Effects Of Heat On Seven Endodontic Sealers

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Abstract

Purpose: To examine the microscopic surface features, chemical composition, and thermodynamic profile of seven endodontic sealers (AH Plus, Adseal, MTA-Fillapex, RoekoSeal, GuttaFlow 2, GuttaFlow BioSeal, and EndoRez) exposed to high-temperature changes using an endodontic obturation device.

Methods: The thermal properties were examined using scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Then, six disc-shaped specimens of each sealer were prepared and divided into two groups – a room temperature group and a heat exposure group – for analysis of surface and chemical changes using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS).

Results: DSC analysis showed that AH Plus had the highest exothermal signal (122.9°C), while TGA analysis showed that MTA-Fillapex was most affected by increased temperature (32.4% mass loss at 230°C). SEM analysis showed that while AH Plus and GuttaFlow BioSeal maintained their surface integrity after heat exposure, the EDS profiles demonstrated changes in the chemical composition of the sealers after heat exposure for 5 s. High-temperature exposure had a negative impact on the properties of five of the sealers (Adseal, MTA-Fillapex, RoekoSeal, GuttaFlow 2, and EndoRez).

Conclusion: AH Plus and GuttaFlow BioSeal showed minimal changes upon high-temperature exposure, suggesting their suitability for thermal endodontic obturation techniques.

Keywords: differential scanning calorimetry, endodontic root canal sealers, energy-dispersive X-ray spectroscopy, scanning electron microscopy, thermogravimetric analysis

Introduction

Thermal endodontic obturation techniques include carrier-based obturation and warm vertical condensation (WVC). WVC is one of the obturation techniques most frequently employed by endodontics clinicians [1], and involves the use of a gutta-percha core and sealer to prevent potential leakage [Ørstavik D, Obtration of root canals. In: Chugal N, Lin LM, editors. Endodontic Prognosis. Cham: Springer International Publishing, 141-159, 2017]. Because some microorganisms can penetrate the coronal portion of root canal fillings, prevention of leakage is essential for successful root canal treatment [Sundqvist G et al., Endodontic treatment of apical periodontitis. In: Ørstavik D, Pitt Ford TR. Essential endodontology: prevention and treatment of apical periodontitis. London: Blackwell Publishing, 242-269, 1998]. As reported previously, small voids in the obturation (often undetected by radiography) may be responsible for rapid recontamination of the root canal system [2]. As both apical and coronal leakage can be primarily responsible for treatment failure [3], it is essential to examine how heat application can affect endodontic sealer materials.

It is known that the heat generated using WVC may negatively affect the physical and chemical properties of some root canal sealers [4]. Most of the available obturation devices offer a thermal working range of 150-250°C, with preferential use at 200°C [5]. Physical changes caused by heat have been evaluated using thermogravimetric analysis (TGA) [6,7] and differential scanning calorimetry (DSC) [6,8]. Also, changes in the surface morphology and material elements due to heat have been analyzed using scanning electron microscopy (SEM) in combination with energy-dispersive spectroscopy (EDS) [9-10]. Although choosing the right endodontic sealers for WVC is imperative, only a few selected endodontic sealers have been studied previously [4,6-8,10,11].

The effects of heat application can vary depending on the type of endodontic sealer employed. Such sealers are categorized on the basis of setting reaction and composition [12]. AH Plus (Dentsply Sirona, Konstanz, Germany), an epoxy sealer also known as TopSeal in Central/South America and Europe [12], offers low solubility and shows some apatite deposits despite the absence of calcium release and alkalizing activity [13]. Although AH Plus has been studied for the effects of heat application [4,7,11], no other epoxy resin product has been examined in this way. MTA-Fillapex (Angelus, Paraná, Brazil) is a salicylate resin-based sealer containing calcium silicate particles (mineral trioxide aggregate, MTA) and silicon dioxide. It has been reported to show suitable flow, good sealing, and low solubility [9,14]. However, few studies showed heat application effect in SEM/EDS studies [12,15-17], and changes were observed in the chemical composition and setting times after heat application [18]. A previous report [8] on the effect of heat application is available for EndoRez (Ultradent, South Jordan, UT, USA), which is a methacrylate resin-based sealer, and GuttaFlow 2 (Coltene/Whaledent, Altstätten, Switzerland), which is a silicone-based sealer. GuttaFlow 2 was introduced as an improved version of GuttaFlow, having a slightly different composition and containing gutta-percha powder with a particle size of less than 30 μm. It has shown higher porosity than EndoRez and RealSeal [19] and poor wettability because of the presence of silicone, which possibly produces high surface tension forces, making spreading on the root dentin surface difficult [20]. While silicone-based endodontic sealers have better sealing properties than AH Plus, little has been reported regarding the impact of heat application [6,12]. GuttaFlow BioSeal (Coltene/Whaledent) is a silicone-based endodontic sealer with a novel formulation of polydimethylsiloxane-gutta-percha doped with calcium silicate particles. It has shown alkalizing activity together with negligible solubility and slight calcium release. Therefore, nucleation of apatite and apatite precursors can be related to the interaction of CaSi particles with polysiloxane, conferring both intrinsic bioactivity-related and extrinsic apatite-forming ability [9]. However, no heat application effect has been reported in a SEM/EDS study [21] either.

To address the gap of knowledge about how heat application affects various silicone-based sealers and additional resin-based products both in vitro and clinically, it is important to test them using different evaluation methods. Therefore, the present study investigated seven endodontic sealers: AH Plus, Adseal, MTA-Fillapex, RoekoSeal, GuttaFlow 2, GuttaFlow BioSeal, and EndoRez. It was hypothesized that TGA, DSC, and SEM/EDS analysis would show that AH Plus remained stable to heat in com-
before the application of heat. Samples were heated under nitrogen gas and weighed using the built-in highly sensitive balance of the TGA unit. Approximately 6 mg of each mixed sealer was placed in a platinum pan. TGA analysis and thermodynamic profiles were obtained by determining the respective temperatures used among different commercial endodontic obturation devices. The onset temperature (To) (at which the weight loss begins) and the inflection point (Tp) (the point showing the most significant rate of change on the weight loss curve) were also recorded for comparison among the seven sealers. The data were analyzed using the TGA software (Universal Analysis 2000 for Windows 2000/XP/Vista version 4.5, TA Instruments), and the calorimetric curves were obtained.

Materials and Methods

The seven endodontic sealers investigated in this study included epoxy resin-based, salicylate-based, silicone-based, and methacrylate-based sealers. The brand names, manufacturers, and compositions of the sealers are listed in Table 1.

DSC analysis

Sealers were mixed in accordance with the manufacturers’ instructions, and 4 mg of each sealer was placed in an aluminum DSC crucible. Immediately after the crucibles had been sealed, the samples were placed in a DSC unit Q200 (TA Instruments, New Castle, DE, USA). Thermal scans were started at 20°C, followed by heating at a rate of 10°C/min up to a final temperature of 230°C. Three samples of each endodontic sealer were analyzed. The data were evaluated using thermal analysis software (Universal Analysis 2000 for Windows 2000/XP/Vista version 4.5, TA Instruments), and thermodynamic profiles were obtained by determining the respective thermal peak areas.

TGA analysis

Approximately 6 mg of each mixed sealer was placed in a platinum pan and weighed using the built-in highly sensitive balance of the TGA unit (Q500, TA Instruments). Three samples of each sealer were placed in the TGA furnace, and the sealer weight was recorded via the TGA analyzer before the application of heat. Samples were heated under nitrogen gas from room temperature (20°C) to a maximum of 1,000°C at a rate of 20°C/min, and the changes in weight were monitored. For each TGA curve, the mass loss at 180°C, 200°C, and 230°C was recorded to evaluate the temperatures used among different commercial endodontic obturation devices. The onset temperature (To) (at which the weight loss begins) and the inflection point (Tp) (the point showing the most significant rate of change on the weight loss curve) were also recorded for comparison among the seven sealers. The data were analyzed using the TGA software (Universal Analysis 2000 for Windows 2000/XP/Vista version 4.5, TA Instruments), and the calorimetric curves were obtained.

SEM/EDS analyses

Figure 1 shows the sample preparation technique, where the two components (paste/paste) were thoroughly mixed in a mixing pad, or using the manufacturer’s auto mixing tips when available. Six disc-shaped specimens of each sealer, 5 mm in diameter and 3 mm in height, were prepared and divided into two groups. In the Room Temperature (RT) group, samples were allowed to polymerize under controlled laboratory conditions (21°C and 80% humidity) for 24 h. For the Heat Exposure (HE) group, the upper surface of each sealer sample was immediately exposed to the activated metal tip of a heated endodontic obturation device (Alpha II, B&L Biotech, Fairfax, VA, USA) for 5 s at 230°C to simulate the clinical procedure used in the continuous wave obturation technique. Next, the samples were allowed to polymerize under the same conditions as those for Group 1. After the 24-hour setting period, all samples were labeled and prepared for SEM and EDS analyses.

Samples randomly selected for SEM analysis were sputter-coated with a gold-palladium powder alloy, placed on aluminum stubs with carbon-adhesive tape, and placed in a scanning electron microscope operating at 10 kV (ASEM Microscopy JEOL JSM-6390LV, Peabody, MA, USA).
Images of the upper surfaces of the sealer specimens were captured at >2,000. Elemental analysis was also performed with an energy-dispersive spectrometer (Oxford INCA X-Sight 7582 M, Oxford, UK) using new non-coated specimens.

Results

DSC analysis showed differences in thermodynamic profiles among the sealers (Fig. 2). The absence of impurities and/or external contaminants in the mixtures was confirmed after repeated analyses of the same sealer yielded similar results. All seven sealers showed exothermic signals before reaching 150°C, indicating that the setting reaction was accelerated by heat; however, the specific changes differed depending on the sealer. Once the exothermic signals were attained, most of the samples exhibited thermal stability within the range 180-230°C. Specific signals and temperatures are shown in Fig. 2.

TGA curves are shown in Fig. 3. AH Plus (Fig. 3a) and Adseal (Fig. 3b), both epoxy resin-based sealers, revealed different logarithmic trends: AH Plus showed a less steep mass loss curve (<5%) before a sudden drop of the curve, whereas Adseal displayed a continuous increase in mass loss before reaching a mass loss of 15% and then dropping. Logarithmic trends for Roeko Seal (Fig. 3d), GuttaFlow 2 (Fig. 3e), and GuttaFlow BioSeal (Fig. 3f) were similar with a slow mass loss for the thermogravimetric run-up to 400°C, where a steeper curve was observed. Table 2 summarizes the To, Tp and percentage mass losses of the sealers at different temperatures. All observed To values were within the range 140.5-399.8°C, displaying wide variability among the sealers. The To values for the sealers increased in the order MTA-Fillapex > EndoRez > Adseal > AH Plus > RoekoSeal > GuttaFlow BioSeal > GuttaFlow 2. Although most of the sealers showed a To superior to the temperatures employed in continuous wave obturation techniques, MTA-Fillapex in particular was suggested to be thermally vulnerable.

SEM images showed that the surface characteristics of the seven studied sealers varied widely at room temperature and after exposure to heat (Fig. 4). The surfaces of the epoxy resin-based sealers (AH Plus and Adseal) resembled a smooth matrix (Fig. 4a and c), but when heat was applied, only AH Plus maintained its original appearance (Fig. 4b); Adseal (Fig. 4d) showed a disrupted pattern with irregular voids ranging in size from 5 µm to 20 µm. These voids were also evident in EndoRez after heat had been applied (Fig. 4n) and smaller voids were seen in RoekoSeal (Fig. 4h) and GuttaFlow 2 (Fig. 4j). No voids were detected in GuttaFlow BioSeal after exposure to heat (Fig. 4l). MTA-Fillapex showed a more significant change in surface appearance (Fig. 4f); although no voids were observed after heat had been applied, the surface displayed a broken glass-like appearance (Fig. 4f). Like AH Plus, GuttaFlow BioSeal showed no surface disruption or irregular voids between the RT (Fig. 4k) and HE (Fig. 4l) samples.

The EDS profiles for the randomly selected sealer samples are presented in Fig. 5, with element signals identified for each sealer in both groups. Both the epoxy resin- and salicylate-based sealers showed a reduction in the proportional percentage of C after heat had been applied. In contrast, the silicone- and methacrylate-based sealers exhibited an increase in the proportional percentage of C after heat application. AH Plus and Roeko Seal, both of which contain zirconium oxide, showed an increase in the proportional percentage of Zr after heat had been applied to the unset sealer mix. Silicon (Si) increased after exposure to heat in sealers such as AH Plus, GuttaFlow 2, and GuttaFlow BioSeal. In the salicylate-based sealer (MTA-Fillapex), Ti from the titanium dioxide compound contained in paste A of the sealer was identified in both groups.

Discussion

Successful root canal treatment is contingent upon preventing sealer leakage and infection. The heat generated from thermal endodontic techniques has been shown to impact the properties and sealing abilities of some endodontic sealers. Hence, this study was designed to evaluate and compare different sealers to which heat was applied under the same conditions. The results of TGA showed that the percentage weight loss increased in all sealer groups as the temperature increased from 180°C to 230°C. Overall, exposure to high temperatures decreased the stability of the materials. The weight loss upon heating was lowest for silicone-based sealers (RoekoSeal, GuttaFlow 2, and GuttaFlow BioSeal), and highest for the salicylate-based sealer (MTA-Fillapex). The percentage weight loss upon heating of a methacrylate resin-based sealer (EndoRez) and epoxy resin-based sealers (AH Plus and Adseal) was intermediate between the two. Although the methodology used in previous studies has differed, the present pilot study found a weight loss of 2.2% at 180°C and 2.5% at 200°C, which was similar to the results obtained by Aksel et al. [7] for AH Plus, i.e. 1.7% at 180°C and 1.8% at 200°C, however, Atteh et al. [6] reported that the weight loss for AH Plus upon heating was 1.2% at 250°C. In the present study, TGA analyses revealed that the salicylate-based sealer (MTA-Fillapex) had the lowest To (140°C) and Tp (193°C) among the seven sealers. These low To and Tp values were below the applied temperature (180°C, 200°C, and 230°C), which may explain the significant weight loss compared to other sealers tested. The present TGA results show that heat application during obturation induced significant changes in the properties of MTA-Fillapex sealer. Although previous DSC results have been limited, Roberts et al. [8] reported that the exothermic peaks of EndoRez and GuttaFlow 2 were 52°C and 60°C, respectively. The result for EndoRez was in agreement with the present study, whereas GuttaFlow 2 had a lower thermal peak. The DSC results for GuttaFlow 2 reflected the manufacturer’s recommendations for a cold obturation technique due to concerns about decomposition after a high thermal challenge [8]; however, this study did not use SEM/EDS equipment to evaluate the topography and surface composition of the material.

SEM/EDS analyses revealed similarities between the elements found and the primary compounds described by the manufacturers before appli-
Table 2  Thermogravimetric (TGA) analysis of the examined sealers

<table>
<thead>
<tr>
<th>AH Plus</th>
<th>Adseal</th>
<th>MTA-Fillapex</th>
<th>RoekoSeal</th>
<th>GutaFlow 2</th>
<th>GutaFlow BioSeal</th>
<th>EndoRez</th>
</tr>
</thead>
<tbody>
<tr>
<td>Onset temperature (To) (°C)</td>
<td>333.7</td>
<td>313.5</td>
<td>140.5</td>
<td>343.3</td>
<td>399.8</td>
<td>373.7</td>
</tr>
<tr>
<td>Inflection point (Tp) (°C)</td>
<td>362.7</td>
<td>369.6</td>
<td>193.0</td>
<td>429.0</td>
<td>453.1</td>
<td>428.8</td>
</tr>
<tr>
<td>Tp-To (°C)</td>
<td>29.0</td>
<td>56.1</td>
<td>52.6</td>
<td>85.7</td>
<td>53.4</td>
<td>55.1</td>
</tr>
<tr>
<td>Mass loss at 180°C</td>
<td>2.2%</td>
<td>4.0%</td>
<td>14.7%</td>
<td>0.3%</td>
<td>0.3%</td>
<td>0.3%</td>
</tr>
<tr>
<td>Mass loss at 200°C</td>
<td>2.3%</td>
<td>5.0%</td>
<td>23.1%</td>
<td>0.4%</td>
<td>0.3%</td>
<td>0.3%</td>
</tr>
<tr>
<td>Mass loss at 230°C</td>
<td>2.5%</td>
<td>6.5%</td>
<td>32.3%</td>
<td>0.5%</td>
<td>0.4%</td>
<td>0.5%</td>
</tr>
</tbody>
</table>

Fig. 3  Thermogravimetric (TGA) curves for each examined sealer in terms of weight percentage (%) by temperature (°C). Specific mass loss at 180°C, 200°C, and 230°C is presented. Onset point (To) and inflection point (Tp) (calculated from the 1st derivative of weight percentage (%/°C)) for each sealer are also shown. 3a AH Plus. 3b Adseal. 3c MTA-Fillapex. 3d RoekoSeal. 3e GuttaFlow 2. 3f GuttaFlow BioSeal 3g EndoRez.
Fig. 4 Scanning electron microscopy (SEM) images for each sealer at ×2,000. 4a AH Plus room temperature, 4b AH Plus heat exposure. 4c Adseal room temperature, 4d Adseal heat exposure. 4e MTA-Fillapex room temperature, 4f MTA-Fillapex heat exposure. 4g RoekoSeal room temperature, 4h RoekoSeal heat exposure. 4i GuttaFlow 2 room temperature, 4j GuttaFlow 2 heat exposure. 4k GuttaFlow BioSeal room temperature, 4l GuttaFlow BioSeal heat exposure. 4m EndoRez room temperature, 4n EndoRez heat exposure.
Fig. 5 Energy-dispersive spectroscopy (EDS) elemental analysis histograms for the evaluated sealers in terms of the number of X-rays counts by energy (keV). 5a AH Plus room temperature, 5b AH Plus heat exposure, 5c Adseal room temperature, 5d Adseal heat exposure, 5e MTA-Fillapex room temperature, 5f MTA-Fillapex heat exposure, 5g RoekoSeal room temperature, 5h RoekoSeal heat exposure, 5i GuttaFlow 2 room temperature, 5j GuttaFlow 2 heat exposure, 5k GuttaFlow BioSeal room temperature, 5l GuttaFlow BioSeal heat exposure, 5m EndoRez room temperature, and 5n EndoRez heat exposure
cation of heat at room temperature. However, the SEM images and EDS analyses demonstrated apparent heat-induced compositional alterations and ultrastructural changes for several sealers, i.e. Adseal, RoekoSeal, EndoRez, GuttaFlow 2, and MTA-Filexap. This study found no apparent heat-induced compositional alterations or ultrastructural changes for AH Plus and Gutaflow BioSeal, indicating that both sealers can be heated even to 230°C. SEM observations showed that, after heat application, AH Plus maintained a regular surface and that Gutaflow BioSeal maintained a uniform distribution of elements with globular-like particles of different sizes and shapes. A number of previous studies analyzing the impact of heat exposure on AH Plus have produced some contradictory findings. For example, the use of SEM/EDS has suggested possible chemical changes after heat exposure, as well as an impact on surface features [4,10,11].

In contrast, Viapianta et al. [4] have reported that AH Plus sustained changes to its chemical structure after exposure to heat. Heran et al. [22] concluded that AH Plus should not be subjected to high temperature due to deterioration of its properties and an increased incidence of voids. In this connection, Adseal, RoekoSeal, Gutaflow 2, and EndoRez demonstrated disrupted irregular voids after heat application. Adseal is an epoxy resin sealer, as is the case for AH Plus. However, the previous study found that Adseal had a low radiopacity value (3.09 mm of aluminum). On the other hand, AH Plus was found to have high radiopacity (10.14 mm of aluminum) [23], possibly explaining the difference in chemical elements between the RT and HE samples demonstrated by the present EDS. The presence of elements with a high atomic number in AH Plus may explain its high radiopacity [16]. RoekoSeal and Gutaflow 2 are silicone-based sealers, as is Gutaflow BioSeal (also known as Gutaflow 3), which was developed to improve bioactivity and promote the regeneration of periapical tissues by including bioactive glass ceramic in the composition [21].

Due to the bioactive glass ceramic component of Gutaflow BioSeal, the EDS results in the present study indicated a higher content of calcium and a lower content of carbon than for RoekoSeal and Gutaflow 2. Also, SEM observation of Gutaflow BioSeal without heat application revealed bioactive glass-ceramic particles with pointed edges, in agreement with the study by Hoikkala et al. [24]. Similar to the results of Sampaio et al. [15], the present EDS study showed that MTA-Filexap has considerably lower calcium levels. Because MTA-Filexap contains only 15% MTA powder and its composition is primarily resin, it should not be considered as a tricalcium silicate sealer [12].

The present in vitro results are of considerable clinical significance in terms of the choice of sealer types and obturation techniques. Within the limitations of the DSC/TGA and SEM/EDS results, heat application caused minor changes in the properties of AH Plus and Gutaflow BioSeal.

Heat application significantly changed and negatively affected the physical and chemical properties of MTA-Filexap. DSC/TGA and SEM/EDS analysis revealed the effect of temperature on the tested endodontic sealers, which could also have been influenced by the type of obturation used. Endodontists and general dentists can choose from several obturation techniques; the most common include cold lateral condensation obturation, single-cone obturation, carrier-based obturation, and warm vertical obturation. The present findings show that AH Plus and Gutaflow BioSeal can be used with warm vertical obturation and carrier-based obturation. MTA-Filexap can be used with cold lateral condensation obturation because heat-induced changes could adversely affect the quality of other obturation techniques.

Even within the same type of sealer group, heat-induced changes differed among the sealer products. When a clinician decides to use WVC, adherence to a specific sealer’s temperature setting and gutta-percha point is recommended. For example, based on the To and Tp values obtained by TGA for AH Plus and Gutaflow BioSeal, even when a clinician requires the high heat cutting efficiency of gutta-percha, the heating device temperature should be set below 300°C. If a clinician is comfortable with a lower temperature (180°C), this is better for minimizing weight loss and changes in sealer properties than a higher temperature (230°C). Although the number of samples was limited, the findings of this study are informative for future research on how heat application affects sealer efficacy. Additional variables analyzed by DSC would also have been desirable (e.g., the impact of a fast heating rate or a heating plateau at a specific temperature) and use of an ex vivo model with extracted teeth. Future studies using a larger number of samples and different sealers such as zinc oxide-eugenol and tricalcium silicate, as well as the experiments proposed above, would be desirable.

Under the present experimental conditions, heat transfer had a negative impact on five endodontic sealers (Adseal, MTA-Filexap, RoekoSeal, Gutaflow 2, and EndoRez); however, AH Plus and Gutaflow BioSeal exhibited minimal structural change and appear to be an appropriate choice for endodontic obturation techniques such as carrier-based obturation and warm vertical condensation.

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Conflict of interest

None.

References

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