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Functional materials by electrospinning of polymers

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ABSTRACT

About a decade ago electrospinning was primarily concerned with the preparation of nanofibers from synthetic polymers and to a lower degree from natural polymers targeting predominantly technical applications areas such as textiles and filters as well as medical areas such as tissue engineering and drug delivery. Since then strong progress has been made not only in the understanding and theoretical modeling of the complex processes governing electrospinning and in the strict control of fiber formation by material and operating parameters but also in the design of a broad range of technical spinning devices. These achievements have in turn allowed for an extension of electrospinning towards fiber formation based not only on polymers – of synthetic, biological nature – but also on metals, metal oxides, ceramics, organic/organic, organic/inorganic as well as inorganic/inorganic composite systems. Here not only preparation schemes were investigated but properties and functions of the nanofibers were analyzed and potential applications were evaluated. As far as technical applications are concerned nanofibers composed of such materials can today be designed in a highly controlled way to display specific structural features. They include phase morphology and surface topology as well as unique functions including in particular magnetic, optical, electronic, sensoric, catalytic functions specific for one-dimensional architectures. Significant developments have also been achieved towards the exploitation of such functional nanofibers in applications involving among others fuel cells, lithium ion batteries, solar cell, electronic sensors as well as photocatalysts. One major target is currently the incorporation of such functional nanofibers in micrometer-sized electronic devices or even the construction of such devices purely from nanofibers.

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1. Introduction

Within the last decade electrospinning of polymers has become an internationally highly recognized method for the preparation of polymer nanofibers with diameters down to a few nanometers and of a broad range of complex architectures of nanofibers and nonwovens [1–7]. This is obvious from the ever growing number of papers published amounting currently to 2000 publications per year. These papers reflect significant progress which has been made in a variety of topics within the last years. Such topics include (a) the understanding and modeling of the complex processes governing electrospinning, (b) the control of fiber formation by material and operating parameters, (c) improvements and multiple extensions made to technical spinning devices and (d) the extension of electrospinning towards fiber formation based not only on polymers – of synthetic, natural, biological nature – but also on metals, metal oxides, ceramics, organic/organic, organic/inorganic as well as inorganic/inorganic composite systems. Here not only preparation schemes were investigated but properties and functions of the nanofibers were also evaluated and potential applications discussed.

Such applications include medical areas such as tissue engineering and drug delivery not discussed in this paper in view of existing reviews [8–10] as well as technical areas relying on nanofibers with specific photonic, electronic, photocatalytic and magnetic properties. Fuel cells, lithium ion batteries, solar cells, electronic sensors, energy storage systems are assumed to benefit strongly from nanofiber-based architectures. It is frequently pointed out in corresponding papers that key features which make nanofibers and nonwovens of interest for such types of applications are the 1D-confinements characteristic of nanofibers, the high orientations of structural elements induced along the fibers via electrospinning, strongly restricted material and electronic diffusion distances perpendicular to the fiber axis, high surface area as well as the high porosities of up to 90% observed for electrospun nonwovens. Substantial progress has, of course, also been made in a range of other areas including textile applications, filter applications, fiber reinforcement and many more [11–14]. Yet in view of the more than 10,000 papers published within the last decade and the correspondingly large number of issues treated in them a selection of specific topics to be addressed in this review had to be made.

2. The electrospinning system

2.1. Understanding and modeling the complex processes governing electrospinning

Of general importance is the recognition that fiber formation processes in electrospinning differ fundamentally from the ones in conventional technical approaches which rely predominantly on mechanical forces and geometric boundary conditions. Such conventional techniques include extrusion with in general follow-up elongations, melt blowing or techniques based on converging flow. In contrast, fiber formation in electrospinning is governed by self-assembly processes as induced by electric charges. All the key features characteristic of the spinning process including not only the evolution of the final diameter of the nanofibers in electrospinning but also undulations of the fiber diameter, the formation of beaded structures with droplets located along the fibers in a regular fashion can be attributed to the presence of repulsive Coulomb interactions between charged elements of the fluid jet. Self assembly happens according to the general Earnshaw theorem of electrostatics. It states that it is impossible to prepare stable fluid structures such as, for instance, stable fluid jets in which all elements interact only by Coulomb forces [15,16]. Charges within the fluid jet subject the charged polymer elements to motions along complex pathways so that the Coulomb interaction energy becomes minimized. Self-assembly processes in electrospinning take place not only in simple fibers but also in fibers of complex shapes such as flat fibers, in fibers with vertical protrusions, splayed fibers. Detailed theoretical [16–25] as well as experimental investigations [26–55] on the nature of the processes governing fiber formation have advanced electrospinning significantly in the last decade. Identified were as key processes (1) droplet deformation at the feeding units/tip of die, onset of jetting, (2) development of a rectilinear jet, (3) onset of bending deformations with looping, spiralling trajectories, (4) deposition on counter electrodes/substrates. Yet additional processes also exist which affect fiber geometries considerably including the Rayleigh type instability, the