

Preparation of Melt Spun Conductive Polypropylene/Polyaniline Fibres for Smart Textile Applications

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ABSTRACT

Blends of polypropylene/Panipol™ were prepared and melt spun to fibres under different processing conditions including mixing parameters (time and temperature) and draw ratio of prepared fibre. Morphology of blends and fibres was found to consist of two phases using TEM, SEM and optical stereomicroscopy. Two factors showed substantial effects on electrical resistance of fibres: size of the dispersed Panipol™ rich phase, which was controlled by melt blending conditions, and applied force to form them to the fibrillar morphology, which was controlled by draw ratio of the fibre. Both factors were shown to be optimum, in order to maintain continuous conductive fibril structure.

AUTHOR KEYWORDS

Conductive fibre, smart textile, polyaniline, polypropylene, blend, melt spinning, morphology, draw ratio.

INTRODUCTION

Smart and functional textile fibres have attracted interest worldwide because of their potential applications such as in electrotherapy [1], health monitoring shirts [2], dust and germ free clothing [3], heat generation [4], cooling systems [5], data transfer in clothing, electrochromic display, sensors and military applications like stealth technology [6]. For all the mentioned applications, producing conductive fibres is a basic element. The electrical conductivity can be established in conventional insulating thermoplastic

polymers using different techniques. Electrically conductive fibres have been produced by wet spinning, melt spinning or coating fibres with electrically conductive materials such as metal powders, carbon black, carbon nanotubes or intrinsically conductive polymers (ICP) such as polyaniline or polypyrrole. Among all methods, there are a few researches on melt spinning of ICP/insulating polymer blends. One of the most common ICPs is Polyaniline emeraldine base (EB). It becomes conductive by protonating the non-conductive EB using a strong acid such as dodecyl benzene sulphonic acid (DBSA) or camphor sulphonic acid (CSA), and this salt is called PANI-complex. The PANI-complex is processable and can be blended with thermoplastics such as polypropylene (PP), polystyrene (PS), or polyethylene (PE) [7]. Polyaniline shows also high chemical and thermal stability in the conductive form, its production cost is low and easily it can be doped with inorganic and organic acids [8]. PANI doped with dodecyl benzene sulphonic acid (DBSA) arouse great interest, it can be doped in solid state. In the prepared complex, PANI occurs as a salt and the complex is like a paste, dark green and soluble in organic solvents [9–11]. Kim et al. [12] prepared melt spun fibres from polyaniline salt /polypropylene blend, the electrical conductivity was not satisfactory due to the homogeneity problems, it was suggested to optimize melt mixing process and possibly improve homogeneity by several extended mixing steps.

In the present study, we have used a proprietary plasticized polyaniline, Panipol™, and polypropylene. First, we blended polypropylene with different polyaniline contents, and then blends were extruded into fibres using melt-spinning technology and under different draw ratio conditions. Electrical resistance of fibres was measured. Morphology of fibres was examined with a stereoscopic zoom microscope (SZM), scanning electron microscopy (SEM), and a transmission electron microscope (TEM).

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EXPERIMENTAL

Materials and Blending

Panipol CXL polyaniline-complex (from Panipol, Finland) and fibre grade polypropylene (HF350FB from Borealis) were melt mixed using a DSM Explore twin-screw compounder. Two sample series were prepared: A-samples at 200°C and with a screw rotation rate of 70 rpm for 12 min. The concentration of Panipol was chosen between 1 to 25 wt-%. The B-samples were processed at 220°C and with screw rotation rate of 70 rpm for 15 min, with 20 wt-% Panipol.

Fibre Spinning

Fibres were melt spun at suitable processing conditions and drawn between two Godet rolls with draw ratios of 2, 3, 4, 5 and 6.

Electrical Resistance

Resistance for both single fibre and bundles of 16 fibres was measured with resistance meter METRISO2000, the electrical current was applied between two clips holding 100 mm of fibres.

Morphology Analysis

For scanning electron microscopy and optical stereomicroscopy both cross-sections and fibre surfaces were analysed. Fibre cross-sections were also analysed by transmission electron microscopy.

RESULTS

In samples containing 1 wt-%, 5 wt-%, and 10 wt-% of polyaniline-complex, no change was observed in electrical resistance with increasing the polyaniline concentration or draw ratio, all showed the same value around $1\text{E}+10\ \Omega$, actually the resistance was very high and not measurable using present resistance meter, therefore they are not reported here. Table 1 and 2 show electrical resistance of fibres containing 15 wt-%, 20 wt-% and 25 wt-% of PANI, both single fibres and bundles of 16 fibres. With increasing the draw ratio, first the resistance is decreased, then after passing a minimum starts to increase. For mentioned compounds the appropriate draw ratio is 4 or 5 which shows minimum resistance.

In order to see the influence of mixing quality on conductivity, sample 20A (containing 20 wt-% polyaniline under A-mixing condition) was compared to 20B. Table 3, Table 4 and Figure 1 show electrical resistance of these samples. Results show that the lowest electrical resistance is observed in B-sample, which is due to a better mixing and dispersion of the conductive polyaniline throughout the insulating PP matrix. On the other hand the minimum electrical resistance has been shifted to lower draw ratios 2 or 3. As will be seen in the microscopic images, it could be related to better dispersion, which can result in smaller domains of PANI rich phase, so a lower tension is required to draw PANI rich phase along the fibre axis to get fibril-like phases of conductive materials.

Table 1. Resistance-R (Ω) for single fibre, 100 mm.

No.	draw ratio (DR)				
	2	3	4	5	6
15A	3.2E+9	1.3E+10	3.5E+9	2.5E+9	4.5E+9
20A	1.1E+10	5.4E+9	7.4E+8	1.5E+9	6.8E+9
25A	8.2E+9	9.5E+7	2.4E+7	4.1E+9	-

Table 2. Resistance-R (Ω) for a bundle of 16 fibres, 100 mm.

No.	draw ratio				
	2	3	4	5	6
15A	5.7E+9	9.3E+9	3.2E+9	6.5E+8	1.5E+9
20A	4E+9	1E+8	6E+7	7.5E+7	1E+9
25A	4.9E+9	6.8E+6	1.9E+6	4.2E+8	-

Table 3. Resistance-R (Ω) for single fibre, 100 mm.

No.	draw ratio				
	2	3	4	5	6
20A	1E+10	5.4E+9	7.4E+8	1.5E+9	6.8E+9
20B	1.6E+8	2.1E+8	1E+9	3.4E+9	6E+9

Table 4. Resistance-R (Ω) for a bundle of 16 fibres, 100 mm.

No.	draw ratio				
	2	3	4	5	6
20A	4E+9	1E+8	6E+7	7.5E+7	1E+9
20B	9.7E+6	1.7E+7	8.4E+7	4E+8	1.1E+9

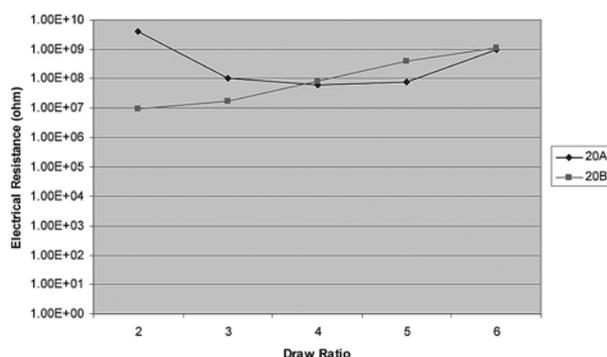


Figure 1. Electrical resistance of 20A and 20B made under different draw ratios.

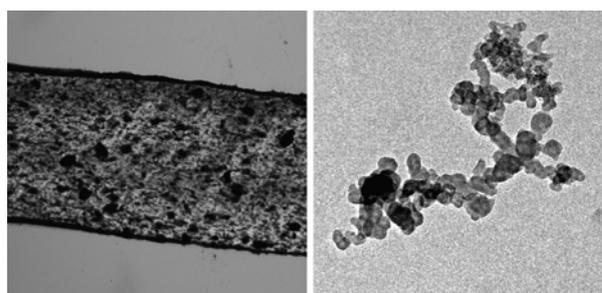


Figure 2. Stereoscopic image and TEM diagram for sample 20A2.

For all prepared blends of polypropylene/polyaniline-complex, SMZ images (Figure 2), TEM and SEM micrographs (Figure 2 and 3) show a two phase morphology containing a continuous PP rich phase and a dispersed polyaniline rich phase.

In optical microscopic images (Figure 4), When draw ratio is two (DR=2), fibres show a droplet phase morphology, dark droplets are the polyaniline rich phase, and light can easily pass through the transparent PP phase. When the draw ratio is increased, the morphology seems to change from droplet to fibril morphology and dark phase will be stretched along the fibre axis, does not let light to pass easily through the fibre and so represent darker and more uniform micrographs. (Figure 4)

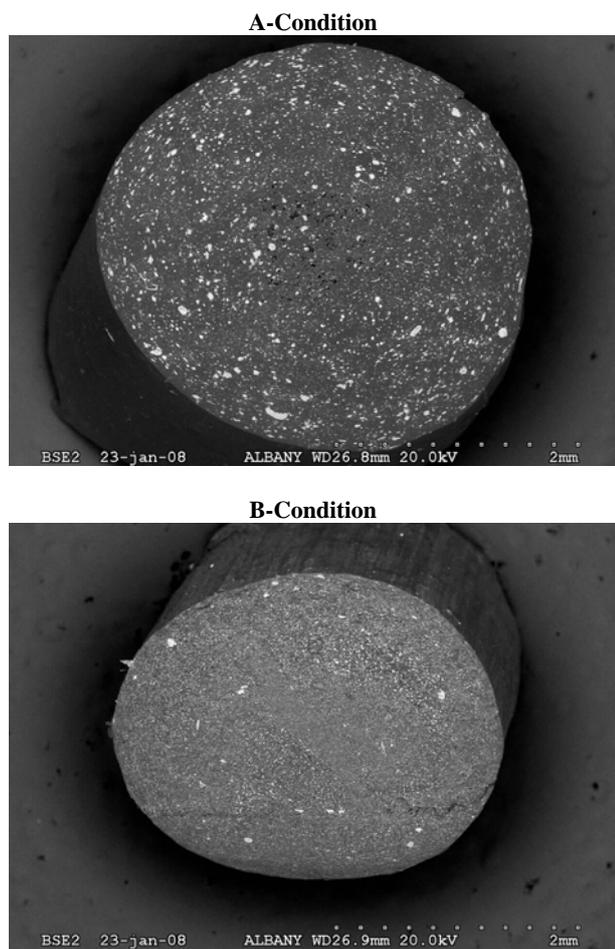


Figure 3. SEM micrographs of blends: 20 wt-% polyaniline/ A-or B condition.

Figure 3 is SEM micrographs of compounds prepared under A and B conditions, it is obvious in the images that sample- A has bigger average size dispersed phase compare to sample B. Figure 5 and 6 show micrographs for mentioned compounds when they are processed to fibres under different draw ratios. With increasing draw ratio, dispersed phase is stretched to fibrils and shows smaller size droplets in fibre cross section.

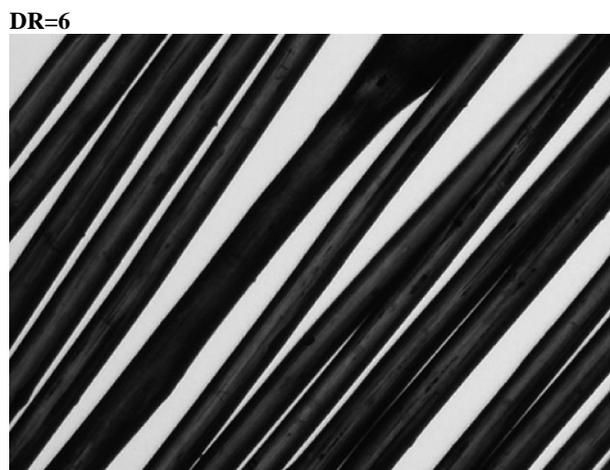
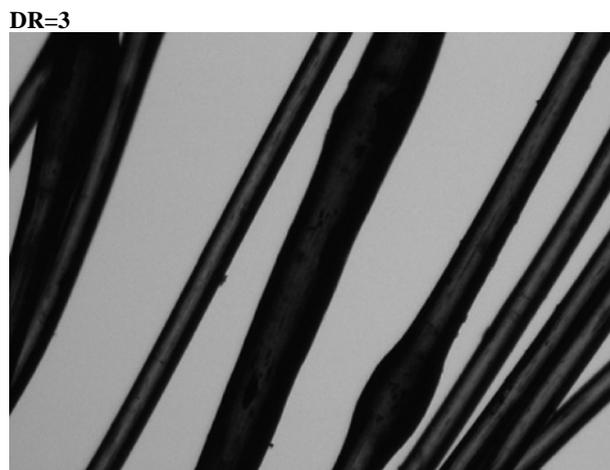
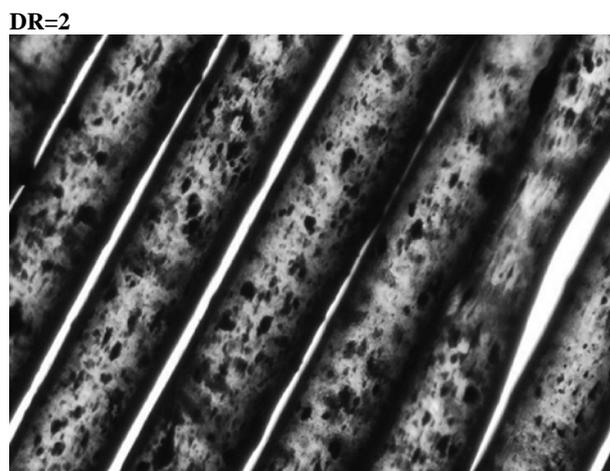


Figure 4. Stereoscopic images of fibers from PP and 10 wt-% Panipol with different draw ratios: DR=2, 3, 6.

Better dispersion and more sever mixing in B sample, has reduced the average size of the conductive phase. This may explain why a better mixing has given lower electrical resistance in lower draw ratios. During the compounding we observed that with increasing the content of PANI, the melt shows a higher viscosity, so the PANI rich phase in the fibre has a higher viscosity compare to the PP rich phase, when the size of the droplets are small, they need less force to change their shape to fibrils and consequently a lower draw ratio is

needed to orient them along the fibre axis. On the other hand, the diameter of these fibrils is small (because they are made from small size droplets) and under a higher draw ratio, the pathway of conductive materials will disconnect soon, this can show why a better mixed blend is not as good as a less mixed blend when the fibre is prepared under high draw ratio. As Figure 5 and 6 show, 20A2 has bigger average size disperse phase compare to 20B2 due to different mixing conditions (both samples have 20 wt-% polyaniline and are made under draw ratio of 2). When draw ratio is

changed from 2 to 4, its influence on resistance is different, because in A-sample has lead to more fibril formation and better conductivity, while for B- sample it may result in more fibril breakage and less conductivity.

Actually the size of the first conductive droplets and applied force to orient those to fibril-like morphology should be optimum to have an appropriate balance of fibrils formation/breakage. In other words, there is an optimum draw ratio for each compound to have a fibrillar pathway of conductive phase in fibre, which is depended on morphology of the blend.

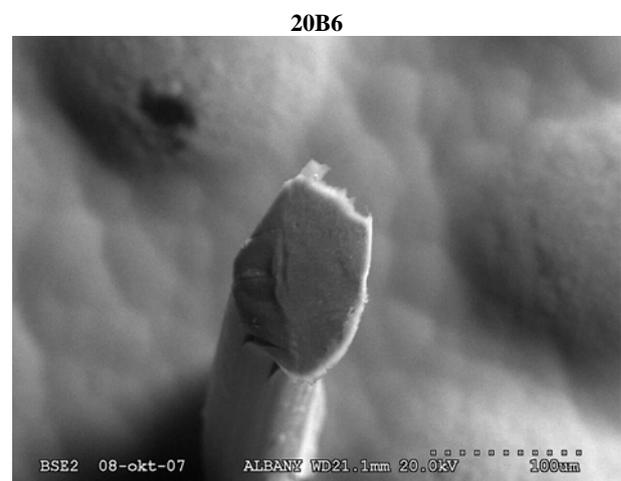
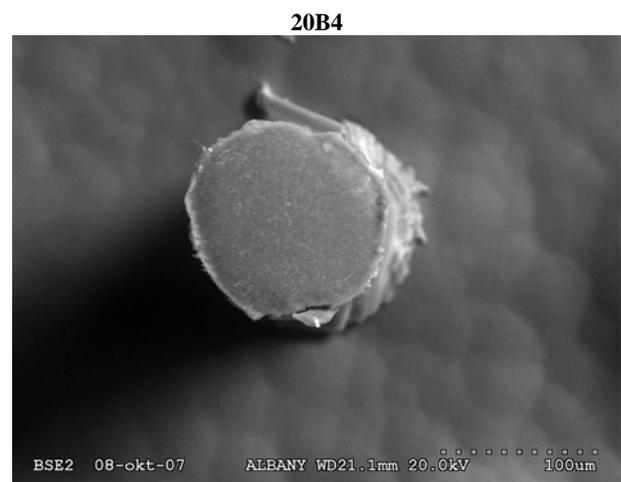
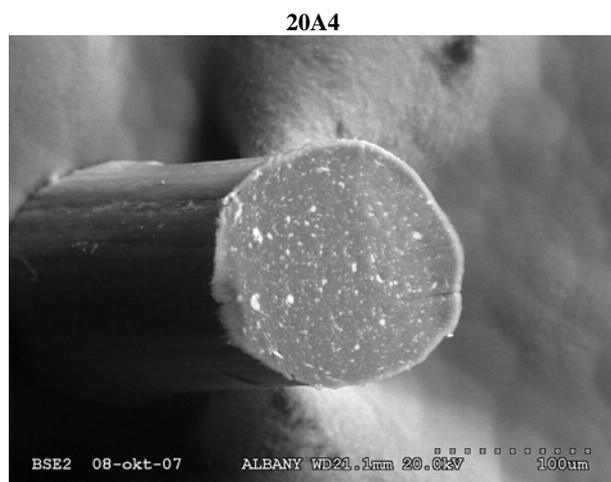
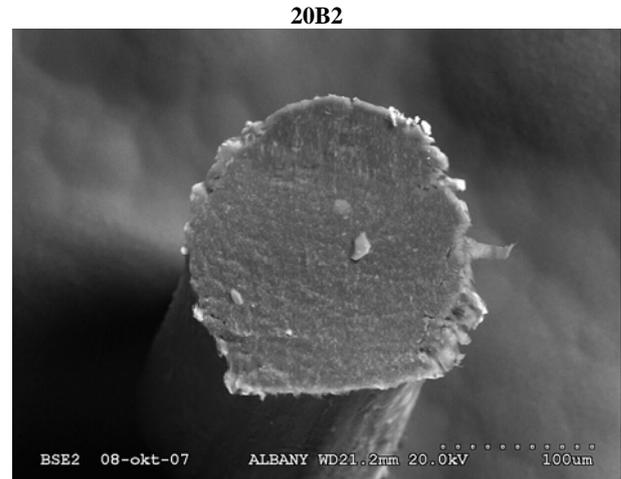
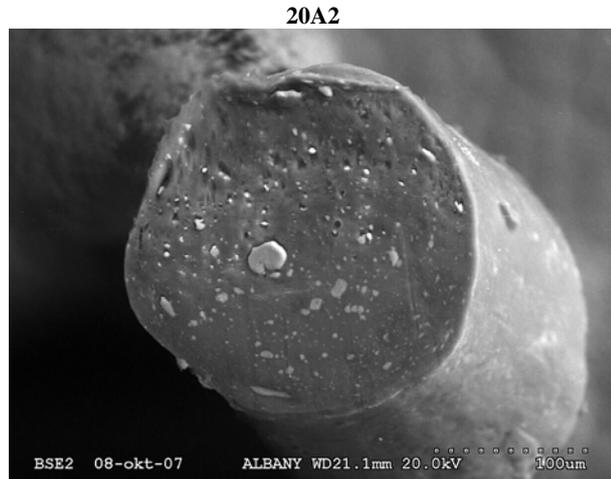


Figure 5. SEM micrographs of fibres: 20 wt-% polyaniline/ A- condition/ draw ratio of 2, 4 or 6.

Figure 6. SEM micrographs of samples: 20 wt-% polyaniline/ B- condition/ draw ratio of 2, 4 or 6.

CONCLUSION

PP/Panipol is a two phase blend of dispersed conductive PANI rich phase in the insulating PP rich matrix. Electrical resistances of fibres prepared of this blend made under different mixing conditions and draw ratios, show that for each compound there is an optimum draw ratio to obtain minimum resistance. Two factors are shown to control resistance of fibres: average size of dispersed polyaniline rich phase, which depends on blending conditions, and applied force to change these conductive domains to fibrillar morphology, which is controlled by draw ratio of the fibre. These two factors can control conductive fibrils formation/breakage along the fibre axis to make a continuous pathway in order to conduct electricity. Other factors such as matrix viscosity and proper selection of it, is expected to have important influence on fibre resistance, which would be studied in our future investigation.

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