Conductive Polymer Tape Containing Highly Oriented Carbon Nanofillers

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ABSTRACT: The effect of the orientation of carbon fillers with different aspect ratios on the resistivity and morphology of conductive polymer composites (CPCs) based on polypropylene was investigated in this study. Multiwall carbon nanotubes (MWNTs) and carbon black (CB) were used as conductive fillers. The CPCs were made by melt compounding, hot pressing, and solid-state drawing. The alignment of the filler was observed after solid-state drawing. The resistivity of the composites increased with the draw ratio at relatively low carbon filler loadings (<20 wt %), whereas it remained unchanged at a high filler loading (20 wt % CB). Orientation-promoted anisotropy of the conductive network was observed in both the morphology and resistivity. MWNTs were found to be better at maintaining a percolating network under large deformations than CB because of their larger aspect ratio and their entangled network structure. The experimentally obtained resistivity was analyzed with percolation theory, and this indicated that the initial three-dimensional conductive network was deformed into a two-dimensional network after solid-state drawing for the composites containing CB. The three-dimensional network was found in isotropic CPCs containing MWNTs with the same analysis. Theoretical analysis using excluded volume theory was in good agreement with results obtained experimentally. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 742–751, 2009

Key words: morphology; orientation; poly(propylene) (PP)

INTRODUCTION

Polymer composites reinforced with carbon nanotubes (CNTs) have been investigated extensively over the last decade. Bulk composites reinforced with CNTs have been investigated with respect to mechanical, thermal, electrical, and other properties.[1–3] The processing methods used are mainly solution-based *in situ* polymerization and melt compounding. The mechanical reinforcement potential of CNTs in bulk polymer composites is high, but the theoretical strength of CNTs is approached only if a high level of dispersion, interfacial interaction, and alignment of nanofillers is achieved in oriented systems such as polymer fibers and tapes.[4–6] In a recent study by Wang et al.,[4] it was demonstrated that very high reinforcing efficiencies of single-wall nanotubes are possible when these nanotubes are embedded in highly oriented tapes.

Conductive polymer composites (CPCs) are conventionally made by the addition of carbon black (CB), metal powder, or carbon fiber into a polymer matrix. Even with the polymer matrix being an insulator; the conductivity of the composites can demonstrate a sudden jump when a critical filler content is reached. This phenomenon is often described as percolation.[7] The percolation threshold of composites has been shown both experimentally and theoretically to decrease with the filler aspect ratio.[8–11] CNTs have become some of the most interesting fillers for CPCs. Their large aspect ratio and excellent conductivity can lead to bulk CPCs with percolation thresholds as low as 0.0025 wt %.[12–14]

Oriented polymer fibers have been an important topic of research since the 1970s.[15,16] Much research on oriented polymers has led to successful commercial products, including Kevlar,[17] Dyneema,[15,18] and, more recently, single polymer composites such as Curv[19,20] and PURE.[21–28] Solid-state drawing is the most common and efficient way of achieving orientation in flexible chain polymers. The drawing of CNT–polymer composites was first considered by Ajayan et al.[29] as a method of aligning CNTs. Since then, polymer fibers containing CNTs have been extensively studied. Similar to polymer molecules, CNTs provide much more effective reinforcement when they are uniaxially aligned versus isotropic organization in bulk composites.[1,3,4,6] Similarly to their mechanical behaviors, it is also thought that oriented CNT networks should improve thermal and

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electrical transport properties in that particular direction.[4] Few works have been published on conductive oriented polymer fibers containing CNTs. Some investigations of oriented polymer fiber have involved the use of vapor-grown carbon fibers.[30] The percolation threshold in these studies was found to be relatively high: 5 wt % for CNTs and 15 wt % for vapor-grown carbon fibers in highly oriented (draw ratio up to 15) polymer fibers.[30,31] During the spinning of CNT–polymer composites, the lowest resistivity occurs for slightly aligned, rather than isotropic, CNT networks, as shown by Du et al.[32]

In comparison with the very low percolation threshold reported for isotropic bulk polymer composites (typically < 1 wt %),[12–14,33] a percolation threshold of around 5 wt % is high for CNT–polymer composites. Such an increase in the resistivity (or percolation threshold) during fiber drawing or spinning has been reported in the literature: highly drawn fibers containing CNTs have much higher resistivity than identical isotropic materials before drawing.[31,33,34] Morphological evidence has shown that the probability of multiwall carbon nanotubes (MWNTs) forming a network is reduced by drawing, and it is thought that a certain amount of a conducting network is vital to maintain the conductive network when the composites are stretched.[31,33]

This study was carried out to gain insight into the formation of a conductive network during a highly oriented CPC fabrication process and to draw a systematic comparison between conductive nanofillers with different aspect ratios through a combination of electrical, morphological, and theoretical studies. In this study, CPCs were fabricated through the melt compounding of MWNTs or CB with a polypropylene (PP) matrix. The formation of a conductive network during composite tape fabrication was studied with scanning electron microscopy (SEM). Highly oriented CNT bundles were observed in the oriented polymer tapes. The change in the resistivity with the draw ratio was investigated. Classical percolation theory and excluded volume theory were used to analyze the experimental results obtained.

EXPERIMENTAL

Materials

MWNTs (Nanocyl 7000) were kindly provided by Nanocyl S.A. (Belgium). These MWNTs had a diameter of 10 nm, a length of 1.5 μm, and a surface area of 250–300 m^2/g.[35] The PP was an ethylene–polyprolene copolymer (weight-average molecular weight = 320 kg/mol, melt flow index = 5.5 g/min).The conductive CB was Printex XE-2, a highly structured CB supplied by Grolman, Ltd. (United Kingdom). A full characterization study of several CBs, including Printex XE-2, was carried out by Pantea et al.,[36] and they showed that Printex XE-2 has good conductivity in comparison with other CBs because of its large surface area (910 m^2/g).

Composite preparation

MWNTs or CB was melt-blended with PP (as pellets) in a microextruder (Explore Micro 15, DSM) at 200°C and 200 rpm for 10 min. The extruded strand was then cut and hot-pressed into sheets 150 μm thick at 200°C for 5 min. Rectangular samples of 5 mm × 20 mm were then cut from these sheets and subsequently hot-drawn into tapes with different draw ratios (i.e., drawn tape length/original tape length). Drawing was conducted on an Instron (Bucks, United Kingdom) 5584 equipped with an environmental chamber at a crosshead speed of 50 mm/min at 120°C.

Composite characterization

Morphological studies were carried out on a JEOL JSM-6300F scanning electron microscope to investigate the formation of a conductive network during tape fabrication. A high accelerating voltage was applied for the SEM study. MWNTs or CB in the polymer matrix material was charged to give an enriched secondary electron, as demonstrated by Loos and coworkers.[37,38] SEM imaging of cross sections of cut samples (in longitudinal and transverse directions) was performed. The as-prepared nanocomposite samples were sectioned with an ultramicrotome (Ultracut E, Reichert-Jung).

The morphology of CB and MWNTs fillers was examined with a JEOL JEM-2010 transmission electron microscope. Specimens were prepared by the dispersion of CB and MWNT powders in ethanol with ultrasonication. The specimen was picked up with a copper grid, and the solvent was allowed to evaporate. The nanoparticles that remained on the copper grid were studied with transmission electron microscopy (TEM).

Direct-current electrical resistivity was measured for the composites at different stages of processing. A two-point method with a voltage scan from 1 to 10 V was conducted for the resistivity measurements. Silver paint was applied to both ends of the sample to ensure good contact. As a result, contact resistance was negligible in comparison with sample resistance. The dimensions of the sample were not uniform in this study as the thickness and width varied with the draw ratio. The resistance was measured with an Agilent 6614C programmable voltage source in combination with a Keithley 6485 picoammeter (Keithley Instruments Inc. Ohio, USA). All equipment was interfaced with a computer to record

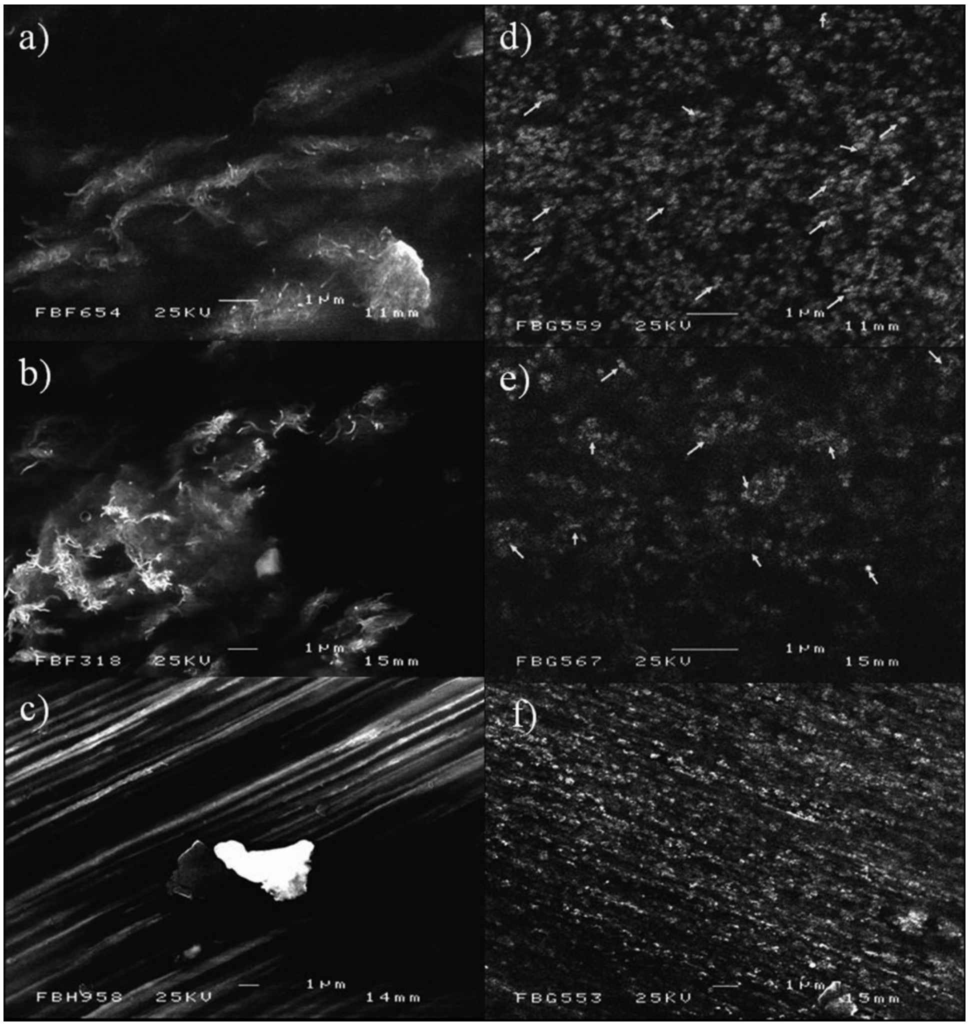

Figure 1 SEM pictures of PP composite surfaces containing 5.3 wt % MWNT [(a) as-extruded strand, (b) hot-pressed film, (c) solid-state drawn tape (draw ratio = 8)] or 15 wt % CB [(d) as-extruded strand, (e) hot-pressed film, and (f) solid-state drawn tape (draw ratio = 8).

the current–voltage curve to calculate the resistivity. All current–voltage curves were linear in this study. For a specimen with a resistivity higher than 10^6 Ω m, electrical resistivity was not measurable, and the tapes were considered nonconductive. At least three specimens were measured for each group of experiments, and the average value was reported.

RESULTS AND DISCUSSION

Morphology

The morphology of the composites and fillers was investigated with SEM and TEM, as shown in Figures 1–3. It is worth mentioning that SEM was used in a high accelerating voltage mode for Figures 1 and 2; thus, the morphology of the conductive network is shown in three dimensions so that the nanoparticle network underneath the polymer matrix can be observed.[37,38] Figure 1 shows the formation of a conductive network for both MWNTs and CB in the polymer matrix during tape fabrication. Most of the MWNTs are dispersed as complex entangled networks in the polymer matrix. CB is dispersed as relatively large aggregates in comparison with individual particles. Slightly aligned MWNT bundles are found on the surface of the as-extruded composite strand [Fig. 1(a)], and this is probably caused by shear during extrusion. Highly aligned MWNTs and CB networks are achieved by solid-state drawing (draw ratio = 8), as shown in Figure 1(c,f). Figure 2 shows the cross-section morphology of a CPC tape with MWNTs. The MWNT bundles are highly oriented and are distributed evenly through the tape. However, the dispersion of MWNTs in the polymer matrix is still relatively poor as most of the tubes are dispersed as bundles.

A TEM study of MWNTs and CB (as received) was carried out to demonstrate the difference in the aspect ratio between the fillers, as shown in Figure 3.

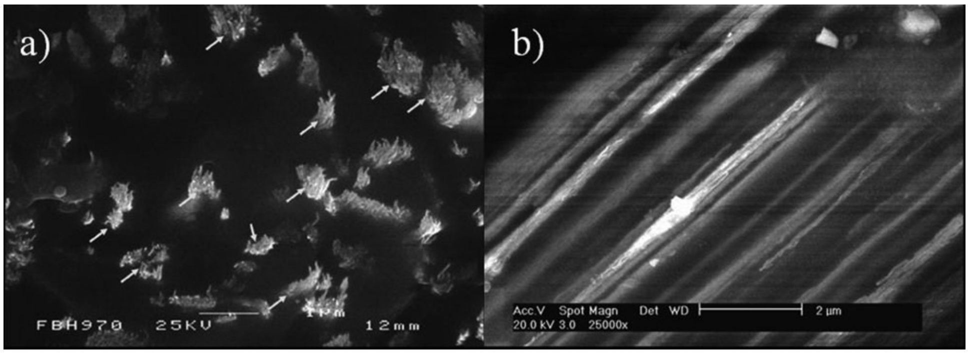

Figure 2 SEM pictures of a cross section of solid-state drawn PP tape with 5.3 wt % MWNT (draw ratio = 20): (a) perpendicular to the drawing direction (transverse) and (b) parallel to the drawing direction (longitudinal).

MWNTs are thought to be more efficient than CB in forming a conductive network in polymer matrices because of their higher aspect ratio. The large overlap length between adjacent MWNTs and their entangled network structure is the key to keeping the conducting network intact under large deformations.

Electrical properties of the CPCs

The electrical resistivity of tapes containing MWNTs or CB as a function of the draw ratio is shown in Figure 4. The resistivity for 5.3 wt % MWNT loaded composites increases rapidly with increasing draw ratio. However, the resistivity remains nearly constant for composites containing 20 wt % CB at draw ratios ranging from 3 to 13. The resistivity of composites containing 10 or 15 wt % CB significantly increases with the draw ratio. The increase in resistivity during drawing is believed to be caused by the breakdown of local contacts in the conductive network. The resistivity of the specimen is no longer measurable for the setup used in this study when the draw ratio exceeds 8 or 10 for composites containing 10 or 15 wt % CB, respectively. The resistivity of the drawn tapes with low MWNT loadings (1.44, 1.82, 2.3, and 3.1 wt %) is not measurable with the experimental setup used in this study. This study is focused on relatively low MWNT contents ($\leq$ 5.3 wt %), as large amounts of MWNTs result in poor filler dispersion and poor composite processability.

To conclude this resistivity study on composite tapes, the conductive network formed by either CB or MWNTs was deformed to a certain draw ratio. The resistivity of composite tapes at different draw ratios demonstrated the ability of different carbon nanofillers to form conducting networks. MWNTs have been found to form much stronger conducting networks in terms of maintaining these networks during stretching. Because the CB used in this study has a larger surface area than MWNTs, it demonstrates the importance of the filler aspect ratio rather than the surface area for maintaining a percolating network in highly oriented tapes.

Upon drawing, it can be expected that electrical anisotropy will be stimulated by the alignment of the polymer chains and CNT. The development of anisotropy in electrical resistivity upon drawing is shown in Figure 5. The anisotropy index is defined as $R_{\mathrm{Transverse}}/R_{\mathrm{Longitudinal}}$, where $R_{\mathrm{Transverse}}$ and $R_{\mathrm{Longitudinal}}$ are the resistivity of the CPC in the transverse direction and the resistivity of the CPC in the longitudinal direction with respect to the drawing direction, respectively. It is considered an index

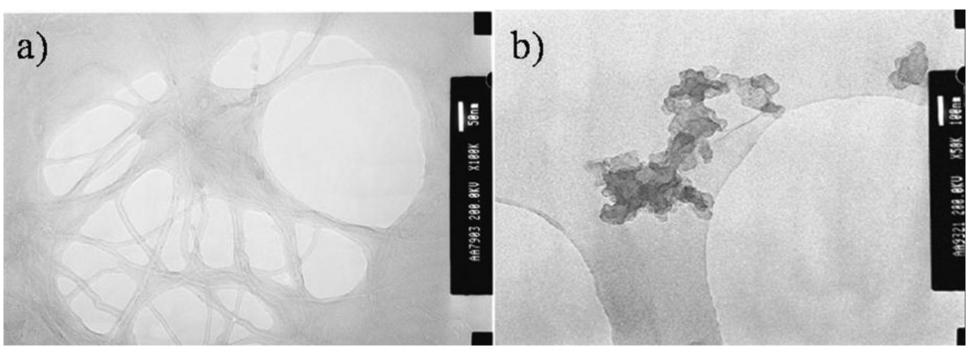

Figure 3 TEM pictures of (a) MWNTs and (b) CB used in the study.

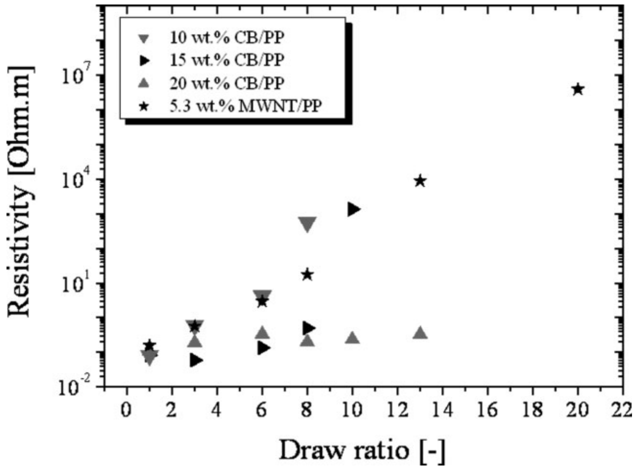

Figure 4 Longitudinal (along the drawing direction) electrical resistivity of oriented PP tapes containing MWNTs or CB in different draw ratios.

used to describe the anisotropy of the conductive network to give some information on the orientation of the filler itself and the network that it forms. Clearly, the higher the anisotropy index is, the more anisotropic the conductive network is.

As shown in Figure 5, anisotropy can be observed in both MWNT- and CB-filled composite systems. Anisotropy is more pronounced in MWNT-filled composites because of the alignment of the high-aspect-ratio fillers induced by the drawing process. In contrast, CB, possessing a lower aspect ratio, does not show such significant alignment during the drawing process [see Fig. 1(f)]. However, also in the case of CB, the conductive network still develops some level of anisotropy, as shown in Figures 1(f) and 5. Another issue to be noted in Figure 5 is that a high CB content leads to a stable anisotropy index with increasing draw ratio. This indicates the presence of a more stable conductive network upon deformation. Similar effects can be expected for CPCs containing MWNTs in high loadings (> 5.3 wt %), but there are no data available in that loading range in this study.

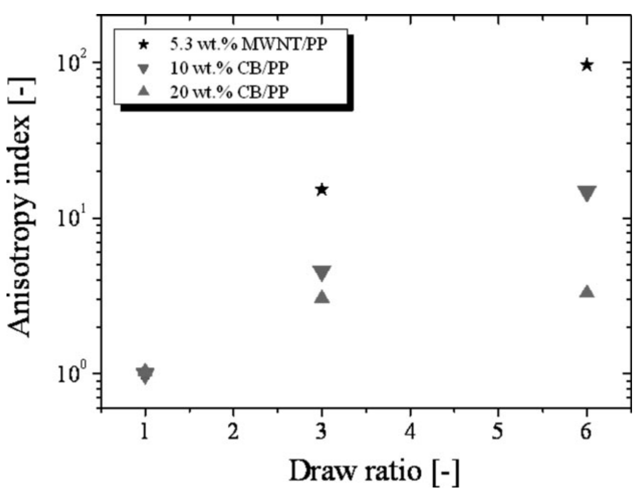

Figure 5 Anisotropy index ($R_{\mathrm{Transverse}}/R_{\mathrm{Longitudinal}}$) of PP tapes containing MWNTs or CB as a function of the draw ratio, showing higher anisotropy for MWNT composites.

The percolation threshold was investigated for composites containing MWNTs or CB (Fig. 6). For composites containing MWNTs, the percolation threshold is 1.5 wt %, between 3.1 and 5.3 wt %, and greater than 5.3 wt % for tapes with draw ratios of 1, 8, and 13, respectively. No precise percolation threshold value could be obtained for oriented tapes containing MWNTs on the basis of the current data. It can be considered to be between 3.1 and 5.3 wt % as no measurable resistivity data were observed at loadings less than 5.3 wt %. In the case of CB, the percolation threshold is around 3.2, 10, and 20 wt % for draw ratios of 1, 8, and 13, respectively. Clearly, the percolation threshold increases more with the draw ratio for composites containing CB than for those incorporating MWNTs.

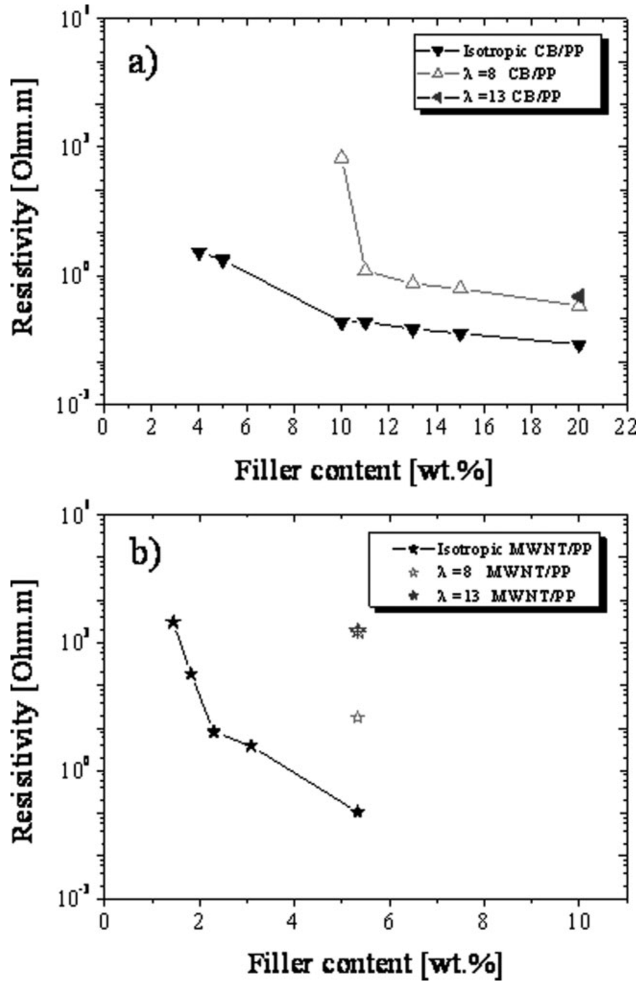

Figure 6 Percolation thresholds of composites containing (a) CB or (b) MWNTs at different draw ratios, with lower values for MWNT composites.

Comparison with theory

Classical percolation theory

The increasing conductivity (1/resistivity) of composite materials with increasing conductive filler content can be described by a scaling law according to classical percolation theory:

$$\sigma = \sigma_0 (P - P_c)^t \tag{1}$$

where σ_0 is a scaling factor, P_c is the percolation threshold of the CPC, σ is the conductivity of the CPC, and P is the content of the filler in the CPC.[7] t is an exponent that depends on the dimensionality of the conductive network. It is expected to vary with different materials, with calculated values of $t \approx 1.3$ and $t \approx 2.0$ in two and three dimensions, respectively. Therefore, the percolation threshold of CPCs can be determined accurately, and information on the dimensionality of the conducting network can be obtained before and after drawing through the fitting of classical percolation theory to experimentally obtained conductivity data.

Percolation threshold P_c and exponent t have been calculated with eq. (1) (see Fig. 7). Isotropic MWNT/PP systems give $t \approx 3$ and $P_c = 1.2$ wt %. The t value is relatively high, and this can be interpreted as a broad distribution of tunneling resistance within a three-dimensional network.[39] For isotropic composites containing CB, $t \approx 2.0$ and $P_c = 3.2$ wt % have been calculated, whereas for composites with a draw ratio of 8, $t \approx 1.3$ and $P_c = 10$ wt % have been calculated. It is clear that exponent t decreases from 2 to 1.3 when composites containing CB are drawn from an isotropic state to an oriented state (draw ratio = 8). This indicates that the conductive network has been deformed from a three-dimensional random network into a two-dimensional network according to classical percolation theory. The percolation threshold increases from 3.2 to 10 wt % when composites containing CB are drawn from their isotropic state to an oriented state at a draw ratio of 8. Comparing the percolation thresholds of composites containing MWNTs and those containing CB, we observe much lower percolation thresholds for both isotropic and oriented systems based on MWNTs. As discussed earlier, the high-aspect-ratio MWNTs clearly form a more entangled network than CB and therefore maintain conductivity upon drawing.

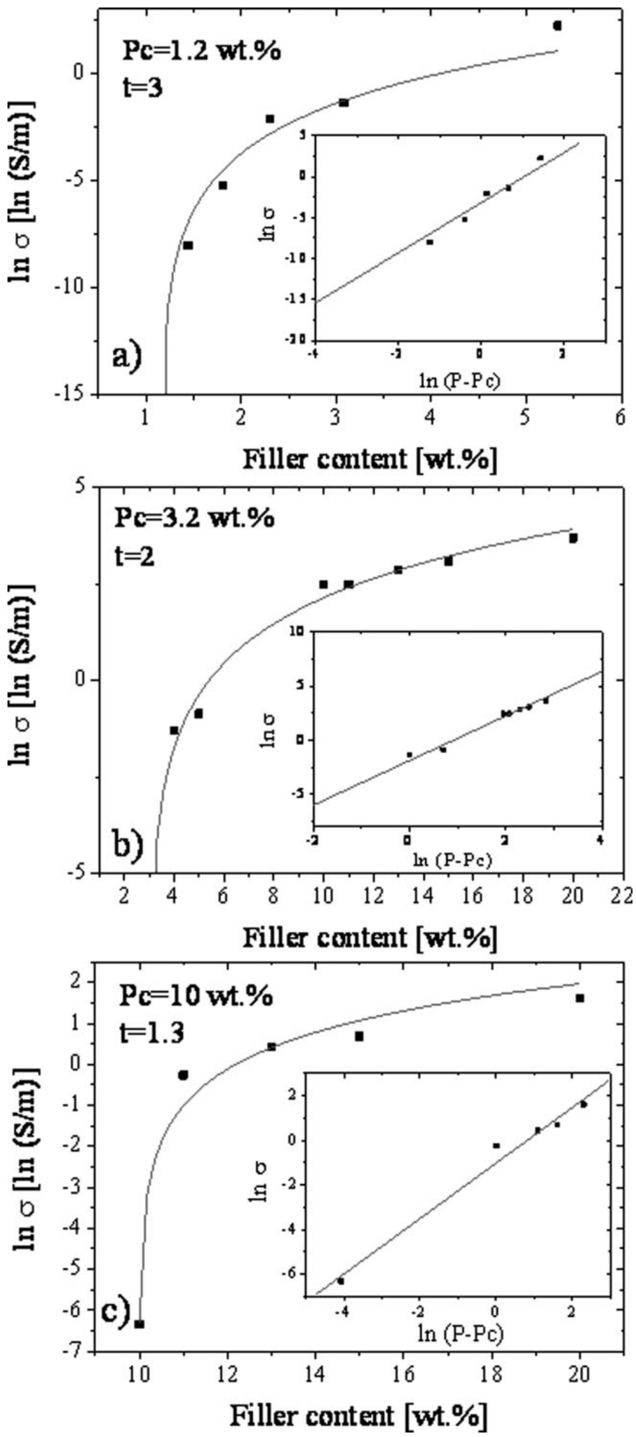

Figure 7 Percolation threshold (P_c) values of (a) isotropic composites containing MWNTs, (b) isotropic composites containing CB, and (c) oriented composites (draw ratio = 8) containing CB.

Excluded volume theory

To model the effect of the filler aspect ratio and filler orientation on the percolation threshold of CPCs, analytical models such as excluded volume theory[8] can be used. The excluded volume of an object is defined as the region of space that the center of another similar object is not allowed to enter if overlapping of these two is to be avoided.[40] It is capable of predicting the percolation threshold of high-aspect-ratio cylindrical particles embedded in a noninteracting matrix, as shown in Figure 8.

It has been extensively used to describe both microsize and nanosize composite systems.[8,11,40–45]

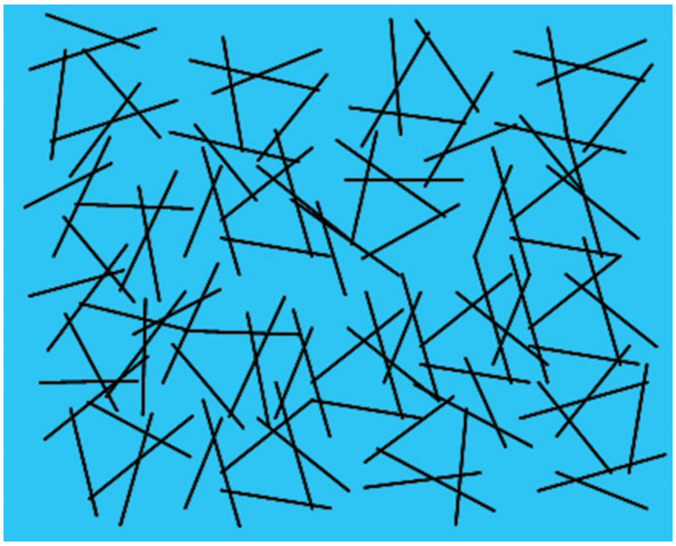

Figure 8 Randomly dispersed, cylinder-shaped, high-aspect-ratio rods in a matrix as described by Celzard et al.[8] [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Here, the nanotube and CB clusters are modeled as capped cylinders of diameter W and length L, as shown in Figure 9. The excluded volume ($\langle V_e \rangle$) is expressed as follows:[8]

$$\langle V_e \rangle = \frac{4\pi}{3} W^3 + 2\pi W^2 L + 2WL^2 \langle \sin \gamma \rangle \qquad (2)$$

where γ is the angle between the two cylinders in contact with each other and $\langle \sin \gamma \rangle$ is calculated to be $\pi/4$ for randomly oriented cylinders.[40] The values of $\langle \sin \gamma \rangle$ for oriented systems with maximum disorientation angles of 0, 30, 45, and 90° are 0, 0.44, 0.60, and $0.78 = \pi/4$, respectively.[8] Thus, the excluded volume of an isotropic system can be written as follows:

$$\langle V_e \rangle = \frac{4\pi}{3} W^3 + 2\pi W^2 L + \frac{\pi}{2} WL^2 \qquad (3)$$

It was shown by Celzard et al.[8] that the percolation threshold of an infinitely thin cylinder system is expressed as follows:

$$1 - \exp\left(-\frac{1.4V}{\langle V_e \rangle}\right) \le \phi_c \le 1 - \exp\left(-\frac{2.8V}{\langle V_e \rangle}\right) \qquad (4)$$

The volume of the MWNTs ($\langle V \rangle$) is written as follows:

$$\langle V \rangle = \frac{\pi}{6} W^3 + \frac{\pi}{4} W^2 L \qquad (5)$$

Hence, the percolation threshold of such a high-aspect-ratio filler system can be calculated according to eqs. (2)–(5) (Fig. 10).

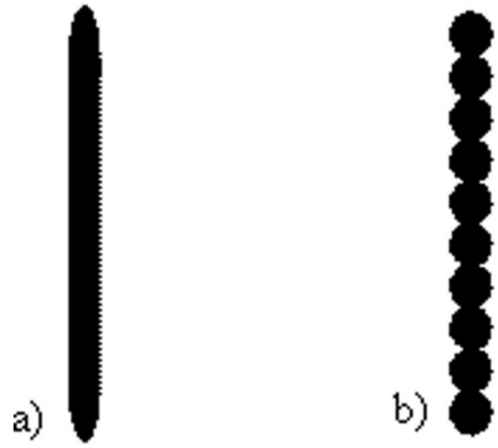

Figure 9 Model considered in this study for (a) MWNTs and (b) CB clusters.

As shown in Figure 10, some of the results reported in the literature[12,13,46] lie well below the percolation threshold predicted by excluded volume theory. In such systems, particle movement and reaggregation are allowed to induce the formation of a conductive network.[47] These systems can be defined as systems with a kinetic percolation threshold.[46] Other data[31,39,45,48–52] fit the theory quite well and are defined as systems with a statistical percolation threshold[46] in which the conductive phase is randomly dispersed.

Effect of waviness of MWNTs

All the theoretical work previously introduced deals with straight and rigid cylinder-shaped rods. However, this is clearly not the reality in CPCs based on

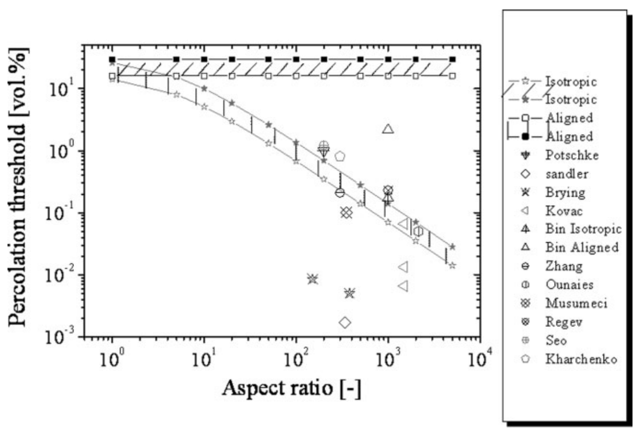

Figure 10 Theoretical percolation threshold for aligned and isotropic composite systems (the shadowed area) according to Celzard et al.[8] together with experimental data reported by Potschke et al.,[50] Sandler et al.,[13] Brying et al.,[12] Kovacs et al.,[46] Bin et al.,[31] Zhang et al.,[39] Ounaies et al.,[45] Musumeci et al.,[49] Regev et al.,[51] Seo and Park,[52] and Kharchenko et al.[48]

TABLE I
Theoretical Predications Based on Excluded Volume Theory Versus the Experimental Data[8]

Type of filler	P (vol %) Experimental	P (vol %) Calculated	Diameter (nm)	Length (nm)
CB (Printex XE 2)	1.62	—	30	1270–2640
MWNTs (Nanocyl 7000)	0.62	$0.46 \leq \phi_c \leq 0.91$	10	1500

The lengths for the CB system were calculated, whereas the diameter and length of the MWNTs were obtained from the supplier.[35]

CNTs. MWNTs have a relatively large aspect ratio and are flexible. The entangled structure that they form in the polymer matrix (see Fig. 1) is complicated and makes them more difficult to be modeled than rigid rods. Some efforts have been made by Dalmas et al.[10] and Berhan and Sastry[53] regarding this issue, and the results from Dalmas et al. show that the percolation threshold is not significantly influenced when the aspect ratio of the fiber is above 100. For wavy fibers, the percolation threshold increases when the aspect ratio is below 100. In contrast to the work of Dalmas et al., the results generated by Berhan and Sastry suggest something different. Therefore, the percolation threshold of high-aspect-ratio wavy fibers is expressed as follows:

$$\phi_{\text{wavy}} = \phi_{\text{straight}}/\alpha \tag{6}$$

where $\alpha < 2$ depends on waviness only and ϕ_{wavy} and ϕ_{straight} are the theoretical percolation thresholds for CPCs with wavy fibers and straight fibers, respectively.

Therefore, excluded volume theory, describing rigid and straight fibers, is used in this study as results reported in the literature for fiber waviness have shown a negligible effect on the percolation threshold. Through the fitting of the experimental data with excluded volume theory, the effects of the filler aspect ratio and filler orientation on the percolation threshold of CPCs could be obtained. With the dimensions of MWNTs (W = 10 nm, L = 1.5 μm),[35] the percolation threshold for MWNT systems can be calculated with eqs. (2)–(5) to be between 0.46 and 0.91 vol % (MWNT density = 1.75 g/cm^3).[54] Clearly, this theoretical value fits the experimental data of 0.62 vol % (equivalent to 1.2 wt %) for our composites quite well. The effect of fiber waviness is not considered this study because of the complexity of the network structure.

For the CB system, the percolation threshold of a perfectly sphere-shaped filler has been calculated to be between 14 and 26 vol % with eqs. (2)–(5) (CB diameter = 30 nm[55]). However, the percolation threshold values reported in the literature range from 0.06 to 39 vol %. The large differences in the percolation threshold depend on the structure of the CB and the composite processing conditions.[41,56] CB is distributed in the polymer matrix in aggregated form,[57] and hence this aggregated structure should be considered in the percolation threshold theory. The size of the aggregates is noticed to be different for similar CB systems under different processing conditions. This is explained by reaggregation of CB aggregates.[56] If the CB aggregates (as shown in Fig. 9) are considered cylindrical shapes in a matrix,[8] the size of the aggregates can be calculated with the aforementioned method and the experimentally obtained percolation threshold value. The theoretical results together with the experimental data for the MWNT system are listed in Table I. The observed CB cluster size for this study is shown in Figure 11 and matches the calculated value (1270–2640 nm) taking into account that most of the network observed by SEM is buried in the polymer matrix.

Finally, the theoretical percolation thresholds, calculated with eqs. (2)–(5), are compared with the experimental data (Fig. 12). The isotropic CB and MWNT data fit quite well the theoretical predictions. Comparing the data obtained in this study

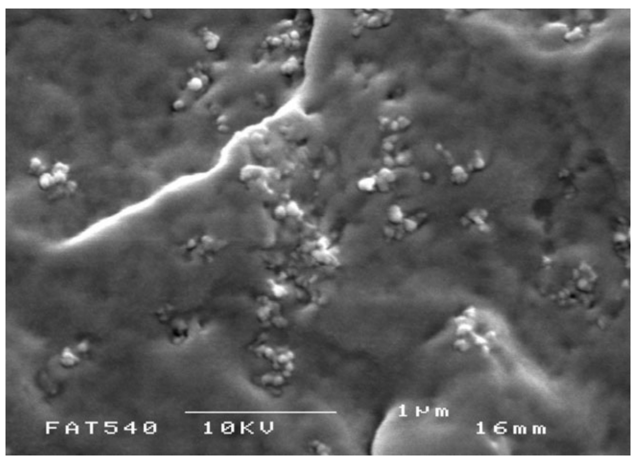

Figure 11 SEM of 3 wt % CB/PP composites showing local conductive networks on a cold fracture surface.

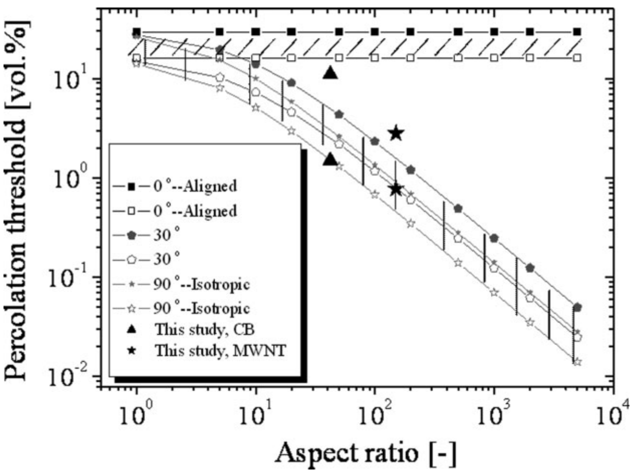

Figure 12 Theoretical percolation threshold for aligned and isotropic systems (the shadowed area)[8] versus isotropic and oriented PP/MWNT and PP/CB. The higher values for each of the nanofillers are for the oriented system (draw ratio = 8). The percolation threshold of the oriented PP/MWNT system is between 3.1 and 5.3 wt %; this is identical to the theoretical predication using the excluded volume theory for the systems with filler disorientation angles between 0 and 30°.

with previous data reported in the literature (see Fig. 10), we find that the viscous PP (or polycarbonate[50]) matrix does not seem to allow much reaggregation of the conductive fillers during melt processing. The percolation threshold is much lower when filler reaggregation is allowed in low-viscosity polymer matrices (e.g., epoxy[12,13,54]). The percolation threshold of the oriented systems lies well within those of a perfectly aligned system and a system with a maximum disorientation angle of 30°, and this agrees well with data reported in the literature (see Figs. 10 and 12).

CONCLUSIONS

The morphology and electrical resistivity of PP composites filled with MWNTs and CB have been studied. Highly oriented MWNTs have been observed after solid-state drawing, together with a highly organized CB network. The resistivity of the composites has been observed to increase with the draw ratio at relatively low carbon filler loadings, whereas it remains nearly unchanged with an increasing draw ratio for CPCs containing a large amount of fillers (20 wt % CB).

According to classical percolation theory, conductivity exponent t decreases from 2 to 1.3 after composites containing CB are drawn into tapes with a draw ratio of 8. This indicates the formation of a two-dimensional conducting network during tape fabrication. On the other hand, t is found to be 3 for isotropic composites containing MWNTs, and this could indicate a three-dimensional network with a large distribution of tunneling resistance.

According to excluded volume theory, the percolation threshold of oriented systems (for both MWNTs and CB) lies between the values predicted for systems having a maximum filler disorientation angle of 0–30°.

In short, it can be concluded that the percolation threshold of oriented CPCs tapes is relatively high because of distortion of the percolating network upon solid-state drawing (MWNTs, between 3.1 and 5.3 wt %; CB, ~ 10 wt %). As such, alternative approaches are needed for the development of conductive fibers that combine high polymer orientation through solid-state drawing with good conductivity at relatively low filler contents.[58,59]

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References

1. Thostenson, E. T.; Ren, Z.; Chou, T. W. Compos Sci Technol 2001, 61, 1899.
2. Ahir, S. V.; Terentjev, E. M. In Polymeric Nanostructures and Their Applications; Nalwa, H. S., Ed.; American Scientific Publisher: California, USA, 2005.
3. Coleman, J. N.; Khan, U.; Gun'ko, Y. K. Adv Mater 2006, 18, 689.
4. Wang, Z.; Ciselli, P.; Peijs, T. Nanotechnology 2007, 18, 455709.
5. Chae, H. G.; Kumar, S. Science 2008, 319, 908.
6. Ciselli, P.; Wang, Z.; Peijs, T. Mater Technol 2007, 22, 10.
7. Stauffer, D.; Aharony, A. Introduction to Percolation Theory; Taylor & Francis: Washington, DC, 1985.
8. Celzard, A.; McRae, E.; Deleuze, C.; Dufort, M.; Furdin, G.; Mareche, J. F. Phys Rev B 1996, 53, 6209.
9. Munson-McGee, S. H. Phys Rev B 1991, 43, 3331.
10. Dalmas, F.; Dendievel, R.; Chazeau, L.; Cavaille, J. Y.; Gauthier, C. Acta Mater 2006, 54, 2923.
11. Foygel, M.; Morris, R. D.; Anez, D.; French, S.; Sobolev, V. L. Phys Rev B 2005, 71, 104201.
12. Bryning, M. B.; Islam, M. F.; Kikkawa, J. M.; Yodh, A. G. Adv Mater 2005, 17, 1186.
13. Sandler, J. K. W.; Kirk, J. E.; Kinloch, I. A.; Shaffer, M. S. P.; Windle, A. H. Polymer 2003, 44, 5893.
14. Grossiord, N.; Miltner, H. E.; Loos, J.; Meuldijk, J.; Mele, B. V.; Koning, C. E. Chem Mater 2007, 19, 3787.
15. Peijs, T.; Jacobs, M. J. N.; Lemstra, P. J. In Comprehensive Composites; Chou, T. W.; Kelly, A.; Zweben, C., Eds.; Elsevier Science: Oxford, 2000; p 263.
16. Ward, I. M. Plast Rubbers Compos 2004, 33, 189.
17. Kwolek, S. L.; Morgan, P. W.; Schaefgen, J. R.; Gularich, L. W. Macromolecules 1977, 10, 1390.
18. Smith, P.; Lemstra, P. J. J Mater Sci 1980, 15, 505.
19. Ward, I. M.; Hine, P. J. Polymer 2004, 45, 1413.
20. Curv. http://www.curvonline.com (accessed Oct 2008).
21. Alcock, B. Ph.D. Thesis, Queen Mary University of London, 2004.
22. Alcock, B.; Cabrera, N. O.; Barkoula, N.-M.; Loos, J.; Peijs, T. J Appl Polym Sci 2007, 104, 118.

23. Alcock, B.; Cabrera, N. O.; Barkoula, N.-M.; Peijs, T. Compos Sci Technol 2006, 66, 1724.
24. Alcock, B.; Cabrera, N. O.; Barkoula, N.-M.; Spoelstra, A. B.; Loos, J.; Peijs, T. Compos A 2006, 37, 716.
25. Alcock, B.; Cabrera, N. O.; Barkoula, N.-M.; Spoelstra, A. B.; Loos, J.; Peijs, T. Compos A 2007, 38, 147.
26. Barkoula, N.-M.; Schimanski, T.; Loos, J.; Peijs, T. Polym Compos 2005, 261, 114.
27. Loos, J.; Schimanski, T.; Hofman, J.; Peijs, T.; Lemstra, P. J. Polymer 2001, 42, 3827.
28. Lankhorst Pure Composites. http://www.pure-composites.com (accessed Oct 2008).
29. Ajayan, P. M.; Stephan, O.; Colliex, C.; Trauth, D. Science 1994, 265, 1212.
30. Gordeyev, S. A.; Ferreira, J. A.; Bernardo, C. A.; Ward, I. M. Mater Lett 2001, 51, 32.
31. Bin, Y.; Mine, M.; Ai, K.; Jiang, X.; Masaru, M. Polymer 2006, 47, 1308.
32. Du, F. M.; Fischer, J. E.; Winey, K. I. Phys Rev B 2005, 72, 121404.
33. Potschke, P.; Brunig, H.; Janke, A.; Fisher, D.; Jehnichen, D. Polymer 2005, 46, 10335.
34. Haggenmueller, R.; Gommans, H. H.; Rinzler, A. G.; Fisher, J. E.; Winey, K. I. Chem Phys Lett 2000, 330, 219.
35. Nanocyl. http://www.nanocyl.com (accessed Oct 2008).
36. Pantea, D.; Darmstadt, H.; Kaliaguine, S.; Roy, C. Appl Surf Sci 2003, 217, 181.
37. Loos, J.; Alexeev, A.; Grossiord, N.; Koning, C. E.; Regev, O. Ultramicroscopy 2005, 104, 160.
38. Loos, J.; Grossiord, N.; Koning, C. E.; Regev, O. Compos Sci Technol 2007, 67, 783.
39. Zhang, R.; Baxendale, M.; Peijs, T. Phys Rev B 2007, 76, 195433.
40. Balberg, I.; Anderson, C. H.; Alexander, S.; Wagner, N. Phys Rev B 1984, 30, 3933.
41. Balberg, I. Carbon 2002, 40, 139.
42. Berhan, L.; Sastry, M. Phys Rev E 2007, 75, 041120.
43. Bug, A. L. R.; Safran, S. A.; Webman, I. Phys Rev Lett 1985, 54, 1412.
44. Neda, Z.; Florian, R. Phys Rev E 1999, 59, 3717.
45. Ounaies, Z.; Park, C.; Wise, K. E. Compos Sci Technol 2003, 63, 1637.
46. Kovacs, J. Z.; Velagalaa, B. S.; Schulte, K.; Bauhofer, W. Compos Sci Technol 2007, 67, 922.
47. Martin, C. A.; Sandler, J. K. W.; Shaffer, M. S. P.; Schwarz, M. K.; Bauhofer, W.; Schulte, K.; Windle, A. H. Compos Sci Technol 2004, 64, 2309.
48. Kharchenko, S. B.; Douglas, J. F.; Obrzut, J.; Grulke, E.; Migler, K. B. Nat Mater 2004, 3, 564.
49. Musumeci, A. W.; Silva, G. G.; Liu, J. W.; Martens, W. N.; Waclawik, E. R. Polymer 2007, 48, 1667.
50. Potschke, P.; Dudkin, S.; Alig, I. Polymer 2003, 44, 5023.
51. Regev, O.; Elkati, N. B.; Loos, J.; Koning, C. E. Adv Mater 2004, 16, 248.
52. Seo, M.; Park, S. Chem Phys Lett 2004, 395, 44.
53. Berhan, L.; Sastry, M. Phys Rev E 2007, 75, 041121.
54. Shaffer, M. S. P.; Windle, A. H. Adv Mater 1999, 11, 937.
55. Gojny, F. H.; Wichmann, M. H. G.; Fiedler, B.; Kinloch, I. A.; Bauhoferc, W.; Windle, A. H.; Schulte, K. Polymer 2006, 47, 2036.
56. Schueler, R.; Petermann, J.; Schulte, K.; Wentzel, H.-P. J Appl Polym Sci 1997, 63, 1741.
57. Liang, J. Z.; Yang, Q. Q. J Appl Phys 2007, 102, 083508.
58. Peijs, T.; Deng, H., PCT/EP2008/064460, Patent ending, Conductive Polymer Composites, 2008
59. Zhang et al. Conductive network formation in the melt of carbon nanoutbe/thermoplastic polyurethane composite, Composites Science and Technology, 2008, doi:10.1016/j.compscitech.2008.11.039