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Intraradicular dentine silanization by a new silicon-based endodontic sealer

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ABSTRACT

We synthesize a new silicon-based endodontic sealer that reacts at room and body temperature. The sealer is initially hydrophilic allowing flowing and filling every accessory tubule of the root canal and turns hydrophobic during polymerization. A hydrophobic surface of dentinal walls could limit fluid penetration by reversing capillary pressure and reducing the space between the intraradicular dentinal wall and the endodontic sealer by covalent bonds. For this purpose, we did a surface treatment on dentinal walls to expose hydroxyl groups usable for silanization by a covalent attachment between the tetraethyl orthosilictate (TEOS) and dentinal wall, transforming dentin walls in a hydrophobic surface; while TEOS also acts as cross-linking of the sealer which ensured a good sealing. The sealer polymerization was followed by Fourier transform infrared spectroscopy (FTIR), Quartz crystal microbalance (QCM-D), water contact angle (WCA) and rheological analysis. Radiopacity, resistance to dislodgment and dimensional alterations are in accordance with international standards (ISO standard 6876/2002). Working and setting time may be manipulated by varying TEOS and catalyst concentration. Zero filtration was obtained in the liquid filtration test.

1. Introduction

The aim of endodontic sealer in the root canal system is to prevent bacterial growth and fluids filtration, thus to prevent endodontic treatment failure. These are usually achieved by creating a monoblock system between the endodontic sealer and the wall of the intraradicular dentine. An ideal endodontic sealer should be the following: a non-irritant to tooth and periapical tissues, insoluble in tissue fluids, non-staining to the tooth, dimensionally stable, non-resorbable, no setting shrinkage, radiopaque, good mixing consistency, bactericidal active and soluble in a solvent (xylene) to aid removal of set material, if necessary. Additionally, it should exhibit biocompatibility, if not bioactivity, and maintain a hermetic sealing [1–3]. As is known, quite different chemical formulations have served as bases for root canal sealers whose main components are ZnO-eugenol, resin, glass ionomer, calcium hydroxide and silicone.

Polydimethylsiloxanes (PDMS) is a polymer that has elastic behavior, excellent biocompatibility, capability to seal materials of a various nature, resistance to high temperatures, to light degradation, to electricity, to weathering and to chemical attack. These exceptional characteristics make PDMS suitable for a wide range of applications such as building industries, medical applications, in sealants and adhesives compositions in fields as aerospace and electronics [4–7]. PDMS may produce very hydrophobic films with a good surface covering [8]. The hydrophobic property is useful in several fields: such as textile, building construction, food and drug delivery, this property prevents water and gas microfiltration. Recently, this was used to protect tooth surface against acid erosion using octadecyltrichlorosilane (OTS) [9]. The hydrophilic nature of the root canal environment [10] inhibits an adequate

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wetting, good seal and adhesion to the root canal by hydrophobic materials.

In this work, we synthesize a new hydrophobic sealer that reacts at room and body temperature; and we propose a strategy to overcome the incompatibility between hydrophilic and hydrophobic materials: we use carboxyterminal domains to do a surface treatment to hydrophobicize the dentinal walls by expose hydroxyl groups usable for silanization by a covalent attachment between the hydrophobic sealer and hydrophilic dentine, which ensured an adequate sealing that may produce null liquid permeation. The characterization of the sealer was followed by Fourier transform infrared spectroscopy (FTIR) to identify the functional groups, by Quartz crystal microbalance (QCM-D) to quantify the loss of ethanol during the curing process, by water contact angle (WCA) to analyze the hydrophobicity; and a study of the rheological properties of the endodontic sealer was conducted, which may help to assess the formation of the structure and the time-dependence behavior.

2. Materials and methods

2.1. Chemical products

Chemical reagents from Sigma-Aldrich (Munich, Germany) were the following: polydimethylsiloxane hydroxy terminated (PDMS-OH, 750 cSt at 25 °C), zinc oxide (≥ 99.0%), barium sulfate (99%), red iron oxide (≥ 99%), polydimethylsiloxane (PDMS, 200 cSt at 25 °C), dibuthyl tin dilaurate (DBTDL, 95%, 1.066g/ml at 25 °C), tetraethyl orthosilicate (TEOS, 99.0%), sodium hypochlorite (6–14%), ethylenediaminetetraacetic acid (≥ 99%) and ethanol (96%). All of them were used as received.

2.2. Endodontic sealer synthesis

The endodontic sealer was prepared using poly (dimethysiloxane) hydroxy terminated (PDMS-OH) as precursors, tetraethyl orthosilictate (TEOS) as tetra-functional cross-linkers, dibutyltindilaurate (DBTDL) as catalyst, ZnO as bactericide, $BaSO_4$ as radiopaque agent, and Fe_2O_3 as inorganic fillers.

The endodontic sealer was composed of paste and liquid. The paste contains PDMS-OH (21.15% w/w), zinc oxide (50% w/w), barium sulfate (15% w/w), red iron oxide (0.32% w/w), and PDMS (13.53% w/w). All reagents were mixed thoroughly and ground with a mortar until becoming a homogenous paste. The liquid was formed by DBTDL (5 g) and TEOS (5 g), which was heated under reflux for an hour, at a temperature of 120 °C, at ambient pressure, in a nitrogen atmosphere, free from air and moisture. The product was allowed to cool; then 3.36 g of the preceding product was mixed with 13.39 g of TEOS and 8.25 g of PDMS. Finally, the liquid was prepared as follow: for each milliliter of the last mixture, 6.2 mL of PDMS and 7.2 mL of TEOS were added. To study the effect of the concentration of TEOS and catalyst DBTDL in sealing properties, six samples were prepared: 0.46 g of paste was mixed to 10 μL of liquid (sample S1), 0.46 g of paste plus 20 μL of liquid (sample S2), 0.46 g of paste plus 30 μL of liquid (sample S3), 0.46 g of paste plus 40 μL of liquid (sample S4), 0.46 g of paste plus 50 μL of liquid (sample S5) and 0.46 g of paste plus 60 μL of liquid (sample S6).

2.3. Water contact angle measurement (WCA)

All samples were evaluated for water affinity with the water contact angle. After mixing the paste with the catalyst liquid, the endodontic sealer was deposited by spin coating technique on coverslips quartz (thickness of 0.2 mm and 25 mm in diameter), forming a homogeneous and uniform film. The WCA was measured immediately after mixing the sealant and once the polymerization was completed. To analyze the evolution of hydrophobicity degree, sample S5, which contains a high proportion of the cross-linking agent, was monitored from the start to the end of polymerization. The WAC was performed with 6 replicates of each sealer sample (each replica was taken with 6 drops of water) by placing 5 μl of distilled water on the surface of the substrates and measured at 25 °C using a goniometer (RAMÉ-HART, model 100-00-115, serial number 2017); images and angle were processed with DROPimage standard software. A mathematical model of fluid penetration at the dentine-sealer interface gives information about the importance of hydrophobic surfaces. According to Jurin's law, capillary pressure depends on the surface water contact angle:

$$P_c = \gamma \frac{(\cos\theta_d + \cos\theta_s)}{d} \quad (1)$$

where P_c is capillary pressure, γ is surface tension, θ_d is dentine contact angle, θ_s is sealer contact angle and d is interstice width [10]. According to this law, hydrophobicity should reduce water penetration by reversing capillary pressure.

2.4. Spectrophotometry analysis (FTIR)

Fourier transform infrared spectroscopy (FTIR) was used to verify the expected condensation reaction and to identify functional groups. Infrared spectroscopy analysis was performed using a spectrometer Nicolet Nexus 470 FTIR (Nicolet, Madison, WI, USA). The interferograms, covering a spectral range of 4000–525 cm^{-1} at a resolution of 2 cm^{-1} with 80 scans, were collected at room temperature. The processing and analysis of the spectra band regions were performed with the OMNIC E.S.P.5.1 software (Nicolet).

2.5. Rheological measurements

The working time was measured from the start of mixing sealant components, during which time it is possible to manipulate the root canal sealer without causing any adverse effect on its properties, to ensure that the sealant can be manipulated without suffering changes, the working time was considered as the time during which the viscosity has a horizontal behavior over time. Viscosity is a property that will allow us to determine when the sealant begins to suffer changes in its structure. The experiments of working time were performed at room temperature (25 °C). The setting time is the point where the viscosity stops the constant growth and was performed at body temperature (37 °C) [11]. In order to determine viscosity-time behavior, the samples were subjected to complete 360° revolution of the upper plate at a constant speed of 1 rpm until complete sealant polymerization [12]. Rheological measurements on the materials tested were performed using a mechanical spectrometer (Anton-Paar Rheometer MCR 300, Stuttgart, Germany). The endodontic sealer sample was placed on stainless steel parallel plate geometry (Anton Paar, Graz, Austria) with a diameter of 25 mm, the gap between the plates was 0.55 mm. The temperature was controlled by a Peltier System located in the base of the equipment. To examine the effect of steady shear rate (rpm) on viscosity-time behavior, sweeps at 0.1, 1 and 5 rpm were conducted.

To determine the stress–strain behavior and to determination of the storage (elastic) shear modulus (G') and loss (viscous) shear modulus (G''), the endodontic sealer sample was placed on stainless steel parallel plate geometry with a diameter of 25 mm, the gap between the plates was 0.55 mm. Samples were allowed to stand 16 h to ensure that the sealer was fully cured and then a