HIGH ELECTRIC FIELD USED IN MATERIAL SCIENCE

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Abstract - The objective of this paper is to bring together divers examples showing the importance of novel material preparation and interactions with high electric field. In the present work we report a versatile and precise method to produce nanometer to micrometer scale fibrous scaffolds with high electric field and the development of smart polymer composites that show spinning in static uniform field. A microscopic motor of which operation is based on the principle of Quincke rotation

Index - Elecrorotation, Electrospinning , fibers, smart polymer, polysuccinimid, Quincke rotation

I. INTRODUCTION

The point of view taken in this paper is based on chemical approaches including preparation and phenomena that can be utilized for further technological developments. Beside many possible application of electric field in material science we focus on two basically different phenomena: reactive electrospinning and micro-motor powered by electric field. The common in these topics discussed here is the application of high electric field. All materials experience forces and torques when subjected to high electric field, electrophoretic- and dielectrophoretic forces and torques acting on the materials. The terms of electrophoresis and dielectrophoresis imply the interplay between electrical phenomena and motion. Dielectrophoresis is the migration of neutral particles in non-uniform electric field due to polarisation. Although polarisation effects are often considered to be weak, they are far more effective than Coulomb forces, since polarisation forces can act directly on an uncharged material including solids and fluids.

II. ELECTRO SPINNING

Electro spinning is a versatile and precise method to produce nanometer to micrometer scale fibrous scaffolds [1]. The process utilizes electrostatic forces to fabricate artificial fibers. The most basic setup of electrospinning machine consists of a syringe and a syringe pump, a high DC voltage supply and a grounded metal collector plate (Fig. 1. a). Electrospinning has a wide spectrum of research interests and applications ranging from industrial filters to artificial tissues for bio-medicine. Protein-based polymers that have desirable chemical, mechanical and biological properties have recently emerged as promising new class of biomaterials in multiple biomedical fields such as tissue engineering and regenerative medicine. In this work we prepared chemically crosslinked poly(succinimide) and poly(aspartic acid) electrospun scaffolds that may provide unique platform for design of biomimetic fibrous scaffold for cell growth and tissue engineering.

In the process of electrospinning the high DC voltage is attached to the metal needle through which the viscous polymer solution is pumped. If the electrical field strength is high enough, the surface charges and the electrical forces can overcome the surfacetension of the fluid and a thin jet is ejected in the direction of the collector. This jet than starts a whirling movement while it is constantly elongated and the solvent evaporates till it reaches the collector plate. There are many parameters affecting this process related to solution (polymer concentration, viscosity, etc.), processing (applied voltage, feeding rate, etc.) and ambient (temperature, humidity, etc.) parameters. Poly(succinimide) based fibers can be electrospun from DMF solution effectively just as it was shown in our previous work [2]. However the quality of the resulting product is strongly dependent on polymer concentration. In the case where the poly(succinimide) concentration was 15 w/w% only polymer particles were obtained (Fig. 1. b).

The reason for this, is that due to the low polymer concentration the polymer entanglement was low, and thus the polymer jet was split into small particles by the surface tension. At higher concentration (20 w/w%) fibers were obtained, however small beads were incorporated into these fibers (Fig. 1. c). In this case the jet dried out just when the jet started splitting up to small particles leading to deformed fibers. However 25 w/w% polymer concentration proved to be ideal for smooth fiber formation. There were no particle nor any beads along the fibers (Fig. 1. d). The average diameter of the fibers were 800 ± 40 nm. Another interesting parameter which is easily varied is the distance between the collector and the needle. A series of experiments were carried out with a 25 w/w% poly(succinimide)/dymethilformamide solution where all the electrospinning parameters were kept constant except the collector distance from the needle. We found that with rising distance the deposition area of fibers rises as well (Fig. 1. e). At 5 cm distance the diameter of the area where fibers were deposited was only 2 centimeters, whereas at 20 cm it was approximately 15 cm.

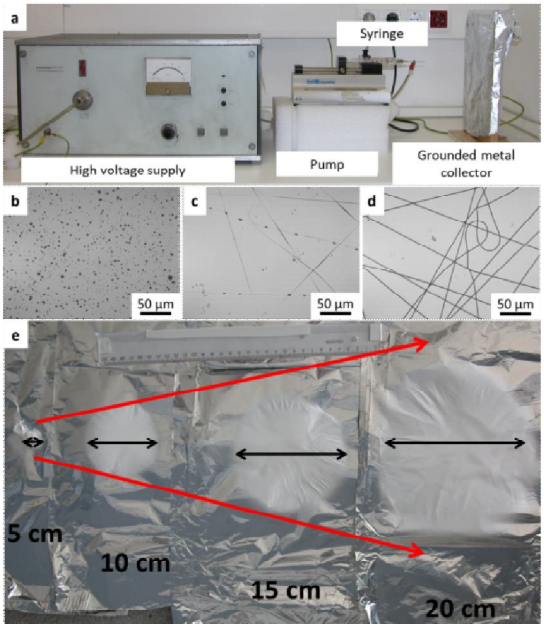

Fig. 1. Basic setup of electrospinning (a); poly(succinimide) electrospun from 15 w/w% (b) 20 w/w% (c) and 25 w/w% (c) dimethylformamide solution; polysuccinimide electrospun at different needle-to-target distances (e)

With high collector distance the jet needs more time to reach the collector and thus it has longer time for elongation and solvent evaporation, leading to thinner fibers. While lower distance leads to higher electric field strength and thus faster jet movement and lower time for the jet to reach the collector which can result in fused fibers due to partial evaporation of the solvents [3]. Average diameter of the fibers prepared at different collector distances are collected in Table I. It seems that the larger the collector distance, the thinner are the PSI fibers which is in line with the previous statements, however the experimental data available for the PSI/DMF system is not yet enough for proper justification.

Distance	Volume rate 0.4 ml/h Average fiber diameter
10 cm	1.47 ± 0.03 µm
15 cm	1.48 ± 0.03 µm
20 cm	1.39 ± 0.03 µm

Table I. Average fiber diameters of PSI membranes prepared at different collector distances

Poly(succinimide) turns into poly(aspartic acid) in mild alkaline environment and dissolves. This is a huge drawback of this polymer if we consider any bio-medical application. One of the solutions for this problem is the creation of cross-links between the polymer chains inside the fibers, and thus creating hydrogel fibers. Such fibrous membranes would not dissolve upon immersion into their solution (in the case of poly(succinimide) as hydrolysis takes place) just uptake the surrounding fluid and swell. These soft and rubberlike materials are called gels or if the fluid swelling the matrix is water they are called hydrogels.

Preparation of such cross-linked fibers has no straightforward method. If appropriate chemistry is available, it is possible to cross-link the polymer chains during the electrospinning process. This technique is called reactive electrospinning, since there is a reaction ongoing during fiber formation. In our case poly(succinimide) was modified with cysteamine which is a small molecule with a thiol group and an amine group at its ends. Poly(succinimide) can be easily modified with primer amine group containing molecules at room temperature [4]. However with cysteamine the reaction mixture was kept under Ar atmosphere to prevent the auto cross-linking of thiol groups in oxidative reaction (Fig. 2.). The solution was prepared in a way that the final polymer concentration was 15 w/w% and the ratio of mols of monomer units to mols of cysteamine was 10. This mixture was stirred for 45 minutes then filled into the needle for electrospinning (PSICYSE). As the polymer solution left the needle, electrospinning started and also cross-linking due to the presence of aerial oxygen. In the process the resulting fibers consist of poly(succinimide) cross-linked by disulfide bonds (PSICYS).

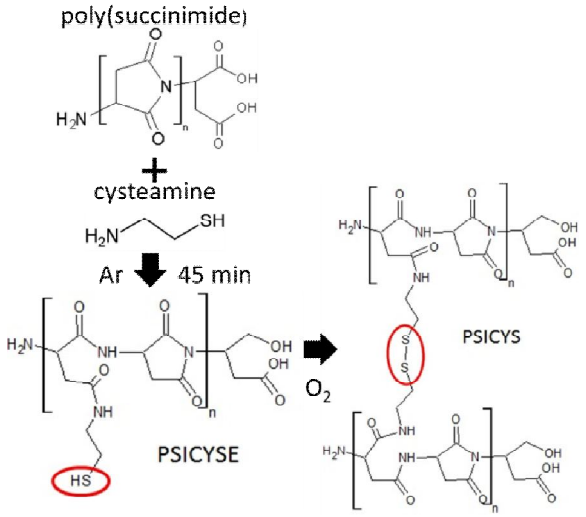

Fig. 2. Modification of poly(succinimide) with cysteamine and the auto cross-linking reaction of the thiol side-chains on the modified polymer during electrospinning

The resulting membrane looks like any other membrane in dry state (Fig. 3. a) and is composed of smooth fibers with an average diameter of 900 ± 35 nm according to scanning electron microscopy (Fig. 3. b). However upon hydrolysis these membranes will not dissolve anymore, they only uptake the surrounding mild alkaline solution and swell. The resulting hydrogel membrane can be even transparent depending on the fluid used for swelling (Fig. 3. c). Scanning electron microscope showed that the fibrous structure of the membrane was only partly retained due to the fusion and deformation of fibers. Still these membranes have a very loose structure which can be considered as fibrous (Fig. 3. d). The drawback of hydrogels, especially for those composed of polymers of low molecular weight, is that they can be very

brittle and prone to break [5]. However the gel fiber membranes have the advantage of being very flexible and thus they could be very useful as flexible implants for wound dressing or soft tissue replacement in medical application.

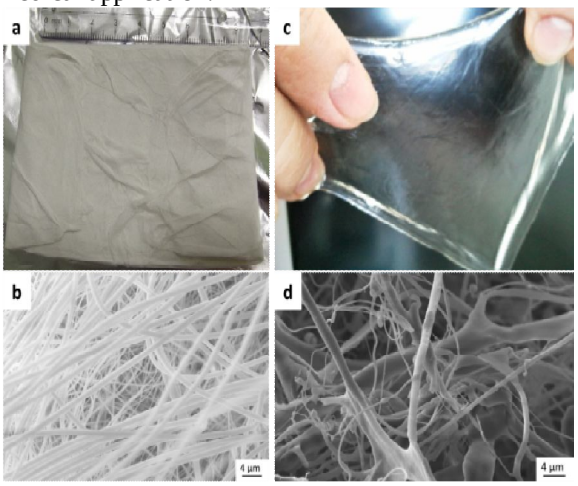

Fig. 3. PSICYS fibrous membrane in dry state (a); scanning electron microscope picture taken from PSICYS membrane (b); PSICYS membrane in wet state after hydrolysis (c) and scanning electron microscope picture of the same sample after freeze-drying (d)

A. Concluding remarks

Electrospinning is a fascinating tool for the preparation of fibers with diameters as low as tens of nanometers. It has been research extensively in the past few decades, however there is still room for improvement. In this paper we report new method for the preparation of gel fibers via reactive electrospinning, in which case cross-linked polymeric fibrous membranes could be prepared in one step. The reported method based on thiol chemistry could be applied for any other polymeric system if appropriate chemistry is available.

III. CONSTRUCTION OF MICROMOTOR BASED ON ELECTROROTATION

The first impulse to build micro- or nanomotor was given by R.P. Feynman in 1959 [6]. The early attempts to miniaturize the electromotors were achieved by making a scale reduction of existing motor parts. On the basis of this technique the first micromotor was developed by L.S Fan and Y.C. Tang in 1988 [7]. Their electrostatic driven motor had a diameter of 120 μm and the rotation speed of 500 rpm with a torque of some pNm. Due to their complicated construction, the coils of traditional electromagnetic motor are rather difficult to miniaturize. Despite several works have been devoted to develop and manufacture micromotors, there are only few studies available in literature about their design and performance. In order to construct a novel type of micro-motors, we have exploited the electrorotation phenomenon (Quincke rotation) and intend to use polymers as rotors. As early as in 1896 G. Quincke observed that some solid particles (glass, aragonite, sulphur, topaz, tourmaline…) can spontaneously rotate in certain media (ether, carbon disulfide, benzyl, and different oils), if a large uniform electric field is applied [8,9]. The phenomenon exhibits a threshold value of the electric field and occurs only if certain conditions concerning to the conductivity and permittivity of the particles and of the liquid are satisfied [9]. Due to these special criteria of material characteristics, it is not easy to observe the phenomenon. Only a limited number of experimental studies are available. In order to utilize the spontaneous rotation for micro-motor applications several requirements have to be fulfilled. The most important are: the rotating material has to have a suitable shape (wheel, shaft...) by means of which the torque may be transmitted. Suitable control which the rotation can either starts or stops. It is also a requirement that the speed of circular motion may be controlled in wide range. Taking into account the above requirements we have successfully fabricated micron sized disks, hollow cylinders and gears with asymmetric teeth from electroactive polymer (EAP), as well as miniaturized cubic motor from EAP polymer composite. In our previous works, we have reported the orthorhombic FeO(OH) particles immersed in oil has shown intensive rotation in uniform DC electric field

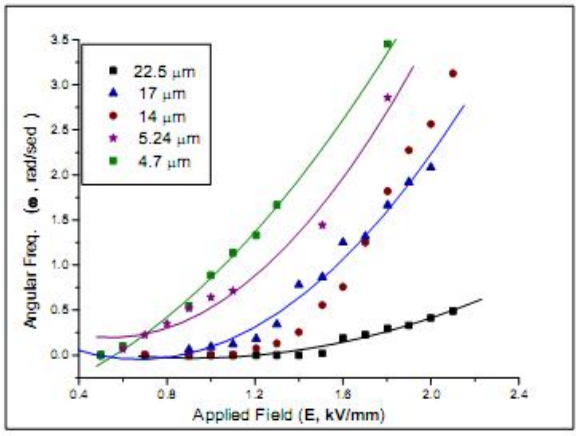

Fig.4.Dependence of angular frequency of FeO(OH) particles on the DC electric field intensity [10]. The solid lines represent guide to eyes.

It can be seen on Fig. 4. that solid particles perform intensive rotation and the rotation speed is higher for smaller particles than for larger particles, despite the theoretical prediction[9], the angular velocity strongly depends on the particle size. In our first EAP polymer rotor we have FeO(OH) particles loaded in different polymers. We obtained best rotation characteristics for gelatin as host polymer of solid particles. When comparing the angular frequency of solid FeO(OH) particles with the filler loaded circular polymer disks it was found that at the same electric field intensities the rotation of polymer disk is significantly faster than that of single particle. Due to presence of solid particles in the composite systems locally different mechanical and stiffness properties occurred and therefore it made difficult fabrication of the rotors in adequate size and

shape. To overcome this problem we have succeeded in developing a novel polymer showing electrorotation phenomena without dispersed solid particles [11].
We have found that the SU8 2075 photoresists with SU8 developer are good candidate to prepare rotors for micro-electromotor. Disk, hollow cylinders and gear with asymmetric teeth of different size as prototypes were successfully manufactured by mask lithography technique [11,12] (Fig.6).

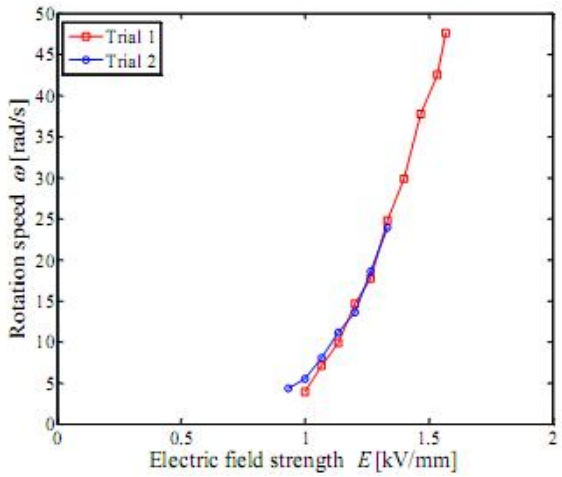

Fig. 5. Dependence of rotation frequency of filler loaded polymer disks as a function of electric field intensity E [11].

The electric field was provided between two electrodes. The gap distance between the electrodes was 3 mm. The space between the electrodes was filled up with special oil mixture containing substantial amount of triglicerid of oleic-, palmitic-, and linoleic acids, with conductivity of $\sigma_1 = 9.56 \cdot 10^{-10}$ S/m and relative permittivity of $\varepsilon_1 = 3.32$, respectively.

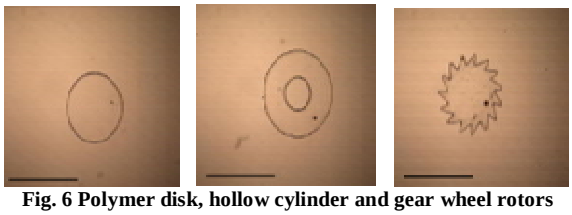

Fig. 6 Polymer disk, hollow cylinder and gear wheel rotors made of SU-8 polymer. The bar indicates 500 microns. The dot close to the edge of the micro tools was used to determine the speed of rotation.

Uniform DC electric field was supplied by a high voltage DC power supply (TREC, USA). We have increased the electric field intensity step by step up to 2.2 kV/mm. The rotation of floating micro-rotors in the oil was followed by optical microscope (OLYMPUS, Japan) equipped by a high speed camera (4500 fps, Photron, Japan. In order to visualize the rotation and to determine the angular frequency, a visible sign close to the edge of the disk was used. The angular frequency of the rotation was determined by recording the spinning motion of the disk. If the inertia of the rotor is accounted for, its dynamics is governed by the relaxation time of the polarization, as well as the characteristic mechanical time related to the relaxation of the angular velocity. The competition of these two characteristic times leads to a complex dynamics of the rotor. If the strength of static DC field is accounted for, three regimes have been observed.

1. Below a threshold value, Ec of the electric field, the disk does not show any motion.
2. At the threshold value and slightly above, the disk begin to rotate, but the angular displacement was found to be less than 2π. The angular displacement occurred either in clockwise or counter-clockwise direction, as a seesaw. The clockwise angular displacement is always followed by regular counter-clockwise rotation. In this regime the speed of rotation is not constant, but keeps on changing. Similar behaviour was observed under AC electric field when the frequency did not exceed 1.7 Hz.
3. At DC field intensities much higher than the threshold value continuous rotation was observed. The disk rotates around itself with an axis pointing in any direction perpendicular to the DC field.

In some cases we have observed not only spinning, but also slow migration of the disk. When repeating the experiment several times, the direction of rotation was found to be completely random. Above a threshold value Ec, of the electric field, the disks rotate at constant velocity either in clockwise or counter-clockwise direction.

We have determined the dependence of rate of spinning on the electric field intensity. Above a critical value of electric field intensity, the rotors begin to rotate at constant rate. This rate is sensitive to the field intensity. With increasing field intensities the angular velocity of both types of rotors linearly increases with the field intensity (Fig.3). Our work clearly indicates that decreasing the size of the rotor, the speed of rotation increases as shown in Fig. 4
For the cubic motor, which has significantly larger size and consequently less intensive rotation, it is worth to mention that the height of cylinder plays a decisive role. The shortest rotor height performs most intensive rotation. It suggests that a set of hollow disk fixed on axis could perform more intensive rotation (Fig.3(b)).
We have succeeded in controlling the rotational direction using two extra electrodes (Fig.5). Their role is to break the symmetry of spatial distribution of electric field, resulting in clockwise and counter clockwise direction of rotation. We have found that the cubic motor generates a maximum torque of 0.2 (?)Nm when the electric field of 2.35 kV/mm was applied. The SU-8 rotors were immersed in a special oil, containing substantial amount of triglyceride of oleic-, palmitic-, and linoleic acids. Above a critical value of electric field intensity, the rotors begin to rotate at constant rate. This rate is sensitive to the field

intensity. With increasing field intensities the angular velocity of both types of rotors linearly increases with the field intensity (Fig.7,8). Our work clearly indicates that decreasing the size of the rotor, the speed of rotation increases as shown in Fig. 8.

We have also prepared miniaturized cubic micro-motor of 3x3x7 mm inner size with a cylindrical EAP composite rotor has been fabricated (Fig.9). The EAP composite is made of gelatin loaded with micron sized FeO(OH) particles. For the cubic motor, which has significantly larger size and consequently less intensive rotation, it is worth to mention that the height of cylinder plays a decisive role. The shortest rotor height performs most intensive rotation. It suggests that a set of hollow disk fixed on axis could perform more intensive rotation. We have succeeded in controlling the rotational direction using two extra electrodes (Fig.10).

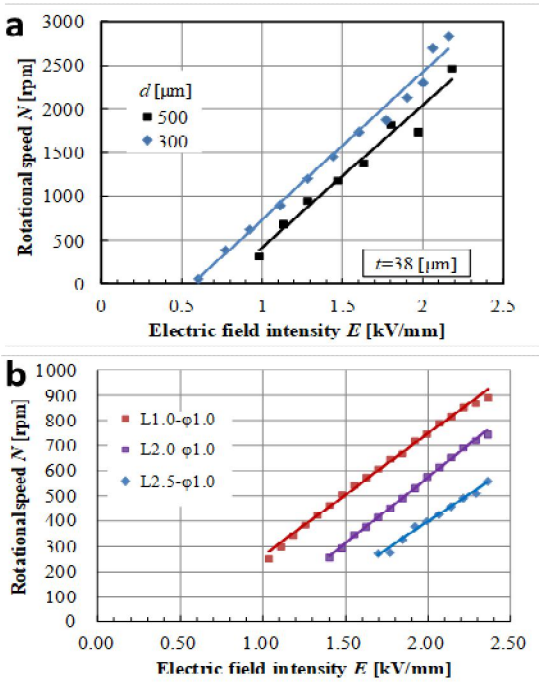

Fig. 7 Rotational speed N as a function of electric field intensity E: effect of diameter d of gear wheels (a), effect of rotor height L in cubic motor without load (b)

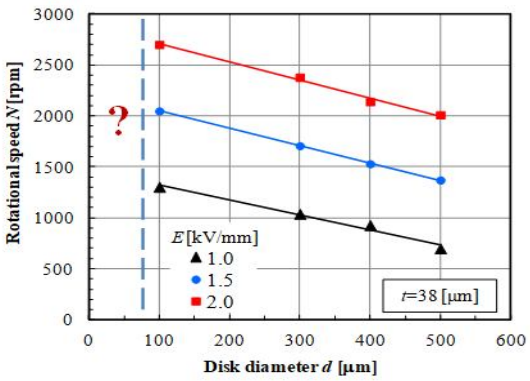

Fig.8. Dependence of speed of rotation on the diameter of SU8 disks. Thickness is 38 μm. The question mark indicates the size range that we could not observe with light microscope.

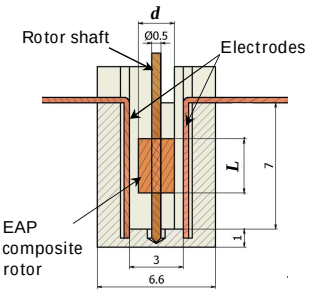

Fig. 9 Cubic micro-motor of 3mm square and 7mm in height with cylindrical EAP composite rotor.

Their role is to break the symmetry of spatial distribution of electric field, resulting in clockwise and counter clockwise direction of rotation. We have found that the cubic motor generates a maximum torque of 0.2 □Nm when the electric field of 2.35 kV/mm was applied.

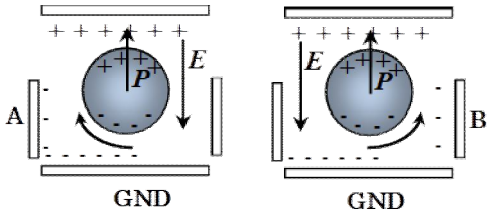

Fig.10 Alteration of the rotational direction by extra electrodes that modify the field distribution.

A. Concluding Remarks

Regarding the novel driving principle of the micro-motors presented here, it may open new perspectives for their use in several MEMS applications[3,4]. At this point, we are not able to provide a theoretical background to interpret the complexity of the electro-rotation phenomena. All these measurements provide fundamental information on micro-motor characteristics which is important for further micro-engineering development. A microscopic electric motor of which operation is based on the principle of electro-rotation is just one step away.

ACKNOWLEDGEMENTS

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