Published online: 2019-09-25

Chemical composition and thermal behavior of five brands of thermoplasticized gutta-percha

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ABSTRACT

Objective: The aim of this study was determine the chemical composition and thermal behavior of Thermafil (TH), Microseal Cone (MC), Microseal Microflow (MF), Obtura (OB) and Obtura Flow (OF). In addition, their thermal behavior in response to temperature variations was studied by differential scanning calorimetry (DSC) to determine the temperature at which gutta-percha switches from the beta to alpha form, and from the alpha to the amorphous phase. **Materials and Methods:** The organic and inorganic fractions were separated by dissolution in chloroform. Gutta-percha (GP) was precipitated with acetone. The inorganic fraction was analyzed via Elemental Microanalysis. Energy Dispersive X-ray Microanalysis and X-ray Diffraction were used to identify the chemical elements and compounds ($BaSO_4$ and ZnO). Thermal analysis was conducted using DSC. **Results:** The organic and inorganic fractions ranged from 21.3% and 26.9% of weights, respectively. MC and MF showed the highest percentages of organic compounds ($P = 0.0125$). All specimens exhibited two crystalline transformations when heated from ambient temperature to 130ºC. MC presented the highest percentage of GP. **Conclusions:** No correlation was observed between chemical composition and thermal behavior. Each of the products showed thermal behavior that is typical of beta-phase gutta-percha.

Key words: Chemical composition, gutta-percha, root canal filling materials, thermal behavior, thermoplastic obturation

INTRODUCTION

Thermoplastic obturation techniques have the potential to produce a complete filling of root canal space, including irregularities and lateral canals.[1-4] Several techniques have been proposed to obtain optimal adherence of gutta-percha (GP) to root canal walls[5-7] to minimize microbial leakage[8] and to ensure treatment success.[8-10] Since the introduction of the warm vertical condensation technique by Schilder, in 1967,[10] a number of clinical placement techniques involving warm GP have been developed.[4,9,11] However, there are no reports comparing different brands of thermoplasticized GP with respect to their chemical composition and thermal behavior.

Heating GP is known to result in changes to the molecular structure (phases) and polymer volume of the compound.[9,12-14] GP expands slightly when heated, a desirable trait for endodontic filling material.[15] This physical property manifests itself

How to cite this article: Maniglia-Ferreira C, Gurgel-Filho ED, de Araújo Silva JB, de Paula RM, de Andrade Feitosa JP, de Sousa-Filho FJ. Chemical composition and thermal behavior of five brands of thermoplasticized gutta-percha. Eur J Dent 2013;7:201-6.

 DOI: 10.4103/1305-7456.110173

as an increase in volume of material that can be compacted into a root canal cavity.[10]

GP is a *trans*-1, 4-polyisoprene polymer obtained from the coagulation of latex produced by trees of the family Sapotaceae and is primarily derived from *Palaquium gutta* bail.[16] The crystalline phase appears in two forms: 1) the alpha (α) phase and 2) the beta (β) phase. During thermal manipulation, the structure of the compound transforms into the crystalline structure of the polymer from the β-form to the α-form and from the α-form to the amorphous phase. The forms (β and α) differ only in the molecular repeat distance and single-bond form.[17-18]

Some studies have demonstrated the thermal properties of dental GP[13,18-20] and have shown that changes in the crystalline form may lead to irreversible volumetric change.[21]

The purpose of the present study was to determine the chemical composition (organic and inorganic components), as confirmed by X-ray Diffraction and Energy Dispersive X-ray microanalysis (EDX), of Thermafil, Microseal (cone and microflow), Obtura and Obtura flow. In addition, their thermal properties in response to temperature variations were studied via Differential Scanning Calorimetry (DSC) to determine the temperature at which GP changes from the β- to the α-form and from the α-form to the amorphous phase. Finally, analyses were conducted to ascertain whether there is a significant correlation between chemical composition and thermal behavior.

MATERIALS AND METHODS

Five GP brands were analyzed three times each before the expiration dates established by the manufacturer. These brands consisted of three thermoplastic GP systems, as listed: Thermafil (TH) (Dentsply Maillefer, Tulsa, OK, USA); Obtura (OB) (Obtura Corporation, Penton, Missouri, USA); Obtura Flow (OF) (Obtura Corporation, Penton, Missouri, USA); Microseal Cone (MC) and Microseal Microflow (MF) (Analytic Endodontics, Glendora, CA, USA).

Quantitative chemical analysis

The chemical components of the GP brands were determined in accordance with the procedures described by Friedman *et al.*[6] and modified by Gurgel-Filho *et al.*[22] 1 g of commercial GP points was dissolved in 10 ml of chloroform for 24 hours; the resulting solution was then centrifuged for 15 min at 6000 rpm. This allowed for separation of the solid phase (inorganic components: Zinc oxide and metal sulfates) from the supernatant (organic components: GP, resins and waxes) remaining in solution.

GP, insoluble in acetone, was coagulated by the addition of this solvent and weighed after total solvent evaporation. The mass of soluble material in acetone (wax/resin) was determined after solvent evaporation using a microbalance (XP56 Microbalance, Mettler-Toledo Int Inc, Brazil).

The organic fraction (GP and wax/resin) was determined by use of the procedure described by Gurgel-Filho *et al.*[22] Barium sulfate content was determined by sulfur percentage (Elemental Microanalysis) using Equation 1. Zinc oxide content was calculated using Equation 2 when the specimen contained sulfur or using Equation 3 when it did not.

- Equation 1: $BaSO_4\% = S\% \times (BaSO_4 \text{ molar mass})/(S \text{ atomic mass}) = S\% \times 7.28$
- Equation 2: $ZnO\% = 100\% - (GP \text{ polymer}\% + \text{wax/resin}\% + BaSO_4\%)$
- Equation 3: $ZnO\% = 100\% - (GP \text{ polymer}\% + \text{wax/resin}\%)$

Energy dispersive X-ray microanalysis

Energy Dispersive X-ray Microanalysis (EDX) was applied to qualitatively establish the presence of chemical elements in the samples. The analyses were made in sections, with all specimens mounted on aluminum stubs and carbon coated using a DSM-940A Scanning Electron Microscope (Carl Zeiss, Jena, Germany) and a Link System 3.34 Series 300 with Si (Li) detector. The sections were analyzed at ×1000 magnification.

X-ray diffraction

The apparatus used for the X-ray Diffraction Analysis was a Philips MDR Pro (Eindhoven, Holland) with 40 kV and 20 mA using a copper tube. The equipment was calibrated to produce 10^2 cps.

Elemental microanalyses

Quantitative determination of carbon, hydrogen, nitrogen and sulfur chemical elements in the samples was carried out in a CHNS/O Carlo Erba, model 1110 microanalyzer (Carlo Erba, Rodano, Italy) with combustion at 1000°C, in atmospheric oxygen. A thermal conductivity detector was used and all of the analyses were repeated three times for all materials.

Differential scanning calorimetry

The thermal analyses of all samples were carried out by Differential Scanning Calorimetry (DSC) (Shimadzu DSC-50, Shimadzu Corporation, Japan) and the calibration of each was verified using a calcium oxalate standard. For each material, duplicate samples between 40 and 50 mg were analysed using 25 mg alumina as the reference material.[21]

All specimens were heated from room temperature to 70ºC at a rate of 1ºC/min, with the endothermic peaks being recorded for each material. This was followed by rapid heating up to 130ºC, rapid cooling to room temperature and heating up again back to 70ºC, at a rate of 1ºC/min., with the endothermic peaks of the materials recorded once again.

Thermogravimetric analysis

Simultaneously, Thermogravimetric Analysis (TGA) (Shimadzu TGA-050, Shimadzu Corporation, Japan) was performed to determine the amount of weight lost (organic fraction) during the heating cycles.[21] This analysis was made to confirm the results obtained by quantitative chemical analyses of the organic fraction.

Statistical analysis

The data collected for each sample were entered into a spreadsheet and analyzed statistically using SPSS 12.0 for Windows (SPSS Inc., Chicago, Ill, USA). The ANOVA test was used to test the null hypothesis that there is no difference between the compositions of all GP brands analyzed.

RESULTS

Quantitative chemical analysis and energy dispersive X-ray microanalysis

A heterogeneous concentration of compounds in the GP brands was noted, as is illustrated in Table 1. The Microseal cone showed the highest percentage of GP (P = 0.0001), followed by Obtura, Microseal microflow (P = 0.0022), Thermafil and Obtura flow (P = 0.0022). Thermafil, Obtura flow and Microseal microflow showed high concentrations of wax and resins (P = 0.0022) in their compositions when compared with the remaining groups. With regard to the percentages of organic compounds, it was noted that Microseal (cone and microflow) showed the highest percentages (P = 0.0125). These results appear in an inverted position when the analyses were made with the other remaining organic compounds.

X-ray diffraction and elemental microanalyses

The results obtained from X-ray Diffraction and Elemental Microanalysis are presented in Table 2. X-ray diagrams and EDX Microanalysis qualitatively confirmed the chemical components of GP brands. The presence of Barium and Sulfur were noted for all specimens. Quantitative analysis was carried out *via* Elemental Microanalysis.

Differential scanning calorimetry

All products showed thermal behavior typical of β-phase GP, with two endothermic peaks during the

Table 1: Mean and standard deviation of percentage weights from chemical assay of all GP brands analyzed

GP brands	GP (mean±SD)	Wax/Resin (mean±SD)	Inorganic fraction (mean±SD)	ZnO (mean±SD)	$BaSO_4$ (mean±SD)
TH	15.2±0.23	7.7±0.60	77.8±0.10	72.6±0.10	5.19±0.09
OB	17.9±0.30	3.4±0.26	78.6±0.33	75.9±0.25	2.62±0.02
OBF	15.7±0.50	7.1±0.60	79.1±0.39	77.3±0.35	1.72±0.02
MC	22.4±0.35	4.5±0.70	72.5±0.60	67.3±0.32	5.21±0.04
MF	18.2±0.14	7.8±0.40	73.7±0.10	66.2±0.15	7.57±0.04

GP: Gutta-percha

Table 2: Elemental microanalysis and X-ray diffraction of all GP brands analyzed. ZnO and $BaSO_4$ were detected in all specimens analyzed (X)

GP brands	Percentage of chemical elements (mean±SD)				X-ray diffraction	
	Carbon	Hydrogen	Nitrogen	Sulfur	ZnO	$BaSO_4$
TH	19.68±0.45	2.52±0.51	-	0,72±0.03	X	X
OB	19.96±0.32	2.48±0.53	-	0,36±0.08	X	X
OBF	18.56±0.42	2.35±0.36	-	0,28±0.06	X	X
MC	24.70±0.71	3.21±0.11	0.21±0.01	0,72±0.09	X	X
MF	22.95±0.25	3.02±0.07	0.23±0.05	1,04±0.07	X	X

first run. Dental GP transitions occurred when the GP was heated from 50.7ºC to 53.4ºC (β- to α-phase) and from 60.6ºC to 62.9º (α- to amorphous-phase), depending on the specific compound.

After replication, all specimens analyzed showed similar thermal behavior (DSC and TGA), presented in Table 3. TGA showed that none of the materials had measurable weight loss under the experimental conditions (from ambient temperature up to 130º).

DISCUSSION

The Thermafil, Obtura and Microseal GP systems were used in this study due to their widespread clinical use in root canal systems and their excellent filling properties [1,4,23] even in oval-shaped root canals.[7] They also show high apical sealing capabilities, as showed in a microbiological model.[8] The constituents of these materials were identified by qualitative chemical analysis (X-ray Diffraction and EDX) and their relative percentages were determined by elemental microanalysis and chemical composition, using a slow dissolution process due to the low dissolving rate of GP.[23] Any resins and/or waxes present in the materials were not analyzed.

X-ray and Elemental Microanalyses provided an overview of the elemental composition of the GP brands. Elemental Microanalysis is the most popular technique for quantifying Sulfur and has been described by several authors in the literature.[3,13,24-25]

Despite the relevance and importance of the X-ray, microanalysis and diffraction techniques in the screening of some chemical elements and compounds present in GP brands, there are some limitations to the use of these techniques for quantitative analysis. For rigorous quantitative X-ray microanalysis, the atomic number of the analyzed element must be greater than 11. Thus, important elements such as hydrogen, carbon, nitrogen and oxygen could not be correctly quantified. In addition, the element concentration has to be greater than 5% and the specimen must be homogeneous in the volume sampled.[22,24-25] Assumptions concerning the relative contents of elements present in the material were made based on the results and zinc was found to be universally present in large amounts. These results indicate that zinc oxide is the main ingredient in these brands, which is in accordance with many studies.[3,6,9,13,23] Despite the differences in chemical compositions of the materials analyzed, there were no differences in their thermal behavior. This fact leads us to believe that gutta-percha percentages above 15% of the chemical composition probably determine the thermal behavior of the sample. In the present study, all specimens showed two typical major endothermic peaks in the first DSC run [Table 3], indicating that they are a β-form material. These results are in line with the data obtained by Schilder *et al.*[18] and Maniglia-Ferreira *et al.*;[19] however, during the second run, no peaks occurred at a temperature higher than 53.7ºC, which contradicts the findings of Combe *et al.*[21]

DSC allows for an appraisal of the estimated thermal range required to plasticize GP between 40ºC and 60ºC.[17] In endodontic therapy, dental GP is plasticized by a heat carrier (System B, Obtura II, Thermafil and Microseal microflow) or by Thermomechanical compaction (Microseal cone), which heats to a temperature higher than the maximum allowed to avoid partial degradation (100ºC), according to the Merck index[26] and Maniglia-Ferreira *et al.*[27]

The low fusion temperature of the tested materials is due to the high percentage of organic compounds in their composition (GP and wax/resins). The high quantities of wax and resins found in TH, OBF and MF can jeopardize the longevity of the endodontic treatment, as they are easily degraded, damaging the dimensional stability of the obturation material.[19,25,27-28]

Our DSC results, which are similar to those of Schilder *et al.*,[18] indicated that GP in the β-phase begins its transition to α-phase when heated from 51ºC to 53ºC, and the α-phase material begins its transition to an amorphous phase when heated between 60ºC and 62ºC. Our results suggest that after the material has cooled off and is heated up again, beginning a new heating cycle, the amorphous GP finds itself crystallized into the α-phase and is therefore, not able to return to the β-phase. Alternatively, its chemical structure may have changed in such a way

Table 3: Temperatures (ºC) at which endothermic peaks occurred (DSC analysis) and percentage of weight loss (TGA)

GP brands	DSC run 1		DSC run 2		TGA
	Peak 1	Peak 2	Peak 1	Peak 2	
TH	50.7	61.7	53.7	-	78.11
OB	53.4	62.4	51.9	-	77.35
OBF	51.6	60.6	52.7	-	78.13
MC	51.7	61.8	53.5	-	70.65
MF	52.4	62.9	51.7	-	72.94

TGA: Thermogravimetric analysis

that it became a *cis*-1, 4 polyisoprene, as only one endothermic peak appeared, which often occurs when the material has been submitted to too many thermal cycles.[29] A typical heating cycle of up to 130ºC caused changes in the behavior of the material due to the decrease in molar mass, which indicated polymer degradation by the backbone cleavage of polyisoprene.[27,30]

Combe *et al*.[21] also noted that fewer endothermic peaks were present during reheating of the polymer. It is thought that this new heating cycle breaks the chain of covalent bonded atoms,[11] changing its molecular structure and causing such behavior.[12] This covalent bonding along with natural physical entanglement of the long chains, produces unique and interesting properties in the bulk specimen.[11,21]

The nature and amount of inorganic components in dental GP strongly influence its clinical (i.e. brittleness, stiffness, tensile strength, radiopacity, flow, plasticity, elongation and inherent tension force) and thermal behavior and also allows for good control of its mechanical properties. According to Marciano *et al*.[17] the existence of discrepancies among the thermomechanical behaviors of fresh and thermally treated samples, demonstrates the importance of the thermodynamic properties of dental GP. As a consequence, the thermal history of these materials is important for its clinical properties. The results of this study show that this parameter is important in clinical applications and suggest that the high percentage of organic components found in dental GP may influence its degradation, although no correlation was identified between thermal behavior and chemical composition.

The concentration of wax and resins should not surpass 2% of the chemical composition,[10,20] therefore all tested materials showed excessive percentages of waxes and resins. In the 2008 study,[27] Maniglia-Ferreira *et al*. demonstrated advanced degradation of the GP polymer present in their formulations, which could have occurred due to excessive heating during the manufacturing process.

In practice, the endodontist can develop a continuously tapering conical form in the root canal preparation with a regular dentine wall, allowing for the use of GP cones with the ideal composition and avoiding preparations with a high percentage of inorganic elements, which make the cones rigid. Such a strategy would facilitate the performance of the three-dimensional root canal system obturation with thermoplastic techniques.[31] To date, the ideal composition has not been determined and/or identified; however, it has been noted clinically that when dental GP with excessive percentages of organic compounds are used, they become loose and can easily be deformed during their intra canal adaptation. In contrast, high percentages of inorganic compounds (higher than 85%) make the thermo plasticization of the obturation material more difficult. Further studies in this area are essential, as the supply of natural GP is in decline. Synthetic products, such as Resilon™ and Guta-Flow™, reflect this reality.

CONCLUSIONS

Results of the present study showed that: (i) MC presented the highest percentage of GP, followed by the MF, OB, OBF and TH; (ii) all tested materials showed excessive percentages of waxes and resins; (iii) no correlation was observed between chemical composition and thermal behavior; (iv) all the products showed thermal behavior typical of ß-phase GP and (iv) heating dental GP to 130ºC causes physical changes.

REFERENCES

1. Anbu R, Nandini S, Velmurugan N. Volumetric analysis of root fillings using spiral computed tomography: An *in vitro* study. Int Endod J 2012;43:64-8.
2. Goldberg F, Artaza LP, Silvio A. Efectiveness of different obturation techniques in the filling of simulated lateral canals. J Endod 2001;27:362-4.
3. Gurgel-Filho ED, Feitosa JP, Gomes BP, Ferraz CC, Souza-Filho FJ, Teixeira FB. Assessment of different gutta-percha brands during the filling of simulated lateral canals. Int Endod J 2006;39:113-8.
4. Tanomaru-Filho M, Pinto RV, Bosso R, Nascimento CA, Berbert FL, Guerreiro-Tanomaru JL. Evaluation of the thermoplasticity of gutta-percha and Resilon(®) using the Obtura II System at different temperature settings. Int Endod J 2011;44:764-8.
5. De Deus GA, Gurgel-Filho ED, Maniglia-Ferreira C, Coutinho-Filho T. Penetração intradentinária de quatro cimentos endodônticos. Braz Oral Res 2002;16:332-6.
6. Friedman CE, Sandrick JL, Heuer MA, Rapp GW. Composition and physical properties of gutta-percha endodontics filling materials. J Endod 1977;3:304-8.
7. Ozawa T, Taha N, Messer HH. A comparison of techniques for obturating oval-shaped root canals. Dent Mat J 2009;28:290-4.
8. Brosco VH, Bernardineli N, Torres SA, Consolaro A, Bramante CM, Moraes IG, *et al*. Bacterial leakage in obturated root canals-part 2: A comparative histologic and microbiologic analyses. Oral Surg Oral Med Oral Pathol Oral Radiol Endod 2010;109:788-94.
9. Chandrasekhar V, Morishetty PK, Metla SL, Raju RV. Expansion of gutta-percha in contact with various concentrations of zinc oxide-eugenol sealer: A three-dimensional volumetric study. J Endod 2011;37:697-700.
10. Schilder H. Filling root canals in three dimensions. Dent Clin North Am 1967;11:723-44.
11. Goodman A, Schilder H, Aldrich W. The thermomechanical properties of guta-percha: II: The history and molecular chemistry of guta-percha. Oral Surg Oral Med Oral Pathol 1974;37:954-61.
12. Cohen BD, Combe EC, Lilley JD. Effect of thermal placement techniques on some physical properties of dental gutta-percha. Int Endod J 1992;25:292-6.
13. Maniglia-Ferreira C, Valverde GB, Silva Jr JB, Paula RC, Feitosa JP,

Souza-Filho FJ. Clinical relevance of trans 1,4-polyisoprene aging degradation on the longevity of root canal treatment. Braz Dent J 2007;18:97-101.
14. Schilder H, Goodman A, Aldrich W. The thermomechanical properties of gutta-percha. Part V. Volume changes in bulk gutta-percha as a function of temperature and its relationship to molecular phase transformation. Oral Surg Oral Med Oral Pathol 1985;59:285-96.
15. Gurney BF, Best EJ, Gervasio E. Physical measurements on gutta-percha. Oral Surg Oral Med Oral Pathol 1971;32:260-70.
16. Marciano J, Michailesco PM, Abadie JM. Stereochemical structure characterization of dental gutta-percha. J Endod 1993;19:31-4.
17. Marciano J, Michailesco PM, Charpentier E, Carrera L, Abadie JM. Thermomechanical analysis of dental gutta-percha. J Endod 1992;18:263-70.
18. Schilder H, Goodman A, Aldrich W. The thermomechanical properties of gutta-percha. III: Determination of phase transition temperatures for gutta-percha. Oral Surg Oral Med Oral Pathol 1974;38:109-14.
19. Maniglia-Ferreira C, Gurgel-Filho ED, Silva Jr JB, Paula RC, Feitosa JP, Gomes BP, *et al*. Brazilian gutta-percha points. Part II: thermal properties. Braz Oral Res 2007;21:29-34.
20. Marciano J, Michailesco PM. Dental gutta-percha: Chemical composition, X-ray identification, enthalpic studies and clinical implications. J Endod 1989;15:149-53.
21. Combe EC, Cohen BD, Cummings K. Alpha-and beta-forms of gutta-percha in products for root canal filling. Int Endod J 2001;34:447-51.
22. Gurgel-Filho ED, Feitosa JP, Teixeira FB, Paula RC, Silva Jr JB, Souza-Filho FJ. Chemical and X-ray analyses of five brands of dental gutta-percha cone. Int Endod J 2003;36:302-7.
23. Möller B, Ørstavik D. Chemical and Energy Dispersive X-ray analyses of gutta-percha points. J Endod 1984;10:413-6.
24. Lyman CE, Goldstein JI, Romig Jr AD, Echlin P, Joy DC, Newbury DE, *et al*. Scanning electron microscopy, X-ray microanalysis, and analytical electron microscopy. New York, NY: Plenum Press; 1990. p. 33-41.
25. Maniglia-Ferreira C, Silva Jr JB, Paula RC, Feitosa JP, Cortez DG, Zaia AA, *et al*. Brazilian gutta-percha points. Part I: Chemical composition and X-ray diffraction analysis. Braz Oral Res 2005;19:193-7.
26. Budavari S, O'Neil MJ, Smith A, Heckelman PE, Kinneary J. Merck index 12nd ed. New Jersey: Merck and Co. Inc.; 1996.
27. Maniglia-Ferreira C, Valverde GB, Silva Jr JB, Paula RC, Feitosa JP, Souza-Filho FJ. Degradation of trans-polyisoprene after root filling with thermoplasticized techniques. Int Endod J 2008;41:296-302.
28. Stevens MP. Polymer chemistry, an introduction. New York: Oxford University Press; 1999.
29. Ivan G, Meghea A, Giurginka M, Iftimie N. Thermo-oxidative degradation of some elastomers with a high content of 3,4 isoprene units. Pol Degrad Stab 2003;80:397-402.
30. Silva Jr JBA, Paula RC, Feitosa JP, Gurgel-Filho ED, Maniglia-Ferreira C, Souza-Filho FJ. *In vivo* aging of gutta-percha endodontic cone. J Appl Pol Sc 2006;100:4082-8.
31. Maniglia-Ferreira C, Almeida-Gomes F, Sousa BC, Lins CC, Santos RA. A case of unusual anatomy in second mandibular molar with four canals. Eur J Dent 2008;2:217-9.

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Source of Support: Nil.
Conflict of Interest: None declared