Revista Colombiana de Materiales

ISSN 2256-1013, No 14, pp.66-80, 2019.

DETERMINACIÓN DEL TIEMPO DE FRAGUADO DE CEMENTOS BASE HIDROXIAPATITA Y EXTRACTO DE GALACTOMANANO A PARTIR DE SEMILLAS DE Adenanthera pavonina L POR EL MÉTODO DE CAVIDAD RESONANTE

L.R.C Aquino¹, A.A.M. Macêdo², C. C. Silva^{1*}

1: Federal University of Maranhão – UFMA. Social Science, Health, and Technology Center (CCSST) - Imperatriz – MA - Brazil

2: Federal Institute of Education, Science, and Technology of Maranhão – IFMA – Imperatriz – MA– Brazil

* E-mail: ccsilva@fisica.ufc.br

RESUMEN

El tiempo de fraguado de cementos odontológicos es un parámetro clínico importante debido a que estima el tiempo disponible para llevar a cabo el procedimiento luego de la preparación del cemento, el cual no puede ser extenso o corto. Actualmente, este parámetro puede ser determinado mediante las normas ISO 6876/2001 y ADA 57/2000, estas técnicas solo realizan un análisis superficial para la determinación el tiempo de fraguado, por lo que no es posible indicar si el cemento ha secado completamente. El objetivo de este estudio era determinar el tiempo de fraguado mediante el método de cavidad resonante de cementos base Hidroxiapatita (Hap) y galactomanano (Gal) extraído de semillas de Adenanthera pavonina L. Se prepararon tres compuestos: HAG (75 % de HAp and 25 % Gal en peso como fase sólida y 0,30 mL de agua destilada como fase líquida), HAGJET (75 % de Hap, 2% en peso de Gal en polvo con 0.10 mL de catalizador comercial JET (metacrilato de metilo and dimetil-ptoluidina) y 0.20 ml de agua destilada), HAGLS (60% de HAp + 40% en peso de una solución de Galactomannan (Gal) + 0.10 mL de ácido fosfórico, óxido de zinc, hidróxido de aluminio y agua (catalizador comercial LS). La fase sólida en cada material fue disuelta en el líquido correspondiente para cada compuesto formado. La inserción de los cementos HAG y HAGJET generó una perturbación en el campo eléctrico debido a la presencia de agua libre en la muestra, esta perturbación disminuye a medida que el cemento endurece debido a la evaporación del agua libre. Un proceso contrario ocurrió cuando con la inserción del cemento HAGLS en la cavidad, ya que la presencia de agua en el material es estructural. De acuerdo con los resultados, el cemento HAG tuvo el mayor tiempo de fraguado debido a la falta de un activador químico durante la preparación, mientras los cementos HAGJET y HAGLS que tenían activadores en su procesamiento mostraron tiempos de fraguado inferiores.

Palabras clave: Tiempo de fraguado, cavidad resonante, cemento, hidroxiapatita, galactomanano.

DETERMINATION OF SETTING TIME OF CEMENT-BASED HYDROXYAPATITE AND GALACTOMANNAN EXTRACTED FROM Adenanthera pavonina L. SEEDS BY THE RESONANT CAVITY METHOD

ABSTRACT

The setting time of odontological cement is a clinically important parameter because it suggests the time available to perform the treatment after cement preparation. This time cannot be long

or short. Currently, this parameter can be determined by two specifications such as ISO 6876/2001 and ADA 57/2000. These techniques perform only a superficial analysis in determining the setting time, so, it is not possible to indicate whether the cement dries completely. The aim of this study was to determine the setting time of the cement-based hydroxyapatite (Hap) and galactomannan (Gal) extracted from Adenanthera pavonina L. seeds, by the method of the resonant cavity. Three composites were prepared: HAG (75 wt% of HAp and 25 wt% of Gal were used for the solid phase, while the liquid phase comprised 0.30 mL of distilled water), HAGJET (75 wt% of Hap, 25% of Gal powder with 0.10 mL of catalyst commercial JET (methyl methacrylate and dimethyl-p-toluidine) and 0.20 ml of distilled water were used), and HAGLS (60 wt% of HAp + 40 wt% Galactomannan (Gal) solution + 0.10 mL of phosphoric acid, zinc oxide, aluminum hydroxide and water (LS catalyst commercial). The solid phase in each material was dissolved in the liquid corresponding to each composite formed. The insertion of HAG and HAGJET cement in the cavity caused a disturbance in the electric field due to the presence of free water in the sample. This disturbance decreases as the cement harden due to evaporation of free water. The reverse process occurred with the insertion of HAGLS cement into the cavity, since the presence of water in the material is structural. This characteristic caused perturbation in the cavity to increase with the cement hardening. On the basis of the results, the HAG cement had the highest setting time due to the absence of the chemical activator in its preparation; while HAGJET and HAGLS cement that had activators in their production showed the lowest setting times.

Keywords: Time setting, resonant cavity, cement, hydroxyapatite, galactomannan.

1. INTRODUCTION

When water is added in the cement solid phase, the hydration reactions start, acquiring gradually consistency and forming a plastic paste; with the course of time, the mixture will lose its consistency until reaching its hardening state. The hardening occurs due to loss of free water present in the composition of the cement [1].

The phenomenon that covers the development of the mechanical properties of the cement at the start of hardening is called setting time [2]. There are two periods that distinguishes this event is the start and the end of the setting time [3]. The first is defined by the time between the additions of the liquid until the start of the reactions with the constituents of cement. This period occurs through the increase of sudden viscosity [4–5].

The end of the setting time is characterized when the cement becomes visibly dry and is presented as a monolithic block (hard). This setting time may not be as extensive because the same should return their constructive activity in a reasonable time [4–5].

The setting time of sealers is a clinically important parameter because it suggests the time available to perform the treatment after cement preparation. Some factors as temperature, the relationship between the liquid phase and the solid phase, particle size, environment, and the pH may interfere with the setting time of cement [6].

There must be a temporal balance in the cement setting time of the cement, since a prolonged setting time may damage the clinical behavior and promote degradation of the material, thus, can benefit the penetration of irritants substances and promote the release of probable toxic products. On the other, a very short time may not be sufficient for complete treatment of the root canal [7].

The International Organization for Standardization – ISO specification 6876/2001 [8] for dental root canal sealing materials and the American Dental Association – ADA specification n° 57/2000 [9] for endodontic sealing materials are techniques used to determine the setting time

of sealers. In this study, we used the resonant cavity method to determine the setting time of the cement-based hydroxyapatite $(Ca_{10}(PO_4)_6(OH)_2 - HAp)$, bioceramics bioactive and biocompatible, with the biological system, and natural biopolymer – galactomannan (Gal) extracted from *Adenanthera pavonina* L. seeds.

The technique is based on a resonant cavity delimited by a dielectric region demarcated by conductive walls that can store energy. Characterized by a fundamental resonance frequency (f_0) and a quality factor (Q) [10]. The central frequency of the cavity not only absorbs energy at the center frequency, where absorption is maximum but also absorb certain frequency range, designated bandwidth of the resonant cavity (W) [11]. Thus, $f_0 = QW$ [10].

Insertion of a sample in the cavity occurs a disturbance of the electric field due to the properties of the material making up the sample [12]. This disturbance is both more measured greater electric field in the space [13]. For that, the insertion of the sample in the cavity produces a disturbance in frequency and presents acceptable results. It is necessary that the material has adequate conditions, i.e. the sample must have dimensions very small compared with the own cavity [14].

The cavity perturbation technique is based on the changes in the resonant frequency and quality factor of the cavity due to the presence of a sample inside the cavity. This method was designed for fully inserted samples but occupying a narrow volume inside the cavity [15–17].

The resonant perturbation method is widely used in the characterization of microwave dielectric properties of various materials [18–20]. The success of this method to calculate the microwave dielectric properties relies on measuring the values of resonant frequency f and quality factor Q accurately, before and after the insertion of the sample into the cavity. The parameters of the cavity depending on the volume, geometry, mode of operation, shape, dimensions, and location of the object inside the cavity. For a given cavity and a sample of regular shape and well-defined dimensions, we can determine the permittivity of the material [21]. Microwave resonant cavities have been used for evaluating the dielectric properties of geometrically defined samples when the cavity is calibrated with a dimensionally identical sample of known permittivity (ε).

The quality factor of a cavity filled is the ratio of its resonant frequency (f_0) and the side frequency at which the power drops to half the target, i.e. the bandwidth of the cavity resonance frequency (W). Thus, the higher the quality factor, the smaller the bandwidth and consequently, more is selective is the cavity in relation to the excitation frequency. The quality factor (Q) of the standard sample and of the material formed was calculated by equation 1.

$$Q = \frac{f_0}{W} \tag{1}$$

Known the center frequency of the empty cavity and sample of HAG, HAGJET and HAGLS cement, the internal volume of the resonant cavity and the specimen volume is possible to calculate the dielectric constant (ε ') of each material at a different time interval (Equation 2). The insertion of the sample inside a cavity provokes the change of the transmission response. The shift in the cavity resonant frequency, $\Delta f (f_2 - f_1)$, is related to the real part of the complex permittivity ε ' where f_l is the center frequency of the empty cavity, f_2 is the center frequency of the disturbing cavity with the sample, V is the internal volume of the resonant cavity, v is the specimen volume.

$$\epsilon' = 1 + \frac{1}{2} \left(\frac{f_1 - f_2}{f_2} \right) \frac{V}{v}$$
 (2)

The aim of this study was to determine the setting time of the cement-based hydroxyapatite and galactomannan extracted from *Adenanthera pavonina* L. seeds, by the method of the resonant cavity.

2. MATERIALS AND METHODS

2.1. Galactomannan extraction from Adenanthera pavonina L. seeds and Preparation of the Gal Solution

Gal was extracted from *Adenanthera pavonina* L. seeds (1.25 cm of diameter in the mean - see Figure 1), because this seed has galactomannans with mannose/galactose 1:35 ratio, and contain small amounts of other monosaccharides such as rhamnose, fucose, arabinose, xylose and glucose. Its molecular mass is equal to 1.17×10^6 Da and has 97.9% carbohydrates [22]. We opted for this polymer because *Adenantera pavonina* seed contains about 97% Gal and is abundantly found in our region. The technique of obtaining is simple, greatly reducing its cost. The method consisted of heating the seeds in distilled water for 30 minutes to 100 °C and subsequent swelling for a period of 24 hours. Then, the seeds were washed and the endosperms were separated manually from the embryo and integument. Afterward, the endosperms were dehydrated and sprayed in order to prepare the cement [23,24]. The galactomannan solution (10%) was prepared by the solubilization and homogenization of 0.5 g of the Gal powder in 5 ml of distilled water.



Figure 1. Adenanthera pavonina L. seeds.

2.2. Synthesis of Hydroxyapatite (HAp)

Hydroxyapatite $[Ca_{10}(PO_4)_6(OH)_2]$ was synthesized by mechanical milling with a high-energy planetary ball mill, a Fritsch Pulverisette 5. The components used were calcium hydroxide – $[Ca(OH)_2]$ (Sigma/Aldrich) and calcium mono-hydrogen phosphate $[CaHPO_4]$ (Sigma/Aldrich) in stoichiometric amounts (reaction 1). The milling was carried out for 20 hours at 370 rpm rotation and 10-min break followed every 30 min of milling, in order to avoid excessively heating up the mill [25-27]. The ratio of the mass of the powder to the mass of the balls was 1/6. Every 30 minutes of milling, 10-minute breaks were carried out to avoid excessive heat from the mill.

$$4 Ca(OH)_2 + 6 CaHPO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 6 H_2O$$
 (reaction 1)

2.3. Preparation of Cement

The cement was formulated from a solid phase and a liquid phase. The solid phase comprised hydroxyapatite and galactomannan extracted from *Adenanthera pavonina* L. seeds, while the liquid phase consisted of distilled water, liquid JET (methyl methacrylate and dimethyl-p-toluidine) and liquid LS (phosphoric acid, zinc oxide, aluminum hydroxide). Three types of cement were developed, for which the amounts of liquid and solid varied. For the preparation of the first cement, called HAG, 75 wt% of HAp and 25 wt% of Gal were used for the solid phase, while the liquid phase comprised 0.30 mL of distilled water (see Table 1). The second cement, designated HAGJET, was produced using 75 wt% of HAp and 25% of Gal powder. For the liquid phase, 0.10 mL of catalyst commercial JET (Clássico, Brazil) and 0.20 ml of distilled water were used (see Table 1). The solid phase of the third cement (HAGLS) comprised 60 wt% HAp; the liquid phase was formed with 40% Gal solution and 0.10 mL of commercial LS (Coltene, Brazil) as a catalyst. These amounts were determined using empirical methods. The samples were prepared according to the traditional method. The solid phase in each material was dissolving in the liquid corresponding to each cement formed.

	L .				
Material	Description				
HAG	75 wt% of HAp and 25 wt% of Galactomannan (Gal) + 0.30 mL water				
HAGJET	HAG + 0.10 mL of methyl methacrylate and dimethyl-p-toluidine (JET catalyst commercial) and 0.20 mL water				
HAGLS	60 wt% of HAp + 40 wt% Galactomannan (Gal) solution + 0.10 mL of phosphoric acid, zinc oxide, aluminum hydroxide and water (LS catalyst commercial)				

Table 1. Composites Nomenclature.

2.4. Resonant Cavity Method

The choice of experimental data was performed using the network analyzer of Hewlett-Packard – HP 8753D a rectangular cavity of 2.45 GHz and standard time 180 min. The samples of HAG, HAGJET and HAGLS cement were obtained center frequency (f_0) of the cavity with the standard sample from the fit Lorentzian curve in each experimental point of resonance peaks at a different time interval, the quality factor (Q) and real dielectric permittivity (ϵ '). As a standard sample to compare, the data obtained regarding the cement (HAG, HAJET, and HAGLS) was used polytetrafluoroethylene (PTFE) because doesn't this polymer resonate in this type of cavity.

3. RESULTS AND DISCUSSION

3.1. HAG Cement

The method of the resonant cavity was used to determine the setting time of the HAG, HAGJET and HAGLS cement. Figure 2 shows the frequency spectrum for the cavity in the range 2.45 GHz of the HAG cement, at different times. In the graph, is observed the transmission of the empty cavity, with the standard sample (Teflon) and the HAG cement.

In Figure 2 it can be observed that the insertion of the cement in the cavity produces a disturbance clear reflecting in the resonance peaks dislocated to lower frequencies, due to the

presence of free water in the material, where water is a substance that has the highest dielectric constant (ϵ ' = 80).



Figure 2. Cavity transmission; (A) – Empty; (B) – Standard (Teflon); (C) – HAG cement.

The free water displays a relaxation in the microwave region, thus reflecting in the imaginary component of the full permittivity, ε ". Therefore, the greater the amount of water present in the material, the greater the perturbation of the electric field within the resonant cavity [14]. This disturbance varies as function of cement hardening, i.e. the measure that the free water will disappear. Figure 3 shows, detach in C (figure 2) with more clearly how the resonance frequency of the cavity is affected by the insertion of the HAG cement, where the arrow indicates the displacement of the curve in relation to the exposure time of the cement sample.



Figure 3. Cavity transmission of the HAG cement in a different time.

In Figure 3, it is observed that in the analysis end time (170 min) there has been, practically, no peak shift to higher frequencies, close to the standard sample, indicating that free water present in the material was disappearing, suggesting the end of the setting time of the cement HAG. Comparing with the standard setting time measure (Gilmore Needle Method [28]), this sample took 183.33 min to dry, demonstrating that the resonant capacitance method is more accurate.

Table 2 presents the data concerning the quality factor (Q), center frequency (f_{θ}) and dielectric constant (ϵ ') of the empty cavity, standard sample, and HAG cement. The calculation of the center frequency was obtained from the Lorentzian curve fit to the experimental points acquired by resonance peaks of the cement in each time interval. The quality factor and the dielectric constant were acquired by equations 1 and 2, respectively.

HAG Cement	<i>Q</i> ₁ (10 ³)	<i>f</i> ₁ (GHz)	<i>Q</i> ₀ (10 ³)	<i>f</i> ₀ (GHz)	ε'
Empty	-	-	1,928	2,7877	-
Standard	1,947	2,7869	1,928	2,7877	1,017
00 min	1,677	2,7841	1,928	2,7877	1,015
05 min	1,684	2,7841	1,928	2,7877	1,015
10 min	1,685	2,7841	1,928	2,7877	1,015
30 min	1,685	2,7841	1,928	2,7877	1,015
50 min	1,688	2,7841	1,928	2,7877	1,015
70 min	1,689	2,7841	1,928	2,7877	1,015
90 min	1,691	2,7841	1,928	2,7877	1,015
110 min	1,698	2,7841	1,928	2,7877	1,015
130 min	1,705	2,7841	1,928	2,7877	1,015
150 min	1,707	2,7841	1,928	2,7877	1,015
170 min	1,709	2,7841	1,928	2,7877	1,015

Table 2. Values of the Quality factor (Q), center frequency (f) and dielectric constant (ε ') at different times for the HAG cement. The index 0 e l is empty and the cement sample cavity, respectively.

The data in Table 2 shows that quality factor of the HAG cement increases with the time indicating that the conductivity of the material is decreased by virtue of the reducing the amount of free water, thereby, suggesting the cement hardening over time. However, the values concerning the center frequency of the cement show that the same remains constant over time, changing only for the standard sample, and the resonance peaks of the materials, change virtually in the same frequency with the passage of time. Thus, confirms that in 170 min the HAG cement wasn't hardened completely in setting time.

The values of dielectric constant depend on the center frequency and this does not change with the passage of time. Therefore, is observed in Table 2 that the data the dielectric constant of HAG cement remains constant over time. These data confirm also that in 170 min the cement not hardened completely.

3.2. HAGJET Cement

Figure 4 shows a disturbance caused by the insertion of the HAGJET cement inside of the cavity, from of the measurement of the pattern cavity transmission and of the empty cavity. Observed the displacement of resonance peaks to lower frequencies. This perturbation is caused due to the presence of free water in the sample.



Figure 4. Cavity transmission; (A) – Empty; (B) – Standard (Teflon); (C) – HAGJET cement.

Figure 5 shows, detach in C (figure 4) more clearly, how the resonance frequency of the cavity is affected by the insertion of the HAGJET cement, where the arrow indicates the displacement of the curve in relation to the exposure time of the cement sample.

In the first minutes of observation, the resonance peaks virtually echo at the same frequency approximately between 130 to 150 min initiating a move to the highest frequencies next standard sample (Teflon). Comparing with the standard setting time measure (Gilmore Needle Method [28]), this sample took 143.33 min to dry between the standard method and the resonant cavity due to the action of the JET catalyst. It is also possible to verify that with the increase of time, we observe in the narrowing of the curves, due to evaporation of free water, that the reduction of the width in graphic indicating that sample contains less water and consequently the cement hardening.



Figure 5. Cavity transmission of the HAGJET cement in a different time.

Table 3 presents the data concerning the quality factor (Q), center frequency (f_{θ}) and dielectric constant (ϵ ') of the empty cavity, standard sample, and HAGJET cement. The calculations of the center frequency were obtained from the Lorentzian curve fit to the experimental points acquired by resonance peaks of the cement in each time interval. The quality factor and the dielectric constant were acquired by equations 15 and 16, respectively.

The data in Table 3 confirm the perturbation inside of the cavity when is insert the HAGJET cement, due to the center frequency of the empty cavity of the standard sample and the cement prowl around 2.7877 GHz, 2.7869 GHz, and 2.7848 GHz, respectively. In 150-170 min, this perturbation is minimized and the central frequency values of the cement begin to an approximation of the standard sample, 2.7851 GHz, and 2.7869 GHz, respectively.

HAGJET Cement	<i>Q</i> ₁ (10 ³)	<i>f</i> ₁ (GHz)	Q ₀ (10 ³)	f ₀ (GHz)	ε'
Empty	-	-	1,926	2,7877	-
Standard	1,947	2,7869	1,928	2,7877	1,055
00 min	1,739	2,7847	1,926	2,7877	1,013
05 min	1,746	2,7847	1,926	2,7877	1,013
10 min	1,748	2,7847	1,926	2,7877	1,013
30 min	1,750	2,7847	1,926	2,7877	1,013
50 min	1,758	2,7848	1,926	2,7877	1,012
70 min	1,763	2,7848	1,926	2,7877	1,012
90 min	1,768	2,7848	1,926	2,7877	1,012
110 min	1,775	2,7848	1,926	2,7877	1,012
130 min	1,777	2,7848	1,926	2,7877	1,012
150 min	1,797	2,7851	1,926	2,7877	1,011
170 min	1,797	2,7851	1,926	2,7877	1,011

Table 3. Values of the Quality factor (Q), center frequency (f) and dielectric constant (ε ') at different times for the HAG cement. The index 0 e l is empty and the cement sample cavity, respectively.

This event occurs because of the presence of free water in material, as the components used for the preparation of cement, decreasing when to substance evaporates and the disturbance in the cavity decreases. Dielectric constant values are shown in Table 3.

The data relating to the quality factor show that over time there is an increase in this parameter because the amount of free water in the sample is minimized due to a decrease in conductivity and the perturbation of the resonant cavity. These data suggest that about 130 minutes the HAGJET cement begins to get their setting time and increases with time.

3.3. HAGLS Cement

Figure 6 shows the change in frequency of the resonance peaks with the insertion of the HAGLS cement causing a disturbance of the electric field inside of the cavity. Between 00 to 110 min, the displacement of the curves for lower frequency regions is not as significant and peaks resonate practically the same frequency of the standard sample. However, over time, this disturbance is increased, shifting the peak to low-frequency regions. This analysis is observed with most clearly in Figure 7.



Figure 6. Cavity transmission; (A) – Empty; (B) – Standard (Teflon); (C) – HAG cement.

Is observed in the Figure 7, detach in C (figure 6) showed the developing of setting time in HAGLS cement resonance peaks shift to low-frequency regions with the inverse phenomenon for the HAG and HAGJET cement. This fact occurs due to the densification of the cement and by water not present as free water and your structure is present in the composition of the commercial catalyst LS, used as a one the liquid phase to the production of the HAGLS cement, where the arrow indicates the displacement of the curve in relation to the exposure time of the cement sample.



Figure 7. Cavity transmission of the HAGLS cement in a different time.

As it has been described, the free water in the sample affects the displacement of the resonance peaks for regions of high frequencies the extent that the cement hardens, due to reducing of the dielectric constant. Therefore, the results of this sample it was observed that when water present in the cement is not free, the reverse occurs, i.e. structurally bound water shifts the peaks of the material to low-frequency regions with the evolution of the HAGLS cement. Besides, it looks like the end of the time setting of the cement was approximately 170 min, because from the time 130 min did not observe any change in the resonance peaks.

Table 4 presents the data concerning the quality factor (Q), center frequency (f_0) and dielectric constant (ϵ ') of the empty cavity, standard sample, and HAGLS cement. The calculations of the center frequency were obtained from the Lorentzian curve fit to the experimental points acquired by resonance peaks of the cement in each time interval. The quality factor and the dielectric constant were acquired by equations 15 and 16, respectively.

The data contained in Table 4 confirm that first peaks resonate about the same frequency of the standard sample: 2.7862 GHz to the HAGLS cement and 2.7869 GHz to the standard sample. Furthermore, in 130 min confirm that the curves deviate off the resonance peaks of the standard sample. Between 130 min and about 170 min of the center frequency values remain constant (2.7854 GHz), suggesting the end of the setting time of the material.

The data concerning the material quality factor reveals that this decreases over time, so the curves increase the width and shift to lower frequencies. The values of the dielectric constant also confirm these data, because it increases with the passage of time due to the presence of structural water in the HAGLS cement. Moreover, the dielectric constant becomes constant from 130 min, indicating the end of the setting time of the material. Comparing with the standard setting time measure (Gilmore Needle Method [28]), this sample took 116.66 min to dry between the standard method and the resonant cavity due to the action of the LS catalyst.

HAGLS Cement	<i>Q</i> ₁ (10 ³)	<i>f</i> ₁ (GHz)	<i>Q</i> ₀ (10 ³)	<i>f</i> ₀ (GHz)	ε'
Empty	-	-	1,876	2,7877	-
Standard	1,947	2,7869	1,928	2,7877	1,017
00 min	1,512	2,7862	1,876	2,7877	1,007
05 min	1,522	2,7862	1,876	2,7877	1,007
10 min	1,513	2,7862	1,876	2,7877	1,007
30 min	1,517	2,7862	1,876	2,7877	1,007
50 min	1,524	2,7862	1,876	2,7877	1,007
70 min	1,522	2,7862	1,876	2,7877	1,007
90 min	1,523	2,7862	1,876	2,7877	1,007
110 min	1,526	2,7862	1,876	2,7877	1,007
130 min	1,308	2,7854	1,876	2,7877	1,010
150 min	1,314	2,7854	1,876	2,7877	1,010
170 min	1,318	2,7854	1,876	2,7877	1,010

Table 4. Values of the Quality factor (Q), center frequency (f) and dielectric constant (ε ') at different times for the HAG cement. The index 0 e l is empty and the cement sample cavity, respectively.

4. CONCLUSION

On the basis of the results, the HAG cement had the highest setting time due to the absence of the chemical activator in its preparation; while HAGJET and HAGLS cement that had activators in their production showed the lowest setting times. The method of the resonant cavity is presented as an additional technique to determine the setting times of cement in the odontological field.

In the cement where the liquid phase is mainly composed of water, this method provides more results accurate, because the technique analyzes a possible perturbation of the electric field with results of dielectric permittivity (ϵ) that may occur due to properties in the material and the disturbance decreases the extent that cement get the set time, i.e. the extent that the free water evaporates. While the techniques available to determine the setting time of cement, such as ISO and ADA performs only a cursory review, not being possible to indicate whether the material is dry completely.

5. ACKNOWLEDGMENTS

The authors thank CAPES (Coordenanção de Aperfeiçoamento de Pessoal de Nível Superior – Brazil), FAPEMA (Fundação de Amparo à Pesquisa e Desenvolvimento Científico do Maranhão) Brazilian agencies and Physics Department of Aveiro University, I3N (Aveiro, Portugal).

6. REFERENCES

[1] Mehta, R.K, Monteiro, P.J.M., *Concrete Microstructure, Properties, and Materials*, 3th ed., São Paulo, Brazil, 2008.

[2] Paiva, D., Introduction to spectroscopy, 4th ed., CA: Cengage Learning, USA, 2009.

[3] Vedacit. Technical Manual, 5th ed., 2005

[4] Muniz, M.V., *The influence of additives and accelerators handle retardants on Portland cement paste.* Feira de Santana, Brazil, 2008.

[5] Segre, N.C., Joekes, I., "Use of tire rubber particles as an addition to cement paste", *Cement and Concrete Research*, vol. 30, pp 1421-1425, 2000.

[6] Faroni, G., Finger, M.S., Masson, M.C., Victorino, F.R., "Comparative evaluation of flow and setting time of MTA Fillapex[®] cement", *RFO*, vol. 18, pp 180-184, 2013.

[7] Allan, N.A., Walton, R.E., Shaffer, M., "Setting time for endodontic sealers under clinical usage and in vitro conditions", *J. Endod.*, vol. 27, pp 421-423, 2001.

[8] International Organization for Standardization, ISO-6876. Dental root canal sealing materials. Geneva: ISO; 2001.

[9] *American Nacional Standard*. American Dental Association Specification nº 57 for endodontic sealing materials. Chicago: ADA, 2000.

[10] Montgomery, C.G., *Principles of microwave circuits*. Dover Publications Inc., New York, USA, 1965.

[11] Calla, O.P.N., Mishra, S.K., Bohra, D., Khandelwal, N., Kalla, P., Sharma, C., Gathania, N., Bohra, N., Shukla, S., "Design a tunable cavity resonator for complex permittivity measurement of low-loss material at L-band.", *Indian Journal of Pure & Applied Physics*, vol.46, pp 134-138, 2008.

[12] Costa, L.M.C. *Electrical properties of some glasses with rare earth ions*. Ph.D. Thesis Aveiro University, Aveiro, Portugal, 1995.

[13] Devesa, S.M. *Electrical properties of polymers for industrial applications in the microwave band.* MsC. Thesis, Aveiro University, Aveiro, 2007.

[14] Reis, M.F.S. *Study of prey cement by electrical measurements*. Aveiro University, Aveiro, Portugal, 2007.

[15] Bethe, H.A., Schwinger, J., *Perturbation theory for cavities, NRDC report D1–117*, Cornell University, USA, 1943.

[16] Kahan, T., Méthode de perturbation appliqué a étudier des cavite's electromagnétiques, Comptes Rendus, 221, Paris, France, 1945.

[17] Slater, J, Microwave Electronics, Van Nostrand Co. Ltd., New York, USA, 1950.

[18] Chen, L., Ong, C.K., Tan, B.T.G., "A resonant cavity for high accuracy measurement of microwave dielectric properties", *Meas Sci Technol*, vol. 7, pp 1255-1259, 1996.

[19] Costa, L.C., Devesa, S., Andre', P., Henry, F., "Microwave dielectric properties of polybutylene terephthalate (PBT) with carbon black particles", *Microwave Opt Tech Lett*, vol. 46, pp 61-63, 2005.

[20] Costa, L.C., Correia, A., Viegas, A., Sousa, J., Henry, F., "Dielectric characterization of plastics for microwave oven applications", *Mater Sci Forum*, vol. 480, pp 161-164, 2005.

[21] Kraszewski, A.W., Nelson, S.O., "Observations on resonant cavity perturbation by dielectric objects", *IEEE Trans Microwave Theory Tech*, vol. 40, pp 151-155, 1992.

[22] Cerqueira, M.A.; Pinheiro, A.C.; Souza, B.W.S.; Lima, A.M.P.; Ribeiro, C.; Miranda, C.; Teixeira, J.A.; Moreira, R.A.; Coimbra, M.A.M.; Gonçalves, P.; Vicente, A.A., "Extraction, purification and characterization of galactomannans from non-traditional sources", *Carbohydrate Polymers*, vol. 75 (3), pp 408-414, 2009.

[23] Sombra, A.S.B., Mazzetto, S.E., C.C. Silva., "Influence of the polysaccharide galactomannan on the dielectrical characterization of hydroxyapatite ceramic", *Composites B*, vol. 44, pp 95-99, 2013.

[24] Soares, C.E.A. Structural Characterization and Potential of galactomannan Adenanthera pavonina L. as the raw material for the production of bioactive edible films, Fortaleza, Brazil, 2009.

[25] C.C. Silva, Thomazin, D., Pinheiro, A.G., Lanciotti, J.R.F., Sasaki, J.M., Góes, J.C., Sombra, A.S.B. "Optical properties of hydroxyapatite obtained by mechanical alloying", *Journal of Physics and Chemistry of Solids*, vol. 63, pp 1745-1757, 2002.

[26] C.C. Silva, Pinheiro, A.G., Miranda, M.A., Góes, J.C., Sombra, A.S.B. "Structural properties of hydroxyapatite obtained by mechanosynthesis", *Solid State Sciences*, vol. 5, pp 553-558, 2003.

[27] C.C. Silva, Graça, M.P.F., Sombra, A.S.B., Valente, M.A., "Structural and electrical study of calcium phosphate obtained by microwave radiation assisted procedure", *Physica B*, vol. 404, pp 1503-1508, 2009.

[28] Aquino, L.R.C.; Macêdo, A.A.M.; Graça, M.P.F.; Valente, M.A.; C.C. Silva; "

Preparation and Characterization of Cement-Based Hydroxyapatite and Galactomannan Extracted from *Adenanthera pavonina* L. Seeds", *Rev. LatinAm. Metal. Mat.*, Vol. 37(1), pp 102-110, 2017.