Carbohydrate Polymers 85 (2011) 862–868

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Rheological and micro-DSC studies on the aqueous mixtures of methylcellulose and ammonium poly(3-thiophene acetic acid)

Renliang Lv, Tu Luan, Fengyuan Yu, Hongbin Zhang*

Advanced Rheology Institute of SJTU, Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Min Hang, Shanghai 200240, China

ARTICLE INFO

Article history:
Received 9 February 2011
Received in revised form 10 March 2011
Accepted 4 April 2011
Available online 12 April 2011

Keywords:
Viscous synergism
Polymer gels
Rheology
Methylcellulose
Polythiophene

ABSTRACT

In the present work aqueous mixtures of polysaccharide of methylcellulose (MC) and conductive polymer of ammonium poly(3-thiophene acetic acid) (PTAA-NH_4) were prepared and the effect of PTAA-NH_4 on the rheological and thermal properties of MC solution were investigated. Significant viscous synergism depending on shear rate and concentration of PTAA-NH_4 was found for the mixtures, indicating a special interaction between the two amphiphilic polymers of MC and PTAA-NH_4. In comparison with pure MC solutions, the mixtures showed much more evident shear thinning characteristics. When the concentration of PTAA-NH_4 added was higher than 0.15%, weak gel-like behavior of the mixtures was also observed at low temperatures. In addition, though the gelation and degelation patterns of MC were not changed by the addition of PTAA-NH_4, both rheological and calorimetric measurements showed that the presence of PTAA-NH_4 shifted the sol–gel transition temperature of MC solution to higher temperature with increasing of the concentration of PTAA-NH_4.

1. Introduction

Methylcellulose (MC) is a cellulose ether formed by the alkali treatment of cellulose (Peressini, Bravin, Lapasin, Rizzotti, & Sensidoni, 2003). Commercial MC is a heterogeneous polymer consisting of highly substituted zones called “hydrophobic zones” and less substituted ones called “hydrophilic zones” (Desbrières, Hirrien, & Ross-Murphy, 2000). MC exhibits thermal gelation and has excellent film-forming properties, which has been widely used as a binder or thickener in paints, oil recovery, cosmetics, foods (Hirrien, Chevillard, Desbrières, Axelos, & Rinaudo, 1998), ceramics (Lin et al., 2009), injectable gel for tissue engineering scaffolds (Tang et al., 2010), *in situ* forming gel for ophthalmic drug delivery (Bhowmik et al., 2010; Kumar, Haglund, & Himmelstein, 1994), etc. MC has been proven currently to support some nerve regeneration and can also be linked with proteins which encourage axonal extension (Martin, Minner, Wiseman, Klank, & Gilbert, 2008). Moreover, MC has shown good biocompatibility when used as scaffolds in traumatic brain injury and peripheral nerve regeneration (Gupta, Tator, & Shoichet, 2006).

Over the last 50–70 years there have been many reports that indicate that electrical stimulation of tissues can elicit enhanced cellular activity. There are many tissues that have been targeted for regeneration, including nerve, bone, skin, liver, heart, cartilage, vascular, tendon, and ligament (Svennersten, Bolin, Jager, Berggren, & Richter-Dahlfors, 2009). Tissue engineers are interested in making interactive scaffolds that not only perform a mechanical and physical role, but also a biological function. It is known that electrical stimulation *in vivo* and *in vitro* leads to enhanced regeneration of some tissues include peripheral nerves (Green, Lovell, & Poole-Warren, 2010; Onoda, Abe, & Tada, 2009; Xiao, Li, Wang, Shi, & Ooi, 2010). Conducting polymers, especially those based on polyanilines, polypyrroles, polythiophenes and polyphenylenes, have received significant attention throughout the course of the past 3 decades owing to the tunable electro-optical properties and high degree of processability. Among many materials that have been developed during this period, poly(3-thiophene acetic acid) (PTAA) is one of the most successful polythiophene derivatives because of its interesting properties. PTAA has been largely used in several applications such as dye-sensitized solar cell, polymer solar cells, optical sensors and chemically modified electrodes. Such a wide range of applications is based on properties, for instance, thermochromism, fluorescence, conductivity in its doped state, photoluminescence and absorption in the UV–vis region (Malitesta, Guascito, Mazzotta, & Picca, 2010). Mukherjee, Dawn, and Nandi (2010) reported the preparation and properties of a DNA-PTAA hybrid, whose optical and conducting properties might be useful for DNA hybridization, gene therapy, and DNA diagnostic study. The anion of PTAA was reported to bind with many biomolecules like insulin, lysozyme, and so on (Nilsson, Herland, Hammarstrom, & Inganas, 2005). PTAA cannot dissolve in water, but it is ready to get the water-soluble ammonium

---

* Corresponding author. Tel.: +86 21 54745005; fax: +86 21 54741297.
E-mail address: hbzhang@sjtu.edu.cn (H. Zhang).

0144-8617/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2011.04.009

poly(3-thiophene acetic acid) (PTAA-NH_4) by treating PTAA with aqueous ammonia solution.

Polysaccharides are naturally produced polymers of simple sugar building blocks with inherently desirable bioactivity, biocompatibility and biodegradability. It has been reported that conducting polymer–polysaccharides composites could be electroactive, biodegradable, and biocompatible materials and used to enhance the regeneration of severed peripheral nerves and other tissues (Alemán et al., 2009; Guimard, 2008; Kim, Wiler, Anderson, Kipke, & Martin, 2010). In light of the above work, the aqueous mixtures of MC and PTAA-NH_4 may have academic importance and potential applications in many fields as mentioned. In this work, the properties of the mixture solutions of MC and PTAA-NH_4 were studied, and the effects of PTAA-NH_4 on steady flow, dynamic rheological behaviors and the sol–gel transition of MC were discussed rheologically and micro-thermally.

2. Experimental

2.1. Materials

MC was kindly provided by Shin-Estu Chemical Co., Ltd., Japan, with the commercial name of SM4000. According to the manufacturer, this MC has an average degree of substitution (DS) of 1.8 and a viscosity of 4.54 Pa s at 20 °C for a 2 wt% aqueous solution. Its weight-average molecular weight (M_w) is ca. 3.8×10^5 g/mol determined by light scattering (Kobayashi, Huang, & Lodge, 1999; Li et al., 2001; Yin, Zhang, & Nishinari, 2007). SM4000 has been proven to be highly pure by Kobayashi et al. (1999) and Li (2002), therefore, the material was used as received without further purification. Prior to use, it was vacuum-dried at 55 °C for 24 h and kept in a desiccator at room temperature.

3-Thiopheneacetic acid (purity > 99%) was purchased from Anhui Hua Fu Chemical (Anhui, China) and used as received. Dichloromethane was of analytical grade, purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC, China), dried by anhydrous sodium sulphate for at least 4 weeks before use. All other reagents were of analytical grade, purchased from SCRC, and used as received. Distilled deionized water from a Millipore water purifier was used throughout.

2.2. Synthesis of ammonium poly(3-thiopheneacetic acid) (PTAA-NH_4)

PTAA was synthesized via a chemical oxidation method (de Souza & Pereira, 2001; Giglioti, Trivinho-Strixino, Matsushima, Bulhões, & Pereira, 2004; Zhang & Srinivasan, 2005). A mixture of 3-thiopheneacetic acid (0.71 g, 5 mmol) and anhydrous $FeCl_3$ (4.06 g, 25 mmol) in 100 ml dry CH_2Cl_2 was stirred at room temperature (25 °C) under nitrogen for 4 h. Then most of the solvent was removed in vacuo, and then100 ml ethanol was added and stirred for another 4 h. The mixture was filtered and the filter cake was washed with 100 ml 1 M aqueous HCl, ethanol, refluxed in ethanol for 2 h and then dried overnight at 30 °C under vacuum. The resulting reddish brown powder was subsequently dissolved in 100 ml 2 M aqueous NaOH, heated for 24 h at 100 °C. The mixture was centrifugalized to remove the insoluble part. 100 ml concentrated HCl was added to the solution and stirred for 10 h, standing for 2 days and filtered, washed repeatedly with distilled deionized water and ethanol and finally dried at 40 °C under vacuum for 2 days. The obtained PTAA was dissolved in 200 ml 1.5% aqueous ammonia solution, stirred for 20 h and lyophilized to give PTAA-NH_4 (76% yield). Successful synthesis was confirmed by FTIR spectra recorded on a Spectrum 100 FTIR spectrometer (Perkin Elmer, Inc., USA) and the weight average molecular weight of PTAA-NH_4 obtained was 1.57×10^4 detected by using a HLC-8320GPC GPC system (TOSOH Corporation, Japan).

2.3. Sample preparation

The weight percentage (versus water) is used to represent all the polymer concentrations in this work because of the convenience and accuracy. The MC concentration was fixed to be 1% within the appropriate concentration range of 0.3–2.5% (Li et al., 2002), and the PTAA-NH_4 concentration was varied in order for us to compare the effects of different concentrations of PTAA-NH_4 on the properties of MC solution.

Each solution was prepared by dispersing the weighed PTAA-NH_4 and MC powders in water in turn, stirring for 10 h and mixing on a roller mixer for 24 h at 5–15 °C. Since the MC could not be completely dissolved for a short period of time at room temperature, the dispersion was transferred to a refrigerator with a temperature at 4 °C and kept for a minimum period of 48 h prior to measurements. All the solutions obtained were clear and transparent at room temperature (25 °C) or below. The samples were used up within a week to prevent the degradation of MC.

2.4. Rheological measurements

The rheological measurements were carried out using a controlled stress rheometer AR G2 (TA Instruments, USA) with a parallel plate geometry (40 mm in diameter and 0.9 mm in gap). The temperature was regulated by a circulate water bath and peltier system. To reduce the evaporation of water from the samples during the measurement, a thin layer of low-viscosity silicone oil was placed on the periphery surface of the solution held between the plates.

Steady shear viscosity curves were measured over a shear rate range of 0.01–1000 s^{-1} at 5 °C. Steady state is assumed to be attained only when the variation of torque is less than 5% throughout three consecutive sampling periods (30 s) and the maximum point time was set as 6 min.

The dynamic viscoelastic functions such as the shear storage modulus G' and loss modulus G'' were measured as a function of temperature during a temperature cycle between 5 and 80 °C with the ramp rate of 5 °C/min. All the dynamic viscoelastic measurements were carried out in the oscillatory shear mode at a frequency of 1 Hz and a low shear strain of 1% to ensure the linearity of viscoelasticity. Prior to the data collection, these settings were checked at different temperatures with the strain-sweep and angular frequency-sweep measurements.

2.5. Differential scanning calorimetry

Calorimetric experiments were performed with a micro differential scanning calorimeter SETARAM (France) DSCIII during a thermal cycle from 10 to 80 °C with a heating and cooling rate of 1 °C/min. Each temperature cycle was sequentially repeated at least 3 times in order to ensure and check the reproducible response of the instrument. The microcalorimeter is designed for liquid samples, where the sample is injected into a sample cell and the reference cell is filled with pure water or the same solvent used for the sample solution. In this work, we employed the distilled deionized water as the reference. After each cycle was completed for the sample, the sample cell was cleaned by distilled deionized water for several times, followed an ultrasonic washing for at least 10 min in distilled deionized water, then washed by ethanol and dried. Before the next sample was injected and measured, cleanliness of the sample cell was confirmed by measuring deionized water. If necessary, the cleaning procedure was repeated.

3. Results and discussion

3.1. Steady shear flow

The steady shear viscosity as a function of the shear rate for the pure aqueous 1% MC and the mixed solutions of MC (1%) and PTAA-NH_4 at various PTAA-NH_4 concentrations was depicted in Fig. 1. The results demonstrated shear thinning behavior in all the solutions. This type of behavior was reported for many hydrocolloid solutions, due to formation of aggregates of the polymers in solutions and their high molecular weight. At low shear rates, the aggregates can be remained as strongly associated but they could be easily broken up with the effect of high shear (Yasar, Kahyaoglu, & Sahan, 2009). The typical steady shear viscosity plots of pure PTAA-NH_4 solutions were also included in Fig. 1, the viscosity values of which were much lower than those of both MC and mixture solutions.

It is known that MC exists in solution as aggregated bundles, held together by the hydrophobic clustering of methyl groups in regions of heavy substitution and by unsubstituted regions of native cellulose structure (Haque & Morris, 1993). A recent theoretical study dealing with adsorption of surfactants on a semiflexible polymer proposes that the bound molecules may modify local characteristics of polymer conformation, thereby altering its stiffness (Diamant & Andelman, 2000). Synergistic interactions between components in a blend or a mixture are generally governed by intermolecular interactions (Bresolin, Milas, Rinaudo, & Ganter, 1998). The viscosity increase of the mixed system corresponding to the PTAA-NH_4 concentration in Fig. 1 might be due to the occurrence of interaction between MC and PTAA-NH_4 yielding conformational expansion of the polymer chains. In order to describe the variation in the rheological properties of the samples under steady shear, the experimental data were fitted to the well-known power law (Eq. (1)) (Yasar et al., 2009):

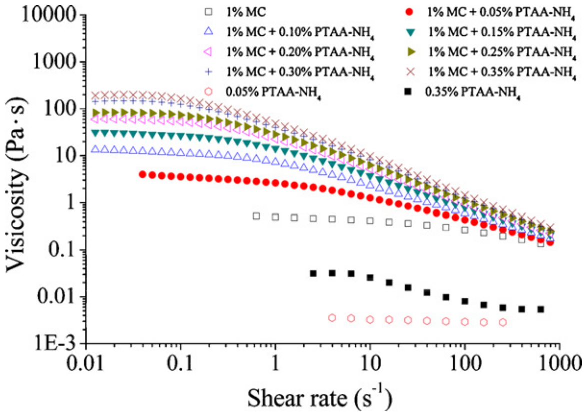

Fig. 1. Viscosity curves of pure PTAA-NH_4 solutions and 1% MC as a function of shear rate at various PTAA-NH_4 concentrations at 5 °C.

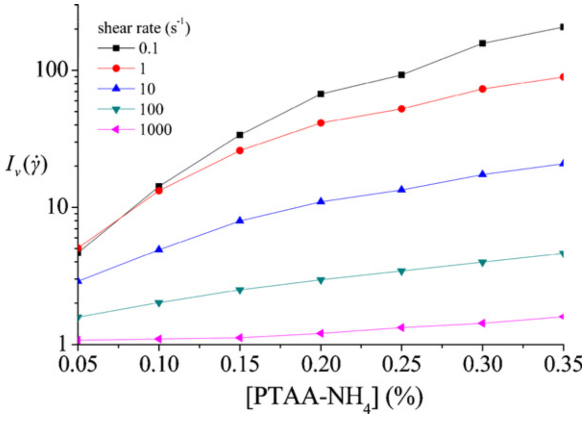

Fig. 2. Viscous synergism index $I_\nu(\dot{\gamma})$ of PTAA-NH_4 + MC (1%) systems at various shear rates as a function of PTAA-NH_4 concentrations at 5 °C.

$$\sigma = K\dot{\gamma}^n \tag{1}$$

where σ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (s^{-1}), K is the consistency index (Pa s^n), and n is the flow behavior index (dimensionless). The power law was shown to provide good fittings for the various curves in Fig. 1 with coefficient of determination $R^2 > 0.98$. This model has allowed study of the effect of the concentration increase on the consistency index K and shear rate index n of the corresponding power law (lower fitting limit 1 s^{-1}). The obtained K and n were listed in Table 1. The value of K, which is a measure of consistency, increases with increasing the PTAA-NH_4 concentration, showing a remarkable synergistic viscosity behavior, while the value of n decreases, showing stronger shear thinning characteristic (Zhang & Zhou, 2006).

Cross model was also used to fit as precisely the most general pseudoplastic behavior of the polymer solutions. According to this model, four characteristic parameters representative of the pseudoplastic behavior of a polymer solution were obtained by

$$\sigma = \left[\eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (\lambda\dot{\gamma})^p}\right]\dot{\gamma} \tag{2}$$

where η_0 is the zero shear viscosity, corresponding to the first Newtonian region, η_∞ is the infinity shear viscosity, p is the shear rate index characterizing the shear thinning properties of the polymer solutions, and λ is a time parameter corresponding to the inverse ratio of the critical shear rate $\dot{\gamma}_0$ for which the transition between Newtonian and non-Newtonian behavior occurs. The λ parameter may be considered as being the longest relaxation time of the Rouse spectrum for a given polymer solution (El Ghzaoui, Trompette, Cassanas, Bardet, & Fabregue, 2001). The fitting result (coefficient of determination $R^2 > 0.99$) was also shown in Table 1.

It can be observed in Table 1 that η_0, p and λ of the mixed aqueous solutions increased with increasing PTAA-NH_4 concentration. As expected, for all the samples the larger the PTAA-NH_4 concentration the lower the $\dot{\gamma}_0$ value, i.e., pseudoplastic character became more pronounced as the concentration of PTAA-NH_4 increased, which could be further attributed to the occurrence of intermolecular interactions including the hydrophobic interaction between hydrophobic backbone of PTAA-NH_4 and the methyl groups of MC, and the hydrogen bonding induced by the $-COO^-$ groups of PTAA-NH_4 and the –OH groups of MC, leading to the formation of pseudonetwork in solution.

Synergistic effects have been observed in studies involving different non-Newtonian mixed systems (Rojas, Muller, & Saez, 2008; Tako, 1992). These effects lead to an increase of viscosity and dynamic modulus of mixed systems, compared with the values corresponding to single components alone, at the same concentration (Donati et al., 2007). The quantification of nonadditive behavior of viscosity is particularly advantageous in industry, where products are very often formulated with more than one additive to achieve the desired physical structure and properties (Pellicer et al., 2000; Sovilj & Petrovic, 2007). Since polymer solutions, pure or in the form of a mixture, exhibit non-Newtonian flow behavior even at low solute concentration, the intensity of any synergistic or antagonistic effect can have shear rate dependency. Viscosity depends on both concentration and shear rate. Therefore the parameter quantifying viscous synergism will also be dependent upon these

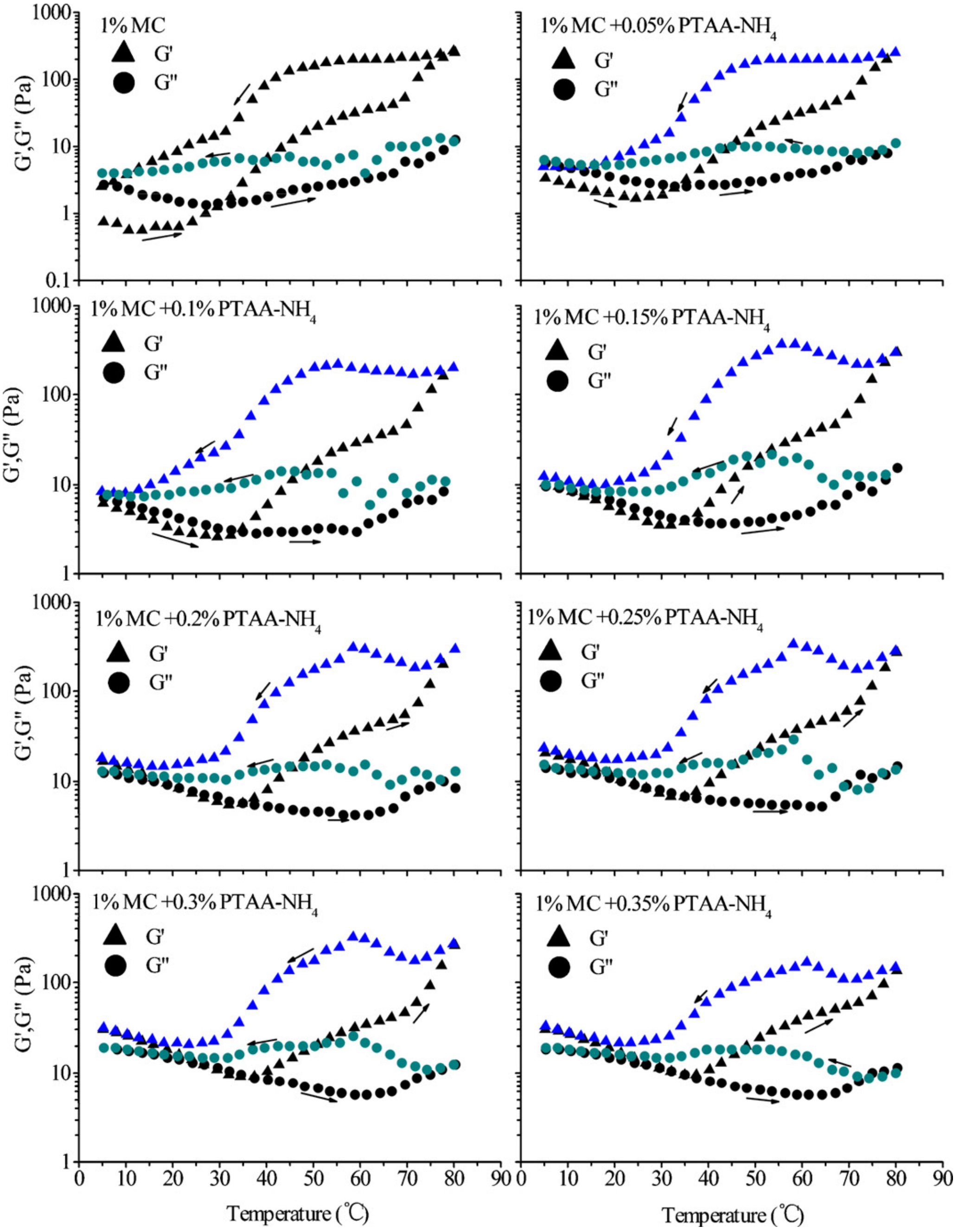

Fig. 3. G' and G'' of 1% MC as a function of temperature without and with addition of various concentrations of PTAA-NH_4 in the heating and cooling processes.

variables. Several kinds of viscosity synergism index have been reported (Dolz, Hernández, Pellicer, & Delegido, 1995; Jiménez, Fresno, & Ramirez, 2007; Kaletunc-Gencer & Peleg, 1986). Accordingly, in order to quantify viscous synergism in our mixed systems, a viscosity synergism index $I_v(\dot{\gamma})$, was defined as follows:

$$I_v(\dot{\gamma}) = \frac{\eta_{i+j}(\dot{\gamma})}{\eta_i(\dot{\gamma}) + \eta_j(\dot{\gamma})} \qquad (3)$$

where $\eta_{i+j}(\dot{\gamma})$, $\eta_i(\dot{\gamma})$ and $\eta_j(\dot{\gamma})$ are the steady shear viscosity corresponding to systems of components i, j, and $i+j$ at concentrations c_i, c_j and $c_{i+j} = c_i + c_j$, respectively. According to this definition, when $I_v(\dot{\gamma}) > 1$, the viscosity of the mixed system would be larger than the sum of the viscosities of the two simple systems, i.e., synergism would result.

The $I_v(\dot{\gamma})$ for various shear rates were calculated according to Eq. (3) and the viscosity data from Fig. 1. Here, instead of using determined viscosity data of pure PTAA-NH_4 solutions, we simply used 0.05 Pa s in all the calculations due to the measurement difficulty at low shear rate for these solutions. It could be seen in Fig. 1 that the viscosities of all the pure PTAA-NH_4 solutions were lower than 0.05 Pa s, therefore the calculated $I_v(\dot{\gamma})$ would be smaller than the actual value. Fig. 2 represents the variation of $I_v(\dot{\gamma})$ in PTAA-NH_4 + MC (1%) systems corresponding to various shear rates as a function of PTAA-NH_4 concentrations at 5 °C. With the increase in concentration of PTAA-NH_4, intermolecular interactions between MC and polythiophene increased, which enhanced the stability of the molecular entanglements, suppressing phase separation, and improving shear tolerance and the viscosity of the solution. Therefore, at all shear rates, $I_v(\dot{\gamma})$ increased with the concentration of

Table 1
The fitting parameters of the power law and Cross model.

[PTAA-NH$_4$] (%)	Power law		Cross model			
	K (Pa s^{-1})	n	η_0 (Pa s)	λ (s)	p	$\dot{\gamma}_0$ (s^{-1})
0	1.50	0.62	0.52	0.009	0.60	111
0.05	4.45	0.49	4.12	0.43	0.57	2.33
0.1	8.59	0.42	13.09	1.12	0.65	0.89
0.15	15.24	0.36	31.35	1.64	0.72	0.61
0.2	22.91	0.31	60.39	2.15	0.78	0.47
0.25	29.01	0.29	83.73	2.39	0.80	0.42
0.3	39.58	0.25	149.48	3.26	0.83	0.31
0.35	48.59	0.24	195.39	3.52	0.84	0.28

PTAA-NH$_4$. In addition, in comparison with the cases for low shear rates where the viscosity synergistic effect is much more evident, the cross-link density of the network in solution would be depleted at high shear rates, thus the viscosity was reduced remarkably, as a result, the increase in $I_v(\dot{\gamma})$ with the concentration of PTAA-NH$_4$ was not so significant.

3.2. *Dynamic viscoelastic measurements*

In order to investigate the effect of PTAA-NH$_4$ on the gelation of MC, dynamic viscoelastic measurements were performed at different temperatures for the aqueous 1% MC solution at different polyanion concentrations. In Fig. 3, both moduli of G' and G'' for the 1% MC solutions at various PTAA-NH$_4$ concentrations were shown as a function of temperature in the heating and cooling processes.

According to Fig. 3, on heating, G' decreased log-linearly with temperature from 5 °C to ca. 40 °C. This was attributed to the increase in MC chain mobility and weakened hydrogen bonding between the hydroxyl groups on the glucopyranosyl residues and water (Owen, Tung, & Paulson, 1992). On further heating the gradual increase in G' observed above 40 °C can be considered to be caused by the partial formation of aggregates or clusters through the hydrophobic association (Kobayashi et al., 1999). On the other hand, G'' slightly decreased with temperature while G' began to increase. This difference between G' and G'' in this region suggests that the evolution of the hydrophobic association mainly contributes to the increase in the elasticity of the system. The thermally induced increase in the number of hydrophobically associative aggregates made the solution undergo the critical point at which G' began to override G'' and the connectivity of the polymer chains across the system volume was then established (Li et al., 2001). The temperatures at the crossover of G' and G'' as a function of PTAA-NH$_4$ concentration were plotted in Fig. 4. The crossover temperature (crossover temperature 1) could be approximately expressed as a positive function of PTAA-NH$_4$ concentration, PTAA-NH$_4$ showing an effect of somewhat salt-in similar to that of some salts as revealed by Li, Liu, and Lim (2007). Interestingly, when the concentration of PTAA-NH$_4$ was higher than 0.15%, weak gel-like behavior of the mixtures with $G' > G''$ could be observed in low temperature range. This phenomenon disappeared upon further heating with $G' < G''$ (this crossover temperature 2 corresponding to the crossover point of G' and G'' was also shown in Fig. 4). As an amphiphilic polymer, PTAA-NH$_4$ may interact with water and MC by hydrogen bonding at low temperatures. It is expectable that PTAA-NH$_4$ might act as bridges between the MC chains, playing the role of cross-linking points. As shown in Fig. 4, with the increase of the concentration of PTAA-NH$_4$, the interaction became stronger, resulting in the crossover temperature 2 shifting to higher temperatures.

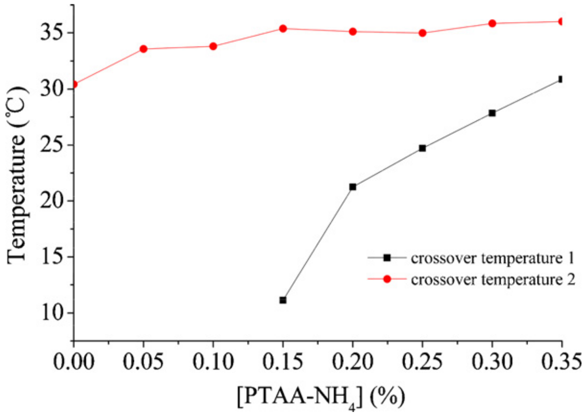

Fig. 4. Crossover temperature of G' and G'' as a function of PTAA-NH$_4$ concentration for 1% MC aqueous solutions containing PTAA-NH$_4$ during a heating process at 5 °C/min.

In Fig. 3, a remarkable increase in G' on heating was observed at high temperatures due to significant induction of the phase separation of the hydrophobic parts from the hydrophilic matrix. In contrast to the sharp increase of G' on heating in the high temperature range, the gradual decrease in G' with temperature on cooling showed an outstanding deviation from the heating curve. This clearly indicates that the thermally induced hydrophobic dissociation is not an exact reversal of the hydrophobic association occurring in the heating process (Xu & Li, 2005). In addition, a re-entrant change in G' in high temperature range of 80–60 °C on cooling was found in the presence of PTAA-NH$_4$, which needs to clarify further.

In order to further understand the effect of PTAA-NH$_4$ on the rheological properties of MC solutions, the G' of 1% MC without and with addition of various concentrations of PTAA-NH$_4$ was shown as a function of temperature in the heating and cooling cycle, respectively, in Fig. 5. With the increase in the concentration of PTAA-NH$_4$, G' increased significantly at the temperatures lower than ca. 30 °C whereas at higher temperatures, the G' curves did not change significantly with the PTAA-NH$_4$ content; this indicates that while the addition of PTAA-NH$_4$ influenced the rheological properties of MC, the strength of gels formed would not be affected so much by the addition of polyanions. The addition of PTAA-NH$_4$ did not change the patterns of the gelation and degelation of MC, but it suppressed the sol–gel transition of MC by shifting to higher temperatures (Fig. 4).

3.3. *Thermal behavior*

Fig. 6 shows the calorimetric thermograms for PTAA-NH$_4$ solutions and 1% MC solutions without and with addition of various concentrations of PTAA-NH$_4$ on heating and cooling, respectively. While no peaks were found on the curves of pure PTAA-NH$_4$ solutions, for MC and the mixed solutions, pronounced endothermic and exothermic peaks were observed in both heating and cooling processes, respectively. The endothermic peaks at on heating corresponded to the sharp increase in G' (cf. Fig. 5a). The endothermic

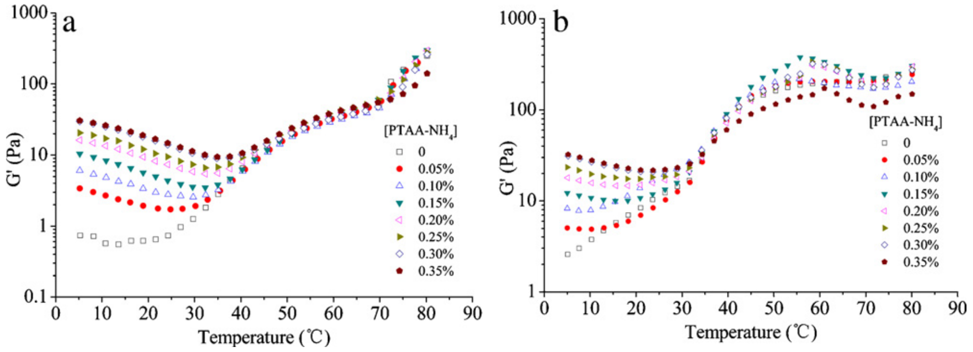

Fig. 5. *G*′ of 1% MC as a function of temperature without and with addition of various concentrations of PTAA-NH$_4$ in heating (a) and cooling (b) processes. Legend shows the different concentrations of PTAA-NH$_4$ used.

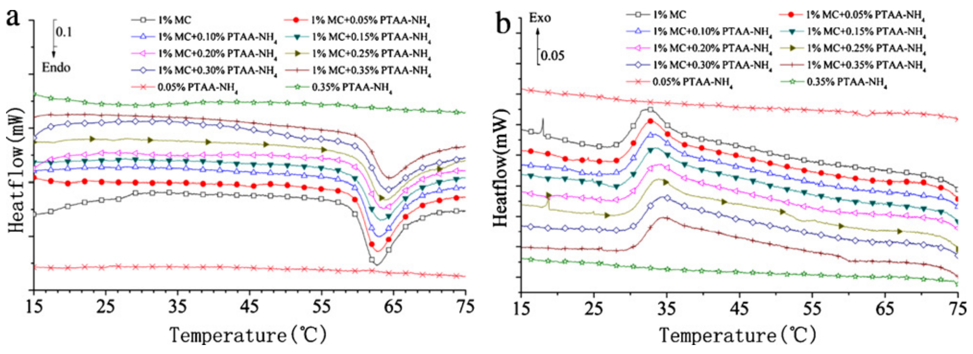

Fig. 6. Calorimetric thermograms for pure PTAA-NH$_4$ solutions and 1% MC solutions without and with addition of various concentrations of PTAA-NH$_4$ during heating (a) and cooling (b) processes at 1 °C/min.

energy is consumed to break the cage structures formed between the methyl groups of MC and water molecules. The exothermic peaks on cooling corresponded to the sharp drop in *G*′ (cf. Fig. 5b); this step can be considered as the massive destruction of the whole gel network. Below this gel–sol transition temperature, all the hydrophobic junctions were disintegrated so that MC chains became free again. Simultaneously, the arrangement of water molecules for the re-formation of the cage structures takes place so that the large exothermic heat is required (Li et al., 2002). As for as the influence of PTAA-NH$_4$ on the sol–gel transition of MC was concerned, Fig. 7 shows the endothermic and exothermic peak temperatures in the heating and cooling processes for 1% MC solutions with different concentration of PTAA-NH$_4$. As showed in Fig. 7, with PTAA-NH$_4$ content increasing, both the endothermic and exothermic peaks shifted to higher temperatures. That is, PTAA-NH$_4$ exhibited the symptom of a salt-in behavior that delays the occurrence of the sol–gel transition. Therefore, on heating it is more difficult for MC to form hydrophobic aggregates compared with pure MC solution at the same temperature. To reach the critical requirement for intermolecular hydrophobic association, more energy is needed, thus leading to a higher sol–gel transition temperature. On cooling the gel formed in the presence of PTAA-NH$_4$ could be molten at relatively high temperature compared with pure MC gel as revealed in Fig. 7.

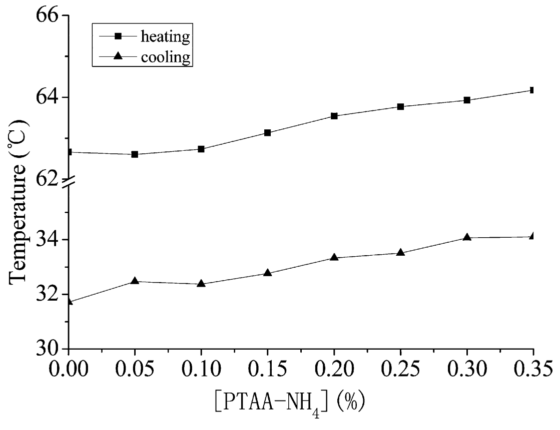

Fig. 7. Endothermic and exothermic peak temperatures in the heating and cooling processes for 1% MC solutions with various concentrations of PTAA-NH$_4$.

4. Conclusion

The present work investigated the steady flow, dynamic rheological behaviors of MC solutions at different concentrations of PTAA-NH$_4$. The effect of PTAA-NH$_4$ on the thermoreversible sol–gel transition behavior of MC was also studied rheologically and microcalorimetrically.

The flow curves could be satisfactorily fitted by the power law and Cross model. The mixture solutions of MC and PTAA-NH$_4$ showed more remarkable shear thinning behavior than pure MC solutions at low temperatures. The pseudoplastic character of the mixtures became more pronounced as the concentration of PTAA-NH$_4$ increased. Remarkable viscous synergism was found in the mixtures and the viscous synergism index evidently increased with the PTAA-NH$_4$ concentration especially at low shear rates.

Rheological dynamic measurements revealed the occurrence of two kinds of crossover temperatures corresponding to the cross points of *G*′ and *G*″ in the temperature ranges of 10–30 °C and 30–35 °C, respectively, depending on the concentration of PTAA-NH$_4$. At low temperatures, PTAA-NH$_4$ with sufficient concentrations more than 0.15%, might act as bridges between the MC chains, giving rise to weak gel-like behavior of the mixtures. At relatively high temperatures, PTAA-NH$_4$ showed a salt-in effect, thereby suppressing the sol–gel transition of MC. Calorimetric thermograms showed that no peaks could be found on the DSC curves of pure PTAA-NH_4 solutions, but in comparison with pure MC solutions, for the mixed solutions of MC and PTAA-NH_4, with the increase of PTAA-NH_4 content, both the endothermic peak on heating and the exothermic peak cooling shifted to higher temperatures, indicating that PTAA-NH_4 delayed the occurrence of the sol–gel transition of MC as consistent with the rheological results.

Acknowledgements

The authors are thankful for the financial support for this work from the National Natural Science Foundation of China (Grant no. 21074071) and the Shanghai Leading Academic Discipline Project (no. B202).

References

Alemán, C., Teixeira-Dias, B., Zanuy, D., Estrany, F., Armelin, E., & del Valle, L. J. (2009). A comprehensive study of the interactions between DNA and poly(3,4-ethylenedioxythiophene). *Polymer*, *50*(8), 1965–1974.

Bhowmik, M., Das, S., Sinha, J., Bag, S., Chattopadhyay, D., & Ghosh, L. K. (2010). Methyl cellulose based sustained release thermosensitive in situ fast gelling ocular delivery of ketorolac tromethamine. *Asian Journal of Chemistry*, *22*(3), 2147–2154.

Bresolin, T. M. B., Milas, M., Rinaudo, M., & Ganter, J. L. M. S. (1998). Xanthan–galactomannan interactions as related to xanthan conformations. *International Journal of Biological Macromolecules*, *23*(4), 263–275.

de Souza, J. M., & Pereira, E. C. (2001). Luminescence of poly(3-thiopheneacetic acid) in alcohols and aqueous solutions of poly(vinyl alcohol). *Synthetic Metals*, *118*(1–3), 167–170.

Desbrières, J., Hirrien, M., & Ross-Murphy, S. B. (2000). Thermogelation of methylcellulose: Rheological considerations. *Polymer*, *41*(7), 2451–2461.

Diamant, H., & Andelman, D. (2000). Self-assembly in mixtures of polymers and small associating molecules. *Macromolecules*, *33*(21), 8050–8061.

Dolz, M., Hernández, M. J., Pellicer, J., & Delegido, J. (1995). Shear stress synergism index and relative thixotropic area. *Journal of Pharmaceutical Sciences*, *84*(6), 728–732.

Donati, I., Haug, I. J., Scarpa, T., Borgogna, M., Draget, K. I., Skjak-Braek, G., et al. (2007). Synergistic effects in semidilute mixed solutions of alginate and lactose-modified chitosan (chitlac). *Biomacromolecules*, *8*(3), 957–962.

El Ghzaoui, A., Trompette, J. L., Cassanas, G., Bardet, L., & Fabregue, E. (2001). Comparative rheological behavior of some cellulosic ether derivatives. *Langmuir*, *17*(5), 1453–1456.

Giglioti, M., Trivinho-Strixino, F., Matsushima, J. T., Bulhões, L. O. S., & Pereira, E. C. (2004). Electrochemical and electrochromic response of poly(thiophene-3-acetic acid) films. *Solar Energy Materials and Solar Cells*, *82*(3), 413–420.

Green, R. A., Lovell, N. H., & Poole-Warren, L. A. (2010). Impact of co-incorporating laminin peptide dopants and neurotrophic growth factors on conducting polymer properties. *Acta Biomaterialia*, *6*(1), 63–71.

Guimard, N. (2008). *Biodegradable electroactive materials for tissue engineering applications*. TX, United States: The University of Texas at Austin. (Ph.D. Dissertation).

Gupta, D., Tator, C. H., & Shoichet, M. S. (2006). Fast-gelling injectable blend of hyaluronan and methylcellulose for intrathecal, localized delivery to the injured spinal cord. *Biomaterials*, *27*(11), 2370–2379.

Haque, A., & Morris, E. R. (1993). Thermogelation of methylcellulose. Part I: Molecular structures and processes. *Carbohydrate Polymers*, *22*(3), 161–173.

Hirrien, M., Chevillard, C., Desbrières, J., Axelos, M. A. V., & Rinaudo, M. (1998). Thermogelation of methylcelluloses: New evidence for understanding the gelation mechanism. *Polymer*, *39*(25), 6251–6259.

Jiménez, M. M., Fresno, M. J., & Ramirez, A. (2007). Rheological study of binary gels with Carbopol (R) Ultre (TM) 10 and hyaluronic acid. *Chemical & Pharmaceutical Bulletin*, *55*(8), 1157–1163.

Kaletunc-Gencer, G., & Peleg, M. (1986). Rheological characteristics of selected food gum mixtures in solution. *Journal of Texture Studies*, *17*(1), 61–70.

Kim, D. H., Wiler, J. A., Anderson, D. J., Kipke, D. R., & Martin, D. C. (2010). Conducting polymers on hydrogel-coated neural electrode provide sensitive neural recordings in auditory cortex. *Acta Biomaterialia*, *6*(1), 57–62.

Kobayashi, K., Huang, C. I., & Lodge, T. P. (1999). Thermoreversible gelation of aqueous methylcellulose solutions. *Macromolecules*, *32*(21), 7070–7077.

Kumar, S., Haglund, B. O., & Himmelstein, K. J. (1994). In situ-forming gels for ophthalmic drug delivery. *Journal of Ocular Pharmacology*, *10*(1), 47–56.

Li, L. (2002). Thermal gelation of methylcellulose in water: Scaling and thermoreversibility. *Macromolecules*, *35*(15), 5990–5998.

Li, L., Liu, E., & Lim, C. H. (2007). Micro-DSC and rheological studies of interactions between methylcellulose and surfactants. *Journal of Physical Chemistry B*, 6410–6416.

Li, L., Shan, H., Yue, C. Y., Lam, Y. C., Tam, K. C., & Hu, X. (2002). Thermally induced association and dissociation of methylcellulose in aqueous solutions. *Langmuir*, *18*(20), 7291–7298.

Li, L., Thangamathesvaran, P. M., Yue, C. Y., Tam, K. C., Hu, X., & Lam, Y. C. (2001). Gel network structure of methylcellulose in water. *Langmuir*, *17*(26), 8062–8068.

Lin, J., Wen, Z. Y., Liu, Y., Xu, X. G., Song, S. F., & Li, N. (2009). Rheological behavior of aqueous polymer-plasticized gamma-$LiAlO_2$ pastes for plastic forming. *Ceramics International*, *35*(6), 2289–2293.

Malitesta, C., Guascito, M. R., Mazzotta, E., & Picca, R. A. (2010). X-ray photoelectron spectroscopy characterization of electrosynthesized poly(3-thiophene acetic acid) and its application in molecularly imprinted polymers for atrazine. *Thin Solid Films*, *518*(14), 3705–3709.

Martin, B. C., Minner, E. J., Wiseman, S. L., Klank, R. L., & Gilbert, R. J. (2008). Agarose and methylcellulose hydrogel blends for nerve regeneration applications. *Journal of Neural Engineering*, *5*(2), 221–231.

Mukherjee, P., Dawn, A., & Nandi, A. K. (2010). Biomolecular hybrid of poly(3-thiophene acetic acid) and double stranded DNA: Optical and conductivity properties. *Langmuir*, *26*(13), 11025–11034.

Nilsson, K. P. R., Herland, A., Hammarstrom, P., & Inganas, O. (2005). Conjugated polyelectrolytes: Conformation-sensitive optical probes for detection of arnyloid fibril forrnation. *Biochemistry*, *44*(10), 3718–3724.

Onoda, M., Abe, Y., & Tada, K. (2009). New fabrication technique of conductive polymer/insulating polymer composite films and evaluation of biocompatibility in neuron cultures. *Thin Solid Films*, *518*(2), 743–749.

Owen, S. R., Tung, M. A., & Paulson, A. T. (1992). Thermorheological studies of food polymer dispersions. *Journal of Food Engineering*, *16*(1–2), 39–53.

Pellicer, J., Delegido, J., Dolz, J., Dolz, M., Hernandez, M. J., & Herraez, M. (2000). Influence of shear rate and concentration ratio on viscous synergism. Application to xanthan–locust bean gum–NaCMC mixtures. *Food Science and Technology International*, *6*(5), 415–423.

Peressini, D., Bravin, B., Lapasin, R., Rizzotti, C., & Sensidoni, A. (2003). Starch-methylcellulose based edible films: Rheological properties of film-forming dispersions. *Journal of Food Engineering*, *59*(1), 25–32.

Rojas, M. R., Muller, A. J., & Saez, A. E. (2008). Synergistic effects in flows of mixtures of wormlike micelles and hydroxyethyl celluloses with or without hydrophobic modifications. *Journal of Colloid and Interface Science*, *322*(1), 65–72.

Sovilj, V., & Petrovic, L. (2007). Interaction and phase separation in the system HPMC/NaCMC/SDS. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *298*(1–2), 94–98.

Svennersten, K., Bolin, M. H., Jager, E. W. H., Berggren, M., & Richter-Dahlfors, A. (2009). Electrochemical modulation of epithelia formation using conducting polymers. *Biomaterials*, *30*(31), 6257–6264.

Tako, M. (1992). Synergistic interaction between xanthan and konjac glucomannan in aqueous media. *Bioscience, Biotechnology, and Biochemistry*, *56*(8), 1188–1192.

Tang, Y., Wang, X., Li, Y., Lei, M., Du, Y., Kennedy, J. F., et al. (2010). Production and characterisation of novel injectable chitosan/methylcellulose/salt blend hydrogels with potential application as tissue engineering scaffolds. *Carbohydrate Polymers*, *82*(3), 833–841.

Xiao, Y., Li, C. M., Wang, S., Shi, J., & Ooi, C. P. (2010). Incorporation of collagen in poly(3,4-ethylenedioxythiophene) for a bifunctional film with high bio- and electrochemical activity. *Journal of Biomedical Materials Research – Part A*, *92*(2), 766–772.

Xu, Y., & Li, L. (2005). Thermoreversible and salt-sensitive turbidity of methylcellulose in aqueous solution. *Polymer*, *46*(18), 7410–7417.

Yasar, K., Kahyaoglu, T., & Sahan, N. (2009). Dynamic rheological characterization of salep glucomannan/galactomannan-based milk beverages. *Food Hydrocolloids*, *23*(5), 1305–1311.

Yin, Y. M., Zhang, H. B., & Nishinari, K. (2007). Voltammetric characterization on the hydrophobic interaction in polysaccharide hydrogels. *Journal of Physical Chemistry B*, *111*(7), 1590–1596.

Zhang, F. X., & Srinivasan, M. P. (2005). Cross-linked polyimide-polythiophene composite films with reduced surface resistivities. *Thin Solid Films*, *479*(1–2), 95–102.

Zhang, L. M., & Zhou, J. F. (2006). Synergistic viscosity characteristics of aqueous mixed solutions of hydroxypropyl- and carboxymethyl hydroxypropyl-substituted guar gums. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *279*(1–3), 34–39.