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(54) **Title:** MORPHOLOGICALLY OPTIMIZED NONWOVEN TEXTILES BASED ON NANOFIBRES

(57) **Abstract:** The prepared space nanostructures contain drop-like spacing microspheres and/or are made of a combination of micro- and nanofibres and/or consist of nanofibres of polymers eventually polymeric mixtures that ensure formation of more voluminous space structures that may be prepared by a suitable combination of variables at the electrospinning process. The more voluminous space structures embody a larger thickness and area mass of the filtration material in comparison with planar structures, hence, the so much required enhancement of mechanical properties and of manipulability with the filtration nanomaterial. However, if we compare the planar and space nanostructures that have the same pressure drop, then the materials with space morphology have a larger effective surface of fibres and better filtration properties in elimination of ultrafine particles (filtration efficiency and, hence, also the quality factor).



MORPHOLOGICALLY OPTIMIZED NONWOVEN TEXTILES BASED ON NANOFIBRES

Technical field

The invention concerns the morphologically optimized nonwoven textiles on the basis of nanofibres that can be produced by electrospinning and that embody an increased quality factor of filtration nanofibre nonwoven textiles (nNT).

Background of the invention

The processing of polymer solutions in the electrostatic field (electrospinning) is currently the most used technique that enables preparation of fibres with diameters of tens of nm. The first patent – US1975504 concerning this technology dates to 1934. The increased interest in the nanostructures from the early nineties of the past century is related to the possibilities of decreasing the size, material saving and achieving new properties unachievable by other techniques.

Currently, the requirements for elimination of ultrafine particles, bacteria and viruses from the air and potable water are increasing because they are responsible for the increasing number of allergies and diseases of the respiratory tract in industrial agglomerations as well as for spreading of various pandemics. It may be assumed that the nanofibre structures will find application particularly in the area of microfiltration (i.e. for removing particles sized from 100 nm to 15 μ m) and ultrafiltration (for particles from 5 to 100 nm). However, the optimization of nanofibre structures is necessary with regards to this application.

Due to the fact that the dominant mechanism that takes effect at capturing the ultrafine particles is diffusion, it may be assumed that due to a longer path of an ultrafine particle performing Brownian motion the capture probability on the surface of nanofibres or a drop-like spacers will be increased.

In this relation, solutions aiming at formation of three dimensional nanofibre structures given in the US7828539 are interesting. In this patent, there is among others discussed also the tendency towards formation of drops or beads within the nanofibre structure using spinning solutions of low viscosity or solutions of low-molecular polymers.

However, the randomly spread drop-like spacers were, in general, so far considered rather defects (bead defects) that can be removed by e.g. a suitable solution additivation. A distinctive suppression of drop-like defect may be achieved by the use of a modification additive (borax and/or citric acid) to enhance the conductivity of polyurethane spinning solution (15 wt. % in dimethylformamide) (refer to Figs. 1, 2). The presence of drop-like defects in the PU structures may be also very effectively eliminated by an addition of surface active compounds, e.g. ionic liquids (Figs. 3 and 4). The change has been achieved by adding 1 wt. % (related to solid of the polymer) 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide of the IoLiTec Ionic Liquids Technologies company, FRG.

Therefore, neither the solution in accordance with the cited patent US7828539 can be considered an aimed optimization of nanofibre structures for the purpose of enhancing their filtration effect.

Only general principles are currently known and applied from the viewpoint of the optimization of electrospinning techniques of the produced nanofibre structures:

For example, it is known that the largest changes in the planar nanofibre structures may be achieved at the electrostatic fibre formatting process by the change of processed solution properties (polymer concentration and, hence, solution viscosity, polymer molar weight, solution conductivity, polymer permittivity...) and of the process parameters themselves (applied voltage, kind and distance of electrodes, quality and electric conductivity of the collecting substrate...). It is by addition of various additives, solvents, modifying polymers and by a suitable combination of process variables not substantially changing the process intensity that nanofibre nonwoven textile (nNT) with high homogeneity, with required nanofibre diameter and organized space arrangement may be prepared in a continual process.

However, as already shown, a sufficiently effective optimization of nanofibre structures for the purpose of enhancing their filtration effect is so far not performed.

Basic idea of the invention

The morphologically optimized nonwoven textiles on the basis of nanofibres in accordance with the invention that show in particular an increased filtration effect contribute

to removal of the above mentioned deficiency of the existing technology status. The invention principle consists of the fact that these nonwoven textiles include nanofibre structure with the morphologically separated nanofibres, as:

- a) nanofibre structure with nanofibres physically separated by drop-like spacers and/or nanoparticles dispersed within the nanostructure that form regular structures with drop-like spacers and/or nanoparticles dispersed within the nanostructure, cumulated in columns interconnected by nanofibres into regular morphological arrangements,
- b) nanofibre structure with nanofibres physically separated by drop-like spacers and/or nanoparticles dispersed within the nanostructure that form regular structures with drop-like spacers and/or nanoparticles dispersed within the nanostructure,
- c) nanofibre structure based on fibres with a broad distribution of diameters of rigid polymers with high modulus of elasticity composed with mechanically maintained distances in the organized space morphological arrangements,
and/or
- d) structure with bimodal distribution of fibre diameters based on combination of micro- and nanofibres forming organized space morphological arrangements.

A morphologically optimized nonwoven textile containing nanofibre structure with nanofibres physically separated by drop-like spacers that form regular structures with drop-like spacers cumulated in columns interconnected by nanofibres into regular morphological arrangements similar to honey combs is with an advantage polycarbonate nanofibre structure that may be prepared by the electrospinning technology from a spinning solution of polycarbonate in tetrachlorethane containing an addition of chloroform and borax.

It was found that at preparation of polycarbonate (PC) nanostructures an increase of nanofibres contents between the drop-like defects and formation of regular structure, where the drop-like defects are cumulated in columns interconnected by nanofibres is achieved by the change of the solvent system (chloroform addition to tetrachlorethane) and by addition of borax (ref. to Figs. 5, 6). Such organized space arrangement similar to that of honey combs results in filtration material thickness increase, increase of area mass, increase of solid volume fraction (SVF), while the free volume fraction (FVF) does not substantially differ from planar nanofibre structures. Furthermore, this morphology substantially contributes to the increase of the specific surface and, hence, positively influences the filtration properties.

The organized space structure with arranged drop-like spacers (Fig. 6) with area mass 3,42 g/m² had a permeability of aerosol 0,762% at a pressure drop of 35 Pa, which corresponds to $qF = 139$ (measured on the Lorenz equipment in accordance with EN 143).

(Note: At the assessment of the filter quality, it is necessary to take into account both pressure drop (Δp) and filtration efficiency (E). The interrelation of these two characteristics is best described by the quality factor $qF = \ln(1/P)/\Delta p$, where the permeability $P = 1 - E$).

The organized space structures with spacers arranged into structures of honey combs (ref. to Fig. 7) may be prepared also from the polyurethane spinning solution in mixture of solvents dimethylformamide and tetrachlorethane.

The enhanced filtration features in comparison with planar structures show also organized space structures with spacers without honey combs morphology (as for example on Fig. 3).

The elegant method of formation of structure with polymer distance spacers consists in combination of two polyurethane types with different average molar weight, where the one of them (with a lower M) under given electrospinning conditions forms globular microspheres and the other the nanofibres. It is possible to use also one of rigid polyurethane with a content of hard segments at least 20 wt. %.

Also, nanoparticles may be with advantage used as distance spheres (e.g. titanium dioxide, silver, phthalocyanine agglomerates, clay (refer to structure on Fig. 8) or jet milled clay (refer to structure on Fig. 9) that may be surface modified e.g. by chlorhexidine or zinc dioxide) dispersed in the nanofibre structure. In this way, materials may be prepared with additional added value, e.g. antibacterial properties. The incorporation of the nanoparticles into the fibrous composites during electrospinning under optimum conditions is very efficient (ca. 95%).

In the table 1, there are summarized the filtration properties and size characteristics of the planar polyurethane (ref. to Fig. 4) and space polycarbonate (refer to Fig. 6) nanostructure. To compare the structure influence on the filtration efficiency, structures with the same pressure drop ~90 Pa were compared.

The compared nanostructures (Table 1, Fig. 10) that show the same pressure drop at filtration of ultrafine particles are formed by fibres with a comparable average diameters and distribution of pores in the nanostructure (D_n , D_w) but they substantially differ in area mass,

thickness and filter effective area, which is the reason of enhancement of the filtration efficiency of the space nanostructure, and hence, of the filter quality factor.

Table 1: Characterization and properties of organized space and planar nanostructure

Nanostructures with a pressure drop of ~90 Pa		
Sample	Space PC nanostructures with distance microspheres	Planar PU nanostructure
Area mass (g/m^2)	6,80	0,807
Thickness (μm)	30,2*	9,2*
Solid volume fraction SVF (m^3/m^3)	0,188	0,080
Free volume fraction FVF (%)	81,2	92,0
Filtration properties in the area of ultrafine particles		
Most penetrating particle size MPPS (nm)	100	70
Pressure drop (Pa)	81 - 95	90
Filtration efficiency in MPPS (%)	98,90	90,35
Quality factor in MPPS (1/kPa)	51	26
Morphological characteristics of nanostructures acquired by digital image analysis of SEM images		
Average size of fibres diameter (nm)	120,2	124,7
Pore size distribution (nm)	D_n	202,5
	D_w	740,0
	D_z	1 269,0
	D_{z+1}	1 721,0
Filter effective area (m^2)	188,9	23,6

* measured from SEM images

As already shown before, due to the fact that the dominant mechanism of capturing the ultrafine particles is diffusion, it may be assumed that due to a longer path of an ultrafine particle performing Brownian motion the capture probability on the surface of nanofibres or a drop-like spacer will be increased.

As the proof of mechanism, by which the enhancement of filtration abilities of voluminous structures occurs, distributions of fibre diameters have been determined (ref. to Fig. 11) and has been monitored, how the pore sizes and their distribution vary for structures with microscopic spacers (ref. to Fig. 12). For the determination, digital analysis of SEM images of the nanostructures has been used. A detailed description of the applied technique is

given in the publication W. Sambaer, M. Zatloukal and D. Kimmer, The use of novel digital image analysis technique and rheological tools to characterize nanofibre nonwovens, *Polymer Testing* 29, 82-94 (2010). The analysis is based on an examination of the change in richness of grey halftones caused by a change in the thickness of nanofibre nonwoven textiles. In more detail, all nanostructure pores are loaded with fractions of model spheres to identify pore size distribution.

From the comparison of the pores distribution in prepared nanostructures (Fig.12) it is obvious that the pore distribution of the nanostructure organized space arrangement with drop-like spacers is broader, includes bigger pores but the average value of the distribution does not substantially differ from the planar nanostructures. Nevertheless, the space nanostructure has approximately 15 times larger area mass and 11 times larger thickness. The space arrangement results in physical separation of nanofibre layers increase of the distance between the nanofibres and angles, under which they are embedded in the nanostructures. Such morphology results in the enhancement of the nanostructures filtration properties.

The fibres with a diameter in units of micrometres can also provide the function of distance spacers that form the space structure. Such arrangements that provide thickness and volume increase of the filtration material and that are created by fibres with a broad distribution of their diameters show also enhanced filtration properties. First of all, the rigid polymers with high modulus of elasticity, as e.g. polymethylmetacrylate (PMMA), styrene - acrylonitrile copolymer (SAN) as well as polyurethane with a high contents of hard segments, have tendency to form such arrangements – ref. to Figs. 13 through 15. The space arrangements originate in both the area of nanofibres (Fig. 13, magnification 5 000x) as well as the area of microfibers with fibre diameters of units of μm (Fig. 14, magnification 1 500x) and/or diameters of tens of μm (Fig. 15, magnification only 500x).

Pressure drop of such structures characterized in Table 2 is approximately half of the pressure drop of the materials listed in the Table 1. The attention is purposefully focused on the low pressure drop – due to potential application of these nanostructures in face halfmasks and as the mask filters. In Table 2 and in Fig. 16, there are properties of material with morphology shown in Fig. 14 compared with properties of planar structure. The combination of globular microspheres, nanofibres and microfibers (Fig. 14) leads to an enhancement of material filtration properties as well.

Table 2: Characterization and properties of planar nanostructure and combined micro- and nanofibre structure

Nanostructures with a pressure drop of ~ 45 Pa		
Sample	Combined PMMA space nanostructure with a broad distribution of fibres	Planar PU nanostructure
Area mass (g/m^2)	6,92	0,403
Thickness (μm)	34,7	4,6
Solid volume fraction SVF (m^3/m^3)	0,169	0,080
Free volume fraction FVF (%)	83,1	92,0
Filtration properties in the area of ultrafine particles		
Most penetrating particle size MPPS (nm)	50	100
Pressure drop (Pa)	48	45
Filtration efficiency in MPPS (%)	97,52	78,77
Quality factor in MPPS (1/kPa)	77	44
Morphological characteristics of nanostructures acquired by digital image analysis of SEM images		
Average size of fibres diameter (nm)	758,6	124,7
Pore size distribution (nm)	D_n	672
	D_w	2564
	D_z	4409
	D_{z+1}	6151
Effective surface area (m^2)	30,9	11,8

* measured from SEM images

The compared materials differ in distribution of fibre diameters (Fig. 17) and distribution of pore sizes (Fig. 18). The more voluminous structures are in the area of ultrafine particles capturing more effectively maintaining the same pressure drop.

Morphologically optimized nonwoven textiles may also contain structure with bimodal distribution of fibre diameters on the basis of combination of polymeric microfibers and nanofibres that form voluminous morphological arrangements. The Fig. 19 shows a structure with the bimodal distribution of fibre diameters containing polymethylmetacrylate microfibers and of polyurethane nanofibers. By this structure it is possible to achieve the same filtration efficiency and lower pressure drop as by planar structures that are prepared from polyurethane nanofibers only.

List of figures in drawings

The enclosed drawings serve for clarification of the invention principle. They represent:

Fig. 1 - polyurethane nanostructure with drop-like defects – without additives, magnification 1 500x

Fig. 2 - polyurethane nanostructure with eliminated drop-like defects by addition of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ and citric acid, magnification 1 500x

Fig. 3 - polyurethane nanostructure with drop-like defects – without additives, magnification 5 000x

Fig. 4 - polyurethane nanostructure with eliminated drop-like defects by adding of ionic liquid, magnification 5 000x

Fig. 5 - polycarbonate nanostructure prior to the optimization process, magnification 1 500x.

Fig. 6 - polycarbonate nanostructure after the optimization – regular structures of drop-like spacers, magnification 1 500x

Fig. 7 - polyurethane nanostructure with regular structures of drop-like distance spheres prepared from the mixture of solvents dimethylformamide/tetrachlorethane, magnification 1 500x

Fig. 8 - composite nanostructure based on copolymer of ethylenvinylacetate (EVA) And vermiculite (undersize 40 μm), magnification 500x

Fig. 9 - composite nanostructure based on copolymer of ethylenvinylacetate (EVA) And jet milled vermiculite, magnification 500x

Fig. 10 - comparison of filtration efficiency of planar and space nanostructure (ref. Table 1); pressure drop of compared nanostructures $\sim 90 \text{ Pa}$

Fig. 11 - comparison of distributions of fibre diameters of the planar and space nanostructures (ref. Table 1); columns represent the measured values, the line chart is a function based on Gauss approximation

Fig. 12 - comparison of distributions of pores of the planar and space nanostructures (ref. Table 1); columns represent the measured values, the line chart is a function based on Gauss approximation

Fig. 13 - combined space nanostructure based on polyethersulphone fibres with a broad

distribution of diameters, magnification 5 000x

Fig. 14 - combined space nanostructure based on polymethylmetacrylate fibres with a broad distribution of diameters, magnification 1 500x

Fig. 15 - combined space structure based on fibres of copolymer styrene- acrylonitrile with a broad distribution of diameters, magnification 1 500x

Fig. 16 - comparison of filtration efficiencies of the planar nanostructure and structure based on polymethylmetacrylate combining microfibres and nanofibres, pressure drop of the compared materials ~45 Pa

Fig. 17 - comparison of the distribution of the fibre diameters of the filter based on planar and pace nanostructure (ref. Table 2)

Fig. 18 - comparison of pores distribution of planar and pace nanostructure (ref. Table 2)

Fig. 19 - combined nanostructure based on polymethylmetacrylate microfibers and polyurethane nanofibres – bimodal distribution of fibre diameters, magnification 5 000x

Examples

Example 1

The example of the polycarbonate nanofibre structure with nanofibres physically separated by drop-like spacers forming regular structures with drop-like spacers cumulated in columns interconnected by nanofibres into regular morphological arrangements similar to honey combs may be characterized by the following conditions of preparation and end-use properties:

a) spinning solution: Polycarbonate (Macrolon 2458, Bayer, Leverkusen, Germany, $\rho = 1,2 \text{ g.cm}^{-3}$) electrospinning solution has been prepared using the mixture of two solvents – tetrachlorethane and chloroform in the ratio of 3:1 and modified by a mixture of ionic liquids 1-ethyl-3-methylimidazolium-bis(trifluoromethylsulfonyl)imid and 1-ethyl-3-methylimidazolium triflate in the ratio of 2:1 (IoLiTec Ionic Liquids Technologies, Heilbronn, Germany) and 1 wt. % borax. The polycarbonate solution had viscosity of 0,3 Pa.s and electric conductivity of $10,5 \mu\text{S.cm}^{-1}$.

b) conditions of electrospinning process: electrospinning equipment Nanospider (Elmarco, Liberec, Czech Republic), rotating electrode with three cotton cords (in accordance with PCT/CZ2010/000042), the voltage in solution bath $U = 25 - 75$ kV, distance of electrodes $D = 15 - 25$ cm, rotating speed of the electrode = $7 - 14$ rpm, shift velocity of the collecting substrate (antistatically modified polypropylene nonwoven (PPNT) or polyester nonwoven or viscose nonwoven fabrics) = $16 - 32$ cm/min.

c) characterization of prepared nanostructure: In addition to calculations of the area mass, solid phase fraction (SVF), free volume fraction (FVF) and filter effective area, also the scanning electron microscope (SEM) Vega 3 (Tescan, Brno, CZ) has been used for the characterization of the nanostructures. The SEM images have been subsequently used for determination of the nanofibres layer thickness and distribution of the fibre diameters/pore size using the technique of digital image analysis in accordance with the publication W. Sambaer, M. Zatloukal and D. Kimmer, The use of novel digital image analysis technique and rheological tools to characterize nanofibre nonwovens, *Polymer Testing* **29**, 82-94 (2010).

d) measuring of filtration efficiency: the produced filtration materials have been tested for aerosol penetration (diethyl hexyl sebacate with a particle diameter of $0,45\ \mu\text{m}$) at a flow rate of $30\ \text{l}\cdot\text{min}^{-1}$ (face velocity $5,7\ \text{cm}\cdot\text{s}^{-1}$) by means of filtration measuring system LORENZ (Germany) adjusted for EN 143. Measurement in the range of ultrafine particles has been made with the aerosol of ammonium sulphate using the pulveriser (AGK, PALAS, Germany), the electrostatic classifier (EC 3080, TSI, USA) and the condensation particle counter (UCPC 3025 A, TSI, USA) at the face velocity of $5,7\ \text{cm}\cdot\text{s}^{-1}$. The filtration efficiency and pressure drop have been determined for nine fractions of particles with diameters 20, 35, 50, 70, 100, 140, 200, 280 and 400 nm.

Penetration (measured in accordance with EN 143) of nanoparticles of diameter 450 nm through such space structure having area mass of $3,42\ \text{g}\cdot\text{m}^{-2}$ was 0,762%. The pressure drop was of 35 Pa, which corresponds to a quality factor $qF = 139\ \text{kPa}^{-1}$. Material with a area mass of $6,8\ \text{g}\cdot\text{m}^{-2}$ has shown the filtration efficiency of 99,9% for MPPS (maximum particle penetration size) of 100 nm and pressure drop of 90 Pa, which corresponds to a quality factor of about $qF = 51\ \text{kPa}^{-1}$. The filtration properties of the materials with such space structure outperform the potency of the planar nanofibre materials.

Example 2

All the conditions have been the same as in Example 1, only the experimental equipment manufactured by SPUR a.s. is equipped with spinning nozzles instead of rotating cotton cord electrode.

Example 3

Organized space nanostructures based on nanofibres and globular spacers have been prepared from highly elastic polyurethanes as well – combination of two or more polyurethanes with different distribution of molar weight, when at least one of them forms fine fibres and, at least one of them forms rather spheres or drop-like spacers under given electrospinning conditions. The polyurethane solution contains dimethylformamide as solvent. Polyurethane (PU 918) was synthesized using 4,4'-methylene-bis(phenylisocyanate) (MDI), poly(3-methyl-1,5-pentanediol)-alt-(adip, isophthalic acid) (PAIM) and 1,4 butandiol (BD) in molar ratio of 9:1:8. Synthesis took place at 90°C and lasted 5 hours (per partes synthesis method, when the prepolymer of MDI and PAIM is prepared in the first step and, subsequently, BD and the remaining amount of MDI are added). Density of PU 918 was $\rho = 1,1 \text{ g.cm}^{-3}$. Such prepared solution has been mixed with polyurethane solution in dimethylformamide, synthesized from MDI : polyester diol : chain extender in molar ratio of 4:1:3 (density $\rho = 1,05 \text{ g.cm}^{-3}$) eventually in a molar ratio of 3:1:2 (density $\rho = 1,04 \text{ g.cm}^{-3}$). The prepared mixtures with solid content of 10,5 - 19 wt. % and viscosity of 0,35 - 2,7 Pa.s has generated (under electrospinning conditions from Example 1) required organized space structures. These materials have shown the same filtration efficiency as nanostructures without globular distance spacers but substantially lower pressure drop.

Example 4

Another space structure has been prepared by electrospinning using PU 918, synthesized in accordance with Example 3 and solved in a mixture of solvents dimethylformamide and tetrachlorethane in ratio of 98,5:1,5 by weight. The processing conditions was: solution concentration = 12,5%, voltage = 55 kV, distance of electrodes = 21 cm, electrical conductivity of solution = 16,5 $\mu\text{S/cm}$.

Such space arrangement has shown an increase of filtration efficiency in the area of ultrafine particles from 90,4% to 97,8% for MPPS 70 nm keeping the same pressure drop of 100 Pa in comparison with a planar arrangement.

Example 5

Space structure has been prepared by ellectrospinning at conditions of Example 1. The solution of PU 918 in dimethylformamide containing 1,5 wt. % of jet milled nanoclay has been used. In comparison with the planar arrangement, the space one shows an increase in quality factor of the filtration material to more than doubled values at the same pressure drop of 80 Pa (measured by Lorenz equipment, adjusted in accordance with EN 143).

Example 6

Conditions of Example 6 have been the same as of Example 5 but instead of polyurethane solution the solution of copolymer ethylene-vinylacetate (EVA) in the solvents mixture toluene/tetrachlorethane in ratio 3:1 by weight has been used.

Example 7

All the conditions have been the same as in Example 5 but instead of nanoclay nanoparticles of titanium dioxide with an average diameter of 60 nm have been used.

Example 8

All the conditions have been the same as in Example 5 but instead of nanoclay nanoparticles of silver with an average diameter of 45 nm have been used.

Example 9

All the conditions have been the same as in Example 5 but instead of nanoclay agglomerates of zinc phtalocyanine (COC, Rybitví, Czech Republic) with an average diameter of 180 nm have been used.

Example 10

All the conditions have been the same as in Example 5 but the used nanoclay have been surface treated by chlorhexidine.

Example 11

All the conditions have been the same as in Example 5 but the used nanoclay have been modified by zinc dioxide.

Example 12

The example of nanofibre structure based on fibres with a broad distribution of diameters of rigid polymers with high modulus of elasticity composed with mechanically maintained distances in the organized space morphological arrangements may be characterized by following conditions of preparation and end-use properties:

- a) spinning solution: There have been prepared the solution of polymethylmethacrylate (PMMA, Altuglas V 046, Altuglas International, La Garenne-Colombes cedex, France) with density $\rho = 1,18 \text{ g.cm}^{-3}$ in a mixture of solvents – dimethylformamide and toluene – in the ratio of 1:1 by weight. The concentration of polymer solution was 20 wt. %, viscosity 0,11 Pa.s and conductivity $1,3 \mu\text{S.cm}^{-1}$.
- b) the electrospinning conditions and the characterization of prepared nanostructures were similar as in Example 1.
- c) Penetration (measured in accordance with EN 143) of nanoparticles of diameter 450 nm through such space structure with a broad distribution of fibre diameters having area mass of $6,92 \text{ g.m}^{-2}$ was 1,095%. The pressure drop was of 45 Pa, which corresponds to a quality factor $qF = 181 \text{ kPa}^{-1}$.

The material has shown the filtration efficiency of 97,52% for MPPS (maximum particle penetration size) of 50 nm and pressure drop of 48 Pa, which corresponds to a quality factor of about $qF = 77 \text{ kPa}^{-1}$. The filtration properties of the materials with such space structure and a broad distribution of fibre diameters outperform the potency of the planar nanofibre materials as well.

Example 13

Another space structure based on fibres with a broad distribution of diameters of rigid polymers with high moduli of elasticity has been prepared from 20% solution of polyethersulphone in dimethylformamide (Ultrason, BASF, Germany) with viscosity of 0,84 Pa.s, and electric conductivity of $159 \mu\text{S}\cdot\text{cm}^{-1}$ using SPUR's jet electrostatic spinning equipment.

Conditions of electrospinning process: Voltage $U = 75 \text{ kV}$, distance of electrodes $D = 21 \text{ cm}$, electrode rotation speed = 7 rpm, relative humidity = 25%, temperature = 28°C , shift velocity of the collecting substrate (viscose nonwoven fabrics) = 14 cm/min.

Example 14

All the conditions have been the same as in Example 12 only polyvinylidenefluoride (PVDF, Kynar 451, Arkema, PA, USA) has been used instead of polymethylmetacrylate.

Example 15

All the conditions have been the same as in Example 12 but the copolymer of styrene-acrylonitrile (SAN, Luran HH-120 Natural, BASF, Germany) solved in dimethylformamide has been used for preparation of the space structure with a broad distribution of fibre diameters.

Example 16

The space structure with a broad distribution of fibre diameters on the base of bicomponent fibre has been prepared from copolymer styrene-acrylonitrile (SAN- Luran) and PU 918 in a solvent system dimethylformamide/toluene. The prepared nanostructure has shown, in addition to the required filtration properties, also substantially better mechanical properties due to the use of elastic polyurethane.

Example 17

The solution of polyamide 11 (PA11, Rilsan D, Arkema, Great Britain) and PU 918 (2–5 wt. % in dry residue of PA11) in a mixture of solvents trifluoroacetic acid/dimethylformamide in the ratio of 92-99 : 1-8 has been used for the preparation of the

voluminous structure with a broad distribution of fibre diameters. While PA11 alone has formed under electrospinning conditions of Example 1 planar nanostructures, together with a small amount of polyurethane, an organized space structure has been formed that has shown a more than doubled enhancement of the quality factor in comparison with the planar structure at the same pressure drop.

Example 18

The space structure formed by combination of microfibres and nanofibres has been prepared using the SPUR's electrospinning equipment with four rows of nozzles. The solution of polymethylmetacrylate in mixture of solvents dimethylformamide/toluene in the ratio of 1:1 generating microfibers has been dosed into the first and third rows of nozzles. The solution of polyurethane in dimethylformamide generating nanofibres has been dosed in the second and fourth rows of nozzles. The electric conductivity of PU solution has been adjusted by borax and citric acid to the value about $150 \mu\text{S}\cdot\text{cm}^{-1}$.

The electrospinning conditions have been identical to those of Example 1.

Example 19

All the conditions have been the same as in Example 16, only copolymer of styrene-acrylonitrile (SAN) has been used instead of polymethylmetacrylate.

Example 20

All the conditions have been the same as in Example 16, only polyvinylidenefluoride (PVDF) has been used instead of polymethylmetacrylate.

Example 21

All the conditions have been the same as in Example 16, only the polyurethane with a high content of hard segments which is able under given electrospinning conditions produce microfibers has been used instead of polymethylmetacrylate.

Example 22

All the conditions have been the same as in Examples 18 - 21 but the process has been realized using SPUR's equipment equipped by only one row of nozzles instead of four rows of nozzles. The solutions have been dosed alternately to individual nozzles.

P A T E N T C L A I M S

1. The morphologically optimized nonwoven textiles on the basis of nanofibres showing in particular an increased filtration effect characterized by the fact that they include nanofibre structure with morphologically separated nanofibres, as:
 - a) nanofibre structure with nanofibres physically separated by drop-like spacers and/or nanoparticles dispersed within the nanostructure that form regular structures with drop-like spacers and/or nanoparticles dispersed within the nanostructure, cumulated in columns interconnected by nanofibres into regular morphological arrangements,
 - b) nanofibre structure with nanofibres physically separated by drop-like spacers and/or nanoparticles dispersed within the nanostructure that form regular structures with drop-like spacers and/or nanoparticles dispersed within the nanostructure,
 - c) nanofibre structure based on fibres with a broad distribution of diameters made of rigid polymers with high modulus of elasticity composed with mechanically maintained distances in the organized space morphological arrangements,and/or
 - d) structure with bimodal distribution of fibre diameters based on combination of micro- and nanofibres forming space morphological arrangements.
2. The morphologically optimized nonwoven textiles in accordance with claim 1 characterized by the fact that they contain polycarbonate nanofibre structure with nanofibres physically separated by drop-like spacers forming regular structures with drop-like spacers cumulated in columns interconnected by nanofibres into regular morphological arrangements similar to honey combs is nanofibre structure that may be prepared by the electrospinning technology from a spinning solution of polycarbonate in tetrachlorethane containing an addition of chloroform and borax.
3. The morphologically optimized nonwoven textiles in accordance with claim 1 characterized by the fact that they contain polyurethane nanofibre structure with

nanofibres physically separated by drop-like spacers and/or nanoparticles dispersed in the nanostructure forming regular structures with drop-like spacers cumulated in columns interconnected by nanofibres into regular morphological arrangements similar to honey combs is with an advantage polycarbonate nanofibre structure that may be prepared by the electrospinning technology from a spinning solution of polyurethane in dimethylformamide or in a mixture of dimethylformamide and tetrachlorethane.

4. The morphologically optimized nonwoven textiles in accordance with claim 3 characterized by the fact that the nanoparticles dispersed in the nanostructure are nanoparticles selected from the group comprising nanoparticles of titanium dioxide, zinc dioxide, silver, phtalocyanine agglomerates, exfoliated clay and jet milled clay, while these clays are eventually modified by substances with biocidal effect, in particular by chlorhexidine.
5. The morphologically optimized nonwoven textiles in accordance with claim 1 characterized by the fact that they contain polyurethane nanofibre structure with nanofibres physically separated by drop-like spacers forming irregular structures with drop-like spacers that may be prepared by the electrospinning technology from a spinning solution of two types of polyurethanes with different average molar weight and/or one rigid polyurethane with a contents of hard segments at least 44 wt. %.
6. The morphologically optimized nonwoven textiles in accordance with claim 1 characterized by the fact that they contain polymeric nanofibre structure with nanofibres physically separated by nanoparticles dispersed in the nanostructure forming irregular structures with spacers.
7. The morphologically optimized nonwoven textiles in accordance with claim 6 characterized by the fact that the nanoparticles dispersed in the nanostructure are nanoparticles selected from the group comprising nanoparticles of titanium dioxide, zinc dioxide, silver, phtalocyanine agglomerates, exfoliated clay and jet milled clay, eventually modified by chlorhexidine.

8. The morphologically optimized nonwoven textiles in accordance with claim 1 characterized by the fact that they contain polymeric nanofibre structure based on fibres with a broad distribution of diameters made of rigid polymers with a high modulus of elasticity, as polyethersulphone, polymethylmethacrylate, copolymer styrene – acrylonitrile and polyurethane with a high contents of hard segments organized with mechanically maintained distances in voluminous morphological arrangements.
9. The morphologically optimized nonwoven textiles in accordance with claim 1 characterized by the fact that they contain structure with bimodal distribution of diameters of fibres based on combination of microfibers made of rigid polymers and polymeric nanofibres forming voluminous morphological arrangements, while this structure may be prepared by a parallel or subsequent spinning of the spinning solutions of microfibers and nanofibres.

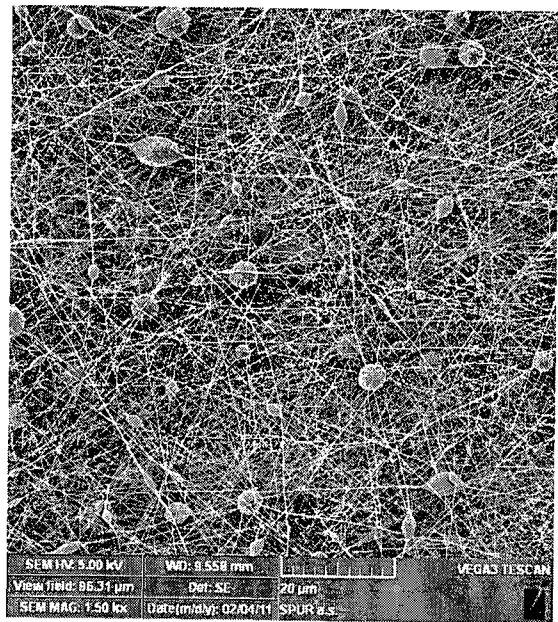


Fig. 1

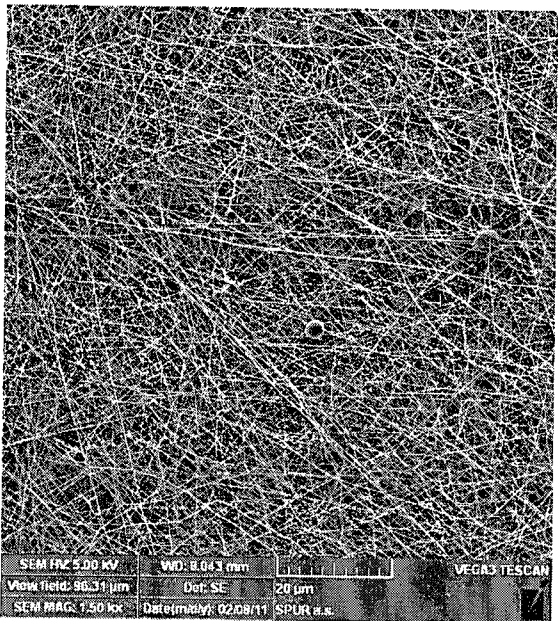


Fig. 2

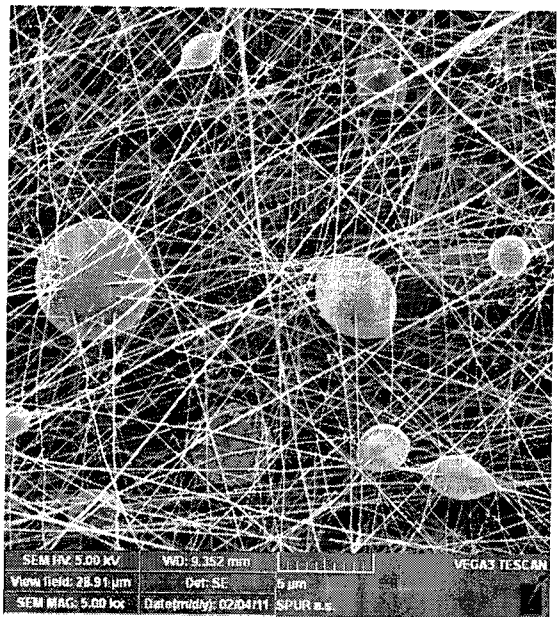


Fig. 3

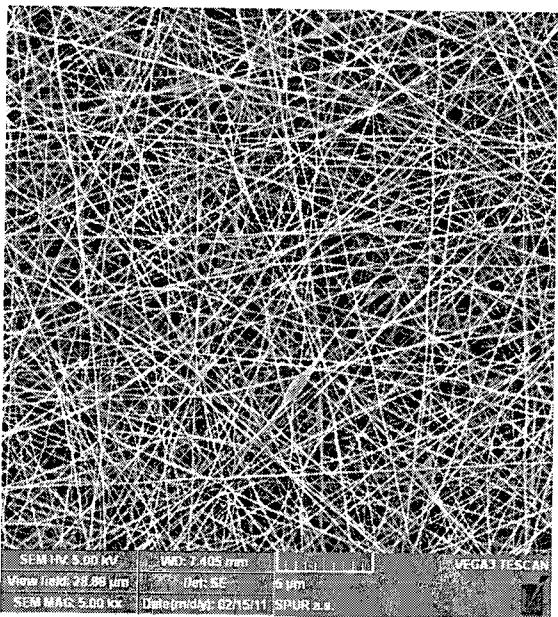


Fig. 4

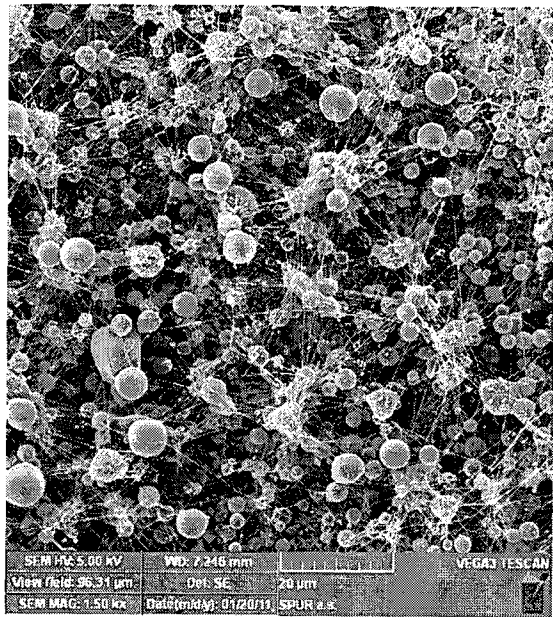


Fig. 5

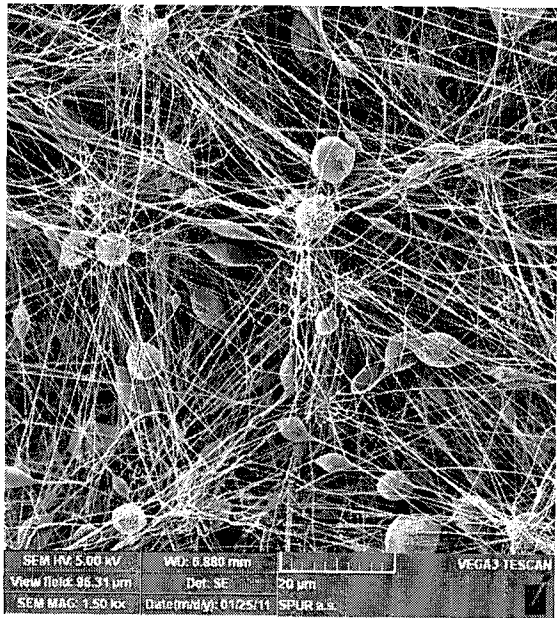


Fig. 6

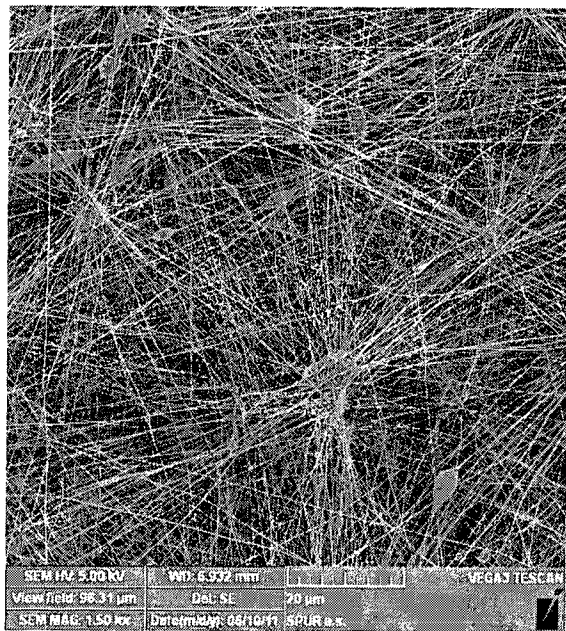


Fig. 7

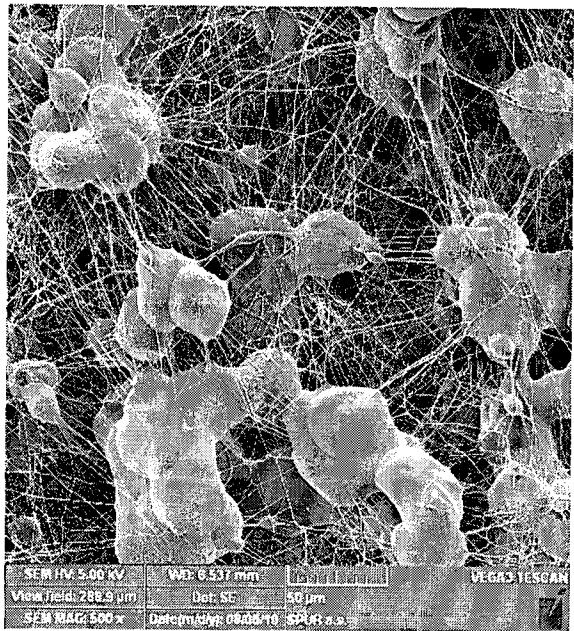
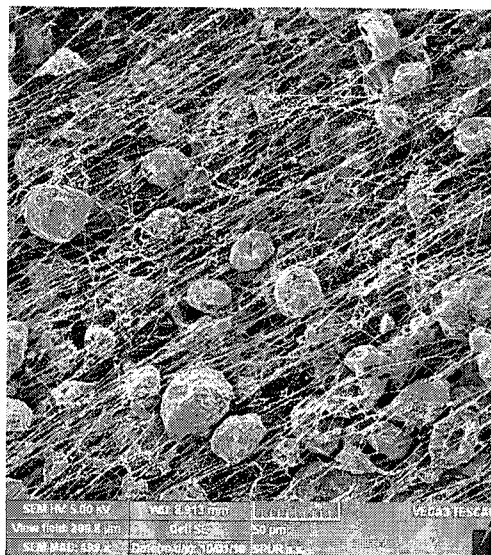
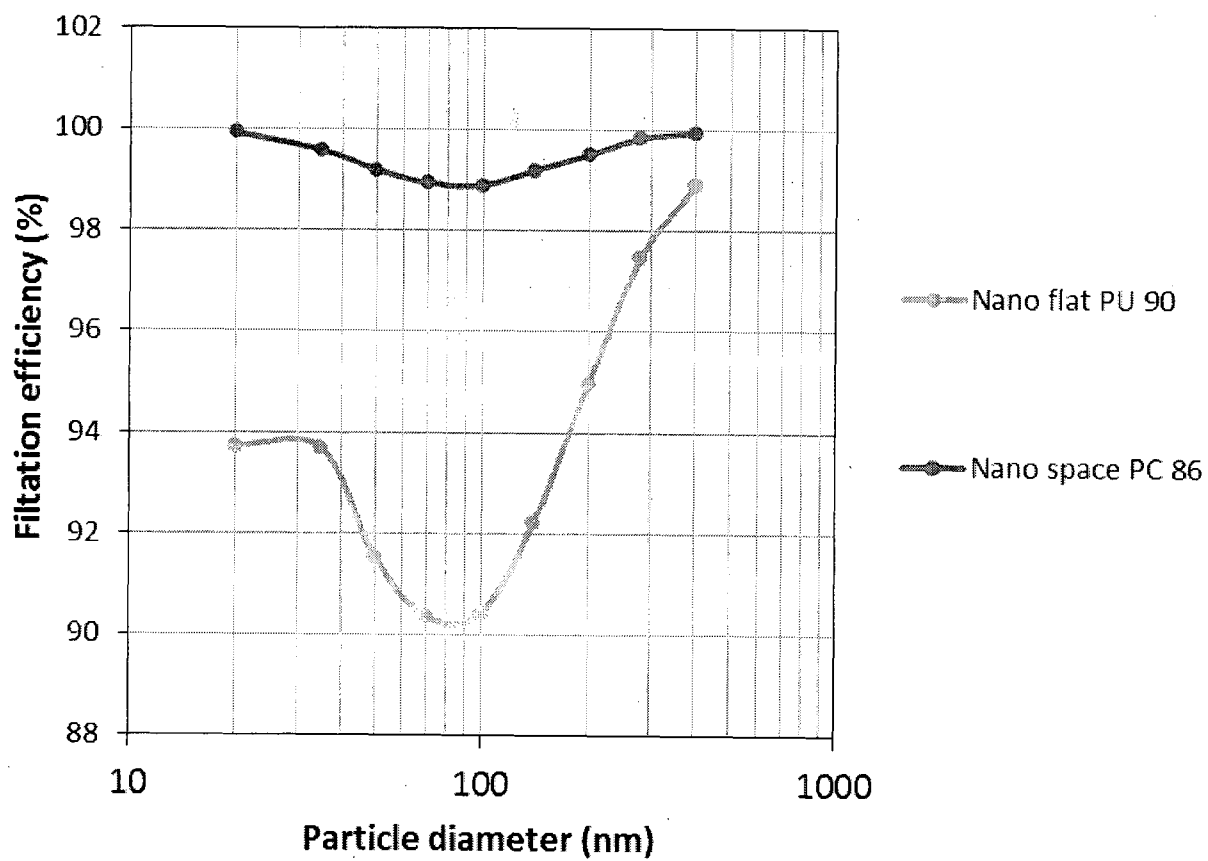


Fig. 8

**Fig. 9****Obr. 10**

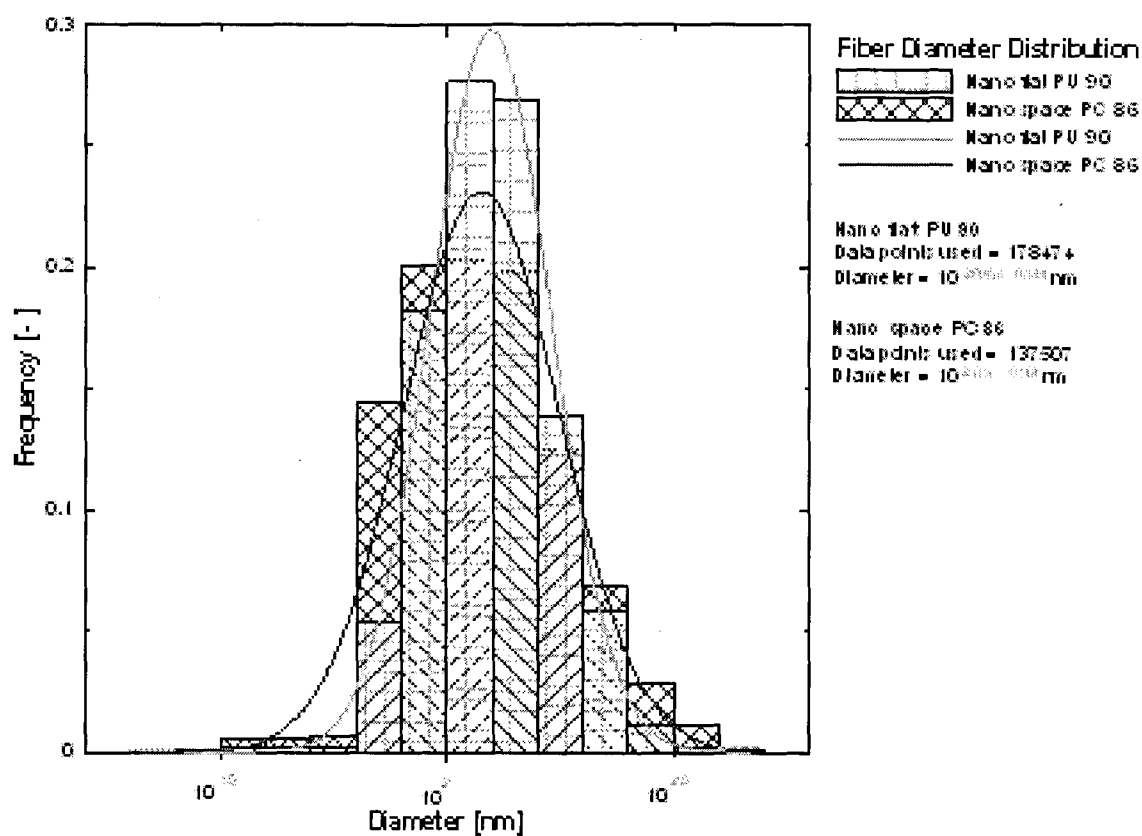


Fig. 11

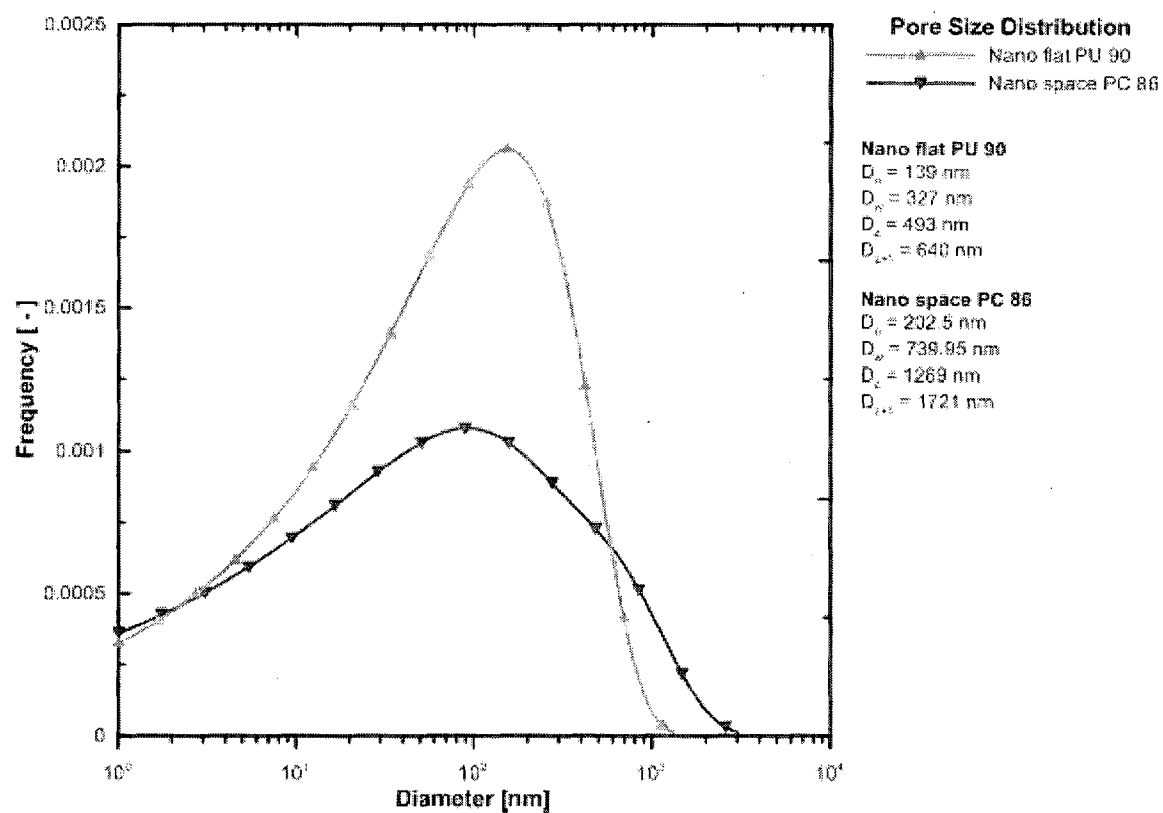
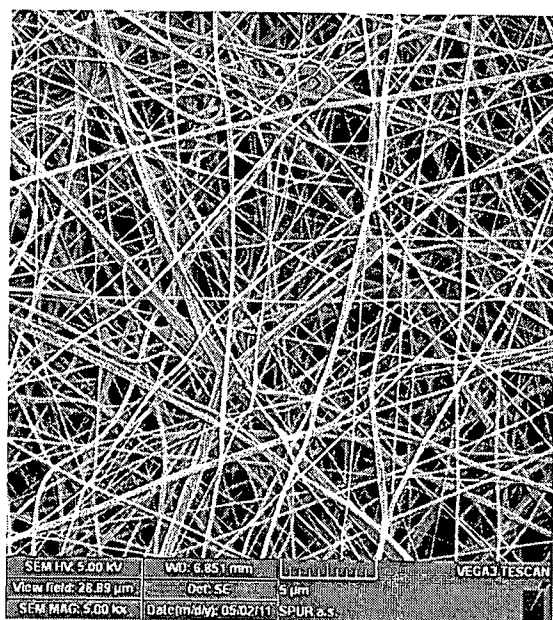
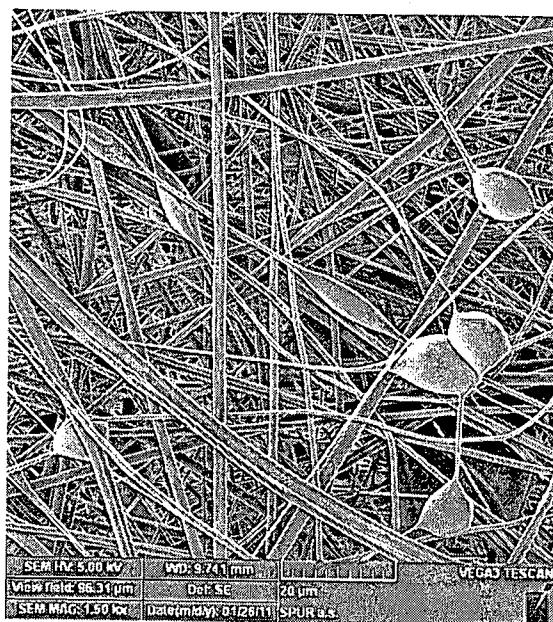
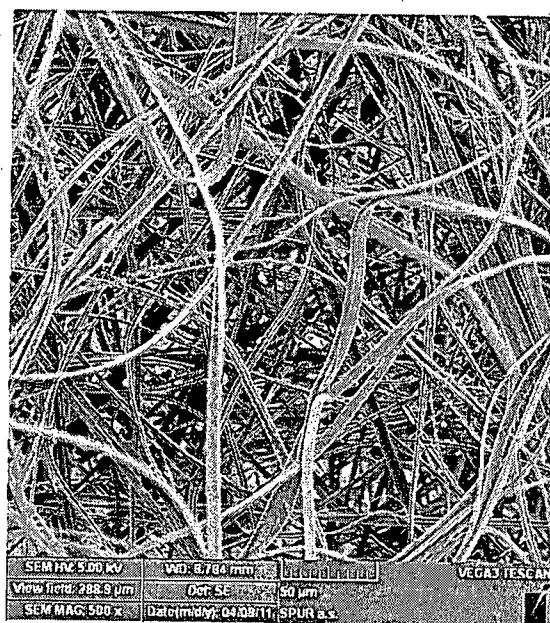
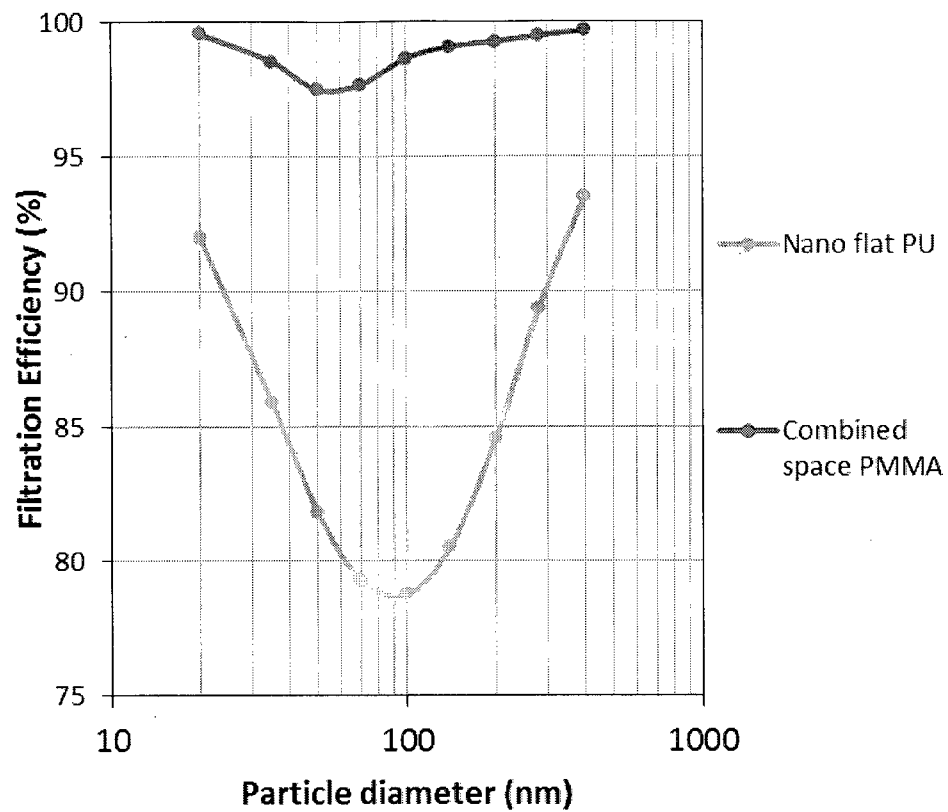
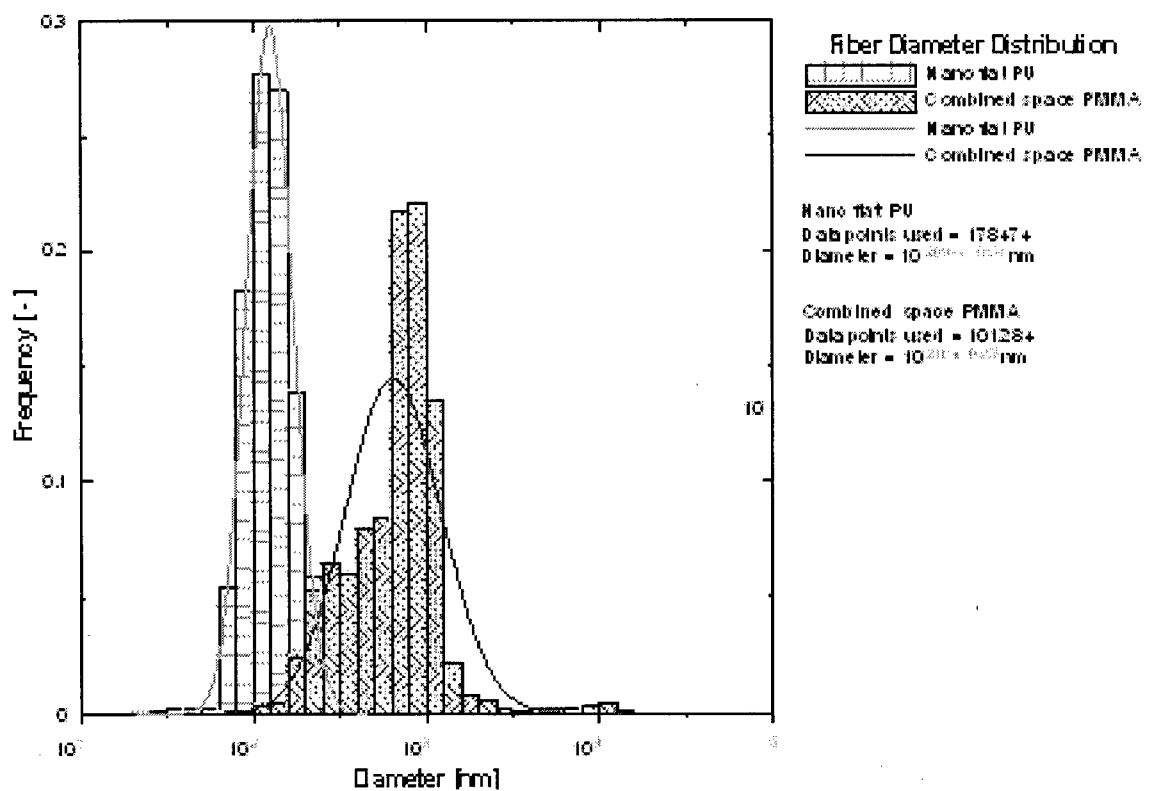
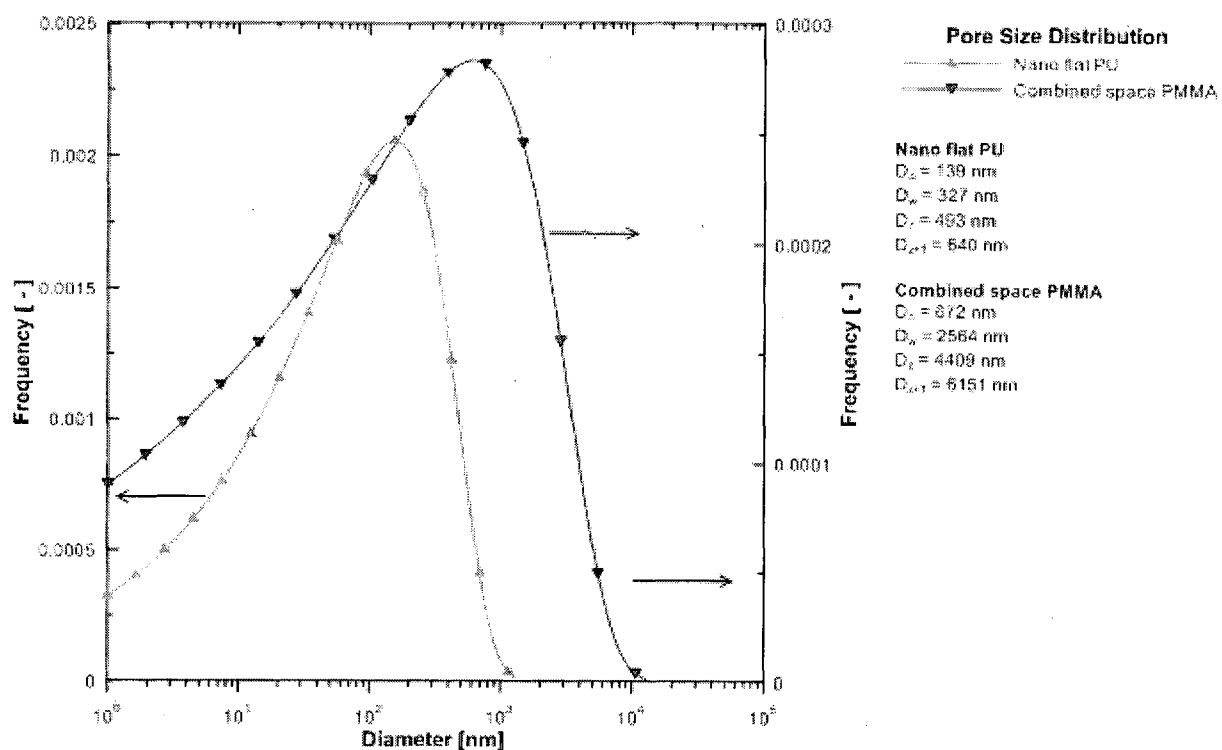


Fig. 12

**Fig. 13****Fig. 14****Fig. 15**

**Fig. 16****Fig. 17**

**Fig. 18****Fig. 19**