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Development of polyester and polyamide conductive fibre

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Conducting polyester PET and polyamide PA-6 fibre and fabrics were prepared by *in-situ* chemical oxidative polymerisation using super critical fluid assisted process. The fibre materials and cloths produced were characterized by means of FTIR, WAXD, SEM, and DSC and two-probe resistivity. The samples were studied also by means of washing them several times. Homogeneous treated fibre materials with sustainable properties were produced. Melt spun fibre material of inherently conducting polymer blends have been reported earlier. Reasonable mechanical and electrical properties (resistance of $10^5 \ldots 10^7$ Ω/cm) are typical for blend of polypropylene and polyaniline. With bi-component extrusion technology the fibre as good as $10^3 \ldots 10^5$ Ω/cm is reachable.

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Conducting fibre applications

Industrial applications of conducting fibre are mainly in electrostatic discharge (ESD 10^{-9} S/cm) applications in work-wear, dust-free garments, automotive decorations, carpets and upholstery. Typical bi-component fibres containing carbon black or white metal reach the requirement also in mixed fibre materials. However the conductive polymer materials reach 10...100 S/cm conductivity, and can be used in electromagnetic impulse (EMI 10^{-3} S/cm) protection.

Belltron commercial products have introduced carbon-black based sandwich structures having electric resistance $10^8 \ldots 10^{10}$ Ω/cm and $10^6 \ldots 10^8$ Ω/cm in 2,5 g/d tenacity polyester and nylon fibre respectively. The comparable values for white metal powder construction were $10^8 \ldots 10^{10}$ Ω/cm for both co-centric and side-by-side nylon based bi-components 3 g/d tenacity fibre.

Truly conducting fibre is needed for MEMS. No applicable synthetic polymer fibre is yet known. For the application is proposed draw blending of metal slivers 10^5 Ω/cm, metallic salts such as copper sulphide or iodide $10^{-6} \ldots 10^{-1}$ Ω/cm, galvanic coating $>10^4$ Ω/cm, coating fibre with conductive particles suspended in a resin $10^0 \ldots 10^5$ Ω/cm, and pure carbon 10^2 Ω/cm [1].

The conductive polymers were based on conjugated electron structure, first created in the early 1980's in polyacethylene, non-processable oxygen sensitivity polymer. Today the inherently conductive polymers, such as polyaniline PANI, polypyrrole PPy, polytiophene PT, and poly (per-naphthalene) PNa can be processed and are used in industrial applications. Typically the conductive polymer materials are, however, semiconductors. Novel conductive inherently conducting polymers are able to emit light as well [5, 17, 18]

Manufacturing of inherently conducting polymer fibre

The spinnability of the polymer melt has shown to be a very complex dilemma even for the homogeneous thermoplastic. [2] Both conductivity and spinnability of the PANI blend are limited for obvious reasons, and have left the door open for other than melt spin processes, e.g. solution spin, and solution fibre coating.

The conductive polyaniline complex in plastized form has irreversible degradation at high temperature, such as 235°C requested for the PP, PA, or PBT, reduces the allowed processing time only by 60–100 s. The shear and heat stress also seems to be additive, and between the process steps the material do not recover from the earlier process stresses. [8]

However higher melting polymer blends suffer heat sensitivity of polyaniline, such as polyamide PA6 and polyester copolymer PBT with resistivity of $10^8 \ldots 10^{10}$ and $10^9 \ldots 10^{11}$ Ω/cm respectively. Simultaneously the mechanical strength of fibre is lost in certain extend.

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Fibre dipped with PANI toluene solution conductivities in a range of $10^{-2} \ldots 10^{1}$ S/cm have been reported. The materials have original mechanical properties, but poor wearing resistance [21–24].

Blending and melt spinning the matrix with PANI is possible in limited and controlled cases. Certain technologies, e.g. direct spinning in a single step or bi-component technology are possibilities to develop more robust spin methods for PANI fibre [6, 25, 26].

The *in-situ* polymerised PANI systems have been indicated close to metallic conductivities. [13–16]. Recently the systems have been possible to be spin of dispersions through electrostatic spinning of certain solvents. [28]

Self-organizing systems forming certain structures in nano-scale are the latest development in the field of conductive polymers. The formation of IPN is now less dependent on the external macro process conditions. This provides more possibilities in the fibre and fibrous material processing it self. [7–12]

Finnish the fibre with PANI solution is an interesting alternative for ESD applications, due to low electric polymer consumption and relative good electrical conductivities. Adhesion on the fibre should be further improved. Improved surface treating fibre with PANI solution and fixatives provides improved wear resistance but $10^{6} \ldots 10^{8}$ Ω/cm. All the previous mentioned fibres have severe conductivity loss after few base washing steps. [27]

Impregnation [29, 30] and polymerisation [31–35] of PANI and PPy from solution and gas phase on glass, cotton, and nylon textile has been reported. Recently has been developed a method for polymerising inherently conducting polymer on fibre or textile utilizing supercritical carbon dioxide aided processing [36]. In this paper is tested the latest developed fibre and discussed their properties.

Supercritical phase of carbon dioxide appears above the critical pressure and temperature (+31°C, 73.8 bar).In supercritical state the physical properties of the fluid are between the gaseous and the liquid phases. Moreover, the "solvent power" the fluid can be adjusted by changing the pressure and temperature. Supercritical carbon dioxide can be used instead of common organic solvents to swell the structure of the fibre and open the way for the monomer to penetrate into the polymer i.e. to impregnate the fiber. The polymerisation reaction can be take place in the supercritical phase if the polymerisation reagents (oxidants, dopants) are made soluble in CO_2 or in a separate process step utilizing e.g. simple aqueous reagent paths for monomer impregnated fibers [36]. In this paper the samples were prepared by the latter process using 0.5 M aqueous ferric chloride path.

Polymerisation reactions in supercritical carbon dioxide have been under extensive research in the recent years. The motivation has been to eliminate the emissions of volatile organic compounds (VOCs). The first example of a $scCO_2$-solvent based industrial polymerisation process is the Dupont's fluoropolymer plant opened year 2002.

Experimental

In the experiments was utilized Aniline and Pyrrole from Merck and Acros Organics, respectively. Monomers were distilled before use.

Samples of PET and PA fibre were of commercial technical product suitable for manufacturing of certain filter fabrics.

The PET samples and about 15 μl of the monomer were placed in 30 ml reactor. The reactor was equipped with sapphire observation window and magnetic stirrer. Both monomers formed a homogenous solution or dispersion with $scCO_2$ which could be verified visually through the observation window.

Supercritical carbon dioxide aided monomer impregnation was performed at temperature +80°C and pressure between 110–140 bar over 2 h.

Polymerisation and doping were conducted by oxidative reaction in 0.5–1 M $FeCl_3$ aqueous path or 0.013–0.053 M APS, 2 M p-toluenesulfonic acid path over 2 h. Samples were washed with excess distilled water to remove oxidant residues.

Resistivity of PET fibre was measured of 24 h conditioned samples with resistance meter METRISO 2000. Resistivity of other samples was measured with MEGGER BM80/2 equipment. Testing was made according to standard DIN 54345 Teil 5. The testing conditions are temperature $T = 23 \pm 1^{\circ}$C, relative moisture HR = 25 ± 2%. Actual testing time moisture was in range of 22,5 and 30,0%, while temperature was in range of 22,5 and 22,9°C too low. Measuring voltage was $U = 100$ V and measuring time 15 s. Bundle of approximately 100 fibres and 10 separate fibres were measured between two pressure clips applying a certain distance. Average values of 10 measurements were reported.

Fibre samples were test washed according to SFS-EN ISO 6330 7A standard modified in respect of washing powder. In these tests OMO Sensitive with pH 8 was used. Samples were placed in washing bags, and in one washing batch were used 50 ml of washing powder and 2 kg of filling cloths. Standard washing machine ELECTROLUX WASCATOR FOM71MP-Lab was used. After the washing the fibre samples were dried and conditioned before measuring the conductivities.

Fibre samples

Polyester fibre samples were coated with polyaniline according to the method described above. Four different derivates were prepared differentiating in the composition and time in the after treatment according to the Table I.

TABLE I Polyester fibre *in-situ* polymerisation

	Oxidation			
Sample	Media	C (mol/dm^3)	Time	Doping
1 PET 240403	APS	0,0131	2	PTSA
2 PET 240403	APS	0,0263	2	PTSA
3 PET 240403	APS	0,0526	2	PTSA
4 PET 240403	$FeCl_3$	1,0	2	Cl−

TABLE II Resistivity of the fibre before and after the washing

Sample 10 mm	Bundle	Fibre	Color	Washed bundle	Washed fibre	Color
1 PET 240403	58E + 6	88E + 6	Green	1E + 14	1E + 14	Light blue
2 PET 240403	52E + 4	94E + 6	Greenish	75E + 6	41E + 8	Bluish
3 PET 240403	45E + 4	2E + 6	Dark	9E + 6	4E + 8	Dark
4 PET 240403	15E + 4	83E + 4	Dark green	10E + 8	1E + 10	Dark blue

TABLE III Washing effect on the PPy-c-PA6 fibre resistance on 5 mm and 10 mm samples

	0.5 cm		1 cm		5 cm		10 cm	
Washing (times)	Bundle	10 fibers	Bundle	10 fibers	Bundle	10 fibers	Bundle	10 fibers
0	3E + 4	4E + 4	4E + 4	6E + 4	9E + 4	21E + 4	13E + 4	50E + 4
1	4E + 4	6E + 4	5E + 4	8E + 4	14E + 4	40E + 4	33E + 4	52E + 4
2	4E + 4	5E + 4	5E + 4	7E + 4	17E + 4	20E + 4	23E + 4	77E + 4
3	6E + 4	13E + 4	7E + 4	20E + 4	22E + 4	76E + 4	45E + 4	2E + 6
4	6E + 4	38E + 4	7E + 4	40E + 4	25E + 4	1E + 6	47E + 4	3E + 6
5	3E + 4	13E + 4	4E + 4	16E + 4	13E + 4	92E + 4	18E + 4	2E + 6
10	2E + 4	21E + 4	3E + 4	48E + 4	13E + 4	1E + 6	65E + 4	2E + 6

After the preparation was collected green and dark fibre, which were washed with distilled water. The resistance of the fibre was measured according to the standard DIN 54345 Teil 5. The fibre was washed according to the method described above, and the resistance of the fibres was measure after drying and conditioning. The resistivity values for the fibre measured of 10 mm samples are collected in Table II.

Clearly can be seen the sample 1 was insufficiently reacted, and remains open if the conductive material has reached the fibre inner layers. The strength of the oxidation defines amount of conductive polymer formed, the related conductivity, and sustainability in washing on the benefit of sample 3.

In another set of experiments, which was performed according was used poly-ε-caprolactone (PA6) fibre which was *in-situ* polymerized with pyrrole. The respective fibre treatment conditions were as follow.

Supercritical carbon dioxide aided pyrrole impregnation was carried out (+60°C, 150 bar, 2 h). Monomer volume fraction in the reactor was about 0.2 vol%. The polymerisation was carried out in a simple 0.5 M $FeCl_3$ path. After the synthesis the dark colored chlorine doped PPy coated fibre was washed in turn several times with distilled water and acetone.

The PPy coated PA6 samples where washed 10 times with the same procedure as the above described PET samples. Between the washing steps the fibre was dried, conditioned and the resistivity was measured. In the Table III is expressed the resistivity changes on fibre bundles.

In the Fig. 1 is expressed the respective values which are tabulated in the Table III as well. Clearly can be seen the PPy-c-PA6 resistivity very robust in washing. Compared with the result of PANi-c-PET difference is very clearly better, indicating marked difference on benefit of modified polyamide fibre.

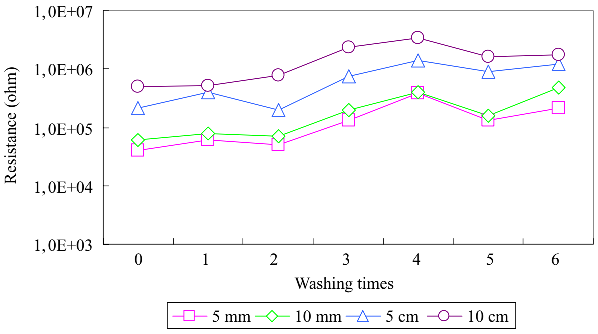

Figure 1 Washing effect on the PPy-c-PA6 fibre resistance on 5 mm and 10 mm samples.

Cloth samples

Polyester cloth was *in-situ* coated with polypyrrole. The preparation was as described above. The actual conditions were as follows: Supercritical carbon dioxide aided pyrrole impregnation was carried out (+75°C, 130 bar, 2 h). Monomer volume fraction in the reactor was about 0.6 vol%. The polymerisation was carried out in a simple 1 M $FeCl_3$ path.

Prepared cloth was measured, and after that it was washed ten times. After each washing the cloth was dried, conditioned, and resistivity measured. The results are expressed in the Table IV. Clearly can be seen also the result is comparable the resistance loss in fibre tests even if made with different monomers. Thus is concluded the inherently conductive polymers are less interactive with polyester than with polyamide. Result can be explained through NH-groups in polyamide.

TABLE IV Washing effect on the PPy-c-PET cloth resistance

	Measuring gap	
Washing (times)	5 mm	10 mm
0	11E + 2	10E + 2
1	1E + 4	1E + 4
2	4E + 4	3E + 4
3	7E + 4	6E + 4
4	11E + 4	12E + 4
5	37E + 4	33E + 4
10	1E + 6	2E + 6

TABLE V Differential scanning calorimetric DSC results

	PET reference	PET modified	PA reference	PA modified
Tm, 1, °C	225,1	254,8	222,1	220,5
Tm, 2, °C	255,8	254,3	220,3	211,1
ΔH, 1, J/g	49,8	73,8	69,3	64,0
ΔH, 2, J/g	35,7	45,6	49,7	49,9

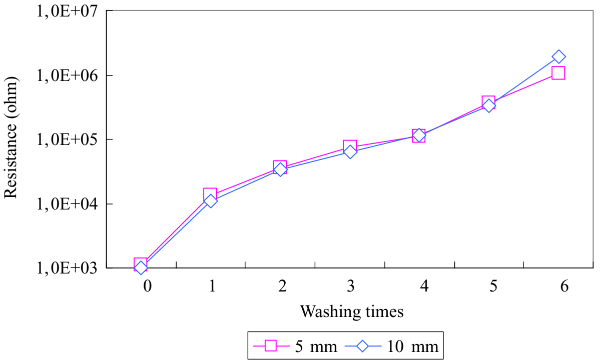

Figure 2 Washing effect on the PPy-c-PET cloth resistance.

Concentration of washing media in the cloth might have also a minor effect.

Microscopy

Polyamide fibre samples treated with PPy were fixed with fill vinyl acetate fibre in a bundle and microtome cut. The result has been studied in double polarized light. In the Fig. 3 is shown the micrographs of the fibre cross section. In sample where side reflections were removed it was possible to observe the originally 17 dtex (40 micron) fibre was covered with 3.88±0.8 micron dark cladding layer increasing the fibre size 9.4%. Cross-section of fibre clearly indicates the outer layer that is smooth, and covers whole fibre.

SEM

Scanning electron microscopy of fibre surface are shown in the Fig. 4. In the scanning electron microscopy of Bhat et al. [35] has been expressed evenly distributed small globules of polyaniline on the cotton fibre surface. The size of the particles was approximately 0,3...0,5 microns. Surface structure was flaky which indicates some PANi material out of phase and possibly loose. The SEM micrographs of the now reported fibre are markedly smoother on the surface.

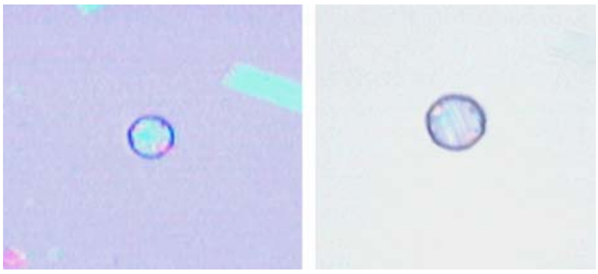

Figure 3. The micrographs of the polyamide + PPy -fibre cross section.

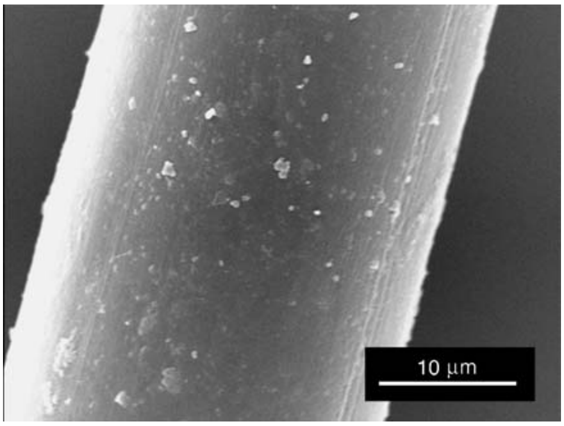

Figure 4 Scanning electron microscopy of the Pa + PPy -fibre surface.

FTIR

Fibre was analysed in solid state with FTIR, which gives also indication of the surface characteristics of the system. Polyaniline has characteristic broad and intensive absorption at 1589,1 cm^{-1}. Additionally the benzenoid has peaks at 1482,4 and 1405,9 cm^{-1}, while the peak of C-N stretching is at 1298,8 cm^{-1}. Sift from these positions should mean interaction with polymer material of base fibre. In the Fig. 5 is shown FTIR results of pure and modified PET fibres. Measurements were made fibre *in-situ* of fibre as such. Most of the typical PANi characteristic peaks are mixed with those of PET fibres. Clear indication of PANi is available at 2980 cm^{-1} wavelength regions a broad peak. Low concentration on surface leads us to idea of structure where PANi is mainly inside the fibre.

The FTIR spectrum of polyamide and respective polypyrrole modified fibre are shown in Fig. 6. In the spectrums are the typical peaks of polyamide and interactions especially at 1039 and 1013 cm^{-1} for polypyrrole. Differences also in the case are small and the polypyrrole is also in this mainly inside the fibre. In both cases it is reasonable the inherently conducting polymer content is some 5...8% of the total mass of fibre.

WAXD

Wide-angle x-ray diffraction was measured from both PET and PA samples and the result of unmodified and modified samples were compared in Fig. 7. The polyaniline typical crystal diffractions at 38,55 and 44,80° are not observed in the modified fibre. In the modified PET fibre is however observed marked increase in crystallinity increase, which has to be new fraction of co-crystals.

In the Fig. 8 are shown WAXD results the polyamide and polypyrrole system. While pyrrole has no marked crystal structure no clear difference between modified and unmodified product was observed. The sample comparison clearly shows that the inherently conducting polymer has formed intimately dispersed system with the polyamide.

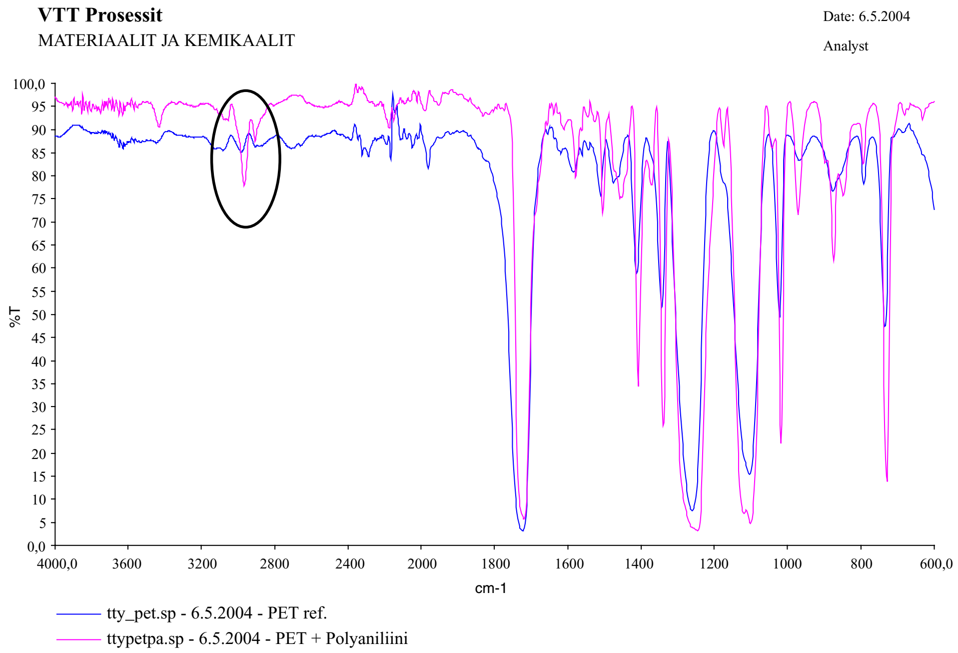

Figure 5 FTIR results of pure and modified PET fibres.

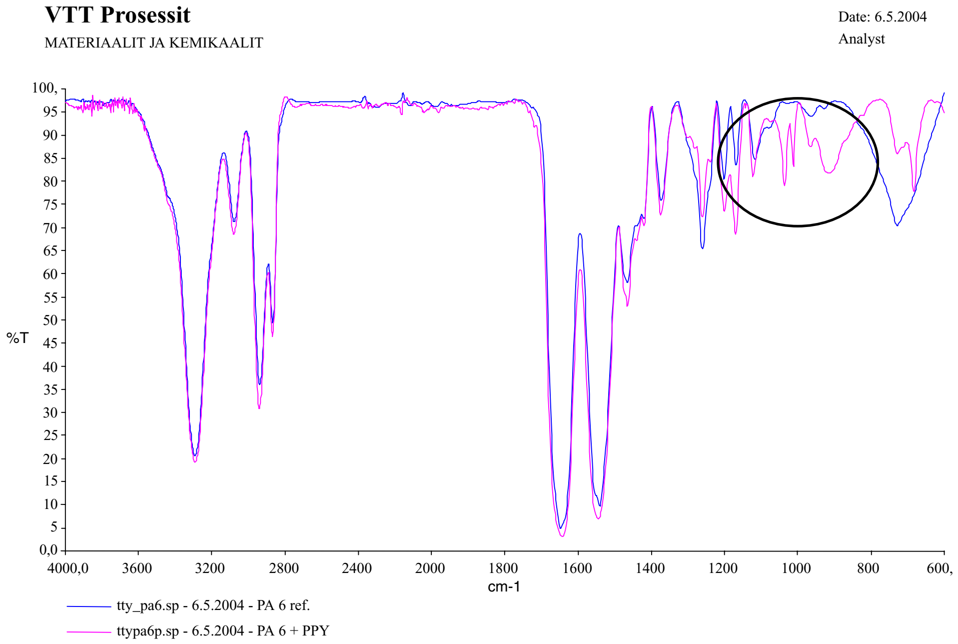

Figure 6 FTIR spectrum of polyamide and polypyrrole modified polyamide fibre.

DSC

Differential scanning calorimetric DSC results with unified peaks structure does not promote idea of phase separation. Especially in the case of polyamide modified with polypyrrole melting peak has broadened and there is clear melt temperature reduction typical for unified blend phase. PPy seems to be even able of softening the polyamide fibre. Modified PET, even if in other analysis is well-distributed system, indicates here more spinodal kind blend behaviour.

In the second melting the melting fibre orientation is lost and observed in lower enthalpies. What is surprising is the actual value of non-molten modified PET fibre sample having a high enthalpy. This may be related to the modification in the crystallinity and seen also in WAXD results above. PANi nucleates the PET polymer in fibre system.

Comparison with references

Bhat et al. [35] has produced conductive PANi + cotton fabrics by means of *in-situ* chemical oxidative polymerisation of aniline in mixed bath. Water compatible natural fibre made utilization of solution obvious. In the present work hydrophobic man made fibre materials monomers were introduced to the surface layer of fibre by means expanding the matrix. The fibres were treated especially under super critical carbon dioxide.

There are marked similarities between the results. Microscopy, FTIR, and crystal structure results

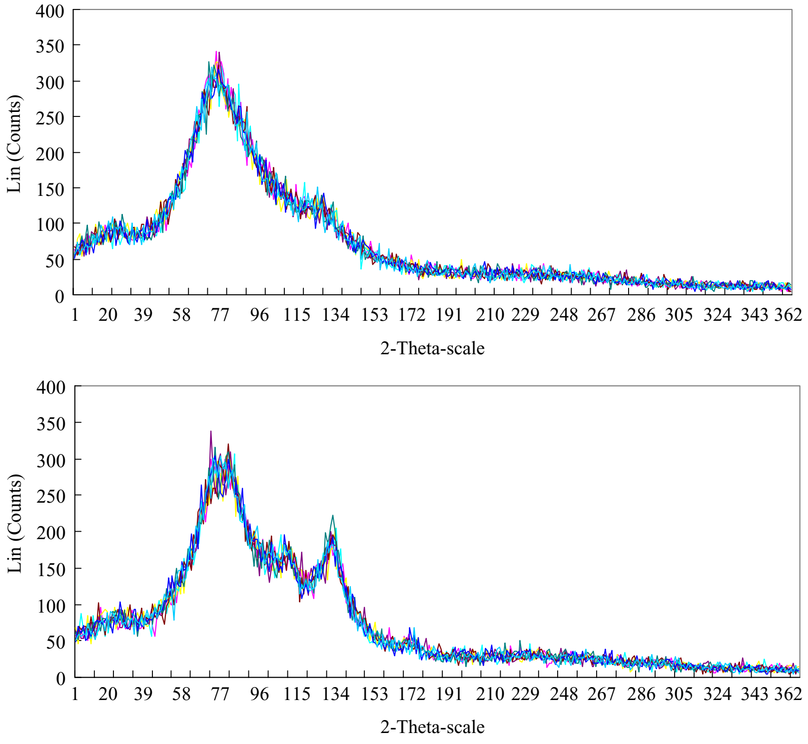

Figure 7 WAXD of unmodified PET fibre (left) and PANi modified PET (right).

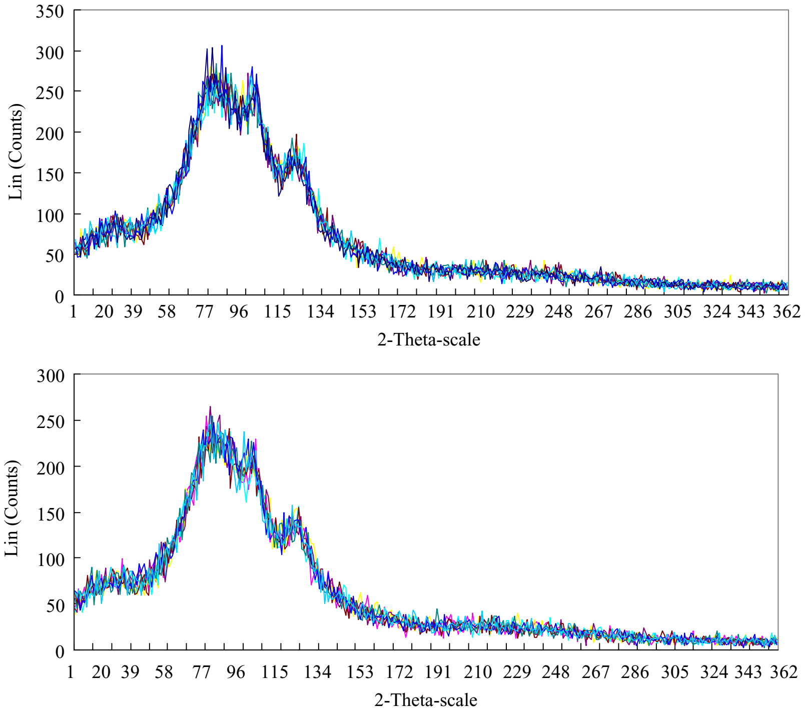

Figure 8 WAXD of unmodified PA fibre (upper) and PPy modified PA (lower).

support each other without any major complications. In both cases it was possible to produce fibre materials where the inherently conducting polymer is *in-situ* polymerised on the outer layer and fine structure of a fibre. The resent study shows also man-made fibre can be coated by means of *in-situ* polymerisation with both aniline and pyrrole. New results show evidently also man-made fibre can be treated.

Differentiation is the washing treatment, which was made in the reference with distilled water only. The known weakness of PANi is the reduction of conductivity while washed with base. Typically the change is reversible, when re-doped with acid. This is however undesired for most of the cloths. This is why in the present study is used pH 8 washing media.

The novel results indicate, however less resistance increase even with base washing. New development is reported of wear resistant conductive polyamide PA6 polypyrrole and polyester PET polyaniline having $1*10^3\ldots3*10^4$ and $9*10^4\ldots3*10^5$ Ω/cm respectively. Conductivity of the novel fibres are tested in cascade of washing steps according to SFS-EN

ISO 6330 7A except adopting pH=8. Most promising are the results were the conductivity remains well in ESD specification and the resistivity is increased only on level $1{*}10^{6}\ldots2{*}10^{7}$ Ω/cm after 10 washing cycles.

EMI results were not produced, but it is reasonable to believe they follow the conductive material concentration and respective conductivity. Further it is reason to believe there is improvement in the flame retardancy.

Discussions

Man-made fibre, PET and PA, can be coated with inherently conducting polymer, like polyaniline PANi and polypyrrole PPy, layer means of super critical *in-situ* polymerisation. The products have improved washing resistivity increase markedly also when used base washing media. The results are limited to certain polymer systems, but the concept should be possible for other synthetic fibre and inherently conducting polymers. Benefit compared to other methods is fully polymeric fibre, and similar methods that expand the polymer fibre like solvents. The manufacturing method is simple and the material costs are low. Even further it is possible to treat different kinds of textiles, cloths and films as such and remain their original mechanical properties.

Polyaniline has two distinct conformations: the crystalline, which is extended coil conformation and highly conducting, and the amorphous, compact coil conformation which is less conductive. It seems that in the case of PET/PANi fibre the first conformation is formed.

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