SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF ACETYLATED GUAR GUM

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This research aimed to acetylate guar gum (GG) in granular form in order to improve its hydrophobicity. Acetylated guar gum (AGG) was synthesized using acetic anhydride as acetylating reagent and pyridine as solvent to obtain better property combination. By polarized light microscopy, infrared spectrometry, differential scanning calorimetry and thermogravimetric analyses, the appearance, structure and thermal properties of AGG were observed, characterized and measured, respectively. The most suitable process conditions for preparing AGG were found to be: reaction time of 3 h, reaction temperature of 90 °C and amount of pyridine of 50%. The acetylation reduced the freeze-thaw stability and the swelling power of GG, but increased its retrogradation and cold and hot viscosity stability. The appearance of GG was not changed by the acetylation. The acetylation was able to increase the onset decomposition temperature, peak temperature, final decomposition temperature and melting enthalpy of guar gum, but lowered the thermal stability of guar gum.

Keywords: guar gum, acetylation, acetic anhydride, synthesis, property

INTRODUCTION

Guar gum (GG) is extracted from the endosperm of *Cyamopsis tetragonalobusa*, a non-ionic hydrophilic polygalactomannan, with the ratio of galactose to mannose of approximately 1:2, in which the galactose units are randomly distributed on the polymannose backbone.[1] GG and its derivatives have been used in many fields, such as textiles, paper, explosives, pharmaceuticals, hydraulic fracturing, mining and cosmetics, owing to their environmental benefit, unique molecular structure, natural characteristics and the ability to produce highly viscous, pseudoplastic aqueous solutions even at the low concentrations.[2-8] One of the advantageous properties of GG is that it thickens spontaneously without the application of heating. Water suspensions of GG exhibit non-Newtonian viscosity. However, in practical application of guar gum, it is difficult to achieve satisfactory results because of shortcomings such as slow dissolution rate, high water insoluble content, difficult to control viscosity and susceptibility to microbial contamination. As a result, this urged researchers to seek ways to improve its performance. At present, guar gum is mainly modified by etherification, esterification, oxidation, cross-linking, enzymatic hydrolysis in order to improve its performance.[9-11] Among the various chemical modifications, the acetylation of guar gum is an outstanding modification method. The introduction of acetyl groups reduces the bond strength between guar gum molecules and thereby alters the properties. Guar gum is acetylated by acetic acid, acetic anhydride, ketene, vinyl acetate, or a combination of these reagents. Acetic anhydride is commonly used as an acetylating reagent. Acetylated guar gum is more hydrophobic than native guar gum, and acetylated guar gum (AGG) with a low degree of substitution (DS) may be used for food, biomaterials, waste water treatment and papermaking due to its important characteristics. However, only little information is available about acetylated guar gum. Therefore, this study

investigated first the influence of selected reaction conditions on the acetylation extent of guar gum, and then the effects of acetylation on the functional properties of guar gum, thus exploring the use of AGG as an eco-friendly, renewable additive in the industry.

EXPERIMENTAL

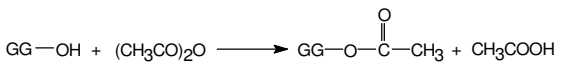
Materials

Guar gum was purchased from Binzhou Zhongbo Chemical Co., Ltd. Sodium hydroxide and ethanol were purchased from Shenyang Xinhua Reagent Factory. Acetic anhydride was purchased from Tianjin Chemical Reagent One Factory. Hydrochloric acid was purchased from Shenyang Paier Fine Chemical Factory. Pyridine was purchased from Tianjin Ruijinte Chemicals Co. Ltd. All above reagents were of analytical grade.

Methods

Acetylation of guar gum (AGG)

An amount of 16.8 g of guar gum powder (water content 11.0%) was weighed, and put into a 250 mL three-necked flask. First, a quantity of pyridine (the percentage mass ratio of pyridine to slurry was maintained similar hereinafter) was added. Second, a quantity of water was also added into the mixture in order to produce a suspension with a mass concentration of 25%. The obtained suspension was stirred and heated in a water bath to the required temperature. Then the required amount of acetic anhydride (the percentage mass ratio of acetic anhydride to dry guar gum was maintained similar hereinafter) was added dropwise into the suspension within 20 minutes. The reaction was carried out for a certain time. After the reaction was ended, vacuum filtration of the slurry was conducted. The obtained filtered cake was washed with ethanol aqueous solutions with a mass concentration of 95% until the pH of the washing liquid was within 6.5-7.0. The resultant cake was dried at 100 °C for about 2 h in a 1010-2 electrothermal constant-temperature dry box (Jintan City Dadi Automation Instrument Factory), to a moisture content could be less than 12%. The dried cake was ground and screened. Finally, acetylated guar gum was obtained.[12] The reaction formula of guar gum with acetic anhydride was as follows:



Acetyl content

An amount of 2 g of AGG sample was weighed, transferred to a 250 mL conical flask and dispersed in 50 mL of distilled water. A few drops of phenolphthalein as indicator were added and titrated with 0.1 mol/L sodium hydroxide to a permanent pink color. Then, 25.0 mL of 0.2520 mol/L NaOH was added into the mixture. The conical flask was plugged by a stopper, and shaken vigorously for half an hour. The stopper and the neck of the flask were flushed with a little distilled water and then the excess alkali was titrated with 0.1541 mol/L HCl to the disappearance of the pink color. A total of 25.0 mL of 0.2520 mol/L NaOH was titrated as blank. The acetyl content and the degree of substitution were calculated as follows:[13-14]

$$W_{AC} = \frac{(V_2 - V_1) \times C_{HCl} \times 0.043 \times 100}{m \times (1 - H)} \quad (1)$$

$$DS = \frac{162 \times W_{AC}}{4300 - 42W_{AC}} \quad (2)$$

where W_{AC} is the acetyl content (%), V_2 is the volume of 0.1541 mol/L HCl used to titrate the blank (mL), V_1 is the volume of 0.1541 mol/L HCl used to titrate the samples (mL), C_{HCl} is the concentration of HCl, m is the mass of the samples (g), H is the moisture content.

Freeze-thaw stability

A paste was prepared by mixing 4 g of dry guar gum or acetylated guar gum with 100 g distilled water. The paste was heated in the water bath to 95 °C until it became uniform, and then cooled to the ambient temperature. 10 g of the paste precisely weighed was added into each of the pre-weighed 10 mL centrifuge tubes, and these paste samples were frozen at -18 °C in a freezer for 24 h. All tubes were removed from the freezer and thawed at 30 °C in the water bath for 2 h. After the above freeze-thaw procedure was repeated for five times, three tubes from each thawing of these samples were centrifuged by a TDL80-2B desk centrifuge (Shanghai Anting Scientific Instrument Factory, China) at 3000 r/min for 15 min. The clear liquid was decanted, and the residue was weighed. The separated water percentage was then calculated as the ratio of the mass of the decanted liquid to the total mass of the paste before centrifugation and multiplied by 100. The low separated water percentage means high freeze-thaw stability.[15-16]

Solubility and swelling power

An amount of 0.1 g of dry sample weighed precisely was added in a pre-weighed 25 mL centrifugal tube, and 19.9 g of distilled water was then added. After that, the centrifugal tube was immediately placed in the water bath, whose temperature was controlled at 85 °C, and the tube was continuously shaken for 30 min. The centrifugal tube was then placed on a balance, followed by the addition of distilled water to bring to a total weight of 20 g, and then it was wiped dry. After capping, the centrifugal tube was centrifuged by a TDL80-2B desk centrifuge

(Shanghai Anting Scientific Instrument Factory, China) at 3000 r/min for about 15 min. To measure the solubility, the supernatant from the tube was transferred into an evaporating Petri dish and dried overnight in a 1010-2 electrothermal constant-temperature dry box (Jintan City Dadi Automation Instrument Factory, China) at 105 °C. The dried residue was then cooled in a desiccator and weighed. To measure the swelling power, the residual supernatant was carefully removed and discarded. The bottle with the sediment paste was then weighed to give the weight of the swollen sample granules. The result was expressed by the calculation as:[17-18]

$$\text{swelling power}(\%) = \frac{\text{mass of sediment paste} \times 100}{\text{mass of sample on dry basis} \times (100 - \%\ \text{solubility})} \quad (3)$$

$$\text{solubility}(\%) = \frac{\text{mass of dried residue of supernatant} \times 100}{\text{mass of sample on dry basis}} \quad (4)$$

Stability of hot and cold viscosity

The viscosity was measured by a NDJ-1A rotational viscometer (Shanghai Balance Instrument Factory, China). The cold viscosity and hot viscosity were defined as the viscosity of a sample measured at 50 °C and 95 °C, respectively. The stability of the viscosity was determined by the following formula:

$$\text{Stability of viscosity}(\%) = 100 - \text{FRV} \quad (5)$$

The fluctuation ratio of the viscosity was expressed as:

$$\text{FRV}(\%) = \frac{\max|\eta - \eta'|}{\eta''} \times 100 \quad (6)$$

where FRV is the fluctuation ratio of the viscosity (%), η'' is the viscosity measured by keeping the temperature constant for 1 hour at 95 °C or 50 °C, $\max|\eta - \eta'|$ is the maximum viscosity difference measured by keeping the temperature constant for 60 min, 90 min, 120 min, 150 min, and 180 min at 50 °C or 95 °C, respectively.[19]

Retrogradation

A slurry with the concentration of 0.5% by dry acetylated guar gum or guar gum was produced with distilled water. 50 mL of the slurry was put into a 100 mL beaker and heated in the boiling bath for 10 min; and the volume of the slurry was kept at this level during heating. The paste was cooled to 25 °C. The transparency of the supernatant was measured by a VI-1501 spectrophotometer (Tianjin Gangdong Sci. & Tech. Development CO. LTD, China) at the different standing times. The more transparent the paste was, the stronger the retrogradation of the samples, and vice versa.[20-21]

Infrared spectroscopy

An IR Prestige-21 infrared spectrometer (Shimadzu Corporation, Japan) was used to record the IR spectra within the range of 4000-400 cm^{-1}. The IR spectra were recorded in the solid state using the KB pellet method. The dry sample was blended with KBr in a ratio starch/KBr 1:100. The blend was pressed to obtain a pellet.[22]

Particle morphology

Particle morphology was observed by an XPL-2 transflective polarizing microscope (Nanjing Jiangnan Yongxin Optics Company Limited). About 5 mg of the samples was placed on a clean slide. A few drops of ethanol were added onto the slide. A cover glass was placed on the sample particles, and then moved back and forth until these particles were uniformly dispersed on the slide. The cover glass was then removed. The lighting power of the polarizing microscope was opened. The appropriate magnification was selected, and then the light source was adjusted and focused. The slide with the sample particles was put and moved under the object lens of the polarizing microscope. The appropriate viewing area was selected to observe the size and the shape of the sample particles.[23]

Thermal analysis

The thermal analysis of guar gum and its derivatives was carried out with a TGA Q50 V20.10 Build 36 thermogravimetric analyzer and a DSC Q20 V24.4 Build 116 differential scanning calorimeter (TA Instruments) in a nitrogen atmosphere. To properly characterize the thermal properties of guar gum, guar gum derivatives, the mixture needed to be analyzed in a sealed pan in order to prevent the loss of water from the formulation during heating.

Analysis conditions of DSC: sample mass 4.0-5.0 mg, heating rate 10 °C/min, temperature range 10-200 °C, nitrogen flow 50.0 mL/min.[24]

Analysis conditions of TGA: sample mass 6.0-7.0 mg, heating rate 10 °C/min, temperature range 10-800 °C, nitrogen flow 60.0 mL/min.[25]

Statistical analysis

The data were expressed as means of triplicate determinations. The statistical significance was assessed with the one-way analysis of variance using SPSS 11.5 for Windows. The treatment means were considered to present significant difference at $P \leq 0.05$.

RESULTS AND DISCUSSION

Effect of reaction time on substitution degree of acetylated guar gum

The effect of the reaction time on the substitution degree of acetylated guar gum (AGG) is shown in Figure 1. As may be observed, the degree of substitution of AGG reached 0.049, when the reaction time was 0.5 h. This suggests

that the acetylation of GG was quick. The substitution degree of AGG increased with the increase of the reaction time, when the reaction time was less than 3 h. This increase was nonlinear. However, the substitution degree of AGG decreased with the increase of the reaction time, when the reaction time was more than 3 h. The causes for this could be explained as follows: as the reaction time increased when the reaction time was short, the effective contact between the molecules of GG and the molecules of acetic anhydride also increased. It promoted the esterification reaction, so that the substitution degree of AGG increased. However, the acetic anhydride was gradually depleted, and the numbers of the reactive sites on the guar gum particles reduced as the acetylation reaction proceeded. At this time, the substitution degree of AGG increased slowly. When the reaction time was long, the AGG was deacetylated slightly, owing to the alkalinity of the suspension. As a result, the substitution degree of AGG decreased a little, owing to the above-mentioned causes. Thus, the most suitable reaction time was considered to be 3 h.

Effect of reaction temperature on substitution degree of acetylated guar gum

The effect of the reaction temperature on the substitution degree of AGG is illustrated in Figure 2. The reaction temperature was varied from 70 to 95 °C to examine the temperature effects. From Figure 2, it is clear that the maximum reaction temperature of this system was only 95 °C, because of the azeotrope formation of pyridine with water. When the reaction temperature was less than 90 °C, the substitution degree of AGG increased with increasing the reaction temperature. However, when the reaction temperature was more than 90 °C, the substitution degree of AGG decreased with increasing the reaction temperature. The reason might be explained as follows: when the reaction temperature increased, the thermal motion of acetic anhydride molecules was accelerated, which was in favor of the esterification reaction. However, the elevated temperature resulted in more side reactions of acetic anhydride and large expansion of the guar gum grains. As a result, this influenced the esterification. Therefore, the most suitable reaction temperature was considered to be 90 °C.

Effect of amount of pyridine on substitution degree of acetylated guar gum

The effect of the amount of pyridine on the substitution degree of AGG is shown in Figure 3. The amount of pyridine was varied from 50 to 100% to examine the effects of the amount of pyridine. It may be noted from Figure 3 that the substitution degree of AGG decreased with the increase of the amount of pyridine. The causes for this could be explained as follows. When the amount of pyridine increased, it meant that the water content in this system decreased. However, the low water content was unfavorable to the reaction since the guar gum granules could not swell moderately. When the amount of pyridine was less than 50% in the experiment, it was found that the mixture easily formed into a colloid, owing to the high water content during the esterification.

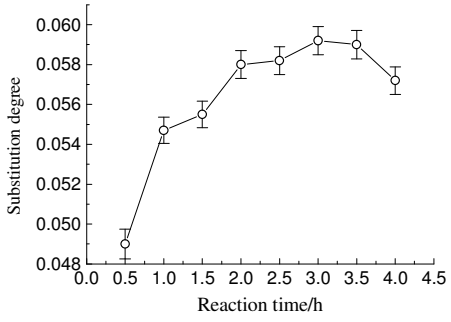


Figure 1: Effect of reaction time on substitution degree of AGG (reaction conditions: reaction temperature 90 °C, amount of pyridine 50%, amount of acetic anhydride 16%)

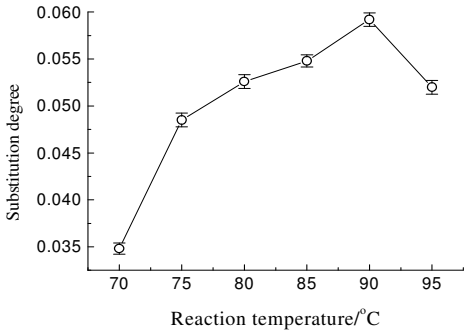


Figure 2: Effect of reaction temperature on substitution degree of AGG (reaction conditions: reaction time 3 h, amount of pyridine 50%, amount of acetic anhydride 16%)

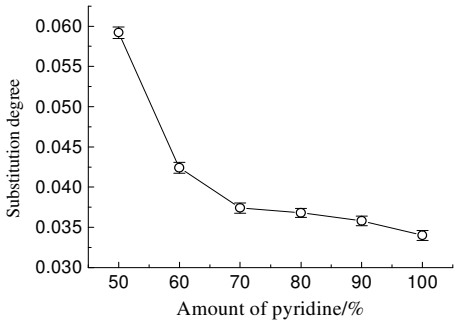


Figure 3: Effect of amount of pyridine on substitution degree of AGG (reaction conditions: reaction time 3 h, reaction temperature 90 °C, amount of acetic anhydride 16%)

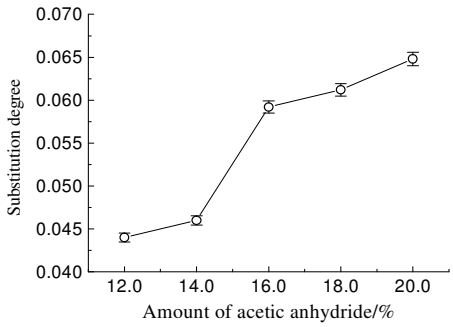


Figure 4: Effect of amount of acetic anhydride on substitution degree of AGG (reaction conditions: reaction time 3 h, reaction temperature 90 °C, amount of pyridine 50%)

Table 1
Analysis of variance

Source	Sum of squares	Degree of freedom	F value	P value
Between groups	0.001	3	5.267	0.007
Within groups	0.001	21		
Total	0.002	24		

Not only it was not conducive to the liquid-solid reaction, but also the formation of the colloid was not helpful to the post-processing of AGG. So, the most suitable amount of pyridine was considered to be 50%.

Effect of amount of acetic anhydride on substitution degree of acetylated guar gum

The effect of the amount of acetic anhydride on the substitution degree of AGG is presented in Figure 4. The amount of acetic anhydride was varied from 12% to 20% to examine the effects of acetic anhydride. From Figure 4, it is clear that the substitution degree of AGG increased with the increase of the amount of acetic anhydride. So, considering the actual needs of AGG, the amount of acetic anhydride was selected to be 16%.

One-way analysis of variance

The one-way analysis of variance was used to assess the statistical significance. The results were presented in Table 1. According to Table 1, the F value was 5.267, which was greater than 1. This suggested that the difference between groups was statistically significant. The P value between groups was 0.007, which was less than 0.05. It indicated that above these factors influencing the substitution degree of AGG were significant terms.

Effect of acetylation on freeze-thaw stability and swelling power

The freeze-thaw stability and the swelling power of GG and AGG are exhibited in Table 2. When the pastes of GG and AGG were frozen, phase separation occurred with the formation of ice crystals. The extent of the phase separation rose with increasing the additional freeze-thaw cycles due to an increase in the retrogradation of GG or AGG in the rich GG or AGG phase. According to the data of Table 2, the acetylation reduced the freeze-thaw stability and swelling power of GG. Also, the freeze-thaw stability and swelling power of AGG decreased as the substitution degree increased. The acetyl groups were in favor of the phase separation of the GG paste after the AGG paste was frozen and then thawed. Meanwhile, the swelling results suggested that the swelling power of GG in aqueous medium was reduced because of the introduction of the hydrophobic acetyl groups.

Effect of acetylation on cold and hot viscosity stability

The cold and hot viscosity stability of GG and AGG is shown in Table 3. After GG was acetylated, the fluctuation ratio of the cold and hot viscosity decreased. The fluctuation ratio of the

hot viscosity was higher than that of the cold viscosity. Also, the fluctuation ratio of the cold and hot viscosity was reduced with increasing the substitution degree of AGG. It was suggested that the cold and hot viscosity stability of GG increased by acetylation.

Effect of acetylation on retrogradation

The retrogradation of GG and AGG is illustrated in Figure 5. The retrogradation took place in the solution of the polymer when the chains were realigned, causing the liquid to turn into gel. The retrogradation could expel water from the polymer network, and was induced by the low temperature and the presence of polar substances, such as salts. On the other hand, the surfactants hindered the retrogradation. Of course, GG susceptibility to retrogradation was also controlled by its molecular weight, concentration, temperature, and the presence of non-guar gum components. As may be seen in Figure 5, the retrogradation of GG was obviously improved by the acetylation modification, namely, the retrogradation was strengthened by the acetylation. In addition, as the substitution degree of AGG increased, the retrogradation increased too.

Infrared spectroscopy analysis

IR spectra of GG and AGG (DS = 0.0598) are shown in Figure 6. The absorption peaks of GG and AGG at the wavenumber 3440 cm^{-1} was attributed to the stretching vibration of the O-H groups. Obviously, the peak intensity of the O-H groups in the IR spectrum of AGG became weaker, compared with that of the O-H groups in the spectrum of GG. It suggested that the numbers of the O-H groups decreased after the GG was acetylated. The absorption peaks of GG and AGG at the wavenumber 2927 cm^{-1} were assigned to the stretching vibration of the C-H bond.

Table 2
Freeze-thaw stability, swelling power of GG and AGG

Samples	Separated water percentage, %	Swelling power, %
GG	86.1	87.5
AGG (DS=0.0352)	91.4	50.2
AGG (DS=0.0598)	92.8	36.9

Table 3
Cold and hot viscosity stability of GG and AGG

Samples	Fluctuation ratio of hot viscosity, %	Fluctuation ratio of cold viscosity, %
GG	37.5	6.4
AGG (DS=0.0352)	30.0	4.7
AGG (DS=0.0598)	11.0	3.2

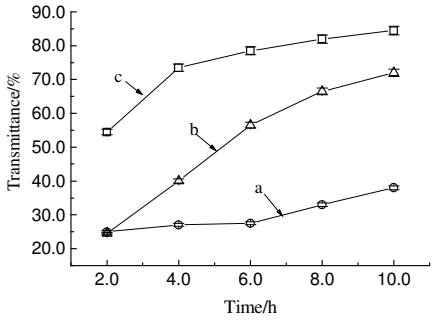


Figure 5: Retrogradation of GG and AGG (a: GG, b: AGG (DS = 0.0352), c: AGG (DS = 0.0598))

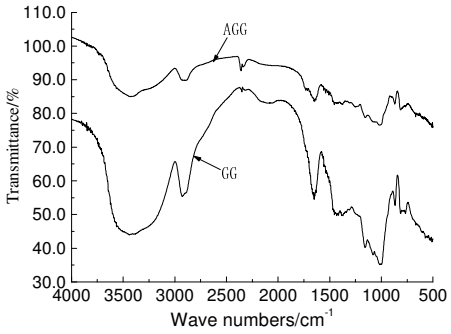


Figure 6: IR spectra of GG and AGG

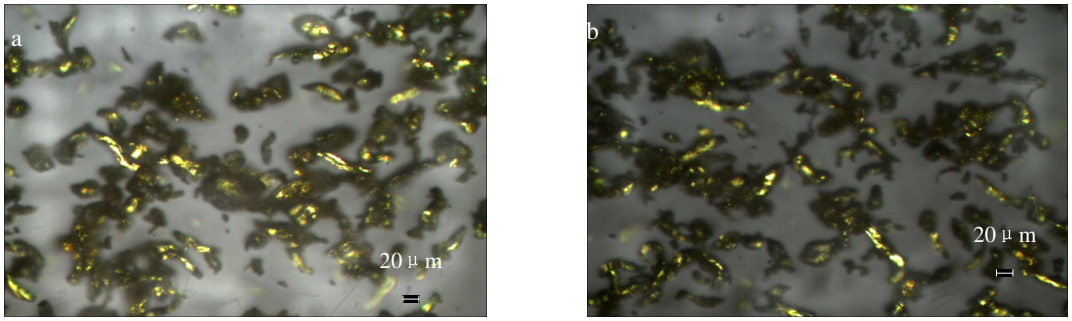


Figure 7: Polarizing microscope images of GG and AGG (a: GG, b: AGG)

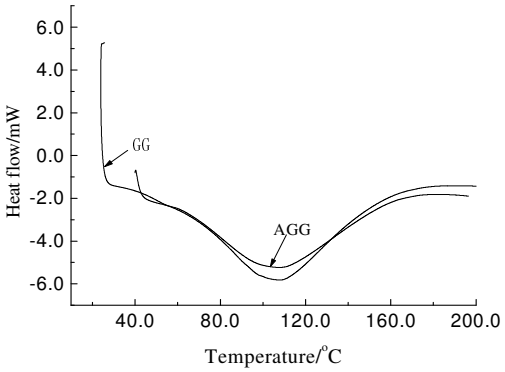


Figure 8: DSC curves of GG and AGG

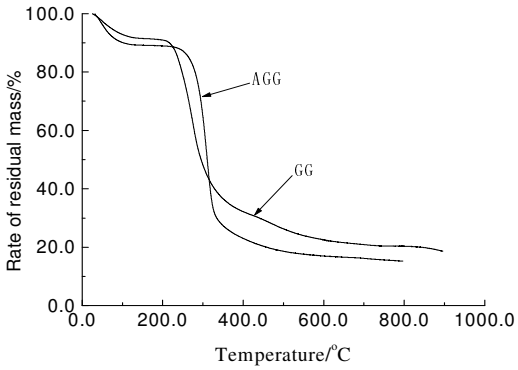


Figure 9: TGA curves of GG and AGG

The absorption peaks at 1642 cm^{-1} in the spectra of GG and AGG were attributed to the H-O-H bending vibration, those at 1010 cm^{-1} to the C-O-C stretching vibration, and those at 1740 cm^{-1} to the characteristic peak of carbonyl groups. This proved that the acetyl groups were introduced into the molecules of GG owing to the acetylation.

Particle morphology

Polarizing microscope images of GG and AGG (DS = 0.0598) are shown in Figure 7. As may be noted, there was no Maltese cross on the surface of the particles of GG, which were very different from the particles of starch. The shape of the GG particles was irregular and thick. According to the images, the appearance and size of GG granules was little influenced by the acetylation.

DSC and TGA analyses

The DSC and TGA curves of GG and AGG (DS = 0.0598) are presented in Figures 8 and 9. After GG was modified by acetylation, its decomposition onset temperature, peak temperature, final temperature, melting enthalpy and thermal stability were all changed. The corresponding thermodynamic parameters calculated from the above-mentioned figures were listed in Tables 4 and 5. The thermogravimetric analysis of GG and AGG essentially revealed two distinct zones of mass loss. The initial mass loss occurred due to the moisture presented in the samples. The second step represented the degradation of the polymer backbone.

Table 4
Decomposition onset temperature, peak temperature, final temperature and melting enthalpy

Samples	Onset temperature, °C	Peak temperature, °C	Final temperature, °C	Melting enthalpy, $J.g^{-1}$
GG	27.89	106.77	163.96	227.6
AGG	44.15	107.94	167.36	290.0

Table 5
Decomposition onset temperature, final decomposition temperature and mass loss rate

Samples	Onset temperature, °C	Final temperature, °C	Mass loss rate, %
GG	227.60	440.35	60.71
AGG	274.90	327.90	69.90

According to the data from Tables 4 and 5, the decomposition onset temperature, peak temperature, and final temperature, as well as the melting enthalpy of AGG, were higher than those of GG, which was due to the acetylation. The acetylation increased the onset decomposition temperature and rate of mass loss within the temperature range. However, the final decomposition temperature was reduced owing to acetylation. The above data proved that the thermal stability of GG was reduced by the acetylation.

CONCLUSION

The acetylation of GG was influenced by the reaction temperature, reaction time, amount of pyridine and acetic anhydride. The maximum reaction temperature of GG with acetic anhydride was 95 °C, because of the azeotrope formation of pyridine with water when pyridine was used as solvent. The most suitable process conditions for preparing AGG were: reaction time = 3 h, reaction temperature = 90 °C and amount of pyridine = 50%. After GG was acetylated by the acetic anhydride, the freeze-thaw stability and swelling power were reduced, but the retrogradation, as well as cold and hot viscosity stability, increased. The IR spectrum of AGG proved that acetyl groups were introduced into the molecules of guar gum owing to the acetylation. The appearance of GG was not changed by the acetylation according to the polarizing microscope images. The acetylation could increase the onset temperature, peak temperature, end temperature and melting enthalpy of GG. The acetylation, however, lowered the thermal stability of GG.

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