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Electrospun nanofibrous structures and their composites

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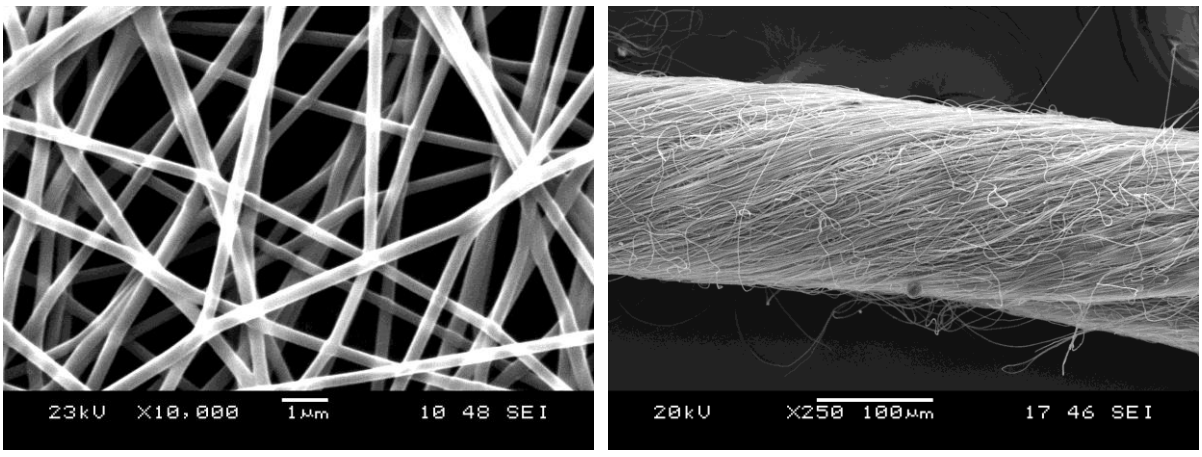
1. Introduction

Nowadays nanotechnology receives distinguished attention in technology. Engineers try to influence the construction at possibly more structural levels and today frequently the nano-structure of the materials is consciously designed by engineering methods, as exemplified by the appearance and extensive use of nanotube reinforced composites, nano-crystalline materials etc.

Electrostatic fiber spinning (*electrospinning*) basically belongs to the field of nanotechnology. First appearance of this technology is the patent of Cooley and Morton submitted in 1902.The method was later perfected by the inventions of Formhals in the 1930's but in the absence of modern characterization methods and due to the limited potential fields of application the electrospun nanofibers gained considerable attention only in the past two decades.

At present mostly polymer and ceramic fibers can be produced by electro-spinning in the diameter range of some nanometers to some micrometers, with a pre-designed diameter, which have also several application areas. At present the research work concentrates on medical and filtering applications which are already important in the practice. Morphologically the two dimensional fiber mat structure is the most widespread, but there are other forms, e.g. fiber bundles or yarns (see the Figure).



a) **b)**

Scanning electron micrographs of electrospun poly(acrylonitrile) nanofibers – a) web, b) yarn

A coherent nano-fibrous structure does not mean a danger of silicosis, it is not carcinogenic and no other harmful effects for health are known – in contrast to other nanoparticles (as at e.g. carbon nanotubes, etc.). Even if the individual fibers cannot be recognized by naked eye

the nanofibrous structure itself can be well observed visually and can be touched. The production technology of properly homogeneous products has not yet reached a level of maturity. Further processing of the nanofibrous intermediate product has not yet been solved either. This could be done by standard textile technologies (spinning, twisting into yarns, weaving etc.).

Electrospinning is a fairly stochastic technological process lacking precise description which hampers precision applications. There are no laws allowing the design of spinning plate or fiber collector belonging to this technology, there are no descriptive or design methodologies allowing the description of the mass, energy or entropy transport of the process.

Strength design and failure process description of nanofibrous structures are virtually absent from the literature. Known methods of testing and sizing are frequently time-consuming and require very expensive test equipment. Re-consideration of the models devised for traditional fibers, fiber bundles and fiber mats may solve several problems in this field.

The average surface of 1 g nanofiber is about 40 m^2, which allows excellent adhesion between the composite matrix and such reinforcing fibers, which may, among others, reduce delamination tendency. Nanofibers and nano-pores may also provide excellent hindrance against crack propagation. Due to their unique properties electrospun materials may play an important role in industrial composite applications.

2. Short analysis of the literature, goals of the thesis

A literature search has shown that several research works have been devoted to the application of nanofibers in composites, which are briefly reviewed in the literature section, but was also summarized in a book chapter of mine [1]. The general goals of nanofiber related research can be summarized as follows: the fiber diameter distribution should be as narrow as possible, the average diameter should be controllable, the surface of the fibers should be fault-free or at least the surface quality should be controllable and the individual continuous fibers should be collected. These are important requirements from the morphological viewpoint, but in my opinion for a real use of the nanofibers these goals should be re-defined.

In my opinion electrospinning will remain cost-effective and industrially useful technology if its basic features are taken into account. Defect-free fibers are even more required for composite applications but now we know enough of the process that it can be usually easily

achieved by properly selecting the process parameters. In my opinion it is not worth to strive for a very narrow fiber diameter distribution or for ideally oriented individually formed fibers, as in this case we may lose the highest advantage of the process, namely that fibers and the web are formed simultaneously. It should be accepted instead that the fibers are formed randomly and become ordered on the fiber collector, which is the consequence of several stochastic instabilities occurring during fiber formation. Similarly the distribution of fiber diameters should be viewed as a characteristic of the process, as it derives from the branching of liquid streams. Spreading of the fibers is proven to be a consequence of field strength trajectories, but these are not known, not even statistically and not even for the simplest case. Understanding the fiber spinning parameters has been aimed at in several research projects related to electrospinning but there is no general theory describing the relations between them. There have been several innovative ideas recently to improve the throughput, a part of which have been taken over by the industry. Based on the literature it can be recognized, however, that the construction of the fiber spinning head (spinneret) is not mature, therefore the solution concentrates, the dispersed particles tend to settle, the surface density of the product is frequently inhomogeneous. Fiber bundles, yarns, threads etc. could be utilized by the composite and textile industries, as these can be easily processed, even manually but we have no mature technology for their production, as the web formation and the process itself should be modified. Some publications deal with these problems but these ideas are not followed by others, they rather start again form the beginning along different lines. Besides limitations of the technology applications in the composite industry are limited also by the fact that we do not really know the mechanical behavior of nanofibrous materials, as the available test methods are under-developed and expensive: they need special micro-manipulators, force sensors or even atomic force microscope.

The main goal of the thesis is to give clear-cut answers to the majority of these problems after a careful investigation and to provide easily applicable knowledge and tools to the industrial experts. In order to achieve these goals the following technology development, experimental testing and modeling tasks were defined:

1. Design and fabrication of a self-developed electrospinning equipment based on preliminary experiments and own innovation ideas.

2. Selection of proper raw materials and development of optimum solution preparation methods including the dispersion of carbon nanotubes. Production of carbon nanotube filled, so-called composite nanofibers.

3. Development of hybrid composites reinforced also by traditional micro-fibers which are combined with nanofibers and to study the effect of such combinations on the behavior under static and dynamic loads.

4. Development of carbon nanofiber structures. Observation and evaluation of chemical and structural transformations during the pyrolysis of nanofibrous structures. Development of a proper model describing the pyrolytic process. Investigating the effect of carbon nanotube loading on the kinetics of the pyrolytic process of the nanofibers.

5. Determining the advantageous carbonization parameters based on the developed model. Determining the possibilities of industrial scale production and application.

6. Continuous production of oriented, linear nanofibrous structures and improvement of the selected method to achieve better strength properties and the quality of longitudinal homogeneity.

7. Development of testing and modeling methods that allow drawing conclusions on the micro-level behavior from the macroscopic mechanical tests. For example drawing conclusions on the strength of single fibers and on the degree of fiber utilization from the tensile test of nano-fibrous mats or bundles. Development of fiber-bundle cell model to describe the tensile test of products.

3. Overview of the materials and methods used

I used poly(acrylonitrile) (PAN) obtained directly from a carbon fiber manufacturer and a polyamide 6 (PA-6, Schulamid 6MV13F, Germany) for nanofiber production. In the case of PAN the solvent was 95% dimethyl formamide (DMF), while in the case of PA-6 it was 85% formic acid. Based on preliminary experiments the optimum concentration was 12 m% for PAN and 16 m% for PA-6, as these values resulted in minimum fiber diameters and fault-free fibers.

In order to produce composite nanofibers I have admixed multi-walled carbon nanotubes (MWCNT) into PAN solutions. The carbon nanotube (CNT) used was Bayer Baytubes BT C150HP (Germany).

I have prepared hybrid composites in which PAN nanofiber mats were placed between traditional carbon fiber reinforcing layers so that the carbon fiber textiles were covered by nanofibers. When preparing nanofiber-hybridized composites two kinds of reinforcements were selected and used. One was a unidirectional structure Panex35 (PX35FBUD300, Zoltek

Plc., Hungary), the other was a plain weave textile: Sigratex KDL 8003 (SGL Technologies GmbH, Germany). As a matrix material FM20 epoxy resin (P+M Polimerkémia, Hungary) was selected together with the corresponding T16 crosslinker, the mixing ratio was 100:20 m/m. For the embedding of nano-carbon fibers a low viscosity AH12 epoxy resin was selected with the corresponding T-111 crosslinker, the mixing ratio was 100:116 m/m.

During the research various kinds of electrospinning equipment were used – mostly designed and developed by myself – to prepare the samples. Among these there is a "single capillary" device, another device for producing nanofibrous yarns and a proprietary equipment (patent pending) allowing high throughput production of nanofibers. For the continuous production of PAN nanofibrous materials I have used a pilot-plant scale Nanospider equipment with open liquid surface, developed by the Department of Nowoven Textiles of the Technical University of Liberec.

For the metering of the solution a medical infusion pump of Aitecs SEP-10S Plus type (Lithuania) was used. The flow rate could be adjusted between 0.1 and 750 ml/h, with a precision of 0.1 ml/h (for a 20 ml syringe). A HVDC supply was used to produce the high voltage electric field. The voltage of the DC supply built by me varies between 24 and 29 kV (without load). Additionally DC supplies of MA2000 NT 35/P and NT 65/P type (Hungary) with adjustable voltage in the 10-35 kV, and 5-65 kV ranges were used respectively. The current can be read in 100 μA units.

Scanning electron microscopic (SEM) studies were carried out in all cases by a JEOL 6380 LA type (Japan) equipment. Optical microscopic studies were made by an Olympus BX 51M type (Japan) microscope. Based on the SEM micrographs the fiber diameters were determined by UTHSCSA Image Tool 3.0, and ImageJ 1.46 image analysis software.

The strength tests, such as tensile, three point bending and tape tearing tests, etc. were performed by a Zwick Z005 universal tester (Germany).

For the Fourier Transform Infrared (FTIR) spectroscopic studies a Bruker Tensor 27 (USA) type transmission spectrometer was used having a DTGS detector capable of measuring in the 400-4000 cm^{-1} wavenumber range.

In order to determine the static mechanical behavior of hybrid composites interlaminar shear strength (ILSS) and 3 point bending tests were performed.

The effect of dynamic loads was studied by Charpy impact and falling dart impact tests. Charpy impact tests were made on a Ceast Resil Impactor Junior (Italy) instrument equipped

with a DAS 8000 data collector. Impact speed of the pendulum was 2.9 m/s, its energy was 2 J.

The instrumented falling dart tests were performed on a Ceast Fractovis type (Italy) computer controlled impactor together with a DAS 8000 type data collector. In addition to the penetration test other impact tests at lower (sub-critical) energy were also performed.

The fiber content was determined by incineration method, according to ISO 3451-1 by heating the test samples at 600°C for 1 hour, using a Nabertherm type (Germany) oven.

The viscosity of the solutions used for sample preparation were measured by a TA Instruments AR 2000 type (USA) rotation viscometer at 25°C as the electrospinning experiments were also made at room temperature. Measurement of the viscosity curves was a part of the optimization of the dope solution.

When preparing the CNT-PAN composite nanofibers an own dispersion method was developed for dispersing the CNTs in the solution. A Lehfeldt-GTS 22/125 type (Germany) ultrasonic equipment was used for ultrasonication with a DBK 16P type generator and a cylindrical sonotrode. Solutions containing 1 m% and 2 m% CNT (with respect to the PAN content) were prepared.

The structure of the nanofibers was studied by X-ray diffraction and by FTIR spectroscopy. The first was performed by a PANalytical (Netherlands) X'pert Pro MDP X-ray diffractometer, using Cu-Kα radiation (1,542 Å) and Ni filter. The voltage used was 40 kV, while the current was 30 mA. The samples were studied in the angle range from 2° to 42°(2θ).

When optimizing the stabilization program I used a SETARAM LabSysTG type thermogravimeter, where the studies were performed in the temperature range of 30-900°C, at a heating rate of 10°C/min in air atmosphere.

In order to study the chemical processes during the stabilization process DSC studies were also performed in air atmosphere. These tests were made in a Setaram (France) DSC 92 type instrument in the temperature range of 25-350°C, at a heating rate of 5°C/min. These studies were also performed in N_2 atmosphere as in this case the cyclization processes could be monitored alone, as in inert atmosphere dehydrogenization does not occur. These measurements were made in the temperature range of 0-350°C in tow subsequent heating runs, at heating and cooling rates of 10°C/min using TA Instruments DSC Q2000 (USA) equipment. The effect of the stabilization time was studied by isothermal DSC studies, also using the TA Instruments equipment.

For the structural study of the carbon nanofibers developed, Raman-spectroscopy was used. A Horiba Jobin-Yvon LabRAM Raman microscope (France) was used mounted on an Olympus BX-40 type optical microscope with an outer laser diode source (wavelength 785 nm, power 80 mW). Magnification of the objective was 100x, while the diameter of the laser beam was about 800 nm.

The composites hybridized with the carbon nanofibers developed by myself were prepared by hand layup technique. The electrical conductivity of the composites was determined on samples of 30x200 mm size with 4 point conductivity tests. Heat conductivity was determined on 80x80 mm samples using the hot plate method, according to the ISO 8302 standard.

On the samples of PA-6 and PAN tape tearing tests were made in the longitudinal direction using a Zwick Z005 (Germany) tensile tester. The width of the tapes were selected to be 5-6 mm, their length was 20-25 mm. In the case of the PAN fiber flow samples of about 30 mm length were cut and used as test specimens.

The mass of the test samples were measured by PerkinElmer Autobalance AD-2 type equipment at precision of 1 μg (in the test range of 20 mg), their length was measured by a caliper at a precision of 0.1 mm.

When modeling the strength and failure processes of the nanofibrous web I have used fiber-bundle cell model of Vas and the related FiberSpace software performing the relevant calculations.

4. Theses

1. I have demonstrated that by interleaving a poly(acrylonitrile) type nanofibrous mat of 20 μm average thickness between the layers carbon fiber reinforced epoxy composites the Charpy impact strength (measured along the edge of the specimen), the specific energy belonging to the maximum impact force, in the case of subcritical impact the absorbed energy all increase (at 5% significance level) without a considerable increase of the laminate size mass or carbon fiber content. I have proved by scanning electron micrographs that the nanofibers in these composites prevent the crack propagation process, they exhibit excellent adhesion to the epoxy matrix and locally make the material during the failure process tougher and, in the fabrication process they participate in the resin infiltration process [2-7].

2. I have proved by differential scanning calorimetry and thermogravimetric analysis that the poly(acrylonitrile) nanofibers are more sensitive to thermal degradation than microfibers of identical composition, as the peak intensity of the energy released during the cyclization is by 75% higher in the case of nanofibers and the cyclisation temperature is 14°C closer to the decomposition temperature of poly(acrylonitrile). The reason of this difference is the higher specific surface area of nanofibers in comparison to micro-fibers. By using 2 wt% carbon nanotube loading the expected intensity of the heat effect of cyclization is reduced by 30% and the temperature of the exothermal peak is reduced by 16°C therefore the degradation sensitivity of nanofibers as compared to micro-fibers could be essentially eliminated. In case of complete stabilization the peak value of the most intense exothermal peak was reduced by 9 and 17% by the addition of 1 and 2 m% carbon nanotube, respectively. Therefore their use means technological advantage during the carbonization of PAN nanofibers [7-14].

3. Using differential scanning calorimetry, Fourier transformation infrared spectroscopy and color tests I proved that in the case poly(acrylonitrile) fibers at a certain transformation temperature (taken as a probabilistic variable), provided that enough time is allowed for the completion of the stabilization reactions – that is at least 10 minutes based on isothermal differential scanning calorimetric results – in the conversion temperature range of 50-300°C the conversion ratio can be quantitatively described by a normal (Gaussian) distribution. I have proved by Fourier transformation infrared spectroscopy that the disruption of the nitrile groups and the formation of cyclic structures, as far as they ratio is concerned, can be

described by a properly parameterized normal distribution function and its complementary pair [7, 8, 10, 12].

4. I have developed and optimized a multistep pyrolytic technology that can produce continuously carbon nanofibrous webs from both poly(acrylonitrile) and poly(acrylonitrile) containing 2 wt% carbon nanotube solutions. I have proved the results by Raman spectroscopy and by scanning electron microscopy [7-12, 15].

5. I have further developed the yarn-formation technology of Smith *et al*. I have demonstrated that by using an auxiliary electrode and an elongating fiber-flow winding method the tensile modulus of the linear nanofibrous fiber flows increased by 100%, their tensile strength by 80% in comparison to those produced by the original equipment. It can be explained by the improved longitudinal uniformity (due to the use of the auxiliary electrode) and by the better ordering of the fibers within a fiber bundle and by the altered friction conditions between the fibers [4, 16, 17-19].

6.a I have demonstrated that the fiber-bundle model of Vas, using traditional tape tensile tests, can be used to determine the geometrical distribution and orientation (general fiber inclination and its standard deviation) of the nanofibers and the quality of inter-fibrillar relations (fraction of out-slipping and disassembling fibers and the fraction of broken fibers). According to the fitted bundle model the failure process of nanofibrous structures occurs mostly by the initial orientation of slanted and wavy fibers, then by the disruption of interfibrillar joints and finally by the disassembly of the structure itself. The validity of the bundle model is supported by comparing the results with electron micrographs [19-26].

6.b I have proved that by using the fiber-bundle model of Vas some main strength parameters (tensile modulus, tensile strength, elongation at break etc.) of the single nanofibers can be determined from tape tearing tests performed on samples cut from fiber mats. The feasibility of this precise method is supported by test results of other researchers performed on individual nanofibers of similar composition using special atomic force microscope. In the case of nanofibrous samples the fiber utilization factor can also be determined by the model [19-21].

5. List of the most important publications related to the topic of the thesis

1. **Molnár K**., Vas L.M.: Chapter 10 - Electrospun Composite Nanofibers and Polymer Composites. Bhattacharyya D., Fakirov S. (szerk.) Synthetic polymer-polymer composites. Hanser, München, 301-350 (2012).
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5. Fejős M., **Molnár L.**, Karger-Kocsis J.: Epoxy/polycaprolactone systems with triple-shape memory effect: electrospun nanoweb with and without graphene versus co-continuous morphology. Materials, 6, 4489-4504 (2013).
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7. **Molnár K**.: Development of carbon nanofiber reinforced hybrid composites for aerospace applications. Oral presentation, PRECARB-12 - Surface Chemistry and Performance of Carbon Materials Conference, Budapest (2012).
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10. **Molnár K**., Szolnoki B., Toldy A., Vas L.M.: Thermochemical stabilization study of continuously electrospun carbon nanotube-loaded polyacrylonitrile nanofibers for high performance carbon nanofiber mass production. Submitted to Journal of Thermal Analysis and Calorimetry.
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