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Improvement of the mechanical, tribological and antibacterial properties of glass ionomer cements by fluorinated graphene

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ABSTRACT

Objective. The aim of this study was to improve the mechanical properties, wear resistance and antibacterial properties of conventional glass ionomer cements (GICs) by fluorinated graphene (FG), under the premise of not influencing their solubility and fluoride ion releasing property.

Materials and methods. FG with bright white color was prepared using graphene oxide by a hydrothermal reaction. Experimental modified GICs was prepared by adding FG to the traditional GICs powder with four different weight ratios (0.5 wt%, 1 wt%, 2 wt% and 4 wt%) using mechanical blending. Compressive and flexural strength of each experimental and control group materials were investigated using a universal testing machine. The Vickers microhardness of all the specimens was measured by a Vicker microhardness tester. For tribological properties of the composites, specimens of each group were investigated by high-speed reciprocating friction tester. Fluoride ion releasing was measured by fluoride ion selective electrode methods. The antibacterial effect of GICs/FG composites on selected bacteria (*Staphylococci aureus* and *Streptococcus mutans*) was tested with pellicle sticking method.

Results. The prepared GICs/FG composites with white color were successfully fabricated. Increase of Vickers microhardness and compressive strength and decrease of friction coefficient of the GICs/FG composites were achieved compared to unreinforced materials. The colony count against *S. aureus* and *S. mutans* decreased with the increase of the content of FG. And the antibacterial rate of *S. mutans* can be up to 85.27% when the FG content was 4 wt%. Additionally, fluoride ion releasing property and solubility did not show significant differences between unreinforced and FG reinforced GICs.

Significance. Adding FG to traditional GICs could not only improve mechanical and tribological properties of the composites, but also improve their antibacterial properties. In addition, the GICs/FG composites had no negative effect on the color, solubility and fluoride ion releasing properties, which will open up new roads for the application of dental materials.

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1. Introduction

Glass ionomer cements, since invented by Wilson and Kent in 1969 [1], have been widely used in clinical dentistry as tooth-colored luting and restorative materials owing to their direct chemical adhesion to tooth structure and base metals [2,3], favorable coefficient of linear thermal expansion, dynamic fluoride ion releasing [4] and low cytotoxicity [5]. Dental applications of GICs include restoration of deciduous teeth [6], anterior class III and V restorations [7,8], cementation (luting) of crowns, bridges and orthodontic appliances [9–11], restorations of non-carious teeth [12], and as materials for atraumatic restorative therapy (ART) [13]. Not only so, GICs have shown their potential in other medical areas, such as ear ossicles and bone substitute plates for craniofacial reconstruction [14].

However, their high brittleness, poor physico-mechanical properties and wear resistance, and moisture sensitivity in the early stages of setting limited their further application in dentistry as permanent filling materials in stress-bearing areas. To overcome these drawbacks, many researchers have focused on optimization of composition of the glass cements over the years. In 1977, the addition of amalgam alloy to glass ionomer was proposed to increase their strength [15]. Likewise, some researchers added other mental fillers, such as Ag, Ti and Pd and found that the materials were limited in some of properties due to the poor esthetics and poor interfacial bonding between the mental fillers and the matrix [16]. In 1980s, the resin-modified glass ionomer cements (RMGICs) were developed. They showed better mechanical properties and lower solubility [17], but the presence of resin reduced the biocompatibility [18] and lead to lower fluoride ion releasing [19]. Also, volumetric shrinkage during polymerization of the RMGICs [20] affected the bond strength of this material to dentin. Some antibacterial fillers such as Ag, ZnO and TiO_2 nanoparticles [21,22] have been incorporated to dental restorations [23]. However, ZnO and $nTiO_2$ have been supposed to be cytotoxic [24,25]. These modifications have various inevitable drawbacks, which would restrict their applications. Obviously, a tooth-colored material with sufficient mechanical properties, wear resistance and antibacterial properties is in demand.

Graphene, a two-dimensional (2D) material consisting of carbon atoms which was arranged in honeycomb lattice, has been studied extensively to enhance performances of other materials due to their unique properties, such as excellent mechanical properties (breaking strength of 42 N/m and Young's modulus of 1.0 TPa) [26], extreme chemical stability, superior biocompatibility, good antibacterial properties [27,28], and favorable tribological properties by reducing wear and friction. For example, the addition of graphene nanosheets could improve the hardness and mineralization of bioactive calcium silicate cements [29] and hydroxyapatite [30]. The graphene nanoplatelet (GNP)/biphasic calcium phosphate (BCP) composite has significantly enhanced fracture toughness compared to original BCP [31]. Recent studies have shown that graphene and graphene-based composites (especially graphene oxide, GO) possess a series of merits in biomedicine field. For example, graphene was found to be non-toxic for human osteoblasts and mesenchymal stromal cells [20], suitable for adhesion and proliferation of osteoblasts [32], and could induce the expression of osteoblastic-related genes and osteogenic differentiation in dental pulp stem cells [33]. A study showed that certain concentration of polyethylene glycol (PEG)-GO nanosheets have potential in treatment of bone cancer [34]. Also, it was found that GO nanosheets were highly effective in inhibiting the growth of dental pathogens [35,36] and promoting the proliferation and cellular activity of periodontal ligament stem cells (PDLSCs) [36].

Fluorinated graphene (FG), an up-rising member in the family of graphene derivatives, is a kind of one-molecule-thick material [37] and shows many unique properties. Compared to pristine graphene or graphene oxide (including reduced graphene oxide), the research of FG is still in its infancy, so there are little reports on its properties and applications especially in biology or biomedicine. For example, Nair et al. reported that the Young's modulus and intrinsic strength of FG are lower than that of graphene but still higher than that of other materials (e.g., structural steel) [38]. FG also has low friction coefficient [39]. In biology field, Loh et al. used FG as scaffold for the growth of mesenchymal stem cells (MSCs) and found that FG could enhance cell adhesion and proliferation of MSCs and exhibited a neuro-inductive effect via spontaneous cell polarization. Graphene has been reported to be highly cytotoxic for bacteria and can thus serve as an antibacterial material [40], so we could speculate that as a member of graphene family, FG may also have similar effect. What's more, FG can enhance proliferation and polarization of mesenchymal stem cells [41] and neuroinduction of stem cells [42], indicating that FG has favorable biocompatibility. Based on these studies, it is reasonable to assume that FG may be beneficial for reinforcing GICs and improving its performance as dental materials.

The objective of this work was to investigate the effect of fluorinated graphene on the physico-chemical properties, wear resistance, fluoride ion releasing property, solubility and antibacterial properties of conventional GICs. The hypothesis tested was that FG can increase these properties without compromising the intrinsic properties, such as the color.

2. Materials and methods

2.1. Raw materials

Graphene oxide was purchased from Nanjing XF Nano Technology Co., Ltd., China. Commercial GICs (conventional, Shanghai Dental Material Company, China) are composed of powder and relevant liquid before use. The main components of the powder are silicon oxide, calcium chloride, sodium fluosilicate and aluminum phosphate. The liquid consists of polyacrylic acid, tartaric acid and deionized water. The components of the artificial saliva are showed in Table 1 (ISO/TR10271-2011). The raw materials were dissolved in distilled water and diluted to 1 L. All the chemicals used were of analytical grade. All aqueous solutions in experiments were prepared using threefold-distilled water. Other reagents were commercially available.