

Polymer Communication

Effect of spinning temperature and blend ratios on electrospun chitosan/poly(acrylamide) blends fibers

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ABSTRACT

We report the formation of non-woven fibers without bead defects by electrospinning blend solutions of chitosan and polyacrylamide (PAAm) with blend ratios varying from 75 wt% to 90 wt% chitosan using a modified electrospinning unit wherein polymer solutions can be spun at temperatures greater than ambient up to 100 °C. Electrospinning at elevated temperature leads to further expansion of the processing window, by producing fibers with fewer defects at higher chitosan weight percentage in the blends. Effects of varying blend ratios, spinning temperatures, and molecular weights on fiber formation were studied and optimum conditions for formation of uniform non-woven fiber mats with potential applications for air and water filtration were obtained. Uniform bead-less fiber mats with fiber diameter as low as 307 ± 67 nm were formed by spinning 90% chitosan in blend solutions at 70 °C.

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1. Introduction

Chitosan is a naturally occurring nontoxic and biodegradable biopolymer made from the second most abundant polysaccharide chitin [1,2]. Chitosan, a polycation, is a copolymer of *N*-acetyl-D-glucosamine and D-glucosamine, and the D-glucosamine content is dependent on the degree of deacetylation (DDA) of chitin to chitosan. Chitosan has been widely studied owing to its unique properties of binding toxic heavy metal ions [3] and its ability to inhibit the growth of a wide variety of fungi, yeasts and bacteria making it an anti-microbial polymer [4]. These properties are a result of the polycationic nature of chitosan arising from the protonation of $-NH_2$ groups on the chitosan backbone [5] and demonstrate the need for fabrication of non-woven filter media from chitosan for air and water filtration applications.

Electrospinning is a widely studied and sought after process for making nanometer sized non-woven fiber mats. A polymer solution, when electrostatically charged, can produce non-woven polymeric fibers in desired size ranges by controlling the physical properties of the polymer solution and the spinning process parameters [6,7]. A wide variety of research has been done in this field optimizing the spinnability of numerous synthetic polymers for potential applications in a broad variety of fields such as filtration, tissue engineering etc. [8,9]. Fiber formation is primarily governed by the viscosity of the polymer solution and strength of the applied electric field. The viscosity of the polymer solution

depends on the concentration of polymer in the solution and the structure of the polymer. The concentration of polymer in solution must be well above the critical chain overlap concentration (c^*) near the entanglement limit for the formation of uniform bead-less nanofibers [10].

Electrospinning of chitosan has been a topic of immense interest in recent years and is limited by its insolubility in common organic solvents used for electrospinning. Pure chitosan has been electrospun from acetic acid [11], environmentally harmful solvent trifluoroacetic acid [12] and 1,1,1,3,3,3-hexafluoro-2-propanol [13]. However, fibers formed using trifluoroacetic acid are readily dissolved in aqueous solutions and had to be cross-linked [14]. Chitosan has been blended with other synthetic polymers like poly(ethylene oxide) and poly(vinyl alcohol) [15,16] to form nanometer sized chitosan fiber mats. We have also recently reported the fabrication of bead-less nanofibers using 95% chitosan in chitosan/poly(ethylene oxide) and demonstrated their applicability to bind chromium (Cr(VI)) metal ions [17] using chitosan with high molecular weight ($M_v \sim 1400$ kDa).

The present study focuses on the spinnability of chitosan/poly(acrylamide) (PAAm) blend solutions. Poly(acrylamide) is a hydrophilic, high molecular weight synthetic polymer which like chitosan has $-NH_2$ groups on its side chain and can form hydrogen bonds with other polymers. PAAm has been widely used for waste water treatment as a flocculent to bind heavy metal ions by forming coordination bonds [18] and cationic polyacrylamide has also been used for anti-microbial applications [19]. As chitosan is soluble only in aqueous acids, we modified the conventional electrospinning unit allowing us to heat the charged solution being ejected through the needle and be able to spin solutions at higher temperatures as

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shown in Fig. 1 [17]. Heating the solution would enable us to reduce the viscosity and increase the concentration of polymer in solution. Blends of chitosan/PAAm were prepared in aqueous acetic acid and electrospun at varying blend ratios, solution temperatures and molecular weights.

2. Experimental part

2.1. Materials

Chitosan with two different molecular weights was used. Chitosan of molecular weight $M_v = 1400$ kDa (HMW) with 80% DDA was used as received from Primex Inc, chitosan of lower molecular weight $MW = 100$ kDa (LMW) and 70–80% degree of deacetylation was used as received from Sigma. Polyacrylamide of molecular weight $MW = 5000$ kDa was used as received from Scientific Polymer Inc. The solvent for electrospinning i.e. acetic acid (AA) was used as received from Sigma.

2.2. Electrospinning

The electrospinning apparatus consisted of a metered flow pump (Harvard Apparatus Pump II), a high D.C. voltage supply (Gamma High Voltage Research, Inc. Model HV ES 30P/DAM), and aluminum foils as targets for fiber collection. Electrospinning solutions were prepared by dissolving the required polymers on weight percentage basis in the solvent and stirring the solutions for 24 h to make a well mixed homogenous solution. While making electrospinning solutions the strength of the acid solvent was adjusted to maximize solubility of polymer in solution. The solution was then ejected through a syringe using a syringe flow pump at feed rate of 0.08 ml/min and applying a voltage of 30 kV and tip-target distance of 15 cm.

2.3. Characterization

The electrospun fiber mat was characterized using field emission scanning electron microscope (FESEM, LEO 1525) to study the fiber morphology. The SEM samples were sputter coated with gold to prevent charging during SEM imaging. Image processing software ImageJ was used to measure the fiber diameter from the SEM micrographs. For each sample, fiber diameter was measured at 60 different points. The bead density of the fibers was also measured using the ImageJ image processing software using the SEM micrographs. To measure the bead density the images were first

converted to binary and then thresholded so that there would be a contrast in the beads and the fibers and we would get measure of the fraction of area covered by beads using the analyze particle routine in the software. Measurements were done in triplicates. Shear viscosity of electrospinning solutions was measured using a TA instruments (AR 2000) rheometer. Solutions were subjected to a step shear rate of 0.01 s^{-1} – 100 s^{-1} and zero-shear viscosity and rate index (n) of the solution was calculated by fitting the data to a Carreau model which describes relationship between viscosity and shear rate for pseudoplastic fluids [20]. The compositional analysis of the fiber mats was done using a Mettler Toledo (TGA/SDTA 851^c) thermo gravimetric analyzer (TGA). Samples were weighed and heated at $10 \text{ }^\circ\text{C}/\text{min}$ from $40 \text{ }^\circ\text{C}$ to $500 \text{ }^\circ\text{C}$ and weight loss for each polymer fraction in the fiber measured by calculating area under the respective polymer melting/degradation temperature peak. Fiber diameter and bead density were analyzed using the one-way Anova Tukey–Kramer test to see if there was statistical difference in means between different sample groups using the JMP 6.0 statistical analysis software.

3. Results and discussion

We have reported the difficulties in spinning fibers out of pure chitosan solution and the need for making chitosan blends elsewhere [17]. Chitosan/PAAm blend solutions were prepared with the goal of forming fibers with maximum chitosan content in the blend. Blend solutions were prepared by dissolving both polymer fractions in dilute acetic acid solutions. Initial studies at room temperature showed that both high and low molecular weight chitosan/PAAm blend fibers were formed with 75% chitosan content, but higher chitosan percentage did not lead to uniform fiber formation due to an unstable jet. Fibers obtained with LMW chitosan/PAAm blends were thicker ($421 \text{ nm} \pm 153$) compared to HMW chitosan/PAAm blends ($132 \text{ nm} \pm 55$) due to higher solution concentration resulting in higher viscosity. To produce fibers with increased chitosan content, hot air was blown around the charged needle at various temperatures. Under the spinning conditions used here, it is estimated that the residence time of the solution in the heated needle is of the order of 15 s while it is estimated that the time for the solution in the needle to reach thermal equilibrium with the heated air is of the order of 5 s. Therefore, it can safely be assumed that the solution temperature matches that of the heated air before leaving the needle.

Blowing of hot air helps reduce solution viscosity and increase evaporation rate of the solvent [21]. If temperature is increased closer to the boiling points of the solvent, drying of the jet could cause a large localized increase in viscosity at the tip of the needle. For this reason, we limited the maximum air temperature to $70 \text{ }^\circ\text{C}$ in this study. The air-blowing rate helps improve fiber formation as it improves the spin-draw ratio allowing further stretching of the charged polymer jet during the whipping process [22].

3.1. Effect of blend ratios and solution temperature

Blend solutions were prepared with reducing weight fractions of chitosan in blend starting with 95% chitosan down to chitosan level which allowed formation of nanometer sized, uniform, beadless fibers. Fig. 2 summarizes the effect of blend ratios and spinning solution temperature on fiber formation. It can be seen that with increase in temperature the fiber diameter increases slightly and the bead density decreases. SEM images of electrospun solutions containing 95% chitosan (Fig. 2a) show poor fiber formation at room temperature, and very few fibers are collected on the target. As the temperature is increased (Fig. 2b and c) fiber formation is improved with bead-less fibers formed at $70 \text{ }^\circ\text{C}$. When chitosan content was reduced to 90% (Fig. 2d–f) with

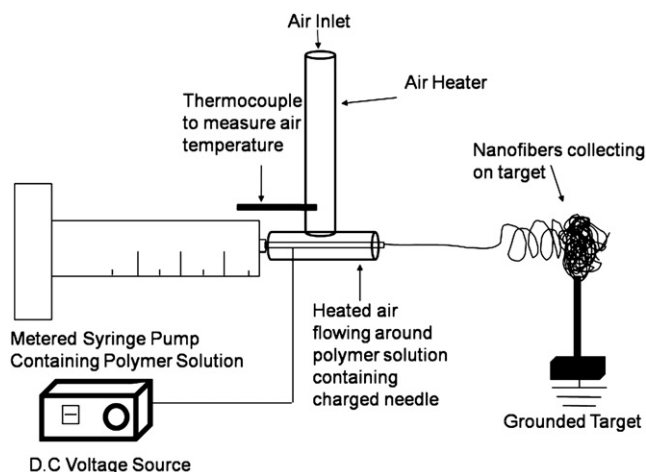


Fig. 1. Schematic outline of the designed electrospinning set up.

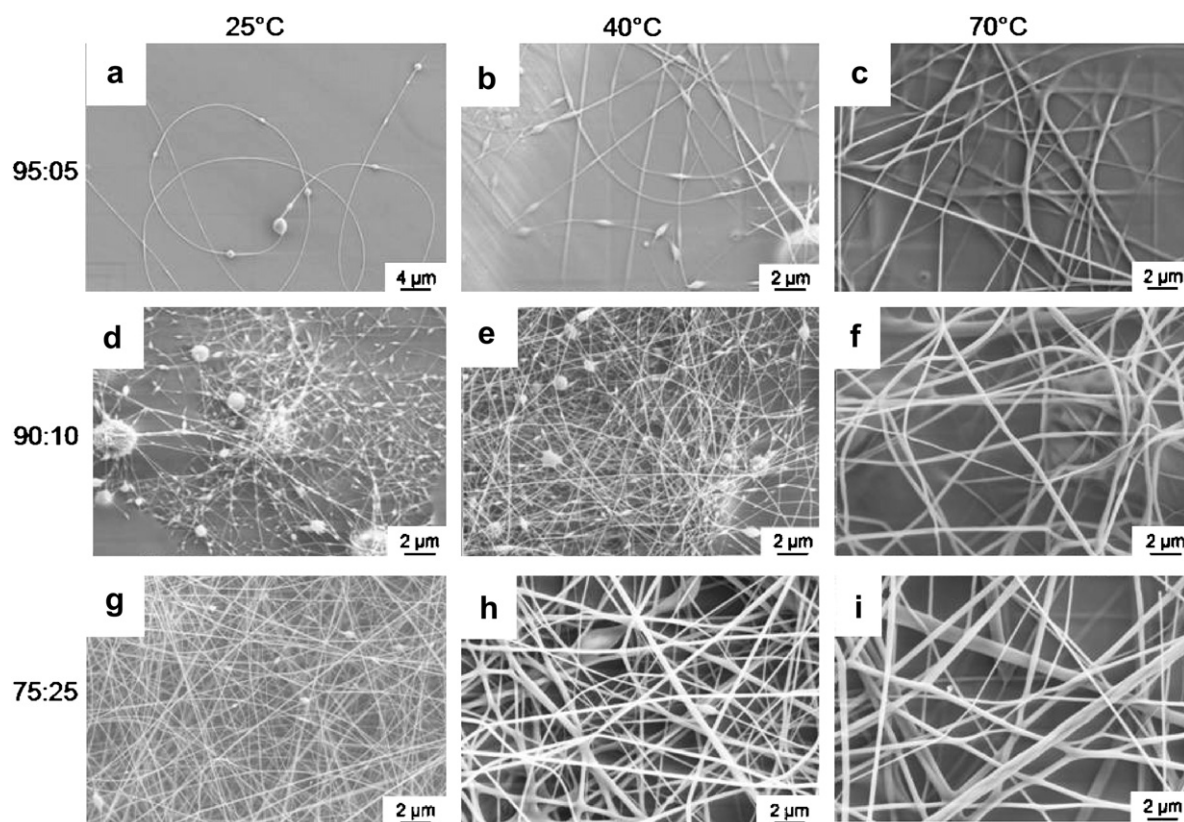


Fig. 2. SEM images of 1.4 wt% HMW chitosan/PAAm blends at different blend ratios and hot air blown at 25 ft³/h at different temperatures; (a)–(c) are HMW chitosan/PAAm 95:05 blend ratio, (d)–(f) are HMW chitosan/PAAm 90:10 blend ratio, and (g)–(i) are HMW chitosan/PAAm 75:25 blend ratio fibers.

increasing spinning temperature, we see the transformation from beaded fibers to uniform bead-less fibers. Further reduction to 75% chitosan in the blend leads to formation of bead-less fibers at room temperature (Fig. 2g). As spinning temperature is increased (Fig. 2h and i), an increase in fiber diameter is seen. At higher temperature there is a faster evaporation of solvent leading to faster drying of the charged jet and increased chain entanglements which is validated by the reduction in rate index of solutions at constant blend ratio with increasing temperature as shown in Table 1 [23]. Table 1 also details the zero-shear viscosity data of chitosan/PAAm blend solutions at different processing conditions. Reneker et al. have observed that spinning polymer solutions with high viscosity leads to formation of polymer skin on the outside of the jet subsequently leading to formation of a flat ribbon like structure [24]. SEM images of the chitosan/PAAm fibers formed at high temperature also show some flat ribbon shaped fibers which would contribute to the apparent increase in fiber diameter at higher temperatures. The chitosan molecule is

rigid in nature due to its high inter- and intra-chain hydrogen bonding. Addition of a synthetic polymer helps break down some of these by forming new hydrogen bonds between chitosan and the synthetic polymer, and with reduced chitosan content fiber formation is improved [16]. With increasing solution temperature, for constant chitosan percentage the overall viscosity of the solution decreases which along with the blown air helps in formation of uniform defect free fibers as the charged jet upon exiting the needle is further stretched, elongated and stabilized during the chaotic whipping motion that occurs as the jet travels to the target. There is no discernable trend in viscosity as a function of chitosan percentage at constant solution temperature, due to competing effects of higher molecular weight of PAAm compared to chitosan and hydrogen bonding between chitosan and PAAm chains. Air flow rate was kept constant at 25 ft³/h as it has been previously seen that increasing it to 70 ft³/h did not have significant effect on fiber formation [17]. Fig. 3 shows quantitatively the fiber diameter and bead density data, respectively, of electrospun chitosan/PAAm solutions at different blend ratios and increasing spinning solution temperatures.

Table 1
Zero-shear viscosity of chitosan/PAAm blends

Sample	Solution temperature (°C)	η_0 (Pa s)	n
1.4 wt% HMW chitosan/PAAm (95:5) in 50% AA	25	3.208	0.3561
	40	1.539	0.3089
	70	0.611	0.2229
1.4 wt% HMW chitosan/PAAm (90:10) in 50% AA	25	4.325	0.3691
	40	2.486	0.2961
	70	0.780	0.2589
1.4 wt% HMW chitosan/PAAm (75:25) in 50% AA	25	3.446	0.895
	40	2.082	0.3208
	70	0.6863	0.2476

3.2. Compositional analysis of fibers using TGA

TGA analysis of the blend fibers confirmed the presence of both the polymer fractions in the blend (Fig. 4). Pure chitosan was found to thermally decompose at ~240 °C and pure PAAm shows two degradation peaks one at ~240 °C (due to melting of polymer chains and onset of degradation) and other broad peak at 350 °C (due to further polymer degradation) [25]. For both pure chitosan and PAAm the raw TGA curve shows presence of unburnt material residue. Although we can confirm the presence of both polymers in the fibers it is difficult to quantify the exact fractions of both

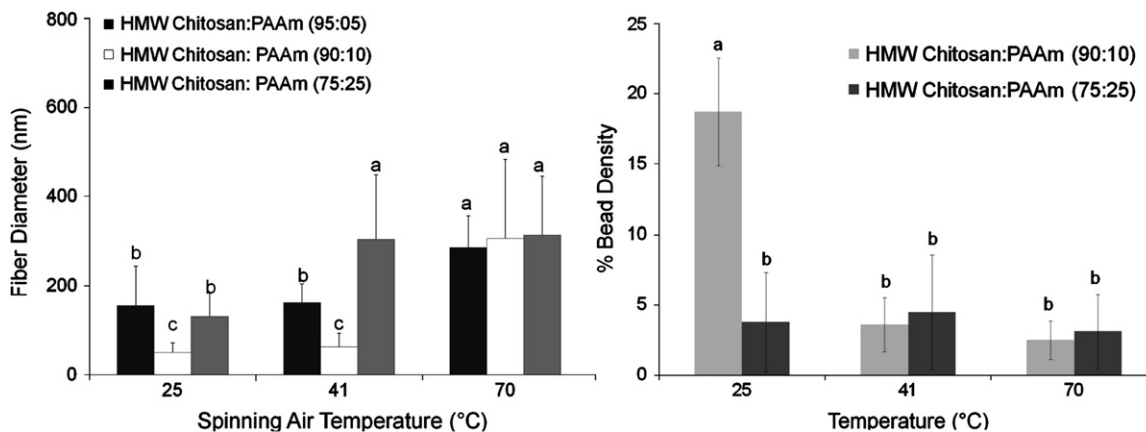


Fig. 3. Fiber diameter (left) and bead density (right) of 1.4 wt% HMW chitosan/HMW PAAm blend fibers at different air temperature. (Error bars represent standard deviation ($n = 60$ for FD, and $n = 3$ for BD), letters indicate significant difference at $p < 0.05$.)

polymers in fiber due to overlapping peaks (~ 240 °C) of both polymers. The derivative curve for the 90% and 75% chitosan blend fibers showed absence or very small PAAm peak at 350 °C. This suggests that there is a low PAAm and higher chitosan content in the electrospun fibers and our previous work quantifies that the fraction of polymers in fibers and blend solutions is not significantly altered during electrospinning [17].

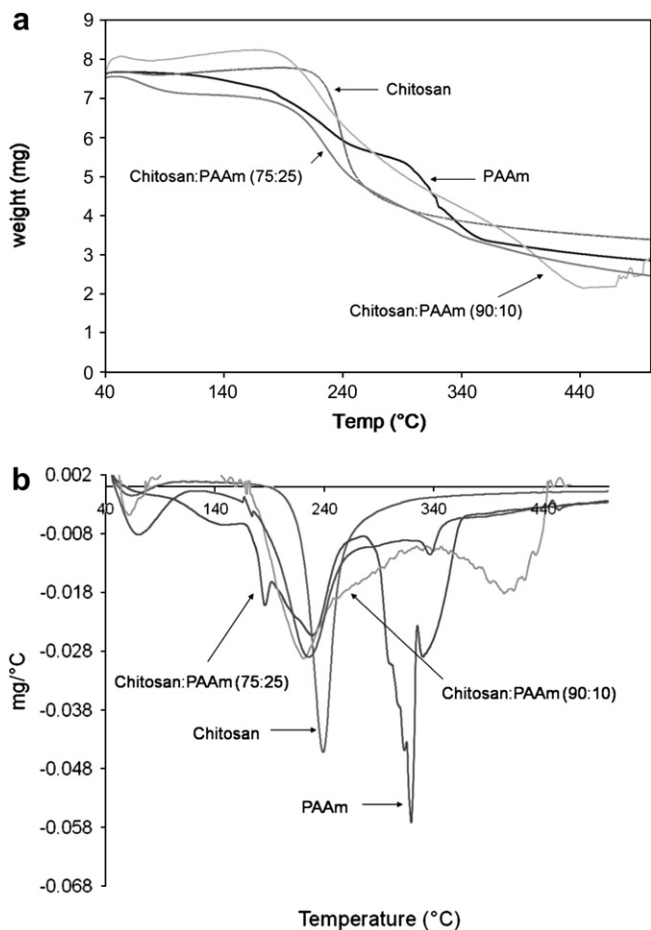


Fig. 4. TGA analysis of chitosan/PAAm blend fibers (a) raw TGA scans showing presence of unburnt polymer, (b) first order derivative of TGA scans.

4. Conclusions

Fairly uniform nanometer to sub-micron sized fibers of chitosan/PAAm blend solutions were successfully fabricated using electrospinning by optimizing the polymer blend ratios and spinning solution temperatures. Fiber formation and size was strongly influenced by the blend ratio of the two polymers, and hot air-blowing conditions. The blowing of hot air around the charged needle containing the polymer solution helped in stabilizing the jet and improving the spinnability of blend solutions at higher chitosan contents. Uniform bead-less fibers in the sub-micron range (250–300 nm) were obtained using blend solutions with 90% chitosan. Preliminary studies of these nanofiber mats for Cr(VI) metal binding showed high binding efficiencies (4 mg chromium/g chitosan). Further studies will be conducted by fabricating filter media using a layer of electrospun fibers on a conventional spun-bonded non-woven filter mat and the effect of blend ratios, fiber diameter and chitosan molecular weight on the metal binding and anti-microbial properties of these novel filter mats will be determined. The surface properties of these non-woven filter media will be correlated to their structure and morphology by studying their surface chemistry using XPS (X-ray photoelectron spectroscopy).

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References

- [1] Cauchie HM. *Hydrobiologia* 2002;470(1–3):63–96.
- [2] Roberts GAF. *Chitin chemistry*. London: The MacMillan Press Ltd; 1992.
- [3] Selmer-Olsen Er HC, Pehrson R. *Water Science and Technology* 1996;34:33–40.
- [4] Angelova Nm N, Rashkov I, Maximova V, Bogdanova S, Domard A. *Journal of Bioactive and Compatible Polymers* 1995;10(4):285–98.
- [5] Sorlier P, Denuziere A, Viton C, Domard A. *Biomacromolecules* 2001;2(3):765–72.
- [6] Reneker DH, Yarin AL, Fong H, Koombhongse S. *Journal of Applied Physics* 2000;87(9):4531–47.
- [7] Doshi J, Reneker DH. *Journal of Electrostatics* 1995;35(2–3):151–60.
- [8] Gibson P, Schreuder-Gibson H, Rivin D. *Colloids and Surfaces A: Physico-chemical and Engineering Aspects* 2001;187–188:469–81.
- [9] Boland ED, Wnek GE, Simpson DG, Pawlowski KJ, Bowlin GL. *Journal of Macromolecular Science Part A – Pure and Applied Chemistry* 2001;38(12):1231–43.
- [10] Gupta P, Elkins C, Long TE, Wilkes GL. *Polymer* 2005;46(13):4799–810.
- [11] Geng XY, Kwon OH, Jang JH. *Biomaterials* 2005;26(27):5427–32.
- [12] Ohkawa K, Cha DI, Kim H, Nishida A, Yamamoto H. *Macromolecular Rapid Communications* 2004;25(18):1600–5.

- [13] Min BM, Lee SW, Lim JN, You Y, Lee TS, Kang PH, et al. *Polymer* 2004;45(21):7137–42.
- [14] Schiffman JD, Schauer CL. *Biomacromolecules* 2007;8(2):594–601.
- [15] Li L, Hsieh YL. *Carbohydrate Research* 2006;341(3):374–81.
- [16] Bhattarai N, Edmondson D, Veisoh O, Matsen FA, Zhang MQ. *Biomaterials* 2005;26(31):6176–84.
- [17] Desai K, Kit K, Li J, Zivanovic S. *Biomacromolecules* 2008;9(3):1000–6.
- [18] Siyam T. *Designed Monomers and Polymers* 2001;4(2):107.
- [19] Gao BJ, He SX, Guo JF, Wang RX. *Journal of Applied Polymer Science* 2006;100(2):1531–7.
- [20] Carreau P, Kee D, Chabra P. *Rheology of polymeric systems: principles and applications*. Munich, Germany: Hanser Publishers; 1997.
- [21] Wang XF, Um IC, Fang DF, Okamoto A, Hsiao BS, Chu B. *Polymer* 2005;46(13):4853–67.
- [22] Um IC, Fang DF, Hsiao BS, Okamoto A, Chu B. *Biomacromolecules* 2004;5(4):1428–36.
- [23] Cho JY, Heuzey MC, Begin A, Carreau PJ. *Journal of Food Engineering* 2006;74(4):500–15.
- [24] Koombhongse S, Liu W, Reneker DH. *Journal of Polymer Science, Part B: Polymer Physics* 2001;39(21):2598–606.
- [25] Xiao C, Lu Y, Jing Z, Zhang L. *Journal of Applied Polymer Science* 2002;83(5):949–55.