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The Effect of Conductive Network on Positive Temperature Coefficient Behaviour in Conductive Polymer Composites

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Abstract

Flexible and controllable self-regulating heating devices with positive temperature coefficient (PTC) behaviour are potentially excellent candidates in applications like healthcare, soft

robotics, artificial skin and wearable electronics. Although extensive studies have been carried out in this field to understand the mechanism of PTC effect, rather limited conclusions have been reached. Many controversies remain on the dominating factors that influence the PTC performance of composites, hence limiting their design and broader applications. Herein, we propose a systematic study to explore the PTC phenomenon and the underlying mechanism, from a conductive network viewpoint, taking account of both conductive fillers and polymer matrices. Three representative conductive fillers with distinct dimensions and shapes (0D silver coated glass sphere, 1D carbon nanotubes and 2D graphene nanoplatelets), in combination with three different polymer matrices (high density polyethylene, thermoplastic polyurethane and polycarbonate) were selected to elucidate the effect of the “robustness” of different conductive networks on PTC behaviour in conductive polymer composites (CPCs). The desired conductive network can be obtained by selecting preferentially larger filler size, lower filler aspect ratio and/or selective distribution of filler (e.g. in the amorphous region of semi-crystalline polymers). The highest PTC intensity was observed around the “critical” percolation threshold, in correspondence of networks with the lowest number of inter-particle contacts. This study can serve as a guideline in the selection of the most appropriate conductive filler and polymer matrix for various self-regulating heating requirements and final applications.

Keywords: Nanocomposites; Pyroresitivity; Positive temperature coefficient; Electrical conductivity; Graphene nanoplatelets; Carbon nanotubes.

Introduction

With the rapid development of functional and intelligent devices, there is an increasing demand for technological progress on new materials and devices, which can respond to external stimuli spontaneously. Benefiting from a large variety of polymer matrices and conductive fillers

available, conductive polymer composites (CPCs) can be easily fabricated with desired properties, fulfilling a broad spectrum of requirements in various applications. By combining different polymer matrices and conductive fillers, not only the electrical and mechanical properties of CPCs can be tuned and tailored to specific target requirements, but other functionalities can also be introduced such as sensitivity to a number of external stimuli including strain [1-3], humidity [4], temperature [5-7], liquid [8] and damage [9-11].

Certain CPCs, in particular, can show a pyroresistive behaviour (“pyro” is a Greek word meaning “fire/heat”), with their electrical resistivity changing with temperature. Pyroresistivity can manifest in two ways: (i) an increase in electrical resistivity with increasing temperature – known as positive temperature coefficient (PTC) effect – and (ii) a decrease in electrical resistivity with increasing temperature – known as negative temperature coefficient (NTC) effect [12, 13]. PTC effect in most cases refers to a switching type transition, where the resistivity of the polymer nanocomposite changes by several orders of magnitude at the critical temperature. The change in resistivity is defined by the PTC intensity, which is quantified as the maximum resistivity (ρ_{max}) over the room temperature resistivity (ρ_{RT}). Although many researchers have dedicated efforts in this field and in studying this physical phenomenon, up until now, the underlying mechanism of the PTC effect is still not well understood [14]. ~~Conflicting explanations have been proposed and systematic and direct supporting evidence for this critical phenomenon is still insufficient.~~

Different hypotheses on the factors dominating the PTC effect have been proposed, based on experimental observations from different systems, some showing evident inconsistencies. For instance, some researchers in early studies found that the polymer crystalline phase change with temperature has a strong influence on the electrical conductivity of CPCs [15, 16]. Luo *et al.* investigated composites based on carbon black (CB) and polymers with different degree of crystallinity; from high to low, high density polyethylene (HDPE), low density polyethylene

(LDPE), LDPE/ethylene-vinyl acetate (EVA) blends and amorphous polymethylmethacrylate (PMMA). The results have showed a correlation between polymer crystallinity and PTC intensity, namely the higher the crystallinity the higher the PTC intensity. Amorphous PMMA/CB composites showed the smallest PTC intensity, usually below one order of magnitude [15]. This finding is in agreement with the work on CB-based polymer composites by Meyer in early 1970s [17]. Thermal volume expansion is phenomenologically one of the leading factors for the polymeric PTC transition, as reported by Yi *et al.* for HDPE/CB systems [18]. In semicrystalline polymers, the change of crystallites to an amorphous melt around the melting temperature leads a step change in volume expansion and an increase in the coefficient of thermal expansion (CTE). No such step change occurs instead in an amorphous polymer. However, although polymer crystallinity has been widely believed to be a dominant factor for the PTC effect, contrasting results have also been reported from literature, in which no correlation between PTC intensity and crystallinity was found [19, 20]. For example, a surprisingly large PTC intensity (five orders of magnitude) has been reported for an amorphous CPC system based on PMMA containing 40 wt.% Ag coated glass beads by Kar *et al.* [21]. The same group reported a three orders of magnitude change in resistance in a nickel coated graphite (40 wt.%) filled polycarbonate (PC). ~~Xiong *et al.* has reported that a CB-filled amorphous polyurethane (PU) can have a PTC intensity of three orders of magnitude by adding reactive low molecular crystals stearic acid as crystalline phase into amorphous polymers [19].~~ Overall, it is understandable and reasonable to believe that although the polymer matrix crystallinity has a significant influence on the PTC effect, other factors such as filler size and topology might also play a role, and in some cases a more dominant one.

Many researchers have revealed that CPCs with larger average filler size exhibit a higher PTC intensity and higher resistivity at room temperature than those systems with smaller filler size at similar filler content, possibly linked to the increase of average interparticle distance with

increasing particle size [22, 23]. The effect of different filler content and the use of a combination of different conductive fillers were shown to have an even more complex influence on the PTC effect [24]. It is believed that the PTC behaviour of conductive composites relies on the “robustness” of the conductive network formed within the polymer matrix [25, 26]. Therefore, the conductive network in the CPCs can be considered the real dominating factor that influences the PTC effect, containing effects from both filler and matrix. Unfortunately, to date, a comprehensive study of the effect of the matrix, the filler and its formed conductive network on the PTC effect is still lacking.

Herein, an investigation into the understanding of how the conductive network affects the PTC behaviour has been performed. The contributions and influences of different types of filler and polymer matrix on the PTC performance are considered, exploring effects arising from the use of conductive fillers with different shapes and dimensions as well as different polymer matrices. Three classes of conductive fillers with distinct dimensional features have been employed in this work, ranging from spherical zero-dimensional (0D) silver coated glass spheres (AgS), 1-dimensional (1D) carbon nanotubes (CNT), and 2-dimensional (2D) graphite nanoplates (GNP) [27]. The motivation behind this selection is to explore the influence of dimensionality of the fillers on the electrical properties of the composites, the different conductive networks formed and their subsequent pyroresistive behaviour. In addition, three representative polymer matrices with distinct structure and properties have been selected: high density polyethylene (HDPE), thermoplastic polyurethane (TPU) and polycarbonate (PC). HDPE is a typical semicrystalline polymer widely used for PTC materials, while TPU is a thermoplastic elastomer for flexible applications, with the presence of hard blocks, acting as physical crosslinks upon crystallisation. PC is a typical amorphous engineering polymer with outstanding strength, and impact resistance. With this systematic and comprehensive study, the factors that affect the pyroresistive (both PTC and NTC) behaviours as well as their underlying

mechanisms are explored, providing a material selection guideline for self-regulating heating applications in the fields like healthcare, robotics, and smart heater.

Experimental

Materials

The materials used in this study are listed in Table 1. All the polymers are in the form of pellets and dried overnight at 80 °C before compounding.

Table 1. Information on polymers and conductive fillers used in this study.

	Materials	Trade name	Information
Polymer	Thermoplastic polyurethane (TPU)	Lubrizol Estane® 58437	Density 1.19 g/cm ³
	High density polyethylene (HDPE)	Rigidex® HD5218EA	Density 0.95 g/cm ³
	Polycarbonate (PC)	Bayer Material Science Makrolon 2805	Density 1.20 g/cm ³
Conductive filler	Multi-wall carbon nanotubes (MWCNTs)	Nanocyl® NC7000™	Average diameter of 9.5 nm, carbon purity 90% [28]
	Silver coated glass spheres (AgS)	Potters Industries Ltd.	Average diameter of 2.5 µm, 50 µm, 100 µm with the density of around 3.6, 2.6 and 2.5 g/cm ³ , respectively
	Graphite nanoplates (GNPs)	xGnP® Grade M	Average particle diameters of 15 µm, density 2.2 g/cm ³ , carbon content >99.5%

Fabrication of composites

A Collin Lab twin-screw compounder P (ZK25, 25mm, L/D=40) was used to produce masterbatches of TPU with 5 wt.% CNT and of HDPE with 24 wt.% GNP. Extruder throughput was 2 kg/h using a screw speed of 50 rpm and 220 rpm for CNT and GNP, respectively, with a temperature profile ranging from 190 °C to 240 °C, over 8 heating zones [29]. Apart from the masterbatches, the remaining compounds and diluted composites from the masterbatches were prepared by melt mixing using a DSM X'plore MC 15 micro-compounder (Netherland).

Both HDPE and TPU based composites were melt compounded at 200 °C using a screw speed of 50 rpm for 5 min in nitrogen atmospheres, while PC based composites were processed at a temperature of 280 °C. The composites prepared in this study are listed in Table 2. The extruded strands were chopped into pellets and subsequently compression moulded into rectangular shaped samples with dimensions of 30 × 10 × 2 mm, using a Collin hot press P300E, at 220 °C for 5 min under 60 bar pressure. Two pieces of copper mesh (0.16 mm aperture wire diameter) were embedded at mid-depth and on both sides of each specimen during compression moulding and used as the electrodes for all electrical characterisations.

Table 2 List of composite systems.

HDPE based composites	TPU based composites	PC based composites
HDPE/AgS (2.5 µm, 50 µm, and 100 µm)	TPU/AgS (2.5 µm, 50 µm, and 100 µm)	PC/AgS (2.5 µm, 50 µm, and 100 µm)
HDPE/GNP	TPU/GNP	-
HDPE/CNT	TPU/CNT	-

Characterisation

Scanning electron microscopy (FEI Inspector-F, Netherlands) was used to observe the morphology of as-received materials, as well as the fabricated conductive composite specimens. Filler size distributions of as-received silver coated glass spheres were characterised by SEM imaging, after having deposited the spheres on a conductive substrate (SI Figure 1, see Supporting Information). All the morphologies of CPCs in this research were observed on cryo-fractured surfaces, which were induced by immersing the specimens into liquid nitrogen for 10 min before fracture to expose the internal microstructure. All the surfaces analysed were gold sputtered before imaging. The images were taken at different magnifications with an accelerating voltage of 20 kV.

Thermal analysis of the samples was performed using differential scanning calorimetry (DSC) (DSC4000, PerkinElmer, Massachusetts, USA). All samples were heated from 20 °C to 200 °C at 10 °C/min under nitrogen atmosphere and then cooled back to room temperature (RT) at the same rate, for two heating cycles. The second heating curve was used in examining the melting behaviour of the composite to eliminate differences in thermal history.

Dynamic mechanical analysis (DMA) was performed on a TA Instruments DMA Q800 machine (USA), equipped with a fixture for three-point bending. A frequency of 1 Hz, a strain of 1 % and a heating rate of 3 °C/min, between -150 °C to 100 °C, were chosen for these tests. The samples were compression moulded into rectangular bars with the dimensions of 30 × 10 × 2 mm.

Electrical resistance was measured by the two-point probe technique and used to calculate the electrical resistivity, obtained using a picoammeter (Keithley 6485, USA) and a DC voltage source (Agilent HP 6614C, USA). As the electrodes are embedded into the compression moulded CPC, the contact resistance between the materials and electrodes are consistent and relatively low.

The pyroresistive behaviour of all samples was tested with an apparatus consisting of a temperature-controlled oven (heating rate of 2 °C/min) and an *in-situ* two-point resistance measurement unit, obtained by combining a picoammeter (Keithley 6485, USA) with a DC voltage source (Agilent HP 6614C, USA). A thermocouple was placed close to, but not touching, the specimen to ensure reliable temperature reading. A constant voltage (1 V) was applied during heating and cooling cycles on the rectangular samples (30 × 10 × 2 mm), while the current and temperature were monitored and recorded simultaneously. Since the size difference induced by thermal expansion of the matrix during heating is very small compared to the sample dimension, it has been neglected from the electrical resistivity calculation.

Voltage was applied with 1 second on/off intervals, to avoid electric field-induced filler alignment and network alteration. A minimum of three samples was tested for all characterisations.

Results and discussion

Morphology

It is essential to investigate the microstructure of the composites in order to obtain a better understanding of the conductive networks formed within the polymer matrices and their influence on the electrical and pyroresistive properties of CPCs. Figure 1a-e shows the micrographs of as-received fillers of different size (AgS 2.5 μm , 50 μm , and 100 μm) and shape (AgS as spherical 0D filler, CNT as 1D filler and GNP as 2D filler). The size distributions of AgS are summarised in Supporting Information (SI Figure 1).

Figure 1. SEM micrographs of conductive fillers: (a) 2.5 μm AgS; (b) 50 μm AgS; (c) 100 μm AgS; (d) GNP, and transmission electron microscopy (TEM) image of (e) CNT [28].

In order to understand the effect of filler size on the microstructure of the composite and any preferential distribution of conductive fillers within the matrix, AgS fillers with distinctly different diameters (2.5 μm , 50 μm , and 100 μm) were selected. Figure 2 shows images of PC based composites containing 2.5 μm , 50 μm , and 100 μm AgS, respectively. The dispersion of up to 30 wt%/12.5 vol.% (above percolation) of 2.5 μm AgS dispersed in PC matrix is generally rather uniform (Figure 2b), with the exception of some more concentrated regions (red circles in Figure 2a). Figure 2c-d show the morphologies of PC composites containing 40 wt%/24.2 vol.% loading 50 μm AgS (above percolation) and 40 wt%/24.2 vol.% loading (below percolation) of 100 μm AgS, respectively. It is worth noting that, for the same filler concentration in a given volume of composite, smaller sized fillers (i.e. 50 μm) are present in larger numbers compared to larger fillers (i.e. 100 μm). This also implies that smaller (spherical)

fillers present a higher specific surface area, with more potential contact points (or points close enough for tunnelling) between fillers to form conductive pathways (Figure 2c), as compared to larger spherical fillers (Figure 2d). This difference in the number of contact points is believed to have a significant impact on the electrical properties of the CPCs.

Figure 2. SEM images of cold-fractured cross-sectional areas of PC based composites containing 30 wt.% (above percolation) of 2.5 μm AgS, at a magnification of (a) 500x and (b) 2000x; (c) 40 wt.% (above percolation) of 50 μm AgS, showing several contact points between fillers; and (d) 40 wt.% (below percolation) of 100 μm AgS, without obvious contact points between fillers.

As mentioned earlier, filler shape can also greatly affect the conductive network and hence the subsequent PTC behaviour of the composite. The effect of filler shape has been explored with representative fillers (distinct aspect ratio) from 0D to 2D in TPU matrix: 40 wt. % of AgS as 0D filler (50 μm), 15 wt.% of GNP as 2D filler and 3 wt.% of CNT as 1D filler, respectively, as shown in Figure 3a-c. The filler loading was chosen based on the respective percolation threshold: 40 wt.% for AgS, 15 wt.% for GNP and 3 wt.% for CNT, which are all just above each of their corresponding percolation thresholds in TPU matrix (percolation thresholds have been presented in Figure 5 and SI Figure 3). SEM images reveal that the number of contact points between the AgS fillers is rather limited (Figure 3a), compared to GNPs where a larger number of contact points and a more easily formed percolated network can be expected (Figure 3b). This difference between 0D AgS and 2D GNPs is believed to be due to their different aspect ratios, where a higher aspect ratio is generally desired for electrical conductivities as the percolation threshold is lower. Figure 3c shows a rather uniform dispersion within the TPU matrix, consistent with our previous findings [30]. The shape, size and high aspect ratio of CNTs allow the formation of an even more robust network, with a larger number of contact points at a relatively low volume fraction [16].

Figure 3. SEM images of the cold-fractured cross-sectional area of TPU based composites containing (a) 40 wt. % of AgS as 0D filler (50 μm); (b) 15 wt.% of GNP as 2D filler; (c) 3 wt.% of CNT as 1D filler, ~~showing a clear positive relationship between the number of contact points and filler aspect ratios;~~ (d) unfilled TPU as reference.

Apart from the influence of filler size and shape on the conductive network formed, the effect of the polymer matrix has also been explored. Figure 4 shows SEM images of HDPE, TPU and PC composites containing the same amount of 50 μm AgS. HDPE shows the worst interfacial bonding between filler and matrix while TPU shows the best. This finding is believed to be due to a combined effect of several intrinsic polymer properties, including wetting and surface tension (PC>TPU>HDPE) [31], ductility of the polymer matrix (TPU>HDPE>PC) and thermal

contraction coefficient upon cooling (HDPE>PC) [32]. There is no significant difference in filler distribution between the three polymer matrices, although the AgS in TPU and PC are slightly more homogeneously distributed than in HDPE. In HDPE composites, some polymer rich areas can be found, which are believed to be associate with the semicrystalline and apolar nature of the polymer generating inhomogeneity in filler dispersion [15, 33]. The location of the spheres as well as cavities (left after debonding of the AgS particle) are all marked with coloured circles to highlight the distribution of the AgS within the polymer matrix.

Figure 4. SEM images of cold-fractured cross-sectional areas of 40 wt.% of 50 μm AgS filled (a) HPDE; (b) TPU; and (c) PC. The coloured circles indicate the locations of the AgS particles in the polymer matrix.

Although no distinct difference in conductive filler networks was observed for this 50 μm AgS filled HPDE, TPU, PC matrices, due to the large size of the filler, it is expected that the nature of the host polymer can in general play an important role in the PTC effect. Therefore, the

intrinsic polymer properties have been characterised and analysed here. The variation of storage modulus of the polymer matrix with temperature is one of the potentially important physical properties (see SI Figure 2a-b). The degree of crystallinity is another one. The relatively high crystalline content of HDPE (about 57% crystalline phase melting at a T_m of around 130 °C) is expected to result in the selective distribution of filler in the amorphous phase only. On the contrary, TPU and PC are two amorphous polymers (see in SI Figure 2c). The characterisation on the main physical properties of the polymer matrices is important as it establishes a baseline for better understanding the PTC behaviour.

Electrical and pyroresistive properties of AgS particles of different sizes in HDPE, TPU and PC

Figure 5a-c show the electrical conductivity of HDPE, TPU, PC composites containing AgS (2.5 μm , 50 μm and 100 μm), as a function of filler content. All the percolation curves show a very sharp “on-off” behaviour, going from a not measurable value of electrical conductivity to a maximum plateau above a specific AgS filler loading. This is in accordance with studies by Ambrosetti *et al*, who observed that a sharp cut-off applies to CPCs made of large conducting particles [34].

Figure 5d summaries the percolation threshold values of each composite system. It shows a clear increasing trend of percolation threshold values with increasing AgS filler dimensions, which is attributed to the decrease of their specific surface areas, as suggested by many researchers [35, 36]. Clearly, with a smaller filler dimension, a higher surface area and hence a larger number of connecting pathways can be expected, resulting in a more “robust” conductive network compared to fillers with the same loading but larger dimensions. The obtained percolation thresholds of HDPE/AgS composites with 2.5 μm , 50 μm and 100 μm filler dimension are 5.5 vol.%, 16.9 vol.% and 18.9 vol.%, respectively. A similar trend is

observed in TPU/AgS and PC/AgS composites, where filler dimensions of 2.5 μm , 50 μm and 100 μm give the percolation thresholds of 9.9 vol.%, 24.0 vol.% and 28.0 vol.% for TPU and 12.5 vol.%, 24.2 vol.% and 28.2 vol.%, respectively. These findings are consistent with earlier morphological observations, where a higher number of contact points between fillers was observed for smaller sized filler.

Regarding the three different polymer matrices, it can be noted that HDPE has the lowest percolation thresholds. This is believed to be due to their semicrystalline nature, which leads to high effective concentration of filler in the amorphous phase (consequence of exclusion from the crystalline phase), and hence a lower overall percolation threshold. For instance, the 2.5 μm AgS filled HDPE composites show a percolation threshold of around 5.5 vol.%, which is approximately half the percolation threshold of TPU and PC (around 9.9 and 12.5 vol.%). This is in agreement with the amount of crystalline phase in HDPE, which is 57.5 % calculated from DSC measurement (see SI Figure 2c). For larger fillers dimensions (50 μm , 100 μm), which are much larger than the size of the crystalline domains, considerably lower percolation thresholds were observed in semi-crystalline HDPE than the other amorphous systems, although this was not as obvious as for the 2.5 μm filler system.

Figure 5. Electrical percolation curves of HDPE, TPU, and PC filled with (a) 2.5 μm AgS; (b) 50 μm AgS; (c) 100 μm AgS; and (d) percolation threshold values (in volume fraction) of the three types of composites, error bars indicate the possible range of percolation threshold. The shaded area indicates the non-measurable electrical conductivity range.

To examine the pyroresistive behaviour of AgS (2.5 μm , 50 μm and 100 μm) filled HDPE, TPU and PC composites, the electrical resistivity of the composites was monitored as a function of temperature (Figure 6). The effect of both polymer matrix and filler size on the observed pyroresistive behaviour have been studied, in order to establish a systematic understanding of their influence on PTC behaviour. Figure 6a-c compares the effect of different polymer matrices with the same filler, while Figure 6d-f compares the effect of varying filler sizes in the same polymer matrix.

As shown in Figure 6a, AgS (2.5 μm) based composites exhibit a relatively small PTC intensity, regardless of the polymer matrix. Among the three composites, HDPE/2.5 μm AgS (25 wt.%) shows the highest PTC intensity (about two orders of magnitude), more than one order of magnitude higher than for TPU and PC based AgS (2.5 μm) composites. This difference is attributed to polymer crystallinity and the greater thermal expansion associated with the melting of the crystal phase. However, as known from the morphological study, small-sized AgS (2.5 μm) with a larger number of contact points build more robust conductive networks, which are more difficult to disrupt under the effect of the matrix thermal expansion. This explains, phenomenologically, why the PTC intensity of HDPE/AgS (2.5 μm) composite is much lower than the PTC intensity of HDPE composites containing larger AgS spheres (50, 100 μm). The same is true for the other polymer matrices. All the 50 μm and 100 μm AgS based composites, independently on the polymer matrix (HDPE, TPU, and PC), show a very high PTC intensity, of about eight orders of magnitude (Figure 6b and c). It is suggested that spherical conductive fillers of large size can induce a high PTC intensity as the number of conductive filler contact points is limited, which makes the conductive network more sensitive to perturbations, regardless of the polymer matrix. This is consistent with previous studies by our group and the concept of “robustness” of the conductive filler network [25]. The smaller the filler size, the more “robust” the conductive network is, as the number of specific conductive pathways increases, and the more difficult it is for the conductive network to be disrupted. However, the PTC intensity is not a monotonic function of filler size. In fact, the PTC behaviour of composites based on the 50 μm and 100 μm AgS is very similar.

For what concerns the switching temperature, it can be observed that this is associated with a main phase transition of the polymer matrix (melting, softening, and/or glass transition temperature). For examples, the switching temperature of HDPE based composites shows a switching temperature around 130 $^{\circ}\text{C}$, which is in the proximity of the melting temperature of

HDPE (129.8 °C from the DSC curve). The switching temperature of TPU based composites corresponds to the Vicat softening temperature of TPU (90 - 100°C) [37]. While the switching temperature of PC based composites is above 140 °C, close to the glass transition temperature of PC. The switching temperature of amorphous polymer-based systems seems slightly higher than the corresponding polymer phase transition temperature. This is believed to be related to the absence of a step change in specific volume, with only a slope change in TEC with temperature at around T_g . Overall, all the composites based on 50 µm and 100 µm AgS are attractive pyroresistive materials and exploitable in self-regulating heating devices.

With the aim of having a tailored performance to suit various applications, the three different polymer matrices (HDPE, TPU and PC) can be considered as model systems with distinct switching temperatures and mechanical properties, which can be used to tailor the performance of the device to suit various applications.

Figure 6. The pyroresistive behaviour of HDPE, TPU and PC filled with (a) 2.5 μm AgS (25 wt.%, 30 wt.% and 35 wt.%); (b) 50 μm AgS (50 wt.%); and (c) 100 μm AgS (50 wt.%).

Pyroresistive behaviour of 2.5 μm , 50 μm and 100 μm AgS filled composites in the matrix of (d) HDPE, (e) TPU and (f) PC.

Electrical and pyroresistive properties of GNP and CNT in HDPE and TPU

Apart from 0D AgS, the other two fillers, 1D CNTs and 2D GNPs, are also investigated in order to examine the effect of filler shape on pyroresistive behaviour.

As expected, much lower percolation thresholds were found for HDPE composites containing GNPs and CNTs, with values of 8.8 wt.% (4.0 vol.%) and 1.67 wt.% (1.0 vol.%) for these two fillers, respectively (see SI Figure 2), due to their much larger aspect ratios as compared to 0D AgS micro-sized fillers. It is worth noting that dispersed GNPs are not necessarily completely rigid and flat when dispersed in a polymer matrix, while they are prone to folding and wrinkling during the melt compounding in addition to breaking (probably the main effect) [38], which reduces its effective aspect ratio and in turn affects the percolation threshold. This morphological feature of GNPs also has a significant impact on their formed conductive networks, and the subsequent pyroresistive properties of the corresponding composites.

The pyroresistive behaviour of both HDPE/GNP composites and HDPE/CNT composites are shown in Figure 7a-b, with three different filler concentrations for both systems to understand better the effect of the conductive network on their PTC behaviours.

HDPE/GNP composites (Figure 7a) at filler loadings of 18, 22, and 24 wt.% show a similar trend of pyroresistive properties, with an increase of resistivity at around 130 °C for all three loadings. With decreasing GNP filler content, both the initial resistivity and the PTC intensity of the HDPE/GNP composites increase due to their less “robust” conductive network. This is consistent with previous findings where a lower number of contact points can lead to a higher

PTC intensity due to an easier disruption of conductive pathways. Although the composites can exhibit a higher PTC intensity value at lower filler content, the subsequent NTC effect also becomes more apparent. The hypothesis here is that the increased inter-particle spacing, as a consequence of reduced filler content, allows GNP particles to exhibit more mobility in order to re-agglomerate at higher temperatures [39-41].

Conversely, CNT/HDPE composites show only a minimal gradual increase in resistivity upon heating for all filler loadings, due to the difficulty in breaking down the “robust” conductive networks formed by high aspect ratio 1D CNTs. Among all three CNT loadings, the lowest filler content (2 wt.% CNT) displays a relatively high initial resistance and a more pronounced NTC effect, due to a re-establishment of the conductive network upon heating [40, 42].

A considerable variation of PTC intensity has been observed for different filler shapes, ranging from eight orders of magnitudes, two orders of magnitude, to less than one order of magnitude, for AgS (50 μ m), GNP and CNT in HDPE composites, respectively (Figure 7c). This finding can be explained from the viewpoint of how the conductive network (or contact points between fillers) behave upon heating. Comparing the conductive network for 0D, 1D, and 2D fillers, it can be concluded that 0D AgS has the least number of contact points due to their lowest specific surface area. On the other hand, 1D nanotubes, exhibiting the highest aspect ratio and largest surface areas, can form robust, entangled and interconnected networks, leading to a large number of contact points which are the least likely to be separated by thermal expansion of the polymer matrix. 2D GNPs present an intermediate case in terms of both aspect ratio and number of contact points but without the possibility of entanglements, forming a network that is partially affected by the temperature approaching the PTC switch point with a trace of associated NTC behaviour. A similar trend was found in amorphous TPU, with a reduced PTC intensity or even a predominant NTC effect alongside an increasing number of contact points

between conductive fillers, i.e. a more robust and interconnected network when moving from 0D to 1D fillers (see SI Figure 3).

Figure 7. The pyroresistive behaviour of (a) HDPE/GNP composites (18, 22, and 24 wt.%); (b) HDPE/CNT composites (2, 3 and 5 wt.%). (c) A comparison between the effect of 0D, 1D, and 2D filler conductive networks on the pyroresistive behaviour of HDPE/AgS (50 μm), HDPE/GNP and HDPE/CNT composites.

Conclusions

A systematic study into the effect of different conductive networks on pyroresistive performance of polymer composites has been reported. Three representative conductive fillers

with distinct dimensions and shapes, in combination with three different polymer matrices were selected to form different conductive networks. A more “robust” filler conductive network results in a reduced disruption from the thermal expansion of the polymer matrix and a less pronounced (or absent) PTC effect. These “robust” filler networks can be the consequence of smaller filler size, higher aspect ratio and/or distribution of filler (due to intrinsic polymer properties such as crystallinity). Similar to the well-known percolation theory, which implies that electrical resistivity changes the most at filler loadings around the percolation threshold, the highest PTC intensity was also observed around the “critical” percolation threshold with conductive pathways established with a minimum number of contacts. Excessive “contact” points together with highly inter-connected or entangled networks as in the case of CNTs can result in no PTC or even a NTC effect upon temperature increase. This systematic study can be instrumental in providing a better understanding of the effect of the conductive network on pyroresistive behaviour of CPCs as well as the selection of the most appropriate conductive filler and polymer matrix for various applications requiring temperature and current self-regulation.

Conflicts of interest

The authors declare no conflict of interest.

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