The Effect of Heating Time and Temperature on Epoxy Resin and Calcium Silicate–based Endodontic Sealers

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Abstract

Introduction: With the growing use of warm obturation techniques during endodontic treatment, more interest is directed toward sealers' compatibility with heat. This study aimed to evaluate the effect of heat application duration and temperature on epoxy resin– and calcium silicate–based sealers using chemical and thermogravimetric analyses. **Methods:** Freshly mixed samples (n = 5/group) of each sealer were heated at 200°C or 250°C for 30 or 60 seconds. Additional 2 sets of samples were examined directly after mixing or after setting without heat exposure. Raman spectroscopy was used to identify changes in the chemical structure, and a 2-way analysis of variance was performed to compare values of measurable peaks that exhibited changes. Additionally, Thermogravimetric Analysis (TGA) was used to evaluate the effect of heat on mass change where sealers were heated to 250°C at a rate of 20°C/min (11-minute duration) or maintained at 37°C for 8 hours. **Results:** No differences were detected among all the spectra of calcium silicate samples of different groups, while TGA revealed 15% and 18% weight loss upon heating at 250°C and 37°C, respectively. For the resin sealer, significant differences were detected when samples were heated for 60 seconds, involving bonds of benzene rings and aromatic amines in the uncured resin. TGA revealed minimal changes in the sealer mass (1.2% and 1.8%) on heating at 250°C and 37°C, respectively. **Conclusions:** Heat application duration and temperature can affect the chemical structure of epoxy resin sealers. The consideration of endodontic sealer compatibility as well as the duration of heat application is essential when warm vertical obturation is used. *(J Endod 2017;■:1–7)*

Key Words

Calcium silicate, endodontic sealers, epoxy resin, heat application time, Raman spectroscopy, warm vertical obturation

Significance

Heat application during obturation has been widely used, triggering attention about its compatibility with sealers. Chemical and thermogravimetric analysis revealed the effect of time and temperature on tested endodontic sealers, which may reflect on the way sealers are used.

As the final step of root canal treatment, obturation aims to provide an adequate seal for the chemo-mechanically prepared canal system. It intends to restrict the movement of surviving bacteria and their products out of the canal, as well as the inverse movement of fluids and accompanying nutrients into it (1). Ideally, achieving such environment requires a root filling material that can flow into all the spaces of root canal system to create a fluid-tight seal (2), which no single obturation material has been proven to achieve (3). This allowed gutta-percha, despite its poor adaptability and lack of adhesion to dentine (3), to remain the most commonly used obturation material along with different endodontic sealers (4). Efforts to develop new materials have been made in parallel with attempts to improve performance of gutta-percha by adopting alternative application techniques, such as the continuous wave heating.

Epoxy resin–based endodontic sealers have been widely used due to their good handling properties, low toxicity and solubility, and compatibility with gutta-percha (5). They are principally composed of epoxy monomers that are cross-linked on mixing with amine hardeners through an addition reaction (Fig. 1) (6). A commonly used epoxy resin sealer is AHPlus (Dentsply, Konstanz, Germany) which is dispensed in 2 pastes. Paste A is composed of diglycidylether of bisphenol-A and bis-(4-[-2,3-epoxypropoxy]phenyl)-methane (Bisphenol-F) monomers (Fig. 1*A*), whereas paste B contains aminoadamantane, aromatic amine hardeners (dibenzyldiamine and tricyclodecane) (Fig. 1*B*), and calcium tungstate and zirconium oxide fillers. Calcium silicate–based endodontic sealers have been recently introduced after gaining good reputation as restorative materials for their biocompatibility and bioactivity (7). A new member of this family is BioRoot RCS (Septodont, Saint Maur Des Fosses, France); a tricalcium silicate–based powder containing zirconium oxide filler dispensed in a fixed powder-liquid ratio. On mixing with the liquid that is composed of water and contains calcium chloride, the setting hydration reaction takes place (8) to produce a matrix of calcium silicate hydrate (CSH) that holds other constituents (9).

During obturation, using heat while applying gutta-percha was first suggested by Schilder (10) in 1967 to enhance its adaptability to root canal walls though thermoplasticization. With the subsequent advances in this technique, the principle of applying heat directly to the material remained the same despite the advancements introduced over the years. Clinically, no conclusive evidence has been provided to support a better

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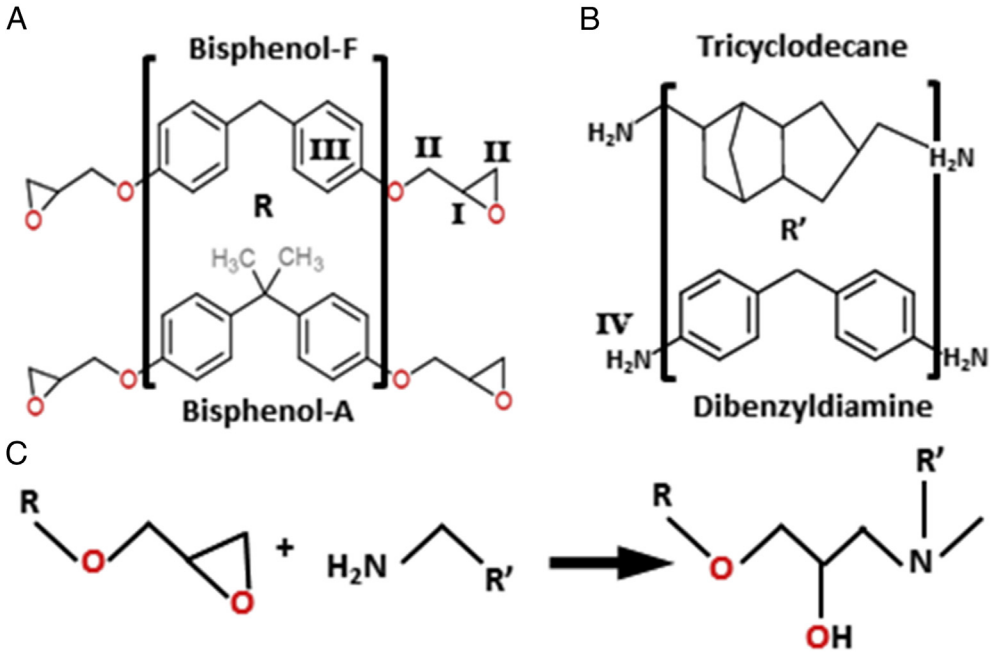

Figure 1. Molecular structure of the main chemical components of epoxy resin–based endodontic sealer AHPlus. (*A*) The epoxy molecules bisphenol-A and bisphenol-F with characteristic epoxy rings on both ends. I, CH group of epoxide; II, C-H bond in CH_2; III, C=C bonds in benzene rings. (*B*) Aromatic amine epoxy resin hardeners; dibenzyldiamine and tricyclodecane with characteristic 2 amine functional groups. IV, N-H bond in aromatic amine. (*C*) Epoxy resin setting (curing) reaction induced by the amine hardeners that cross-link the epoxy monomers together after opening epoxy rings to form the resinous matrix.

treatment outcome (11, 12). On the contrary, recent studies have reported that heat application during obturation may induce changes in the properties of some sealers (13, 14).

This study aimed to analyze the potential effect of heat application on the structure of epoxy resin– and calcium silicate–based endodontic sealers, as well as compare the effect of heat application duration and temperature on these changes. Raman spectroscopy, which has been a very useful tool to investigate the chemical bonds and structures of materials (15), was used along with Thermogravimetric Analysis (TGA). TGA allows evaluation of the effect of heat on the mass of tested matter, which can reflect chemical changes in its composition, whether due to reactions or material loss (16). TGA along with Raman spectroscopy thus provides complementary information to help in understanding the effect of heat on endodontic sealers.

Materials and Methods

Sample Preparation

Two endodontic sealers with different chemical composition were used in this study: epoxy resin–based (AHPlus) and calcium silicate–based (BioRoot RCS). For each type, 6 groups with 5 samples each were prepared. In the "cold" group, sealers were examined directly after mixing at room temperature without exposure to heat. In the "H200-30s" and "H200-60s" groups, sealers were heated in an electric oven with a temperature control (Blue M, Blue Island, IL) at a 200 ± 10°C temperature for 30 and 60 seconds, respectively. In the "H250-30s" and "H250-60s" groups, sealers were heated at a 250 ± 10°C temperature for 30 and 60 seconds, respectively. In the "set" group, sealers were left to set for 48 hours under ambient conditions before testing: this time was sufficient for both sealers to set. The sealers were mixed as per manufacturers' instructions and applied in thin films on clean glass slides for imaging. Heated samples were left to cool for 45 minutes before imaging.

Raman Spectroscopy

Raman scans were acquired using a surface-enhanced Raman scattering spectroscope (LabRAM HR EVO; Horiba Scientific, Kyoto, Japan), equipped with 688-nm helium neon laser beam at room temperature. A ×50/0.75 numerical aperture objective lens was used with 11 mW power laser beam and a 600 grooves/mm diffraction grating, with 12 acquisitions per point of 5 seconds each. Acquired spectra were all uploaded into optical spectroscopy analysis software (SpectraGryph 1.0 [Spectroscopy Ninja, Oberstdorf, Germany]) and normalized to the 177 cm^{-1} Raman peak area. Spectral data from the same experimental group were averaged and plotted together with other average spectra of the same sealer for comparison, which was performed by 2 examiners who were not involved in the acquisition of the spectra. For each peak that exhibited visible changes on the averaged spectra, the ratio of each peak's area to the reference peak area was calculated, and the percentage of change in relation to the control "cold" samples was measured and plotted.

Statistical Analysis

Analysis of variance was performed using SPSS-20.0 (IBM, Chicago, IL), followed by *post boc* Tukey test to show the significance of specific mean with respect to each group. The unpaired *t*-test was also applied to determine mean differences in values representing peaks in relation to time and temperature. *P* values (≤.05) were considered statistically significant differences in means.

Thermogravimetric Analysis

Two samples of each sealer were tested using a thermogravimetric analyzer (TGA/DSC-2; Mettler-Toledo International Inc, Greifensee, Zurich, Switzerland) to evaluate changes in the mass of sealers on heating. Freshly mixed samples of each sealer were placed in polycrystalline alumina oxide crucibles and heated under helium gas from room