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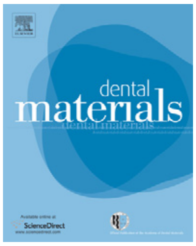

Effects of N-vinylpyrrolidone (NVP) containing polyelectrolytes on surface properties of conventional glass-ionomer cements (GIC)

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ABSTRACT

It has been found that polyacids containing an N-vinylpyrrolidinone (NVP) comonomer produces a glass inomer cement with improved mechanical and handling properties. The objective of this study was to investigate the effect of NVP modified polyelectrolytes on the surface properties and shear bond strength to dentin of glass ionomer cements.

Poly(acrylic acid (AA)-co-itaconic acid (IA)-co-N-vinylpyrrolidone) was synthesized by free radical polymerization. The terpolymer was characterized using ^{1}H NMR, FTIR spectroscopy and viscometry for solution properties. The synthesized polymers were used in glass ionomer cement formulations (Fuji II commercial GIC). Surface properties (wettability) of modified cements were studied by water contact angle measurements as a function of time. Work of adhesion values of different surfaces was also determined. The effect of NVP modified polyacid, on bond strength of glass-ionomer cement to dentin was also investigated. The mean data obtained from contact angle and bonding strength measurements were subjected to one- and two-way analysis of variance (ANOVA) at $\alpha = 0.05$.

Results showed that NVP modified glass ionomer cements showed significantly lower contact angles ($\theta = 47^\circ$) and higher work of adhesion (WA = 59.4 erg/cm^2) in comparison to commercially available Fuji II GIC ($\theta = 60^\circ$ and WA = 50.3 erg/cm^2, respectively). The wettability of dentin surfaces conditioned with NVP containing terpolymer was higher ($\theta = 21^\circ$, WA = 74.2 erg/cm^2) than dentin conditioned with Fuji conditioner ($\theta = 30^\circ$, WA = 69 erg/cm^2). The experimental cement also showed higher but not statistically significant values for shear bond strength to dentin (7.8 MPa), when compared to control group (7.3 MPa). It was concluded that NVP containing polyelectrolytes are better dentin conditioners than the commercially available dentin conditioner (Fuji Cavity Conditioner, GC). NVP containing terpolymers can enhance the surface properties of GICs and also increase their bond strength to the dentin.

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1. Introduction

Glass-ionomer cements (GICs) have been successfully used as a dental restorative material since their invention by Wilson and Kent in early 1970 [1,2]. GICs are well-known for their unique properties such as direct adhesion to tooth structure and base metals [1–3], anticariogenic properties due to release of fluoride [3], minimized microleakage at the tooth–enamel interface due to low shrinkage, thermal compatibility with tooth enamel and dentin because of low coefficient of thermal expansion similar to that of tooth structure [4,5], biological compatibility, and low cytotoxicity [6,7]. Besides their advantages they have disadvantages compared to composite resins and resin modified glass ionomer cements (RMGICs) such as brittleness. Significant improvements have been made since the invention of GICs and further improvements are required in order to enhance the physical properties of glass ionomer cements [1–8].

One of the most important characteristics of GICs is their adhesion to tooth structure and their relatively good surface wetting properties as compared to hydrophobic nature of composite resins. The exact mechanism of adhesion has not been established for glass ionomer dental cements. However, studies have shown that adhesion occurs between glass ionomer cements and collagen in which pendant COO^- groups of collagen can be cross-linked to the GIC matrix by Ca^{2+} from the glass [9,10]. It has been indicated that polyacrylic acid (PAA) chains are absorbed on to collagen through hydrogen bonding and no primary bond is necessary for the formation of poly salt bridges.

Polysalt bridge formation is the mechanism of adhesion of polyelectrolyte cement to hydroxyapatite, which is also applied for the hydroxyapatite component of dentin [11,12]. Wilson et al. (1983) reported that during adsorption, polyacrylate ions entered the surface of hydroxyapatite by displacing and replacing surface phosphate groups [13]. This is the mechanism of adhesion of polyelectrolyte cement to hydroxyapatite and to the hydroxyapatite component of dentin. Carboxylic acid groups (COO^-) react with the hydroxyapatite of enamel and form ionic bonds, calcium and phosphate are displaced from the enamel. The result is the formation of an intermediate layer between cement and surface of enamel, which is rich in calcium and phosphate. Negm et al., 1982 in their studies reported that the composition of this layer is different from the composition of enamel, dentin, and glass ionomer cement [14]. It has been confirmed by IR studies that strong ionic bonds form between COO^- groups of the poly acrylic acid and calcium ions of the hydroxyapatite in the enamel and dentin structures. Further investigations showed that the initial adhesion between the glass ionomer cement and tooth is due to hydrogen bondings by free carboxyl groups which are presented in the fresh paste. As the cement matures and becomes harder the hydrogen bonds are progressively replaced by ionic bonds [15,16].

NVP (N-vinylpyrrolidone) has the ability to be polymerized with free-radical initiators, affording a non-ionic, water soluble, synthetic polymer. NVP polymers have wide range of applications in medicine because of the hydrophilic and non-toxic nature of the NVP molecule. NVP polymers are easily soluble in water due to some degree of compensation between the strong hydrogen bonding capability, specifically hydrogen bonding between the cyclic amide group and water protons, and hydrophobic interactions that exist between water and the NVP polymer backbone and cyclic methylene groups. In addition, NVP containing polymers have the ability to absorb water [17,18], where the absorption center is the amide group. In contrast to water-soluble poly(acrylic acid) or poly(methacrylic acid), NVP polymer does not precipitate from aqueous solution, without salts, even upon heating to 100 °C [17]. According to previously mentioned properties of NVP, Culbertson (2001) has reported that NVP is a good comonomer to incorporate in polyelectrolytes glass-ionomer formulations [18].

The ability of NVP containing polymers to enhance the properties of glass ionomer cements, is probably due to their ability to form hydrogen bonds leading to enhanced surface properties, adhesion and bond strength to dentin. Various reports by Culbertson, Yamazaki et al., Xie et al. [18–20] and more recently by Moshaverinia et al., 2007 [21] have suggested that NVP modified polyacids can significantly enhance the mechanical strength of glass ionomer dental cements.

It is expected that the presence of NVP molecules in the GIC polyacid composition, has the ability to enhance the surface properties (wettability), surface free energy and bond strength of the resulting material. Hence, the main aim of this study has been to synthesize NVP modified copolymer of acrylic acid and to assess the effect of this modification on the surface properties (contact angle and work of adhesion) and bond strength to dentin compared to conventional glass ionomer cements.

2. Materials and methods

2.1. *Materials*

The glass powders, all liquids and dentin conditioner (GC) 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 synthesis. Commercially available dentin conditioner (Fuji Cavity Conditioner, GC) was used as received from GC International, Tokyo, Japan.

2.2. *Methods*

2.2.1. *Synthesis of NVP containing polymers*

Experimental procedure employed in this study is the method reported by Crisp et al., 1980, Yamazaki et al., 2005 and more recently by Moshaverinia et al. [19,22,31]. 0.4 moles (27.43 mL) of acrylic acid (density of 1.05 g cm^{-3}), 0.05 mole (6.5 g) of itaconic acid and 0.05 moles (5.31 mL) of NVP (density of 1.045 g cm^{-3}) were measured and dissolved in distilled water. Ammonium persulfate (2 wt%) was used as an initiator for the polymerization reaction. The molar ratio was kept at 8:1:1 for the final product AA–IA–NVP terpolymer. The reaction mixture