acetylated konjac glucomannan
Thermoplastic
Melt rheological property

ABSTRACT

A series of acetylated konjac glucomannan (AKGM) with different degrees of substitution (DS) were prepared by the reaction of konjac glucomannan (KGM) and acetic anhydride catalyzed with methanesulfonic acid. The degree of acetylation was enhanced with increase of substitution degree (DS), which affected markedly on the thermal stability, thermoplastic and melt rheological properties of AKGM. The thermal stability of KGM and AKGM was increased in the following sequence: AKGM2 (DS 1.25), AKGM1 (DS 0.37), KGM and AKGM3 (DS 2.48) and the AKGM3 with the highest DS had the best thermal stability. Only the AKGM with DS more than 1.25 possessed thermoplastic property and could melt before thermal decomposition. The melt rheological properties of AKGM2 and AKGM3 were influenced by temperature and frequency. The melt fluidness of AKGM3 was better than AKGM2, and the processing flow of AKGM3 can be adjusted by regulating the temperature.

1. Introduction

Konjac glucomannan (KGM) is one of the richest natural polysaccharide isolated from the tubers of *Amorphophallus konjac* C. Koch (Nishinari, 2000). It consists of D-mannose and D-glucose in a molar ratio of 1.6:1, respectively, with a β-1,4-linkage (Kato & Matsuda, 1969; Maeda, Shimahara, & Sugiyama, 1980). There may be certain short side branches at the C-3 position of the mannoses and acetyl groups randomly present at the C-6 position of a sugar unit. The acetyl groups frequently range from 1 per 9 sugar units to 1 per 20 sugar units (Koroskenyi & Mccarthy, 2001; Smith & Srivastava, 1959). Because of its renewable capabilities, good biocompatibilities and biodegradable activities, KGM is a promising material on the degradable plastics. However, KGM itself is difficult to process by conventional thermoplastic methods, because of the strong interchain interactions which exist due to extensive hydrogen bonding (Vipul, Mihir, Stephen, Jo, & David, 1998). These interactions result in a KGM system absent of thermoplasticity, which typically undergoes thermal decomposition before reaching its glass transition temperature (T_g) and melting temperature (T_m). Therefore, it is worthwhile to develop thermoplastic KGM through physical or chemical modifications.

The thermoplasticity of KGM would be supposed to increase by reducing the hydrogen bonding. Chemical modifications of KGM including esterification, etherification and graft copolymerization, are efficacious methods to reduce the hydrogen bonding and improve the properties of KGM (Matsuda, 1987). We have recently reported that thermoplastic KGM (TKGM) was synthesized by graft copolymerization of vinyl acetate and methyl acrylate onto KGM (Luo, Liu, Zhang, & Lin, 2009; Xu, Luo, Lin, Zhuo, & Liang, 2009), and the etherified KGM (EKGM) was synthesized with KGM and 1-bromopropane in lithium chloride/dimethyl sulfoxide (LiCl/DMSO) (Wu, Lin, Luo, & Chen, 2009). They showed T_g around 26.6 and 18.8 °C, respectively. Lu and Zhang (2002) and Lu, Zhang, and Xiao (2004) reported that the benzyl konjac glucomannan (B-KGM) were prepared by the reaction of KGM with benzyl chloride in the presence of odium hydroxide, and showed T_g around 124 °C. Acetylation of KGM can effectively reduce the hydrogen bonding in KGM, so that it is supposed to be one of the efficient methods to improve thermoplasticity of KGM. However, at present, there are no reports available on thermoplastic and melt rheological properties of AKGM. Acetylation of KGM, possessing simply and easily large-scale operation properties, is extensively studied in food processing in regard to gelation and water solubility of acetylated KGM with different degrees of substitution. Gao and Nishinari (2004a, 2004b) synthesized AKGM with low degree of substitution (DS) by using acetic anhydride in the presence of pyridine as catalyst, and investigated the gel rheological properties of low DS AKGM. Balint and Stephen (2001) reported that high DS AKGM was prepared by reaction with acetic anhydride catalyzed with sodium hydroxide, and had good water resistance. Whether degrees of substitution of AKGM affect on thermoplastic and melt rheological properties of AKGM is still little understood.

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doi:10.1016/j.carbpol.2010.04.053

In the present study, a series of AKGM with different DS were synthesized by the reaction of KGM, pretreated by 50% (v/v) ethanol, and acetic anhydride catalyzed with methanesulfonic acid in order to explore influence of substitution degrees of AKGM on thermoplastic and melt rheological properties of AKGM. The thermal properties of AKGM with different DS were investigated by thermogravimetric analyzer (TGA) and differential scanning calorimeter (DSC). Additionally, the melt rheological properties of AKGM were tested by rotary rheometer.

2. Experimental

2.1. Materials

The KGM sample was donated by Mianyang Konjac Co. (Sichuan, China) and used without further purification. All chemical reagents used in the study were of analytical grade and purchased from commercial sources in Mianyang, China.

2.2. Preparation of AKGM

Six grams of KGM was mixed with 60 ml of 50% (v/v) ethanol for 2 h and then filtered. The pretreated sample and a certain amount of glacial acetic acid were added into a round-bottom three-neck flask equipped with a mechanical stirrer. After stirring for 5 min, acetic anhydride was added into the flask and mixed for 5 min. The predetermined amount of methanesulfonic acid used as catalyst was added, and the reaction was controlled at required temperature for 2 h. The reaction was terminated by pouring into distilled water. The precipitate was gathered, washed with excess distilled water to neutral pH, and dried at 50 °C for 24 h (Chi et al., 2008).

2.3. Determination of degree of substitution (DS)

The degree of substitution of modified KGM products was determined by titration according to Chen, Zong, and Li (2006). Acetyl content (ω) was calculated according to the following equation:

$$\omega\% = \frac{(V_2 - V_1) \times N_{\mathrm{HCl}} \times M_{\mathrm{acetyl}}}{m_s} \times 100 \qquad (1)$$

where V_1 is the volume of hydrochloric acid consumed for the sample in liters, V_2 represents the volume of hydrochloric acid consumed for the blank in liters, N_{HCl} stands for the normality of the hydrochloric acid, $M_{\mathrm{acetyl}} = 43$ g/mol and m_s is the mass of the sample in grams.

The DS was calculated as follows:

$$\mathrm{DS} = \frac{162 \times \omega}{4300 - (43 - 1) \times \omega} \qquad (2)$$

2.4. Fourier transform infrared spectroscopy

Fourier transform infrared spectra of dried KGM and AKGM were measured on a Nicolet 6700 FTIR spectrometer in the range of 400–4000 cm^{-1}.

2.5. X-ray diffraction

The X-ray diffraction was obtained from an X'Pert PRO X-ray diffractometer (PANalytical, Holland). The X-ray diffraction patterns with CuKα at 40 kV and 40 mA were recorded from 2θ of 5.00–90.00°.

2.6. Thermogravimetric analysis

Thermogravimetry experiments were performed using a TA Instruments thermogravimetric analyzer (Q500 TGA, USA). The sample weight varied from 5 to 10 mg. Samples were heated from 40 to 600 °C at a heating rate of 10 °C/min. All the TGA scans were carried out under a nitrogen atmosphere.

2.7. Differential scanning calorimetry

Differential scanning calorimetry (DSC) analyses were carried out using a DSC Q200 apparatus of TA Instruments under nitrogen conditions. A sample for DSC was weighed (5–10 mg) on a small aluminum pan, followed by sealing the pan. The heat capacity was scanned from −20 °C to 200 °C at the rate of 10 °C/min, and then the sample was cooled to −20 °C at the rate of 10 °C/min. Subsequently, a second identical heating and cooling cycle was carried out. The glass transition temperature (T_g) was determined as the midpoint of the heat-capacity increase of the second heating process.

2.8. Dynamic rheological measurements

Dynamic rheological measurements were carried out using the HAAKE MARS II rheometer (ThermoHaake, Germany) in dynamic oscillation mode with a parallel plate geometry (20 mm diameter).

In order to determine the linear viscoelastic region of AKGM (DS 2.48, DS 1.25), a dynamic oscillatory test was done in which the applied stress ramped from 0.001 to 1000 Pa at a frequency of 1 Hz. Once the linear viscoelastic region is defined, the dynamic frequency sweeps and the temperature sweeps were performed in the linear viscoelastic region, respectively.

3. Results and discussion

3.1. FTIR analysis of AKGM

In order to synthesize AKGM with high DS by reaction of KGM and acetic anhydride catalyzed with methanesulfonic acid, KGM was pretreated with 50% (v/v) ethanol solution for 2 h before the reaction, so that acetic anhydride can penetrate into the molecular chain of KGM and react completely. Mechanism of the reaction can be represented in Fig. 1.

A series of AKGM with various degrees of substitution (DS 0.37, DS 1.25, DS 2.48) were obtained and coded as AKGM1, AKGM2 and AKGM3. FTIR spectra of AKGM1, AKGM2, AKGM3 and KGM are shown in Fig. 2. The absorption at about 1751 cm^{-1}, which was assigned to the C=O stretching vibration of carbonyl groups, was remarkably increased with an increase of DS values of AKGM. Concomitant with the increase of the carbonyl stretching vibration, the absorptions at about 1243 and 1077 cm^{-1}, assigned to the C–O–C stretching vibration of carbonyl groups, also was increased with an increase of DS values of AKGM. The absorption at about 1371 cm^{-1}, which was assigned to the CH_3 symmetric deformation vibration, was increased with an increase of DS values of AKGM. These results indicated that acetylation of KGM proceeded and degree of acetylation was enhanced with increase of substitution degree.

3.2. X-ray diffraction pattern of AKGM

X-ray diffraction measurements were performed to check if chemical modification altered the aggregation structures of KGM. The X-ray diffraction spectra of AKGM1 (DS 0.37), AKGM2 (DS 1.25), AKGM3 (DS 2.48) and KGM are presented in Fig. 3.

The XRD pattern of KGM showed a diffusion peak at about 2θ of around 20.5°, and several weak peaks appeared at 11.6° and 36.3° (Lu, Wang, & Xiao, 2008). The pattern of AKGM showed a diffusion peak at about 2θ of around 20.5° and 9.7°, respectively. Comparing the patterns of AKGM1, AKGM2 and AKGM3 to that of KGM, it was obvious that the diffraction peak at about 9.7° became stronger with an increase of DS values of AKGM. The X-ray diffraction indicated

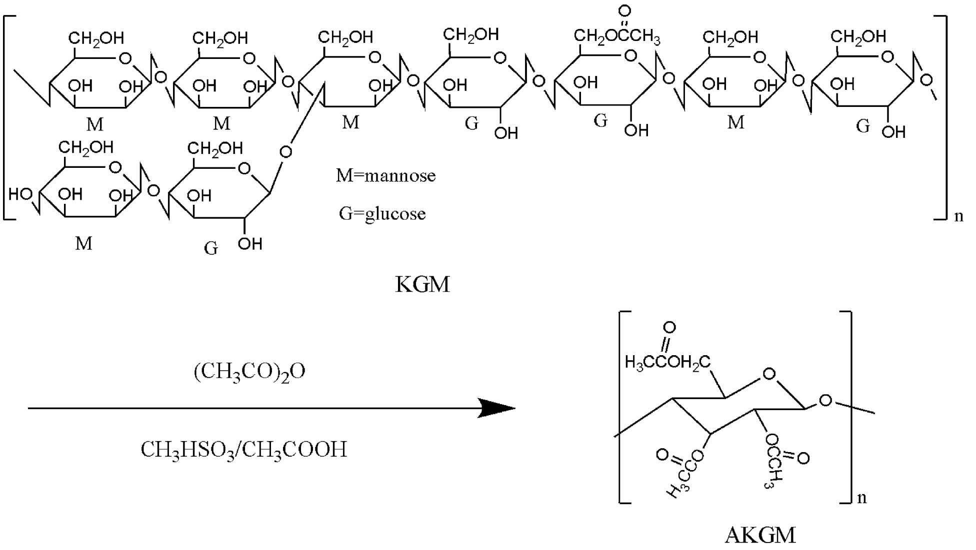

Fig. 1. Scheme for reaction of KGM with acetic anhydride.

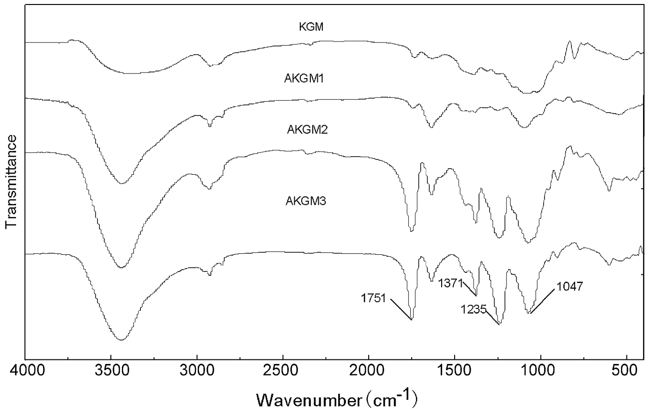

Fig. 2. FTIR spectra of AKGM1 (DS 0.37), AKGM2 (DS 1.25), AKGM3 (DS 2.48) and KGM.

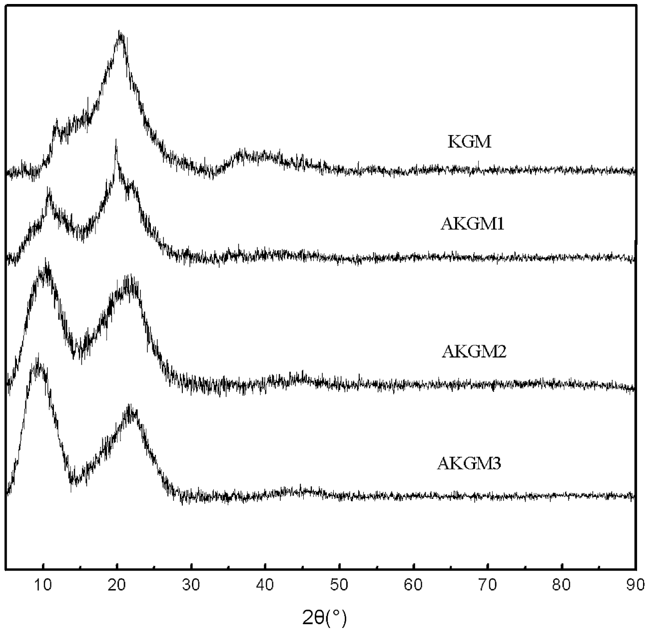

Fig. 3. XRD curves of AKGM1 (DS 0.37), AKGM2 (DS 1.25), AKGM3 (DS 2.48) and KGM.

that with acetylation processing, the aggregation structures of KGM were modified, and the hydrogen bonding of KGM was weakened.

3.3. Thermogravimetric analysis of AKGM

Thermogravimetric analysis (TGA) has been widely used for many years for evaluation of thermal stability of materials, and is one of the main methods which evaluate the thermal properties of materials. The thermal decomposition behavior under a nitrogen atmosphere of AKGM1, AKGM2, AKGM3 and KGM is illustrated in Fig. 4. According to TGA curve of KGM, there were two stages of weight loss. The first one (4.4%) occurred in the range of 40–125 °C probably coming from the loss of moisture, which was due to extensive hydrogen bonding in KGM. The subsequent one stage of weight loss was 61.0%, and occurred in temperature range of 220–422 °C. For the AKGM, AKGM1 (DS 0.37) and AKGM2 (DS 1.25) showed weight loss in two stages. The two stages of AKGM1 (DS 0.37) was 1.3% and 64.9%, and occurred in the temperature range of 50–102 and 182–376 °C, respectively. The two stages of AKGM2 (DS 1.25) was 0.78% and 74.9%, and occurred in the temperature range of 35–82 and 181–372 °C, respectively. AKGM3 (DS 2.48) showed only one stage of weight loss about 83.3% in

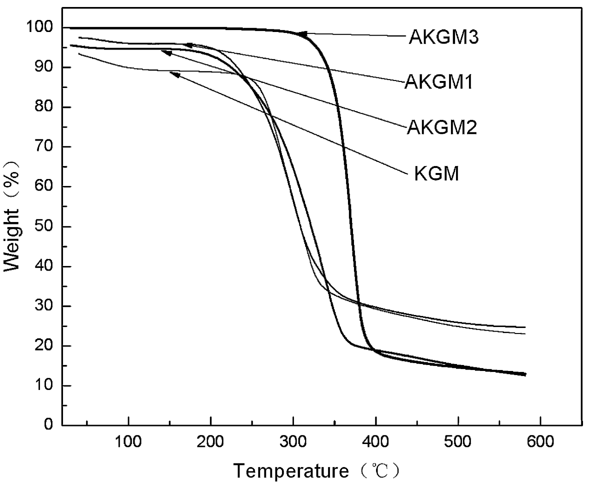

Fig. 4. TGA curves of AKGM1 (DS 0.37), AKGM2 (DS 1.25), AKGM3 (DS 2.48) and KGM. The heating rate was 10 °C/min.

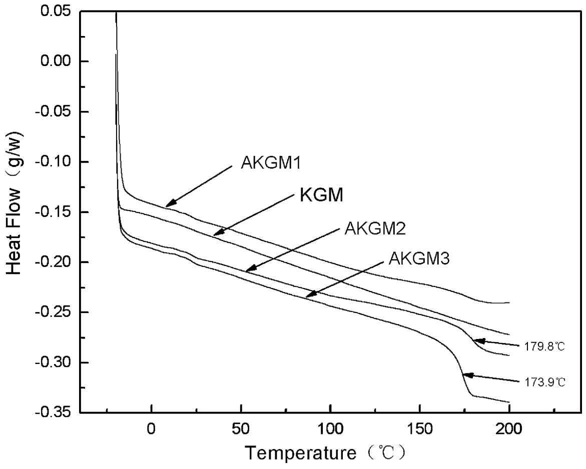

Fig. 5. DSC thermograms of AKGM1 (DS 0.37), AKGM2 (DS 1.25), AKGM3 (DS 2.48) and KGM; the second heating process is presented. The heating rate was 10 °C/min; arrows indicate glass transition points.

temperature range of 276–442 °C. Thermal stability of KGM and AKGM is estimated by onset decomposition temperature or weight loss in similar temperature range of TGA curves of KGM and AKGM. The onset decomposition temperature of 220 °C of KGM was higher than those of 182 °C of AKGM1 and 181 °C of AKGM2, but lower than that of 276 °C of AKGM3. The onset decomposition temperature of 181 °C for AKGM2 was almost the same as 182 °C for AKGM1, but weight loss of 74.9% for AKGM2 was greater than 64.9% for AKGM1 in similar temperature range. Compared with the KGM and AKGM, the onset decomposition temperature of AKGM3 was 56, 94 and 95 °C higher than those of the KGM, AKGM1 and AKGM2, respectively. Therefore, the AKGM3 (DS 2.48) with the highest DS had the best thermal stability. The thermal stability of KGM and AKGM was increased in the following sequence: AKGM2, AKGM1, KGM and AKGM3.

3.4. *Differential scanning calorimetry analysis of AKGM*

The glass transition temperature (T_g) of a polymer is a very important parameter for material applications and engineering design and processing, and is determined by factors such as chain structure and conformation, intermolecular interactions, the efficiency of molecular packing in the amorphous state and by the degree of crystallinity (Zilberman, Siegmann, & Narkist, 1995; Zhou & James, 1999). Fig. 5 shows DSC thermograms of AKGM1, AKGM2, AKGM3 and KGM. KGM and AKGM1 (DS 0.37) did not exhibit any transition until 200 °C, whereas AKGM2 (DS 1.25) and AKGM3 (DS 2.48) had different glass transition temperatures (T_g) at 179.8 and 173.9 °C, respectively. The T_g of AKGM was slightly decreased with an increase of DS. It may be because the interchain interactions, which exist due to extensive hydrogen bonding, were weakened with acetylation processing. These results suggested that AKGM with DS more than 1.25 (DS 1.25, DS 2.48) had a thermoplastic property and could melt before thermal decomposition.

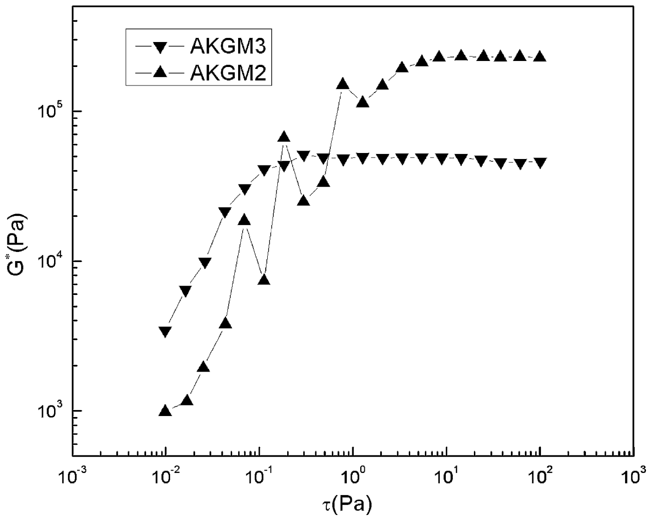

Fig. 6. Complex modulus G^* as a function of stress for AKGM2 (DS 1.25) and AKGM3 (DS 2.48) melts at 210 °C (f = 1 Hz).

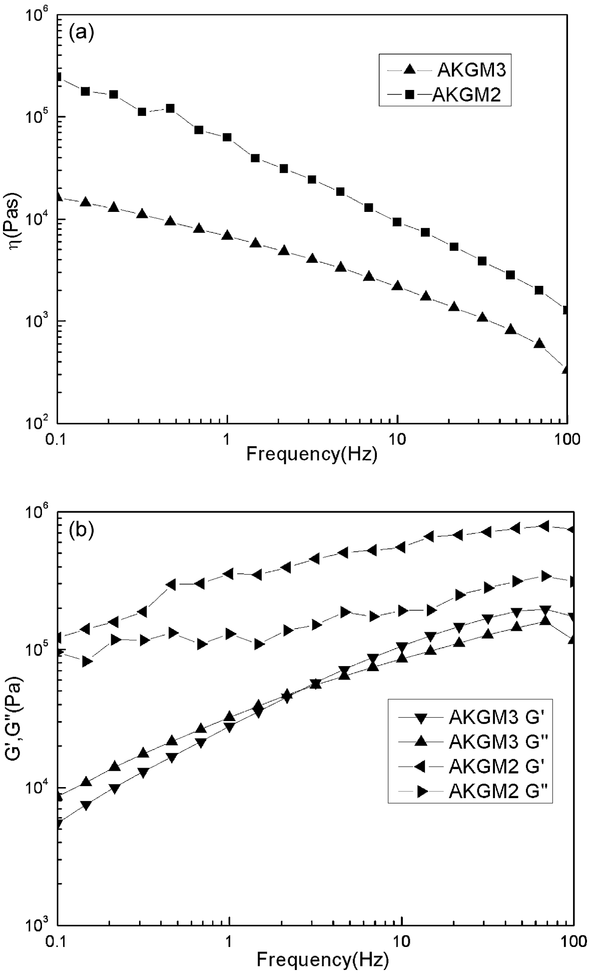

Fig. 7. Shear viscosity η, storage modulus G', and loss modulus G'' as a function of frequency for AKGM2 (DS 1.25) and AKGM3 (DS 2.48) melts at 210 °C.

3.5. *Dynamic rheological analysis of AKGM*

In the injection, extrusion and other molding process, the melt rheological properties of polymer are important parameters for selecting process equipment and determining the process conditions. Before reaching their glass transition temperatures and melting temperatures, KGM and AKGM1 (DS 0.37) undergoes thermal decomposition, and cannot form the melts. Therefore, only melt rheological properties of AKGM2 (DS 1.25) and AKGM3 (DS 2.48) were investigated using a rotary rheometer.

3.5.1. *Determination of the linear viscoelastic regime*

Before determination of dynamic rheological properties, the linear viscoelastic regime must be determined. In the linear

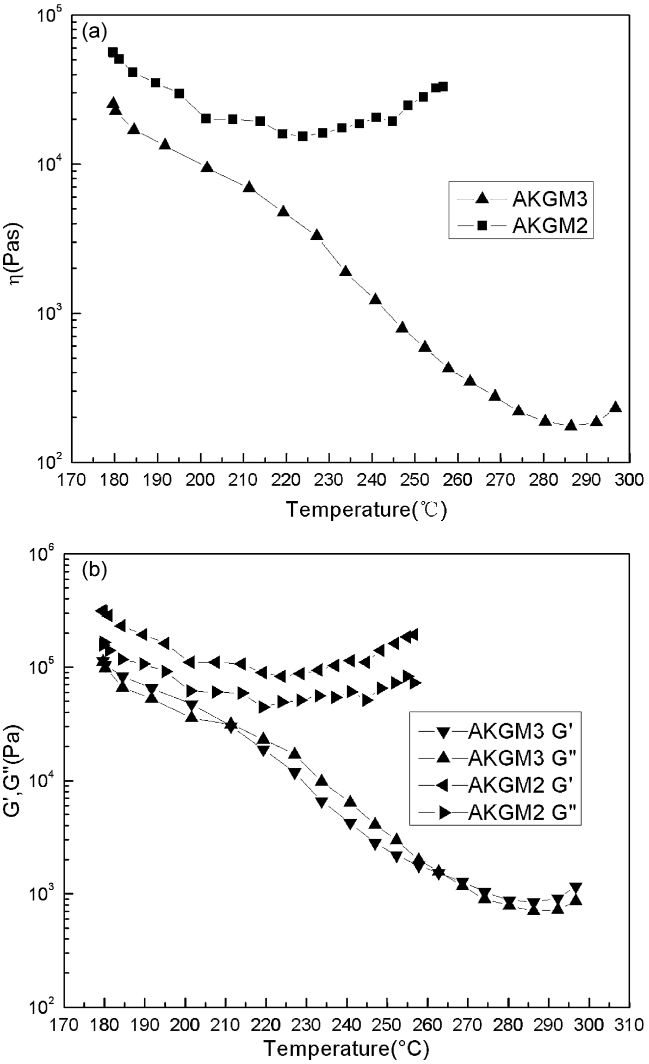

Fig. 8. Shear viscosity η, storage modulus G', and loss modulus G'' as a function of temperature for AKGM2 (DS 1.25) and AKGM3 (DS 2.48) melts at 1 Hz.

viscoelastic regime, the complex modulus G^* ($G^* = G' + iG''$) does not changed with the oscillatory stress or strain (Sundaram & Mehmet, 2000). A dynamic stress sweep carried out at a frequency of 1 Hz was shown in Fig. 6. It could be observed that the complex modulus G^* of AKGM2 (DS 1.25) and AKGM3 (DS 2.48) was constant in the range of stress 12–100 and 0.81–100 Pa, respectively, which were included in the linear viscoelastic regime. Therefore, all experimental results were obtained under applied stresses of 30 Pa.

3.5.2. *Effect of frequency on the rheological properties*

The shear viscosities for AKGM2 (DS 1.25) and AKGM3 (DS 2.48) at different frequencies are shown in Fig. 7a. The shear viscosities decreased with the increase of frequency, indicating a non-Newtonian behavior and pseudoplastic characteristics of AKGM2 (DS 1.25) and AKGM3 (DS 2.48). The shear thinning behavior may be attributed to the orientation of the rigid molecular chains which disturbed the formation chain entanglements of AKGM during the applied shear force and the shear viscosities of AKGM3 (DS 2.48) were always smaller than the AKGM2 (DS 1.25), indicating that the fluidness of AKGM3 (DS 2.48) had better than AKGM2 (DS 1.25).

The shear deformation of materials was characterized by the shear modulus, which was calculated by the ratio of stress and strain. If the shear modulus was greater, the deformation was more difficult. The storage modulus G' and loss modulus G'' for AKGM2 (DS 1.25) and AKGM3 (DS 2.48) at different frequencies were presented in Fig. 7b. It was apparent that the modulus (G', $''$) of AKGM2 (DS 1.25) were always greater than AKGM3 (DS 2.48). This showed that the shear deformation of AKGM2 (DS 1.25) was more difficult than AKGM3 (DS 2.48).

3.5.3. *Effect of temperature on the rheological properties*

To determine the effect of temperature on the viscosities of AKGM2 (DS 1.25) and AKGM3 (DS 2.48), dynamic temperature ramp tests were performed. The shear viscosities for AKGM2 (DS 1.25) and AKGM3 (DS 2.48) at different temperatures are shown in Fig. 8a. It can be observed that the shear viscosities of AKGM2 (DS 1.25) and AKGM3 (DS 2.48) remarkably decreased with the increase of temperature. This may be because the activity of molecular chain of AKGM2 (DS 1.25) and AKGM3 (DS 2.48) was increased with the increase of temperature. The melt shear viscosity η of AKGM3 was very sensitive to temperature, indicating that processing flow of AKGM3 can be adjusted by regulating the temperature.

The storage modulus G' and loss modulus G'' for AKGM2 (DS 1.25) and AKGM3 (DS 2.48) at different temperatures are shown in Fig. 8b. It can be observed that the modulus (G', G'') of AKGM2 (DS 1.25) was always greater than AKGM3 (DS 2.48). It may be attributed that hydrogen bonding of AKGM2 (DS 1.25) was stronger than AKGM3 (DS 2.48).

4. Conclusions

A series of acetylated konjac glucomannan (AKGM) with different degrees of substitution (DS) were synthesized. The structure and properties of AKGM and KGM were characterized by FTIR, XRD, TGA, DSC and rotary rheometer. The results showed that the degree of acetylation of KGM, namely substitution degree (DS), had an obvious influence on the aggregation structure, thermal stability, thermoplastic and melt rheological properties of acetylated konjac glucomannan. The diffraction peak of AKGM at about 9.7° became stronger with increasing DS. The thermal stability of KGM and AKGM was increased in the following sequence: AKGM2 (DS 1.25), AKGM1 (DS 0.37), KGM and AKGM3 (DS 2.48) and the AKGM3 with the highest DS had the best thermal stability. Only the AKGM with DS more than 1.25 had a clear glass transition temperature and possessed thermoplastic property and could melt before thermal decomposition. The melt rheological properties of AKGM2 and AKGM3 were affected by temperature and frequency. The melt fluidness of AKGM3 was better than AKGM2, and the processing flow of AKGM3 could be adjusted by regulating the temperature. The AKGM3 is a promising natural polymer, which can be molded by melt-processing or casting method.

Acknowledgements

This research was supported by the Nature Science Foundation of China (Grant No. 29876017) and National Key Technology R&D Program of China (No. 2007BAB18B08). Experiments were conducted at Sichuan Provincial Engineering Research Center for Biomass-modified materials.

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