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(54) High performance electrospun nanofibers from polyaniline/polyamide

(57) The invention relates to a method of producing a electrospun conductive polymer fibre by coating a non-conductive polymer fibre with conductive polymer. This can be done by a batch or a continuous process.

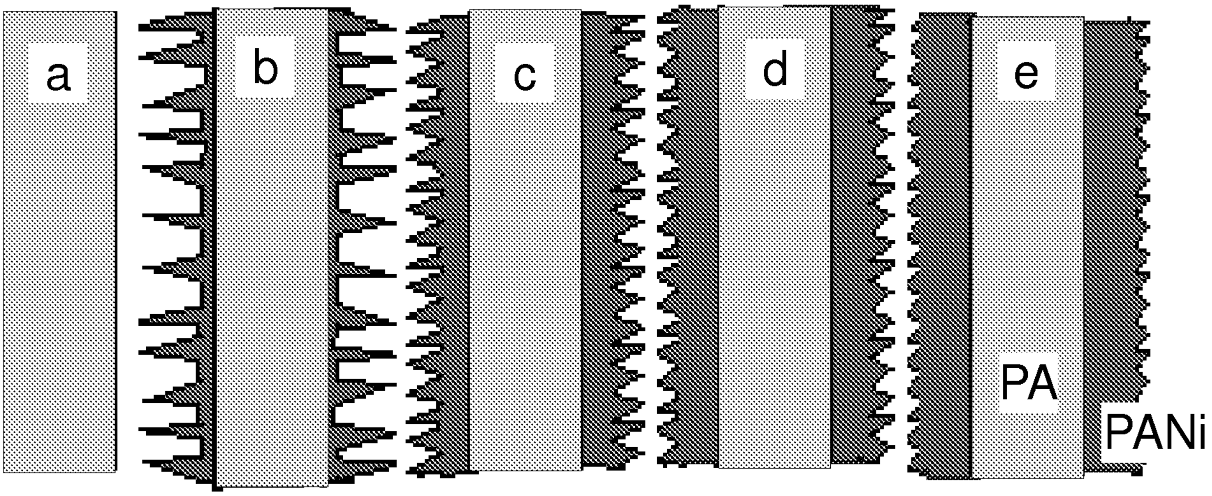

Fig8. Schematic diagram of PA/PANi core/shell fiber model grown from different aniline concentration, a)0M, b)0.02M, c)0.04M - 0.08M, d)0.16M, e) 0.32M, f)0.64M

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Description

Introduction

[0001] Electrospun nanofibers have attracted great attention recently, due to its small diameter and long length. The non-woven from these micro or nanometer fibers showed high specific surface area and porousity and can be applied for diverse applications in a wide range area, which was summarized in recent reviews[1]. For different applications require special properties, such as conductivity, mechanical, biocompatible, thermal, optical and surface properties etc. in case of special application, it had to sacrifice other properties for sake of functional properties, for example, the highly rough surface electrospun nanofibers had to sacrifice its mechanical properties.

[0002] Herein, we introduce an extremely simply method to produce high performance electrospun nanofibers combined high electrical conductivity and specific surface area, good mechanical and thermal properties, excellent biocompatibility. Conducting nano-fibrillar PANi was successfully grown on the surface of electrospun polyamide (PA) nanofibers to form a core/shell structure by simple chemical oxidative polymerization for the first time. The green color of uniform nanofiber non-woven demonstrated that it is in the highly conductive emeraldine salt state (Fig1).Electrospun nanofibers with electrical conductivity of 84.7 $S.cm^{-1}$ (vs. measuring thickness) were obtained, which outperformed conducting electrospun nanofibers produced by directly electrospinning of blends containing high molecular weight polymer and conducting polymer or carbon nanotubes[2-4], by adsorption of carbon nanotube on electrospun nanofibers[5], and by vapor phase deposition/polymerization of conducting polymer on electrospun nanofibers[6].

[0003] It was well known that polyaniline (PANi) is unique among the family of conducting polymer, due to the simple way of synthesis, environment stability, reversible doping/de-doping chemistry. [7, 21] Nanostructured PANi, especially nano-fibrillar PANi has received growing interest in recent year [8-13]. There are several approaches to make nano-fibrillar PANi, for example, chemical oxidative polymerization, including interfacial polymerization[14], nanofiber seeding[11], oligomer-assisted polymerization[15], surfactant-assisted polymerization[16] and non-template polymerization[17, 18], electrochemical polymerization and electrospinning. It is being or potential for many applications such as electrode in batteries and supercapacitors[19, 20], sensors[14], actuators, catalysis, electromagnetic shielding, antistatic coating, corrosion protection, separation membranes, electro-optic and electrochromic decices[21].

[0004] Polymerization of aniline is particular prone to fibrillar polymer growth. [10, 13, 22] It was shown in one report that nano-fibrillar PANi was obtained when the oxidant and aniline was mixed rapidly, while granular PANi was got when oxidant was added drop-wise[13]. It has recently reported that nano-fibrillar PANi was able to grow on normal substrates during dilute chemical[9]or electrochemical[23] polymerization. In this work, uniform nano-fibrillar PANi was grown on the electrospun nanofibers for the first time by simple chemical oxidataive polymerization to make high performance electrospun nanofibers. These findings combined the advantages of electrospinning technique and functional properties of polyaniline. The intrinsic properties of PANi contribute the highly electrical conductivity and good biocompatibility[3] to the composite nanofibers. The electrospun PA nanofiber showed good mechanical properties and serve as ideal substrate for growth of nano-fibrillar PANi to make high strength nanofiber non-wovens. The intrinsic nano-fibrillar morphology of PANi grown uniformly onto the smooth surface of PA electrospun nanofibers and showed toothed club shape. This made the composite nanofibers possessed more than two times specific surface area as that of pure PA nanofibers and pure PANi nanowires. The both materials showed good thermal properties. These made the PA / PANi composite nanofibers possessed more than five excellent properties together.

[0005] There are other polymers possible. As a monomer acetylene, benzene, naphthalene. pyrrole, aniline, thiophene, phenylene sulphide, naphthalene and others, and their derivatives,such as sulphoaniline, ethylene dioxythiophene, thienothiophene and others, and their alkyl or alkoxy derivatives or derivatives with other side groups, such as sulphonate,phenyl and other side groups are useable. Combinations of the above named monomers can also be used as a monomer to form polymers or copolymers. All of them showing as a polymer a conjugated electron system and can be put in a ionic form by oxidation (iodine, peroxides, Lewis and proton acids), by reduction (sodium. Potassium, Calcium) or by protonation. The ionic form shows a conductive effect.

[0006] Examples of intrinsically conductive polymers according to the invention are those named at the beginning of this description. There can be named in particular as examples: polyaniline (PANi), polythiophene (Pth), poly(3,4-ethylenedioxythiophene) (PEDT), polydiacetylene, poly-acetylene (PAc), polypyrrole (Ppy), polyisothianaphthene(PITN), polyheteroarylenevinylene (PArV), wherein the heteroarylene group can be e.g. thiophene, furan or pyrrole, poly-p-phenylene (PpP), polyphenylene sulfide (PPS),polyperinaphthalene (PPN), polyphthalocyanin (PPc), among others, as well as their derivatives (which are formed e.g. from monomers substituted with side chains or groups), their copolymers and their physical mixtures. Polyaniline(PANi), Polythiophene (PTh), poly(3,4-ethylenediox-ythiophene) (PEDT), polythienothiophene (PTT) and their derivatives are particularly preferred. Polyaniline is most preferred.

[0007] The non-conductive polymers can be any polymer which may be electrospinnable. For example polyamide (PA), polymethylmetacrylate (PMMA), polylactide, polyurethane, poly-p-xylylene, polyvinylidenhalogenide, polyester, polyolefine, polyether, polycarbonate,natural polymers, polycarbonacids, polysufonacids, sulfated polysaccharids, polyglycosids, polyacrylnitrile, polymethacrylnitrile, polyacrylamide, polyimide, polyphenylene, polysilane, polysiloxane, polybenzimidazole, polybenzothiazole, polyoxazole, polysufide, polyesteramide, polyarylenvinylene, polyetherketone, polysulfone, silicone, poly(alkyl)acrylate, poly(alkyl) methacrylate, polyhydroxyethylmethacrylate, polyvinylacetate, polyvinylbutyrate, polyisoprene, polytetrafluoroethylen, natural or synthetic rubber, polyvinylalcohols, polyalkylenoxide, poly-N-vinylpyrrolidon,cellulose and combinations of these polymers as copolymers or blockpolymers.

[0008] The invention comprises a continuous process for the coating of the electrospun fibre. After the electrospun process the fibre will be guided into a solution with aniline and an acid (hydrochlorid acid - HCl) and afterwards in a separate solution with ammonium peroxydisulfate in HCl. The reaction process of the two solutions occur directly on the electrospun fibre and results in a conductive coating of the electrospun fibre. A better way is spraying or rinsing the two solutions onto the polymer fibre. In this case the solutions can be mixed before.

[0009] Instead of Hydrochloric acid also inorganic acids (e.g. sulfuric acid H2SO4), organic acids (e.g. HCOOH) are Useable. Instead ofAmmonium-peroxydisulfat also ferric chloride is useable.

[0010] The electrospun polymerfibre have diameters from 20,50,80,100,150,180,210,300,500,700,1000 to 20000 nm.

[0011] If the conductive polymer consists of fibres, they have a diameter from 10, 20 to 50 nm. It is tightly attached to the electrospun polymerfibre.

Experimental

Electrospinning

[0012] Polyamide B24 from BASF was dissolved in $CH_3COOH/HCOOH$ (weight ratio of 2/1) mixed solvents to form a uniform solution with weight concentration of 20%. The electrospinning of polyamide B24 was carried out under high voltage electrical field of 166kV/m from a positive voltage of +25kV and negative of 0kV with distance of 15cm. The formed nanofibers were collected of non-aligned non-woven by a drum with low rotated speed of 0.5m/s and of highly aligned belts by a disc with flat rim of 10mm with high collecting speed of 15m/s. All nanofiber samples were dried under vacuum at 50°C.

Growth of nano-fibrillar PANi on electrospun polyimide nanofibers

[0013] Aniline was purified by distillation under reduced pressure. Other chemicals were of analytical grade and used as received. Reactions were carried out in 80ml beaker. Typically, an aqueous solution of aniline in 20ml 1M HCl doping acid and another solution of ammonium peroxydisulfate in 20ml the same doping acid as oxidant were prepared. Rapidly mixed the two solutions by pouring them together and immediately stirred or shook to ensure sufficient mixing before polymerization begins. The mol ratio of aniline/oxidant was 4/1. Then stopped stirring or shaking and put nanofiber mats into the mixed solution. After reaction, the nanofibers were washed three times using distilled water and dried under vacuum at 50°C for further characterization.

Characterization

[0014] The morphology of composite nanofibers was characterized by JSM-7500 Scanning Electron Microscopy (SEM). The structure and crystallinity of PANi was characterized by FTIR (DIGLAB Excalibur series) and XRD (SIEMENS Diffraktometer D5000). The electrical conductivities of composite nanofber non-wovens were calculated from their resistances which were measured by four probe method using Keithley 2000 multimeter at room temperature. The mechanical properties of nanofiber non-wovens and belts were measured by Zwick/ Roll with stretch model, stretching speed was $20mm.min^{-1}$. The thickness determined by two ways, one was calculated from weight and density following ref [24] which called calculating thickness δ_c, another was measured by micrometer (Mitutoyo-MDC-25M), which called measuring thickness δ_m.

[0015] The mechanical properties data were reported using calculation thickness δ_c, the conductivity data were reported using two kinds thickness for comparison. Samples used for the XRD measurements were highly aligned belt form, while for FTIR and conductivity measurements were non-aligned non-woven form.

Results and discussion

Growth of nano-fibrillar PANi on PA electrospun nanofibers

[0016] Polyaniline in highly conductive emeraldine salt state (green color) was able to get easily in aqueous solution with presence of oxidant and doping acid. Nanofibrillar PANi with diameter of 35nm was obtained when the oxidant and aniline solutions mixed rapidly (Fig2B). Previous reports showed that nano-fibrillar PANi was able to grown on normal macroscopic substrate, such as metals, glasses, polymer films by during dilute electrochemical[23] or chemical[9] polymerization. Here, we investigated the growth of nano-fibrillar PANi on microscopic substrates. The good mechanical properties PA electrospun nanofiber was chosen as the microscopic substrate. When a piece of PA electrospun non-woven was quickly put into the rapidly mixed solution, after the solution became dark green, the white PA non-woven also turned to green color. It was found by SEM that the smooth surface of PA nanofibers (Fig2A) was uniformly covered by a layer of PANi nanowires showed toothed club morphology. SEM image of broken composite nanofiber was showed in Fig2C which nicely illustrate that the composite nanofibers exhibit core/shell structure.

FTIR analysis

[0017] Polymerized from the aniline monomer, polyaniline can be found in different oxidation states. Emeraldine (EM) base is regarded as the most useful form of polyaniline due to its high stability at room temperature and the fact that upon doping the emeraldine salt form of polyaniline is electrically conducting. The FTIR spectra of PA nanofibers, PA/PANi composite nanofibers and PANi powder were shown in Fig3. For the PA/PANi composite nanofibers (Fig3B), the absorption at 3291 cm^{-1} is attributed to N-H stretch mode, in the case of protonated base EM, it showed long absorption tail from above 2000 cm^{-1}. While the C=C and C-C stretching and bending mode for the quinonoid unit occur at 1338 and 1307 cm^{-1}, for the benzenoid unit at 1150 cm^{-1} which have been associated with high electrical conductivity[7].

Morphology, fiber diameter, content of PANi in composite nanofibers

[0018] The properties of composite nanofibers obtained from different aniline concentration were summarized in table1. The color differences of composite nanofibers formed at different aniline concentration are noteworthy, as shown in Fig4, the color changed from light green (Fig4A), green (Fig4B, C), dark green (Fig4D), to black (Fig4E, F). The morphology of PA/PANi composite nanofiber also displayed greatly different, as shown in Fig5. The nano-PANi grown in low aniline concentration solution displayed a thin PANi layer and long nano-fibrillar PANi, while in high aniline concentration tend to form a thick PANi layer with short nano-fibrillar PANi nanofibers, which also could find proof from increase of PANi content and fiber diameter with increasing aniline concentration. Fig6 showed that the weight percent of PANi in the composite nanofibers was increased with increasing aniline concentration, as well as the nanofiber diameter (Fig7). Based on the results reported a schematic explanations of PANi grown on PA nanofiber at different aniline concentration is suggested in Fig8. At dilute aniline solution (0.02M), the polymerization speed was low, the solution became dark green after about 30min, the PANi tended to grow as intrinsic fibrillar shape [10, 25] and formed long length but sparse PANi wires (Fig5A, Fig8A), the PANi layer on the PA nanofiber was very thin about 30nm calculated from the diameter data. Increasing aniline concentration, the reaction speed accelerated and reaction time decreased, the secondary growth of PANi happened, the length PANi nanowire shortened and thickness of PANi layer increased (Fig 5B, C, D, E, F and Fig 8B, C, D, E, F). So, the fiber diameter and PANi content increased, from 230 nm to 448nm and from 2.51% to 19.11%, respectively.

Surface area

[0019] The fibrillar shape PANi grown on PA6 nanofibers led to a very rough fiber surface and showed high specific surface area, the specific surface area vs. aniline concentration was shown in Fig9. The surface area increased with increment of aniline concentration and was up to maximum of 160.08 m^2/g which was obtained from 0.16M aniline solution, which was more than twice as that of pure PA nanofibers (80.2 m^2/g) and pure PANi powder (60.89 m^2/g) formed by its nanowires. The reason was that the content of PANi nanowires on the PA fibers was increased with increase of aniline concentration. But, further increase of aniline concentration would cause decrease of specific surface area due to the PANi nanowires became short (Fig5b, c, d, e), even vanished at very high aniline concentration of 0.64M (Fig5f), it formed a thick PANi layer.

Crystallinity and electrical properties of composite nanofibers

[0020] The both materials PA and PANi are crystalline polymers, their XRD spectra were shown in Fig10A, C, respectively. The XRD pattern of PA aligned nanofiber belt showed two peaks at $2\theta \sim 9.5°$, 22°, while the HCl doped PANi power showed 4 peaks at $2\theta \sim 9.5°$, 15 °, 20.5 °, 25.7 °, which was consistent to previous report [26]. In the case of PA/PANi composite nanofiber Fig10B, four peaks were observed $2\theta \sim 9.5°$, 20.5 °, 22 °, 24 °, the peak at 20.5° was derived from PANi, the peak at 22° was attributed to PA nanofibers, while the peak at 24 ° might be formed by the overlay of peak 22 ° from PA aligned nanofibers and peak 25.7 ° from PANi. It demonstrated that the composite nanofibers crystalline.

[0021] The conductivity trend of composite nanofibers with different PANi content was shown in Fig11. Most papers used measuring thickness which was measured by micrometer, SEM, or thickness meter to report the conductivity of electrospun non-woven [2, 4-6]. But, the non-woven was composed of nanofibers and highly porous. So the thickness determined by measuring method was not real thickness, and it would change with change of porosity. So, here we introduced another thickness determining method, calculation by weight and density following ref[24], to evaluate the thickness of electrospun nanofiber non-woven. This thickness was same as the thickness of film pressed from the non-woven, which could be regarded as the "real" thickness of the non-woven. Meanwhile, measuring thickness was also used to compare the conductivity results with that reported in papers. Two kinds conductivities of composite non-woven were reported, σ_c (vs. calculating thickness) and σ_m (vs. measuring thickness), as shown in Fig11. The conductivity of composite nanofiber non-woven was increased with increment of PANi content. Because higher

PANi content, thicker PANi layer on PA nanofibers, led to higher conductivity. The maximum conductivity of composite non-woven was up to 84.27 S.cm^{-1} (vs. measuring thickness) and the "real" conductivity was got up to 308.8s.cm^{-1} (vs. calculating thickness).

Mechanical properties

[0022] The nano-PANI grown on the electrospun PA nanofibers shows a little effect on its mechanical properties, the mechanical properties data were listed in table2, the stress-strain curves were shown in Fig12. After growth of nano-PANi, the strength and modulus of non-aligned non-wovens showed a little improvement, the tensile strength increased from 77.5MPa of PA nanofiber non-woven to 82.88MPa of composite nanofiber non-woven and the modulus from 0.79GPa to 1.18GPa. While the strength of highly aligned belts increased greatly, from 113.61MPa of pure PA to 161.75MPa of composite nanofiber belts. The improvements on the mechanical properties of PA/PANi composite nanofibers were attributed to the nano-PANi which enhanced the connections between fibers, and the connections in belts were more than that of in non-wovens, see Fig. 5,13.

Thermal and biocompatibility property

[0023] The PA and PANi both are thermal stability polymers. The composite nanofibers from PA and PANi also shown good thermal property, the 5% weight loss temperature was over 400 °C, as shown in Fig 14.

[0024] More recently, there is a growing interest in conductive polymers for diverse biomedical applications. Polyaniline was one of most studied conducting polymer, it was also biocompatible and could be used for tissue engineering applications[3] and as anode in microbial fuel cells (MFCs)[27, 28]. In an upcoming communication we will investigate the electrochemical properties of this high performance electrospun non-woven as electrode in MFC.

Conclusion

[0025] A novel and simple method of preparation high performance electrospun nanofibers was developed. Nano-fibrillar PANi was successfully grown on electrospun PA nanofibers by normal oxided polymerization for the first time. It formed a core/shell structure with highly rough surface. It also was the first time to grow nano-fibrillar PANi on microscopic substrate by simple oxided polymerization.The resulted PA/PANi composite nanofibers possessed more than five good properties, high conductivity of 84.27 S.cm^{-1}, high specific surface area of 160 m^{2}.g^{-1}, good strength of 82.88MPa for non-wovens and 161.75MPa for highly aligned belts, good thermal properties with 5% weight loss temperature up to 415°C and excellent biocompatibility.

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[0026]

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Claims

1. Method for producing a conductive electrospun polymer fibre comprises an electrospun non-conductive polymer fibre which is afterwards coated with conducting polymer.

2. A method according to claim 1 comprises that the electrospinning and or the coating process are a continuous process.

3. A polymer fibre comprises a non-conductive polymer fibre with a coating of conductive polymer.

4. A polymer fibre according to claim 3 comprises that the conducting polymer consists of fibres.

5. A polymer according to claim 3,4 comprises that the conducting polymer have an diameter of 10 to 40 nm and the non-conducting polymer fibre have an diameter of 10 nm to 50 μm.

6. A polymer fibre according to claims 3 to 5 comprises a non-conductive polymer choosen from: polyamide (PA), polymethylmetacrylate (PMMA), polylactide, polyurethane, poly-p-xylylene, polyvinylidenhalogenide, polyester, polyolefine, polyether, polycarbonate,natural polymers, polycarbonacids, polysufonacids, sulfated polysaccharids, polyglycosids, polyacrylnitrile, polymethacrylnitrile, polyacrylamide, polyimide, polyphenylene, polysilane, polysiloxane, polybenzimidazole, polybenzothiazole, polyoxazole, polysufide, polyesteramide, polyarylenvinylene, polyetherketone, polysulfone, silicone, poly(alkyl)acrylate, poly(alkyl)methacrylate, polyhydroxyethylmethacrylate, polyvinylacetate, polyvinylbutyrate, polyisoprene, polytetrafluoroethylen, natural or synthetic rubber, polyvinylalcohols, polyalkylenoxide, poly-N-vinylpyrrolidon,cellulose and combinations of these polymers as copolymers or blockpolymers.

7. A polymer fibre according to claims 3 to 6 comprises a conductive polymer choosen from:

> polyaniline (PANi), polythiophene (Pth), poly (3,4-ethylenedioxythiophene) (PEDT), polydiacetylene, poly-acetylene (PAc), polypyrrole (Ppy), polyisothianaphthene(PITN), polyheteroarylenevinylene (ParV), wherein the heteroarylene group can be e.g. thiophene, furan or pyrrole, poly-p-phenylene (PpP), polyphenylene sulfide (PPS),polyperinaphthalene (PPN), polyphthalocyanin (PPc), among others, as well as their derivatives (which are formed e.g. from monomers substituted with side chains or groups), their copolymers and their physical mixtures. Polyaniline(PANi), Polythiophene (Pth), poly(3,4-ethylenediox-ythiophene) (PEDT), polythienothiophene (PTT) and their derivatives.

8. Use of a polymer according to claim 3 to 7 as an electrode in batteries and supercapacitors, sensors, actuators, catalysis, electromagnetic shielding, antistatic coating, corrosion protection, separation membranes, electro-optic and electrochromic decices.

Tables and figures

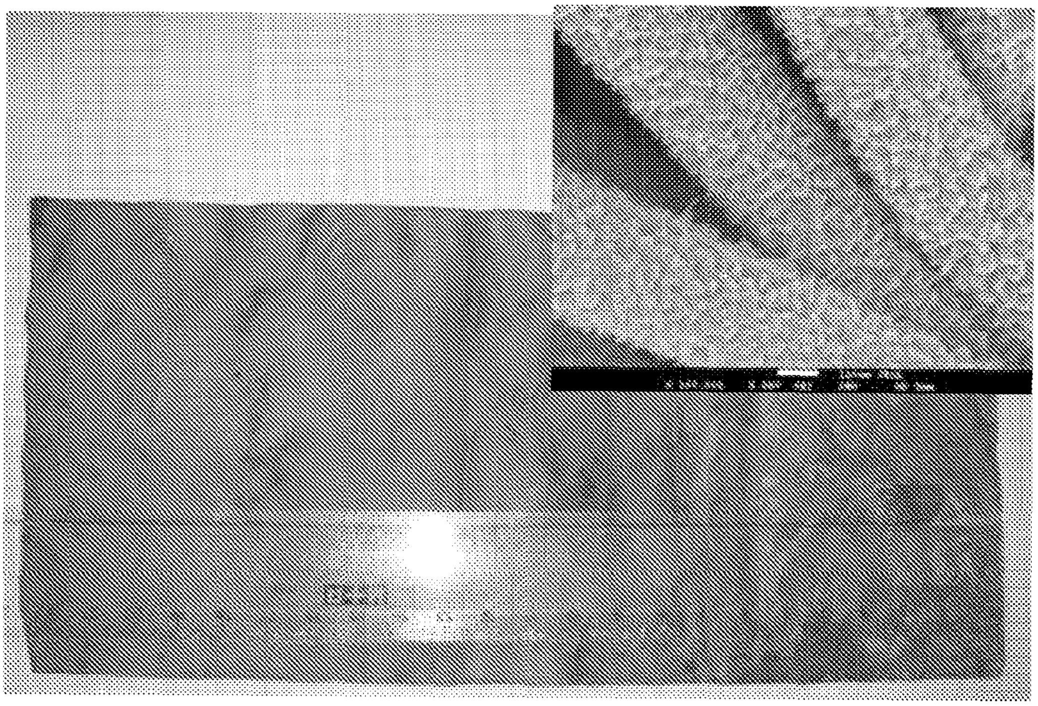

Fig1.Camera picture of a piece of PA electrospun nanofiber mats grown with nano-fibrillar PANi, with size of 10.5cm × 23cm. The inlet is the SEM image of composite fibers.(polymerization condition: 0.04M aniline in 1M HCl at room temperature)

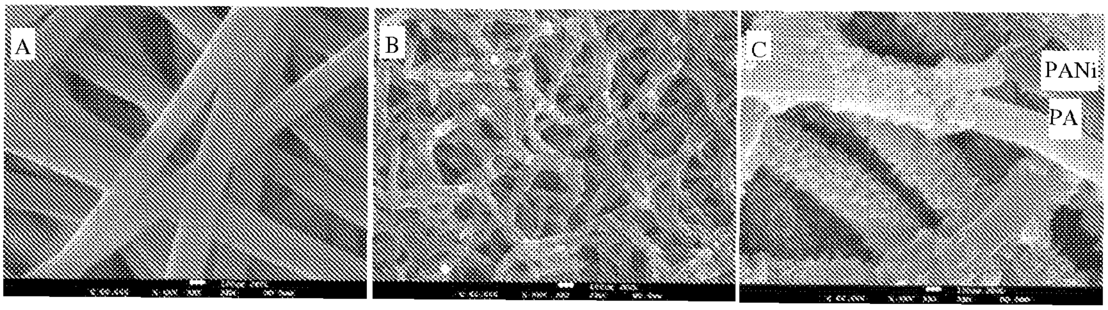

Fig2. SEM images of A) PA nanofibers, B) PANi nanofibers, C) PA/PANi core/shell nanofibers with brokenshell scale bars were 100nm

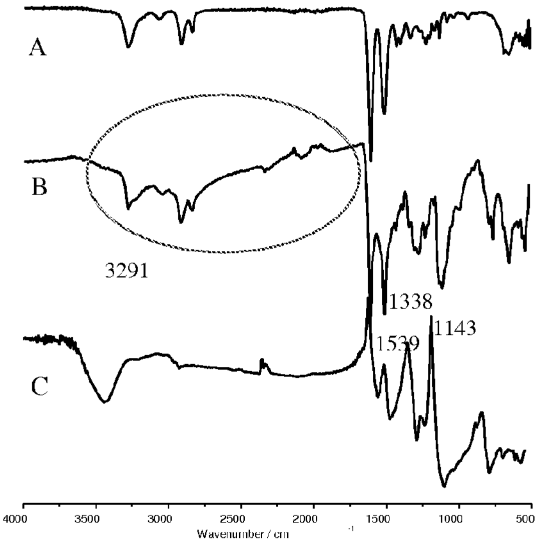

Fig3. IR spectrum of A) PA nanofibers, B) PA/PANi nanofibers, C) PANi powder (HCl doped)

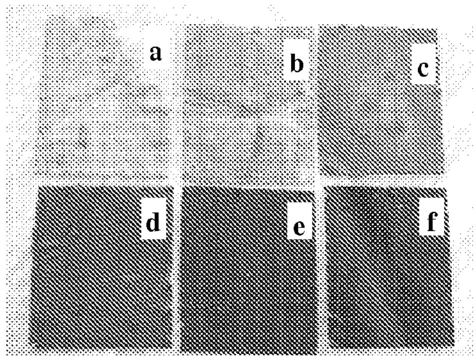

Fig4. PA/PANi composite nanofibers from different aniline concentration, a)0.02M, b)0.04M, c)0.08M, d)0.16M, e)0.32M, f)0.64M.

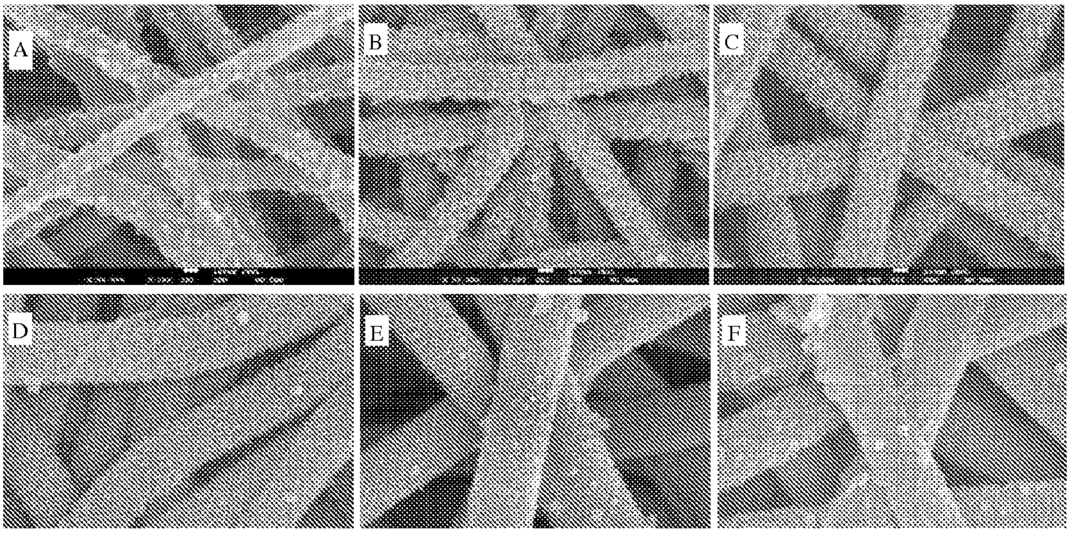

Fig5. SEM images of nano-fibrillar PANi grown on Polyamide 6 nanofibers from different aniline concentration A) 0.02M, B) 0.04M,C) 0.08M, D) 0.16M, E) 0.32M , F) 0.64M, at room temperature in 1M HCl. scale bars were 100nm.

Table 1 properties of PA/PANi composite nanofibers

Samples from different aniline concentration	Weight percent of PANi / %	Fiber diameter / nm	Surface area / $m^2.g^{-1}$	Conductivity / $S.cm^{-1}$			
				$^a\sigma_m$	measuring thickness/ μm	$^b\sigma_c$	calculating thickness/ μm
PA nanofibers(0M)	0	201	80.2	0	——	0	——
0.02 M	2.51	230	132.94	0.138	96.3	0.54	24.67
0.04 M	2.85	288	137.76	0.223	83.0	0.805	23.96
0.08 M	4.1	334	153.33	1.06	82.8	3.59	24.50
0.16 M	8.7	376	160.08	17.95	88.8	61.84	25.78
0.32 M	13.4	419	144.84	32.76	87.5	87.5	25.30
0.64 M	19.11	448	100	84.27	96.3	308.8	26.28
PANi nanorod (1M)	100	35	60.89	——	——	——	——

a. conductivity vs. measuring thickness
b. conductivity vs. calculating thickness

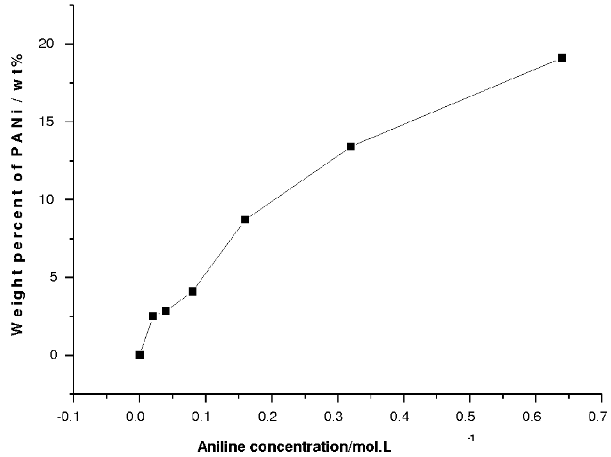

Fig6. Content of PANi in PANi/PA composite nanofibers mats

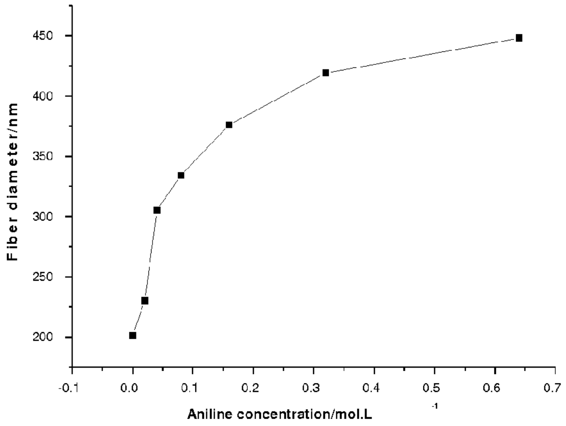

Fig7. Diameter of composite nanofibers from different aniline concentration solution

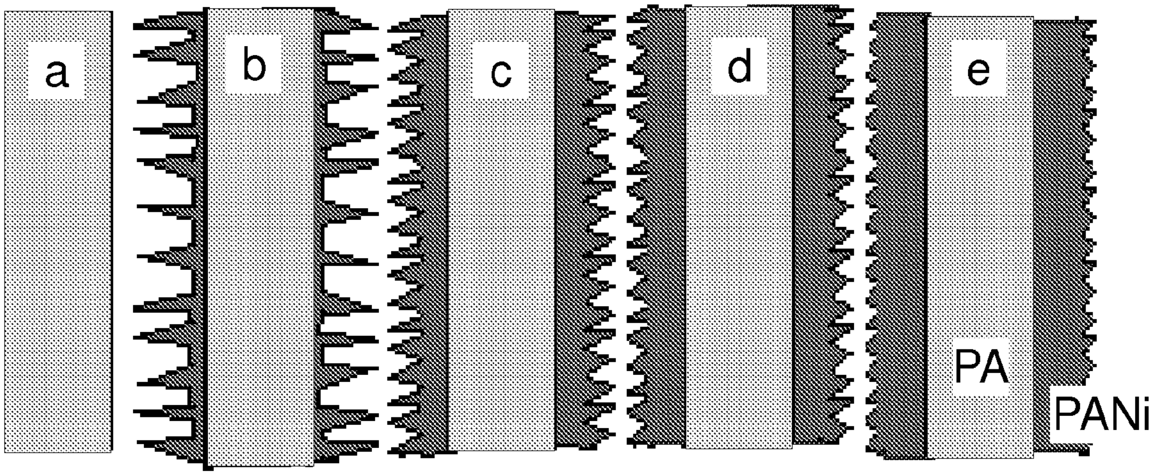

Fig8. Schematic diagram of PA/PANi core/shell fiber model grown from different aniline concentration, a)0M, b)0.02M, c)0.04M - 0.08M, d)0.16M, e) 0.32M, f)0.64M

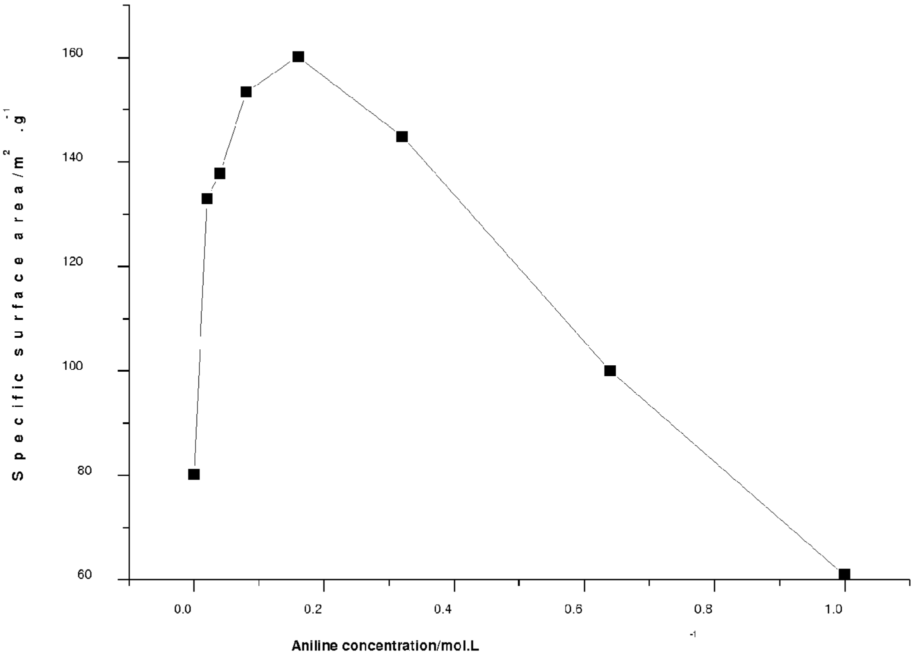

Fig9. Specific surface area of non-aligned composite nanofiber mats polymerized from different aniline concentration. The value at 1 mol/L was the surface area of pure PANi.

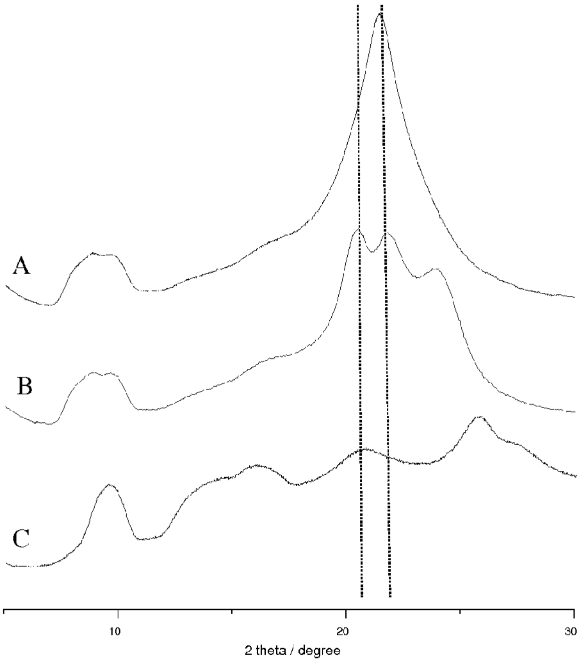

Fig10. X-ray diffraction of A) PAnanofibers, B) PA/PANi nanofibers, C) PANi powder (HCl doped)

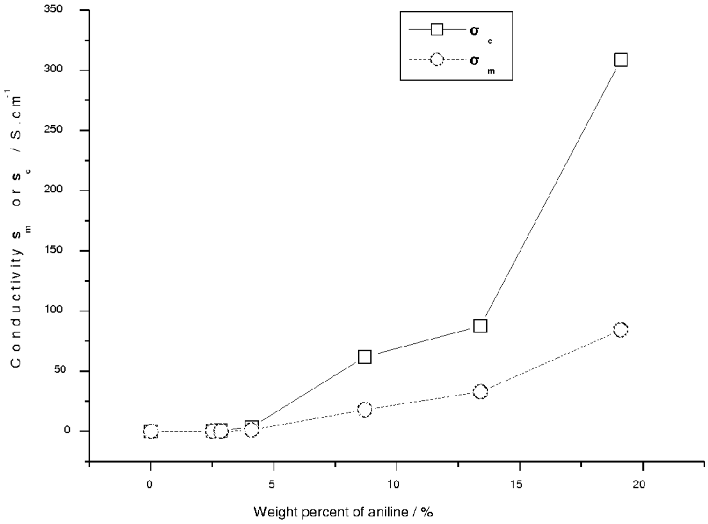

Fig11. Conductivity of PA/PANi composite nanofiber mats vs. PANi content.
σ_m: conductivity vs. thickness measured by micrometer; σ_c: conductivity vs. thickness calculated by weight and density.

Table 2. Mechanical properties of PANi/PA composite nanofibers

Samples	Thickness/ μm	Content of PANi / %	Strength/MPa	Modulus/GPa	Elongation to break/%
PA non-aligned non-woven	15.03	0	77.55	0.23	121.9
PA/PANi non-aligned non-woven	15.03*	2.85	82.88	0.49	124.8
PA aligned belts	10.28	0	113.61	0.79	17.6
PA/PANi aligned belts	10.28*	2.43	161.75	1.18	58.0

*The thickness of mats or belts grown with PANi was same as that of before

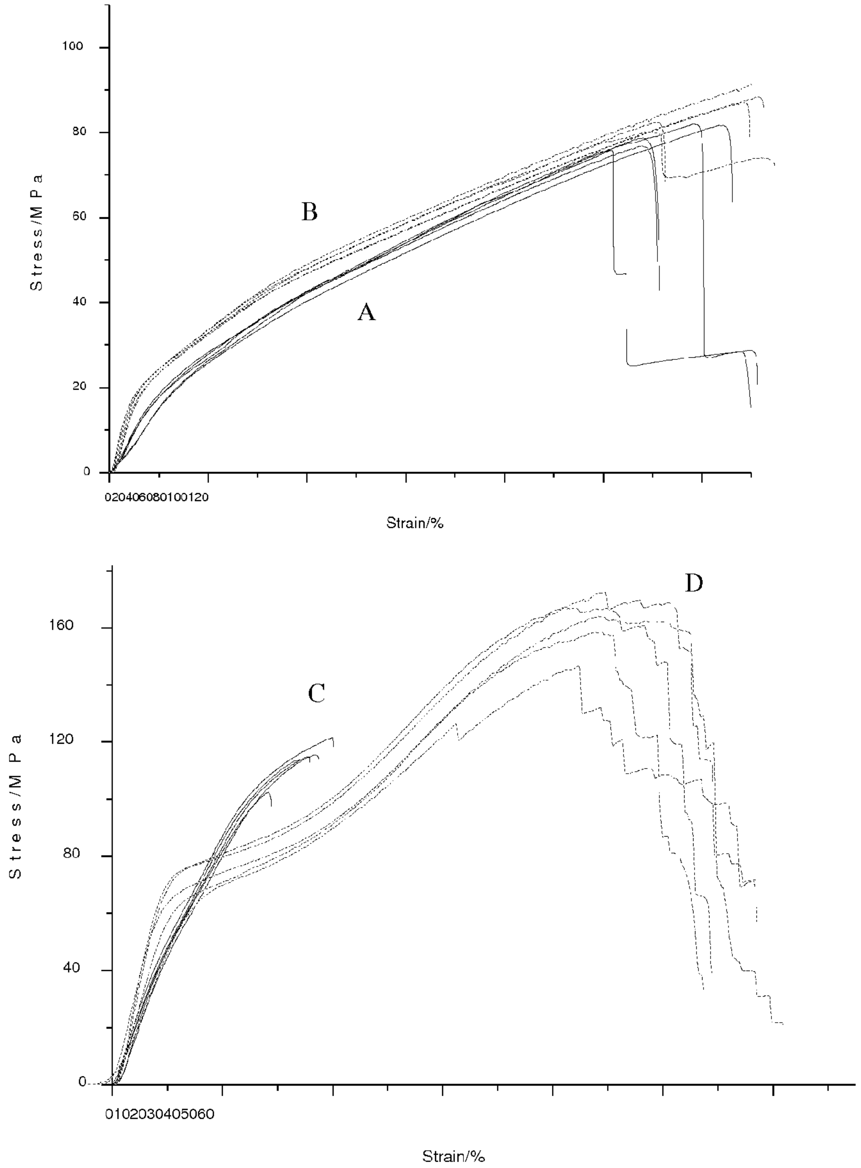

Fig12. Stress- strain curves of pure PA nanofibers and PA/PANi composite nanofibers; A) PA non-aligned non-woven; B) PA/PANi non-aligned non-woven; C) PA aligned belts; D) PA/PANi aligned belts. (0.02M aniline in 1M HCl, at room temperature)

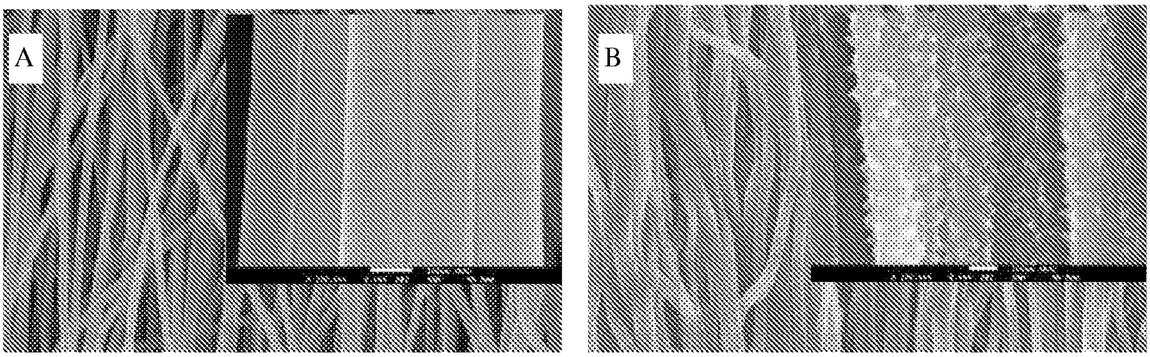

Fig13. SEM images of aligned A) PA nanofibers and B) PA nanofibers grown nano-fibrillar PANi, scale bar were 1μm. The inlets are images at high magnification, scale bar were 100nm.

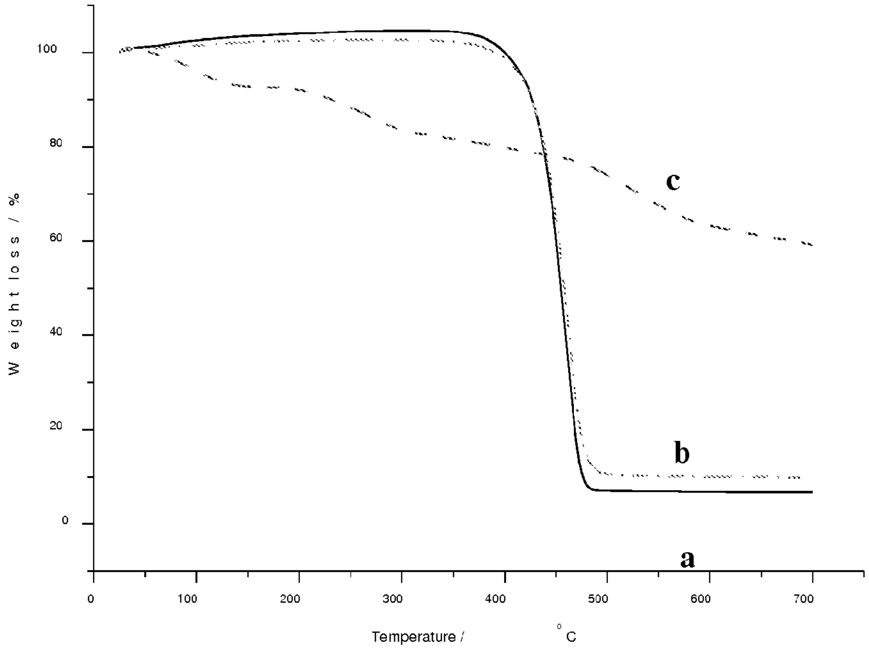

Fig14.TGA thermographs of a) PAnanofibers, b) PA/PANi nanofibers, c) PANi powder (HCl doped)

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EUROPEAN SEARCH REPORT

Application Number
EP 09 15 3057

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Place of search	Date of completion of the search	Examiner
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