

Conducting Bicomponent Fibers Obtained by Melt Spinning of PA6 and Polyolefins Containing High Amounts of Carbonaceous Fillers

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ABSTRACT: Melt spinning of conductive polymer composites (CPCs) is coupled with some difficulties such as a decrease of conductivity upon drawing and a reduced spinnability with increasing filler concentration. Applying bicomponent technology may provide the possibility to produce fibers from CPCs with a high filler concentration. A pilot-scale bicomponent melt spinning set-up was used to produce core/sheath fibers with fiber titers between 13 and 47 dtex. The sheath material was polyamide 6 (PA6) or polypropylene (PP) and the core material was a CPC. Two CPCs were used, polypropylene (PP) with carbon black (CB), denoted by PP/CB, and polyethylene (PE) with multiwalled carbon nanotubes (MWNT), denoted by

PE/MWNT. The results showed that both materials could be used with a filler concentration of 10 wt % to obtain melt draw ratios up to 195. The volumetric fraction of core material in the bicomponent structure was 28%. A heat treatment of PP/CB fibers restored the conductivity to the level of the undrawn material, corresponding to an increase in conductivity by a factor 5. The same heat treatment had a positive effect on the conductivity of PE/MWNT fibers although the conductivity was not restored. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 936–943, 2012

Key words: carbon black; multiwalled carbon nanotubes; fibers; conductivity; percolation; melt spinning

INTRODUCTION

In our previous work,¹ it was found to be difficult to process conducting polymeric composites (CPC) with filler concentrations higher than 8 wt % carbon black (CB) into usable fibers (produced with melt draw ratio (MDR) >100), mainly due to spin line breaks. Using multiwalled carbon nanotubes (MWNT) as conducting particles instead of CB provided no advantages in this respect. The reduction in spinnability with increasing filler content was correlated with increasing melt elasticity (elastic modulus). In summary, the problems encountered were the following: (i) spin line breaks at low MDRs and an unstable spin line resulting in diameter variations, (ii) the electrical conductivity vanished (MWNT) or decreased (CB) in the melt drawing and solid-state drawing processes, and (iii) the fibers had

an insufficient strength considering the demands of the textile industry, where processes like yarn twisting, crimping, knitting, and weaving generally require fibers with rather high tenacity.

Here, we explore the possibility to remediate these shortcomings by employing bicomponent technology where the processability and strength are provided by the sheath material and the conductivity by the core material. Bicomponent technology is well-known for producing antistatic fibers,² usually with CB as the conductive filler. In this case, the aim was to increase both the volumetric ratio of CPCs in the fiber and the conductivity of the CPCs (i.e., higher filler concentration or fillers with higher conductivity) to create fibers with functionality (e.g., power and signal transmission, heating capability, and EMI shielding) beyond what is required for antistatic applications. It would also be interesting to see whether the shortcomings of MWNT (loss of conductivity upon melt drawing) in the production of single-component monofilaments^{3–5} could be overcome by using the bicomponent technology. To the best of our knowledge, there has been no study on using MWNT as filler material in bicomponent fibers.

Ziabicki⁶ examined the influence of surface tension and melt elasticity on the spinnability (although the

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surface tension has little effect on the spinnability of highly viscous materials, such as polyolefins). It seems possible that the spinnability of the CPCs could be improved if the elasticity of these materials was to be counteracted by the viscous forces of a surrounding material, such as in a bicomponent melt spinning line, allowing the use of a material with low spinnability (high filler concentration) as the core. This would solve problem (i) and (iii) allowing higher filler concentrations, but not problem (ii). However, recent findings⁷⁻⁹ indicate that if a conductive polymer composite, which has solidified under strained conditions, is heated above the melting point of the polymer, the conductivity will be restored, at least partially. This behavior is attributed to conformational changes of the polymer molecules and diffusion of filler particles, which lead to reorientation of the filler particles, if these are small enough, and thereby to formation of new contact points and a new conducting network of particles (secondary agglomeration).¹⁰ If the material surrounding the CPC (as in a sheath-core fiber) has adequate mechanical and thermal properties, the fibers would retain their original shape during a postprocessing heat treatment which would lead to a reformation of the conducting network, thereby increasing the conductivity of the drawn material.

For this purpose, we used a pilot scale melt spinning line to produce bicomponent sheath-core fibers where the core was a CPC and the sheath was a polymer with high viscosity and high melting point (polyamide 6). CB and MWNT were used in concentrations up to 10 wt % in the core for producing fibers at MDRs from 44 to 195, resulting in fibers with linear densities (titers) between 13 and 47 dtex (g/km). Solid-state drawing of the yarns was explored as a means to increase the strength of the fibers. The fibers were then subjected to a heat treatment to enhance the conductivity.

EXPERIMENTAL

Materials

The carbon black (CB)-grade was Ketjenblack EC 600JD from AKZO NOBEL, the Netherlands, with aggregate size 10–50 nm, density 1800 kg/m³, apparent bulk density 100–120 kg/m³, BET surface area 1250 m²/g, pore volume 480–510 cm³/100 g, and pH 8–10. These characteristic data were provided by the supplier. polypropylene (PP) was HG245FB from Borealis, Belgium, (MFI_{2/230} 26 g/10 min, melting point 163°C, density 910 kg/m³). High Density Polyethylene (HDPE) was Aspun 6835 A from the Dow Chemical Company, Belgium, (MFI_{2.16/190} 17 g/10 min, melting point 129°C, density 950 kg/m³). PA6 was Ultramid B33L from BASF, Germany. The

relative viscosity (RV) number in 96% sulfuric acid was 3.19 and the density 1120 kg/m³.

A masterbatch containing HDPE and multiwalled carbon nanotubes (MWNT) was used; MB3520-00 from Hyperion Catalysis, Cambridge, USA, using Fibril™ Nanotubes (denoted H-MWNT). The MB3520-00 contained 20 wt % MWNT, which was confirmed by us using thermogravimetric analysis (TGA). The nanotubes were produced by chemical vapor deposition (CVD). The MWNT in MB3520-00 had been dispersed by melt compounding. The molecular characteristics of the HDPE in the masterbatch are however unknown and thus probably deviates from the HDPE used to obtain the different filler concentrations in this study. Experiments were also performed with a MWNT concentrate, Nanocyl 9035, obtained from Nanocyl, Belgium. Nanocyl 9035 contained 31 wt % MWNT (denoted N-MWNT) and the nanotubes had been dispersed in HDPE by *in situ* polymerization.¹¹

Mixing

The conductive polymer composites used in the core were prepared by melting the polymer in a mixing chamber and then adding the conductive filler, either pure (CB) or as a masterbatch/concentrate (MWNT). The mixing time was 10 min, the temperature was 200°C, and the rotational rate was 100 rpm.

Melt spinning of bicomponent fibers

Melt spinning was performed using a pilot scale extrusion spinning machine, model Labspin II, from ESL, England, schematically described in Figure 1. The following settings were used: Extruder 1 (core extruder) held at 240°C in the final zone. Melt pump 1 (core melt pump) held at 240°C and the melt volume flow rate from the pump was 10 cm³/min. Extruder 2 (sheath extruder) held at 270°C in the final zone. Melt pump 2 (sheath melt pump) held at 270°C and the melt volume flow rate from the pump was 26 cm³/min. Thus, each fiber consisted of 72 vol % sheath material and 28 vol % core material upon exiting the spinneret. The diameter of the holes in the spinneret was 0.6 mm and there were 24 holes. The calculated exit speed from the die was 5.3 m/min and the spinneret temperature was kept at 270°C. The ratio between the tangential velocity of take-off wheel and the calculated exit speed from the spinneret was taken as the MDR, see Figure 1. Varying the speed of the take-off wheel between 233 and 1034 m/min gave fibers with MDRs between 44 and 195. The ratio between the tangential velocities of the first two pairs of godet rolls (cold drawing between the first and second pair of godet rolls) was taken as the solid-

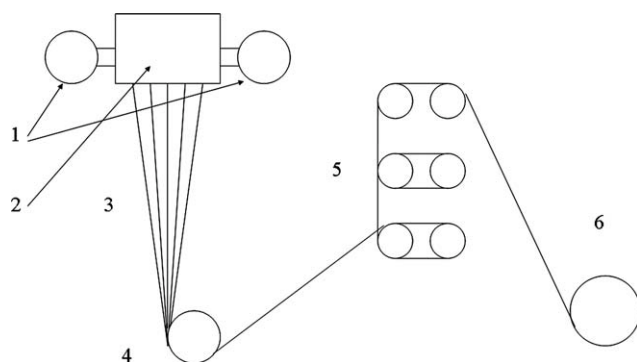


Figure 1 Schematic picture of the fiber spinning line. Two melt pumps, (1) each fed by a single screw extruder maintains a constant volumetric flow rate in the spinneret. (2) Filaments of molten polymer emerge from the spinneret and are drawn to fibers (3) by the take-off wheel. (4) By varying the speed and temperature of the godet rolls (5) the fibers can be further drawn in the solid state to increase the tenacity before they are wound up on a bobbin (6).

state draw ratio (SSDR), see Figure 1. Solid-state drawing was performed using SSDRs of 1, 2, and 3, where a SSDR of 1 implies no solid-state drawing. Increased SSDR was compensated by a lower MDR to obtain fibers with similar titers.

The temperature of the first and second pairs of godet rolls was kept at 70°C. An alternative route was also tried by which the fibers were heat treated inline by increasing the temperature of the second pair of godet rolls to 150°C. The third pair of godet rolls was always kept at room temperature. Table I

summarizes the different material combinations used and the applied draw ratios.

Electric conductivity of the fibers

The conductivity of the fibers was determined using the two-point method. The measurements on the undrawn material (sampled directly from the spinneret) were performed on the strands one by one, but for the drawn fibers, measurements were made on a bundle of fibers (about 20 mg/cm) cut with a razor blade at its ends, after applying silver paint on both ends of the fiber bundle. Three samples were tested for each data point.

A power supply (Leek, Netherlands) applied a voltage (U) over the specimen, measured by a multimeter (Everett, Washington). The voltage was varied in the range 5 (low resistance) to 450 V (high resistance) depending on the conductivity of the specimen. The current (I) was measured by an electrometer (Cleveland, Ohio). The conductivity (σ_v) was calculated from the mass (m) of the fiber bundle (yarn) between the silver paint spots, the length (l) of the bundle and the measured voltage and current according to

$$\sigma_v = \frac{I\rho l^2}{Um} \quad (1)$$

where ρ is the calculated density of the filaments. The length (l) was around 10 cm, measured with a ruler.

TABLE I
Parameters Used for the Production of Fibers

Sample	Calc. fiber titre (dtex)	MDR : SSDR	Core material	Sheath material
PP/PPCB1	47	44 : 1	PP/CB7	PP
PP/PPCB2	23.5	88 : 1	PP/CB7	PP
PP/PPCB3	12	175 : 1	PP/CB7	PP
PP/PPCB4	23.5	44 : 2	PP/CB7	PP
PP/PPCB5	23.5	88 : 1	PP/CB10	PP
PP/PPCB6	23.5	44 : 2	PP/CB10	PP
PA6	20	67 : 2	PA6	PA6
PA6/PE	20	67 : 2	PE	PA6
PA6/PPCB1	38	67 : 1	PP/CB10	PA6
PA6/PPCB2	26	100 : 1	PP/CB10	PA6
PA6/PPCB3	13	195 : 1	PP/CB10	PA6
PA6/PPCB4	13	100 : 2	PP/CB10	PA6
PA6/PPCB5	13	67 : 3	PP/CB10	PA6
PA6/PEMWNT1	38	67 : 1	PE/H-MWNT10	PA6
PA6/PEMWNT2	26	100 : 1	PE/H-MWNT10	PA6
PA6/PEMWNT3	13	195 : 1	PE/H-MWNT10	PA6
PA6/PEMWNT4	13	100 : 2	PE/H-MWNT10	PA6
PA6/PEMWNT5	13	80 : 2.5	PE/H-MWNT10	PA6
PA6/PEMWNT6 ^a	13	80 : 2.5	PE/H-MWNT10	PA6
PA6/PEMWNT7	13	67 : 3	PE/H-MWNT10	PA6

PP/CB7 denotes a material with 7 wt % CB in PP and PE/H-MWNT10 denotes a material with 10 weight-% H-MWNT in PE. The godet roll temperature (70°C) refers to the second pair of rollers.

^a Godet roll temperature 150°C.

Heat treatment of fibers

Some specimens were subjected to a heat treatment at 180°C for 10 min to increase their conductivity. A shorter treatment time (1 min) was also tested. The conductivity of the specimens was measured before and after the heat treatment.

Microscopy

Samples for scanning electron microscopy (SEM) were prepared by embedding the fibers in an epoxy matrix and subsequently cryo-fracturing in liquid nitrogen before coating with 20 nm of gold using an ion sputter JEOL JFC-1100, Japan. SEM-micrographs of the fracture surfaces were then obtained with a JEOL JSM 5300, Japan.

Tensile properties

The fiber titers were determined on individual filaments using a Vibroscope (Lenzing, Germany) using at least 10 filaments collected from different areas along the fiber tow. The tenacity (ultimate tensile strength) of the filaments were then determined using a tensile test apparatus, Vibrodyn (Lenzing, Germany). The distance between the clamps was 20 mm and the test speed was 20 mm/min. A small weight (200 mg) was attached to the end of each filament and was used as a preload to make sure that the specimens were mounted straight.

RESULTS

Spinnability

The spinnability was expected to improve when a sheath material was used compared to the single component system. All the processing conditions described in Table I could be maintained for an extended period of time although occasional spin line breaks were seen at higher draw ratios, meaning that 10 wt % H-MWNT/PE and 10 wt % CB/PP could be melt drawn to a MDR of almost 200, when used as the core component, and that it was possible to perform solid-state drawing of the bicomponent fiber up to a SSDR of 3.

When using the same filler concentration, but using N-MWNT/PE as the core, it was however not possible to stretch the melt sufficiently to produce fibers of any technical interest, even when reducing the filler content to 6 wt %. In our earlier work,¹ it was shown that the loss of spinnability of the N-MWNT-containing system was paralleled by a significant melt elasticity of the material, i.e., an increase of the elastic modulus of the melt. This marked elasticity was associated with the formation of an elastic particle network. Such networks were

formed both in the CB- and the MWNT-systems, but were especially pronounced with N-MWNT¹.

Tensile properties of bicomponent fibers

Table II shows the tenacity of the bicomponent fibers produced. Without any solid-state drawing, i.e., SSDR = 1, the strength of the fibers was in many cases low as expected. PP/PPCB1, for example, had a tenacity of 4.6 cN/tex (40 MPa), which is in the range of the ultimate tensile strength of most isotropic isotactic grades of PP. Increasing the MDR significantly (to 175 or more) without applying any solid-state drawing increased the tensile strength only to a minor extent. However, when PA6 was used as the sheath material (and H-MWNT as the conducting filler), increasing MDR led to a more pronounced increase of the strength. Increasing the SSDR leads to orientation of crystalline regions, connected by tie molecules (the amorphous region), in the draw direction and significantly increasing the strength of the bicomponent fibers (and of the sheath).⁶ Changing the CB-concentration from 7 to 10 wt % for fibers with PP sheath had no substantial influence on the strength. Note that in the case of PP, as the sheath material, the bicomponent fibers did not fail at an elongation of 250% which was the maximum strain that could be attained with the tensile tester used. The tenacity given in Table II thus refers to the maximum stress measured during the test.

Commercial PA6-fibers usually have tenacities in the range 30–70 cN/tex.¹² When PA6 was used in the sheath and PE in the core, the fiber strength was reduced to 23.5 cN/tex (300 MPa), which can be associated with the poorer mechanical performance of the core material as well as the lack of adhesion between these two incompatible polymers. This trend was confirmed by comparing the tenacities of the PA6 fibers with those of the PA6/PEMWNT fibers, c.f. Table II.

In this context, it is certainly interesting to note that 10 wt % H-MWNT could be used in a core of HDPE with PA6 as the sheath material and tenacities exceeding 35 cN/tex could be achieved if a solid-state drawing of more than 2.5 was applied, see Table II. Increasing the godet temperature from 70 to 150°C had virtually no effect on the tenacity, but seemed to improve the conductivity of the core material.

The effect of the heat treatment at 180°C for 10 min on the mechanical properties is also shown in Table II. Clearly, the tensile strength of all the investigated fibers was reduced by this treatment, although the decrease appeared to be somewhat less pronounced in case of the fibers that had been subjected to the solid-state drawing. The reduction in

TABLE II
Mechanical and Electrical Properties of Bicomponent Fibers Before and After Subjected to a Heat Treatment (denoted HT) for 10 min at 180°C

Sample	Measured titre (dtex)	Conductivity (S/cm)	Conductivity after HT (S/cm)	Tenacity (cN/tex)	Elongation (%)	Tenacity after HT (cN/tex)	Elongation after HT (%)
PP/PPCB1	46	36×10^{-3}	NM	4.6 (NB)	250	NM	NM
PP/PPCB2	21	38×10^{-3}	NM	4.8 (NB)	250	NM	NM
PP/PPCB3	11	31×10^{-3}	NM	5.0 (NB)	250	NM	NM
PP/PPCB4	21	$<10^{-5}$	NM	15.4 (NB)	250	NM	NM
PP/PPCB5	25	51×10^{-3}	NM	4.6 (NB)	250	NM	NM
PP/PPCB6	25	$<10^{-5}$	NM	14.8 (NB)	250	NM	NM
PA6	20.0 ± 2.2	NM	NM	35.4 ± 3.4	145 ± 22	24.7 ± 5.7	119 ± 40
PA6/PE	21.0 ± 2.2	NM	NM	23.5 ± 2.9	148 ± 13	NM	NM
PA6/PPCB1	NM	175×10^{-3}	241×10^{-3}	NM	NM	NM	NM
PA6/PPCB2	NM	165×10^{-3}	235×10^{-3}	NM	NM	NM	NM
PA6/PPCB3	14.3 ± 3.1	155×10^{-3}	246×10^{-3}	22.9 ± 7.9	157 ± 26	NM	NM
PA6/PPCB4	12.3 ± 2.2	118×10^{-3}	223×10^{-3}	28 ± 3.2	62 ± 20	NM	NM
PA6/PPCB5	16.0 ± 3.8	46×10^{-3}	221×10^{-3}	36.8 ± 5.3	56 ± 20	NM	NM
PA6/PEMWNT1	40.3 ± 5.2	13×10^{-3}	57×10^{-3}	10.6 (NB)	250	5.7 ± 0.6	74 ± 43
PA6/PEMWNT2	24.7 ± 3.7	9.3×10^{-3}	22×10^{-3}	16.1 ± 2.1	229 ± 22	8.3 ± 1.8	95 ± 59
PA6/PEMWNT3	17.3 ± 5.0	5.6×10^{-3}	26×10^{-3}	20.1 ± 4.1	192 ± 26	8.6 ± 1.4	61 ± 26
PA6/PEMWNT4	14.1 ± 2.2	9.7×10^{-3}	22×10^{-3}	32.0 ± 4.7	91 ± 22	21.0 ± 4.1	61 ± 28
PA6/PEMWNT5	14.5 ± 3.6	9.4×10^{-3}	22×10^{-3}	38.5 ± 5.9	48 ± 12	30.0 ± 6.0	36 ± 7
PA6/PEMWNT6	15.5 ± 3.1	16.4×10^{-3}	21×10^{-3}	28.6 ± 3.6	62 ± 12	19.9 ± 4.5	60 ± 13
PA6/PEMWNT7	13.1 ± 2.3	10.6×10^{-3}	24×10^{-3}	38.1 ± 3.9	70 ± 18	31.1 ± 4.2	37 ± 13

NB, no break; the value thus reflects maximum stress recorded.
 NM, not measured. Mean values are shown.

mechanical performance can be interpreted in terms of reorientation of crystalline regions, changes in crystallinity, and a decrease of the orientation of the amorphous phase.

Contact resistance and its effect on the conductivity measurements

Measuring the conductivity of bicomponent fibers with a conductive core and an insulating sheath is coupled with some experimental difficulties. Usually, the 4-point method is used to measure the conductivity of a material to reduce the effect of the contact resistance. For bicomponent fibers having an insulating sheath, conductive material will only be found at the fiber ends. The ends were contacted with silver paint and the conductivity was measured at several voltages starting from the low side, as shown in Figure 2. The conductivity increased with increasing voltage towards a plateau value, indicating a high contact resistance despite the silver paint. After heat treating the fibers for 1 min at 180°C, the conductivity plateau had increased and the nonlinearity diminished, see Figure 2. However, when the heat treatment was increased to 10 min, the measured conductivity became independent of the voltage. This result can be interpreted as the formation of a good electrical contact between the conductive core material and the silver paint. At 180°C the core material melts and protrudes

(volume expansion) out from the fiber into the paint and the contact resistance is significantly reduced. One minute of heat treatment was obviously not enough to establish a perfect contact. This interpretation is verified by the curve measured for a sample contacted with silver paint after heat treatment for 10 min at 180°C. In this case, the high voltage plateau conductivity is approaching the value for a similar sample contacted with silver paint before the heat treatment for 10 min at 180°C

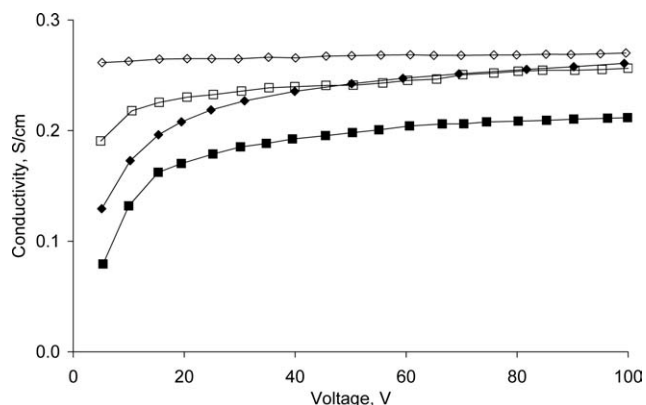


Figure 2 The conductivity at different voltages for samples prepared with PA6/PPCB2 fibers. (■) Contacted with silver paint, (□) heat treated 1 min, (◇) heat treated 10 min, then ends were cut off and contacted with silver paint again. The temperature during the heat treatment was 180°C. The measurements were performed starting from a low voltage.

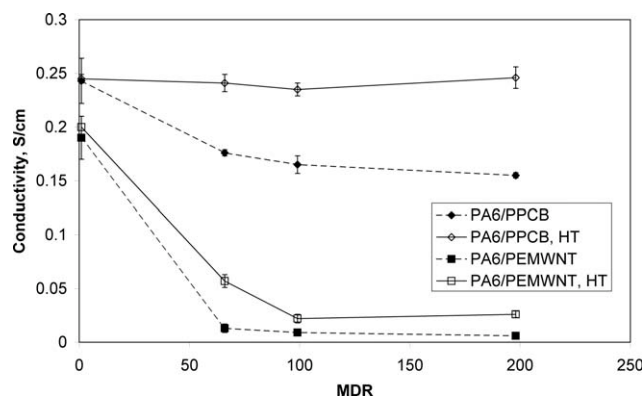


Figure 3 The electrical conductivity as a function of MDR for melt spun bicomponent fibers with 10 weight% filler in the core material and PA6 as sheath material. HT denotes here heat-treated fibers. SSSR was 1 for all fibers.

and the nonlinearity is as severe as for the untreated sample. In parallel to the improvement of the electrical contact, the conductivity of the CPC material itself increased due to the heat treatment above the melting point of the matrix polymer. This observation is attributed to conformational changes of the polymer molecules, leading to redistribution of particles and thereby to formation of a more efficient conducting network of particles. In the following, to reduce the effect of contact resistance on the conductivity measurements, high voltages were used. However, the voltage was always kept below levels producing a noticeable heating effect in the fibers.

Conductivity of the fibers

In the case of the CB-filled fibers, regardless of the sheath material, the electrical conductivity decreased somewhat with increasing MDR and more markedly with increasing SSSR. Both these reductions in conductivity can be recovered after heat treating the fibers for 10 min at 180°C, as shown in Figures 3 and 4, cf also Table II. In fact, many authors^{7,10,13,14} have found that the conductivity of conductive polymer composites can be increased by a heat treatment. In the case of the MWNT-filled fibers, the electrical conductivity was significantly reduced by the melt drawing. The low conductivity of the MWNT-containing fibers is in agreement with the results reported in our previous work.¹ The MWNT-filled fibers responded somewhat to the heat treatment (Figs. 3 and 4), although it was not possible to recover the conductivity, as with PP/CB in the core, within the time frame used. The effect of the heat treatment of MWNT-filled fibers was somewhat more pronounced at low MDR.

Microscopy of bicomponent fibers

Figure 5 is a SEM micrograph of the cross-section of a PA6/PPCB4 fiber, containing 10 wt % CB in the core. The CB particles were apparently homogeneously distributed across the cross-section of the core. Spherically shaped clusters of CB particles, approximately 100 nm in size, formed interconnected chains leading to conductive paths through the material. When H-MWNTs were used as filler some alignment of the nanotubes occurred, as indicated in Figure 6. This micrograph shows the cross-section of the core region of a PA6/PE fiber with 10 wt % H-MWNT in the core. Our interpretation of Figure 6 is that the small bright dots (related to charging effects due to differences in conductivity and/or topography) are carbon nanotube ends, protruding from the fractured cross-section. The dots are well below 100 nm in size which would correspond with the thickness of a bundle of MWNTs.¹⁵ Very similar patterns were seen in other samples whenever MWNTs were used as fillers, whereas if CB was used as the filler, the generated patterns were more like the one in Figure 5. The distribution of the H-MWNTs was relatively uniform over the cross-section, but where the CB formed small, close to spherical, clusters, the H-MWNT appeared to form oriented bundles which are indicated by the regions of tightly packed white dots seen in Figure 6.

DISCUSSION

As shown in Table I it was possible to extend a material with high concentrations of filler to high draw ratios by using bicomponent fiber spinning. For instance, in the case of a single-component PP/CB10 containing 10 wt % CB, it was possible to obtain a maximum MDR just below 20¹ whereas a maximum

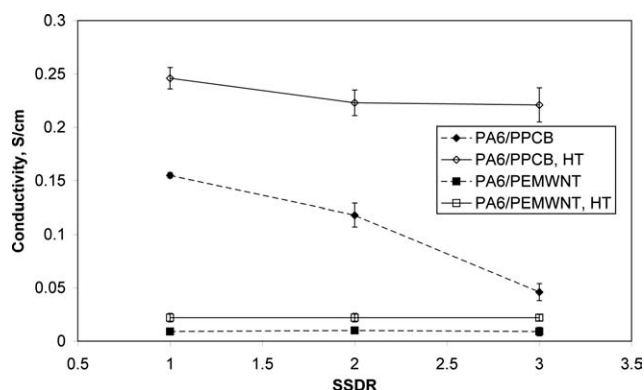


Figure 4 The electrical conductivity as a function of SSSR. The MDR was adjusted to obtain a total draw ratio of ~ 200 . The loss in conductivity created by the different drawing steps is almost completely regained by heat treatment (denoted HT) for 10 min at 180°C in case of the CB-filled core material.

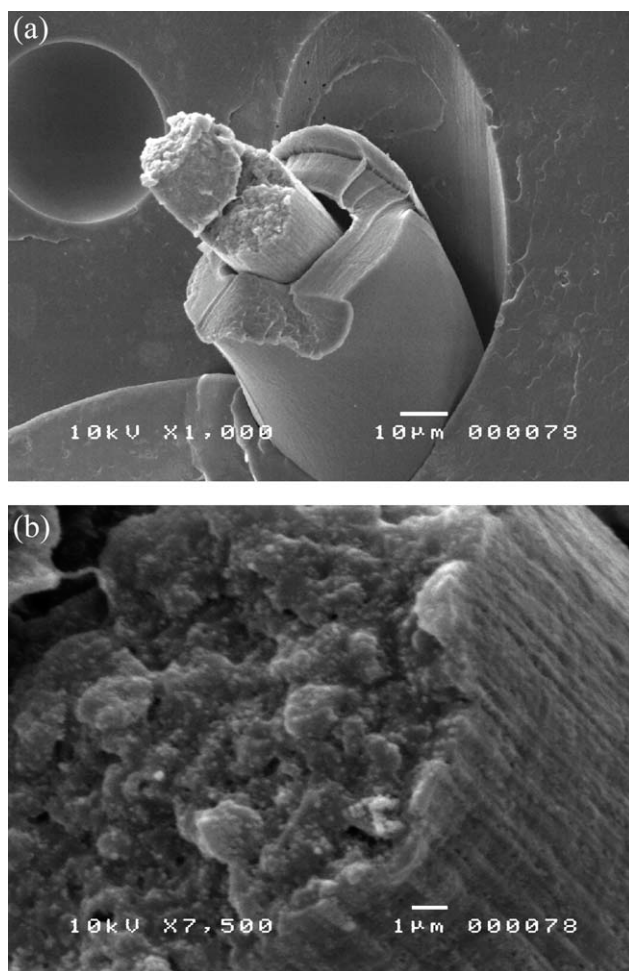


Figure 5 (a): Scanning electron micrograph showing the core-shell structure of a PA6PPCB4 fiber fractured in liquid nitrogen. (b): Close-up view of the fractured core. An even distribution of CB-clusters, about 100 nm in size, is seen (lighter dots) over the whole cross section.

MDR of at least 195 could be obtained using the bicomponent technology and by that surrounding the less spinnable core material with a readily spinnable sheath material. It must however be noted that a higher processing temperature was used in this study compared to the earlier¹ (270°C versus 210°C) although this was not expected to improve the spinnability.¹⁶ The reason is most likely that the rheological properties of the sheath material govern the spinnability and thus the sheath material bears a major share of the spin line force. The pronounced elastic modulus and the related yield stress behavior of the core material, creating a limited drawability, were thus counteracted by the sheath material. It should be noted that a relatively high molecular weight PA6 was here selected to counteract the high flow resistance of the filled core material. We have noted that the spinnability improved with increasing volumetric sheath/core ratio and became poorer with a lower viscosity sheath material, which is not

unexpected. It is important to note that the extensibility of the highly filled core material appeared to be high. The main problem encountered in our previous study,¹ when spinning monocomponent filaments from PP/CB10 creating spin line breaks, was not a limited extensibility *per se*, rather the fact that the extension was localized to a very narrow segment of the extruded thread in which the yield stress was exceeded leading to an unstable catastrophic extension and rupture.

The instability along the spin line described in our earlier work¹ was also noted during the bicomponent spinning, although the resulting variations in diameter were much less pronounced. This supports the assumption that counteractive forces from the sheath helped preventing a localized stretching of the core melt, leading to improved spinnability.

Pötschke et al.⁴ and Haggemueller et al.⁵ studied melt spinning of multiwalled carbon nanotubes in polycarbonate, MWNT/PC, and singlewalled carbon nanotubes in polymethylmethacrylate, SWNT/PMMA. Compression molded films of SWNT/PMMA had conductivities in the range 0.0012–0.12 S/cm for SWNT-contents from 1.3 to 6.6 wt %. Upon melt spinning of fibers at draw ratios from 400 (1.3 wt % SWNT) to 60 (6.6 wt % SWNT), the conductivity fell below the detection limit. A compounded MWNT/PC-composite containing 2 wt % MWNT had a conductivity of 0.002 S/cm. Also in this case the conductivity fell below the detection limit upon melt spinning the material to fibers. This behavior was explained by nanotube orientation and alignment during melt spinning and a resulting loss of conducting pathways through the fibers.⁴ It is interesting to note that in our case (with 10 wt % H-MWNT), the conductivity did not fall below the

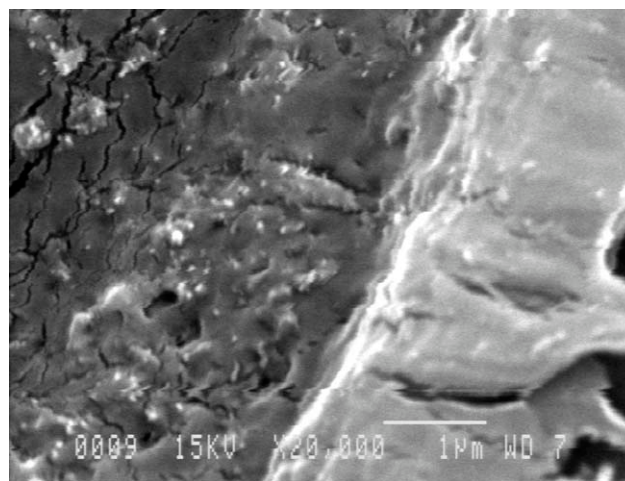


Figure 6 Scanning electron micrograph showing the core of PA6/PEMWNT4. Protruding ends of carbon nanotubes are seen as small white dots, which are mainly distributed in bundles, oriented along the fiber direction.

detection limit. Whether this was a result of the sheath-core structure or the high filler concentration may only be speculated upon without further studies. It is also interesting that the PP/CB-composites in the present work did not exhibit such a severe loss of conductivity upon melt drawing as the MWNT filled composites. This can be attributed to the morphology of CB particles which can find new contact points when the material is in a molten state and are less sensitive to orientation effects.

Varying the filler content indicated that the reduction in conductivity with increasing MDR was larger closer to the percolation threshold (i.e., at lower filler concentrations). Percolation curves of the materials can be found in our previous study¹ and the threshold values (in wt %) for CB/PP, CB/PE, H-MWNT/PE, and N-MWNT/PE were 1.8, 1.9, 2.9, and 0.7, respectively. This is not surprising since the conductivity at these concentrations is to a great extent dependent on the interparticle conduction mechanisms¹⁷ and small changes in particle alignment can have a large influence on the bulk conductivity.⁴

The effect of heat treatment on the conductivity of the bicomponent fibers was stronger when CB was used as the filler material, completely restoring the conductivity of the core in less than 10 min. Admittedly, PP and PE have different structures and different melting points, but this was not believed to have any significant influence on the result from the heat treatment. In the case of CB (small, almost spherical particles) we believe that relaxation of polymer molecules combined with an associated diffusion-like motion of the particles is responsible for the rapid restoration of a conductive network. To restore contacts between aligned MWNTs rotational diffusion would be needed. A reorientation of MWNTs due to such rotational diffusion would be exceedingly slow in a viscous medium due to the high aspect ratio as shown by Broersma.¹⁸

CONCLUSIONS

- With bicomponent technology it is possible to attain a higher MDR with a high filler concentration in the core compared with melt spinning of monofilaments using the same material. A suitably chosen sheath material permits melt-spinning of materials beyond the normal strain at rupture of the core polymers and will also

add significant mechanical strength to the fiber, increasing its usefulness in textile processing.

- Drawing in the molten state reduced the electrical conductivity of CPC more when MWNT was used as the filler than when CB was used; the conductivity decreased with increasing draw ratio.
- The conductivity was completely restored upon heat treatment of the drawn PA6/PPCB-fibers whereas the corresponding PA6/PEMWNT-fibers exhibited a modest increase.
- Drawing in the solid state had a more significant impact on the conductivity than drawing in the molten state when CB was used as filler. In the molten state, filler particles formed new conductive paths supported by the mobility of the matrix, while in the solid-state elongation leads to a permanent separation of filler particles.

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