Characterization of novel dental obturation materials

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Abrasion behavior of new nanohybrid polymer+ceramic dental materials designed for filling dental cavities is reported. The polymer matrix is a polyurethane while the dispersed phases include particles of silica and alumina with the diameters below 100 nm. Several commercial obturation materials are investigated by the same technique. The authors' new nanohybrids show clearly superior resistance to abrasion wear – in one case some 20 times better than a commercial sample. Moreover, the new materials exhibit low toxicity, short curing times (<10 min), good dimensional stability (low contraction), high chemical resistance and good pigmentation capacity and they are easy to prepare and show good adhesion to the substrate (dentine or enamel).

Introduction

The present paper begins with a general perspective on the results reported below. As noted by Deng and Shalaby, polymeric materials have been used in dentistry already in the middle of the nineteenth century.[1] Thus, in 1848 gutta-percha was used for dental impressions and today still is a useful material for root canal fillings. However, as argued by Castaño and one of the authors, in many instances when one class of materials was used in the past, polymer+ceramic or other composites and hybrids are now seen.[2] These include nanohybrids in which one of the phases consists of dispersed particles with the diameter up to 100 nm (Ref. 3). Nanohybrids can be particularly useful in applications in which tribological properties are important. Polymeric materials are known to have poorer tribological properties than metals or ceramics, although methods of improvement of polymer tribology exist.[4,5] Polymer+ceramic systems also have the advantage of an unusually wide range of properties and component sizes, from obturation in dentistry through prostheses to construction materials.[2,6–10]

Focusing now on dental obturation materials based on polymers, addition of ceramic particles should improve tribological properties.[11–13] As argued by Zweifel, impact strength is typically improved at the same time.[14] Moreover and particularly important in applications in dentistry, ceramic particles improve dimensional stability by reducing warpage and shrinkage. Thus, the selected polymeric resin has to be able to accept large amounts of ceramic particles; this means that the resin should 'wet' the surface of the nanoparticles to incorporate them into the polymeric matrix. To achieve this goal, the ceramic particles have to have the appropriated chemical groups to allow a good dispersion into the organic matrix.[2]

Apart from tribological properties such as investigated by the authors, dental materials should fulfill other requirements:[15–17] good biocompatibility, high chemical resistance, high dimensional stability, good adhesion to the substrate (dentine or enamel) to avoid microfiltration (leaks), low toxicity, short curing time, easiness in preparation, gloss and the possibility to be pigmented to match the color with the substrate. Pigments are colored particles insoluble under processing conditions, with the primary particle size between 0·01 and 1 μm (Ref. 14). They often improve the stability with respect to UV and visible radiation, as well as reduce the resulting elongation if injection molding is applied.[14] Thus, pigments are in general allies for dental materials in service.

Relation to previous work

Several so called high tech materials have been designed for use as filling materials in dentistry.[18,19] All are ceramic modified polymeric materials because of the advantageous combination of properties already noted above and also discussed by Saenz and his colleagues.[6]

In the previous work several dental obturation materials have been investigated.[20,21] In the work reported below a new series of such materials have been described. The authors investigated their behavior under abrasion, a property not studied earlier while paying more attention to scratch resistance determination.[20–22] At present abrasion behavior of several widely used commercial obturation materials is also determined. As

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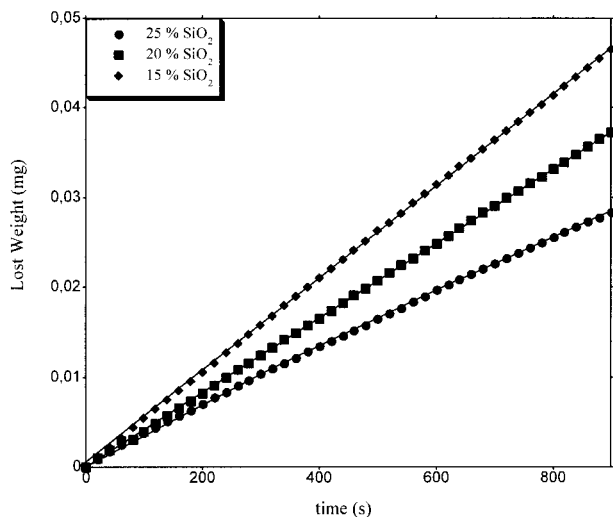
1 Plot of weight loss as function of time for silica based samples

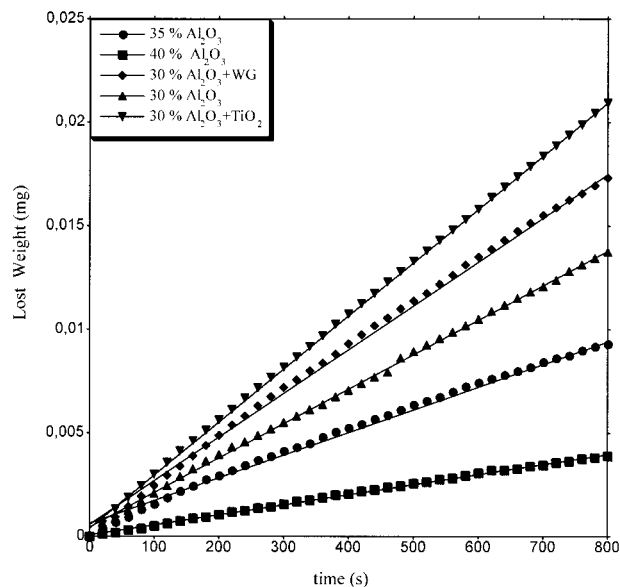**2 Plot of weight loss as function of time for alumina based samples**

discussed by Petraikiene and Pekarskas, other experiments such as determination of surface roughness are not substitutes for abrasion, while abrasion of teeth occurs as a result of interaction with toothbrush and dentrifice.[23,24]

Experimental

Synthesizing the new polymer for the obturation nanohybrid, the authors have largely followed a procedure described by Jang and co-workers.[25] Briefly, a polyurethane based material (PU) has been created. The selected resin was a commercial polyol resin (2000 M, Bayer, Leverkusen, Germany); n-methyl 2 pyrrolidone was used as the solvent and the catalyst was polyisocyanate added in the ratio 4:1 (resin:catalyst). Thus, a polyester PU with low toxicity was produced. It has good adhesion to a considerable number of different substrates, particularly so on surfaces containing OH groups, since the isocyanate reacts with the OH groups, including those of the substrate, to produce the polyurethane. This is important for the application since the main component of the teeth is hydroxyapatite (HAp) which contains 2 OH groups in each repetitive unit.[26]

Two types of ceramic particles were added to the resin: the first was alumina (Cabot, Billerica, MA, USA) with 4 μm in diameter, at concentrations 30, 35 and 40 wt-%; these particles had surfaces previously modified in order to disperse them well in the resin. It is necessary to reduce the number of original OH groups to a certain level to make the particles oleophilic (i.e. hydrophobic), leaving enough OH groups just to anchor the particles with the resin through the reaction with the isocyanate. Once the particles have been chemically modified, they are added slowly to the resin, stirring at a high shear rate.

Silica particles (Degussa, Hanau, Germany) with 16 nm in diameter were also used. Because the size of the silica particles is considerably smaller than the alumina, and the surface area is considerably higher, it is not possible to incorporate high concentrations of silica particles into the resin. Silica particles were added at concentrations 15, 20 and 25 wt-% under the same conditions as for alumina.

At these ceramic concentrations, both systems were moldable pastes, with curing times at room temperatures of ≈10 min. The curing time is the key characteristic of the crosslinking process; the extent of conversion can be predicted as a function of both temperature and time.[27] The consistency of the paste can be modified by adding somewhat more solvent. The paste was molded using a Teflon container with inner dimensions $1.5 \times 1.0 \times 0.3$ cm, and kept there for 30 min before demolding. Commercial samples were placed in a Teflon mold and cured with a UV lamp for 40 s according to the manufacturer specifications.

Abrasion results

The abrasion results were obtained using the Taber method according to the appropriate ASTM standard (D-1242). Other authors have used this method for dental materials before.[24] The abrasive test was performed using a Fandeli F-120 sand paper in dry conditions; the machine was operated at 250 rev min^{-1} with the load of 10.0 g. The weight loss was determined every 20 s with the accuracy of $\pm 1.0 \times 10^{-5}$ g. Additionally, after each weight loss determination, the sample surface was wiped up with a dry soft cloth, and the sand paper was also cleaned with a soft brush in order to remove the dust particles. All experiments were performed at room temperature of 25°C. Five sets of abrasion experiments were performed for each sample to obtain averages.

Figure 1 shows the results for the abrasion experiments in silica based samples for all concentrations of silica. The weight loss is plotted as a function of the abrasion time. It is seen that the rate of the material removal decreases along with the increasing concentration of silica; the material becomes more wear resistant. The rate of the mass removal, given by the slopes of the lines in the diagram, is 51.6, 43.6 and 33.6 μg s^{-1} for silica concentrations of 15, 20 and 25 wt-% respectively.

In the case of alumina based materials, the abrasion results are shown in Fig. 2. Here it is interesting to note that the addition of white graphite (WG) or TiO$_2$ in
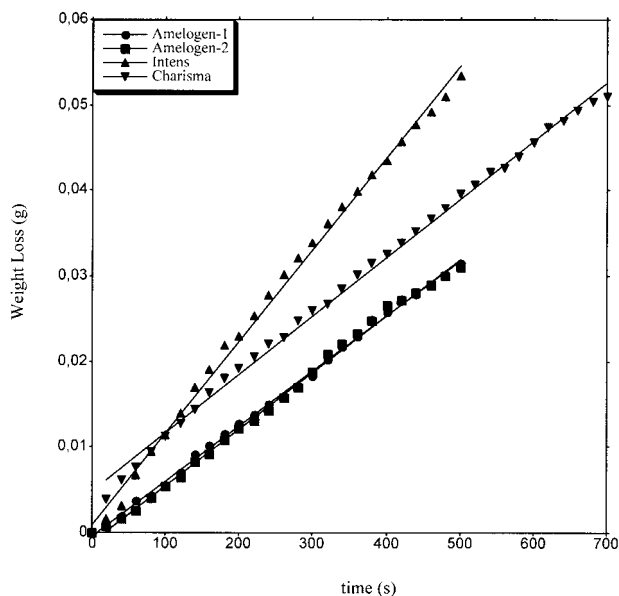
3 Plot of weight loss as function of time for commercial samples

small proportions (1 wt-%) produces a negative effect on the abrasion resistance: the worse behavior for this type of samples corresponds to those added with WG and TiO_2; for these samples the slopes are 24·1 and 26·7 $\mu g\ s^{-1}$. In the case of the other alumina based materials the slopes were 19·8, 15·2 and 5·0 $\mu g\ s^{-1}$ for samples containing 30, 35 and 40% alumina. As can be noticed, a small percentage of WG or TiO_2 indeed deteriorates the abrasion performance of the alumina based material; this effect has to be taken into account when some pigments or other additives are added to the hybrid composite. The results for the material containing WG can be explained by softness of the additive. In fact, the name of this experimental material comes from the fact that it can be a substitute of graphite when a solid lubricant is useful.

Figure 3 shows results of abrasion experiments for several widely used commercial samples: Amelogen 1 and Amelogen 2 (Ultradent, South Jordan, Utah, USA), Intens (Vivadent, Saint-Jorioz, France) and Charisma (Kulzer, Hanau, Germany).

It is seen in Fig. 3 that the commercial samples loose weight rapidly. The rate of the weight lost is 64·4, 65·9, 68·5 and 107·3 $\mu g\ s^{-1}$ respectively for Amelogen 1, Amelogen 2, Charisma and Intens. The numbers are much higher than those for the silica and alumina based nanohybrids.

To get a complete picture, the rate of weight loss in the abrasion experiments for all samples investigated is presented as a block diagram in Fig. 4. Consider the extreme cases – the nanohybrid containing 40% alumina and Intens. The latter looses weight some 2100% faster than the former.

Concluding remarks

Consider now the use of a dental material in service somewhat more in detail. As briefly noted above, abrasion resistance is an important property. The obturation material is subjected to a practically continuous abrasion process, not only during the chewing but also when the teeth are in contact with each other.
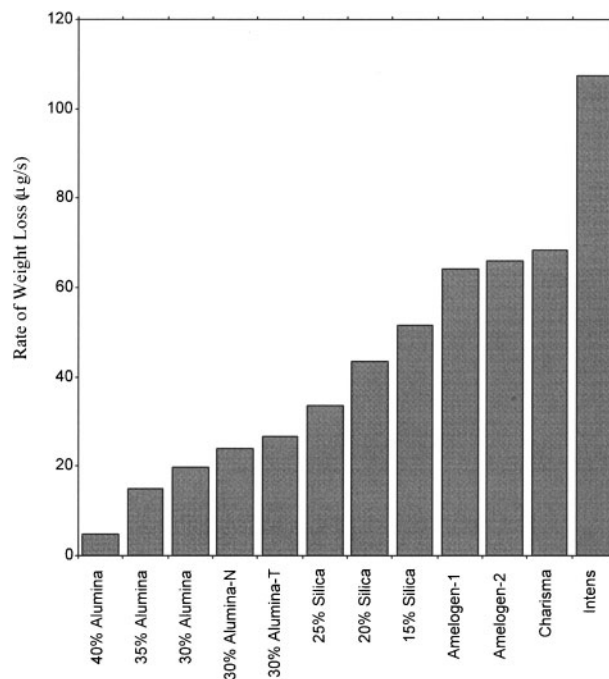
4 Rate of weight loss for all samples, $\mu g\ s^{-1}$

Additionally, during the brushing process, teeth are subjected to an intense abrasion process since the toothpaste is a highly abrasive material. The dental enamel is regenerated in a standard biochemical process taking place in the human body. Since this does not happen with the obturation material, such a material has to 'survive' as much as possible the abrasion process. This is one to the most important requirements for an obturation material.

In a separate paper the authors analyze results of scratch resistance experiments on a similar group of materials, including the same commercial materials.[28] The technique has been described before.[22,29,30] One of the properties obtained is the residual depth R_h which remains after healing of the scratch groove created by the passage of a diamond indenter. In this case the same commercial samples show low values of R_h, along with the nanohybrids containing Al_2O_3. The samples containing silica have deeper residual scratches, as do those containing WG. Thus, abrasion wear tests probe a different kind of material behavior than the scratch resistance tests.

Acknowledgements

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