THERMAL BEHAVIOR OF ELECTROSPUN GELATIN AND CHITOSAN COMPLEX

by

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This paper studied the thermal behavior of gelatin, chitosan, and their complex. Thermal stability was analyzed by thermogravimetric analysis, and the results showed that gelatin and chitosan raw materials exhibited two decomposition stages while as-electrospun nanofibrous mats had three decomposition stages. Moreover, chitosan raw material had better thermal stability than gelatin. However, its electrospun partner revealed its opposite trend. X-ray diffraction was used to analyze the crystalline property and the result showed that the crystallinity decreased due to the interaction with the solvents, and thus the thermal stability sharply decreased. In addition, incorporation of gelatin could improve the thermal stability of chitosan.

Key words: chitosan, gelatin, thermal, electrospinning

Introduction

Electrospinning is an effective method that utilizes electronic force to drive the solutions or melts to produce fibers with diameter ranging from nanometers to micro meters [1, 2]. Most synthetic and natural polymers have been successfully electrospun into nanofibers, moreover, incorporation with spinnable polymers makes it possible to obtain honey and milk nanofibers [3, 4]. However, seldom research focused on the thermal behavior during electrospinning. Karim et al. [5] found that the addition of poly(vinyl alcohol) could improve the thermal stability of pullulan. Correia et al. [6] investigated the effect of electrospinning conditions on the thermal behavior, and found that electrospinning conditions had no influence on the polymer degradation. Gelatin and chitosan have been used as polymeric biomaterials in a wide range of applications [7, 8]. Our previous study showed that gelatin and chitosan complex had been successfully electrospun into nanofibers, and gelatin and chitosan formed hydrogen bond between molecules [8]. In the present work, the thermal behaviors of gelatin, chitosan, and their complex were investigated.

Experimental

Materials

Gelatin (Type A, 300 bloom) and chitosan (Mη, about 10^6) with a degree of deacetylation (DD = 85%) was purchased from Sigma-Aldrich (St. Louis, Mo., USA) and Haide-
Preparation of solutions and electrospinning

Gelatin was dissolved in pure HFP. The mixed solvents HFP and TFA (with v/v = 9/1) were used to dissolve chitosan and chitosan/gelatin complex (CS/Gel) with weight ratio of 50/50. All the solution concentration was 0.08 g/ml. The electrospinning method was referred in [2]. In brief, the solutions were fed into a plastic syringe, which was controlled by a syringe pump (789100C, Cole-Parmer, USA), and the feeding rate was set as 0.6 ml/h. A positive high voltage of 24 kV which was supplied by a high voltage power (BGG DC high-voltage generator) was applied at the tip of the syringe needle. A piece of aluminum foil was used to collect the electrospun nanofibers with the distance of 13 cm below the tip. The electrospinning was conducted under the ambient conditions.

Characterization of the electrospun matrix

The thermal behavior of chitosan, gelatin raw materials, and their electrospun complex was investigated by thermal analyzer (TG209F1). Thermogravimetric (TG) curves of chitosan, gelatin, and their complex were recorded in nitrogen from ambient temperature to 700 °C at a scanning rate of 10 °C per minute. The structural study was performed through X-ray diffraction (XRD) (D/max-2500PC) in the 2θ range of 5-60° at a scanning rate of 6° per minute.

Results and discussion

As fig. 1 shows, both gelatin and chitosan raw materials decomposed in two steps. The onset decomposition temperatures of gelatin and chitosan raw materials were 275.8 °C and 284.8 °C, respectively. The mass loss of the first stage was due to the loss of being absorbed water in gelatin and chitosan raw materials, while that of the second stage was associated with the degradation and carbonization. When gelatin and chitosan were electrospun into nanofibrous mats, the TG curves exhibit being decomposed in three steps, as shown in fig. 2. The upper curve of the thermo-gravimetric analysis data represents the pure gelatin and the lower
one stands for the pure chitosan, while the middle one represents CS/Gel. The first stage was also due to the loss of absorbed water, the second stage was corresponded to the degradation of polymers and the third stage was associated with the thermal decomposition [6]. The onset decomposition temperatures were 261.6 °C, 195.3 °C, and 201.9 °C, respectively for electrospun gelatin, chitosan, and their complex nanofibrous mats. Compared with raw materials, as-spun gelatin nanofibrous mat had better thermal stability than chitosan. The solvents utilized to dissolve chitosan were HFP and TFA (with v/v 90/10), of which HFP was a strong polar solvent and TFA could form ammonium salt with chitosan.

Figure 3 shows X-ray patterns of chitosan raw material and its casting film. Chitosan raw materials showed two sharp peaks at 2θ of 10° and 20°, while the casting film showed one broad peak at 2θ of 20°, in addition, the intensity of the peak at 2θ of 20° decreased. Therefore, the solvents decreased the interaction of molecules and crystallinity of chitosan, and thus the thermal stability decreased sharply.

Conclusion

The thermal behaviors of gelatin, chitosan and CS/Gel were studied in this paper. Electrospun gelatin, chitosan and their complex nanofibrous mats exhibit three decomposition stages while gelatin and chitosan raw materials had two stages. Chitosan raw material had better thermal stability than gelatin, however chitosan exhibit lower stability than gelatin when electrospun into nanofibrous mats due to the decreased crystallinity. Moreover, the addition of gelatin could improve the thermal stability of electrospun nanofibrous mats.

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Reference


