Preparation of ZnO/thermoplastic polyurethane composite nanofibers by electrospinning

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Abstract

ZnO/thermoplastic urethane (TPU) composite nanofibers were prepared by electrospinning process based on TPU doping with ZnO NPs. Two kinds of ZnO/ TPU composite nanofibers were developed. One was prepared by directly adding ZnO NPs powder, while another was by surfactant-assist ZnO NPs. The doping of ZnO NPs worked as nano-filler with a decreased hydrophilicity, which increased the tensile strength and decreased the elongation. When the content of ZnO NPs was 3 wt%, the innhibitory rates of them were more than 90% of Escherichia coli and over 80% of Staphylococcus aureus, respectively.

Keywords

ZnO nanoparticles, thermoplastic polyurethane, electrospinning, antibacterial.

1. Introduction

Among the various elastomers, thermoplastic polyurethane (TPU) is the most widely used in biomedical applications [1]. Due to the high elasticity, good flexibility, and abrasion resistance of TPU, many researchers use it for the repair of matrix materials such as skin [2], blood vessels, achilles tendons [3] and other tissues. However, during the practical application and preservation of TPU, the bacteria are easily grown and propagated on the surface under suitable temperature and humidity conditions [4], which seriously threatens human health and limits its application in biomedical materials. Therefore, the researchers are committed to the selection of antibacterial agents [5-6] and antibacterial treatment methods [7] in TPU composites.

In this paper, the novel ZnO/ TPU composite nanofibers were prepared by electrospinning. Then, the effects of different doping processes on the structure of composite nanofibers were investigated. More importantly, the antibacterial properties of ZnO/TPU were also measured by absorbance tests.

2. Experimental Procedure

2.1 Materials

TPU was obtained from Lubrizol® 2363-80AE, ZnO nanoparticles (NPs) were synthesized by small molecular solvothermal method from the previous work [8]. *Escherichia coli (E. coli,* ATCC 25922*)* and *Staphylococcus aureus (S. aureus,* ATCC 25923*)* were obtained from South China Agricultural University. DMF, span 80, LB broth medium and other chemicals of analytical grade were commercially available and were purchased from Guangzhou chemical reagent factory, china. All other chemicals were of analytical grad and used without further purification.

2.2 Preparation of ZnO/TPU composite nanofibers

The preparation of ZnO/TPU composite nanofibers by electrospinning is as follows: The TPU was first dissolved in DMF to obtain a 10% solution, and then 0.3 wt% ZnO was added. Three methods of adding ZnO were designed: ZnO-P/TPU for the direct addition of ZnO powder, ZnO-S for the addition of ZnO powder and a small amount of surfactant dispersion, ZnO-sol for the addition of ZnO precursor sol. The electrospinning voltage was 18 kV, the solution flow rate was 0.5 mL/h, the receiving distance was 12 cm, and the spinning time was 4 h.

2.3 Characterizations

The morphology and structure of the ZnO/TPU was observed using FRSEM (Ultra 55, Zeiss) and XRD (MiniFlex 600, Rigaku, performed at 36 kV and 20 mA with a Cu Kα radiation source, λ = 1.5406 Å). Tensile properties by the universal testing machine (AG-1, SHIMADZU), antibacterial properties were measured by absorbance tests [9], inhibition rate (α) was calculated according to the following formula.

$$\alpha(\%) = \frac{D_t - D_n}{D_p - D_n} \times 100\%$$

where *Dt*, *Dp* and *Dn* represent the absorbance of the experimental group, the positive control group and the negative control group, respectively.

3. Results a and Disscussion

3.1 Morphology and structure of ZnO/TPU

Three kinds of ZnO/TPU XRD patterns are shown in Fig. 1. ZnO-P/TPU and ZnO-S/TPU had three strong peaks with d = 2.8136, 2.6028, and 2.4784 Å, which could be indexed as the (100), (200) and (101) of ZnO, respectively. These diffraction peaks were not observed in the ZnO-sol/TPU. This indicates that ZnO in the first two kinds of ZnO/TPU is present as hexagonal crystal form, and ZnO is present as Zinc ions in the last case.

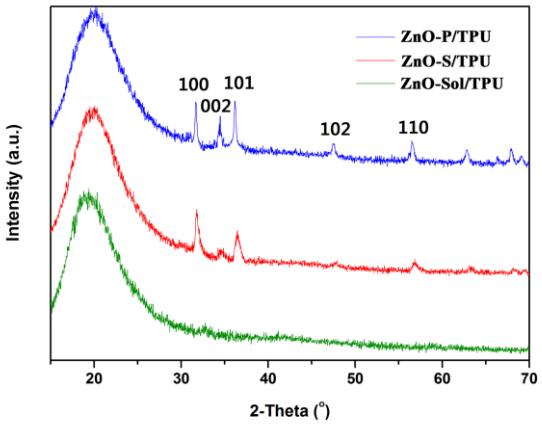

Fig. 1 XRD patterns of ZnO/TPU

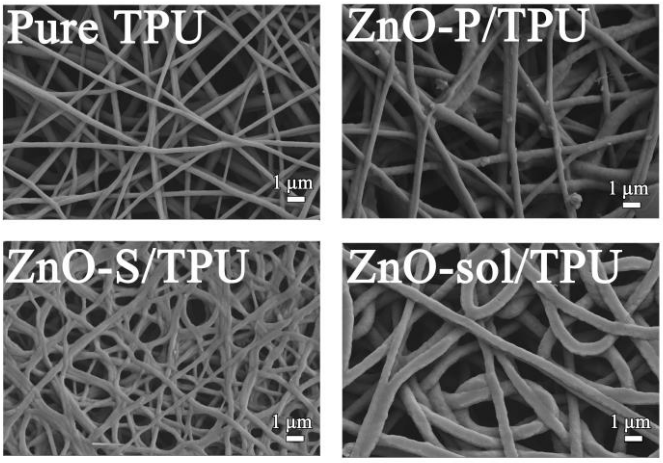

Fig. 2 SEM images of pure TPU and ZnO/TPU

Fig. 2 shows the SEM images ZnO/TPU obtained from three methods. It can be observed from the figure that, doped ZnO will increase the diameter of nanofibers. Compared with the SEM images of ZnO-P and ZnO-S, surfactant (span 80) can reduce the agglomeration of ZnO NPs, but also make the

nanofibers easier to stick. The diameter of ZnO-sol/TPU is the largest, since the spinning solution increases volatilically after the addition of the ZnO sol.

3.2 Mechanical and antibacterial properties of ZnO/TPU

The average tensile strength of each sample is shown in Table 1. Compared with pure TPU, the tensile strength of the ZnO-P/TPU and ZnO-S/TPU is obviously improved. This may be due to the doping of ZnO NPs. The ZnO NPs as a nano-filler in the polymer matrix and part of the tensile load from the TPU fiber transfer to the ZnO NPs, enhance the mechanical strength of the composite. There was no significant difference in the strength between the ZnO-sol/TPU and pure TPU. This may be due to the absence of crystalline ZnO NPs in the sol, and the increase in the diameter of the nanofibers also causes the tensile strength to decrease.

Table 1 The average tensile properties of the composite fibers

Sample	Tensile Strength (MPa)	Elongation at break (%)	Tensile modulus (N/mm2)
Pure TPU	6.92±1.50	369.3±40.9	1.87
ZnO-P/TPU	15.47±3.06	156.7±38.6	9.87
ZnO-S/TPU	17.55±1.13	237.4±37.5	7.39
ZnO-Sol/TPU	9.14±0.82	282.3±26.9	3.24

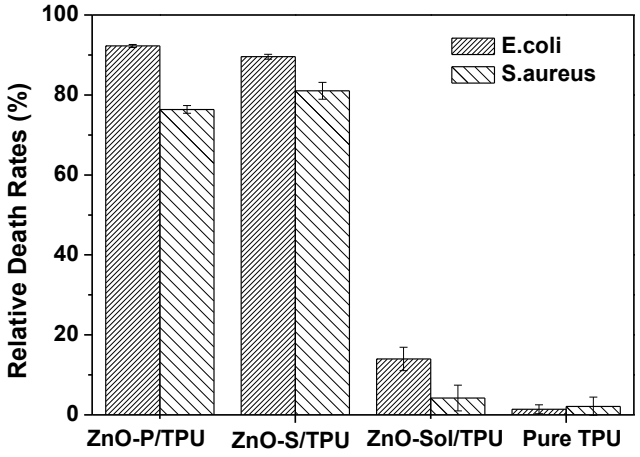

Fig. 3 The inhibition rate of ZnO/TPU and pure TPU on bacteria

The inhibitory rate of the samples with 10^5 CFU/mL bacteria for 24 h was shown in Fig. 3. The inhibitory rate of ZnO-P/TPU and ZnO-S/TPU was also more than 90% on *E. coli*, and was 76% and 81% on *S. aureus*, respectively. It was proved that the doping of ZnO NPs could significantly enhance the antibacterial properties of TPU nanofibers.

Compared with the other two groups, the inhibition rate of ZnO-Sol/TPU on bacteria was not improved obviously. This is because, for ZnO NPs, photocatalytic release of reactive oxygen species (ROS) and hydroxyl radicals is one of the most important antimicrobial mechanisms [10], and the photocatalytic action takes place in the electron vacancy of ZnO crystal. For ZnO precursor sol, Zn was present as zinc ions, so the antibacterial activity is significantly lower than that of ZnO NPs.

4. Conclusion

Three kinds of novel ZnO/TPU composite nanofibers were prepared by electrospinning. Among these nanofibers, ZnO-S/TPU have the best tensile property and the highest antibacterial property. The inhibitory rate of ZnO-S/TPU on *E. coli*. And *S. aureus* can be as high as 90% and 81%. This provides a new idea for the preparation of antibacterial TPU composites.

Acknowledgements

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