Carbohydrate Polymers 85 (2011) 276–279

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Short communication

Effect of intermolecular interaction on electrospinning of sodium alginate

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ARTICLE INFO

Article history:
Received 7 January 2011
Received in revised form 20 January 2011
Accepted 27 January 2011
Available online 3 February 2011

Keywords:
Sodium alginate
Electrospinning
Nanofiber

ABSTRACT

Fabrication of sodium alginate (SA) nanofibers from its aqueous solutions by electrospinning is still a challenge, because of its rigid chain conformation and lack of chain entanglements. In this study, the electrospinnability was improved by introducing Ca^{2+} cations to SA solutions. Rheological behavior of the electrospinning solutions was investigated. The physical properties of the solutions were also studied by a surface tension meter and a conductivity meter. The results showed that Ca^{2+} cations enhanced the intermolecular interactions of SA solutions, and improved the electrospinnability of SA solutions.

1. Introduction

Electrospinning is a technique that could fabricates fibers with the diameters in range of a few hundred nanometers. Due to the high surface-to-volume ratio, nanofibers have been already applied in many difference areas (Agarwal, Greiner, & Wendorff, 2008; Li & Xia, 2004). Various biopolymers have been electrospun into nanofibers for an extensive applications, for instance in tissue engineering (Blasioli, Kaplan, Kim, Kim, & Wang, 2006), drug delivery (Recum & Sill, 2008), wound dressing (Jafari, Rezaeian, Ranaei-Siadat, Supaphol, & Zahedi, 2010), etc.

Sodium alginate (SA) is naturally derived linear copolymer of 1,4-linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) units (Fig. 1) in various composition and sequence, and exists widely in brown seaweeds (Shull & Webber, 2004). SA has been widely used in bio-applications including tissue engineering (Mooney & Lee, 2001) and drug delivery (Chen et al., 2004) in the form of alginate hydrogels, due to its excellent biocompatibility, biodegradability and nontoxicity.

Many research groups have successfully fabricated SA electrospun fibers by blending SA with poly(ethylene oxide) (PEO) or poly(viny alcohol) (PVA) (Islam & Karim, 2010; Lee & Lyoo, 2009). The important effect of conductive, surface tension and viscosity of the solutions in electrospinning of SA/PEO system were also investigated (Guo, Hu, Lu, Yu, & Zhu, 2006). In addition, He et al. (2009) studied the effect of chain entanglements on electrospinnability of SA by blending SA with PEO. However, few articles have reported to fabricate pure SA fibers via electrospinning because of poor electrospinnability of the solutions. Nevertheless, He et al. (2008) fabricated pure SA nanofibers by introducing a strong polar co-solvent, glycerol into the SA aqueous solutions. They emphasized entanglement on improving electrospinnability of SA.

The chain entanglement was considered as a key factor for improving the electrospinnability of SA solutions (Bates, Frisch, Shenoy, & Wnek, 2005; He et al., 2009). However, we considered chain entanglement as one of intermolecular interactions, and insisted that the way to improve the interactions, for instance hydrogen bond or electrostatic force could also improve the electrospinnability. Considered the polyanion structure of SA chains, electrostatic force was used to increase the intermolecular interactions of SA chains, thus improving the electrospinnability.

In this study, a divalent cation, Ca^{2+}, was used to increase the intermolecular interactions via increasing the ionic interactions among SA chains. SA fibers were successfully obtained by introducing Ca^{2+} cations and a complex solvent to SA solutions. The effect of Ca^{2+} cations on improving electrospinnability of SA solutions was studied. Furthermore, the influence of solution physical properties on the electrospinnability and fiber morphology was also investigated.

2. Materials and experimental

2.1. Materials

Sodium alginate (SA 1.28 Pa s for a 2 wt% aqueous solution at 30 °C) was purchased from Sinopharm Chemical Reagent Co.

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doi:10.1016/j.carbpol.2011.01.054

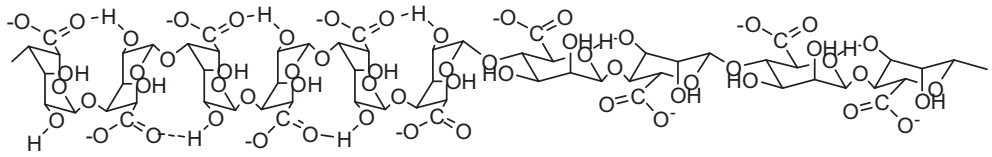

Fig. 1. Chemical structure of SA chain conformation.

Ltd. Ethanol obtained from Danfeng Chemical Reagent Co. Ltd. (Jiangsu China). N,N-dimethylformamide (DMF) was supplied by Zhejiang Sunrise Chemicals Co. Ltd. (Zhejiang, China). Calcium chloride ($CaCl_2$) was obtained from Beijing Chemical Co. Ltd. (Beijing China). All the materials were used without further purification.

2.2. Electrospinning

SA solutions were prepared by dissolving SA powder into deionized water with stirring. Then a complex solvent ($m_{\text{deionized water}}/m_{\text{ethanol}}/m_{\text{DMF}} = 75/15/10$) was added. $CaCl_2$ was introduced into the solutions by dropping $CaCl_2$ aqueous solutions slowly, and the mass ratio of $CaCl_2$ to SA varied from 0.5 wt% to 2 wt%. The concentration of SA solutions was fixed at 1.5 wt%. A high voltage power supply (BGG4-21, BMEI Co. Ltd.) was employed to generate the high voltage, and the voltage was 20 kV in this study. The tip-to-collector distance was fixed at 10 cm. The SA solutions were loaded into 5 mL syringe, and the inner diameter of metal needle was 0.7 mm. After electrospinning, the SA fibers were dried in vacuum oven at temperature 40 °C overnight to dry off remaining solvent.

2.3. Characterization

The morphologies of the fibers were observed by field emission scanning electron microscopy (FE-SEM, S-4700, Hitachi) at accelerating voltage of 20 kV. Each sample was coated with gold for analysis.

The conductivity of SA solutions was measured by conductivity meter (DDS-307A, Rex Shanghai, China).

The surface tension of the SA solutions was measured by surface tension meter (DCAT21, EASTERN-DATAPHY).

The rheological properties of SA solutions were analyzed on AR Rheometer (TA Instruments, USA) at 30 °C. Frequency sweeps were carried out for angular frequencies $\omega = 0.1–100\ \text{rad}\ \text{s}^{-1}$ at strain

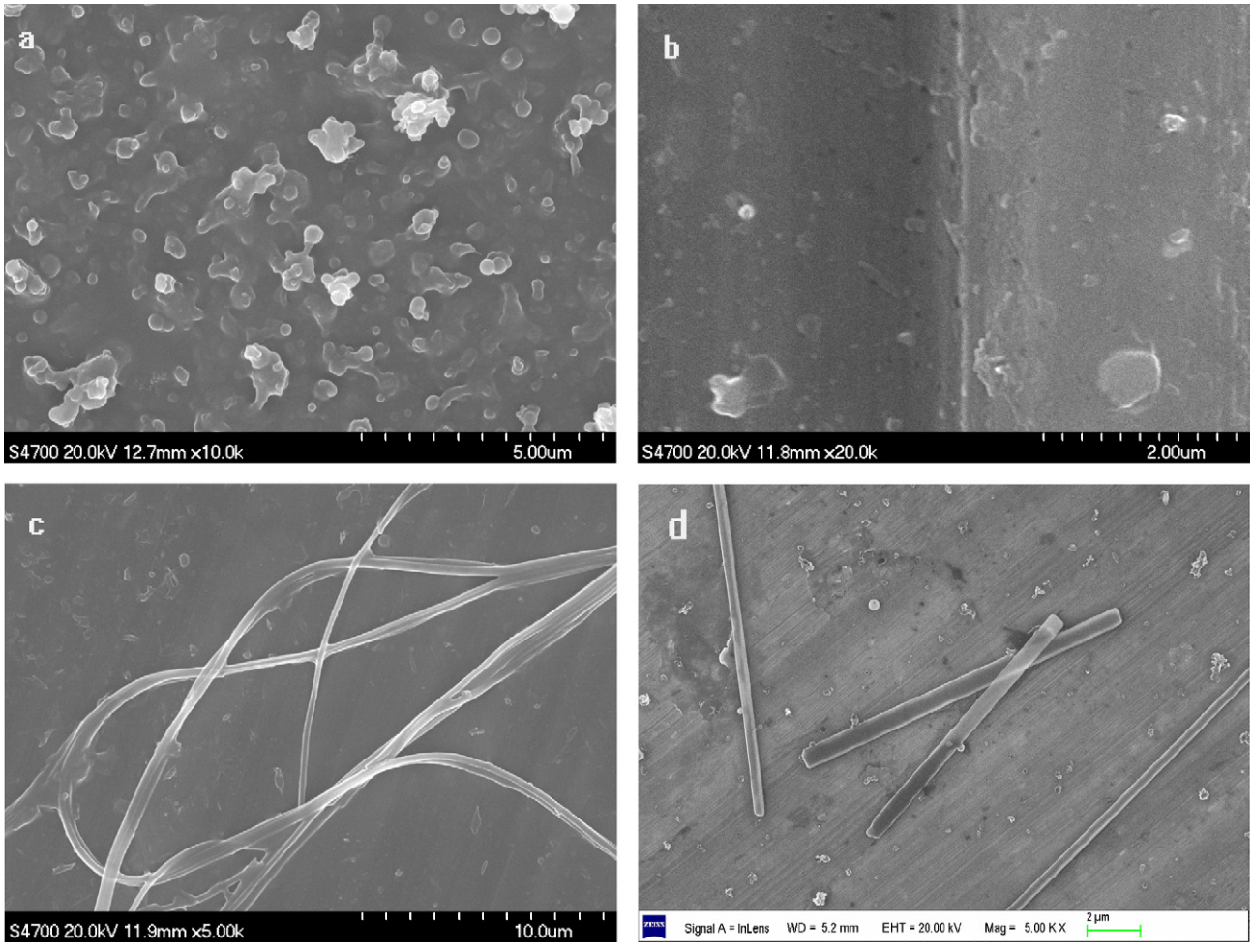

Fig. 2. SEM images of SA fibers electrospun from SA solutions with different mass ratio of $CaCl_2$ to SA (a) 0, (b) 0.5 wt%, (c) 1 wt% and (d) 2 wt%.

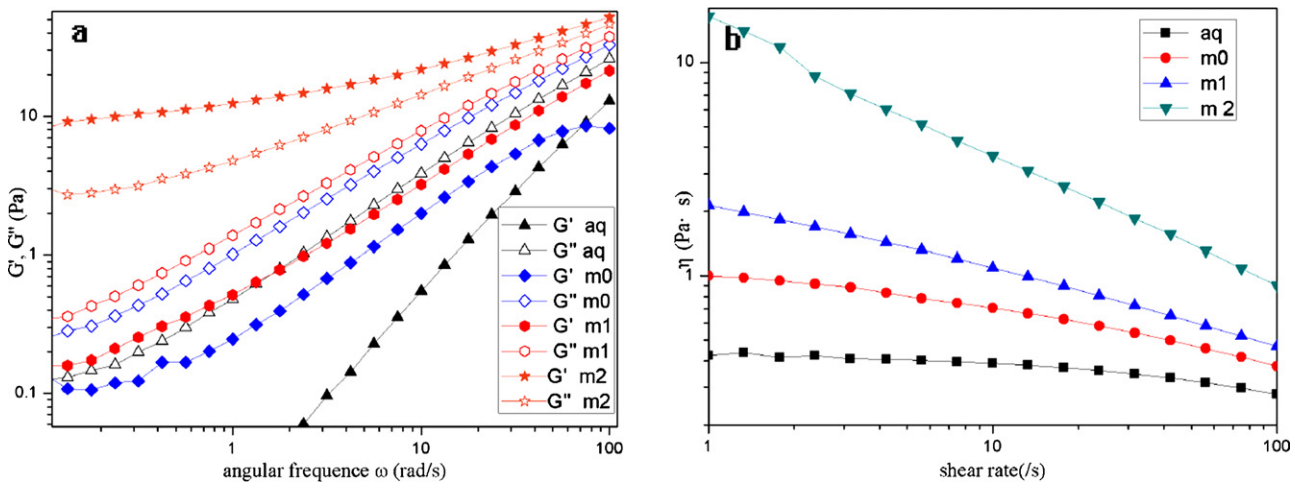

Fig. 3. Storage (G') and loss (G'') modulus (a) of SA solutions as functions of frequency at 30 °C and viscosity (b) of SA solutions as a function of shear rate. 'aq' represent SA aqueous solutions, '*m*0', '*m*1' and '*m*2' represent SA complex solvent solutions with the mass ratio of $CaCl_2$ to SA was 0, 1 wt% and 2 wt%, respectively.

Table 1
Physical properties of SA solutions.

$M_{DW}/m_{EtOHI}/m_{DMF}$	R_{CaCl_2} (wt%)	Conductivity (μS/cm)	Surface tension (mN/m)	Viscosity[a] (Pa s)
100/0/0	0	2.75×10^3	60.5	0.42
75/15/10	0	1.75×10^3	47.6	1.00
75/15/10	1	2.0×10^3	48.0	2.13
75/15/10	2	0.38×10^4	–	16.4

[a] Viscosity was measured by AR rheometer at shear rate of 1 s^{-1}; – the date was not measured.

amplitude of 1%. Shear measurements were performed in a range of shear rates from 1 to100 s^{-1}.

3. Result and discussion

The effect of Ca^{2+} cations on the electrospinnability of SA solution was studied by varying the mass ratio of $CaCl_2$ to SA. Only irregular droplets were collected when the solutions without $CaCl_2$, as shown in Fig. 2a. As the mass ratio of $CaCl_2$ to SA was 0.5 wt%, fibers were still not obtained (Fig. 2b), but the fallen droplets were disappeared. And the Taylor cone tended to break up when the applied voltage increased. The 1 wt% of the ratio led to continuous electrospinning and long fibers (Fig. 2c). However, when the ratio grew up to 2 wt%, the jet was not found. As increased the electrospinning voltage to 30 kV, the jet was observed, whereas the fibers were cracked into short nano-rod (Fig. 2d). The results showed that Ca^{2+} cations improved the electrospinnability of SA solutions. However, the electrospinnability of SA solutions decreased when the ratio of Ca^{2+} cations to SA surpass a critical value. The reason might be that the SA solution was gelled by Ca^{2+} cations, and the molecular chain could not move independently. The intermolecular interactions of SA were enhanced by Ca^{2+} cations via increasing the ionic interactions (Draget et al., 2000). It could be inferred that the increase of the intermolecular interactions of SA chains could improved the electrospinnability of SA solutions.

Fig. 3 compares the rheological behavior of the electrospinning solutions with and without Ca^{2+} cations. As expected, lack of Ca^{2+} cations led to low value of both G' and G''. As the Ca^{2+} cations introduced to the solutions the value was increased, and when the ratio of $CaCl_2$ to SA was 2 wt%, the value of G' was greater than G'' which indicated that the solution had partly gelled. In Fig. 3b, an approximate Newtonian liquid behavior was observed in SA aqueous solution. As the increase of Ca^{2+} cations content in SA solutions, the shear-thinning behavior was became apparently. The rheological results proved that the intermolecular interactions were enhanced by introducing Ca^{2+} cations to the solutions. The

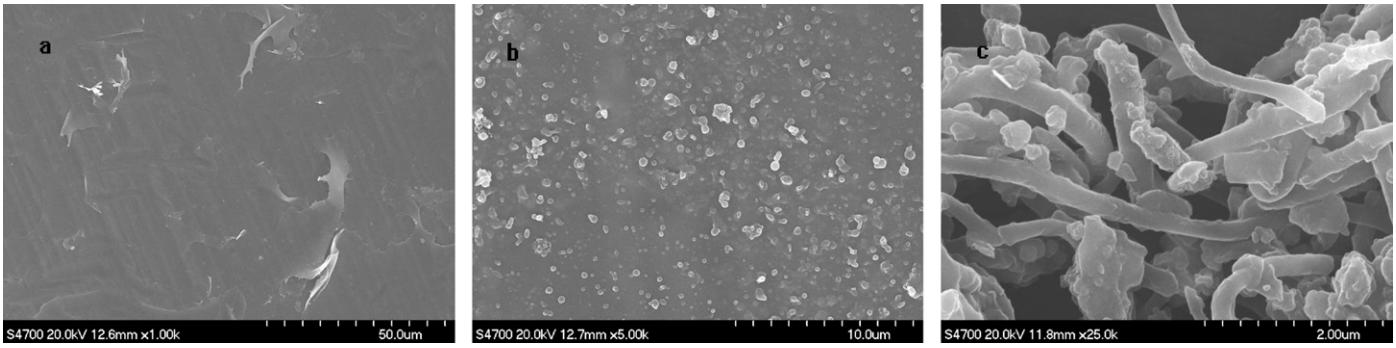

Fig. 4. SEM images of SA fibers electrospun from SA solutions with different solvent composition (a) SA aqueous solutions without component solvent added in, (b) SA solution with component solvent added in and without $CaCl_2$ added in and (c) SA aqueous solution with component solvent and $CaCl_2$ added in the concentration of SA solutions were fix at 1.5 wt%.

contribution of enhanced intermolecular interactions was considered as the key reason for improving the electrospinnability of SA solutions.

The effect of complex solvent was also investigated. Table 1 showed the physical properties of SA solutions with different solvent composition. It is showed that the surface tension and conductivity of the solutions were obviously decreased after adding complex solvent. The influence of complex solvent on the morphology of electrospun fibers showed in Fig. 4. The results proved that the complex solvent could not improve the electrospinnability of the solution. In addition, Fig. 3 showed that the complex solvent was not significant increased the chain entanglement. The critical voltage of fluid jet initiated tend to increase linearly with the surface tension of the polymer solutions (Bang, Jung, Kim, Lee, & Lee, 2003). Thus, the main contribution of the complex solvent was that it could obviously decrease the surface tension of the solutions, and help to form a continuous fluid jet.

4. Conclusions

In this study, pure SA fibers were obtained by electrospinning via introduced Ca^{2+} cations to SA aqueous solutions. The results of rheological showed that Ca^{2+} cations increased the storage modulus, loss modulus and viscosity of the solutions by increasing ionic interactions among SA chains. The increase of intermolecular interactions and decrease of surface tension were the key factor of improving the electrospinnability of SA solutions. The study provided a method to electrospinning pure SA solutions.

Acknowledgements

The author would like to thank the project supported by the Natural Science Foundation of Jiangsu Province (BK2010190) for its financial support. This study was also supported by Open Fund from State Key Laboratory of Chemical Resource Engineering.

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