

A PARAMETRIC STUDY ON ELECTROSPINNING AND ITS APPLICATION TO CARBON/EPOXY COMPOSITES

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Abstract. This study investigated the synthesis of nanomembranes using the electrospinning technique. Polyamide-66 (PA-66) was used in the parametric study (considering the impact of polymer concentration, applied voltage, solution flow rate, and the gap between needle and collector) on the morphology of nanofibers. An additional parameter investigated was the graphene effect into nanofiber diameter. The results showed that the mean diameter of nanofibers is directly proportional to the flow, the polymer concentration and the applied voltage. The addition of carbon-based nanoparticles caused the growth of the mean diameter of nanofibers. The mean diameters for graphene concentrations of 0 wt%, 1 wt% and 2 wt% ranged from 57 nm (0 wt%) to 141 nm (2 wt%). Moreover, the mean diameters of the nanofibers were 37% lower than those reported in the literature.

Keywords: electrospinning, nanofibers, nanomembranes, graphene, nanostructured composites

1. INTRODUCTION

Due to their high surface area to volume ratio, the interconnectivity of their fibers and the existence of interstitial space, nanomembranes are interesting for a large number of applications where high porous structures are needed: some examples are structural composites, nanobiology, air purification systems, bioengineering, environmental engineering and electronics, energy industries, defense and security (Huang *et al.*, 2003; Ramakrishna *et al.*, 2005; Andradý, 2008; Li *et al.*, 2008; Shivakumar *et al.*, 2009).

Although the synthetic fibers manufacture technique using electric discharges have been discovered in the last century (Cooley, 1902; Morton, 1902; Formhals, 1934), only recently electrospinning has become the focus of a large number of researchers around the world (Ko, 2004). The operating principle of the electrospinning process is relatively simple, which makes it quite advantageous in comparison to other methods (Ramakrishna *et al.*, 2005). In addition, the dimensional control of generated nanofibers, the reproducibility of results and great potential for industrial-scale have made the electrospinning process to become quite “popular” in recent years.

The technique of electrospinning involves applying a strong electric field between the polymer and a metal collector (Norris *et al.*, 2000; Ayutsede, 2005; Andradý, 2008), as shown in Fig. 1. Generally, the melted or dissolved polymer is contained in a reservoir with a capillary tube (hypodermic needle), and it is forced to flow through a needle by gravity or with the aid of an infusion (metering) pump.

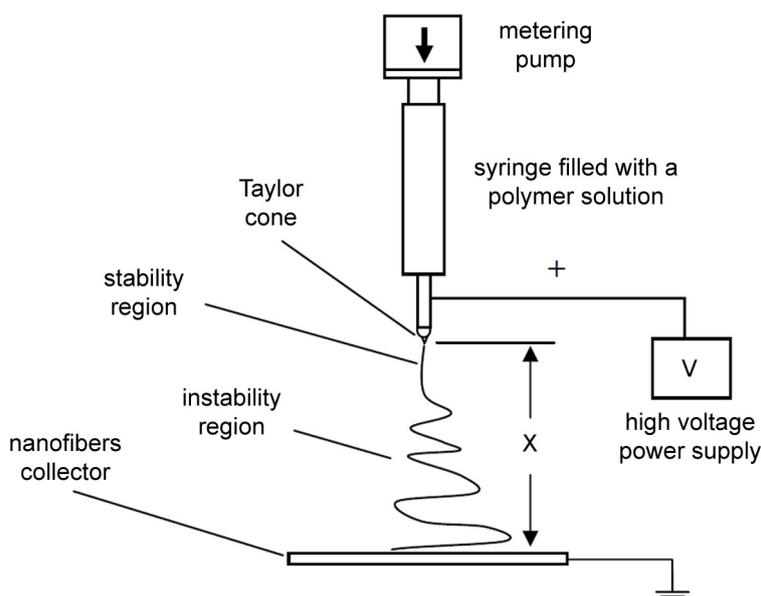


Figure 1. Schematic assembly of a typical electrospinning system (Lam, 2004)

When applying a high voltage in the capillary tube (syringe needle), which is located at a certain distance from the collector (a stationary flat surface or a rotating cylinder), there is a polarization in the polymer molecules. When the voltage between the capillary and the collector exceeds a critical value, the electrostatic force acting on the polymer becomes greater than the surface tension of the solution at the tip of the needle, forming the so-called Taylor cone and leading to the formation of a jet that is drawn toward the collector. The electric field is responsible for stretching the jet, making it increasingly thin, leading to fibers diameters of micro or nanoscale (Doshi and Reneker, 1995).

To make the electrospinning process possible, the polymer has to be melted or dispersed in a solution. It is evident that the properties of the solution (polymer molecular weight, viscosity, surface tension and electrical conductivity of the solution, and the solvent dielectric effect) will play an important role in the generation of the nanofibers. Other factors of great influence in the electrospinning process are related to the operating parameters of the process. Among these factors, we can mention the potential difference used to generate the electric field, the solution flow rate, temperature, the type of collector used, the diameter of the syringe needle and the distance between the syringe and the collector. Finally, environmental factors such as relative humidity, pressure and the atmosphere composition (in the case of using different gases), may also influence the results obtained by the electrospinning process (Ramakrishna *et al.*, 2005; Reneker and Yarin, 2008).

An other parameter that can have an impact on the morphology of nanomembranes generated by electrospinning is the addition of nanoparticles in the polymer solution. Carbon nanotubes, graphene, silver nanoparticles, nanoceramic, quantum dots, colloidal gold and silica are among the nanoparticles most widely used today. Graphene, which has mechanical, thermal and electrical properties similar to those of carbon nanotubes, are 500 times cheaper and are becoming a promising alternative (Yasmin and Daniel, 2004; Mack *et al.*, 2005; Kotov, 2006; Wei *et al.*, 2009).

Due to its excellent physical, chemical and thermal properties (Shivakumar *et al.*, 2009), the polymer used in the study was the polyamide-66 (PA-66), also known as Nylon-66[®]. As solvent, a mixture containing 75% of formic acid (CH₂O₂) and 25% of chloroform (CHCl₃) was used (Lingaih *et al.*, 2008).

2. EXPERIMENTAL

2.1 Materials

The polymer polyamide-66 (Nylon-66[®]) was obtained from Rhodia. Formic acid (CH₂O₂) and chloroform (CHCl₃) were obtained from Synth[®]. The expanded graphite HC 11-IQ was provided by National Graphite.

2.2 Electrospinning

The electrospinning was carried out with the aid of electrospinning unit of the “Laboratory of Nanocomposites” at UFMG. Among the various operating parameters available, we chose to vary only those who have greater influence on the fiber morphology (Ávila Júnior, 2010), namely: the concentration of polymer in solution, the applied voltage, the flow rate of the solution, the distance between the needle tip and collector and the concentration of nanoparticles in the polymer solution. The speed of transverse displacement of the syringe holder and the rotation of the collector were fixed at 6.25 cm/min and 19 rpm, respectively. Based on the results obtained in the literature (Huang *et al.*, 2006; Heikkilä and Harlin, 2008; Lingaih *et al.*, 2008; Park *et al.*, 2009; Shivakumar *et al.*, 2009), we generated PA-66 nanomembranes as shown in Tab. 1.

The solutions used for electrospinning were obtained by dissolving the PA-66 in formic acid/chloroform (75%:35%) for 1 h 30 min at room temperature using a magnetic stirrer IKA[®] CERAMAG Midi at 600 rpm. Once the PA-66 was dissolved in formic acid/chloroform, we added expanded graphite HC 11-IQ (graphene) nanoparticles to the solutions X to XV which, again, returned to the magnetic stirrer for additional 1 h 30 min at 600 rpm. Once homogenized, the polymer solutions “rested” for 1 h, so that all air bubbles, created during the mixing process, could be released. Then, 10 ml of the polymer solutions were placed in 20 ml syringes with stainless steel needles with G18 tip (inner and outer diameters of 0.84 mm and 1.27 mm, respectively) to be used in the electrospinning process.

The nanomembranes were deposited by electrospinning for 2 h on the cylindrical collector, which was covered with aluminum foil for easy removal of the generated nanomembranes. The drying process of nanomembranes took place in a vacuum oven Quimis Q-819V2 for a period of 2 h at a constant temperature of 70 °C.

2.3 Morphological Characterization

The morphological characterization of the generated nanomembranes was performed by scanning electron microscopy (SEM) using a FEI Quanta[®] 200-FEG microscope. The nanomembranes samples were mounted in aluminum stubs and coated with an extremely thin layer (1 nm) of gold through the Bal-Tec/Leica MED 020 Coating System, to avoid electric loading of the images during scanning.

Using the image analysis software ImageJ (Abramoff *et al.*, 2004), the mean diameter of the fibers of the nanomem-

Table 1. Parameters used in the fabrication of nanomembranes by electrospinning

Sample	Polymer concentration (wt%)	Applied voltage (kV)	Flow rate (ml/h)	Tip to collector distance (cm)	Graphene concentration (wt%)
I	10	25.0	0.17	15.0	0
II	12	25.0	0.17	15.0	0
III	15	25.0	0.17	15.0	0
IV	10	20.0	0.17	15.0	0
V	10	22.5	0.17	15.0	0
VI	10	25.0	0.34	15.0	0
VII	10	25.0	0.51	15.0	0
VIII	10	25.0	0.17	10.0	0
IX	10	25.0	0.17	12.5	0
X	10	25.0	0.17	15.0	1
XI	10	25.0	0.17	15.0	2
XII	12	25.0	0.17	15.0	1
XIII	12	25.0	0.17	15.0	2
XIV	15	25.0	0.17	15.0	1
XV	15	25.0	0.17	15.0	2

branes was determined. Fifty measurements of diameters in the SEM images were taken from each sample.

3. RESULTS AND DISCUSSION

Table 2 summarizes the average diameter of each set of nanofibers after elimination of outliers (inconsistent data or extreme values that differ substantially from the behavior of the remaining data).

Table 2. Mean diameters of electrospun nanofibers samples

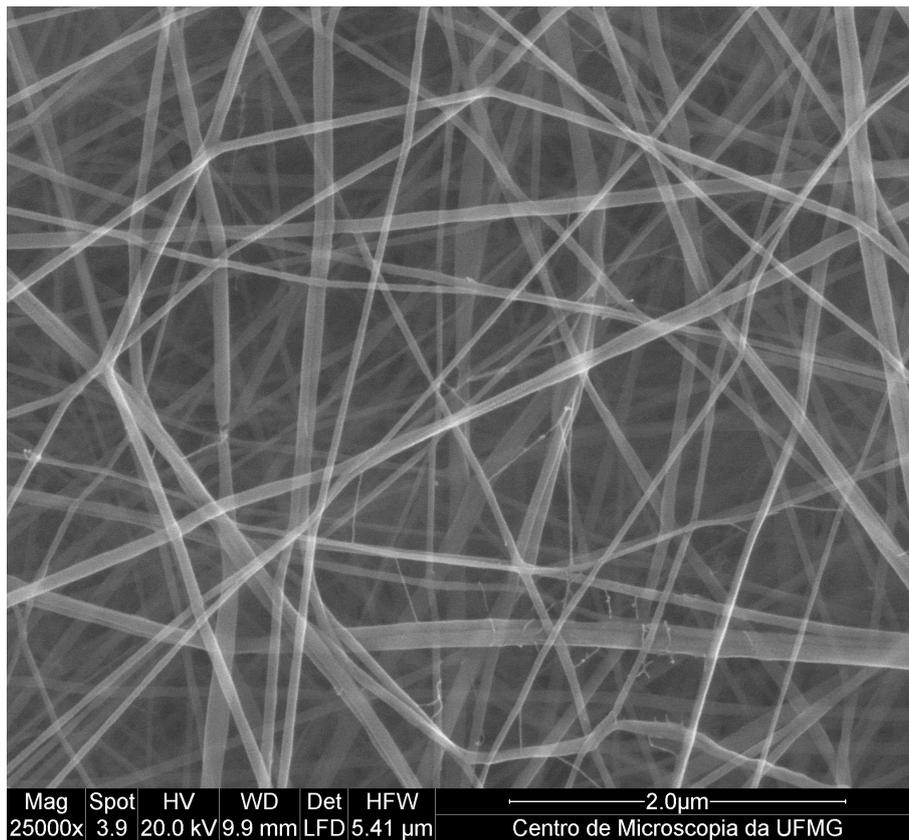
Sample	n	Mean diameter (nm)	Standard deviation (nm)	Coefficient of variation (%)
I	48	57	15	26.3
II	46	98	23	23.5
III	46	95	16	16.8
IV	48	49	11	22.4
V	46	54	15	27.8
VI	47	69	17	24.6
VII	50	81	28	34.6
VIII	48	52	12	23.1
IX	50	50	13	26.0
X	46	72	19	26.4
XI	48	57	9	15.8
XII	49	67	15	22.4
XIII	45	88	11	12.5
XIV	43	137	37	27.0
XV	50	141	44	31.2

Figure 2 shows the SEM image of sample I and the distribution of diameters in the nanomembrane.

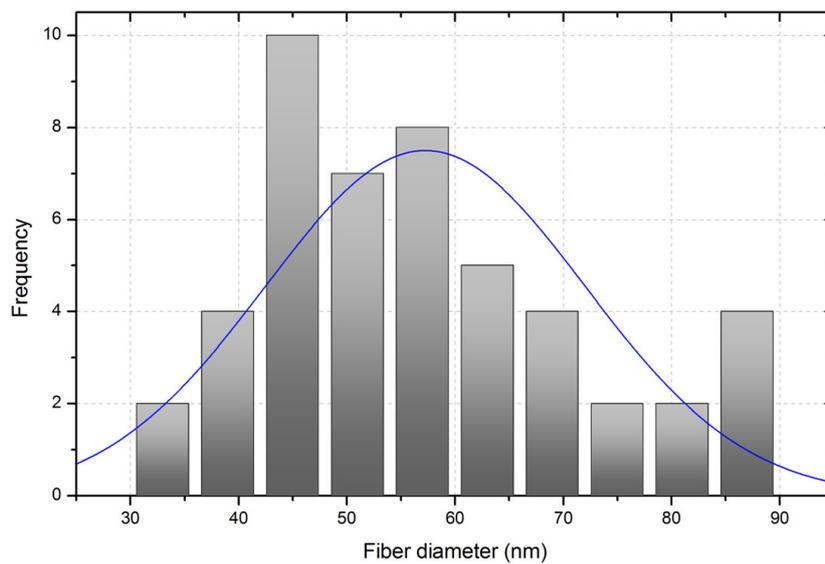
3.1 Influence of Polymer Concentration

As shown in Fig. 3, comparing independently samples II and III with the control sample I, it was observed a statistically significant increase (according to an analysis of variance, $P = 0.000 < 0.05$) of mean fibers diameters with increasing of PA-66 concentration in the polymer solution. this result is in agreement with the experimental results in the literature (Li *et al.*, 2007; Tao and Shivkumar, 2007; Lingaiah *et al.*, 2008; Wang *et al.*, 2009).

As it can be noticed, the mean nanofibers diameters of samples I and II are much smaller than the values obtained by Lingaiah *et al.* (2008) for the same polymer (ranging from 60 to 120 nm and from 120 to 240 nm for 10 wt% and 12 wt%



(a) SEM image (25.000x)



(b) Distribution of found diameters

Figure 2. Morphology of the fibers of the sample I

PA-66, respectively).

3.2 Influence of Applied Voltage

Comparing samples IV and V with the control sample I, as shown in Fig. 4, it was observed a statistically significant increase ($P = 0.019 < 0.05$) on the mean diameter of the fibers with the increase of applied voltage, as noted by Li *et al.* (2007).

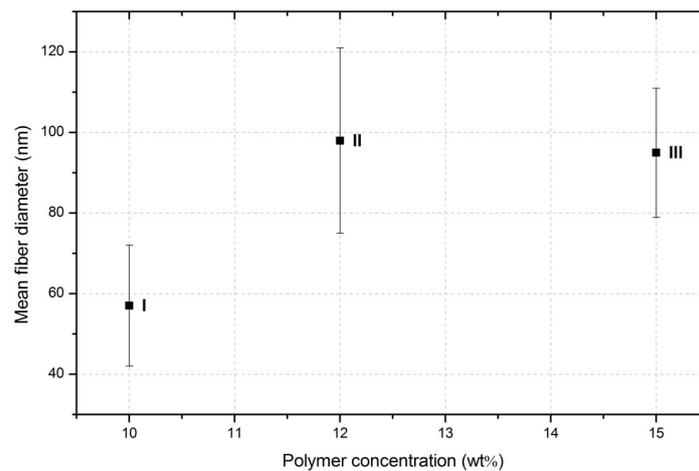


Figure 3. Variation of the mean nanofibers diameter with the polymer concentration (error bars indicate one standard deviation of uncertainty)

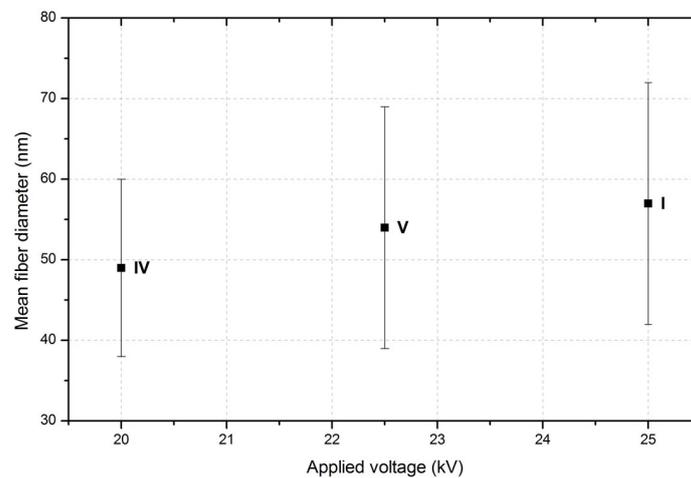


Figure 4. Variation of the mean nanofibers diameter with the applied voltage (error bars indicate one standard deviation of uncertainty)

3.3 Influence of Solution Flow Rate

Comparing samples VI and VII with the control sample I, there was a statistically significant and continuous increase ($P = 0.000 < 0.05$) on the fibers mean diameter (Fig. 5) with increasing polymer solution flow rate. These results are consistent with the behavior described in theory Ramakrishna *et al.* (2005).

3.4 Influence of Distance Between the Needle and the Collector

Comparing the samples VIII and IX with the control sample I, it was observed that there was a statistically significant change ($P = 0.028 < 0.05$) on the mean fibers diameter, as shown in Fig. 6. According to Ramakrishna *et al.* (2005), the effect of varying the distance between the needle and the collector may or may not be significant. In most cases, the decrease on the distance between the needle and the collector leads to an increase on the electric field, which is responsible for stretching the nanofibers during the deposition process, causing a decrease on the mean fibers diameter. Although it is possible to observe an increase on the diameter when the distance was reduced from 12.5 cm to 10.0 cm, there was no statistically significant variation ($P = 0.553 > 0.05$) between the results of samples VIII and IX.

3.5 Influence of Graphene Concentration

Comparing sample X with the control sample I, it was observed a significant ($P = 0.000 < 0.05$) increase on the mean fibers diameter (Fig. 7), which increased from 57 nm to 72 nm. Similar behavior was found by Wang *et al.* (2009)

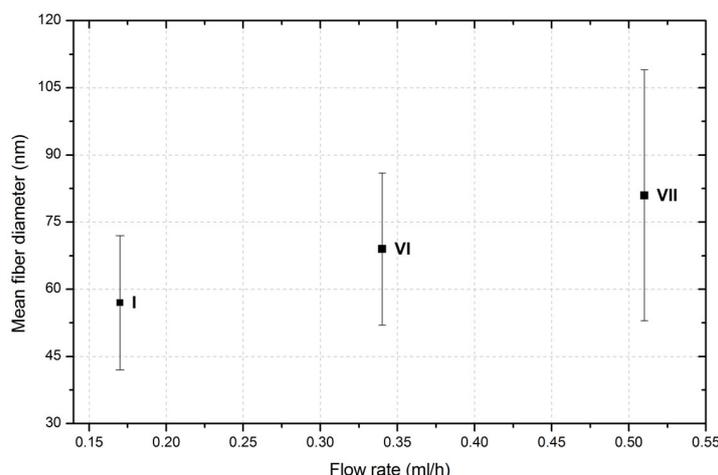


Figure 5. Variation of the mean nanofibers diameter with the polymer solution flow rate (error bars indicate one standard deviation of uncertainty)

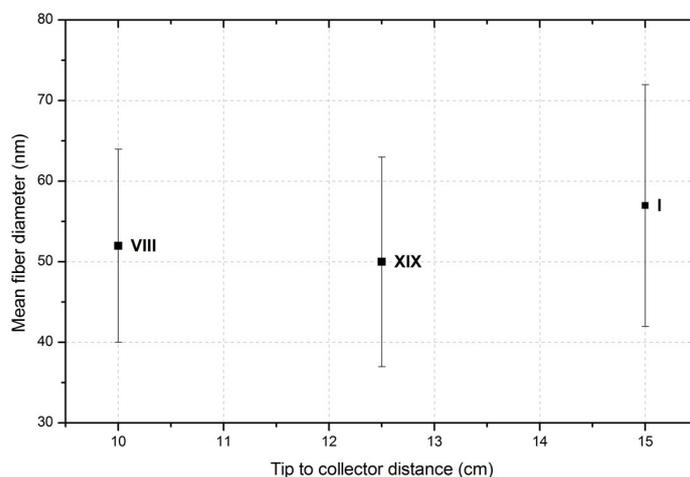


Figure 6. Variation of the mean nanofibers diameter with the needle to collector distance (error bars indicate one standard deviation of uncertainty)

for polylactic acid (PLA), nanomembranes containing montmorillonite (MMT). Comparing sample XI with the control sample I, there was no statistically significant change ($P = 0.908 > 0.05$) on the mean diameter of the fibers, which may have been caused by partial and temporary clogging of the needle due to the increase on the solution viscosity during the deposition process via electrospinning, producing fibers thinner than expected. In fact, SEM images confirmed the occurrence of the partial clogging of the needle, which led to a reduction in the number of fibers deposited on the collector.

Although there was a statistically significant change ($P = 0.000 < 0.05$) of mean diameter of the 12 wt% of PA-66 fibers with the increase on the concentration of polymer solution with graphene, the variation in the results may have been caused by the change of the relative humidity (ranging from 62% to 70%) in the environment where the deposition of fibers by electrospinning was being conducted. Similarly, the increased viscosity of the solution decreased its flow and thus reduced the effect of adding graphene.

Comparing samples XIV and XV with the control sample III, it was observed a significant ($P = 0.000 < 0.05$) and continuous increase on the mean diameter of fibers with the increase on the concentration of graphene in 15 wt% of PA-66 polymer solutions. These results are consistent with the behavior described by Ramakrishna *et al.* (2005). Once again, the variation in climatic conditions (26.3 °C and 60% relative humidity for samples XIII and XV and 23.9 °C and 70% relative humidity for sample XIV) may have influenced the results, not allowing a large increase in the mean diameter of fibers generated with the increase of 1 wt% to 2 wt% of graphene in the polymer solutions.

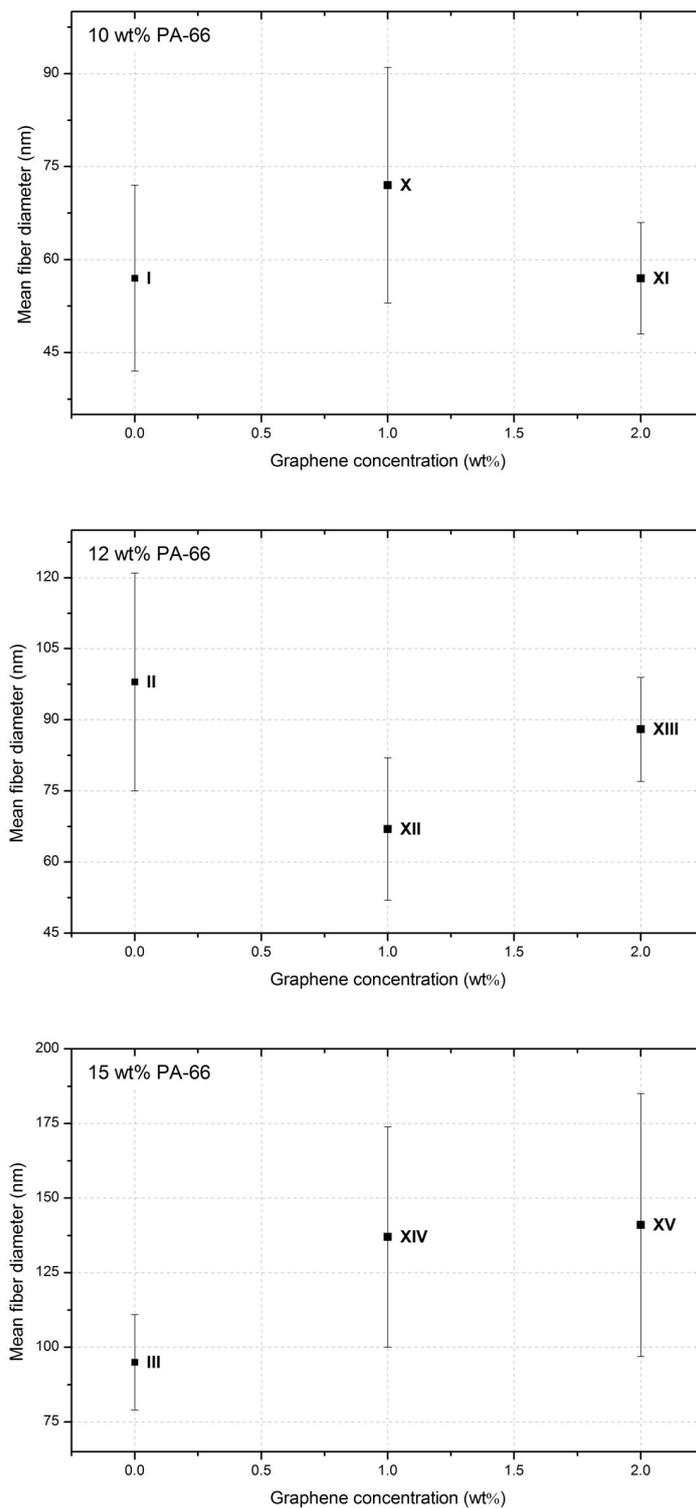


Figure 7. Variation of the mean nanofibers diameter with the graphene concentration (error bars indicate one standard deviation of uncertainty)

4. FINAL CONSIDERATIONS

To make possible the evaluation of the electrospinning process and its influence on the morphology of the nanofibers formed, we used polyamide-66 (PA-66). The results showed that the following operational parameters of the electrospinning technique are proportional to the diameter of the nanofibers: applied voltage, polymer solution flow rate and the concentration of polymer in the solution. The results also showed that the distance between the collector and emitter

(needle tip) is inversely proportional to the diameter of the nanofiber formed.

The diameters of the nanofibers presented a quasi-normal distribution and ranged from 49 nm to 141 nm. These values were 37% lower than those reported in the literature. Changes in diameters were also observed with the addition of carbon-based nanoparticles (in this case, the graphene) in proportions of 1 wt% and 2 wt% in the PA-66 solutions. For the 10 wt% concentration of PA-66, the addition of 1 wt% graphene resulted in an increase in the mean diameter from 57 nm to 72 nm, which was expected. However, the addition of 2 wt% of graphene did not result in significant increase in diameter. Rather, the diameter remained stable at around 57 nm. One possible explanation is the increased viscosity of the solution, which caused the reduction of the flow and thereby the effect of addition of the nanoparticles was almost neutralized. For the concentration of 12 wt% of PA-66, it was observed the reduction of the mean diameter of nanofibers from 98 nm to 67 nm and to 88 nm for concentrations of 1 wt% and 2 wt%, respectively. The increased viscosity caused the reducing of the flow and thereby the addition of carbon-based nanoparticles was a secondary effect. For the concentration of 15 wt% of PA-66 polymer solution, the addition of graphene resulted in an increase in diameter from 95 nm to 137 nm and to 141 nm for 1 wt% and 2 wt%, respectively. The increased concentration of carbon-based nanoparticles was not an important factor, since the increase from 1 wt% to 2 wt% of graphene led us to have a variation in diameter of only 5% over the original diameter. The main factor in this case seems to be the concentration of PA-66 in solution. This is a highly desired result since we can still have thin nanofibers in spite of the addition of nanoparticles (graphene) to improve nanomembranes properties.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

- Abramoff, M.D., Magalhaes, P.J. and Ram, S.J., 2004. "Image processing with ImageJ". *Biophotonics International*, Vol. 11, No. 7, pp. 36–42.
- Andrady, A.L., 2008. *Science and Technology of Polymer Nanofibers*. John Wiley, New Jersey, USA.
- Ávila Júnior, J., 2010. *Nanomembranas Interlaminares Para Compósitos de Alto Desempenho*. Master's thesis, Universidade Federal de Minas Gerais, Belo Horizonte, Brazil.
- Ayutsede, J.E., 2005. *Regeneration of Bombyx Mori Silk Nanofibers and Nanocomposite Fibrils by The Electrospinning Process*. Ph.D. thesis, Drexel University, Philadelphia, USA.
- Cooley, J.F., 1902. "Apparatus for electrically dispersing fluids". US Patent 692.631.
- Doshi, J. and Reneker, D.H., 1995. "Electrospinning process and application of electrospun fibers". *Journal of Electrostatics*, Vol. 35, pp. 151–160.
- Formhals, A., 1934. "Process and apparatus for preparing artificial threads". US Patent 1.975.504.
- Heikkilä, P. and Harlin, A., 2008. "Parameter study of electrospinning of polyamide-6". *European Polymer Journal*, Vol. 44, No. 10, pp. 3067–3079.
- Huang, C., Chen, S., Lai, C., Reneker, D.H., Qiu, H., Ye, Y. and Hou, H., 2006. "Electrospun polymer nanofibres with small diameters". *Nanotechnology*, Vol. 17, pp. 1558–1563.
- Huang, Z.W., Zhang, Y.Z., Kotaki, M. and Ramakrishna, S., 2003. "A review on polymer nanofibers by electrospinning and their applications in nanocomposites". *Composites Science and Technology*, Vol. 63, pp. 2223–2253.
- Ko, F.K., 2004. "Nanofiber technology: Bridging the gap between nano and macro world". In S.I. Guceri and Y. Gogotsi, eds., *Nanoengineered Nanofibrous Materials*, Kluwer Academic Book Publishers, Dordrecht, Netherlands, Vol. 169, chapter 1.1, pp. 1–18.
- Kotov, N.A., 2006. "Carbon sheet solutions". *Nature*, Vol. 442, pp. 254–255.
- Lam, H.L., 2004. *Electrospinning of Single Wall Carbon Nanotube Reinforced Aligned Fibrils and Yarns*. Ph.D. thesis, Drexel University, Philadelphia, USA.
- Li, G., Li, P., Yu, Y., Jia, X., Zhang, S., Yang, X. and Ryu, S., 2008. "Novel carbon fiber/epoxy composite toughened by electrospun polysulfone nanofibers". *Materials Letters*, Vol. 62, pp. 511–514.
- Li, Q., Jia, Z., Yang, Y., Wang, L. and Guan, Z., 2007. "Preparation and properties of poly(vinyl alcohol) nanofibers by electrospinning". In *Proceedings of IEEE International Conference on Solid Dielectrics*. Winchester, UK.
- Lingaiah, S., Shivakumar, K.N. and Sadler, R.L., 2008. "Electrospinning of nylon-66 polymer nanofabrics". In *Proceedings of 49th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics and Materials Conference*. Schaumburg, USA.
- Mack, J.J., Viculis, L.M., Ali, A., Luoh, R., Yang, G., Hahn, H.T., Ko, F.K. and Kaner, R.B., 2005. "Graphite nanoplatelet reinforcement of electrospun polyacrylonitrile nanofibers". *Advanced Materials*, Vol. 17, No. 1, pp. 77–80.

- Morton, W.J., 1902. "Method of dispersing fluids". US Patent 705.691.
- Norris, I.D., Shaker, M.M., Ko, F.K. and Macdiarmid, A.G., 2000. "Electrostatic fabrication of ultrafine conducting fibers: Polyaniline/polyethylene oxide blends". *Synthetic Metals*, Vol. 144, pp. 109–114.
- Park, S.W., Bae, H.S., Xing, Z.C., Kwon, O.H., Huh, M.W. and Kang, I.K., 2009. "Preparation and properties of silver-containing nylon 6 nanofibers formed by electrospinning". *Journal of Applied Polymer Science*, Vol. 112, No. 4, pp. 2320–2326.
- Ramakrishna, S., Fujihara, K., Teo, W.E., Lim, T.C. and Ma, Z., 2005. *An Introduction to Electrospinning and Nanofibers*. World Scientific, Singapore.
- Reneker, D.H. and Yarin, A.L., 2008. "Electrospinning jets and polymer nanofibers". *Polymer*, Vol. 49, pp. 2387–2425.
- Shivakumar, K., Lingaiah, S., Chen, H., Akangah, P., Swaminathan, G., Sharpe, M. and Sadler, R., 2009. "Polymer nanofabric interleaved composite laminates". In *Proceedings of 50th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics and Materials Conference*. Palm Springs, USA.
- Tao, J. and Shivkumar, S., 2007. "Molecular weight dependent structural regimes during the electrospinning of pva". *Materials Letter*, Vol. 61, pp. 2325–2328.
- Wang, C., Ko, F.K. and Alcock, M., 2009. "Nanoclay reinforced pla nanocomposite by electrospinning". In *Proceedings of 24th Annual ASC Technical Conference*. Newark, USA.
- Wei, T., Fan, Z., Luo, G., Wang, S. and Song, L., 2009. "Dispersibility and stability improvement of graphite nanoplatelets in organic solvent by assistance of dispersant and resin". *Materials Research Bulletin*, Vol. 44, pp. 977–983.
- Yasmin, A. and Daniel, I.M., 2004. "Mechanical and thermal properties of graphite platelet/epoxy composites". *Polymer*, Vol. 45, pp. 8211–8219.

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