Carbohydrate Polymers 90 (2012) 696–702

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

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

Viscosity properties of acetylated carboxymethyl starch

Yuanhao Wang, Benzhi Ju, Shufen Zhang*

State Key Lab of Fine Chemicals, Dalian University of Technology, Dalian 116024, PR China

A R T I C L E I N F O

Article history:
Received 3 March 2012
Received in revised form 14 May 2012
Accepted 30 May 2012
Available online 6 June 2012

Keywords:
ACMS
Viscosity-stability
Salt-tolerance
Shear-resistance

A B S T R A C T

The viscosity properties of acetylated carboxymethyl starch (ACMS) aqueous solution with different *DS* (degree of substitution) at concentration of 2.0% (w/w) were investigated using Brookfield R/S+ Portable rheometer. All flow curves of ACMS are well fitted to Power law model. Arrhenius model was used to describe temperature sensitivity. Furthermore, the parameters, which influenced the viscosity properties of the solutions, including temperature, *DS* of carboxymethyl group (DS_{cm}), *DS* of acetyl group (DS_{ac}), presence of salt (NaCl) and shear rate were discussed in detail. Specifically, the viscosity-stability, salt-tolerance and shear-resistance of ACMS with DS_{cm} (0.76) and DS_{ac} (0.34) were compared with that of sodium alginate as thickener in food or non-food applications. The results indicate that the viscosity properties of ACMS ($DS_{cm} = 0.76$, $DS_{ac} = 0.34$) were similar to that of sodium alginate and ACMS with DS_{cm} (0.76) and DS_{ac} (0.34) may be considered as a substitute for sodium alginate in certain application.

1. Introduction

Starch and its derivatives have attracted much attention due to their low cost, biocompatibility, biodegradability and non-toxicity. Carboxymethyl starch (CMS), one of the most important starch derivatives, has been applied for many years in industry as food thickening (Bhattacharyya, Chhaya, Singhal, & Kulkarni, 1995), textile sizing (Mostafa & Morsy, 2004), paper coating (Reinisch, Radics, & Roatsch, 1995), and water-based adhesives (Zhang, Chen, Lin, & Zhang, 2008). However, there are still some problems during applications of CMS due to its low salt-tolerance and shear-resistance. So, sodium alginate, which has good resistance to salt and shear, is still the main candidate in wide range of food and non-food applications (Çaykara, Demirci, Eroğlu, & Güven, 2005). While, the requirements of sodium alginate are gradually growing in recent years. Considering that CMS and sodium alginate are similar in hydrophilic group (carboxyl), CMS with good salt-tolerance and shear-resistance is hopefully to be the substitute for sodium alginate. Normally, the introducing of non-ionic group in the starch molecule can improve its salt-tolerance because of the non-ionic group is immune to salt solutions (Sheu, 1992), and offer more resistance to flow due to the starch molecular chain is more stretching (Daniel, Whistler, Chaplin, & Setser, 1985) by the sterical hindrance of non-ionic group. As an ideal non-ionic group, acetyl group was widely used to reduce the sensitivity of starch to salt and enhance its stability due to the breakage of hydrogen bonds between starch chains and the steric hindrance of acetyl group, resulting in that the starch derivatives with water-solubility (Liu, Ramsden, & Corke, 1997), viscosity stability (Hoover & Sosulski, 1985; Lawal & Adebowale, 2005; Liu, Ramsden, & Corke, 1999), thermal stability (Singh, Kaur, & Singh, 2004) and resistance to retrogradation (Lawal, 2004). Therefore, acetylating is an important substitution method to starch that imparts the thickening needed in food (Bemiller, 1997; Shogren & Biswas, 2010) and non-food applications (Boutboul, Giampaoli, Feigenbaum, & Ducruet, 2002). In most cases, however, acetylated starch were difficult to dissolve in cold water because of its surface reaction and lack of hydrophilic group on starch chains. Hence, by introducing of acetyl group into CMS molecule, the resulting starch derivatives, which have both carboxymethyl and acetyl group and we call it acetylated carboxymethyl starch (ACMS) here, would have good water-solubility, viscosity stability, salt-tolerance and shear-resistance.

The objectives of this work were to prepare ACMS by introducing both carboxymethyl and acetyl group on starch molecule to improve its thermal stability, viscosity-stability, salt-tolerance, shear-resistance and the modified starch may be a potential substitute for sodium alginate.

2. Materials and methods

2.1. Materials

Potato starch was obtained from Huanglong Food Company (Changchun, PR China). Sodium alginate under study (High viscosity grade) was supplied by Yantai Runlong Marine Biological Products Co., Ltd. (Yantai, PR China). All other reagents used in

---

* Corresponding author. Tel.: +86 411 84986265; fax: +86 411 84986264.
E-mail address: zhangshf@dlut.edu.cn (S. Zhang).

0144-8617/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2012.05.099

the preparation and analysis of modified starch were AR grade and without further purification.

2.2. Methods

2.2.1. Preparation of ACMS

CMS was prepared by method of Tijsen (Tijsen, Kolk, Stamhuis, & Beenackers, 2001) and DS_{cm} was determined by method of Kessel (1985).

4.0 g CMS was dissolved in 100 mL deionized water with agitation at 25 °C. Acetic anhydride was added drop-wise while the pH value was controlled at 8.5–9.0 (Betancur, Chel, & Cañizares, 1997) with 5.0% (w/w) NaOH solution. The reaction continued at 25 °C until the pH value was stabilized. After reaction, the pH value was adjusted to 9.0 and the mixture was poured to ethyl alcohol, washed twice with 80% aqueous alcohol and anhydrous ethyl alcohol, then the solid was oven-dried at 45 °C for 24 h.

2.2.2. Determination of degree of substitution

The DS_{ac} of ACMS was determined by hydrolysis method based on the hydrolysis of the ester bonds in sodium hydroxide solution (Elomaa et al., 2004). ACMS and CMS (0.50 g) were weighted accurately and added into the sodium hydroxide solution (25 mL, 0.5 M). The mixture was stirred for 72 h at room temperature. After indicator (3–5 drops of 1% thymolphthalein) was added the solution was immediately titrated with 0.1 M hydrochloric acid to the thymolphthalein endpoint. Reference sample was treated in a similar way. Acetyl group content (A) was calculated according to Eq. (1):

$$A\,(\%) = \frac{(V_2 - V_1) \times 10^{-3} \times C \times 43}{m} \times 100 \tag{1}$$

The degree of substitution (DS_{ac}) was calculated by content of acetyl group (A), according to Eq. (2):

$$DS_{ac} = \frac{M_{cms} \times A}{43 - 42A} \tag{2}$$

where V_1 and V_2 are the volume of 0.1 M HCl in mL used for titration of 0.50 g CMS and 0.50 g ACMS, C is the normality of HCl solution, m is the weight of the sample, M_{cms} is the molecular weight of CMS ($161 + 80DS_{cm}$), and 43 is the molecular weight of the acetyl group.

2.2.3. Fourier transforms infrared (FT-IR) spectroscopy

The change in chemical structure of the starch was qualitatively analyzed by using FT-IR (FT/IR-430, JASCO, Japan). Samples were prepared by grinding the finely powdered starch with KBr. The spectrum was recorded over the wave numbers range of 400–4000 cm^{-1}.

2.2.4. Thermalgravimetry analysis (TGA)

The analyses were performed with a simultaneous thermal analyzer TGA/SDTA 851 (Perkin-Elmer, USA). Samples (20 mg) were placed in corundum crucibles non-hermetically closed with lids, and heated under argon from room temperature to 400 °C at 5 °C/min rate of the temperature increase.

2.2.5. Dynamic viscosity determination

Rheological measurements were carried out using a Brookfield R/S + Portable rheometer and analyzed with RHEO3000 software. The solution was prepared by dissolving samples in the deionized water. The flow curves were obtained by registering viscosity and shear stress at shear rate which was increased from 0 to 500 s^{-1}. All measurements were performed in twice, at a temperature of 25 ± 0.1 °C. Viscosity was expressed in mPa s.

3. Results and discussion

3.1. FT-IR and TG analysis

The infrared spectra of CMS (DS_{cm} = 0.76) and ACMS (DS_{cm} = 0.76, DS_{ac} = 0.34) are presented in Fig. 1(A). The bands at 1642 cm^{-1} and 1420 cm^{-1} are the stretching vibration of the carbonyl functional group, which indicate the introduction of —COO⁻ group on the starch molecules (Kittipongpatana, Sirithunyalug, & Laenger, 2006). Compared with the IR spectrum of CMS, the ACMS have new absorption bands at 1735 cm^{-1} and 1247 cm^{-1}, corresponding to C═O and C—O—C of the typical stretching vibration of ester carbonyl group (Biswas et al., 2008). The broad band between 3600 and 3000 cm^{-1} is assigned to O—H stretching and it is due to hydrogen bonding involving the hydroxyl groups on the starch molecules. These evidences suggest that carboxymethyl and acetyl group were both introduced to starch molecules.

The TG curves of the native starch, CMS (DS_{cm} = 0.76) and ACMS (DS_{cm} = 0.76, DS_{ac} = 0.34) are shown in Fig. 1(B). These curves show that both native starch and starch derivatives involve two steps of weight loss. The first slight weight loss below 100 °C can be attributed to the dryness procedure, and the subsequent second major weight loss occurring could be attributed to the decomposition of the starch derivatives. It is instructive that initial decomposition temperature (IDT) of carboxymethyl starch is lower than the IDT of the native. This results due to the substitution on the hydroxyl group on the native starch with carboxymethyl group (Li, Gao, Huang, Wang, & Liu, 2010). The IDT of ACMS (260 °C) is higher than that of CMS (230 °C), which indicates the thermal stability of ACMS was enhanced after acetylating. After etherification by acetyl group, hydroxyl groups on starch molecules continue to be partly acetyl-substituted. Dehydration reaction between hydroxyl groups was reduced when the number of hydroxyl group on starch molecules decreased (Morita, 1956). So, the thermal stability of CMS was improved after acetylating reaction and IDT of ACMS is similar to that of sodium alginate (240–260 °C) (Soares, Santos, Chierice, & Cavalheiro, 2004).

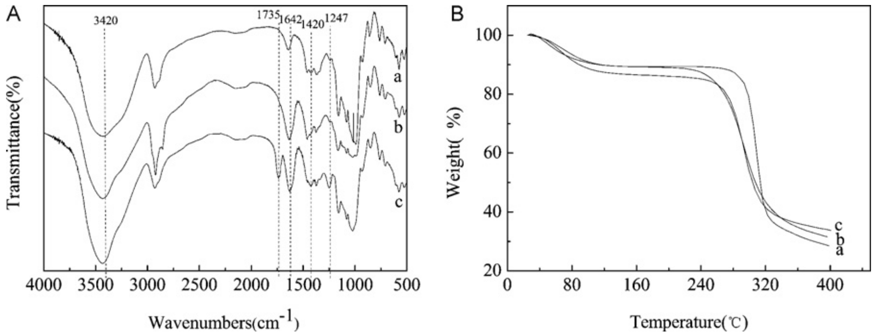

Fig. 1. IR spectra (A) and TG curves (B) of native starch (a), CMS (b) and ACMS (c).

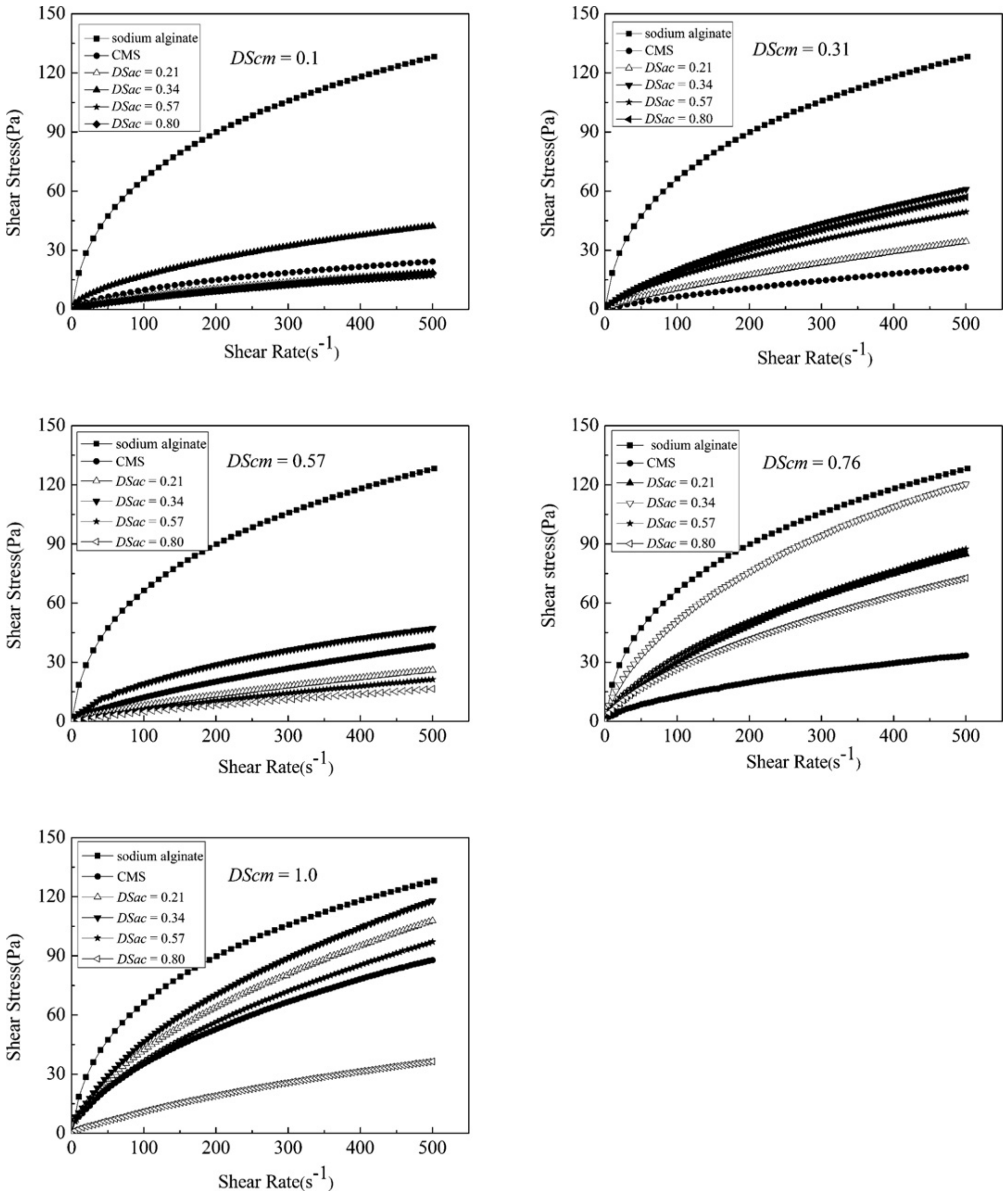

Fig. 2. Flow curves of ACMS and sodium alginate ($c = 2.0\%$, $T = 25\ ^\circ\text{C}$).

3.2. Rheological measurements

3.2.1. Determination of flow properties

The flow curves of ACMS, CMS and sodium alginate (Fig. 2) were described using Power-law model in Eq. (3):

$$\sigma = K \cdot \gamma^n \tag{3}$$

where σ is the shear stress (Pa), γ is the shear rate (s^{-1}), K is the consistency index (Pa s^n), and n is the flow behavior index (dimensionless) (Steffe, 1996).

Fig. 2 shows flow curves of ACMS, CMS and sodium alginate. It was observed that all curves are fit to the well-known Power law model ($r^2 > 0.99$) well, which is used extensively to describe the flow properties of non-Newtonian liquids in theoretical analysis as well as in practical engineering applications. It can be seen from Fig. 2 that the introduction of acetyl group can improve the flow properties and the flow curve of all ACMS with DS_{ac} at 0.34 is more close to that of sodium alginate. When DS_{cm} of ACMS is 0.76, its flow curve is the most close to that of sodium alginate. So, the Power-law model parameters of ACMS with DS_{cm} of 0.76 were compared with that of sodium alginate and the results were listed in Table 1.

The parameters in Table 1 indicate that all solutions are exhibited non-Newtonian behavior. This behavior is defined as shear-thinning, which causes the structure of starch chains to be broken down, as evidenced by $n < 1$. The flow behavior index (n) decreases first with DS_{ac} increasing, when DS_{ac} exceeds 0.34, the

Table 1
Power-law model parameters for different DS_{ac} of ACMS ($DS_{cm} = 0.76$), CMS ($DS_{cm} = 0.76$) and sodium alginate ($T = 25\ ^\circ\text{C}$, $c = 2.0\%$ (w/w)).

DS	*K* (Pa s^n)	*n*	r^2
Sodium alginate	9.23 ± 0.64201	0.42582 ± 0.00466	0.99639
CMS	0.83766 ± 0.0109	0.59484 ± 0.00225	0.99924
0.21	1.84182 ± 0.02947	0.6227 ± 0.00276	0.99898
0.34	4.17528 ± 0.07675	0.54437 ± 0.00319	0.99814
0.57	2.04399 ± 0.01561	0.60507 ± 0.00132	0.99975
0.80	1.50689 ± 0.01389	0.62497 ± 0.00159	0.99966

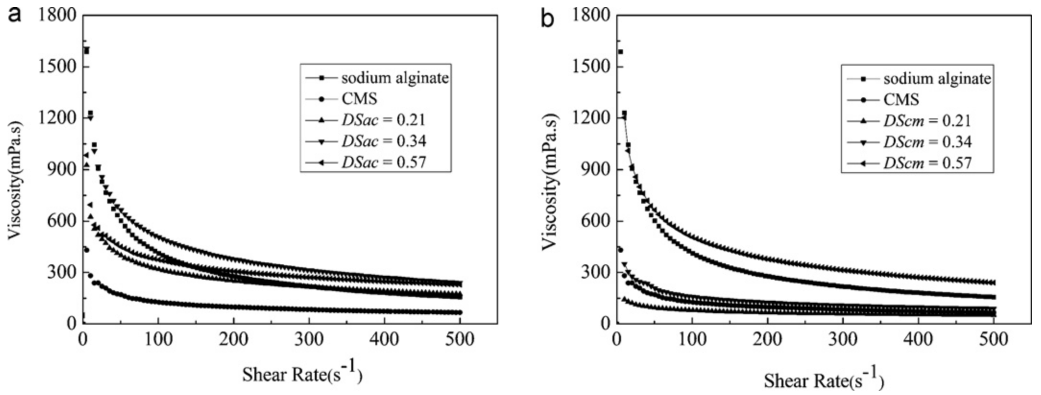

Fig. 3. Viscosity with shear rate of ACMS (DS_{cm} = 0.76) with different DS_{ac} (a), DS_{cm} (b), CMS (DS_{cm} = 0.76) and sodium alginate (c = 2.0%, T = 25 °C).

value of n increased. On the contrary, the consistency index (K) increases at first and then decreases. The lowest value of n and the highest value of K indicate the minimum structure viscosity and the maximum thickening effect. These results are caused by the rigidity of starch molecules and the hydrophobic association of acetyl groups in solution. When DS_{ac} is lower than 0.34, acetyl group is acting mainly as a steric hindrance group in starch chains. As the number of acetyl group increased, the starch chains became more and more stretching and the rigidity of the starch molecules increased. As a result, the intrinsic viscosity increased. When DS_{ac} exceeded 0.34, the rigidity of starch molecules decreased because of the weak hydrophobic association (Sengül & Fatih Ertugay, 2005) caused by hydrophobic interaction of the acetyl group. The structure viscosity increases with the increase of the flexibility of starch chains. Therefore, the value of n and the viscosity decreased because of the less stretching of starch chains. It can be seen that the steric hindrance and weak hydrophobic association may be in an appropriate proportion when DS_{ac} is 0.34. This may be the reason that all flow curves of ACMS are mostly close to sodium alginate when the DS_{ac} is 0.34.

3.2.2. Influence of DS_{ac} and DS_{cm} on viscosity of ACMS

The viscosity with shear rate range of 0–500 s^{-1} of ACMS, CMS and sodium alginate at 25 °C are shown in Fig. 3(a). An obvious shear-thinning behavior was observed for all solutions. The hydrophobic association between starch chains increases as the number of acetyl group increases and leads to increase of viscosity. The flexibility of starch chains was reduced due to the steric hindrance effect of acetyl group. Therefore, the chances of starch chains contact each other increase. When DS_{ac} is 0.34, the effect of acetyl group as a hinder group reaches a maximum. So the viscosity of ACMS with DS of 0.34 is the highest among the synthesized ACMS. When DS_{ac} is up to 0.57 the viscosity of ACMS decreased due to insolubility and flexibility of starch chain.

The viscosity of ACMS (DS_{ac} = 0.34) with different DS_{cm} at 2.0% (w/w) concentration is shown in Fig. 3(b). The starch samples with high DS_{cm} possessed higher apparent viscosities than the sample with low DS. The more the number of carboxymethyl group existed, the greater the electrostatic repulsion among the molecules and starch chain is more extending because of the electrostatic repulsion between carboxymethyl. Another reason is that the interplay between carboxymethyl group and water is enhanced with increase of DS_{cm}. These two reasons cause the higher viscosity of ACMS. The influence of DS_{cm} on viscosity consists with the result reported by Sangseethong, Ketsilp, and Sriroth (2005) and Tatongjai and Lumdubwong (2010), that is, the improvement of viscosity in CMS might be due to the presence of negative charges on their molecules.

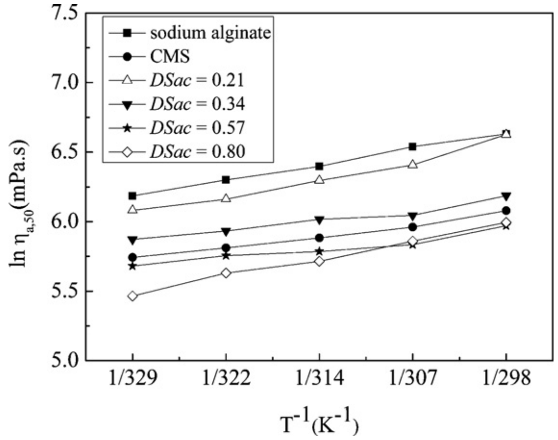

Fig. 4. The relationship of ln $\eta_{a,50}$ to T^{-1} (DS_{cm} = 0.76, γ = 50 s^{-1}, c = 2.0%).

3.2.3. Influence of DS_{ac} on temperature sensitivity

The influence of temperature on the apparent viscosity at a specified shear rate for liquid or semi-solid foods can be calculated using the Arrhenius equation in Eq. (4) (Pongsawatmanit, Temsiripong, Ikeda, & Nishinari, 2006)

$$\eta = A \cdot \exp\left(\frac{E_a}{RT}\right) \tag{4}$$

where η is the apparent viscosity at a specific shear rate, A is the frequency factor, E_a is the activation energy (kJ mol^{-1}), R is the gas constant (8.3144 J mol^{-1} K^{-1}), and T is the absolute temperature (K).

The relationship of ln $\eta_{a,\,50}$ (apparent viscosity at 50 s^{-1}) to T^{-1} was shown in Fig. 4. The E_a and A values were calculated from the slopes and intercepts on straight lines. The temperature sensitivity of different DS_{ac} was evaluated by the activation energy (E_a) and the results were listed in Table 2. Activation energy (E_a) for the flow process is related to chain flexibility (Lee & Nielsen, 1977). High r^2 values indicate that the viscosity of solutions in relation with

Table 2
Arrhenius model for different DS_{ac} of ACMS at shear rate of 50 s^{-1} (DS_{cm} = 0.76, c = 2.0%).

DS_{ac}	A (Pa s)	E_a (kJ mol^{-1})	r^2
0	2.046	2.143	0.9912
0.21	6	1.27	0.954
0.34	0.325	0.623	0.96
0.57	5.6054	0.194	0.90
0.80	5.3805	0.175	0.91
Sodium alginate	4.2364	0.198	0.9963

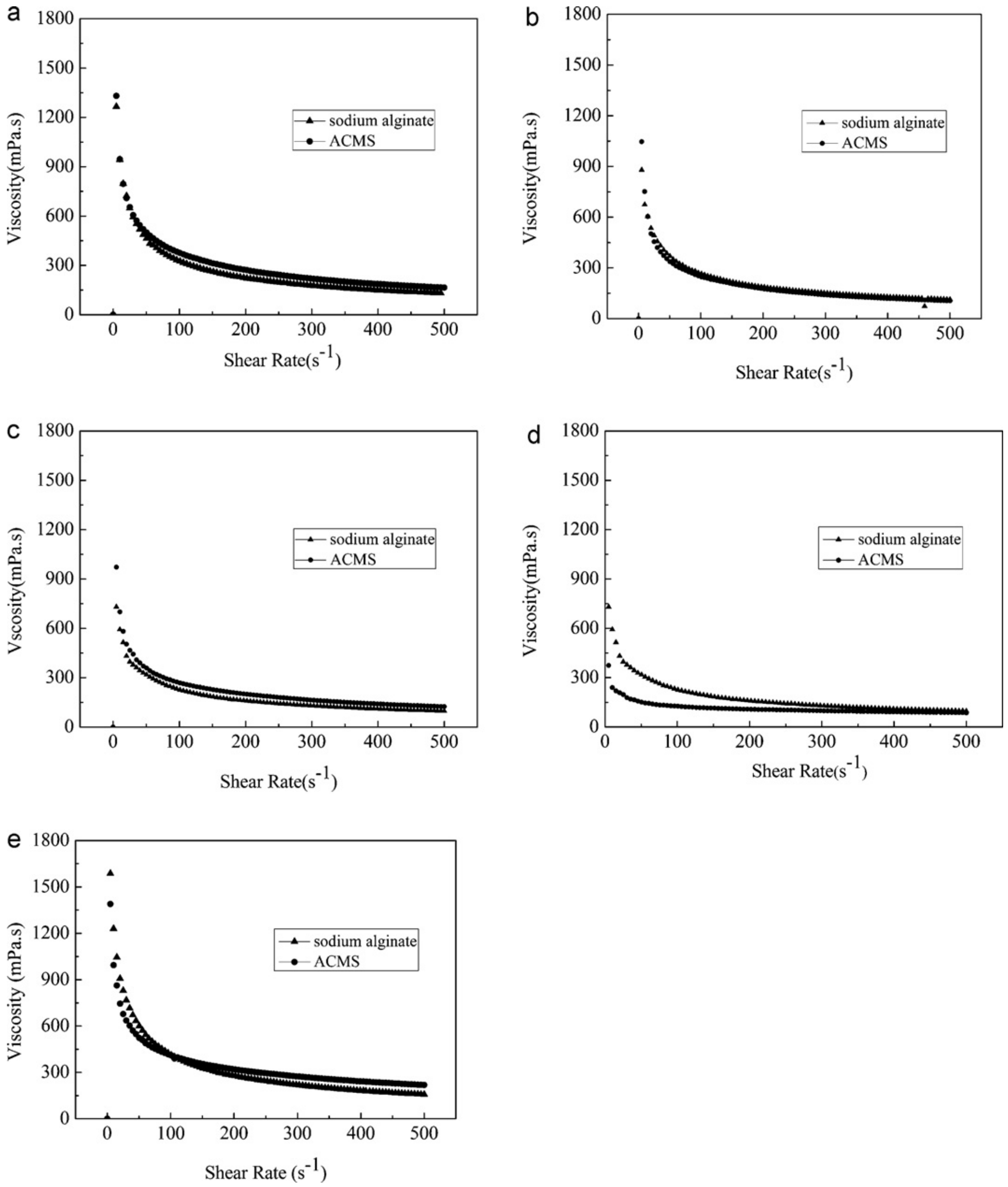

Fig. 5. The salt-tolerance (salt content – a: 0.1%; b: 0.25%; c: 0.50%; d: 0.75%) and shear-resistance (e) of ACMS and sodium alginate at different salt content ($c = 2.0\%$, $T = 25\,^{\circ}\mathrm{C}$).

temperature fit the Arrhenius type equation. The value of E_a decreased with the increase of DS_{ac}. This result showed that the temperature sensitivity of ACMS decreased with the increase of DS_{ac}. It was due to the hydrophobic association of acetyl group when the solution temperature was increased. The flexibility of starch chains enhanced with the temperature increasing and the viscosity decreasing. But the hydrophobic association caused by increasing temperature can offset this decrease of viscosity in certain extent. Therefore, the increase of DS_{ac} is beneficial to temperature sensitivity improvement. The temperature sensitivity of ACMS is improved when DS_{ac} exceeds 0.34 due to the hydrophobic association of acetyl group.

3.3. Comparison the solution properties of ACMS with that of sodium alginate

It can be seen from the discussion in Section 3.2 that the flow properties and viscosity of ACMS with $DS_{cm} = 0.76$ and $DS_{ac} = 0.34$ is similar to that of sodium alginate. So, the solution properties of this particular DS_{cm} and DS_{ac} of ACMS were compared with that of sodium alginate.

3.3.1. Salt-tolerance and shear-resistance of ACMS

Fig. 5 shows the dependence of viscosity upon addition of NaCl. The viscosity of solution decreased as the ionic strength increased. Upon addition of NaCl, carboxymethyl group combined with Na^+. The chance of starch chains interacting with each other reduced as the rigidity of starch chains weakened. So, the increase of salt concentration resulted in a decrease in viscosity. When the salt addition is between 0.1 and 0.5%, the sensitivity to salt of ACMS is similar to that of sodium alginate. This is due to the steric exclusion and hydrophobic association of acetyl group in ACMS. It was reported that the acetyl group introduced in rice starch chains impeded the formation of the helical structure of amylose in some areas, by sterical hindrance (Gonzalez & Perez, 2002). On the other hand, the polarity of solution increased with the addition of salt, the hydrophobic association of acetyl group enhanced. As a result, the sensitivity of ACMS to salt is similar to that of sodium alginate.

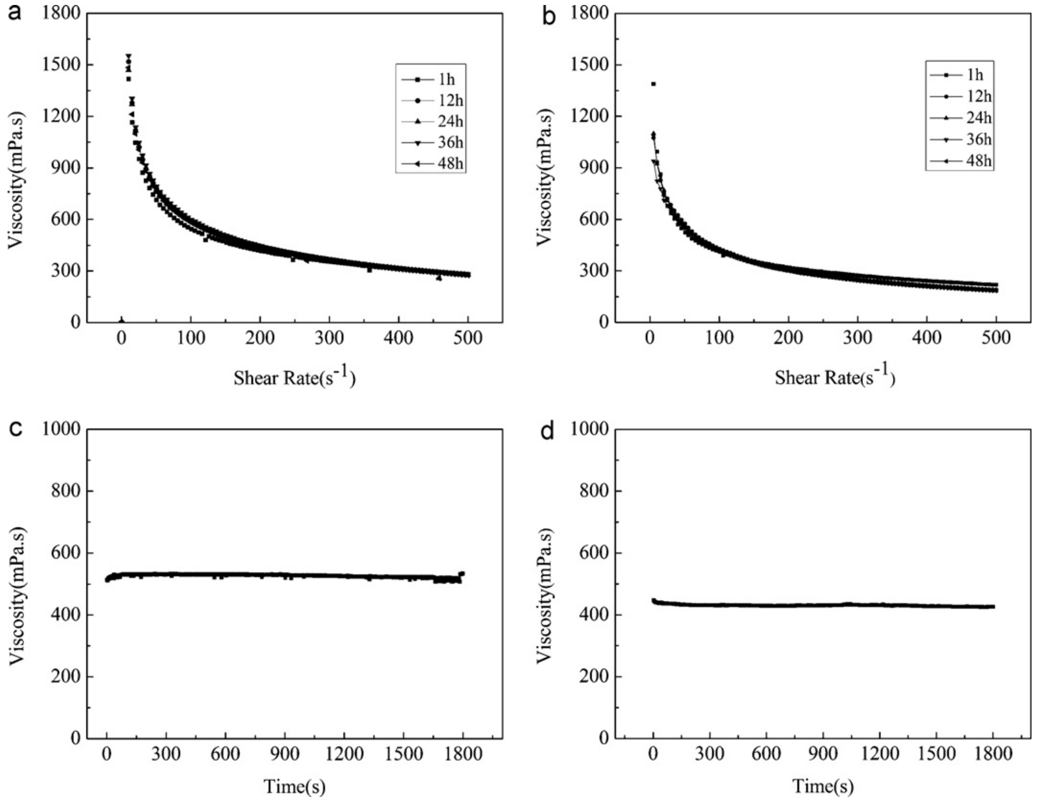

Fig. 6. Storage stability (a, b) ($c = 2.0\%$, $T = 25\,^{\circ}\mathrm{C}$) and shear stability (c, d) ($c = 2.0\%$, $\gamma = 100\,\mathrm{s}^{-1}$, $T = 25\,^{\circ}\mathrm{C}$) of ACMS (a, c) and sodium alginate (b, d).

However, the decrease of ACMS in viscosity is greater than that of sodium alginate when the salt content reaches 0.75%. This result may be attributed to less carboxymethyl group content on ACMS chains compared with that of sodium alginate at the same concentration. The existence of the remaining carboxymethyl group of sodium alginate chains in combination with salt may maintain the extending of starch chains. Hence, the viscosity decrease of sodium alginate is less than that of ACMS when the salt addition exceeds 0.75%.

The shear-resistance of ACMS and sodium alginate in shear rate range of 0–500 s^{-1} is shown in Fig. 5(e). It can be seen from Fig. 5(e) that the shear-resistance of ACMS is better than that of sodium alginate. Introducing of acetyl group is beneficial to the stretching of starch chain and their interactions. Consequently, decrease of the viscosity caused by shear force is reduced. On the other hand, acetyl groups may effectively prevent the parallel arrangement between the amylase and reduce the viscosity drop which causes destruction of parallel structure by shear rate. Therefore, the shear-resistance of ACMS is better than that of sodium alginate in the shear rate range of 0–500 s^{-1}.

3.3.2. Viscosity-stability of ACMS

Fig. 6 shows the storage stability and shear stability of ACMS and sodium alginate. It is possible to observe from Fig. 6 that the viscosity of ACMS (Fig. 6(a)) is almost constant within 48 h, which is similar to the stability of sodium alginate (Fig. 6(b)). Moreover, the shear rate stability of ACMS at 100 s^{-1} is also similar to that of sodium alginate. Compared shear stability of ACMS (Fig. 6(c)) with that of sodium alginate (Fig. 6(d)), the apparent viscosity of ACMS at 100 s^{-1} is higher than that of sodium alginate. This also proved that the shear-resistance of ACMS is better than that of sodium alginate. This kind of good storage stability and shear stability is due to the contribution of acetyl group. After esterification of CMS with acetyl group, the hydrogen bond and the parallel arrangement between starch chains were reduced. Therefore, the storage stability and shear stability were enhanced.

4. Conclusions

Introduction of acetyl group into carboxymethyl starch (CMS) changed the rheological behavior of CMS. Both appropriate proportion of carboxymethyl to acetyl and the steric hindrance to weak hydrophobic association of acetyl group on starch chains are crucial factor for the viscosity properties of ACMS. The flow curve of ACMS with $DS_{cm} = 0.76$, $DS_{ac} = 0.34$ is similar to that of sodium alginate. The viscosity properties, including thermal stability, viscosity stability, salt-tolerance and shear-resistance of ACMS with $DS_{cm} = 0.76$, $DS_{ac} = 0.34$ were compared with that of sodium alginate under 25 °C, at 2.0% concentration. The result indicates that the viscosity properties of ACMS with $DS_{cm} = 0.76$, $DS_{ac} = 0.34$ are similar to that of sodium alginate. Hence, ACMS with $DS_{cm} = 0.76$, $DS_{ac} = 0.34$ may be a potential substitute for sodium alginate in the practical application that shows the requirements of good viscosity properties and low the cost.

Acknowledgment

This work was supported by the State Key Program of National Natural Science of China (20836001).

References

Bemiller, J. N. (1997). Starch modification: Challenges and prospects. *Starch/Stärke*, *49*(4), 127–131.

Betancur, A. D., Chel, G. L., & Cañizares, H. E. (1997). Acetylation and characterization of *Canavalia ensiformis* starch. *Journal of Agricultural and Food Chemistry*, *45*(2), 378–382.

Bhattacharyya, D., Chhaya, P., Singhal, R., & Kulkarni, P. (1995). Studies on reduction in oil content in deep-fat fried legume based snack using carboxymethyl starch (CMS). *Lipid/Fett*, *97*(11), 432–434.

Biswas, A., Shogren, R., Selling, G., Salch, J., Willett, J., & Buchanan, C. M. (2008). Rapid and environmentally friendly preparation of starch esters. *Carbohydrate Polymers*, *74*(1), 137–141.

Boutboul, A., Giampaoli, P., Feigenbaum, A., & Ducruet, V. (2002). Influence of the nature and treatment of starch on aroma retention. *Carbohydrate Polymers*, *47*(1), 73–82.

Çaykara, T., Demirci, S., Eroğlu, M. S., & Güven, O. (2005). Poly (ethylene oxide) and its blends with sodium alginate. *Polymer*, *46*(24), 10750–10757.

Daniel, J., Whistler, R., Chaplin, M., & Setser, C. (1985). Carbohydrates. *Food Chemistry*, 70–137.

Elomaa, M., Asplund, T., Soininen, P., Laatikainen, R., Peltonen, S., Hyvärinen, S., et al. (2004). Determination of the degree of substitution of acetylated starch by hydrolysis, ^{1}H NMR and TGA/IR. *Carbohydrate Polymers*, *57*(3), 261–267.

Gonzalez, Z., & Perez, E. (2002). Effect of acetylation on some properties of rice starch. *Starch/Stärke*, *54*(3–4), 148–154.

Hoover, R., & Sosulski, F. (1985). A comparative study of the effect of acetylation on starches of *Phaseolus vulgaris* biotypes. *Starch/Stärke*, *37*(12), 397–404.

Kessel, H. (1985). Determination of the functional group and the average degree of substitution of carboxymethyl starch. *Starch/Stärke*, 37.

Kittipongpatana, O. S., Sirithunyalug, J., & Laenger, R. (2006). Preparation and physicochemical properties of sodium carboxymethyl mungbean starches. *Carbohydrate Polymers*, *63*(1), 105–112.

Lawal, O., & Adebowale, K. (2005). Physicochemical characteristics and thermal properties of chemically modified jack bean (*Canavalia ensiformis*) starch. *Carbohydrate Polymers*, *60*(3), 331–341.

Lawal, O. S. (2004). Succinyl and acetyl starch derivatives of a hybrid maize: Physicochemical characteristics and retrogradation properties monitored by differential scanning calorimetry. *Carbohydrate Research*, *339*(16), 2673–2682.

Lee, B. L., & Nielsen, L. E. (1977). Temperature dependence of the dynamic mechanical properties of filled polymers. *Journal of Polymer Science: Polymer Physics Edition*, *15*(4), 683–692.

Li, X., Gao, W., Huang, L., Wang, Y., & Liu, C. (2010). Preparation and physicochemical properties of carboxymethyl *Fritillaria ussuriensis* Maxim. starches. *Carbohydrate Polymers*, *80*(3), 768–773.

Liu, H., Ramsden, L., & Corke, H. (1997). Physical properties and enzymatic digestibility of acetylated ae, wx, and normal maize starch. *Carbohydrate Polymers*, *34*(4), 283–289.

Liu, H., Ramsden, L., & Corke, H. (1999). Physical properties of cross-linked and acetylated normal and waxy rice starch. *Starch/Stärke*, *51*(7), 249–252.

Morita, H. (1956). Characterization of starch and related polysaccharides by differential thermal analysis. *Analytical Chemistry*, *28*(1), 64–67.

Mostafa, K. M., & Morsy, M. S. (2004). Tailoring a new sizing agent via structural modification of pregelled starch molecules. Part 1. Carboxymethylation and grafting. *Starch/Stärke*, *56*(6), 254–261.

Pongsawatmanit, R., Temsiripong, T., Ikeda, S., & Nishinari, K. (2006). Influence of tamarind seed xyloglucan on rheological properties and thermal stability of tapioca starch. *Journal of Food Engineering*, *77*(1), 41–50.

Reinisch, G., Radics, U., & Roatsch, B. (1995). Rationelle stärkeacetat-synthesen. *Die Angewandte Makromolekulare Chemie*, *233*(1), 113–120.

Sangseethong, K., Ketsilp, S., & Sriroth, K. (2005). The role of reaction parameters on the preparation and properties of carboxymethyl cassava starch. *Starch/Stärke*, *57*(2), 84–93.

Sengül, M., & Fatih Ertugay, M. (2005). Rheological, physical and chemical characteristics of mulberry pekmez. *Food Control*, *16*(1), 73–76.

Sheu, J. J. (1992). *Cables such as optical fiber cables including superabsorbent polymeric materials which are temperature and salt tolerant*. Google Patents.

Shogren, R. L., & Biswas, A. (2010). Acetylation of starch with vinyl acetate in imidazolium ionic liquids and characterization of acetate distribution. *Carbohydrate Polymers*, *81*(1), 149–151.

Singh, J., Kaur, L., & Singh, N. (2004). Effect of acetylation on some properties of corn and potato starches. *Starch/Stärke*, *56*(12), 586–601.

Soares, J., Santos, J., Chierice, G., & Cavalheiro, E. (2004). Thermal behavior of alginic acid and its sodium salt. *Eclética Química*, *29*(2), 57–64.

Steffe, J. F. (1996). Rheological methods in food process engineering. *Freeman Press*.

Tatongjai, J., & Lumdubwong, N. (2010). Physicochemical properties and textile utilization of low- and moderate-substituted carboxymethyl rice starches with various amylose content. *Carbohydrate Polymers*, *81*(2), 377–384.

Tijsen, C., Kolk, H., Stamhuis, E., & Beenackers, A. (2001). An experimental study on the carboxymethylation of granular potato starch in non-aqueous media. *Carbohydrate Polymers*, *45*(3), 219–226.

Zhang, F., Chen, Y., Lin, H., & Zhang, D. (2008). Performance of cotton fabric treated with an amino-terminated hyperbranched polymer. *Fibers and Polymers*, *9*(5), 515–520.