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Modification of conventional glass-ionomer cements with N-vinylpyrrolidone containing polyacids, nano-hydroxy and fluoroapatite to improve mechanical properties

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ABSTRACT

Objective. The objective of this study was to enhance the mechanical strength of glass-ionomer cements, while preserving their unique clinical properties.

Methods. Copolymers incorporating several different segments including *N*-vinylpyrrolidone (NVP) in different molar ratios were synthesized. The synthesized polymers were copolymers of acrylic acid and NVP with side chains containing itaconic acid. In addition, nano-hydroxyapatite and fluoroapatite were synthesized using an ethanol-based sol–gel technique. The synthesized polymers were used in glass-ionomer cement formulations (Fuji II commercial GIC) and the synthesized nanoceramic particles (nano-hydroxy or fluoroapatite) were also incorporated into commercial glass-ionomer powder, respectively. The synthesized materials were characterized using FTIR and Raman spectroscopy and scanning electron microscopy. Compressive, diametral tensile and biaxial flexural strengths of the modified glass-ionomer cements were evaluated.

Results. After 24 h setting, the NVP modified glass-ionomer cements exhibited higher compressive strength (163–167 MPa), higher diametral tensile strength (DTS) (13–17 MPa) and much higher biaxial flexural strength (23–26 MPa) in comparison to Fuji II GIC (160 MPa in CS, 12 MPa in DTS and 15 MPa in biaxial flexural strength). The nano-hydroxyapatite/fluoroapatite added cements also exhibited higher CS (177–179 MPa), higher DTS (19–20 MPa) and much higher biaxial flexural strength (28–30 MPa) as compared to the control group. The highest values for CS, DTS and BFS were found for NVP-nanoceramic powder modified cements (184 MPa for CS, 22 MPa for DTS and 33 MPa for BFS) which were statistically higher than control group.

Conclusion. It was concluded that, both NVP modified and nano-HA/FA added glass-ionomer cements are promising restorative dental materials with improved mechanical properties.

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1. Introduction

Glass-ionomer cement (GIC) was invented by Wilson et al. at the Laboratory of the Government Chemist in early 1970 [1,2]. These materials are water-based cements, known as polyalkenoate cements [3]. Their generic name is based on the reaction between silicate glass and polyacrylic acid, and the formation arises from an acid/base reaction between the components [4,5]. These cements are translucent and adhesive to tooth structure [6–11]. Glass-ionomer cements have unique properties such as, biocompatibility, anticariogenic action (due to fluoride release) and adhesion to moist tooth structure. In addition, the coefficient of thermal expansion for glass ionomers is low and close to the values of tooth structure [12–15]. Besides their advantages they have some disadvantages such as brittleness and inferior mechanical strength. Significant improvements have been made since the invention of GIC and further improvements are required in order to enhance their physical properties. Although stronger and more aesthetic materials with improved handling characteristics are now available, lack of strength and toughness are still major problems [16–18]. The concept that NVP modified polyacids would result in improved strength of glass-ionomer cements has been found valid in dentistry [19,20]. Culbertson et al. reported that acrylic acid–itaconic acid-*N*-vinylpyrrolidone polymers with the different molar ratio have the ability to increase the mechanical properties of the glass-ionomer cements [19]. In another study Yamazaki et al. showed that AA-MA-NVP polymer resulted in modified glass-ionomer cements with higher CS and DTS in comparison to Fuji IX commercial glass-ionomer cement [24].

In this study, a method employed to synthesis NVP containing polymers, which is a modification of the procedure reported by Culbertson et al. and Yamazaki et al. In this modified method, novel NVP modified polyacids with a new molar ratio (8:1:1 and 8:2:2) and altered monomeric sequences (AA-NVP-IA) were synthesized, and incorporated into glass-ionomer liquid formulations. Previous studies have shown that neither 7:3:1 nor 7:1:3 molar ratios, exhibited optimum mechanical strength values (highest compressive, diametral tensile strength and biaxial flexural strength) [19]. Therefore, in this study, polymers with 7:2:2, 8:2:2 and 8:1:1 molar ratios were synthesized and the resulting data were compared to each other and previous data. It was envisaged that NVP molecules interspersed between the itaconic and acrylic acid, would act as a spacer to decrease the degree of steric hindrance of carboxylic acid groups. Subsequently, the probability of ionic bond formation and poly-salt bridge formation within the final set cement would be increased significantly.

Lucas et al. in their work showed that the addition of the hydroxyapatite particles to the glass-ionomer powder has the ability to increase the fracture toughness of the cement which maintained long-term bond to dentin [21]. Furthermore, Gu et al. reported that glass-ionomer cements containing 4%w hydroxyapatite particles exhibited enhanced mechanical properties in comparison to commercial glass-ionomer cements [22,23]. Therefore, in this study nano-hydroxyapatite and fluoroapatite were synthesized and the effect of incorporation of these bioceramic nanopowders into GIC formulations upon the mechanical properties was investigated. The mechanical strength (compressive, diametral tensile and biaxial flexural strength) of the GICs were evaluated and the effect of incorporation of NVP modified polymers and HA/FA nanopowders on the mechanical values of resulted cements were investigated.

2. Materials and methods

2.1. Materials

The glass powders and all liquids which were used in the experiments were of commercial grade obtained from Fuji II (GC International, Tokyo, Japan). All the other chemicals in this study were in analytical grade and applied as received from Sigma–Aldrich Chemical Co. Acrylic acid (AA), itaconic acid (IA), *N*-vinylpyrrolidone (NVP), ammonium persulfate, methanol (CH_3OH) and anhydrous ethyl acetate ($CH_3COOC_2H_5$) were used for polymer syntheses. For nano-hydroxyapatite and fluoroapatite syntheses, calcium nitrate tetrahydrate [Ca $(NO_3)_2{\cdot}4H_2O$], $(NH_4)_2HPO_4$, ammonium fluoride (NH_4F), ethanol (C_2H_5OH), and ammonium hydroxide (NH_4OH) were used as obtained.

2.2. Methods

2.2.1. Polymer synthesis

Experimental procedure employed in this study is a modification of the method first reported by Crisp et al. and Yamazaki et al. [24,25]. Details are as follows: initially 0.075 g (0.1% wt) of ammonium persulfate was dissolved in 75 ml of distilled water in a 250-ml three-neck flask. In the next step, 0.4 mol (27.43 ml) of acrylic acid (density of 1.05 g cm^{-3}), and 0.05 mol (5.31 ml) of NVP (density of 1.045 g cm^{-3}) were measured and partially dissolved in 37.5 ml of distilled water in a beaker. A third solution was made up, consisting of 0.022 g of ammonium persulfate and 0.05 mol (6.5 g) of itaconic acid dissolved in 22.5 ml of distilled water in a beaker. The first solution was stirred with a magnetic stirrer (IKA Werke magnetic stirrer/heater) and heated continuously up to 98 °C under flowing nitrogen. The second solution containing acrylic acid and NVP added to the flask after the temperature reached 98 °C. The third solution which contained the initiator and itaconic acid was then added to the three-neck flask in a dropwise manner using a glass dropping funnel at ca. 3 ml/min rate. After the addition was complete, polymerization was allowed to proceed for an additional 12 h by maintaining stirring under the blanket of nitrogen at 98 °C. Different molar ratios were synthesized for the polymers. Using the previously mentioned process (Crisp et al. and Yamazaki et al.) the copolymer of acrylic acid and NVP with side chains containing itaconic acid groups was synthesized. In order to synthesize an AA-IA-NVP polymer with 8:1:1 molar ratio, the same basic procedure as used by Yamazaki et al. was applied, albeit with different molar ratios [24].

The polymers were freeze-dried for 24 h at 266 mbar (Wizard 2.0 SP Industries Co. The Virtis Company, NY, USA), dissolved in anhydrous methanol (Sigma–Aldrich) and then