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EFFECT OF AMBIENT PARAMETERS ON MORPHOLOGY OF POLY(Ε-CAPROLACTONE) ELECTROSPUN NANOFIBERS

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ABSTRACT

The effect of temperature(10 ºC-35 ºC, 5 ºC intervals) and relative humidity(20% -70%, 10% intervals) on the morphology of poly(ε-caprolactone) (PCL) electrospun nanofibers is investigated. Acetic acid/pyridine mixture is used as solvent. Surface morphologies and diameters of PCL nanofibers are examined by Field-emission scanning electron microscopy (FESEM). The average diameter of PCL nanofibers increases with increasing relative humidity (RH) at all temperatures. As the temperature increase, the average diameter of PCL nanofibers firstly increases then decreases at all RH values. The electrospun PCL nanofibers are circular shaped with smooth surface without bead formation for all RH and temperature values.

KEYWORDS

Electrospinning; Poly(ε-caprolactone); Morphology; Ambient temperature; Relative humidity

1. INTRODUCTION

Electrospinning technique has become the most dominant technique for nanofiber production because of its advantageous properties: repeatability, simplicity, low cost, and continuous nanofiber production (Formhals, 1934; Taylor, 1964; Baumgarten, 1971; Doshi et al., 1995). Electrospun nanofibers have unique characteristics such as small diameters, high specific surface area and high porosity (Wang et al., 2002, Jin et al., 2007). Important electrospinning parameters can be divided into three groups: process, polymer and ambient parameters (Deitzel et al., 2001; Tan et al., 2005).

There is limited number of studies about effect of ambient parameters on morphology of electrospun nanofibers. In these studies, ambient temperature (Huang et al., 2008; Amiraliyan et al., 2009), relative humidity (RH) (Casper et al., 2004; Yang et al., 2006; Tripatanasuwan et al., 2007; Medeiros et al., 2008; De Schoenmaker et al., 2013) and RH and temperature together (De Vrieze et al., 2009; Hardick et al., 2011; İçoğlu and Oğulata, 2013; Oğulata and İçoğlu, 2015) are investigated.

With increasing of RH, the average diameter of polyamide 4.6, polyamide 6.9 (De Schoenmaker et al., 2013) polyethylene oxide (PEO) (Yang et al., 2006; Tripatanasuwan et al., 2007) and poly(vinylpyrrolidone) (PVP) (De Vrieze et al., 2009) decreases, while that of cellulose acetate (CA) (De Vrieze et al., 2009; Hardick et al., 2011) and polyetherimide (PEI) (İçoğlu and Oğulata, 2013) increases.

The average diameters of poly (vinylidene fluoride) (PVDF) (Huang et al., 2008) and polyetherimide (PEI) (İçoğlu and Oğulata, 2013) decrease with increasing of temperature.

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PCL is aliphatic polyester having biodegradability, biocompatibility and good physical properties (Lee et al., 2003) Hence, several studies about electrospinning of PCL with different solvents have been performed (Wu and Gan, 1998; Lee et al., 2003).

2. MATERIAL AND METHODS

2.1. Materials

The concentration of PCL (Mn: 80000) was kept at 15% (wt/v) in the mixture solution of acetic acid/pyridine 99.5/0.5 (v/v). PCL solution was prepared at 35ºC by stirring magnetically for 24 hours. PCL, acetic acid and pyridine were purchased from Sigma Aldrich.

2.2. Nanofiber fabrication

The electrospinning apparatus includes two high voltage power supplies (+50 kV and -50 kV), a syringe infusion pump and a collector plate. Positive and negative high voltage power supplies are connected to the needle tip and the collector, respectively. The electrospinning apparatus is in a closed cabin. The walls of the cabin are coated with an insulating material. The temperature in the cabin is controlled via a heating and cooling system. An ultrasonic humidifier and a dehumidifier are used for setting the desired relative humidity in the cabin. A fan is used for obtaining a homogeneous RH and temperature in the cabin.

PCL solution was electrospun at ambient temperatures of 15–35 °C (5 °C intervals) and RH of 20–70% (10% intervals). Applied voltage, tip-collector distance (TCD), needle diameter and flow rate were selected as 12 kV, 15 cm, 0.7 mm and 0.7 ml/h, respectively.

2.3. Characterization

Surface tension, viscosity, and electrical conductivity of PCL solution were determined by Attention Theta optical tensiometer, Brookfield DV-III Ultra rheometer, and Orion 4 Star Plus meter, respectively.

The morphological appearances of the PCL nanofibers were investigated by using field- emission scanning electron microscopy (FE-SEM, Zeiss Supra 55) after platinum coating with an ion sputter. Image-Pro Plus 6.0 program was used for the measurement of the nanofiber diameters.

2.4. Statistical Analyses

The data obtained are subjected to statistical analyses of variance (ANOVA) and Pearson Correlation Test to assess the effects of ambient temperature and RH on morphology of PCL nanofibers using SPSS statistical software (IBM SPSS Statistics 22.0.0 trial version; IBM, Chicago, USA). For all statistical tests, the results are considered significant at $p \leq 0.01$.

3. RESULT AND DISCUSSION

Electrical conductivity, viscosity, and surface tension values (at 25ºC) of the PCL solution are determined as 15.93 µS/cm, 725 cP, and 26.75 mN/m respectively.

FESEM images of electrospun PCL nanofibers produced at three different RH values (30%, 50% and 70%) and three different temperature values (10 ºC, 20 ºC, 30 ºC) were shown as an example (Figure 1).

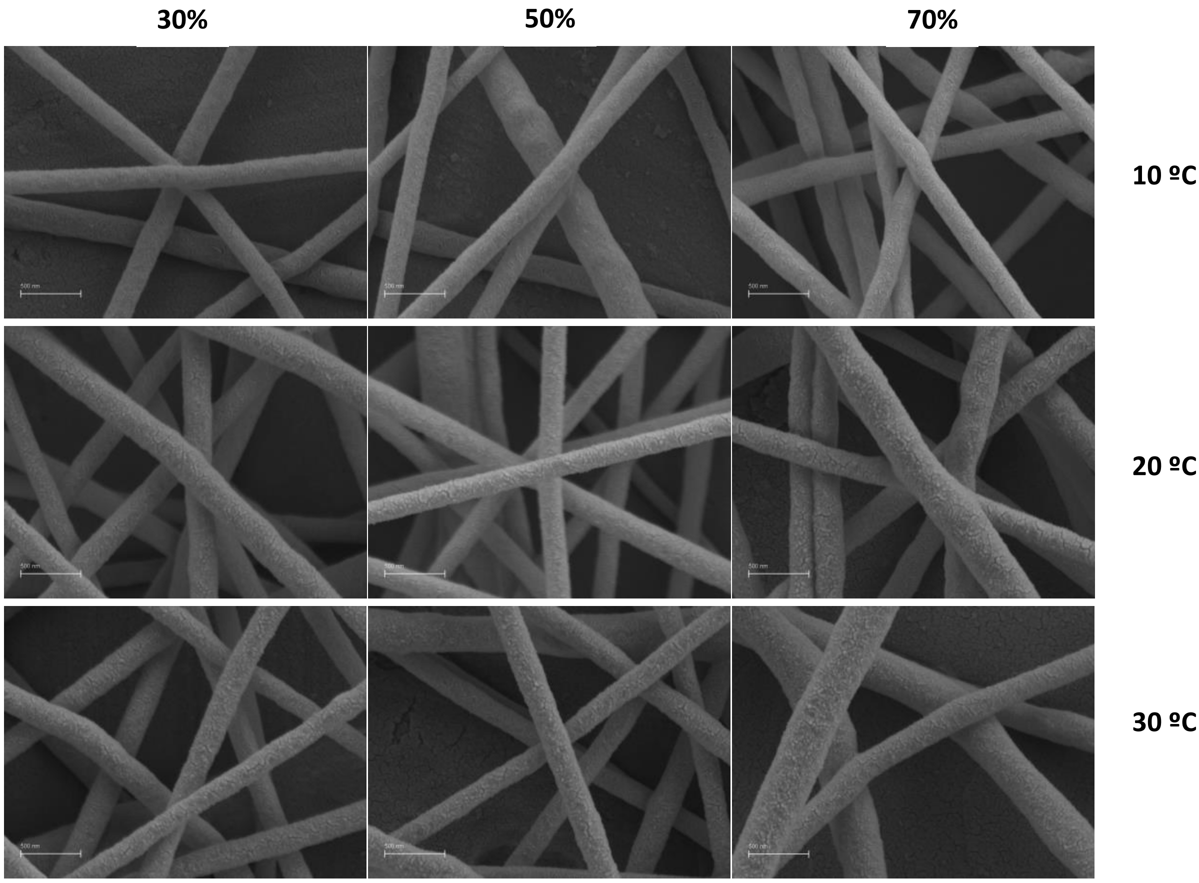

Figure 1: FESEM images of PCL nanofibers (100kX)

The obtained PCL nanofibers are circular shaped with smooth surface for all RH and temperature values. Also no bead formation is seen for all of the electrospun PCL nanofibers. Figure 2 shows the average nanofiber diameter according to relative humidity (RH). Also Table 1 shows the average diameter results of the PCL nanofibers according to RH and temperature.

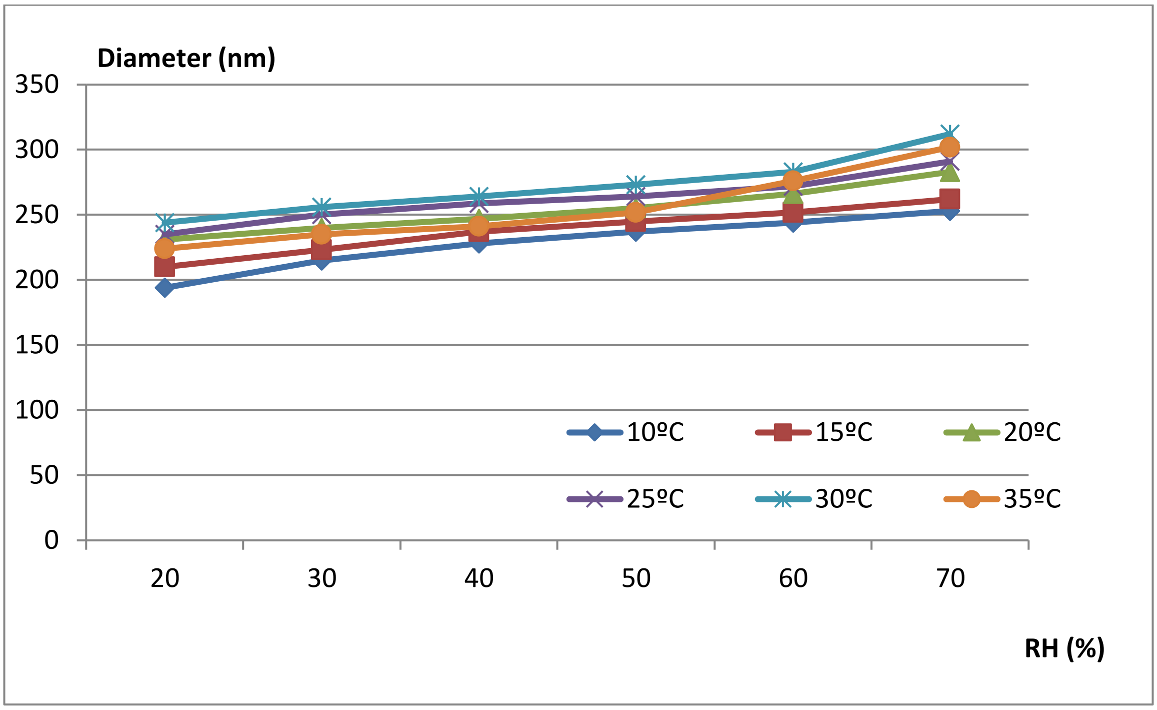

Figure 2: Average diameter of electrospun PCL nanofibers according to relative humidity(RH)

Table 1: The average diameters (nm) of PCL nanofibers according to temperature and relative humidity

Temperature (ºC)	RH					
	20%	30%	40%	50%	60%	70%
10	194 ± 33	215 ± 30	228 ± 38	237 ± 45	244 ± 46	253 ± 74
15	210 ± 23	223 ± 44	237 ± 46	245 ± 45	252 ± 52	262 ± 63
20	231 ± 26	240 ± 34	247 ± 36	255 ± 44	266 ± 39	283 ± 38
25	235 ± 31	250 ± 32	259 ± 29	264 ± 28	272 ± 46	291 ± 50
30	244 ± 37	256 ± 38	264 ± 37	273 ± 37	283 ± 45	312 ± 60
35	224 ± 21	235 ± 32	241 ± 38	252 ± 36	276 ± 45	302 ± 48

Average diameter of PCL nanofibers increases with increasing relative humidity (Figure 2 and Table 1). These results are similar to the studies of CA, PS, PAN, PSU ve PEI polymers (De Vrieze et al., 2009; Hardick et al., 2011; Kim et al., 2005; Huang et al., 2011; İçoğlu and Oğulata, 2013). The reason may be related to the fast precipitation of PCL dissolved in acetic acid/pyridine by adding of water. With increase in RH, the amount of water surrounding in the air is increased, resulting in more water absorption. It may possibly cause precipitation of the nanofibers in the polymer solution jet quickly and decrease of elongation of the jet. Increase in amount of water, which has molecular polarization property, also gets lower the electrostatic discharge between needle tip and the collector. As a result, thicker PCL nanofibers are obtained with increasing of RH. Figure 3 shows the average nanofiber diameter according to ambient temperature.

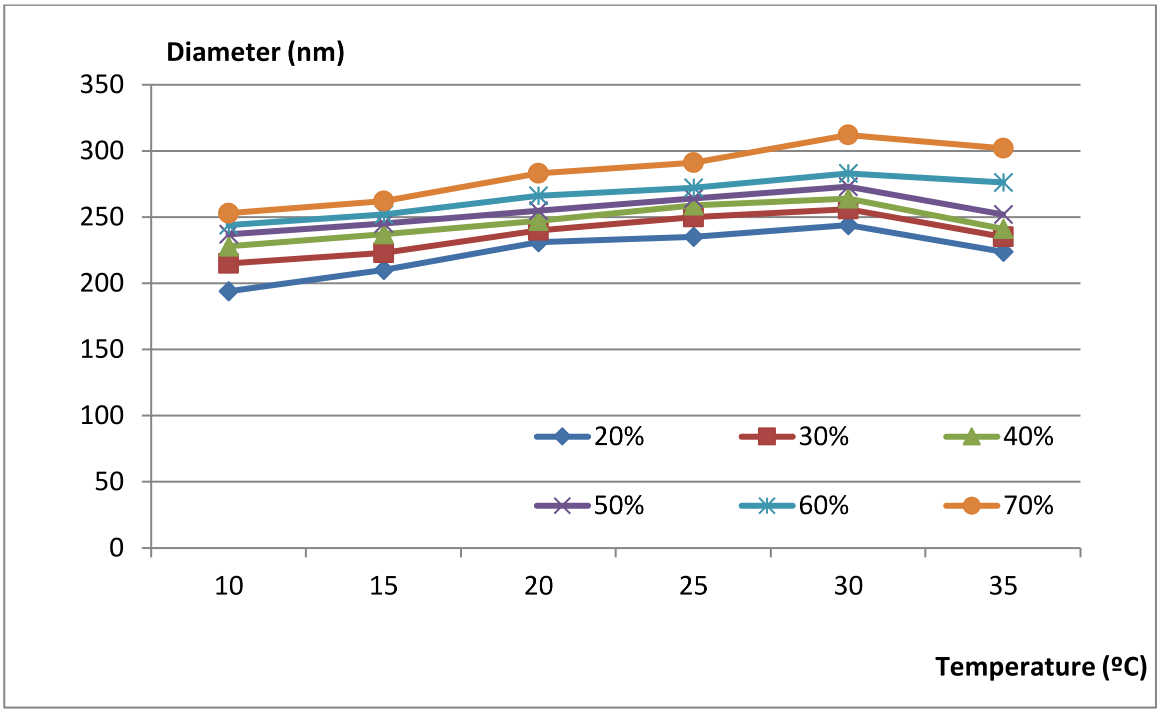

Figure 3: Average diameter of electrospun PCL nanofibers according to ambient temperature

It is also clearly seen that the average diameter of PCL nanofibers firstly increases than decreases with increasing temperature (Figure 3). These results are similar to the studies of CA polymers (De Vrieze et al., 2009). Change in ambient temperature has two different effects. The evaporation rate increases when ambient temperature increases. Hence, stretching of the polymer solution jet decreases, resulting in thicker fibers. Solution viscosity and surface tension decrease with the increase of temperature (Mit-uppatham et al., 2004; Huang et al., 2008). Lower surface tension and viscosity reduce the resistance to electric force applied; hence stretching of the polymer solution jet increases, resulting in thinner fibers.

According to the statistical analysis of variance (ANOVA), temperature and RH are significantly effective ($p \leq 0.01$) on the diameter of the PCL nanofibers. Also it is obtained that increasing of RH increases the diameter significantly according to Pearson Correlation Test ($p \leq 0.01$).

4. CONCLUSION

In this study, effects of ambient temperature and RH on morphology of electrospun PCL nanofibers are investigated. Average diameter of electrospun PCL nanofibers increases with increasing relative humidity (RH). Also the average diameter of PCL nanofibers firstly increases than decreases with increasing of the ambient temperature. All of the obtained electrospun PCL nanofibers are circular shaped with smooth surface without bead formation for all RH and temperature values.

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