

Electrospun Self-Assembled Nanofiber Yarns

Abhijit Mondal, Ritutapan Borah, Avishek Mukherjee, Sandip Basu, Manjeet Jassal, Ashwini K. Agrawal

Department of Textile Technology, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India

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ABSTRACT: A technique for making self-assembled electrospun (E-spun) nanofiber yarns from poly(acrylonitrile) in a single step is described. The process involved formation of the nanofiber yarn directly within the electrospinning zone and its removal before it can reach the counter-electrode. The yarn is presumably formed due to splitting of the main jet into numerous nanojets and their reassembly into a single entity midway between the two electrodes. The process was found to occur at a particular

field strength, which varied considerably with the concentration of the polymer dope. The gross morphology of yarns and the alignment of nanofibers in the yarn were evaluated by scanning electron microscopy (SEM). The rationale behind the formation of the yarn like structure has been explained. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 603–607, 2008

Key words: fibers; nanotechnology; self-assembly

INTRODUCTION

Electrospinning is a fiber forming process, which utilizes a high voltage electric field to produce an electrically charged jet of polymer fluid. An electrode charges the polymer fluid droplet; which ejects into a fine fluid jet when the repulsive forces induced by the electrostatic charge overcome the cohesive surface tension forces of the polymer fluid. The jet elongates as it accelerates under the electric field. During its travel from the jet electrode, it solidifies and produces a nanofiber, which is deposited in a form of a web on the oppositely charged collecting counter electrode placed at a distance. Although the first patent¹ for the fundamental idea of this process was awarded in 1934, however, the process of electrospinning was used for the formation of nanofibers² only in the mid-1990s. Since then there has been an upsurge in research in this area to find the potential of electrospun fibers for various applications.³ The electrospun fibers/mats have found application in filters, biomaterials, composite reinforcements, semipermeable membranes, protective textiles, and other fields.^{4–12}

For many of the textile based applications, the electrospun fibers are required to be produced as a continuous fiber bundle or filament yarns. However,

due to the delicate nature of the individual nanofilaments, converting them into yarns or other geometries is extremely challenging. It is desirable to produce bundle of nanofibers or yarns to enable their easy handling and processability into useful textile products. Various approaches have been reported¹² to obtain aligned electrospun fiber bundles e.g., spinning onto a rotating drum; spinning onto the sharp edge of a thin rotating wheel; introducing an auxiliary electrode or electrical field; rapidly oscillating a grounded frame within the jet; and using a metal frame as the collector.

Fennessey and Farris¹³ performed electrospinning and collected unidirectional aligned and oriented tows of nanofibers of 270–290 nm diameter spun into yarns using an electric spinner. This allowed the testing of the effects of twist on the tensile strength and other properties of the yarn. Dalton et al.¹⁴ have collected aligned polycaprolactone fibers between two grounded rings and twisted them into a yarn. However, all of these approaches result in the formation of only short tows of aligned nanofibers. Ko et al.^{15,16} manufactured continuous yarns of composites of polylactic acid and polyacrylonitrile with single wall carbon nanotubes but no detailed description of the process or the resulting yarns was given. Electrospinning continuous fiber bundle yarn onto a liquid reservoir and then collecting the fibers has also been reported.^{17–19} A simple technique for producing continuous nanofiber yarns was proposed by Pan et al., where they formed a yarn from fibers coming out of two oppositely charged and oppositely placed needles.²⁰ The resulting yarn was then taken up on a cylinder rotating at a high speed.

Correspondence to: M. Jassal (manjeetjassal@gmail.com) or Ashwini K. Agrawal (ashwini_agrawal@yahoo.com).

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In this article, we are reporting an alternative approach, where a yarn consisting of electrospun nanofibers was allowed to self-assemble within the spinning path. This process is being referred to as E-spinning and the product as E-spun yarn. The continuous electrospun yarns (E-spun yarns) were obtained by a process of self-assembly where the spinning fluid underwent multiple splitting into nanojets followed by assembly under the influence of a strong electric field. The assembly of the split nano-jets was initiated by an insulated rod placed between the top and counter electrode. This process of yarn formation takes place spontaneously under certain electrospinning conditions, which are reported below.

EXPERIMENTAL

Fiber grade commercial acrylic terpolymer with M_w of 75,000 was procured from Pasupati Acrylon Ltd., India and used for the experiments. The terpolymer had about 8% methyl acrylate and 1% 2-acrylamido 2-propane sulfonate as comonomers in addition to acrylonitrile. Laboratory grade reagent *N, N*-dimethylformamide (DMF) was used as a solvent for the acrylic terpolymer. The terpolymer was dissolved in DMF to obtain homogeneous spinning dope concentrations of 4–22% (w/w). The electrospinning was carried out using an infusion syringe pump (KDS 100 from KD Scientific) with a needle (ID = 0.55 mm) as the spinning head and 40 kV dual polarity high voltage power supply (from Gamma HV). The syringe pump was used to control the flow rate, while the high-voltage supply was used to charge the needle and the collector, as needed. To initiate the formation of E-spun yarn, a glass rod was introduced between the two electrodes and was slowly moved out. The yarn was formed on one end of the glass rod and was continuously removed manually by moving the glass rod away from the spinning zone or automatically by attaching the yarn end from the glass rod to an endless belt made up of wire mesh. The belt was made to roll on a pair of rotating rollers driven by a motor insulated from the wire mesh. The polymer solution was forced through the needle at a flow rate of 0.2 mL/h. The distance between the collector and needle was maintained at 10 cm for all the experiments. In some of the experiments a circular ring attachment was used with the needle, as shown in Figure 1. The ring was placed surrounding the needle just above the orifice. The electrospinning dope was conditioned at the room temperature (27°C) before spinning. Polymer dopes of concentrations more than 16% (w/w) were electrospun using preheated dope at 70°C. For dope concentration of 22 wt % a special heating arrangement was incorporated, as shown in Figure 1, to maintain the spinning environment temperature at 70°C.

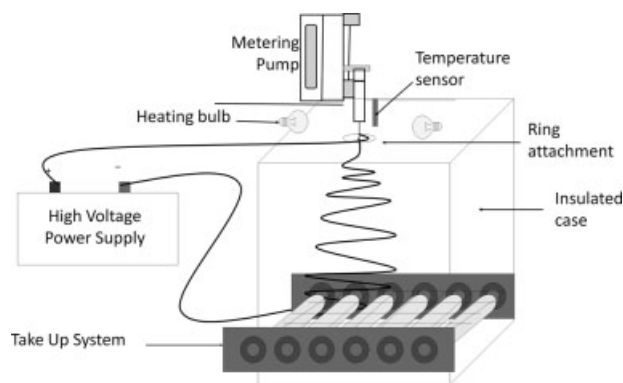


Figure 1 Electrospinning set-up with heating arrangement, ring attachment around the needle and take up device.

RESULTS AND DISCUSSION

During spinning, the collector was maintained at a negative potential while the needle was at positive potential, however their magnitudes were kept the same. It was observed that the electric potential required to get the self assembled E-spun yarn structure was different for different dope concentration. In contrast to the electrospinning of a typical nanoweb, where counter electrode could be kept grounded, a high opposite collector potential was found necessary for producing E-spun yarn. The E-spun yarn formation was triggered by manually placing a glass rod in the electric field between the two electrodes (i.e., jet and the collecting wire mesh and pulling it out slowly.) Once the yarn formation began, the first end of E-spun yarn was slowly placed on the moving endless wire-mesh (serving as the counter electrode) and the E-spun yarn could be mechanically removed in a continuous manner. The conditions required for E-spun yarn formation are reported in Table I.

Solution properties such as viscosity, elasticity and surface tension govern the transformation of polymer dope into nanofibers. To understand the underlying mechanism of E-yarn formation, the polymer dope concentration was varied between 6 and 22 wt %. At polymer concentration lower than 6 wt %, only droplets and beads were formed. This was attributed to low entanglement density of the polymer at lower concentrations and possibly the incomplete evaporation/removal of the solvent from the electrospun fibers at the collection site. The formation of beads has been observed during electrospinning by the other authors as well.²¹ The presence of high amount of solvent causes complete relaxation of the charged polymer jet to a bead, once it is neutralized on reaching the collector electrode. Bead formation is significantly high at lower polymer concentrations.

TABLE I
Electrospun Yarn Properties

Polymer concentration (wt %)	Dope temperature (°C)	Electric potential (kV)	Morphology	Fibre diameter (nm)	Coefficient of variation (CV%)
4	27	20	Only droplets and no fiber formation	–	
6		20	Continuous yarn formation	105	9
8		24	Continuous yarn formation	365	13
10		26	Yarn formation with breakages	456	8
12		28	Yarn formation with frequent breakages	480	7
16		70	30	Only short lengths of yarn formation	504
22	36		Yarn forms but of very short length	561	14

Therefore, a dope concentration of 6 wt % was found to be necessary for the formation of fiber and yarn type structure. At 6 wt % dope concentration, it was possible to obtain continuous E-spun yarn at low field strength (of 2 kV/cm). At lower concentrations, the nanofibers in the yarn were observed to possess textured surface. Also due to the high amount of solvent and short spinning path, the yarn structure was fused.

In our endeavor to improve the nanofiber properties (like producing strong, bead free and unfused fibers), electrospinning was performed at higher polymer concentrations. Although these problems could be easily overcome by increasing the polymer dope concentration, the nanofiber diameter in E-yarn was found to increase. The fibers constituting the E-spun yarns were not as fine and were fewer in number. Clearly, the increase in dope concentration had made the splitting of fluid jet (i.e., jet splaying) more difficult. Therefore, with increasing polymer dope concentration, significantly higher electric fields were required to generate the E-yarn as reported in Table I.

The E-spun yarns produced using 6 wt % dope was found to be somewhat fragile. The low strength was attributed to the poor entanglement density of the polymer network at this concentration during spinning. Similar low strengths were also found in regular diameter fibers, when the above polymer was wet-spun in DMF-water system using laboratory set-up. A nanofiber electrospun from a higher polymer dope concentration is expected to form better e-spun yarn because of higher entanglement density. It was hoped that at higher dope concentration during E-spinning may help in improving the yarn strength. The same was observed when the dope concentration was increased to 8 wt %. However, at dope concentrations higher than 10 wt %, frequent breakages were experienced during the collection of continuous E-spun yarn. Consequently, with increasing dope concentrations, the spinning of continuous E-spun yarn became progressively difficult. This behavior contradicted our expectation based on entanglement density and network formation of

polymer chains during electrospinning. The possible reasons for this deviation may be that at the polymer dope concentration of 10 wt % or higher the extruding jet is split into fewer filaments, which are not able to hold the strand together and have a tendency to remain separate from each other. This leads to poor cohesiveness of the E-spun yarn resulting in poorer mechanical properties.

As shown in SEM micrographs (Fig. 2), the electrospun yarn consisted of a bundle of nanofibers.

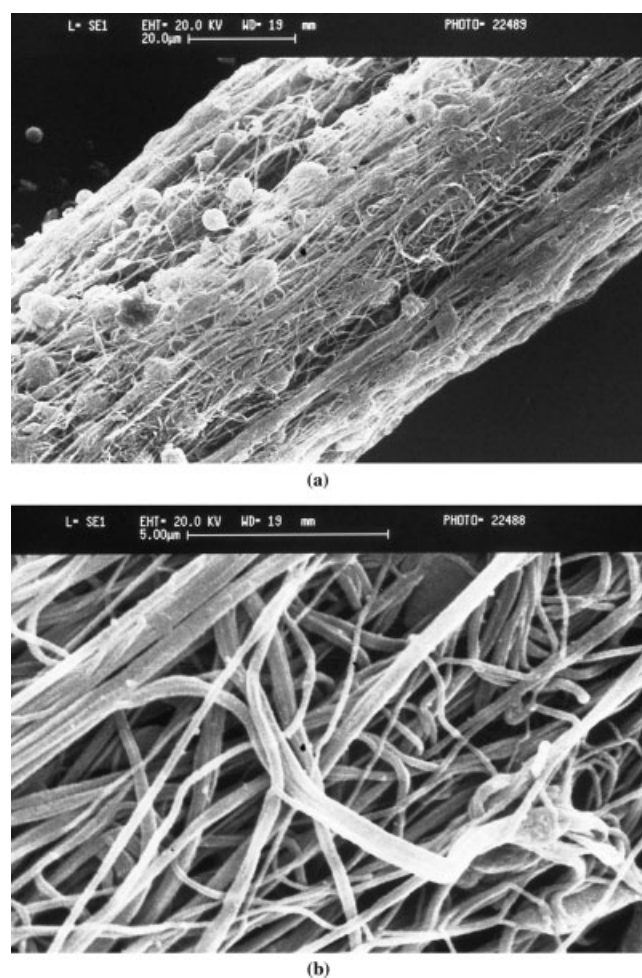


Figure 2 SEM of E-spun Yarn at magnification (a) 12,000 X, and (b) 26,000 X.

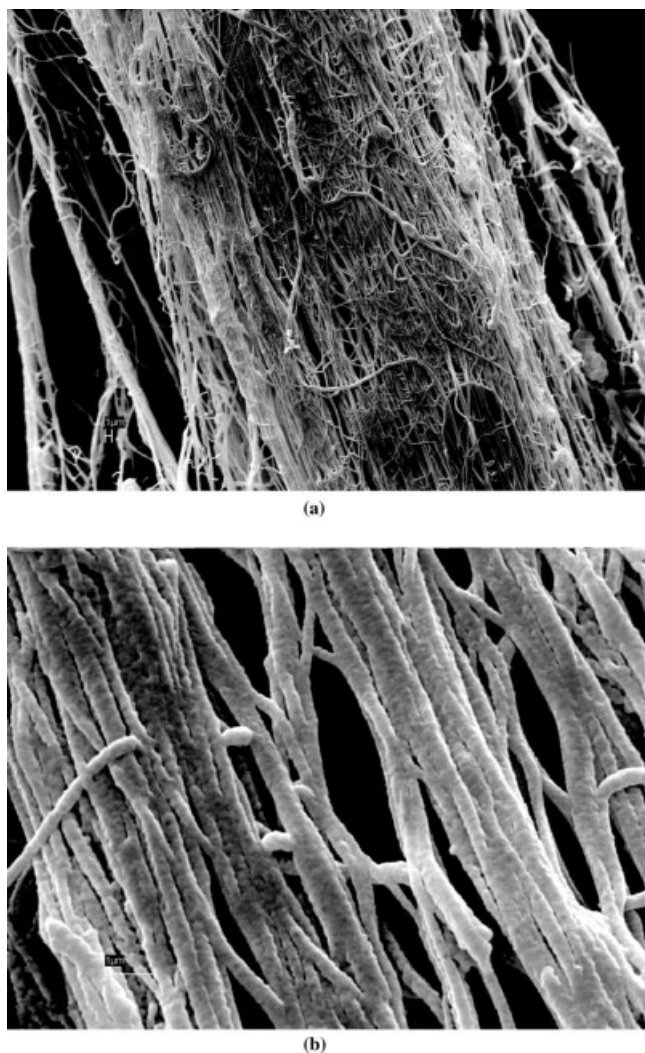


Figure 3 SEM of E Spun yarn electrospun with ring attached to needle at magnification (a) 12,000 X, and (b) 26,000 X.

The first set of SEM images shows that the arrangement of the nanofibers is not very well aligned along the axis of the E-spun yarn. During electrospinning process the similar charges in the jet may diverge the nanofibers and produce uneven, fluffy structure. To improve the yarn structure an additional circular electrode was placed around the spinning needle. This electrode was also kept at the same potential as needle. The introduction of the extra electrode resulted in formation of a more uniform and compact yarn structure, where nearly all nanofibers were aligned along the axis of the E-spun yarn. The scanning electron micrographs of the E-spun yarns with additional electrode are shown in Figure 3.

There are two possible mechanisms by which the formation of the said E-spun yarn may take place. In one possible mechanism, a single jet of the polymer fluid may start to deposit on the glass rod tip in a zigzag fashion to form a E-spun yarn with lamellar

type structure (Fig. 4). In this case there is no splitting of the fluid jet and the multiple nanofibers seen in the bundle are actually the same filament running to and fro. The micrographs shown in Figure 2 may support such a mechanism because many nanofibers appear to undergo many U-type turns in the yarn bundle. The second possible mechanism is that as the polymer fluid jet ejects out of the needle, it undergoes excessive splitting into numerous nano-jets. The splitting occurs only when a certain amount of charge is accumulated on the polymer fluid jet. Under normal set-up, once split, the numerous nano-jets must go to counter electrode and deposit randomly as a web. When a glass rod is placed in the spinning zone, it alters the electrostatic lines of force. There is a net induced charge on the glass electrode, which makes it a point of collection. As soon as the electric field is interrupted by the presence of glass rod in between the two electrodes, all the nano-jets try to deposit at the same point on the glass rod. In their attempt to deposit at the same point, they recombine to form the E-spun yarn structure (Fig. 5). The presence of a glass rod tip may create, by induction, a strong negative potential in presence of negatively charged counter electrode

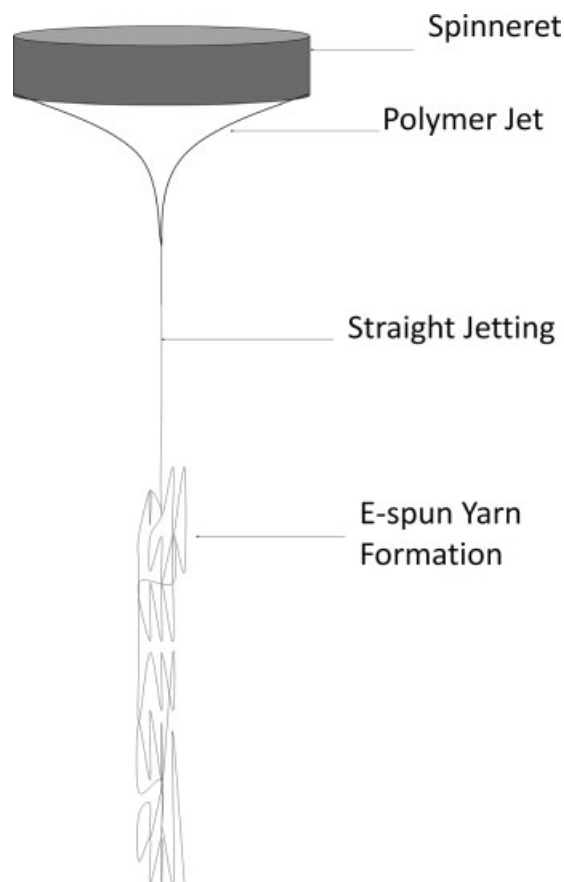


Figure 4 Mechanism of lamellar type structure formation.

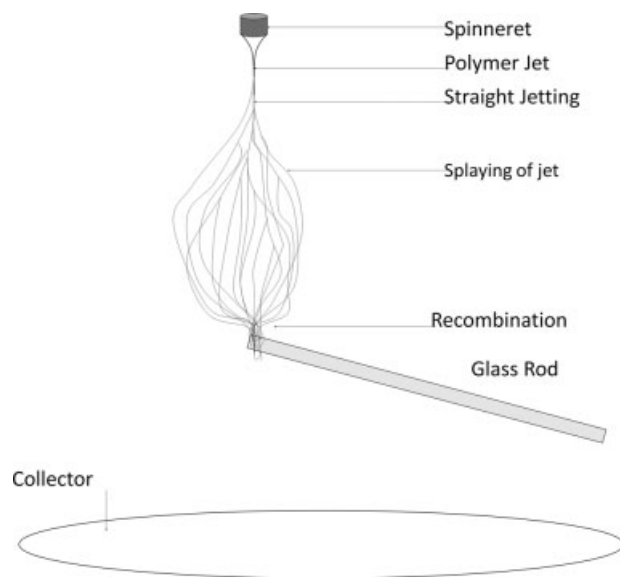


Figure 5 Mechanism of splitting and recombination of fluid jet.

below it. Therefore, the presence of large area counter-electrode having negative polarity is important to initiate such a process. As the glass rod is pulled out, the deposition point moves from the tip of the glass rod to the forming end of the E-spun yarn and the deposition continues. This gives a continuous yarn. Since the path between the needle and the glass rod is much shorter than the distance between the two electrodes, the solvent from the nano-jets are not completely evaporated and partly fused filaments with textured surface are produced.

Among the two mechanisms, the second mechanism appears to be responsible for the E-spun yarn structure reported here. This is based on several observations: (a) A significantly higher voltage (electric field) was needed to start the process of E-spun yarn than normal electrospinning nanowebs. The higher voltage would help in splitting the jet as it comes out of the spinning zone. (b) The SEM micrographs show the filaments of nanometers which is possible only if a long spinning path is provided to the spinning jet. Here the path is very short and the jet is unlikely to undergo elongation to achieve diameter of the order of nanometers. Only splitting of the jet may result in formation of such fine fibers. (c) The polymer dope of higher concentration was found to produce fewer strands of higher diameter in the E-spun yarns. This can be easily explained on the basis that higher dope concentration causes lower splitting due to higher entanglement density. (d) As seen in the micrographs in Figure 3, the zigzag turns of the nanofibers vanished as the additional ring electrode was placed at the needle which suggests that the spinning filaments are not under-

going zigzag turns. (e) The careful SEM scan of the E-spun yarn along its axis revealed continuous and uninterrupted runs of the nanofibers. Therefore, it is likely that E-spun yarns are being formed by the second mechanism.

CONCLUSIONS

Electrospinning has been used to generate a variety of structures from the same raw material when spun under different conditions. We have reported the formation of a novel structure, an E-spun yarn, with a commercially available acrylic polymer and a simple setup. The reported process is a consequence of recombination of the split jets of nanofibers formed during electrospinning. The self-assembly is initiated by the presence of a pointed insulator in the electrospinning zone. The formation of the E-spun yarn is spontaneous and is controlled by dope properties. The E-spun yarns, thus formed can be easily handled and put to use in a variety of applications where random nanoweb structures are of limited utility, for example, formation of carbon nanofiber yarns by carbonization of the E-spun acrylic yarns.

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