SYNERGISTIC EFFECTS IN TERNARY POLYMER NANOCOMPOSITES[†]

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[†] Dedicated to the memory of an exceptional materials scientist and friend Dr. Daniela Tabuani.

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Abstract

In this paper, the electrical properties of ternary nanocomposites based on thermoplastic polyurethane (TPU) and multi-walled carbon nanotubes (MWNTs) are studied. In particular two nanofillers – differing in shape and electrical properties - are used in conjunction with MWNTs: an electrically conductive CB and an insulating needle-like nanoclay, sepiolite. The ternary nanocomposites were manufactured in a number of forms (extruded pellets, filaments, and compression moulded films) and their morphological and electrical properties characterised as function of time and temperature. The presence of both secondary nanofillers is found to affect the formation of a percolating network of MWNTs in TPU, inducing a reduced percolation threshold and tuneable strain sensing ability. These ternary nanocomposites can find application as conductive and multi-functional materials for flexible electronics, sensing films and fibres in smart textiles.

1 Introduction

Carbon nanotubes (CNT) have attracted substantial interest since the 1990s [1], for a combination of outstanding properties, including high mechanical properties [2, 3] and high electrical [4] and thermal conductivity [5]. Several application fields like anti-static, electro-static painting, EMI shielding [6] as well as sensing [7, 8], flexible electronics [9], field emission [10], transparent and conductive thin films [11] and organic thermoelectric materials [12] have been explored.

The high electrical conductivity combined with their large aspect ratio, have made CNT a particularly interesting candidate as filler for conductive polymer composites (CPCs) [13]. In fact, according to statistic percolation theory [14], the percolation threshold is inversely proportional to the particle aspect ratio. Percolation thresholds below 0.01 % have been

reported for specific systems [13]. Nevertheless values of about 1-3 wt.% are typically found for composites based on thermoplastic polymers and produced with industrially-viable methods like melt compounding/extrusion [15]. The several orders of magnitude variation in the values of percolation thresholds reported in the literature can often be attributed to the phenomenon of dynamic percolation. Dynamic percolation has been observed in both CNT-[16, 17] and carbon black-loaded [18] polymer composites and describes the dynamic process of conductive network formation.

It was previously demonstrated by our group [15] that a partial reduction in percolation threshold, and a subsequent increase in electrical conductivity in correspondence of a fixed filler content, could be achieved and predicted by controlling simple processing parameters during polymer extrusion, which affect the dynamic percolation. This is interesting as it reduces the overall filler content, improves the processability and reduces the cost of the final product. There is certainly the necessity and industrial drive to reduce even further the percolation threshold of CNT in polymer nanocomposites.

Recently a strategy has been proposed, which involves the addition of a second filler/nanofiller working in synergy with CNT, and is defined as mixed (nano-)fillers systems. This is extremely interesting from an application view point since the selection of a secondary filler can not only assist the CNT conductive network formation but can also provide additional functionalities to the polymer matrix. For instance the addition of nanoclays could modify rheological properties and provide improved barrier properties and fire retardancy [19, 20].

Limiting our focus to electrical properties, the advantage of the mixed-fillers approach has been shown phenomenologically for several systems however the explanations for the underlying physical mechanisms have been diverse and often contradictory.

The main explanations given in literature can be summarised as: i) Excluded volume/confinement effect [21], ii) Improved dispersion [22] and iii) Improved network connectivity [23].

The current manuscript partially rejects the previous hypotheses and offers an original explanation for mixed-fillers systems. In order to draw more general conclusions, two very different nanofillers - in terms of shape and physical and electrical properties - have been used as additives for polymer/CNT composites: an electrically conductive CB and an insulating needle-like nanoclay, sepiolite. The ternary nanocomposites were manufactured in a number of forms and their electrical properties studied as function of time and temperature in order to analyse the process of dynamic percolation.

By understanding the effect of addition of a second nanofiller to a polymer/CNT composite, it is demonstrated how to control the dynamic percolation of CNT in a polymer matrix. This all gives practical benefits in producing low filler content, conductive and multi-functional polymeric materials. In particular the tuneable strain sensing ability of such ternary nanocomposites, in the form of filaments for smart textiles, was demonstrated.

2 Experimental

2.1 Materials

The MWNT used are supplied by Nanocyl, Belgium (Product No. NC7000), while the thermoplastic polyurethane (TPU) is the Estane®, by Lubrizol, USA (Product No. X4280). Carbon black (CB) and sepiolite (Sep) nanoclays are, respectively, Printex® XE-2 (by Grolman Ltd) and Pangel® (by Tolsa, Spain).

2.2 Sample Preparation

TPU composites were prepared using a DSM X'plore 15 Mini-extruder (The Netherlands), at 190°C for 4 min at 50 rpm. The so produced compounded strands were successively palletised by hand and compression moulded into films using a Collin hot press P300E (Germany), at 210°C for 7 min.

2.3 Characterisation

The conductivity of all samples (strands or films) was measured by a simple two-point measurement with a combination of a picoameter (Keithley 6485) and a DC voltage source (Agilet 6614C).

Dynamic percolation experiments were conducted on extrusion compounded nanocomposite strands (3 mm in diameter and 10 mm in length), as described in our previous work [15, 16].

Nanocomposite pellets, from these extruded strands, were successively used in a set-up for filament extrusion composed of a single-screw extruder connected to a melt pump and a circular die of 1 mm diameter. Throughput was accurately controlled by extruding through a melt pump connected to an inlet channel and a die. In analogy with our previous publications [7, 15], the strain-sensing tests were performed by loading the filaments in an Instron tensile test machine (up to 50% strain, at a strain rate of 100% min^{-1}) while simultaneously measuring the conductivity by a 2-point measurement. The electric contacts were obtained by brass plate electrodes attached to pneumatic tensile grips (set at 50 psi) and insulated from the tensile test machine frame.

3 Results and Discussion

3.1Morphology: CNT Dispersion

Figure 1 shows the cross-sectional area of binary and ternary thermoplastic polyurethane (TPU) nanocomposites filled by CNT, CB and/or sepiolite nanoclay. All composites present a relative good dispersion of the different nanofillers into the polymeric host matrix. Up to 4 wt.% of CNT is distributed within the TPU as small bundles or, partially, as individual nanotubes (Figure 1.a).
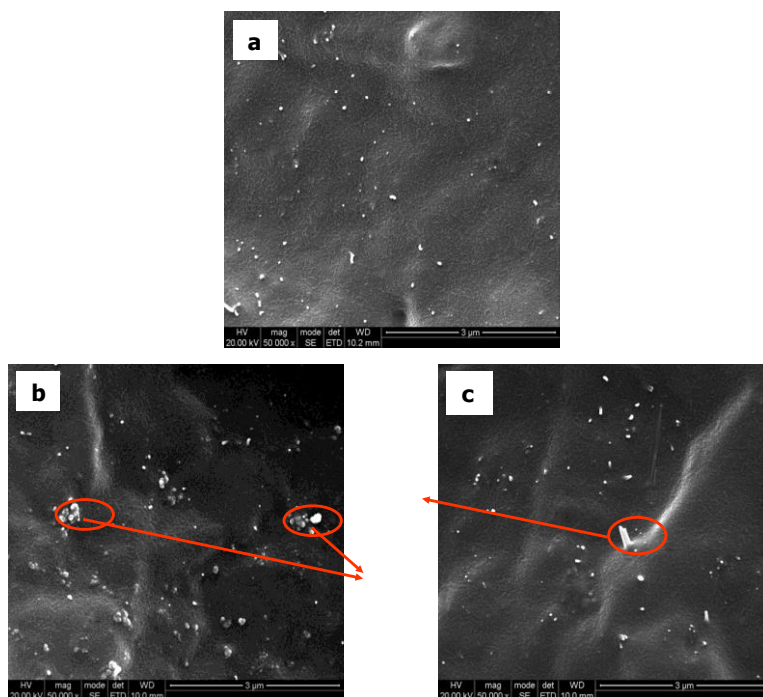

Figure 1. SEM micrographs of: a) TPU/4%CNT, b) TPU/3%CNT/1%CB, c) TPU/3%TPU/1%clay.

Sepiolite nanoclay shows the typical shape of a rigid needle [24-28] and are also dispersed as small bundles (Figure 1.c). CB is partially agglomerated into sub-micron spherical units (Figure 1.b). The presence of a second nanofiller (CB or clay) does not appear to modify the dispersion state of CNT (Figure 1).

These direct morphological observations contradict the hypothesis of Liu *et al.* [29] and Sumfleth *et al.* [22] on the effect of nanoclay (MMT) and titania nanoparticles on the exfoliation of CNT.

3.2 Conductivity and Dynamic Percolation: CNT Network

The effect of the secondary nanofiller is truly unveiled when using time-temperature dependent conductivity measurements (Figure 2). In analogy with previous publications [16], the conductivity shows a sharp increase with time, under isothermal conditions, which can be attributed to CNT network formation (dynamic percolation). Interestingly, the presence of minute amounts of secondary nanofiller (CB or clay), independently from their electrical properties, results into an accelerated dynamic percolation process, where the sharp increase in conductivity is shifted towards shorter times.
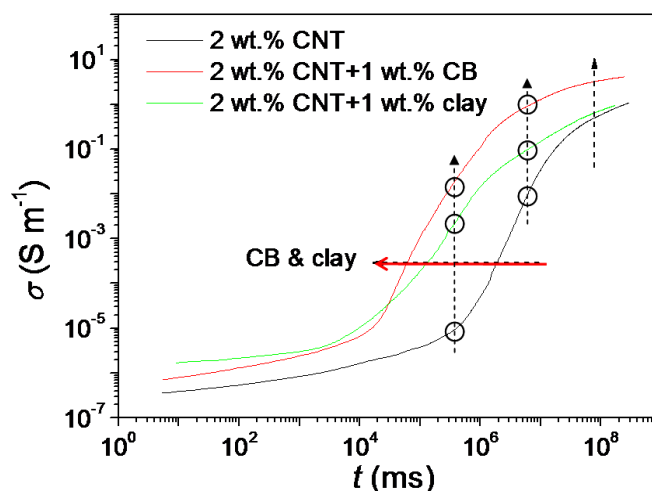
Figure 2. Influence of secondary nanofiller (CB or clay) on the time-dependent conductivity behaviour of TPU/MWNT nanocomposites.

The above phenomonon was partially intuited by Konishi *et al.* [30], which suggested that organo-clay could induce CB network self-assembly within PA6 matrices. However, for the first time this statement is better understood thanks to dynamic percolation experiments (Figure 2), which are able to monitor the evolution of the conductive network with time, given a certain activation energy (related to temperature [15]).

It is believed that small amounts of secondary nanofillers such as clay or CB can trigger the natural tendency of CNT to partially re-agglomerate in the polymer melt - which causes the increase in electrical conductivity - by altering the surface energy balance of the polymer/CNT system.

However, we can certainly exclude any effect of the viscosity change upon secondary nanofiller addition. It was previously demonstrated that the dynamic percolation is a process highly depended and limited by polymer melt viscosity [15]. The addition of a second filler

increases the overall viscosity which would decelerate the dynamic percolation, contrarily to what is observed (see supporting materials).

We can also exclude any direct participation of the secondary filler to the conductive network. In fact it can be observed from Figure 2 that the conductivity of the different samples is very similar both in the initial and final region of the curves. In order to further confirm this observation, the electrical conductivity of the composites in two different forms is measured: pellets of the as-extruded compound, representative of a relatively well-dispersed state (relating to the initial region of Figure 2), and compression moulded films, representative of an annealed and re-aggregated dynamically percolated state (relating to the final region of Figure 2) [15, 16].
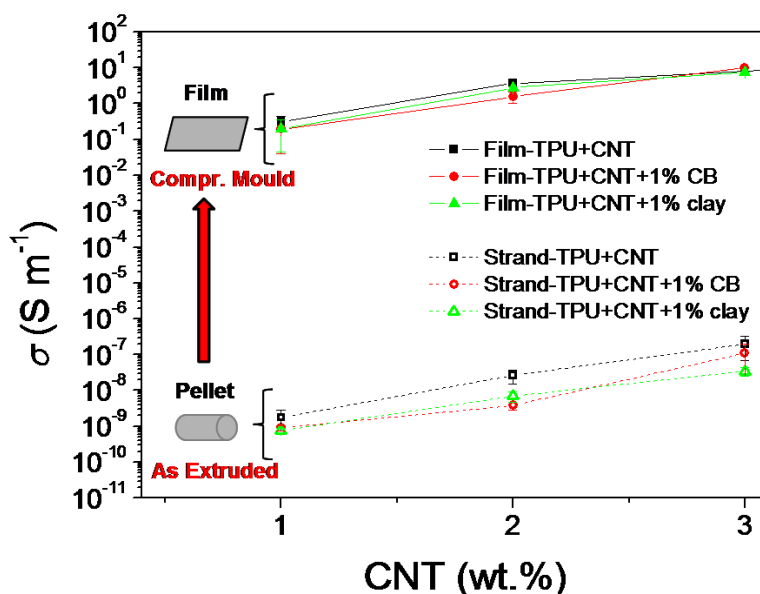
Figure 3. Conductivity of TPU/CNT composites, with or without second filler (CB or clay), directly after extrusion compounding or as fully annealed films.

As expected the conductivity of films is higher (up to eight orders of magnitude) than the conductivity of pellets (Figure 3). However, the conductivity of both pellets and films is, within experimental error, independent from the presence of either conductive CB or insulating clay. This demonstrates that CNT form the main conductive network and the presence of the secondary nanofiller (in small amounts) has little or no effect. In other words none of the two secondary nanofillers directly contribute to the conductive network, unlike as suggested by Konishi *et al.* [30], who envisaged the formation of CB/clay 'nano-unit' structures, able to affect the electron hopping pathways. In our opinion the modification of the slope in the static percolation curves observed by the same authors can simply be explained by the alteration of the dynamic percolation phenomenon instead.

3.3 Manufacture of Conductive and Strain Sensing Fibres

Understanding the effect of the addition of a secondary nanofiller on the dynamic percolation of CNT in a polymer matrix can have important implications for the manufacture of low filler content conductive polymer products such as extruded filaments. Filament extrusion requires always a partial melt drawing upon collection. This process negatively affects the CNT

network formation [31] as this is destroyed upon drawing, which explains why conductive polymer fibres generally require relatively high loadings of conductive filler.

This can be observed in Figure 4, in which the conductivity of TPU/CNT filaments, collected at different draw down speeds, is reported. As the speed increases, the conductivity of the filaments decreases by more than three orders of magnitude, as the melt drawing increases and the CNT network is destroyed.

Interestingly, the conductivity of the ternary nanocomposites filaments, within the range tested does not decrease with draw down speed. In this case, the addition of CB makes the filament processable at higher speeds preventing the reduction in conductivity. This can again be explained by the acceleration of dynamic percolation induced by the presence of CB.
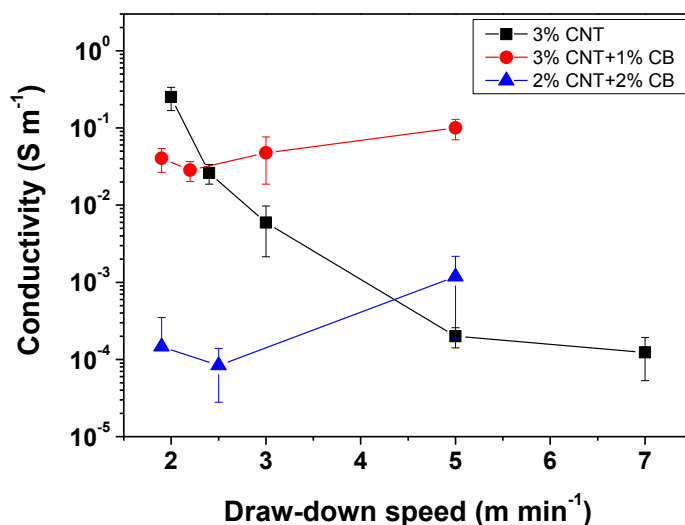
Figure 4. Conductivity of TPU/CNT binary and ternary nanocomposites, in the form of extruded filaments, collected at different draw down speeds. The addition of CB prevents the reduction in conductivity with speed.

The filaments produced are not only electrically conductive but also sensitive to strain. Figure 5.a shows the change in resistivity of TPU/CNT/CB filaments upon application of elongational strain as high as 50%. A typical exponential relationship can be observed, which is attributed to the increase of the average tunnelling distance induced by macroscopic strain, as demonstrated elsewhere [7].
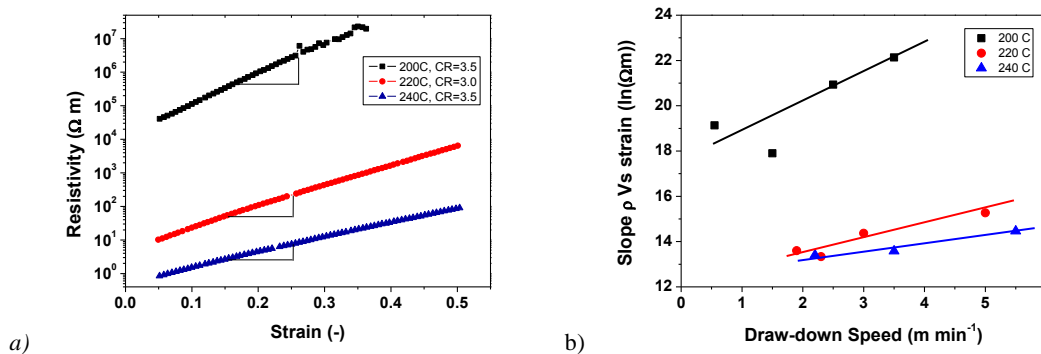
Figure 5. a) Resistivity-strain dependence and b) slopes of the resistivity-strain curves, relative to TPU/3% CNT/1%CB filaments extruded at different temperatures and collected at different draw down speeds.

Interestingly, the slope of these curves (straight lines in a semi-logarithmic plot) varies as a function of both the extruding temperature and draw down speed, as reported in Figure 5.b.

The sensitivity of polymer/CNT composites to strain has been previously reported to be dependent on a number of parameters like CNT loading [32] and CNT alignment [33]. In our case the concentration of CNT is invariant and the change in draw down ratio is insufficient to justify significant differences in particle orientation. Nevertheless the different processing conditions certainly affect the conductive network formed as well as the interparticle distance distribution.

For tunnelling-percolating materials like polymer/CNT composites it has been suggested that if the tunnelling distances are sufficiently widely distributed, this can lead to non-universality (percolation exponent *t* greater than 2 in 3D), which can be intimately related to the sensitivity of the conductive composite upon strain [34]. In particular it has been demonstrated both theoretically and experimentally that the piezo-resistive response becomes logarithmically divergent when the transport is non-universal [34].

In analogy, it is believed that the variation in strain sensitivity experimentally observed in this paper is to be explained by an increased distribution of interparticle distances induced, in the mixed fillers systems, by both extrusion temperature and draw down speed.

4 Conclusions

It was demonstrated that the addition of a secondary nanofiller, independent from its shape and electrical properties, is able to accelerate the dynamic percolation of CNT in a polymeric matrix. This dismisses alternative hypotheses, previously suggested in the literature, on the effect of secondary nanofillers on the electrical properties of polymer/CNT composites, like improved dispersion and improved network connectivity. The rapid network reformation in systems incorporating secondary nanofillers is of particular interest in high-speed polymer processes such as filament extrusion. Effectively, it was shown that the presence of a secondary nanofiller is able to significantly decrease the amount of CNT necessary to guarantee conductivity in extruded polymer filaments, with obvious cost and performance benefits, and at the same time induce strain sensing ability with tuneable sensitivity. These encouraging results suggest the use of ternary CNT-based nanocomposites filaments as promising multifunctional strain sensors for applications like smart textiles.

5 Acknowledgments

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