

# Influence of the Structure of Nanofibre Based Composites on Their Strength Properties

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## Abstract

*In this work, preliminary investigations on the influence of the structure of nanofibre based composites on their strength properties were made. As a 'matrix' material, needle punched nonwoven from classical polypropylene fibres was used. Polyamide 6.6 nanofibres electrospun directly onto 'matrix' nonwoven were used as a reinforcement. In order to obtain composites, the nanofibre/'matrix' multilayer structures of different architecture but with the same weight percentage of nanofibres were pressed. On the basis of the investigations realised, it was found that collecting the nanofibres spun in the electrospinning process directly onto the 'matrix' nonwoven is more advantageous than transferring the layer of nanofibres from the collector onto the nonwoven. The tensile test indicates the influence of the composite structure on its strength properties. The composite obtained from the multilayer structure consisted of two thin layers of nanofibres uniformly arranged between the layers of 'matrix' nonwoven, characterized by a higher value of tensile stress and Young's modulus than a composite based on one thicker layer of nanofibres. From the results comes that the use of a higher number of nanofibre layers between the layers of 'matrix' nonwoven gives a more uniform arrangement of nanofibres in the composite space, favouring more the precise wetting of nanofibres by the matrix.*

**Key words:** nanofibres, electrospinning, nonwoven, composite structure, tensile stress.

## Introduction

In the technology of fibrous composites more often the fibres with unique characteristics, i.e. nanofibres, are used. The transverse dimension of nanofibres produced using an electrostatically driven jet of polymer solution or melt can be in the range of a few nanometers to several micrometers. In comparison with traditional fibres, the nanofibres possess a higher ratio of the length to fineness and a specific surface to weight/volume and their mechanical properties are more excellent. For this reason and also because of a large available surface area, specific surface morphology and potential homogeneous dispersion in the matrix, the nanofibres become a valuable filling material of composite matrices, which ensures better reinforcement than comparable traditional fibres. As reinforcement of polymer composites, three different types of nanofibres, i.e. polymer nanofibres, carbon nanofibres and carbon nanotube composite nanofibres are enumerated. A large spectrum of applications is open for single continuous nanofibres or uniaxial fibre bundles, especially in reinforced composites. In nanofibre science literature, the technical solutions for aligned electrospun nanofibre obtainment are mentioned, e.g. a cylinder collector with a high rotating speed, an auxiliary electrical field, a thin wheel with sharp edge, a frame collector, the multiple field technique etc. Nanofibres spun in the classical electrospinning process lie on the collector in an undetermined way forming a very thin nonwoven layer. The nanofibres in a nonwoven form are

used in filter materials, textiles for special applications, elements of nanoelectronics, tissue engineering, and wound dressing materials. The nonwoven structure, where between fibres irregular voids exist, can ensure better load transfer between the matrix and nanofibres in composites and, consequently, can have an effect on the mechanical performance of composites. Moreover, polymer composites reinforced by nanofibres have very good transparency [1, 2]. Kim and Reneker, using polybenzimidazole (PBI) nanofibres of 400 nm diameter in the form of a nonwoven layer with a mass per unit area of a few tens of g/m<sup>2</sup>, as a 15 wt.% reinforcement of the epoxy matrix, concluded that the reinforcing effect is bigger than in the case of PBI fibroids (whisker-like particles) as a reinforcement. They also found a very good reinforcing effect for the rubber matrix (styrene-butadiene). According to Fong, the addition of 5 wt.% PA 6 nanofibres in BIS-GMA/TEGDMA (50/50, mass ratio) dental restorative composite resins improves the flexural strength of the composite by 36%, the elastic modulus by 26% and the work of fracture by 42%. Bergshoef i Vancso fabricated transparent composites with an epoxy matrix using Nylon-4,6 nanofibres as a reinforcement [3, 4].

Nanofibres in the form of a plane fabric can be used as one of the composite components, ensuring specific properties. Among mechanical properties, besides the tensile strength of such composites, the bending strength and delaminated

fracture also decided about their usability. Composites fabricated from nanofibres as a reinforcement, especially from biodegradable polymers, can be dedicated for medical applications. PA 6 nanofibres improve the mechanical properties of dental materials, and PA 6.6 nanofibres give the desirable mechanical properties of transparent material e.g. face shields, body shields, protective eye wares [5 - 7]. A very important problem concerns the electrospinning process of nanofibres with suitable characteristics and their connection with other components in such a way as to prevent any damage. In the case of reinforced composites, where nanofibres as the reinforcement have an effect on the strength properties, the avoidance of nanofibre damage is a significant matter. For composite technology a solution to the problems mentioned above is very important and requires detailed study of the electrospinning of nanofibres from the solution of a given polymer to develop a method and conditions of the connection of composite components as well as to establish the most advantageous composite structure giving possibilities to utilise the strength properties of nanofibres effectively. Until now, however, there have been no publications related to that matter. In this study, the method of manufacturing plane textile fabrics with nanofibre layer/layers and a preliminary analysis of the influence of the fibrous layer arrangement on the tensile stress of thermoplastic composites are presented. The investigations were carried out for polypropylene nonwovens/polyamide 6.6 nanofibre composites.

## Experimental

### Materials

As the material of the composite matrix, polypropylene was chosen. It is the polymer often used as the composite component, characterised by a relatively low melting point (within a temperature range of 160 - 190 °C). The composite matrix was formed from nonwoven consisting of polypropylene fibres (PP) with a length of 60 mm and linear density of 6 dtex.

Polyamide 6.6 nanofibres were used as a reinforcing material. For manufacturing the nanofibres, a 10 wt.% spinning solution [4, 8, 9] of polyamide 6.6 (PA6.6) (with a melting point of about 250 °C) in 85 wt.% formic acid was used.

### Manufacturing of composites

Thermoplastic model composites were obtained from the multilayer structures of fibrous materials on a hydraulic press machine with a water-cooling system. The multilayer structures were formed by collecting nanofibres spun in the electrospinning process directly onto the 'matrix' nonwoven. This method is more advantageous than transferring the nanofibre layer from the collector onto the nonwoven. Transferring by hand is hazardous because during the process of separating the nanofibres from the collector or from the fibrous sublayer placed on the collector, as well as during the later uniform overlaying on the 'matrix' nonwoven, nanofibres could be damaged.

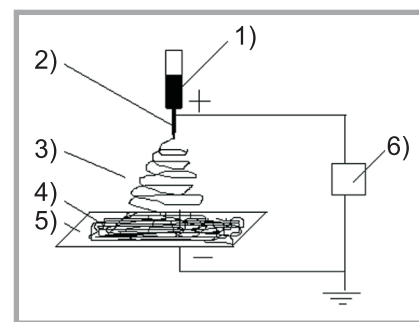
Multilayer structures with a diversified arrangement of layers but with the same weight percentage of nanofibres as reinforcement were manufactured to make a comparison of the tensile properties of composites obtained from them.

### 'Matrix' nonwoven

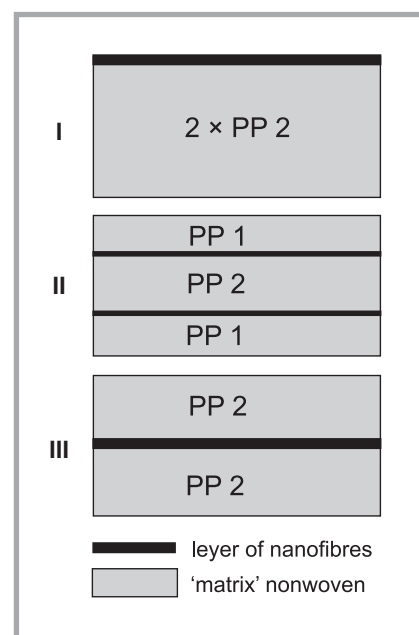
Needle punched nonwoven used as the composite matrix was manufactured from the fleece of the longitudinal direction of fibres, obtained on a roller card. Needle punching of the fleece layer was carried out on a needle punching machine at the following technological parameters: type of needle - 15 × 18 × 40 × 3<sup>1</sup>/<sub>5</sub> RB, number of needle punching - 40/cm<sup>2</sup>, and depth of needle punching - 12 mm. Due to the needle punching process, the density and strength of the material were increased. In order to make diversified variants of the multilayer structure but with similar thickness, two nonwovens of different area weight (about 100 and 200 g/m<sup>2</sup>) were produced.

### Layer of nanofibres

A layer of nanofibres was obtained from the polymer solution by the electrospinning process from a motionless metal capillary with an external diameter of 0.6 mm, shown in **Figure 1** [10]. Nanofibres were electrospun directly onto 'matrix' nonwoven placed on the plane metal collector. Dimensions of the nonwoven sample were 6 × 12 cm, and the mass fraction of the electrospun nanofibres was controlled on a laboratory balance. Technological parameters of the electrospinning were determined on the basis of preliminary tests in order to ensure the correct course of the process, without any disturbances. The parameters used



**Figure 1.** Scheme of electrospinning: 1) polymer solution, 2) capillary, 3) solution jet, 4) nanofibre web, 5) collector, 6) high voltage power supply.



**Figure 2.** Scheme of layers in the multilayer structures.

were as follows: power supply voltage - 15 kV, distance between the capillary tip and nonwoven placed on the collector - 20 cm, ambient temperature - 19.6 °C, and relative humidity - 28%.

### Multilayer structures

The multilayer structures with the same weight ratio of the matrix nonwoven to nanofibres, shown in **Figure 2**, were formed by electrospinning nanofibres directly onto the "matrix" nonwoven. Variant I consists of two layers of PP 2 nonwoven covered by one layer of nanofibres; variant II consists of one PP 1 nonwoven, one layer of nanofibres, one PP 2 nonwoven, one layer of nanofibres and one PP 1 nonwoven, and variant III consists of one PP 2 nonwoven, one layer of nanofibres and one PP 2 nonwoven. In variant II the thickness of individual nanofibre layers is lower than in the case of variants I and III.

According to nanofibre science literature, the weight percentage of nanofibres in thermoplastic composites should be in the range of 1 ± 5 wt.% in relation to the matrix weight, [1]. The mass fraction of nanofibres could be higher, but even that content has a positive influence on the strength properties of the composites. In this study, the weight percentage of nanofibres in each multilayer structure was 2 wt.%. The use of a higher content of nanofibres could lengthen the time of composite manufacturing as well as increase the energy consumption.

### Pressing

The composites were obtained by pressing particular multilayer structures consisting of 'matrix' nonwoven layers and nanofibre layers on a hydraulic press machine with a water-cooling system. To check the scale of improvement of the composite tensile properties by PA 6.6 nanofibre addition, comparatively pure polypropylene nonwoven was pressed.

The optimal thermal and pressure conditions were determined on the basis of experiments and literature [11]. The multilayer structure placed on the metallic plate was wrapped in teflon foil to prevent of molten polymer propagation during the pressing process performed under the following conditions:

1. consolidation time 15 min, pressure during consolidation 0.0166 MPa, temperature 180 °C,
2. cooling time 15 min, pressure during cooling 0.0166 MPa, temperature decreasing to 20 °C.

### Testing methods

The area weight of the 'matrix' nonwoven was established according to PN-EN 29073-1 (ISO 9073-1), the thickness according to ISO 9073-2 and the air permeability according to PN-EN ISO 9237:1998. The diameters of PA6.6 nanofibres produced by the electrospinning technique were determined by means of SEM microphotography (scanning microscope JEOL JSM 5200 LV, Jeol LTD., Japan) and the Lucia G image analysis

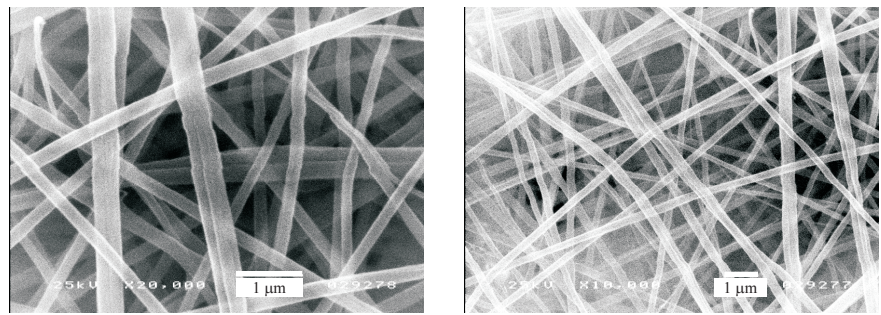


Figure 3. SEM image of PA6.6 nanofibres.

Table 1. Characteristics of 'matrix' nonwovens.

Nonwoven	Average area weight, g/m <sup>2</sup>	Standard deviation of area weight, g/m <sup>2</sup>	Var. coeff. of area weight, %	Average thickness, mm	Average air permeability, dm <sup>3</sup> /(m <sup>2</sup> s)
PP 1	111.13	15.32	11.3	4.69	5436.77
PP 2	211.59	12.66	7.2	9.63	2588.94

software program (Laboratory Imaging s.r.o., Czech Republic). In order to study the influence of the composite structure with nanofibres on their strength properties, a unidirectional tensile test according to PN-EN ISO 527-4 was performed with 'INSTRON' tensile tester series 4204 equipment with PC control. The tensile stress at maximum load, strain and Young's modulus were determined. For the sake of small thickness and small surface area of the composite plate, the dimensions of the samples tested were smaller than according to the standard. Five samples of 15 mm × 120 mm were cut from each composite plate, and the cutting direction was the same as the fibre direction in the 'matrix' nonwoven. The sample width was 15 mm, and the sample thickness, measured by a micrometer screw, was in the range of 0.24 to 1.13 mm. The process parameters were as follows: gauge length - 50 mm, and cross-head velocity - 50 mm/min.

## Results and discussion

In order to obtain multilayer structures with the planned diversified arrangement of layers, two polypropylene needle punched nonwovens with the characteristics presented in Table 1 were manufactured.

The area weight of PP 2 nonwoven was higher by about 100% than that of PP 1 nonwoven. Similar relationships were found for the thickness and air permeability of these nonwovens. Polyamide 6.6 nanofibres were characterised by a lack of defects, smoothness and a regular shape, and their average diameter was about 227 nm (min: 95.59 nm, max: 391.34 nm, standard deviation: 52.34 nm), shown in Figure 3.

The thickness of the model composites varied, usually lower than 1 mm. The results of the tensile test are shown in Table 2.

Values of the tensile stress at the maximum load and Young's modulus clearly indicate the influence of the multilayer arrangement on the strength properties of the composite. From the study results, the composite obtained from multilayer structure II is characterised by the highest value of tensile stress and Young's modulus, achieved because the arrangement of nanofibre layers in the composite space was more uniform than in the case of other composites. For this variant the tensile stress is higher by about 109% and Young's modulus by about 156% in comparison with the pure polypropylene sample. The highest value of strain was

Table 2. Tensile properties of the model composites.

Variant of multilayer structure	Tensile stress at max. load, MPa	Standard deviation of tensile stress, MPa	Var. coeff. of tensile stress, %	Strain at max. load, %	Standard deviation of strain, %	Var. coeff. of strain, %	Young's modulus, MPa
I	36.62	7.80	21.3	17.79	11.87	66.7	1499
II	46.60	8.57	18.4	13.86	10.99	79.3	1862
III	22.21	3.34	15.0	5.11	1.55	30.3	1336
PP	22.31	1.70	7.6	7.48	1.23	16.5	727

noted for the composite obtained from multilayer structure I, the reason for which being the higher thickness of the matrix layer, which is not divided by a layer/layers of nanofibres. That layer has a greater influence on the strain value of the composite than the layer of nanofibres. Two layers of nanofibres in the composite structure also have a larger influence on the increase in tensile stress of the composite than only one layer, in spite of their weight being comparable. On the basis of the results, variant II is the most advantageous structure of thermoplastic composite with polyamide 6.6 nanofibres as a reinforcement. This variant is composed of three layers of matrix material separated by two layers of nanofibres. The weight percentages of the matrix and nanofibres are the same in variant II and in the other two variants. The composite of variant II shows the highest value of tensile stress, which results from the uniform arrangement of nanofibres in the composite space. Variant III is characterised by the lowest tensile stress, comparable with the value determined for the pure polypropylene sample and by a Young's modulus 84% higher than for pure polypropylene.

## Conclusions

Collecting the nanofibres spun in the electrospinning process directly onto the 'matrix' nonwoven is considerably more advantageous than transferring the layer of nanofibres from the collector onto the nonwoven.

The values of tensile stress and Young's modulus found clearly indicate the considerable influence of the composite structure on its strength properties. The composite from the multilayer structure, consisting of two thin layers of nanofibres uniformly arranged between the layers of 'matrix' nonwoven, is characterised by higher value of tensile stress than composites based on one thicker layer of nanofibres. From the results, it can be concluded that the use of a higher number of nanofibre layers between 'matrix' nonwoven layers gives a more uniform arrangement of nanofibres in the composite space, favouring more precise wetting of nanofibres by the matrix.

As a result of pressing of one thicker layer of nanofibres covering the layer of 'matrix' nonwoven, a composite is obtained with higher tensile properties than in the case of one thicker layer of

nanofibres placed in the middle of the thickness of the multilayer structure. The layer of nanofibres, being at the side of the stamping plate, is pressed into the matrix. Consequently, the binding of composite components is more effective than if the layer of nanofibres is shifted from the middle to the outer bottom part of the composite.



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Received 30.06.2011 Reviewed 23.01.2012

## Technical University of Lodz Faculty of Material Technologies and Textile Design

### Department of Clothing Technology and Textronics

The Department was established in 2009, combining the departments of: Clothing Technology and Automation of Textile Processes.

The Department offers research and cooperation within the following fields:

- physical and biophysical properties of clothing (modelling the microclimate under clothing packages)
- creating a basis for engineering fashion design (e.g. actions to improve design processes)
- unconventional structures of clothing with regard to use and manufacturing
- analysis of the operating conditions of machines for clothing production (e.g. optimisation of the gluing parameters process working conditions of sewing threads)
- creating analysis and design processes for the industrial production of garments
- basic problems of general and technical metrology
- instrumentation of measurements, the construction of unique measurement device and system
- measurement and control computer systems, including virtual instruments of the fourth generation
- textronics as synergetic connecting textile technologies with advanced electronic systems and computer science applied in metrology and automatics
- identification of textile and clothing objects with the use of advanced microprocessor measurement techniques
- modelling of objects and their computer simulation, methods of experimental research, especially experiment design of experiments and computer analysis of results

The Department is active in the following educational and scientific fields: textile engineering, pattern design, education of technology and information engineering, materials engineering, health and safety at work, and logistics.

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