Electrospun Nanofibers for artificial scaffolds and reinforcement of rubbers

Ulrike Wangenheim, Ulrich Giese, Robert H. Schuster

Deutsches Institut für Kautschuktechnologie e.V. -DIK- Eupener Straße 33, D-30519 Hannover

Robert.Schuster@DIKautschuk.de

Introduction

Interest in producing small-diameter fibers came about the interest in engineered nanomaterials. The process of electrospinning introduces a new level of versatibility and a key platform that yields products for electronics, drug delivery, chemical sensors, microfiltration and tissue scaffolding.[1] The value of the technology is given by smallest fiber diameter that can be fabricated and manipulated under practical conditions.[2] Although key material related parameters (viscosity, dielectric constant, conductivity, surface tension and volatility) and process-related parameters (electric field strength, geometry of the electrodes, gap distance, feed rate) were recognized in early work, the present understanding is due to investigations on fluid dynamics [3], electrostatics[4] and viscoelastic solution properties.[5] Taking into account the high surface area of nanofibers good composite characteristics could be expected in polymer matrices. The finding that biodegradable or even bio-identical polymers can be electrospun into nanofibers and that cell types have been shown to ad-here and proliferate encourages research in tissue en-gineering. Engineered tissues consist of cells and scaffold, which substitute the native extracellular ma-trix (ECM). Scaffolds can be prepared via electrospin-ning by creating a nano scaled network structure. [5] The advantage of the process is its flexibility for both the selection of the polymer and the variety of the non-woven topology.

The objective of this work is to explore (i) the interplay of molecular parameters and fiber morphology, (ii) functionalize electrospun fibers, (iii) the reinforcing potential of the fibers in rubbers and (iv) investigate the use of polysialic acid for bio-identical scaffolds for peripheral nerve regeneration.

Experimental

PS, PAN, PMMA, CEAc were used for preparing reinforcing electrospun fibers. For artificial scaffolds polysialic acid PSA (Mw: 30,000 g/mol) was used as delivered by Nacalai or converted to poly-2,8-N-pentenoylneuramic acid (PEN) in order to become photocrosslinkable by UV-light irradiation. PAN nanofibers were functionalized and carbonize. The expe-rimental set-up consists in a high voltage power supply (Matsusada, AU-502P2-L) connected to a spinneret and a collector (shallow container or rotating drum) for discharge of the deposited fibers. The feed rate is adjusted by a syringe pump (NE-500 OEM). The electrical field strength was varied in the range from 5kV to 40 kV. Elastomer nanocomposites were prepared by incorporating fibers into rubber on an internal mixer and subsequent curing. Intrinsic viscosity, conductivity and surface tension of the solutions were measured conventionally. Fiber morphology and the diameter were investigated by using a SEM (EVO MAIO; Fa. Zeiss, Germany) at 5 kV and a sample stream of 10 pA. In vitro cell tests were performed with neuronal cell models on PSA or PNA mats deposited on disinfected glass slides. After 6 day incubation in cell suspension the cell viability was measured by a MMT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazoliniumbromide) assay.

Results and discussion

Fiber morphology

The influence of the solution concentration on fiber morphology is shown in Fig. 1. In the dilute and semi-dilute solutions the most common morphological features are beads (surface tension overcomes coulomb repulsion forces). At higher concentrations a transition to beaded nanofibers is observed.

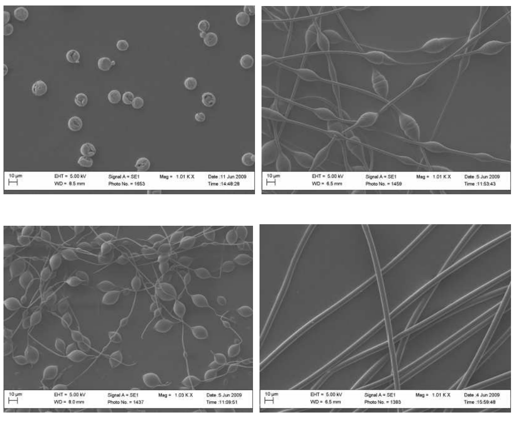

Fig. 1 Influence of polymer concentration on the morphology of electrospun fibers

By increasing the concentration the diameter of fibrils between the beads becomes steadily larger.

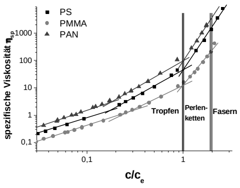

Fig. 2 Fiber morphology as a function of concentration and viscosity.

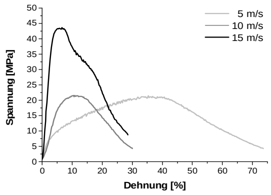

Fig. 3 Stress-strain curves for differently oriented lectrospun mats.

Investigations undertaken with PS, PMMA and PAN revealed that smooth fibers are formed only above the concentration $2C_e$ where 2-3 entanglements per chain occur. However, by increasing the electrical field strength a transition from "beads on string" to smooth fibers is reached. An increase of solvent viscosity as well as surface tension (opposing coulomb repulsion) results in a larger "beads on string" regime.

Physical properties of non-woven mats

Unlike with crosslinked polymer films of plates subjecting a non-woven mat to tensile deformation results merely in rearrangements of the nanofibers. Tensile properties demonstrate a strong correlation to fiber orientation gained during the spinning process (Fig.3)

Carbon-Nanofibers

After superficial oxidation PAN nanofibers were submitted to anaerobic annealing at 900°C. As a result (i) the fiber diameter shrinks to 200-250 nm, (ii) a semi-crystalline structure is formed,(iii) small amounts of functional oxygen groups remain on the surface. Different to CNTs the novel C-nanofibers can be easiliy dispersed in polymer matrices (Fig. 4).

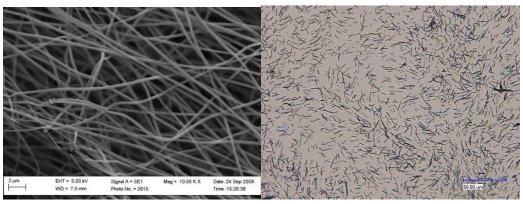

Fig. 4 a) C-Nanofibers and b) Dispersion in rubber

Reinforcement by fibers

By incorporating less than 5 vol.% of electrospun fibers in the rubber matrix the Young's modulus is signifycantly increased, the stress values at 100 to 300% elongation are at least doubled and the tensile strength is increased also (Fig. 5). Partially oriented and anisotropic effects were recorded for the modulus and tensile strength.

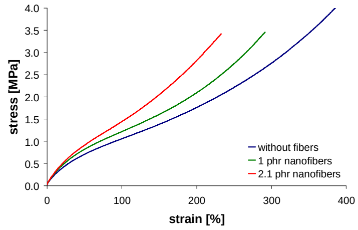

Fig. 5 Reinforcement by electrospun fibers

Cell tests

Cultivation of cells on glass sildes reveal a random cell growth and cell clusters without the PSA/PEO fibers. On the slides coated with fibers the cell growth in the direction of the fibers can be noticed. (Fig. 6a).

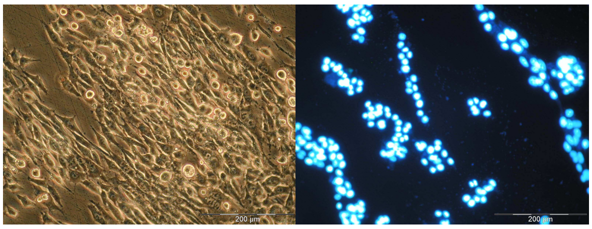

Fig. 6 Orientation of immortalized Schwann cells on electrospun PSA/PEO

Considering the pictures were the cell nuclei were stained with DAPI it can be seen how the cells grow along the detached fibers, even if no statement about the cell density on the substrate can be made (Fig. 6b).

Acknowledgements
The authors thank to Deutsche Kautschuk-Gesellschaft DKG and the Deutsche Forschungsgesellschaft DFG for financial support of the project.

References
[1] Ch. Burger, B. S. Hsiao, Annu. Rev. Mater. Res. 26,222 (2006)
[2] D. H. Reneker and I. Chun, Nanotechnology 7, 216 (1996)
[3] M. M. Hohmann, Phys. Fluids 13,2201 (2001)
[4]Y. M. Shin et al, Polymer 42,9955 (2001)
[5]J. Doshi and D. H. Reneker, J. Electrostatics 35,151 (1995)
[6] W. J. Li et al, J. Biomed. Mater. Res. 60,613 (2002)