Degradation of *trans*-polyisoprene after root filling with thermoplasticized techniques

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Abstract

Maniglia-Ferreira C, Bönecker G, Silva JBA Jr, de Paula RCM, Feitosa JPA, Souza-Filho FJ. Degradation of *trans*-polyisoprene after root filling with thermoplasticized techniques. *International Endodontic Journal*, **41**, 296–302, 2008.

Aim To evaluate *ex vivo* degradation of gutta-percha following six thermoplastic obturation techniques.

Methodology Ninety human-extracted mandibular premolars were selected and divided randomly into nine groups for filling. Group 1: thermomechanical compaction for 3 s with Konne gutta-percha points (Konne Ind. e Com. de Mat. Odontol., Belo Horizonte, MG, Brazil); Group 2: thermomechanical compaction for 3 s with Dentsply TP gutta-percha points (Dentsply Indústria e Comércio Ltda, Petrópolis, R.J. Brazil); Group 3: thermomechanical compaction for 10 s with Konne; Group 4: thermomechanical compaction for 10 s with Dentsply TP; Group 5: warm vertical condensation using System B (EIE/Analytic, Richmond, WA, USA) with Konne; Group 6: warm vertical condensation using System B with Dentsply TP; Group 7: vertical condensation with Konne; Group 8: vertical condensation with Dentsply TP; Group 9: Microseal cone (Analytic Endodontics, Glendora, CA, USA). A further four groups were assessed without using teeth, Group 10: Microseal microflow (Analytic Endodontics); Group 11: Obtura (Obtura Corporation, Penton, MO, USA); Group 12: Obtura flow (Obtura Corporation); Group 13: Thermafil (Dentsply Maillefer, Tulsa, OK, USA). The filling material was removed from the root canal and *trans*-1,4-polyisoprene isolated by solubilization of the root filling remnants in chloroform followed by filtration and centrifugation. By gel permeation chromatography and infrared spectroscopy, the occurrence and degree of degradation were assessed. The results were analysed statistically using the Kruskal–Wallis test. With differential scanning calorimetry, the thermal behaviour of the gutta-percha was determined.

Results A significant decrease in polymer molar mass and the production of carboxyl and hydroxyl groups in the polymer were observed with thermomechanical compaction used for 10 s and vertical condensation filling techniques ($P = 0.0001$ and $P = 0.0005$, respectively). Other techniques caused no polymer degradation.

Conclusion Polyisoprene degrades with high temperature. Thermomechanical compaction for 10 s and vertical condensation were associated with the greatest degradative process.

Keywords: root-canal filling techniques, root-canal therapy, *trans*-polyisoprene degradation.

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Introduction

The main objective of root-canal treatment is to prevent or cure apical periodontitis by cleaning, shaping and filing the root-canal space. The root-canal system has a complex anatomy, characterized by the occurrence of

curvatures, accessory and lateral canals, deltas and isthmuses (Schilder 1967). Root-canal filling procedures should fill the main root canal and accessory canals (Weine 1984, Goldberg *et al.* 2001, De Deus *et al.* 2002).

Gutta-percha and sealer are currently the filling materials of choice, but they can be used in a variety of ways to fill root canals (Nguyen 1994). Cold lateral condensation relies on sealer to fill accessory anatomy because the core filling material will not move out of the main canal (Gurgel-Filho *et al.* 2006) and into canal irregularities (Reader *et al.* 1993). Studies have shown that thermoplasticized gutta-percha is more capable of replicating the intricacies of the root-canal system (Gutmann *et al.* 1993) and has the potential to produce a complete filling of root-canal space including lateral canals (Schilder 1967, Goldberg *et al.* 2001, Gurgel-Filho *et al.* 2006).

A number of warm gutta-percha methods are available for filling root canals. These include warm lateral condensation, warm vertical condensation, coated carrier system, injections systems and thermomechanical compaction (Gilhooly *et al.* 2001). Unfortunately, the improved flow characteristics of warm gutta-percha can result in reduced apical control. Extrusion of material beyond the apical limits of the root-canal space is a common finding with these techniques (Gulabivala *et al.* 1998). Although the commonly used materials are generally well tolerated by periradicular tissue, overextension of a root filling prejudices a successful outcome (Hauman & Love 2003).

Polyisoprene (*trans*-1,4) is one of the components of dental gutta-percha and represents 14.5–21.8% of its weight (Friedman *et al.* 1977, Gurgel-Filho *et al.* 2003, Maniglia-Ferreira *et al.* 2005). Unfortunately, degradation of polyisoprene can occur as a result of several factors such as aging, increase in temperature, exposure to light, as well as to chemical and biological environmental changes (Sawada 1987, Somers *et al.* 2000, Bode *et al.* 2001, Enoki *et al.* 2003, Sato *et al.* 2003, Maniglia-Ferreira *et al.* 2007b).

The aging of dental gutta-percha has been studied in order to verify the effect of time on its mechanical properties (Oliet & Sorin 1977), and the synergistic action of age and moisture on the material (Arvanitoyannis *et al.* 1993). Arvanitoyannis *et al.* (1993) studied commercial brands of gutta-percha stored in different laboratory environmental conditions (time, temperature and humidity) to prevent degradation before root-canal filling. Recently, chemical aspects of *in vivo* aging of gutta-percha cones have been reported (Silva *et al.* 2006, Maniglia-Ferreira *et al.* 2007b). However, the consequence of this degradation of gutta-percha during the heating process by themoplasticized root-canal filling techniques was not discussed.

The purpose of this *ex vivo* study was to study the degradation of dental gutta-percha (*trans*-1,4-polyisoprene) according to the increase in temperature after using different thermoplastic filling techniques.

Materials and methods

Sampling procedures

The Ethical Committee in Research of the Dental School of Fortaleza (University of Fortaleza) approved a protocol describing the sample collection for this investigation.

This study included root-filling techniques based on thermomechanical compaction, warm vertical condensation, coated carrier systems and injection systems. Ninety human-extracted mandibular premolars were selected and divided randomly into nine groups for filling. After cleaning and shaping procedures, the root canals were filled using different gutta-percha brands (Table 1) and techniques (Table 2) and pulp canal sealer. Group 1: thermomechanical compaction for 3 s with Konne gutta-percha points (Konne Ind. e Com. de Mat. Odontol., Belo Horizonte, MG, Brazil); Group 2: thermomechanical compaction for 3 s with Dentsply TP gutta-percha points (Dentsply Indústria e Comércio

Table 1 Dental gutta-percha brands selected for study

Product	Manufacturer	Expiry date
Konne (M)	Konne Ind. E Com. De Mat. Odontol., Belo Horizonte, MG, Brazil	Jan/2008
Dentsply TP (M)	Dentsply Indústria e Comércio Ltda, Petrópolis, R.J. Brazil	Nov/2008
Microseal (cone)	Analytic Endodontics, Glendora, CA, USA	Aug/2007
Microseal (microflow)		Sept/2007
Obtura	Obtura Corporation, Penton, MO, USA	Jul/2007
Obtura flow		Sept/2007
Thermafil	Dentsply Mailleffer, Tulsa, OK, USA	Oct/2007

Table 2 Groups, techniques and dental gutta-percha (GP) brands selected for study

Groups	Techniques	GP brands
1	TC (3 s/6000 rpm)	Konne
2	TC (3 s/6000 rpm)	Dentsply TP
3	TC (10 s/6000 rpm)	Konne
4	TC (10 s/6000 rpm)	Dentsply TP
5	WC (System B, 180 °C)	Konne
6	WC (System B, 180 °C)	Dentsply TP
7	VC	Konne
8	VC	Dentsply TP
9	MC	Microseal
10	Microseal microflow	Microseal
11	Obtura	Obtura
12	Obtura flow	Obtura flow
13	Thermafil	Thermafil

TC, thermomechanical compaction; WC, wave of condensation; VC, vertical condensation; MC, microseal cone.

Ltda, Petrópolis, R.J. Brazil); Group 3: thermomechanical compaction for 10 s with Konne; Group 4: thermomechanical compaction for 10 s with Dentsply TP; Group 5: warm vertical condensation using System B (EIE/Analytic, Richmond, WA, USA) with Konne; Group 6: warm vertical condensation using System B with Dentsply TP; Group 7: vertical condensation with Konne; Group 8: vertical condensation with Dentsply TP; Group 9: microseal cone (Analytic Endodontics, Glendora, CA, USA). A further four groups were made up of those whereby gutta-percha heating occurs prior to insertion into the root canal, and therefore a group of teeth was not required; Group 10: Microseal microflow (Analytic Endodontics); Group 11: Obtura (Obtura Corporation, Penton, MO, USA); Group 12: Obtura flow (Obtura Corporation); Group 13: Thermafil (Dentsply Maillefer, Tulsa, OK, USA).

The thermomechanical compaction technique was adopted with the use of a gutta-condenser (Dentsply Maillefer, Ballaigues, Switzerland) attached to an electric micro-motor (Easy Endo, Belo Horizonte, MG, Brazil) at 6000 rpm. The vertical compaction technique was accomplished by heating condensers in an alcohol lamp (5 s) as described by Schilder (1967).

Gutta-percha from the apical portion of 5 mm only was removed from the root canal using Hedströem files (Dentsply Maillefer, Ballaigues, Switzerland) without solvent. The samples were then submitted to dissolution in chloroform (Synth, Diadema, São Paulo, Brazil) over night by stirring at room temperature (28 °C). After this, the mixture was passed through a cotton filter to remove inorganic or insoluble materials. The solution was centrifuged (Andreas Hettich GmbH & Co., KG, Tuttlingen, Germany) at 6000 rpm for 10 min to separate the small solid particles that remained after filtration and to obtain clear solutions.

Gel permeation chromatography (GPC) and infrared spectroscopy (FT-IR) were used to analyse the materials. Gutta-percha was purified by dissolution in chloroform and precipitated with methanol (Synth, Diadema, SP, Brazil). This raw gutta-percha obtained for each group was included in the study as a control group, and degradation took place in order to compare them with the groups that were heated. The samples of each group had similar results.

Gel permeation chromatography (GPC)

The chromatographic study was performed using a high-performance liquid chromatographic system with a refractive index detector, RID-6A (LC-10AD, Shimadzu, Tokyo, Japan). A series connected system including a pre-column and two Phenomenex columns (Linear/Mixed 5 and 5U) was used, and toluene (Synth, Diadema, São Paulo, Brazil) was employed as an eluent at a flow rate of 1 mL min^{-1} at 25 °C. All sample solutions were filtrated in politetrafluoretilene (PTFE) membranes (Sigma-Aldrich Co., St. Louis, MO, USA). The instrument was calibrated with polystyrene standards (Shodex-Showa, Orlando, FL, USA), with molar mass (M_w) ranging from 1.13×10^3 to 2.15×10^6 g mol^{-1}.

Gel permeation chromatography is a method used to determine the molecular weight of polymers. It employs a liquid chromatography that separates molecules according to molecular weight (Elias 1997).

FT-IR spectroscopy analysis

FT-IR spectra of gutta-percha film were registered in an 8300 spectrometer model (Shimadzu, Tokyo, Japan) in the range of 4000 to 400 cm^{-1}. The films were prepared by successive casting and solvent evaporation from polymer solutions in CHCl$_3$ on KBr window. Unaged *trans*-1,4-polyisoprene from purified raw gutta-percha was heated into films at 140 °C in air at different periods and thermal oxidations. The samples were then studied by FT-IR spectroscopy (Table 3).

Chemical groups were identified by FT-IR spectroscopy, which is an analysis based on the vibrational and rotational motions of a molecular bond (Pavia *et al.* 1996).

Table 3 Means of FT-IR (M_{pk}) and GPC (elution volume) results obtained from polyisoprene extracted from filling materials

Groups	Techniques	M_{pk} (g mol^{-1}) Before	After	Elution volume (mL)
1	TC (3 s)	6.2×10^5	6.1×10^5	13.54
2	TC (3 s)	5.5×10^5	5.5×10^5	13.89
3	TC (10 s)	6.2×10^5	1.7×10^5	19.34
4	TC (10 s)	5.5×10^5	1.8×10^5	19.79
5	WC	6.2×10^5	5.3×10^5	13.66
6	WC	5.5×10^5	5.5×10^5	13.83
7	VC	6.2×10^5	1.5×10^5	19.60
8	VC	5.5×10^5	1.4×10^5	19.60
9	MC	5.7×10^5	5.5×10^5	13.56
10	Microflow	1.3×10^5	1.1×10^5	16.62
11	Obtura	4.8×10^5	4.3×10^5	13.15
12	Obtura flow	1.2×10^6	1.2×10^6	16.45
13	Thermafil	1.9×10^5	1.5×10^5	16.69

TC, thermomechanical compaction; WC, wave of condensation; VC, vertical condensation; MC, microseal cone.

Differential scanning calorimetry (DSC)

The thermal analyses of all samples were carried out by differential scanning calorimetry (DSC; Shimadzu DSC-50, Shimadzu Corporation, Japan), the calibration of each was checked out 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 (Combe *et al.* 2001).

The principle involved is that when a material is heated and undergoes a physical change, such as fusion or transitional crystallization from one form into another, it absorbs or generates heat (Marciano & Michailesco 1989). DSC is constructed to measure the enthalpic energy of these transformations. The material is kept steady at the same temperature by cooling or heating it under the control of a computer. When a physical change occurs in the test material (endothermic or exothermic reaction), the device equalizes the temperature with the control. This three-unit device consists of heating, controlling and recording systems (Marciano & Michailesco 1989).

Samples were heated in the analyser to determine the occurrence of endothermic peaks. The transformation temperatures of dental gutta-percha compounds were determined to be 42–52 °C for the β- to α-form, and 53–62 °C for the α- to amorphous form (Schilder *et al.* 1974, Maniglia-Ferreira *et al.* 2007a).

All specimens were heated from room temperature to 70 °C at a rate of 1 °C min^{-1} being the endothermic peaks recorded for each of them. This was followed by

Table 4 Temperatures (°C) at which endothermic peaks occurred (DSC analysis), indicating β-form for all samples

	DSC run 1		DSC run 2	
Gutta-percha brands	Peak 1	Peak 2	Peak 1	Peak 2
Konne	51.7	61.1	51.8	—
Dentsply TP	48.6	61.0	50.0	—
Microseal (cone)	51.3	61.2	52.9	—
Microseal (microflow)	51.6	60.9	53.1	—
Obtura	52.9	61.7	52.3	—
Obtura Flow	51.3	61.4	52.1	—
Thermafil	51.9	61.2	52.6	—

DSC, differential scanning calorimetry.

rapid heating up to 130 °C and rapid cooling to room temperature, and heating back again up to 70 °C, at a rate of 1 °C min^{-1} being the endothermic peaks recorded once again.

The results from this analysis can be found in Table 4, indicating that all analysed materials (gutta-percha) were found to be in β phase. In order to have gutta-percha in α phase, a continuous and controlled heating source is required to avoid overheating that causes the appearance of an amorphous phase and thermal degradation, as seen in the second set of the analysed materials (Table 4).

All analysed samples showed thermal degradation, indicating only one peak change of phase transformation in the second cycle of heating.

Statistical analysis

The data collected for each sample were entered into a spreadsheet and analysed statistically using SPSS for Windows (SPSS Inc., Chicago, Il, USA). The Kruskal–Wallis test was used to test the null hypothesis that there is no relationship between degradation of *trans* 1,4-polyisoprene and heating promoted by thermoplastic filling techniques.

Results

Data obtained from FT-IR spectrum (Fig. 1) and GPC (peak molar mass and elution volume) for the root-filling samples are shown in Table 3. The GPC curve of the unheated gutta-percha was a unimodal with a maximum peak at 13.56 mL, corresponding to a molar mass peak (M_{pk}) of 1.7×10^6 g mol^{-1}, in agreement with the values reported, ranging from 1×10^5 to 2.5×10^6 g mol^{-1} (Tanaka 1989).

A maximum peak shift to higher elution volume for root canals filled at different techniques was noted. The
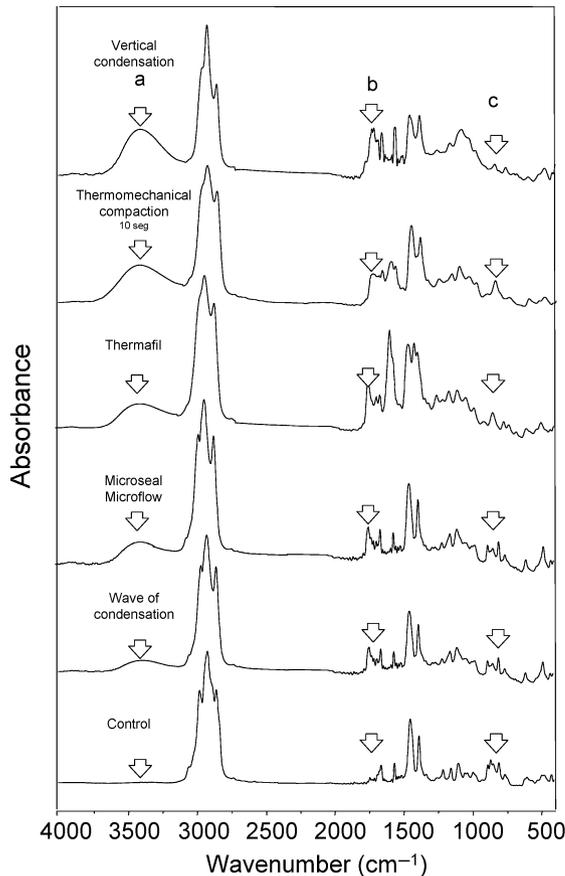
Figure 1 FT-IR spectra of no heated dental gutta-percha and polymer (*trans*-polyisoprene) extracted from root canal after using different thermoplastic obturation techniques.

consequent decrease in molar mass indicated that polymer degradation by the backbone cleavage of polyisoprene occurred (Table 4). The results were statistically analysed (SPSS for windows) and decrease in polymer molar mass and production of carboxyl and hydroxyl groups in the polymer were observed after use of thermomechanical compaction (10 s; $P = 0.0001$), vertical compaction ($P = 0.0005$) for both gutta-percha brands.

Moreover, Thermafil ($P = 0.0275$), Microseal microflow ($P = 0.0275$) and Obtura flow ($P = 0.0275$) filling techniques showed polymer degradation before the heating process took place (control). These degradations were also seen in the GPC and FT-IR previously. It is common knowledge that these techniques are supposed to be safe because of the controlled heating source used; therefore, degradation should not occur.

Discussion

The degradation of *trans*-1,4-polyisoprene occurs because of temperature, exposure to light, as well as to chemical (oxygen, ozone, metal; Somers *et al.* 2000, Rodrigues *et al.* 2004) and biological environmental shifts (microorganisms, enzyme) (Bode *et al.* 2001, Enoki *et al.* 2003, Sato *et al.* 2003, Silva *et al.* 2006, Maniglia-Ferreira *et al.* 2007b).

Care must be taken when applying heating techniques on gutta-percha cones during filling procedures. Thermocompaction (10 s/6000 rpm) and vertical condensation with uncontrolled heat sources promote excessive intracanal heating, causing degradation of gutta-percha polymer.

Surprisingly, many techniques employing controlled heat sources, such as the Thermafil, Microseal microflow and Obtura flow, showed unexpected high polymer degradation. It may be the case that the degradation occurred because of excessive heating during the manufacturing process.

This degradation can be seen through the FT-IR analysis (Fig. 1), which shows formation of degradation products including volatile ones. The GPC analysis showed breakage of carbon chains in the gutta-percha polymer, with formation of short- and low-molecular-weight chains. This conclusion is based on the comparison with polyisoprene 1,4-*trans* polymer molecular weight that has carbon chains with variations in molecular weight from 1×10^5 to 2.5×10^6 g mol^{-1} (Tanaka 1989), clearly observed in all brands before use.

After using previous techniques, it was observed that thermocompaction (10 s) and vertical condensation techniques caused formation of carbon chains with low molecular weights. Consequently polymer degradation occurred, forming new compounds with low molecular weights such as peroxides and volatile products. A result of this is loss of stability of the material and molar mass reduction that will jeopardize the sealing capability of root filling with the risk of root-canal reinfection (Silva *et al.* 2006).

The degradation reaction includes chemical changes that can be analysed by FT-IR. Three important regions, using the FT-IR spectra (Fig. 1), could be considered after aging: (i) 3400–3420 cm^{-1} attributed to OH stretching; (ii) 1715–1737 cm^{-1}, because of C=O stretching; and (iii) 797–881 cm^{-1}, attributed to =C–H bending from *trans*-1,4-isomer. All analysed materials demonstrated the presence of OH and C=O groups after using the different obturation techniques.

These groups correspond to degradation products such as alcohols, carboxylic acid, hydroperoxide, aldehyde, ketone, ether or ester. Some of these substances are present in the oxidation of polyisoprenes (Alam *et al.* 2000). The presence of groups containing oxygen indicates that the degradation process includes oxidation, as reported by Silva *et al.* (2006).

Another important effect of volatile product formation during degradation is polymer weight loss. Determination of residual weight of the *cis*-1,4-polyisoprene sample degraded by bacteria, for example, showed weight losses up to 18% after 10 weeks of incubation at 30 °C (Enoki *et al.* 2003). More weight loss (80%) was also verified in the oxidation of vulcanized rubbers in lipid peroxidation (Sato *et al.* 2003). The weight loss in gutta-percha polymer could make the cone material more porous and could reduce its root-canal sealing property.

Unheated gutta-percha is more crystalline than the overheated material, showing an amorphous polymer profile. The formation of peroxide products, crosslinking and cleavage of main chain are factors that might be responsible for reducing crystallinity (Richardson & Sacher 1953).

In thermal oxidation of *trans*-1,4-polyisoprene films at 140 °C an increase in C = O stretching (1720 cm^{-1}; Fig. 1a) and OH stretching (3448 cm^{-1}; Fig. 1b) absorbance was observed, as well as a decrease in =C–H bending (835 cm^{-1}; Fig. 1c). There is also an increase in the region around 1100 cm^{-1}. The same spectral changes are observed in *in vivo* aging of gutta-percha cones, according to Silva *et al.* (2006). Some differences between the *in vivo* aging of cones and thermal oxidation of gutta-percha polymer were noted. Firstly, OH and C=O bands are relatively more intense in polymer when heated. This is the end of thermal oxidation, because all C=C have been consumed. Second, the region around 1300–1800 cm^{-1} in aged material *in vivo* is much more complex. Finally, the band intensity for heated material has a clear tendency (increase in OH and C=O and decrease in =C–H) with time of heating, not shown for *in vivo* aging. As expected, the *in vivo* degradation is slower and occurs in a more complex manner.

The results of this study show which parameter is important in clinical applications, during root filling steps, when choosing the ideal temperature to make the gutta-percha cone flow. During clinical treatment, gutta-percha should be plasticised under adequate and controlled conditions so as not to be permanently altered and/or lose its chemical characteristics.

The use of uncontrolled heat sources can overheat gutta-percha up to 300 °C causing its degradation (Bode *et al.* 2001). Heat source should be used carefully and instrument should be heated for a few seconds only before use, if overheated periodontal tissue damage might occur (Mc Cullagh *et al.* 2000).

Conclusion

Trans-1,4-polyisoprene in gutta-percha cones degrades with high temperatures. The degree of degradation is dependent on the increase of temperature. The technique of root filling can be an important factor affecting the durability of gutta-percha, principally because of possible early degradation of gutta-percha by excessive heat.

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