

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.

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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]:



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, Copenhagen) and Charisma (Kulzer, Hanau, Germany).

3. Experimental

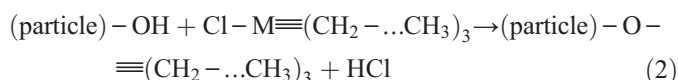
3.1. Polymer synthesis

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 μ m 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



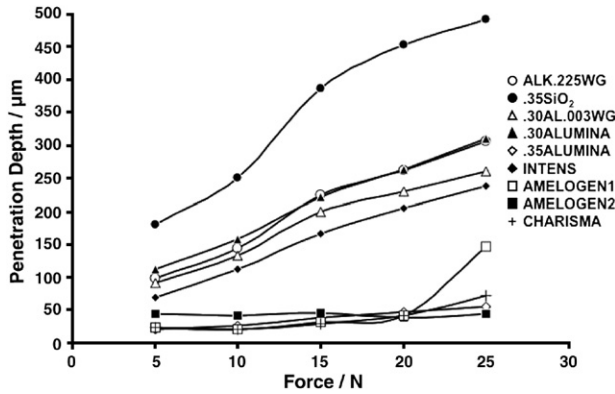


Fig. 1. Plot of the penetration depth R_p as a function of the applied force.

so that some hydrophilic OH groups now become parts of oleophilic end groups ending with CH_3 . Because the size of the silica particles is considerably smaller than that of the alumina, the surface area is considerably higher in the former case and it is not possible to incorporate as high concentrations of silica particles into the resin as in the case of alumina particles.

The nanohybrid materials were prepared as follows: once the particles have been chemically modified, they were added slowly to the polyurethane, stirring with a high shear rate for 30 min until the final concentrations were reached. At these large contents of ceramic particles, the composite increases significantly its viscosity, producing a moldable paste. The final viscosity of this paste was adjusted changing the solvent content; the curing time for these systems was less than 10 min. The paste was molded using a Teflon contained with the inner dimensions: $1.5 \times 1.0 \times 0.3$ cm, and kept there for 30 min before removal. An additional sample was prepared mixing the alumina particles with 0.3 wt.% of an experimental product called white graphite (WG).

The commercial samples named at the end of Section 2 were placed also in the Teflon mold and cured with a UV lamp for 40 s according to the manufacturer's specifications. Four samples of each type were prepared for reproducibility purposes.

4. Tribology results

A survey of tribology of materials containing polymers is available [30]. Our scratch resistance determination experiments were performed in a microscratch tester from CSEM, Neuchatel, Switzerland, with their Version 2.3 software. Scratches of 5.00 mm length were performed using a diamond tip with a 200 μm diameter. Several constant loads were applied: 5, 10, 15, 20 and 25 N. The procedure in each test was the same as described before [31–33]. Briefly, a pre-search is performed to determine the texture (topology) of the surface at a very low load (0.03 N). The scratching is performed to determine the penetration depth R_p at a constant load such as 5.0 N. Since the experiments have shown that healing occurs within 3 min or so [31], after 5 min the viscoelastic recovery depth R_h is determined using again a very low load.

The experimental values allow us to calculate the percentage recovery ϕ defined [31] as:

$$\phi = (R_p - R_h) \cdot 100\% / R_p \quad (3)$$

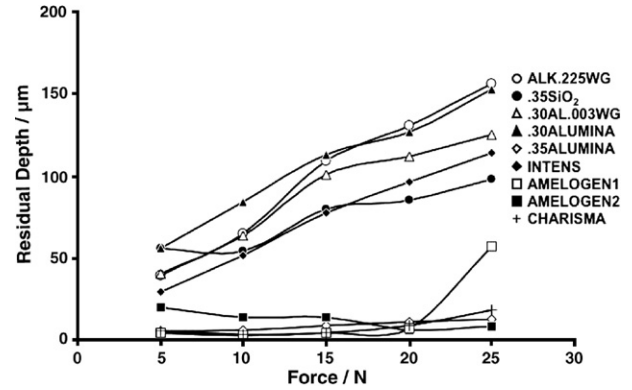


Fig. 2. Plot of the residual depth R_h as a function of the applied force.

Each of the results reported below represents an average for a series of identical samples (between 4 and 9, in most cases 6 samples). Before presenting the results let us introduce some symbols to define the samples: .30 alumina = our PU containing 30 wt.% Al_2O_3 ; similarly .35 alumina = our PU with 35 wt.% Al_2O_3 ; SiO_2 = PU with 35 wt.% SiO_2 ; WG = PU containing 30 wt.% Al_2O_3 and 0.3 wt.% white graphite; the other symbols correspond to the commercial dental materials named above.

Fig. 1 shows the penetration depth R_p plotted as a function of the applied force. As can be seen, our sample with 35 wt.% SiO_2 is penetrated the most deeply, this even during scratching even at low applied forces. Samples loaded with alumina and WG behave in a similar way but with significantly less penetration. The best samples are Charisma, Amelogen 1 (except at forces above 20 N), Amelogen 2 and our .35 alumina. Thus, more alumina lowers the penetration depth.

More important for the user (= owner of a set of teeth) is the residual depth displayed for the same materials in Fig. 2, also here as a function of the applied force. In this case, the samples containing white graphite particles exhibit poor behavior, particularly so at high forces, followed by .30 alumina. WG is a solid lubricant, in fact the name reflects its potential use similar to graphite, and apparently the WG particles are relatively soft. Our .35 alumina and three commercial samples (Amelogen 1 and 2, Charisma) are the best, again except for Amelogen 1 at forces exceeding 20 N. Thus, also in healing more alumina results in lower depth.

The percentage recovery defined by Eq. (3) is another important variable and is plotted in Fig. 3. If we roughly divide the materials into two groups, then the group with higher recovery includes Amelogen 1,

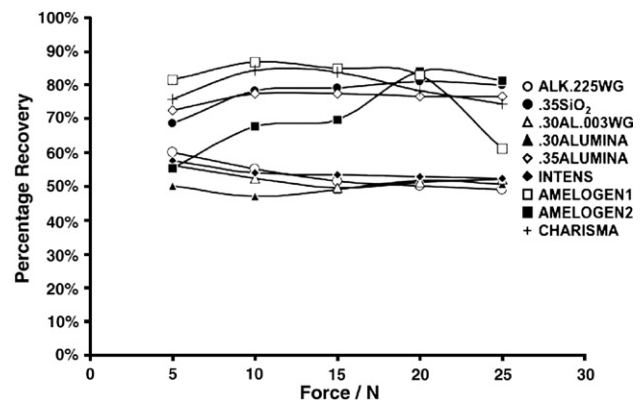


Fig. 3. Plot of the percentage recovery ϕ (Eq. (3)) as a function of the applied force.

Charisma, and our materials with 35% Al₂O₃ and with 35% SiO₂. Amelogen 2 seems, between the upper and the lower groups, to have good recovery at lower loads and worsening above 20 N, while Amelogen 1 behaves in the opposite way. Adding white graphite improves somewhat the recovery of our material with 30% Al₂O₃, apparently the softness of the white graphite helps scratch healing of the surrounding polymer chains. We recall here the healing of macroscopic cracks; as explained by Wool [34], crack healing occurs by diffusion of chains across the interface.

5. Concluding remarks

A literature review suggests that evaluation of performance in service of dental obturation materials is difficult, with various manufacturers typically claiming great advantages of their respective products. We find that the resistance to scratching and also the extent of recovery (healing) after scratch determined with the CSEM microscratch tester (MST) we have used constitute objective measures of expected service performance of dental obturation materials. This is particularly true since MST allows also the repetition of scratching along the same groove and thus determines sliding wear [35,32,33]. The depth accuracy determination in the MST, namely ± 7.5 nm, is some orders of magnitude more accurate than the scratch depths our materials have.

Our new materials fulfill important conditions: low toxicity, high chemical resistance, and they can be easily pigmented to match the teeth color. As for the scratching results, it turns out that the addition of white graphite to the nanohybrid containing alumina particles results in deeper cracks but somewhat better scratch recovery. We have explained this by the softness of the WG nanosize particles. Increasing the concentration of alumina in our nanohybrids improves scratch resistance, while the dependence of recovery on the load applied is insignificant. Our new PU polymer is clearly promising and has advantages of short curing time, low toxicity, chemical resistance and ease of coloration. In the future we intend to use the same polyurethane but with further variation of the nanopowder nature and more detailed exploration of the effects of concentration of the nanoparticles.

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