

Polyaniline–Polypropylene Melt-Spun Fiber Filaments: The Collaborative Effects of Blending Conditions and Fiber Draw Ratios on the Electrical Properties of Fiber Filaments

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ABSTRACT: A melt-processable polyaniline complex was blended with polypropylene under different mixing conditions and melt-spun into fiber filaments under different draw ratios. The conductivity, electrical resistance at different voltages, and morphological characteristics of the prepared fibers were investigated. The morphology of this two-phase blend was demonstrated to have a large effect on the conductivity level and the linearity of the resistance–voltage relationship of the blend fibers. Two factors had substantial effects on the morphology and electrical properties of the fibers. They were the size

of the initial dispersed conductive phase, which depended on the melt blending conditions, and the stress applied to orient this phase to a fibril-like morphology, which was controlled by the draw ratio of the fiber. The two factors were shown to be associated with each other to maintain an appropriate balance of fibril formation and breakage and to create continuous conductive pathways. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 558–564, 2011

Key words: blends; conducting polymers; drawing; fibers

INTRODUCTION

Electroconductive fibers have potential applications in smart and interactive textiles, such as in sensors,^{1–5} electrotherapy,⁶ health-monitoring shirts,⁷ dust- and germ-free clothing,⁸ heat generation,⁹ and cooling systems.¹⁰ Conductive fibers based on polymers have been produced by the coating of the fiber with a conductive material and by the wet- or melt-spinning of polymers that are compounded with electrically conductive fillers, such as metal powders or carbon black. The use of these fillers in polymeric fiber filaments has made it possible to increase the conductivities of the fibers from 10^{-12} to 10^{-6} S/cm.¹¹ With the discovery of intrinsically conductive polymers (ICPs), such as polyacetylene, polypyrrole, and polyaniline (PANI), it seems that the level of conductivity can be raised to 10^{-1} S/cm or even higher.¹¹ Higher conductivities are usually achieved by coating the fiber. Because of the continuous circular topology of a conductive coating on the fiber, the continuous connection between ICP chains is more easily maintained than in the case of a

coated surface.¹² The wet-spinning of PANI,^{13–16} PANI/poly(ω -aminoundecanoyle),¹⁷ and PANI/poly(*p*-phenylene terephthalamide)¹⁸ have been studied previously. However, the use of melt-blended ICPs with common fiber-forming polymers and then the melt-spinning of these blends into fibers, in place of the solution blending and wet-spinning methods, is an interesting approach. If a homogeneous, conducting blend is achieved, the fiber should also be homogeneously conducting, with no percolation threshold levels. Preparing such conductive fibers with the melt-spinning process is more difficult but still potentially interesting, as melt spinning is the major process used to produce continuous textile fibers. Some reports on this approach can be found in the literature. Kim et al.¹² prepared melt-spun fibers from PANI salt/polypropylene (PP) blends, but the electrical conductivity was unsatisfactory because of homogeneity problems. PANI is a well-known ICP. PANI is infusible, but under special conditions, it can be made processable.¹⁹ Wide-angle X-ray scattering and transmission electron microscopy characteristics of melt processable PANI/PP have been reported by Passiniemi et al.²⁰ Conductive fibers based on PANI have potential applications in chemical sensors, electrically or chemically active actuators, electrostatic discharge protective clothing, and textile resistive heating elements.

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In this study, PP and a commercial PANI compound, Panipol CXL, were used to prepare blends under different blending conditions. The blends were then extruded into fibers with melt-spinning technology under different solid-state draw ratios. The electrical conductivity of the fibers, the electrical resistance at different voltages, and the fiber morphology determined by scanning electron microscopy (SEM) were characterized.

EXPERIMENTAL

Materials and blending

A PANI compound (Panipol CXL from Panipol, Oy, Porvoo) and a fiber-grade PP (HF350FB from Borealis, Kongens Lyngby, Denmark) were melt-mixed with a 15-cc twin-screw microcompounder (DSM Xplore, Geleen, The Netherlands). The Panipol CXL compound was based on a proprietary technology with PANI doped by means of protonation with dodecylbenzene sulfonic acid to render it electronically conductive (the total PANI content in the Panipol CXL compound was 25 wt %).

Two sample series were prepared with PP and Panipol CXL. The first samples were processed at 200°C with a screw rotation rate of 70 rpm for 12 min. These samples are referred to as the A series. The second group of samples, the B series, was processed at 220°C with a screw rotation rate of 70 rpm for 15 min. Panipol CXL, the conductive component, accounted for 20% of the weight of the samples of both series.

Fiber spinning

Fibers were melt-spun from the processed compounds through a 0.2-mm spinneret die attached to a microcompounder barrel. The fibers were then drawn over two Godet rolls (Fourné Polymertechnik, Alfter, Germany). The first Godet was heated to a temperature of 120°C. The rotational speed of the Godet rolls was adjusted so that draw ratios of 2, 3, 4, 5, and 6 were obtained.

Electrical resistance

To obtain the conductivity of single fibers, the resistance was measured at a constant voltage of 10 V with a METRISO 2000 resistance meter (Wolfgang Warmbier e.K., Hilzingen, Germany). The electrical current was applied between two clips holding 100 mm of fibers. The conductivity (C ; $\Omega^{-1} \text{ cm}^{-1}$ or S/cm) of single fibers was calculated with the formula $C = L/RA$, where R is the resistance measured (Ω), L is the length, and A is the cross section of the fibers. The mean value of conductivity measured for five samples is reported.

To determine the resistance–voltage relationship, bundles of 16 fibers were attached to clips at a dis-

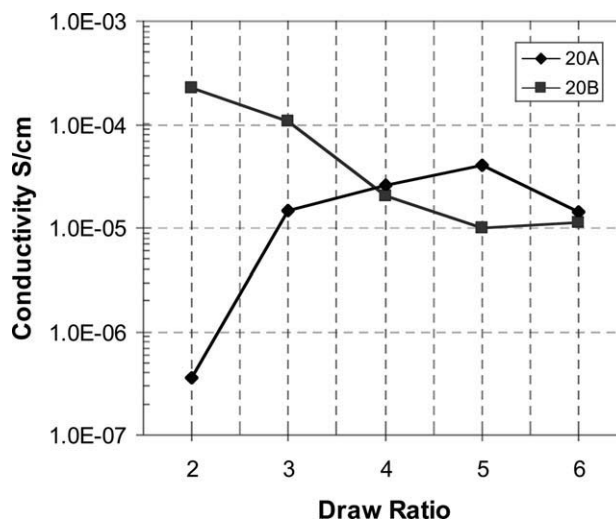


Figure 1 Electrical conductivity of fibers containing Panipol CXL at 20 wt % made from A or B blends and drawn to fibers at different draw ratios.

tance of 100 mm. The resistance was measured with a Keithley 6487 (Cleveland, Ohio, USA) resistance meter at voltages ranging from 0.1 to 500 V. (the Keithley meter was used because the METRISO's voltage range was limited.) All resistance measurements were conducted under ambient conditions (temperature = 21°C, relative humidity = 12%).

Morphology and mechanical analysis

Scanning electron microscopy was used to study the fiber cross sections and fiber surfaces. The morphology of the compounded granulates was also examined. The micrographs were analyzed by NIS-Elements-D (Nikon Instruments Europe, Badhoevedrop, the Netherlands) image analysis software. The number of visible domains representing the PANI-containing phase in each sample's cross section was calculated. The image analysis was done on micrographs of the same magnification. The mean values of three cross sections are reported for each sample. To study the mechanical properties, we used a Favimat single-fiber tester (Textechno, Mönchengladbach, Germany) with a 1200-cN load cell and a test speed of 30 mm/min. A total of 25 fibers and a gauge length of 10 mm were measured for each sample.

RESULTS AND DISCUSSION

Figure 1 shows the conductivity of single fibers containing Panipol CXL at 20 wt % mixed under condition A or B and then drawn into fibers under different draw ratios (2, 3, ...6). The standard deviations varied from $\pm 1\%$ up to $\pm 10\%$, depending on the fiber's conductivity. The more conductive fibers

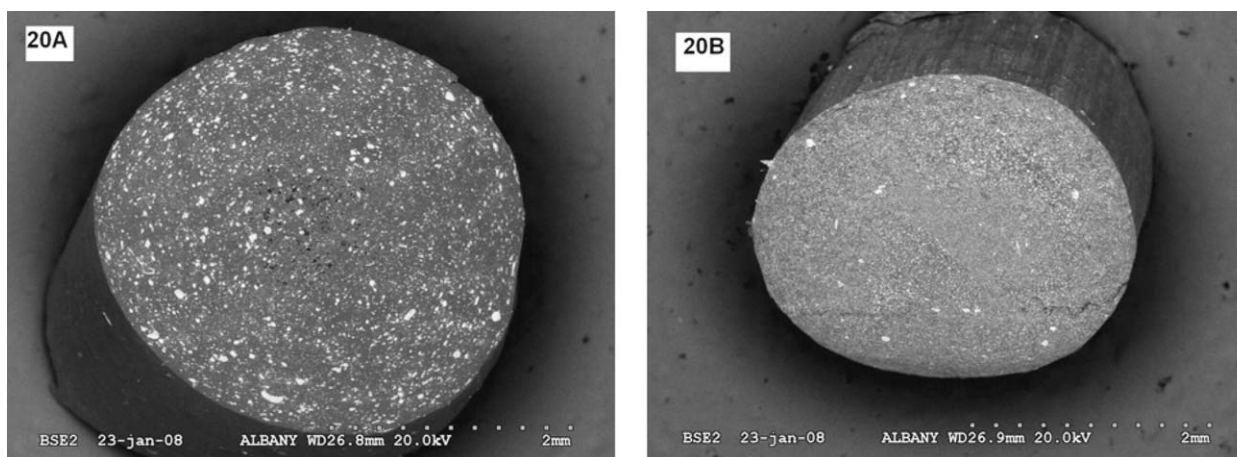


Figure 2 SEM micrographs of cross sections of the blend granulates: 20 wt % of Panipol CXL/processed at 200°C (A condition) and 220°C (B condition).

showed a lower deviation from standard when the conductivity and resistance were measured.

Figure 1 shows that for each compound, there was an optimum draw ratio to obtain the maximum conductivity in the prepared fibers. For 20A compounds (mixed under condition A), the maximum conductivity was obtained in fibers made under a draw ratio of 5, whereas for 20B, such a maximum was observed at a draw ratio of 2. Furthermore, a comparison of the two maximum conductivities obtained for the A and B series showed that the highest conductivity was observed in the B series, which was mixed under more vigorous processing conditions than in the A series. This might have been due to better mixing and dispersion of the conductive PANI throughout the PP matrix. Figure 1 shows this observed maximum conductivity (20B at a draw ratio of 2) and its place to reflect a lower draw ratio than that of the maximum conductivity obtained in the 20A series.

As will be discussed in greater details later, drawing could increase the possibility of the formation of conductive pathways. This was beneficial to fiber conductivity, but on the other hand, excess drawing could cause disconnections and decrease conductivity.

According to our previous study with transmission electron microscopy and SEM,²¹ polypropylene/Panipol CXL compound is a two-phase blend containing a dispersed PANI-containing phase in a continuous PP phase. Figure 2 shows the SEM micrographs for the cross sections of the granulated compounds processed under conditions A and B. Both images use the same scale. Light domains represent the conductive PANI-containing phase dispersed in the dark continuous PP matrix. As Figure 2 shows, the granulates processed at 200°C showed more visible domains than the granulates processed at 220°C. Table I shows the results of image analysis for the cross sections of granulates processed according to conditions A and B (and the fibers made from these blends). The mean value of

measurements for three samples is reported in each case. Calculations of the visible domains in the 20A and 20B blend granulates' cross sections showed that more vigorous mixing in the sample processed at 220°C, 20B, decreased the number of visible domains compared to that in sample 20A. This indicated that a more homogeneous structure and smaller PANI droplet phase were obtained in 20B.

To investigate the influence of the drawing and mixing parameters on the fiber morphology, SEM micrographs of the fibers were studied (Fig. 3), and images were analyzed (Table I). The samples were named according to their Panipol CXL content, the blending conditions (A or B), and the draw ratio. For example sample, 20A2 is PP blended with 20 wt % Panipol CXL under condition A and drawn into fibers with a draw ratio of 2.

SEM micrographs of the fiber cross sections at the same scale (100 μ m) and the calculation of the mean values of the visible domains in three samples of each fiber (Fig. 3 and Table I, respectively) showed

TABLE I
Image Analysis of the Granulates and Fibers
Cross-Section Micrographs

	Number of domains	Standard deviation
Blend		
20A	142	5.89
20B	32	2.94
Fiber made of A		
20A2	97.5	4.5
20A4	70	6.33
20A6	11	4.97
Fiber made of B		
20B2	9.67	3.86
20B4	4.67	1.7
20B6	2	1.63

The number of visible PANI droplets in the cross section was counted.

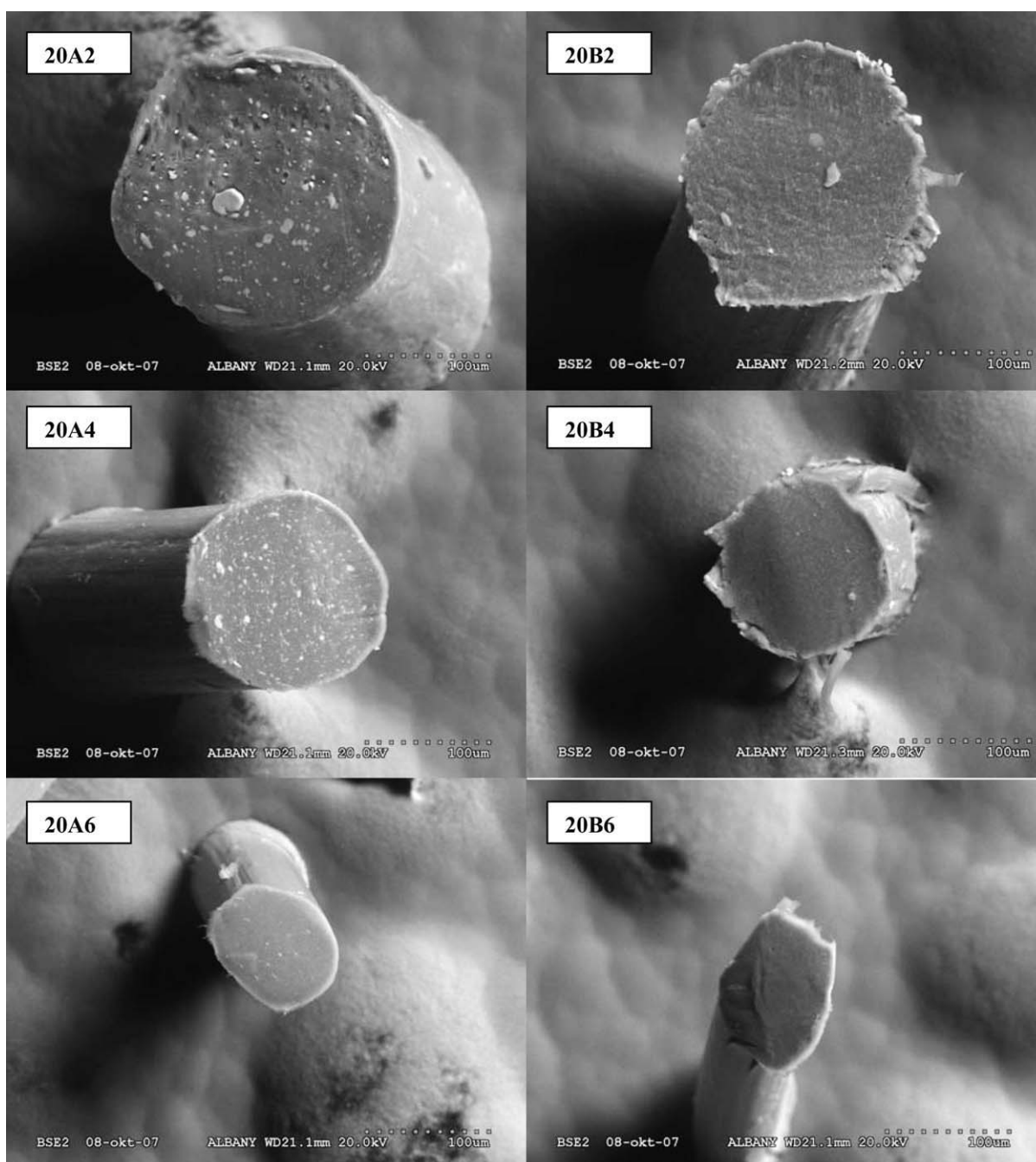


Figure 3 SEM micrographs of the cross sections of the fiber samples: PP/20 wt % Panipol CXL, condition A or B, and draw ratios of 2, 4, and 6 (label of SEM images: working distance (WD) 21.1 mm, 20.0 kV, 100 μm).

that increasing the draw ratio from 2 to 6 reduced the number of visible droplets in the fiber's cross section. The following discussion shows that fewer droplets in the cross section of fibers in the A series was a sign of more conductive fibril formation, whereas in the B series, there was a sign of more conductive fibril breakage; that is why the conductivity of the A and B series showed reversed trends with draw ratios (Fig. 1).

The reduced number of visible droplets in the cross section could be attributed to fibril formation,

fibril breakage, or both. Actually, a lower number of visible spots meant that their size was so decreased that they were not visible with this SEM resolution. The volume of the droplet phase in the fiber was constant, and when one dimension was decreased (i.e., the cross-sectional area), the other dimension (i.e., along the fiber axis) was increased; this could show rod or fibril formation. The other possibility resulting in a decreased droplets size was that the droplet was first stretched to form a rod and then a fibril and was finally broken into two smaller

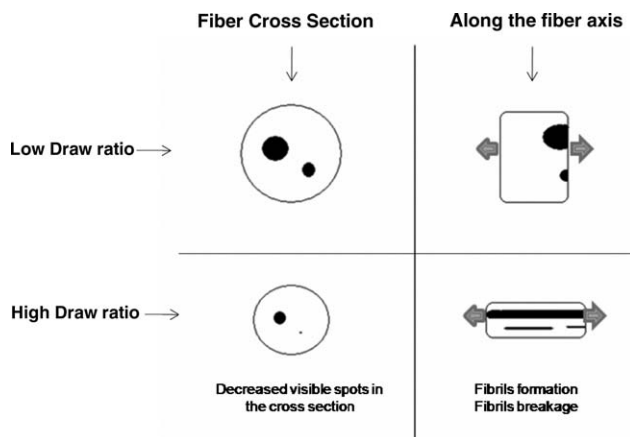


Figure 4 Comparative scheme of morphological changes during fiber drawing and their influence on visible spots in the fiber cross section.

droplets, a phenomena that can be termed *fibril breakage*. As result, both fibril formation and breakage could decrease the size of the cross section of the droplets and result in fewer visible domains. A comparative scheme of morphological changes during fiber drawing and its influence on the number of visible spots in the cross section is illustrated in Figure 4.

The high-resolution SEM images in Figure 5 also show that the dispersed phase in 20A represented smaller size droplets when it was stretched under a draw ratio of 4 rather than 2.

These explanations, based on the formation and breakage of fibrils, could explain the previously observed difference in the conductivity–draw ratio relationship of fibers made from the blends 20A and

20B. To conduct electricity well, it is desirable to have a continuous pathway of conductive phase. In PP/Panipol CXL, which was a two-phase blend containing a conductive dispersed phase in an insulating matrix, such conductive pathways could be achieved by the creation of a fibrillar morphology. As indicated before in Figure 1, the fibers made of 20B (small-size dispersed phase) possessed higher conductivity at low draw ratios and poor conductivity at high draw ratios. During compounding, the processing parameters and extruder output showed that with increasing content of Panipol CXL, the melt exhibited a viscosity that was much higher than that of pure PP. Consequently, the PANI-containing phase of the fiber obviously possessed a higher viscosity than the PP phase. When high-viscose droplets were small in size, such as in the 20B samples, less stress was required to reform their shape to rods and, then, fibrils. Consequently, a low draw ratio was enough to orient them along the fiber axis and create conductive pathways. On the other hand, the diameter of these fibrils was small (because they were made from small-size droplets), and under higher draw ratios, some pathways of the conductive fibrils were broken. This explained why an increase in the draw ratio decreased the conductivity in the 20B fibers, shown in Figure 1. In fibers made of 20A, which had large-size droplets, the behavior was quite different. These high-viscose large droplets needed a greater stress to be oriented to rods and then fibrils along the fiber. Increasing the draw ratio to 5 increased the stress applied and the formation of the conductive fibrils so that the conductivity of the fibers increased gradually.

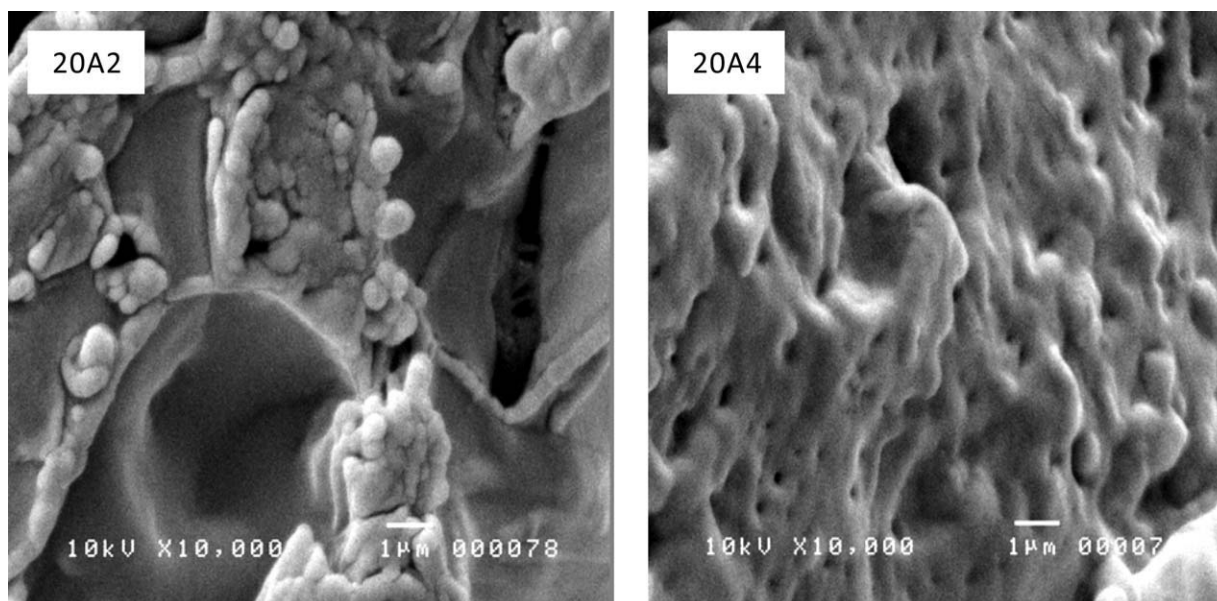


Figure 5 High resolution SEM micrographs of cross sections of fiber samples: PP/20 wt % Panipol CXL, blended under condition A, fiber draw ratio of 2 and 4.

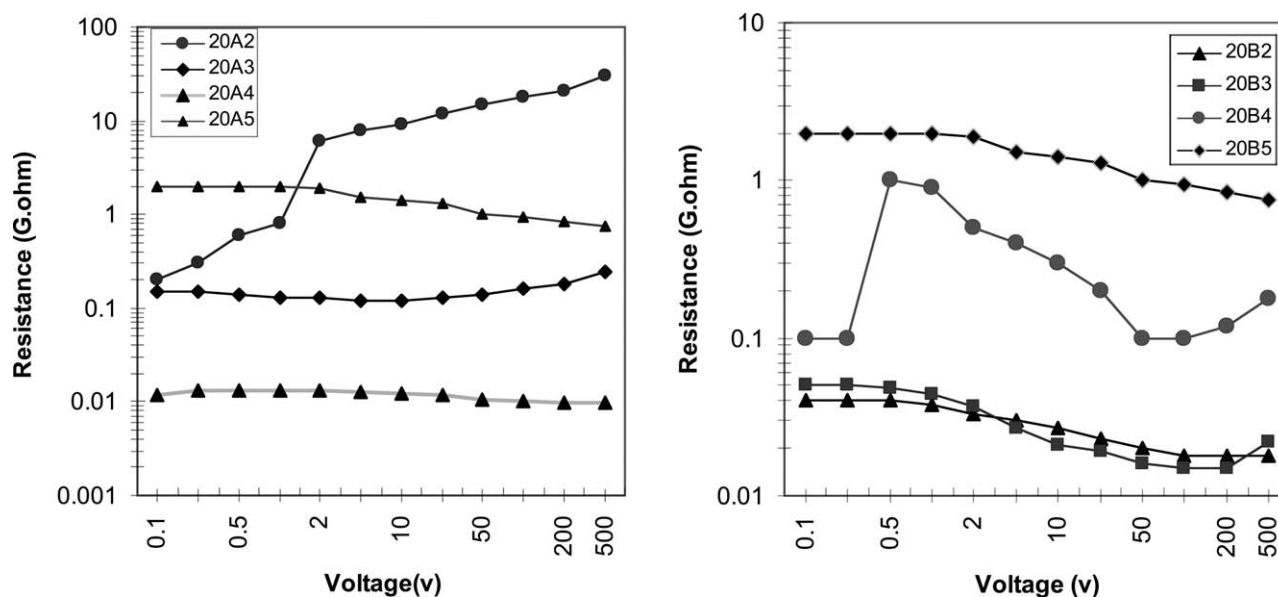


Figure 6 Resistance versus voltage for fibers 20B and 20A made under different draw ratios

However, at a draw ratio of 6, the breakage of fibrils exceeded formation, and a decreased conductivity was observed.

When the draw ratio was increased from 2 to 4 or 6, although both the 20A and 20B series showed less visible droplets in the fiber cross section (Fig. 3), the draw ratio effect on conductivity was different for different blend fibers (Fig. 1) because a decreased number of visible domains could have indicated fibril formation or fibril breakage. With increased draw ratio, there were more fibrils formed and better conductivity in the samples that had bigger size droplets (20A), whereas the samples with smaller size droplets (20B) had more fibril breakage and a lower conductivity. Actually, to conduct electricity, the size of the initially formed conductive droplets and the stress applied to orient them to a fibril-like morphology should be matched to give an appropriate balance of fibril formation-breakage. This also explained the difficulties and critical factors in the preparation of melt-spun fibers from such two-phase blends.

To determine the effects of the mixing conditions and dispersed phase size on the voltage-resistance relationship, graphs of samples 20A and 20B are presented in Figure 6. In A samples, the most linear resistance-voltage plot was obtained for fibers made

under a draw ratio of 4 (20A4), whereas such behavior was observed in B samples for fibers made by draw ratios of 2 and 3 (20B2 and 20B3). On the other hand, 20A4, 20B2, and 20B3 were among the most conductive fibers in each series, as indicated previously in Figure 1.

This suggests that fibers with higher conductivities had a more linear resistance-voltage relationship. Fibers showing a higher conductivity actually had more conductive pathways or closer conductive domains. It seemed that smaller interdomain distances (less insulating distance between the conductive domains) resulted in less dependency of the resistance on the applied voltage. On the other hand, the interdomain distance depended on such different factors as concentration of the conductive phase, the size of the domains, and the distribution and shape of the conductive phase. All of these factors could be controlled in the compound by the PANI content, the mixing conditions, and the draw ratio of the fiber.

Initial mechanical tests for the fibers made under the same draw ratio showed that the tenacity of PP and the well-mixed PP/Panipol CXL fibers (20B) were roughly the same and higher than the value obtained for the 20A fibers. Furthermore, the modulus of the neat PP fiber was higher than those of

TABLE II
Mechanical Properties of the Fibers Prepared at a Draw Ratio of Five with PP/Panipol CXL

Fiber sample	Panipol content and mixing condition	Draw ratio	dtex	Force (cN)	Elongation (%)	Modulus (cN/dtex)	Tenacity (cN/dtex)
20A5	20 wt %, A	5	137	278	140	13.80	2.03
20B5	20 wt %, B	5	104	226.46	126	13.24	2.2
PP5	—	5	63	147.06	140	17.43	2.3

both blend fibers. The results for five-time drawn fibers are presented in Table II. A study of the mechanical properties is underway and will be reported in the future.

CONCLUSIONS

The electrical properties of fibers obtained by the melt blending and melt spinning of PP/PANI complex blends depended greatly on the morphology of these two-phase blends. The final morphology was controlled by two main factors, the average size of the dispersed PANI complex phase, which depended on the blending conditions, and the stress applied to deform these conductive domains to fibrillar morphology. The latter was controlled by the draw ratio of the fiber. These two factors preserved the conductive fibril formation–breakage balanced along the fiber axis to form a continuous pathway of conductive material to conduct electricity. Depending on the initial droplet phase size, an optimum draw ratio was necessary to obtain a maximum conductivity by the promotion of fibril formation (sufficient stress) and the prevention of fibril breakage (no excess stress). When the draw ratio was increased, both fiber series, made of large- and small-droplet-size blends, showed fewer droplets in the cross section of the fibers in SEM images, but their conductivity showed reversed trends with draw ratios because fewer visible droplets in the former was a sign of more fibril formation (which was beneficial to the conductivity), whereas in the latter, it was a sign of more fibril breakage (which decreased the conductivity).

Resistance–voltage plots showed that fibers with higher conductivity exhibited less dependency of resistance on the applied voltage, which could have referred to a more homogeneous structure and smaller interdomain distances. Initial mechanical tests showed that the tenacity of PP and well-mixed PP/Panipol CXL fibers was roughly the same, whereas the modulus of the neat PP was greater than that of the blend fibers. To fully investigate the

potential of these fibers in textile applications, it is necessary to study the conductivity of fibers aged under different environmental conditions and also the possibility of manufacturing textile fabrics from the fibers. This investigation is currently in progress, and the results will be reported in the near future.

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References

1. Mattmann, C.; Clemens, F.; Tröster, G. *Sensors* 2008, 8, 3719.
2. Barman, J.; Guha, S. K. *Sens Actuators A* 2006, 125, 210.
3. Hu, N.; Karube, Y.; Yan, C.; Masuda, Z.; Fukunaga, H. *Acta Mater* 2008, 56, 2929.
4. Knite, M.; Hili, A.; Hili, J.; Pas, J.; Teteris, V.; Zavickis, J. *Mater Sci Eng* 2006, 26, 771.
5. A-Li, Y.; Cheng, X.; Leung, M. *Synth Met* 2005, 155, 94.
6. Wha, K.; Park, H. J.; Kim, S. H. *J Appl Polym Sci* 2003, 88, 1225.
7. Bowman, D.; Mattes, B. R. *Synth Met* 2005, 154, 29.
8. Xue, P.; Park, K.; Tao, X.; Chen, W.; Cheng, X. *Compos Struct* 2007, 78, 271.
9. Hakansson, E.; Kaynak, A.; Lin, T.; Nahavandi, S.; Jones, T. *Synth Met* 2004, 144, 21.
10. Hu, E.; Kaynak, A.; Li, Y. *Synth Met* 2005, 150, 139.
11. Bhat, N. V.; Seshadri, D. T.; Nate, M. M.; Gore, A. V. *J Appl Polym Sci* 2006, 102, 4690.
12. Kim, A.; Koncar, B.; Devaux, V. *Synth Met* 2004, 146, 167.
13. Hsu, C. H.; Cohen, J. D.; Tietz, R. F. *Synth Met* 1993, 59, 37.
14. Hsu, C. H.; Epstein, A. J. *Synth Met* 1997, 84, 51.
15. Mattes, B. R.; Wang, H. L.; Yang, D.; Zhua, Y. T.; Blumenthal, W. R.; Hundley, M. F. *Synth Met* 1997, 84, 45.
16. Zhang, F.; Halverson, P. A.; Lunt, B.; Linford, M. *Synth Met* 2006, 156, 932.
17. Zhang, Q.; Wang, X.; Chen, D.; Jing, X. *J Appl Polym Sci* 2002, 85, 1458.
18. Andreatta, A.; Heeger, A. J.; Smith, P. *Polym Commun* 1990, 31, 275.
19. Paul, K.; Raji, C. *Polym Int* 2001, 381.
20. Passiniemi, P.; Laakso, J.; Österholm, H.; Pohl, M. *Synth Met* 1991, 84, 775.
21. Soroudi, A.; Skrifvars, M. *Proceedings of Autex 2008 World Textile Conference, Città Studi, Biella, Italy, CD version, June 24–26, 2008.*