Are the Electrospun Polymers Polymeric Fibers?

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In this short communication, an attempt is undertaken to demonstrate that the widely used practice to call the electrospun polymers from their solutions and melts "polymer nanofibers" is hardly correct for the following reasons. The polymer fibers prepared by means of the common melt-spinning are characterized by perfect molecular orientation of the parallel aligned macromolecules leading to superior mechanical performance. The electrospun polymers are also flexible cylindrical formations but with macromolecules in isotropic, non-oriented state and distinguished by poor mechanical properties, frequently inferior than those of the same polymer in isotropic state. For this reason, it is suggested to call these materials "*fiber-like nanomaterials*" instead of "polymer nanofiber". The real target of the communication is to challenge the electrospinning community to modify the manufacturing process in such a way that the final nanomaterial is characterized by perfect molecular orientation resulting in excellent, typical for polymer fibers mechanical properties, which will offer wide real applications of these nanofibers.

Polymeric materials, contrasting all other materials, are comprised of large chain-like molecules. In addition, in majority of cases, these macromolecules are very flexible formations and thus they can adopt various conformations – from coiled state to extended parallel-aligned chains. The first state is realized in case of absence of any external forces applied to polymer body. If elongational forces act (drawing), the macromolecules are extended parallel aligned and thus transformed into highly oriented state as schematically shown in **Fig. 1**.

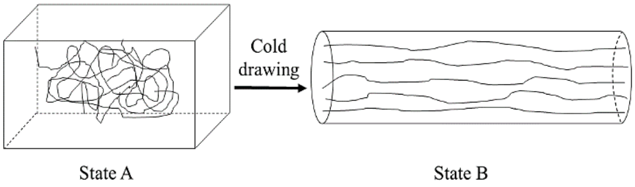

Fig. 1. Schematic the transition from isotropic non-oriented state of macromolecules (State A) into anisotropic highly oriented state (State B).

One of the best techniques for analysing the conformational state of macromolecules is the wide-angle X-ray scattering (WAXS). For the state A (**Fig. 1**), one should expect a scattering pattern in the form of circular reflections characterized by isointensity. For the state B (**Fig. 1**) – the reflections have to be in the form of single spots; their length in azimuthal direction is a quantitative measure for the degree of orientation. In **Fig. 2** are demonstrated such scattering patterns for a polypropylene (PP)/poly(ethylene terephthalate) (PET) blend (70/30 by wt.). **Fig. 2a** reflects the situation just after the melt blending and extrusion, and **Fig. 2b** - after the subsequent cold drawing.

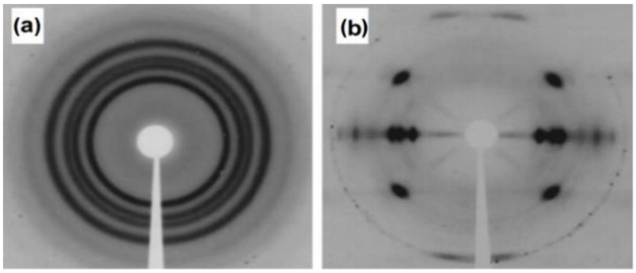

Fig. 2. WAXS patterns of PP/PET (70/30 by wt.) blend bristle: (a) after extrusion (no drawing) and (b) after extrusion and cold drawing.

It is important to remind that state A (Fig. 1) is characterized by an isotropy of all properties while state B (Fig. 1) shows strong anisotropy of the properties. In addition, the mechanical properties, for example tensile properties, in the direction of orientation are much higher than those of the isotropic state.

The conformational transition from state A to state B (Fig.1) is performed usually by means of drawing at temperatures above glass transition temperature (T_g) of the polymer but far below its melting temperature (T_m) ("cold drawing"). For majority of polymers (excluding the elastomers), this transition takes place via the necking phenomenon [**1**]. For this reason, the commercial manufacturing of synthetic polymer fibers comprises two basic steps: (i) extrusion trough spinnerets (melt-spinning), and (ii) cold drawing via necking. The final textile fibers are characterized by very high molecular orientation leading to superior mechanical properties. For example, PET single fibers prepared via the common melt-spinning have a modulus of elasticity (E) of 15000 MPa and a tensile strength (σ) of 1100 MPa [**2**]. Quite similar is the situation with single fibers of Nylon 6 (PA 6) and Nylon 6,6 (PA 6,6) manufactured in the same way for which the $E = 6000$ MPa and $\sigma = 1000$ MPa [**2**]. At the same time, the mechanical performance of these three polymers in a bulk isotropic state are as follows: for PET - $E = 2000 – 3000$ MPa, $\sigma = 50 – 150$ MPa and for PA 6 and PA 6,6 - $E = 2000 – 2500$ MPa, $\sigma = 50 – 80$ MPa [**3**].

Based on the above considerations, we can define the *polymer fibers* as flexible anisotropic formations with cylindrical symmetry and molecular structure distinguished by high molecular orientation of extended parallel aligned molecules leading to superior mechanical performance. The last one is because in the formation of mechanical strength are involved also the covalent chemical bonds, while in the isotropic materials (Fig. 1, State A) the strength is due mostly to van der Waals forces.

What about the electrospun materials prepared from polymer solutions and melts? They are also flexible cylindrical formations belonging to the category of nanomaterials since they satisfy the definition suggested by European Commission of 2011: "… *50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 – 100 nm …*" [**4**]. At the same time, they are distinguished by rather poor molecular orientation (if any!). Using various techniques, the local molecular orientation of the polymer chains within the fibers has been measured and found that the degree of orientation of the polymer chains with respect to the fiber axis increases with decreasing fiber diameters [**5-9**]. Although it has been shown by various researchers that electrospinning can induce some level of chain orientation in fibers based on flexible chain polymers, these levels are often rather low [**5**]. Of particular importance for the issue discussed are the results of small-angle neutron scattering (SANS) studies on chain extension in electrospun polystyrene fibres [**10**]. These results are summarised in the excellent review of Ton Peijs *et al.* [**5**] on high strength and high modulus electrospun nanofibers in the following way: "…*The SANS was used to quantify the size and shape of the chain conformation in electrospun fibers of deuterated atactic polystyrene prepared from solutions. Although the orientation parameter* $<P_2>$ *was found to increase with increasing collecting speed, the maximum value of about 0.15 was well below the orientation parameter expected for high performance polymer fibers with values typically approaching 1. When the tangential velocity of the rotating collector was greater than the flight velocity of the fibers some degree of orientation of the polymer coils was induced. However, even at the highest collector speeds the ratio of the radii of gyration increased only by 20% from for bulk (17 nm) to fibers (20 nm), showing limited coil deformation. As the diameters of these fibers were much greater than the polystyrene radius of gyration these effects can be solely contributed to flow-induced orientation, excluding size or confinement effects as a result of nanosized fiber diameters*".

The findings by using SANS [**10**] are of a paramount importance. They demonstrate that the prepared via electrospinning technique extremely fine cylindrical formations with diameters in the nano-range represent an isotropic material. Polymer fibers, as discussed above, comprise highly extended macromolecules aligned parallel to each other and thus demonstrate superior mechanical properties. The lack of molecular orientation in the electrospun materials is obviously the main reason for their inferior mechanical performance. As stated in a review on polymer nanofibers by electrospinning and their applications in nanocomposites [**11**], the mechanical properties of most electrospun polyamide and polyester fibers are not comparable with conventional microfibers manufactured by melt-spinning, which again can be ascribed to the low degree of chain orientation in these as-spun nanofibers and the absence of a post-drawing step in the electrospinning process. In fact, in many cases the properties of electrospun fibers are even inferior to that of the bulk polymer. For example, the E modulus of electrospun single nanofiber of PA 6 is reported to be 1320 ± 152 MPa and the tensile strength $\sigma = 78.1 \pm 6.0$ MPa [**12**]. Quite similar are the results for electrospun single nanofibers of the same polymer ($E = 902$ MPa, $\sigma = 304$ MPa) of another report [**13**]. Almost the same values ($E = 950 \pm 390$ MPa, $\sigma = 150 \pm 49$ MPa) have been found for electrospun PA 6,6 single nanofibers [**14**].

Obviously, in addition to the general problem of the proper dispersion of nanomaterials into matrix [**15**], the electrospun polymer nanofibers cannot be used as reinforcement for manufacturing of polymer nanocomposites because their mechanical properties are close or even worse than those of the polymer matrix. It turned out that *"nano-sized"* does not mean necessarily "*superior mechanical performance*". The sizes only are not enough, something more is needed!

In conclusion, the use of the term "*polymer fibers*" to electrospun polymers is misleading because this term assumes superior mechanical properties due to the perfect orientation of the parallel aligned macromolecules. Such an orientation in the case of electrospun polymers is missing and therefore their mechanical performance is poor – close to or below than that of the same materials in an isotropic state. For this reason, with respect of their molecular structure and mechanical behavior, the famous electrospun nanofibers represent sooner "nano-sized macaroni"

Possibly, it would be more correct if the electrospun polymeric materials will be called "*fiber-like nanomaterials*" instead of electrospun nano*fibers*.

Genuine polymer nanofibers can be manufactured by using the concept of "*converting instead of adding*" [**16,17**] developed for overcoming the practically non-soluble problem of proper nanomaterial dispersion during preparation of polymer nanocomposites via blending the reinforcing and matrix components [**15,18**]. For this purpose, two thermodynamically non-miscible polymers (usually in a ratio 70/30 by wt.) are melt blended, extruded and cold drawn (via necking) when the dispersed minor component is converted into fine fibrils (diameters between 50 and 250 nm) [**19**]. Neat polymer nanofibers can be easily prepared via extraction of the dominating second blend component.

Because these nanofibers are prepared via necking process during the cold drawing, they are characterized by perfect molecular orientation, as can be concluded from the WAXS pattern shown in **Fig. 2b** for the PP/PET blend, and thus they are characterized by superior mechanical performance. For example, single polymer composites (SPCs) prepared from parallel aligned and compression molded neat PET nanofibers (dia. between 50 and 150 nm) demonstrate an *E* modulus of 10570 MPa (what is ten times higher than the data cited above for electrospun polyamides!) and a tensile strength of 89.00 ± 11.58 MPa [**20**].

Obviously, in order to be able to understand each other properly in our contacts and discussions on topics of joint interest, we are supposed to use terms and definitions in their precise content. A good example for bad practice in this respect is the misuse of the term "phase" instead of "component" as it is frequently observed in the composite's community, although both terms have precise definitions in thermodynamics [**21**]. Such a task requires the efforts of all researchers and mostly the support of Editors of the scientific journals, as for example, the journal *Materials Today* does [**22**].

Finally, it must be stressed that the above considerations do not concern the meaning of the word "fiber" used in the everyday life (according to Oxford Dictionary there are 5 different meanings). The current comments concern the scientific community only, and more specific, the polymer materials researchers involved in the manufacturing, study and application of synthetic textile fibers as well as those dealing with electrospinning of polymers or interested in polymer nano-size materials. All these specialists are involved in the improvement of mechanical properties of the discussed materials.

In author's opinion, it is a high time that the electrospinning community offers, in addition to the fantastic photos (and practically not that much else!), a valuable nanomaterial, characterized by superior mechanical properties and suitable for many new important applications where the mechanical performance counts. This challenge can be realized by introducing to the traditionally used setup for electrospinning [**23-25**] a drawing step (via necking, not drawing of the concentrated solution or melt) ensuring a perfect molecular orientation. Only in such a case the electrospun nanomaterial could be considered as *polymer nanofibers* since their mechanical properties will be superior as those of the textile polymer fibers.

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Keywords

Polymer fibers, electrospinning, nanofibers, orientation, mechanical properties, fiber-like nanomaterials.

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