ELECTROSPINNING OF ANTIBACTERIAL POLYURETHANE/ZnO NANOFIBERS

DOI: 10.35530/TT.2021.29

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Abstract: *In this study, it is aimed to produce and characterize antibacterial polyurethane (PU)/Zinc oxide (ZnO) nanofibers by electrospinning method. Firstly, polymer solutions were prepared at various ZnO concentrations such as 0, 0.2, 0.4, 0.6, 0.8, 1. Then solution properties (conductivity, viscosity, surface tension) were determined and analysed the effects of ZnO concentration on the solution properties. PU/ZnO nanofibers produced via electrospinning under the optimum process parameters (voltage, distance between electrodes, feed rate and atmospheric conditions). Finally, the nanofibers were characterized in terms of fibre morphology, thermal stability, permeability and antibacterial activity using SEM-EDS, DSC-TGA, water vapour permeability and disk diffusion methods. According to the solution results; it was observed that conductivity and surface tension decrease significantly with ZnO addition. On the other hand, solution viscosity increases as the ZnO concentration increases. From the SEM images, it has been seen clearly that average fibre diameter increases with ZnO concentration and incorporation of ZnO particles to the fibre structure was verified by SEM-EDS. According to the thermal analyse result, nanofibers begin to degrade between 271.94 °C and 298.73 °C. In addition, water vapour permeability increases as the ZnO concentration increase. Lastly antibacterial activity against gram negative (E.coli) and gram positive (S. aureus) was determined with specific zone diameter.*

Keywords: antibacterial, electrospinning, nanofiber, polyurethane, Zinc oxide

1. INTRODUCTION

Protective textiles are the materials to prevent the risk of exposure to harmful substances (virus, bacteria etc.) and bad environmental conditions, to protect them from this risk and/or to reduce this risk. Especially fibre structure, thermal, chemical, microbiological, pore size, air permeability, barrier etc. properties are important for this aim [1].

In recent years, various polymers can be easily electro spun to obtain advanced fibrous materials [2,3]. Among them, polyurethane based nanofibers are the most common and functional materials due to their high elasticity, good mechanical, protective and barrier properties. Polyurethane based nanofibers are especially used in medical, filtration, protective textiles, etc. [4-6]. Antibacterial nanofibers are also important for these application areas. In the literature, there are many studies about PU nanofibers containing various antibacterial agents [7,8].

For this study, ZnO was chosen as an antibacterial agent because of its non-toxicity, compatibility with the skin, and its chemical stability when exposed to both high temperatures and UV [9]. There are some studies on ZnO based nanofibers in the literature. Lee studied PU/ZnO based nanofibers to obtain UV protective textile materials. He noted that very thin electro spun ZnO nanocomposite fibre layer significantly

increased UV blocking for both the UV-A and UV-B ranges and exhibited excellent UV protection. In addition, it was observed that the UV protective properties increased with increasing ZnO concentrations [10]. Wu and Pan also prepared ZnO nanofibers by electrospinning. They found that the fibre diameter increased with ZnO content and the morphology of inorganic ZnO fibres was affected by the calcination time.

2. MATERIALS AND METHODS

In this study, polyurethane (PU) was used as a polymer, dimethylformamide (DMF) was used as a solvent and zinc oxide (ZnO) was used as an additive to provide antibacterial activity. During the experimental studies, PU polymer concentration was kept constant at 15 wt % and this value was determined from our preliminary studies. Zinc oxide concentrations such as 0, 0.2, 0.4, 0.6, 0.8 and 1 wt % were applied to the PU/DMF solutions. All solutions were prepared under the same conditions (mixing time, temperature, etc.).

First of all, solution properties such as conductivity, viscosity (shear rate 5 s^{-1}) and surface tension were measured. Then, nanofiber production was carried out by electrospinning method under the optimum process parameters. During the spinning process, 24 kV voltage, 0.2 ml/h solution feed rate and 22 cm distance between the electrodes were applied for all solutions. In addition, all nanofibers were produced under ambient conditions of $36 \pm 2\%$ humidity and $23 \pm 2^\circ\text{C}$ temperature. All nanofibers were produced for 30 minutes and collected on an aluminium foil.

Nanofiber morphology such as fibre diameter, diameter uniformity and nanoweb surface structure were analysed by Scanning Electron Microscopy (SEM). Fibre diameter histograms were obtained from the SPSS program. The presence of ZnO was determined by EDS and the thermal behaviour of nanofibers was analysed by DSC and TGA. In addition, the water vapour permeability test was performed according to BS 7209, BS 3424 standards. Finally, antibacterial activity against gram negative (*E. coli*) and gram positive (*S. aureus*) was determined by disc diffusion method.

3. RESULTS AND DISCUSSIONS

Viscosity, conductivity and surface tension results of PU/DMF solutions with various ZnO wt % concentrations are given in table 1.

Table 1. Solution results of PU/DMF with various concentrations of ZnO wt %

Samples	Viscosity (mPa.s) (Shear rate: 5 s^{-1})	Conductivity ($\mu\text{S/cm}$)	Surface Tension (mN/m)
PU0	2240	5.16	36.4
PU0.2	3970	1.01	6.74
PU0.4	4570	0.93	7.63
PU0.6	5680	0.82	7.29
PU0.8	5080	1.17	6.77
PU1	7680	0.72	7.53

Also figure 1 shows the changing of viscosity, conductivity and surface tension of PU/DMF solutions with ZnO concentrations.

Figure 1. Graphical representation of: a - viscosity and conductivity of PU/ZnO solutions; b - surface tension of PU/ZnO solutions

It is clearly seen that from table 1 and figure 1, solution viscosity increases with ZnO concentration while conductivity decreases. On the other hand, with the initial addition of ZnO, conductivity and surface tension decreases significantly, but is not affected by the ZnO concentration increase. This result is compatible with literature [11]. Figure 2 shows the SEM images and histograms of PU/ZnO nano webs.

PU0

PU0.2

PU0.4

PU0.6

PU0.8

PU1

Figure 2. SEM images and fibre diameter histograms of PU/DMF nanofibers

From the SEM images, it was observed that the fibre diameter and stickiness increased with the addition of ZnO. Average fibre diameter was calculated as 550 nm for PU/DMF without ZnO (PU0). On the other hand, average fibre diameter increased to approximately 750 nm with addition of various concentrations of ZnO. It is clearly seen

from the SEM images that incorporation of ZnO particles to the nanofibers were achieved successfully. Unimodal histogram curves were obtained from PU0, PU0.2, PU0.8 samples.

The changing of average fibre diameter and fibre diameter uniformity with ZnO concentration increase is shown in figure 3.

Figure 3. Average fibre diameter and diameter uniformity coefficient of PU/ZnO nanofibers

Figure 3 presents that average fibre diameter increased significantly with the first addition of ZnO to the PU nanofibers. Fibre diameter uniformity coefficient is not effected from ZnO concentration. It is possible to say that uniform PU/ZnO nanofibers were obtained. From the water vapour permeability test results, it was determined that water vapour permeability increased with addition of ZnO (PU0: 2484.62 g/m²/day and PU0.8: 2910.28 g/m²/day).

ZnO particles can be seen clearly into the fibre structure and also ZnO existence was verified by SEM-EDS (figure 4).

Figure 4. SEM-EDS Spectroscopy of PU nanofibers with 0.8 wt % ZnO

Elemental analysis results of Pu/ZnO nanofibers are given in table 2. Thermal behaviour of Pu/ZnO nanofibers were analysed by DSC-TGA (figure 5, figure 6).

Table 2. SEM-EDS results of PU/ZnO nanofiber samples

Sample code	C (%)	N (%)	O (%)	Zn (%)	Mg (%)	Al (%)	Na (%)
PU0.2	68.13	7.20	19.95	-	0.27	3.89	0.55
PU0.4	75.76	-	23.25	0.99	-	-	-
PU0.6	76.41	-	21.02	1.38	-	1.19	-
PU0.8	70.87	6.57	20.22	2.34	-	-	-
PU1	70.63	7.28	20.01	2.07	-	-	-

Figure 5. TGA analysis of PU nanofibers with various concentrations of ZnO

As shown, the amount of ZnO is visibly changing the temperature of any thermal resistance value. The major mass loss for PU/ZnO is around 275-280°. In the PU/ZnO curve, after 430 degrees, PU1 % containing the most zinc oxide remained the most residues and this ratio was 25%. PU0, PU0.2 and PU0.4 left the least residues close to each other. This rate is 1%.

Figure 6. DSC analysis of PU nanofibers with various concentrations of ZnO

Thermal characterization of polymers was investigated in nitrogen atmosphere using differential scanning calorimetry (DSC) and glass transition temperature (T_g) and melting temperature (T_m) were determined. Analysis -50°C to 350°C at a scan rate of 10°C/min has been carried out. In general, the temperatures at which nanofibers begin to degrade are between 271.94°C and 298.73°C. Similarly, the temperature at which the mass loss ends is close to each other and varies between 308.11°C and 330.90°C.

Lastly, antibacterial activity against gram negative (*E.coli*) and gram positive (*S. aureus*) was determined with specific zone diameter for PU nanofibers with 0.8 wt % ZnO.

4. CONCLUSION

This study was carried out for the fabrication and characterization of antibacterial PU/ZnO nanofiber surface with various ZnO concentrations by electrospinning. According to the solution results; viscosity increased with ZnO concentration while conductivity and surface tension decreased. In addition, average fibre diameter increased and fibre stickiness was observed with ZnO concentration increase. On the other hand, fibre diameter uniformity was not affected from ZnO addition. ZnO incorporation to the PU nanofibers was shown by SEM images and ZnO presence was verified via SEM-EDS. Also it was determined that water vapour permeability increased with ZnO addition. Thermal behaviour of PU nanofibers with various concentrations of ZnO was investigated by DSC-TGA analysis. Lastly, good antibacterial activity against gram negative (*E. coli*) and gram positive (*S. aureus*) was determined.

ACKNOWLEDGMENT

The authors would like to express appreciation for the financial support of the Süleyman Demirel University Scientific Researches Project Unit [Project Number = FYL-2020-8206]. I would like to thank the Scientific and Technological Research Council of Turkey for their support to the 2247-C Trainee Researcher Scholarship Program (STAR) 2020/1.

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