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Effect of particle size and shape on positive temperature coefficient (PTC) of conductive polymer composites (CPC) — a model study

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ABSTRACT

More than four decades since the discovery of the positive temperature coefficient (PTC) effect in conductive polymer composites (CPC), many fundamental aspects related to this phenomenon are still poorly understood, though there is consensus on the important contribution of the mismatch of the thermal expansion coefficients of the polymer matrix and filler. The aim of this paper is to study a model system able to explain the PTC effect and more in particular the effect of the filler size and shape on the PTC intensity of a CPC. Silver coated glass particles (spheres and flakes) are used as model conductive fillers due to the ease in controlling uniform size and shape. For the first time in a controlled system it is demonstrated that the PTC intensity increases with increasing filler size and with decreasing filler content, both for spherical and platelet-like conductive fillers.

1. Introduction

With the increase of functionality and 'smartness' of electronic consumer products, there is an urgent need for technological progress in fields like wearable electronics, flexible displays and sensors, which require new materials and devices able to respond, possibly autonomously, to a number of stimuli. Conductive polymer composites (CPC) promise to address some of the above challenges, as they have already demonstrated capability in sensing strain [1], liquids and gases [2,3], damage [4–6] and even degradation [7]. CPCs can also show interesting pyroresistive behaviour with large positive temperature coefficient (PTC) effects, as demonstrated since the 1970s [8], which have found applications in self-regulative heaters and over-current protectors [9–11].

Different theories have been proposed for the origin of the PTC effect, all somehow addressing the mismatch of the thermal expansion coefficients of polymer matrix and filler but from different perspectives; in terms of percolation behaviour [12], void formation [13] interfacial polarisation [14], tunnelling current [15,16], or potential tunnel barrier height [17]. Nevertheless, none of the above concepts are able to fully explain the PTC effect, indicating there is still a lack of understanding after more than four decades. We believe this is partially caused by the fact that often too complicated systems have been studied, including polymer blends [18–22], segregated phases and networks [23–29], fillers of non-uniform size and shape, aggregates, mixed fillers [30–34] and chemical and physical crosslinking [35,36], which might hinder cause-effect relationships. Moreover it is widely recognised that the PTC effect is affected in a complicated manner by many factors like the nature of the polymer matrix, the conductive filler as well as processing, among others [24,37].

The aim of this paper is to propose and study a model system able to unravel some of the complicated relationships and ultimately able to better explain the PTC effect in terms of structure-property relationships. In particular, the effect of the size and shape of a model conductive filler on the PTC effect of a polymer composite will be studied.

The relationship between size and shape of a conductive particle and its percolation threshold in a polymer is well understood in terms of percolation theories [15,16,38]. Still unclear is the relationship between particle size and shape and PTC effect even though many different conductive particles have been studied [3,17–20]. Luo and Wong [37] have suggested that PTC intensity increases with particle size. Unfortunately the conductive particles studied in this paper were five different grades of carbon blacks (CB) of unknown size, shape and their distributions. CB is a complicated filler to study and draw conclusion from since it exhibits rather complex and inhomogeneous shapes and structures, both at the particle level and the aggregate level [37].

In this study silver coated glass particles (spheres and flakes) are used as model conductive fillers due to the ease in controlling size and

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shape. This offers for the first time the possibility to establish a deterministic relationship between the size and shape of a relatively uniform conductive filler in a polymer composite and its PTC intensity.

2. Experimental

The high density polyethylene (HDPE) (MF1: 18 g/10 min 2.16 kg load, density: 952 kg/m^3) used in this study was the grade Rigidex HD5218EA from Ineos. Silver coated glass flakes (AgF) of different sizes were procured from Glassflake Ltd. (20 μm and 100 μm) or kindly donated by Nippon Glass Flakes (NGF) Europe (5 μm). Three different sizes of silver coated spherical glass spheres (AgS) were supplied by Potters Industries Ltd.

The composites were prepared via a melt compounding process using a DSM Xplore 15 mini twin-screws extruder with screw speed of 50 rpm, processing temperature of 170 °C and a residing time of 15 min. The extruded strands were pelletised and compression moulded into rectangular shaped bars (25 mm × 4 mm × 2 mm) using a Collin P300E hot press at 200 °C and 60 bar for 5 min. Brass electrodes were attached to the ends of the sample, after application of silver paste, in order to reduce contact resistance between the electrodes and the sample.

Particle size distribution of the conductive particles was characterised, before and after melt compounding, using an optical light microscope. To estimate the particles size after melt compounding, particles were isolated from the composites by at least three cycles of dissolution in xylene (at 90 °C) and centrifuging/filtering.

The morphology of the samples was studied by a FEI Inspect-F scanning electron microscope (SEM) after fracturing it in liquid nitrogen.

Positive temperature coefficient (PTC) effect of the samples was studied by measuring electrical resistance while the sample was subjected to a certain temperature ramp, when placed onto a mini hot-stage as the resistivity/temperature experiments in [1]. Electrical resistivity was measured by a simple two-point measurement using a combination of a picoameter (Keithley 6485) and a DC voltage source (Agilent 6614C). A minimum of three samples were tested and the average PTC intensities and standard deviations reported.

3. Results and discussion

3.1. Particle size distribution

The distribution of diameters of silver coated glass sphere AgS$_M$ is shown in Fig. 1. The distribution is relatively narrow, with most of the particle diameters between 40 μm and 60 μm and a D50 of 48 μm, in agreement with data sheet values from manufacturer. The measured values for all the conductive particles are reported in Table 1. The D50 value measured for the silver coated glass sphere particles were comparable to the average particle size given by the manufacturers. No major damage of the spheres was observed after melt compounding, thanks to the mild compounding process.

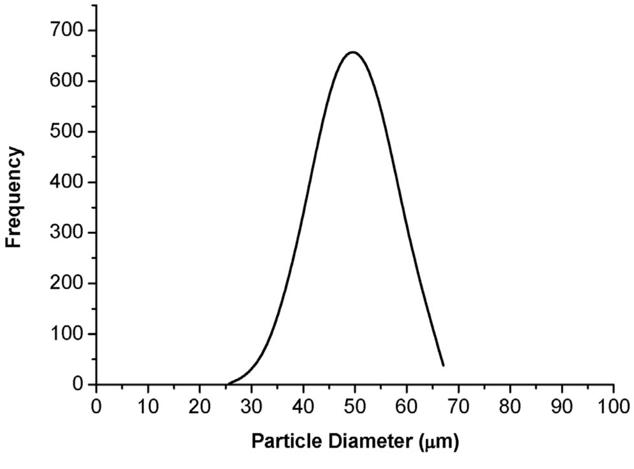

Fig. 1. Size distribution (diameter) for silver coated glass sphere (AgS$_M$).

Table 1
Diameters of the three silver coated glass spheres.

Particle	D10 (μm)		D50 (μm)		D90 (μm)	
	Supplier	Measured	Supplier	Measured	Supplier	Measured
AgS$_S$	N/A	5	8	9	N/A	13
AgS$_M$	N/A	40	50	48	N/A	56
AgS$_L$	N/A	80	100	87	N/A	95

Silver coated glass flakes were instead, as expected, more sensitive to melt compounding. Fig. 2 shows the particle size distribution before and after compounding for the large flakes (AgF$_L$). The bigger the flakes experienced the larger the extent of damage; the D50 of AgF$_L$ is reduced by approximately 50% (Table 2). Interestingly, though, the size distribution curve becomes narrower, leading to a more uniform flake size (Fig. 2).

3.2. Morphology

Fig. 3. a shows the SEM image of high density polyethylene (HDPE) filled with AgF$_L$. The orientation of the silver coated glass flakes (as for all the different sized particles) in the polymer matrix was observed to be random. No damage to the silver coating was observed on the lateral surfaces of the flakes even though the size was reduced after melt compounding (Table 2). Dispersion of silver coated glass spheres in HDPE is shown in Fig. 3.b. Only minor damage to the silver coating on the glass spheres was observed after cold fracture. A poor interfacial interaction was noticed for all composites, with clear signs of failure at the interface and debonding (void formation).

3.3. Electrical properties

Fig. 4 shows the electrical percolation curves of composites containing each of the six conductive fillers. As expected, all the prepared composites showed a similar trend of an increase in electrical conductivity

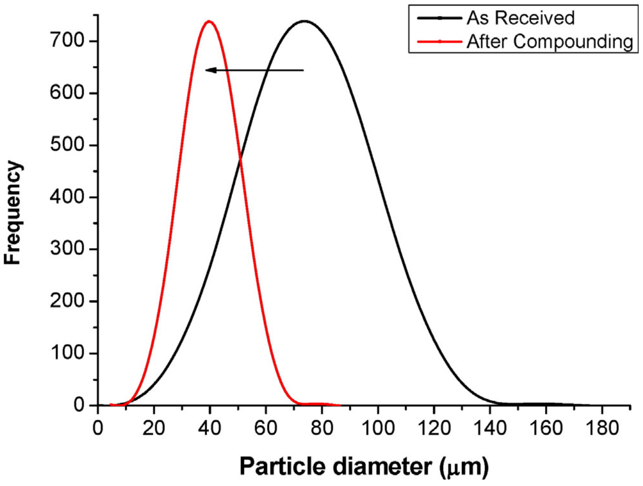

Fig. 2. Particle size (lateral dimension) distribution of AgF$_L$ before and after compounding. The average size decreases but the distribution curve becomes narrower.