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# Morphology and properties evolution upon ring-opening polymerization during extrusion of cyclic butylene terephthalate and graphene-related-materials into thermally conductive nanocomposites

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## ABSTRACT

In this work, the study of thermal conductivity before and after *in-situ* ring-opening polymerization of cyclic butylene terephthalate into poly (butylene terephthalate) in presence of graphene-related materials (GRM) is addressed, to gain insight in the modification of nanocomposites morphology upon polymerization. Five types of GRM were used: one type of graphite nanoplatelets, two different grades of reduced graphene oxide (rGO) and the same rGO grades after thermal annealing for 1 h at 1700 °C under vacuum to reduce their defectiveness. Polymerization of CBT into pCBT, morphology and nanoparticle organization were investigated by means of differential scanning calorimetry, electron microscopy and rheology. Electrical and thermal properties were investigated by means of volumetric resistivity and bulk thermal conductivity measurement. In particular, the reduction of nanoflake aspect ratio during ring-opening polymerization was found to have a detrimental effect on both electrical and thermal conductivities in nanocomposites.

## 1. Introduction

The high corrosion resistance, ease of processing, lightweight and low cost of polymers attracted scientific community and industry for the preparation of thermally conductive materials for the replacement of metallic parts [1–3], despite their intrinsic low thermal conductivity. For this purpose, polymer composites or nanocomposites are typically used, exploiting different types of conductive fillers/nanofillers, including carbon nanotubes, graphite, graphene-related materials, boron nitride, metal particles, aluminum oxide, diamond and silicon nitride [3].

In the last decade, scientists focused their attention on graphene [4,5], a single-atom-thick sheet of hexagonally arranged sp<sup>2</sup>-bonded carbons, due to its extraordinary thermal, electrical and mechanical properties [6–8]. Unluckily, although various preparation approaches have been studied [5,9–12], the industrial scale up of graphene, required for its exploitation in polymer nanocomposites, remains highly challenging. For this reason, different synthesis techniques have been developed during years: chemical reduction of graphene oxide (GO) [13], thermal exfoliation and reduction of GO [14], ball milling [15], liquid phase

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exfoliation of graphite [11] and other methods [16]. However, all of these methods often lead to flakes of relatively low quality (low to limited single layer yield, large thickness distribution, chemical defectiveness in the  $sp^2$  structure, limited lateral size). Indeed, techniques allowing kg scale production typically lead to so-called graphene-related materials (GRM), including graphite nanoplatelets (GNP), reduced graphene oxide (rGO), multilayer graphene (MLG), which sometimes are misreferred to graphene, while a more accurate nomenclature should be used [17].

Despite the obvious scatter of results, owing mainly to their different structural features, graphene-related materials appear to be more efficient than carbon nanotubes (CNT) for the preparation of thermally conducting polymer nanocomposites [18]. However, for carbon based material families, parameters like particle aspect ratio and quality, interfacial thermal resistance, distribution and alignment of nanoparticles are generally recognized to play a key role for the final thermal conductivity of polymer nanocomposite [1,2]. The quality of nanoparticles exploited is obviously crucial: while the effect of lateral size is well known [2,19,20], in our previous work we demonstrated the increase of the intrinsic thermal conductivity of rGO upon annealing at 1700 °C in vacuum [21]. This in turn leads to higher thermal conductivities with respect to nanocomposites containing pristine rGO (2-fold and 4-fold increase when pristine or annealed nanoparticles, respectively, were used) [18].

While homogeneous distribution of conductive particles into the polymer matrix is an obvious need, it is worth noting that nanoparticle dispersion, intended as the separation of nanoparticles into isolated individual primary particle, is expected to be detrimental for conductivity, either thermal or electrical. In fact, the existence of a percolating network is essential for electrical conductivity and generally also recognized as required for efficient thermal transfer, despite heat transfer may also include a role of the matrix between conductive particles. However, when using nanoparticles with a high aspect ratio, e.g. carbon nanotubes or graphene, the percolation threshold is very low and a network of nanoparticles in contact with each other is typically obtained in composites containing a few wt.% nanoparticle loading. Despite this fact, improving contacts between nanoparticles by controlled particle segregation is one of the possible strategies for the enhancement of thermal conductivity in nanocomposites [22]. For instance, Eksik et al. [23] added chemically reduced graphene oxide (c-rGO) coated poly (methyl methacrylate) microspheres to epoxy resin (with a final content of c-rGO of 1 wt.%) and obtained a 7-fold increase in the thermal conductivity of pure epoxy resin while the increase was about 3-fold when a traditional epoxy + 1 wt.% c-rGO nanocomposite was prepared, thus indicating that the formation of a well-organized pathway is crucial for the enhancement of thermal conductivity in polymer nanocomposites.

In the last years, scientists focused their attention on reactive extrusion of polymer nanocomposites, taking advantage of the starting low viscosity of oligomers/monomers and its increase during polymerization reaction, which could result in a higher dispersion and distribution of nanoparticles [24–26]. A wide interest was focused to the *in-situ* ring-opening polymerization (ROP) of cyclic butylene terephthalate (CBT) oligomers for the preparation of poly (butylene terephthalate) (pCBT) nanocomposites [27–30]. In particular, Noh et al. [26] and Colonna et al. [18] demonstrated the possibility to distribute and disperse GNP and rGO via ROP of CBT. The high dispersion and distribution degree of these electrically and thermally conductive nanoparticles resulted in nanocomposites with excellent electrical and thermal conductivities [18,26]. However, it is worth noting that the presence of graphene-related materials was proven to decrease polymerization rate [31] and/or decrease molecular weight [32].

Despite pCBT nanocomposites have been widely studied, the evolution of nanoparticle dispersion and thermal/electrical conductivities during ring-opening polymerizations were not previously reported, to the best of our knowledge. Even though CBT is a solid at room temperature, unpolymerized CBT nanocomposites cannot be regarded as materials for real application owing to their low mechanical properties. Nevertheless, it is important to study how nanocomposite properties change upon the ring-opening polymerization, to be able to develop and optimize reactive extrusion processing of pCBT nanocomposites. With this aim, in the present paper we report a comparison between CBT and pCBT nanocomposite properties, focusing our attention on electrical and thermal properties of nanocomposites containing GNP, rGO and thermally annealed rGO.

## 2. Experimental

### 2.1. Materials

Cyclic butylene terephthalate oligomers [CBT100,  $M_w = (220)_n$  g/mol,  $n = 2-7$ , melting point = 130–160 °C] were purchased from IQ-Holding<sup>1</sup> (Germany). Butyltin chloride dihydroxide catalyst (96%,  $m_p = 150$  °C, CAS # 13355-96-9) was purchased from Sigma-Aldrich while acetone (99 + %) was purchased from Alfa Aesar.

Three types of graphitic nanoparticles were used for this study. GNP (Surface Area =  $22 \pm 5$  m<sup>2</sup>/g, Raman  $I_D/I_G \approx 0.16$ , Oxygen content  $\approx 1.8$  at.%,<sup>2</sup>  $T_{Oxid} \approx 632$  °C<sup>3</sup>), RGO (Surface Area =  $210 \pm 12$  m<sup>2</sup>/g, Raman  $I_D/I_G \approx 0.88$ , Oxygen content  $\approx 3.2$  at.%,<sup>2</sup>  $T_{Oxid} \approx 558$  °C<sup>3</sup>) were research grades synthesized by AVANZARE (Navarrete, La Rioja, Spain) accordingly with the procedure previously reported [18]. Another thermally reduced graphite oxide grade, EXG98 350R (Surface Area > 300 m<sup>2</sup>/g, Raman  $I_D/I_G \approx 0.80$ , Oxygen content  $\approx 7.0$  at.%,<sup>2</sup>  $T_{Oxid} \approx 471$  °C<sup>3</sup>), was purchased from Graphite Kropfmühl (Germany) and here referred to as RGO-2.

Part of the RGO and RGO-2 were annealed, in a closed graphite box, at 1700 °C for 1 h at 50 Pa in a vacuum oven (Pro.Ba., Italy) with graphite resistors to decrease the defectiveness in the  $sp^2$  structure, as previously reported [21]. Annealed material are from now

<sup>1</sup> Distributor of products previously commercialized by Cyclics Europe GmbH.

<sup>2</sup> XPS,  $O_{1s}$  signal.

<sup>3</sup> Onset TGA plots in air, 10°C/min heating rate, sample mass = 2mg.

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