Int. J. Environ. Res., 3(4):663-670, Autumn 2009
ISSN: 1735-6865

Recycling of Used Bottle Grade Poly Ethyleneterephthalate to Nanofibers by Melt-electrospinning Method

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Received 18 Feb. 2009; Revised 15 June 2009; Accepted 25 June 2009

ABSTRACT: Used PET bottles disposal is an unsolved environmental problem, and there are many efforts for finding an applicable solution for it. Many researches have showed that the degradation rate of the polymers increase with the smaller size of fibers. This work was carried out to convert used PET bottles into nanofibers by melt-electrospinning method. Uncolored, washed and chipped PET bottles and the PET granule was used for experiments. The temperature of melted PET at extruder nozzle and spinning area were set in the range of 245-255 °C and 200-235 °C respectively. The melting point of the polymer was determined by DSC. The potential difference was fixed at 25 kV and the distance between the nozzle and the collector were 3-9 cm. The morphology and fineness of produced fibers investigated by SEM. Although the producing fibers were not completely in the rang of nano-size fibers, but the results have showed that the nanofibers with diameter between 61-93 nm can be achieved by the melt-electro spinning method. Comparing the effects of different flow rates of melting polymer as well as the distance between the nozzle to the collector have shown more proportion of finer fibers in flow rate less than 0.1 mL/min and the distance in the range of 3-5 cm. It was concluded however the melt electrospinning production of nanofibers has some difficulties but it can be considered as an applicable and environmental friendly way to recycling the used PET bottles so it can prevent more pollution of the environment.

Key words: Environmental Pollution, Nonofiber, PET, Disposal Bottle, Polymers

INTRODUCTION

Poly ethylene-terephthalate (PET) has been used increasingly in recent years, especially to produce PET bottles (Silva *et al.,* 2005). Many companies produce virgin PET globally giving it different trade names. In the year 2000, a total amount of about 30 millions tons of PET was commercially produced in worldwide including packing which only less than 30% percent of it has been recycled (Claudio, 2005). The most of PET polymer is used in the field of textiles. Polyester fibers ranked the first place in the worldwide production of synthetic textile fibers with an output of 18.9 million tons which corresponds to 60% of market share (Torres *et al.,* 2000). Post consumer PET bottles are considered as one of the most important waste material in the past two decades due to rapid growth in its use. It is regarded as an excellent tensile and impact strength, chemical resistance, clarity, process ability, color ability and reasonable thermal stability (Firas *et al.,* 2005). Three to 5% of waste occurs during PET fiber production (Incarnato *et al.*,2000; Byung *et al.*,2007). Those wastes can be classified into three distinct groups. These groups can be named as follows: a) Polymer cakes or lump wastes, b) POY (Partially Oriented Yarn) wastes or hard wastes, c) Fiber wastes or soft wastes (Jang-Ho *et al.,* 2007).

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Commercial PET has a wide range of intrinsic viscosity [η] that varies from 0.45 to 1.2 dlg^{-1} with polydispersity index generally equal to 2. The chain is considered to be stiff above the glass transition temperature (T_g) unlike many other polymers. The low flexibility of the PET chain is a result of the nature of short ethylene group and the presence of the p-phenylene group (Torres *et al.*, 2000).

Many efforts have been done to produce nanofibers from synthetic materials by electrospinning method in recent years. A fiber having a diameter less than 10 μm is called an "ultra-fine fiber," and a fiber having diameter less than 100 nm is called a "nanofiber" (Reneker *et al.*, 2007). By virtue of its surface area, ultra-fine fiber has many applications, including high-performance filters, membranes optics, vascular grafts, protective clothing, molecular templates, tissue scaffolds and raw material for carbon fibers (Ji-Huan *et al.*, 2004). Nanofiber, which has not only greater surface area than ultra-fine fiber, but also a possibility of good biocompatibility and low fluid resistance, is expected to find advance application (Elamri *et al.*, 2007).

Electrospinning is novel process for forming superfine fibers with diameters ranging from 10 down to 10 by forcing a melting or solution polymer through a spinneret with an electric field. The technology has attracted much attention recently. Techniques for in-situ alignment of as-spun nanofiber/nanotube using electrostatic repulsion force are demonstrated as route for alignment of nanofiber/nanotube (Thompson *et al.*, 2006). While most of the previous work on electrospinning has involved polymer solution, but not enough progress has been made in polymer melt-electrospinning (Wen Zhang *et al.*, 2007). The melt-electrospinning method is more attractive for industrial application because it is environmental friendly, it eliminates the solvent recovery and treatment cost, and there is a wider selection of polymer available, including such important system as polyethylene (PE), polypropylene (PP) and polyethyleneterephthalate (PET) which do not have appropriate solvents at room temperature(Holzmeister *et al.*,2007).

MATERIALS & METHODS

This study was focused on the production of nanofibers from recycling of post-consumer PET bottles by melt-electrospinning method. Two types of materials were investigated in this study. Used grade PET bottles and the PET granule were used. Crushed and cleaned bottles chips were purchased from an industrial plastic collector and used as the source for recovered PET materials. The PET granules made by Hawollan Company PET producer purchased from the market. For determine a melting point of samples the DSC experiment was used.

This system was set up by using a pyrex piston and a cylinder which was connected to a changeable conic aluminum nozzle under it. A circular ceramic heater installed around a silicon oil bath was used to unify heating of cylinder for melting the polymers. The silicon oil bath temperature adjusted in the range of 255-255 °C by installing submerged thermocouple in it. An agitator used to agitate the silicon oil continuously to homogenize the temperature and allow the cylinder reaches the required temperature, i.e. to the melting point of samples in all side evenly. The melted polymer exits from the aluminum nozzle by its gravity and the pressure of piston weight. Another heating area with a range of 200-235 °C was prepared around the exiting melted PET to prevent sooner solidification of it. A dielectric high voltage field was prepared by a high voltage power supply to convert the melting PET to nano-fibers. A schematic diagram of the melt-electro spinning setup is shown in (Fig.1). It consists of five major component: packed melting system, heating area for spun jet, high voltage power supply, spinneret (aluminum nozzle), and a collector plate.

The polymer was melted in the cylinder due to hot silicon oil around it and exit from the nozzle with a flow rate depend on nozzle diameter, piston weight and the melting temperature. As the melting jet is going down, the high voltage electric field produce an electrostatic forces which overcome the surface tension and viscoelastic properties of the melt resulting in converting the melting polymer to fine fibers. Of course in the beginning of the operation the applied voltage cause a cone formation at the apex of capillary or spinneret and it needs to find the critical voltage for better fiber

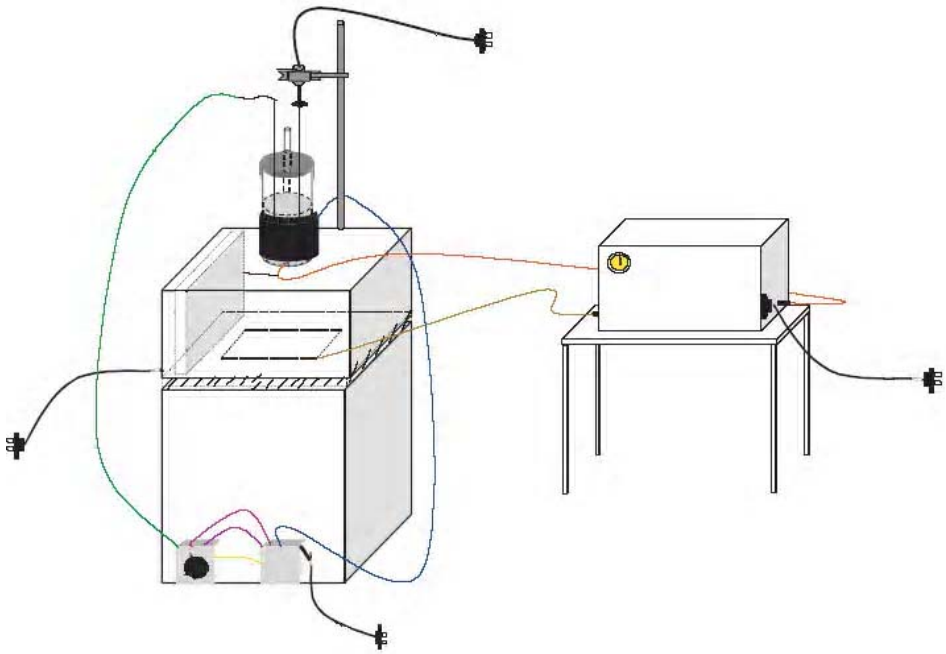

Fig. 1. schematic diagram describing the melt-electrospinning technique

formation. Similar to solution based electrospinning, the main driving force for fiber formation is attenuation of the spin line under electrostatic forces. The melting jet diameter is continually reduced due to the electrostatic forces acting on it in the spinning area, unless the viscosity once again overcomes the electrostatic forces as a result of jet solidification from cooling. So it needs to keep the spinning area warm enough during the fiber production. Scanning Electron Microscope (SEM, Philips, XL-30) was used to study the morphology of dried mat. Beam strength of 20 kV with spot size of 3 was used to take the micrographs. The average diameter of fibers and the respective distributions were determined from 50 measurements of random fibers at each spinning condition.A Differential Scanning Calorimetric (DSC) analysis was carried out on a Perkin-Elmer 7 instrument. Ultrahigh purified nitrogen was purged through the calorimeter. The PET sample (H"5 mg) was heated to 296 °C at a rate of 25 C/min, then cooled to 25 °C at the same rate. subsequently, a second heating cycle was conducted at a heating rate of 25 °C/min.

RESULTS & DISCUSSION

Fiber morphology such as bead structure, radius cross section and fiber structure can be affected by production condition including flow rate, viscosity, applied voltage, and polymer specifications. Also applying a suitable melting temperature can result in better product.

Experimental consideration showed that viscosity affects much more on diameter of electro-spun fibers than the others. Baumgarten (2004) point out that as the viscosity increased, the spinning drop changed from approximately hemispherical to conical, the length of the jet increased as well. We also found that the fiber diameter will increased with increasing the melt viscosity and is approximately proportional to jet length. The jet length was measured from the tip of the spinning drop to onset of waves in the fiber. Those phenomena have recently been subjected to theoretical treatment and it was shown that the fiber diameter depends on solution viscosity (Reneker, *et al.*, 2006).

There are limitations to reducing the viscosity of a melting polymer without sacrificing the properties of fibers produced. Increasing the temperature of melting polymer was used to reduce the viscosity, but it was very critical because it may lead to polymer burning. Other melt-electro spinning experiments for PET were performed at a processing temperature of 200°C (Jason *et al.*,2004), therefore all processing temperatures were kept in the range of 200-225

C. It was found that the processing temperature is more effective at lower electric field strengths. As the electric strength was increased the fiber diameter differential between both temperatures was significantly low. This result was according to finding of the other research (Chin Pong *et al.*, 2007). At lower electric field strengths before the critical point, the electrostatic forces are trying to untangle molecular chains and begin the formation of linear structure. At this stage, the viscosity plays a very significant role as the ease of disentanglement will be directly related to viscosity of the melt; a lower viscosity will be more easily untangled (Theron *et al.*, 2004). However, at electric field strength of 20 kV/cm, a majority of molecular chains are untangled and the electrostatic forces are being utilized to further attenuate the molecular chains, so a majority of the chain entanglement will be removed (Hong *et al.*, 2001) and the average fiber diameter remains smaller for the higher processing temperature but the variation is significantly reduced.

The experiments have been done at three different distances (3, 5, and 9cm) between nozzle and collector. The produced fibers were really different in shape and diameter as well with changing the distance between nozzle and collector. As it has shown in fig. 2 - 4 increasing the distance between the nozzle and collector from 3 to 9 cm results in producing finer fibers but the best fiber shape or morphology was achieved at distance of 5 cm.

Increasing the applied voltage during melt-electrospinning while maintaining a constant spinning distance, will increase the electrostatic forces acting on the jet. This was according to other studies in this regards (Zuwei *et al.*, 2005; Paul *et al.*, 2007). If greater forces are acting on the jet, there exists a greater potential for electric field strength to overcome the chain entanglement of the polymer melt (Freng *et al.*, 2003; Elamri *et al.*, 2007). If a group of chain can be removed from the bulk of the polymer and attenuated in electric field, it is possible for smaller diameter fibers to be produced. Fig. 3. shows the effect of electric field strength on fiber diameter for the PET samples that were melting electro-spun.

In order to determine the feasibility of utilizing existing commercial equipment to melt-electrospinning, therefore one melting packed was used to perform the melt-electrospinning in our work. One of the major faults of electrospinning,

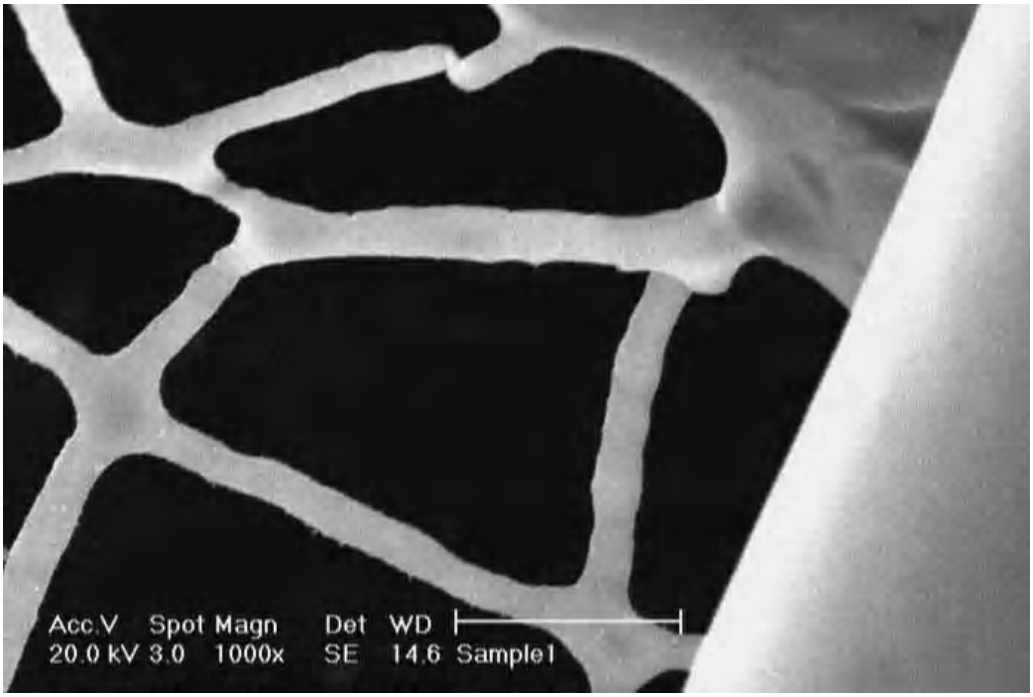

Fig. 2. SEM photo micrograph of submicron fibers produced from PET at 3 cm distance between nozzle and collector and 225 °C temperature of spinning area

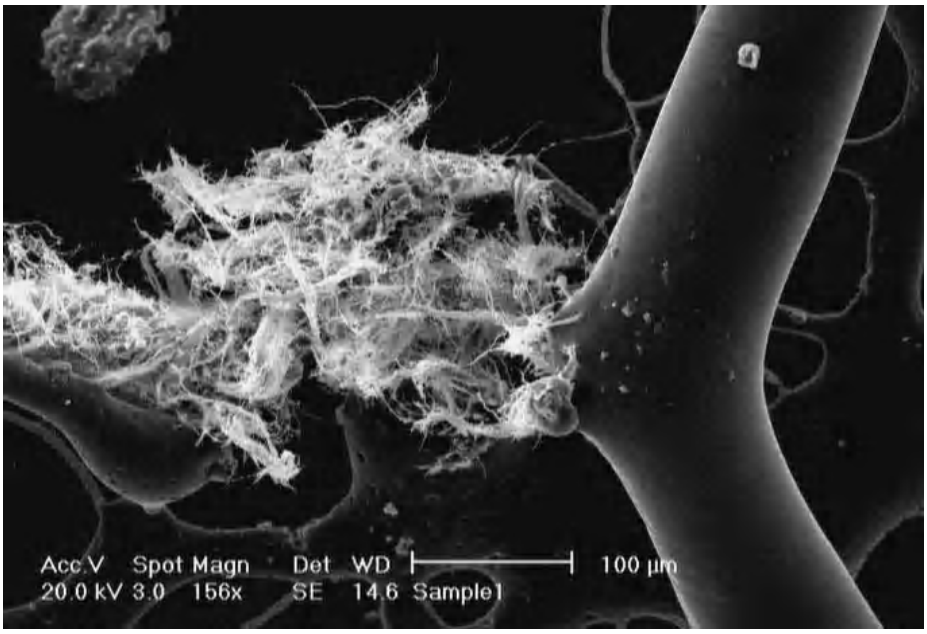

Fig. 3. The SEM micrograph of morphology and diameter of PET fibers at electric field strength of 20 kV/cm and 9 cm distance between nozzle and collector

in general, is the exceptionally low output associated with the process; solution electrospinning yields approximately 0.01 g/min/ nozzle (Bhattarai *et al.,* 2006) and melt-electro spinning, as a result of zero loss to evaporation would be significantly higher. To further increase productivity, it may be possible to simply increase the amount of polymer being fed into the system (Yarin *et al.*, 2001). The flow rate of the polymer feed is therefore and important parameter that must be studied (Hohman *et al.,* 2001). The size of the enveloped cone has a significant effect on fiber diameter. The smallest fibers as seen in Fig. 4. were produced when the least amount of volume was present. This phenomenon is not unexpected because the electrostatic forces remain constant and are more capable of deforming a smaller volume because of the forces required.

This realization is significant because it shows that supplying more polymers to the spinneret will increase the productivity of melt-electrospinning to a point, but at the sacrifice of the collected fiber diameter. In order to become competitive in productivity to melt-blown nonwoven, a comparable technology with a production rate of 0.5 g/min/nozzle, multi- spinneret electrospinning must be considered (Yarin *et al.,* 2007; Reneker *et al.,* 2006). This finding is in agreement with the studies by other researcher [Kirichenko, 1986] on lower viscosity fluids that concluded that the asymptotic limit of the fiber diameters is a function of the flow rate and not of the nozzle size.

The temperature range of spin pack was set 245-255 °C and in spinning area was adjust in the range of 200-225 °C. Temperature has indirect effect on fiber diameter, when temperature was increased then the viscosity of melt-electro spun has decreased so the diameter of produced fibers were reduced. It appears that the processing temperature is more influential at lower electric field strength. (Deitzel *et al.*, 2001). As the electric field strength was increased the fiber diameter differential between low and higher temperatures was significantly low. At lower electric field strengths before the critical point, the electrostatic forces are trying to untangle molecular chain and begin the formation of linear structure (Yu *et al.,* 2006). At this stage, the viscosity plays a very significant role as the ease of disentanglement will be directly related to viscosity of the melt; a lower viscosity will be more easily untangled. However, at electric field strength of 20 kV/cm, a majority of the molecular chains are untangled and the electrostatic forces are being utilized to further attenuate the molecular chains; a majority of chain entanglements have already been removed (Bognitzki *et al.,* 2001). The average fiber

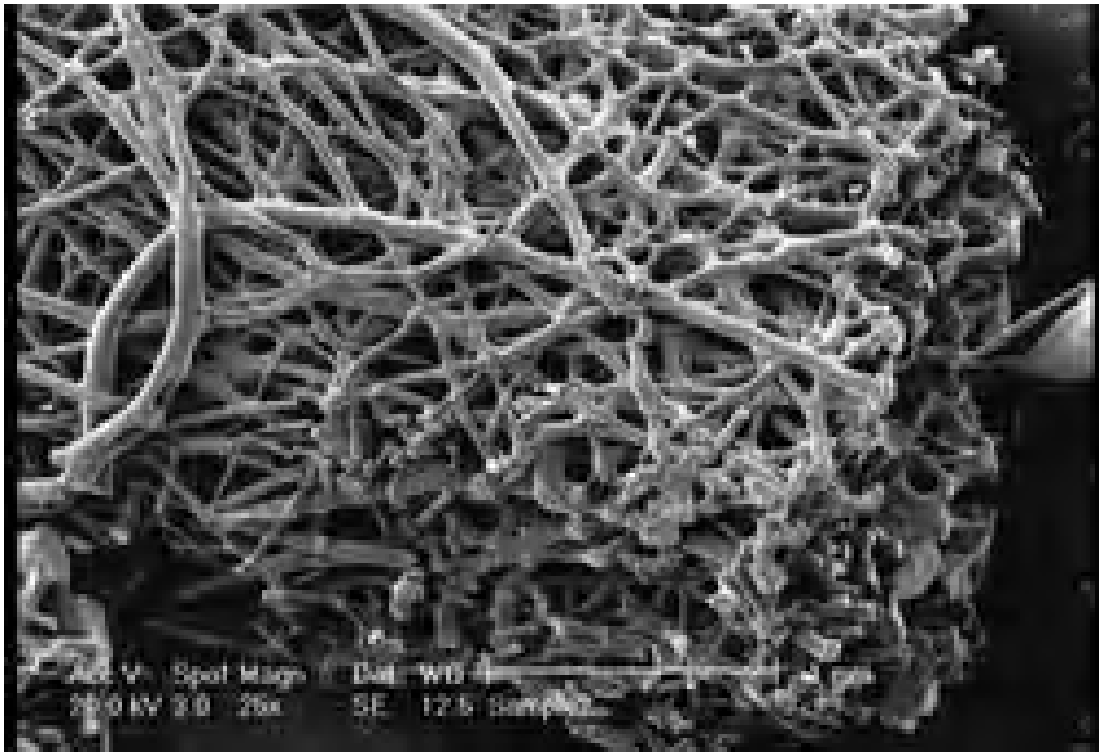

Fig. 4. SEM photo micrograph for significant effect of flow rate (less than 0.1 mL/min) on fiber diameter at distance between nozzle and collector of 5 cm

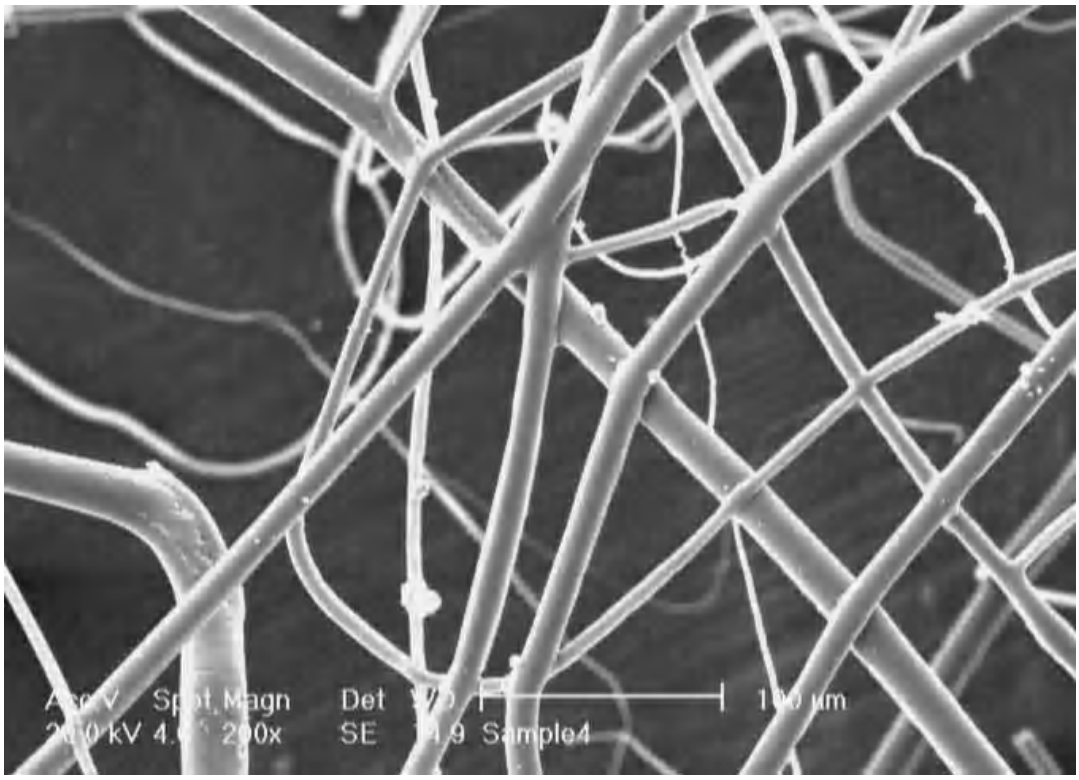

Fig. 5. SEM photo micrograph for significant Effect of Processing Temperature on Fiber Diameter

diameter remains smaller for the higher processing temperature fibers but the variation is significantly reduced (Fig. 5).

CONCLUSION

Using electro spinning to produce nano-fibers from polymer fluids has been well known and extensively studied. Most of polymers dopes are prepared by using a solvent which may be creates an additional environmental problem. Melt-electro spinning is seems to be a more environmental friendly method but there is another challenge due to its difficulty for treating with a melt polymer. It can be concluded from the result of this study that the melt-electro spinning method is capable to be used to produce nano-fibers from melting PET. In order to become competitive in productivity to other conventional methods, a comparable technology with multi- nozzle must be considered. The surface morphology and diameter distribution of produced nanofibers are a function of various electrospinning parameters including electric field strength, melt temperature, viscosity and flow rate, and polymer specification, which among them the melting temperature and dielectric properties of polymer are dominant. It would be helpful to develop a model relating fiber diameter to processing parameters and polymer properties. It can be seen that with the aid of this method many thermoplastic polymers considered as pollutants can be safely convert to profitable nanofibers. According to great specific surface of nanofibers, they have high rate of degradability, and are not threatening the environment.

REFERENCES

Bhattarai, S. R., Bhattarai, N., Yi, H. K., Hwang, P. H., Cha, D. I. and Kim, H. Y. (2004). Nonverbal biodegradable electrospun membrane. Scaffold for tissue engineering. Biomaterials, **25 (13)**, 2595-2602.

Bognitzki, M., Czado, W., Frese, T., Schsper, A., Hellwing, M. and Steinhart, M. (2007). Nanostructured fibers via electrospinning. Adv. Mater., **13(1)**, 70-72.

Jo, B. W., Tae, G. H. and Kim, C. H. (2007). Uniaxial creep behavior and prediction of recycled-PET polymer concrete. Constr. Build. Mater., **21**, 1552-1559.

Chang, C. P. and Lin. S. M. (2007). The formation and growing properties of poly (ethylene terephthalate) fiber growing media after thermo-oxidative treatment. Mater. Sci. Eng., **457**, 127-131.

Claudio, B. (2005), Recycling PET; Bottle to Bottle Process Application. Paper presented at, 10th World Congress of Polyester, Amsterdam, The Netherlands.

Deitzel, J. M., Kleinmeyer, J., Harris, D. and Beck Tan, N. C. (2001). The effect of processing variable on the morphology of electrospun nanofibers and textiles. Polymer, **42(1)**, 261-272.

Elamri, A., Lallam, A., Harzalllah, O. and Bencheikh, L. (2007). Mechanical characterization of melt spun fibers from recycled and virgin PET blends. J. Mater. Sci., **42(19)**, 8271-8278.

Awaja, F. and Pavel, D. (2005). Statistical models for optimization of properties of bottles produced using blends of reactive extruded recycled PET and virgin PET. European polymer journal, **41**, 2097-2106.

Freng, J. J. (2003). Streching of a straight electrically charged viscoelastic jet. J. Non-Newtonian Fluid Mechanics, **116(1)**, 55-70.

Hohman, M. M., Shin. M., Rutledge, G. and Brenner, M. P. (2001). Electrospinning and electrically forced jets. I. Stability theory. Phys. Fluids., **13**, 2201-2220.

Holzmeister, A., Rudisile, M., Greiner, A. and Wendorff, J. H. (2007). Structurally and chemically heterogeneous nanofibrous nonwoven via electrospinning. European Polymer journal, **43(12)**, 4859-4867.

Chen, H., Cao, Y. and Xianwei, X. (2001). formation of AIN nano-fibers. J. Crystal Growth., **224**, 187-189.

Incarnato, L., Scarfato, P., Di maio, L. and Acierno, D. (2000). Structure and rheology of recycled PET modified by reactive extrusion. Polymer, **41(18)**, 6825-6831.

Jang-Ho, J. K., Chan-Gi, P., Si-Won, L., Sang-Woo, L. and Jong-Pil, W. (2007). Effects of the geometry of recycled PET fiber reinforcement on shrinkage cracking of cement-based composites. Composites, **10**, 05-001.

Jason, L., Christopher, L. and Frank, K. (2004). Melt-electrospinning part I: processing parameters and geometric properties. Polymer, **45**,7597-7603.

Ji-Huan, H., Yu-Qin, W. and Jian-Yong, Y. (2004). Application of vibration technology to polymer electrospinning. Int. J. Nonlin. Sci. Num. Simulation, **5(3)**, 253-262.

Dalton, P. D., Grafahrend, D., Klinkhammer, K., Klee, D. and Moller, M. (2007). Electrospinning of polymer melts: Phenomenological observations.polymer, **48**, 6823-6833.

Reneker, D. H., Yarin, A. L., Zussmna, E. and Xu, H. (2007). Electrospinning of nanofibers from polymer solution and melts. Adv. Appl. Mech., **41**, 43-195.

Silva, D. A., Betioli, A. M., Gleiza, P. J. P., Roman, H. R., Gomez, L. A. and Ribeiro, P. (2005). Degradation of recycled PET fibers in Portland cement-based materials. Cement and Concrete Research, **35**, 1741-1746.

Theron, S., Zussman, E. and Yarin, A. L. (2004). Experimental investigation of the governing parameters in the electrospinning of polymer solution. Polymer, **45**, 2017-2030.

Thompson, C. (2006). An analysis of variable effects on theoretical model of the electrospin process for making nanofibers. Ph. D. Thesis, The university of Akron, Akron, Ohio, USA.

Torres, N., Robin, J. J. and Boutevin, B. (2000). Study of thermal and mechanical properties of virgin and recycled poly(ethylene terephthalate) before and after injection molding. European Polymer journal, **36**, 2075-2082.

Kirichenko, V. N., Petryanov–Sokolov, I. V., Suprun, N. N. and Shutov, A. A. (1986). Asymptotic radius of a slightly conducting liquid jet in an electric field. Sov. Phys. Dokl., **31**, 611-613.

Wen, Z., Zonghao, H., Eryun, Y., Cheng, W., Yi, X., Qiang, Z. and Yanbin, T. (2007). Preparation of poly(phenylene vinylene) nanofibers by electrospinning. Mater. Sci. Eng., **443**, 292-29.

Yarin, A. L., Koombhongse, S. and Reneker, D. H. (2001). Taylor cone and jetting from liquid droplets in electrospinning of nanofibers. J. Appl. Phys., **90**, 4839-4846.

Yarin, A. L. and Zussman, E. (2004). Upward needleless electrospinning of multiple nanofibers. Polymer, **45**, 2977-2980.

Yu, J. H., Fridrikh, S. V. and Rutledge. G. C. (2006). The role of elasticity in the formation of electrospun fibers. Polymer., **47**, 4789-4797.

Zuwei, M., Masaya, K., Thomas, Y., Wei, H. and Seeram, R. (2005). Surface engineering of electrospun polyethethylene terephthalate (PET) nanofibers towards development of a new material for blood vessel engineering. Biomaterials, **26**, 2527-2536.