

## **Polythylene (PE)/MWCNT-composites: Spectral, morphological, mechanical and electrical properties**

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### **ABSTRACT**

*In this research article, we have described the synthesis of non-covalent functionalization of multi-walled carbon nanotubes (MWCNTs) with a polymer dispersant and obtained a powder of polymer-wrapped MWCNTs. The UV-vis absorption spectrum was used to investigate the optimal weight ratio of the MWCNTs and polymer dispersant. The powder of polymer-wrapped CNTs had improved the drawbacks of MWCNTs of being lightweight and difficult to process, and it can re-disperse in a solvent. Then, we blended the polymer-wrapped MWCNTs and polyethylene (PE) by melt-mixing and produced a conductive master batch and MWCNT/PE composites. The polymer-wrapped CNTs showed lower surface resistivity in composites than the raw MWCNTs. The structure of PE/c-MWCNT composites was characterized by UV-vis spectra, Scanning electron microscopy showed that both the thinner fibrous phase and the larger block phase could be observed. The ultimate mechanical properties might be compromised by the addition of CNTs to the perfect structure of the polymer fibre.*

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### **INTRODUCTION**

Since the discovery of carbon nanotubes (CNT) in 1991 by Iijima [1], they have been considered as ideal reinforcing fillers in nanocomposite materials. Some key properties include high mechanical strength, high aspect ratio, small diameter, light weight, high electrical and thermal conductivities, and high thermal and air stabilities [2–13]. They have the potential to be used in areas such as field emitters [14], probe tips for SPMs [15], nanoelectronic devices [16, 17], and nanotube-based composites [10, 18]. In recent years, considerable research has been undertaken on the preparation of novel nanocomposites with CNTs as fillers in composite materials. A wide range of host materials have been used, including polymers, ceramics, and metals [19–22]. Several methods have been developed to prepare these polymer/CNT composites, such as melt mixing [20], in situ polymerization [23], mini-emulsion polymerization [24], electrochemical [25], electrospinning [26, 27], and other methods [28, 29].

By optimizing the process conditions, polyethylene fibres could be produced possessing Young's moduli approaching that of the theoretical maximum for polyethylene crystals. The introduction of nanofibres in such high strength fibres would lead to materials that are truly inspired by nature. Natural materials such as bone and tooth are composites of proteins, which exhibit many levels of hierarchical structures and use nano-scale fibres as building blocks for micron-sized fibres. The creation of such 'man-made' nanostructured fibres could be used for the creation of newly 'designed' composite materials with additional levels of hierarchy. Furthermore, it is expected that nanocomposites might exhibit improved stiffness without sacrificing toughness. This is extremely important for anti-ballistics which is the main application area for these polymer fibres.

In this research work, one of the best known organic solvents for nanotubes, namely *N,N*-dimethylformamide (DMF) and xylene will be mixed together and used as a mixed solvent in the gelation/ crystallisation process in order to improve the dispersion of MWNTs and dissolve the PE. The nanocomposite film will be drawn to obtain highly

oriented tapes. These materials will be characterized in terms of electrical and mechanical properties. Finally, an assessment of the real reinforcement potential of CNTs in highly oriented PE fibres will be presented.

## MATERIALS AND METHODS

PE was supplied by DSM, Multiwall nanotubes used as supplied. They are produced by CVD and their purity is 95%. Xylene and *N,N*-dimethylformamide (DMF), supplied by Romil, were used as solvents.

### COMPOSITE PREPARATION

Nanocomposite films were fabricated by a gelation/ crystallisation casting technique using xylene or a mixture of xylene and DMF. A typical sample preparation procedure is described for mixed solvents. MWNTs were dispersed in 19 g of DMF by ultrasonication using a high power tip. The MWNTs concentration needed in DMF was calculated in order to obtain a range of loadings between 1 and 5 wt% in the final composite. The DMF/MWNT mixture was added to 1 g of Stanyl UH 610 polyethylene reactor powder in a large neck flask and topped up to 100 g with xylene. The mixture was degassed for 1 hour in a sonication bath and left overnight. The mixture was heated in an oil bath at 126-127 °C under gentle stirring and as the polymer started swelling, the mixture was left for 45 minutes. When the swelling process was complete, the mixture was stirred vigorously and the temperature was increased to 130 °C. Once PE was totally dissolved, the sample was poured into a crystallisation basin at room temperature. After 2-3 hours DMF was extracted using xylene. The gel was dried at room temperature for several days [30].

### CHARACTERISATION

#### AGGLOMERATES SIZE DETECTION

The size distributions of the suspended MWNT agglomerates in different solvents were measured by a laser particle size instrument (Malvern Zetasizer Nano ZS, measuring range 0.6 nm to 6 μm).

#### SCANNING ELECTRON MICROSCOPE (SEM)

The SEM (XL30 ESEM-FEG, Fei Co., The Netherlands) was equipped with a field emission electron source. High vacuum conditions were applied and a secondary electron detector was used for image acquisition. The SEM was operated either in conventional high-voltage or low-voltage mode.

#### ELECTRICAL MEASUREMENT

Bulk electrical measurements were conducted on a rectangular specimen with planar dimensions of 15 mm × 5 mm. The sample ends were gold coated in order to measure the resistance in the axial direction. Agilent DC power supply E3612A was used as voltage source and Keithley 6517A Electrometer was used for voltage and current measurement. Each resistance measurement was made from the slope of the voltage-current plot within the linear range.

#### TENSILE TEST

Tensile tests were conducted on tapes at room temperature on an Instron 5586. The samples were rectangular with approximate planar dimension of 15 mm × 5 mm. For all samples at least five specimens were measured, the results analysed and the mean and standard deviation calculated.

## RESULTS AND DISCUSSION

### DISPERSION QUALITY

Figure 1 shows the aggregate size distribution as detected from light scattering measurements. Ultrasonication of MWNTs in pure xylene gave a poor degree of dispersion. The solvent can only swell the nanotube agglomerates and loosen them up, but they are still visible and in large number. Their size is outside the measuring range of the machine. However, when DMF is employed to disperse MWNTs, a better dispersion of tubes is produced and light scattering measurements produce a sharp peak at around 250 nm. The addition of xylene to DMF worsens the dispersion, in fact the peak is broadened, however the size of the agglomerates is drastically reduced as compared to the case of pure xylene.

These measurements are very useful for the identification of the best solvent to process the composites, because they give a good indication of the level of aggregate dispersion of nanotubes in solution. However, the degree of dispersion in solution may not reflect the final dispersion within the polymer matrix. Electrical measurements, however, can serve as a good indicator of the state of dispersion of nanotubes within the polymer matrix. Hence, the state of dispersion of nanotubes in order to establish the best processing condition of melt mixed polycarbonate (PC)/MWNT composites [31].

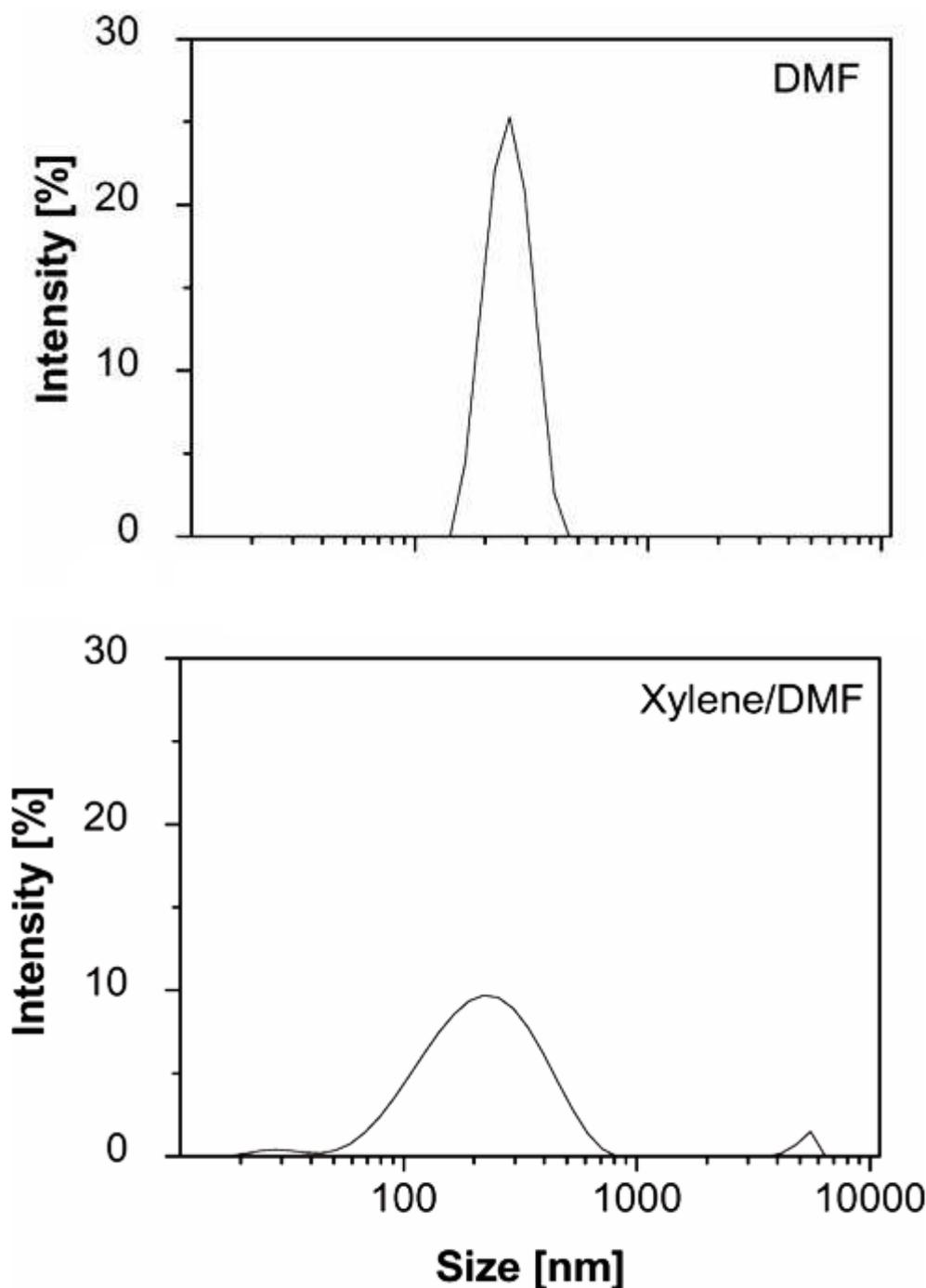


Figure 1: Aggregate size distributions for MWNTs dispersed in pure DMF and a mixture of DMF and xylene (1:4)

Figure 2 shows the real part of AC conductivity (as calculated from the real part of the admittance) as a function of the angular frequency  $\omega$  for PE composite films containing 5 wt% MWNTs processed from different solvents. For the composite film processed with pure xylene, the conductivity is frequency dependent in the frequency range studied. This is in good agreement with the expression valid for dielectric materials. Electrical measurements show clearly that the presence of DMF plays a crucial role in the state of dispersion of MWNTs, in fact the same amount of nanotubes lead to a conductive specimen when dispersed with a mixture of solvents, while the sample remains an insulator when the composite is prepared from pure xylene.

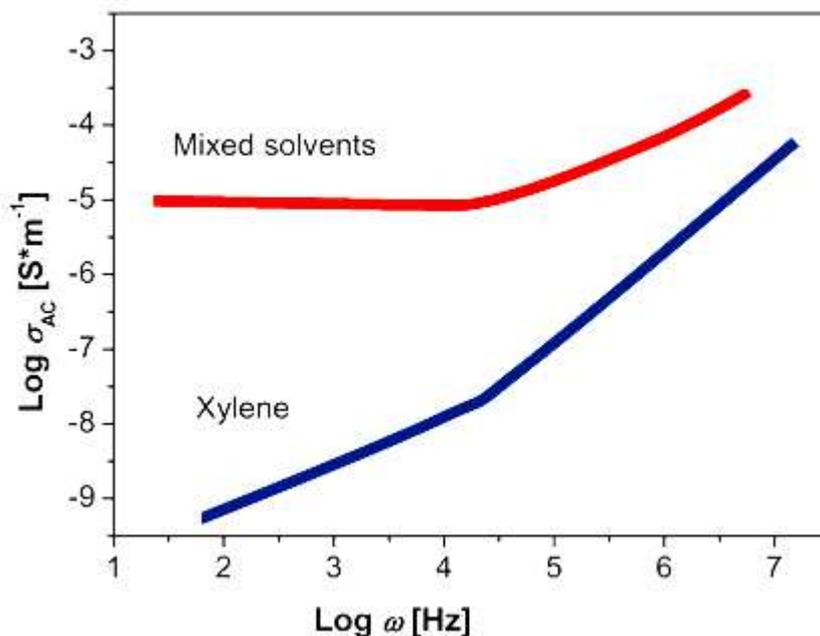


Figure 2: Frequency dependant conductivity for PE containing 5 wt% MWNTs prepared using different solvents

**Electrical properties of composites**

The percolation threshold is a basic characteristic of a conductive composite, as mentioned in the introduction. The percolation model describes the behaviour of conductive polymer composites. Its conductivity ( $\sigma$ ) at and above the percolation threshold ( $p_c$ ) is generally described by a power law relationship

$$\sigma = \sigma_0 (p - p_c)^t \quad \text{for } p > p_c$$

where  $\sigma_0$  is a constant,  $p$  is the weight fraction of the conductive filler and  $t$  is the critical exponent.  $p - p_c$  is known as the reduced mass.

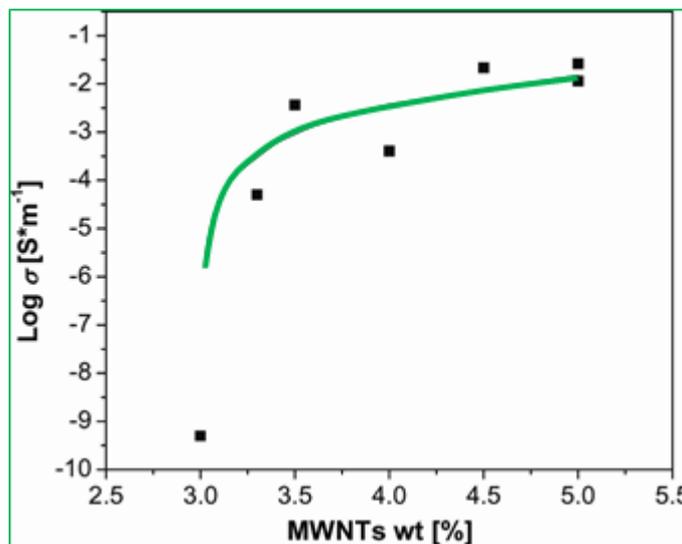
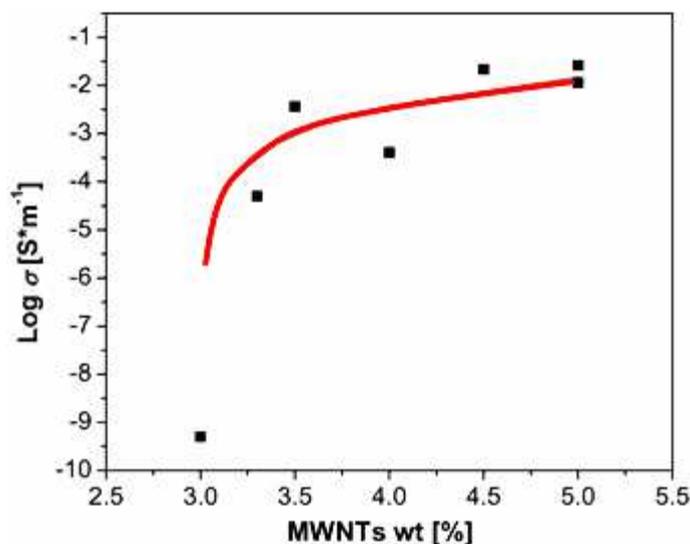
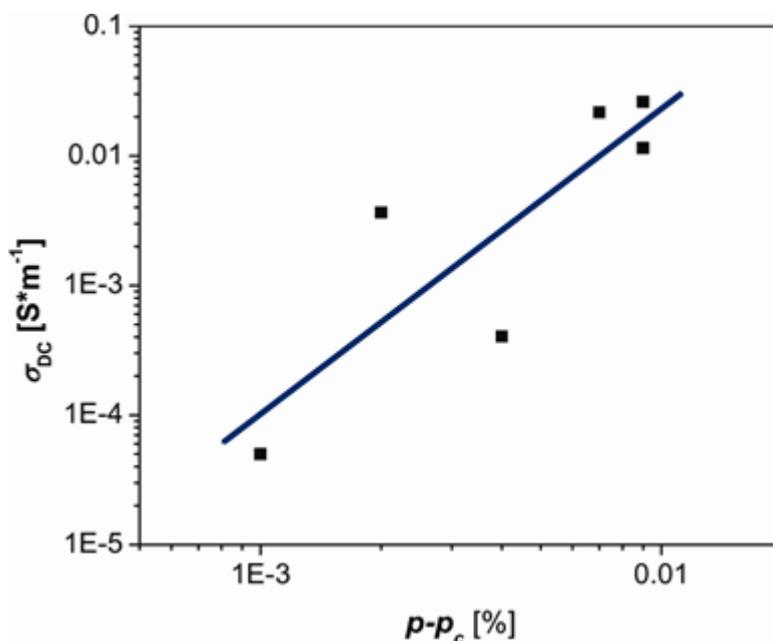


Figure 3: Electrical conductivity as a function of MWNT weight fraction  
The squares are experimental data and the solid line

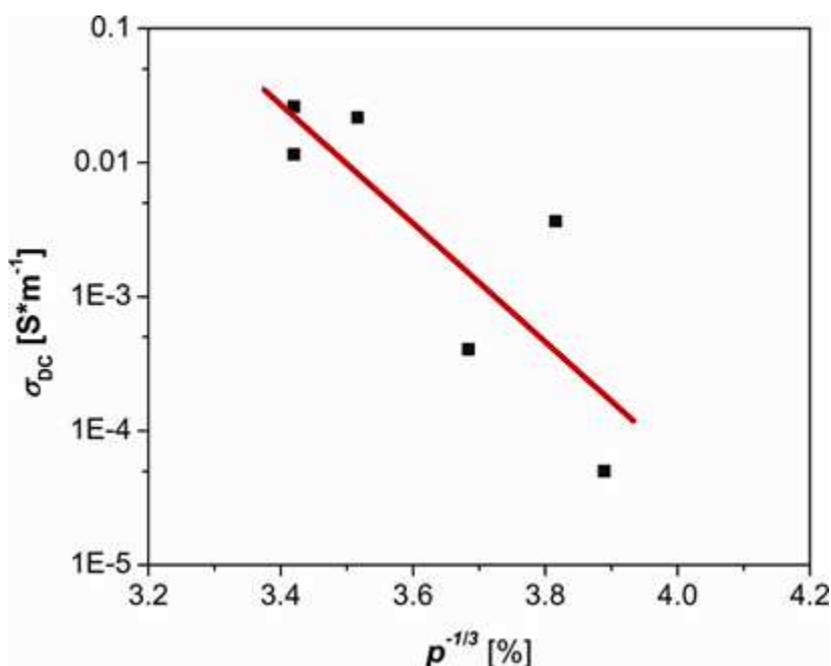


**Figure 3: Electrical conductivity as a function of MWNT weight fraction**  
The squares are experimental data and the solid line is a fit of the data



**Figure 4: Plot of conductivity vs.  $p-p_c$ , reduced mass**  
The squares are experimental data and the solid line is a linear fit of the data

Figure 3 and 4 shows the DC conductivity of PE/MWNTs composite films as a function of weight fraction of MWNTs. A linear relationship can be clearly seen. The best fitted values are for  $p_c = 3.1$  wt % and  $t = 1.97$ . The percolation threshold value falls within the range of percolation thresholds calculated for cylindrical conductors in an insulating matrix. In this study statistical analysis was used to show that a percolation threshold in the region of 1-5% is expected for a system of conductive fillers of aspect ratio between 40 and 130, consistent with the aggregation state of nanotubes used in this study. The conductivity exponent  $t$  generally reflects the dimensionality of the system with values typically around 1.3 and 2.0 for two and three-dimensions, respectively. Here the conductivity critical exponent's value is close to the universal value for three-dimensional percolation systems. Furthermore,  $\sigma_0$  can be extrapolated when  $p = 100\%$ , i.e. for a nanotube film.  $\sigma_0 = 1 \times 10^3$  S/m is lower than the expected conductivity for nanotube mats, 105 S/m. This might be due to the morphology of the nanocomposite, where large conductive nanotube agglomerates are separated by regions of insulating matrix. Hence, conduction is limited by tunnelling between potential barriers between conductive regions [32,33].



**Figure 5: Plot of the log of conductivity as a function of  $p^{-1/3}$**   
The squares are experimental data and the solid line is a fit of the data

They found conductivity for nanotube film of  $10^{-3}$  S/m by extrapolation and ascribed this result to the formation of a thick crystalline polymer layer, which prevented direct contact between nanotubes. They modelled this behaviour with the fluctuation induced tunnelling model, which takes into account tunnelling through potential barriers of different heights due to local temperature fluctuations. If temperature is constant, they obtain a simple relation between conductivity and internanotube gap width,  $w$

$$\ln \sigma_{DC} \propto \sigma$$

Due to spatial consideration, the inter-nanotube gap width is proportional to  $p^{-1/3}$ , which combined with the previous equation lead to

$$\ln \sigma_{DC} \propto \sigma p^{-1/3}$$

Figure 5 shows in a semi-logarithmic scale conductivity as a function of  $p^{-1/3}$ , where a linear relationship can be clearly seen.

#### SEM:

The different capabilities for charge transport of the conductive MWNTs and the insulating polymer matrix, the secondary electron yield is enriched at the location of the nanotube, which results in the contrast between the MWNT network and the polymer matrix. The mechanism operating is not totally understood, in fact from a theoretical point of view, the contrast should be inverted, with dark MWNTs within a bright charged polymer matrix. However, this imaging mode is very efficient in the visualisation of the nanotube organisation within the matrix. 6 shows a general view of a tape ( $\lambda=30$ ) containing 5 wt% MWNTs. A high degree of alignment can be clearly seen. The solid state drawing is indeed very efficient in aligning the nanotubes. In fact, at a relatively low draw ratio, the MWNTs are already perfectly aligned in the axial direction, thus creating the ultimate uniaxial nanocomposite [34].

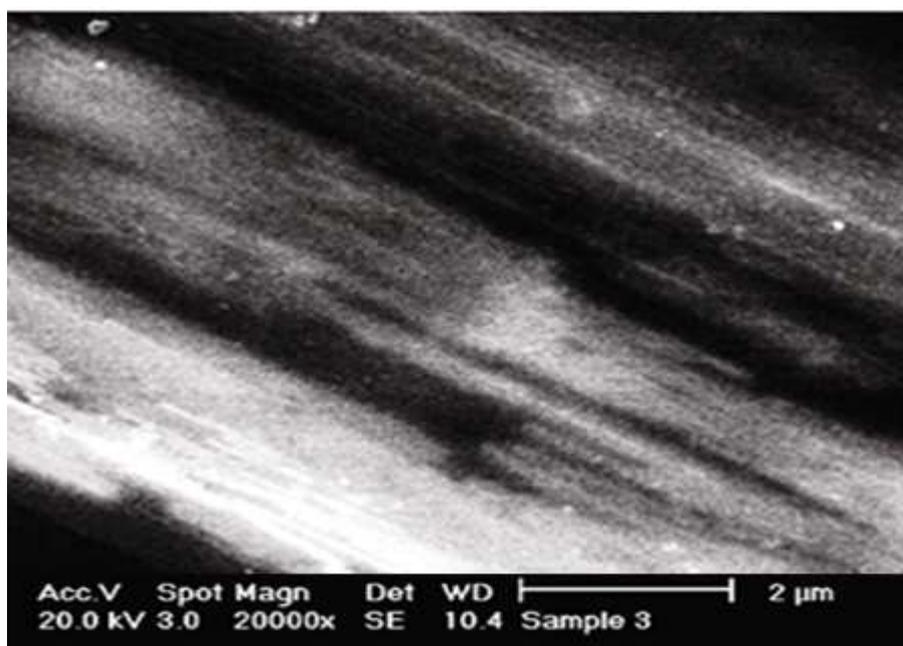


Figure 6: SEM image of PE containing 5 wt% MWNTs tape ( $\lambda=30$ ) showing highly oriented nanotubes

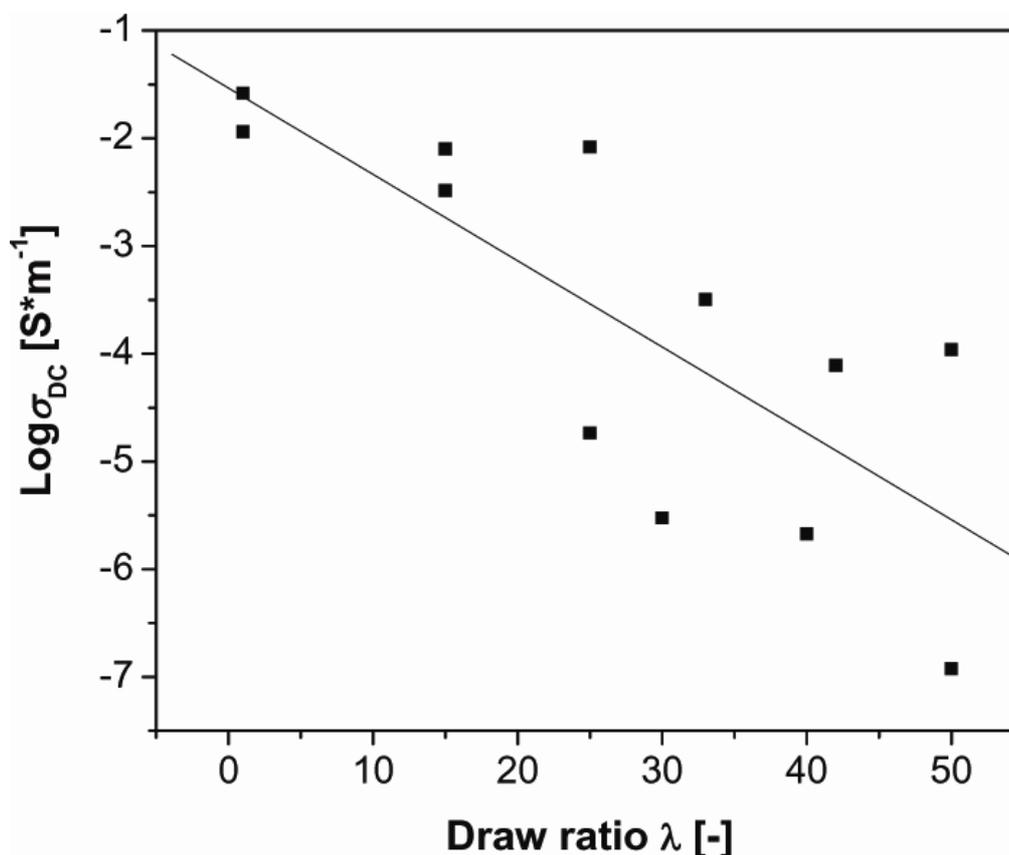


Figure 6: Electrical conductivity of PE containing 5 wt% MWNTs as a function of draw ratio  $\lambda$ . Black squares are the experimental data and the solid line is a linear fit.

#### Electrical properties of drawn tapes

Figure 7 shows the electrical conductivity as a function of the draw ratio for a composite containing 5 wt% MWNTs. The conductivity was measured along the stretching direction with the two-terminal method. The conductivity of undrawn sample ( $\lambda=1$ ) is improved drastically as compared to pure PE film (5 wt% > percolation threshold), however the conductivity was gradually decreased with increasing draw ratio. As shown in the previous paragraph, solid state drawing is responsible for a change in distribution and alignment of MWNTs. It could be

thought that drawing of PE/MWNT nanocomposites decreases the number of possible conduction paths present above the percolation threshold with a resulting decrease in conductivity. In fact, for pure PE films, a draw ratio of 80-100 could be reached, while for the nanocomposites containing 5 wt% MWNTs only 50 could be achieved. Furthermore, as it will be shown in the next paragraph, the addition of MWNTs is accompanied by a decrease of the mechanical properties.

### Mechanical properties of drawn tapes

Figure 7 shows the stress-strain curves for PE tapes drawn to a draw ratio of 30. Nanocomposite tape of PE containing 5 wt% MWNTs is compared to its reference material, PE processed from a mixture of xylene and DMF, and also to the standard PE tape processed from pure xylene. As compared to the PE processed from mixed solvents, both Young's modulus and tensile strength are affected by the presence of nanotubes. MWNT agglomerates act as stress concentrators and result in a reduction of the ultimate properties. When compared to the PE tape prepared from xylene, the effect is even bigger.

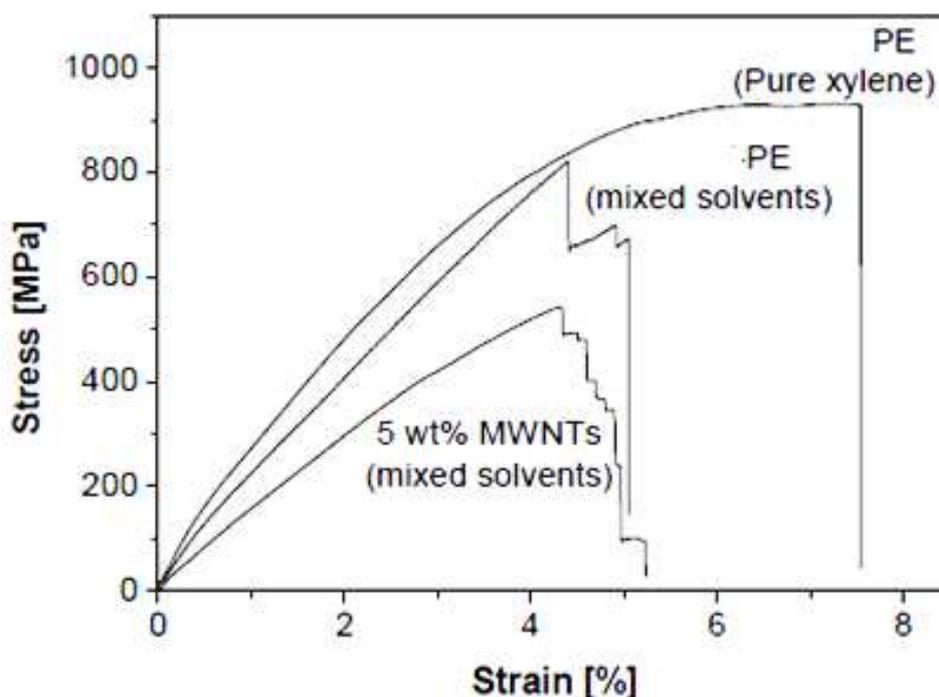


Figure 7: Stress-strain curves of pure PE crystallized by xylene and by a xylene/DMF mixture and PE containing 5 wt% MWNTs crystallized from a mixture of xylene and DMF

### CONCLUSION

In conclusion, CNTs can be used as fillers in PE in order to create conductive fibres. However, the idea of using CNTs, especially MWNTs, as reinforcing Manufacturing and characterisation of PE/MWNT composites nanofibres for PE should be carefully reconsidered, since the ultimate mechanical properties might be compromised by the addition of CNTs to the perfect structure of the polymer fibre. These results are not completely surprising. As already mentioned in the introduction, the amazing mechanical properties of PE fibres are a result of the perfect structure obtained by gel-spinning followed by solid state drawing. If the structure is compromised by the addition of a filler, then there will be a decrease in properties of the matrix and the gain that results from the use of a reinforcing filler might be nullified. In addition, the reinforcing potential of MWNTs can be modest, depending on the effective load carrying capabilities of the multiple layers. It would be interesting to assess from a theoretical point of view whether SWNTs could be used to reinforce high-strength PE fibres.

### REFERENCES

- [1] Iijima S, *Nature* 354:56(1991)
- [2] Despres JF, Deguerre E, Lafdi K, *Carbon* 33:87(1995)
- [3] Treacy MMJ, Ebbesen TW, Gibson JM, *Nature* 381:678(1996)
- [4] Overney G, Zhong W, Tomanek D (1993) *Z. Phys D* 27:93
- [5] Robertson DH, Brener DW, Mintmire, JW, *Phys Rev B* 45:12592(1992)

- [6] Chopra NG, Benedict LX, Crespi VH, Cohen ML, Louie SG, Zettl A, *Nature* 377:135(1995)
- [7] Wagner HD, Lourie O, Feldman Y, Tenne R, *Appl Phys Lett* 72:18(1998)
- [8] Iijima S, Brabec C, Maiti A, Bernholc J, *Chem Phys* 104:2089(1996)
- [9] Lourie O, Wagner HD, *J Mater Res* 13:2418(1998)
- [10] Wong EW, Sheehan PE, Lieber CM, *Science* 277:1971(1997)
- [11] Poncharal P, Wang ZL, Ugarte D, de Heer WA, *Science* 283:1513(1999)
- [12] Meyyappan M Carbon nanotubes: science and applications. ,CRC Press, Boca Raton, FL(2005)
- [13] Salvétat JP, Andrew G, Briggs D, Bonard JM, Basca RR, Kulik AJ, Stočkli T, Burnham NA, Forró, *L Phys Rev Lett* 82:944(1999)
- [14] Fan S, Chapline MG, Franklin NR, Tomblor TW, Cassell AM, Dai H, *Science* 283:512(1999)
- [15] Dai H, Hafner JH, Rinzler AG, Colbert DT, Smalley RE, *Nature* 384:147(1996)
- [16] Frank S, Poncharal P, Wang ZL, de Heer WA, *Science* 280:1744(1998)
- [17] Tans SJ, Verschueren ARM, Dekker C, *Nature* 393:49(1998)
- [18] Ajayan PM, Stephan O, Colliex C, Trauth D, *Science* 265:1212(1994)
- [19] Tang BZ, Xu HY, *Macromolecule* 32:2569(1999)
- [20] Jin Z, Pramoda KP, Xu G, Goh SH (2001), *Chem Phys Lett* 337:43
- [21] Hwang GL, Hwang KC, *J Mater Chem* 11:1722(2001)
- [22] Dong SR, Tu JP, Zhang XB *Mater Sci Eng A Struct Mater Prop Microstruct Process* 313:83(2001)
- [23] Jia ZJ, Wang ZY, Xu CL, Liang J, Wei BQ, Wu DH, Zhu SW *Mater Sci Eng A* 271:395(1999)
- [24] Barraza HJ, Pompeo F, O'Rear EA, Resasco DE (2002) *Nano Lett* 2:797
- [25] Gao M, Huang SM, Dai LM, Wallace G, Gao RP, Wang ZL *AngewChemInt Ed* 39:3664(2000)
- [26] Ge JJ, Hou HQ, Li Q, Graham MJ, Greiner A, Reneker DH, Harris FW, Cheng SZD *J Am, Chem Soc* 126:15754(2004)
- [27] Salalha W, Dror Y, Khalfin RL, Cohen Y, Yarin AL, Zussman E, *Langmuir* 20:9852(2004)
- [28] Kong H, Gao C, Yan DY, *Macromolecules* 37:4022(2004)
- [29] Qu LW, Lin Y, Hill DE, Zhou B, Wang W, Sun XF, Kitaygorodskiy A, Suarez M, Connell JW, Allard LF, Sun YP, *Macromolecules* 37:6055(2004)
- [30] Hsiao AE, Tsai SY, Hsu MW, Chang SJ. *Nanoscale Res Lett.* 6;7(1):240. 2012
- [31] Harel Y, Azoubel S, Magdassi S, Lellouche JP. *J Colloid Interface Sci.*;390(1):62-9. 2013
- [32] Jin Y, Zhang Y, Zhang Q, Zhang R, Li P, Qian W, Wei F. *Nanoscale.* 7;5(13):6181-6. 2013
- [33] Arslantunali D, Budak G, Hasirci V. *J Biomed Mater Res A.* 102(3):828-41 2014
- [34] Vinodh R, Sangeetha D. *J Nanosci Nanotechnol.* ;13(8):5522-33.2013