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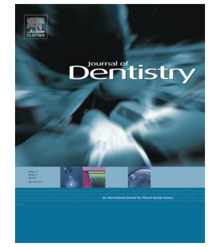

In vitro investigation of coupling-agent-free dental restorative composite based on nano-porous alumina fillers

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ABSTRACT

Objectives: The study aims at demonstrating the feasibility of a novel type of coupling-agent-free resin composite based on nano-porous fillers.
Methods: The fillers were obtained by ball-milling anodic alumina membranes. Composites were prepared with standard resin at maximum loading of 50% by weight. The resin matrix penetration into the pores was verified visually by scanning electron microscopy and mechanically by atomic force microscopy in force modulation mode. The dynamic flexural modulus at 1 Hz was measured by dynamic mechanical analysis. Silver nanoparticles were also synthesized in the pores and their release was investigated with inductive coupled plasma optical emission spectrometry.
Results: A storage modulus of 5 GPa was measured, similar to the ∼6 GPa ones of two coupling-agent-based dental restorative composites used for comparison, which is a promising starting point, additionally showing better one-year equivalent ageing as compared to both commercial materials. Loading the pores with silver nanoparticles was demonstrated as well as their subsequent release in a model system.
Significance: The alumina micro-particles with interconnected nano-pores allow mechanical interlocking between fillers and matrix without the need for chemical bonding. This material is also promising for being made bio-active, after pore filling with different agents.

1. Introduction

In conservative dentistry, during the last two decades the dental amalgams have been progressively replaced by resin composites,[1] due to both aesthetical and health reasons, the latter being recently stressed by the European Council that prohibited the use of mercury in dentistry.[2] However, in practice there is still no dental composite with the same clinical success of amalgam in posterior restorations.[3]

Most restorative composites have a modulus of 7–10 GPa, 30–50% lower than dentine (∼15 GPa),[4] to absorb part of operative stress and releave it from the dentine interface. The major limitation of dental composites is in stability,[5] showing a real average lifetime of 3–5 years as opposed to the 7–10 years of amalgams. Whereas recurrent caries if the major problem for all restorations,[6] another relevant issue of restorative composites is their chemical degradation occurring on absorption of water through the matrix and subsequent hydrolysis at the fillers.[7] In addition to decreasing the mechanical properties over time, degradation of the coupling agent releases in the patient's mouth chemical products such as methacrylic acid and formaldehyde among the others,[8] which are a mid-long term risk factor for health.

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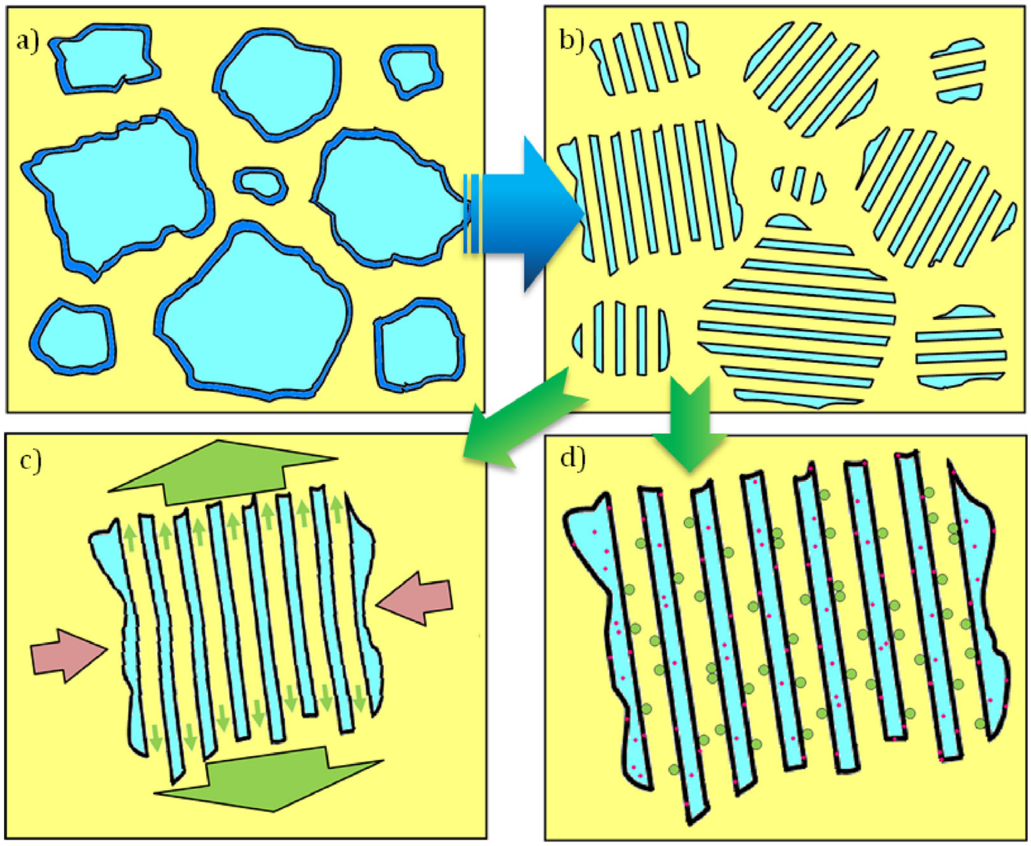

Fig. 1 – Sections of a filling composite: (a) traditional one, based on bulk fillers coated with bonding agent, and (b) experimental one, based on porous fillers; (c and d) single porous filler close-up, showing possible strengthening and bioactive action, respectively.

Porous particles have already found application in different tasks such as dentine hypersensitivity.[9] The idea of using porous fillers in dental restorative composites to improve bonding to resin dates back to the father of modern dentistry and inventor of Bis-GMA Dr. R.L. Bowen, who first proposed semi-porous glass fillers obtained by controlled phase separation of different glass components.[10] Recently,[11] meso-porous fillers (~4 nm diameter) from silica were fabricated in a non-surfactant templating route,[12] by using glucose molecules similar to a 'resist' to be degraded afterwards. Other authors obtained porous glass–ceramic fillers by chemical etching with hydrofluoric acid.[13,14] Whereas this process is simpler, it gives poor control on pore size and uniformity, and the pores are limited to the particle surface only, not allowing for passing-trough matrix fibres. Other works on porous fillers are based on bottom-up assembly of nanoparticles by sintering,[15–18] with porosity given by the remaining interstitial voids. While it should be considered that sintering for alumina is not easy, given the high required temperature (>1500 °C instead of e.g. ~800 °C for glass-based particles), a major issue of sintered porous fillers could be resin inter-penetration, and the welded nano-particles could remain a weak point of the fillers, likely weaker than a natively continuous porous material. Pores were obtained during synthesis of the material by Brostow et al.,[19] who fabricated ~5 mm diameter hydroxyapatite fillers with much larger pores (100–250 μm), which could rather be good for dental or orthopaedical implants to allow for vascularization, but showed reduced mechanical properties. Nanoporous alumina fillers for dental composites were also fabricated by Azevedo et al., via a special thermal treatment in the presence of mercury.[20] However, the authors still used these fillers with silane coupling-agent coating.

We describe a new nano-structured dental restorative composite that is coupling-agent-free same as amalgam but is promising in biocompatibility, thanks to the properties of the individual components. This material is built from a conventional dental resin and an innovative filler of anodic porous alumina (APA), also known to have high biocompatibility.[21,22] Our method is simple as no complex chemistry is required, is prone to industrial scale application based on the existing APA fabrication technology,[23] and is versatile given the APA pore size tunability in the range of 10–400 nm, with typical dispersion limited to ~±13%.[24]

The surface of our APA micro-particles with the presence of interconnected nano-pores allows mechanical interlocking fillers and matrix without the need for chemical bonding. Fig. 1b represents a section of the novel composite, as compared to a traditional one in Fig. 1a. The frame formed by the filler (Fig. 1c) promises to allow for high deformation with low risk of fracture at the filler-matrix interface. Additionally, the composite can be made bioactive by inserting into the nano-pores appropriate molecules or nanoparticles (Fig. 1d), enabling either antibacterial action (e.g. by silver particles or fluoride ions) or re-mineralization (e.g. by phosphate ions).