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ELECTRICAL PROPERTIES OF ZnO/NYLON-6 SPIDER-WAVE-LIKE NANO-NETS PREPARED VIA ELECTROSPINNING

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In this work, ZnO nanoparticles (NPs) incorporated electrospun nylon-6 spider-wave-like nanonets with improved electrical properties were successfully fabricated by simple blending of ZnO NPs with nylon-6 solution. Proper dispersion of ZnO NPs with nylon-6 solution not only produce well distributed ZnO NPs on/into the fibres but also accelerate the formation of large number of thin fibres in the form of spider-wave-like nanonets. The incorporation of ZnO NPs through spider-wave-like nylon-6 nanonets was verified by FE-SEM, EDX, TEM, TGA, FT-IR analysis. The electrical properties of pristine nylon-6 and ZnO/nylon-6 composite fibres was investigated by current-voltage (I-V) characteristic measurement. It was found that ZnO incorporated nylon-6 composite mats had better electrical conductivity than pristine nylon-6 mat. This result was due to the influence of ultrathin nanofibers and well incorporated ZnO NPs through electrospun nylon-6 fibers. The significant enhanced electrical properties of composite mat may open a new direction for future polymer electronics.

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Keywords: Electrospinning, Electrical property, Zinc oxide, Nylon-6, Nanocomposite

1. Introduction

Over the last few years, considerable polymer nanofibres have been effectively utilized in a wide range of applications in the fields of sensor, electronic, catalysis, protective clothing, filtration, bioengineering and biotechnology[1-3]. Various polymers have been fabricated by electrospinning which is an efficient and facile technique for the production of nanofibres. Elecrospinning is carried out using high voltage on a polymer solution or its blend that leads to drive the solution to be stretched into fibres by spinning. Recently, polymer based composite nanofibres, especially by incorporation of metal or metal oxide NPs through electrospun nanofibres is being widely investigated because of their enhanced properties and potential application in catalysis, sensor, energy storage, and electronics [4-6]. Several NPs such as Ag, Au, Fe, TiO_2, ZnO, SiO_2, etc. have been incorporated in various polymer nanofibres using blend solution of NPs and polymer [7].

Nylon-6, a polyelectrolyte, has good physical and mechanical properties [8] and it is a potential candidate for the fabrication of efficient practical nanofibres with high aspect ratio in the form of spider-wave-like nano-nets by varying process/material parameters during electrospinning [9-15]. However, the electrical property of pristine nylon-6 fiber under electronic field is very low. Therefore, this study was investigated on the fabrication of large amount of true nanofibres (<50 nm in diameter) in the form of spider-wave-like structure and enhance the electrical properties of

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mat using the unique properties of ZnO NPs provided to nylon-6 fibres. Zinc oxide (ZnO), an inorganic compound which is widely used as an additive in various materials, has considerable properties including a direct wide band gap of 3.3 eV, high exciton binding energy of 60 meV [16]. Therefore, the combination of ZnO and nylon-6 composite is useful to enhance the electrical conductivity of electrospun nylon-6 mat. Spider-wave-like nano-nets of nylon-6 using electrospinning and the impregnated ZnO NPs into nylon-6 nanofibres was carried out to extend interact structure and increase the electrical conductivities of ZnO/nylon-6 composite mat. The schematic diagram of experimental process for the fabrication of ZnO/nylon-6 nanocomposite is shown in Fig. 1.

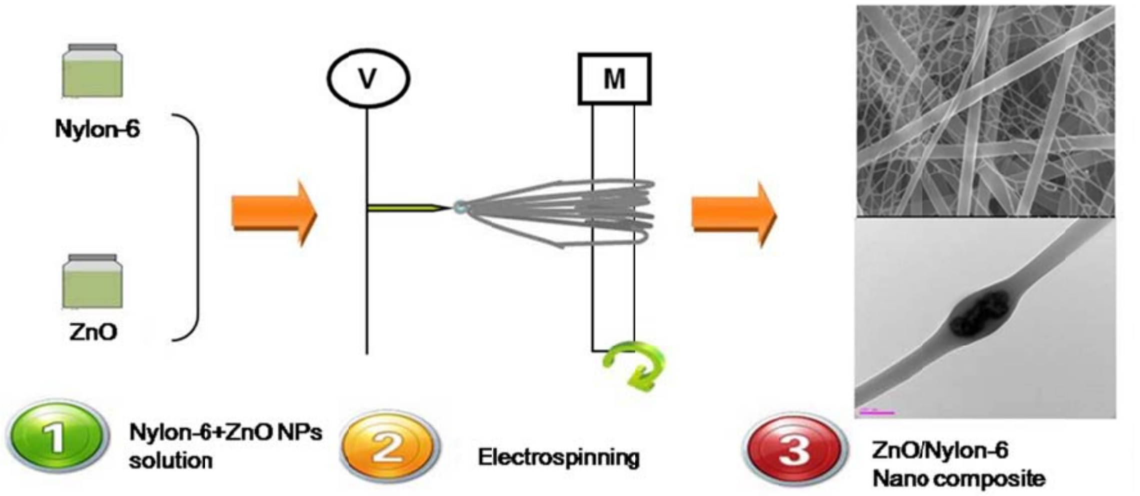

Fig. 1. Schematic diagram for the fabrication of ZnO/Nylon-6 spider-wave-like nanonets.

2. Experimental procedure

2.1 Materials and methods

Commercial nylon-6 (Mw ≈ 35000, Kolon, Korea), ZnO NPs (Aldrich, particle size of ≈ 30 nm), formic acid, and acetic acid were used as they received. Different nylon-6 mats were electrospun from 20 wt% nylon-6 solution dissolved in 4:1 formic acid/acetic acid (by wt) solvents that contain 0, 5, 10, and 20 wt % ZnO NPs with respect to nylon-6. Polymer solution was fed through the metal capillary (nozzle) having di = 0.21 mm (21 G) attached to a 1-D robot-system that moves laterally controlled by LabVIEW 9.0 program (National Instrument). The feeding rate via a controllable syringe pump was maintained at 0.3 ml/h. Electrospinning process was carried out at 20 kV electric voltage and 18 cm working distance between the collector and the tip of the syringe. The fibres were collected on polyethylene sheets attached on the surface of rotating drum. After vacuum drying for 12 h at 30˚C, the mat was used for further analysis and measurement.

2.2. Characterization and measurements

The surface morphology of pristine nylon-6 and ZnO/nylon-6 electrospun mats was analyzed by using field-emission scanning electron microscopy (FE-SEM, S-7400, Hitachi, Japan) and transmission electron microscopy (TEM, JEM-2010, JEOL, Japan). The conductivity and viscosity of the solutions were measured by an EC meter CM 40G Ver. 1.09 (DKK, TOA, Japan) and Rheometer (DV-III Ultra, Brookfield, UK), respectively. The incorporation of ZnO NPs through nylon-6 fibers was evaluated by means of thermo-gravimetric analysis (TGA, Perkin-Elmer, USA) and Fourier-transform infrared (FT-IR) (ABB Bomen MB100 spectrometer, Bomen, Canada). The current-voltage (I-V) characteristic was measured in two-probe configuration using Keithley 2400 semiconductor characterization system to study the electrical properties of as-prepared mats. The synthesized mats were cut into small pieces (same dimension) and they were contacted by 25 μm thick Au wires with an assistance of silver paste.

3. Results and discussion

Zinc oxide has been recognized as excellent materials for electronic and good filler to organic materials [17]. Therefore, effective incorporation of ZnO NPs through nylon-6 fibres not only increase the electrical conductivity of nylon-6 matrix but also make some changes in morphology of the electrospun fibres. The morphological structure of electrospun fibres is very important characteristics because it ultimately affects many physical properties of materials such as permeability, thermal stability, mechanical properties, and so on. Fig. 2 shows typical FE-SEM images of as-spun pristine nylon-6 and ZnO/nylon-6 nanofibrous composite mats. It is clearly shown in Fig. 2a that the pristine nylon-6 mat has no any thin nanofibres (true nanofibres, fibre diameter <50 nm) whereas the addition of ZnO NPs led the formation of highly interconnected thin (true nanofibres) and thick fibres in the form of spider-wave-like structure. Spider-wave-like nanonets can easily increase total surface area of electrospun nylon-6 mat. The formation of spider-wave-like nanonets is due to the fast solvent degradation of nylon-6 caused by dispersed ZnO NPs throughout the polymer solution which was explained in author's previous report [13, 15]. The solvent degradation of nylon-6 (caused by formic acid) might be accelerated when a suitable amount of ZnO is properly dispersed throughout the nylon-6 solution [14, 15]. Since a large amount of solvent degraded ionic oligomer molecules of nylon-6 were formed during the solution preparation, there might be two fraction of solution (higher and lower molecular weight fractions) during jet whipping. The fraction of lower molecular weight polymer solution could form true nanofibers during phase separation [14]. The proper loading of ZnO NPs on/into as-fabricated fibres was carried out by transmission electron microscopy (TEM). Fig. 3a shows that pristine electrospun nylon-6 fibre is smooth whereas fibre obtained from blend solution containing 10 wt% ZnO NPs shows that these NPs were loaded on fibres (Fig. 3b). However, agglomeration of NPs was observed on fibers when 20 wt% ZnO NPs was added to the electrospinning solution (Fig. 3c). At this point, the spinability of nylon-6 solution was decreased and agglomerated ZnO NPs had blocked the tip of the syringe. The conductivity and viscosity of nylon-6 solution containing different amounts of ZnO NPs were measured and the result was expressed in Table 1. The highest conductivity of the solution at 10 wt% ZnO NPs is attributed to the proper mixing of ZnO NPs with nylon-6 at this concentration. Further increasing of ZnO NPs (20 wt%) showed the decrease in conductivity of the solution due to the agglomeration of NPs. Therefore, we concluded that 10 wt% ZnO containing nylon-6 solution was suitable for the formation of smooth nylon-6 fibers containing effectively loaded ZnO NPs.

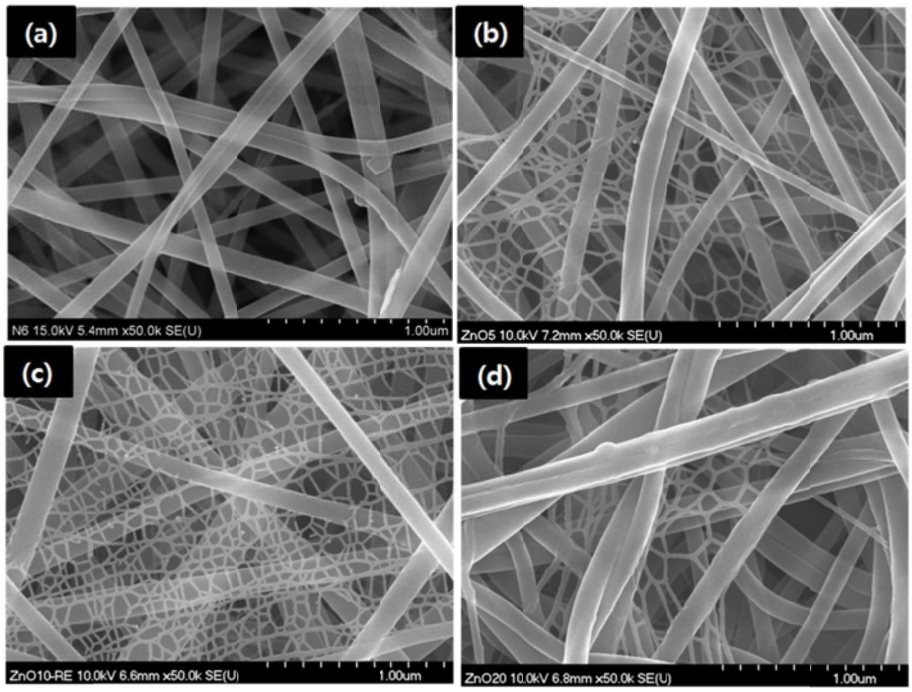

Fig. 2 . FE-SEM images of electrospun nanofibres obtained from the nylon-6 solution containing (a) 0, (b) 5, (c) 10, (d) 20wt% ZnO NPs.
(b)

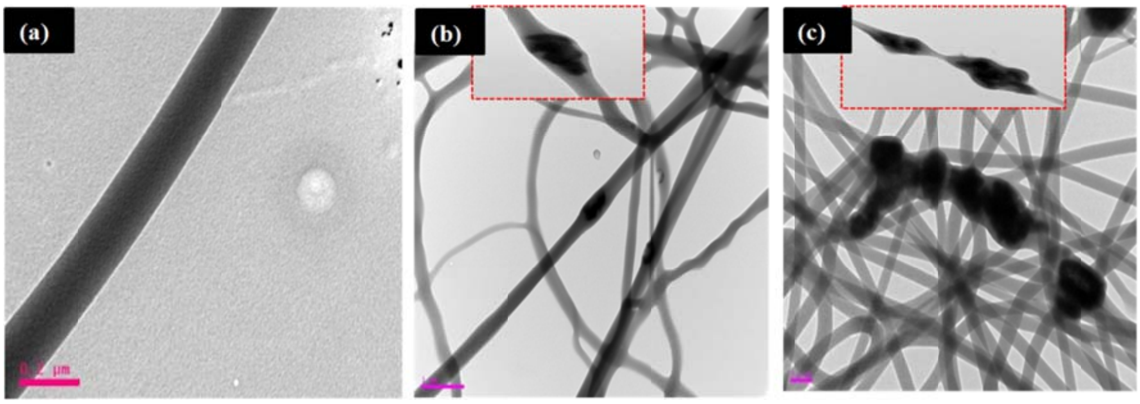

Fig. 3. TEM images of electrospun nanofibres obtained from the nylon-6 solution containing (a) 0, (b) 10, and (c) 20wt% ZnO NPs.

Table 1. Comparison of conductivity of Nylon-6 and ZnO/Nylon-6 mats.

Sample	**Viscosity (cP)**	**Conductivity**
Pristine Nylon-6	1017	191.4 s/m
Nylon-6+ 5 wt% ZnO	1042	196.1 ms/m
Nylon-6+ 10 wt% ZnO	1217	196.8 ms/m
Nylon-6+ 20 wt% ZnO	1636	181.4 ms/m

The incorporation of ZnO NPs through nylon-6 fibres was further conformed by TGA analysis. Fig. 4 shows that, as the ZnO component increases, the onset decomposition temperature of nylon-6 composite mat is decreased. This indicates that ZnO/nylon-6 nanocomposites have less thermal stability than pristine nylon-6 mat. The decrease in thermal stability can be attributed to the decrease in intermolecular hydrogen bond strength caused by ZnO NPs. The proper intermixing of ZnO NPs with nylon-6 solution could rupture the intermolecular hydrogen bond of nylon-6 molecules. Interestingly, it was observed that the thermal stability of 10 and 20 wt% ZnO containing nylon-6 mat is almost same, however, weight loss present of 20 wt% ZnO containing mat is less than that of 10 wt% ZnO containing mat. This result indicated that in 20 wt% ZnO containing nylon-6 solution, ZnO NPs were not effectively uploaded through the electrospun fibres and supported the results obtained from the TEM analysis where NPs were seen to be agglomerated only on certain part of fibres (Fig. 3c). From this result, we can conclude that 10 wt% ZnO is suitable amount to make effective nanocomposite fibres with nylon-6. Furthermore, lower decomposition temperature of composite mat is attributed to the decomposition of ZnO and formation of its by-product around 400 ^{0}C which can accelerate the decomposition of nylon-6 matrix. Similar result was reported by Kim *et al.* when ZnO NPs were incorporated through polyurethane acrylate film [18].

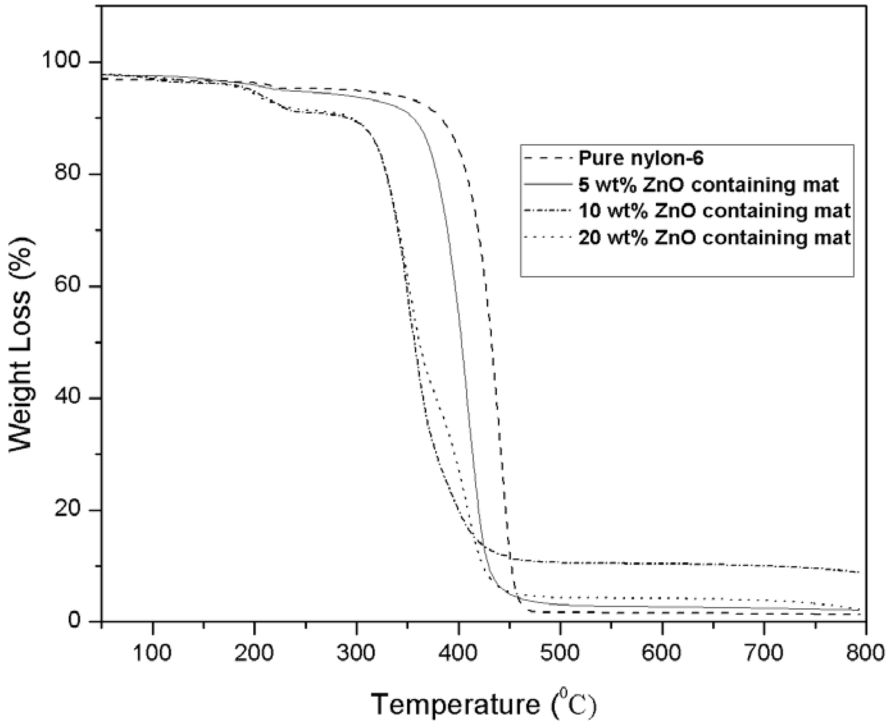

Fig. 4. TGA spectra of different electrospun nylon-6 mats.

The loading of ZnO NPs and their proper interaction with polymer matrix was further confirmed by FT-IR spectra. Fig. 5 shows the comparison of the FT-IR spectra of pristine nylon-6 mat and ZnO/nylon-6 composite mats. It shows that the functionalities of nylon-6 molecules can easily interact with ZnO NPs through the formation of hydrogen bonding or donor-acceptor complexes which was clearly observed from the shifting of different IR bands of nylon-6 in composite mats (Fig. 5). The characteristic peaks of pristine nylon-6 fibres are explained in our previous work [10]. Compared with the pristine nylon-6 mat, ZnO NPs containing mats showed the shifting of different peaks towards higher values (Fig. 5) and signifying an interaction between ZnO NPs and nylon-6 molecules [10, 19]. This shifting was pronounced in 10 wt% ZnO NPs containing mat compared to others. Therefore, the result indicated that at 10 wt% ZnO concentration there was proper interaction of ZnO with nylon-6 molecules which was also supported by TEM and TGA analysis as described above.

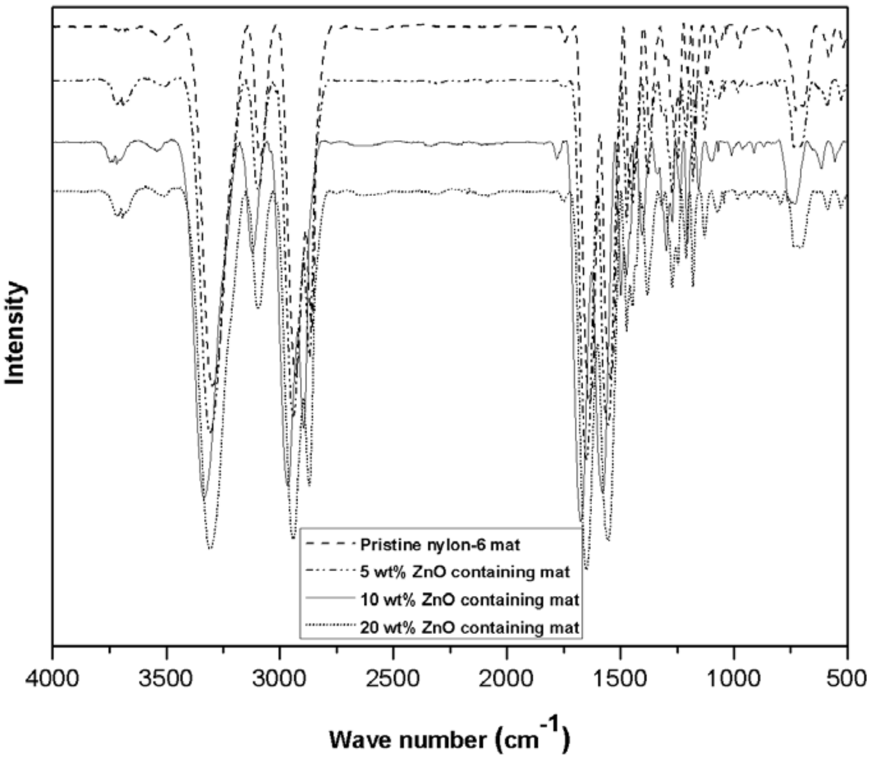

Fig. 5. FT-IR spectra of different electrospun nylon-6 mats.

The electrical characteristics of pristine nylon-6 and 10 wt% ZnO NPs containing nylon-6 composite mats were measured by a current-voltage (I-V) characterization. Small pieces of individual mats with equal dimension were taken and they are separately contacted by 25 μm thick Au wires with an assistance of silver paste for current-voltage (I-V) characterization. The I-V characteristic was measured for the applied bias voltage ranging between -25 to +25 V and the data obtained from the first measurement for each probe pair is shown in Figure 6. Here, current tendency of pristine nylon-6 mat shows almost rectilinear movement to increased voltage (V). On the other hand, comparing to the pristine nylon-6 mat, current (I) of ZnO/nylon-6 mat shows similar linear characteristics at lower range of voltage (up to 2 volt) whereas its current values (I) shows a great difference of about two times or over after 3 volt. From this, it is confirmed that the conductivity of nylon-6 fibres is increased when ZnO is incorporated with nylon-6 fibres. The increased electrical conductivity of ZnO/nylon-6 composite mat is attributed to the formation of denser spider-wave-like nanonets (Fig. 2c) as well as incorporation of ZnO NPs which can enhance the electrical pathways thought the mat. The measured current (I) as a function of applied bias voltage (V) was normalized by the aspect ratio of width to length (w/l), and absolute values of I were plotted in logarithmic scale for better comparison of positive and negative biases (Fig. 7). Hysteric behaviour was observed for the ZnO/nylon-6 mats by a cyclic voltage sweep. This might be due to trapping sites inside the samples caused by large number of true nanofibres and ZnO NPs. Furthermore, this curve resembles the cyclic I-V characteristics of memory devices. The decreased in sheet resistance in composite mats suggests that ZnO loading boosts the electron conduction path. Moreover, possibility of bridging between the nylon-6 nanofibres due to the spider-wave structure and ZnO particles can increase the amounts of charge carrier and reduces hopping distance of conduction electrons which favours percolation phenomenon. Jeong *et al.* also observed the similar result when MWNTs were incorporated through electrospun nylon fibers [20]. By the basis of our experimental analysis, we can strongly conclude that the present of ZnO particles and the spider-wave-like nanonets on electrospun nylon-6 fibrous mat play significant roles on the electrical properties of nylon-6 composite fibres. These results show that the spider-wave-like ZnO/nylon-6 composite can be applicable for the future electronic and memory device applications.

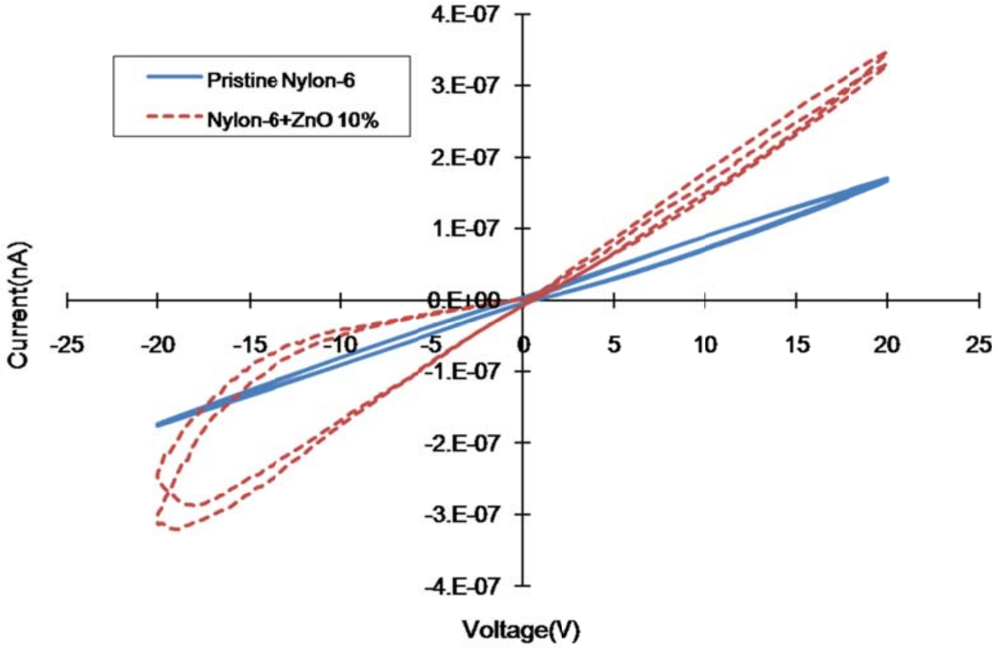

Fig. 6. I-V Characteristics of pristine nylon-6 and ZnO (10 wt%) incorporated nylon-6 electrospun mats.

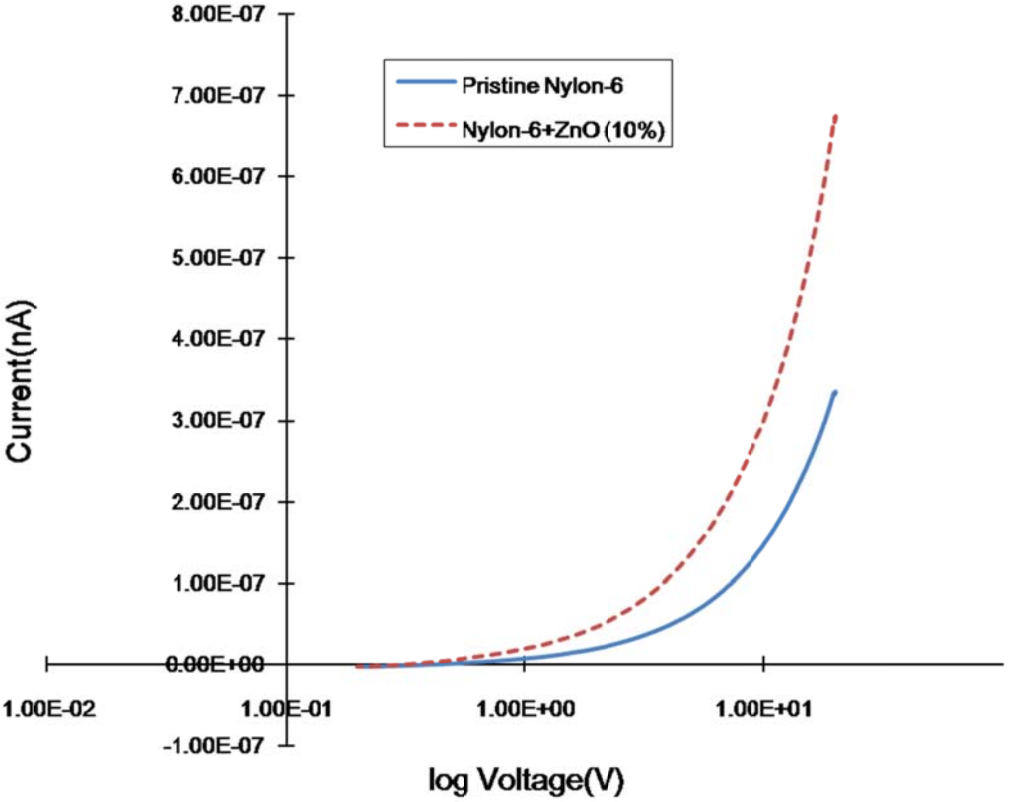

Fig. 7. Sweeping-down traces of current-voltage characteristics of pristine nylon-6 and ZnO(10 wt%) incorporated nylon-6 electrospun mats.

4. Conclusions

This study reports the electrical properties and unique morphology of ZnO NPs loaded nylon-6 spider-wave-like nanonets. We investigated the optimized conditions for the fabrication of ZnO loaded nylon-6 composite nanofibres with continuous and smooth fibre morphology. Well-dispersed ZnO NPs (up to 10 wt%) with nylon-6 solution could allow effective uploading of NPs through fibres and obviously formed spider-wave-like nano-nets of nylon-6. The incorporation of ZnO NPs through electrospun fibres were confirmed by FE-SEM, TEM, TGA, and FT-IR analysis. The electrical characteristics of pristine nylon-6 and ZnO/nylon-6 composite mats were investigated by a current-voltage (I-V) characteristic and it was found that ZnO/nylon-6 nanofibres had better electrical conductivity than pristine nylon-6 mat. Therefore, this work indicates that ZnO/nylon-6 composite nanofibres can be utilized for future electronic devices and sensor applications.

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References

[1] S. Ramakrishna, K. Fujihara, W. E. Teo, T. C. Lim, Z. Ma, An introduction to electrospinning and nanofibers, World Scientific Pub., Singapore, 2005.
[2] A. Greiner, J.H.Wendorff, Angew. Chem. Inter. Ed. **46**, 5670 (2007).
[3] N. Bhardwaj, S. C. Kundu, Biotech. Adv. **28**, 325 (2010).
[4] H.R. Pant, M.P. Bajgai, K. T. Nam, Y.A. Seo, D.R. Pandeya, S.T. Hong, H.Y. Kim, J. Haz. Mater. **185**, 124 (2011).
[5] K. Kim, H. Ryoo, K. S. Shin, Langmuir **26** (13), 10827 (2010).
[6] S. Shahgaldi, Z. Yaakob, D. J. Khadem, W. R. W. Daud, Int. J. Hydrogen Energy, **37**, 11237 (2012).
[7] N. A. M. Barakat, M.F. Abadir, F.A. Sheikh, M.A. Kanjwal, S.J. Park, H.Y. Kim, Chem. Eng. J., **156**, 487 (2010).
[8] H.R. Pant, M.P. Bajgai, C. Yi, R. Nirmala, K.T. Nam, W. Baek, H.Y. Kim, Colloids Surf. A. **370**, 87 (2010).
[9] B. Ding, X. Wang, J. Yu, M. Wang, J. Mater. Chem. **21**, 12784 (2011).
[10] H.R. Pant, M.P. Bajgai, C. Yi, R. Nirmala, K.T. Nam, W. Baek, H.Y. Kim, Colloids Surf. A. **370**, 87 (2010).
[11] H.R. Pant, M.P. Bajgai, K.T. Nam, K.H. Chu, S. Park, H.Y. Kim, Mater. Let. **64**, 2087 (2010).
[12] N.A.M. Barakat, M.A. Kanjwal, F.A. Sheikh, H.Y. Kim, Polymer **50**, 4389 (2009).
[13] H.R. Pant, K. Nam, H. Oh, G. Panthi, H. Kim, B. Kim, H.Y. Kim, J. Colloid. Interf. Sci. **364**, 107 (2011).
[14] H.R. Pant, C. H. Park, L. D. Tijing, A. Amarjargal, D. H. Lee, C. S. Kim, Colloids Surf. A **407**, 121 (2012).
[15] H.J. Kim, H.R. Hem, C.H. Park, L.D. Tijing, N.J. Choi, C.S. Kim, Ceramics Int. (2012) (in press) DOI: http://dx.doi.org/10.1016/j.ceramint.2012.09.089.

[16] R. Thangavel, V. Sabarinathan, S. Ramasamy, J. Kumar, Mater, Lett. **61**, 4090 (2007).
[17] Z.L Wang, ACS Nano **2**, 1987 (2008).
[18] D. Kim, K. Jeon, Y. Lee, J. Seo, K. Seo, H. Han, S. Khan, Prog. In Org. Coatings **74**, 435 (2012).
[19] H. Zhang, S. Li, C. J. Branford White, X. Ning, H. Nie, L. Zhu, Elect. Acta **54**, 5739 (2009).
[20] J.S. Jeong, S.Y. Jeon, T.Y. Lee, J.H. Park, J.H. Shin, P.S. Alegaonkar, A.S. Berdinsky, J.B. Yoo, Diamond Related Mater. **15**, 1839 (2006).