Graphene nanoplatelets as economical alternative in the reinforcement of PMMA bone cements

E.Paz,*[1], Y. Ballesteros[1], S. López de Armentia[1], J.C. del Real[1]

[1] Institute for Research in Technology/Mechanical Engineering Dept., Universidad Pontificia Comillas, Alberto Aguilera 25, 28015 Madrid, Spain; sara.lopez@comillas.edu

* Correspondence: eva.paz@comillas.edu

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INTRODUCTION

The reinforcing effect of G and GO has attracted considerable interest during recent decades, giving rise to advanced nanocomposites with enhanced mechanical properties [1,2]. In previous studies, it was demonstrated that the incorporation of well-dispersed Graphene (G) and Graphene oxide (GO) powder can be a promising solution in augmenting the mechanical performance of PMMA bone cement in an attempt to enhance the long-term survival of the cemented orthopaedic implants [3].

It has been demonstrated that the presence of G and GO nanoparticles within a polymer matrix produces a deviation and detention of crack fronts during their propagation, increasing the required energy for failure [4]. In addition, it has been proven that these nanoparticles do not significantly influence the thermal properties and biocompatibility of PMMA bone cements, potentially allowing its clinical progression.

One of the most important constraints in the large-scale production of nanocomposite applications is that the industrial production of G and GO currently is limited by two main aspect: the scalability of the chemical production process and the cost. A wide variety of cheaper and easier-to-produce graphene derivatives have emerged as is the case of graphene nanoplatelets (GnPs).

GnPs exhibit exciting properties such as light weight, high aspect ratio, electrical and thermal conductivity, mechanical toughness, low cost, and planar structure. As such, they are attractive options to replace different nanostructured fillers [5]. They are appealing for nanocomposites since they can easily and successfully be included in polymeric matrices by solvent or melt compounding. GnPs are cheaper than G and GO; and are comparable in modifying the mechanical properties of polymers.

The objective of this study is to make a comparison of the effect that the addition of GnPs has on the mechanical performance of bone cements, compared to the use of other carbon-based nanoparticles such as G and GO.

EXPERIMENTAL

The PMMA bone cement used in this study was a two-phase bone cement. The solid phase was composed of 3.64 g of barium sulphate (Sigma Aldrich, UK) and 36.36 g of Colacryl B866 (Lucite International Ltd., UK), which contained the pre-polymerised PMMA and initiator (benzoyl peroxide, BPO). The liquid phase was composed of 19.9 mL of the methyl methacrylate (MMA) and 160 µL of an activator, N,N-Dimethyl-p-toluidine (Sigma Aldrich, UK).

PMMA bone cements without filler (Control), with G (Avanzare Nanotechnology, Spain), GO (NanoInnova Technologies, Spain) and GnPs (Avanzare Nanotechnology, Spain) at different levels of loadings (0.1, 0.05, 0.025 and 0.01 wt.% were prepared. In each case, the nanoparticle powder was dispersed into the liquid phase of the bone cement using ultrasonication at 50% amplitude for 3 min at intervals of 30 sec ON and 10 seconds OFF. To prevent overheating, the liquid monomer was placed in a water bath that was held at 22 ± 1 °C. Following sonication, the suspension was placed in an ultrasonic bath for 1 min, to reduce the incidence of bubble formation.

The bending strength and fracture toughness of each kind of cement was studied. A four-point bending load arrangement was used to determine bending properties in accordance with ISO 5833 [36]. Specimens were in the form of rectangular bars with dimensions of 80.0 ± 0.1 mm length, 10.0 ± 0.1 mm width and 4.0 ± 0.1 mm thickness. The fracture toughness was determined according to the standard [38]. Single edge notch bend specimens (SENB) were used to calculate the fracture toughness (K_{IC}). The tests were performed under three-point bending loading arrangement. The tests were conducted using a Universal Testing Machine IBTH/500 (Ibertest, Madrid, Spain) using a load cell of 5 kN, which operated at a crosshead speed of 5 mm/min. A total of three batches were tested for each cement composition with a minimum of five samples per batch.

Finally, the fracture surface of the tested specimens was evaluated using an Olympus DSX1000 digital microscope (Olympus, Shinjuku, Tokyo, Japan).

RESULTS

As each type of nanoparticle has a different density, the optimum level of loading in each case could be different. Consequently, the effect of the level of loading has been studied for each case adding different amounts of filler between 0.1 - 0.01 wt.%.

In all cases, it was observed that when the load decreased, there was an increase in fracture toughness. Figure 1 shows the average fracture toughness in the case of GnPs for the different load levels. As can be seen, the best results were obtained for the low loading (0.01 wt.%), in this case the fracture toughness was 20% higher than for 0.1 wt.%.

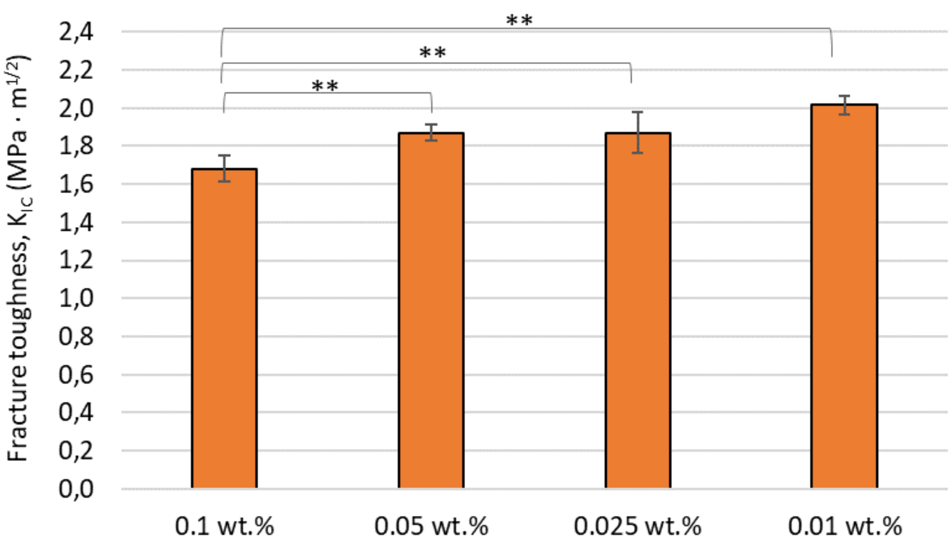

Figure 1. *Fracture toughness of the PMMA bone cement reinforced with GnPs at different levels of loading (0.1, 0.05, 0.025 and 0.01 wt.%). The variation in comparison with the control cement also indicated. ** meaning a p-value < 0.001.*

In view of the results, the effect of the different nanofillers at the optimum obtained level of loading (0.01 wt.%) were compared. In Figure 2 it is represented the fracture toughness of the bone cements with 0.01 wt. % of the different nanoparticles. It can be observed that in all cases the fracture toughness was improved in comparison with the control cement. In the case of the GO and GnPs, these significantly increased the fracture properties (p<0.001) by 30% and 40% respectively. This result demonstrated that the addition of GnPs is even better that the use of G and GO at this level of loading.

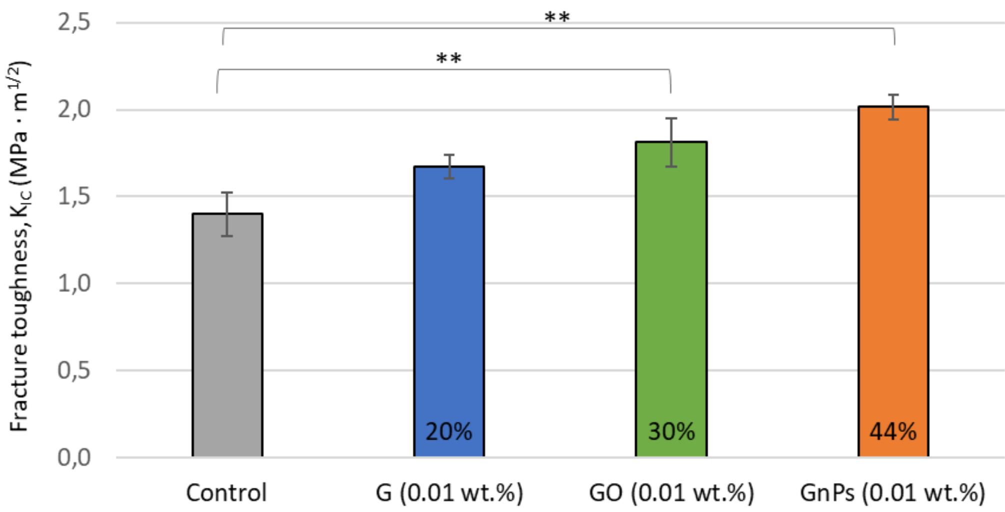

Figure 2. *Fracture toughness of the different PMMA bone cement with the different nanofillers (G, GO and GnPs) with 0.01 wt.% of load. The variation in comparison with the control cement also indicated. ** meaning a p-value < 0.001.*

The bending tests were carried out at two different levels load, wt.% and 0.01 wt.% and in both cases the resultant trend was similar to that obtained in the fracture tests could be observed - the addition of low loadings produced better results, and the improvement was significantly higher in the case of GnPs than G and GO.

The analysis of the fracture surfaces showed that fewer agglomerations of nanoparticles were found in the case of the addition of low level of load, which could explain the reason of the obtained increase in the mechanical performance with the low levels of load.

The better reinforcement effect observed in the GnPs could be related with a lower tendency of these to form agglomerates, as they are less exfoliated and are more stable, and with the better dispersability ot them within the polymeric matrix.

In future researches the effect of the GnPs on the fatigue life and other fundamental properties of the bone cements as are the mechanical properties and the biocompatibility should be studied.

CONCLUSIONS

The use of GnP as a reinforcing agent for bone cements produces very promising results with significant improvements in the properties of resistance to fracture and bending of these bone cements. Compared to other carbon-based nanomaterials (G and GO), GnPs have been shown to produce even better results, being a very interesting alternative with a lower cost.

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