Dental Materials (2005) **21**, 145–155

dental materials

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Barium and strontium leaching from aged glass particle/resin matrix dental composites

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Received 28 August 2003; received in revised form 16 January 2004; accepted 19 February 2004

KEYWORDS
Dental material; Composite resin; Leaching; Barium; Strontium; Wavelength dispersive spectroscopy; Energy dispersive spectroscopy; Aging

Summary *Objectives*. This study characterizes the loss of Ba and Sr from glass particle/resin-matrix dental composites during simulated aging.

Methods. X-ray wavelength dispersive spectrometry and secondary ion mass spectrometry were used to analyze the Ba and Sr content from the surfaces of three commercial dental composites after aging for 4 and 8 months in humid air, artificial saliva, water, and 50% ethanol.

Results. Aging in artificial saliva caused the greatest leaching of Ba or Sr for all the specimens, compared with either lesser or no leaching for aging in ethanol and water. Differences in leaching were observed between the different composites. Composites aged in artificial saliva also picked up elements in the saliva solution and displayed crystallite formation on the surface. Samples aged in ethanol displayed cracking which was not observed for water or artificial saliva.

Significance. Dental composites display ion leaching from their surfaces over periods of four to eight months. Three mechanisms are proposed to explain differences in leaching for the various composites and aging solutions. Surface mineralization is also proposed to occur as a self-repair mechanism in artificial saliva.

Introduction

Dental composites consisting of a polymerizable resin matrix, reinforcing glass particle fillers, and silane coupling agents, are becoming more popular in modern dentistry.[1] These glass particle/resin matrix composites have good aesthetic properties and strength, making them the most widely used materials for restorations of anterior teeth.[2] The polymerizable resin matrix typically contains one or more monomers such as ethylene glycol dimethacrylate (Bis-GMA), urethane dimethacrylate (UDMA) and triethylene glycol dimethacrylate (TEGDMA). Polymerization of the resin matrix may be chemically initiated in 'self cure' composites, light activated, or a combination of both. Various inorganic materials such as glass fillers are utilized as fine or micro-fine particles and serve as reinforcing components. These fillers make up the bulk of the composites and they vary in size and composition among different composites. In addition to silica (SiO_2), these composites also incorporate barium (Ba) and strontium (Sr) glasses, which add

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doi:10.1016/j.dental.2004.02.009

X-ray opacity to facilitate radiological monitoring of the composite in vivo.

During exposure to the oral environment, dental composites are subjected to material property changes due to degradation and erosion over time. Problems include shrinkage, which could result in fracturing and lead to leakage as well as the leaching of water soluble components. These changes may result from chemical breakdown by hydrolysis,[3] chemical breakdown by stress induced effects associated with swelling and applied stress,[4] chemical composition changes by leaching,[4] precipitation and swelling phenomena to produce voids and cracks, leaching of the interface,[5] and loss of strength due to corrosion.[6]

Different analytical techniques have been used to analyze the elemental composition changes of the composites during their degradation in the oral environment. A change in weight of dental composites[7] indicated that the source of leachable components was the uncured resin at the bottom of the specimens. Studies on the absorption of water and the leaching of inorganic ions from several commercial dental composites analyzed the elemental composition of the inorganic filler composition in the aqueous leachate by optical emission spectroscopy.[8] The results showed that silicon was the major element in all the fillers except one, which had both silicon and strontium as major elements. Atomic absorption and inductively coupled plasma spectroscopies are both effective techniques[9] for analyzing the leached components into the aging solution. These studies generally found that the elements prevalent at the surface of the composite were those predominantly released into the leachate solution. However, analysis of the leachate does not describe from which portion of the composite leaching occurs.

The present study evaluated elemental and structural changes on the surface and cross-sections of several dental composites after aging for several months in different solutions that simulate the oral environment. Leaching and aging propagate from the surface and cracks of a dental composite, so any composition change on the surface will eventually affect the bulk properties of dental composites. It follows that elemental surface analysis can be applied to the degradation of dental composites in the oral environment. Wavelength X-ray dispersive spectroscopy (WDS), secondary ion mass spectroscopy (SIMS), energy dispersive spectrometry (EDS), and secondary electron microscopy (SEM) are surface analysis techniques used here to study aging at the surface of these dental composites. Quantification of WDS is achieved by the use of standards combined with matrix correction factors. The penetration depth of the incident electron beam defines the analysis depth of WDS, which is much deeper than the instantaneous analysis depth of SIMS. SIMS has been used in the analysis of dental hard tissue for over two decades.[10] However, it is difficult to obtain reproducible and accurate quantitative information from SIMS due to fluctuations in ionization efficiency and ion collection efficiency.[11] Although absolute quantification of an element remains difficult, a relative quantitative approach is possible by using C^+ (m/z 12) as an internal reference.[12] The dynamic internal standard SIMS method is applied here by employing C^+ (m/z 12) and CH_3CO^+ (m/z 43) as internal reference ions due to their ubiquitous appearance in spectra of the embedding resin. Quantification of the SIMS data is completed by preparation of specific standards of dental composites with known concentrations of Sr and Ba. Use of the WDS and SIMS methods for the analysis of dental composites are contrasted with each other and other surface analysis methods.

Materials and methods

Three dental composites with different glass fillers, resins and composition were evaluated: a hybrid filler (Micronew, Bisco Inc., Schaumburg, IL, USA), a microfill (Renew, Bisco), and a composite resin cement (Choice, Bisco). The glass filler particles varied in size and distribution among the three different dental composites shown in Table 1, whose glass filler and resin composition are described in Table 2. Micronew and Choice specimens contain Sr but no Ba, while Renew contains Ba but no Sr. Three series of four calibration samples were prepared for SIMS experiments, with their filler and resin compositions as shown in Table 3. All the specimens were polished with 320 grit silicon carbide grinding paper and then cleaned ultrasonicly in water for five minutes. Specimens were aged in sealed polyethylene containers with 200 ml of solution at 37 °C in a water bath for 4 and 8 months. The aging media were air, distilled water, 50% ethanol in water, and artificial saliva. The artificial saliva was an aqueous solution prepared with 0.4 g/l NaCl, 0.4 g/l KCl, 0.795 g/l $CaClPO_4 \cdot 2H_2O$, 0.78 g/l $NaH_2PO_4 \cdot 2H_2O$, 0.005 g/l $Na_2S \cdot 9H_2O$, and 1.0 g/l $CO(NH_2)_2$.[13] Aging in humid air over a water bath at 37 °C was used as the baseline because it compensates for polymer or composite reorganization as well as some swelling due to water adsorption (as water is adsorbed into