Polymer Bulletin 61, 277–285 (2008)
DOI 10.1007/s00289-008-0950-6

Polymer Bulletin

# Synthesis and Flocculation Characteristics of Konjac Glucomannan-g-Polyacrylamide

**Dating Tian**[a, b] (✉), **Hong-Quan Xie**[a]

[a] Department of Chemistry, Huazhong University of Science and Technology, Wuhan 430074, P R China
[b] School of Chemical and Environmental Engineering, Hubei Institute for Nationalities, Enshi 445000, P R China

Received: 20 September 2007 / Revised version: 6 May 2008 / Accepted: 12 May 2008

## Summary

A flocculant was synthesized by graft copolymerization of acrylamide onto konjac glucommannan using potassium permanganate/thiourea redox system as an initiator. The effects of the concentration of monomer, initiator, $H_2SO_4$, as well as reaction time and temperature on the graft copolymerization were studied. The optimum synthesis conditions were: the concentrations of acrylamide, $KMnO_4$ and $H_2SO_4$ were 2.0 mol.$L^{-1}$, 20 mmol.$L^{-1}$ and 3.0 mmol.$L^{-1}$, respectively, and the molar ratio of $KMnO_4$/thiourea was 2/1 at 60 °C for 3 h. Compared with polyacrylamide, the graft copolymer had better flocculating effect on the kaolin suspensions, as well as the local Qinjiang river water and the machine water in paper making.

## Introduction

Polymeric flocculants are extensively used for the treatment of industrial effluents and mineral water. The flocculants based on natural polymer, which are of low cost, pollution-free, biodegradable, and of widespread applicability, have attracted extensive attention in recent years. Currently, researchers are focusing on the development of starch, chitosan, cellulose and other natural materials to obtain the natural polymer flocculants[1-6]. Polyacrylamide is a very efficient flocculent, however, it suffers from poor shear stability. On the other hand, polysaccharides are shear stable but poor flocculants. So graft copolymer between the two makes a match, apart from the biodegradability. Konjac, belonging to the branch of amorphophallus plants, is an abundant renewable resource of natural polymers behind the starch and cellulose. Konjac glucomannan (KGM), the main constituent of konjac, is a kind of compound polysaccharide containing β-D-glucose and β-D- mannose in a molar ratio of approximately 2 : 3 linked by β-1, 4 glycoside. Because its hydrosol has high viscosity and a variety of properties, such as thickening, gelation and film formation, KGM has been extensively applied in medicine, textiles, petroleum chemicals, food and other fields. Generally, KGM and its modified products have been studied by many researchers recently[7-12]. However, although C Xie[7] reported a flocculant from phosphate esterification of KGM recently, there are almost no reports on the preparation of flocculants using KGM as a raw material.This paper deals with the synthesis of the graft copolymer of KGM and AM using a cheap redox system of potassium permanganate/thiourea as initiator, acrylamide as graft monomer, KGM as backbone and the study of its flocculation characteristics in order to obtain a new type of water treatment agent.

## Experimental

### *Materials*

Konjac glucomannan (KGM), supplied by Hubei Hongye Konjac company, China, was purified with ethanol and then dried under reduced pressure until it reached constant weight. Acrylamide (AM), chemically pure, with the number average molecular weight ($M_n$) of $2.5\times10^6$, was recrystallized with benzene before use. Kaolin, industrial product, was provided by Suzhou kaolin production company, China. Other reagents were analytically pure and used as received without further treatment.

### *Graft copolymerization*

To a three-necked flask, equipped with a mixer, a thermometer and a constant pressure separatory funnel, a certain amount of deionized water and a certain mass of KGM were added sequentially and mixed thoroughly. After the mixture was heated to 40 °C so as to make KGM swell enough and then cooled to room temperature, a certain amount of AM was added. Under the $N_2$ atmosphere, a certain amount of potassium permanganate and thiourea (TU) solution with the molar ratio at 2 : 1 was also added to the flask. At an appropriate temperature, $H_2SO_4$ was dropped into the flask through the constant pressure separatory funnel in order to start the reaction. The reaction was carried out for 3 h. After cooled to room temperature, the crude product was precipitated and washed with ethanol and filtered with a Buchner funnel. Then the product was dried in vacuum at 60 °C to constant weight.

### *Evaluation of graft efficiency (GE) and content of PAM in the graft copolymers*

The product obtained was extracted with a mixture of 1, 2-ethylene glycol and acetic acid (volume ratio 60 : 40) in a Soxhlet extractor for 30 h to remove the AM homopolymers. The extract was precipitated with methanol , washed repeatedly with ethanol and then dried in vacuum for 24 h. The residue was weighed accurately to obtain the mass of homopolymers in the graft polymers. The total amount of polyacrylamide (PAM) in the product was determined by the following sequence: 2 g graft polymer were refluxed with 200 mL of 1 mol.L$^{-1}$ $H_2SO_4$ for 2 h to remove KGM, filtered, washed with ethanol, and dried at 60 °C vacuum, followed by weighing accurately. The grafting efficiency (GE) was calculated according to the following equation:

$$\text{GE}=\frac{m_1-m_0}{m_1}\times100\%$$

where $m_0$ is the mass of AM homopolymers in the graft copolymers, $m_1$ the total mass of PAM in the graft copolymers.

The mass percentage of grafted PAM in the graft copolymers was calculated using the following equation:

$$\omega_{PAM}=\frac{m_1-m_0}{m_2}\times 100\%$$

where $m_2$ is the mass of graft copolymers.

### *Number average molecular weight ($M_n$)*

The number average molecular weight ($M_n$) of graft copolymers were determined by gel permeation chromatography (GPC) using Waters GPC 2000 with Sephadex G-100 column and NaCl solution as mobile phase at a flow rate 0.6 $mL.min^{-1}$.

### *FTIR analysis*

FTIR spectra of the samples were taken by Avatar370 of Thermo Nicolet, USA, using KBr disc method.

### *Flocculation testing*

A certain amount of flocculants was added to a 250 mL beaker containing 2% of the kaolin suspensions. After the solution was stirred for 1 min by a mechanical stirrer at a fast speed of 200 $r.min^{-1}$, it was stirred for 2 min at a slow speed of 60 $r.min^{-1}$. The upper clear liquid was taken after standing for 5 min, then its percent transmittance (T%) was measured by a 722 spectrophotometer.

## **Results and discussion**

### **Synthesis of the graft copolymer**

Effects of synthesis conditions such as concentration of monomer, concentration of initiator, acidity and reaction time as well as temperature on the graft copolymerization were shown in Figure 1. Figure 1 (a) indicated the effect of concentration of AM on the graft efficiency (GE). When [AM] was less than 2.0 $mol.L^{-1}$, the GE increased faster with the rising [AM]. However, when [AM] was higher than 2.0 $mol.L^{-1}$, the GE declined slightly. This phenomenon could be interpreted as follows: As the monomer concentration increased, the diffusion of the monomer molecules into the KGM molecules also increased, which led to a higher GE. When the monomer concentration rose to a certain extent, the homopolymerization competing with the graft copolymerization would probably increased, so the GE did not increase any more, and tended to level off or declined slightly.

Figure 1 (a) also showed the effect of amount of $KMnO_4$ on the graft efficiency at the molar ratio of $KMnO_4$ to TU fixed at 2 : 1. Evidently, the GE increased significantly as the $KMnO_4$ concentration increased, but after reaching a maximum, it decreased with further addition of $KMnO_4$. As well known, free radicals occurred as a result of the reaction of $KMnO_4$ with TU. On the one hand, with the increases of initiator concentration, the number of free radicals generated in the system increased greatly, which favored the graft copolymerization and led to an increasing GE. On the other hand, when the initiator concentration was too high, the excess radicals were produced, and the homopolymerization would be initiated directly by those radicals, and thus the GE decreased.

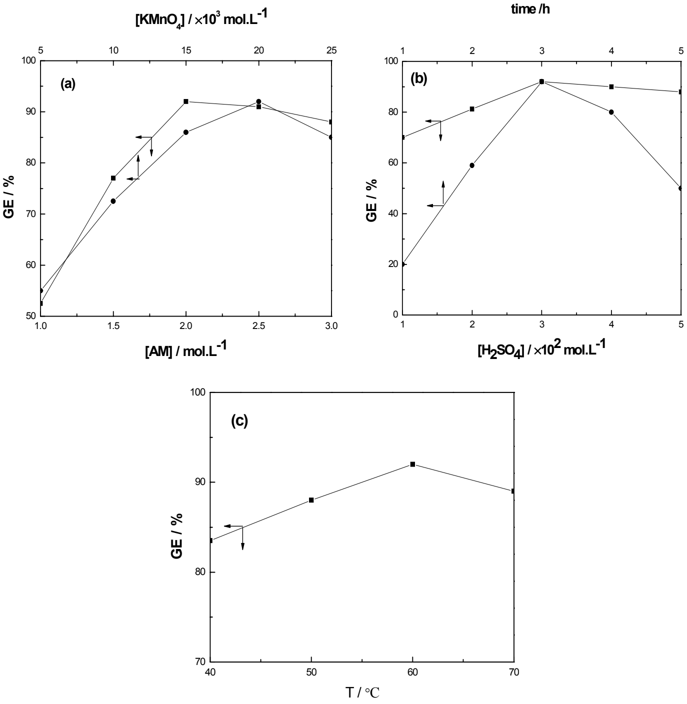

**Figure 1.** Effect of synthesis conditions on the graft efficiency

Figure 1 (b) indicated the effect of acidity on the graft copolymerization. There existed a maximum value of GE with increasing amount of $H_2SO_4$ used in the polymerization. The formation of radicals in this system depends on the [$H^+$] in the solution. At the low acidity, the number of free radicals was relatively small, thereby, the initiation effect was not strong . However, at too high acidity, the acidolysis of KGM and AM might occur in the meantime, which was not favorable to the graft copolymerization, and the GE became less.

The reaction time played a significant role on the GE, as also shown in Figure 1 (b). With the extension of the reaction time, the GE increased significantly and exhibited a maximum value at 3 h. At the initial stage of reaction, the amount of both AM and radicals were high and the rate of graft copolymerization was quick. However, at too longer reaction time, the amount of both AM and radicals decreased, and moreover, side reaction such as the hydrolysis of KGM might occur, which lowered the GE. The appropriate reaction time was 3 h.

Figure 1 (c) showed the effect of reaction temperature on the graft efficiency. It could be seen that the GE increased with increasing reaction temperature and showed a maximum value at 60 °C. This fact could be interpreted as follows: With the increase of the reaction temperature, the formation rate of initiators increased and the concentration of radicals also increased, which accelerated the initiation and propagation of the polymerization. In the meantime, the free volume of KGM increased, which caused the active points to be fully exposed. However, if the temperature is too high, although the chain propagation reaction grew fast, the reaction rate of chain transfer and chain termination increased more quickly, and the homopolymerization rate of AM also rose, thus the GE decreased. Therefore, the optimum reaction temperature was 60 °C.

### *FTIR spectra of KGM-g-AM and KGM*

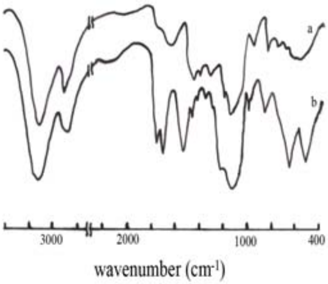

**Figure 2.** FTIR analysis of samples (a, KGM; b, KGM-g-PAM)

Comparing the FTIR spectra of KGM-g-AM and KGM shown in Figure 2, we could see that KGM exhibited a weak absorption peak at 1700 cm$^{-1}$, which came from the small amount of acetyl group in KGM, whereas KGM-g-AM exhibited two strong absorption peaks at 1670 cm$^{-1}$ and 1640 cm$^{-1}$, which were the characteristic absorption peaks of $–CO-NH_2$. The former was stretching vibration peak of –CO, and the latter was the deformation vibration absorption peak of $–NH_2$. Thus the FTIR spectra verified that AM has been grafted onto the KGM.

### *Flocculation Characteristics of the graft copolymer*

### *Effect of amount of flocculants used on the flocculation*

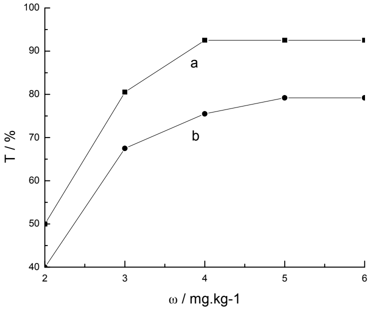

**Figure 3.** Effect of amount of flocculants used on the flocculation (a, KGM-g-PAM; b, PAM)

At room temperature and pH=6, the flocculating effects of KGM-g-PAM and commercial PAM on the high-turbidity water containing kaolin suspensions were shown in Figure 3. The ordinate axis in the Figure 3 indicated the percent transmittance (T%) of the supernatant, where T=0 exhibited that the flocculant had no flocculability and T=100% represented full flocculability. It could be seen from the Figure 3 that the flocculating effects of two kinds of flocculants increased with the increasing of amount of flocculants used. Moreover, the graft copolymer KGM-g-PAM showed better flocculating effect than the commercial PAM. The best dosage of KGM-g-PAM was 4 mg.kg$^{-1}$and that of PAM 5 mg.kg$^{-1}$, respectively.

The explanation of this observation is based on a particle-polymer-particle complex formation in which polymer serves as a bridge[13,14]. When a polymer comes into contact with a colloidal particle, some of its groups adsorb at the particle surface, leaving the remainder of the molecule extending out into the solution. If a second particle with some vacant adsorption sites contacts these extended segments, adsorption can occur, which forms a bridge. When the amount of flocculant was too low, it could not form a bridge between the suspended kaolin particles, therefore the flocculating effect was weak. However, with the increasing dosage of flocculant, the PAM chains of KGM-g-PAM could fully contact and strongly combine with suspended particles in aqueous solution, which made all suspended particulates in water enter into the range of bridging flocculation and settle from aqueous solution. With excess dosage the suspended particulates were occluded and enveloped by PAM chain, and the solution was re-stabilized. Then, bridging flocculation was no longer possible and the flocculating effect decreased[13]. Of course, the viscosity generated at high dosage might also inhibit the sedimentation of flocculated particles[15].

The reason why the flocculation of KGM-g-PAM was better than that of commercial PAM may be explained as follows: For the flocculant KGM-g-PAM, the molecular chain of KGM was semi-rigid. When a flexible graft of PAM was introduced into this framework, then a polymer network with both flexible graft and rigid backbone was formed via hydrogen bonding. Moreover, the comb-like structure of the graft copolymer favored the formation of bridging of particle-polymer-particle in three dimensional. Thus the flocculating effect was improved.

### *Effect of pH on the flocculation*

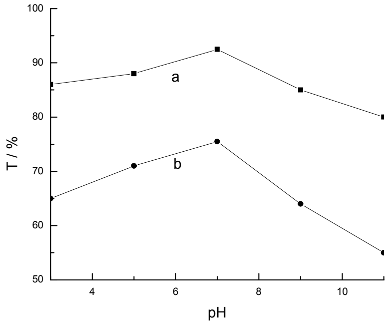

**Figure 4.** Effect of pH on the flocculation (a, KGM-g-PAM, 4 mg.kg$^{-1}$; b, PAM, 5 mg.kg$^{-1}$)

At room temperature, 2% kaolin suspensions with a certain amount of flocculants was formulated, and their pH values were adjusted by either NaOH or HCl. The effects of pH on the flocculating effect of the KGM-g-PAM and PAM with the best dosage of both flocculants were shown in Figure 4. The results showed that the best flocculating effect occurred at the neutral condition. At the acidic condition the rate of settlement decreased gradually, whereas at the alkaline condition, the rate of settlement decreased seriously, which means that the two flocculants are better to be used in the neutral or slightly acidic condition. Moreover, the flocculating effect of KGM-g-PAM was better than that of PAM within the whole range of pH probably due to the non-ionic character of KGM which was not sensitive to pH[13].

*Effect of settling time on the flocculation*

For the optimum dosage of both KGM-g-PAM and commercial PAM, the influence of settling time on the flocculation was investigated, as shown in Figure 5. With increasing settling time, the flocculation increased, and the optimum flocculation time was found at 5 min for both flocculants. If the settling time was longer than 5 min, the flocculation almost did not change any more.

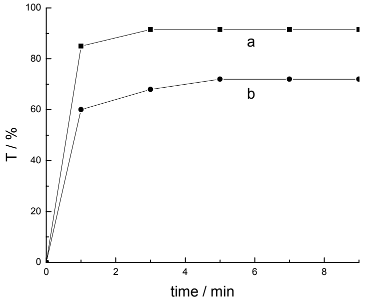

**Figure 5.** Effect of settling time on the flocculating effect (a, KGM-g-PAM, 4 mg.kg$^{-1}$; b, PAM,5 mg.kg$^{-1}$)

*Effect of amount of PAM in the KGM-g-PAM on the flocculating effect*

**Table 1.** Effect of amount of PAM graft in the KGM-g-PAM on the flocculation (KGM-g-PAM dose= 4 mg.kg$^{-1}$)

| $\omega_{PAM}$ / % | Number average molecular weight of the graft copolymer ($M_n \times 10^{-6}$) | T / % |
|---|---|---|
| 20.5 | 1.5 | 83.5 |
| 35.0 | 1.9 | 90.5 |
| 42.5 | 2.3 | 91.5 |
| 50.2 | 2.9 | 88.6 |

Table 1 compared the effect of amount of PAM graft in the KGM-g-PAM on the flocculation efficiency. The results showed that, with the increase of PAM graft in the KGM-g-PAM, the flocculation efficiency of KGM-g-PAM increased gradually with increase of PAM from 20.5 to 42.5 and decreased with further increase. The initial rise in the flocculation efficiency may be due to the rising molecular weight of KGM-g-PAM (as shown in Table 1) or the increasing length of PAM chains on the KGM, which therefore could be easily absorbed on the surface of suspended kaolin particulates and the bridging action between flocculant chains and colloid particles occurred more easily[13,16]. However, an excess of PAM would induce too high a molecular weight of KGM-g-PAM and segmental overlapping of some grafted chains would occur simultaneously, which would weaken the bridging flocculation and impair the flocculation[13].

### *Effect of concentration of NaCl on the flocculation*

Figure 6 showed the effect of salt concentration on the flocculation in the case of the dosage of kaolin fixed at 2%. In comparison with distilled water, the flocculation was significantly enhanced at initial increase of salt concentration, and turned to level off at 10 mmol.L$^{-1}$ of NaCl, and then decreased slightly for further increase of NaCl. Several researchers also observed this phenomenon[1,17]. The initial increase of flocculation might be attributed to the partial neutralization of colloidal particles by Na$^+$ in aqueous solution, which weakened the repulsion of charges at the aggregation of kaolin particles and made the bridging occur more easily. However, at a too high salt concentration, the chain segments of polymers could not easily extend and became curled, which made the bridging fail and thus decreased the flocculation. In all, because the graft copolymer is a kind of nonionic polymer and is not sensitive to electrolyte, it showed a good flocculation within a wide range of salt concentration, which is very useful in the practical application.

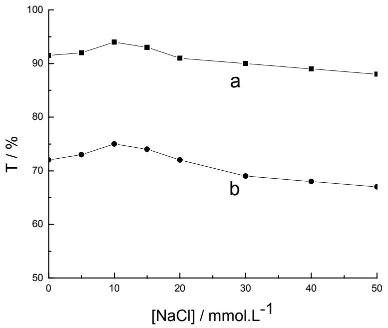

**Figure 6.** Effect of concentration of NaCl on the flocculation (a, KGM-g-PAM, 4 mg.kg$^{-1}$; b, PAM, 5 mg.kg$^{-1}$)

### *The flocculating effect on the local water samples*

The flocculating effects of both KGM-g-PAM and PAM with the best dosage used on the local water samples such as the Qingjiang River and the machine water in paper making were studied, as shown in Table 2. For both the Qingjiang River and the

**Table 2.** The flocculating effect on the local water samples

| Flocculants | $T_1$ / %* | $T_2$ /%* |
|---|---|---|
| KGM -g- PAM | 91.5 | 90.0 |
| PAM | 74.4 | 72.0 |

*$T_1$, the percent transmittance of the Qingjiang river treated by the flocculants; $T_2$, the percent transmittance of the machine water in paper making treated by the flocculants. KGM-g-PAM dose= 4 mg.kg$^{-1}$; PAM dose=5 mg.kg$^{-1}$

machine water in paper making, the flocculating effect of KGM-g-PAM was much better than that of commercial PAM.

## Conclusions

A new kind of flocculant was synthesized by the graft copolymerization of AM onto KGM. The optimum synthesis conditions were: the concentrations of acrylamide, $KMnO_4$ and $H_2SO_4$ were 2.0 $mol.L^{-1}$, 20 $mmol.L^{-1}$and 3.0 $mmol.L^{-1}$, respectively, and the molar ratio of $KMnO_4$/thiourea was 2/1 at 60 °C for 3 h. The effects of amount of flocculants, pH, and temperature on the flocculatiion of both KGM-g-AM and PAM on the kaolin suspensions, as well as those on the local water samples were studied. The results showed that the graft copolymer flocculant had better flocculating effect than the commercial PAM.

*Acknowledgements.* This work was supported by the Scientific Research Funds from Education Committee of Hubei Province, China (Grant No. D200629003) and Hubei Institute for Nationalities, China.

## References

1. Kumar K, Verma M (2007) J Appl Polym Sci 103: 1025
2. Adhikary P, Tiwari KN, Singh RP (2007) J Appl Polym Sci 103: 773
3. Riske F, Schroeder J, Belliveau J, Kang, X, Kutzko J, Menon MK (2007) J Biotechnol 128: 813
4. Anuradha M, Malvika B (2006) Colloid Polym Sci 284:443
5. Krentz DO, Lohmann C, Schwarz S, Bratskaya S, Bert T, Laube J, Heinze T, Kulicke WM (2006) Starch, 58: 166
6. Anuradha M, Rajani S, Malvika B, Rashmi D (2004) Colloid Polym Sci 282:722
7. Xie C, Feng Y, Cao W (2007) Carbohydr Polym 67: 516
8. Lu J, Xiao CB (2007) J Appl Polym Sci 103: 2954
9. Yu H, Huang Y, Ying H (2007) Carbohydr Polym 69: 29
10. Yang XH, Zhu WL, Yan JF (2006) J Biomater Sci 17: 53
11. Li B, Kennedy JF, Jiang QG, Xie BJ (2006) Food Res Int 39: 544
12. Tian D, Hu W, Zhen Z, Xie HQ (2006) J Appl Polym Sci 100: 1323
13. Hao X, Chang Q, Zhang Y (2007) Starch 59: 251
14. Xie C, Feng Y, Cao W, Xia Y, Lu Z (2007) Carbohydr Polym 67: 566
15. Yim JH, Kim ST, Ahn SH, Lee HK (2007) Bioresource Technol 98: 361.
16. Pal S, Mal D, Singh RP (2007) J Appl Polym Sci 105: 3240
17. Chen Y, Liu S, Wang G (2007) J Appl Polym Sci 105: 2841