UNIVERSIDADE FEDERAL DE PELOTAS
Faculdade de Odontologia
Programa de Pós-Graduação em Odontologia

Tese

Síntese e caracterização de tensoativos para uso odontológico

Aline de Oliveira Ogliari

Pelotas, 2016

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Tese apresentada ao Programa de Pós-Graduação em Odontologia da Faculdade de Odontologia da Universidade Federal de Pelotas, como requisito parcial à obtenção do título de Doutor em Odontologia, área de concentração de Materiais Odontológicos.

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Co-orientador: Prof. Dr. Fabrício Aulo Ogliari

Pelotas, 2016

Universidade Federal de Pelotas / Sistema de Bibliotecas
Catalogação na Publicação

O35s Ogliari, Aline de Oliveira

Síntese e caracterização de tensoativos para uso odontológico / Aline de Oliveira Ogliari ; Rafael Ratto de Moraes, orientador ; Fabrício Aulo Ogliari, coorientador. — Pelotas, 2016.

95 f. : il.

Tese (Doutorado) — Programa de Pós-Graduação em Materiais Odontológicos, Faculdade de Odontologia, Universidade Federal de Pelotas, 2016.

1. Síntese orgânica. 2. Ângulo de contato. 3. Tensoativos. 4. Silicone por adição. 5. Hidrofilia. I. Moraes, Rafael Ratto de, orient. II. Ogliari, Fabrício Aulo, coorient. III. Título.

Black : D151

Elaborada por Fabiano Domingues Malheiro CRB: 10/1955

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Tese apresentada, como requisito parcial, para obtenção do grau de Doutor em Odontologia, Programa de Pós-Graduação em Odontologia, Faculdade de Odontologia de Pelotas, Universidade Federal de Pelotas.

Data da defesa: 29/07/2016

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Dedico este trabalho ao meu
esposo e a minha filha.

Agradecimentos

À **Universidade Federal de Pelotas** por meio do Magnífico Reitor, Prof. Dr. Mauro Augusto Burkert Del Pino.

À **Faculdade de Odontologia** por meio da Senhora Diretora, Profª Drª Adriana Etges.

Ao **Programa de Pós-Graduação em Odontologia** por meio do Senhor coordenador Prof. Dr. Rafael Ratto de Moraes.

Ao meu orientador, professor **Rafael Ratto de Moraes,** pela orientação prestada, pelos conselhos dados, pelo conhecimento compartilhado e pela ajuda que sempre tive em todos os períodos da minha formação, tanto na graduação quanto no mestrado e doutorado, somando 7 anos de convivência e aprendizado.

Ao meu co-orientador **Fabrício Aulo Ogliari**, pelo incentivo e troca de conhecimentos diários, pelo apoio incondicional em todas as etapas da minha formação e aprimoramento profissional.

Ao Prof. **Cesar Liberato Petzhold** por ter disponibilizado o Instituto de Química- UFRGS, para a realização de parte do nosso estudo e ter feito parte dessa etapa da primeira etapa do trabalho.

Ao Prof. **Fabrício Mezzomo Collares** por ter disponibilizado o LAMAD para que eu pudesse realizar parte das metodologias apresentadas na tese.

Ao laboratório **CDC-Bio**, por ter aberto as portas para que a minha tese pudesse ser realizada em sua maior parte.

Ao **CNPq e a Capes**, pelas bolsas de estudos que recebi durante meu período de doutoramento.

Agradeço em especial, alguns **professores e colegas de trabalho** que tive o prazer de conviver e de crescer profissionalmente ao lado deles: Prof. Victor Feitosa, Gabriel Abuna, Prof. Salvatore Sauro, Prof. Douver Michelon, Prof. Eduardo Castilhos, Prof. Fabrício Collares, Prof. Evandro Piva, Prof. César Zanchi, Prof. Alexandre Masotti, Profª. Patrícia Jardim, Prof. André Faria e Silva, Prof. Rafael Lund, Profª. Giana Lima, Prof. Maximiliano Cenci, Prof. Neftali Carreño, Débora Meinck, Fernanda Leal, Carine Meereis, Katerine Pilownic, Andressa Goicochea, Carianne Almeida, Juliana Ribeiro, Giselle Reis, Fernanda Silva, Bruno Noremberg, Igor Cherubin, Viviane Duarte, Natalia Marins e Ricardo Marques.

Agradeço aos **orientados** de TCC que tive o prazer de compartilhar um pouco do conhecimento que adquiri durante essa última jornada e também de aprender muito com eles: Bruno Noremberg, Vinícius Heming, Andressa Goicochea, Carianne Almeida, Manuela Ferrari, Julia Schwantz, Maísa baggio e Ana Paula Gonçalves.

Agradeço aos **colegas de pós-graduação** que sempre estiveram dispostos a ajudar e trocar ideias, são eles: Fernanda Leal, Carine Meereis, Ana Paula Gonçalves, Luciana Conceição, Katerine Pilownic, Cristina Isolan, Sônia Peralta, Vinícius Salgado, Wellingtom Rosa, Eliseu Münchow, Débora Simonetti, Andressa Goicochea, Simone Oliveira, Marina Kaizer, Juliana Ribeiro.

Agradeço sobretudo, a **minha família**, em especial o meu marido Fabrício, pela sua amizade, pela sua compreensão e pelo seu amor; e a minha filha Julia, por ser a minha motivação de vida! Amo muito vocês!

“A melhor maneira de prever o futuro é criá-lo”

(PETER DRUCKER)

Notas Preliminares

A presente tese foi redigida segundo o Manual de Normas para Dissertações, Teses e Trabalhos Científicos da Universidade Federal de Pelotas de 2013, adotando o Nível de Descrição 4 – estrutura em Artigos, descrita no Apêndice D do referido manual. http://sisbi.ufpel.edu.br/?p=documentos&i=7 Acesso em: 29/05/2016.

O projeto de pesquisa contido nesta tese é apresentado em sua forma final após qualificação realizada em 06 de agosto de 2013 e aprovado pela Banca Examinadora composta pelos Professores Doutores André Luís Faria e Silva, Carlos José Soares e Rafael Ratto de Moraes.

Resumo

OGLIARI, Aline de Oliveira. **Síntese e caracterização de tensoativos para uso odontológico**. 2016. 95f. Tese (Doutorado em Odontologia, área de concentração de Materiais Odontológicos) – Programa de Pós-Graduação em Odontologia, Faculdade de Odontologia, Universidade Federal de Pelotas, Pelotas, 2016.

O objetivo deste estudo foi sintetizar e caracterizar diferentes classes de tensoativos não-iônicos e avaliar a influência nas propriedades e características de materiais de moldagem experimentais a base de polivinilsiloxanos (VPS). Os tensoativos sintetizados e avaliados podem ser utilizados, ainda, para modificação de outros materiais odontológicos. Esta tese foi dividida em dois estudos, apresentados em dois artigos originais. No primeiro estudo, foi realizada a síntese de fluortensoativos com diferentes balanços hidrofílico-lipofílico (HLB) e avaliado o efeito no VPS, enquanto no segundo foi realizada avaliação do desempenho de diferentes tensoativos comerciais não-iônicos do tipo fluorcabono (F), siloxano (S) e hidrocarboneto (H) em uso isolado ou combinado (mais de um tensoativo) adicionados ao VPS. No primeiro estudo, seis fluortensoativos foram sintetizados utilizando polietilenoglicóis com diferentes massas molares (variando de 200 a 1.000.000 g/mol) na porção polar. Os tensoativos sintetizados foram caracterizados e adicionados em concentração de 3% em massa no VPS. No segundo estudo, oito grupos de tensoativos comerciais foram adicionados no VPS, de forma simples ou combinada, em diferentes concentrações: 1%, 3% e 5% em massa. Foram realizadas diferentes metodologias para análise dos tensoativos e dos materiais de moldagem, incluindo espectroscopia no infravermelho, ressonância magnética nuclear de ^{1}H e ^{19}F, tensão superficial, ângulo de contato, viscosidade, capacidade de cópia, resistência mecânica à tração e resistência elástica. Os dados quantitativos foram analisados por Análise de Variância e teste *post hoc* de Tukey ($P<0,05$). No primeiro estudo, a síntese dos tensoativos foi confirmada por espectroscopia no infravermelho e ressonância magnética nuclear. Os fluortensoativos, no geral, apresentaram baixa tensão superficial e reduziram a resistência à tração do VPS quando comparados ao grupo controle (sem tensoativo), porém propiciaram excelente capacidade de cópia ao VPS. Foram encontrados diferentes padrões de molhabilidade e obtidos reduzidos ângulos de contato com a água nos grupos FS 200 e FS 400 (fluortensoativos sintetizados com polietilenoglicol de massa molar 200 e 400, respectivamente). A viscosidade foi reduzida com a adição de FS 400 e FS 500; no entanto, foi verificado aumento no tempo de indução do material. No segundo estudo, a menor tensão superficial foi encontrada no grupo que combinou os três tensoativos (F+S+H). Em geral, os grupos que combinaram tensoativos apresentaram menores ângulos de contato e menor viscosidade. O tempo de indução aumentou com o aumento da concentração de tensoativo e nem todos os grupos obtiveram resultados satisfatórios na análise de capacidade de cópia. Os VPS modificados com tensoativos na forma isolada, em geral, apresentaram maior resistência à tração. Em conclusão, a adição de FS 200 e FS 400 melhorou significativamente a molhabilidade do VPS, reduzindo a viscosidade sem alterar o tempo de trabalho significativamente; no entanto, reduziu a resistência à tração. No segundo estudo ficou evidente que a correta seleção do tipo de tensoativo e sua concentração podem melhorar significativamente a molhabilidade dos VPS com pouca interferência em suas propriedades mecânicas.

Palavras-Chave: síntese orgânica; ângulo de contato; tensoativos; silicone por adição; elastômero; hidrofilia.

Abstract

OGLIARI, Aline de Oliveira. **Synthesis and characterization of surfactants for dental use.** 2016. 95p. Thesis (PhD in Dentistry, Dental Materials Area) – Graduate Program in Dentistry, Federal University of Pelotas, Pelotas, Brazil, 2016.

The aim of this study was to synthesize and characterize different classes of non-ionic surfactants and evaluate their influence on properties and characteristics of experimental impression materials based on vinylpolysiloxanes (VPS). This thesis was divided in two studies, presented as two original articles. In the first study, we synthesized fluorosurfactants with different hydrophilic-lipophilic balances (HLB) and evaluated the effect on the VPS, whereas in the second study we evaluated of the performance of different fluorocabon (F), siloxane (s), and hydrocarbon (H) commercial non-ionic surfactants used alone (one surfactant) or in combination (more than one surfactant) added to the VPS. In the first study, six fluorosurfactants were synthesized using polyethylene glycols of different molar mass (varying from 200 to 1,000,000 g/mol) in the polar portion. The surfactants were characterized and added at a 3 wt% concentration to the VPS. In the second study, eight groups of commercial surfactants were added alone or in combination to the VPS at different concentrations: 1 wt%, 3 wt%, or 5 wt%. Different methods were used to analyze the surfactants and impression materials, including infrared spectroscopy, ^{1}H and ^{19}F nuclear magnetic resonance, surface tension, contact angle, viscosity, detail reproduction tensile strength, and elastic strength. Quantitative data were analyzed using Analysis of Variance and Tukey's *post hoc* test ($P<0.05$). In the first study, the synthesis was confirmed by infrared spectroscopy and nuclear magnetic resonance. The fluorosurfactants, in general, showed low surface tension and reduced the VPS tensile strength when compared to the control group (without surfactant), but yielded excellent copy capacity to the VPS. Different wettability patterns were found and low contact angles were obtained for FS 200 and FS 400 groups (fluorosurfactants synthesized using polyethylene glycol with 200 and 400 molar masses, respectively). The viscosity also decreased with the addition of FS 400 and FS 500; however, an increase in the induction time of the material was observed. In the second study, lower surface tension was found in the group that combined the three surfactants (F+S+H). Overall, the groups that combined surfactants had lower contact angle and lower viscosity. The induction time increased with increased surfactant concentration and satisfactory results on the analysis of copy capacity were not observed for all groups. The VPS modified with surfactants alone, in general, had higher tensile strength. In conclusion, the addition of FS 200 and FS 400 significantly improved wettability of the VPS, reducing viscosity without changing the working time significantly; however, the surfactants reduced the tensile strength. In the second study, it was evident that the correct selection of the surfactant type and its concentration may significantly improve the VPS wettability without major interference on the mechanical properties.

Key-words: organic synthesis; contact angle; surfactant; polyvinylsiloxane; elastomer; hydrophilicity.

Sumário

1 Introdução

Elastômeros do tipo silicone polimerizado por reação de adição são muito utilizados para a realização de moldagens na Odontologia. Estes materiais são constituídos de polímeros polivinilsiloxanos (VPS) reticuláveis em temperatura ambiente por meio de sistema de catálise à base de um complexo platínico. Os VPS são capazes de copiar tecidos moles e duros, áreas retentivas e interdentais, permitindo ainda a obtenção de mais de um modelo de gesso a partir do mesmo molde. Dessa forma, são materiais com grande versatilidade na Odontologia, sendo utilizados em diversos procedimentos clínicos e laboratoriais.

De forma geral, os silicones de adição atendem satisfatoriamente as propriedades de estabilidade dimensional, resistência ao rasgamento e biocompatibilidade. No entanto, sua capacidade de cópia, uma das principais exigências para materiais de moldagem (HOSSEINPOUR; BERG, 2009), ainda é deficiente em situações críticas de umidade, como em moldagens de término cervical especialmente em áreas intrassulculares. Isso se deve à diferença entre o ambiente oral polar e o material de moldagem altamente hidrófobo (apolar), ocasionando incompatibilidade de polaridade que pode afetar a molhabilidade e o escoamento do silicone na superfície a ser moldada.

A elevada hidrofobia dos silicones de adição, advinda das suas ligações polissiloxanas apolares (RUPP et al., 2005), além de reduzir a precisão da impressão, pode também gerar falhas de moldagem em decorrência do aprisionamento de ar (KESS; COMBE; SPARKS, 2000). Bolhas podem ser formadas tanto no momento da moldagem quanto no vazamento do gesso no molde (MICHALAKIS et al., 2007). Estas limitações, em última instância, podem resultar falhas em procedimentos clínicos de confecção de restaurações e próteses (MONDON; ZIEGLER, 2003, RAGAIN et al., 2000), acarretando em maiores custos de tratamentos.

Para conferir caráter mais hidrófilo aos silicones, alguns fabricantes adicionam agentes tensoativos não-iônicos na formulação dos VPS (KESS; COMBE; SPARKS, 2000, MANDIKOS, 1998, RUBEL, 2007). A escolha por tensoativos não-iônicos se dá em função destes não se complexarem com o catalisador platínico da reação, diferentemente dos tensoativos aniônicos e catiônicos. Diversos tipos e concentrações de tensoativos não-iônicos podem ser utilizados com o intuito de atribuir hidrofilia ao material. Sua ação se dá na superfície do silicone, alterando sua polaridade e melhorando o molhamento pela água (YUNFEI et al., 2012). As estruturas químicas dos tensoativos invariavelmente apresentam um segmento polar etóxi que fica orientado para a área superficial do material, enquanto o outro segmento, apolar, fica orientado para o interior hidrófobo. Na extremidade voltada para a porção hidrófoba, os segmentos hidrófobos mais utilizados são os fluorcarbonos, hidrocarbonetos e siloxanos. Os tensoativos fluorados são conhecidos por terem mais eficiência na redução da tensão superficial da água, seguidos pelos siloxanos, enquanto os hidrocarbonetos são os menos eficientes (SALAGER, 2002). Além disso, tensoativos fluorados são mais estáveis e aptos a condições adversas devido à estabilidade da ligação de carbono-flúor (HU; ZHANG; WANG, 2010).

Essas fortes interações exibidas pelas cadeias de fluorcarbonos, aliada às fracas interações de van der Waals, aumenta drasticamente a tendência dessas moléculas ambifílicas em se autoalinharem à água, apresentando forte atração superficial quando comparadas aos hidrocarbonetos (GRANIER, 2009). Além disso, existem evidências de que os fluorcarbonos podem reduzir pela metade a tensão superficial da água quando comparados a tensoativos de segmento hidrofóbico hidrocarboneto (KISSA, 1994, YOSHIMURA; OHNO; ESUMI, 2006). Adicionalmente, a elevada eletronegatividade dos fluorcarbonos favorece a redução da polaridade, o que não os torna tão suscetíveis às forças de dispersão de London quanto os hidrocarbonetos.

Todas essas excelentes características nos levam a crer que fluorcarbonos poderiam ser adicionados a VPS com o objetivo de melhorar a hidrofilia do material e consequentemente gerar resultados mais satisfatórios de moldagem, nas mais diferentes ocasiões clínicas. Para desenvolver um VPS com melhores propriedades é necessário, primeiramente, realizar estudos (*screening*) com diferentes tipos, concentrações e combinações de tensoativos para entender o comportamento do material frente a condições adversas. Para isso, é necessário avaliar a influência do balanço hidrofílico-lipofílico das diferentes classes de tensoativos não-iônicos; o possível efeito sinérgico quando adicionado mais de um tipo de tensoativo ao VPS, isto é, aumento da eficiência hidrofílica; a relação da concentração desses tensoativos nas principais propriedades do VPS, como resistência ao rasgamento, capacidade de cópia, viscosidade e ângulo de contato. Todas essas avaliações podem ajudar a responder algumas questões a respeito de quão hidrofílico é o VPS modificado, perfazendo assim algumas das metas deste trabalho.

2 Projeto de pesquisa

2.1 Introdução

Elastômeros do tipo silicone por adição são muito utilizados para a realização de moldagens na Odontologia. Estes materiais são constituídos de polímeros polivinilsiloxanos (VPS) reticuláveis em temperatura ambiente por um sistema de catálise à base de um complexo platínico. Os VPS são capazes de copiar tecidos moles e duros, áreas retentivas e interdentais, permitindo ainda construção de mais de um modelo de gesso a partir de um mesmo molde. Dessa forma, são materiais com grande versatilidade Odontologia, utilizados em diversos procedimentos clínicos.

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Para conferir caráter mais hidrófilo aos silicones, os fabricantes adicionam agentes tensoativos não-iônicos na formulação dos VPS (KESS; COMBE; SPARKS, 2000; MANDIKOS, 1998; RUBEL, 2007). A escolha por tensoativos não-iônicos se dá em função destes não se complexarem com o catalisador platínico da reação, diferentemente dos tensoativos aniônicos e catiônicos. Diversos tipos e concentrações de tensoativos não-iônicos são utilizados com o intuito de atribuir hidrofilia ao material. Os tensoativos agem na superfície do silicone, alterando sua polaridade e melhorando o molhamento pela água (YUNFEI et al., 2012). Suas estruturas químicas invariavelmente apresentam um segmento polar etóxi que fica orientado para a área superficial do material, e outro apolar orientado para o interior hidrófobo. Na extremidade voltada para a porção hidrófoba, os segmentos hidrófobos mais utilizados são os hidrocarbonetos, siloxanos e fluorcarbonos. Os tensoativos fluorados são os mais eficazes na redução da tensão superficial da água, seguidos pelos siloxanos e tendo os hidrocarbonetos como os menos eficientes (SALAGER, 2002). Além disso, são mais estáveis e aptos a condições adversas, devido à estabilidade da ligação de carbono-flúor (HU; ZHANG; WANG, 2010).

O presente estudo tem o objetivo de testar a hipótese que a correta seleção do tensoativo não-iônico pode conferir ao VPS hidrofilia suficiente para a obtenção de um reduzido ângulo de contato com a água e, ainda, ser potencializada através da combinação de diferentes tensoativos.

2.2 Objetivo

2.2.1 Objetivo Geral

O objetivo do presente estudo é sintetizar e caracterizar diferentes classes de tensoativos não-iônicos e avaliar sua influência em propriedades e características de materiais de moldagem experimentais baseados em VPS.

2.2.2 Objetivos Específicos

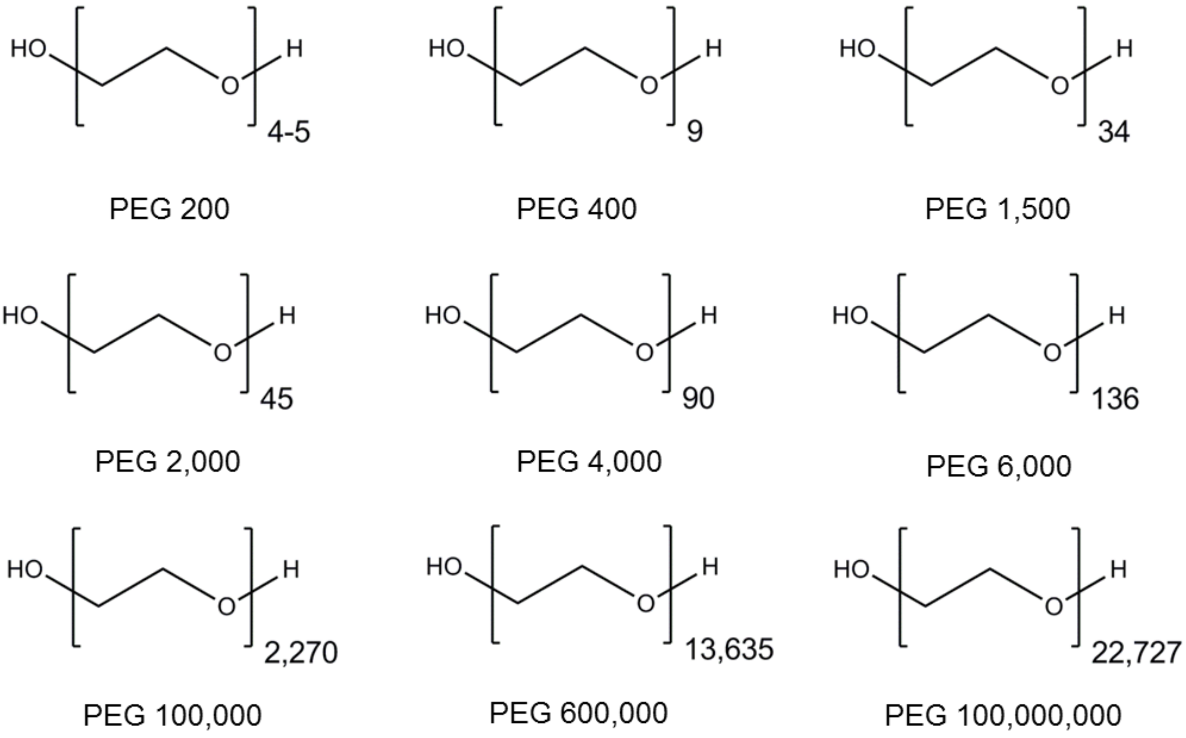
- Sintetizar diferentes fluortensoativos;
- Avaliar o desempenho de diferentes classes de tensoativos;
- Investigar a sinergia entre tensoativos.

2.3 Metodologia

2.3.1 Síntese de diferentes fluortensoativos

2.3.1.1 Reagentes

Serão sintetizados aproximadamente 10 tensoativos fluorados. Para isso será necessária a utilização de diversos polietilenoglicois (PEG) com diferentes massas molares, conforme apresentado na Figura 1. Para conferir a fração apolar fluorada do tensoativo, será utilizado o ácido perfluoroctanóico (APFO) como reagente (Figura 2).



PEG 200
PEG 400
PEG 1,500
PEG 2,000
PEG 4,000
PEG 6,000
PEG 100,000
PEG 600,000
PEG 100,000,000

FIGURA 1. Estrutura molecular dos polietilenoglicóis (PEG).

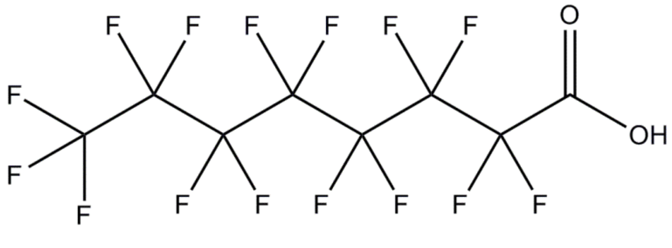


FIGURA 2. Estrutura molecular do ácido perfluoroctanóico (APFO).

2.3.1.2 Síntese

Para a obtenção dos tensoativos fluorados, a rota sintética selecionada será uma convencional esterificação de Fischer. Com o objetivo de ilustração, seguem abaixo dois exemplos do método.

- Tensoativo Fluoro-PEG400: Em um balão de 10mL acoplado a um aparato Dean-Stark, será adicionado 0,96g (2 mols equiv.) de PEG400. Sob agitação, o balão será aquecido a 130°C por 30min. Na sequência, será adicionado 0,015g de ácido p-tolueno sulfônico e 0,5g de ácido perfluoro-octanóico. A reação será mantida nesta temperatura sob agitação por 48h.
- Tensoativo Fluoro-PEGME5000: Em um balão de 25mL acoplado a um aparato Dean-Stark será adicionado 7,2g de PEGME5000 (1,2 mols equiv.). Sob agitação, a reação será mantida a 130°C por 30min. Na sequência será adicionado 0,015g de ácido p-tolueno sulfônico e 0,5g de ácido perfluoroctanóico. A reação será mantida nesta temperatura sob agitação por 48h.

2.3.1.3 Purificação

A purificação dos tensoativos fluorados será realizada por meio de filtração e ponto de fusão utilizando dois possíveis métodos. Com o objetivo de ilustração, seguem abaixo dois exemplos dos métodos.

- Tensoativo Fluoro-PEG400: O produto será filtrado em coluna de alumina básica compactada em uma pipeta de Pasteur. Para remover o excesso de PEG400, será investigado o ponto de solidificação do éster, considerando o ponto de fusão já conhecido do PEG400 entre 4 e 8°C. A estrutura molecular do produto purificado será confirmada por FTIR e RMN H^+. A pureza do isolado será avaliada por cromatografia gasosa.
- Tensoativo Fluoro-PEGME5000: O produto será filtrado a quente em coluna de alumina básica compactada em uma pipeta de Pasteur. Na sequência nova filtração será realizada a frio em coluna de celite compactada em uma pipeta de Pasteur. A estrutura molecular do produto purificado será confirmada por FTIR e RMN H^+. A pureza do isolado será avaliada por cromatografia gasosa.

2.3.1.4 Formulação do VPS experimental

Para avaliar o desempenho dos tensoativos sintetizados, será formulada uma base experimental de VPS de acordo com a Tabela 1. As análises físico-mecânicas do material de moldagem serão realizadas utilizando esta mesma composição. Como controle, será utilizado VPS sem a presença de tensoativo.

Tabela 1. Composição do VPS experimental

Pasta base	Pasta catalisadora
Polivinilsiloxano	Polivinilsiloxano
Quartzo	Quartzo
Dióxido de silício	Dióxido de silício
Polimetil hidrogênio siloxanos	Complexo platínico
Tensoativo*	

*A composição da pasta base pode variar conforme concentração do tensoativo utilizada.

2.3.1.5 Caracterização

2.3.1.5.1 Espectroscopia no infravermelho

Os produtos obtidos serão caracterizados por meio de espectrofotômetro no infravermelho por Transformada de Fourier (Prestige21, Shimadzu, Tóquio, Japão) equipado com dispositivo de refletância total atenuada (ATR). As amostras dos reagentes e dos fluortensoativos sintetizados serão individualmente analisadas em uma faixa espectral entre 700 e 4000cm^{-1}. Os espectros dos produtos serão comparados nas frequências correspondentes aos grupos carboxílicos e álcoois, ambos na faixa de 3200cm^{-1}. O desaparecimento dos picos nestas frequências será um indício do sucesso na obtenção dos ésteres.

2.3.1.5.2 Ressonância magnética nuclear

Os espectros de RMN serão obtidos em um espectrômetro (Varian, Inova 300MHz, Palo Alto, CA, EUA) operando a 75MHz para RMN^{13}C e 300MHz para RMN H^{+}. Serão utilizados tubos de vidro com 5mm de diâmetro e clorofórmio deuterado como solvente a temperatura ambiente, na concentração de 1% em massa.

2.3.1.5.3 Ângulo de contato

Os ângulos de contato serão mensurados por meio de um tensiometro (Theta Lite TL101, Biolin Scientific Inc., Finlândia) em dois tempos (t) distintos:

- t 0s: o espécime de VPS experimental será depositado no porta-amostra e o ângulo de contato será mensurado após processo de automistura.
- t1h: o espécime de VPS experimental será depositado no porta amostra após processo de automistura, e o ângulo de contato mensurado após tempo de presa final.

Para ambos os tempos uma gota de 3µL de água destilada será dispensada na superfície do VPS. Assim que o software (OneAttension, Biolin Scientific Inc) detectar a deposição da gota, a mensuração dos ângulos direito e esquerdo será feita em tempo real durante 60s. Esse processo será repetido por três vezes (n=3) para cada VPS experimental.

2.3.1.5.4 Tensão superficial

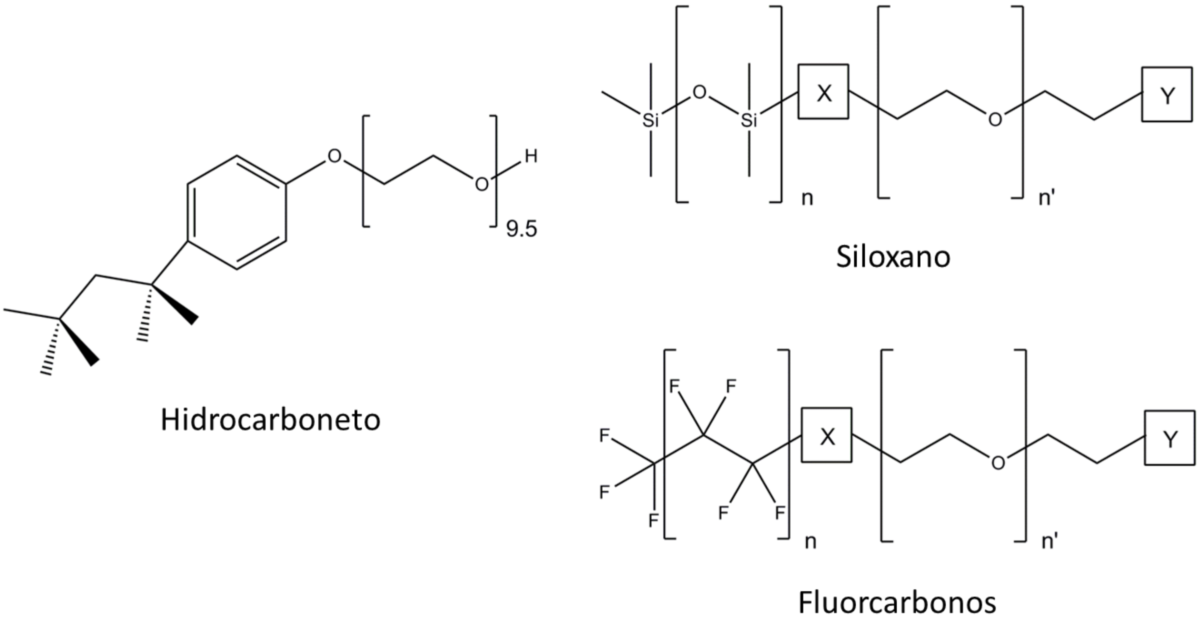
A tensão de superfície de cada surfactante será analisada utilizando o tensiometro por meio do método de gota pendente invertida. A gravação de vídeo será acionada e uma gota será dispensada através da agulha. Tanto o volume da gota quanto a tensão superficial serão mensurados em tempo real, através do software que automaticamente detectará a curva em torno da gota e calculará a média e desvio padrão através de funções estatísticas.

2.3.2 Desempenho de diferentes classes de tensoativos

2.3.2.1 Formulação do VPS experimental

Para a investigação do desempenho das diferentes classes de tensoativos, será formulada uma base experimental de VPS, conforme a Tabela 1. Essa mesma composição será utilizada para as análises físico-mecânicas. Nessa composição serão então adicionados diferentes tipos de tensoativos, bem como em diferentes concentrações. Serão utilizados três tipos de surfactantes comerciais não-iônicos: hidrocarboneto (Triton X100, Vetec, Duque de Caxias, RJ, Brasil), siloxano (Silwet

L77, Momentive, Columbos, OH, EUA) e fluorcarbonos (Hydroflu, Yller, Pelotas, RS, Brasil), conforme apresentados na Figura 3. Estes surfactantes serão adicionados à formulação de VPS experimentais em três diferentes concentrações 0,5%, 1% e 3%. Como controle, será utilizado VPS sem a presença de tensoativo.



Hidrocarboneto

Siloxano

Fluorcarbonos

FIGURA 3. Estruturas moleculares representativas das classe de surfactantes não-iônicos. X indica a possibilidade das ligações do tipo éter, éster, C-C, amida e uretana dentre outras, enquanto Y indica a possibilidade de ligações OH, metil éter e acetóxi, dentre outras.

2.3.2.2 Ângulo de contato

Os ângulos de contato serão mensurados conforme método descrito anteriormente no item 2.3.1.5.3.

2.3.2.3 Tensão superficial

A tensão de superfície de cada surfactante será analisada conforme método descrito anteriormente no item 2.3.1.5.4.

2.3.2.4 Resistência mecânica ao rasgamento

O teste de resistência mecânica ao rasgamento será conduzido de acordo com a norma ASTM D624 (2001), conforme descrição tipo C. Este método é utilizado para mensurar a resistência ao rasgamento de materiais elastoméricos a partir de ruptura inicial que se propaga em um local de alta concentração de tensão, provocando um corte localizado. Para a confecção das amostras (n=5) será utilizada uma matriz acrílica que será preenchida com o VPS experimental após processo de automistura. A superfície será planificada com uma lâmina de vidro e, após 5min, os corpos-de-prova serão removidos da matriz e submetidos imediatamente ao teste de resistência ao rasgamento em máquina de ensaios mecânicos (DL500; EMIC, São José dos Pinhais, PR, Brasil). A amostra será apreendida por duas pinças, que se movimentarão em sentidos opostos à velocidade de 0,5mm/min, até a ruptura. Os valores de resistência ao rasgamento serão calculados em N/cm.

2.3.2.5 Reprodução de detalhes

O teste de reprodução de detalhes será realizado de acordo com a norma ISO 4823 (2000). Este método será utilizado para determinar a reprodução de detalhes dos materiais elastoméricos do tipo 3 (pasta leve), por meio da avaliação da intersecção da linha horizontal com a vertical do bloco de teste. Para a confecção das amostras (n=3) será utilizada uma matriz metálica que apresenta três linhas horizontais medindo 20µm, 50µm e 75µm de largura e duas linhas verticais que cortam suas extremidades. As duas pastas do VPS experimental serão misturadas e depositadas sobre um molde em forma de anel, e este encaixado no bloco de teste umedecido. Após 5min, o molde será retirado do bloco de teste para análise. O molde será observado com auxílio de lupa estereoscópica, sob aumento de 40× para avaliação da impressão. Será considerada satisfatória a impressão que reproduzir as intersecções da linha de 20µm continuamente.

2.3.2.6 Recuperação elástica

O teste de recuperação elástica será realizado de acordo com a norma ISO 4823 (2000). Este método é utilizado para determinar a recuperação elástica de materiais elastoméricos, calculada de acordo com a seguinte equação:

$$k\text{=100-}\left[100\left(\frac{\text{h}_1\text{-h}_2}{\text{h}_0}\right)\right],$$

onde:

k representa a constante de recuperação elástica, h_0 a altura do modelo dividido, h_1 leitura do indicador em t + 55s (imediatamente antes da amostra ser deformada) e h_0 leitura do indicador em t + 180s (115s depois da força de deformação ter sido removida da amostra). Para a confecção das amostras (n=5) será utilizada uma matriz cilíndrica medindo 2cm × 1,25cm, que será preenchida com o VPS experimental que, após a polimerização, será removido para o teste.

2.3.3 Sinergia entre tensoativos

2.3.3.1 Formulação do VPS experimental

Para a investigação da sinergia entre tensoativos, também será formulada uma base experimental de VPS, conforme a Tabela 1 do item 2.3.1.4. Essa mesma composição será utilizada para as análises físico-mecânicas. Nessa composição serão adicionados diferentes tipos de tensoativos, em concentrações que serão definidas com o decorrer do projeto, combinados da seguinte forma:

- Hidrocarboneto + siloxano
- Hidrocarboneto + fluorcarbono
- Fluorcarbono + siloxano.

Como controle será utilizado VPS sem a presença de tensoativo.

2.3.3.2 Ângulo de contato

Os ângulos de contato serão mensurados conforme método descrito anteriormente no item 2.3.1.5.3.

2.3.3.3 Tensão superficial

A tensão de superfície de cada surfactante será analisada conforme método descrito anteriormente no item 2.3.1.5.4.

2.3.3.4 Resistência mecânica ao rasgamento

O teste de resistência mecânica ao rasgamento será conduzido conforme método descrito anteriormente no item 2.3.2.4.

2.3.3.5 Reprodução de detalhes

O teste de reprodução de detalhes será realizado conforme método descrito anteriormente no item 2.3.2.5.

2.3.3.6 Recuperação elástica

O teste de recuperação elástica será realizado de acordo com o método descrito anteriormente no item 2.3.2.6.

2.3.4 Análise estatística

Os dados quantitativos serão analisados utilizando testes paramétricos caso a homoscedasticidade seja atingida. Dados qualitativos serão analisados de forma descritiva. O nível de significância de 5% será considerado em todas as análises.

2.4 Referências

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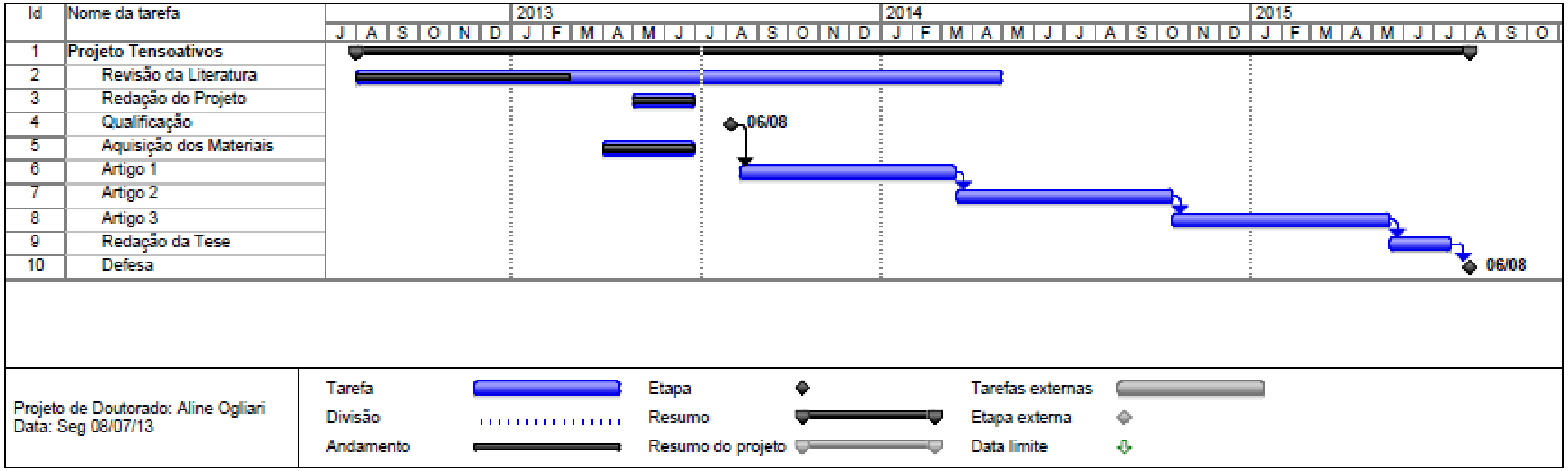
2.5 Orçamento

Item	Quantidade	Preço unitário	Total, R$
PEG200	1L	797,50	797,50
PEG400	1Kg	42,60	42,60
PEG1500	1Kg	41,50	41,50
PEG2000	1Kg	355,00	355,00
PEG4000	1Kg	49,10	49,10
PEG6000	1Kg	67,80	67,80
PEG100.000	250g	575,00	575,00
PEG600.000	250g	517,00	517,00
PEG1.000.000	250g	629,00	629,00
APFO	25g	736,00	736,00
PTSA	500g	345,10	345,10
PEGME5000	250g	254,00	254,00
Balão 10mL	12un	9,00	108,00
Balão 25mL	12un	9,00	108,00
Dean-Stark	2un	95,00	190,00
Coluna cromatográfica	2un	100,00	100,00
Alumina básica	1Kg	446,60	446,60
Pipeta de Pasteur	100un	13,00	13,00
Micropipeta graduada	1un	597,98	597,98
Ponteiras de 0,5µl a 10µl	1pct	28,96	28,96
Polivinilsiloxano	1Kg	400,00	400,00
Quartzo	1Kg	140,00	140,00
Dióxido de silicone	1Kg	300,00	300,00
Polimetil hidrogênio siloxano	1Kg	400,00	400,00
Complexo platínico	100g	1.500,00	1.500,00
Hidrocarboneto	1L	40,00	40,00
Siloxano	1Kg	600,00	600,00
Fluorcarbono	1L	1.200,00	1.200,00
Espátula	3un	7,22	21,66
Material para acondicionamento	-	-	200,00
Material de escritório	-	-	50,00
Material descartável	-	-	150,00
Impressão gráfica	500un	1,00	500,00
Diária e passagem para congresso	-	-	4.000,00

TOTAL: **R$ 15.503,80**

2.6 Cronograma



Id	Nome da tarefa
1	**Projeto Tensoativos**
2	Revisão da Literatura
3	Redação do Projeto
4	Qualificação
5	Aquisição dos Materiais
6	Artigo 1
7	Artigo 2
8	Artigo 3
9	Redação da Tese
10	Defesa

Projeto de Doutorado: Aline Ogliari
Data: Seg 08/07/13

3 Relatório do trabalho de campo

Os objetivos específicos propostos no projeto foram todos realizados. As diferenças entre o projeto de pesquisa apresentado no item 2 e os artigos a seguir apresentados no item 4 se referem à inclusão e exclusão de algumas metodologias. Além disso, os dois últimos artigos propostos no projeto foram unificados para possibilitar uma discussão mais aprofundada acerca dos dados encontrados.

4 Artigo 1[1]

Rendering vinylpolysiloxanes hydrophilic

Short title: Hydrophilic vinylpolysiloxanes

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Keywords: Contact angle; hydrophilicity; impression materials; vinylpolysiloxanes; surface tension; surfactants; wetting.

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[1] Artigo formatado segundo as normas de periódico *Dental Materials.*

Abstract

Objectives: This study evaluated the use of nonionic surfactants to render vinylpolysiloxane (VPS) impression materials hydrophilic. Other material properties were analyzed.

Methods: Fluorocarbon (F), hydrocarbon (H), and siloxane (S) surfactants were tested and the surface tension of the surfactants diluted in water was analyzed. F, H and/or S, alone or in combination, were added at 1 wt%, 3 wt%, or 5 wt% to both base and catalyst pastes of an experimental VPS impression material. In the control group no surfactant was added. Water contact angles formed with the non-polymerized (t=0) and polymerized VPS (t=60min) were evaluated. The other properties tested were tensile strength, detail reproduction, and viscosity. Data were analyzed statistically ($p<0.05$).

Results: All surfactants alone or in combination reduced the water surface tension between 42% (H) and 86% (F+S+H). At t=0, all surfactants reduced dramatically the water contact angles compared with the control VPS, particularly when used in combination. At t=60, the S+H group had no synergistic effect and did not reduce the contact angle as efficiently as the other groups did. The surfactants decreased viscosity, delayed the induction time, and generally reduced the mechanical strength of the VPS. When the surfactants were used alone, the detail reproduction was satisfactory, whereas F+S 3% and 5%, all H+S or F+S+H combinations apparently did not polymerize.

Significance**:** Nonionic surfactants were able to render the VPS hydrophilic, both before and after polymerization. Increased hydrophilicity was observed when surfactants were combined. The reduced mechanical strength of the modified VPS needs attention.

Introduction

A surfactant is defined as a material that can greatly reduce the surface tension of water when used at very low concentrations. The surfactants have an inherent amphiphilic character due to the polarity difference between the head and tail of the molecules. In the head, a water-soluble section confers a polar character, whereas in the tail there is a non-polar end, i.e. a water insoluble moiety [1]. Due to these characteristics, surfactants are amongst the most versatile chemicals and are used in a diverse range of products, including pharmaceuticals, detergents, and bio medical technologies.

In dentistry, surfactants are seldom used in dental materials. The academic research on this topic, in dentistry, is also very scarce. Some companies (e.g. 3M ESPE, Dentsply, Kettenbach) have paid attention to the surfactants technology, with some patents deposited [2-4]. It is known that some manufacturers add non-ionic surfactants to confer a more hydrophilic profile to vinylpolysiloxane (VPS), for example [5-7]. The choice for using nonionic surfactants lays in the fact that they do not complex with the platinum catalyst during VPS polymerization, unlike anionic and cationic surfactants. The surfactants act in the silicone surface by changing its polarity and improving wettability by water [8].

VPS impression materials have good properties such as dimensional stability, tear resistance [9], and biocompatibility. However, the detail reproduction, one of the main requirements for impression materials [10], is still deficient under critical moisture conditions, such as in the impression of abutment cervical lines in subgingival areas. This is as effect of the incompatibility polarity caused by the difference between the polar oral environment and the nonpolar, highly hydrophobic impression material. This incompatibility might affect the wetting and flow of the VPS over the dental and periodontal surfaces.

The high hydrophobicity of the VPS, derived from its nonpolar polysiloxane links [11], might also generate impression failures due to air entrappment [5]. Air bubbles can be formed either during impression or fabrication of stone models [12]. These limitations may ultimately result in failures in the restorative treatments [13,14]. When added to VPS, the non-ionic surfactants exhibit an ethoxy polar segment that is oriented to the surface, while the nonpolar segment is oriented to the hydrophobic interior. The most commonly used hydrophobic segments are hydrocarbons, siloxanes, and fluorocarbons. It is known that fluorinated surfactants are the most effective in reducing the surface tension of water, followed by siloxanes and hydrocarbons [15]. Fluorosurfactants also are more stable and able to withstand adverse conditions due to the stability of the C–F bond [16]. In order to render dental VPS hydrophilic, it is necessary to investigate the impact of different nonionic surfactants classes and hydrophobic-hydrophilic balance of the surfactant.

The aim of the study was to evaluate which of the nonionic surfactant types (fluorocarbon, hydrocarbon, or siloxane) is the most suitable to be added, individually or in combination, to an experimental dental VPS impression material to render it hydrophilic without significantly affecting its other properties.

Materials and methods

Surfactants added to the VPS

The experimental VPS impression material without surfactants (light-bodied consistency) was produced by the company Yller (Yller Biomaterials, Pelotas, RS, Brazil). The basic composition of the VPS is described in Table 1. Three different types of nonionic surfactants were added to the VPS: fluorocarbon (F), hydrocarbon (H), and/or siloxane (S) surfactants, all supplied by Yller. The surfactants were added at mass fractions of 1%, 3%, or 5% to both paste and catalyst pastes. In a first series, the addition of each surfactant was evaluated separately. In a second series, the combination of more than one type of surfactant was tested. The surfactants were added to the pastes, mixed for 60 s at 3500 rpm using a centrifugal mixer (SpeedMixer DAC150; FlackTek, Landrum, SC, USA) and packed into cartridges. For all tests, the base and catalyst pastes were mixed using dispensing guns and automix syringes.

Surface tension of the surfactants

Surface tension of each surfactant was measured using a tensiometer (Theta Lite TL101; Biolin Scientific Inc., Finland) by the inverted pendant drop method. The surfactant was dissolved in deionized water (1:10 ratio) and automatically sucked into a syringe of the equipment. Recording started when the volume of the droplet was 4 µL. The surface tension was measured in real time for 10 s using 12 frames/s. The software automatically detected the curve formed around the drop and the means and standard deviations were calculated. The resulting data were analyzed comparatively.

Evaluation of the modified VPS

Water contact angles formed in the surface of the VPS were measured with the tensiometer using the sessile drop method, in two different times: immediately after mixing the base and catalyst pastes of the VPS (t=0, non-polymerized material) and 1 h after (t=60, polymerized, crosslinked material). The mixed VPS was placed onto the sampler and a 4 µL drop of deionized water was dropped on the VPS surface. The contact angle formed between the water droplet and the VPS was monitored in real time for 60 s using 2 frames/s. Data were analyzed qualitatively.

The viscosity of VPS was analyzed using a parallel plate rheometer (R/S-CPS+; Brookfield Inc., Middleboro, MA, USA) equipped with a temperature controller. A 0.5 mL volume of each VPS material was dispensed onto the lower plate and the upper plate, with 25 mm in diameter, was positioned with a 0.05 mm gap between plates. Viscosity (Pa.s) was measured for 600 s using 75 counts, 100 s^{-1} constant shear rate, and 23°C temperature. Data were analyzed qualitatively.

Detail reproduction test was carried according to ISO 4823:2000 standard using a metallic mold with three horizontal lines (widths 50 µm, 20 µm, and 75 µm) and two vertical lines (width 75 µm) intersecting the horizontal lines. An impression of the mold was carried and the intersection of the 20 µm horizontal line with the vertical lines was evaluated. After polymerization, the specimens (n=3) were removed and stored at room temperature (23°C) for 24 h. The specimens were observed using a stereomicroscope with 40× magnification. Continuous reproduction of the intersection with the 20 µm line (positive copy) was considered satisfactory detail reproduction.

Specimens for tensile strength and elastic strain analyses were obtained using a rectangular mold (50 mm × 16 mm × 1.5 mm) with a central constriction (8 mm), which formed hourglass-shaped specimens. The mold was filled with the experimental VPS and covered with a polyester strip and glass slide. The specimens (n=10 per group) were stored at room temperature for 24 h then tested in a mechanical testing machine (DL500; EMIC, São José dos Pinhais, PR, Brazil). For the test, two claws seized the ends of samples and moved them in opposite directions at a crosshead speed of 0.5 mm/min until failure. Data were analyzed using One-Way Analysis of Variance and Tukey’s *post hoc* test (α=0.05).

Results

Figure 1 shows the results for surface tension for the surfactants, used alone or in combination, dissolved in water. In all cases the surfactants reduced the surface tension as compared to water alone. The H surfactant presented the highest surface tension and the drop volume was 7.19 µL. The group that combined all types of surfactants (F+S+H) was the most efficient in reducing the surface tension, consequently leading to the formation of the smallest water drop volume (1.74 µL). The other groups presented intermediate results.

The contact angle presented different patterns of wettability, as shown in Figures 2 to 5 (Figs. 2, 3: surfactants added alone; Figs. 4, 5: surfactants added in combination). All groups had the contact angles drastically reduced 10 s after the initial of analysis (Fig. 2). The lowest contact angle at t=0 in groups with surfactants added alone was found for F 5% (~15º). The contact angle of many groups with surfactant added was reduced to zero after the first 25 s (Fig. 3), with F3%, F5% and S5% groups had faster reduction, reaching zero in the first 10 s. The synergy between surfactants at t=0 (Fig. 4) indicates excellent results in rendering the VPS hydrophilic, with the exception of S+H groups and F+H 1%. In the analysis at t=60 (Fig. 5), it was observed that the S+H group had no synergistic effect and did not reduce the contact angle as efficiently as the other groups did. F+H 1% and F+S 1% presented an initial resistance to reduce the contact angle but reached final contact angles of zero. In all cases, the control VPS kept a high water contact angle (90º) for all analysis and times.

Results for viscosity are shown in Figures 6 (surfactants used alone) and Figure 7 (surfactants used in combination). The viscosity decreased and the induction time was delayed with increasing surfactant concentration. The S groups had the most appreciable reduction in viscosity. The induction times of H groups and F 1% were less affected as compared with the other materials. The modified VPS, irrespective of surfactant type or concentration, had higher polymerization time as compared to the control VPS. In some cases, no detectable change in viscosity was observed during the 10 min analysis, suggesting no appreciable crosslinking.

All VPS materials modified with surfactants used alone, irrespective of their concentration, reproduced continuously the 20 μm line, presenting satisfactory detail reproduction. The same did not happen for some combinations and concentrations of surfactants: F+S 3% and 5%, all H+S or F+S+H combinations did not copy the 20μm line since these materials apparently did not complete polymerization and crosslinking in the time frame of the test (up to 10 min).

Table 2 shows the results of the mechanical tensile strength test. The VPS with F surfactant showed no significant differences between three different concentrations analyzed. When surfactants were added at 1 wt%, groups with surfactants alone were statistically similar and showed greater tensile strength than surfactants combined. The F+S+H presented the poorest results in all concentrations. For concentrations of 3% and 5%, the groups F and H were similar.

Discussion

Surface tension is a physical phenomenon characterized by an elastic tendency of the fluid surface in acquiring the smallest area possible. This phenomenon occurs because while the molecules located inside the liquid are attracted equally in all directions, the molecules located at the surface suffer only side and internal attraction forces. This behavior can be easily observed when a water droplet is dispensed and while in free fall it assumes a perfectly spherical shape. Likewise, when deposited onto a nonpolar surface, the attractive forces between the water molecules are stronger than the attraction forces with the substrate, thus generating difficulty for the drop to spread on the surface.

For water to spontaneously spread over a solid surface it is necessary that the surface tension is less than the surface energy of the solid. Water has a surface tension of about 72 mN/m. Substrates such as silica-based glasses, with surface energy close to 78 mN/m, are easily wet by water, while polydimethylsiloxanes, with surface energies between 19 and 22 mN/m [17,18], are highly water repellent. The dynamic liquid–solid interfacial behavior has direct implications on the use of VPS impression materials in dentistry.

According to a study by Hrncir and Rosina [19], human blood has a surface tension of 52 mN/m at 37°C. Kawai et. al [20] showed that human saliva normally has a surface tension of approximately 49 mN/m. Although having lower surface tension than water itself, blood and saliva still have higher surface energy than VPS, leading to a difficult interaction between the oral tissues with VPS. When considering the preparation of stone models, the difficulty of interaction between materials is even more pronounced since the aqueous dispersion of calcium sulfate in water has a surface tension of approximately 111 mN/m [21].

Surfactants, when dissolved in water, form aggregates known as micelles, in which the hydrophobic tail lines in the center of the aggregate and the hydrophilic head of the surfactant stays in contact with the liquid on the outside. This mechanism reduced the cohesive forces of water, leading to reduced surface tension. As can be observed in Figure 1, the surface tension of water was drastically reduced upon mixture with all surfactants. Even the less efficient surfactant in reducing water surface tension (H) showed a reduction of as least 42%. When using surfactants alone, it was possible to obtain surface tension below 17 mN/m (F), i.e., a value lower than the surface energy of the VPS. In an endeavor to seek synergistic effect of the different surfactants, binary and ternary compositions were formulated, with only the ternary component demonstrating synergistic effects. The combination of the three surfactants caused a significant synergistic effect in reducing the surface tension of water to 9.54 mN/m.

Having in mind the ability of the surfactants in reducing the water surface tension, understanding the contact angle data observed in this study is easier. As shown in Figure 2 (analysis of the non-polymerized VPS), the control group showed a water contact angle of approximately 90° during the 60 s observation. The addition of surfactants, regardless of their type or concentration, significantly reduced the contact angles. It is clearly observed that the H surfactant type was less efficient than the S or F types, which generated contact angles below 30°. The same pattern of behavior can be observed in Figure 3 (analysis of the polymerized VPS). However in this case, it was possible to observe 0° contact angles, probably due the ability of the surfactant molecules to align themselves with the hydrophobic tail into the material and the hydrophilic head to the surface. A hydrophilic character before polymerization is necessary for the wetting of the material with the moist oral surfaces; hydrophilicity after polymerization is important to allow proper wetting of the gypsum material when obtaining stone models.

When the surfactants were combined (Figs. 4 and 5) a synergistic effect in reducing the contact angles was observed. Overall, when the combinations had fluorocarbon surfactants, contact angles near 0° were observed for both polymerized and non-polymerized VPS. This can be explained by their greater capacity of the fluorosurfactants in reducing the surface tension of water and self-aligning with the hydrophobic part, leaving the hydrophilic domains at and silicone surface.

Due to the complexity of the combined actions of different surfactants, it is difficult to explain the mechanism by which this synergistic effect occurs. However, the observed data are consistent with other studies in the literature [22,23]. As shown in the control group on Figure 6, the polymerization of VPS has an induction period in the first seconds after mixing; although hydrosilation reactions are occurring, it is still not possible to observe an increase in the VPS viscosity. Afterwards, the viscosity starts to increase at an accelerated rate. It was possible to verify that all surfactants used, regardless of their concentration or used alone or in combination, delayed the viscosity development. For many groups, this delay led to incomplete polymerization, interfering with the study of the detail reproduction. It is hypothesized that the presence of surfactants, which invariably presents –OH groups in their structure, has led to a delay in the crosslinking by poisoning or inhibiting the platinum catalyst, in turn affecting the overall properties of the final product. These competing agents or impurities can bind to the platinum catalyst avoiding it to coordinate with the alkene C=C groups, thereby inhibiting effective crosslinking.

As shown in Table 1, the addition of surfactants significantly reduced the mechanical strength of the VPS. The presence of –OH groups in the surfactant chain makes, during the addition reaction, the hydrogens of the crosslinker to be released as H_2 gas, incorporating a large number of bubbles in the material [24]. These bubbles, together with the delay in the polymerization, are primarily responsible for the drastic reduction in the tensile strength. Regardless of the class of surfactants used, there is a presence of residual –OH groups, alcohols, or water incorporated into the material due to its hygroscopic behavior. Additionally, it should be considered that the surfactants used could have acted as a plasticers because they are unreactive from the viewpoint of crosslinking. In order to solve this problem and keep the gain hydrophilicity, surfactants with blocked ethoxylated groups without the presence of –OH should be pursued; The ideal surfactant would be absolutely anhydrous and have reactive functional groups for the crosslinking process.

Conclusions

The addition of up to 5 wt% of nonionic fluorocarbon, siloxane, and/or hydrocarbon surfactants was able to render a vinylpolysiloxane experimental impression material hydrophilic, both before and after polymerization. Increased hydrophilicity was observed when the three surfactants were used in combination. The reduced mechanical strength of the modified materials, however, still needs attention.

Acknowledgments

A.O.O is grateful to CNPq/Brazil for a PhD scholarship. R.R.M. is grateful to CNPq/Brazil (grant 305890/2014-0). The authors thank LAMAD from UFRGS/Brazil for support with the tensiometer.

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Table 1. Composition of the experimental vinylpolysiloxane impression material tested*

Base paste	Catalyst paste
Vinylpolysiloxane	Vinylpolysiloxane
Quartz	Quartz
Silicon dioxide	Silicon dioxide
Polymethyl hydrogen siloxane	Platinum complex
Surfactant**	Surfactant**

*The material was produced by Yller Biomaterials (Pelotas, RS, Brazil).

**The synthesized surfactants were added to both base and catalyst pastes at 1 wt%, 3 wt%, or 5 wt%.

No surfactant was added to VPS control material.

Table 2. Means (standard deviations) for tensile strength (MPa) of the VPS impression materials (n=10)

VPS tested	Surfactant concentration		
	1 wt%	3 wt%	5 wt%
F	1.10 (0.12) ^{A,a}	1.05 (0.25) ^{A,ab}	1.06 (0.14) ^{A,a}
H	1.16 (0.14) ^{A,a}	1.25 (0.20) ^{A,a}	0.92 (0.18) ^{B,ab}
S	0.95 (0.15) ^{A,ab}	0.61 (0.06) ^{B,c}	0.48 (0.12) ^{C,d}
F+S	0.48 (0.06) ^{A,c}	0.33 (0.05) ^{B,d}	0.30 (0.03) ^{B,e}
F+H	0.84 (0.12) ^{AB,b}	0.89 (0.08) ^{A,b}	0.74 (0.10) ^{B,bc}
S+H	0.87 (0.12) ^{A,b}	0.62 (0.15) ^{B,c}	0.62 (0.13) ^{B,c}
F+S+H	0.17 (0.03) ^{B,d}	0.22 (0.03) ^{A,e}	0.22 (0.04) ^{A,f}

Distinct lowercase letters in the same column indicate significant differences between the VPS materials; distinct uppercase letters in a same row indicate significant differences between the surfactant concentrations ($P<0.05$). The reference value for the control group was 1.41 (0.19) MPa according previous study not yet published.

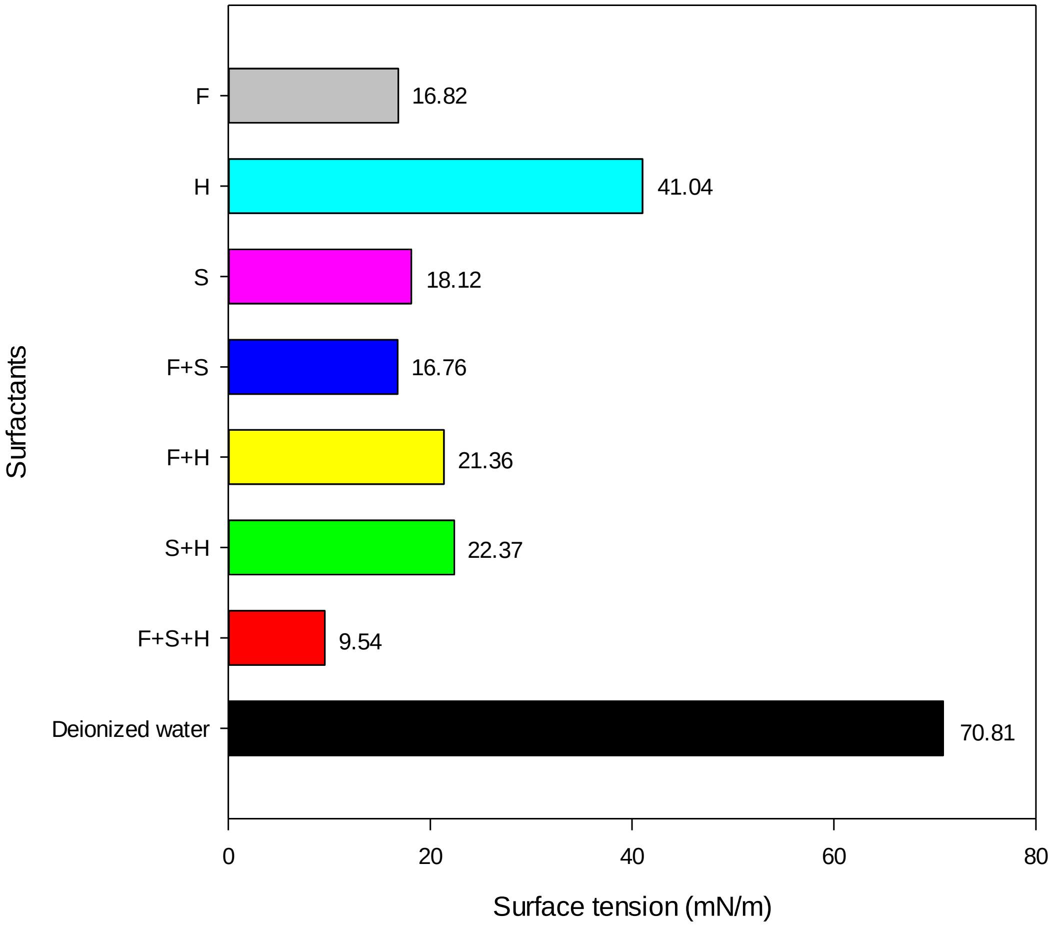

Figure 1 – Surface tension of the fluorosurfactants (alone or in combination) dissolved in water: F (fluorocarbon), H (hydrocarbon), (S) siloxane.

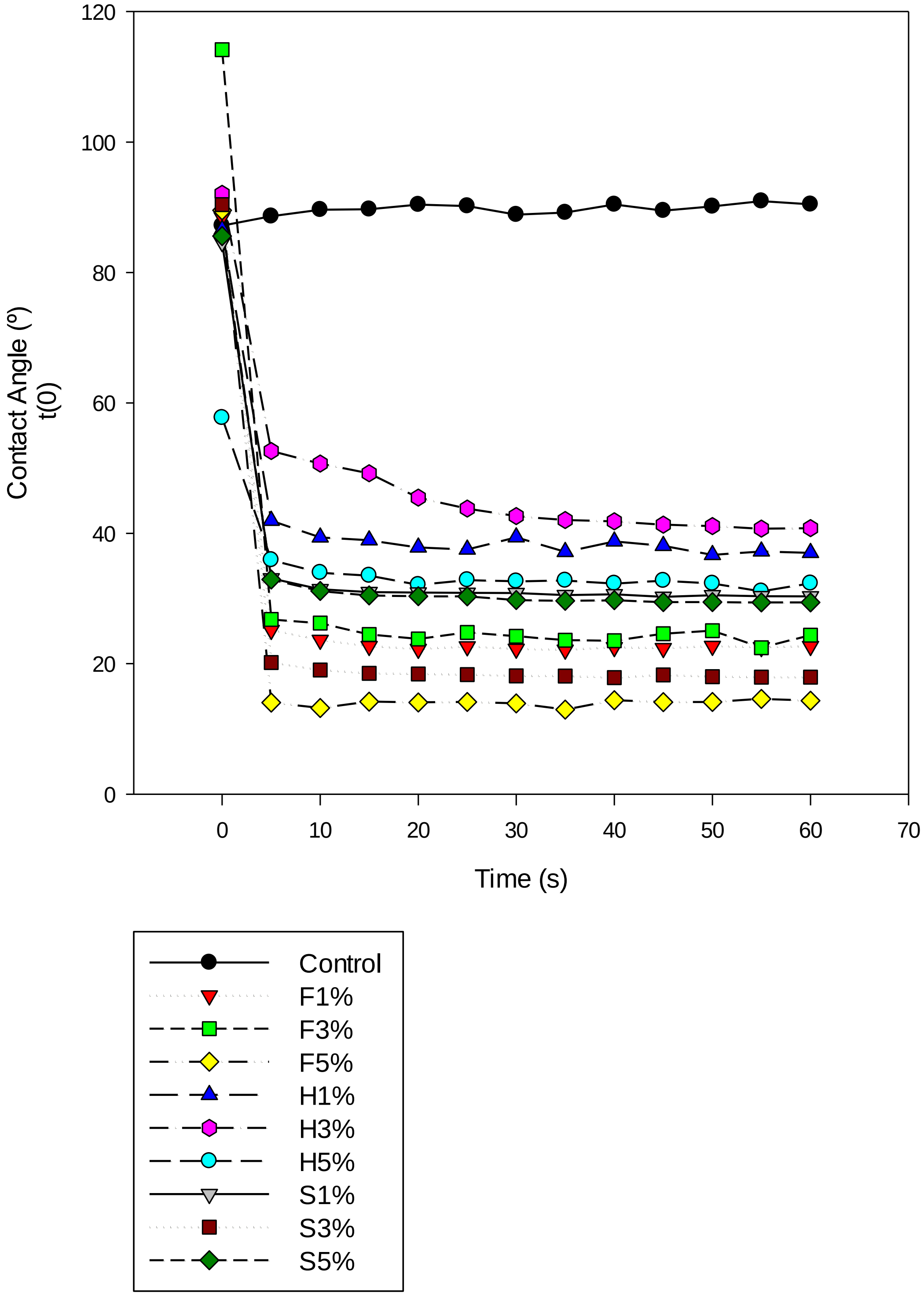

Figure 2 – Results for water contact angle formed with the VPS impression materials immediately after mixing the base and catalyst pastes at t=0 (non-polymerized VPS): F (fluorocarbon), H (hydrocarbon) and S (siloxane). Surfactants used alone are shown.

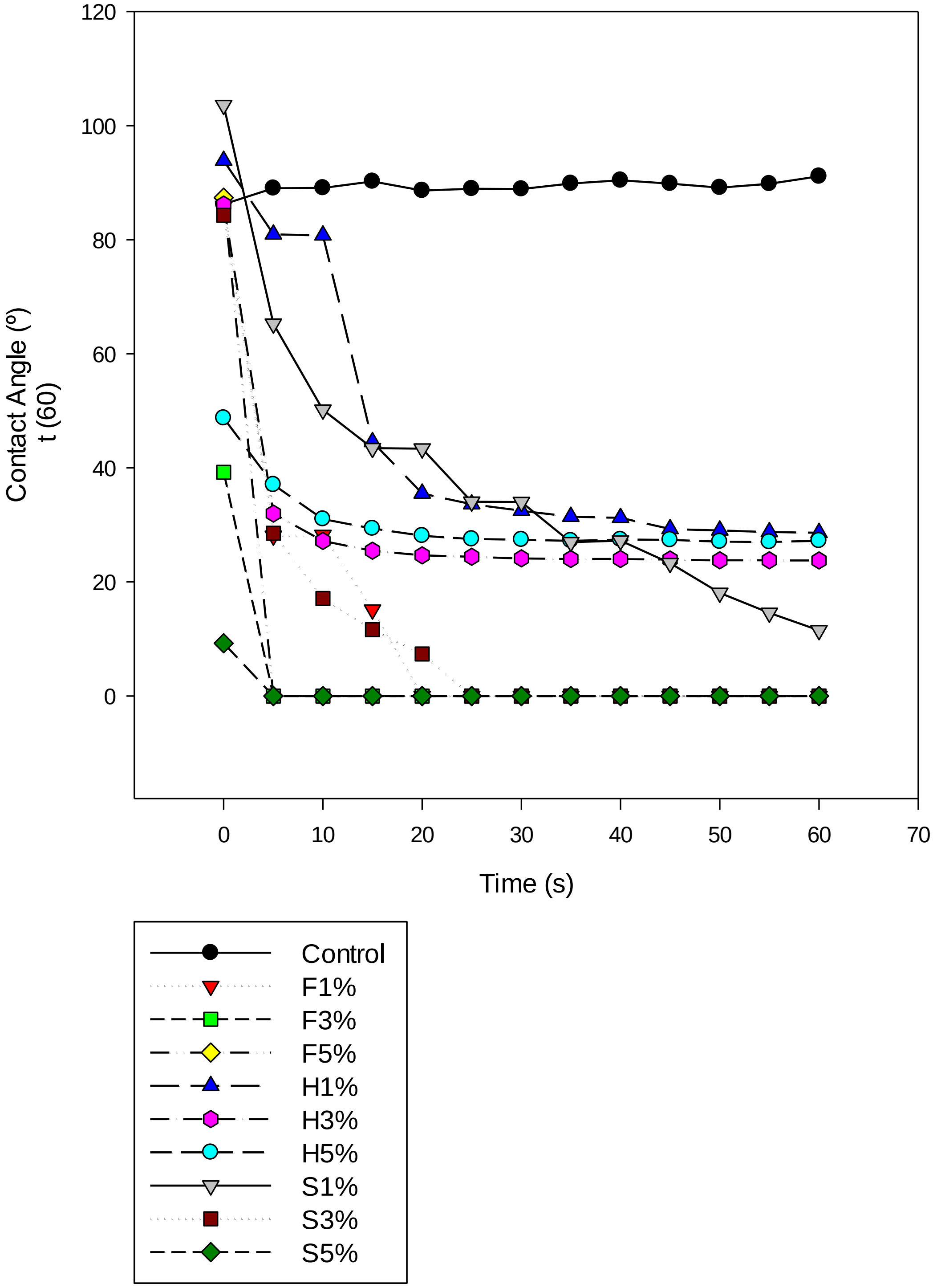

Figure 3 – Results for water contact angle formed with the VPS impression materials at t=60: F (fluorocarbon), H (hydrocarbon) and S (siloxane). Surfactants used alone are shown.

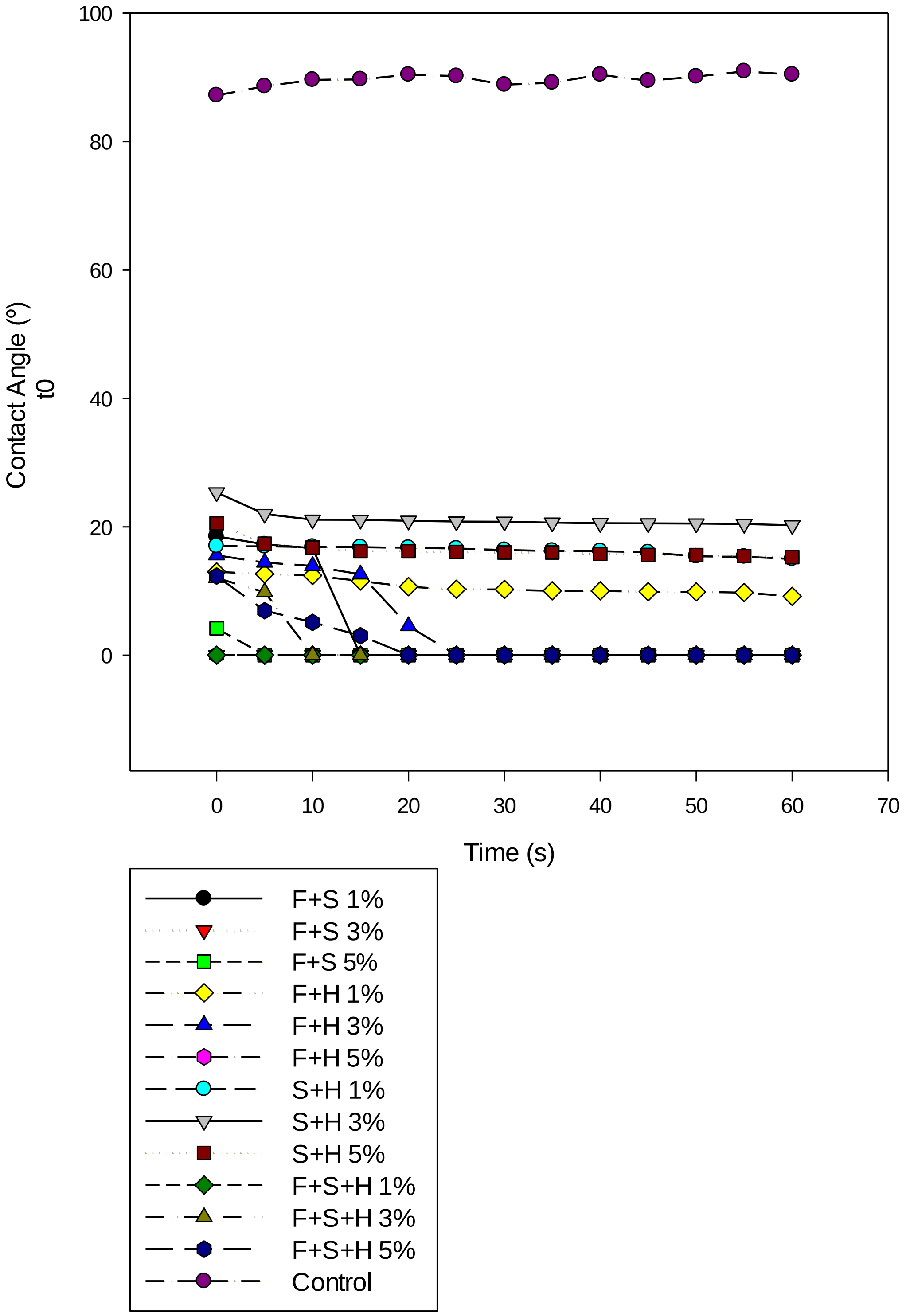

Figure 4 – Results for water contact angle formed with the VPS impression materials immediately after mixing the base and catalyst pastes at t=0 (non-polymerized VPS): F (fluorocarbon), H (hydrocarbon) and S (siloxane). Surfactants used in combination are shown.

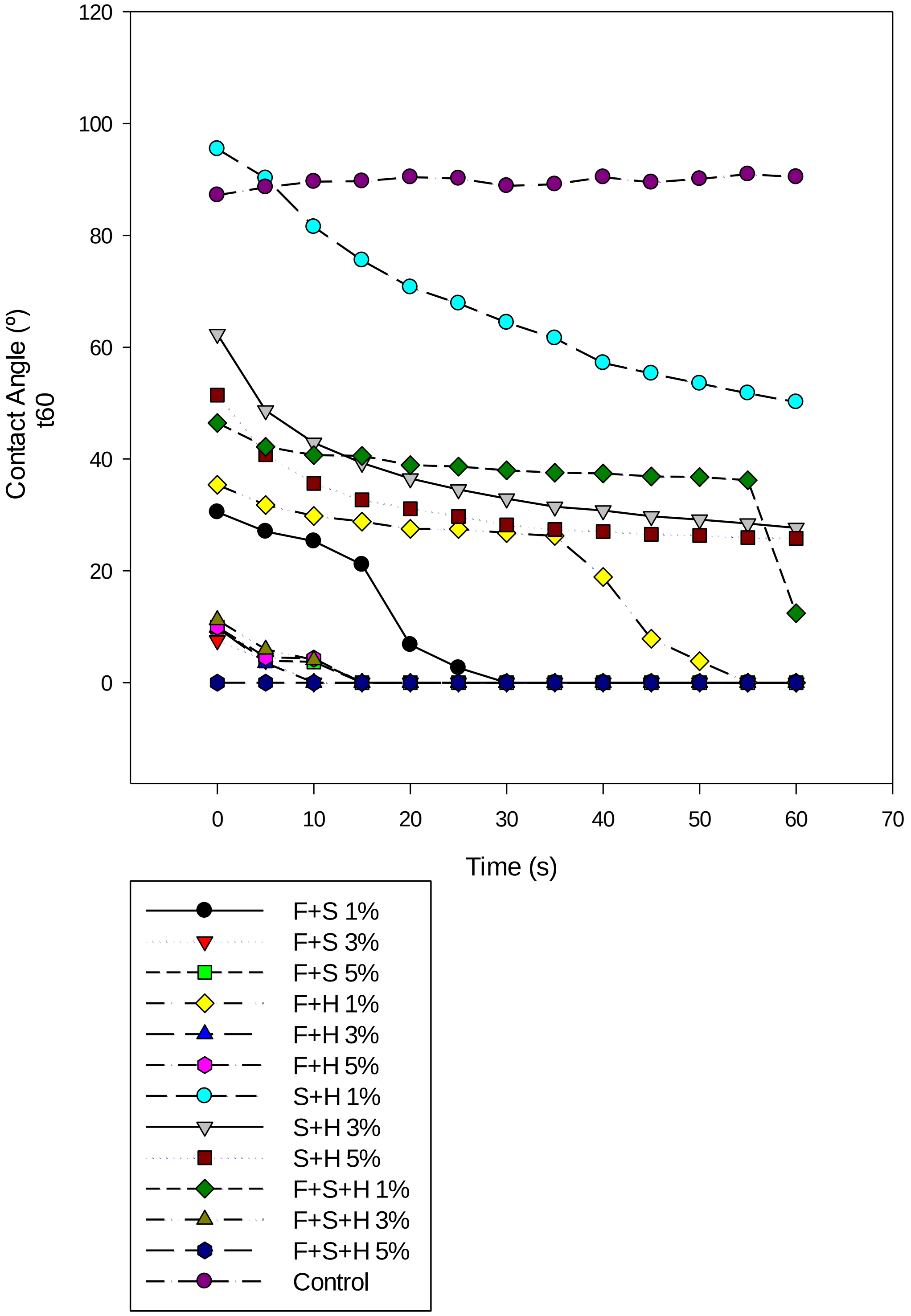

Figure 5 – Results for water contact angle formed with the VPS impression materials at t=60: F (fluorocarbon), H (hydrocarbon) and S (siloxane). Surfactants used in combination are shown.

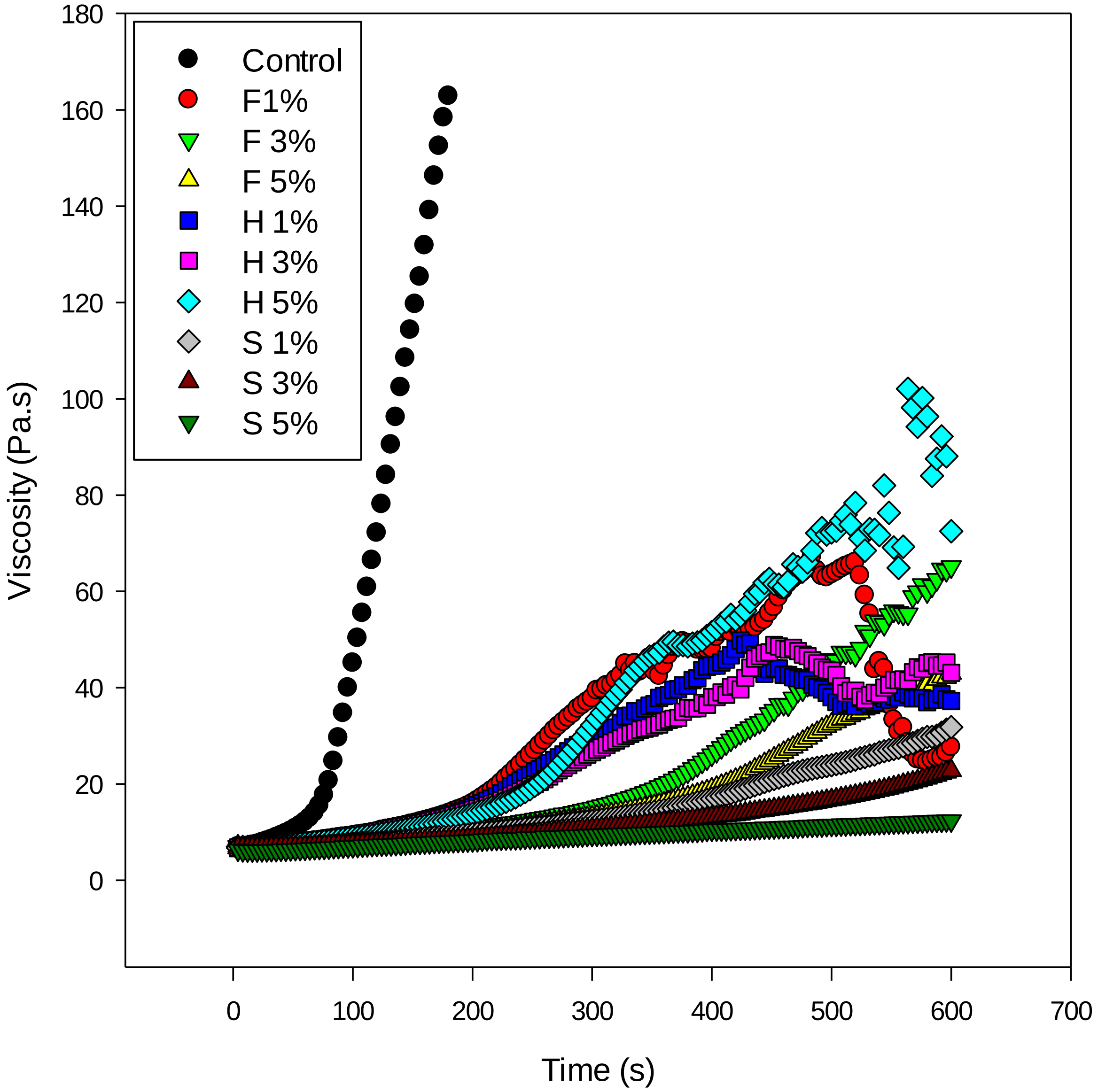

Figure 6 - Viscosity curves during mixture of the base and catalyst pastes of the VPS impression material modified with surfactants used alone.

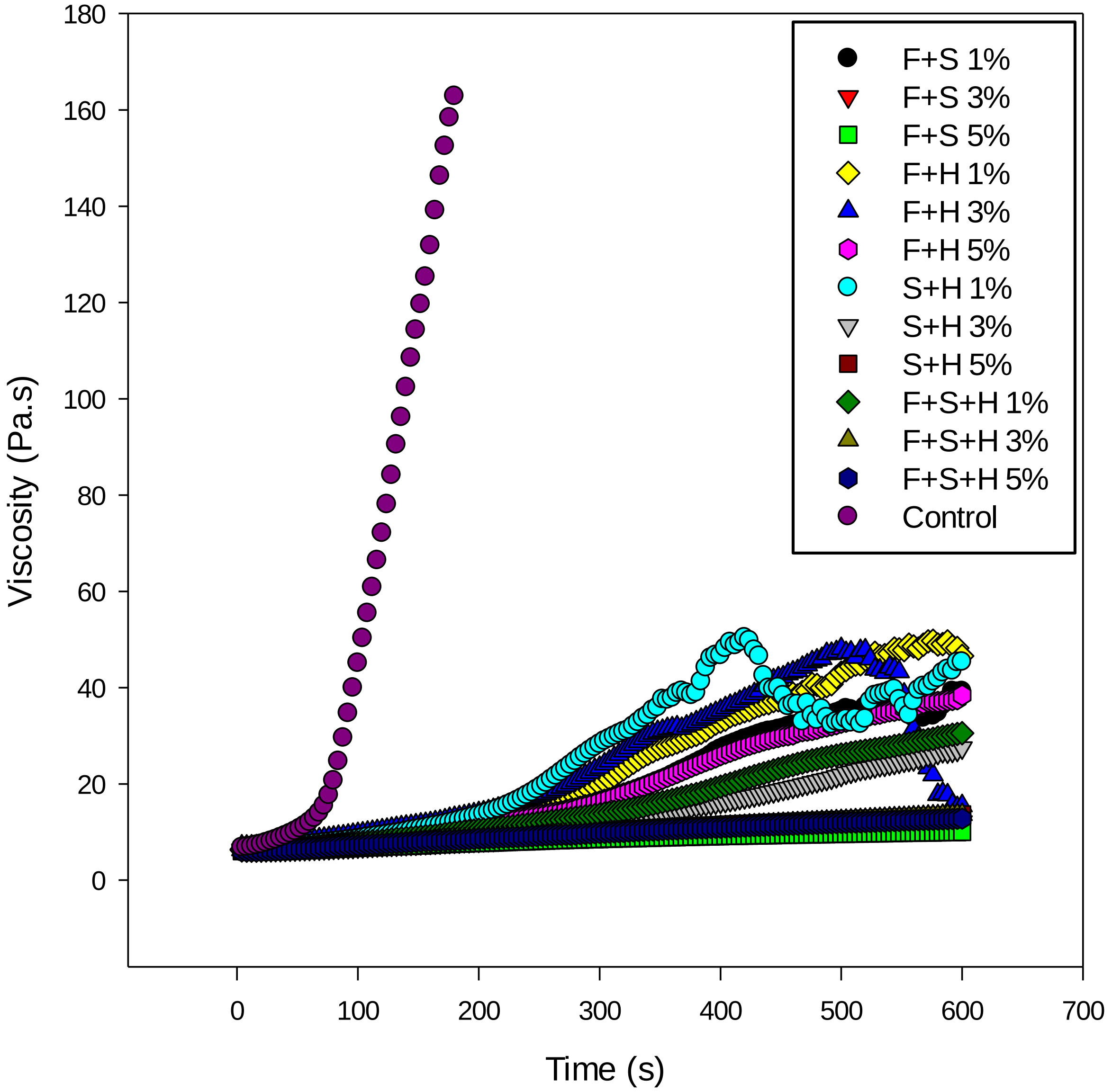

Figure 7 - Viscosity curves during mixture of the base and catalyst pastes of the VPS impression material modified with surfactants used in combination.

5 Artigo 2[2]

Synthesis of fluorosurfactants for use in dentistry

Short title: Synthesis of fluorosurfactants

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Keywords: Contact angle; fluorosurfactants; hydrophilicity; impression materials; NMR; vinylpolysiloxanes; synthesis; surface tension; surfactants; wetting.

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[2] Artigo formatado segundo as normas de periódico *Dental Materials.*

Abstract

Objectives: The aim of this study was to synthesize and characterize fluorosurfactants and evaluate their impact on properties and characteristics of vinylpolysiloxane (VPS) experimental impression materials.

Methods: Six fluorosurfactants were synthesized using polyethylene glycols of molar masses varying from 200 to 1,000,000 g/mol. The synthesis was followed by Fourier-transform infrared spectroscopy and confirmed by ^{1}H and ^{19}F NMR. Surface tension of the surfactants diluted in water was analyzed. The surfactants were added at 3 wt% to the base and catalyst pastes of a light body VPS material. In the control group no surfactant was added. The VPS properties evaluated were tensile strength, elastic strain, detail reproduction, water contact angle, and viscosity. Data were analyzed statistically ($p<0.05$).

Results*:* The fluorosurfactants reduced dramatically the surface tension of water, except for FS 600,000 and FS 1,000,000. The control group presented the highest tensile strength. All groups showed good detail reproduction. FS 200 and FS 400 rendered the VPS hydrophilic, reducing the water contact angle up to 85% compared to the control material. FS 400 e FS 500 reduced the viscosity and increased the VPS induction time.

Significance**:** The addition of FS 200 and FS 400 improved significantly the wettability, reduced the viscosity without changing the working time or elastic strain, but significantly reduced the tensile strength of the VPS. Fluorosurfactants may be used to tune the properties of VPS impression materials.

Introduction

Surfactants are amphiphilic organic compounds, i.e. substances that exhibit a double affinity and can be defined as molecules containing both hydrophobic (tails) and hydrophilic groups (heads) [1,2]. On one hand, this characteristic allows these molecules to have strong affinity to water since it yields lower surface tension between two liquids or between a liquid and a solid. On the other hand, these molecules may also have strong affinity to hydrophobic compounds, which is the case in most dental materials. The double affinity character of the surfactants is perfect to allow formation of a close contact between hydrophobic dental materials and the moist oral structures [3].

The use of surfactants is poorly explored in dentistry. There are many dental materials that could benefit from this technology, including dental adhesives [4,5], resin-based cements, periodontal cements, bleaching agents, and impression materials. Impression materials based on vinylpolysiloxane (VPS), for instance, are widely used in dentistry [3]. However, for some specific situations, such as impression in subgingival areas, the use of VPS is challenging [6]. The clinical accuracy of dental impressions depends on the flowing and wetting properties of VPS [7], which sometimes does not have proper wettability, dimensional stability, and working time.

To overcome limitations of VPS, a few manufacturers developed technologies and started adding nonionic surfactants to their VPS formulations [8-10]. Nonionic surfactants are the most suitable for use in VPS because they do not complex with the platinum catalyst present in the material. Some patents have reported the use of hydrocarbon, siloxanes, or fluorocarbon surfactants to render hydrophilicity to VPS [11-14]. Nevertheless, in unpublished pilot studies conducted by our group, it was noticed that only one of the commercial VPS impression materials analyzed showed a water contact angle of 20°, whilst all the other VPS materials had contact angles greater than 60°. This finding indicates a need for studies to improve the wetting properties of dental VPS impression materials.

Among the nonionic surfactants, the fluorosurfactants class is more efficient in reducing the surface tension [15] and improving the surface wettability [2]. Fluorosurfactants are amphiphilic molecules with fluorocarbon chains as the hydrophobic segment. The strong hydrophobic interactions and low van der Waals interactions exhibited by fluorinated chains dramatically increase the tendency of fluorinated amphiphiles to self-assemble in water and collect at interfaces, displaying stronger surface activity compared to hydrocarbon surfactants [16]. Fluorosurfactants can lower the surface tension of water down to a value half of what is attainable by using hydrocarbon surfactants [17,18]. This ability is derived from the lipophobic nature of fluorocarbons. The electronegativity of fluorine reduces the polarizability of the surfactants' fluorinated molecular surface, making them not as susceptible to London dispersion forces as hydrocarbon surfactants are. Fluorine has a large size atom and is the more electronegative element in periodic table [15]; the C–F bond is also the most stable single bond in organic chemistry [19,20]. For this reason, one disadvantage of fluorosurfactants in industrial use is their persistence in the environment. Nonetheless, due to its numerous advantages of fluorosurfactants used as additives in various materials, many new products with improved properties and biocompatibility appeared in recent years [21-25].

The aim of this study was first to synthesize and characterize a new series of fluorosurfactants with different molar masses and hydrophile-lipophile balance (HLB) values. The second purpose of the study was to identify which of the synthesized fluorosurfactants would be able to yield greater wettability to an experimental VPS impression material without significantly affecting its properties. The hypothesis tested was the use of fluorosurfactants would successfully improve the wettability of VPS.

Materials and methods

Synthesis of the fluorosurfactants

Different polyethylene glycol (PEG) molecules of varied molecular mass (Sigma-Aldrich, St. Louis, MO, USA) were used in the synthesis to compose the polar portion of the fluorosurfactants. For the apolar fraction, perfluorooctanoic acid (PFOA, Sigma-Aldrich) was used. Six different types of surfactants were synthetized, by Fischer esterification, transforming a carboxylic acid and an alcohol to an ester using 1 wt% *p*-toluenesulfonic acid (Vetec, Duque de Caxias, RJ, Brazil) as catalyst. The synthesis scheme is shown in Figure 1. The reagents and manufacturers are detailed in Table 1. The different fluorosurfactants were labelled as FS followed by the respective number of PEG used in the synthesis (e.g. FS 200 - fluorosurfactant synthesized with PEG 200).

PEG and PFOA were mixed at a 1:1 molar ratio in a 50 mL round bottom vessel connected to a reflux condenser, and kept under constant stirring at 600 rpm and 110°C temperature, for 24 h. The products' conversion was followed by thin layer chromatography and Fourier-transform infrared spectroscopy (Prestige 21 spectrometer; Shimadzu, Tokyo, Japan) equipped with an attenuated total reflectance device. The solvent was eliminated in a rotary evaporator connected to a vacuum cold trap (Marconi Ltda., Piracicaba, SP, Brazil) and the product was purified in a vertical glass column with alumina. Representative molecular structures of the fluorosurfactants synthesized are shown in Figure 1.

The obtained products were characterized by ^{1}H and ^{19}F nuclear magnetic resonance (NMR) spectroscopies (Varian-VXR 300 MHz; Agilent Technologies, Palo Alto, CA, USA), using deuterated chloroform as solvent and trifluoroacetic acid as an internal standard. The HLB of each nonionic surfactant synthesized was calculated according to the Griffin's formula: HLB = [20 × MWH/(MWH + MWL) = wt% hydrophile / 5], where MWH is the molar weight of the hydrophile and MWL is the molar weight of the hydrophobe.

Surface tension of each surfactant was measured using a tensiometer (Theta Lite TL101; Biolin Scientific Inc., Finland) by the inverted pendant drop method. The surfactant was dissolved in deionized water (1:10 ratio) and automatically sucked into a syringe of the equipment. Recording started when the volume of the droplet was 4 µL. The surface tension was measured in real time for 10 s using 12 frames/s. The software automatically detected the curve formed around the drop and the means and standard deviations were calculated. The resulting data were analyzed comparatively.

Fluorosurfactants added to VPS impression material

The experimental VPS without surfactants used in this study (light-bodied consistency) was produced by the company Yller (Yller Biomaterials, Pelotas, RS, Brazil). The basic composition is described in Table 2. The surfactants were added to both base and catalyst pastes of the VPS material at a 3 wt% concentration. The materials were mixed for 60 s at 3500 rpm using a centrifugal mixer (SpeedMixer DAC150; FlackTek, Landrum, SC, USA) and packed into cartridges. For all tests, the base and catalyst pastes were mixed using dispensing guns and automix syringes.

Specimens for tensile strength and elastic strain analyses were obtained using a rectangular mold (50 mm × 16 mm × 1.5 mm) with a central constriction (8 mm), which formed hourglass-shaped specimens. The mold was filled with the experimental VPS and covered with a polyester strip and glass slide. The specimens (n=10 per group) were stored at room temperature for 24 h then tested in a mechanical testing machine (DL500; EMIC, São José dos Pinhais, PR, Brazil). For the test, two claws seized the ends of samples and moved them in opposite directions at a crosshead speed of 0.5 mm/min until failure. Data were analyzed using One-Way Analysis of Variance and Tukey's *post hoc* test (α=0.05).

Detail reproduction test was carried according to ISO 4823:2000 standard using a metallic mold with three horizontal lines (widths 50 µm, 20 µm, and 75 µm) and two vertical lines (width 75 µm) intersecting the horizontal lines. An impression of the mold was carried and the intersection of the 20 µm horizontal line with the vertical lines was evaluated. After polymerization, the specimens (n=3) were removed and stored at room temperature (23°C) for 24 h. The specimens were observed using a stereomicroscope with 40× magnification. Continuous reproduction of the intersection with the 20 µm line (positive copy) was considered satisfactory detail reproduction.

Contact angles formed with water were measured with the tensiometer using the sessile drop method. The mixed VPS was placed onto the sampler and a 4 µL drop of deionized water was dropped on the VPS surface. The contact angle formed between the water droplet and the VPS was monitored in real time for 60 s using 2 frames/s. Data were analyzed qualitatively.

The viscosity of VPS was analyzed using a parallel plate rheometer (R/S-CPS+; Brookfield Inc., Middleboro, MA, USA) equipped with a temperature controller. A 0.5 mL volume of each VPS material was dispensed onto the lower plate and the upper plate, with 25 mm in diameter, was positioned with a 0.05 mm gap between plates. Viscosity (Pa.s) was measured for 300 s using 75 counts, 100 s^{-1} constant shear rate, and 23°C temperature. Data were analyzed qualitatively.

Results

Synthesis of the fluorosurfactants

After 24 h, end of the synthesis was detected in the FTIR taking into account the disappearance of the perfluorooctanoic acid carbonyl peak at ~1754 cm^{-1} and appearance of peaks in the 1780 cm^{-1} region due to the formation of carbonyl ester. In Figure 2, representative FTIR spectra of these peaks are shown. The syntheses were confirmed by ^{19}F and ^{1}H NMR spectroscopies, as shown in Figure 3.

The reactions produced fluorosurfactants of different molar masses and different HLB values, resulting in molecules with characteristics of unique wettability. Results of the HLB calculations are displayed in Table 1. The HLB value increases up to 306% with increased PEG molar masses, but no increase in HLB occurs from PEG 100,000 until PEG 1,000,000. As regards the surface tension analysis (Figure 4), Most fluorosurfactants reduced dramatically the water surface tension. FS 600,000 and FS 1,000,000 had higher values of surface tension than the other surfactants. Deionized water alone had a surface tension well above the values for all surfactants diluted in water.

Properties of the VPS impression materials

Table 3 shows the results of the tensile strength and elastic strain tests carried out with the VPS impression materials. The control VPS (no surfactant) presented significantly higher tensile strength than all modified VPS materials. Reduced elastic strain as compared to the control VPS was observed only for VPS modified with FS 1,000,000. All VPS materials tested reproduced continuously the intersection with the 20 µm line, presenting satisfactory detail reproduction. Results for the water contact angle formed with the impression materials indicate different patterns of wettability

(Figure 5). The groups FS 1,000,000, FS 600,000, and Control showed higher contact angles, around 90°. In contrast, groups FS 200 and FS 400 had very low contact angles, around 15º. The water contact angles were reduced up to 84.75% in the modified VPS as compared with the Control material. The groups FS 200, FS 400, and FS 500 showed lower maximum viscosity (near to 60 Pa.s) than the Control material (Figure 6), but only FS 400 and FS 500 increased the VPS induction time. The other groups presented viscosities and induction times similar to the Control group.

Discussion

Direct Fischer esterification was the method used for the synthesis of the fluorosurfactants this study [26]. For the viability of the reaction (Figure 1), a carboxylic acid group, an alcohol, and an acid catalyst are necessary. The reaction is initiated by the protonation of carbonyl in the carboxylic acid, making it more electrophilic. In this state, the oxygen of the alcohol function promotes a nucleophilic attack on the carbon of the protonated carbonyl, creating a tetrahedron intermediate. With the instability of this intermediate, the alcohol oxygen is deprotonated and the hydrogen abandoning facilitates departure of the –OH group of the tetrahedron intermediate, allowing elimination of an H_2O molecule. The carbonyl is then finally deprotonated, resulting in the desired ester product and H_3O by-product. For the quantitative success of the reaction, continuous removal of H_3O by-products is desirable since the reaction mechanism is reversible and the ester can be hydrolyzed by an acidic medium.

PFOA was selected as carboxylic acid, with an 8-carbon structure protected by 15 fluorine atoms. The apolar character of this segment becomes hydrophobic; a lipophobic effect is also possible due to the fluorocarbons that are less susceptible to London dispersion forces than hydrocarbons. As alcohol for the reaction and formation of the polar portion of the surfactant, polymers derived from ethylene oxide (PEGs) were selected, with different molar masses, containing –OH groups at both ends. The use of different PEGs lead to different HLB value, which was the main objective of this study. This design allowed the obtaining of fluorosurfactants with large amplitude of HLB values, ranging between 6.5 and 19.9.

Use of the surfactants synthesized in this study promoted a dramatic reduction in the surface tension of water. The surfactants reduce the cohesive forces between water molecules, thereby reducing the surface tension of the liquid. This effect was more evident for surfactants synthesized using PEG with molar masses up to 100,000 g/mol. For FS 600,000 and FS 1,000,000, it is hypothesized that the high molecular weight may have limited the reduction in water surface tension by two factors: 1) due to the high molar mass, there is a difficulty in complete dissolution of the products in water; 2) the high molar mass leads to increased viscosity of the fluid, consequently influencing the surface tension.

One of the desirable characteristics of a VPS is to present high compatibility with moist oral tissues during intraoral application. The VPS without surfactant (control) had a contact angle formed with water of approximately 90°. When FS 200 and FS 400 were added, water contact angles around 20° were observed, indicating the surfactants increased to a large extent the hydrophilicity of the VPS. FS 500, with a similar molar mass to FS 400, was not able to render the same effect to the VPS. This finding is likely a result of the methylation of the hydrophilic end in the ethoxy chain. Similarly, the surfactants with high molar masses showed little effectiveness in reducing the contact angles, most likely due to the difficulty of solubility of these compounds in the silicon substrate and a greater difficulty for the alignment of the hydrophilic portion on the surface of the material.

Besides rendering increased hydrophilicity, the surfactant should not interfere with the mechanical properties of the VPS. Irrespective of the molar mass, all fluorosurfactants led to significant reductions in tensile strength. The main reason for that behavior is interference of the surfactant in the silicone crosslinking reaction. During addition polymerization of the VPS, the –OH groups of the surfactant chain cause the hydrogen atoms of the crosslinker to be released as H_2 gas, incorporating a large number of air bubbles in the material [27]. These bubbles are the main responsible for the reduction in tensile strength. In addition, it needs to be considered that purification of fluorosurfactants is technically complex. The possible presence of intermediate species and other impurities may also potentially interfere in the polymerization process.

Another point that may help to elucidate the strength reduction is that due to the high hygroscopic nature of surfactants, it is possible that the presence of H_2O, even in small concentrations, may contribute to the release of hydrogen during crosslinking. The crosslinking kinetics was evaluated indirectly by analyzing the evolution of viscosity after mixing the base and catalyst pastes. As can be seen in Figure 6, the control group showed an induction period (i.e., no detectable crosslinking) of approximately 75 s; after this point, fast viscosity evolution was observed. After approximately 180 s, it is observed an apparent viscosity reduction of the material, which in fact reflects the mechanical fragmentation of the material due to the continuous shear stress imposed by the rheometer. When comparing the induction periods, groups FS 400 and FS 500 showed induction periods longer than 100 s. This delay in crosslinking may be a result of contamination or inhibition of the platinum catalyst by other reagents, affecting the overall properties of the final product. These competing agents or impurities can bind to the platinum catalyst avoiding its coordination with the alkene C=C groups, thereby inhibiting effective crosslinking.

Fluorosurfactants with lower molar masses HLB values below 10 promoted effective wetting effect of water on the surface of VPS. Even in the first seconds after the contact of water with the silicone contact angles less than 20° could be observed. This condition, from a clinical point of view, is highly desirable because even in moist conditions the material could be capable of flowing on the surface and establishing intimate contact with the oral structures. However, a major challenge still remains: to render a low water contact angle without compromising the mechanical properties of

VPS. In order to achieve this goal, we suggest further studies focusing on the development of techniques for separation and purification of fluorosurfactants to obtain these with high purity and, if possible, with complete absence of free –OH groups.

Conclusions

Fluorosurfactants of varied hydrophile-lipophile balance (HLB) values, successfully obtained by Fischer esterification, were able to dramatically alter the hydrophilicity of dental vinylpolysiloxane impression materials (surfactants with HLB below 10 were the most efficient).Thus, the hypothesis tested in this study was accepted. However, as the addition of the fluorosurfactants also interfered with the mechanical properties of the elastomer material, there is still a challenge to obtain fluorosurfactants that may simultaneously increase the hydrophilicity without affecting the mechanical properties of elastomers.

Acknowledgments

A.O.O is grateful to CNPq/Brazil for a PhD scholarship. R.R.M. is grateful to CNPq/Brazil (grant 305890/2014-0). The authors thank the Chemical Institute of UFRGS/Brazil for NMR analysis and LAMAD from UFRGS/Brazil for contact angle support.

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Table 1. Reagents used in the synthesis and results for HLB calculation of the synthesized fluorosurfactants

Reagent	Average molar mass (g/mol)	Linear formula	Supplier	HLB
PEG 200	200	$H(OCH_2CH_2)_nOH$	Sigma-Aldrich	6.5
PEG 400	400	$H(OCH_2CH_2)_nOH$	Sigma-Aldrich	9.8
PEG methyl eter	500	$CH_3(OCH_2CH_2)_nOH$	Sigma-Aldrich	10.9
PEG 100,000	100,000	$H(OCH_2CH_2)_nOH$	Sigma-Aldrich	19.9
PEG 600,000	600,000	$H(OCH_2CH_2)_nOH$	Sigma-Aldrich	19.9
PEG 1,000,000	1,000,000	$H(OCH_2CH_2)_nOH$	Sigma-Aldrich	19.9
Perfluorooctanoic acid	414.17	$CF_3(CF_2)_6COOH$	Sigma-Aldrich	-
p-toluenesulfonic acid	190.22	$C_7H_8O_3S.H_2O$	Vetec	-

PEG: polyethylene glycol. HLB: hydrophile-lipophile balance calculated for the synthesized surfactants.

Table 2. Composition of the experimental vinylpolysiloxane impression material tested*

Base paste	Catalyst paste
Vinylpolysiloxane	Vinylpolysiloxane
Quartz	Quartz
Silicon dioxide	Silicon dioxide
Polymethyl hydrogen siloxane	Platinum complex
Surfactant**	Surfactant**

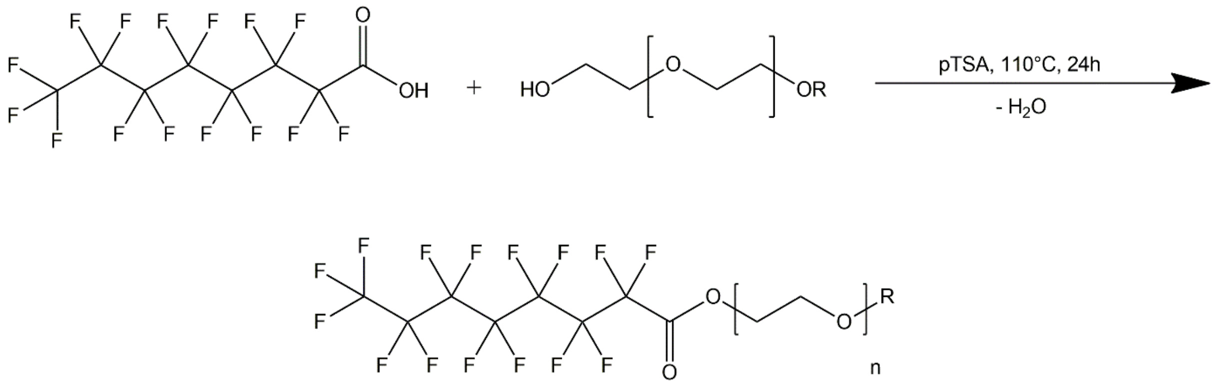
*The material was produced by Yller Biomaterials (Pelotas, RS, Brazil).

**The synthesized surfactants were added to both base and catalyst pastes at 3 wt%. No surfactant was added to VPS control material.

Table 3. Means (standard deviations) for tensile strength and elastic strain of the VPS impression materials (n=10)

VPS tested	Tensile strength, MPa	Elastic strain, mm
FS 200	0.86 (0.17)^{BC}	23.1 (4.6)^{A}
FS 400	0.86 (0.13)^{BC}	21.8 (4.2)^{A}
FS 500	0.68 (0.13)^{C}	19.0 (4.8)^{AB}
FS 100,000	0.75 (0.25)^{BC}	19.2 (4.8)^{AB}
FS 600,000	0.95 (0.15)^{B}	20.9 (3.1)^{AB}
FS 1,000,000	0.74 (0.13)^{BC}	15.2 (3.2)^{B}
Control	1.41 (0.19)^{A}	23.1 (3.9)^{A}

Distinct letters in the same column indicate significant differences between the materials (P<0.05).



n= 5; 9; 11; 34; 136; 2,273; 13,636; 22,727
R = H or CH_3

Figure 1 – Synthesis scheme of the fluorosurfactants by Fischer esterification (pTSA: *p*-toluenesulfonic acid).

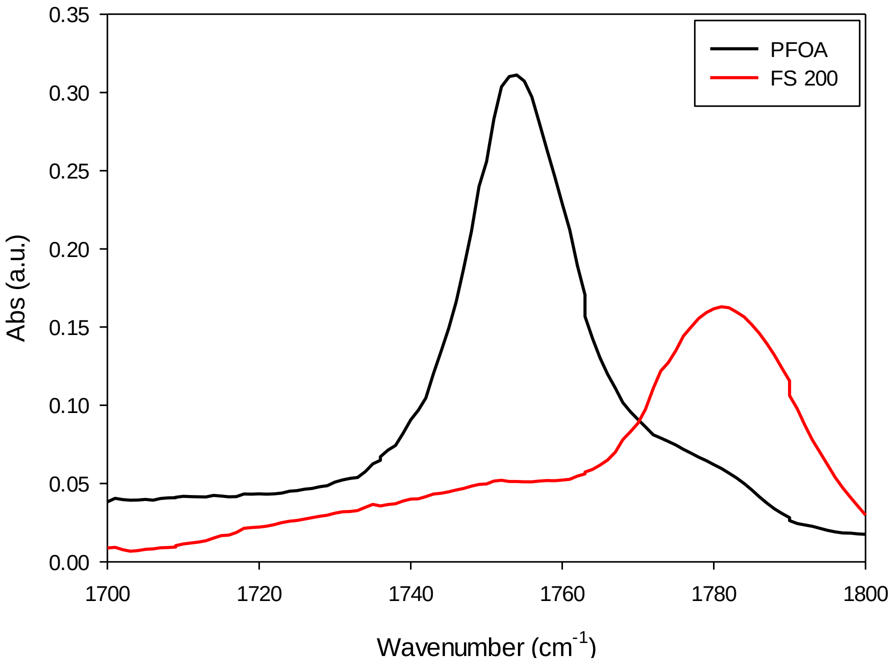


Figure 2 – Representative FTIR spectrum of the synthesized fluorosurfactant FS 200 (red line). Disappearance of the perfluorooctanoic acid carbonyl peak at ~1754 cm^{-1} (black line) and appearance of the a peak at ~1785 cm^{-1} due to the formation of carbonyl ester indicated the end of the synthesis reaction.

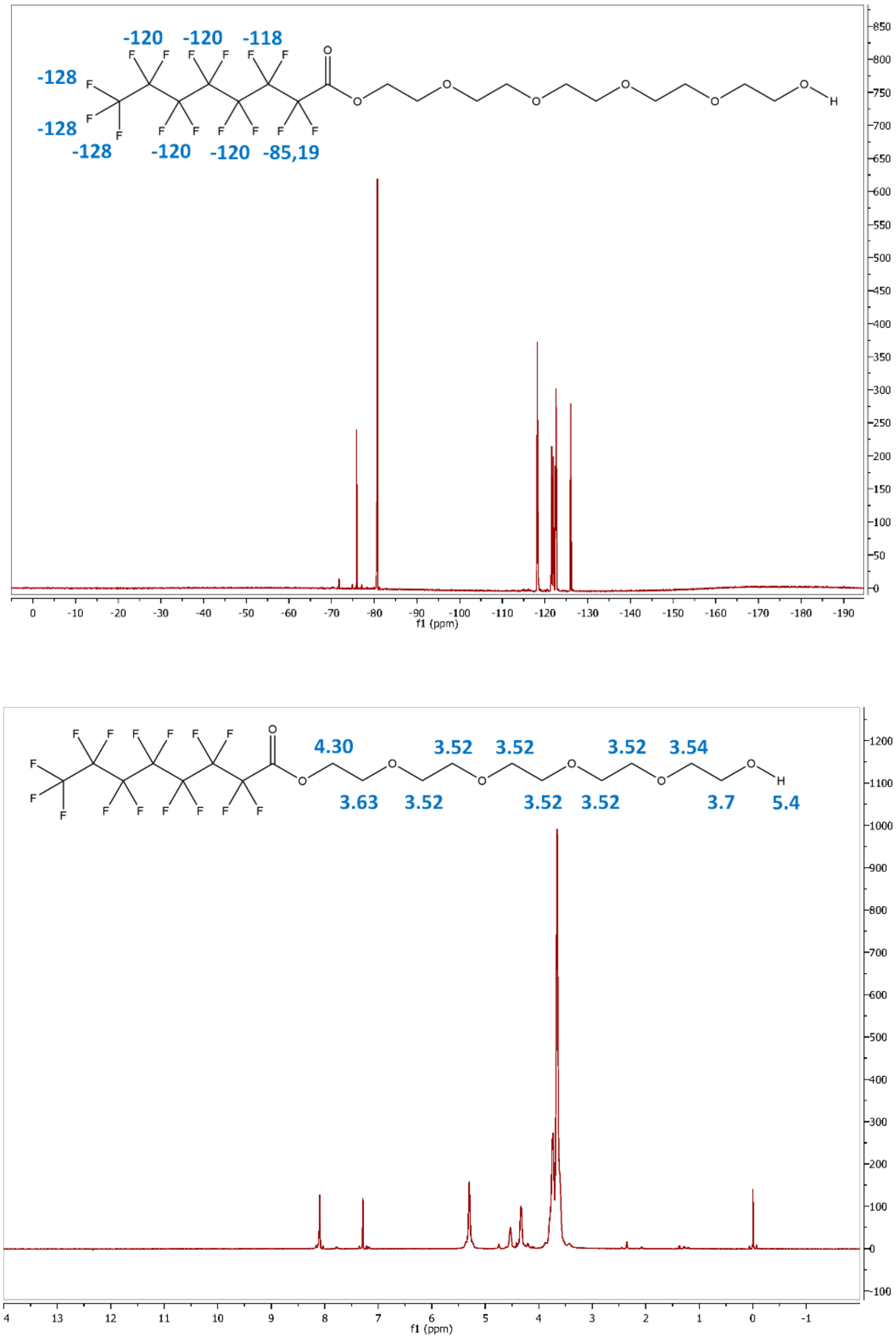


Figure 3 – Representative ^{19}F (top) and ^{1}H (bottom) nuclear magnetic resonance spectra of the synthesized fluorosurfactant FS 200.

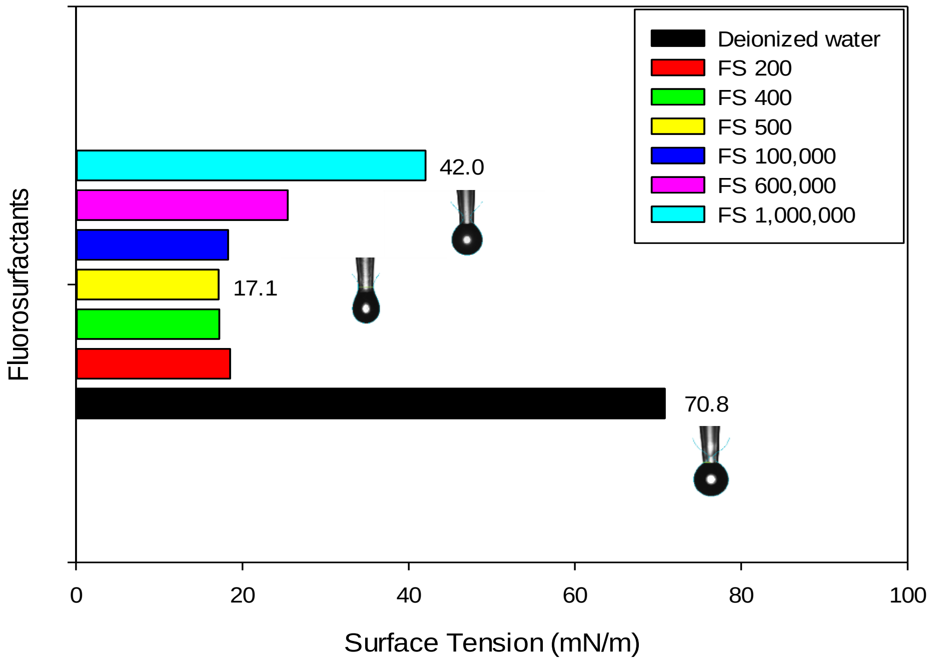


Figure 4 – Surface tension of the synthesized fluorosurfactants dissolved in deionized water.

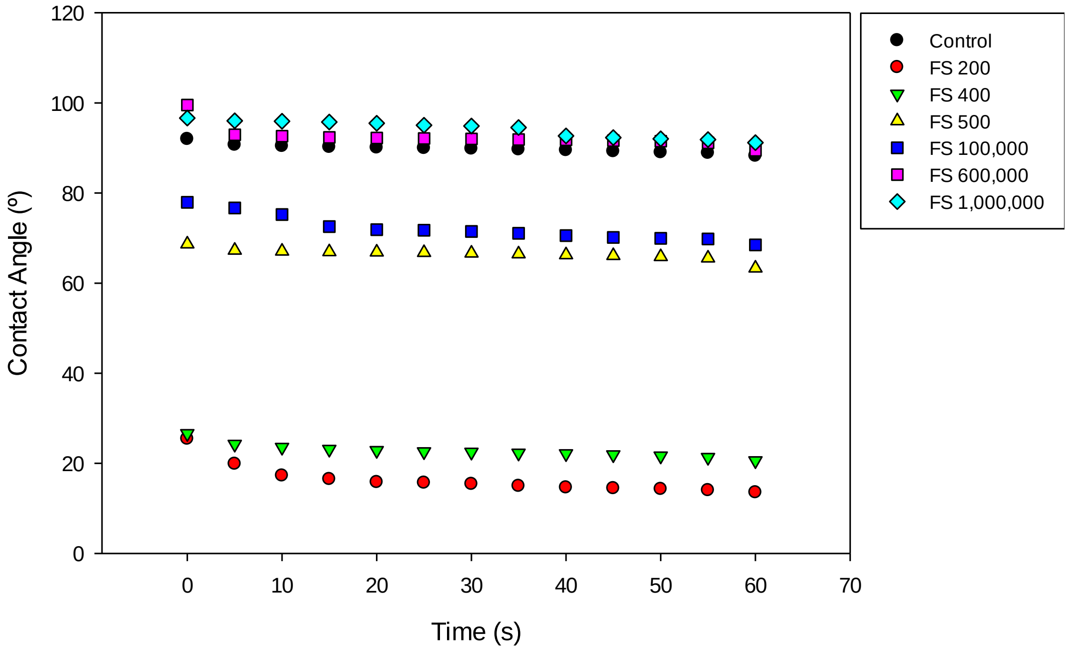


Figure 5 – Results for water contact angle formed with the VPS impression materials.

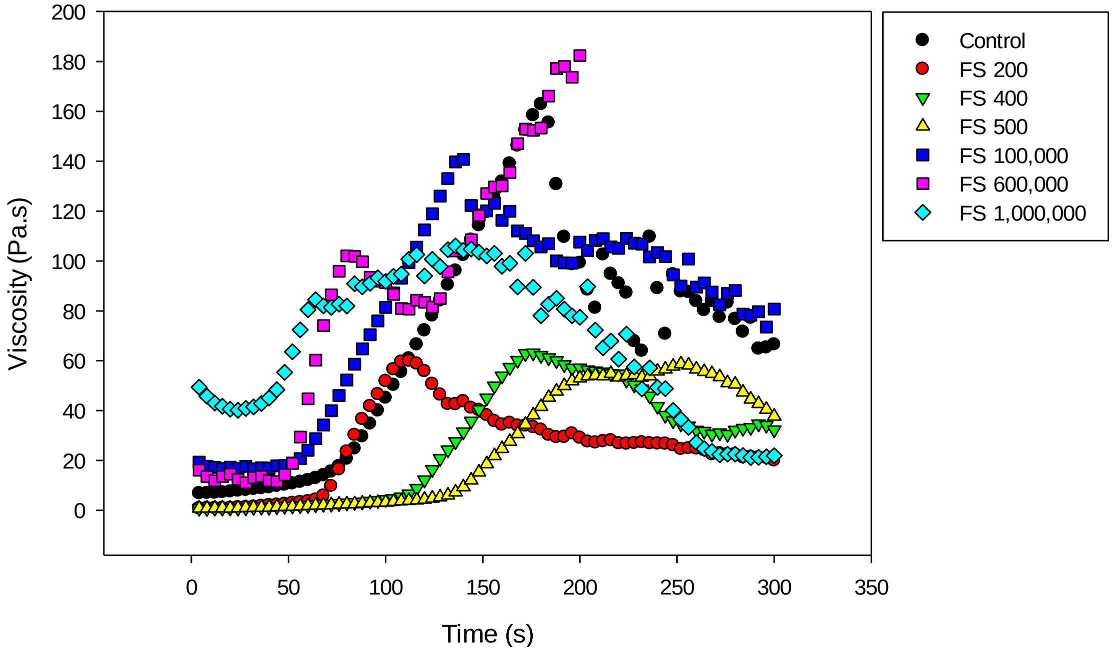


Figure 6 – Viscosity curves during mixture of the base and catalyst pastes of the VPS impression material.

Conclusão

O presente estudo mostrou que é possível promover diferentes níveis de hidrofilia ao silicone por adição por meio da incorporação de tensoativos não-iônicos do tipo fluorcarbono, siloxano e/ou hidrocarboneto. Os resultados encontrados foram muito satisfatórios e de extrema relevância, uma vez que o objetivo principal foi atingido, ou seja, foi possível atribuir caráter hidrofílico a um material extremamente hidrofóbico por natureza, tanto com a adição dos tensoativos sintetizados neste estudo quanto com os diferentes tensoativos comerciais. Além disso, foi possível estabelecer uma nova linha de pesquisa, uma vez que esses tipos de tensoativos podem ser introduzidos em uma ampla gama de materiais odontológicos com o intuito de melhorar a hidrofilia e as propriedades dos materiais, como por exemplo: adesivos dentais, cimentos resinosos, cimentos periodontais e clareadores dentais.

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Apêndices

Apêndice A – Nota de defesa

Título da nota	Uso de tensoativos não-iônicos em materiais odontológicos *Use of non-ionic surfactants in dental materials*
Conteúdo	Foram utilizados no estudo, diferentes tipos de tensoativos não-iônicos do tipo fluorcarbono, siloxano e hidrocarboneto com o intuito de atribuir características hidrofílicas aos materiais de moldagem do tipo silicone por adição. Os dados encontrados são extrema relevância, uma vez que o objetivo principal foi atingido, ou seja, foi possível atribuir caráter hidrofílico a um material extremamente hidrofóbico por natureza. Além disso, foi possível estabelecer uma nova linha de pesquisa, uma vez que esses tipos de tensoativos podem ser introduzidos em uma ampla gama de materiais odontológicos (adesivos dentais, cimento resinoso, cimentos periodontais, clareadores dentais, dentre outros) para promover maior hidrofilia e melhora das propriedades.
Área do conhecimento do CNPq	4.02.00.00-0 Odontologia 4.02.09.00-8 Materiais Odontológicos
Candidato a Doutora	Aline Ogliari. Mestre em odontologia, área de concentração Dentística - Universidade Federal de Pelotas. Graduação - Universidade Federal de Pelotas.
Data da defesa e horário	29/07/2016, às 14:00 horas
Local	Auditório do Programa de Pós-graduação em Odontologia – 5º andar da Faculdade de Odontologia de Pelotas. Rua Gonçalves Chaves, 457.
Membros da banca	Prof. Dr. Cesar Henrique Zanchi, Universidade Federal de Pelotas, Doutor em Odontologia, Área de concentração Dentística. Prof. Dr. Fabrício Mezzomo Collares, Universidade Federal do Rio Grande do Sul, Doutor em Odontologia, Área de concentração Materiais Dentários. Profª. Drª. Patrícia dos Santos Jardim, Universidade Estadual Paulista Júlio de Mesquita Filho, Doutora em Odontologia, Área de concentração Dentística Restauradora. Prof. Dr. Rodrigo Varella de Carvalho, Universidade Federal de Pelotas, Doutor em Odontologia, Área de concentração Dentística. Dr. Gregori Franco Boeira, Universidade Federal de Pelotas, Doutor em Odontologia, Área de concentração Dentística (suplente).

	Prof. Drª. Noéli Boscato, Universidade Estadual de Campinas, Doutora em Clínica Odontológica, Área de concentração Prótese Dental (suplente).
Orientador	Prof. Dr. Rafael Ratto, de Moraes, Universidade Estadual de Campinas, Doutor em Materiais Dentários.
Co-orientador	Prof. Dr. Fabrício Aulo Ogliari, Universidade Federal de Pelotas, Doutor em Odontologia, Área de concentração Dentística.
Informação de contato	Aline de Oliveira Ogliari, Rua Gonçalves Chaves, 457 – Laboratório CDC-Bio. CEP 96015560, Pelotas, RS, Brasil.

Apêndice B – Nota da Tese

Síntese e caracterização de tensoativos para uso odontológico

Synthesis and characterization of surfactants for dentistry use

A presente tese de doutorado desenvolveu tensoativos fluorados por meio de síntese, por esterificação de Fischer, apresentando diferentes balanços lipofílico-hidrofílico e avaliou a utilização de diferentes tensoativos não-iônicos comerciais dos tipos fluorcarbono, siloxano e hidrocarboneto adicionados em silicones por adição. Foi realizado um *screening* acerca das propriedades desses tensoativos e a interação deles quando adicionados ao material de moldagem. Foi possível obter resultados muito satisfatórios e de extrema relevância, uma vez que o objetivo principal foi atingido, ou seja, foi possível atribuir caráter hidrofílico a um material extremamente hidrofóbico por natureza, tanto com a adição dos tensoativos sintetizados quanto com os diferentes tensoativos comerciais. Além disso, foi possível estabelecer uma nova linha de pesquisa, uma vez que esses tipos de tensoativos podem ser introduzidos em uma ampla gama de materiais odontológicos (adesivos dentais, cimento resinoso, cimentos periodontais, clareadores dentais, dentre outros) para promover maior hidrofilia e melhora das propriedades.

Campo da pesquisa: Materiais Odontológicos.

Candidato: Aline de Oliveira Ogliari, Cirurgiã-dentista pela Universidade Federal de Pelotas (2010), Mestre em Odontologia – área de concentração Dentística pela Universidade Federal de Pelotas (2012).

Data da defesa e horário: 29/07/2016 às 14:00 horas.

Local: Auditório do Programa de Pós-graduação em Odontologia da Universidade Federal de Pelotas. 5º andar da Faculdade de Odontologia de Pelotas. Rua Gonçalves Chaves, 457.

Membros da banca: Prof. Dr. Cesar Henrique Zanchi, Prof. Dr. Fabrício Mezzomo Collares, Profª. Drª. Patrícia dos Santos Jardim, Prof. Dr. Rodrigo Varella de Carvalho, Dr. Gregori Franco (suplente) e Prof. Drª. Noéli Boscato (suplente).

Orientador: Prof. Dr. Rafael Ratto de Moraes

Co-orientador: Prof. Dr. Fabrício Aulo Ogliari

Informação de contato: Aline de Oliveira Ogliari, alineoliveiraogliari@gmail.com, Rua Gonçalves Chaves, 457- Laboratório CDC-Bio – 1º andar.

Apêndice C – Súmula do currículo do candidato

Súmula do currículo

Aline de Oliveira Ogliari nasceu em 25 de outubro de 1982, em Rio grande – RS. No ano de 2005 ingressou na Faculdade de Odontologia da Universidade Federal de Pelotas, atuou como aluna de iniciação científica sob orientação do professor Rafael Ratto de Moraes, tendo sido graduada cirurgiã-dentista em 2010. No ano de 2011, ingressou no Mestrado do Programa de Pós-graduação em Odontologia da Universidade Federal de Pelotas, área de concentração Dentística, sob orientação do professor mencionado acima. No mestrado foi bolsista da CAPES e desenvolveu trabalhos científicos na área de materiais dentários. Durante o período de mestrado também realizou MBA em Gestão Empresarial na Fundação Getúlio Vargas. Atualmente, além de aluna de doutorado do Programa de Pós-Graduação em Odontologia da Universidade Federal de Pelotas, na área de concentração de Materiais Odontológicos é também sócia-proprietária da indústria de materiais odontológicos Yller Biomateriais SA.

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