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Local mechanical properties of graphene/polyethylene-based nanocomposites by depth-sensing indentation

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ABSTRACT

Local mechanical properties of modified-graphene high-density polyethylene nanocomposites are investigated using depth-sensing indentation. Three different chemical routes are employed to boost filler dispersion by functionalizing graphene with polyethylene brushes and incorporating a small amount of free short-chain polyethylene. At large penetration depths the results reveal distinct mechanical properties for the different chemical approaches. Hardness, modulus and creep resistance are discussed in terms of filler dispersion, polymer nanostructure and plasticization of the amorphous regions by the short-chain polyethylene. By reducing the indentation size, maps of the surface mechanical properties are generated, and graphene agglomerates that appear in some nanocomposites can be clearly identified. However, these agglomerates present significantly inferior mechanical properties than those usually reported for graphene, and results at the nanoscale suggest that modification of graphene together with the viscous "liquid-like" character of the polymer host represent strong impediments for effective reinforcement. Notwithstanding, one of the nanocomposites (from the thiol-ene click reaction) overcomes these issues, achieving a macroscopic mechanical performance similar to that of the neat polymer, combined with outstanding electrical conductivity.

1. Introduction

In recent years considerable effort has been engaged to effectively incorporate graphene as a nanofiller in polymer matrices. It is known that graphene can enhance electrical, thermal, mechanical, and barrier properties of a polymer host, as well as change its water affinity [1–4]. Good dispersion of graphene and strong interaction with the matrix are understood as the necessary conditions to optimize nanocomposite properties and, in this respect, covalent strategies have been suggested as one of the most potentially successful routes [5–7].

The case of nanocomposites incorporating high density polyethylene (HDPE) and graphene is especially challenging, and advances on materials with superior properties have occurred at a much slower pace than with other polymer matrices. It has been found that the combination of these particular constituents by conventional mixing methods or simple chemical

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reactions leads to modest improvements in nanocomposite performance [8–12]. Very recently, work in our laboratory on the preparation of graphene/HDPE nanocomposites with improved properties using a combination of click chemistry and adequate mixing protocols has been reported [13,14]. Graphene modified with brushes of short-chain polyethylene (PE) using three different click reactions is more easily incorporated into a high density polyethylene matrix due to an enhancement of the interfacial interactions. The most relevant changes in properties have been obtained using a two-step mixing procedure that includes the addition of small amounts of free short polyethylene chains. This procedure creates a so-called "gradient interphase" as compared with the direct incorporation of pristine or functionalized graphene. Nanocomposites with modified-graphene using the thiol-ene click reaction have shown excellent electrical conductivity with a low percolation threshold and conductivity values almost three orders of magnitude higher than those reported for other graphene/PE nanocomposites with the same filler content [14]. With regard to the macroscopic mechanical performance, the elongation at break of all clicked-reinforced samples is higher than that of the neat polymer, whilst the Young's modulus decreases, except in the case of thiol-ene modified graphene. All these results demonstrated that, both the chemical strategy chosen to provide graphene with functionalities common to the polymer matrix and the engineering of the nanoscale interface play key roles that determine the properties of the nanocomposites [13]. Therefore, the evaluation of mechanical properties at the nanoscale could provide very important information in order to understand the origin of their variations as a function of chemical strategies and processing methodologies employed.

Depth-sensing indentation (DSI), also commonly known as "instrumented indentation" or simply "nanoindentation", allows the evaluation of the local mechanical properties of materials and is especially helpful for specimens with reduced dimensions or containing heterogeneities [15,16]. The size of the indentation depth ranges from only a few tens of nanometres up to the micrometre scale. The application of DSI to polymer-based materials is most challenging due to their time-dependent character that requires the development of specific strategies [17–21].

There are many examples in the literature where DSI is employed to evaluate the reinforcing effect of the filler in polymer-based nanocomposites, and one of the most attractive features of the technique lies in the small quantities of material required [22]. The study of mechanical creep is interesting because the response of a polymer material inherently includes a time dependent deformation, and the use of instrumented indentation for this purpose is especially valuable because the same small specimen can be tested at different locations using a range of conditions (for example different strain rates). Penetration depths in the micron range are preferred when the interest is focused on mechanical properties representative of those of the bulk, because the volume of deformation encompasses a significant amount of material. In contrast, to date there has been only limited effort in the exploitation of the capabilities of this technique to spatially resolve the mechanical properties, even though this is crucial to the understanding of the average macroscopic properties. Surface effects, material heterogeneities, inhomogeneous filler distribution, etc. can be readily detected by means of DSI. For example, in graphene-reinforced polyvinyl alcohol (PVA) nanocomposites, nanoindentation has allowed the detection of a reverse plasticization effect of graphene on the hydrophilic matrix [23]. Moreover, both uniform [24,25] or inhomogeneous [26,27] nanofiller distribution across the sample thickness in different nanocomposites have been recognized on the basis of DSI measurements. In hierarchical composites, a gradient of mechanical properties within a region of a few microns away from the microscale reinforcement has also been detected by DSI [28,29].

The aim of the present study is to evaluate the effect of modified graphene on HDPE nanocomposites by means of indentation studies and generate a map of the surface mechanical properties. As mentioned above, the graphene/HDPE nanocomposites show relevant differences in their macroscopic properties depending on the procedure adopted to incorporate short polyethylene chains to the graphene sheets. This work explores the local mechanical properties and correlates them with morphological observations and, as a consequence, provides a comprehensive understanding of the final macroscopic performance.

2. Experimental

2.1. Materials

Graphene (Angstron Materials, Inc., USA), polyethylene monoalcohol (PEOH, $M_n = 460 \times 10^{-3}$ kg mol^{-1}, Sigma–Aldrich Corp.) and a commercial high density polyethylene (HDPE, MFI = 1.5×10^{-5} m^3/10 min (2.16 kg), density = 945 kg m^{-3}) kindly supplied by Repsol S. A. (Spain), were used. The preparation of PE-brushes "clicked" to graphene and graphene/HDPE nanocomposites has been described in detail elsewhere [13,14]. Three approaches were addressed to click graphene with PE. In approach 1 (CuAAC), graphene was furnished with alkyne groups, while the azide-terminated polymer was prepared by bromination of PEOH and subsequent nucleophilic attack with sodium azide; this modified graphene was denominated GAA. In approach 2 (thiol-ene), pristine graphene representing a hyper-conjugated alkene and a thiol-terminated PE (PE-SH) were used and the modified graphene was denominated GTE. In approach 3 (thiol-yne), the same polymer as in approach 2 and the alkyne-modified graphene of approach 1 were used; this graphene was denominated GTY. Additional information on these modified graphenes is provided in the supplementary material (see Scheme S1 and Fig. S1).

Nanocomposites of HDPE, a small amount of PEOH, and one modified graphene (GAA, GTE or GTY) were prepared using the protocol described in Ref. [13]. In short, modified graphene was mixed with PEOH in hot xylene (90 °C) under vigorous stirring and precipitated in methanol, filtered, washed and thoroughly dried under vacuum. These mixtures with a graphene/