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Controlling the Dynamic Percolation of Carbon Nanotube based Conductive Polymer Composites by Addition of Secondary Nanofillers: The Effect on Electrical Conductivity and Tuneable Sensing Behaviour†

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

ABSTRACT

In this paper, the electrical properties of ternary nanocomposites based on thermoplastic polyurethane (TPU) and multi-walled carbon nanotubes (MWCNTs) are studied. In particular two nanofillers – differing in shape and electrical properties - are used in conjunction with MWCNTs: 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 MWCNTs 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.

KEYWORDS

A. Polymers; A. Carbon Nanotube; A. Nanoclay; E. Melt-spinning; Dynamic Percolation

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1. Introduction

Carbon nanotubes (CNT) have attracted substantial interest since the 1990s [1], for a combination of outstanding properties, including high mechanical properties [2-5] and high electrical [6] and thermal conductivity [7, 8]. Several application fields like anti-static, electro-static painting, EMI shielding [9] as well as sensing [10-13], flexible electronics [14], field emission [15], transparent and conductive thin films [16-18] and organic thermoelectric materials [19, 20] 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) [21-24]. In fact, according to statistic percolation theory [25], the percolation threshold is inversely proportional to the particle aspect ratio. Percolation thresholds below 0.01 % have been reported for specific systems [22]. 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 [26]. 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- [27-32] and carbon black-loaded [33-35] polymer composites and describes the dynamic process of conductive network formation.

It was previously demonstrated by our group [26] 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 [36-39].

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 [40, 41], ii) Improved dispersion [42, 43] and iii) Improved network connectivity [44, 45].

Bao *et al.* [40] showed that the addition of different inert fillers to a polypropylene (PP)/MWNT composite could significantly lower its electrical resistivity and percolation threshold, which was explained by a volume exclusion effect. The concept of effective concentration of MWNT was introduced (localised higher MWNT concentration) and quantitatively related to the percolation threshold. Unfortunately this approach can only justify the effect of relatively high loadings of secondary inert fillers (20-30 wt.%).

Feller *et al.* [46] studied the effect of montmorillonite (MMT) nanoclays on the electrical and mechanical properties of CPC based on carbon black (CB). Again it was suggested (four years before Bao *et al.* [40]) that the presence of a non-conductive secondary filler (MMT) increased the exclusion volumes of the conductive filler (CB) and therefore their percolation threshold. Moreover it was suggested that CB aggregates could adsorb onto MMT platelets thus modifying both the level of CB dispersion and flow properties.

Konishi *et al.* [47] also studied a polymer/CB/MMT ternary composite. A substantial shift of percolation threshold to lower CB volume fractions was observed in the presence of optimum concentrations of MMT. Organoclay/CB constituted "nano-unite" structures which induced CB network self-assembly within PA6 matrices. MMT behaved effectively as a dispersion control agent in these polymer/carbon systems to induce self-assembly of CB network at low CB content.

Liu *et al.* [43] studied the effect of addition of nanoclays to an epoxy/single-walled carbon nanotube (SWCNT) composite. It was proposed that SWCNT become more exfoliated and better networked in these composites, because of its affinity with nanoclay.

Also *Sumfleth et al.* [42] proposed the same hypothesis. The authors stated that the dispersion of small amounts of MWCNT (0.01 vol.%) could be improved by the addition of titania nanoparticles. This was again attributed to the intrinsic chemical interactions between MWCNT and titania nanoparticles which formed a hybrid structure, characterised by an attachment of titania nanoparticles onto the surface of MWCNTs and their agglomerates. It must be noted that the last two papers worked on a thermoset matrix (epoxy resin). This makes the comparison with other systems non trivial.

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 MWCNT 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 (referred to as Sep or simply as Clay) nanoclays are, respectively, Printex® XE-2 (by Grolman Ltd) and Pangel® (by Tolsa, Spain).

2.2. Samples 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 [26, 29].

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 [10, 26], 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 Discussions

3.1. Morphology: 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). Sepiolite nanoclay shows the typical shape of a rigid needle [48-52] 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.* [43] and Sumfleth *et al.* [42] on the effect of nanoclay (MMT) and titania nanoparticles on the exfoliation of CNT in epoxy matrix.

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

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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 [29], 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.* [47], 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 [26]).

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 [26]. 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) [26, 29].

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.* [47], 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.

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3.3. Manufacture of Conductive and Strain Sensitive 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 [53] 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 [10].

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 [54] and CNT alignment [55]. 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 [56]. In particular it has been demonstrated both theoretically and

experimentally that the piezo-resistive response becomes logarithmically divergent when the

transport is non-universal [56].

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.

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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.

SUPPORTING INFORMATION PARAGRAPH

It can be observed from Figure S1 that the addition of a second filler (CB) increases the overall viscosity of the TPU/CNT nanocomposite. This is particularly obvious when comparing the curves relative to TPU/3%CNT and TPU/3%CNT/1%CB. It was previously demonstrated that the dynamic percolation is a process highly depended and limited by polymer melt viscosity [26]. An increase in viscosity would therefore decelerate the dynamic percolation, contrarily to what is observed (Figure 2).
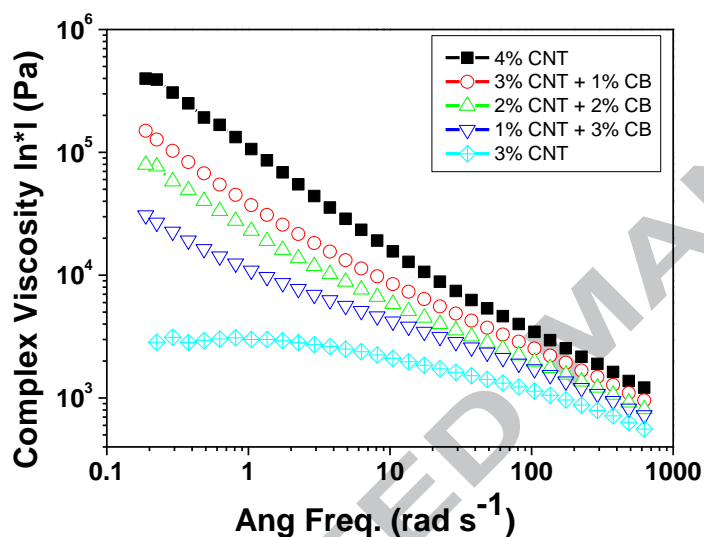

Figure S1. Frequency sweep tests of TPU nanocomposites with different amounts of CNT and CB.
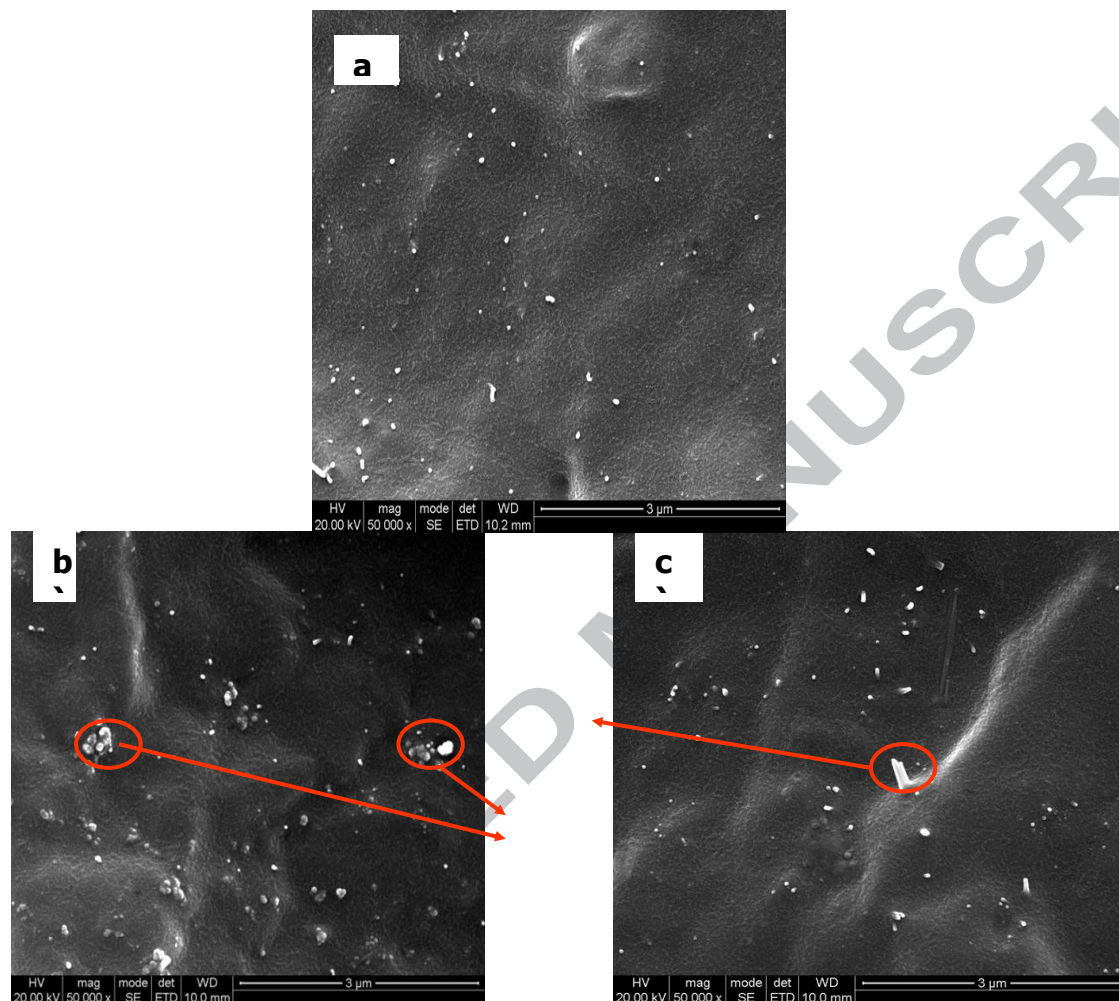
FIGURE CAPTIONS

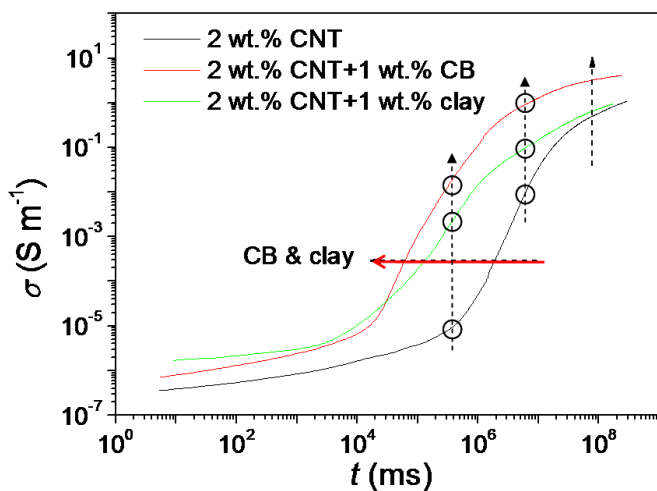**Figure 1.** *SEM micrographs of: a) TPU/4%CNT, b) TPU/3%CNT/1%CB, c) TPU/3%TPU/1%clay.*

Figure 2. *Influence of secondary nanofiller (CB or clay) on the time-dependent conductivity behaviour of TPU/MWNT nanocomposites.*
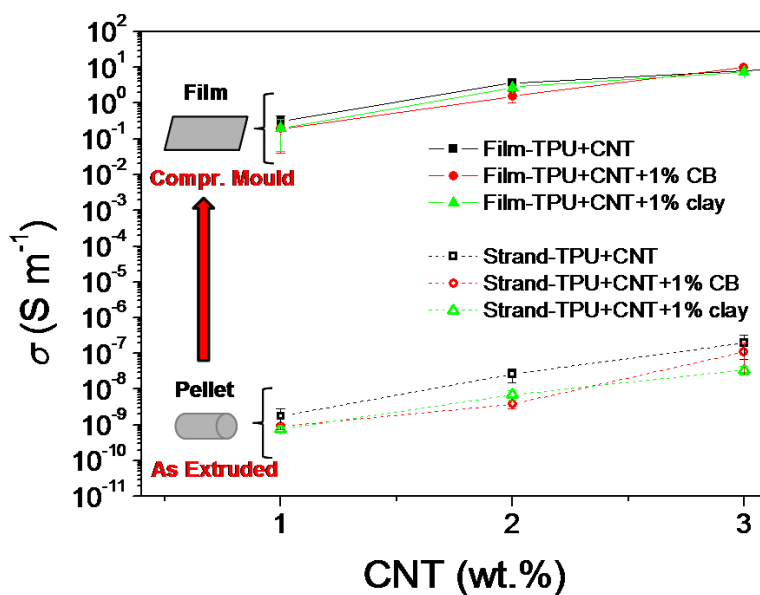
Figure 3. *Conductivity of TPU/CNT composites, with or without second filler (CB or clay), directly after extrusion compounding or as fully annealed films.*
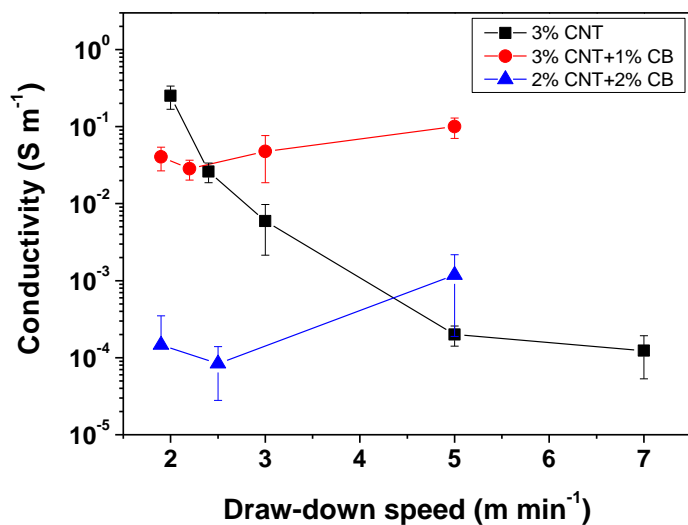
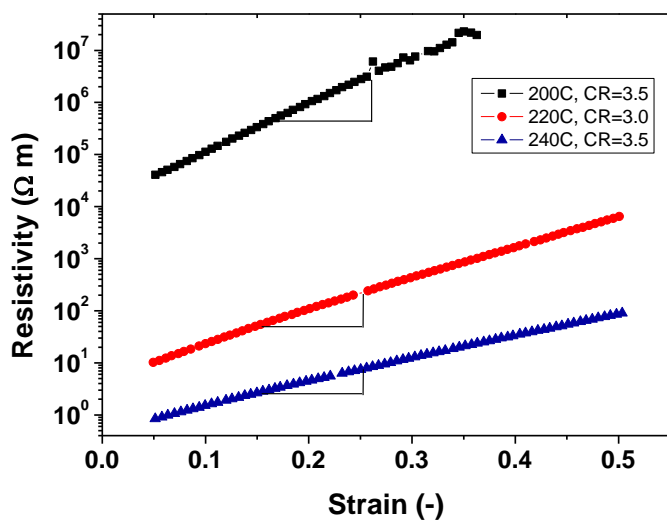**Figure 4**. *Conductivity of TPU/CNT binary and ternary nanocomposites, in the form of extruded filaments, collected at different draw down speeds. The addition of CB prevents the reduction in conductivity with speed.*
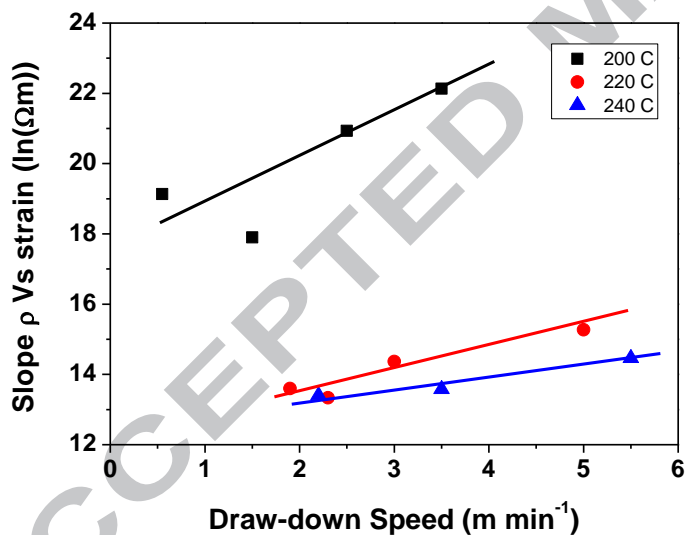
a)

b)

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.

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