



RAFAEL PINO VITTI

“STUDY OF COMMERCIAL AND EXPERIMENTAL MTA-  
BASED SEALERS FOR ROOT CANAL FILLING”

*“ESTUDO DE CIMENTOS COMERCIAIS E EXPERIMENTAIS  
À BASE DE MTA PARA OBTURAÇÃO DE CANAIS  
RADICULARES”*

PIRACICABA

2013





UNIVERSIDADE ESTADUAL DE CAMPINAS  
FACULDADE DE ODONTOLOGIA DE PIRACICABA

RAFAEL PINO VITTI  
“STUDY OF COMMERCIAL AND EXPERIMENTAL MTA-BASED  
SEALERS FOR ROOT CANAL FILLING”

Orientador: Prof. Dr. Mário Alexandre Coelho Sinhoreti

*“ESTUDO DE CIMENTOS COMERCIAIS E EXPERIMENTAIS À  
BASE DE MTA PARA OBTURAÇÃO DE CANAIS RADICULARES”*

TESE DE DOUTORADO APRESENTADA À FACULDADE DE  
ODONTOLOGIA DE PIRACICABA DA UNICAMP PARA  
OBTENÇÃO DO TÍTULO DE DOUTOR EM MATERIAIS  
DENTÁRIOS.

DOCTORATE THESIS PRESENTED TO THE PIRACICABA  
DENTAL SCHOOL OF THE UNICAMP TO OBTAIN THE PhD  
GRADE IN DENTAL MATERIALS.

Este exemplar corresponde à versão final  
da Tese defendida pelo aluno Rafael Pino Vitti  
e orientada pelo Prof. Dr. Mário Alexandre Coelho Sinhoreti

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PIRACICABA

2013

FICHA CATALOGRÁFICA ELABORADA POR  
JOSIDELMA F COSTA DE SOUZA – CRB8/5894 - BIBLIOTECA DA  
FACULDADE DE ODONTOLOGIA DE PIRACICABA DA UNICAMP

V835e Vitti, Rafael Pino, 1984-  
Estudo de cimentos comerciais e experimentais à base de  
MTA para obturação de canais radiculares / Rafael Pino Vitti. --  
Piracicaba, SP : [s.n.], 2013.

Orientador: Mário Alexandre Coelho Sinhoreti.  
Tese (Doutorado) - Universidade Estadual de Campinas,  
Faculdade de Odontologia de Piracicaba.

1. Fosfatos de cálcio. 2. Propriedades físicas e químicas. 3.  
Materiais dentários. I. Sinhoreti, Mário Alexandre Coelho, 1969-  
II. Universidade Estadual de Campinas. Faculdade de  
Odontologia de Piracicaba. III. Título.

Informações para a Biblioteca Digital

**Título em Inglês:** Study of commercial and experimental MTA-based sealers  
for root canal filling

**Palavras-chave em Inglês:**

Calcium Phosphates  
Physical and Chemical Properties  
Dental Materials

**Área de concentração:** Materiais Dentários

**Titulação:** Doutor em Materiais Dentários

**Banca examinadora:**

Mário Alexandre Coelho Sinhoreti [Orientador]  
Murilo Baena Lopes  
Cesar Henrique Zanchi  
Mario Fernando de Goes  
Caio Cezar Randi Ferraz

**Data da defesa:** 27-02-2013

**Programa de Pós-Graduação:** Materiais Dentários



UNIVERSIDADE ESTADUAL DE CAMPINAS  
Faculdade de Odontologia de Piracicaba



A Comissão Julgadora dos trabalhos de Defesa de Tese de Doutorado, em sessão pública realizada em 27 de Fevereiro de 2013, considerou o candidato RAFAEL PINO VITTI aprovado.

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Prof. Dr. CESAR HENRIQUE ZANCHI

Prof. Dr. MARIO FERNANDO DE GOES

Prof. Dr. CAIO CÉZAR RANDI FERRAZ

*Dedico este trabalho aos meus pais,  
**José Urbano** (in memoriam) e **Maria Helena**,  
exemplos de caráter e dedicação.  
Jamais mediram esforços para a minha  
formação profissional e pessoal.  
Agradeço por todo incentivo, orientação,  
compreensão e amor.*

*A minha irmã **Fernanda**, presente  
em todos os momentos da minha vida,  
pela amizade, companheirismo e amor.*

## AGRADECIMENTO ESPECIAL

A **Deus**, pelo conforto nos momentos difíceis e por iluminar e guiar meus passos, colocando sempre em meu caminho pessoas corretas, tornando possível mais uma conquista.

Ao **Prof. Dr. Mário Alexandre Coelho Sinhoreti**, Titular da Área Materiais Dentários, do Departamento de Odontologia Restauradora, da Faculdade de Odontologia de Piracicaba, Universidade Estadual de Campinas, pelo inestimável apoio, dedicação e paciência a mim dispensados nos ensinamentos durante esses nove anos de trabalho em conjunto, na orientação deste estudo e principalmente pela amizade, transformando as horas de trabalho em momentos de agradável convivência. Obrigado por tudo o que você me proporcionou durante minha Graduação e Pós-graduação, pela confiança em mim depositada e por tornar possível meu crescimento humanístico e científico.

## AGRADECIMENTOS

À direção da Faculdade de Odontologia de Piracicaba, da Universidade Estadual de Campinas, na pessoa do seu Diretor **Prof. Jacks Jorge Junior** e do Diretor Associado **Prof. Dr. Alexandre Augusto Zaia**, por todos os momentos que aqui passei desde a Graduação.

À coordenadoria geral de Pós-Graduação da Faculdade de Odontologia de Piracicaba da Universidade Estadual de Campinas na pessoa da sua coordenadora **Profa. Dra. Renata Cunha Matheus Garcia**, e do coordenador do Programa de Pós-Graduação em Materiais Dentários **Prof. Dr. Marcelo Giannini**.

Ao **Prof. Dr. Simonides Consani**, Titular da Área de Materiais Dentários, do Departamento de Odontologia Restauradora, da Faculdade de Odontologia de Piracicaba, Universidade Estadual de Campinas, grande educador, pela sua dedicação durante o curso e pela contribuição em meu crescimento científico e pessoal, sempre incentivando a busca pelo conhecimento.

Ao **Prof. Dr. Lourenço Correr-Sobrinho**, Titular da Área de Materiais Dentários, do Departamento de Odontologia Restauradora, da Faculdade de Odontologia de Piracicaba, Universidade Estadual de Campinas, pela amizade, incentivo e contribuição para a minha formação, além dos agradáveis momentos de lazer proporcionados.

Ao **Prof. Dr. Mario Fernando de Goes**, Titular da Área de Materiais Dentários, do Departamento de Odontologia Restauradora, da Faculdade de Odontologia de Piracicaba, Universidade Estadual de Campinas, pelo convívio e inestimável contribuição em minha formação através de todo conhecimento transmitido e dedicação.

A **Profa. Dra. Regina Maria Puppim-Rontani**, Titular da Área Odontopediatria, do Departamento de Odontologia Infantil, da Faculdade de Odontologia de Piracicaba, da Universidade Estadual de Campinas, pela amizade e por todos os ensinamentos dedicados ao longo desses anos essenciais para a minha formação.

Ao **Prof. Dr. Marcelo Giannini**, Professor do Programa de Materiais Dentários, do Departamento de Odontologia Restauradora, da Faculdade de Odontologia de Piracicaba, Universidade Estadual de Campinas, Coordenador do Programa de Pós-graduação em Materiais Dentários, pela amizade e contribuição em minha formação.

Ao **Prof. Dr. Cesar Henrique Zanchi**, Professor do Departamento de Odontologia Restauradora, da Faculdade de Odontologia, Universidade Federal de Pelotas, pela inestimável contribuição e ajuda na realização deste projeto. Obrigado por confiar em mim, me indicando ao Prof. Dr. Carlo Prati, e principalmente pela amizade criada durante esse tempo e acolhida que me fez sentir em casa todas as vezes que fui para Pelotas trabalhar.

Ao **Prof. Dr. Carlo Prati**, Professor do Departamento de Endodontia, da Faculdade de Odontologia de Bologna, Universidade de Bologna, pela amizade, acolhida e atenção a mim dispensadas durante todo o período de doutorado sanduíche, além da inestimável contribuição científica para a realização deste estudo. Obrigado pela confiança em mim depositada.

A **Profa. Maria Giovanna Gandolfi**, responsável pelo Laboratório de Biomateriais e Patologia Oral, da Faculdade de Odontologia de Bologna, Universidade de Bologna, pela acolhida, atenção, zelo e contribuição científica para a realização deste estudo. Obrigado pela confiança em mim depositada.

Aos Professores Doutores **Lourenço Correr-Sobrinho, José Flávio Affonso de Almeida e Lucas Zago Naves** que participaram da banca do exame de qualificação, pela enorme contribuição no aprimoramento deste trabalho

Ao técnico especializado do laboratório da Área Materiais Dentários, da Faculdade de Odontologia de Piracicaba, engenheiro e mestre em Materiais Dentários **Marcos Blanco Cangiani (Marcão)**, pela amizade, paciência, convívio, sustos diários e grande colaboração na execução de todos trabalhos. Sua ajuda e carisma são de grande importância no convívio diário.

A **Selma Aparecida Barbosa de Souza Segalla**, técnica da Área Materiais Dentários da Faculdade de Odontologia de Piracicaba, Universidade Estadual de Campinas, pela amizade, paciência, convívio e ajuda em todos os momentos solicitados.

Aos colegas, **Francesco Siboni e Manuela Gonçalves de Souza e Silva**, pela imprescindível ajuda na realização deste trabalho.

As minhas amigas, **Polliana Scaffa, Fabianni Apolonio e Rosa Curci** e ao meus amigos, **Stefano Ravaioli e Gabriel Mazzetto (Kiko)**, por toda ajuda e companheirismo durante minha estadia em Bologna. A amizade de vocês foi de suma importância para amenizar a saudade da família e dos amigos.

Aos meus grandes amigos(as) de Pós-graduação, **Ailla Lancelotti, Aloísio Spazzin, Antônio Pedro, Atáis Bacchi, Bruno Bueno, Guilherme Guarda, Lucas Naves, Luciano Gonçalves, Marcos Aurélio, Mateus Bertolini, Murilo Lopes, Rafael Moraes e Renata Bacelar**, pela amizade e companheirismo ao longo desses anos. Sempre presentes e dispostos a ajudar. Obrigado pelos

agradáveis momentos de convívio, os quais suavizaram as dificuldades e renovaram os ânimos.

Aos meus grandes amigos(as) **Bruno Gomes, Carlos Gustavo, Carol Barrichello, Farooque Ahmed, Felipe Degani, Ivan Guedes, Joel Motta, Luciana Berto, Marcelo Fregonesi, Maria do Carmo, Renata Honda, Sulyana Amaral, Vitor Chiamente e Vitor Prado**, pela amizade e torcida durante todo esse tempo.

Aos amigos(as) e colegas da FOP, **Alberto Antunes, Américo Bortolazzo, Ian Matos, Karla Mychellyne, Leonardo Santos, Lucas Tomaselli, Ricardo Guiraldo, Victor Feitosa e William Brandt**, pelos bons momentos de amizade.

Aos amigos da Eurotrip 2012, **Arthur Duarte (Bandola), Jovito Skupien, Rafael Francisco Vitti, Renato Moraes (Muxiba), Rogerio Piazza (Lagosta) e Thiago Yanno**, por toda amizade e parceira antes, durante e após a melhor viagem da minha vida.

A todos os **colegas** de Pós-graduação deste e de outros programas.

À **Fundação e Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES)**, pela bolsa concedida.

A todos os meus **familiares**, pelo apoio e incentivo dispensados durante toda a minha vida.

A **todos** que indiretamente contribuíram ou torceram para a realização deste trabalho.

***Meus sinceros agradecimentos.***

*“Não me envergonho de mudar de ideia,  
porque não me envergonho de pensar.”*

Blaise Pascal

## RESUMO

Os objetivos neste trabalho foram (1) avaliar e comparar propriedades físico-químicas de cimentos endodônticos, sendo um recentemente desenvolvido à base de mineral trióxido agregado (MTA Fillapex, Angelus, Londrina, Brasil) e outro à base de resina epóxica (AH Plus, Dentsply, Konstanz, Alemanha); e (2) desenvolver e avaliar propriedades físico-químicas de três cimentos endodônticos experimentais à base de MTA e uma resina de salicilato com diferentes fosfatos de cálcio (CaP). Os materiais foram manipulados de acordo com as instruções dos fabricantes. Os cimentos experimentais foram compostos de pastas bases e catalisadoras misturadas em 1:1. A pasta base foi composta de 60% de óxido de bismuto e 40% de butilenoglicol dissalicilato. Três diferentes pastas catalisadoras foram formuladas contendo: (1) 60% de MTA, 39% de Resimpol 8 e 1% de dióxido de titânio; (2) 40% de MTA, 39% de Resimpol 8, 20% de hidroxiapatita e 1% de dióxido de titânio e; (3) 40% de MTA, 39% de Resimpol 8, 20% de fosfato dibásico de cálcio diidratado e 1% de dióxido de titânio. MTA Fillapex foi usado como controle. O tempo de trabalho e escoamento foram testados de acordo com a ISO 6876:2001 e o tempo de presa de acordo com a ASTM C266 (n=3 para cada material e teste). Os materiais foram colocados em moldes de PVC (8 mm x 1,6 mm) e armazenados em recipientes contendo 20 ml (testes de solubilidade e absorção de água) ou 10 ml (ensaio de pH e liberação de cálcio) de água deionizada a 37°C (n=10 para cada material e teste). Em 1, 7, 14 e 28 dias as amostras foram removidas dos recipientes e secas para aferição da solubilidade e absorção de água. Após 3 e 24 horas e 4, 7, 14 e 28 dias, a água dos recipientes foi coletada para análises do pH e liberação de cálcio. Os dados foram analisados usando ANOVA um fator e teste de Tukey (5%). MTA Fillapex mostrou menores valores de escoamento e tempos de trabalho e presa em relação ao AH Plus ( $p < 0,05$ ). MTA Fillapex obteve os maiores valores de escoamento e tempos de trabalho e presa em comparação aos materiais experimentais ( $p < 0,05$ ). MTA Fillapex apresentou os menores valores de solubilidade e absorção de água

( $p < 0,05$ ). Todos os cimentos experimentais e o MTA Fillapex apresentaram pH básico e liberação de íons cálcio. MTA Fillapex e AH Plus mostraram valores de acordo com a ISO 6876:2001. Os materiais experimentais apresentaram propriedades físico-químicas satisfatórias.

**Palavras-chave:** Cimento endodôntico, Mineral trióxido agregado, Cimentos à base de resina epóxica, Escoamento, Solubilidade, Absorção de água, pH, Liberação de cálcio.

## ABSTRACT

The aims of this study were (1) to evaluate and to compare physicochemical properties of endodontic sealers, a recent calcium-silicate based sealer (MTA Fillapex, Angelus, Londrina, Brazil) and other an epoxy resin based sealer (AH Plus, Dentsply, Konstanz, Germany); and (2) to develop and to evaluate physicochemical properties of three experimental root canal sealers made by mineral trioxide aggregate (MTA) and a salicylate resin with different calcium phosphates (CaP). The materials were handled following the manufacturer's instructions. The experimental materials were composed of a base and a catalyst pastes mixed in a 1:1. The base paste was made by 60% bismuth oxide and 40% butyl ethylene glycol disalicylate. Three different catalyst pastes were formulated with: (1) 60% MTA, 39% Resimpol 8 and 1% titanium dioxide; (2) 40% MTA, 39% Resimpol 8, 20% hydroxyapatite and 1% titanium dioxide and; (3) 40% MTA, 39% Resimpol 8, 20% dibasic calcium phosphate dihydrate and 1% titanium dioxide. MTA Fillapex was used as control. The working time and flow were tested according to ISO 6876:2001 and the setting time according to ASTM C266 (n=3 for each material and test). The materials were placed into PVC molds (8 mm x 1.6 mm) and stored in containers with 20 mL (solubility and water absorption tests) or 10 mL (calcium release and hydroxyl ions tests) of deionized water at 37°C (n=10 for each material and test). At 1, 7, 14 and 28 days the samples were removed from the solutions and dry for solubility and water absorption tests. After 3 and 24 h and 4, 7, 14, 28 days the soaking water was collected for Ca and pH analysis. The data were analyzed using one-way ANOVA with Tukey's test (5%). MTA Fillapex showed lower values of flow and working and setting times when compared to AH Plus ( $p < .05$ ). MTA Fillapex had the higher values of flow and working and setting times when compared to experimental materials ( $p < .05$ ). MTA Fillapex presented the lowest values of solubility and water absorption ( $p < .05$ ). All experimental cements and MTA Fillapex showed basifying activity and released calcium ions. MTA Fillapex and AH Plus showed values in according to the ISO

6876:2001. The experimental materials showed satisfactory physicochemical properties.

**Key Words:** Endodontic sealers, Mineral trioxide aggregate, Epoxy resin sealers, Flow, Solubility, Water absorption, pH, Calcium release.

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## INTRODUÇÃO

Os materiais utilizados para a substituição e regeneração da estrutura óssea enquadram-se na classe de materiais denominados biomateriais (Guastaldi & Aparecida, 2010). Esses materiais têm contribuído significativamente para o avanço da odontologia moderna e devem apresentar um conjunto de propriedades físicas, químicas e biológicas que permitam desempenhar a função desejada, além de estimular uma resposta adequada dos tecidos vivos através de um reparo histológico (Leonardo *et al.*, 2003; Guastaldi & Aparecida, 2010). Um rápido progresso vem sendo conseguido nessa área, resultando na síntese de novos biomateriais e no conhecimento sobre as interações entre biomateriais e tecidos biológicos. A estrutura dental é um tecido mineralizado onde são realizados diversos procedimentos clínicos com o objetivo de reparar os defeitos de origem congênita ou causados por traumas e doenças, como a cárie (Salgado *et al.*, 2004).

Produtos à base de cálcio têm sido amplamente utilizados por apresentarem propriedades de estímulo, reparação e formação de tecido duro (Stanley & Pameijer, 1997). O agregado de trióxido mineral (MTA) e os cimentos de fosfato de cálcio (CFC) são fontes de cálcio que podem ser utilizadas na composição cimentos endodônticos.

Cimentos à base de MTA são materiais bioativos (Gandolfi *et al.*, 2010a, 2010b, 2010c, 2010d) e biocompatíveis (Torabinejad *et al.*, 2010) que tomam presa em contato com a água, sangue ou outros fluidos, formando hidróxido de cálcio (Fridland & Rosado, 2003; Gandolfi *et al.*, 2009). O hidróxido de cálcio eleva o pH do meio promovendo a ativação da fosfatase alcalina e, conseqüentemente, iniciando o processo de mineralização (Mitchell & Shankwalker, 1958; Tronstad *et al.*, 1981). E mais, em contato com fluidos teciduais esse hidróxido de cálcio se dissocia em íons cálcio e hidroxila (Fridland & Rosado, 2003; Gandolfi *et al.*, 2009). Os íons cálcio, quando em contato com o tecido conjuntivo, determinam uma área de necrose formando o dióxido de carbono. Este, junto com o hidróxido

de cálcio, formam cristais de calcita (carbonato de cálcio) que servem de núcleo de calcificação. A alcalinidade do meio estimula o tecido conjuntivo a secretar uma glicoproteína, chamada fibronectina, que, juntamente com os cristais de calcita, estimulam a formação de colágeno tipo I, o qual, com o cálcio, induz a mineralização (Yaltirik *et al.*, 2004). Entretanto, esses cimentos apresentam algumas limitações clínicas quando utilizados como cimentos endodônticos por apresentarem difícil manipulação (Asgary *et al.*, 2008) e longo tempo de presa (Chng *et al.*, 2005; Bortoluzzi *et al.*, 2006a, 2006b; Islam *et al.*, 2006; Ber *et al.*, 2007; Ding *et al.*, 2008; Gandolfi *et al.*, 2009). A composição dos cimentos à base de MTA pode ser modificada com o intuito de melhorar suas propriedades biológicas e físico-químicas (Ber *et al.*, 2007; Gandolfi *et al.*, 2010; Gandolfi *et al.*, 2011). Alguns estudos mostraram que a adição de outras fontes de cálcio na composição de cimentos à base de MTA pode reduzir o tempo de presa e induzir a formação de apatita (Abdullah *et al.*, 2002; Bortoluzzi *et al.*, 2006a, 2006b; Ber *et al.*, 2007; Bortoluzzi *et al.*, 2009; Gandolfi *et al.*, 2009; Taddei *et al.*, 2009; Gandolfi *et al.*, 2010a, 2010b; Gandolfi *et al.*, 2011).

Os CFC são utilizados na reparação de defeitos ósseos devido as suas excelentes propriedades de biocompatibilidade, bioatividade e osteocondutividade (LeGeros, 1991). Vários estudos mostram o uso desses materiais no tratamento endodôntico (Chohayeb *et al.*, 1987; Sugawara *et al.*, 1990; Sugawara *et al.*, 1995). Existem diversos tipos de CFC que podem ser classificados através da razão molar entre os átomos de cálcio e fósforo (relação Ca/P) (Guastaldi & Aparecida, 2010).

Há certos requisitos desejáveis que um cimento odontológico deve ter para ser utilizado clinicamente: promover selamento hermético, ser insolúvel, possuir facilidade de inserção e remoção, não sofrer contração, ser radiopaco, possuir resistência mecânica adequada, ter pH próximo da neutralidade, possuir ação antimicrobiana, fácil manipulação, ausência de toxicidade, adesão ao dente e não manchar a estrutura dental (Driessens *et al.*, 2002). Isso reduz os tipos de CFC de interesse clínico. A maioria dos fosfatos de cálcio usados *in vivo* pertencem ao

grupo dos ortofosfatos de cálcio por serem cimentos que respeitam a maioria dos requisitos supracitados. Esses materiais contêm o grupo ortofosfato ( $\text{PO}_4$ )<sup>3-</sup> em sua composição química (Bohner, 2000).

A hidroxiapatita (HA) sintética é um tipo CFC muito utilizado na reparação de tecidos ósseos (Campbell, 2003). Esse tipo de cimento foi desenvolvido na década de 80 por meio de misturas de fosfato tetracálcico (TTCP) e fosfato dibásico de cálcio diidratado (DCPD) e anidro (DCPA) (Brown, 1985). É um material que apresenta adesão ao tecido dental e excelentes propriedades de biocompatibilidade e osteocondutividade, permitindo a proliferação de células ósseas, como fibroblastos e osteoblastos (Kawachi *et al.*, 2002; Rey *et al.*, 2007; Best *et al.*, 2008). A HA pode ser adicionada na composição de cimentos endodônticos na tentativa de melhorar as propriedades físico-químicas e biológicas dos materiais (Gandolfi *et al.*, 2009; Collares *et al.*, 2012). A HA sintética tem sido introduzida como componente principal em alguns cimentos endodônticos como Bioseal (Ogna Laboratori Farmaceutici, Muggiò, Itália) e Apatite Root Sealer I, II e III (Dentsply-Sankin, Tóquio, Japão).

O fosfato dibásico de cálcio diidratado (DCPD) é um outro tipo de fosfato de cálcio usado como componente ativo em alguns cimentos endodônticos. É um cimento que apresenta boa osteocondutividade (Bohner, 2000). Alguns estudos relatam resultados satisfatórios no selamento e na resposta celular de cimentos endodônticos contendo DCPD (Kim *et al.*, 2004; Yang *et al.*, 2007; Bae *et al.*, 2010; Bae *et al.*, 2011).

Além da possibilidade de empregar diferentes CFC na composição de cimentos endodônticos à base de MTA, um novo cimento (MTA Fillapex, Angelus, Londrina, Brasil) foi recentemente desenvolvido com um outro componente ativo em sua composição: uma resina de salicilatos. O salicilato é um componente frequentemente utilizado em cremes e géis antiinflamatórios (Vane & Botting, 1998). O MTA Fillapex possui boa viscosidade e bom tempo de trabalho, excelente radiopacidade e solubilidade, além de ser fácil de manipular, segundo o fabricante. Entretanto, há pouca informação científica sobre esse material,

principalmente em relação à função do salicilato na reação química e seus efeitos nas propriedades do cimento.

Diante do exposto, na primeira parte deste estudo (Capítulo 1), foram avaliadas e comparadas algumas propriedades físico-químicas de um novo cimento à base de MTA (MTA Fillapex, Angelus, Brasil) e de um cimento frequentemente utilizado nos tratamentos endodônticos (AH Plus, Dentsply, Konstanz, Alemanha), e na segunda parte (Capítulo 2), desenvolver e avaliar propriedades físico-químicas de três cimentos endodônticos experimentais à base de MTA e de uma resina de salicilato com diferentes fosfatos de cálcio (CaP).

O presente trabalho é apresentado no formato alternativo de dissertação de acordo com as normas estabelecidas pela deliberação 002/06 da Comissão Central de Pós-Graduação da Universidade Estadual de Campinas. O artigo referente ao Capítulo 1 está formatado e foi submetido ao periódico *Journal of Endodontics*. O artigo referente ao Capítulo 2 está formatado e será submetido ao periódico *Dental Materials*.

## **CAPÍTULO 1: Physical properties of MTA Fillapex sealer**

### **Abstract**

**Introduction:** The aim of this study was to evaluate and to compare several physicochemical properties as working and setting times, flow, solubility and water absorption of a recent calcium-silicate based sealer (MTA Fillapex, Angelus, Londrina, Brazil) and an epoxy resin based sealer (AH Plus, Dentsply, Konstanz, Germany).

**Methods:** The materials were handled following the manufacturer's instructions. The working time and flow were tested according to ISO 6876:2001 and the setting time according to ASTM C266. For solubility and water absorption tests the materials were placed into PVC moulds (8 mm x 1.6 mm). The samples (n = 10 for each material and test) were placed in a cylindrical polystyrene-sealed container with 20 mL of deionized water at 37°C. At 1, 7, 14 and 28 days the samples were removed from the solutions and blotted dry for solubility and water absorption tests. The data were analyzed using one-way ANOVA with Tukey's test ( $P < .05$ ).

**Results:** MTA Fillapex showed the lowest values of flow, working and setting times, solubility and water absorption ( $P < .05$ ). The solubility and water absorption increased significantly over time for both materials in 1-28 days period ( $P < .05$ ).

**Conclusions:** MTA Fillapex showed suitable properties to be used as an endodontic sealer.

**Key Words:** Calcium silicate cements, endodontic sealers, epoxy resin sealers, mineral trioxide aggregate, solubility, water absorption

## 1. Introduction

A hermetic 3-dimensional filling must avoid leakage from the oral cavity and/or periapical tissues, thereby reducing periapical inflammation (1). This filling is currently achieved using a combination of endodontic sealer and gutta-percha. Gutta-percha is widely used owing its good physical and biological properties, but the lack of adhesiveness and flow makes necessary the association with endodontic sealers (2).

An ideal endodontic sealer should flow along the entire canal wall surface, fill all voids and gaps between the core root filling material and dentin and should also adhere to both dentin and gutta-percha (3). However, some studies have showed how adhesion of endodontic sealers to gutta-percha can be poor (4) and that all canal fillings may allow bacterial penetration over time (5).

A new calcium-silicate based sealer (MTA Fillapex, Angelus, Londrina, Parana) has been recently proposed as endodontic filling material (6). The strong interest in developing MTA-based endodontic materials is because of the excellent biocompatibility, bioactivity, and osteoconductivity of MTA (7). However, the results related to the biological response of MTA Fillapex are conflicting. When freshly mixed, this material showed high cytotoxicity and genotoxicity (8). Another study showed that when this sealer was implanted in subcutaneous tissues in rats, it remained toxic even after 90 days (9). However a recent study showed that despite these initial toxic effects during setting, the cytotoxicity of MTA Fillapex decreases and the sealer presents suitable bioactivity to stimulate nucleation sites for the formation of apatite crystals in human osteoblast-like cell culture (10).

MTA Fillapex is a sealer that has in the composition MTA, salicylate resin, natural resin, bismuth oxide and silica. A recent study showed that this sealer has suitable physicochemical properties, such as good radiopacity, flow and alkaline pH (11). The manufacturer states that it has great working time, low solubility, and easy handling (6). However, up to now, no scientific studies evaluating these physical properties have been published.

Thus the aim of the present study was to evaluate the working and setting time, flow, solubility and water absorption of MTA Fillapex sealer compared with AH Plus (Dentsply, Konstanz, Germany).

## 2. Materials and Method

### 2.1 Materials

The composition, manufacturers and batch number of AH Plus and MTA Fillapex are shown in Table 1.

**Table 1.** Materials used.

Materials	Composition (MSDS data)	Batch number
AH Plus (Dentsply, Konstanz, Germany)	<b>Paste A:</b> bisphenol-A epoxy resin, bisphenol-F epoxy resin, calcium tungstate, zirconium oxide, aerosol, iron oxide.	1110002296
	<b>Paste B:</b> dibenzyl diamine, adamantane amine, tricyclodecane-diamine, calcium tungstate, zirconium oxide, aerosol, silicon oil.	1110001964
MTA Fillapex (Angelus, Londrina, Brazil)	After the mixture: salicylate resin, natural resin, diluting resin, bismuth oxide, nanoparticulated silica, MTA and pigments.	19595

### 2.2 Flow evaluation

The flow test was performed following the International Organization for Standardization (ISO) 6876:2001 (12). Three determinations were made for each

sealer tested (n = 3). The mean values and standard deviation were calculated and recorded (mm) to obtain the flow rates.

### **2.3 Working time test**

The working time was performed following the same procedure used in flow test (ISO 6876:2001) (12), with the difference of the increase in the intervals between the initial mixing and the setting time. Measurements were made at 10-min intervals and freshly mixed material was used on each time. Three samples for each experimental sealer were made and the mean was taken as sample working time.

### **2.4 Setting time test**

The setting time test was performed according to the C266-03 specification of American Society for Testing and Materials (ASTM) (13). The initial and final setting times of each specimen (n = 3) was tested every hour until the both times were reached.

### **2.5 Solubility**

The solubility test was carried out as described by Gandolfi et al. (14, 15). Briefly, the samples (n = 10) were weighed (Initial weight) and immersed in 20 mL of deionized water at 37°C. At 1, 7, 14 and 28 days the samples were removed from the solutions, rinsed with deionized water, blotted dry and placed in an incubator at 37°C for 48 h and then re-weighed until a constant weight (dry weight). The solubility (percentage weight variation) was calculated according to the following equation:

$$\text{Solubility} = [(Dry\ weight\ at\ each\ time\ point - Initial\ weight) / Initial\ weight] \times 100$$

Any specimen that showed evidence of disintegration was discarded and the test repeated.

## 2.6 Water absorption

The water uptake was determined gravimetrically. The procedure was the same used in solubility test. The samples (n = 10) were weighed (Initial weight) and immersed in 20 mL of deionized water at 37°C. At 1, 7, 14 and 28 days the samples were removed and weighed. Each weight measurement was repeated three times and the mean recorded as Wet weight. Then the samples were blotted dry at 37°C for 48 h until a weight stabilization (Dry weight).

The water absorption at each time point was calculated as follows:

$$\text{Water absorption} = [(Wet\ weight\ at\ each\ time\ point - Dry\ weight) / Dry\ weight] \times 100$$

## 2.7 Statistical analysis

For each test the data were statistically analyzed by one-way ANOVA and Tukey test. The significance level used was  $P < .05$  considered.

## 3. Results

### 3.1 Flow, working and setting times

The mean and standard deviation of flow, working time and setting time are showed in Table 2. A considerable significant difference was found between the materials for all tests ( $P < .05$ ). AH Plus showed the higher values of flow ( $37.97 \pm 0.55$  mm), working time (5.5 h), initial ( $10.18 \pm 0.1$  h) and final ( $18.11 \pm 0.25$  h) setting times when compared to MTA Fillapex (flow =  $29.04 \pm 0.39$  mm; working time = 0.5 h; initial setting time =  $2.27 \pm 0.06$  h; final setting time =  $4.55 \pm 0.05$  h).

### 3.2 Solubility

The solubility of AH Plus (1 day =  $-0.33 \pm 0.03$ ; 7 days =  $-0.36 \pm 0.02$ ; 14 days =  $-0.78 \pm 0.05$ ; 28 days =  $-0.84 \pm 0.03$ ) was significantly higher than MTA Fillapex (1 day =  $-0.09 \pm 0.06$ ; 7 days =  $-0.15 \pm 0.07$ ; 14 days =  $-0.22 \pm 0.08$ ; 28

days =  $-0.25 \pm 0.08$ ) for all tested time points ( $P < .05$ ). The results can be observed in Table 3. Both materials showed the highest values of solubility at 28 days ( $P < .05$ ).

**Table 2.** Flow, working time, initial and final setting times (mean  $\pm$  standard deviation, n = 3 for each material). Data followed by different letters are statistically different ( $P < .05$ ).

Material	Flow (mm)	Working time (h)	Initial setting time (h)	Final setting time (h)
AH Plus	$37.97 \pm 0.55^a$	$5.5^a$	$10.18 \pm 0.10^a$	$18.11 \pm 0.25^a$
MTA Fillapex	$29.04 \pm 0.39^b$	$0.5^b$	$2.27 \pm 0.06^b$	$4.55 \pm 0.05^b$

### 3.3 Water absorption

AH Plus (1 day =  $0.10 \pm 0.01$ ; 7 days =  $0.12 \pm 0.02$ ; 14 days =  $0.19 \pm 0.02$ ; 28 days =  $0.25 \pm 0.01$ ) absorbed significantly more water than MTA Fillapex (1 day =  $0.05 \pm 0.05$ ; 7 days =  $0.08 \pm 0.07$ ; 14 days =  $0.15 \pm 0.08$ ; 28 days =  $0.20 \pm 0.20$ ) for all tested time points ( $P < .05$ ). The results can be observed in Table 3. The highest values of water absorption were found at 28 days for the two materials and the lowest values at 1 day ( $P < .05$ ).

**Table 3.** Solubility and water absorption (mean  $\pm$  standard deviation, n = 10 for each material) expressed as percentage weight variation (%) Data followed by different small letters in column and capital letters in row are statistically different ( $P < .05$ ).

Material	1 day	7 days	14 days	28 days
<b>Solubility</b>				
AH Plus	$-0.33 \pm 0.03^{aD}$	$-0.36 \pm 0.02^{aC}$	$-0.78 \pm 0.05^{aB}$	$-0.84 \pm 0.03^{aA}$
MTA Fillapex	$-0.09 \pm 0.06^{bD}$	$-0.15 \pm 0.07^{bC}$	$-0.22 \pm 0.08^{bB}$	$-0.25 \pm 0.08^{bA}$
<b>Water Absorption</b>				
AH Plus	$0.10 \pm 0.01^{aD}$	$0.12 \pm 0.02^{aC}$	$0.19 \pm 0.02^{aB}$	$0.25 \pm 0.01^{aA}$
MTA Fillapex	$0.05 \pm 0.05^{bD}$	$0.08 \pm 0.07^{bC}$	$0.15 \pm 0.08^{bB}$	$0.20 \pm 0.20^{bA}$

#### 4. Discussion

In relationship with the good properties of calcium silicate MTA cements, MTA-based endodontic sealers for root canal obturation have been developed recently (16) and different MTA-based sealers are marketed (iRoot, Innovative BioCreamix Inc, Vancouver, Canada; Tech Biosealer endo, Isasan, Italy). The present study investigated the physical properties of MTA Fillapex as the latest calcium-silicate MTA-based proposed as endodontic sealer. The working and setting time, flow, solubility and water absorption have been assessed and compared with those of AH Plus.

The working time is the period of time measured between the start of mixing until not be more possible to handle the sealer without promote adverse effects on its properties (12). This time is directly linked with setting time. Both times are dependent on the constituent components, their particle size, the ambient

temperature and relative humidity (15, 17). The setting reactions are complex and even though the sealer surface becomes hard, the inner mass may remain soft for an extended period (18).

Since the extended setting time is an advantageous to root canal sealers, different studies showed the possibility to modify the composition of MTA-based materials in order to delay the setting time (16, 19–21). In this study, the C266-03 was used because this specification provides initial setting time as well as final setting time evaluation; in other hand the ISO 6876:2001 only provides the final setting time evaluation. MTA Fillapex showed initial and final setting times of 2.27 and 4.55 hours, respectively. Both values are shorter than that of AH Plus; however, they are suitable for an endodontic sealer. The initial setting time of AH Plus obtained in this study was in agreement with previous studies (22–24) reporting an initial setting time of 10 hours and a final setting time of 18 hours. AH Plus is a two-component paste material and occurs a slow polymerization reaction of epoxy resin amines with high molecular weight as Bisphenol A and Bisphenol F. Then, the conversion of monomers into polymers occurs gradually (22, 25) and this might explained the long times of this material. Differently, MTA Fillapex is a dual paste (base and catalyst) and it is supposed that in contact promotes two chemical reactions which are responsible to material set: the progressive hydration of the orthosilicate ions ( $\text{SiO}_4^{4-}$ ) and the reaction between MTA and salicylate resin. The MTA reacts with salicylate creating an ionic polymer (26). When calcium silicate particles of MTA react with water, a nanoporous amorphous calcium silicate hydrate gel forms on the cement particles (27). The gel polymerizes and hardens forming a solid network. The differences of setting times between MTA Fillapex and AH Plus could be also related to the resin/filler ratios, as a higher resin/filler ratio leads longer results of working and setting times.

The flowability of an endodontic sealer is a very important property as in relation with its ability to penetrate into the irregularities and accessory canals of the root canal system. Conversely, if the flow is excessive, the risk of material extravasation to the periapex is increased, which could damage periodontal

tissues (2). The ability to penetrate into the root canal system depends on particle size, temperature, setting time, rate of shear, rate of insertion, as well on the internal diameter of the canals (18).

The flow of a material can be evaluated using several methods: viscosity, penetrability, degree of flattening and extrusion. The method used in this study, in accordance with the ISO 6876:2001, was the degree of flattening or extensibility, defined as being the mean area obtained when the materials is subjected to a constant load for a certain time. The present study showed higher values of flowability for AH Plus (37.97 mm) than MTA Fillapex (29.04 mm), and both were in agreement with ISO 6876:2001 requirements ( $> 20$  mm) (12). The reported values for AH Plus were higher than the values reported by both Silva et al. (11) and Versani et al. (23), but lower than values reported by Almeida et al. (2) and Duarte et al (28). This could be explained by variations in the physicochemical properties of AH Plus depending on the portion of the tube where the sealer was taken, in relationship with the findings of Baldi et al. (29) that demonstrated higher flow values when the sealer was collected from the beginning of the tubes in which they were supplied. The flow value of MTA Fillapex was similar to the value obtained by Silva et al (11). This is one of the pioneer studies using MTA Fillapex, so it was difficult to compare the results obtained with previous studies. Moreover, the manufacturer of MTA Fillapex does not provide any information about the composition ratio. A high resin/MTA ratio could leads a form a material with high flow.

The dissolution of a sealer may cause the release of materials that could irritate the periapical tissues (30) and also induce the formation of gaps between root canals and filling materials with the result of the increase in bacterial leakage over time (30). Despite ISO 6786:2001 suggests to evaluate the solubility only at 24 hours, in the present study the solubility test was performed at 1, 7, 14 and 28 days, following a modification previously proposed by Gandolfi et al (14, 15). The findings showed that the solubility of MTA Fillapex was statistically lower than that of AH Plus ( $P < .05$ ), despite the solubility of both sealers was within the ISO

6876:2001 recommended range (less than 3%) at all time points. Such results are in accordance with previous studies that demonstrated a low weight loss in the solubility test for both AH Plus (at different times) and MTA Fillapex (at 24 hours) (30–32). This is the first time that long term solubility test was done on MTA Fillapex. It is important to point out that the standard test methods for solubility recommend immersion of the materials on water only after complete setting (or at least 70% of the initial setting). However, this situation is impossible to be achieved clinically, where the materials are immediately placed into contact with fluids and blood. Therefore, the solubility values in a clinical scenario are probably higher than the ones found *in vitro* tests (33).

Water diffusion into cements may result in deterioration of their physical/mechanical properties, decreasing the life expectancy of the interfaces by hydrolysis and micro-crack formation (34). However, water absorption could be benefic as it promotes an expansion of the material, which may promote a proper sealing. In the current study, AH Plus showed higher water sorption values than MTA Fillapex in all time points ( $P < .05$ ). In general, water absorption properties of the resinous materials are affected by many factors as the chemical composition and the presence of hydrophilic constituents in the resin matrix (14), as well structural parameters of the polymeric network such as crosslinking density and porosity (35). Maybe, a more porous polymeric network and with distant polymeric chains may explain the higher water absorption results for AH Plus.

MTA Fillapex has a shorter but clinically acceptable working time associated to a shorter setting time. MTA Fillapex had a lower flow than AH Plus. MTA Fillapex also showed a lower solubility and water absorption than AH Plus. Solubility and water absorption decreased in rate over 28 days. Both materials showed values in according to the ISO 6876:2001. In conclusion, the results of this study showed that the MTA-based endodontic sealer MTA Fillapex showed suitable physical properties to be used in endodontic therapy.

## **Acknowledgements**

The authors thank the Master in Endodontology of the University of Bologna for providing funds for the research and CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brazil) for financial support. The authors disclose any conflict of interest.

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## **CAPÍTULO 2: Chemical-physical properties of experimental root canal sealers based on butyl ethylene glycol disalicylate and MTA**

### **ABSTRACT**

*Objectives.* The aim of this study was to evaluate the calcium release, pH, flow, solubility, water absorption, setting and working time of three experimental root canal sealers made by mineral trioxide aggregate (MTA) and different calcium phosphates (CaP).

*Methods.* The materials were composed of a base and a catalyst pastes mixed in a 1:1. The base paste was made by 60% bismuth oxide and 40% butyl ethylene glycol disalicylate. Three different catalyst pastes were formulated containing 60% MTA or 40% MTA + 20% CaP (hydroxyapatite HA or dibasic calcium phosphate dehydrate DCPD), 39% Resimpol 8 and 1% titanium dioxide. MTA Fillapex was used as control. The release of calcium and hydroxyl ions, solubility and water absorption were measured during the time up to 28 days. The working time and flow were tested according to ISO 6876:2001 and the setting time according to ASTM C266. The data were analyzed using one-way ANOVA with Tukey's test ( $p < .01$ ).

*Results.* All cements showed basifying activity and released calcium ions. MTA Fillapex showed the highest values of flow ( $p < .01$ ) and working/setting times ( $p < .01$ ) and the smallest values of solubility ( $p < .01$ ) and water absorption ( $p < .01$ ).

*Significance.* All experimental materials showed satisfactory physicochemical properties to be used as endodontic sealers in clinical practice.

**Key Words:** calcium-silicate cement, mineral trioxide aggregate (MTA), endodontic sealer, calcium release, pH

## 1. INTRODUCTION

One of the aims of root canal treatment is to fill the root canal system with an impervious, biocompatible and dimensionally stable sealer [1]. The material is placed on the vital tissues and the tissue response may influence the outcome of treatment [2]. Some materials have been used as root canal sealers as zinc oxide-eugenol, calcium hydroxide, calcium phosphate and calcium silicate cements [3,4]. New root canal sealers are constantly being developed in attempts to improve the physical, chemical and biological properties.

Calcium-silicate cements, such as mineral trioxide aggregate (MTA) cements, demonstrated a wide range of dental clinical applications as root-end filling materials [5], root perforation repair, pulp capping, root canal sealers [6] and dentine hypersensitivity [7,8]. MTA cements consist of a powder with fine hydrophilic calcium silicates particles and are able to set in contact with water, blood or other fluids and release calcium [9,10]. MTA-based cements are bioactive [11-14] and biocompatible [15] materials. It has been shown to induce the differentiation of osteoblasts [5,13], to improve proliferation of periodontal fibroblasts [16] and to stimulate mineralization of dental pulp cells [17].

A root canal sealer must be able to set when is placed in contact with oral fluids and wet tissues to avoid the fast dissolution and removal (wash-out) from the surgical site due fluid contamination [18-23]. Conventional MTA cements showed some clinical limitation when used as endodontic materials due to their poor handling [24] and extended setting time [9,18-23,25]. The composition of MTA-based cements can be properly modified to improve physicochemical properties as well as handling characteristics, to reduce the setting time [9,18-20,26,27] and the solubility by including a resin [28] or to increase the apatite-forming ability [11,13,29,30]. It has been recently demonstrated that MTA cements doped with alpha-tricalcium phosphate support the survival and differentiation of human orofacial bone mesenchymal stem cells [31] and that calcium phosphate have a stimulatory effect on cementoblasts [32].

Root canal sealers based on MTA have been studied [7,14] and new endodontic sealers are now marketed as Tech Biosealer endo (Isasan, Italy) and MTA Fillapex (Angelus, Londrina, Brazil). MTA Fillapex is trade secret, but it is known that the basic composition contains synthetic Portland cement clinkers and a salicylate resin. Other endodontic sealers contain salicylate resin as Sealapex (Sybronendo, Glendora, USA). The salicylate is a chemical compound frequently used in the composition of anti-inflammatory creams and oils [33]. Several derivatives of salicylates resins with differences in molecular structure and size of carbon chain can be used to obtain resins/polymers with different physical characteristics as rheological characteristics and handling properties [34].

MTA Fillapex has been recently developed (2010) in attempt to combine the biological and sealing properties [35,36] of MTA cements with the physicochemical properties required by a root sealer [37]. MTA Fillapex showed to be a biocompatible material [38]. The manufacturer claims that MTA Fillapex has great working time and flow, excellent radiopacity and solubility and is easy handled. However, there is a lack of scientific information/studies, mainly about the effects of salicylate resin on the physicochemical properties.

Calcium phosphates (CPC) are materials that can promote the dissolution and precipitation of calcium and phosphate ions [39]. Some studies have demonstrated that CPC is useful in the composition of sealers used in root canal treatment [40-42]. There are several types of calcium phosphates which can be classified by the molar ratio between the calcium and phosphorus atoms (Ca/P). Most of them used in vivo are calcium orthophosphate [43].

Hydroxyapatite (HA) is a type of calcium orthophosphate and the main mineral component of bone [41] and it has a similarity structural and chemical with the mineral phase present in the teeth [44]. HA is the most biocompatible and stable in aqueous solution [43] and nowadays, the main biomaterial used in the bone tissue repair due to its biological properties. It shows apparent adhesion to dental tissue and excellent biocompatibility and osteoconductivity properties [45]. HA may be added in the composition of root canal sealers to improve the

biological properties of the materials [9,46]. Synthetic HA has been introduced as main component in root canal sealers as Bioseal (Ogna Laboratori Farmaceutici, Muggiò, Italy) and Apatite Root Sealer I, II and III (Dentsply-Sankin, Tokyo, Japan).

Dibasic calcium phosphate dihydrate (DCPD) is an other type of calcium orthophosphate used as active component in root canal sealer. It has a high solubility and reach the stability by the conversion in other calcium phosphate as HA [43,47,48]. DCPD possess good osteoconductivity [43]. Some recent studies reported satisfactory results of sealing ability and cell response to root canal sealers containing DCPD [49-52].

The aim of this study was to develop and to investigate the physicochemical properties of experimental MTA-based root canal sealers containing butyl ethylene glycol disalicylate with or without addition of a calcium phosphate component (HA or DCPD).

## **2. MATERIALS AND METHODS**

### **2.1. Synthesis and characterization of butyl ethylene glycol disalicylate**

The 1,3-butyl ethylene glycol disalicylate was synthesized by the transesterification reaction of methyl salicylate (Synth Laboratory, São Paulo, Brazil) in two different alcohols in a molar ratio of 1:3. The isopropoxide titanium (Sigma-Aldrich, St. Louis, USA) was used as catalyst. The reaction was maintained at 200°C for about 2 h. After the product was purified by vacuum distillation to remove the excess of methyl salicylate. Then the butyl ethylene glycol disalicylate was characterized by Nuclear Magnetic Resonance Spectroscopy (NMR) and by Fourier Transform Infrared Spectroscopy (FTIR) and showed the peak narrow of the hydroxyls in the spectral range from 3300  $\text{cm}^{-1}$ .

### **2.2. Calcium phosphate-based cements formulation**

Three experimental (e) root canal sealers (MTAe, MTAe-HA, MTAe-DCPD) were prepared by mixing a base paste and a catalyst paste. The composition is

shown in Table 1. The catalyst paste contained MTA with or without addition of calcium phosphate, Resimpol 8 resin and titanium dioxide. Three different catalyst pastes were formulated by changing the amount of MTA (60% or 40% in weight) and the type of calcium phosphate (HA or DCPD 20% in weight). The base paste contained the synthesized component 1,3 butyl ethylene glycol disalicylate and the bismuth oxide. MTA Fillapex (Angelus, Londrina, Brazil) was used as control.

### **2.3. Flow evaluation**

The flow and working time tests have been performed following the International Organization for Standardization (ISO) 6876:2001 [53]. After the material handled 0.05 mL of the sealer was dropped on the center of one glass plate (40 x 40 mm and 5 mm in thick). At 180 s after initiating the mixing the second glass plate with same dimensions and weighing 20 g was placed centrally on top of the material followed by a 100 g weight to make a total mass of 120 g. Seven minutes later the weight was removed and the maximum and minimum diameters of compressed disc were measured using a digital paquimeter. Three determinations were made for each sealer tested (n = 3). The test was repeated when the two diameters were different from each other more than 1 mm. The mean values and standard deviation (expressed in mm) were calculated and recorded (mm) to obtain the flow rates.

### **2.4. Setting time test**

Setting time test was performed following the specification n° C266-03 of American Society for Testing and Materials (ASTM) [54]. The different sealers (n = 3) were compacted to excess into PVC moulds (10 mm in diameter and 2 mm thick) placed on flat glass plate (1 mm thick). After 120±10 s from the end of mixing, the sample was placed in incubator at 37°C and 95% relative humidity.

Table 1. Materials used.

Materials	Composition	Manufacturers and batch numbers
MTAe	<b>Base paste:</b>	
	Bismuth oxide (60%)	Vetec, Duque de Caxias, Brazil, 010127-TB
	Butyl ethylene glycol disalicylate (40%)	Prepared at Federal University of Pelotas, Brazil
	<b>Catalyst paste:</b>	
	MTA (60%)	Angelus, Londrina, Brazil, batch number 090605
Resimpol 8 (39%)	Bandeirante Brazmo, São Paulo, Brazil, 81319	
Titanium dioxide (1%)	Vetec, Duque de Caxias, Brazil, 06092005	
MTAe-HA	<b>Base paste:</b>	
	Bismuth oxide (60%)	Vetec, Duque de Caxias, Brazil, 010127-TB
	Butyl ethylene glycol disalicylate (40%)	Prepared at Federal University of Pelotas, Brazil
	<b>Catalyst paste:</b>	
	MTA (40%)	Angelus, Londrina, Brazil, 090605
	Resimpol 8 (39%)	Bandeirante Brazmo, São Paulo, Brazil, 81319
Hydroxyapatite (20%)	Sigma-Aldrich, St. Louis, USA, MKBC4763V	
Titanium dioxide (1%)	Vetec, Duque de Caxias, Brazil, 06092005	
MTAe-DCPD	<b>Base paste:</b>	
	bismuth oxide (60%)	Vetec, Duque de Caxias, Brazil, 010127-TB
	Butyl ethylene glycol disalicylate (40%)	Prepared at Federal University of Pelotas, Brazil
	<b>Catalyst paste:</b>	
	MTA (40%)	Angelus, Londrina, Brazil, 090605
	Resimpol 8 (39%)	Bandeirante Brazmo, São Paulo, Brazil, 81319
Dibasic calcium phosphate dihydrate (20%)	Sigma-Aldrich, St. Louis, USA, 1305078	
Titanium dioxide (1%)	Vetec, Duque de Caxias, Brazil, 06092005	
MTA Fillapex	(MSDS data) salicylate resin, natural resin, diluting resin, bismuth oxide, nanoparticulated silica, MTA and pigments	Angelus, Londrina, Brazil, 19595

At  $150 \pm 10$  s after initiating the mixing the Gilmore needle weighing  $100 \pm 0.5$  g with 2.1 mm diameter was placed carefully on the material surface. This operation was repeated until the indentations could not be observed on the sealer

surface. The elapsed time between the end of mixing and the failure of the indentation was recorded as initial setting time. Then, the Gilmore needle weighing  $456 \pm 0.5$  g with 1 mm diameter was used as previously described and the time recorded as final setting time. The initial and final setting times of each specimen ( $n = 3$ ) were recorded.

## 2.5. Working time test

Working test was performed following the same procedure used in flow test (ISO 6876:2001) [53], with the difference of the increase in the intervals between the initial mixing and the setting time. Freshly mixed material was used on each time. The working time was determined when the specimen diameter was 10% less than flow value. Three samples for each experimental sealer were made and the mean was taken as sample working time.

## 2.6. Solubility

The solubility test was carried out as described by Gandolfi *et al.* [8]. All the materials were handled, placed into PVC moulds with 8 mm of internal diameter and 1.6 mm of height and then weighed using an analytical balance with 0.001 g accuracy (Bel Engineering series M, Monza, Italy). Each weight measurement was repeated three times and the mean recorded as initial weight. PVC matrices were made to serve as support for each sample and to avoid that any surface of the specimen came into contact with the container. So, the entire surface of the sample was in contact with the water. Each sample ( $n = 10$ ) was placed in a cylindrical polystyrene-sealed container with 20 mL of deionized water at 37°C. At 1, 7, 14 and 28 days the samples were removed from the solutions, dry at 37°C for 48 h to constant weight (dry weight) and discarded.

The solubility (percentage weight variation) at each  $t$  time was calculated according to the following equation:

$$\text{Solubility} = [(Dry\ weight\ at\ time\ t - Initial\ weight) / Initial\ weight] \times 100$$

Any specimen that showed evidence of disintegration was discarded and the test repeated [53].

## **2.7. Water absorption**

The water uptake was determined as described by Gandolfi *et al.* [8]. The procedure was the same used in solubility test. The samples were handled and placed into PVC moulds. Each sample ( $n = 10$ ) was placed in a cylindrical polystyrene-sealed container with 20 mL of deionized water at 37°C. There was not contact between the sample and container. At 1, 7, 14 and 28 days the specimens were carefully removed from container, wiped free from any visible surface moisture (blotted dry on filter paper for 3 s to remove the surface water) and weighed. Each weight measurement was repeated three times and the mean recorded as wet weight. Then the samples were dry at 37°C for 48 h until a weight stabilization (dry weight).

The water absorption at each time  $t$  was calculated as follows:

$$\text{Water absorption} = [(Wet\ weight\ at\ time\ t - Dry\ weight) / Dry\ weight] \times 100]$$

Any specimen that showed evidence of disintegration was discarded and the test repeated [53].

## **2.8. pH measurement and calcium ion release evaluation**

All sealers ( $n = 10$ ) were compacted to excess into PVC moulds (8 mm in internal diameter and 1.6 mm thick) and immersed in 10 mL of deionized water in cylindrical polystyrene-sealed container stored at 37°C. After 3 and 24 h and 4, 7, 14, 28 days the soaking water was collected for Ca and pH analysis and renewed. Calcium ions (ppm) and hydroxyl ions (pH) were analyzed in deionized water with a magnetic stirrer using a multi-parameter laboratory meter (inoLab 750WTW, Weilheim, Germany) calibrated with standard solutions and connected to a calcium probe (Calcium ion electrode, Eutech instruments PteLtd, Singapore) or a (selective) temperature-compensated pH probe/electrode (Sen Tix Sur WTW, Weilheim, Germany).

Since the pH changes with temperature, for the pH measurement the probe was inserted into the soaking media and the value recorded at 33°C for all samples. For calcium quantization, 0.200 mL (2%) of 4 mol L<sup>-1</sup> KCl (ISA WTW, Weilheim, Germany) was added to 10 mL of deionized water. The probe was inserted into the soaking media at room temperature and the values were recorded when the data had stabilized to the second decimal.

## **2.9. Statistical analysis**

For each test the data were tabulated statistically and descriptively using graphs and percentage frequencies tables and analyzed using Kolmogorov-Smirnov (K-S test) as nonparametric test and one-way ANOVA with Tukey's test ( $p < .05$ ).

## **3. RESULTS**

### **3.1. Flow, working and setting times**

The mean and standard deviation of flow, working time and setting time are presented in Table 2. A considerable significant difference was found among the sealers for all tests ( $p < .01$ ). MTA Fillapex showed the higher values of flow and working/setting times. MTAe and MTAe-HA had the smallest working time. The smallest final setting time was showed for MTAe. MTAe-HA and MTAe-DCPD presented the lower flow values. There was no significant differences for initial and final setting time between MTAe-HA and MTAe-DCPD ( $p > .05$ ).

Table 2. Flow, working time, initial and final setting times (mean and standard deviation, n = 3 for each material). Data with different superscript letters are statistically different (p<.01).

Material	Flow (mm)	Working time (min)	Initial setting time (min)	Final setting time (min)
<b>MTAe</b>	16.99 (0.18) <sup>b</sup>	3.5 <sup>c</sup>	12.7 (0.58) <sup>b</sup>	56.7 (1.15) <sup>c</sup>
<b>MTAe-HA</b>	13 (0.52) <sup>c</sup>	4 <sup>c</sup>	15.3 (0.58) <sup>b</sup>	66 (1.0) <sup>b</sup>
<b>MTAe-DCPD</b>	13.31 (0.07) <sup>c</sup>	5 <sup>b</sup>	16.3 (0.58) <sup>b</sup>	69.7 (1.15) <sup>b</sup>
<b>MTA Fillapex</b>	29.04 (0.39) <sup>a</sup>	30 <sup>a</sup>	136.3 (4.04) <sup>a</sup>	273.3 (3.21) <sup>a</sup>

### 3.2. Solubility

The solubility of MTA Fillapex was significantly lower than experimental sealers (Table 3) for all times (p<.01). MTAe-HA and MTAe-DCPD showed the higher values of solubility at 1 days and only MTAe-DCPD at 7 days (p<.01), but these materials were not different of MTAe at 14 and 28 days (p>.05).

Table 3. Solubility (mean and standard deviation, n = 10 for each material) expressed as percentage weight variation (%). Data with different superscript small letters in column and superscript capital letters in row are statistically different (p<.01).

Material	1 day	7 days	14 days	28 days
<b>MTAe</b>	-13.82 (1.48) <sup>b, D</sup>	-19.72 (1.28) <sup>c, C</sup>	-29.89 (2.54) <sup>a, B</sup>	-34.24 (2.52) <sup>a, A</sup>
<b>MTAe-HA</b>	-18.31 (1.23) <sup>a, C</sup>	-23.78 (0.59) <sup>b, B</sup>	-32.44 (2.95) <sup>a, A</sup>	-33.26 (1.30) <sup>a, A</sup>
<b>MTAe-DCPD</b>	-19.07 (1.58) <sup>a, C</sup>	-25.53 (1.30) <sup>a, B</sup>	-31.93 (2.47) <sup>a, A</sup>	-34.21 (1.93) <sup>a, A</sup>
<b>MTA Fillapex</b>	-9.31 (0.62) <sup>c, D</sup>	-15.16 (0.79) <sup>d, C</sup>	-22.40 (0.80) <sup>b, B</sup>	-25.55 (0.85) <sup>b, A</sup>

### 3.3. Water absorption

Table 4 shows that MTAe-HA absorbed significantly more water than other materials tested to 7-28 days period ( $p < .01$ ). At 7 days MTAe-DCPD did not differ stastically of MTAe-HA ( $p > .05$ ) and at the same time showed the higher values of water absorption at 1 day ( $p < .01$ ). MTA Fillapex showed the lower values of absorbed water for all times ( $p < .01$ ).

Table 4. Water absorption (mean and standard deviation,  $n = 10$  for each material) expressed as percentage weight variation (%). Data followed by different superscript small letters in column and superscript capital letters in row are statistically different ( $p < .01$ ).

Material	1 day	7 days	14 days	28 days
<b>MTAe</b>	10.30 (1.67) <sup>c, C</sup>	14.93 (1.54) <sup>b, B</sup>	30.24 (4.49) <sup>b, A</sup>	32.99 (3.95) <sup>b, A</sup>
<b>MTAe-HA</b>	14.95 (1.53) <sup>b, C</sup>	20.02 (0.99) <sup>a, B</sup>	35.54 (4.98) <sup>a, A</sup>	36.59 (1.99) <sup>a, A</sup>
<b>MTAe-DCPD</b>	17.01 (1.93) <sup>a, C</sup>	21.42 (1.79) <sup>a, B</sup>	30.03 (3.79) <sup>b, A</sup>	31.90 (3.20) <sup>b, A</sup>
<b>MTA Fillapex</b>	5.22 (0.51) <sup>d, D</sup>	8.93 (0.78) <sup>c, C</sup>	15.88 (0.88) <sup>c, B</sup>	20.57 (2.02) <sup>c, A</sup>

### 3.4. pH

Significant differences were found among the sealers ( $p < .01$ ). Table 5 showed that all materials were able to alkalinize the soaking water initially to approximately pH 9.2-10 (3 h-4 days) and subsequently to pH 8-9 (7-28 days). The pH of the water conditioned by MTAe was significantly higher than other materials up to 1 day as well as the MTA Fillapex showed to 7-28 days period. At 4 days MTAe-DCPD showed the lower value of pH ( $p > .05$ ) and did not differ stastically of MTA Fillapex ( $p < .01$ ). One day presented the highest pH valeus for all materials.

Table 5. pH of soaking water (mean and standard deviation, n = 10 for each material) expressed as percentage weight variation (%). Data followed by different superscript small letters in column and superscript capital letters in row are statistically different (p<.01).

Material	3h	1 day	4 days	7 days	14 days	28 days
<b>MTAe</b>	9.76 (0.06) <sup>a, B</sup>	10.24 (0.12) <sup>a, A</sup>	9.50 (0.18) <sup>a, C</sup>	8.79 (0.11) <sup>b, D</sup>	8.29 (0.23) <sup>b, E</sup>	8.10 (0.05) <sup>b, F</sup>
<b>MTAe-HA</b>	9.36 (0.13) <sup>c, A</sup>	9.28 (0.18) <sup>c, A</sup>	9.42 (0.19) <sup>a, A</sup>	8.68 (0.29) <sup>b, B</sup>	8.43 (0.14) <sup>b, B</sup>	8.11 (0.12) <sup>b, C</sup>
<b>MTAe-DCPD</b>	9.58 (0.05) <sup>b, A</sup>	9.46 (0.12) <sup>b, A</sup>	9.20 (0.17) <sup>b, B</sup>	8.63 (0.14) <sup>b, C</sup>	8.75 (0.11) <sup>a, C</sup>	7.94 (0.10) <sup>c, D</sup>
<b>MTA Fillapex</b>	9.19 (0.07) <sup>d, C</sup>	9.47 (0.07) <sup>b, A</sup>	9.34 (0.08) <sup>ab, B</sup>	9.14 (0.08) <sup>a, C</sup>	8.90 (0.13) <sup>a, D</sup>	8.67 (0.09) <sup>a, E</sup>
<b>deion. Water</b>	7.08 (0.03) <sup>e, B</sup>	7.16 (0.09) <sup>d, A</sup>	6.93 (0.05) <sup>c, D</sup>	7.01 (0.04) <sup>c, C</sup>	7.13 (0.03) <sup>c, A</sup>	7.07 (0.14) <sup>d, B</sup>

### 3.5. Calcium ion release

MTAe presented significantly greater release of Ca<sup>+2</sup> (p<.01) than other materials tested. Table 6 describes the amount of Ca<sup>+2</sup> released at the different experimental times. The amount of leached Ca<sup>+2</sup> increased with the time for all the materials, except for MTAe-DCPD at 28 days where the value of released Ca<sup>+2</sup> was significantly less than 14 days.

Table 6. Calcium (ppm) leaked in the soaking water (mean and standard deviation, n = 10 for each material) expressed as percentage weight variation (%). Data with different superscript small letters in column and superscript capital letters in row are statistically different (p<.01).

Material	3h	1 day	4 days	7 days	14 days	28 days
<b>MTAe</b>	6.70 (1.63) <sup>a, F</sup>	11.24 (1.74) <sup>a, E</sup>	13.31 (1.41) <sup>a, D</sup>	21.74 (0.47) <sup>a, C</sup>	25.55 (1.12) <sup>a, B</sup>	30.61 (1.39) <sup>a, A</sup>
<b>MTAe-HA</b>	6.31 (1.48) <sup>a, C</sup>	6.12 (1.81) <sup>c, C</sup>	7.12 (1.66) <sup>c, C</sup>	12.42 (2.13) <sup>b, B</sup>	13.68 (1.75) <sup>b, B</sup>	21.32 (2.29) <sup>b, A</sup>
<b>MTAe-DCPD</b>	7.13 (1.64) <sup>a, C</sup>	7.67 (1.86) <sup>bc, C</sup>	8.48 (2.04) <sup>bc, C</sup>	22.60 (1.85) <sup>a, A</sup>	23.98 (1.90) <sup>a, A</sup>	13.45 (1.27) <sup>c, B</sup>
<b>Fillapex</b>	7.97 (1.72) <sup>a, B</sup>	8.88 (0.69) <sup>b, AB</sup>	9.57 (0.56) <sup>b, A</sup>	9.36 (0.36) <sup>c, AB</sup>	9.86 (1.30) <sup>c, A</sup>	10.08 (1.38) <sup>d, A</sup>
<b>deion. Water</b>	0.26 (0.07) <sup>b, A</sup>	0.25 (0.04) <sup>d, A</sup>	0.20 (0.01) <sup>d, B</sup>	0.17 (0.02) <sup>d, B</sup>	0.18 (0.01) <sup>d, B</sup>	0.12 (0.01) <sup>e, C</sup>

#### 4. DISCUSSION

MTA-based root canal sealers has been extensively studied since several researches reveal that it presents many of desirable properties, but it showed also drawbacks. In attempt to solve them, new endodontic sealers has been suggested.

The flow ability is influenced by the type of salicylate resin as well as type and size of materials particles. In the present study the MTA Fillapex showed the higher flow values. These differences can be attributed to the peculiar chemical composition of each sealer. Since the manufacture of MTA Fillapex does not provide any information about the composition ratio, it is supposed that this material has a higher resin/MTA ratio than experimental sealers. A low resin/MTA ratio leads a form a material with high flow.

An endodontic sealer must have moderate flow rate, because excessive flow increases the chance of the material extrusion toward the periapical region and insufficient flow reduces the penetration in accessory canals by sealer particles. Greater flow increases the ability to penetrate into irregularities and accessory canals and plays an important role in allowing sealer penetration within confined areas of the root canal system [55]. Further studies showing the sealing ability of these experimental materials may be necessary to corroborate with the flow values.

According of ISO 6876:2001 [53] the working time is the period of time measured between the start of mixing until not be more possible to handle the sealer without promote adverse effects on its properties. This time is directly linked with setting time which is primarily a control test on the stable behaviour of a product and is dependent on the constituent components, their particle size, the room temperature and relative humidity [3]. It seems that the same high resin/MTA ratio that leads the MTA Fillapex has higher flow ability causes the high values of setting and working time for this material.

Since the extended setting time is the major advantageous of MTA-based root canal sealer [18-23,25], in this study was observed a low setting time to all

experimental materials. Some studies [7,18,27] showed these same values to MTA-based root canal sealer only when used the  $\text{CaCl}_2$  as setting accelerator in the material's composition.

The experimental sealers tested have two chemical reactions which are responsible to material set and to provide physicommechanical characteristics: the progressive hydration of the orthosilicate ions ( $\text{SiO}_4^{4-}$ ) and the reaction between MTA and butyl ethylene glycol disalicylate. During the handling these two components come into contact and the calcium reacts with salicylate creating an ionic polymer [29]. The butyl ethylene glycol disalicylate has functionality 2 and therefore the ability to form linear or circular polymers. Resimpol 8 is plasticizer used as diluting resin. Moreover, when calcium silicate particles of MTA react with water a nanoporous amorphous calcium silicate hydrate gel forms on the cement particles [26,55]. During the setting process the soluble  $\text{Ca}(\text{OH})_2$  is released by the cement surface and increases the alkalinity of the surrounding environment [56]. Part of the water in the mix will be consumed, while another part will be trapped in the pores and capillaries and can diffuse and evaporate during and even after the setting process is complete [10,57]. The gel polymerizes and hardens forming a solid network. It was observed also that to take set the all experimental materials need have in their composition a minimum of 1:1 MTA/salicylate resin ratio.

The alkalinity caused by setting process increases the pH which is crucial to show the material's capacity in promote the dissociation of calcium and hydroxyl ions and thus induce mineralized tissue formation [4]. Besides, an alkaline pH creates an adverse environment for bacteria such as *Enterococcus faecalis* that can survive after chemical-mechanical preparation of root maintaining the periapical inflammation [58]. In this study all materials increased the pH of the soaking water to approximately 8-10 with a declining trend over time and slightly higher values recorded during the initial setting period as well as observed in other studies which tested MTA-based root canal sealers [8,27,51,59]. In MTA-based root canal sealers the chemical reaction that takes place during setting results in the formation of calcium hydroxide, which subsequently dissociates into calcium

and hydroxyl ions. The high pH values is not necessarily a positive characteristic of a root canal sealer, because releasing of hydroxyl ion requires the solubilization of the root canal sealers which may damage the dimensional stability [51]. Moreover, the decrease in hydroxyl ion release from experimental materials over time creates a physiological pH. This may provide a positive environment for cell activity [8].

Calcium ion release is another important characteristic of MTA cements. Calcium ion in tissue have been reported to activate Ca-dependent adenosine triphosphatase and may react with tissue CO<sub>2</sub> to form calcium carbonate crystals, which promote mineralization and may be necessary for cell migration and differentiation [60]. In this study all materials released calcium ion with a improving trend over time, except to MTAE-DCPD at 28 days, and provided to release calcium and hydroxyl ions for a period of at least 28 days. The experimental materials released significantly more calcium than MTA Fillapex. Maybe the MTA and calcium phosphate act synergistically to produce calcium hydroxide during the hydrolyzing and setting reactions which could increase the Ca<sup>+2</sup> ion release. Since the pH decreased over time this phenomenon was not easy to interpret. Although there is a tendency to equilibrium, because of a process the solution saturation, the Ca<sup>+2</sup> released in MTA-based root canal sealers modified or no with calcium phosphate is not related to a higher pH. Thus, it is clear that other reactions may occur. The setting reaction of the substances that compose the experimental sealers with a consequent prevention of OH<sup>-</sup> release may explain this phenomenon. It might be also the result among butyl ethylene glycol disalicylate, MTA and water interaction, although the exact mechanism is still unknown.

Bae *et al.* [51] showed that the Ca<sup>+2</sup> ion release decreased over time, but in this study was used experimental MTA-calcium phosphate root sealers with hydroxypropyl methyl cellulose which is different of butyl ethylene glycol disalicylate. Then it is difficult to compare directly the findings of Ca<sup>+2</sup> release when experimental protocols and materials used are different.

All experimental materials showed the highest values of solubility and water absorption. Since the experimental sealers are synthesized in a laboratory a lower

interaction among its components could make the material more soluble. Moisture is supposed to facilitate the hydration reactions of calcium silicates to produce calcium silicate hydrogel and calcium hydroxide which might explain the highest solubility result and  $\text{Ca}^{+2}$  ion release observed in the present study. High solubility is undesirable because dissolution may cause the release of materials that could irritate periapical tissues and may also permit gaps to form between root canals that is likely to increase bacterial leakage [60]. Coomaraswamy *et al.* [61] showed porosities in the resin matrix after the solubility probably because of bismuth oxide that has been related to the reduction of the molecular stability in MTA-based sealers and with the polymer degradation. As a consequence it may facilitate the water absorption.

Although MTA Fillapex and experimental materials are MTA-based sealers, the differences regarding their solubility may be related to the size of the polymer chain formed after setting. The differences may be attributed to the mta/resin ratio, that increases MTA-based sealers solubility as well as the addition of bismuth oxide, which is insoluble in water, and contributes to the insolubility of MTA [10]. Moreover, some studies [27] which used the MTA-based root sealers and showed lower values of solubility and water absorption tested the materials samples in the moulds, reducing the surface area exposed to water, different of this study where the samples were removed from the moulds before the tests. Further studies with SEM and EDX analysis are needed for a better understanding about solubility and water absorption to MTA-based root canal sealers modified with calcium phosphate.

## **5. CONCLUSION**

On the basis of the results obtained, it could be concluded that all experimental materials tested presented good properties as short working and setting time, alkaline pH and ability to  $\text{Ca}^{+2}$  ion release, indicating that composition

of new endodontic sealers studied showed satisfactory results to the properties evaluated.

## **ACKNOWLEDGEMENTS**

The authors thank CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brazil) and the Master in Clinical Endodontology of the University of Bologna for providing the funds for the study. The authors disclose any conflict of interest on this investigation.

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## CONSIDERAÇÕES GERAIS

Com o objetivo de avaliar algumas propriedades de um cimento endodôntico recentemente lançado no mercado (MTA Fillapex), no Capítulo 1, foram realizados alguns ensaios físico-químicos, sendo os resultados comparados a um cimento endodôntico amplamente utilizado em tratamentos endodônticos e pesquisas científicas (AH Plus).

Diferentemente do AH Plus, que é um material à base de resina epóxica, o MTA Fillapex usa como componentes básicos o MTA e uma resina de salicilatos. A associação entre esses dois materiais foi possivelmente a responsável por demonstrar, frente aos resultados desse estudo, as propriedades superiores do MTA Fillapex em relação ao AH Plus. A menor absorção de água e solubilidade por parte do MTA Fillapex poderá conferir ao material melhor estabilidade ao longo do tempo. O tempo de trabalho, apesar de menor, é suficiente para a adequada manipulação do cimento. Já o tempo de presa, além de ser inferior ao AH Plus, minimiza uma das principais limitações de uso do MTA que é o seu longo tempo de presa (Gomes-Filho *et al.*, 2009; Porter *et al.*, 2010) e o consequente risco de dissolução rápida do cimento em um ambiente onde há sangue e outros fluidos (Gomes-Filho *et al.*, 2009).

Devido à falta de informação científica sobre o MTA Fillapex, futuros estudos deveriam ser conduzidos para avaliar outras propriedades físico-químicas e biológicas, além de tentar esclarecer como ocorre a reação química entre o MTA e o salicilato.

O promissor uso da associação MTA e salicilato e a consagrada utilização de diversas fontes de cálcio em tratamentos odontológicos levaram ao estudo do Capítulo 2, onde três cimentos endodônticos experimentais foram desenvolvidos e tiveram suas propriedades avaliadas e comparadas ao MTA Fillapex. A composição básica desses cimentos foi MTA, butilenoglicol dissalicilato e uma segunda fonte de cálcio (hidroxiapatita ou fosfato dibásico de cálcio diidratado).

Esses dois tipos de cálcio foram selecionados devido à sua utilização em Odontologia.

Os resultados encontrados foram surpreendentes, como a significativa redução no tempo de presa e, no geral, liberação de cálcio superior dos cimentos experimentais em comparação ao MTA Fillapex. Entretanto, o MTA Fillapex apresentou resultados superiores em solubilidade, absorção de água e escoamento. Possíveis ajustes na formulação dos materiais experimentais podem ser feitos com objetivo de melhorar essas propriedades. Além disso, novos estudos deveriam ser realizados para avaliar outras propriedades físico-químicas e biológicas desses cimentos experimentais.

## **CONCLUSÃO GERAL**

De acordo com os resultados obtidos, pode-se concluir que os cimentos endodônticos à base de MTA e salicilato podem ser utilizados no tratamento obturador como alternativa ao uso de cimentos endodônticos à base de resina epóxica.

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\*De acordo com a norma da FOP/UNICAMP, baseadas na norma do International Committee of Medical Journal Editors - Grupo Vancouver. Abreviatura dos periódicos em conformidade com o Medline.

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## APÊNDICE

### *METODOLOGIA ILUSTRATIVA*



Fig. 1 – Balança utilizada para o proporcionamento dos reagentes.

## 1. Ensaio para aferição do escoamento e tempo de trabalho (ISO 6876:2001)

A



B

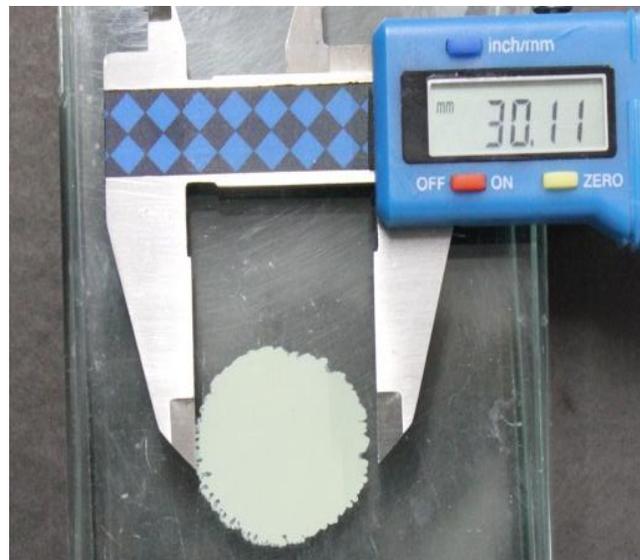


Fig. 2 – (A) compressão dos cimentos; (B) medição do escoamento.

## 2. Teste para medição dos tempos de presa inicial e final (ASTM C266)

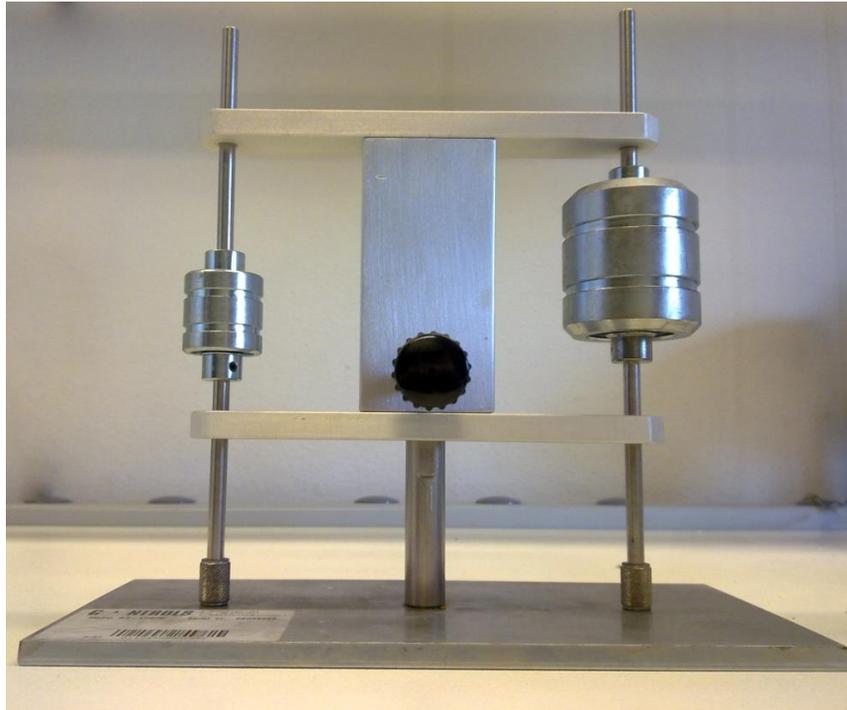


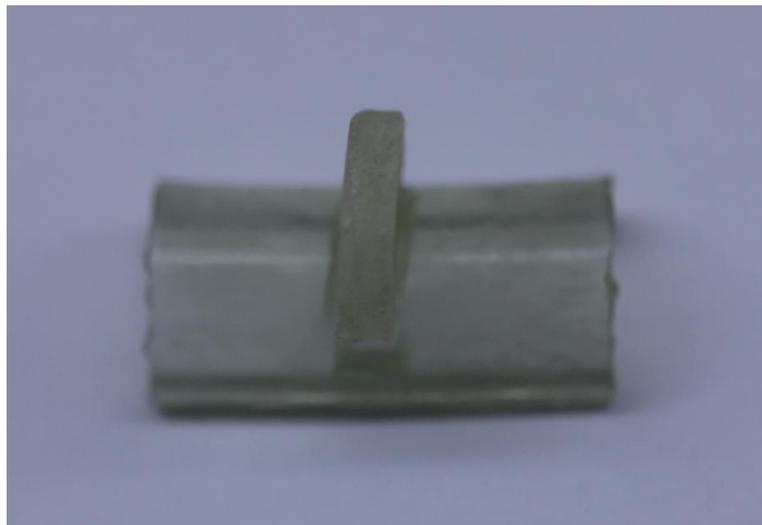
Fig. 3 – agulhas para medição dos tempos de presa inicial (esquerda) e final (direita).

### 3. Ensaio de solubilidade e absorção de água

A



B



C

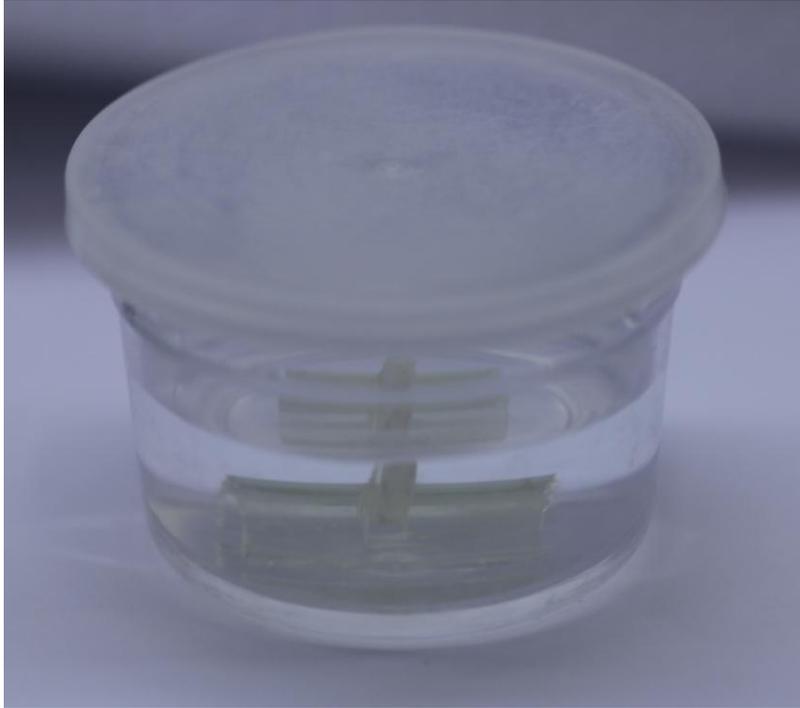


Fig. 4 – (A) confecção da amostra; (B) matriz utilizada; (C) imersão da amostra em água.

#### 4. Testes de pH e liberação de cálcio



Fig. 5 – sondas para medir pH e liberação de íons cálcio.

## ANEXO

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### Submission Confirmation for Physical and chemical properties of MTA Fillapex sealer

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