

Electrospinning of Nylon-6,6 Solutions into Nanofibers: Rheology and Morphology Relationships*

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Abstract The relationship between the rheological properties of nylon-6,6 solutions and the morphology of their electrospun nanofibers was established. The viscosity of nylon-6,6 in formic acid (90%) was measured in the concentration range of 5 wt%–25 wt% using a programmable viscometer. Electrospinning of nylon-6,6 solutions was carried out under controlled parameters. The chemical structure, morphology and thermal properties of the obtained nanofibers were investigated using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and differential scanning calorimetry (DSC), respectively. Entanglement concentration (c_e) was found to be 15 wt% and a power law relationship between specific viscosity and solution concentration was observed with exponents of 2.0 and 3.3 for semi-dilute unentangled ($c < c_e$) and semi-dilute entangled ($c > c_e$) regimes, respectively. The diameter and uniformity of the nanofibers were found to be dependent on the viscosity. Moreover, the average diameter of electrospun nanofibers was found to be dependent on zero shear rate viscosity and normalized concentration (c/c_e) in a power law relationship with exponents of 0.298 and 0.816, respectively. For nylon-6,6 solutions, the entanglement concentration ($c_e = 15$ wt%) provides the threshold viscosity required for the formation of a stable polymeric jet during electrospinning and producing uniform beadless fibers. For concentrations less than c_e , beaded fibers with some irregularities are formed. DSC analysis showed an increase in crystallinity of all electrospun samples compared to original polymer. Furthermore, Based on FTIR spectroscopy, α phase is dominant in electrospun nanofibers and minor amount of β and γ phases is also available.

Keywords: Nylon-6,6 electrospinning; Viscosity; Nanofibers; Entanglement concentration; Crystallinity.

INTRODUCTION

Electrospinning is a very simple and versatile method for producing nano and microfibers from a wide range of polymers. Electrospun polymeric nanofibers have several advantages over regular fibers including very high surface area and controllable porosity and composition with the aim of achieving different characteristics^[1]. This led to the emergence of a large number of research activities involving electrospun nanofibers for different applications such as water and air filtration^[2–5], biosensors^[6–8], tissue engineering and drug delivery^[9–15], wound dressings^[16–18], enzyme immobilization^[19–21] and acoustical damping^[22].

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A large number of research activities have been focused on evaluating the electrospinnability of various polymers' solutions. However, fiber formation mechanism is not yet completely understood in electrospinning. As a general rule, as long as the polymer jet does not break during travelling from spinneret to the collector, electrospinning will be successful^[23].

Solution concentration and viscosity are among the most crucial factors affecting the size and morphology of electrospun nanofibers. There have been some studies focusing on the effect of solution viscosity on fibers' properties for some polymers^[24–27]. It was reported that one of the most commonly used techniques for estimating the spinnability of a solution and morphology of electrospun nanofibers are based on De Gennes' scaling theory^[28]. According to this theory, a logarithmic plot of solution's specific viscosity versus solution concentration will have several areas with various slopes, showing different concentration regimes including dilute, semi-dilute unentangled, semi-dilute entangled and concentrated.

As mentioned before, formation of a stable jet is necessary for a successful electrospinning. However, a stable jet is formed when a considerable overlap among polymer chains exists and such overlapping happens in the semi-dilute area. Therefore, semi-dilute regime is at the focal point of electrospinning studies. For neutral, non-associating, linear polymers, specific viscosity (η_{sp}) is related to the solution concentration in a power law relationship as $\eta_{sp} \sim c^{1.25}$ in the semi-dilute unentangled area and $\eta_{sp} \sim c^{3.7-4.8}$ in the semi-dilute entangled regime, depending on the solvent quality^[29]. The point of this slope change in the plot is known as the entanglement concentration (c_e) and has an important role in predicting the spinnability and the morphology of the electrospun nanofibers from a polymer solution. Hemp *et al.* studied the specific viscosity scaling factor for polyelectrolytes and compared it with that of neutral polymers^[30]. Fong and co-workers conducted an early attempt to understand the effect of solution viscosity on the morphology and diameter of electrospun nanofibers^[24]. Different researchers continued to investigate the effect of viscosity on morphological properties of electrospun nanofibers for various polymers^[31–35].

First detailed investigation about the dependence of fiber morphology on rheological properties of polymeric solutions was carried out by McKee's group^[36]. They studied a series of linear and branched poly(ethylene terephthalate-co-ethylene isophthalate) (PET-co-PEI) copolymers with various molecular weights. The study showed three distinct morphological regimes for fiber formation during electrospinning. For $c < c_e$, the formation of a stable jet did not happen and instead of electrospinning, electrospraying was observed. At $c = c_e$, the formation of fibers started and a mixture of beads and fibers was deposited on the collector. As the solution concentration increased, the ratio of fibers to beads and their average diameter increased until $c = 2-2.5$ times of c_e , where only uniform, bead-free fibers were formed. This relationship later on was called " c_e -regulation" by Zhao *et al.*^[37]. On the other hand, Gupta *et al.* investigated scaling relationships between concentration and viscosity and studied the effect of solution viscosity on electrospinning of poly(methylmethacrylate)^[38]. Their results were not in agreement with McKee's c_e -regulation. Also in another study, Zhao *et al.* found that c_e -regulation is not true for other polymeric systems^[37].

Nylon-6,6 was the first synthetic polyamide having superior thermal and mechanical characteristics qualifying it to be an engineering thermoplastic. This polymer has wide applications in different industries such as fabrication of gears, bearings, fibers, airbags, tires, ropes, conveyor belts and hoses. The hydrophilicity of nylon-6,6 is higher than that of many other polymers because of amide groups present in polymer backbone. This property makes the polymer suitable for making water wetting porous membranes used in various filtration and separation applications^[39].

Nylon-6,6 has already been electrospun in various occasions. For example, Guerrini *et al.* studied the effect of molecular weight and the content of terminal carboxylic and amine groups on the average diameters of the electrospun nanofibers^[40]. Furthermore, Faridi *et al.* used the artificial neural network to find the best conditions for electrospinning of nylon-6,6 in formic acid^[41]. Most recently, Ryu *et al.* studied the effect of solution's electrical conductivity on optimum electrospinning conditions for nylon-6,6. They found that increasing electrical conductivity of nylon-6,6 solutions through adding an organic salt leads to an expansion in the range of other parameters for getting an optimum electrospinning. On the other hand, this electrical conductivity increase

resulted in an increase in average fiber diameter of electrospun nanofibers^[42]. Furthermore, some researchers have been focused on evaluating mechanical properties of electrospun nylon-6,6 nanofibers. For example, Carrizales *et al.* showed that electrospun nylon-6,6 nanofibers have modest mechanical properties which need to be improved^[43]. However, in none of these studies an extensive relationship between concentration regimes of polymeric solutions and their viscosity and morphological properties of the electrospun nanofibers has been addressed.

Electrospun nylon-6,6 nanofibers have been studied for different applications. For example, Goto *et al.* showed that these fibers are good candidates as receptors for infrared spectroscopy (FTIR). They used this property of electrospun nanofibers in quantitative analysis of Orutoran^[44]. Choi *et al.* also used MWCNT-modified nylon-6,6 electrospun nanofibers as sensors to diagnose chemical vapors such as alcohols, acetone and benzene^[45, 46]. Furthermore, Wang *et al.* demonstrated that a two-tier filtration system containing nylon-6,6 nanofibers and PP nonwoven support mat had high filtration efficiency (99.9%) and low pressure drop toward NaCl particles with average size of 300 nm^[47].

Clearly, the viscosity and concentration are very important factors affecting properties of electrospun nanofibers. However the role of entanglement concentration in predicting electrospinnability of polymeric solutions is not completely understood and more studies are required to compare the results of different polymeric systems and give a general rule in this area. Thorough understanding of this relationship could help in predicting the electrospinnability of polymer solutions and acquiring proper concentrations to produce nanofibers with desired properties and morphology for specific applications.

The objective of this research is to study the effect of concentration and viscosity of nylon-6,6 solutions on the morphology and crystallinity of its electrospun nanofibers. Crystallinity of electrospun nanofibers plays an important role in their subsequent modification using techniques such as radiation induced graft copolymerization. Also, a power law relationship between specific viscosity and solution concentration is presented and compared with theoretical predictions. Furthermore, the relationship between average diameter of electrospun nanofibers and zero shear viscosity of the solutions, concentration and normalized concentration (using c_e) is also established.

EXPERIMENTAL

Materials

Technical grade nylon-6,6 (medium viscous, DSM Co., The Netherlands) was used. Formic acid $\geq 98\%$ was purchased from Merck Chemicals Co. and used as received.

Preparation of Polymer Solutions

The nylon-6,6 solutions of 5, 7.5, 10, 12.5, 15, 17.5, 20, 22.5 and 25 wt% concentrations were prepared by dissolving appropriate amounts of polymer in formic acid (90%) under continuous stirring at room temperature in glass reactor for 2 h.

Measurements of Viscosity

The viscosity of nylon-6,6 solutions was measured using a BROOKFIELD DV-II+ Pro programmable viscometer (LV model) with ULA spindle. Measurements were carried out at 30 °C (electrospinning temperature) for each concentration in a specific range of shear rate so that the torque falls between 10% and 100% (valid measurement range for the viscometer). Specific viscosity was calculated using the following equation^[29]:

$$\eta_{sp} = \frac{\eta_0 - \eta_s}{\eta_s} \quad (1)$$

where η_{sp} is the specific viscosity, η_0 is the zero shear rate viscosity and η_s is the viscosity of the solvent used to prepare polymer solutions.

Electrospinning Procedure

Electroris (FNM Ltd.) system was utilized to perform electrospinning process. A schematic diagram of electrospinning set-up is shown in Fig. 1. Electrospinning of the nylon-6,6 solutions was carried out using the following conditions: voltage: 20 kV, flow rate: $0.4 \text{ mL}\cdot\text{h}^{-1}$, tip-to-collector distance: 10 cm, temperature: 30°C and collector drum rotation speed: 200 r/min which was adopted from a previous study^[41]. An aluminum foil on rotating drum with diameter of 8 cm was used as a substrate for collecting the obtained nanofibers.

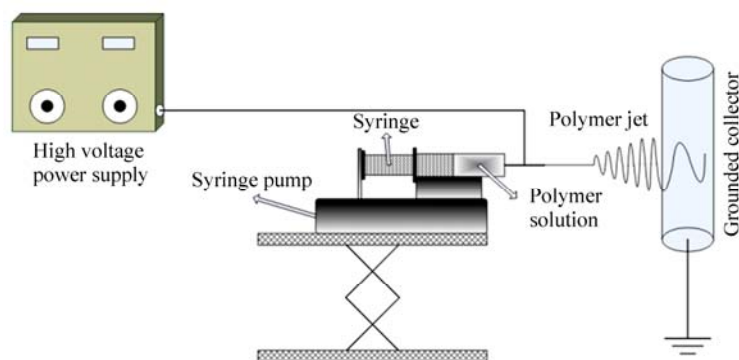


Fig. 1 Schematic diagram of electrospinning set-up

Characterization of Nanofibers

Fourier transform infrared (FTIR) spectrum of the sample was obtained by using a Perkin Elmer spectrometer (model Spectrum 100) in the frequency range of $400\text{--}4000 \text{ cm}^{-1}$. The peaks were identified using a commercial software.

A Hitachi S3400N Scanning Electron Microscope (SEM) with acceleration voltage of 10 kV was used to measure the diameter and diameter distribution of the electrospun nanofibers. A small piece of each sample was coated with a thin layer of gold to make it conductive. Thirty nanofibrous pieces were chosen randomly from each nanofiber mat's image and their diameters were measured. The average diameter was also obtained.

Differential scanning calorimeter (DSC) was used to measure the melting temperature (T_m) and the melting enthalpy (ΔH) of the electrospun nanofibers on a TA Instrument DSC apparatus (model Q200). The samples were heated in the range of $30\text{--}300^\circ\text{C}$ with a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$ under N_2 atmosphere.

The crystallinity of the electrospun nanofibers was calculated using Eq. (2).

$$\% \text{Crystallinity} = (\Delta H / \Delta H_m^0) \times 100 \quad (2)$$

where, ΔH is the melting enthalpy of each sample and ΔH_m^0 is the melting enthalpy of theoretical 100% crystalline nylon-6,6 which is $206 \text{ J}\cdot\text{g}^{-1}$ ^[40].

RESULTS AND DISCUSSION

Dependence of Viscosity on Concentration

Figure 2 shows the variation of the viscosity of nylon-6,6 solutions at 9 different concentrations with shear rate. As expected, the solution viscosity increased with the increase in the solution concentration.

As can be seen, all nylon-6,6 solutions in the concentration range of 5 wt%–17.5 wt% were Newtonian (correspondent to 10%–100% torque of the used spindle). This means, with increasing shear rate, apparent viscosity remained constant and there was no inter-dependency between these two variables. A sign of non-Newtonian behavior was only started to appear for concentrations equal to or more than 20 wt% with the decrease in the viscosities at high shear rates. Such viscosity behavior has been reported for other polymers such as sulfonated polystyrene solutions^[48].

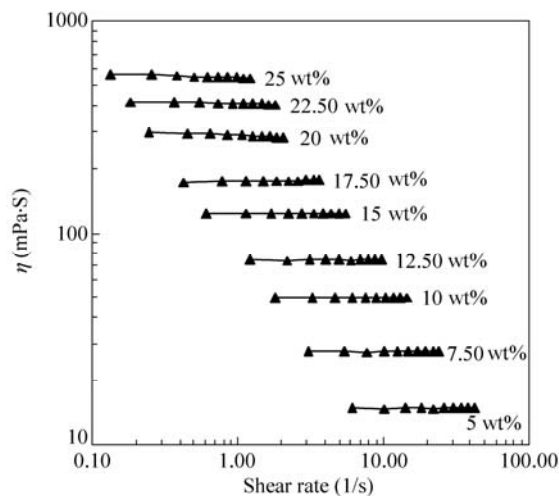


Fig. 2 Viscosity of nylon-6,6 solutions at 9 different concentrations versus shear rate

Figure 3 shows a logarithmic plot of concentration dependence of specific viscosity for nylon-6,6 solutions. In this graph two distinctive regimes for nylon-6,6 solution viscosity can be seen. As the concentration increases from 5 wt% to 15 wt%, a mild viscosity growth occurs, followed by a sudden increase in the line slope. The linear plot of these two discrete regions met at a concentration of 15 wt%, which is the transition from semi-dilute unentangled to semi-dilute entangled regimes and is named as entanglement concentration (c_e). At this concentration, the density of polymeric chains becomes so high in the solution that they start to overlap and form constrained entanglements. This phenomenon results in a sudden increase in the solution viscosity. Similar concentration regime was described by Krause *et al.* who studied the rheology of sodium hyaluronate under physiological conditions^[49].

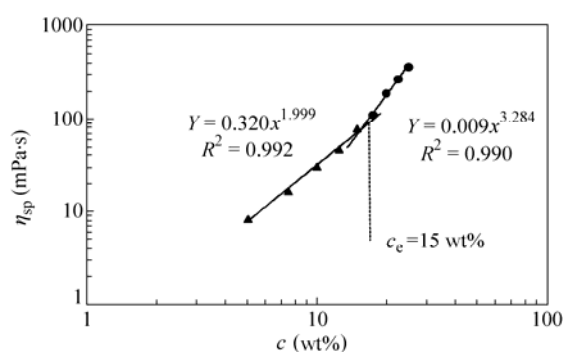


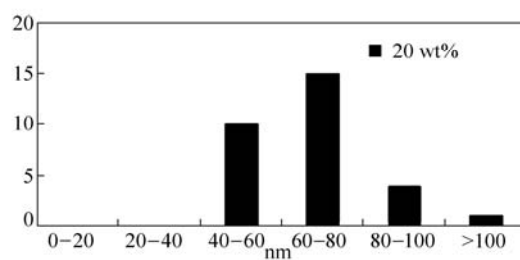
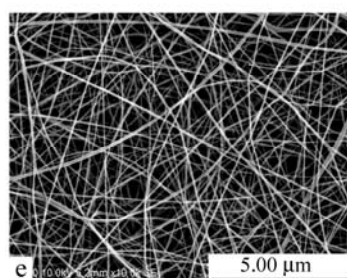
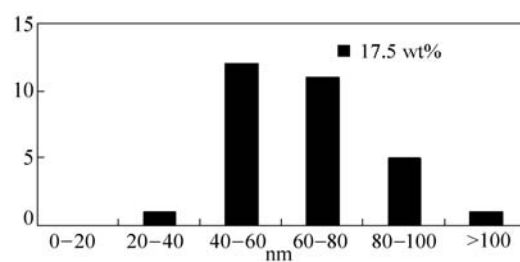
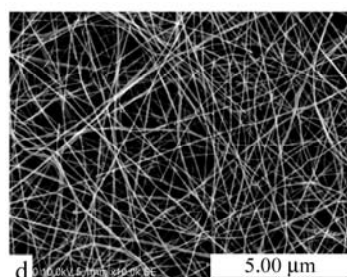
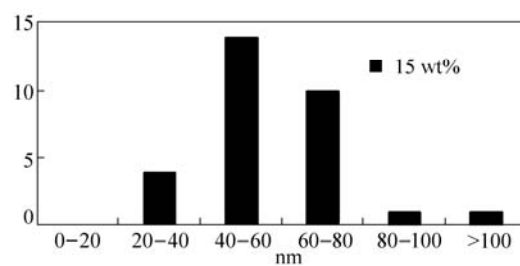
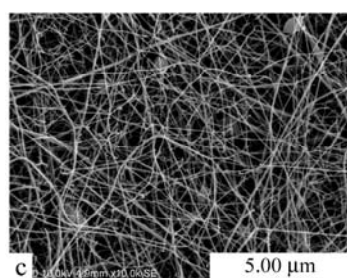
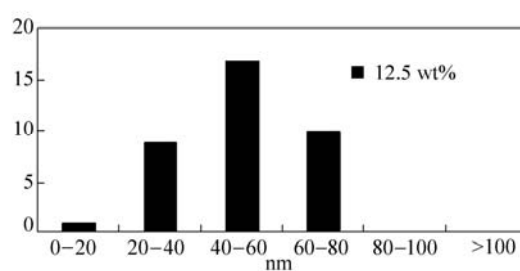
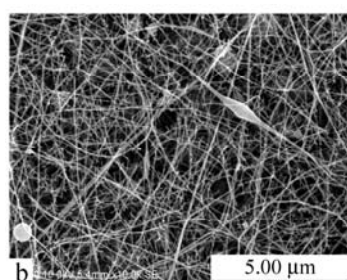
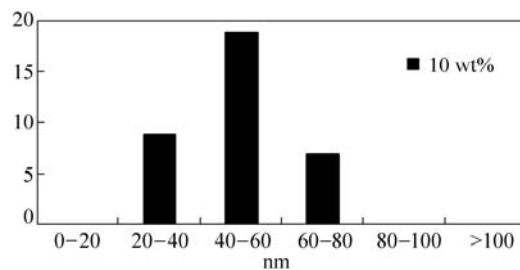
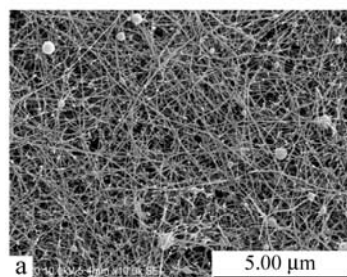
Fig. 3 Concentration dependence of specific viscosity for nylon-6,6 solutions

As can be seen, there is a power law relationship between the specific viscosity and solution concentration with different exponents for these two areas. In the semi-dilute unentangled regime η_{sp} power law exponent was around 2.0, which increased to 3.3 for the entangled regime. These results are in a good agreement with the theoretical predictions^[29].

Dependence of Electrospinning on Viscosity/Concentration

Figure 4 shows the SEM images and fiber size distribution of electrospun nanofibers obtained from 7 different concentrations. For 5 wt% and 7.5 wt% solutions, the viscosity was not high enough to produce a stable jet in the electrospinning and mostly electrospraying happened. For 10 wt% and 12.5 wt% solutions, very thin nanofibers with some irregularities and beads were formed. Solutions with concentrations $15 \text{ wt}\% \leq c \leq 25 \text{ wt}\%$ produced

beadless uniform nanofibers. The average diameter of the electrospun nanofibers increased with the increase in the solution concentration, and the diameter distribution shifted toward larger fibers.



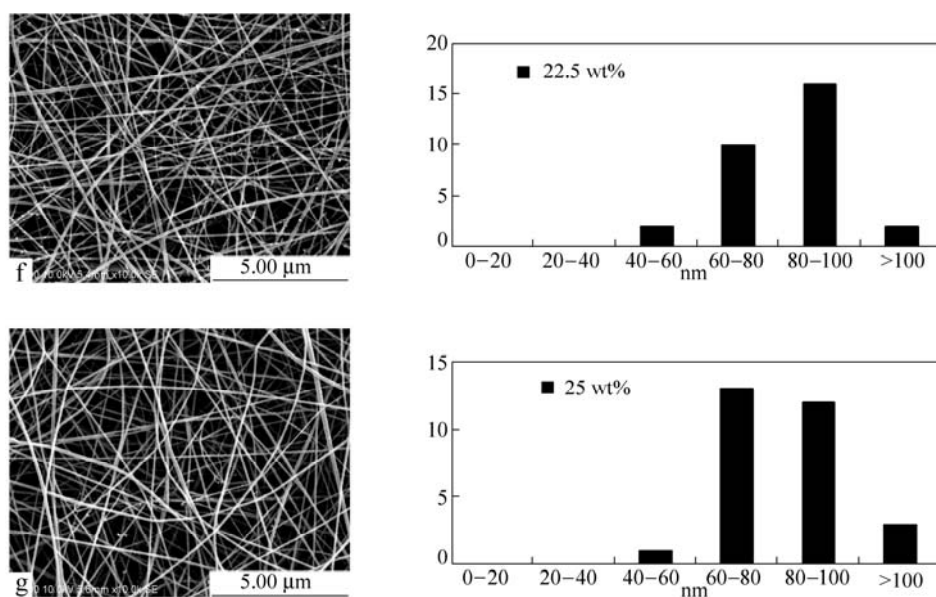


Fig. 4 SEM images and fiber size distribution of electrospun nylon-6,6 nanofibers with different solution concentrations: (a) 10 wt%, (b) 12.5 wt%, (c) 15 wt%, (d) 17.5 wt%, (e) 20 wt%, (f) 22.5 wt% and (g) 25 wt%

At very low viscosities (less than 10 wt% concentrations) formation of a stable jet, which is necessary for electrospinning, was not possible. In this concentration range, polymeric chains are far from each other and there is not considerable overlap among macromolecules.

Between 10 wt% and 15 wt% which is the entanglement concentration, the viscosity was enough for the jet formation, but entanglement between polymer molecules was not high enough and therefore, some beads and irregularities were formed. Above 15 wt% (c_e), the level of macromolecular entanglement became very suitable for electrospinning and very uniform and regular fibers with larger diameters were deposited on the collector.

Clearly, the entanglement concentration has a very crucial role in the electrospinning process; however, its effect on the electrospinnability of polymer solutions differs significantly from one polymeric system to another. Generally, polymers can be categorized into two main groups regarding their solutions' behavior in electrospinning. For the first group, electrospinning will not start until solution concentration reaches to c_e and before that, only electrospraying will happen. For some polymeric solutions inside this group, such as PET-co-PEI solutions, increasing concentration up to 2.0–2.5 times c_e is enough to have uniform bead-free fibers^[36], while for others much higher concentrations are required^[37]. For second group of polymers, like nylon-6,6 in this study, increasing solution concentration up to c_e is necessary for having uniform, bead-free fibers and for concentrations less than entanglement concentration, a mixture of fibers and beads are formed.

Figure 5 shows the average diameter of electrospun nanofibers as a function of solutions' zero shear rate viscosity. As can be seen, with increasing solution viscosity through increasing solution concentration, the average fiber diameter also increased and there was a power law relationship between these two variables as shown in Eq. (3):

$$D \sim [\eta_0]^{0.298} \quad (3)$$

This increasing effect was observed in previous studies, but the exponent of the power law relationship was different ($D \sim [\eta_0]^{0.8}$) for other polymers such as various polyesters^[36], showing less dependence of average fiber diameter on zero shear rate viscosity of nylon-6,6 solutions.

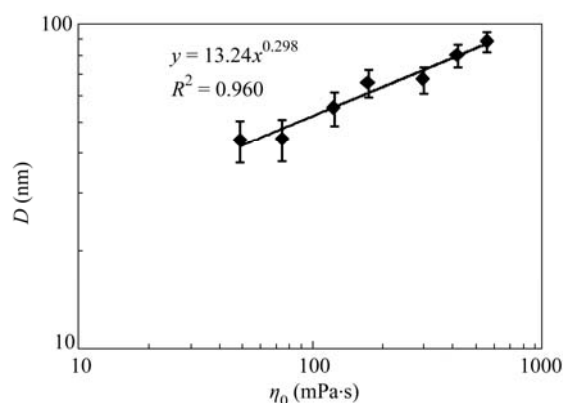


Fig. 5 Average diameter of electrospun nanofibers as a function of zero shear rate viscosity for nylon-6,6 solutions

Figure 6 shows the average diameter of electrospun nanofibers as a function of normalized concentration (c/c_e) for nylon-6,6 solutions. Here also the increase in the normalized concentration led to an increase in the average diameter of the nanofibers and a power law relationship between the average fiber diameter and normalized concentration was observed as in Eq. (4).

$$D \propto \left[\frac{c}{c_e} \right]^{0.816} \quad (4)$$

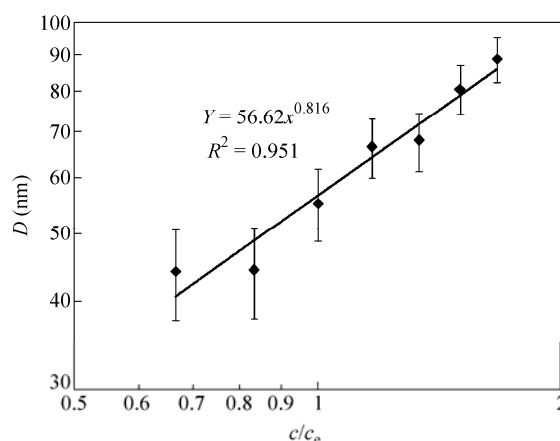


Fig. 6 Average diameter of electrospun nanofibers as a function of normalized concentration for nylon-6,6 solutions

Similar relationship was first established by McKee *et al.* for PTE-co-PEI nanofibers but with different exponent^[29, 36].

Crystallinity of Electrospun Nanofibers

Figure 7 shows the FTIR spectrum of nylon-6,6 electrospun nanofibers from 20 wt% solutions. Table 1 illustrates the main peaks of this spectrum and their assigned functional groups^[40].

The peak at 2936 cm^{-1} shows the dominance of α phase, while very minor amount of β and γ phases is also observed as indicated by the peak at 1430 cm^{-1} . The peaks related to the amorphous phase (922 cm^{-1} and $1128\text{--}1136 \text{ cm}^{-1}$) are not observed probably because of overlapping with the crystalline peaks^[40].

Figure 8 shows the DSC thermograms of nylon-6,6 electrospun nanofibers obtained from solutions of different concentrations. The original nylon-6,6 granules were used as a reference. The melting temperature (T_m)

of the original polymer was at 262.8 °C. For electrospun nanofibers, T_m appeared in the range of 262.4–263.8 °C, suggesting the absence of any clear difference in the melting temperature of original polymer and their corresponding electrospun nanofibers.

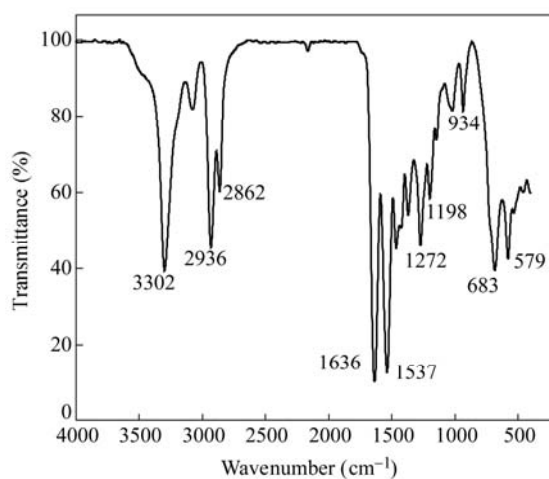


Fig. 7 FTIR of electrospun nanofibrous mat (20 wt%)

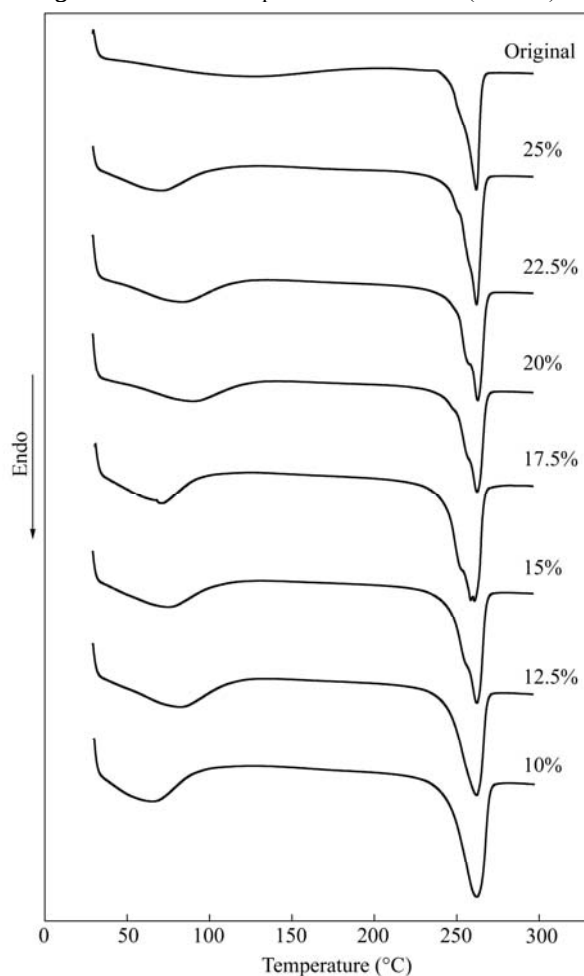


Fig. 8 DSC thermograms of nylon-6,6 electrospun nanofibers

Table 1. Main FTIR peaks and characteristic groups for nylon-6,6 nanofibers electrospun with solution of 20 wt% concentration

Peak (cm ⁻¹)	Characteristics	Peak range (cm ⁻¹)
3302	Free N—H axial deformation	≈ 3330–3060
3082	N—H angular deformation in the plane	≈ 3080
2936	CH ₂ α-NH axial deformation	≈ 2950
2862	CH ₂ β-NH and γ-NH axial deformations	≈ 2858
1636	C=O axial deformation, amide I	≈ 1640
1537	C—N axial deformation and CO—N—H angular deformation, amide II	≈ 1535–1555
1430	γ phase	≈ 1440
1198	Crystalline peak: symmetrical angular deformation out of plane, amide III	≈ 1196–1202
1143	Partially amorphous: angular deformation out of plane of carbonyl groups	≈ 1140–1146
934	Crystalline phase, amide axial deformation (C—C=O)	≈ 932–937

In all samples, there is a very wide peak in range of 31–130 °C which is mostly related to the evaporation of the residual solvent or/and water trapped inside non-woven mats. Because of masking effect of this peak, T_g of nylon-6,6 which normally appears in the range of 45–65 °C was not observed for all samples. The difference in the size of the peaks is because of different amount of the samples used in DSC measurements (between 5 mg to 10 mg).

Table 2 shows a summary of properties of nylon-6,6 solutions and their electrospun nanofibers. As can be seen, the crystallinity for all nanofibrous mats electrospun from solutions of different concentrations is increased compared to that of the the original granular polymer. This effect of crystallinity increase may be ascribed to the high shear stress applied to individual fibers during electrospinning. Similar results were reported in literature^[50]. It can be also seen that there is no clear trend in the crystallinity of the electrospun nanofibers in relation with the solution concentration.

Table 2. Summary of properties of nylon-6,6 solutions and their electrospun nanofibers (solvent viscosity: 1.54 mPa·s)

Concentration (wt%)	Solution		Nanofibers		
	η_0 (mPa·s)	η_{sp}	D (nm)	ΔH (J·g ⁻¹)	Crystallinity (%)
Original polymer	—	—	—	73.34	35.60
10	48.99	30.81	44.13	92.50	44.90
12.5	74.19	47.18	44.35	82.94	40.26
15	123.5	79.19	55.32	96.08	46.64
17.5	173.8	111.86	66.51	91.54	44.44
20	298.8	193.03	67.96	97.67	47.41
22.5	419.1	271.14	80.59	96.13	46.66
25	562.5	364.30	88.80	95.77	46.49

CONCLUSIONS

The effect of different concentration regimes and entanglement concentration (c_e) on electrospinning of nylon-6,6 solutions was studied and the relationship between the viscosity of polymeric solutions and morphology of their electrospun nanofibers was established. It was found that nylon-6,6 solutions show almost Newtonian behavior in the concentration range from 5 wt% to 25 wt%. A power law relationship between the specific viscosity and solution concentration was established with exponents of 2.0 and 3.3 for semi-dilute unentangled ($c < c_e$) and semi-dilute entangled ($c > c_e$) regimes, respectively. For concentrations less than 10 wt%, corresponding to the viscosities less than 49 mPa·s, a stable jet could not be formed. When the concentration was between 10 wt% to 15 wt%, corresponding to viscosities of 49–125 mPa·s, beads and irregular fibers were collected. For 15 wt% (c_e) $\leq c \leq$ 25 wt%, corresponding to viscosities between 125 mPa·s and 550 mPa·s, regular and uniform nanofibers were formed. Therefore, it is necessary to increase the viscosity of the spinning solution of nylon-6,6 above the entanglement concentration of 15 wt% to fabricate regular and uniform nanofibers. The average nanofiber diameter increased with an increase in the solution concentration/viscosity. Particularly, the

average diameter of the electrospun nanofibers was dependent on normalized concentration (c/c_e) and zero shear rate viscosity in a power law relationship with exponents of 0.816 and 0.298 respectively. The crystallinity of all electrospun samples (between 40.26%–47.41%) was found to be higher than that of the original polymer (35.60%), which could be because of high shear stress applied to polymeric jet during electrospinning. These results show that while entanglement concentration has a very important role in predicting spinnability of polymeric solutions, c_e -regulation suggested in literature^[29, 36] is not necessarily valid for all polymeric systems and other parameters than bulk viscosity of the solutions are affecting their electrospinnability.

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