



Impedance as a measure of setting reaction in glass ionomer cements

A. Moguš-Milanković^{a,*}, K. Sklepić^a, M. Čalogović^a, M. Marcuš^b, K. Prskalo^c, B. Janković^c, Z. Tarle^c

^a NMR Center, Ruđer Bošković Institute, Bijenička c. 54, Zagreb, Croatia

^b Division of Materials Chemistry, Ruđer Bošković Institute, Bijenička c. 54, Zagreb, Croatia

^c Department of Endodontic and Restorative Dentistry, School of Dental Medicine, University of Zagreb, Zagreb, Croatia

ARTICLE INFO

Article history:

Received 19 December 2013

Received in revised form 20 February 2014

Available online xxxx

Keywords:

Dental cements;

Impedance spectroscopy;

Electrical conductivity;

Capacitance

ABSTRACT

The setting process for dental glass ionomer cements (GICs) was studied by impedance spectroscopy in a fixed, 10 and 1000 Hz, and wide frequency region, from 0.01 Hz to 1 MHz. For comparison, the setting of the conventional GICs, Fuji IX Fast and Ketac Molar Aplicap, and “resin modified” GIC, Fuji II LC, was investigated. The effect of setting upon electrical conductivity shows a significant decrease and break in conductivity for conventional GICs after the first 15 and 30 min, respectively. For light-activated Fuji II LC, only a drop without any evidence of a break in electrical conductivity was observed. Such behavior is the result of the instantaneous photopolymerization and formation of a rather homogeneous cement matrix. The complex impedance plots obtained for the three GICs studied show the presence of features that are attributed to the structural regions in the samples. Evolution of the impedance spectra and changes in the capacitance values reveal gradual transformations related to the development of various constituent regions during the setting process. Thus, impedance spectroscopy could become an essential technique for the separation of the overall electrical properties into their component parts, which could then serve as the foundation for meaningful clinical impedance measurements in vitro and in vivo. The knowledge of the sequences of the setting reactions in dental cements is important as these will affect the handling and the overall physical properties of the cements.

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1. Introduction

Glass ionomer cements (GICs) were first described for use in dentistry in the early 1970s [1]. They have desirable properties, such as adhesion to moist tooth structure, remineralization effects and anticariogenic action due to fluoride release. However, GICs suffer from the disadvantage of being brittle.

GICs consist of an aluminofluorosilicate glass powder and an aqueous polyacrylic acid. Cement formation arises from the acid–base reaction between the components, glass powder and acid [2,3]. The surface of the glass is attacked by the acid, resulting in the leaching of available cations (e.g., Al^{3+} , Ca^{2+}). Subsequently, the released cations are chelated by the carboxyl groups and serve to cross-link the polycarboxylate chains ionically within the cement matrix. The numbers and types of cations and anions released from the glass determine the extent of the ionic cross-linking of the polysalt matrix and the properties of the cements [4,5]. In addition, a light-cured GIC has also been investigated, where a resin and light-curing catalyst are added to hasten setting and improve esthetic performance. The diffusion of cations controls the

cross-linking of the polymer matrix and enhances the strength, stiffness and insolubility of the cements. Hence, the properties and performance are strongly influenced by the setting and hardening processes. Although a considerable number of papers are available about the effect of glass composition on the GIC setting processes, there is little information on the electrical properties of dental cements.

Impedance spectroscopy (IS), as a nondestructive method for determining changes in a setting mechanism, has been used to study various types of materials, such as Portland cements, mortars and metallic dental materials [6–9]. Previous investigations of the microstructural developments in cement-based materials reported that the analysis of the impedance spectra provides pore structure information [10,11]. It was found that there is a correlation between the pore size in cement paste and the impedance spectra. It was also demonstrated that the pre-drying history of cement paste prior to saturation with solution results in an increase in the total deformation partly due to the pore coarsening effect [12]. Few earlier studies have been focused on the dielectric properties of dental cements using impedance measurements [13–16]. A study of the multi-frequency electrical behavior of glass-polyalkenoate/resin cements reported that ionic conductivity and polarization are the dominant factors in fully solidified cements [17]. Furthermore, it was shown that the electrical measurements are sensitive to the kinetics of the setting reaction and correspond to the time-scale changes in impedance [17].

* Corresponding author. Tel.: +385 1 4561 149; fax: +385 1 4680 114.
E-mail address: mogus@irb.hr (A. Moguš-Milanković).

In some studies, electrochemical impedance spectroscopy (EIS) has been used to investigate the microleakage of dental composite resins, microporosity and ion transport inside pores filled with electrolyte [18–20]. However, despite the published reports, some basic aspects of the setting processes and microstructural features are still not well understood. Reviewing the literature, few studies are dealing with the role of aluminum and silicon in the setting chemistry of GIC [21] in order to establish the critical role of the type and distribution of these species in the glass precursor and the set cement. Furthermore, few investigations are focused on the addition of various particles and their effects on the structure and improvement of mechanical properties and setting reactions [22–24]. In the present study the correlation between microstructure and setting process for three different commercial glass ionomers was investigated during short and long periods of time using impedance spectroscopy.

The objective of this investigation is a detailed analysis of the time and frequency dependence of the progress of setting reactions for Fuji IX Fast, Fuji II LC and Ketac Molar Aplicap. Fuji IX Fast was selected as one of the strongest commercially available restorative GICs, whereas Fuji II LC is well known as a photosensitive glass ionomer cement in which the setting mechanism is light activated. Fuji IX Fast and Ketac Molar GIC are intended for placement in the area of high masticatory forces, and therefore, need to have a high proportion of inorganic filler to withstand the forces of wear during chewing. They are used for making fillings on occlusal surfaces of teeth. Fuji II LC belongs to a group of resin modified GIC and is used in areas where it is not possible to isolate the tooth from moisture, which can cause the porosity in the material. They are commonly used in the cervical region where it is not possible to completely exclude leakage of gingival fluid in the cavity. The addition of HEMA enables the photopolymerization on the surface of fillings which prevents the penetration of moisture in the deeper layers of the material. However, it should be mentioned that Fuji glass ionomer cements contain Sr instead Ca. The substitution of Sr for Ca does not change the GIC structure much but improves the opacity to X-rays because of the similar ionic radii, $\text{Sr}^{2+} = 1.134 \text{ \AA}$ and $\text{Ca}^{2+} = 0.99 \text{ \AA}$. On the other hand, it was found by X-ray diffraction that the Fuji glasses

are completely amorphous, whereas Ketac Molar contains Ca^{2+} cations and shows sharp lines in an XRD pattern that corresponds to the calcium fluoride crystalline phase [25].

In the present paper, changes in electrical conductivity during the setting of GICs were measured by impedance spectroscopy in both a wide frequency region and at a fixed frequency as a function of time. In particular, the special attention was paid on the investigation of the electrical transport in charged molecular species formed during the first hour of setting. This paper attempts to develop a fundamental correlation between changes in structure at the beginning of solidification of GICs and the electrical conductivity. Furthermore, we seek to provide a better understanding of the changes in the electrical properties of GICs and to establish the foundations for meaningful clinical impedance measurements *in vitro* and *in vivo*.

2. Experimental

2.1. Sample preparation

Conventional glass ionomer cements, Fuji IX Fast (GC Corporation, Tokyo, Japan) and Ketac Molar Aplicap (3M ESPE AG, Seefeld, Germany), were prepared at room temperature according to the manufacturers' instructions. The cement capsules were activated and mixed in an AUTOMIX (Kerr, Romulus, USA) mixer for 10 s and then cast into cylindrical Teflon molds, 7.0 mm in diameter and 1, 2 and 3 mm in height as can be seen in Fig. 1(a) and (b). Fuji II LC (GC Corporation, Tokyo, Japan) sample was also prepared by mixing in an AUTOMIX mixer, placed into quartz rings (1, 2 and 3 mm thick) and then light activated for the polymerization of the samples for 20 s using a Bluephase lamp, which produces a blue light of 486 nm, Fig. 1(c). For comparison, the Fuji II LC samples were also investigated without light activation, thereby permitting only an acid–base reaction.

A pair of brass electrodes was attached to the cement samples (facing each other) immediately after preparation. The sample between the two electrodes was placed in an impedance cell. The latter was performed approximately 1 min after activation of the GIC capsules.



Fig. 1. Sample capsule, which contains glass powder and liquid, is first activated and placed into the AUTOMIX mixer to mix the two components (a); using an applicator the paste is extruded into the Teflon mold (b) or quartz ring; the sample in the mold/ring is placed in the impedance cell and activated by Bluephase lamp (c).

2.2. Electrical measurements

The real and imaginary parts of the complex impedance were measured using an impedance analyzer (Novocontrol Alpha-AN Dielectric Spectrometer, Novocontrol Technologies GmbH & Co. KG, Germany) at fixed frequencies (10 and 1000 Hz) over a frequency range from 0.01 Hz to 1 MHz at room temperature. The temperature was controlled to ± 0.5 K.

The impedance spectra were analyzed by means of equivalent circuit modeling and parameters were obtained by the complex non-linear least square (CNLSQ) fitting directly to the measured impedance data using ZView software [26]. An ideal semicircle is generally not observed and the complex impedance plots typical for the most of materials as well as for all investigated samples consist of a single semicircle with the center below the real axis. This behavior is usually associated with a spread of relaxation time and inhomogeneity of the samples [27]. The equivalent circuit that represents such depressed semicircle is a parallel combination of resistor (R) and constant-phase element (CPE). The CPE is an empirical impedance function of the type $Z_{CPE}^* = A(j\omega)^{-\alpha}$, where A and α are the constants, $0 \leq \alpha \leq 1$ [28]. It was shown that using R-CPE in the equivalent circuit, a real value for capacitance, C, of the samples can be calculated by $C = A(\omega_{max})^{\alpha-1}$ where A and α are the CPE parameters obtained by fitting while ω_{max} represents the frequency maximum in the impedance semicircle.

The values of the resistance obtained from the fitting procedures, R and electrode dimensions (d is the sample thickness and A is the electrode area) were used to calculate the dc conductivity, $\sigma_{dc} = d / (R \cdot A)$.

For each sample, about a 1 min delay (time required for sample preparation) was introduced prior to measurement at room temperature and fixed frequency. Electrical measurements were performed at 10 and 1000 Hz over 12 h. For electrical measurements at various frequencies and room temperature, the samples were also placed in the impedance cell at about 1 min after mixing, followed by the start of measurement. Changes in electrical conductivity were recorded by turns every 3.5 min for several hours.

On the other hand, to examine the reproducibility of the IS and the fit to the proposed equivalent circuit, three repetitions of the impedance measurements were performed on the samples.

2.3. Scanning electron microscopy analysis (SEM)

After impedance measurements were performed, the microstructure of the samples was evaluated using an FE-SEM JSM 7000 (JEOL), manufactured by Oxford Instruments Ltd. The samples were not coated with an electrically conductive layer and the accelerating voltage was kept low. Disk-shaped samples were held in air for 3 weeks and then left in a vacuum for 24 h prior the SEM investigations. Some samples were polished using polishers with 63 μm grit of silicone carbide and a 45 μm grit of aluminum oxide in order to obtain better insight into the sample surface.

3. Results

3.1. Electrical measurements at fixed frequency

The time dependence of the electrical conductivity, σ_{ac} , of the Fuji IX Fast samples with three different thicknesses (1, 2 and 3 mm) at 1000 Hz and room temperature for 12 h is shown in Fig. 2. The conductivity spectra generally exhibit a decrease by several orders of magnitude during the first 12 h, regardless of the sample thickness. However, during the first 10–15 min there is a break in electrical conductivity, inset to Fig. 2, reaching the stable minimal values of conductivity at 3.14×10^{-9} , 2.5×10^{-8} and $1.56 \times 10^{-8} (\Omega \text{ cm})^{-1}$ after 12 h for 1, 2 and 3 mm thick samples, respectively. The break in electrical conductivity, as can be seen in the inset to Fig. 2, depends on the thickness of the sample. For thinner samples, conductivity drops after approximately

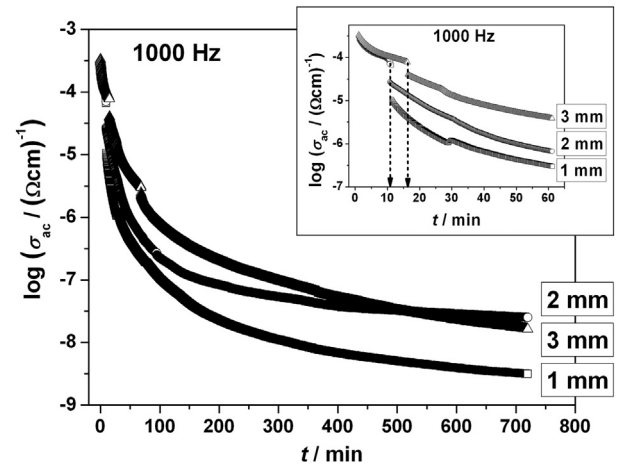


Fig. 2. Time dependence of electrical conductivity, σ_{ac} , for Fuji IX Fast samples with different thicknesses at 1000 Hz during the first 12 h. Inset: evolution of electrical conductivity as a function of time measured during the first hour of setting. Dashed lines designate a time of break in the electrical conductivity. Each curve is a mean curve of three different measurements; the experimental errors are within the symbol size.

11 min by one order of magnitude, whereas for a sample that is 3 mm in height, the drop is observed at about 15 min. The largest change is observed for the 1 mm sample, which leads to the conclusion that setting occurs much faster within thin samples, resulting in the lowest values of electrical conductivity. In addition, after a steep decrease, the electrical conductivity remains almost constant during the first 12 h. This is consistent with the insulating characteristic of the investigated dental cement, which is composed of a polysalt matrix and filler. Similar results were obtained for a Fuji IX Fast sample measured at 10 Hz.

Fig. 3 shows the changes in the electrical conductivity of Ketac Molar samples of various thicknesses measured at 1000 Hz and room temperature over a 1-hour period. There is a break in electrical conductivity that occurs after the first 20–30 min, showing a time shift when compared with the corresponding break for the Fuji IX Fast samples. Although the electrical conductivity is almost identical at the beginning of the measurements, the thinnest sample, 1 mm, displays a significant drop and the lowest electrical conductivity over the first 60 min, $2.21 \times 10^{-7} (\Omega \text{ cm})^{-1}$. The values for the electrical conductivity and corresponding times at the beginning of the

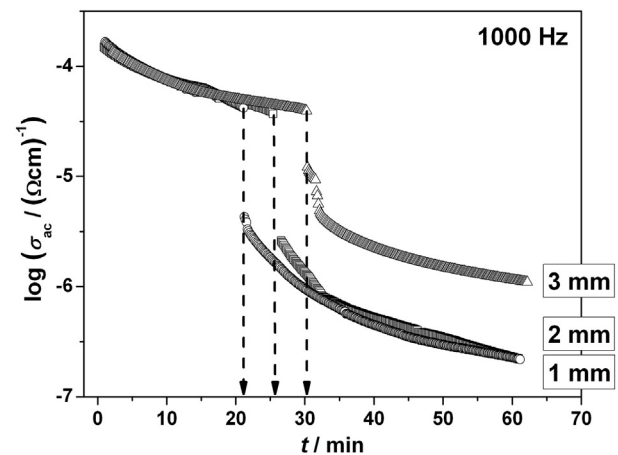


Fig. 3. Time dependence of the electrical conductivity, σ_{ac} , of Ketac Molar samples with different thicknesses at 1000 Hz during the first hour of setting. Dashed lines designate the time of the break in the electrical conductivity. Each curve is a mean curve of three different measurements; the experimental errors are within the symbol size.

Table 1

The values for the electrical conductivity and corresponding times at the beginning of the break for the Fuji IX Fast and Ketac Molar samples of various thicknesses.

Sample thickness/mm	Fuji IX Fast				Ketac Molar	
	1000 Hz		10 Hz		1000 Hz	
	t/min	$\sigma_{ac}/(\Omega \text{ cm})^{-1}$ ($\pm 0.5\%$)	t/min	$\sigma_{ac}/(\Omega \text{ cm})^{-1}$ ($\pm 0.5\%$)	t/min	$\sigma_{ac}/(\Omega \text{ cm})^{-1}$ ($\pm 0.5\%$)
1	11.2	6.64×10^{-5}	12.9	2.22×10^{-5}	25.4	3.69×10^{-5}
2	10.6	7.06×10^{-5}	14.9	4.00×10^{-5}	21.1	4.19×10^{-5}
3	16.2	7.69×10^{-5}	13.6	7.08×10^{-5}	30.2	3.92×10^{-5}

break for the Fuji IX Fast and Ketac Molar samples of various thicknesses are given in Table 1.

The photosensitive Fuji II LC was chosen as the third dental cement in this study. As mentioned earlier, along with the acid–base reaction the setting is light activated. The time dependence of the electrical conductivity of light-activated samples for 20 s, 1 mm in height, measured at 10 and 1000 Hz is presented in Fig. 4. It is worth noting that light activation using 486 nm of light was performed simultaneously at the beginning of measurement. As seen from Fig. 4, at the moment of light activation a corresponding drop in electrical conductivity was observed without any evidence of a conductivity break. For comparison, the changes in the electrical conductivity of a Fuji II LC sample with and without light activation (only acid–base reaction) over 12 h are shown in Fig. 5.

Detailed analysis reveals different behaviors of conductivity for light-activated glass ionomer cement then when only an acid–base reaction took place. For the light-activated Fuji II LC sample, an instantaneous sharp decrease in conductivity occurred and then after 10–15 min the conductivity reached an almost constant value, $5.77 \times 10^{-8} (\Omega \text{ cm})^{-1}$. On the other hand, for the Fuji II LC sample, which is not light-activated, a slower continuous decrease was observed at the beginning of measurement, almost reaching identical conductivity values as for the light-activated sample. Fig. 5(b) shows a different behavior of Fuji II LC light activated and without light activation in comparison with Fuji IX Fast during the first 60 min of setting. In contrast to Fuji II LC, the Fuji IX Fast samples first show a break and then gradual decrease followed by one order of magnitude lower final values of electrical conductivity, $3.14 \times 10^{-9} (\Omega \text{ cm})^{-1}$, observed after 12 h.

It is interesting to note that the analogous measurements over 12 h for the Fuji II LC samples, light activated, with different thicknesses (1, 2, 3 mm) reveal the highest final values of electrical conductivity for a

1 mm sample. However, there is no significant difference in the final conductivity values between the 1 mm ($5.77 \times 10^{-7} (\Omega \text{ cm})^{-1}$) and 3 mm sample ($1.77 \times 10^{-8} (\Omega \text{ cm})^{-1}$), as seen in Fig. 6.

3.2. Electrical measurements in a wide frequency range

It was of interest to confirm the sharp drop and change in the electrical conductivity of glass ionomer cements during short and/or long periods of time. The frequency dependence of electrical conductivity measured for 1 h along with longer periods of time (up to 1 day) for a Fuji IX Fast sample of 2 mm thickness is shown in Fig. 7(a). The electrical conductivity measured by scan every 3.5 min reveals a break during the first 12–18 min. In order to determine the time of the conductivity break more precisely, measurements in a narrower frequency region were performed to collect data every 1 min, as presented in Fig. 7(b). These results correspond well with previously obtained data and confirm that there is a significant change in electrical conductivity between the first 12 and 18 min. Similar data are found for the Ketac Molar samples but the break in conductivity appears after longer periods of time, at about 20–30 min.

As indicated earlier, Fuji II LC behaves differently. Fig. 8(a) shows the frequency dependence of the electrical conductivity measured every 3.5 min for the Fuji II LC sample, 1 mm in height, during 1 h as well as after several hours and 1 day. The sample was light activated for 20 s instantaneously at the beginning of measurement. Light activation causes a significant drop in conductivity, the encircled part in Fig. 8(a), at the moment of the light activation of the sample. After the first drop, the conductivity decreases gradually, reaching the lowest value of $4.24 \times 10^{-7} (\Omega \text{ cm})^{-1}$ after 60 min.

For the Fuji II LC sample, without light activation, the electrical conductivity gradually decreases over 60 min, only showing a rapid decrease in the first 10 min, Fig. 8(b). The final conductivity value $8.77 \times 10^{-7} (\Omega \text{ cm})^{-1}$ after 60 min slightly differs from that for the light-activated Fuji II LC sample.

The decrease in electrical conductivity is accompanied by changes in the conductivity spectra. Generally, the spectra show a universal feature, where at the low frequency region (plateau) the conductivity is independent of frequency and corresponds to the dc conductivity, σ_{dc} , whereas at a higher frequency it exhibits dispersion in the power-law fashion characteristic for ionically conducting materials [29]. The transition point between these two regions is shifted toward the lower frequency with time. The slopes observed at the low-frequency region in the first few minutes are related to the advancement of setting, which is usually caused by ionic mobility.

Going further into the interpretation of the observed electrical changes, conductivity is analyzed in complex impedance plots, known as Nyquist plots. It is accepted that there is a correlation between the shape of the impedance spectra and the nature of the electrical transport. Fig. 9 presents the impedance spectra for the Fuji IX Fast sample, 1 mm thick, obtained at 3.5, 17.5 and 60 min. The spectrum obtained after 3.5 min contains only a low frequency spur, which emanated from ion migration at the beginning of setting, Fig. 9(a). The spectrum of the sample obtained after 17.5 min consists of two overlapping semi-circles related to the bulk and surface layer effects in the sample,

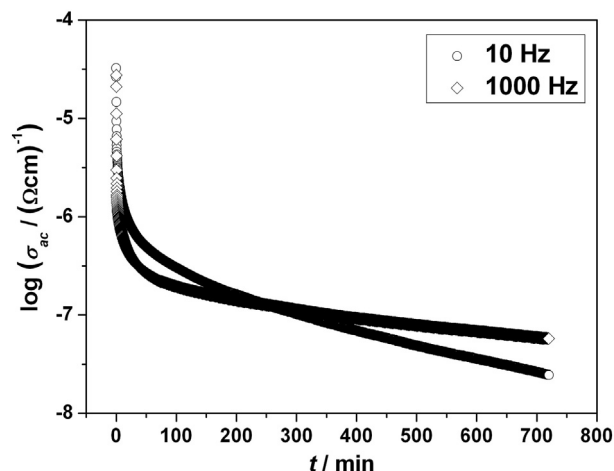


Fig. 4. Time dependence of the electrical conductivity, σ_{ac} , of light activated Fuji II LC samples for 20 s, 1 mm thick, measured at 10 Hz and 1000 Hz. Each curve is a mean curve of three different measurements; the experimental errors are within the symbol size.

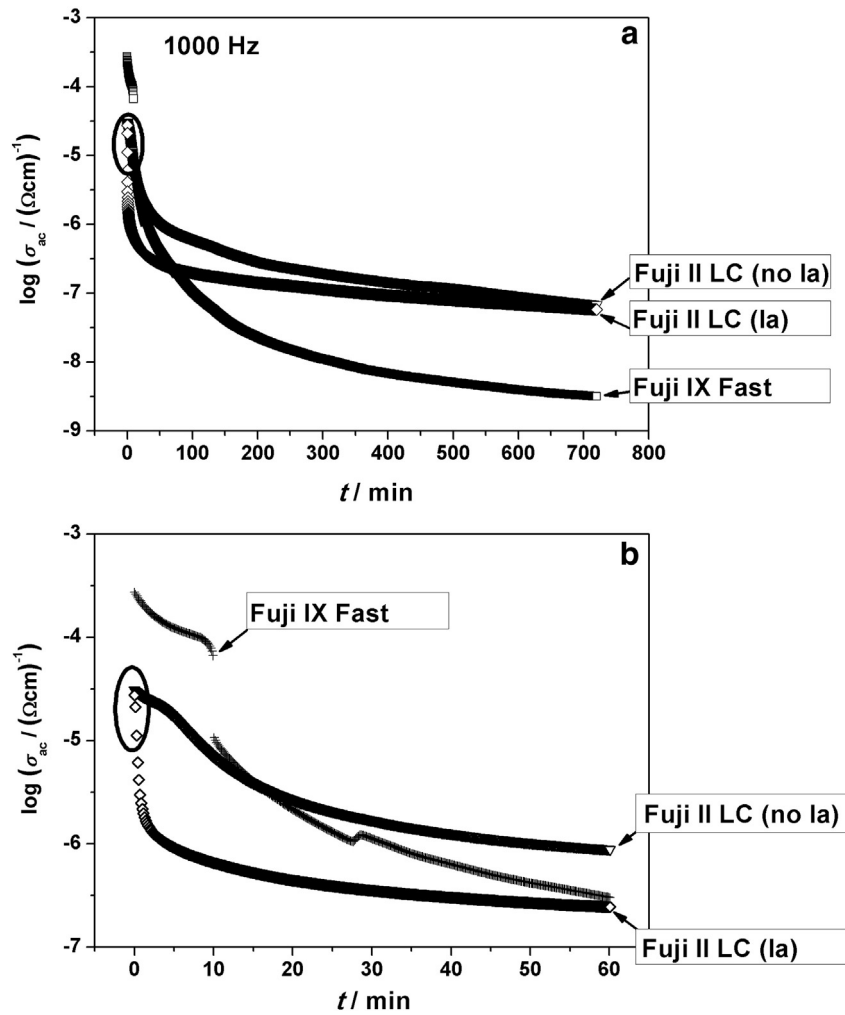


Fig. 5. Time dependence of the electrical conductivity, σ_{ac} , of Fuji IX Fast and Fuji II LC light-activated (la) for 20 s and not light-activated (not la) samples at 1000 Hz, 1 mm thick, for the first 12 h (a). Evolution of electrical conductivity as a function of time measured during the first hour of setting for Fuji IX Fast and Fuji II LC light and not light activated samples. The encircled part represents a drop in electrical conductivity during light activation (b). Each curve is a mean curve of three different measurements; the experimental errors are within the symbol size.

Fig. 9(b). The impedance spectrum of the 63-min-old sample contains two semicircles that are not well resolved, which represent a series of the combination of two component impedances. As mentioned previously, the interpretation of an impedance spectrum usually involves

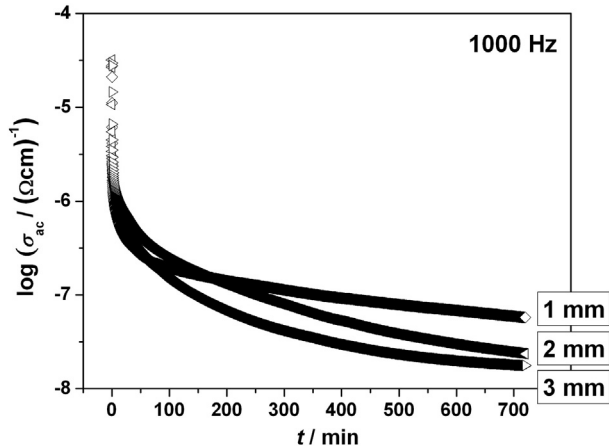


Fig. 6. Time dependence of the electrical conductivity, σ_{ac} , of light-activated Fuji II LC samples with different thicknesses at 1000 Hz during the first 12 h. Each curve is a mean curve of three different measurements; the experimental errors are within the symbol size.

modeling with an equivalent circuit. The values of parameters R_{b1} (the first intercept at high frequency) and $R_{b1} + R_{b2}$ (at a barely detectable minimum between the bulk arc and spur) obtained from fitting are important parameters providing information accompanying the dental cement microstructure. The fitting parameters, R_{b1} and R_{b2} , obtained by ZView software, were used to determine the total resistivity, $R_{tot} = R_{b1} + R_{b2}$, Table 2 [26,28]. The electrical conductivity, which corresponds to the dc conductivity, σ_{dc} , was calculated by $\sigma_{dc} = d / (R_{tot} \times A)$. Furthermore, using the fitting procedure the capacitance of each semicircle in the impedance spectra for the Fuji IX Fast samples obtained after 17.5 and 63 min were calculated and presented in Table 3.

Impedance spectra for a Fuji II LC sample light activated for 20 s and obtained after 2 min and 60 min are shown in Fig. 10. In both cases, the impedance spectra contain two overlapping semicircles associated with the bulk effects of the two components existing in this sample and the low-frequency spur. The fitting was used to calculate the capacitances for each separated semicircle for the Fuji II LC sample and the determined values are listed in Table 3.

3.3. Scanning electron microscopy (SEM)

For further understanding of the setting processes for GICs, in the present study microstructural analysis was performed by SEM. Figs. 11 and 12 show the disk surfaces of Fuji IX Fast and light-activated Fuji II LC, respectively. The SEM micrographs of the polished surfaces of both

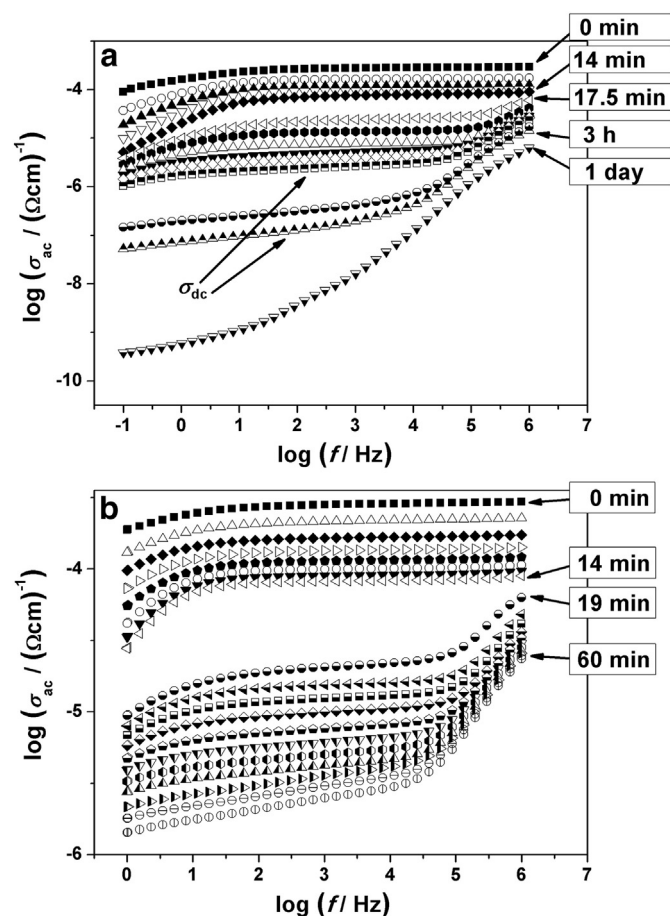


Fig. 7. Frequency dependence of the electrical conductivity, σ_{ac} , of a Fuji IX Fast sample measured at different times, 2 mm thick, scanned every 3.5 min for 1 day (a) and every 1 min for 1 h (b).

GICs in Fig. 11 illustrate the relatively large size of the glass particles embedded in the cement matrix. The particles are sharp-edged, polygonal and range from approximately 1 to 30 μm . Although there are many fractured glass particles, it seems that the glass particles are somehow more uniformly distributed within the matrix for the light-activated Fuji II LC sample.

Fig. 12 shows SEM micrographs for both GICs in nano-scale. As can be seen, the distribution of the pores and homogeneity of the cement matrix for Fuji IX Fast are significantly different than for Fuji II LC. In the case of Fuji IX Fast, the pore size is approximately in the range between 100 and 500 nm in diameter and the pores are randomly dispersed. For Fuji II LC, the pores are more uniformly distributed with an average size that varies from 50 to 200 nm, Fig. 12. The pores are of regular shape, which is probably the result of rapid photopolymerization, as illustrated in the inset to Fig. 12. These pores are surrounded by a smooth and rather homogeneously defined matrix.

4. Discussion

The electrical conductivity properties of three types of GICs, namely Fuji IX Fast, Fuji II LC and Ketac Molar, were determined by ion transport during setting reactions and the solid phase microstructures. The microstructures of the GIC slurries underwent a temporal evolution of structure as a result of chemical reactions, from a flowable state to a solid state during the setting and hardening processes. In such processes, some electrical parameters such as conductivity, resistivity and capacitance varied with time, which was reflected in the development of the internal structure and the change from conductive characteristics to insulating behavior. It should be noted that there are two steps in the

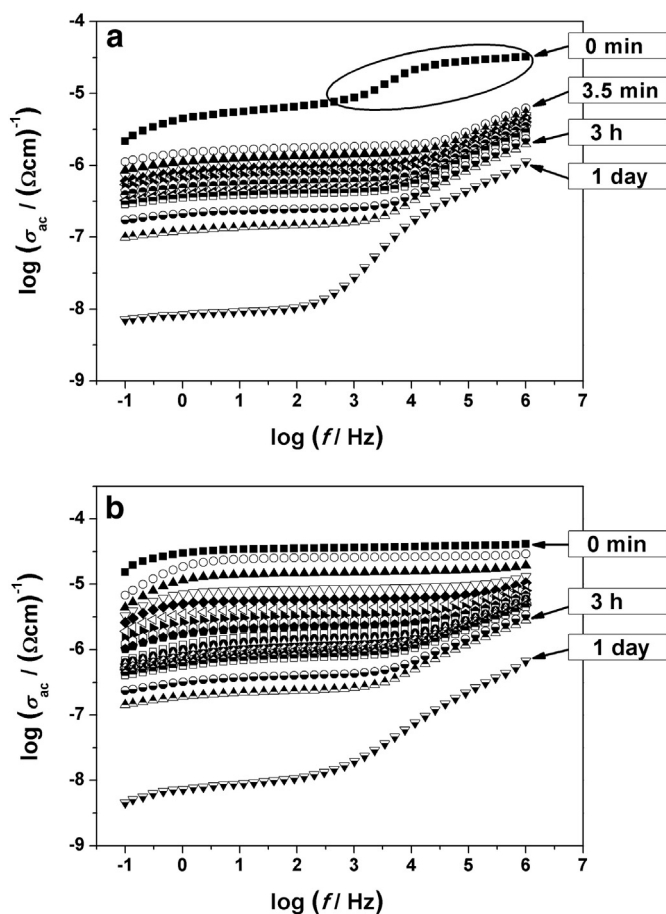


Fig. 8. Frequency dependence of the electrical conductivity, σ_{ac} , of a Fuji II LC sample, 1 mm thick, light activated for 20 s, measured every 3.5 min for 1 day. The encircled part represents a drop in electrical conductivity at the moment of light activation (a). Frequency dependence of the electrical conductivity, σ_{ac} , of a Fuji II LC sample, 1 mm thick, without light activation (b).

setting process: the first is related to the acid attack and ion release and the second is due to the cross-linking between polymeric acid molecules and released Al^{3+} , Ca^{2+} or Sr^{2+} ions.

The setting process was investigated by impedance measurements in a fixed and wide frequency region over short and longer periods of time. For the GICs in the present study, the effect of setting upon change in the electrical conductivity shows a significant decrease over the first 12 h.

The break in electrical conductivity obtained at a fixed frequency for Fuji IX Fast, Fig. 2, depends on the thickness of the sample. With increasing thickness from 1 to 3 mm in height, the time at which the break in electrical conductivity appears is increased from about 11 to 15 min, respectively. On the other hand, the largest change in conductivity is evidenced for a 1 mm sample, indicating that the setting process is faster for thinner samples than for thicker ones. Since the electrical conductivity obtained by impedance spectroscopy is a macroscopic quantity, it seems that the break in electrical conductivity is related to structural changes that occurred within the volume of the samples. Thus, at the beginning of setting, the structural change for a 1 mm sample is a fast process, which takes place within the sample's volume followed by a decrease in the mobility of the charge carriers (ions and molecules) within the solid cement network. It should be pointed out that the mobility gets impaired by the increase in viscosity during reaction and hence it is assumed that a correlation should exist between decreasing conductivity and increasing extent of reaction. However, reduction in the mobility of the charge carriers is related not only to the setting but also to the dehydration process, since measurements are performed in

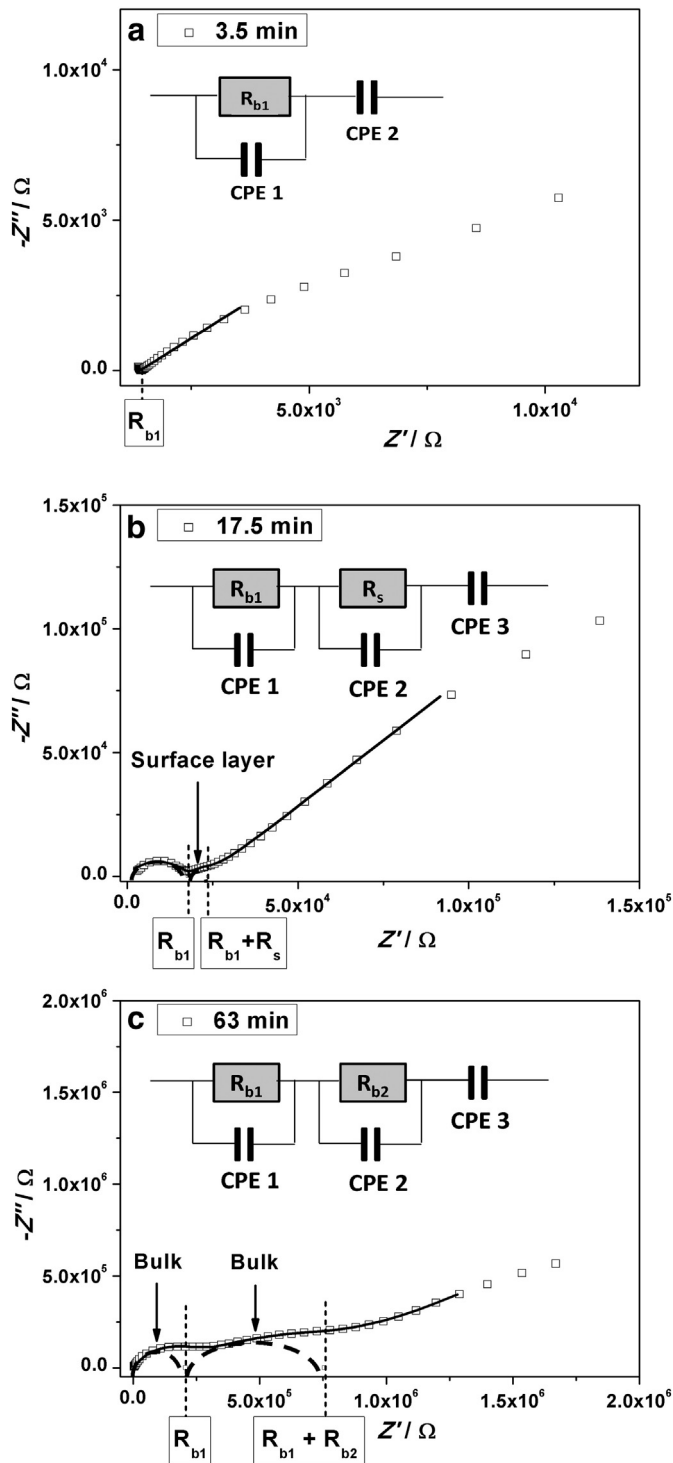


Fig. 9. Complex impedance plots and their corresponding equivalent circuits for a Fuji IX Fast sample, 1 mm thick, measured at 3.5 min (a), 17.5 min (b) and 63 min (c). R_{b1} and R_{b2} are the frequency resistances, whereas CPE 1, CPE 2 and CPE 3 represent the constant-phase elements.

air, and to the pore size distribution. The variation in conductivity of the Fuji IX Fast samples with various thicknesses has a uniform tendency to decrease to the constant values, which indicates that the cement has passed through the final stage of the setting process.

Therefore, changes in electrical conductivity as a function of time correspond to the electrical transport within the slurry structure in the initial stage (before the break) and within the solidified cement structure (continuous decrease in conductivity). The origin of the

electrical conductivity break could be explained by the structural transformations that occur in the cements. The existence of aluminum complex in the initial stage, before the formation of the aluminum polycarboxylates in the GICs, is widely reported in the literature [30–32]. However, it was recently reported for Fuji IX GP that there is a conversion of aluminum from the glass phase, where it has coordination four, Al(IV), into a cement matrix with coordination six, Al(VI) [33]. Also, it was proposed that aluminum forms more stable species with one or two carboxylic groups and fluorine ions along with water or hydroxyl as ligands. Thus, we believe that the conversion of aluminum, specified as a diffusion-controlled process, in the early stage of less than 30 min, along with the cross-linking of the polymeric chains by aluminum and strontium cations, is responsible for the break in the electrical conductivity spectra. Furthermore, cross-linking of the chains is largely completed between 1 and 12 h, resulting in a constant value of conductivity.

For the Ketac Molar samples, the break in conductivity occurs after 20–30 min, which means that the setting process in the initial stage is slower when compared to Fuji IX Fast, Fig. 3. It was previously mentioned that the Ketac Molar glass is partially crystalline and the XRD lines correspond to calcium fluoride (CaF_2). It was assumed that the Ketac Molar glass would first facilitate amorphous phase separation and then subsequent crystallization to fluorite during quenching, which would effectively remove charge balancing calcium cations from the glass and force the Al into a higher coordination state [25]. Therefore, it seems that the release of calcium cations is much slower from crystalline calcium fluoride, resulting in the slower formation of the calcium aluminum silicate cement network during the setting reaction [20]. Consequently, slower structural transformation within the volume of a sample causes a break in the electrical conductivity after 20 min. Generally, calcium silicate cements (such as Portland cement) show slower setting reactions than the acid–base setting reaction of a GIC, causing a lower value of electrical conductivity [7,18,34].

Fuji II LC exhibits a completely different behavior. As mentioned earlier, the polymerization of the resin-modified GIC takes place instantaneously with light activation. The presence of HEMA has an effect on the modification of the microstructure. It is well known that HEMA is an insulating material that can fill the porous network of dental cement, accelerating stabilization of the electrical conductivity [20]. On the other hand, polymerization that is light activated forms a solid network, with more homogenous pore-size distribution. It seems that changes in the sizes of pores and their distribution also influence the sharp decrease in electrical conductivity. This is consistent with the SEM micrograph of Fuji II LC, Fig. 12(b), where the pores are more uniformly dispersed within the cement matrix after 24 h of being dried in vacuum. Thus, the sharp decrease in electrical conductivity is probably a result of the fast polymerization and uniform distribution of pores of approximately 200 nm in size. It is interesting to note that the steady-state value of conductivity is reached instantaneously after this sharp decrease. Furthermore, it was reported that the delay prior to light activation may result in the structural differences and characteristics [35]. Since the Fuji II LC samples were light activated immediately after mixing, with a delay of up to 1 min, the maximal photopolymerization reaction for this GIC is assumed.

In contrast to light-activated Fuji II LC, the samples without light activation do not show a sharp decrease in conductivity, Fig. 5. Electrical conductivity decreases continuously with time, reaching an almost identical final value as for the light-activated samples after 12 h. However, it is a question whether light activation accelerates the acid–base reaction, shifting it to the earlier time, or whether polymerization can obscure the acid–base reaction in the immediately cured samples. Recent results of an investigation of resin-modified GIC setting reactions indicate that the acid–base reaction and photopolymerization in GIC compete with and inhibit one another during the early stage [35]. However, it should be mentioned that the changes in molecular architecture affect impedance i.e. electrical conductivity. It was found that HEMA

Table 2The fitting parameters, R_{b1} , total electrical resistivities, R_{tot} , and dc conductivities, σ_{dc} , for the Fuji IX Fast, Fuji II LC and Ketac Molar samples obtained after various times.

<i>t</i> /min	Fuji IX Fast			Fuji II LC			Ketac Molar		
	R_{b1}^a/Ω	R_{tot}/Ω	$\sigma_{dc}/(\Omega \text{ cm})^{-1}$	R_{b1}^a/Ω	R_{tot}/Ω	$\sigma_{dc}/(\Omega \text{ cm})^{-1}$	R_{b1}^a/Ω	R_{tot}/Ω	$\sigma_{dc}/(\Omega \text{ cm})^{-1}$
3.5	1.42×10^3	1.42×10^3	7.06×10^{-4}	1.01×10^5	5.12×10^5	1.93×10^{-6}	2.86×10^3	2.86×10^3	3.50×10^{-4}
10.5	2.49×10^3	2.49×10^3	4.01×10^{-4}	1.22×10^5	8.18×10^5	1.22×10^{-6}	4.38×10^3	4.38×10^3	2.29×10^{-4}
17.5	1.78×10^4	2.21×10^4	4.52×10^{-5}	9.56×10^4	1.11×10^6	8.16×10^{-7}	5.76×10^3	5.76×10^3	1.74×10^{-4}
31.5	4.76×10^4	8.48×10^4	1.18×10^{-6}	1.68×10^5	1.56×10^6	6.43×10^{-7}	7.80×10^3	7.80×10^3	1.28×10^{-4}
42	1.00×10^5	1.97×10^5	5.07×10^{-6}	2.19×10^5	1.84×10^6	5.43×10^{-7}	3.07×10^5	5.91×10^5	1.69×10^{-6}
52.5	1.42×10^5	4.70×10^5	2.13×10^{-6}	2.85×10^5	2.11×10^6	4.75×10^{-7}	6.39×10^5	1.42×10^6	7.05×10^{-7}
63	2.06×10^5	7.55×10^5	1.32×10^{-6}	3.61×10^5	2.35×10^6	4.25×10^{-7}	2.28×10^6	1.03×10^7	9.70×10^{-8}
119	1.09×10^6	3.64×10^6	2.74×10^{-7}	6.19×10^5	3.83×10^6	2.61×10^{-7}	1.87×10^7	6.99×10^7	1.43×10^{-8}
178.5	5.02×10^6	9.11×10^6	1.10×10^{-7}	6.28×10^5	6.20×10^6	1.61×10^{-7}	1.38×10^8	1.88×10^8	5.32×10^{-9}
1440 (1 day)	8.00×10^8	1.51×10^9	6.62×10^{-10}	5.81×10^7	8.11×10^7	1.23×10^{-8}	–	–	–

^a The fitting parameter errors monitored through the ZView software were in the range of 0.5–6.5%.

added to GIC formulations reduces the activity of polyacids, hence slowing the acid–base reaction [36]. As a result of the addition of HEMA the overall conductivity at the beginning of setting reaction is reduced probably due to the change in intermolecular bonding between individual molecular components present in resin-modified GIC. Generally, the fundamental understanding of the nature and mechanisms of charge migration in reactive system is rather complex. The measured conductivity encompasses contributions from ionic migration and intrinsic migration charges which usually are related to the formation hydrogen-bonding complex whose composition is likely to vary through network created by various molecular groups.

So, it seems that prior to light activation, the acid neutralization process is migration (diffusion) controlled but further acid–base reactant diffusion is significantly reduced after the photopolymer cross-linked network is formed. Thus, the time required for light initiation affects the acid–base reaction rate and extent [35].

Accordingly, the acid–base reaction in Fuji II LC without light activation continues for longer time periods, which results in a continuous decrease in electrical conductivity during the first hour. However, as mention above, after 12 h of setting the obtained electrical conductivity values for Fuji II LC with and without light activation are identical. It should be noted that light activation means using 486 nm of light for 20 s. Therefore, the reason for such behavior of Fuji II LC not exposed to light is probably reduced polymerization due to ambient light influence and/or reduced charge migration in acid–base reaction that is responsible for slowing the setting process. This leads to the conclusion that such polymerization reduction does not significantly affect the electrical properties over longer periods of time. However, it is a question whether or not light activation has an effect on the other properties of photosensitive GICs.

On the other hand, the overall electrical conductivity for the Fuji II LC samples (light activated or not) is one order of magnitude higher than that for the Fuji IX Fast samples. Such behavior can be explained by

the instantaneous formation of a rather homogeneous cement matrix, which enhances electrical transport along the more uniformly distributed pores, Fig. 12(b). Moreover, it seems that the easier motion of ions through conduction pathways formed in Fuji II LC contributes to higher electrical conductivity if compared to the conductivity of Fuji IX Fast.

However, it should be mentioned that in other cement-based material such as Portland cement the smaller pore size and the narrower pore size distribution decreases the electrical conductivity. Such discrepancy is probably result of cement's different microstructure where displacement of calcium silicate hydrate (C–S–H) sheets along with creep process in the absence of water affects the electrical conductivity [12]. It was found that drying even to intermediate humidity causes a partial collapse of C–S–H structure to a greater extend then for the paste cements that have undergone solvent exchange [12]. It is worth noting that the relationship between immersion and pore size distribution for the conventional and “resin modified” GIC using impedance spectroscopy is under investigation.

This research, which evaluated the setting characteristics of three different GICs during both the first hour and longer periods of time, shows that it is possible to examine the evolution of the setting process by measuring electrical conductivity using impedance spectroscopy. Moreover, this method can be used to distinguish the electrical behavior of dental cements in which only the acid–base reaction is responsible for setting from that of photopolymerized dental cements.

Analysis of the complex impedance plots is useful for determining whether the overall electrical conductivity is dominated by bulk or grain-boundary components. Also, this analysis provides information on the quality and homogeneity of dental cements, since there is generally a link between the microstructures and ac response.

The obtained complex impedance spectra in Figs. 9 and 10 show the presence of the distinct features attributable to the structural regions in the samples. This is primarily because the impedance data presented in the form of imaginary Z'' (capacitive) vs. real Z' (resistive)

Table 3

Electrical capacitances of each semicircle in the impedance spectra for the Fuji IX Fast, Fuji II LC and Ketac Molar samples obtained after various times.

<i>t</i> /min	Fuji IX Fast			Fuji II LC			Ketac Molar		
	C_1^b/F	C_2^b/F	C_3^b/F	C_1^b/F	C_2^b/F	C_3^b/F	C_1^b/F	C_2^b/F	C_3^b/F
3.5	4.20×10^{-11a}	–	1.29×10^{-4}	5.73×10^{-12}	1.03×10^{-11}	3.74×10^{-6}	6.28×10^{-11a}	–	2.54×10^{-5}
10.5	2.12×10^{-11a}	–	3.05×10^{-5}	9.35×10^{-12}	8.40×10^{-12}	2.07×10^{-6}	1.63×10^{-10a}	–	1.36×10^{-5}
17.5	6.85×10^{-11}	1.07×10^{-7}	8.64×10^{-6}	8.81×10^{-12}	8.77×10^{-12}	1.69×10^{-6}	2.28×10^{-10a}	–	1.31×10^{-5}
31.5	7.43×10^{-11}	4.64×10^{-9}	4.67×10^{-6}	7.46×10^{-12}	9.55×10^{-12}	1.40×10^{-6}	6.39×10^{-10a}	–	1.13×10^{-5}
42	8.33×10^{-11}	2.26×10^{-9}	2.90×10^{-6}	6.97×10^{-12}	9.66×10^{-12}	1.25×10^{-6}	2.32×10^{-10}	2.01×10^{-9}	1.72×10^{-7}
52.5	8.55×10^{-11}	9.61×10^{-9}	1.73×10^{-6}	6.36×10^{-12}	1.04×10^{-11}	1.12×10^{-6}	3.32×10^{-10}	2.30×10^{-9}	1.01×10^{-7}
63	1.11×10^{-10}	8.31×10^{-9}	1.17×10^{-6}	6.17×10^{-12}	1.08×10^{-11}	1.03×10^{-6}	2.02×10^{-10}	1.23×10^{-8}	1.17×10^{-7}
119	1.71×10^{-10}	4.48×10^{-9}	3.84×10^{-7}	5.97×10^{-12}	1.17×10^{-11}	6.11×10^{-7}	1.32×10^{-10}	3.52×10^{-9}	6.28×10^{-8}
178.5	1.08×10^{-10}	4.43×10^{-9}	2.42×10^{-7}	8.29×10^{-12}	1.24×10^{-11}	3.04×10^{-7}	1.16×10^{-10}	1.88×10^{-9}	3.18×10^{-8}
1440 (1 day)	4.49×10^{-11}	3.45×10^{-10}	–	2.63×10^{-11}	2.53×10^{-11}	3.37×10^{-8}	–	–	–

^a Values obtained by fitting, using the ZView software, represented by CPE.^b The fitting parameter errors monitored through the ZView software were in the range of 0.5–6.5%.

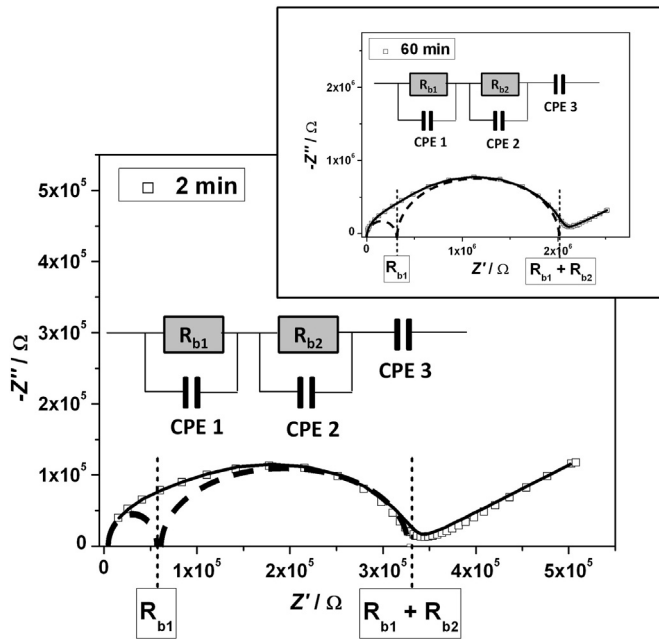


Fig. 10. Complex impedance plot for a Fuji II LC sample, 1 mm thick, light activated for 20 s, measured at 2 min. Inset: complex impedance plot for the Fuji II LC sample at 60 min after light activation.

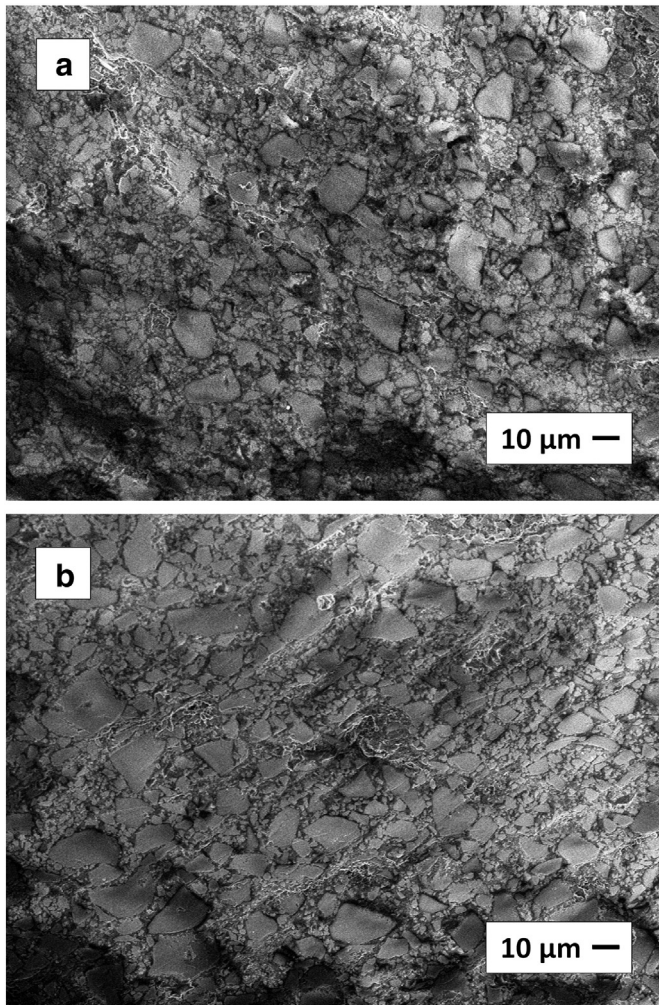


Fig. 11. SEM micrographs of the disk surface of Fuji IX Fast (a) and light-activated Fuji II LC (b).

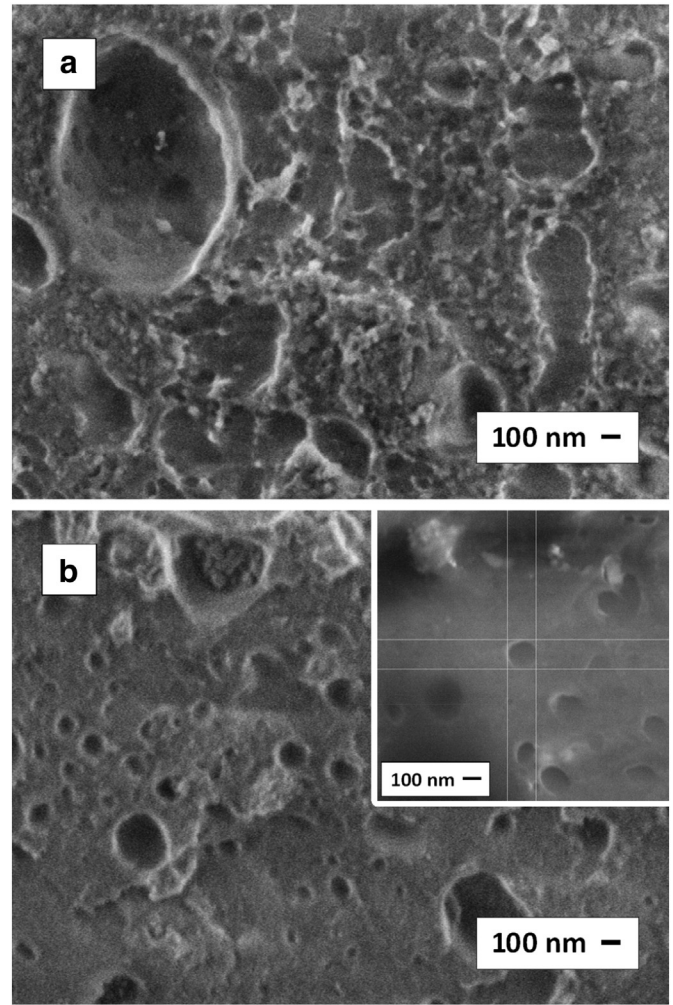


Fig. 12. SEM micrographs for Fuji IX Fast (a) and light-activated Fuji II LC in nano-scale (b). Inset: cement matrix interior of Fuji II LC with pores in the range between 100 and 200 nm.

impedances allow the overall electrical properties to be separated into their component parts. The assignment of the regions is based on the magnitude of the calculated capacitance. As already mentioned, the capacitance, C , for each semicircle was calculated using the values A and α obtained from the fitting and frequency maximum, $\omega_{\max}$, in each semicircle. However, it should be noted that the capacitance for the low frequency spur is represented by the CPE value. Thus, the obtained values of capacitance are related to the regions in the sample. Generally, the suggested assignment is defined as the magnitude of capacitance for ceramics [37] but their interpretation could potentially be used for determining compositional variations within other solid materials. Consequently, the effects related to the microstructures of dental cements can be characterized by their relative capacitance values. The distinction among the components is not always fairly straightforward but depends on the variety of structural regions present in the cements.

From the values obtained for the resistance and conductance components, it is possible to determine the contribution of each separated region to the total resistance, R_{tot} , as shown in Figs. 9 and 10. The determined values for the resistance and capacitance of each GIC in this study obtained after various time periods are listed in Tables 2 and 3.

The calculated value for C_1 of 4.2×10^{-11} F for Fuji IX Fast obtained after 3.5 min is in the range that corresponds to the bulk capacitance of the sample. The semicircle corresponding to the bulk impedance is outside the frequency scale of the instrument. However, the first intercept at high frequency and its associated resistance are attributed to the

sample's bulk. In this case, bulk means the Fuji IX Fast powdered glass. The low frequency spur has an associated capacitance of 1.291×10^{-4} F, which can be attributed to the electrochemical reactions [37].

The impedance plot obtained after 17.5 min contains two separated semicircles and a low frequency spur, Fig. 9(b). The large semicircle corresponds to the released ion conduction through the bulk of the sample, having an associated capacitance, C_1 , of 6.85×10^{-11} F. The small, poorly resolved semicircle with a capacitance, C_2 , of 1.07×10^{-7} F is attributed to the surface layer. This surface-layer capacitance is quite large, indicating the formation of a thin solid cement matrix on the surface. Also, it is known that the GICs are atmospherically unstable and humidity sensitive, and, in fact, can form a hydrated/dehydrated surface layer during the setting reaction. The capacitance value for the low frequency spur is determined to be 8.64×10^{-6} F, which lies in the range from 10^{-7} to 10^{-5} F that corresponds to the motion of the released ions and to the diffusion-controlled acid neutralization.

A sample measured after 63 min also shows two semicircles, where the second one is better defined with a capacitance of 8.31×10^{-9} F, suggesting the formation of a thicker region of the solid cement matrix, Fig. 9(c). It is interesting to point out that the capacitance values for this second semicircle decrease with time, reaching a value of 3.45×10^{-10} F after one day. The value obtained can be compared to the capacitance values of the first semicircle, which are attributed to the bulk of the sample.

Furthermore, analysis of the evolution of the impedance plots and capacitance values obtained shows that after several hours and one day the capacitance values for C_1 and C_2 became very close, indicating that there are two structural regions formed in the Fuji IX Fast samples. The variations of C_2 for different periods of time had a tendency to decrease, which implies a further setting process. Clearly, the variances of capacitance values indicate that the cement experiences a progression from a slurry structure to solid cement. This is in good accordance with the SEM micrographs, Fig. 11(a), which show the presence of two phases, unreacted glass particles and polysalt, which are responsible for the adherence of the particles resulting in the aggregation or networking that leads to the hardening of the cement.

Careful inspection of the C_3 capacitance values related to the low frequency spur reveals a systematic decrease, Table 3, from 1.29×10^{-4} to 2.42×10^{-7} F during the first few hours. Such a decrease in capacitance values is attributed to the transformations that occurred on the surface of the sample. As previously mentioned, the highest capacitance value of 1.29×10^{-4} F is related to the electrochemical reactions on the surface of the particles of powdered glass and corresponds to the acid attack and ion release in the early stage of setting.

The capacitance values obtained after several hours of setting are in the range of $\sim 10^{-7}$ F. These values could be associated with the proton transfers along hydrogen bonds in complex formed from various molecular groups involved in cement network. However, the observed trend in Fig. 9(c) shows that the spur turns over in the form of a semicircle indicating charge migration (or diffusion) through solidified sample. On the other hand the effect of the electrode (blocking or not-blocking) observed at lower frequencies cannot be excluded.

For the light-activated Fuji II LC samples, the impedance plots obtained after 2 and 60 min contain two semicircles and a spur, Fig. 10. It is interesting to note that the capacitance values for both C_1 and C_2 are in the range between 10^{-11} and 10^{-12} F, which are typical values for bulk capacitance, Table 3. Thus, both semicircles with capacitance values of this order indicate that the sample is composed of two phases. The capacitance values of C_1 , which lay in the range between 5.73×10^{-12} and 2.63×10^{-11} F, correspond to the bulk of the powdered glass, whereas the capacitance values of C_2 in the range between 8.40×10^{-12} and 1.03×10^{-11} F are associated with the bulk impedance of the polysalt. Therefore, these two semicircles and its associated resistances, Table 2, are attributed to the bulk properties of the two phases in the Fuji II LC sample. The presence of two phases, glass and polysalt, is presented in the SEM micrograph in Fig. 11(b). In the case

of Fuji II LC, the formation of the second phase was enhanced by the light activation, while the glass phase remains unreacted and amorphous. These results clearly show that light activation causes the almost instantaneous photopolymerization and formation of the cement matrix responsible for the cross-linked structure and solidification. Such behavior is consistent with the formation of pores of an average size from 100 to 200 nm that are uniformly dispersed within the cement matrix, as illustrated in Fig. 12(b).

Furthermore, analysis of the impedance plots confirms that it is possible to separate the overall resistance of GICs into different components and to measure the values of the component capacitances. This is an important point since these results make it possible to determine every step during the setting process, providing information about the time required for the total solidification of dental cements. This is especially important to dentists as the cement needs to remain fluid enough for mixing and accurate placement but is then needed to set sharply.

5. Conclusions

In this work, changes in electrical conductivity/resistivity during setting have been investigated for Fuji IX Fast, Fuji II LC and Ketac Molar Aplicap at fixed, 10 and 1000 Hz, and various frequencies from 0.01 Hz to 1 MHz using impedance spectroscopy. The breaks in conductivity for Fuji IX Fast and Ketac Molar at about 15 and 30 min, respectively, are due to changes in the microstructure during the setting processes. For both GICs, the times at which the breaks in conductivity appeared depend on the thickness of the sample.

The steep drop without break in the electrical conductivity of light-activated Fuji II LC is the result of instantaneous photopolymerization and the formation of a homogeneous cement matrix that contains more uniformly distributed pores, averaging 100–200 nm in diameter.

The complex impedance plots obtained for the three GICs studied show the presence of features that correspond to the structural regions in the samples. The calculated capacitance values for each region in a sample are related to the microstructure of the dental cement. Evolution of the impedance spectra and changes in the capacitance values reveal that it is possible to monitor every step in the solidification of the cements. For Fuji IX Fast, over the first 60 min the impedance spectra exhibit progressive transformations related to the development of different constituent regions during the setting process, whereas light activation causes the instantaneous formation of regions for Fuji II LC.

Finally, impedance spectroscopy could become an essential technique in determining of various processes in dental materials, primarily because it allows the electrical properties of materials to be separated into their component parts, which can then be systematically analyzed. This analysis is useful because the progression and interaction in the setting reaction affect the physical properties of cement especially important in dentistry. The knowledge of the sequence of the setting reactions in dental cements is the base for determining handling characteristics and overall strength of GICs over time.

Acknowledgments

This work was supported by the Croatian National Foundation, project 8/31. A.M.M., K.S. and M.Č. acknowledge partial funding by the Croatian Ministry of Science, Education and Sports, 098-0982929-2916.

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