J Therm Anal Calorim (2011) 103:563–567
DOI 10.1007/s10973-010-0985-4

Thermal analysis of commercial gutta-percha

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Received: 4 May 2010 / Accepted: 26 July 2010 / Published online: 8 August 2010

Abstract The aim of this work is to examine the behaviour of gutta-percha (α–β) after heating, because of the several techniques using the warm gutta-percha as root canal filling material. Samples of gutta-percha have been examined by the thermal analysis. The gutta-percha has been submitted to four runs of heating from the temperature of 25–130 °C, followed by spontaneous cooling. It was found that some products have shown the typical behaviour of the α-gutta-percha; some materials have shown characteristics similar to the conventional β-gutta-percha. The samples have shown a significant mass loss after the first run of heating, while the mass tends to stabilize after the third run. Heating of gutta-percha up to 130 °C causes physical changes; this is due to the presence of additives, which alter the behaviour of the material.

Keywords Gutta-percha · Thermal analysis · Trans-polysoprene

Introduction

The gutta-percha is the filling material more universally approved and used for its properties which are close to the characteristics of the ideal filling material [1, 2]. The polymer of the gutta-percha (trans-polysoprene) can exist in two crystalline forms α and β: they differ by the distance between two consecutive -CH_3 groups placed on the same side in relation to the carbons engaged in the double bonds ("molecular repeat distance") and the two phases (α and β) are inter-convertible.

When β-gutta-percha is thermally analysed, two endothermic peaks occur; the first (between 42 and 49 °C) corresponds to the transformation from β-gutta-percha to α-gutta-percha; the second peak (between 53 and 59 °C) accompanies the conversion of the α-phase to amorphous gutta-percha. It is known that natural gutta-percha occurs as the α-form. If that is cooled at a rate of more than 0.5 °C/h, the molecules rearrange to β-form [3–5]. It is now well established that the conventional gutta-perchas exist in the β-form of trans-polyisoprene.

Since Schilder [6] introduced the warm vertical condensation technique, a number of clinical placement techniques involving warm gutta-percha have been developed [7, 8]. In recent years, a number of manufacturers have formulated gutta-perchas, specifically for warm techniques [9].

α-gutta-percha shows high flowability and low viscosity after heating, and it also acquires adhesion properties. The β-gutta-percha has lower flowability and higher viscosity.

The physical properties of conventional gutta-percha have been widely reported, while there have been few publications with respect to the thermal properties of these new materials (in the commercial preparations for endodontic treatment the actual trans-polysoprene percentage is about 20%).

Cantatore et al. [10] have shown that it is not appropriate to use the terms of alpha or beta gutta-percha, because all types of gutta-percha analyzed, in their study, have shown the same complex polymeric structures.

The thermal analysis is a very useful technique in order to check the quality of different commercial products and

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to perform a comparative analysis. In particular, it is very useful to study properties of dental materials [11–13].

Objectives of the research were to determine the thermal behaviour of some commercial products, to make a deduction about their crystalline structure, and to submit them to cycles of heating simulating the clinical conditions during the root canal filling and to determine the effects of those heating procedures on the material.

Materials and methods

The materials used are reported in Table 1. The measurements were carried out on a thermogravimetric/differential thermal analyser (Model TG/DTA 6300, Seiko Instruments USA Inc. Torrance, CA, USA).

Samples were heated in the analyser to determine the occurrence of endothermic peaks; two peaks would be expected: one between 42 and 49 °C and one between 53 and 59 °C, whereas the α-material would not show the first peak, corresponding to the transformation of the β- to the α-form.

10 samples of each product (number of products = 5) were analyzed (50 samples total analyzed); for each sample of gutta-percha the following cycle of heating and cooling experiments was carried out four times:

(1) Analysis of the sample at standard temperature (25 °C):
(2) Evaluation of the mass (mg).
(3) Heating from the temperature of 30 to 70 °C with an increase of 1 °C/min [14].
(4) Heating from the temperature of 70 to 130 °C with an increase of 5 °C/min with maintenance of the final temperature for 10 min.
(5) Cooling of the sample with spontaneous decrement up to the temperature of 30 °C.

Statistical analysis

Fisher's PLSD, Scheffe and Bonferroni/Dunn methods were used to evaluate the presence of statistically significant differences.

Results

Material 1 (Fig. 1) has shown in the first run two typical major endothermic peaks (48.0 and 61.8 °C); the second, third and fourth analysis have shown one endothermic peak (ca. 62.0 °C). Material 2 in the first run has shown three endothermic peaks (46.0, 55.9, and 66.0 °C), during cooling three corresponding exothermic peaks (59.4, 51.7, and 38.9 °C) have been observed (Fig. 2). The second, third, and fourth run have shown two endothermic peaks (Fig. 3); during cooling two corresponding exothermic peaks (51.5 and 39.6 °C) have been observed.

Materials 3 have a thermal behaviour similar to material 1.

Material 4 (Fig. 4) in the first run has shown three endothermic peaks (44.5, 55.5, and 62.9 °C). The second, third, and fourth run have not shown a third endothermic peak.

Material 5 has shown three major peaks (44.9 and 54.0 °C). The complete results of the differential thermal analysis are presented in Table 2 which also includes the temperatures (°C) at which the endothermic peaks occurred; the temperatures showed in the table were obtained calculating averaged values per each material.

The thermogravimetric analysis has shown an important diminution of the mass of the samples in the first run (3.673–7.534%); the mass tends to stabilize after the fourth run (0.008–0.092%) (Fig. 5). The thermogravimetric results are presented in Table 3.

Discussion

It has been found that shape and the contact surface between used material and plain surface of the tool can influence the final result of the test, since the sensors (thermojunctions of platinum–rhodium) are situated under the crucible. The ideal sample is a thin dust or a very thin foil; this perfectly explains a not linear calorimetric profile of our curves; from the analysis of several runs of the same material a discrepancy emerges in the thermodynamic evaluation who apparently increases with the increase of

Table 1 List of products

Materials	Manufactures	Type
Gutta-percha PD	Produits Dentaires S.A. Vevey, Switzerland	PD Gutta Percha Points 29 mm–30 ∅
Gutta-percha Inline	BM Dentale, Italy	Inline Gutta Percha Points Standardized hand rolled points 28 mm–30 ∅
Gutta-percha Mynol	Mynol, USA	Mynol Gutta Percha Points AAE Style 28 mm–30 ∅
Gutta-percha Microseal	Irvine, USA	Microflow Gp Cone 30 ∅
Gutta-percha Soft-Core	Axis Dental, USA	Soft-Core endodontics obturators 30 ∅

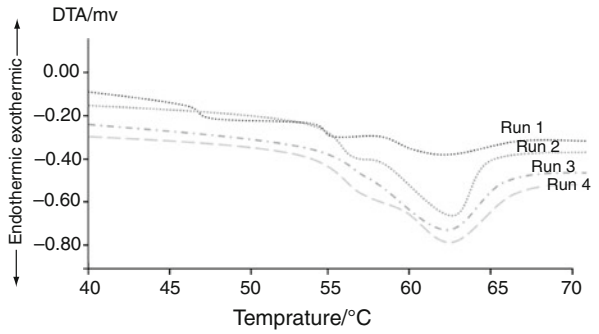

Fig. 1 Differential thermal analysis of material 1. First run, showing two typical major endothermic peaks (48.0 and 61.8 °C), indicating that the material was in β form. Second and third run performed after material had been heated at 130 °C, also showing one endothermic peak (ca. 62.0 °C)

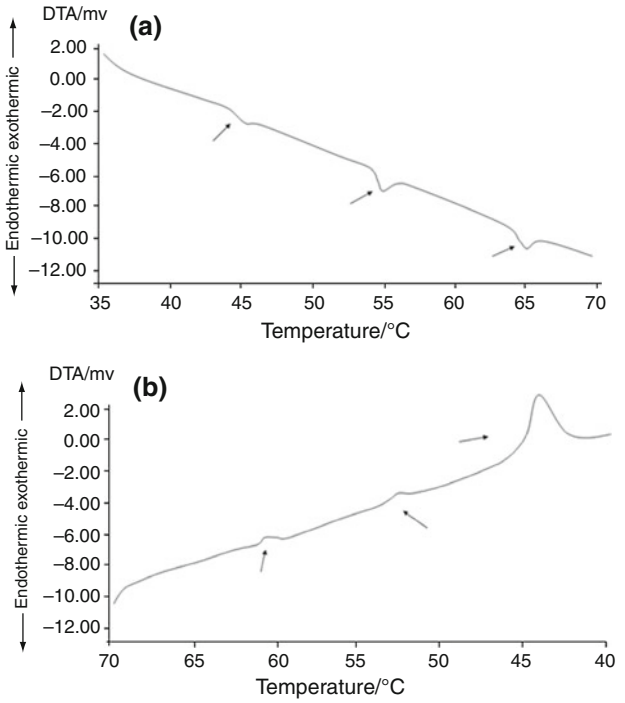

Fig. 2 Differential thermal analysis of material 2. **a** First run showing three endothermic peaks during warming (46.0, 55.9, and 66.0 °C). **b** During cooling, we observe three corresponding exothermic peaks (59.4, 51.7, and 38.9 °C)

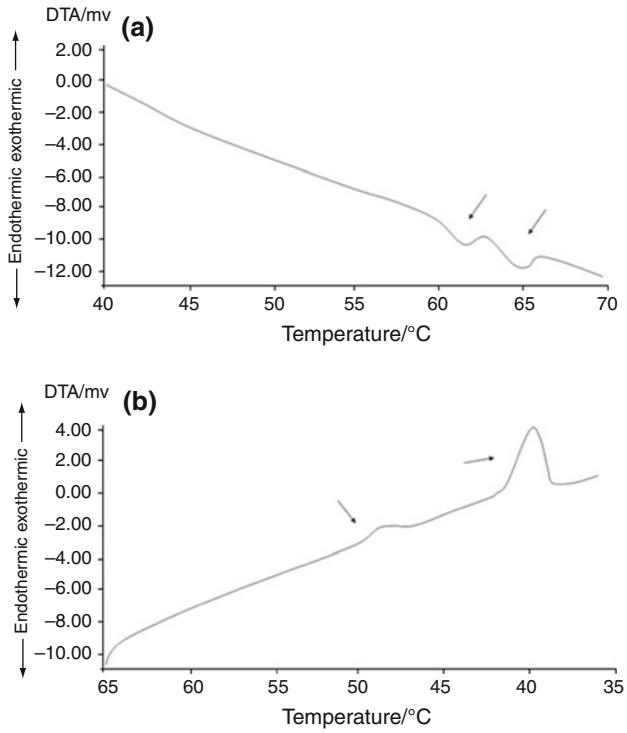

Fig. 3 Differential thermal analysis of material 2. **a** Second run, showing two endothermic peaks during warming (60.9 and 66.6 °C); **b** During cooling, we observe two corresponding exothermic peaks (51.5 and 39.6 °C)

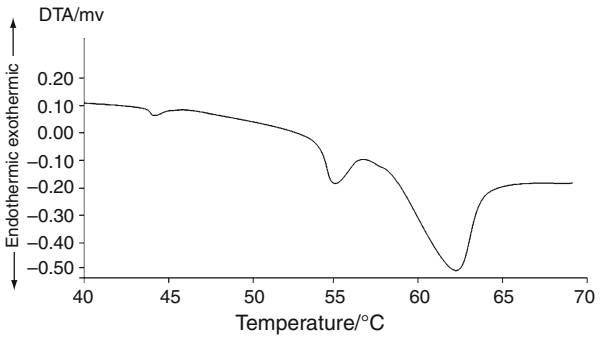

Fig. 4 Differential thermal analysis of material 4. First run, showing three endothermic peaks (44.5, 55.5, and 62.9 °C)

the number of runs. The increase of the temperature provokes in time a bigger surface contact as the sample melts, offering a rational answer to the studied transitions.

When β-gutta-percha is thermally analysed, two endothermic peaks occur; the first (between 42 and 49 °C) corresponds to the transformation from β-gutta-percha to the α-gutta-percha; the second peak (between 53 and 59 °C) accompanies the conversion of the α-phase into amorphous gutta-percha [4].

Furthermore from the results, an interesting event occurred with the analysis of the runs II, III and IV of the material 1. The samples were brought to the temperature of 25 °C with a spontaneous cooling; therefore, in the following analysis, the two endothermic peaks would be expected to appear being separated, instead, as shown in Fig. 1; in the runs II, III and IV, it was possible to observe only one endothermic peak, corresponding to the conversion from the α- to amorphous-gutta-percha.

The disappearance of the β–α conversion peak is due to the kinetics of crystallization; there is not enough time in order to reform the β-phase before the following heating; longer periods of time (months-years) or lower temperatures are needed in order to reform the β-phase. Besides

Table 2 Temperatures at which endothermic peaks occurred

Materials	Temperatures/°C			
	Run 1	Run 2	Run 3	Run 4
Gutta-percha PD	48.0, 61.8	62.1	61.9	61.8
Gutta-percha Inline	(46.0), 55.9, 66.0	60.9, 66.6	60.6, 66.7	60.7, 66.5
Gutta-percha Mynol	49.0, 61.2	62.2	62.6	62.7
Gutta-percha Microseal	44.5, 55.5, 62.9	46.7, 55.8	46.9, 55.8	46.9, 55.7
Gutta-percha Soft-Core	44.9, 54.0	42.9, 53.7	42.8, 53.5	43.4, 53.8

The temperatures shown in the table were obtained calculating the average of data for each material

Data in parentheses represent very small endothermic peaks

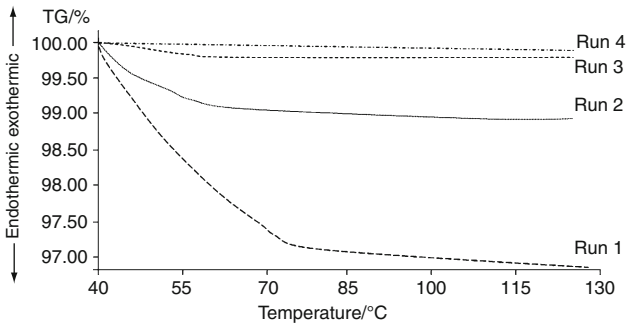

Fig. 5 TG curves of material 1. The curve show mass loss (%) after each run

sufficiently low temperatures, all the materials tend to crystallize. The crystallization makes the material more resistant, but also more fragile. The same happens with gutta-percha, that overtime, undergoes crystallization process which brings to physical–mechanical changes that may influence the root canal filling.

The material 2 in the first run has shown three endothermic peaks 44.5, 55.5, and 62.9 °C (Fig. 2). In the second (Fig. 3), third and fourth run two endothermic peaks have been observed. Also the material 4 has shown three endothermic peaks, to 44.5, 55.4, and 62.9 °C (Fig. 4). Two of them are almost certainly related to the normal transitions of the β-form to the α-form, and of the α-form to amorphous. In the following runs that was a repeated phenomenon. Presumably, the third peak is due to the presence of other substances sensitive to the high temperatures used during the clinical heat-curing procedures; as a matter of fact, in the following runs it has not been possible anymore to observe the presence of such peaks.

It was revealed that many techniques employing controlled heat sources have showed a high polymer degradation; consequently, polymer degradation occurred, forming new compounds with low molecular mass such as peroxides and volatile products [15].

The consequences are a material stability loss and molar mass reduction that will jeopardize the sealing capability of root filling with the risk of root-canal reinfection [16].

Table 3 Thermogravimetric (TG) results after each run

Materials	Mass loss/%	
Gutta-percha PD		
Run 1	3.673 ± 0.016	$P < 0.05$
Run 2	1.104 ± 0.012	
Run 3	0.165 ± 0.007	
Run 4	0.013± 0.006	
Gutta-percha Inline		
Run 1	5.033± 0.048	$P < 0.05$
Run 2	3.401± 0.017	
Run 3	0.294± 0.006	
Run 4	0.092± 0.008	
Gutta-percha Mynol		
Run 1	7.534± 0.069	$P < 0.05$
Run 2	1.897± 0.034	
Run 3	0.048 ± 0.042	
Run 4	0.008 ± 0.001	
Gutta-percha Microseal		
Run 1	5.603 ± 0.145	$P < 0.05$
Run 2	1.027 ± 0.064	
Run 3	0.494 ± 0.033	
Run 4	0.044 ± 0.006	
Gutta-percha Soft-Core		
Run 1	5.312 ± 0.071	$P < 0.05$
Run 2	0.874 ± 0.065	
Run 3	0.515 ± 0.061	
Run 4	0.009 ± 0.006	

It is important to remember that the tips for endodontic use have the following contents in different percentages: gutta-percha from 18.9 to 21.8%, oxide of zinc from 59.1 to 78.3%, sulfates of heavy metals from 1.5 to 17.3% and waxes and resins from 1 to 4% [17–19]. The presence of high quantities of additives and/or impurities may modify the thermodynamic events.

Another important effect of volatile product formation during degradation is polymer mass loss [15].

The gutta-percha expands during the phase of heating and shrinks during cooling [20]; in warm techniques of filling, the gutta-percha is inserted in root canals in the phase of maximum volumetric expansion, and the consecutive and natural cooling brings to a volume loss [21] and to a mass loss that could compromise the apical seal. We have observed a loss of samples-mass from 3.673 to 7.534% in the first run, while the mass tends to stabilize from 0.008 to 0.092% after the fourth run. It is worth mentioning here that, in order to quantify the mass loss, we have repeated four heating cycles for each sample, while it is a common practice in clinical use just to heat and place the material in the root canal. The mass loss in gutta-percha polymer could make the cone material more porous and could reduce its root-canal sealing property. Clinical implications are evident, because we know that the dimensional stability of the filling material is essential to the success of an endodontic treatment [22–27].

Conclusions

The thermal behaviour of all samples was investigated using simultaneous TG/DTA methods. The TG/DTA analysis shows different thermal behaviours between samples. Heating up to 130 °C causes chemical-physical changes of the gutta-percha; this is due to the presence of additives (70–80%), which alter the behaviour of the material. For this reason, the dimensional stability of the filling materials is not guaranteed.

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