2C13

Effect of ZnO nanoparticles on the electrospinning of poly(vinyl alcohol) from aqueous solution: influence of particle size

T. Jamnongkan, R. Shirota, S. K. Sukumaran, M. Sugimoto* and K. Koyama
Graduate School of Science and Engineering, Yamagata University, Yonezawa, 992-8510 Japan.
* E-mail: sugimoto@yz.yamagata-u.ac.jp

Abstract

We have investigated the electrospinning of aqueous PVA solutions with suspended ZnO nanoparticles. ZnO nanoparticles of three different diameters (20, 70 and 100 nm) were used in the study. Interestingly, we found that increasing the diameter of suspended ZnO nanoparticles was accompanied by a decrease in the diameter of the electrospun fibers. FTIR indicated that the ZnO nanoparticles were merely suspended in the aqueous PVA solution without any chemical bonding between the ZnO nanoparticles and the PVA chains. Shear rheometry of the suspensions indicated that, over the relevant range of shear rates, all of the samples exhibited essentially Newtonian behavior. However, the viscosity increased with a decrease in the diameter of the ZnO nanoparticles. We consider that the effect of the nanoparticles on the diameter of the electrospun fibers is through their effect on the viscosity of the suspension.

Introduction

Electrospinning has received a lot of attention in recent years because it is relatively simple to produce continuous fibers from a variety of polymers using this technique. The diameter of the produced fibers can range from a few nanometers to several micrometers [1]. For biomedical applications, human safety concerns are of paramount importance. Poly(vinyl alcohol) (PVA), being biocompatible and biodegradable, is especially attractive and has been successfully used in several biomedical applications [2]. In recent years, materials that combine organic and inorganic components have attracted great interest as they exhibit advantages characteristic to both organic materials, such as good processability, and inorganic materials, such as thermal stability and chemical resistance. Some researchers have successfully produced nanofibers from PVA composited with inorganic materials such as silica, gold and silver for biomedical applications. One such material is ZnO especially in the form of nanoparticles. ZnO not only exhibits superior antimicrobial activity, but is also nontoxic to humans and is environmentally friendly [3]. Owing to these reasons, we expect that nanofibers made from PVA with added ZnO nanoparticles will possess antibacterial properties and hence be potentially attractive for applications such as wound dressings.

Experiment

We have investigated the electrospinning of PVA solutions with suspended ZnO nanoparticles of three different particle diameters. During the electrospinning process, the electrical voltage in the range of 10-25 kV was applied and the tip-to-collector distance was varied between 5 and 15 cm for each applied voltage. The feed rate of the solutions was set at 0.006 mL/min. All electrospinning was performed at room temperature and the relative humidity was maintained at 30%.

Results and discussion

We found at a given electric field strength, the fiber diameter progressively decreased with an increase in the diameter of the added ZnO particles, as can seen in the Fig. 1. To understand of this behavior,

We investigated the chemical structure of the electrospun fibers by using FTIR. The IR spectra of the suspensions did not exhibit any additional peaks.

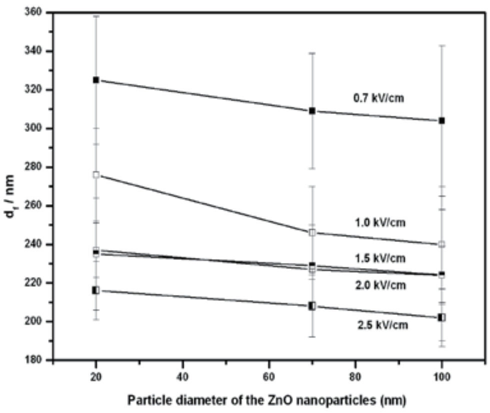

Fig. 1. The average diameter of the electrospun fibers (d_f) as a function of the diameter of the ZnO nanoparticles for different electric field strengths.

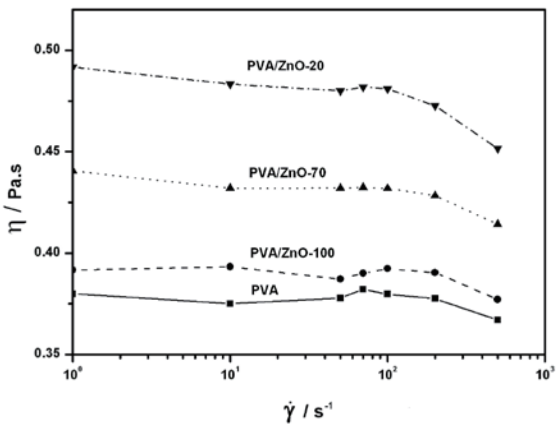

Fig. 2. Variation of the viscosity of the PVA solutions with ZnO particles of three different sizes with shear rate.

This indicates that no chemical reaction has occurred between the ZnO nanoparticles and the PVA polymer chains in the aqueous medium [4].

We also investigated the shear-rate dependent viscosity of the four samples used for producing the electrospun fibers and relate the flow characteristics to the behavior seen in electrospinning. We first determine the approximate apparent shear rate at the wall of the needle using,

$$\dot{\gamma} = \frac{4Q}{\pi r^3} \qquad (1).$$

where, $\dot{\gamma}$ is the shear rate at the wall of the needle, Q is the volumetric flow rate (fixed at 0.006 mL/min in this work) and r is the radius of the needle (0.30 mm). The calculated shear rate is approximately 5 s^{-1}. Hence, we measured the viscosity of the samples for shear rates between 1-500 s^{-1} and the data is shown in Fig. 2. Note that the measured viscosity is essentially independent of the shear rate in this range, indicating that the flow behavior is Newtonian. More interestingly, the viscosity increases with a decrease in the diameter of the ZnO nanoparticles.

Using Fig. 2 and Fig.1, we show propose that the effect of the particle size on the fiber diameter for all of the electric field strengths investigated is primarily through their effect on the viscosity.

Conclusions

Using electrospinning, nonwoven fiber mats were successfully fabricated from an aqueous solution of PVA and suspensions of ZnO nanoparticles in PVA aqueous solutions. Surprisingly, we found that an increase in the diameter of the nanoparticles led to a decrease in the diameter of the corresponding electrospun fiber. The shear viscosity increased with a decrease in the diameter of the suspended nanoparticle in spite of using constant nanoparticle weight fractions in preparing the suspensions. We believe this increase in the shear viscosity can explain the observed increase in the fiber diameter with a decrease in the particle size.

References

1. H. Yoshimoto, Y.M. Shin, H. Terai, and J.P. Vacanti, Biomaterials, 24, 2077 (2003).

2. Y.T. Jia, J. Gong, X.H. Gu, H.Y. Kim, J. Dong, and X.Y. Shen, Carbohyd. Polym., 67, 403 (2007).

3. K.R. Raghupathi, R.T. Koodali, and A.C. Manna, Langmuir, 27, 4020 (2011).

4. T.Jamnongkan, R. Shirota, S.K. Sukumaran, M. Sugimoto and K. Koyama, Polym. Eng. Sci., To be published, 2013.