Fabrication and property prediction of conductive and strain sensing TPU/CNT nanocomposite fibres†

Emiliano Bilotti,*[a] Rui Zhang,[a] Hua Deng,[ab] Mark Baxendale[c] and Ton Peijs*[ad]

Received 9th June 2010, Accepted 9th August 2010
DOI: 10.1039/c0jm01827a

In this study, thermoplastic polyurethane (TPU) fibres containing multi-walled carbon nanotubes (MWNTs) and fabricated *via* an extrusion process were demonstrated to possess a tuneable level of electrical conductivity. A simple approach based on the time–temperature superposition applied to the electrical conductivity of carbon nanotube (CNT) percolating in a thermoplastic polyurethane (TPU) melt was also developed to predict the conductivity of the nanocomposite fibres. The observation of Arrhenius dependence of zero-shear viscosity and the assumption of simple inverse proportionality between the variation of conductivity, due to network formation, and viscosity allow a universal plot of time variation of conductivity to be composed, which is able to predict the conductivity of the extruded fibres. The same TPU/CNT fibres were also demonstrated to possess good strain sensing abilities, which makes them good candidates for applications in smart textiles.

1. Introduction

Carbon nanotubes (CNTs)[1] have attracted substantial attention since the 1990s, catalysing a wide range of research fields.[2–6] The high electrical conductivity together with the large aspect ratio made CNT particularly outstanding candidates as filler for conductive polymer composites (CPCs).[7–9] Several application fields like anti-static, electro-static painting, EMI shielding,[10] as well as sensing,[11,12] flexible electronics,[13] field emission,[14] have been explored.

Despite the extensive research activities on CNT composites manufactured *via* various processes, only limited results have been so far reported on the conductivity of polymer CPC fibres. Du *et al.* achieved a conductivity of $\sim 10^{-3}$ S cm^{-1} for an SWNT and PMMA system with 2 wt% CNTs in the matrix.[15] Potschke *et al.* reported a PC/MWNT composite fibre, oriented in the melt.[16] Due to the deformation on the CNT conductive network induced during spinning, the melt-spun fibres were not conductive for CNT content below 2 wt%. Nevertheless, composite films with similar or even lower CNT concentrations were reported to be conductive.[16] Recently a successful example of highly oriented, mechanically performing and electrically conductive polymeric CPC tapes has been reported by our group.[17–20] This was achieved by a thermal annealing post-treatment, affecting only the outer layers of the tape, formed by a low melting temperature polymer filled with CNT, while retaining the mechanical properties of the core component of the tape (high melting temperature polymer), stretched in the solid-state. It was believed that the thermal treatment facilitated the formation of a CNT conductive network in the outer layer, through a phenomenon defined dynamic percolation.

Percolation theory[21] has been used to describe the insulator–conductor transition in conductive filler polymer composites for the last few decades offering a theoretical explanation to many experimental observations.[11,22–24] However, percolation theory is concerned with static networks so is inadequate when describing the dynamic process of conductive network formation (dynamic percolation). Dynamic percolation has been observed in both CNT-[25–29] and carbon black-loaded[30–32] polymer composites in the melt states. A high shear is often applied during mixing in order to disperse CNT in polymer matrix (*e.g.* during twin-screw melt compounding),[25,26] leaving them separated from each other, resulting in low composite conductivity. These well dispersed and separated CNT are, however, reported to aggregate in the melt given sufficient temperature and time,[27–31] leading to an up to nine orders of magnitude improvement in composite conductivity.[27] This means that, for the same concentration of CNT, a polymer composite can show very different conductivity levels in correspondence of different processing/thermal histories, a fact often neglected in the scientific literature. For the same reason, one should be careful in comparing data reporting conductivity and percolation threshold values.

Many efforts have been made to understand the dynamic process of conductive network formation in these composites due to its impact on the conductivity of composites incorporating nanofillers.[27–34] A common method of studying this behaviour is recording the time-dependent conductivity during isothermal annealing of the composites. Various models have been proposed to explain the experimental data using modified percolation theory[28–30] or a universal interfacial free energy.[32–34] In some

[a]*Centre for Materials Research & School of Engineering and Materials Science, Queen Mary University of London, Mile End Road, E1 4NS London, UK. E-mail: e.bilotti@qmul.ac.uk; t.peijs@qmul.ac.uk; Tel: +44 (0)20 7882 8865; +44 (0)20 7882 5043*
[b]*College of Polymer Science and Engineering, Sichuan University, State Key Laboratory of Polymer Materials Engineering, Chengdu, 610065, Sichuan, China*
[c]*Centre for Materials Research & Physics Department, Queen Mary University of London, Mile End Road, E1 4NS London, UK*
[d]*Eindhoven University of Technology, Eindhoven Polymer Laboratories, PO Box 513, 5600 MB Eindhoven, The Netherlands*
† This paper is part of a *Journal of Materials Chemistry* themed issue on Advanced Hybrid Materials, inspired by the symposium on Advanced Hybrid Materials: Stakes and Concepts, E-MRS 2010 meeting in Strasbourg. Guest editors: Pierre Rabu and Andreas Taubert.

studies, a time (relaxation time[31] or percolation time[32–34]) was obtained from the time-dependent conductivity and its relationship with temperature was described by an Arrhenius equation with activation energies very close to the values obtained from viscosity measurements.[30,32,33] The effect of shearing of the melt was also studied, giving the problem more complexity.[31] Despite the different approaches and details of the models proposed, it is generally accepted that the process can be described as particle re-aggregation in the polymer melt.[27–34]

Although the proposed models have been used to fit experimental data, there are still some problems that remain challenging. The models introduce many physical parameters owing to the complexity of the conductive network formation in composites. This complexity hinders the widespread use of the models for interpreting experimental data and giving useful information that can be correlated with fabrication parameters. In this study, the problem has been simplified by the observation of Arrhenius behaviour of viscosity and the assumption of inverse proportionality between the rate of conductivity change and viscosity. This allowed the composition of a universal conductivity *vs.* time plot using isothermal and scanned temperature data. The universal plot was used, for the first time, to predict the conductivity of composite fibres produced *via* extrusion.

2. Experimental

2.1. Materials

Multiwall CNT (Nanocyl C7000) and thermoplastic polyurethane (TPU) (Estane®, X4280, a polyester-based polyurethane by Lubrizol (USA)) were used as conductive filler and polymer matrix; a loading of 2 and 3 wt% CNT was used throughout this study.

2.2. Sample preparation

The desired amount of CNT (2 or 3 wt%) was mixed with polyurethane at 190 °C in a nitrogen environment for 4 min at 50 rpm using a DSM X'plore 15 ml micro twin-screw compounder. After mixing, the screw speed was set to 5 rpm and kept for 1 min, after which the compounded composite strand was collected without stretching. The typical composite strand diameter was about 3 mm. Pellets of the same compounds prepared were also compression mounded into disc-like specimens (25 mm diameter and 1.5 mm thickness) for rheological characterisation. Nanocomposites with the same CNT contents were also prepared in bigger amounts, by a Dr Collin twin-screw compounder (ZK25, 25 mm, $L/D = 40$), which lead to a CNTs dispersion state comparable to the compounding in the DSM X'plore. The throughput was of 4 kg h^{-1}, with screw speed 35 rpm, and temperatures ranging between 185 °C and 195 °C over 9 heating zones. The composite was directly collected into a water bath for consolidation, and then pelletised inline after removing excess of water with an air-blade. These nanocomposite pellets were successively used in a set-up for fibre extrusion composed of a single-screw extruder connected to melt pump and a circular die of 1 mm diameter. Flow of the melt was accurately controlled by extruding through the melt pump connected to an inlet channel and a die. Slow melt flow rates (40 mm^3 s^{-1}) and gentle inner profile of the die were used to ensure quasi-static conditions for conductive network formation. The inlet channel temperature was 190 °C, and the melt residence time in the inlet channel was 428 s. The polymer residence time in the die was 38 s with the temperature set to 200 °C, 220 °C and 240 °C. All the other conditions were kept constant. Special attention was paid to avoid the conductivity being affected by stretching when the fibre came out of the die as this can break down the conductive networks.[15,16]

2.3. Characterisation

Scanning electron microscope (SEM) images were taken by a FEI Inspector-F. Both the cross-sectional area (fractured in liquid nitrogen) and the lateral surface of the TPU/CNT fibres were examined. For the cross-sectional area investigation, cold fractured fibres were placed vertically on an aluminium stage and gold sputtered, before imaging.

For the lateral surface investigation, the fibres were placed laterally on an aluminium stage without any further treatment and observed by SEM using high accelerating voltage (25 kV). In this way, the carbon nanotubes in the composite can be charged by the high accelerating voltage and emit enriched secondary electrons, which makes the CNT visible.[35]

Dynamic-oscillatory rheological measurements were performed on TPU with a controlled strain rheometer (AR 2000, TA Instrument) equipped with an environmental chamber and parallel plates geometry (25 mm diameter). The specimens were tested temperatures ranging between 170 and 200 °C. The measurements were conducted over a frequency range of 0.1–1000 rad s^{-1} and at the shear strain of 0.1%, within the linear viscoelastic region.

Dynamic percolation tests were conducted on compounded nanocomposite strands (~3 mm in diameter and ~10 mm in length), which were subjected to various heating profiles while the conductivity, time, and sample temperature were monitored simultaneously, as described in our previous work.[27]

The conductivity of the composite fibres was measured by a two-point method, by a combination of a picoameter (Keithley 6485) and a DC voltage source (Agilent 6614C), across a length of 150 mm. Silver paint was applied on the fibre ends as electrodes. A voltage scan was performed for each sample from 0.5 to 10 V and the conductivity was calculated from the linear fit of the current density *versus* electric field curve. At least 10 samples were measured for each data point.

Similarly, the strain-sensing tests were performed by loading the fibre samples (with diameters ranging from 760 μm to 850 μm) in an Instron tensile test machine and simultaneously measuring the conductivity by a 2-point measurement. The electric contacts were obtained by brass plate electrodes attached to the tensile grips and insulated from the tensile test machine frame. The tensile grips were pneumatic, allowing a fine control of the pressure applied to the sample, which was set at 50 psi.

3. Results and discussion

3.1. Morphological analysis

Fig. 1 shows the SEM micrographs of TPU + 2% CNT fibres extruded at 200 °C. The images of the gold coated cross-sectional

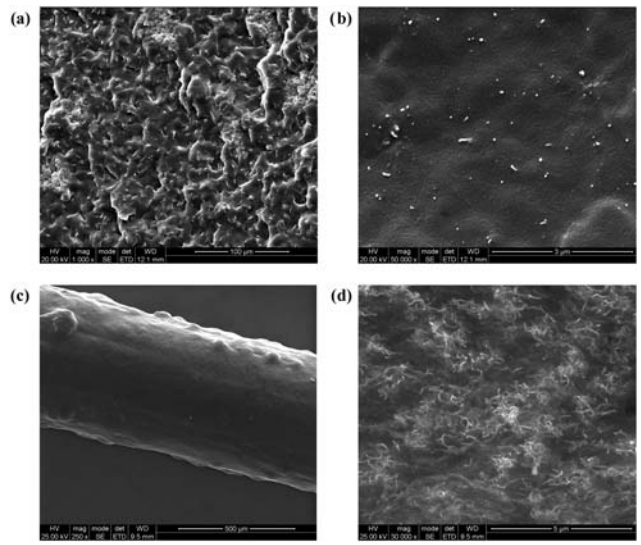

Fig. 1 SEM micrographs of TPU + 2% CNT fibres cross-sectional areas at magnifications of (a) 1000× and (b) 50 000×, and lateral surfaces at magnifications of (c) 250× and (d) 30 000×.

areas (Fig. 1a and b) provide indication of the nanofiller dispersion at the micro- and nano-scale after melt compounding. A relative homogeneous dispersion and morphology across the cross-section of the fibre was found, with no skin effect. CNTs are shown locally well distributed within the TPU matrix (Fig. 1b), but they also exist in the form of densely packed micron-size clusters (Fig. 1a). It is stressed here that, to a certain extent, the existence of a minor nanofiller agglomeration can be beneficial for the electrical properties of the composite, while it is generally demonstrated being detrimental for the mechanical properties.[20,36,37] Fig. 1c and d show the (non-coated) lateral surfaces of the same fibres, imaged at high accelerating voltage (25 kV) by means of the CNT charging effect and emission of enriched secondary electrons.[35] The surface of the fibre appears relatively smooth at low magnifications (Fig. 1c) while a robust interconnected conductive network of CNT is shown at higher magnifications (Fig. 1d).

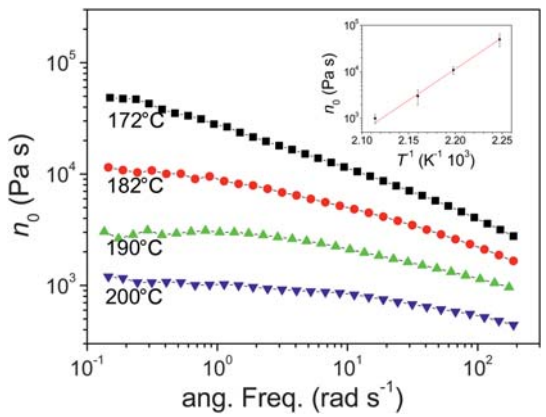

Fig. 2 Viscosity dependence on the angular frequency for TPU. Inset: zero-shear viscosity fitted with Arrhenius equation. Three samples were measured for each data point, and the average was taken. The error bar indicates the highest and the lowest value of the measurements.

3.2. Rheological analysis

Fig. 2 shows the rheological behaviour of pure TPU, tested under rotational oscillatory conditions, within the linear viscoelastic regime. At low frequencies, the complex viscosity of the polymer melt is independent from the angular frequency, for all the temperatures investigated, and it is commonly defined zero-shear viscosity. In the inset of Fig. 2, the values of zero-shear viscosity are plotted as a function of the reciprocal of the temperature, in a semi-logarithmic scale. At temperatures well above the glass transition temperature of the polymer, the relationship between the zero-shear viscosity and the temperature can be described by the Arrhenius equation,[38]

$$\eta_0 = c\exp\left(\frac{\Delta E}{RT}\right), \quad (1)$$

where T is temperature, R is the ideal gas constant, ΔE is an activation energy, and c is a constant. An activation energy ΔE of 249 kJ mol^{-1} can be obtained by fitting the data in Fig. 2 inset using eqn (1).

3.3. Electrical conductivity and dynamic percolation

It was already mentioned that a conductive polymer composite, even with a fixed CNT content, can display very different conductivity values in correspondence of different processing conditions. Often higher conductivity and lower percolation thresholds are found for low viscosity systems (*e.g.* epoxy based composites) rather than simple melt compounding of thermoplastics,[25,26] and for processes involving high temperatures and long times (*e.g.* compression moulding).[27–31,39,40] In this study TPU/CNT fibres were extruded at different temperatures and their conductivity is reported in Fig. 3. Previous published results on the same composite systems but in the form of pellets cut from compounded strands or compression moulded films are also included for comparison.[27] It can be noticed that the fibres conductivity increases with the extrusion temperature and such

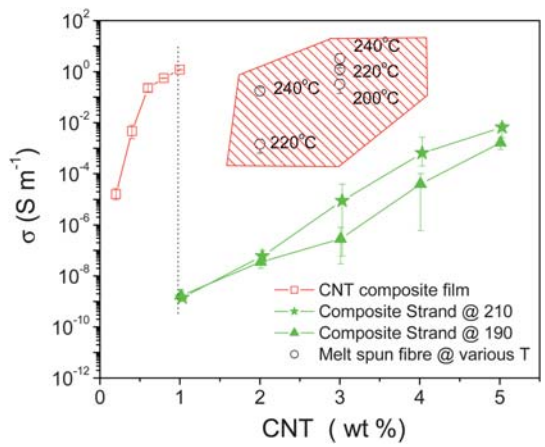

Fig. 3 The effect of different extrusion temperature conditions on the conductivity of TPU/CNT fibres, compared with the conductivity of the same composites prepared by different processing routes (*i.e.* measured directly on the pellets of composite strands, as it comes out of the extruder or on compression moulded films). The data of the composite strands and films are reproduced with permission from Zhang *et al.*[27]

increase is more pronounced in correspondence of a lower filler content. Interestingly, the conductivity of the TPU + 3% CNT fibre extruded at 240 °C is ~3 S m^{-1}, much higher than previously published data for composite fibres,[15,16] and reaching a level of conductivity similar to the hot-pressed film samples containing the same filler content.

This variability in electrical properties is explained by the dynamic percolation of CNT in a polymer melt. Understanding and, possibly, controlling the dynamic process of conductive network formation are of extreme importance due to its practical implication on the final composite properties.[27–34] A common method of studying this process is by monitoring the change in conductivity (time-dependent conductivity) when the sample is subjected to a thermal process. Such tests have been performed on TPU/CNT composite pellets strands coming out from the compounder, which are characterised by a relatively good CNT dispersion, small network re-agglomeration and therefore low conductivity.

Fig. 4a shows the results of the time dependence of the TPU + 3% CNT when three isothermal conditions (Fig. 4a, inset) were used. It can be observed that to obtain the same conductivity the composite reached after 2 h at 172 °C, only a very short time

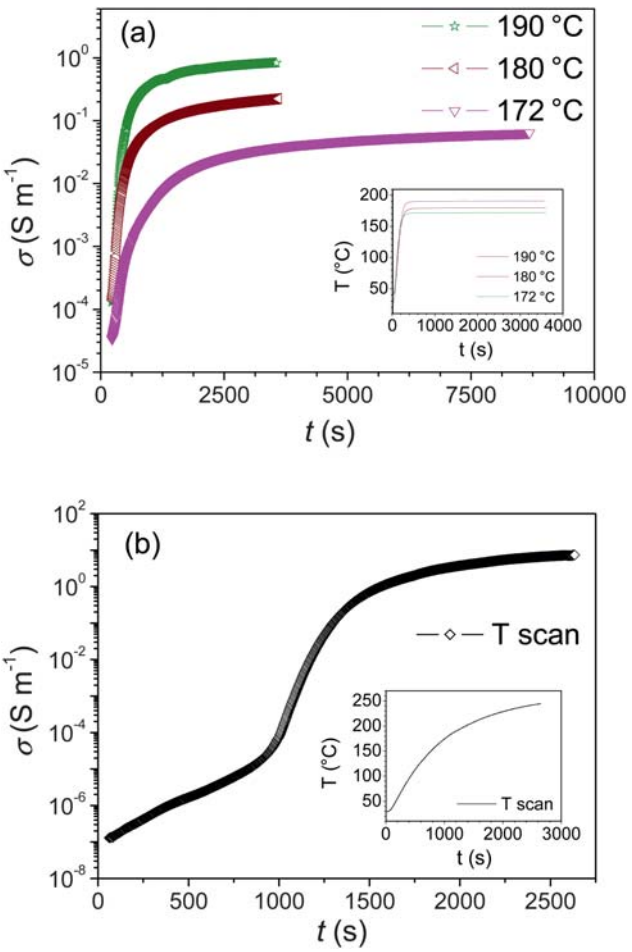

Fig. 4 The conductivity-time dependence of the TPU + 3% CNT composites when subjected to: (a) isothermal condition of 172 °C, 180 °C, and 190 °C and temperature scan (T scan) condition (b). The heating profiles are indicated in the corresponding insets.

(~600 s) is needed if the composite is subjected to 180 °C, and the time needed is even shorter for 190 °C. Fig. 4b shows the conductivity-time dependence result when temperature is continuously increased (T scan test). Before the sharp increase in conductivity, there is a regime where the conductivity gently increases with time. This is attributed to the temperature dependence of the tunnelling resistance.[27] After this regime, the conductivity shows a sharp increase with time which can be attributed to network formation of the conductive filler (dynamic percolation). Due to the higher temperature, the conductivity reached a higher level at shorter times compared with the isothermal data. From this observation, it can be extrapolated that, for constant CNT loading and processing conditions, longer annealing times at higher temperature result in a higher conductivity of the composite.

3.4. Predictive model for the fibre conductivity

Various models have been proposed to explain time-dependence conductivity experiments as in Fig. 4. The main trend has been to fit experimental data with rather complex multi-parameters fitting equations, with limited practical use.[28–30,32,34] There is increasingly more need of simpler predictive tools which are able to provide more useful information and can, for instance, aid the fabrication of highly conductive polymer composite parts (*e.g.* fibres). This requires a simplification of the physical phenomenon.

The CNT network formation process is generally described in terms of conductive filler aggregating and conducting pathway creation. These processes involve filler particle migration in polymer melts. Hence, despite the complexity of the process, it is reasonable to argue that the conductive network formation is regulated by the viscosity of the polymer, which is the main limiting factor.[30,32,34]

Our main assumption is that the conductive network formation is (or is limited by) a first order thermally activated phenomenon. Therefore there will be a simple inverse proportionality between rate of conductivity change and viscosity of the polymer, which can be expressed as:

$$\frac{\Delta\sigma}{\Delta t} \propto \frac{1}{n_0}, \tag{2}$$

and by substituting eqn (1):

$$\frac{\Delta\sigma_T}{\Delta t_T} \propto 1/\exp\left(\frac{\Delta E}{RT}\right). \tag{3}$$

The time required to obtain a given change in conductivity $\Delta\sigma$ at different temperatures can be estimated from eqn (3). This can be expressed, in a similar fashion as the time–temperature equivalence of the T_g viscoelastic behaviour in the WLF theory,[38] as:

$$\Delta t'_{T^*} = \Delta t_T \exp\left(\frac{\Delta E}{RT^*}\right) \Big/ \exp\left(\frac{\Delta E}{RT}\right), \tag{4}$$

where Δt_T is the time required for a certain change in conductivity, $\Delta\sigma$, to take place at a temperature T, and Δt_{T^*} is the time needed for the same change to take place at a different temperature T^*. ΔE is the activation energy which can be obtained from rheological measurements. Here we assume that the activation

energy of the composite is equal to that of the pure polymer matrix since the interaction between CNT will play only a minor role in determining the activation energy of the composite if well dispersed.[41] The value of ΔE for pure TPU was previously estimated in 249 kJ mol^{-1} (Fig. 2, inset).

Eqn (4) can therefore be used for the superposition of the conductivity-time dependence in the case of isothermal tests (Fig. 4a). Even the scanned temperature tests (Fig. 4b) can be transformed into equivalent isothermal curves, when the heating rate is not too fast and each short enough intervals of time Δt_T can be considered as an isothermal test at a certain temperature.

Fig. 5 shows the superpositioned conductivity *vs.* time dependence of TPU + 3% CNT composite strands. Data in Fig. 4a and b were superpositioned to an equivalent isothermal curve at $T^* = 190$ °C (463 K) using eqn (4). The superpositioned plots compose a universal plot (master curve) indicating the underlying assumptions of the analysis are valid despite the heating profiles used. The similar exercise was carried out for TPU + 2% CNT fibres.

Before the fibre extrusion process, the CNT can be considered relatively well dispersed in the pre-compounded composite pellets (Fig. 1), as in the extruded strand samples before thermal annealing (time dependent conductivity tests), which are characterised by a low conductivity. The conductivity of extruded TPU/CNT fibres is controlled by the CNT dynamic percolation during the quasi-static melt flow particularly in the high temperature terminal zone of the die. Using the processing conditions applied during fibre extrusion (temperatures and residence times), a prediction was made for the conductivity of an extruded fibre at different die temperatures based on the universal plot in Fig. 5 and compared with the experimental values. The predicted and the experimentally measured data of TPU + 2% CNT and TPU + 3% CNT fibres are presented in Fig. 6, showing a good agreement.

3.5. Strain sensing

In this section, it is demonstrated how the TPU/CNT fibres are not only electrically conductive but also sensitive to static and dynamic strain stimuli.[11,27] Fig. 7 shows the resistivity-strain dependence of TPU + 3% CNT fibres extruded at different

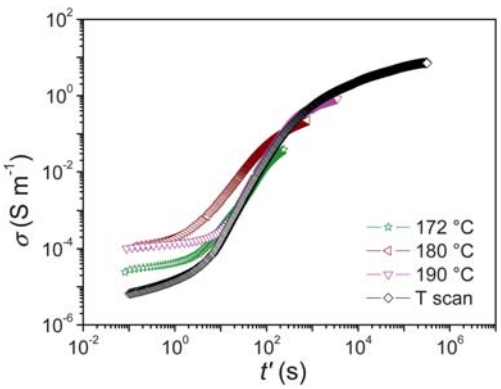

Fig. 5 Universal plot, relative to TPU + 3% CNT fibres, composed by superposition the conductivity-time dependence of three isothermal condition and on temperature scan (T scan) condition from Fig. 4.

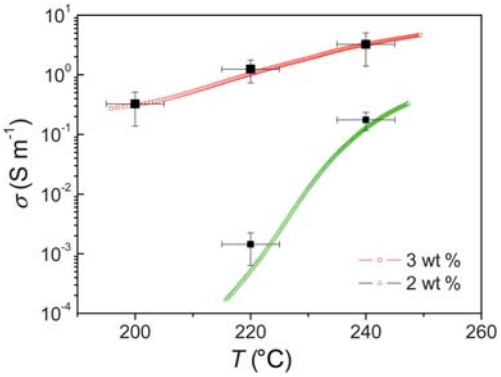

Fig. 6 Predicted and experimental measured composite fibre conductivity dependence on the die temperature, for two different CNT contents. The error bars for the temperature indicate the temperature fluctuation of the die during melt spinning.

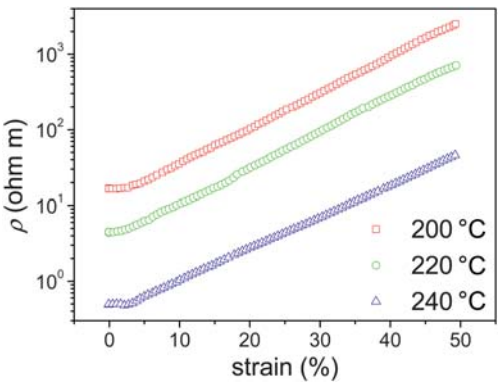

Fig. 7 Resistivity-strain dependence of TPU + 3% CNT fibres extruded at different temperatures.

temperatures. The fibres were stretched up to 50% strain, at a strain rate of 100% min^{-1}, while monitoring the resistivity change. Three specimens were tested for each sample and the medium result among three measurements is presented. An exponential relationship can be clearly observed between resistivity and strain in the range of 5–50% strain. Similar behaviour was observed in our previous publications, and was attributed to the tunnelling junction gap width modulation described by the FIT model.[11] Hence, it is assumed that the conduction mechanism in this fibre can also be described by the FIT model, and resistivity-strain dependence between 5 and 50% can be attributed to the increase of the tunnelling distance induced by macroscopic strain.

Fibres were also subjected to strain sensing tests using a cyclic loading profile with 10% maximum strain and strain rate of 100% min^{-1}. The resistance was normalised by the resistance at zero-strain and plotted against both strain and time.

Fig. 8 shows the normalised resistance-strain dependence during the first cycle. The normalised resistance increased with increasing strain and was only partially recoverable. The fibres extruded at a die temperature of 200 °C showed the highest sensitivity in this cycle, while the fibre extruded at a die temperature of 240 °C shows the lowest sensitivity.

Fig. 9 shows the normalised resistance response to the first 15 cycles, for the same maximum strain amplitude and strain

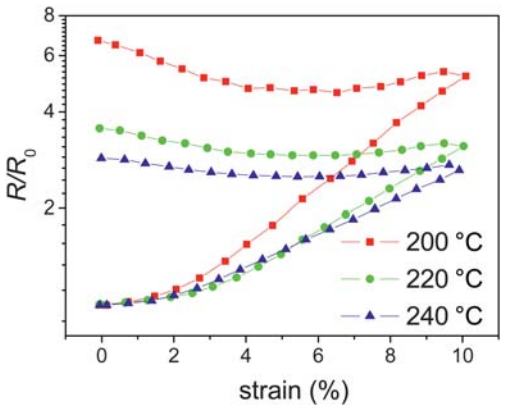

Fig. 8 Relative resistance-strain dependence of TPU + 3% CNT fibres extruded at different temperatures.

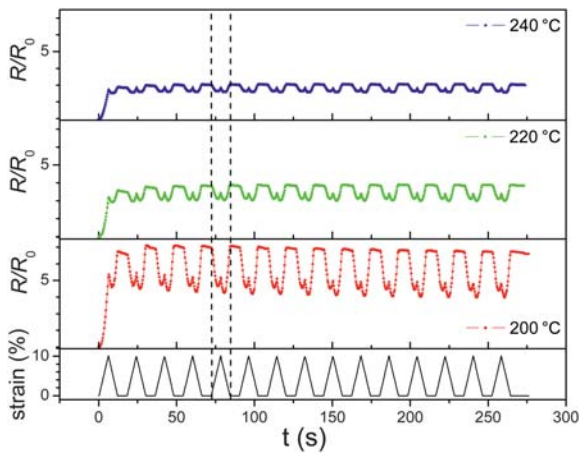

Fig. 9 The strain sensing behaviour of TPU + 3% CNT fibres extruded at different temperatures, subjected to 15 loading cycles.

speed as before. The sensing signal is not monotone with the strain, as already reported in the literature.[27] Upon loading in a given cycle, the fibre resistance first increases with increasing strain (this behaviour can be defined as positive strain effect) but, after a certain strain value, it decreases with increasing strain (this behaviour can be defined as negative strain effect). In analogy with the result in Fig. 8, the fibre extruded at 200 °C presents the highest strain sensitivity, giving the strongest signal. It can also be observed that, for the same fibre, the negative strain effect takes over the positive strain effect, showing almost an inverse relationship between relative resistance and strain. The fine tuning of processing parameters, like the temperature, can lead to CPC fibres with optimal sensing ability, particularly important for applications such as smart textiles.

4. Conclusions

In conclusion, we successfully demonstrated that it is possible to fabricate highly conductive TPU/CNT fibres *via* a continuous extrusion process. The conductivity of such nanocomposites is regulated by the dynamic percolation of the CNT in the polymer melt, which is controlled by the polymer viscosity. The conductive network formation process is a time–temperature dependent process which can be described by a simple Arrhenius equation. This enables the superposition of the conductivity time–temperature dependencies obtained from different heating conditions into a master curve, which gives instructive information for composites fabrication, including optimal processing parameters and possible conductivity values of the resulting composites. These valuable pieces of information can be obtained with minimal experiments and a simple analytical model. Its simplicity and predictive ability provides this approach the potential to be widely introduced in future studies of CPC both theoretically and applied. Finally the extruded TPU/CNT fibres showed interesting strain sensing abilities both under static and dynamic loading conditions.

Acknowledgements

The authors would like to thank Nanocyl (Belgium) and Lubrizol (USA) for supplying the materials used. This study was carried out in the framework of the European Research Program "INTELTEX" (Contract NO. 026626-2) in the Sixth Framework Programme.

References

1 L. V. Radushkevich and V. M. Lukyanovich, *J. Phys. Chem.*, 1952, **26**, 88–95.
2 R. H. Baughman, A. A. Zakhidov and W. A. Heer, *Science*, 2002, **297**, 787.
3 A. E. Aliev, J. Y. Oh, M. E. Kozlov, A. A. Kuznetsov, S. L. Fang, A. F. Fonseca, R. Ovalle, M. D. Lima, M. H. Haque, Y. N. Gartstein, M. Zhang, A. A. Zakhidov and R. H. Baughman, *Science*, 2009, **323**, 1575.
4 M. Zhang, S. L. Fang, A. A. Zakhidov, S. B. Lee, A. E. Aliev, C. D. Williams, K. R. Atkinson and R. H. Baughman, *Science*, 2005, **309**, 1215.
5 T. Hasan, Z. P. Sun, F. Q. Wang, F. Bonaccorso, P. H. Tan, A. G. Rozhin and A. C. Ferrari, *Adv. Mater.*, 2009, **21**, 3874.
6 G. H. Lu, L. E. Ocola and J. H. Chen, *Adv. Mater.*, 2009, **21**, 2487.
7 M. B. Bryning, M. F. Islam, J. M. Kikkawa and A. G. Yodh, *Adv. Mater.*, 2005, **17**, 1186.
8 J. K. W. Sandler, J. E. Kirk, I. A. Kinloch, M. S. P. Shaffer and A. H. Windle, *Polymer*, 2003, **44**, 5893.
9 J. C. Grunlan, A. R. Mehrabi, M. V. Bannon and J. L. Bahr, *Adv. Mater.*, 2004, **16**, 150.
10 R. Ramasubramaniam, J. Chen and H. Y. Liu, *Appl. Phys. Lett.*, 2003, **83**, 2928.
11 R. Zhang, M. Baxendale and T. Peijs, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2007, **76**, 195433.
12 E. T. Thostenson and T. W. Chou, *Adv. Mater.*, 2006, **18**, 2837.
13 S. Razdan, P. K. Patra, S. Kar, L. Ci, R. Vajtai, A. Kukovecz, Z. Konya, I. Kiricsi and P. M. Ajayan, *Chem. Mater.*, 2009, **21**, 3062.
14 T. Connolly, R. C. Smith, Y. Hernandez, Y. Gun'ko, J. N. Coleman and J. D. Carey, *Small*, 2009, **5**, 826.
15 F. M. Du, J. E. Fischer and K. I. Winey, *Phys. Rev. B: Condens. Matter*, 2005, **72**, 12.
16 P. Potschke, H. Brunig, A. Janke, D. Fischer and D. Jehnichen, *Polymer*, 2005, **46**(23), 10355.
17 H. Deng, T. Skipa, E. Bilotti, R. Zhang, D. Lellinger, L. Mezzo, Q. Fu, I. Alig and T. Peijs, *Adv. Funct. Mater.*, 2010, **20**, 1424–1432.
18 H. Deng, R. Zhang, E. Bilotti, J. Loos and T. Peijs, *Synth. Metals*, 2009, **160**, 5–6, 337–344.
19 H. Deng, R. Zhang, C. T. Reynolds, E. Bilotti and T. Peijs, *Macromol. Mater. Eng.*, 2009, **294**(11), 749–755.
20 H. Deng, R. Zhang, E. Bilotti, J. Loos and T. Peijs, *J. Appl. Polym. Sci.*, 2009, **113**(2), 742–751.
21 D. Stauffer and A. Aharony, *Introduction to Percolation Theory*, Taylor & Francis, 4th edn, 1985.
22 R. H. J. Otten and P. Van der Schoot, *Phys. Rev. Lett.*, 2009, **103**(22), 225704.

23 A. V. Kyrylyuk and P. Van der Schoot, *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**(24), 8221–8226.
24 M. A. J. Michels, J. Brokken, W. M. Groenewoud and A. Knoester, *Physica A (Amsterdam)*, 1989, **157**(1), 529–534.
25 G. R. Kasaliwal, S. Pegel, A. Goldel, P. Potschke and G. Heinrich, *Polymer*, 2010, **51**(12), 2708–2720.
26 T. Villmow, P. Potschke, S. Pegel, L. Haussler and B. Kretzschmar, *Polymer*, 2008, **49**(16), 3500–3509.
27 R. Zhang, A. Dawden, H. Deng, M. Baxendale and T. Peijs, *Compos. Sci. Technol.*, 2009, **69**(10), 1499.
28 H. Deng, T. Skipa, R. Zhang, D. Lillinger, E. Bilotti, I. Alig and T. Peijs, *Polymer*, 2009, **50**(15), 3747–3754.
29 I. Alig, D. Lellinger, M. Engel, T. Skipa and P. Pötschke, *Polymer*, 2008, **49**(7), 1902–1909.
30 B. H. Cipriano, A. K. Kota, A. L. Gershon, C. J. Laskowski, T. Kashiwagi, H. A. Bruck and S. R. Raghavan, *Polymer*, 2008, **49**(22), 4846–4851.
31 J. Obrzut, J. F. Douglas, S. B. Kharchenko and K. B. Migler, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2007, **76**(19), 195420.
32 G. Wu, S. Asai, C. Zhang, T. Miura and M. Sumita, *J. Appl. Phys.*, 2000, **88**(3), 1480.
33 X. Y. Tai, G. Z. Wu, H. Yui, S. Asai and M. Sumita, *Appl. Phys. Lett.*, 2003, **83**(18), 3791–3793.
34 G. Z. Wu, S. Asai and M. Sumita, *Macromolecules*, 2002, **35**(5), 1708–1713.
35 J. Loos, A. Alexeev, N. Grossiord, C. E. Koning and O. Regev, *Ultramicroscopy*, 2005, **104**(2), 160.
36 W. Wang, P. Ciselli, E. Kuznetsov, T. Peijs and A. H. Barber, *Philos. Trans. R. Soc. London, Ser. A*, 2008, **366**, 1613.
37 Z. Wang, P. Ciselli and T. Peijs, *Nanotechnology*, 2007, **18**(45), 455709.
38 J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 3rd edn, 1961.
39 F. Inam and T. Peijs, *J. Nanostruct. Polym. Nanocompos.*, 2006, **2**(3), 87–95.
40 F. Inam, M. J. Reece and T. Peijs, *Appl. Phys. A: Mater. Sci. Process.*, 2010, submitted.
41 J. Bicerano, J. F. Douglas and D. A. Brune, *J. Macromol. Sci. Rev., Macromol. Chem. Phys.*, 1999, **C39**(4), 561–642.