Effect of processing conditions on the thermal and electrical conductivity of poly (butylene terephthalate) nanocomposites prepared via ring-opening polymerization

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HIGHLIGHTS

- Thermally conductive pCBT nanocomposites are prepared by ring-opening polymerization.
- Careful optimization of processing parameters is mandatory for the preparation of highly conductive nanocomposites.
- Gentle processing conditions are required to obtain high conductivity values.
- Heat and charge transport performance are correlated with GNP dispersion and fragmentation.

GRAPHICAL ABSTRACT
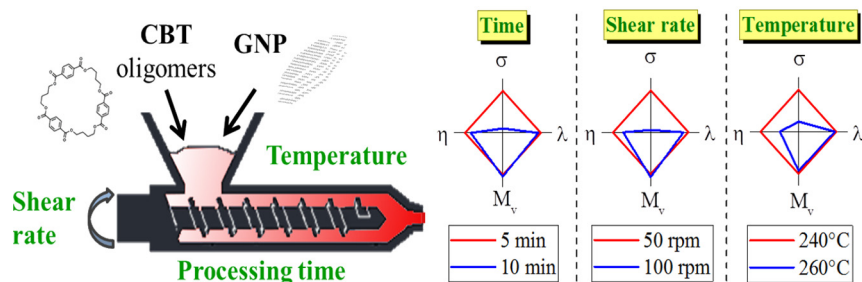
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ABSTRACT

Successful preparation of polymer nanocomposites, exploiting graphene-related materials, via melt mixing technology requires precise design, optimization and control of processing. In the present work, the effect of different processing parameters during the preparation of poly (butylene terephthalate) nanocomposites, through ring-opening polymerization of cyclic butylene terephthalate in presence of graphite nanoplatelets (GNP), was thoroughly addressed. Processing temperature (240 °C or 260 °C), extrusion time (5 or 10 min) and shear rate (50 or 100 rpm) were varied by means of a full factorial design of experiment approach, leading to the preparation of polybutylene terephthalate/GNP nanocomposite in 8 different processing conditions. Morphology and quality of GNP were investigated by means of electron microscopy, X-ray photoelectron spectroscopy, thermogravimetry and Raman spectroscopy. Molecular weight of the polymer matrix in nanocomposites and nanoflake dispersion were experimentally determined as a function of the different processing conditions. The effect of transformation parameters on electrical and thermal properties was studied by means of electrical and thermal conductivity measurement. Heat and charge transport performance evidenced a clear correlation with the dispersion and fragmentation of the GNP nanoflakes; in particular, gentle processing conditions (low shear rate, short mixing time) turned out to be the most favourable condition to obtain high conductivity values.

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1. Introduction

The growing demand for the substitution of metals in those applications where heat exchange coupled with corrosion resistance, ease of process and low cost are required, pushed research on polymer composites and nanocomposites [1–5]. Here, the addition of proper fillers leads to the obtainment of thermally conductive materials, despite pristine polymers behave as heat insulators. Fillers to be used for this application include graphite, carbon fibers (CF), carbon nanotubes (CNT), graphene-related materials (GRM), hexagonal boron nitride (hBN), metal and ceramic powders, etc. and were extensively studied in literature [6]. As carbonaceous fillers are both thermally and electrically conductive, their polymers nanocomposites may also be used as functional materials for applications such as sensors and actuators [7–9], including shape memory polymers [10–12].

The discovery of graphene in 2004 [13], defined as a single-atom-thick sheet of hexagonally arranged sp^2-bonded carbon atoms, and its outstanding thermal, mechanical and electrical properties [14–16] attracted a lot of interest in the scientific community. Despite the development of different synthetic techniques [17–19], the manufacturing of high quality graphene, i.e. low defective flakes with high lateral size, is still associated to the production of very limited quantities of material, whereas exploitation of graphene in polymers for industrial applications requires large scale production. In fact, nanoparticles available in sufficient amount to be exploited in polymer composites are typically from chemical reduction of graphene oxide (GO) [20], ball milling [21] and thermal exfoliation and reduction of GO [22]. However, it is worth noting that these large scale production processes typically lead to the synthesis of so called graphene-related materials rather than single layer graphene, including graphite nanoplatelets (GNP), reduced graphene oxide (rGO) multi-layer graphene (MLG), etc. [23], with various degree of structural and chemical defectiveness.

The improvement of thermal conductivity in polymer/GRM nanocomposites is mainly related to the quality of carbon nanoflakes, their organization in the polymer matrix and the interfacial thermal conductances [24]. The importance of flakes quality was demonstrated by molecular dynamic simulation [25] and recently verified experimentally [26] with a dramatic decreases of the intrinsic thermal conductivity of graphene as a function of defect concentration; furthermore, we reported that reduction of defects upon annealing at 1700 °C in vacuum, raises the thermal conductivity of rGO [27]. Additionally, it was demonstrated in literature that higher lateral size is straightforwardly related to a higher thermal conductivity [28,29]. In a recent paper, we demonstrated that the addition of high-temperature-annealed rGO in a polymer matrix leads to a thermal conductivity which is about 2-fold those of poly (butylene terephthalate) containing pristine rGO (higher defectiveness) or GNP [30], further confirming the need of high quality nanoflakes for the preparation of highly thermally conductive polymer nanocomposites. On the other hand, the control of GRM organization into a polymer matrix remains crucial in terms of nanoparticle distribution and quality of contacts between particles. Attempts in precisely controlling orientation and contacts between nanoparticles indeed resulted in an improvement of thermal transfer [31–33] but the methods adopted for the preparation of these nanocomposites are hardly upscalable or requires very high filler concentrations. Finally, the reduction of interfacial thermal resistance was also pursued by nanoparticle functionalization [34–36], despite the effectiveness of this strategy may be also related to the lateral size of the nanoflakes [37].

Recently, the preparation of polymer nanocomposites was obtained by in situ ring-opening polymerization of cyclic butylene terephthalate (CBT) oligomers into poly (butylene terephthalate), pCBT [38], taking advantage of both the extremely low viscosity of CBT and of the viscosity increase occuring during polymerization, to disperse nanoparticles, including organoclays [39], carbon nanotubes [40], silica [41] and graphene-related materials [30,42]. The presence of GRM was reported to affect the polymerization kinetic of CBT, with increase of the

polymerization time [43] and decrease of the average molecular weight [44]. Furthermore, the exploitation of GRM was described to improve mechanical, electrical and thermal properties [30,42,43,45]. Indeed, in a previous paper we reported a 12-fold increase in the thermal conductivity when 30 wt% of GNP is added to pCBT, while the addition of 5 wt% of rGO annealed at 1700 °C led up to a 4-fold increase [30].

In this work, the optimization of different processing parameters in the preparation of pCBT nanocomposites through ring-opening polymerization of CBT is addressed. In particular, the effect of processing temperature, mixing time and shear rate on electrical and thermal conductivity of nanocomposites are described in this work, aiming at a systematic study of processing conditions vs. material properties, which is still lacking in the field of polymer nanocomposites containing graphene-related materials.

2. Experimental

2.1. Materials

Cyclic butylene terephthalate oligomers [CBT100, Mw = $(220)_n$ g/mol, n = 2–7, melting point = 130 ÷ 160 °C] were purchased from IQ-Holding[1] (Germany). Butyltin chloride dihydroxide catalyst (96%, m$_p$ = 150 °C), chloroform (CHCl$_3$) (≥99.9%) and 1,2 dichlorobenzene (≥99%) were purchased from Sigma-Aldrich; acetone (99 + %), 1,1,1,3,3,3 hexafluoroisopropanol (HFIP, ≥99%) and phenol (≥99.5%) were purchased from Alfa Aesar, Fluka and Riedel-de Haën, respectively.

2.2. Synthesis of graphite nanoplatelets

The GNP used in this work was a research grade (see below for preparation method) synthetized by AVANZARE (Navarrete, La Rioja, Spain) using a rapid thermal expansion of overoxidized-intercalated graphite (ox-GIC). The intercalation of graphite with sulphuric acid to obtain graphite-sulfate is a well-known technology described for the first time by Hofmann and Rüdorff in 1938 [46]. In the present paper, the synthesis of GIC was made by adding 40 g of natural graphite flakes (average lateral size ≈ 1 mm) and 400 g of sulfuric acid (H$_2$SO$_4$) in a 5 L refrigerated glass jacket reactor under continuous stirring at T < 10 °C. Then, 5 g of nitric acid (HNO$_3$) were added drop by drop with a peristaltic pump, keeping the temperature constant. Later, 12.5 g of potassium permanganate (KMnO$_4$) were added to the suspension, keeping the temperature below 10 °C. When KMnO$_4$ was completely added, the system was heated up to 50 °C and stirred at this temperature for 1 h to allow the completion of the reaction (indicated by a change on the color of the suspension, from brown to black). At this point the system was cooled to room temperature and the solution was pumped, with a peristaltic pump, into a tank of H$_2$O (≈2 L), keeping the temperature lower than 70 °C. Hydrogen peroxide (H$_2$O$_2$, 30 g, 30 vol.%) was slowly added to remove the excess of MnO$_4^-$, and the suspension was maintained under stirring for about 30 min at room temperature. The solution was washed in 3 L of 3.3 wt% HCl solution for 1 h. Then, the solid was filtered, rinsed with osmotic water (until the sulfate test gave a negative result), dried in air and then in an oven at 80 °C. The resultant black powder was mechanically milled in a ball mill. The obtained solid, named ox-GIC-1, was then introduced in a tubular furnace under inert atmosphere (N$_2$) at 1000 °C for thermal expansion, obtaining a worm-like solid; this was later mechanically milled, separating nanoflakes and obtaining GNP.

2.3. Nanocomposite preparation

Polymer nanocomposite preparation consisted in a two-step procedure. In a first step, CBT/GNP mixture was prepared by mixing about

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[1] Distributor of products previously commercialized by Cyclics Europe GmbH.