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Novel wear resistant and low toxicity dental obturation materials

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Abstract

Preparation of new polymer (polyurethane)+ceramic nanohybrids for filling dental cavities is reported. Short curing times (below 10 min) are achieved. Some tribological properties are determined and compared with those of commercial dental materials. The new materials provide scratch resistance as well as good adhesion to dentin and enamel, low toxicity and high chemical resistance; additionally, they can be easily pigmented to match the teeth color. Microscratch testing which provides the instantaneous penetration depth, the residual depth after scratch healing and the percentage recovery turns out to be a useful tool for differentiation of quality between dental obturation materials.

Keywords: Nanohybrid; Dental material; Cavities; Adhesion; Microscratch testing

1. Introduction

Caries constitute the most widely spread disease since they affect over 95% of the total human population at some stage of their lives. Thus, there is an important problem in dentistry and an important challenge to public health worldwide [1–3]. Caries is a local demineralization on the tooth surface; the demineralized tissue must be removed, producing a cavity that requires to be filled with an appropriated material. A great deal of effort has been dedicated to prevent caries and to design appropriated obturation materials for repairing cavities. Accordingly, a wide variety of materials have been designed for these purposes [4–6].

Obturation materials have to fulfill several requirements in order to be used for dental applications: good adhesion to the substrate (dentine and/or enamel) to avoid micro-filtration and bacteria growth; good spatial stability to avoid dimensional contraction of the material which results in the creation of empty spaces and consequently leaks; high resistance to abrasion to support the high shear stresses produced during chewing and brushing; low toxicity so as to be used orally in humans; high chemical resistance to support acid conditions with pH values as low as 2.5 (for short periods of time); capacity to receive pigments in order to match the color of the obturation material with the natural color of the dental enamel; short curing time to ensure the material is in normal operation after a few minutes after it was implanted into the mouth [7,8].

Like all bones, teeth are composites of hydroxyapatite (HAp) and an organic matrix [9]. Collagen is the main component of that matrix. Thus, materials which can fulfill the conditions formulated above are ceramics, ceramic-based composites [10] or hybrids. The last category escapes the traditional

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classification of materials into inorganic or organic; it includes nanohybrids in which one of the phases consists of dispersed particles with the diameter up to 100 nm [11]. Strictly speaking, the bone is also a nanohybrid. The presence of HAp in the teeth creates one more requirement for dental obturation materials; if they react with the OH groups of HAp forming chemical bonds with the bone substrate, experience shows that leakage is prevented.

Given the importance of the problem stated in the very beginning, the work of our group went into two directions. One is improvement of the methods of the creation of HAp [12–14]. Another direction is the creation of new dental materials [15,16]. We have tested some of such materials and also bare teeth; in the process we have discovered healing after scratching a bare tooth surface with a diamond indenter [15]. The bottom of the scratch groove goes up, a consequence of the bone viscoelasticity. Viscoelasticity in polymer-containing materials has been extensively discussed in the literature [17,18]. Bone viscoelasticity had been known to manifest itself in mechanical properties [9,19] but thus has been found in a tribological property also [15]. The present work is a continuation of that reported in [15] and [16] but using a different polymer.

2. Choice of the material

Various groups around the world work on obturation materials [20,21]. Generally, such research materials are not easily accessible, but commercially used materials are. Therefore, we shall compare our new materials developed in this work with several commercial ones. In our previous work on the obturation materials [15,16] we have used several types of polymers. Now we have focused on polyurethanes (PUs) since their isocyanate groups react with all OH groups, from the resin and HAp. Moreover, we expected good scratch resistance. Another advantage is that the reactants (NCO and OH groups) react to produce the urethane groups and nothing else [22–25]:

$$\mathrm{R-N{=}C{=}O + R'-OH \rightarrow R-NH-(C{=}O)-O-R'} \qquad (1)$$

Thus, no reaction products need to be removed or eliminated and contraction effects during the polymerization are minimal. A straightforward reaction with the OH groups of the dentine or enamel should occur.

It is well known that this kind of polymer accepts well several kinds of pigments (reactive or passive); the only requirement is that they have to be of low toxicity. Since the NCO groups react with the OH groups (from HAp, resin and/or moisture) the polymer itself is, when all NCO groups are consumed, chemically inert; this means that the only aspect that has to be taken into account is the solvent. The solvent has, apart from being a good solvent for the resin, to be of low toxicity; *N*-methyl-2-pyrrolidone fulfills this requirement [26,27].

Then, the objective of the present work was to design a new obturation material using the appropriate polyurethane matrix that should be able to absorb large quantities of ceramic particles. The latter were expected to provide good wear resistance and also support high shear stresses during the chewing and brushing process [28,29].

As noted above, we needed a reference to evaluate the performance of our new nanohybrid materials. Several new generation commercial products have been used for the purpose: Amelogen 1 and Amelogen 2 (Ultradent, South Jordan, Utah, USA), Intens (Vivadent, Saint-Jorioz, France), ALK.225W (Laegemiddelstyrelsen, Kopenhagen) and Charisma (Kulzer, Hanau, Germany).

3. Experimental

3.1. Polymer synthesis

The polyurethane matrix used to prepare the obturation material was a polyester polyurethane synthesized using a polyol resin (2000 M from Bayer, Leverkusen, Germany) and dimethylol propionic acid (DMPA, from Aldrich Co., USA) in the proportion 10:1 resin:DMPA by volume. As solvent we have used *N*-methyl-2-pyrrolidone for reasons discussed in Section 2; the solvent concentration applied to have the desired consistency to fill cavities was ≈20 vol.%. The resin, DMPA and the solvent were mixed together in a round bottom flask equipped with temperature monitoring, a stirrer and a water-cooled condenser. The mixture was heated to 85 °C and di-cyclo-hexyl-methane-di-isocyanate (DCHMDI) (Bayer) was added dropwise with strong agitation in the ratio 4:1 resin:DCHMDI by volume. The mixture was kept at 85 °C for 4 h; the temperature has to be below 90 °C to prevent gelling and yellowing. Finally, the system was cooled down to room temperature.

Our polyurethane was prepared using DMPA because this compound is both a glycol and a carboxylic acid; thus, the two primary hydroxyl groups of DMPA can react with the NCO groups of the diisocyanate to form an urethane polymer. At the same time, the tertiary hydroxyls in the carboxylic groups can easily be introduced into the backbones of the polymer chains; there is no need to block these hydroxyl groups to prevent their reaction. An advantage here is that a resin formulated with DMPA can be solubilized or dispersed in water by neutralization of the unreacted carboxyl groups with ammonia, amines or other bases.

3.2. Nanohybrid preparation

Several of the samples were prepared using different types of ceramic particles: silica (Degussa, Hanau, Germany) with 16 nm diameter at the concentration of 25 wt.%; and alumina (Cabot, Billerica, MA, USA) with 4 μm diameter at the concentration of 40 wt.%. The alumina particles had previously modified surfaces in order to reduce the original OH groups concentration to a certain level to make the particles oleophilic, but leaving some OH groups to anchor the particles with the resin through the reaction with the isocyanate. This reaction can be schematically represented as

$$\begin{aligned}&\mathrm{(particle)-OH + Cl-M{\equiv}(CH_2-\ldots CH_3)_3 \rightarrow (particle)-O-}\\&\qquad\mathrm{{\equiv}(CH_2-\ldots CH_3)_3 + HCl}\end{aligned} \qquad (2)$$