UNIVERSIDADE ESTADUAL DE MARINGÁ
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PROGRAMA DE PÓS-GRADUAÇÃO EM ODONTOLOGIA INTEGRADA

FERNANDA MIDORI TSUZUKI

OBSERVANDO OS ESTÁGIOS INICIAIS DA DINÂMICA DO PROCESSO DE PRESA EM CIMENTOS DE IONÔMERO DE VIDRO RESTAURADORES QUIMICAMENTE ATIVADOS

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2020

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Dissertação apresentada ao Programa de Pós-Graduação em Odontologia Integrada da Universidade Estadual de Maringá para obtenção do título de Mestre.

Orientador (a): Prof. Dr. Mauro Luciano Baesso
Co-Orientador (a): Profa. Dra. Renata Corrêa Pascotto

MARINGÁ- PR
2020

Fernanda Midori Tsuzuki

Observando os estágios iniciais da dinâmica do processo de presa em cimentos de ionômero de vidro restauradores quimicamente ativados

Este trabalho de conclusão de Mestrado foi julgado e aprovado para obtenção do título de Mestre em Odontologia Integrada através da Universidade Estadual de Maringá.

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BANCA EXAMINADORA

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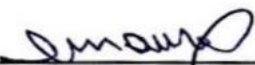
Tsuzuki FM. Observando os estágios iniciais da dinâmica do processo de presa em cimentos de ionômero de vidro restauradores quimicamente ativados [dissertação]. Maringá: Universidade Estadual de Maringá; 2020.

RESUMO

Objetivo: Avaliar os estágios iniciais da dinâmica do processo de presa, o tempo de endurecimento e o tempo de estabilização das ligações químicas de cimentos de ionômero de vidro (CIVs) restauradores quimicamente ativados. **Material e métodos:** Cinco materiais foram avaliados (n = 5): Equia Forte (GC, Japão) [EF], Equia Forte HT (GC, Japão) [HT], Ketac Universal (3M ESPE, Alemanha) [KU], Maxxion R (FGM, Brasil) [MR] e Riva Self Cure (SDI, Austrália) [RV] por meio das técnicas de termografia, espectroscopia no infravermelho por reflectância total atenuada (FTIR-ATR) e teste mecânico de indentação com agulha de Gillmore. Para as medidas de termografia e FTIR-ATR as amostras foram preparadas por meio de um agitador mecânico e a coleta dos dados realizadas no modo resolução temporal, durante 30 minutos. As primeiras leituras foram obtidas aproximadamente 20s após a mistura líquido/pó, monitorando-se o início do processo de reação. O método estatístico "Análise dos Componentes Principais (PCA) " foi utilizado para se avaliar os resultados obtidos com a técnica FTIR-ATR. As mudanças dos espectros FTIR-ATR em função do tempo foram ajustadas com uma função exponencial, fornecendo informações sobre o tempo de evolução das ligações químicas (τ). A câmera termográfica forneceu as imagens do campo de temperatura da amostra ao longo do mesmo intervalo de tempo utilizado nas medidas FTIR-ATR. O tempo de endurecimento dos materiais foi analisado pelo método de indentação com agulha de Gillmore seguindo as recomendações da norma ISO 9917-1:2007. Os dados foram analisados estatisticamente pela ANOVA e Tukey-Kramer (α = 5%). **Resultados e Discussão:** Os resultados permitiram identificar os compostos responsáveis pelas reações químicas ocorridas durante a presa dos CIVs testados. A técnica estatística PCA mostrou diferenças entre as marcas analisadas. Os valores de τ, em segundos, obtidos pela análise espectroscópica foram menores para a estabilização das ligações químicas para o RV (393±58), seguido por MR (632±94), EF (709±36), HT (740±35) e KU (747±92). No entanto, os dados obtidos pelo teste mecânico mostraram que a ordem com que os materiais endurecem seguiu comportamento oposto: KU (210±15,8), HT (212±14,8), EF (258±13,1), MX (324±11,4) e RV (370±14,1). Os resultados com a câmera termográfica demonstraram que o RV, KU, HT e EF apresentaram dois estágios de variação da temperatura, que foram coincidentes com as evoluções dos picos observadas nas medidas FTIR-ATR. No primeiro estágio foi observada uma elevação inicial de temperatura, de 3,9 a 6,6°C, que diminuiu rapidamente após o primeiro minuto. A segunda elevação foi observada após aproximadamente 3 minutos, tendo o RV apresentado maior variação (8°C). Para o MR, houve apenas um estágio e a variação de temperatura foi de aproximadamente 11,5°C. **Conclusão:** As técnicas utilizadas no presente estudo permitiram a análise dos estágios iniciais da reação de presa dos CIVs, auxiliando na compreensão da dinâmica desse processo e do tempo necessário para a estabilização das ligações químicas que indica o endurecimento final do material. O comportamento dos picos de FTIR-ATR ao longo do tempo coincidiu com as variações de temperatura evidenciando os processos endotérmicos e exotérmicos, confirmando a ocorrência de reações químicas nestes intervalos. Os materiais que apresentaram

menor tempo de endurecimento tiveram um período mais longo para a estabilização das ligações químicas, evidência que pode ser muito relevante uma vez que uma força prematura sobre a restauração pode comprometer a sua longevidade. Finalmente, este estudo demonstrou a viabilidade e o grande potencial dessas técnicas no infravermelho para avaliação da dinâmica dos processos de presa de materiais de interesse na Odontologia, com ênfase na relação entre os comportamentos de suas propriedades termodinâmicas e físico-químicas.

Palavras-chave: Cimentos de Ionômeros de Vidro. Estrutura molecular. Tempo de reação.

Tsuzuki FMT. Watching the early stages in the dynamic of the setting process in chemically activated restorative glass-ionomer cements [dissertation]. Maringá: State University of Maringá; 2020.

ABSTRACT

Objective: To evaluate the early stages of the setting process dynamics, the hardening time and the stabilization time of the chemical bonds of chemically activated restorative glass ionomer cements (GICs). **Material and methods**: Five materials were evaluated (n = 5): Equia Forte (GC, Japan) [EF], Equia Forte HT (GC, Japan) [HT], Ketac Universal (3M ESPE, Germany) [KU], Maxxion R (FGM, Brazil) [MR] and Riva Self Cure (SDI, Australia) [RV] by thermography, Fourier Transform Infrared Attenuated Total Reflectance Spectroscopy (ATR-FTIR) and Gillmore needle indentation mechanical testing. For thermography and ATR-FTIR measurements, the samples were prepared using a mechanical stirrer and the data were collected in temporal resolution mode for 30 minutes. The first readings were obtained approximately 20s after the start of the liquid / powder mixture, monitoring the beginning of the reaction process. The statistical method "Principal Component Analysis (PCA)" was used to evaluate the results obtained with the FTIR-ATR technique. The changes in FTIR-ATR spectra as a function of time were adjusted with an exponential function, providing information on the time of evolution of chemical bonds (τ). The thermographic camera provided the temperature field images in the sample over the same time interval as the ATR-FTIR measurements. The hardening time of the materials was analyzed by the Gillmore needle indentation method following the recommendations of ISO 9917-1: 2007. Data were statistically analyzed by ANOVA and Tukey-Kramer (α = 5%). **Results and Discussion:** The results allowed us to identify the compounds responsible for the chemical reactions that occurred during the setting reaction of the GICs. The PCA statistical technique showed differences between the analyzed brands. The values of τ, in seconds, obtained by spectroscopic analysis were lower for the stabilization of chemical bonds for RV (393 ± 58), followed by MR (632 ± 94), EF (709 ± 36), HT (740 ± 35).) and KU (747 ± 92). However, the data obtained by the mechanical test showed that the order in which the materials hardened followed the opposite behavior: KU (210 ± 15.8), HT (212 ± 14.8), EF (258 ± 13.1), MX (324 ± 11.4) and RV (370 ± 14.1). The results with the thermographic camera showed that RV, KU, HT and EF presented two stages of temperature variation, which were coincident with the bands evolutions observed in the ATR-FTIR measurements. In the first stage, an initial temperature rise of 3,9 to 6,6 ° C was observed, which rapidly decreased after the first minute. The second elevation was observed after approximately 3 minutes, and the RV presented largest variation (8 ° C). For MR, there was only one stage and the temperature range was approximately 11.5 ° C. **Conclusion:** The techniques used in the present study allowed the analysis of the early stages of GICs setting reaction, helping to understand the dynamics of this process and the time required for the stabilization of chemical bonds that indicates the final hardening of the material. The behavior of the bands over time coincided with temperature variations, endothermic and exothermic processes, confirming the occurrence of chemical reactions at these intervals. Materials that presented shorter hardening times took longer periods for stabilization of chemical bonds,

which can be very relevant in the clinic, since a great masticatory force performed early on the restoration can compromise their longevity. Finally, this study demonstrated the great viability and importance of the ATR-FTIR and termographic measurements for the evaluation of the dynamic of the reaction setting of dental materials, with focus on its mechasnical and physico-chemical properties.

SUMÁRIO

1. CONTEXTUALIZAÇÃO
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1.1. Desenvolvimento dos cimentos de ionômero de vidro

Até a década de 1960, o cimento de silicato era o material dentário mais utilizado para restauração em dentes anteriores (Nicholson, 2016a). Embora permitissem proporcionar importantes efeitos estéticos, fosse rígidos e oferecesse o benefício terapêutico da liberação de flúor, este cimento apresentava várias desvantagens, entre elas a tendência à formação de manchas, a alta suscetibilidade ao ácido e a ausência de capacidade de adesão ao dente (Wilson e Nicholson, 1993; Nicholson, 2016a).

O desenvolvimento de outros materiais como o cimento de policarboxilato de zinco significou um grande passo para a criação dos cimentos de ionômero de vidro (CIVs). Uma das consequências foi a obtenção de um material que pudesse atuar como cimento e simultaneamente apresentasse adesão aos tecidos dentários (Smith, 1968; Mizrahi & Smith, 1969). Desta maneira, representou um avanço importante para a Odontologia restauradora, pois foi o primeiro material restaurador inerentemente adesivo, o qual demonstrou efetividade para se unir ao esmalte e à dentina (Mizrahi & Smith, 1969; Nicholson, 2016b). O cimento de policarboxilato de zinco permanece até os dias de hoje como um material útil para a odontologia clínica, indicado para a cimentação de coroas protéticas (Lad et al., 2014).

Em 1972, Wilson & Kent observaram que as características do cimento de silicato e do policarboxilato de zinco combinavam a presença de flúor e a baixa alteração dimensional do primeiro, com a adesividade à estrutura dentária proporcionada principalmente pelo ácido poliacrílico do cimento de policarboxilato de zinco. Desta forma, em 1975, o primeiro CIV foi comercializado.

É importante entender a natureza da sua invenção, pois o mesmo não consistiu em simplesmente misturar o pó de vidro do cimento de silicato dental com a solução de ácido poliacrílico do policarboxilato de zinco para se obter um cimento com propriedades melhoradas

(Wilson 1996). A invenção do cimento de ionômero de vidro não foi, de fato, um ato único, mas uma série de etapas inovadoras (Nicholson, 2016a). Um passo importante foi a constatação de que a razão alumina / sílica do vidro controlava a reação. Isso apontou o caminho para a criação do primeiro CIV bem-sucedido, designado de G200 (Wilson & Kent, 1972; Kent et al., 1973).

1.2. Composição

A formação do CIV consiste em uma mistura pó/líquido. Os três componentes essenciais dos CIVs são a sílica, ou óxido de silício (SiO_2), óxido de alumínio ou alumina (Al_2O_3) e fluoreto de cálcio (CaF_2) (De Caluwé, 2014; Nicholson, 2018). Na prática, outros componentes foram adicionados para se melhorar propriedades como taxa de endurecimento, translucidez e resistência final (De Caluwé, 2014).

A propriedade essencial do pó para uso em CIVs é que são vidros básicos que podem reagir com soluções aquosas de ácido (Hill e Wilson, 1988; Sidhu & Nicholson, 2016). Os vidros são preparados por meio de fusão dos componentes de sua formulação como sílica, alumina, flúor e cálcio, utilizando-se temperaturas de fusão entre 1100 °C e 1500 °C (Hill & Wilson, 1988; Nicholson, 2016a). No processo de obtenção do vidro, a mistura dos compostos é aquecida até se obter a fase líquida, que ao ser resfriada por meio de choque térmico, fornece o material vítreo. Em seguida, o vidro é moído até uma granulometria de aproximadamente 20–50 µm, a qual depende da aplicação clínica pretendida para o cimento a ser desenvolvido (Saito, Tosaki & Hirota, 1999; Nicholson, 2016a). Atualmente, os cimentos são preparados a partir de escolha cuidadosa da granulometria misturando-se partículas menores de 4 µm com outras de 25 µm. Esta escolha permite se obter cimentos mais reativos (Saito, Tosaki & Hirota, 1999; De Caluwé et al., 2014)

Em vez de água como empregado no preparo dos cimentos para contrução civil, os cimentos odontológicos CIVs são obtidos adicionado-se um ácido polimérico ao pó de cimento (Wilson e Kent, 1972; Tuzuner, Dimkov & Nicholson, 2019). Atualmente, o ácido poliacrílico ainda é utilizado. Outros ácidos como o tartárico e o cítrico permitem diminuição do tempo de endurecimento em relação ao poliacrílico, resultando em um tempo de trabalho maior (Wilson et al., 1976; Sidhu e Nicholson, 2016).

Desta maneira, o CIV convencional consiste na mistura pó/líquido o qual resulta na reação de presa do material, que consiste numa reação ácido-base formando uma massa homogênea composta por polissais (Tuzuner, Dimkov & Nicholson, 2019).

1.3 Reação de presa

Os ionômeros de vidro se formam imediatamente após a mistura pó/líquido por meio de uma reação ácido-base, que se inicia de forma muito rápida e com duração de poucos minutos (Nicholson, 2018). Os íons de hidrogênio do ácido atacam as partículas de vidro na presença de água, liberando íons Na^+ e Ca^{2+} (ou Sr^{2+}) do vidro para a solução de poliácido e, posteriormente, os íons Al^{3+}. Em seguida, estes íons interagem com as moléculas do ácido para formar reticulações iônicas, e a estrutura final é rígida e endurecida (Sidhu & Nicholson, 2016).

A configuração de elementos de íons de vidro foi estudada por diversas técnicas de espectroscopia, incluindo espectroscopia no infravermelho (Nicholson et al., 1988; Yamakami et al., 2018), espectroscopia Raman (Young, 2000) e Ressonância Magnética Nuclear (RMN) (Stamboulis et al., 2006). A reação química em geral parece ocorrer em duas etapas e por meio de um processo controlado por difusão. Sabe-se que após a reação inicial de endurecimento, outras continuam a ocorrer de forma lenta, em um processo conhecido como reação de maturação (Sidhu & Nicholson, 2016; Nicholson, 2018). É importante destacar que as

propriedades mecânicas dos cimentos, como resistência e rigidez, continuam a aumentar durante o processo de maturação e são consideradas muito importantes do ponto de vista prático para a Odontologia (Nicholson, 2018).

Pesquisas vêm sendo desenvolvidas para se elucidar as características desta reação. Este processo inicial pode estar intimamente associado à várias alterações nas propriedades físicas dos CIVs, daí a importância de seu estudo.

1.4 Aplicação clínica

O CIV encontra-se disponibilizado no mercado nas formas de frascos ou encapsulados. Os CIVs em frascos contêm o pó e o líquido separados, demandando dosagem e manipulação manual do material. Já as cápsulas pré-dosadas são empregadas para se melhorar o proporcionamento entre o pó e o líquido e facilitar a homogeneização. Nessas cápsulas, existe uma membrana que separa as duas partes e ao ocorrer a mistura entre pó e líquido, deve haver manipulação do conteúdo por intermédio de um manipulador mecânico (Sulaiman et al., 2018).

A aplicação clínica dos CIVs engloba as várias áreas da Odontologia, desde o uso em restaurações de dentes decíduos (Pires et al, 2018), em restaurações anteriores de classe III e V (Cefaly, 2006), como agente de cimentação de núcleos e coroas (Nakamura et al, 2016), como acessórios ortodônticos (Pascotto et al, 2004), e para selamento de fóssulas e fissuras (Khudanov, 2018). Este material, por ser adesivo, é amplamente empregado nas técnicas de mínima intervenção, como no Tratamento Restaurador Atraumático (ART) e propiciam, em termos de remoção de tecido dentário, economia do tecidos removidos e diminuição dos preparos cavitários, preservando estruturas dentais saudáveis (Frencken, Leal & Navarro, 2012). A aplicação clínica deste material vai ao encontro das tendências atuais, mostrando-se

intimamente relacionadas aos preceitos da Odontologia Preventiva e Minimamente Invasiva (Burke, 2003; Walsh & Brostek, 2013; Kielbassa et al., 2017).

1.5 Limitações e Tendências futuras

Desde sua criação, as principais vantagens associadas a estes cimentos incluem a biocompatibilidade (Nicholson & Czarnecka, 2008), ação anticariogênica e liberação de flúor (Wiegand,Buchalla & Attin, 2007; Khudanov, 2018), adesão à estrutura dental (Yamakami, 2018), baixo coeficiente de expansão térmica e baixa citotoxicidade (Collado-Gonzalez, 2018). No entanto, algumas de suas propriedades ainda não são totalmente satisfatórias e apresentam algumas limitações mecânicas e clínicas, tais como suscetibilidade inicial à desidratação sob ressecamento ou solubilização e erosão frente a exposição precoce à umidade, baixa resistência à tração e compressão e problemas estéticos devido a sua translucidez limitada (Dyonosipolus et al., 2018).

Desta maneira, pela sua ampla indicação, é necessário que as propriedades dos CIVs sejam estudadas e aprimoradas. Atualmente, a quantidade de pesquisas científicas envolvendo tal material é relevante e novas formulações estão sendo testadas, existindo a tendência de que este material seja cada vez mais utilizado pelos cirurgiões dentistas. Um outro aspecto relevante é que estes estudos podem auxiliar profissionais e órgãos públicos em termos da escolha dos materiais mais adequados para as respectivas aplicações.

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2. ARTIGO

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2.1 INTRODUCTION

Glass ionomer cements (GICs) have been widely used in dentistry since its introduction in the early 70s (Wilson and Kent, 1972). Their main advantages include biocompatibility (Nicholson & Czarnecka, 2008), anti-cariogenic action and fluoride release (Wiegand, Buchalla & Attin, 2007; Khudanov, 2018), adhesion to dental structure (Yamakami, 2018), low coefficient of linear thermal expansion and low cytotoxicity (Collado-Gonzalez, 2018).

The first GIC was developd as a result of the proposal to combine the good properties of two dental materials, mixing the glass powder of the dental silicate cement that presents fluoride release hehavior with the polyacrylic acid solution of the zinc polycarboxylate cement formulation which is responsible for its chemical adhesion (Wilson and Kent, 1972). The invention of the glass ionomer cements was not a single act but rather a series of innovative steps (Nicholson, 2016).

The initial reaction, after cement mixing, is an acid-base reaction between an aqueous polymeric acid solution and an ion-leachable basic glass powder (De Caluwé, 2014; Sidhu and Nicholson, 2016). When mixed with the liquid, the glass powder degrades so that Ca^{2+} and Al^{3+} ions are released. These ions form complexes with acid, resulting in a gel matrix (De Caluwé, 2014). This setting reaction occurs rapidly, usually in the first minutes (Nicholson, 2018). The final cement includes a substantial amount of unreacted glass particles acting as reinforcing fillers in the polymer matrix (De Caluwé, 2014; Cheikh et al., 2019). There is further possibility for improving the properties of these materials to make them still more competitive compared with other restorative systems. Knowledge of the sequences of the setting reaction in dental cements is therefore crucial, as they will affect the handling and overall physical properties of the cements (Cheikh et al., 2019).

According to ISO 9917-1, restorative GICs must have a hardening time of 1.5 to 6 min. However, the fact that GICs harden occurs in a short period of time, does not mean that the material has reached the chemical stability of the setting reaction. Several studies (Stamboulis, 2006; Moberg et al., 2018) analyzed the chemical bonds of the samples 24 hours after handling, considering this period to be the time required for the material to acquire stability. However, recently, Yamakami et al, 2018 demonstrated that the time required for a high viscosity GIC to reach 99% chemical stability was around 150 min. During this time the material is still vulnerable and is in the process of forming chemical bonds with dentin (Yamakami et al., 2018).

Considering that the chemical reaction began at the first moments of the mixture, although the continuity of the setting process may occur slowly, the major variation in the material occurs just after its preparation. This fast process imposes limitation in the current available methods to follow the material formation, specialy in the first seconds of the process. The present study addresses this knowledge gap by examining the very early stages of the dynamics of the cement setting process (down to about 20s after the beginning of the liquid/powder mixture), focusing on stabilization time of chemical bonds of the formed GICs and their relationship with hardening time. This is of clinical relevance as the time for stabilization of chemical bonds can influence material strength and restoration longevity.

2.2 MATERIALS AND METHODS

2.2.1 Specimen Preparation

Measurements were performed in vitro using 5 commercially available restorative GICs (Table 1). The encapsulated materials were handled in a mechanical mixer (SDI, Victoria,

Australia) for 10s. After this time, it took approximately 10s to start the measurements. In order to maintain the same stirring standards and mixing time, MR powder and liquid were inserted into a capsule, maintaining the same ratio recommended by the manufacturer.

Table 1 - Brands and composition of restorative GICs tested (data provided by manufacturers).

Brand / Manufacturer	Code	Powder composition	Liquid composition	Proportion powder / liquid
Equia Forte / GC,Tokyo, Japan	EF	Strontium-fluoro-aluminum-silicate + Polyacrylic acid + Water		Capsule
Equia Forte HT / GC,Tokyo, Japan	HT	Strontium-fluoro-aluminum-silicate + Polyacrylic acid + Water		Capsule
Ketac Universal / 3M ESPE, Seefeld, Germany	KU	Oxide glass	Water + Acrylic acid copolymer - maleic acid + tartaric acid	Capsule
Maxxion R / FGM, Joinville, Brazil	MR	Fluoro-aluminum-silicate glass + Polyacrylic acid + Tartaric acid + Calcium fluoride + Water		1.5:1
Riva Self Cure / SDI,Vitoria, Australia	RV	Fluoro-aluminum-silicate + Polyacrylic acid	Polyacrylic acid + Tartaric Acid + Water	Capsule

2.2.2 Thermographic Camera

A thermographic camera (7300, Infratec, Dresden, Germany), which operates in the wavelength range from 2 to 5.7 µm, was mounted upright and the sample positioned in its lens focal position of 25cm. Possible temperature measurements of this camera ranges from -40ºC to 300ºC, with a resolution of $\pm$ 0.002°C. Measurements were performed at room temperature, around 25°C. The samples were placed on a waterproof paper suitable for GIC handling (SDI, Victoria, Australia). The measurement of each material lasted 30 min with each image taken in intervals of 0.3 s, using the IRBIS® 3 software (Infratec, Dresden, Germany). The same software calculated the average temperature variations of the samples (n = 5).

2.2.3 Fourier Transform Infrared Attenuated Total Reflectance Spectroscopy (ATR-FTIR)

The GICs spectra and their precursors, powder and liquid, were obtained using a Fourier Transform Infrared Spectrometer (FTIR) with Attenuated Total Reflectance attachment (ATR) (Vertex 70v, Bruker Optik GmbH, Ettlingen, Germany) with a diamond ATR crystal. Samples of each material (n = 5) were placed directly on the crystal and a spectrum were collected every 10s for 30 minutes, with 10 scans, resolution of 4 cm^{-1} and the spectral region of 4000 to 400 cm^{-1}, without vacuum.

2.2.3.1 Principal Component Analysis (PCA)

PCA is a multivariate analysis tool that was applied to the ATR-FTIR spectra in order to reduce the dimensionality of a data set (Varmuza & Filzmoser, 2009). ATR-FTIR spectras were baseline corrected, treated using a first derivative with first order polynomial procedure, and applied to PCA using a computer code developed in the software Mathematica 7.0 (Wolfram Research, Illinois, USA). Multivariate statistics package was used for a simplified and comprehensive two-dimensional view of the process dynamics of chemical bonding of GICs.

2.2.3.2 Chemical Bond Stabilization Time

Chemical bond stabilization time (τ) was obtained by adjusting tha ATR-FTIR data with an exponential function (Eq.1):

$$y(t) = y_0 + A\exp[-t/\tau] \qquad (1)$$

In which y(t) is the ATR-FTIR spectral variation as a function of time after the beginning of the reaction, obtained by the PCA method. Here, y_0 is spectral variation value when the material reached stabilization, y (t) the spectral variation with time, t the instant times of the measurements, and τ the characteristic decay time representing the instant t when the spectral variation values decay to 1/e (approximately 37% of y (0) value).

2.2.4 Hardening Time

GICs hardening time measurements followed the recommendation of the ISO 9917-1: 2007 standart. A stainless-steel matrix with an 8mm diameter central hole was placed on a waterproof paper and positioned under a 400g ± 5g Gillmore needle. The cement was inserted into the matrix and, after ninety seconds, the indentator was carefully lowered onto the cement surface and left there for 5s. The indentations were performed at 30s intervals and, as the cement began to harden, the intervals between indentations were reduced to 10s. Hardening time was determined when no circular marks were observed on the material surface (n = 5).

2.2.5 Statistical Analysis

Comparison between different ionomer cements temperature, stabilization of chemical bonds and hardening time were analyzed by ANOVA and Tukey-Kramer ($\alpha = 5\%$).

2.3 RESULTS

The temperature variation as a function of time obtained by measurements made with the thermographic camera is presented in figure 1. Each curve represents a mean value of n = 5 measured samples. RV, EF HT, KU formulations presented two stages of temperature variation, while the MR presented only one. MR was the material that presented the largest temperature variation (11.5°C), that slowly decreased, while the other GICs presented temperature variations from 3.9ºC to 6.6°C at the first stage, followed by a rapid decrease. The

second stage started after about 3 minutes for RV, EF, HT and KU materials, with RV presenting the largest variation (8°C).
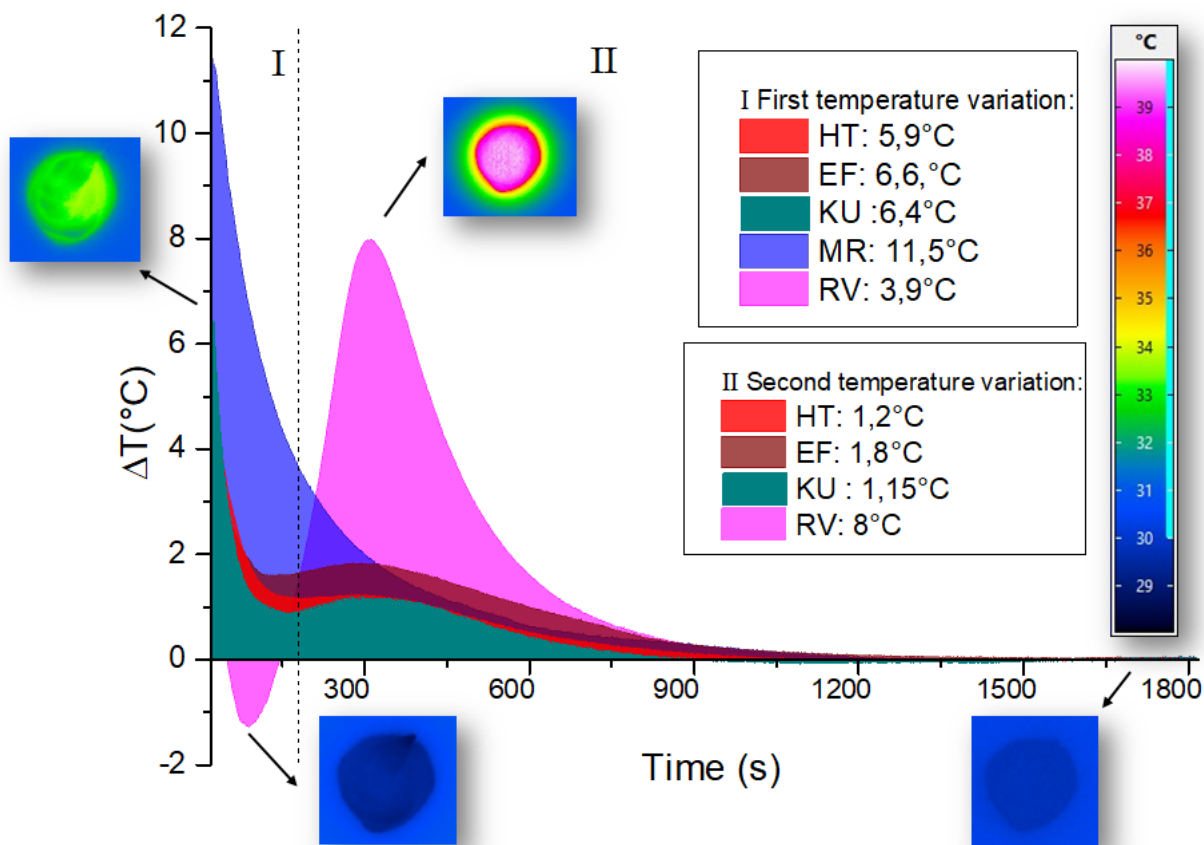

Figure 1 – GICs temperature variation as a function of time. The inserts exemplify images obtained by the thermographic camera.

Precursor (powder and liquid) spectrum of each material assessed by ATR-FTIR technique, are shown in figure 2. All used precursors generally presented the same spectral pattern, except KU powder that exhibited a band centered at 1415 cm^{-1} that was absent in the others.
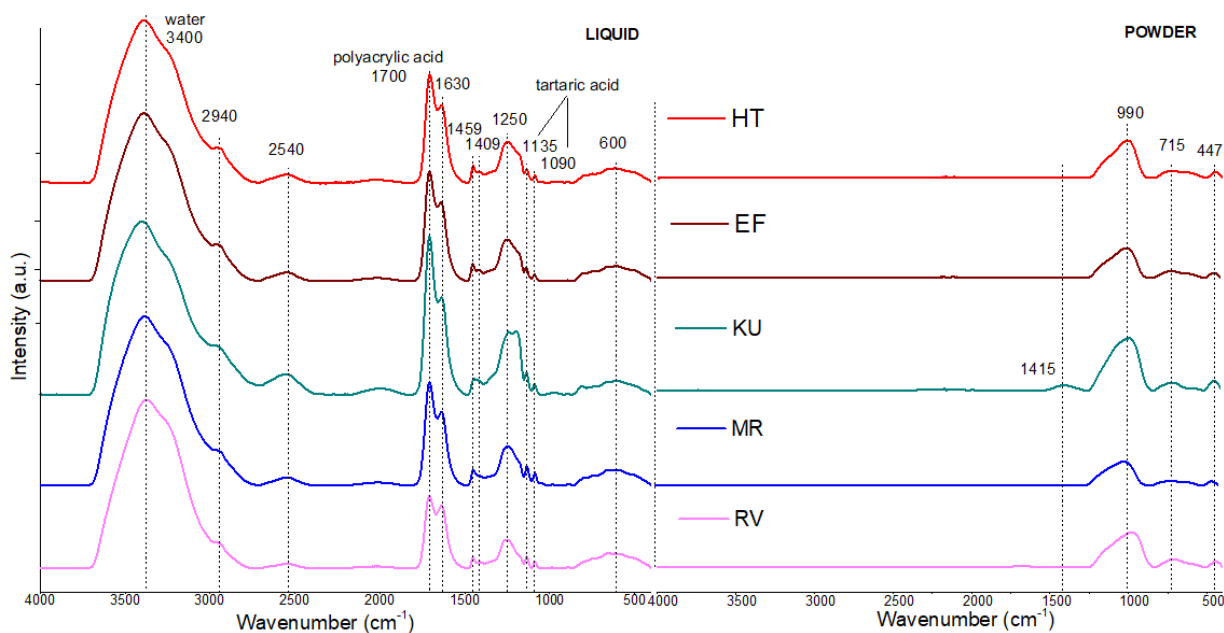
Figure 2- ATR-FTIR spectra of GIC precursors: liquid and powder.

Next, tests that allowed the monitoring of changes of chemical bonds over time were performed, showing that the GICs spectra are changed after mixing the precursors (powder and liquid) and during the hardening process (Figure 3A-B).

The plot of PC1 × PC2 scores representing the spectral changes with time for the five studied cements are shown in the figure 3. The curves represent the spectras at 20s and 1800s, at the beginning and final recorded times of the reaction, respectively. The insert represents the whole spectral change with time for the EF cement. It is noted that, although the powder and liquid spectra show essencially similar behaviors between the different materials (Figure 2), after mixing, the arrangement of the samples in the plot shows that the cement spectra presented significant differences. The plots of PC1 × PC2 scores (figure 3D) at 1800s confirm that the despite the final spectra differed significantly from the initial ones for each sample, they remained clustered, showing low relative variability.
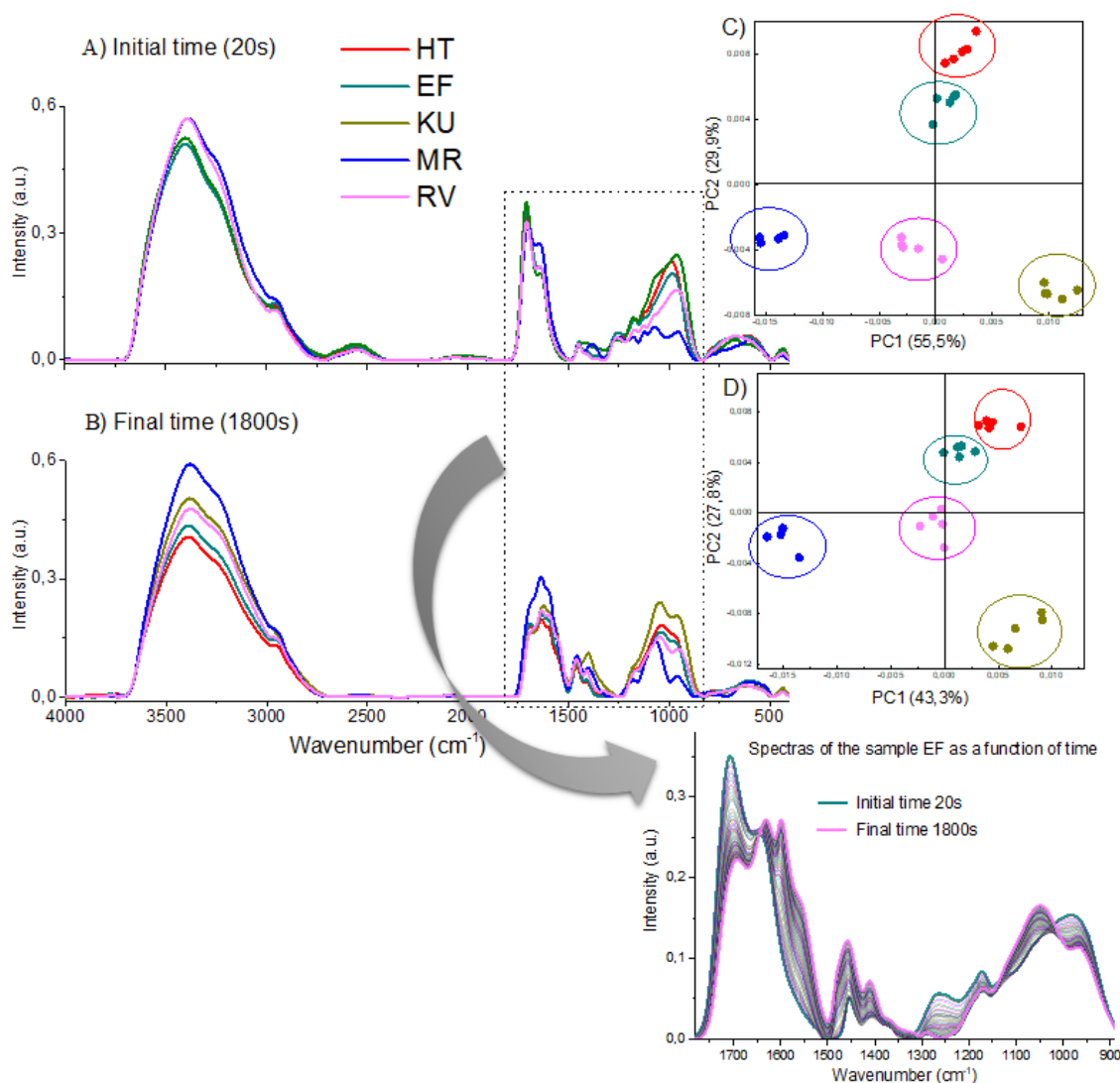
Figure 3 - ATR-FTIR spectral variation of different GICs obtained as a function of the reaction time: (A) at 20s and (B) at 1800s. Respective PC1 and PC2 scores (C and D) are shown on the right side. The insert shows an example for the whole spectral change with time, between 1800 and 900 cm^{-1}, for the EF cement.

Figure 4 shows the loading of PC1 for HT cement, representing the regions responsible for the largest variation among the spectra. It was possible to identify the bands that contributed most to the spectral variation as a function of time. The bands assignments are shown on the

right side (Crisp & Wilson, 1974; Young et al., 2002; Fareed & Stamboulis, 2014; Yamakami et al., 2018; Menezes-Silva, 2019).
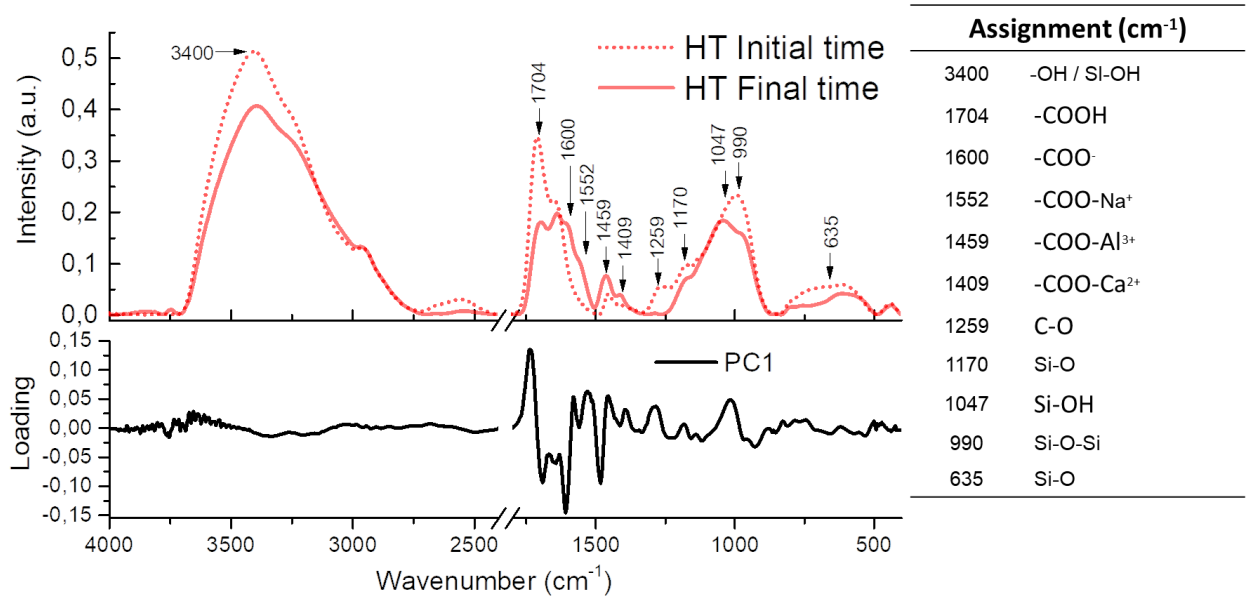

Figure 4 - (A) ATR-FTIR spectra of HT for initial (20s) and final (1800s) times in comparison with the load spectrum of the first principal component PC1. The table shows the bands assignemnts, identifying the functional groups that most contributed to spectral variation as a function of time.

The whole PCA intensity variations as a function of time are shown in the figure 5. Each transient for a specific cement was repeated five times. The average of five measurements is also shown the curve fitting using Eq. 1 allowed to obtain the time in which chemical bonds stabilize. The results show that RV had a shorter chemical bonds stabilization time (τ) in seconds (393 ± 58), followed by MR (632 ± 94), EF (709 ± 36), HT (740 ± 35) and KU (747 ± 92). It can be seen that RV reaction presented different behavior at the beginning of the curves compared with the other studied cements.
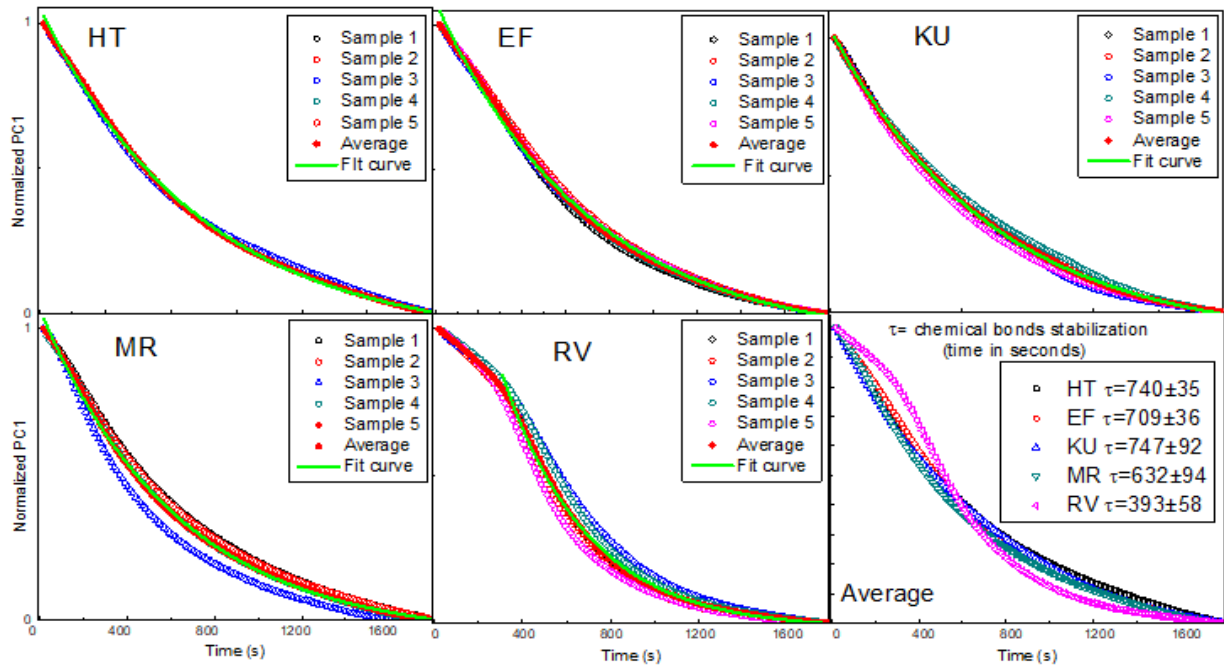
Figure 5 - Curves representing PCA analysis calculated from the ATR-FTIR spectral variation as a function of time. Each curve is an average of five independ measurements (n = 5). The exponential fitting with Eq. 1 provided the stabilization time of chemical bonds (τ) of the GICS.

The hardening times evaluated by Gillmore Needle indentation test can be seen in the figure 6.

Figure 6 - Comparison between the hardening times and the stabilization times. Oposite tendency with time was observed for all five studied cements.

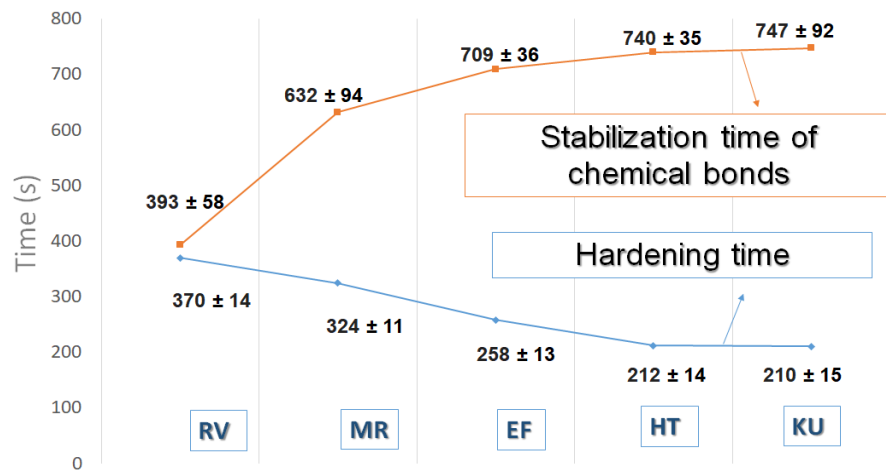Figure 7 shows both the temperature variation for RV obtained with the termografic camera and the most significant ATR-FTIR bands change provided by the PC1 loading. Thus, it was possible to evaluate simultaneously the variation of both temperature and occurrence of chemical reactions (through the increasing or decreasing of the bands) at each specific time interval of the reaction to form the CIV. The possible sequency of the chemical reactions are represented on the illustration, part B of the figure 7.
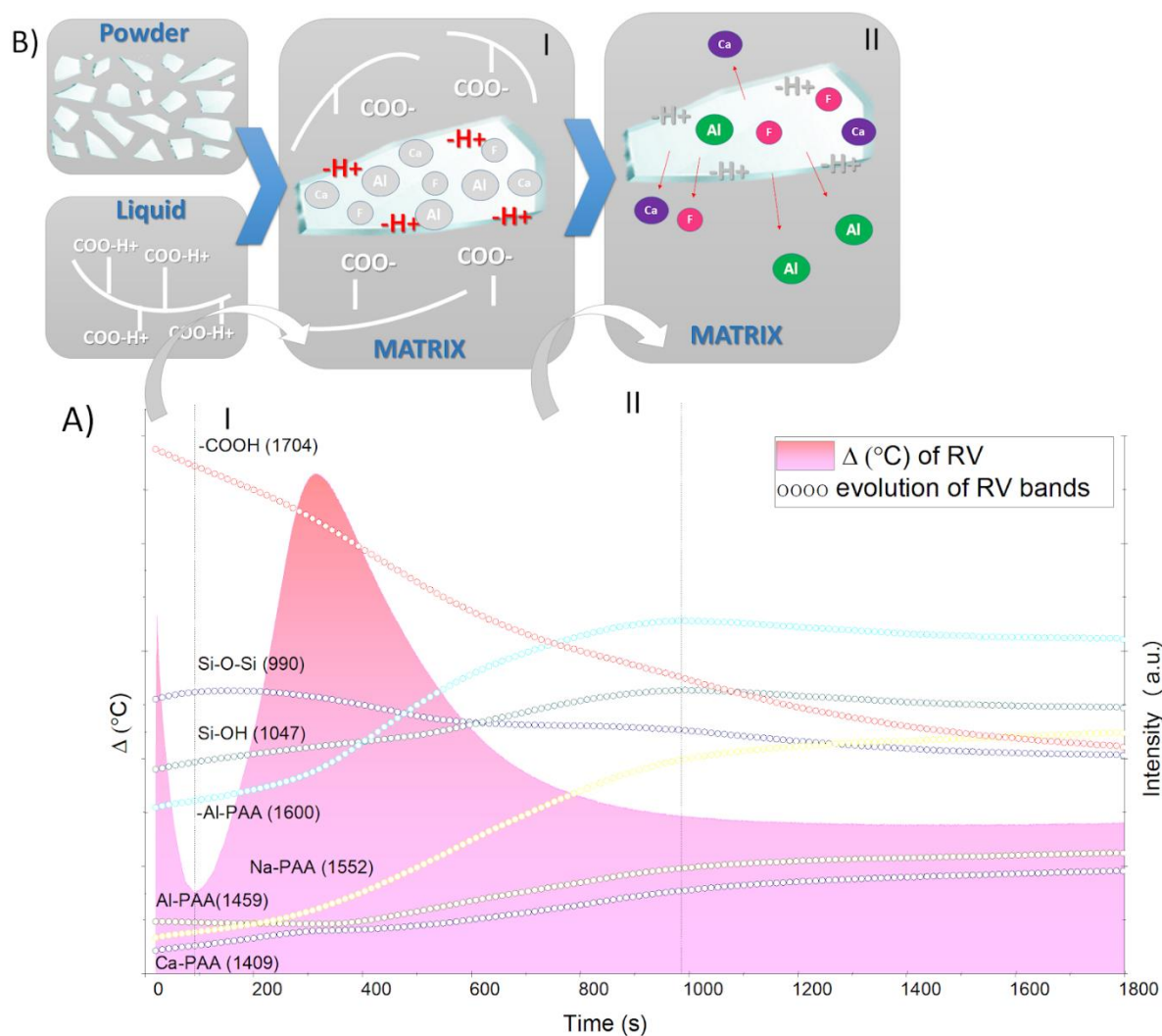

Figure 7 – A) Comparison between the temperature variation of RV and the evolution of the bands as a function of time; B) schematic illustration of possible sequency of the reaction. I) First stage of the reaction which is the acid hydrolysis on the glass particles surfaces, II) Second stage representing the ion release to the matrix.

2.4 DISCUSSION

Data obtained by temperature monitoring in association with ATR-FTIR allowed to explain the dynamics of chemical bonds stabilization in GICs through the formation or changes in absorption bands, revealing the occurrence of chemical interaction from the formation of molecular rearrangements, and also importantly providing its relationship with hardening time. As far as we know, this is the first study to relate, accurately in the first few seconds of the reaction, the changes in temperature and chemical bonds in order to explain the dynamics of GICs setting reaction. The results of this study showed that the values found for stabilization time of the chemical bonds are associated with temperature variation and are different from the cement hardening time, indicating that they should not be used to justify the same processes.

The essential properties of glasses for use in GICs are that they must be basic and able to react with acid aqueous solutions (Hill e Wilson, 1988; Nicholson e Czarnecka, 2008). The Al/Si ratio cannot apparently be greater than 1:1 otherwise there are insuficient tetrahedral SiO_4 for the glass be able to form cements (Burrow, 2016). This condition is necessary to promote sufficient replacement of silica by aluminum to ensure that the glass is basic (De Caluwé et al., 2014). This basicity can be explained in terms of the random network model of Zacheriasen (Zachariasen, 1953). In this model, the glass is considered to be a random assembly of SiO_4 tetrahedra, which are joined at the corners. These joined tetrahedral may be assembled into essentially linear chains. When silica is the only component, the resulting structure is electronically neutral and has no basic character. The addition of alumina changes this and in the presence of sufficient silica, alumina is forced to adopt the tetrahedral geometry of the SiO_4 units. However, since aluminum possesses only three positive charges compared with four for silicon, as a consequence the resulting structure has an overall negative charge (Nicholson & Czarnecka, 2009). To overcome this charge deficiency, additional positive ions (Na^+, Ca^{2+}) are

needed. These render the resulting glass susceptible to acid attack, as required for their role in glass-ionomer cements (Nicholson & Czarnecka, 2009; Nicholson, 2018).

The GIC liquid is a polymeric acid having a carboxylate group (-COOH). The most widely used in GIC was polyacrylic acid (Burrow, 2016), though a variety of other polymers have been studied since this acid was first reported (Young, 2000). The liquid can also contain water or tartaric acid (Sidhu & Nicholson, 2016). The inclusion of tartaric acid was shown to initially reduce the viscosity of the cemet and subsequently increasing it rapidly, almost leading to a snap set (Burrow, 2016). It seems that this action is due to the chelation of ions from the glass powder over the short duration, wich delays the formation of the gel stage of the GIC. This leads to faster cross-linking of the polyacrylic acid component (Nicholson et al. 1988); hence, most GICs contain tartaric acid to improve the working time but reduce the setting time (Young et al. 2000).

It was observed, through the ATR-FTIR spectra and temperature changes, that the initial setting reaction of the GICs occurs in two stages. Immediately after mixing, the cement's liquid moistens and dissolves the outer layer of the glass particles by acid hydrolysis, as observed through the changes in the bands at 1170 cm^{-1} (Si-O), 635 cm^{-1} (Si-O) and 990 cm^{-1} (Si-O-Si) (Sidhu & Nicholson, 2016) (Figure 3). Siloxane groups (Si-O-Si) on the surface of the glass particles react with water to form silanol groups (Si-OH). Thus, the main peak at 990 cm^{-1}, attributed to Si-O-Si stretch vibrations (Fareed & Stamboulis, 2014), is reduced. The intensity of the band at 1047 cm^{-1} is a further evidence of the decomposition of the glass mesh (Crisp et al., 1974). In this phase, a temperature reduction occurs due to the binding energy involved in breaking bonds between atoms or molecules by an exothermic process, which lasts between 100-200s, depending on the material (Figure 6).

The acid hydrolysis of the Si-O-Al bonds in the vitreous network, observed in the ATR-FTIR bands, demonstrated the formation of SiO_4 and AlO_4 tetrahedral structures linked by a

Si-O-Al-type bond in the glass network. When the Al^{3+} replace the Si^{4+} ions in the vitreous network, there is an unbalanced charge which is compensated by positive charges from modifier cations, such as the Ca^{2+} ions present in the glass composition. (Yamakami et al., 2018).

After acid-base reaction, the second phase of the setting reaction occurs. As a consequence, ions are released and the cations from the vitreous network bind to the carboxylic groups forming the polyacrylate salts (Yamakami et al., 2018), resulting in the appearance of absorption bands at 1552 cm^{-1} ($COO-Na^+$), 1459 cm^{-1} ($COO-Al^{3+}$) and 1409 cm^{-1} ($COO-Ca^{2+}$). During this process a temperature increase occurs due to the binding energy involved in the formation of bonds between atoms or molecules through an endothermic process, reaching maximum temperature of reaction. Afterwards, the polyacid gelation by metallic ions occurs, leading to its fixation and, hence, a reduction in temperature (Figure 6).

It has also been shown that water (3400 cm^{-1}) is an important component in the setting reaction of GICs. The presence of water is important in the chemical reaction as it aids in the movement of ions from the glass surface to form compounds with the carboxylic groups of acid (Okada et al., 2001). During the setting of the GIC, the amount of bound water in the matrix also increases. The matrix contains a degree of unbound water, hence the necessity for avoiding dehydratation or desiccation in the first minutes (Okada et al., 2001). Clinically this can be controlled by applying a fluid resin film over the restorative material shortly after removal of the matrix.

The setting reaction tends to a reduction in the number of -COOH groups (1704 cm^{-1}) as they set and reorganize as COO- groups (1600cm^{-1}) (Talal et al., 2009). It is recommended that the insertion of the material in the cavity should be done in the initial stage of this phase while the cement shines, indicating the presence of free carboxylic groups for the chemical bond between ionomer and tooth to occur. The cations released from the vitreous network are chelated by the carboxylic groups and can be observed by forming the absorption band in

1600cm^{-1} atributed to the organic acid polymeric structure. The cement obtained at the end of the reaction has in its constitution glassy particles coated with a layer of silica gel that is present in the formed polyacrylate salt matrices (Cheikh et al., 2019). Silica gel formation by acid degradation was confirmed through the intensity reduction of the band centered at 1060 cm^{-1} (Si-OH), as shown in Figure 3.

GICs, after mixing, go through a rapid initial setting reaction but continue to undergo changes in chemical bonds for some time (Nicholson, 2018). It was observed in this study that hardening time is directly related to the evolution of the aluminum polyacrylate peak (1459 cm^{-1}), which is responsible for the hardening of the material. Therefore, the sooner aluminum begins to be released, the faster the cement will harden (Nicholson & Czarnecka, 2009; Sidhu & Nicholson, 2016). The first challenge to this setting mechanism was discussed by Cook in 1983. His report evaluated freshly prepared cements dissolved in 3% potassium hydroxide solution and the washings were analyzed by atomic absorption spectroscopy. Cook's hypothesis was confirmed by subsequent studies, which involved washing the glasses with dilute ethanoic (acetic) acid (Nicholson e Czarnecka, 2008). Thus, the use of FTIR-ATR in the present research appears to be highly effective for the monitoring of aluminum release, presenting itself as a non-destructible technique of easy application.

The precursors, powder and liquid, of the GICs showed similar ATR-FTIR spectra (Figure 2). However, after mixing, the cement spectra were significantly different, as evidenced by the PCA analysis (Figure 3). The setting speed and final resistance of GICs are influenced by the molecular weight of polymers and copolymers, water concentration and powder/liquid ratio (Algera et al., 2006). Previous studies have shown that when the particle size of glass is reduced, particle reactivity increases considerably (Saito, Tosaki and Hirota, 1999; De Caluwé et al. 2014). The reactivity of such glass structures towards aqueous acids can be increased by including cations such as calcium that can break up the continuous Si-O-Si structural units

(Nicholson, 2016). In this way, the samples presented different stabilization time of the chemical bonds (Figure 5).

Indentations tests are usually used to evaluate the setting characteristics of the cements. However, these methods evaluate the initial superficial strength of the cements once they assess the point when the setting cement has sufficient resistance to indentation (ISO 9917-1:2007). It is important to note that the ability of the cement to resist indentations has a limited clinical relevance once indentation from a small area point load cannot reflect the forces applied to the material used to restore a dental cavity and do not provide insight into kinetics of the setting reaction.

It is worth noting that the hardening time of a material evaluated by means of indentations tests and presented in the package by the manufacturer (setting time) is different from the time to reach chemical bonds stability (completely reacted), which was measured by τ in the present study. From the clinical point of view, the faster the material takes hold, it will be less susceptible to fracture by early mastication on it.

The GICs EF, HT and KU showed fast hardening times, evaluated by the Gillmore test, and longer time to stabilize the chemical bonds. It is possible that the longer the GIC takes to stabilize the chemical bonds during the setting process, the greater the amount of chemical bonds responsible for the increase in the mechanical properties of the material. Hence, according to these results, it would be advisable to develop GICs that have a fast setting time, but that take a longer time for the chemical bonds to achieve great stability.

This information is important because with the knowledge of the instant when each chemical reactions takes place in the setting process, it may be possible to improve the composition of the material.

2.5 CONCLUSION

The techniques used in the present study allowed the analysis of the early stages of GICs setting reaction, helping to understand the dynamics of this process and the time required for the stabilization of chemical bonds that indicates the final hardening of the material. The behavior of the bands over time coincided with temperature variations, endothermic and exothermic processes, confirming the occurrence of chemical reactions at these intervals. Materials that presented shorter hardening times took longer periods for stabilization of chemical bonds, which can be very relevant in the clinic, since a great masticatory force performed early on the restoration can compromise their longevity. Finally, this study demonstrated the great viability and importance of the ATR-FTIR and termographic measurements for the evaluation of the dynamic of the reaction setting of dental materials, with focus on its mechasnical and physico-chemical properties.

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