

Preparation and characterization of electrospun fibers of Nylon 11

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Abstract. Nylon 11 nanofibers mats were successfully prepared by electrospinning process from formic acid solution. The scanning electron microscopy (SEM) images showed that nanofibers with uniform diameter were produced when the polymer concentration was 10% w/v, whereas ribbons were formed at a higher concentration. The crystalline structure of the nanofibers mats was investigated using X-ray diffraction (XRD) and it was found that the nanofibers mats crystallized in γ form. The melt crystallized as well as solution casted films however exhibited α form. The thermal properties of these samples were studied using differential scanning calorimetry (DSC) and it was observed that electrospun fibers showed higher crystallinity than the melt-crystallized samples. However, the crystallinity of electrospun fibers was lower than the solution-crystallized sample.

Keywords: *nanomaterials, biocompatible polymers, electrospinning, Nylon 11*

1. Introduction

Electrospinning process provides a simple route to fabricate polymer fibers with diameters ranging from nanometers to micrometers. The advantage of these fibers is the huge increase in the surface area to volume ratio and recently, electrospinning process has been found to be a cost effective approach for fabrication of polymer fiber mats. Numerous studies have been reported addressing various aspects of electrospinning process [1–5]. The various factors that are known to affect electrospun fibers include solution viscosity, surface tension, electric field intensity and distance. These electrospun fiber mats have wide applications in water filters, textiles, sound absorbers materials, sensors for gas and other chemicals. The use of electrospun nanofibrous mats has also attracted a great deal of attention in biomedical applications. The most important feature of these nanofibrous mats which is exploited in biomedical applications

is their ability to mimic extracellular mass (ECM). As a result, these mats are found suitable for biomedical applications as tissue engineering scaffolding, wound dressing, artificial blood vessels, drug delivery carriers, cosmetic and skin masks [6–10]. Recently, several researchers have reported electrospinning of several biocompatible polymers to explore their use in various biomedical applications. These include polycaprolactone (PCL), polylactic acid (PLA), poly vinyl alcohol (PVA), chitosan, polyhydroxybutyrate and its copolymers [11–19]. However, there is very little information focusing on electrospinning of Nylon 11.

In this communication, we present preparation and characterization of electrospun fibers of Nylon 11 which is a biocompatible polymer. In this study, we investigate the morphology of Nylon 11 fibers under different weight concentrations. The electrospun fibers were characterized for their morphology and structure using scanning electron microscopy

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(SEM), Wide angle X-ray diffraction (WAXD), and differential scanning calorimetry (DSC).

2. Experimental

2.1. Materials

Nylon 11 with a density of 1.026 g/cc, melting point of 189°C and glass transition temperature of about 47°C was purchased from Aldrich Chemicals. Formic acid was procured from Merck. All chemicals were used as received without any further purification.

2.2. Solution preparation

Nylon 11 solutions of 10 and 20 wt% were prepared by dissolving Nylon pellets in formic acid. The solutions were prepared in a constant temperature bath at 70°C for 2 hr. The solutions were cooled to room temperature before electrospinning. The viscosity of solutions was measured using Brookfield viscometer model DV-II+Pro and the viscosity values were found to be 15.5 mPa·s for 10 wt % solution and 29.2 mPa·s for 20 wt% solution.

Films were cast from polymer solution in Petri dish by evaporating the solvent and were used for elucidating the effect of electrospinning process on the structure. For comparison, the melt pressed films were also prepared from Nylon 11 pellets using a laboratory press. Nylon 11 pellets, melt pressed film and solution cast films are coded as P, MP, SC respectively.

2.3. Electrospinning process

The electrospinning apparatus developed in our laboratory was used for this work. The electrospinning setup was horizontal. It consisted of a high voltage supply (0–40 kV) from Gamma Corporation, USA and a syringe pump from Sage instruments (model 351) with flow rate capacity from 0.0015 to 60 ml/min. A glass syringe with 10 ml capacity and a stainless steel needle with 0.8 mm diameter was used. The collector distance was kept at 10 cm from the needle and flow rate was maintained at 0.2 ml/min for experiment. The electrospinning was carried out at 20 kV. The needle was charged to +20 kV and the collector was earthed. Electrospinning process was carried out at room temperature. The electrospun fibers from 10 and 20 wt% solutions are coded as ES10 and ES20.

2.4. Characterization

2.4.1. Scanning electron microscopy (SEM)

The morphology of Nylon 11 electrospun fibers was studied by using Leica-440 scanning electron microscope (SEM). The SEM micrographs of the electrospun fiber were recorded at different magnifications. The sample surfaces were sputtered with gold to avoid overcharging.

2.4.2. X-ray diffraction (XRD)

X-ray diffraction analysis of Nylon 11 melt pressed film, solution casted film and electrospun fiber mats was performed on a Panalytical (XPRT-PRO). The scans were recorded at room temperature with 2θ ranging from 5 to 30°.

2.4.3. Differential scanning calorimetry (DSC)

DSC study of Nylon 11 pellets, melt pressed film, solution casted film and electrospun fibers was performed on Perkin Elmer Differential Scanning Calorimeter (DSC-2) in the temperature ranging from 50–250°C. A controlled heating and cooling rate was maintained at 10°C/min. The test was carried out in nitrogen atmosphere. The melting point of polymer (T_m), crystallization temperature (T_c) and % crystallinity of polymer were determined from the heating and cooling scans.

3. Results and discussion

3.1. Electrospinning process

Electrospinning is a process by which sub-micron polymer fibers are produced using an electro statically driven jet of polymer solution or polymer melt. Metering pump is used to control the flow of polymer solution through syringe. The collector is grounded. When no voltage is applied, the polymer solution through the needle falls like a hemispherical drop due to surface tension. As the intensity electric field is increased, hemispherical surface of fluid starts to elongate to form a conical shape known as Taylor cone [20]. When the threshold value of electrostatic force is reached, it overcomes the surface tension of the polymer solution and a charged jet is ejected from the apex of the cone. The charged jet travels linearly only for a short distance and then undergoes bending instability result-



Figure 1. Electrospinning of Nylon 11

ing in formation of looping trajectory of the jet. The charged jet elongates and the solution dries out and is finally deposited on the collector as fibers. Figure 1 presents the photograph of electrospinning of Nylon 11.

The fibers were collected on the Aluminum collector plate. These electrospun fibers were vacuum dried and then characterized by using SEM, XRD and DSC.

3.2. Scanning electron microscopy

It is well documented that a variety of structures such as beads, fibers and ribbons can be achieved in

electrospinning of polymers as reported earlier by Koombhongse *et al.* [21]. The shape and size of these structures are governed by a number of parameters such as polymer solution properties, vapor pressure of the solvent, humidity and also the process parameters such as feed rate, field strength and geometry of the electrode.

Scanning Electron Micrographs electrospun fibers are shown in the Figure 2. As can be seen from the Figure 2a for ES10 sample, nanofibers with round cross section are formed and the fibers are not aligned. For ES20 samples, nanofibers are not with round cross section but nanofibers show ribbon like structures as shown in Figure 2b. It is also observed from the micrographs that ES10 nanofibers have uniform diameter of the order of about 200 nm whereas ES20 sample shows diameter ranging from about 400 nm to few micrometer are formed as shown in Figure 2c and 2d.

In case of polystyrene, similar flat fibers were obtained for 30% w/v solutions in dimethylformamide [21]. The formation of flat ribbons was attributed to the uneven evaporation of the solvent between the skin and the core of the charged jet

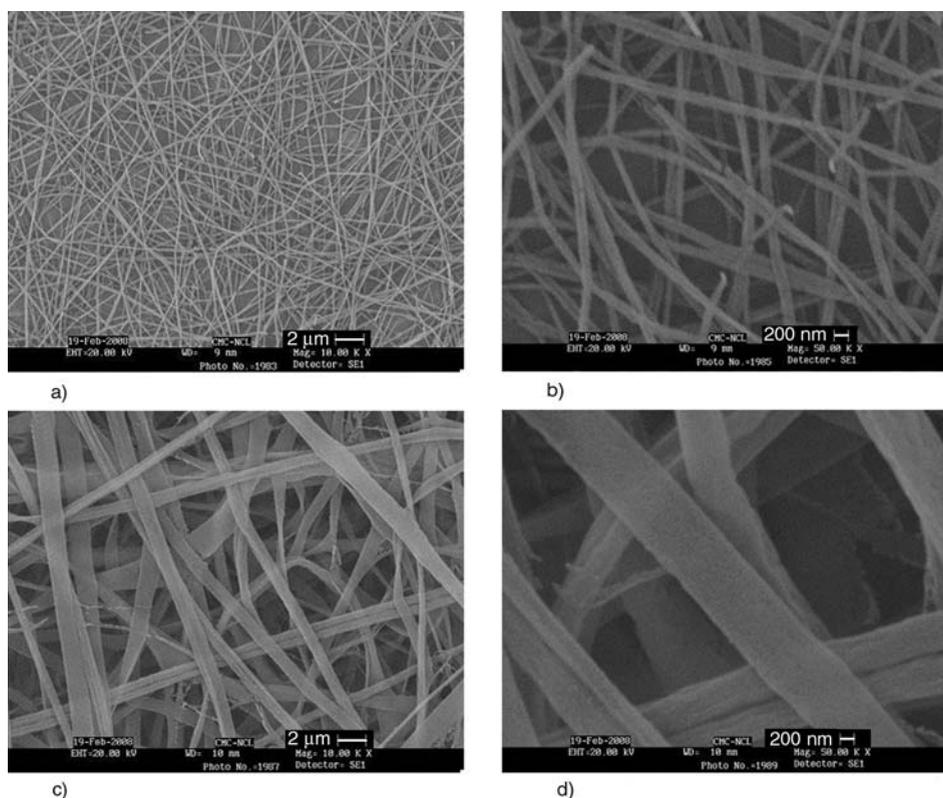


Figure 2. a) Scanning electron micrograph of electrospun fibrous mats of Nylon 11 from 10 wt% solution. b) Magnified scanning electron micrograph of electrospun fibrous mats of Nylon 11 from 10 wt% solution. c) Scanning electron micrograph of electrospun fibrous mats of Nylon 11 from 20 wt% solution. d) Magnified scanning electron micrograph of electrospun fibrous mats of Nylon 11 from 20 wt% solution.

causing the jet to collapse. Flat fibers were also reported in electrospun polyvinyl alcohol fibers from highly viscous solutions [22].

3.3. X-ray diffraction

Nylon 11 is an interesting polymer as it exhibits at least five different crystalline phases such as α , β , γ , δ , δ' and α' . The crystalline structure and polymorphism of Nylon 11 has been studied by several researchers [23–28]. It has been reported that the α form of Nylon 11 exhibits two characteristic reflections at $2\theta = 20.2$ and 23.01° [23] whereas the γ form of Nylon 11 exhibits a characteristic reflection at $2\theta = 21.34^\circ$ [24].

The structure of melt pressed film, solution cast film and electrospun fibers is studied using XRD to ascertain the crystalline form of Nylon 11. Figure 3a and 3b show the diffraction patterns of MP

and SC samples respectively. MP and SC samples exhibit two characteristic reflections around at $2\theta = 20.4$ and 23.01° corresponding to α crystalline phase of Nylon 11.

The XRD patterns of ES10 and ES20 are depicted in Figure 3a and 3b respectively. In these diffraction patterns of the electrospun fibers, a single peak is observed at about $2\theta = 21.63^\circ$. This reflection corresponds to the γ form of Nylon 11 [28].

The XRD results indicate that the electrospinning process transforms the α phase of Nylon 11 to γ phase of Nylon 11 whereas the SC sample exhibits α phase of Nylon 11. This leads to the conclusion that the change in crystal form of Nylon 11 results because of the electrospinning process and not because of solution crystallization. In the electrospinning process, the structure of the fiber is formed under the influence of two simultaneous processes namely the evaporation of the solvent

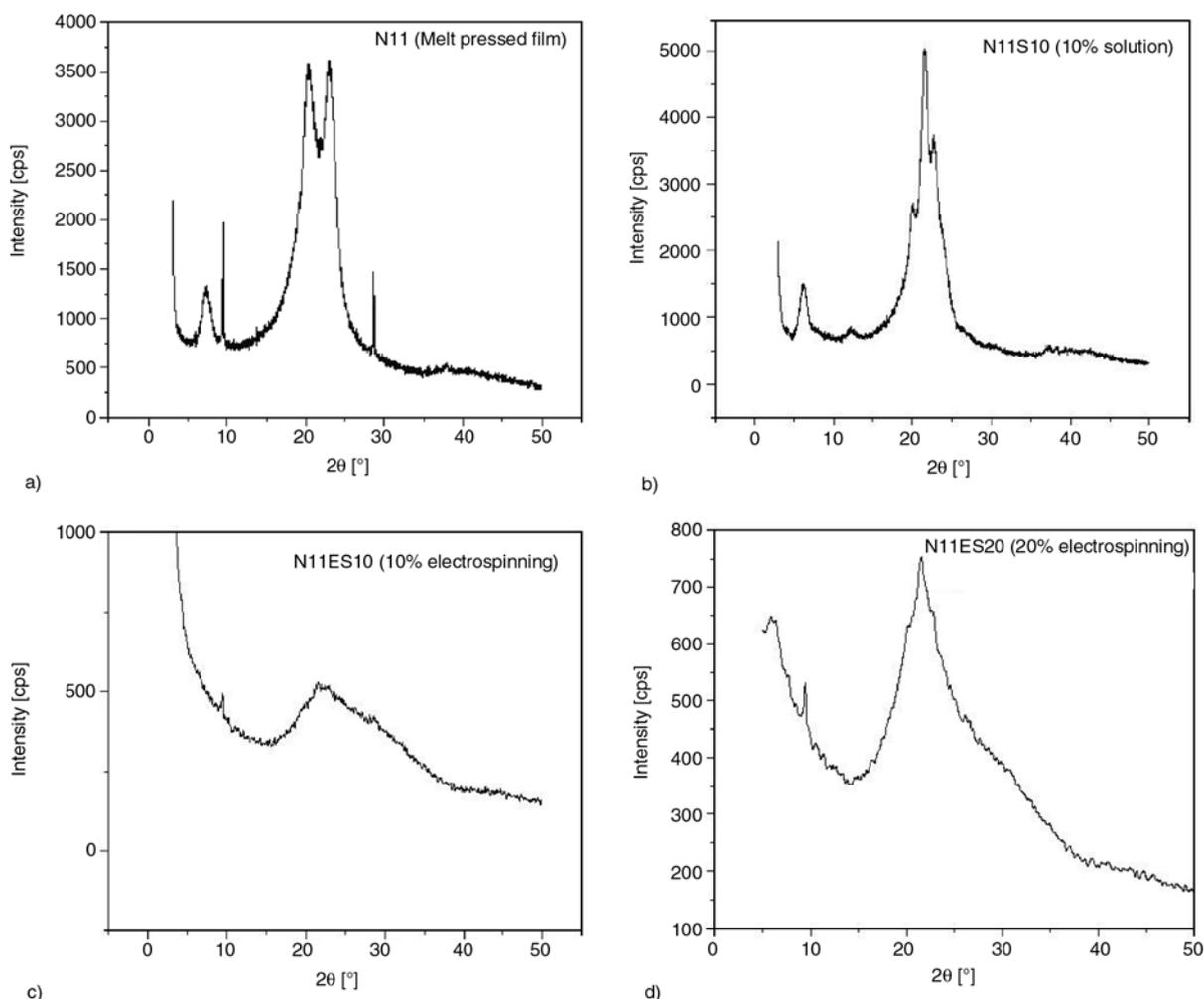


Figure 3. a) XRD scan of melt pressed Nylon 11 film. b) XRD scan of solution casted Nylon 11 film. c) XRD scan of electrospun fibrous mats of Nylon 11 from 10 wt% solution. d) XRD scan of electrospun fibrous mats of Nylon 11 from 20 wt% solution

Table 1. Melting and crystallization parameters of Nylon 11 samples

Sample coding	First heating			Crystalline temperature T _c [°C]
	Heat of fusion ΔH _f [J/g]	Crystallinity χ _c [%]	Melting point T _m [°C]	
P	32.60	15.80	190.90	150.30
MP	40.96	20.00	191.10	160.60
SC10	87.99	41.43	193.68	162.60
ES10	49.32	24.00	188.30	167.90
SC20	84.48	41.20	194.71	161.28
ES20	55.18	26.90	189.40	162.70

and the elongation of the fibers while crystallization from solution takes place under quiescent conditions. Thus, crystallization from solution results in more ordered α form whereas crystallization takes place under mechanical deformation during electrospinning. Similar changes in the crystal form have been noted in Nylon 6, by Stephans *et al.* [29]. They have attributed the formation of γ phase during electrospinning process to the high stress experienced by Nylon 6 during fiber formation.

3.4. Differential scanning calorimetry (DSC)

A thermal analysis of P, MP, SC, ES10 and ES20 is performed on the DSC. The melting and crystallization parameters are presented in Table 1. The crystallinity of samples was calculated by dividing the heat of fusion of polymer samples to heat of fusion of 100% crystalline Nylon 11. The reported value of heat of fusion of 206 J/g for 100% crystalline Nylon 11 was used to calculate the % crystallinity [30]. ES10 and ES20 show higher crystallinity than MP and as received P samples. The crystallization temperature is also higher for electrospun fibers as compared to bulk sample.

It is interesting to note that the solution cast films exhibit highest crystallinity ($\approx 41\%$) as compared to the ES and melt pressed film. This indicates that the ES mats have lower crystallinity than the corresponding solution cast films. The structure formation during electrospinning is governed by the simultaneous processes of evaporation of the solvent and the elongation of the solidifying fiber. In crystalline polymers, solidification is also connected with formation of crystals. The shorter time for crystallization is expected to result in small crystallites with defects and thus lower degree of crystallinity [31]. It can be envisaged, that the rapid solidification of the polymer solution limits the development of crystallinity while the solidification during film casting takes place slowly resulting

in higher degree of crystallinity. Similar results have been reported for poly (lactic acid) (PLLA) [32], Nylon terpolymer [2], Nylon 11 [33] and in PET [34].

4. Conclusions

Nanofibers of Nylon 11 are electrospun at two different solution concentrations. At 10 wt% concentration, uniform nanofibers with diameter of approximately 300 nm are obtained. At higher polymer concentration (20 wt%) formation of ribbons is observed rather than circular fibers. The nanofibers mats so produced exhibit γ crystalline structure as evidenced by the XRD results. The formation of γ crystals is attributed to the possible high rate of elongation experienced by the polymer during electrospinning. The thermal properties of nanofibers show increase in crystallinity as compared to the melt crystallized sample whereas lower crystallinity than that of solution crystallized samples.

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