UNIVERSIDADE FEDERAL DE PELOTAS
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Tese

Desenvolvimento e caracterização de resinas de reduzida tensão de contração

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Clarice Lispector

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 em Artigos, descrita no referido manual, o qual se encontra no site http://sisbi.ufpel.edu.br/?p=manual. Acesso em: 18 de setembro de 2015.

O projeto de pesquisa contido nesta dissertação é apresentado em sua forma final após qualificação realizada em 30 de agosto de 2012 e aprovado pela Banca Examinadora composta pelos Professores Doutores Fabrício Aulo Ogliari, Rafael Ratto de Moraes e Rodrigo Varella de Carvalho.

Resumo

MÜNCHOW, Eliseu Aldrighi. **Desenvolvimento e caracterização de resinas de reduzida tensão de contração. 2015**. 158f. Tese de Doutorado em Odontologia – Programa de Pós Graduação em Odontologia. Universidade Federal de Pelotas, Pelotas, 2015.

O processo de polimerização de materiais resinosos utilizados em odontologia geralmente desencadeia o fenômeno da tensão de contração, o qual pode gerar uma série de eventos negativos, comprometendo o tratamento restaurador. Assim, o objetivo desta tese foi primeiramente revisar a literatura por meio de revisão sistemática com meta-análises acerca das possíveis estratégias existentes para se reduzir a tensão de contração desenvolvida por materiais resinosos; ainda, a presente tese objetivou investigar o efeito de monômeros elastoméricos (exotanos) e nanofibras poliméricas na tensão de contração de resinas experimentais. Quanto à revisão sistemática, a qual foi realizada segundo as normas do PRISMA, 77 estudos foram incluídos na revisão, os quais, coletivamente, demonstraram haver várias alternativas possíveis para se reduzir o fenômeno da tensão de contração de materiais resinosos. Quanto ao efeito dos exotanos, todos os exemplares investigados resultaram em menor tensão de contração quando comparados ao controle (UDMA). Ainda, dependendo do tipo de exotano avaliado, um melhor desempenho da polimerização foi obtido. Quanto ao efeito das nanofibras, que foram fabricadas por meio de eletrofiação, quanto maior a concentração de nanofibras adicionadas nas resinas experimentais, maior o potencial redutor da tensão de contração. Além disso, as nanofibras não alteraram outras propriedades físico-mecânicas avaliadas. Conclui-se que exotanos ou nanofibras poliméricas podem atuar como agentes redutores da tensão de contração de materiais resinosos, demonstrando assim potencial aplicação no desenvolvimento de novos materiais dentários.

Palavras-chave: tensão de contração, estresse de polimerização, agente redutor de tensão, resinas compostas, resinas adesivas, cimentos resinosos, polimerização.

Abstract

MÜNCHOW, Eliseu Aldrighi. **Development and characterization of resins with reduced contraction stress. 2015**. 158p. Thesis of PhD in Dentistry. Graduate Program in Dentistry. Federal University of Pelotas, Pelotas, 2015.

The polymerizaion process of resin-based materials used in dentistry usually produces the contraction stress phenomenon, which may lead to several negative events, thus compromising the restorative treatment. Hence, the aim of this thesis was firstly to revise the literature by means of a systematic review with meta-analyses regarding the possible strategies available for reduce the contraction stress produced by resin-based materials; in addition, the present thesis aimed to investigate the effect of elastomeric monomers (exothanes) and polymer-based nanofibers on the contraction stress of experimental resins. Regarding the systematic review, which was performed following the PRISMA guideliness, 77 studies were included in the review, which collectively demonstrated the existence of several possible strategies to reduce the contraction stress phenomenon of resin-based materials. Regarding the effect of the Exothanes, all Exothanes investigated resulted in lower contraction stress when compared to the control (UDMA). Moreover, depending on the Exothane type, an improved polymerization performance was obtained. Regarding the effect of nanofibers, which were fabricated via electrospinning, the greater the contente of nanofibers incorporated into the experimental resins, the greater the potential to reduce contraction stress. Furthermore, the nanofibers did not alter the other physico-mechanical properties tested. In conclusion, Exothanes and polymeric nanofibers may be used as contraction stress reducing agents of resin-based materials, showing potential application for the development of new dental materials.

Key-words: contraction stress, polymerization stress, stress reducing agent, resin composites, resin adhesives, resin ciments, polimerization.

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Sumário

1 Introdução

De maneira geral, o fenômeno da tensão (estresse) de contração oriundo da reação de polimerização de materiais resinosos utilizados em odontologia ainda é considerado um dos principais problemas que requer atenção do profisisonal. Na verdade, sabe-se que o “estresse” ocasionado na interface dente/restauração pode repercutir em prejuízos ao tratamento restaurador como um todo, seja por falha da adesão propriamente dita ou por motivos secundários, como a perda de continuidade marginal, a qual pode desencadear em eventos de micro-infiltração, sensibilidade pós-operatória e/ou pigmentação marginal da restauração, e a possível deflexão cuspídea ou formação de trincas de esmalte.

Segundo inúmeros estudos presentes na literatura, o fenômeno da tensão de contração destes materiais pode ser significativamente reduzido em magnitude. No entanto, várias são as estratégias existentes, envolvendo desde a simples modificação da técnica de inserção e/ou foto-ativação do material, bem como através da modificação da composição química do mesmo. Esta última estratégia (modificação química), porém, está geralmente associada a processos e mecanismos mais complexos, já que afeta toda a estrutura e dinâmica reacional do material. Ainda, é importante salientar que por muito tempo o profissional tentou controlar/reduzir a tensão de contração por meio da utilização de técnicas operatórias alternativas (técnica incremental, por exemplo); contudo, existem situações clínicas em que técnicas alternativas não surtem efeito algum, como no caso da cimentação de retentores intraradiculares utilizando-se de cimento resinoso. Dessa maneira, a formulação de novos materiais com composição química diferenciada ainda se faz necessária a fim de optimizar o desempenho clínico dos materiais dentários de natureza resinosa, sendo, portanto, foco de vários estudos atuais em odontologia.

Assim, o presente estudo objetiva revisar a literatura acerca das possíveis estratégias existentes para se reduzir o fenômeno de tensão de contração de materiais resinosos, bem como propor novas alternativas para tal propósito.

2 Projeto de pesquisa

2.1 Introdução

Os materiais resinosos utilizados em odontologia são extremamente versáteis, sendo aplicados em diversas situações clínicas, seja como material restaurador (resinas compostas), adesivo (adesivos dentários) e/ou cimentante (cimento resinoso). Eles são constituídos basicamente por uma matriz polimérica (orgânica), a qual pode estar preenchida por partículas inorgânicas (cargas), além de um material capaz de unir quimicamente estas duas fases (geralmente um componente derivado do silano) (FERRACANE, 2011). Desde a sua utilização inicial na forma das resinas compostas, no início dos anos 1960 (BOWEN, 1962), até os dias atuais, diferentes combinações entre as fases orgânica e inorgânica das resinas odontológicas têm proporcionado a obtenção de um equilíbrio de propriedades, tornando estes materiais uma das principais escolhas à realização do tratamento restaurador. Por outro lado, estas resinas, e principalmente as resinas compostas, são materiais que demonstram uma limitação intrínseca bastante problemática: a sua contração de polimerização (DAUVILLIER; AARNTS; FEILZER, 2000).

A contração de polimerização é uma propriedade física intrínseca de materiais resinosos em decorrência da aproximação dos monômeros durante o seu processo de polimerização e conseqüente redução volumétrica (CANEVAROLO JR., 2002). No entanto, o fator mais prejudicial não é a sua simples contração, mas sim esta contração em volume ocorrendo nas circunstâncias de confinamento que uma cavidade dentária ou conduto radicular pode oferecer quando o material é aderido às paredes dentárias (BRAGA; BALLESTER; FERRACANE, 2005). Como conseqüência direta, a contração pode desenvolver uma tensão na interface dente/restauração, causando desde a ruptura desta, com posterior micro-infiltração e sensibilidade pós-operatória, até a deflexão cuspídea do elemento dental (FERRACANE 2008; GONÇALVES et al., 2012). Sendo assim, a tensão de contração é geralmente associada como um dos motivos que levam à falha de uma restauração.

Vários estudos têm sido conduzidos na tentativa de resolver ou minimizar esta problemática. Uma das iniciativas foi o desenvolvimento de materiais à base de monômeros siloxano-oxiranos. Estes monômeros, por terem um processo de polimerização de abertura de anéis (polimerização catiônica), expandem durante a polimerização, ocasionando uma contração volumétrica de apenas 1% (WEINMANN; THALACKER; GUGGENBERGER, 2005). Este valor de contração é menor do que o demonstrado pelos materiais convencionalmente utilizados, cuja contração pode variar de 2 a 6% no caso das resinas compostas (LABELLA et al., 1999). Mesmo assim, a tensão desenvolvida por estes materiais alternativos parece não ter sido solucionada como se esperava, já que ela nãonecessariamente foi menor do que a apresentada pelos materiais convencionais (MARCHESI et al., 2010). Além disso, em um estudo clínico, uma resina composta contendo monômeros siloxano-oxiranos promoveu um selamento marginal pior do que o demonstrado por um compósito nano-híbrido sem este mesmo tipo de monômeros na formulação (SCHMIDT et al., 2011).

Além do uso dos monômeros siloxano-oxiranos, o desenvolvimento de monômeros metacrilatos modificados vem sendo associado com a redução da tensão de contração em compósitos experimentais. Lu (2010) sintetizou um dimetacrilato derivado do ácido dimérico e constatou que a utilização deste como substituto ao trietilenoglicol dimetacrilato (TEGDMA) aumentou o grau de conversão do material e ao mesmo tempo reduziu a contração volumétrica e tensão de contração. Outros estudos nesta mesma linha de pesquisa, porém utilizando-se metacrilato-tiol-eno como monômero base de resinas experimentais, revelaram que a tensão de contração desenvolvida foi menor do que a de resinas contendo dimetacrilatos convencionais, além de terem aumentado a conversão dos grupos funcionais dos materiais (LU et al., 2005; CRAMER et al., 2010). Percebe-se assim que o desenvolvimento de novos constituintes para a formulação da matriz orgânica pode contribuir para o controle da tensão de contração.

Paralelo a estas modificações realizadas na matriz orgânica, o conteúdo inorgânico também é uma variável que influencia o fenômeno da tensão de contração, pois quanto maior a concentração de carga no material, menor será a proporção de matriz orgânica passível de contrair volumetricamente (GONÇALVES; KAWANO; BRAGA, 2010; GONÇALVES et al., 2012). Por outro lado, o maior conteúdo de partículas também aumenta o módulo de elasticidade, o que reduz o escoamento visco-elástico do material, e, conseqüentemente, a sua capacidade de liberar tensão durante a polimerização (BRAGA; BALLESTER; FERRACANE, 2005). Em decorrência disso, alguns estudos incorporaram partículas oligoméricas hiper-funcionalizadas (YE et al., 2012) ou partículas pré-polimerizadas na forma de nanogéis (MORAES et al., 2011) na matriz orgânica de resinas experimentais, constatando que há uma redução significativa no desenvolvimento da tensão gerada. A princípio, estas partículas especializadas participariam do aumento de mobilidade do sistema polimérico, além de permitir a liberação da tensão formada. Além disso, as partículas convencionalmente utilizadas são caracterizadas como uma porção não deformável do material (baixa compliance), o que intensifica a concentração de tensão na sua interface com a matriz resinosa.

Considerando-se todo o recém-exposto, existe uma classe de monômeros derivados do dimetacrilato uretano (UDMA) que pode apresentar características elastoméricas interessantes à formulação de materiais liberadores de tensão. Dependendo das suas características, eles podem atingir grau de conversão acima de 90% e contração volumétrica reduzida, além de apresentarem uma elevada capacidade de alongamento (deformação) (Dados obtidos da Esstech, Inc.). Estes monômeros, por exemplo, poderiam ser utilizados para a formulação da matriz orgânica de materiais resinosos, funcionando como redutores de tensão devido à maior deformação que poderiam suportar. Além disso, eles também poderiam ser transformados em partículas poliméricas, e, assim, ser utilizados como carga das resinas, em substituição total ou parcial às partículas inorgânicas. Outro fator interessante acerca de um monômero elastomérico é que, diferentemente das partículas ou nanogéis sintetizados nos trabalhos de Ye (2012) e Moraes (2011), este tipo de monômero, devido a suas características elastoméricas, apresenta uma temperatura de transição vítrea (Tg) baixa (negativa), típica de um material borrachóide, o que por sua vez tornaria o polímero flexível à temperatura ambiente, favorecendo assim a absorção e liberação de tensão. Dessa maneira, a utilização destes monômeros uretanos poderia contribuir para a formulação de materiais resinosos redutores de tensão de contração.

Quanto à utilização dos monômeros elastoméricos como partículas poliméricas, o processo de obtenção destas partículas depende da obtenção de um material de pequenas dimensões. Então, dentre os diversos métodos existentes, a polimerização em emulsão é aquela em que um monômero é polimerizado em solução aquosa e em presença de substâncias tenso-ativas, originando assim uma dispersão de partículas poliméricas (micro ou nano-esferas) com tamanhos entre 0,05 e 1 µm (BESTETI 2009). As vantagens deste método de polimerização é a possibilidade de se obter, simultaneamente, polímeros de elevado peso molecular e em elevadas velocidades de polimerização, além de utilizar água como meio dispersante, evitando, assim, a utilização de solventes orgânicos (FOWLER et al., 2011). Contudo, este método possui um caráter multi-fásico, com mecanismos complexos e que podem dificultar a modelagem, o monitoramento e o controle reacional (LENZI 2002). Mesmo assim, a polimerização em emulsão pode ser um meio bastante interessante para a obtenção de polímeros de pequenas dimensões, podendo vir a contribuir para a formulação de resinas com elevado nível de polimerização, sem, no entanto, desenvolver elevada tensão de contração.

2.2 Proposição

2.2.1 Objetivo geral

Avaliar a influência, na contração de polimerização e tensão de contração, do uso de monômeros elastoméricos como carga ou constituintes da matriz orgânica de resinas experimentais.

2.2.2 Objetivos específicos

- Caracterizar resinas experimentais contendo monômeros dimetacrilatos elastoméricos (exotanos);
- Sintetizar micro e nano-esferas poliméricas através de polimerização por emulsão e analisá-las quanto a sua granulometria, temperatura de transição vítrea e dispersão na matriz orgânica;
- Analisar o comportamento físico-mecânico de resinas experimentais contendo micro e nano-esferas poliméricas como partículas de carga;

2.3 Materiais e métodos

META-FÍSICA 1 – Caracterização de resinas experimentais

2.3.1. Formulação das resinas experimentais

Diferentes resinas experimentais contendo dimetacrilatos elastoméricos serão formuladas para este projeto. Dentre eles, os uretanos elastoméricos (exotanos) 8, 10 e 26 serão utilizados visto que, quando comparados com os demais exotanos, apresentam elevada capacidade de conversão monomérica, reduzida contração em volume e elevada capacidade de alongamento (Dados obtidos através do site da empresa Esstech, Inc.).

Resinas contendo apenas um dos exotanos listados anteriormente (homopolímeros) serão formuladas utilizando-se uma balança analítica de precisão. Em cada resina, 0,4% de canforoquinona (CQ) e 0,8% de 4-dietilamino benzoato (EDAB) serão adicionados, em peso, para tornar as resinas fotossensíveis. Após sua formulação, elas serão avaliadas quanto a diferentes propriedades físico-mecânicas.

2.3.2. Avaliação do grau e cinética de conversão

A cinética de conversão das diferentes resinas experimentais será avaliada em tempo real por meio de espectroscopia de infravermelho com Transformada de Fourier (RT-FTIR, Shimadzu Prestige21 Spectrometer, Shimadzu, Japão) equipado com dispositivo de refletância total atenuada (RTA), composto por um cristal horizontal de seleneto de zinco (ZnSe) e espelhos de angulação de 45o (PIKE Technologies, EUA). Um suporte será acoplado para fixar um diodo emissor de luz (LED, Radii SDI, Bayswater, VIC, Australia) permitindo a padronização da distância de 2 mm entre a extremidade da ponteira de fibra ótica e a amostra. As amostras serão dispensadas diretamente no cristal de ZnSe, com auxilio de uma micropipeta (~3 μl), e foto-ativadas por 60 segundos (s) . A irradiância será de aproximadamente 900 mW/cm2, sendo mensurada com radiômetro digital (Ophir Optronics, Danvers, MA, EUA). Cada resina será analisada em triplicata. Para o monitoramento de varredura será utilizado o software IRSolution, utilizando a apodizacão de Happ-Genzel, em uma faixa espectral entre 1750 e 1550 cm^{-1}, resolução de 8 cm^{-1} e velocidade de deslocamento de espelho de 2,8 mm/s. Além disso, todas as análises serão realizadas em temperatura (25±1°C) e umidade (60±5%) controladas. O grau de conversão, por segundo, será calculado considerando-se a intensidade da vibração do tipo estiramento da dupla ligação carbono-carbono na frequência de 1635 cm^{-1}. Então, o estiramento simétrico do anel aromático em 1610 cm^{-1} das amostras polimerizadas e não polimerizadas será utilizado como padrão interno. Posteriormente, os dados serão plotados em uma curva ajustada pelo parâmetro regressivo não-linear de Hill 3 e será calculada a taxa de polimerização.

2.3.3. Avaliação da resistência à flexão e módulo de elasticidade em flexão

Para cada resina formulada serão confeccionados espécimes em forma de barra (25 × 2 × 2 mm, n=10) através de uma matriz metálica bi-partida interposta entre duas tiras de poliéster (ISO 4049:2009). Cada espécime será foto-ativado por 120 s nas superfícies superior e inferior utilizando-se o mesmo LED descrito anteriormente e afastado a uma distância de 10 mm. Logo após, os espécimes serão armazenados em água destilada, por 24 horas, e então, serão submetidos ao teste de flexão em três pontos (EMIC DL500, São José dos Pinhais, PR, Brasil), obtendo-se a resistência à flexão (RF) do material, em MPa. Partindo-se da porção linear inicial da curva carga × deslocamento, obtida pelo software Tesc (EMIC), o módulo de elasticidade em flexão (E_f) dos materiais será calculado segundo a fórmula: $E_f = F \times L3 / 4 \times l \times h3 \times d$, onde E_f é o módulo de elasticidade em flexão (MPa), F é a carga registrada no regime elástico (N), L é a distância entre os apoios (mm), l é a largura da amostra (mm), h é a espessura da amostra (mm) e d é a deflexão correspondente a F. As medidas de largura e espessura serão mensuradas com um paquímetro digital (Mitutoyo Corporation, Tóquio, TO, Japão).

2.3.4. Avaliação da micro-dureza Knoop

O número de micro-dureza Knoop (NMK) das resinas será avaliado a partir dos espécimes fraturados no teste de resistência à flexão, que serão embutidos em resina epóxi e polidos com lixas de carbeto de silício de granulação #600 e #1200, sob refrigeração com água. Então, os espécimes serão mensurados em um durômetro (FM 700, Future Tech, Kawasaki, KA, Japão) com uma carga de 50 g durante 15 s, sendo realizadas cinco endentações por espécime, do qual será obtido o valor médio de NMK.

2.3.5. Avaliação da contração volumétrica de polimerização

A contração de polimerização em volume das resinas experimentais será realizada utilizando-se um picnômetro de gás hélio AccuPyc 1330 (Micromeritics Instrument Corporation, Norcross, GA, EUA). Para isso, amostras de cada material (n=3) serão confeccionadas com uma matriz metálica menor do que a câmara de medição do picnômetro (19 mm × 39,8 mm). Então, esta matriz vazia terá o seu volume mensurado através do preenchimento da câmara de medição com gás hélio e consequente deslocamento do gás no interior da câmara. Após isso, o conjunto matriz/amostra terá a sua massa mesurada em balança analítica, como forma de padronizar a quantidade de material utilizado, e, em seguida, este mesmo conjunto será inserido na câmara de medição do picnômetro, onde o gás irá novamente preencher todo o espaço, e, logo após, será transmitido para outro volume interno preciso. Com isso, o volume do material antes da foto-ativação será obtido. Em seguida, a foto-ativação do material será realizada no exterior do picnômetro e com o mesmo LED descrito anteriormente durante 60 s. Então, o conjunto matriz/amostra será novamente inserido no picnômetro para aferição do volume após a foto-ativação. Por fim, a contração de polimerização será calculada utilizando-se a seguinte fórmula: C = ÄV/v + [ÄV], sendo C o coeficiente de contração de polimerização, ÄV a diferença entre o volume da amostra antes e após a foto-ativação e v a diferença entre o volume da matriz metálica vazia e da matriz com a amostra polimerizada.

2.3.6. Avaliação da tensão de contração

O teste de tensão de contração (TC) será realizado em máquina universal de ensaios mecânicos (Electro Puls E3000, Instron, Norwood, MA, EUA), tendo bastões de vidro (5 mm de diâmetro) como substratos de colagem. Estes bastões serão obtidos em dois comprimentos diferentes (13 e 28 mm), sendo que o maior deles será acoplado a uma garra superior, enquanto o menor, na garra inferior da Instron. As imagens das garras devidamente projetadas para a Instron podem ser observadas na Figura 1. As superfícies que serão posicionadas em contato com as blendas experimentais serão asperizadas com lixa #180, enquanto que a superfície oposta do bastão menor será polida na seguinte seqüência: lixas #600, #1200, #1800, #2100 e disco de feltro com pasta de alumina 1 µm.

A inserção dos materiais experimentais nas superfícies asperizadas dos bastões será realizada após a aplicação de silano (Silano, Angelus, Londrina, PR, Brasil). A espessura de cada amostra será de 1 mm, tendo conformação cilíndrica. Um extensômetro (modelo 2630-101, Instron) será acoplado aos bastões a fim de manter-se a distância entre eles constante. A foto-ativação dos materiais será realizada com o mesmo LED descrito anteriormente, que será posicionado entre as garras inferiores (Figura 1) e 0,5 mm afastados do bastão menor. Durante a foto-ativação (40 s), o extensômetro irá manter a espessura da amostra constante, e, com isso, ela não se deformará volumetricamente. Por conseqüência, ela irá desenvolver uma força, cujo valor máximo será dividido pela área de secção transversal do bastão, obtendo-se assim a tensão de contração máxima (n=7). Além disso, a força desenvolvida será monitorada desde 30 s antes da foto-ativação até 10 minutos após.

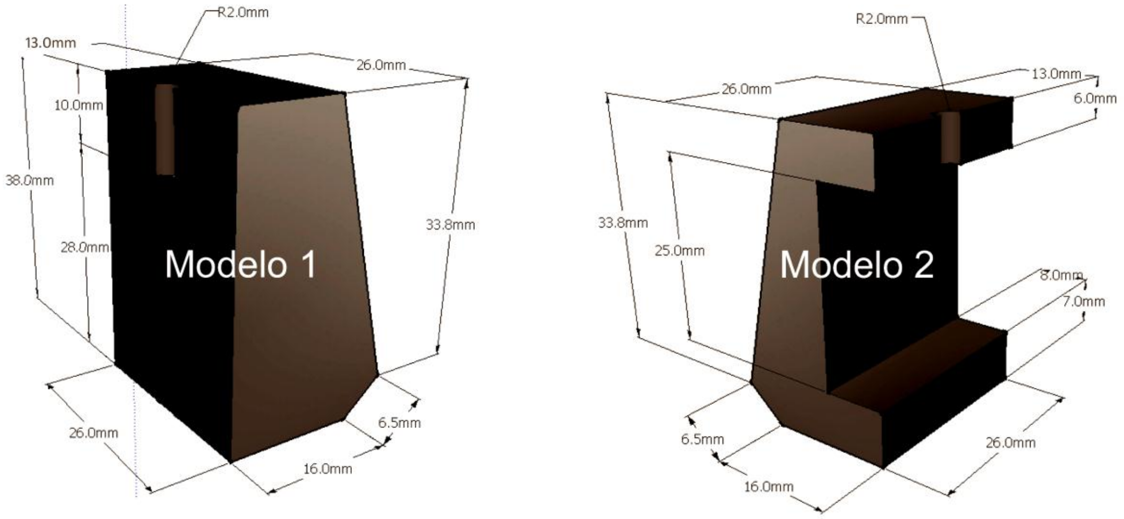

Figura 1. Dispositivos que serão utilizados como garra superior (Modelo 1) e inferior (Modelo 2) da Instron para avaliação da tensão de contração, sendo que dois dispositivos de cada modelo serão utilizados para o posicionamento dos bastões de vidro. Note que o Modelo 2 apresenta um espaço interno, que quando em posição com o seu par, permitirá o acoplamento da luz foto-ativadora.

META-FÍSICA 2 – Síntese de micro e nano-esferas poliméricas através do método de polimerização por emulsão e sua caracterização

2.3.7. Síntese das micro e nano-esferas poliméricas

O método que será utilizado para a síntese das partículas poliméricas é o da polimerização por emulsão. Este método possibilita polimerizar-se um monômero em um meio aquoso através da utilização de uma substância tenso-ativa e um iniciador da reação. O tenso-ativo é responsável pela formação de micelas cujas pontas hidrófobas são direcionadas para dentro e as pontas hidrófilas para fora.

Consequentemente, os monômeros migram para o interior das micelas (região hidrófoba), e, com a adição de um iniciador hidrossolúvel, a polimerização dos monômeros ocorrerá apenas no interior delas, repercutindo na formação de micro-esferas e nano-esferas poliméricas com granulometria na ordem de 0,05 a 1 µm (Reação representada na Figura 2) (CANEVAROLO 2002; BESTETI 2009).

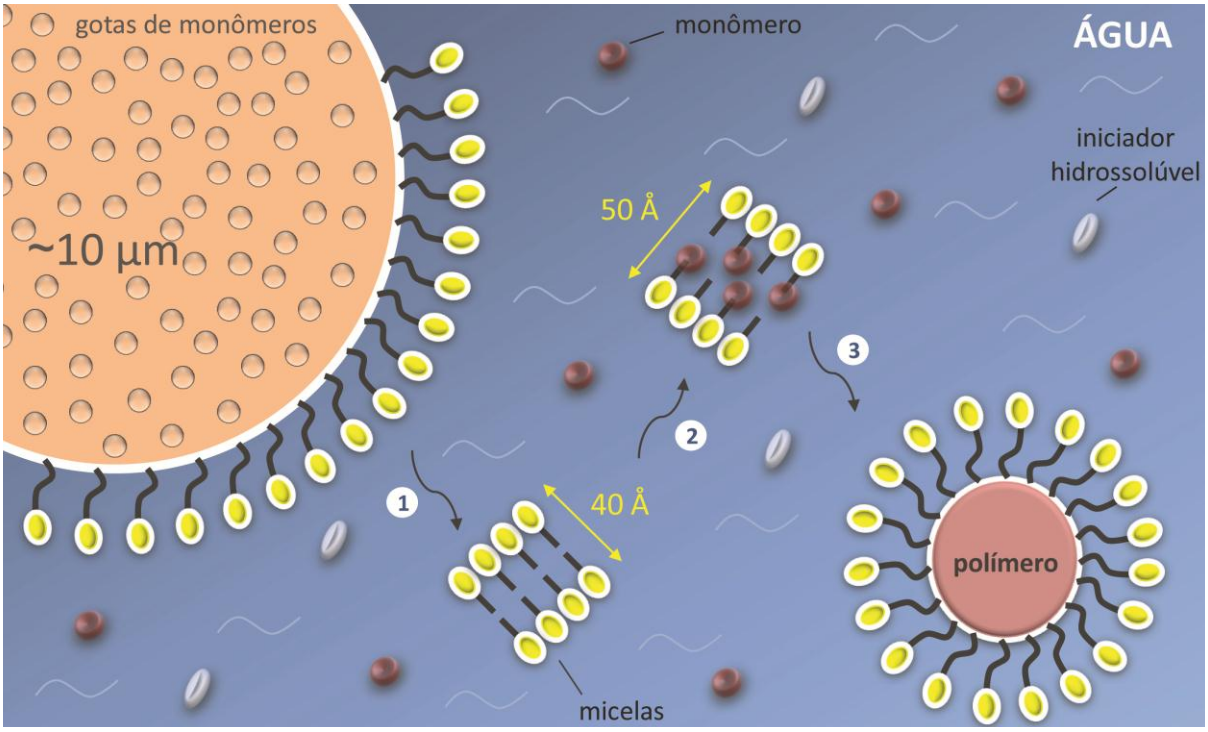

Figura 2. Imagem representando o mecanismo pelo qual polímeros são formados através do método de polimerização por emulsão. A presença de uma substância tenso-ativa forma micelas (1), que por terem uma porção hidrófoba, atraem monômeros para o seu interior (2), que através de substâncias iniciadoras hidrossolúveis, são polimerizados (3).

Sendo assim, lauril sulfato de sódio (SDBS – tenso-ativo) será adicionado em água destilada em uma concentração superior à concentração micelar crítica (CMC). Em seguida, esta solução será mantida em agitador magnético a uma velocidade de 1000 rpm. A partir deste momento, o monômero elastomérico (Exotanos™ 8, 10 ou 26) será incorporado na solução em agitação, e, teoricamente, permanecerá em parte suspenso na forma de gotas e em outra parte aprisionado no interior das micelas, devido a sua migração para uma região mais hidrófoba. Esta parte da reação será realizada com aquecimento da mistura até 70°C. Finalmente, 1% de peróxido de amônio (iniciador hidrossolúvel) será adicionado à mistura, impulsionando a polimerização dos monômeros apenas no interior das micelas. Após o término da reação, e através da evaporação do solvente por meio da utilização de um evaporador rotativo a vácuo (MA 120/TH, Marconi, Piracicaba, SP, Brasil), as partículas serão obtidas e passarão por um processo de purificação, para então serem armazenadas até o uso.

2.3.8. Caracterização morfológica das partículas poliméricas

As micro/nano-esferas poliméricas serão analisadas quanto a sua morfologia através de espalhamento de luz estático e de Microscopia Eletrônica de Varredura (MEV), mas não necessariamente pelos dois métodos. Se a caracterização das partículas quanto ao seu tamanho e dispersão for obtida satisfatoriamente com apenas um dos testes, o outro não será realizado.

As análises de espalhamento de luz serão realizadas através de um goniômetro (BI-200SM, Brookhaven Instruments Corporation) de 200 mm e com uma fonte de luz laser He-Ne 35 mW Spectra Physics (modelo 127) com comprimento de onda (λ) de 632,8 nm. As partículas poliméricas serão solubilizadas em tolueno, devido este apresentar um índice de refração semelhante ao vidro (recipiente onde a solução será formada), que receberão a incidência do laser. Os dados coletados no espalhamento de luz serão analisados por um processador de sinais (BI-9025 AT, Brookhaven Instruments Corporation) que consiste de um hardware para contagem, armazenagem e manipulação dos pulsos provenientes da luz espalhada e um software (BI-ZP versão 4.0) que coleta, analisa, armazena e trata os dados obtidos (RODEMBUSCH 2001).

As imagens em MEV dos espécimes serão realizadas por emissão de campo utilizando-se um microscópio eletrônico de varredura (JEOL, modelo SSZ 550, Shimadzu) operado em 20 kV. Cada amostra será preparada a partir da deposição das micro e nano-esferas em fita dupla face aderida em um porta-amostra de alumínio e posterior metalização com ouro.

2.3.9. Avaliação da temperatura de transição vítrea (Tg) das partículas poliméricas

A análise termogravimétrica das micro e nano-esferas será realizada por calorimetria exploratória diferencial (DSC), utilizando-se um calorímetro modelo 2010 da TA Instruments. Para isso, uma quantidade padrão das partículas será mensurada quanto a sua massa, e, logo após, inseridas em uma panela de alumínio e seladas com uma tampa de alumínio. Então, o calorímetro irá passar por refrigeramento por nitrogênio líquido com varredura de -100°C a 100°C a uma taxa de 10°C/minuto, com duas corridas de temperatura.

META-FÍSICA 3 – Preparo e caracterização de resinas experimentais contendo partículas poliméricas como carga

2.3.10. Formulação das resinas experimentais

Resinas experimentais serão formuladas contendo as partículas poliméricas (micro e nano-esferas) sintetizadas na META-FÍSICA 2 do presente projeto. Por sua vez, a seleção da matriz orgânica a ser utilizada será realizada através da análise do comportamento físico-mecânico das diferentes resinas formuladas na META-FÍSICA 1 do presente projeto, ou utilizando-se uma formulação base de Bis-GMA/TEGDMA (50:50, em peso). Dependendo das características de grau de conversão, resistência à flexão, módulo de elasticidade, contração volumétrica e tensão de polimerização, uma matriz base será proposta como resina padrão na formulação dos materiais experimentais. Não obstante, as partículas poliméricas serão incorporadas em concentrações que variarão de 40 a 80% em peso.

2.3.11. Caracterização físico-mecânica das resinas experimentais

O grau (GC) e cinética de conversão (CC), a resistência à flexão (RF), o módulo de elasticidade em flexão (Ef), o número de micro-dureza Knoop (NMK), a contração volumétrica de polimerização (CV) e a tensão de contração (TC) das resinas experimentais serão realizadas conforme descrito nos tópicos 2.3.2 a 2.3.6 da META-FÍSICA 1 deste projeto, respectivamente.

2.3.12. Tratamento estatístico

Para a realização da análise estatística dos dados que serão obtidos, o programa estatístico Sigmaplot 12 (Systat Software Inc, Chicago, IL, EUA) será utilizado. Os dados serão verificados quanto à distribuição normal de igualdade de variâncias como requisito para a utilização de testes ou análises paramétricas. Quando necessário, o método complementar de Tukey será utilizado.

2.4 Orçamento

O recurso que será utilizado para a execução do presente projeto é proveniente da **Chamada pública MCT/FINEP/AÇÃO TRANSVERSAL – NANOTECNOLOGIA – 05/2009**, nº do convênio: 01.10.0709.01; título do convênio: Biomateriais, no valor de R$ 924.728,00.

A relação de itens de contrapartida do presente projeto está demonstrada na Tabela 1, cujos itens já se encontram disponíveis no local de execução do projeto.

Tabela 1 – Relação de itens de contrapartida do presente projeto

REAGENTES E INSUMOS	
Descrição	**Custo (R$)**
Reagentes orgânicos	1240,00
Reagentes inorgânicos	210,00
Vidrarias para manipulação e análise das formulações	600,00
Equipamentos	750,00
TOTAL	**2800,00**

2.5 Cronograma

O cronograma do presente projeto está apresentado na Tabela 2.

Tabela 2 – Cronograma de atividades

Atividade	2011	2012	2013	2014	2015
Pesquisa Bibliográfica	X*	X*	X*	X*	Jan-Ago
Elaboração do Projeto	Dez	Fev-Abr			
Qualificação		Ago			
META-FÍSICA 1		Set-Dez	Jan-Fev		
META-FÍSICA 2			Mar-Set		
META-FÍSICA 3			Out-Dez	Jan	
Estádio Sanduíche				Mar-Dez	Jan-Abr
Tabulação dos dados		Dez	Out	Jan	Mai
Redação dos artigos					Jun-Ago
Redação da Tese					Set
Defesa					Out

* X: referente a todos os meses do ano.

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3 Relatório do trabalho de campo

Esta seção se refere única e exclusivamente à descrição das atividades que foram realizadas conforme planejado e apresentado no projeto de pesquisa, bem como aquelas que não puderam ser realizadas, e, portanto, foram modificadas e posteriormente acrescentadas.

Inicialmente, cabe salientar que não se planejou realizar uma revisão sistemática, mas devido o tema central deste estudo ser o desenvolvimento de materias resinosos com reduzida tensão de contração, percebeu-se a importância e necessidade de se realizar uma revisão bem delineada sobre as possíveis estratégias capazes de reduzir a tensão de contração de materiais resinosos utilizados em odontologia. De fato, apesar de ser um assunto abundantemente abordado na literatura, notou-se a inexistência de uma revisão sistemática com meta-análise de dados. Portanto, uma revisão sistemática com meta-análise foi planejada posteriormente à qualificação do projeto de pesquisa, tornando-se o primeiro artigo científico deste volume. Certamente, este artigo contribuiu para basear, cientificamente, os demais artigos que foram preparados no estudo.

Quanto à execução da META-FÍSICA 1, a qual teve como foco caracterizar resinas experimentais contendo monômeros dimetacrilatos elastoméricos (exotanos), pode-se dizer que ela foi parcialmente completada nesse estudo. Na verdade, algumas mudanças foram propostas desde a escolha dos exotanos que seriam analisados até os testes utilizados para a sua caracterização. Segundo informações coletadas no website da empresa fornecedora dos exotanos (Esstech, Inc.), planejou-se utilizar apenas os exemplares 8, 10 e 26 já que eles apresentavam características ideais para a formulação de resinas com potencial redutor de tensão de contração. Entretanto, devido à inexistência de estudos na literatura relatando qualquer informação sobre qualquer exotano, resolveu-se caracterizar o desempenho de mais exemplares deles (9, 24 e 32), e, principalmente, quanto à sua cinética de polimerização e capacidade de desenvolver tensão de contração. Ainda, por meio de estudos piloto envolvendo esses exotanos, constatou-se que a reação de polimerização dos mesmos poderia ser desencadeada por diferentes sistemas de fotoiniciação, tornando-se um novo foco da caracterização dos mesmos. Por isso, o presente estudo avaliou o efeito de diferentes exotanos contendo diferentes sistemas de fotoiniciação tanto na cinética de polimerização como no desenvolvimento de tensão de contração de resinas experimentais. As demais metodologias de caracterização planejadas na META-FÍSICA 1, como resistência flexural, módulo flexural, dureza Knoop e contração volumétrica, não foram executadas. Mesmo asism, as informações e resultados obtidos com a META-FÍSICA 1 modificada são importantes e extremamente interessantes à comunidade científica odontológica, pois abrem oportunidades de se utilizar os exotanos não apenas como agentes redutores de tensão, mas também para outras aplicações que foram discutidas ao longo do estudo. Por fim, o segundo artigo do presente estudo retrata da caracterização de resinas experimentais contendo diferentes exotanos e diferentes sistemas de fotoiniciação, avaliando o desempenho destes materiais quanto à sua polimerização e capacidade de desenvolver tensão de contração.

Quanto à execução da META-FÍSICA 2, a qual teve como foco sintetizar micro e nano-esferas poliméricas através de polimerização por emulsão e analisá-las quanto a sua granulometria, temperatura de transição vítrea e dispersão na matriz orgânica, pode-se dizer que ela não foi completada nesse estudo. Várias tentativas utilizando-se de diferentes reagentes e diferentes sequências reacionais foram realizadas; contudo, várias dificuldades foram detectadas com a execução da polimerização por emulsão. Enquanto que algumas tentativas resultaram na obtenção de macro-esferas poliméricas, outras inúmeras tentativas resultaram em um produto amorfo e em estado coloidal, ou seja, morfologicamente diferente daquilo que se esperava obter. Após pesquisa de diversos estudos relacionados à síntese de partículas poliméricas por meio de polimerização por emulsão, constatou-se que não existe um método comum, já que dependendo do estudo, diferentes reagentes e diferentes sequências reacionais são utilizadas. Ainda, muitos estudos relataram a necessidade de se realizar este método de polimerização em sistemas reacionais mais complexos, que no caso, não estavam à disposição na época em questão. Dessa maneira, a ideia de utilizar micro e nano-esferas para compor resinas experimentais com potencial capacidade de reduzir tensão de contração não foi concluída, o que possibilitou a nossa equipe procurar uma estratégia alternativa.

Neste meio tempo entre a experimentação da META-FÍSICA 2 e a decisão por modificá-la surgiu a possibilidade de realizar estágio de doutoramento sanduíche na Indiana University Purdue University of Indianapolis (IUPUI), na cidade de Indianápolis, IN, EUA. Na referida instituição, e sob a coorientação do Prof. Dr. Marco C. Bottino, nanofibras poliméricas foram sintetizadas por meio do método de eletrofiação (em inglês, *electrospinning*). Segundo a literatura atual, não há relatos sobre o efeito de nanofibras poliméricas no fenômeno da tensão de contração, e, por isso, essa se tornou uma alternativa viável para substituir a META-FÍSICA 2 do projeto de pesquisa do estudo. Assim, ao invés de completar a META-FÍSICA com a síntese das micro/nano-esferas poliméricas, nós fabricamos nanofibras poliméricas. Consequentemente, a caracterização das nanofibras não seguiu os mesmos testes prometidos na META-FÍSICA 2 original, isto é, análise granulométrica, análise da temperatura de transição vítrea, e análise da dispersão na matriz orgânica; porém, as nanofibras foram caracterizadas por meio de microscopia eletrônica de varredura e espectroscopia de infravermelho.

Quanto à execução da META-FÍSICA 3, a qual teve como foco analisar o comportamento físico-mecânico de resinas experimentais contendo micro e nano-esferas poliméricas como partículas de carga, em decorrência da impossibilidade de completar a META-FÍSICA 2, a META-FÍSICA 3 também não pôde ser completada na sua forma original. No entanto, ela foi modificada substituindo-se as micro/nano-esferas pelas nanofibras sintetizadas na META-FÍSICA 2 modificada. As resinas experimentais modificadas por nanofibras foram caracterizadas por testes físicos e mecânicos, bem como pelo teste de tensão de contração, conforme planejado nesta etapa do projeto. Consequentemente, a META-FÍSICA 3 modificada permitiu a escrita de um terceiro artigo, o qual integrou o volume final desse estudo.

De maneira geral, o projeto de pesquisa do presente estudo passou por algumas modificações estruturais e metodológicas, porém o conteúdo final obtido foi aceitavelmente semelhante ao prometido. Além disso, a inclusão da revisão sistemática com meta-análise aumentou a relevância desse estudo, pois esta última, no fim das contas, fornece uma sequência lógica do conhecimento básico-aplicado sofre o fenômeno de tensão de contração de materiais resinosos (Artigo 1) até a apresentação de estratégias alternativas para minimizar esse fenômeno negativo dos materiais (Artigos 2 e 3), o que desde o começo era o objetivo central do estudo.

4 Artigo 1

Strategies available to reduce contraction stress of resin-based dental materials – A systematic review with meta-analyses[§]

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Key words: polymerization shrinkage, stress reduction, resin composites, resin cements, resin adhesives, siloranes, low-shrinkage, bulk-fill, fillers, photo-activation mode

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Abstract

The aim of the present review and meta-analyses was first to determine whether the existence of any strategy available to reduce contraction stress development in dental resin-based restorative materials, and second to identify the most effective approach/strategy. Following Preferred Reporting Items for Systematic Reviews and Meta-Analysis (PRISMA) guidelines, we conducted a search in 7 databases (PubMed, Web of Science, Scopus, SciELO, LILACS, Ibecs, and BBO), resulting in 77 studies that reported on a strategy, technique, or alternative formulation (hereafter referred to as “strategy”) that reduced stress. From these studies, meta-analyses were performed with 74 studies only and using RevMan 5.1 (The Cochrane Collaboration, Copenhagen, Denmark). A global comparison was performed with random-effects models at a significance level of $p < 0.05$. The strategies were firstly allocated according to a “technique” or “composition” category, depending on the nature of the modification. Within the technique category (n=29), strategies such as the use of an alternative technique protocol of placing the material, the reduction of the irradiation intensity/energy delivered to the material, the use of an alternative light-curing unit/source, or the use of an alternative photo-activation mode, could be detected. Within the composition category (n=48), several strategies were revealed, which were subdivided according to the part of the material that was modified: the filler phase, the resin-filler interface, or the resin matrix. From the simple modification of the material’s placing technique/photo-activation protocol to the modification of the material’s composition, it seems that the latter main strategy contributes more to minimize stress development than the former. The stress decreasing technology used for the formulation of low-shrinkage and bulk-fill materials has optimized the conventional chemistry of current dental materials, showing promising application for reducing stress development. Finally, there are other formulations that have not been yet translated to commercial materials such as the thiol-ene, thio-urethane, tetraoxaspiroalkane, or trithiocarbonate systems; therefore, it can be expected further improvements in the formulation of new stress decreasing restorative materials. Collectively, contraction stress can be positively reduced in resin-based dental restorative materials.

INTRODUCTION

Resin-based materials have been thoroughly used in dentistry as restorative materials (e.g., resin composites, resin cements, resin adhesives) especially due to their versatility and easiness of application. Differently from other traditional dental restoratives such as amalgam or porcelain, resin materials may present a basic composition comprised of two distinct phases: an organic matrix mainly constituted of resin monomers, and an inorganic phase composed of filler particles; both the organic and inorganic phases can be chemically bonded to each other upon the presence of a coupling agent (Ferracane, 2011). Notably, dental resin formulations have been evolved since their introduction in dentistry, resulting in materials with equilibrated structural characteristics. Notwithstanding, despite all improvements in physic-mechanical properties (e.g., strength, wear resistance) that modern materials exhibit compared to the first ones launched in the market, most resin-based materials still demonstrate a concerning limitation: they shrink in volume (Dauvillier et al., 2000).

Polymerization shrinkage is an intrinsic property of conventional resin-based materials caused by the approximation of monomers during polymerization, i.e., when the distance between monomers is reduced due to the conversion of the weak van der Waals forces into covalent bonds (Kim et al., 2015). However, it is important to note that the polymerization shrinkage itself is not the most deleterious factor, but the stress generated at the tooth/restoration interface while the material is undergoing shrinkage in a confined environment such as tooth cavities or root canals (Braga et al., 2005). This foregoing phenomenon is usually defined as polymerization/contraction stress, and it has been increasingly associated as one of the reasons for failure of resin-based restorations (Cramer et al., 2011), especially for resin composites or resin cements. Indeed, several negative effects may occur, including but not limited to restoration/post de-bonding, cuspal deflection, microleakage, and post-operatory hipersensitivity (Ferracane and Mitchem, 2003; Ferracane, 2008; Goncalves et al., 2012). Consequently, contraction stress should be reduced and/or controlled as much as possible in order to prevent the occurrence of those unpleasant situations and hence, favoring the clinical success of the restorative treatment.

During the last few decades, several strategies have been presented in the literature in an attempt to solve or control the aforementioned problematic. While some of the strategies have reported on changing the placing technique and/or the photo-activation protocol of the material, others have proposed on the modification of its chemical composition. Surprisingly, there is no previous report on a meta-analysis study regarding this subject. Therefore, considering that important information can be collected and produced upon reviewing those studies, the purpose of the present study was to systematically review the literature regarding the potential alternatives to reduce the contraction stress phenomenon associated to resin-based restorative materials.

MATERIALS & METHODS

This systematic review is reported following the guidelines of the PRISMA statement (Moher et al., 2009). The research question was as follows: Is there any strategy available to reduce contraction stress development in dental resin-based restorative materials?

Systematic literature search

This study identified all studies which reported on strategies/techniques/formulations (hereafter referred to as “strategy”) that reduced the contraction stress phenomenon of resin-based materials. The search was systematically performed in seven distinct electronic databases by two independent reviewers, i.e., PubMed, ISI Web of Knowledge, Scopus, SciELO, LILACS, IBECS, and BBO (*Biblioteca Brasileira de Odontologia*). The keywords related to the search strategy in PubMed are listed in Table 1. Two independent reviewers carried out the literature search until August 2015. After the screening of articles in all databases, they were imported into Endnote x7 software (Thompson Reuters, Philadelphia, PA, USA) to remove duplicates.

All abstracts were read to verify the inclusion criteria: in vitro studies that reported on contraction stress reduction after application of an alternative strategy. If this information was not clear in the abstract, the papers were retrieved in full text. Only papers that evaluated contraction stress by direct testing were included; consequently, studies that used only indirect methods (e.g., microleakage and/or cuspal deflection measurements) were excluded. Studies reporting on finite elemental analyses or theoretical/mathematical models were also excluded since they are predictive analyses. Only papers written in English and Portuguese languages were considered for this review, without restriction of year of publication.

Any disagreement regarding the eligibility of the included studies was resolved through discussion and consensus. Only papers that fulfilled all of the eligibility criteria were included.

Data extraction

For each included study, the following data/information was recorded using a standardized form in the Microsoft Office Excel 2013 software (Microsoft Corporation, Redmond, WA, USA): the strategy used to reduce contraction stress and the magnitude of the stress reduction, which was given in approximated percentage values, i.e., range between minimum and maximum values. Data related to the contraction stress mean (±standard deviation/SD) values, in MPa, and number of specimens, were also tabulated. If any information was missing, the authors of the included studies were contacted twice via e-mail to retrieve the missing data; if authors had not given an answer by one month after the first contact, the respective study was promptly excluded from the review.

Quality assessment

The methodological quality of each included study was assessed and adapted from another systematic review of in vitro studies (Downs and Black, 1998). The risk of bias was evaluated according to the articles' description of the following parameters: "informed number of specimens", "informed mean ±SD values", "presence of a clear control group", "informed specimen dimension", "monitored stress kinetic", and "informed about testing compliance". If the authors reported the parameter, the article had a "Yes" on that specific parameter; if it was not possible to find the information, the article received a "No." Articles that reported up to two items were classified as having a high risk of bias, three to four as a medium risk of bias, and five to six as a low risk of bias (Appendice).

Meta-analysis

The values of contraction stress with the alternative strategy were compared to the control(s) used in each study. The alternative strategies were allocated in two main categories: those that modified the technical protocol of placing/photo-activating the material (technique category) or those that modified the chemical composition of the material (composition category). Subgroup analyses were performed in order to decrease heterogeneity.

Pooled-effect estimates were obtained by comparing the mean difference between alternative strategies and the control groups within each study. A *P* value

≤.05 was considered statistically significant. The global analysis was carried out using a random-effect model using Review Manager Software version 5.1 (The Nordic Cochrane Centre, The Cochrane Collaboration, Copenhagen, Denmark). Statistical heterogeneity of the treatment effect among studies was assessed using the Cochran's Q test and the inconsistency I^2 test, in which values greater than 50% were considered as indicative of substantial heterogeneity (Higgins and Green, 2008). Qualitative analysis was performed to elucidate the effect of each alternative strategy on the contraction stress phenomenon.

RESULTS

Study selection and characteristics

The results from the search are shown in Figure 1 according to the PRISMA Statement (Moher et al., 2009). In total, 1,447 publications were retrieved in all databases. From those publications, and after duplicates removal, a total of 914 papers were examined by the titles and abstracts, 808 studies were excluded because they did not fulfill the eligibility criteria, and 106 papers were assessed by full-text reading. From the 106 studies retained for detailed review, 29 studies were not included because of the following reasons: one study was related to theoretical calculation (Alcoutlabi et al., 2003), one study was related to finite elemental analysis (Rees et al., 1999), two studies were presented in a different language (Jodkowska et al., 2012; Kang et al., 2007), three studies did not demonstrate stress reduction results (Pick et al., 2011; Schneider et al., 2009; Spinell et al., 2009), three studies evaluated stress by using indirect measurements (Clifford et al., 2009; Feilzer and Dauvillier, 2003; Kwon et al., 2012), four studies could not be retrieved in full-text version (Bouschlicher et al., 1997; Ernst et al., 2000; Kanca and Suh, 1999; Koran and Kurschner, 1998), six studies did not evaluate contraction stress (Chappelow et al., 2007; De Santis et al., 2010; Deb et al., 2003; Ellakwa et al., 2007; Emami et al., 2003; Lee et al., 2006), and nine studies did not inform some requested information for the qualitative analysis (Chen et al., 2015; Condon and Ferracane, 2000; Liu et al., 1999; Liu and Stansbury, 2014; Park et al., 2010; Park et al., 2012c; Pfeifer et al., 2011; Sun et al., 2011; Szczepanski and Stansbury, 2014). A total of 77 studies were included in the qualitative analysis, and three of these studies (Lu et al., 2005a; Schreck et al., 2011; Xiong et al., 2011) did not inform requested information for the quantitative analysis, so only 74 studies were included for the meta-analyses.

Meta-analyses results

In total, meta-analyses were performed with 74 in vitro studies, which main results are described in Tables 2, 3 and 4. Table 2 shows the results obtained from studies reporting on the use of alternative “technique protocols”, “irradiation intensity/energy”, and “light-curing units/sources”. Statistically significant differences between those alternative strategies and their respective controls were observed ($p<.05$), with substantial heterogeneity among the groups (respectively, I^2 = 99%, 95%, and 93%). For studies that reported on alternative photo-activation protocols, which results are shown in Table 3, the “intermittent light”, “exponential”, “soft-start”, and “pulse delay” photo-activation modes showed statistically significant differences when compared to their respective controls, i.e., standard/continuous polymerization mode, ($p<.05$) with inconsistency (I^2) values of 0%, 86%, 97%, and 94%, respectively. Regarding to studies that reported on alternative/modified chemical composition of resin-based materials, the results were separated into subgroups according to the modified part of the material: “filler phase”, “resin-filler interface”, or “resin matrix”. The results are described in Table 4, which demonstrated statistically significant differences when compared to the respective control groups ($p<.05$), and heterogeneity values that ranged from 0 to 100% depending on the subgroup.

Qualitative/Descriptive analysis

All studies that were included in the review as well as their respective main strategies used to reduce contraction stress and the approximate stress reduction percentage range are demonstrated in Tables 2, 3, and 4. Among all strategies associated with significant contraction stress reduction, two distinct categories were drawn: the modification of the restorative technique (technique category, n=29) or the partial/total modification of the material’s composition (composition category, n=48). Some studies were grouped in both categories and within two or more additional subgroups since they reported on the modification of something related to both the technique and composition categories. Regarding to the former category, four strategies were observed: (1) the use of an alternative technique or additional step of placing the material (n=10); (2) the modification of the irradiation intensity/energy used to photo-activate the material (n=8); (3) the use of an alternative light-curing source (n=2); and (4) the use of alternative photo-activation modes for curing the material, such as the “intermittent light” mode (n=2), the “exponential” mode (n=4), the “soft-start” mode (n=6), and the “pulse delay” mode (n=9). The stress reduction percentage values ranged from 1.3 to 78%. Among the placing technique subgroup, the most effective approach was to pre-heat the material to 40 or 60°C and to photo-activate it for reduced time (5s) (Calheiros et al., 2014); among the irradiation intensity/energy subgroup, reducing the irradiation energy was considered the best approach (Calheiros et al., 2004; Calheiros et al., 2006; Calheiros et al., 2008; Ilie et al., 2007); among the light-curing unit/source subgroup, replacing the conventionally used quartz-tungsten halogen (QTH) source by argon ion laser (Delfino et al., 2009) or light-emitting diode (LED) (Zanchi et al., 2006) sources illustrated an effective method to reduce stress development; finally, among the photo-activation subgroup, all alternative modes presented an overall similar potential to decrease stress, although the pulse delay mode displayed a more concise performance (Table 3).

Within the composition category, which results are shown in Table 4, the stress reduction percentage values ranged from 2.3 to 59.4%, 8.7 to 46.3%, and 0.3 to 98.7% for the filler phase, resin-filler interface, and resin matrix subgroups, respectively. Within the filler phase subgroup, the studies were also subdivided into four classes: (1) studies that increased the content of fillers (Goncalves et al., 2010a; Goncalves et al., 2011); (2) studies that increased the size of fillers (Satterthwaite et al., 2012); (3) studies that incorporated alternative fillers (Ferracane et al., 2003; Garoushi et al., 2008; Szaloki et al., 2013); and (4) studies that incorporated nanogels into the material (Liu et al., 2012; Moraes et al., 2011). From these foregoing classes, the incorporation of nanogels showed the most effective approach to reduce stress development. Within the resin-filler interface subgroup, the studies were subdivided into two additional classes: (1) studies that used non-bonded/unsilanized fillers instead of silanized fillers (Condon and Ferracane, 1998; 2002); and (2) studies that used alternative functionalization systems of fillers (Condon and Ferracane, 1998; Ye et al., 2012). From these studies, the latter strategy resulted in overall higher stress reduction than the former. Lastly, within the resin matrix subgroup, the studies were subdivided according to the following classes: (1) studies that modified the composition ratio of conventional formulations (Braga and Ferracane, 2002; Charton et al., 2007b; Goncalves et al., 2010b; Goncalves et al., 2011); (2) studies that used alternative photo-initiators (Oliveira et al., 2012; Palin et al., 2014); (3) studies that used silorane-based monomers/materials (Eick et al., 2007; Gao et al., 2012; Ilie and Hickel, 2011; Li et al., 2012; Marchesi et al., 2010; Min et al., 2010; Oliveira et al., 2012; Xiong et al., 2011; Yamasaki et al., 2013); (4) studies that used thiol-ene-based monomers (Beigi Burujeny et al., 2015; Boulden et al., 2011; Carioscia et al., 2005; Carioscia et al., 2007; Cramer et al., 2010a; Cramer et al., 2010b; Lu et al., 2005a; Schreck et al., 2011; Ye et al., 2011); (5) studies that used thio-urethane oligomers (Bacchi et al., 2014; Bacchi et al., 2015); (6) studies that used alternative monomers/molecules (Chappelow et al., 2008; Eick et al., 2007; Leung and Bowman, 2012; Park et al., 2012a; Park et al., 2012b; Wilder et al., 2005); (7) studies that used low-shrink compositions (Aleixo et al., 2014; Boaro et al., 2010; Cadenaro et al., 2008; Ernst et al., 2004; Gao et al., 2012; Marchesi et al., 2010; Watts and Alnazzawi, 2014; Yamasaki et al., 2013); and (8) studies that used bulk-fill technology (Cadenaro et al., 2009; El-Damanhoury and Platt, 2014; Ilie and Hickel, 2011; Kim et al., 2015; Taubock et al., 2014; Zorzin et al., 2015). From these foregoing studies, the "alternative monomers" class presented higher potential to reduce stress development when compared to the other technologies/classes.

Quality assessment

Fourteen from the 77 studies (approximately 18%) included in this systematic review were scored with a medium risk of bias, whereas all of the other 63 studies were all considered with low risk of bias (Appendice). The most frequent parameter that was missing in the studies was the use of a clear control group (around 39% of all studies).

DISCUSSION

According to the present systematic review, there are five general factors that may affect the contraction stress phenomenon of light-sensitive resin-based materials, which are illustrated in Figure 2: the technique protocol of placing the material, the irradiation intensity/energy delivered to the material, the type of light-curing unit/source used, the photo-activation mode used, and the chemical composition of the material. While the four former factors were here categorized within the "technique category" since they involve in procedures related to the placing/photo-activation of the material, the latter factor was categorized within the "composition category". Furthermore, within each category, several strategies were found to be positively associated to significant contraction stress reduction, which will be hereafter discussed in order to present the mechanisms and consequences involved in their stress reduction effect.

Technique category

Use of alternative techniques or additional steps for placing the material

Several studies have demonstrated that using a modified technique protocol or adding an additional step during the placing of the material may produce less amount of stress (Table 2). Alster et al. (1992) investigated the effect of porosity in reducing stress under restrained conditions of polymerization. The authors produced different levels of porosity within an unfilled resin, i.e., a pore-free resin (control) and two other resins presenting approximately 40% and 115% higher porosity, and they concluded that the greater the concentration of porosity, the greater the stress relief by voids, thus resulting in significant stress reduction (17 and 42%, respectively). Other studies have reported on the use of a liner (e.g., flowable composite or unfilled resin) (Braga et al., 2003; Cunha et al., 2006) or increased thicknesses of adhesive resin (Choi et al., 2000; Cunha et al., 2006) between tooth and the restorative material; the authors explained that the lower stiffness of the liner allows stress relaxation to occur, thus reducing stress. Regarding to the amount of material placed into the tooth cavity, studies revealed that using less volume of resin cements (Ishikiriama et al., 2013) or less thicknesses of resin composites (Lee et al., 2007) contributed to significantly reduce stress, regardless of the C-factor; this result was explained by the higher flowability that thin layers have as compared to thick layers of material. Considering dual-cure resin cements, Braga et al. (2002) reported on approximately 25 to 38% reduction of stress upon the use of the self-cure mode (without photo-activation) rather than the dual-cure mode (with photo-activation, as manufacturer's directions of use); indeed, the authors suggested that the lower degree of conversion achieved as well as the slower curing speed of the former when compared to the latter resulted in less modulus development, and consequently, less amount of stress. Similarly, Faria-e-Silva et al. (2011) demonstrated that delaying the photo-activation of dual-cure resin cements in 5 minutes delayed the acquisition of a high elastic modulus, allowing the polymer chains to rearrange and accommodate the reduction of volume by plastic deformation, which thereby reduced contraction stress; worth mentioning, degree of conversion was not compromised. Lastly, two studies have demonstrated that pre-heating resin composites to 37°C (Watts and Alnazzawi, 2014) or to 40/60°C (Calheiros et al., 2014) prior to their placing into the tooth cavity expanded the material and increased its free volume, facilitating polymer chain movement and greater compliance of the resin matrix; therefore, contraction stress was reduced.

Overall, the most effective strategy within this subdivision was to pre-heat the material to 40 or 60°C prior to polymerization, showing stress reduction percentage values that ranged from 54 to 70%; moreover, degree of conversion was also progressively increased with greater pre-heating temperatures (Calheiros et al., 2014).

Before moving on to the next strategy division, another aspect that must be stated at this part of the review is the potential applicability of the so-called “incremental technique” of placing resin composites in reducing stress development at the tooth/restorative interface. Considering that the effect of the incremental technique in reducing stress has been evaluated only by indirect testing (i.e., by means of cuspal deflection or microleakage measurements), none studies related to this subject could be included in the systematic review. However, this technique was revealed to be effective in reducing the negative effects of contraction stress of resin-based dental materials (Petrovic et al., 2010), and it has been currently used to minimize those effects.

Modification of the irradiation intensity/energy used to photo-activate the material

All studies included in this subdivision of the review, which are shown in Table 2, demonstrated that decreasing the irradiation intensity (i.e., power density) and/or the irradiation energy (i.e., *irradiation intensity* multiplied by the *exposure time*) during photo-activation of filled/unfilled resins produced considerably less contraction stress values when compared to the use of high levels of irradiation (Bouschlicher and Rueggeberg, 2000; Calheiros et al., 2004; Calheiros et al., 2006; Calheiros et al., 2008; Ilie et al., 2007; Taubock et al., 2014; Witzel et al., 2007; Wydra et al., 2014). Indeed, it is well-known that the irradiation intensity/energy applied to the material directly affects its overall polymerization, and according to Miyazaki et al. (1996), slow polymerization reactions provided by application of low energy density allow the formation of long molecular chains with high flow characteristics, resulting in stress relaxation, and consequently, reduction in overall contraction stress. Notwithstanding, despite all positive effects on producing lower levels of stress, one important aspect that must be considered regarding this strategy is the potential deleterious effect that low irradiant intensities/energies may produce on physic-mechanical properties of the material. For examples, degree of conversion was revealed to be the property more negatively affected (Calheiros et al., 2004; Calheiros et al., 2008; Witzel et al., 2007;

Wydra et al., 2014), as well as flexural strength and hardness, depending on the material tested (Calheiros et al., 2006). Therefore, the use of reduced irradiation intensity and/or energy during photo-activation should be considered with caution as a strategy to reduce/control stress development in order to prevent inferior performance of the restorative material.

Use of alternative light-curing unit/source

During the last few decades, quartz-tungsten-halogen (QTH) light-curing units have been the most common devices used to photo-activate resin-based materials. Nevertheless, QTH units used to waste curing energy and produce excessive heat, so alternative units (e.g., argon ion laser or light-emitting diode/LED) were introduced to dentistry in an attempt to overcome these disadvantages. From the studies included in this review (Table 2), one study investigated the effect of the argon ion laser unit on contraction stress development (Delfino et al., 2009). The authors tested different irradiation intensities (200 or 250 mW/cm^2) applied for different periods of time (10 or 20s) and demonstrated that this light-curing unit produced from 19 to 72% less stress than the QTH unit (control); indeed, the best combination was to apply 250 mW/cm^2 for 10s. The authors stated that the argon ion laser has a monochromatic, coherent, and collimated light that delivers a large concentration of energy in a small area, which may have contributed to produce an overall lower amount of stress. Notwithstanding, it is important to note that the authors did not mention about the irradiation intensity applied with the QTH unit; even so, this latter type of unit usually applies irradiation intensities around 600 mW/cm^2, so it may be also suggested that the lower stress generated by the alternative unit is more related to the lower total amount of irradiation energy delivered to the material, as stated in the last section. Regarding to the second study included in this subdivision of the review (Zanchi et al., 2006), the stress produced by a LED unit was compared to that produced with a QTH unit. Notably, the stress reduction ranged from approximately 10 to 78%, which was attributed by the authors to be due to a reduced conversion degree of the materials. Indeed, the LED unit used in this study had an irradiation intensity of 125 mW/cm^2, i.e., approximately four times lower than that emitted by the QTH unit (507 mW/cm^2); once again, and considering that both light-curing units were applied for the same period of time (40s), the lower irradiation energy delivered by the LED unit led to less development of stress when compared to the QTH unit. Worth mentioning, LED units became the most currently used light-curing devices today, and they have an irradiation intensity much higher than that presented in the study of Zanchi et al. (2006), so it is reasonable to assume that they may not present the same positive effect in reducing contraction stress as demonstrated in that study.

Use of alternative photo-activation mode

Taking into consideration that both the irradiation intensity and the irradiation energy applied/delivered to the material have a considerable influence on the contraction stress phenomenon, alternative photo-activation modes were designed and introduced in dentistry in order to produce less levels of stress. Ultimately, the final irradiation energy was not intended to be modified, but the irradiation intensity applied as well as the duration of the photo-activation process. According to the studies included in the review (Table 3), four distinct modes were mainly observed: “intermittent light” (also known as pulsed curing), “exponential” (also known as ramped curing), “soft-start”, and “pulse delay”. For all studies, the continuous photo-activation mode was considered as the standard mode (control).

Regarding to the first alternative mode, i.e., intermittent light, it refers to the application of a non-continuous light characterized by consecutive light-on and light-off periods. The two related studies included in the review (Cunha et al., 2006; Ilie et al., 2007) used different light-curing sources, and consequently, different protocols of applying the intermittent light; nonetheless, they resulted in a quite similar stress reduction range. It was suggested that the light-off periods reduced the overall rate of polymerization, allowing slower formation of the polymeric chains and accommodation in the initial phase of polymerization, which thereby resulted in reduced stress development. Concerning the second alternative mode, i.e., exponential, it refers to the application of an initial low irradiation intensity that is logarithmically increased until a maximum value, followed by final high irradiation intensity. Four related studies were included in the review: while two of these studies reported on an approximate 30% stress reduction when compared to the control (Bouschlicher and Rueggeberg, 2000; Ilie et al., 2007), which may be considered a significant reduction, the others showed a percentage reduction lower than 8% (Charton et al., 2007a; Ernst et al., 2003). Despite the controversial findings, the authors suggested that the mechanism of reduced contraction stress development was partially due to a prolonged gel point, which allows the material to flow for a longer time period, and also due to a possible reduction in the overall conversion degree of the material. With regards to the third alternative mode, i.e., soft-start, it refers to the application of an initial low irradiation intensity followed by final high irradiation intensity; worth mentioning, the soft-start mode differs from the exponential one because it did not increase the irradiation intensity following a progressive trend. The stress reduction range obtained upon the use of the soft-start mode differed among the included studies: while some reported on very low effectiveness (Bouschlicher and Rueggeberg, 2000; Cunha et al., 2006; Cunha et al., 2007; Taubock et al., 2014), others reported on a moderate to significant stress reduction (Lu et al., 2005b; Zanchi et al., 2006). Once again, it was assumed that the low initial irradiation intensity produced by the soft-start mode reduces the kinetic of the polymerization reaction, thus decreasing the number of polymer growth centers; therefore, the material shows increased opportunity for viscous flow and chain relaxation before mobility is restricted by vitrification, thereby reducing stress development. Lastly, regarding to the fourth alternative mode, i.e., pulse delay, it refers to the application of an initial short pulse of light, followed by a waiting time (hiatus) before the final light exposure is performed. According to the related studies included in the review (Cunha et al., 2007; 2008; Ishikiriama et al., 2012; Lim et al., 2002; Lopes et al., 2008; Lu et al., 2005b; Pfeifer et al., 2006; Taubock et al., 2014; Witzel et al., 2007), they broadly varied with regards to the initial and final irradiation intensities, as well as to the hiatus period used, and the stress reduction results ranged from 2 to 38%. It was suggested that the pulse delay mode allows for an enhanced flow or deformation of the material, reducing residual stress.

Taking all the meta-analyses performed within the “technique category” together, the use of alternative light-curing unit/source demonstrated the highest mean difference (1.39), and consequently, the most effective approach; whereas the use of the exponential photo-activation mode exhibited the lowest mean difference (0.11). Nonetheless, these results should be interpreted with caution since heterogeneity was high for all analyses performed.

Composition category

Dental resin-based materials are usually constituted of three distinct components, namely resin matrix, filler particles, and coupling agent. From the studies that were categorized within the composition category, they were also separated according to the part of the material that was modified/investigated (Table 4).

Filler phase

Increasing the content of fillers

Two studies included in this review demonstrated up to 26% (Goncalves et al., 2010a) or up to 14% (Goncalves et al., 2011) stress reduction upon the increase in the content of fillers. Indeed, there is a strong inverse relationship between filler content and polymerization shrinkage suffered by the resin since the greater the concentration of fillers, the lower the total amount of resin matrix prone to shrink, thus producing less stress. Notwithstanding, this strategy may not be always suggested since increasing the content of fillers may also increase stiffness and modulus development within the material, thus reducing compliance of the system, and consequently, producing higher levels of stress. Important to mention, the stress reduction range presented in Table 4 for the included studies was obtained only from groups that showed double/half filler content compared to each other, method that was intended in order to simplify presentation of data; however, the studies demonstrated that even upon a slight increase (e.g., 5 vol.%) in the concentration of fillers, a significant stress reduction was obtained.

Increasing the size of fillers

Only one of the studies included in this systematic review investigated the effect of the size of fillers on contraction stress (Satterthwaite et al., 2012). According to the study, a decrease in filler particle size directly increases the surface area of the dispersed phase, thus increasing the constraint of fillers upon the resin matrix. This constraint effect concentrates stress, thereby increasing the development of stress within the material. Interestingly, the positive effect that the progressive increase in fillers size have on stress reduction was more pronounced for spherical fillers (from 21 to 48%) over irregular fillers (from 10 to 17%), and this was mainly attributed because the former undergo more translation and rotational movement within the resin matrix than the latter do, thus allowing more stress relaxation to occur. Worth mentioning, current resin-based filled materials have been prepared using quite small fillers especially due to better stability and aesthetical characteristics that may be obtained when compared to larger fillers (Ferracane, 2011). Consequently, the strategy presented here may not be that useful to control/reduce contraction stress in currently used dental materials.

Incorporation of alternative fillers

Conventionally used fillers such as quartz, silica, and glass particles are rigid compounds that increase modulus acquisition within the material, thus developing high levels of contraction stress. However, three studies that were included in this systematic review have demonstrated significant stress reduction upon the application of alternative fillers. One of the studies incorporated up to 20 wt.% of high-density polyethylene (HDPE) spheres (Ferracane et al., 2003), and the authors concluded that because of the less rigid polymeric nature of the HDPE spheres, plastic deformation during stress buildup was more possible to occur, favoring stress relaxation; unfortunately, mechanical properties were also reduced, thus limiting their application as reinforcing fillers. By contrast, the study of Szaloki et al. (2013) have synthesized cross-linked polymeric nanoparticles and tested their effects on several physic-mechanical properties and contraction stress developed by experimental resin composites. The authors demonstrated that upon incorporation of 5 to 25 wt.% of the nanoparticles, volumetric shrinkage was reduced from 7 to almost 30%, and contraction stress was reduced from 2 to 18%; surprisingly, flexural strength and flexural modulus were considerably increased when compared to the control (nanoparticle-free composite). According to the authors, the nanoparticles acted as stress relaxing particles, i.e., they were able to absorb the stress during polymerization; furthermore, it was revealed that the nanoparticles have embedded into the resin matrix by swelling ability, which may have enhanced the cohesiveness of the material, and consequently, the mechanical properties. In summary, the authors suggested that the prepared nanoparticles are attractive for the formulation of new reinforced, resin-based dental materials. The last study included within this subdivision of the review was the study of Garoushi et al. (2008) which investigated the effect of short fiber fillers on contraction stress of resin composites with semi-IPN-polymer matrix. Although stress was only slightly reduced (around 5%), the authors suggested that the fiber fillers may absorb the stress that is transferred from the resin matrix during polymerization shrinkage, thus facilitating stress relaxation. Something important to consider regarding to this subject is that the authors used E-glass fibers which may present similar stiffness/modulus properties when compared to glass fillers (Abdulmajeed et al., 2011); however, the use of polymer-based fibers instead of E-glass fibers may produce, perhaps, a more pronounced effect in reducing stress, which may be worth of future investigations.

Incorporation of nanogels

Two studies included in the review reported on effective stress reduction upon the incorporation of nanogels into experimental resin-based materials (Liu et al., 2012; Moraes et al., 2011). Nanogels are internally cross-linked and cyclized single or multi-chain polymeric particles that allow physical entanglement and chemical cross-linking with the resin network. Despite their polymeric nature, nanogels were revealed to improve mechanical properties of nanogel-modified systems. Moreover, they have the ability to induce delayed production of modulus and vitrification, which in turn results in their successful stress reduction ability; indeed, this potential increases with increasing concentration of nanogels incorporated into the resin, and probably due to lower polymerization shrinkage. Another important aspect of nanogels is their applicability for tissue engineering (Goldberg et al., 2007) and drug delivery systems (Raemdonck et al., 2009), which make them very attractive for biomedical applications.

Resin-filler interface

Use of non-bonded/unsilanized fillers

It is well-known that coupling agents allow stress transfer from the resin matrix to the fillers, thus favoring mechanical reinforcement and chemical stability for the material (Sideridou and Karabela, 2009). On the other hand, intrinsic forces originated from polymerization shrinkage are also transferred to the fillers, especially if a strong interaction between resin and fillers is present. In light of this, and considering that fillers will be constrained by the resin undergoing shrinkage, contraction stress may be produced and concentrated within the resin-filler interface, thereby compromising the stability of the system. Taking this into consideration, two studies included in the review have investigated the effect of non-bonded/unsilanized fillers on stress developed by experimental resin composites (Condon and Ferracane, 1998; 2002). Indeed, the stress reduction range was quite similar for both studies (10–31% and 12–27%, Table 4). The authors explained that the absence of coupling agent increased the stress-relieving ability of the material, and probably due to a higher translation and rotational ability of fillers within the resin; this mechanism may also increase the overall compliance of the system (Goncalves et al., 2008), thus dissipating most of the stress produced. Despite this positive effect on reducing stress phenomenon, it is important to note that the use of non-bonded fillers instead of functionalized fillers may significantly compromise the mechanical performance of the material (Condon and Ferracane, 2002).

Use of alternative functionalization system

Differently from the previous section, some studies have reported on effective stress reduction upon the use of non-functional coupling agents instead of functionalized ones (Condon and Ferracane, 1998; 2002). The main mechanism involved in this positive effect is that non-functional agents may reduce the chemical interaction between resin and fillers, which may increase the compliance of the system. Moreover, it was suggested that non-functional silane facilitates pre-gelation contraction, thus producing less amount of stress. Lastly, it is worth to mention that as compared to non-bonded/unsilanized fillers, non-functional silanized fillers may produce satisfactory strength characteristics to the material.

Resin matrix

Modification of the composition ratio of conventional formulations

Generally speaking, the resin matrix of resin-based materials is the main protagonist responsible for the polymerization shrinkage of the material, so any modification related to its composition ratio may be a potential alternative to minimize/control stress development. According to three from the four related studies included in the review, stress may be reduced from 16 to 46% if TEGDMA content is reduced to approximately the half (Charton et al., 2007b; Goncalves et al., 2010b; Goncalves et al., 2011). Indeed, TEGDMA is a typical dimethacrylate monomer used as diluent of more viscous monomers such as Bis-GMA, UDMA, and Bis-EMA (Ferracane, 2011), and the lower molecular weight and viscosity of the former was revealed to increase the reactivity and the overall polymerization shrinkage of the system, thus contributing to increase the contraction stress phenomenon. Consequently, the reduction in the content of TEGDMA directly affects the total amount of stress developed by the material. Another study that showed a stress reducing effect upon the modification of the ratio of components found within the material revealed that increasing the concentration of inhibitor (e.g., butylated hydroxytoluene/BHT) may decrease the reaction speed, thus extending the pre-gel phase with consequent stress reduction/delay (Braga and Ferracane, 2002). Inhibitors are usually present at small concentrations in light-sensitive resin-based materials, especially as a preventive approach against accidental polymerization. Although the presented strategy showed effectiveness in minimizing stress development, other polymerization parameters may be negatively affected, so this strategy should be cautiously considered before application under clinical conditions.

Use of alternative photo-initiators

Camphorquinone/CQ has been thoroughly used as photo-initiator for resin-based dental materials, especially due to satisfactory reactivity and ability to initiate the polymerization reaction when combined to a co-initiator system. Considering that the type of initiation system has a direct influence on the polymerization kinetic of the resin (Ely et al., 2012; Meereis et al., 2014; Munchow et al., 2013), it is reasonable to assume that alternative photo-initiators may also affect the development of contraction stress. Indeed, two studies included in the review demonstrated that experimental resins containing 1-phenyl-1,2-propanedione/PPD (Oliveira et al., 2012) or monoacylphosphine/MAPO (Palin et al., 2014) produced less stress when compared to a CQ-based system (control). While PPD was revealed to slow down the polymerization reaction of the resin, thus allowing more stress relaxation, MAPO showed a more complicated mechanism for stress reduction, which involved in both the delaying of the diffusion-controlled propagation step of polymerization and in the increase of reaction temperature, allowing higher reaction mobility, greater stress relief, and delayed onset of vitrification when compared to the CQ-based resin. Despite this stress reducing effect (qualitative data), the meta-analysis showed no statistical difference between the alternative photo-initiators and the control ($p=0.57$), thus demonstrating that the presented strategy may not be a significant approach to reduce contraction stress.

Use of silorane-based monomers

Conventional dimethacrylates such as Bis-GMA, TEGDMA, and UDMA usually undergo moderate to severe polymerization shrinkage due to their free radical polymerization reaction; indeed, it has been revealed that homopolymers constituted of each of these foregoing monomers would shrink approximately 5, 14, and 9% in volume, respectively (Chung et al., 2002). As a consequence, their presence in the resin system would account for significant polymerization shrinkage to the material, thus contributing for stress development. Differently from these monomers, low-shrinkage silorane-based monomers polymerize through a cationic ring-opening reaction, resulting in polymerization shrinkage values below 1% (Weinmann et al., 2005), which in turn may produce less stress when compared to dimethacrylate-based materials. According to the nine related studies included in this review, silorane-based resin composites showed an important stress reduction potential of up to 97% (Eick et al., 2007; Gao et al., 2012; Ilie and Hickel, 2011; Li et al., 2012; Marchesi et al., 2010; Min et al., 2010; Oliveira et al., 2012; Xiong et al., 2011; Yamasaki et al., 2013). Besides their cationic ring-opening reaction, the authors also suggested that silorane-based composites have improved ability to flow during initial curing stages and before reaching the gel point, thereby contributing to reduce stress (Eick et al., 2007; Min et al., 2010). Despite the significant stress-reducing potential here presented, there are also some studies that did not demonstrate beneficial effects about using silorane-based materials with regards to stress reduction (Aleixo et al., 2014; Marchesi et al., 2010), and reduced mechanical performance was also reported (Eick et al., 2007). Worth mentioning, siloranes were introduced in dentistry as a promising alternative to overcome the negative effects of contraction stress; however, this technology is not currently as attractive as it was some years ago.

Use of thiol-ene-based monomers

The characteristic chain growth nature of the free radical polymerization process of methacrylate systems is usually associated to important drawbacks, including but not limited to high polymerization shrinkage, presence of extractable, unreacted monomers following cure, early gelation, and inhibition of the polymerization by oxygen; overall, the combination of these drawbacks results in considerably high levels of contraction stress (Ferracane, 2005). Conversely, the step growth nature of thiol-ene and/or methacrylate-thiol polymerization, which involves in a chain-transfer reaction of the thiol group to the ene/vinyl group, allows for more homogeneous network formation with consequent increased conversion of monomers, reduced polymerization shrinkage, and a delayed gel point since most of the shrinkage occurs prior to gelation. Ultimately, the combination of the latter factors promotes significant reduction in contraction stress development. From the nine studies included in the review that used thiol-ene chemistry, two studies presented a low-to-moderate (up to 35%) stress reduction (Boulden et al., 2011; Ye et al., 2011) and the others reported on a much more significant potential to reduce stress (from 37 to 94%) (Beigi Burujeny et al., 2015; Carioscia et al., 2005; Carioscia et al., 2007; Cramer et al., 2010a; Cramer et al., 2010b; Lu et al., 2005a; Schreck et al., 2011). Regarding to thiol-ene systems, it has been revealed that they have rapid rate of polymerization, high overall functional group conversion, and little sensitivity to oxygen inhibition (Lu et al., 2005a), although some reduction in mechanical properties were also reported (Cramer et al., 2010a; Cramer et al., 2010b; Lu et al., 2005a); nonetheless, when combined with methacrylates, the hybrid nature of the methacrylate-thiol-ene polymerization may result in even greater reductions in contraction stress without jeopardizing important mechanical properties of the system (Cramer et al., 2010a; Cramer et al., 2010b). Collectively, the included studies demonstrated that thiol-ene systems have potential applicability for the development of stress-reducing dental materials, which will likely result in superior longevity and clinical performance relative to methacrylate-based systems.

Use of thio-urethane oligomers

Basically, thio-urethanes follow a similar polymerization mechanism as presented for thiol-ene systems, thereby allowing chain-transfer reactions from the pendant thiols to the thio-urethane structure, which delays gelation/vitrification and produces low levels of stress at the later stages of polymerization (Pfeifer et al., 2011). The applicability of thio-urethanes as stress-reducing agents was recently introduced to dentistry, so only two related studies were included in the review. Even so, the included studies showed satisfactory potential to reduce stress: from 23 to 66% (Bacchi et al., 2014) or from 10 to 86% (Bacchi et al., 2015). Differently from thiol-ene systems, thio-urethanes have a urethane composition, which implies in higher toughness and strength characteristics to the material. Moreover, thio-urethanes were revealed to have higher chemical stability than thiol-ene-based monomers, thus overcoming some important drawbacks of the latter systems; as a consequence, they can be interestingly used to minimize/control stress development by resin-based materials without jeopardizing the overall performance of the material.

Use of alternative monomers/molecules

Despite all alternative stress-reducing monomers presented throughout the previous sections (i.e., siloranes, thiol-ene, thio-urethanes), studies have reported on additional alternative compositions that do not fit within those sections but still demonstrate significant effect in reducing contraction stress; these alternatives were all allocated in the present subdivision.

Two studies used monomers based on tetraoxaspiroalkanes, which demonstrated an overall excellent ability to reduce stress: from 48 to 99% in the study of Chappelow et al. (2008) and from 79 to 97% in the study of Eick et al. (2007). The authors explained that tetraoxaspiroalkanes polymerize via cationic reaction, i.e., similarly to siloranes. Furthermore, they reduce elastic modulus development during polymerization, as well as the glass transition temperature and the polymerization rate of reaction; consequently, they increase the gel point and allow stress relaxation, producing very low amount of stress. Other three studies included within this subdivision of the review reported on monomers/functionalities that undergo addition-fragmentation chain-transfer (AFCT) reactions, likewise to thiol-ene and thio-urethane systems. Leung and Bowman (2012) demonstrated that the incorporation of only 1.5 to 2 wt.% of a trithiocarbonate-based monomer into a dimethacrylate-based system allowed network rearrangement to occur, thereby relieving and reducing stress from 25 to approximately 54%. Park et al. (2012b), on the other hand, used the same strategy, but with a considerably higher concentration of the alternative monomer (30 wt.%), resulting in 65% less stress than the conventional Bis-GMA/TEGDMA system used as control. Differently from the trithiocarbonate-based systems prepared in the previous studies, the study of Park et al. (2012a) revealed that the incorporation of an allyl sulfide functional group into a norbornene-methacrylate monomer system reduced stress development from 34 to 96%; in fact, increasing the content of the allyl sulfide-containing species in the resin progressively reduced stress, as well as progressively increased flexural modulus of the system. Therefore, the authors stated that this strategy holds significant promise for the formulation of dental restorative materials. Finally, (Wilder et al., 2005) used an organogelator (i.e., dibenzylidene sorbitol/DBS) to induce physical gelation in the polymer system; indeed, DBS is an organic molecule able to form self-assembled networks, which therefore reduces the total conversion of monomers of the material, thus reducing stress. However, stress reduction obtained by the expenses of lower degree of conversion may not be considered an attractive alternative, thereby limiting the application of DBS molecules as a feasible stress-reducing strategy.

Use of low-shrink compositions

Over the years, several efforts have been made in order to develop resin-based materials that produce minimal levels of stress. For instance, low-shrinkage materials, which are also known as stress decreasing resins (SDR™ technology), became very popular nowadays. The first examples of low-shrinkage materials were the siloranes, but they have been already discussed in a previous subdivision of the review. Even so, there are other certain strategies that may be interestingly used to reduce the polymerization shrinkage suffered by conventional formulations, and consequently, the contraction stress phenomenon produced by the material. From the studies included in this systematic review, eight were allocated within the present subdivision, which will be hereafter discussed. Two related strategies were firstly reported in the study of Ernst et al. (2004), which involved in increasing the filler content of the material or using less reactive solvents. The stress-reducing effect that greater content of fillers has on stress reduction was already discussed before and it is based on the concomitant reduction of the total amount of resin matrix prone to shrink (Goncalves et al., 2011). On the other hand, the use of less reactive solvents was associated to an overall decreased reactivity of the system, directly influencing the stress rate and kinetic of stress development (Ernst et al., 2004). In the study of Cadenaro et al. (2008), the low-shrinkage resin composite Ælite LS (Bisco Inc., Schaumburg, IL, USA) was compared to micro-hybrid (Filtek Z250, 3M ESPE, St. Paul, MN, USA) and nano-filled (Filtek Supreme, 3M ESPE) composites. The low-shrinkage material produced considerably lower stress than the others, which was attributed due to its lower resin matrix volume (26% *versus* 40 and 42% of the other composites, respectively); once again, the lower resin volume that is prone to shrink was accompanied by a higher filler loading, which resulted in less stress. Although the main strategy used to reduce stress was the modification of the filler content, the foregoing materials are recognized by their manufacturers as low-shrinkage materials.

Differently from the aforementioned strategies, there are some alternative monomers that exhibit lower polymerization shrinkage when compared to those conventionally used, so they have also been recognized as low-shrinkage materials. One example is the monomer found in the composition of a nanohybrid composite (Venus Diamond, Heraeus Kulzer GmbH, Hanau, Germany), i.e., bis-(acryloyloxymethyl)tricycle[5.2.1.02,6]decane) (TCD-DI-HEA), which is a low-viscosity monomer that shows potential to replace TEGDMA from dental formulations; indeed, it is well-known the negative effect that TEGDMA, as a very reactive monomer with intrinsic high polymerization shrinkage ability, has on contraction stress development (Charton et al., 2007b), so its replacement by a low-shrinkage component brings potential applicability to reduce stress. According to five studies included in the review, the TCD-DI-HEA-containing material developed less stress than the control materials used in each study (Aleixo et al., 2014; Boaro et al., 2010; Gao et al., 2012; Marchesi et al., 2010; Watts and Alnazzawi, 2014). The authors have also suggested that the TCD-DI-HEA monomer has an increased flexibility due to the presence of three connected rings within its central molecular structure, which accommodates shrinkage; additionally, the low elastic modulus derived from its lower cross-linking potential may also play a significant role in reducing the overall stress produced by the material. Other two examples of low-shrinkage monomers are the so-called DX-511 and the dimer dicarbamate dimethacrylate. While the former is a modified UDMA monomer found in the commercial composite Kalore (GC America Inc., Alsip, IL, USA), the latter is a dimer acid derivative found in N'Durance (Septodont, Louisville, CO, USA). Although both monomers were revealed to reduce contraction stress because of their high molecular weight and consequent low polymerization shrinkage (Boaro et al., 2010; Watts and Alnazzawi, 2014; Yamasaki et al., 2013), different mechanisms are also involved: DX-511 has low reactive group concentration available for reaction (Boaro et al., 2013), whereas the dimer acid derivative allows polymerization-induced phase separation to occur, thus producing heterogeneity within the system, and the greater the heterogeneity, the greater the stress relaxation.

Use of bulk-fill technology

Despite all modifications performed in the organic and/or inorganic content of low-shrinkage materials, which directly contributed for significant contraction stress reduction, there are other modifications that have also improved additional characteristics of these materials. For example, the initiation system and filler amount/size were also modified in order to increase light transmission properties, thus increasing the material's polymerization depth of cure, which is usually inferior to 2.0 mm. To that end, materials known as "bulk-fill" were developed, and they may be placed into the tooth cavity using one layer of up to 4–5 mm in thickness without compromising the polymerization performance (El-Damanhoury and Platt, 2014; Kim et al., 2015). Generally speaking, bulk-fill materials were introduced to dentistry in an attempt to simplify the time-consuming incremental technique, and according to the related studies included in the review, their optimized composition resulted in significant stress reduction (El-Damanhoury and Platt, 2014; Ilie and Hickel, 2011; Kim et al., 2015; Taubock et al., 2014; Zorzin et al., 2015). One important aspect of these materials relates to their overall viscosity: while on one hand low viscous compositions may allow more flow and stress relaxation during polymerization, the low filler content of flowable materials may, on the other hand, increase shrinkage, thus minimizing stress relaxation to occur; the same happens for the inverse situation, since high viscous compositions usually have high filler content, thereby increasing modulus, and consequently, stress. The study of Kim et al. (2015) investigated the effect of viscosity on the stress reducing potential of four bulk-fill resin composites; surprisingly, the authors demonstrated that the high-viscous materials resulted in similar stress values compared to a high-viscous conventional composite, whereas the low-viscous bulk-fill composites produced less stress than the low-viscous conventional composite used as control. Overall, it seems that bulk-fill resins display better potential to reduce stress if materials with low elastic modulus are used, thereby favoring the use of flowable materials. However, and according to Cadenaro et al. (2009), flowability of resin composites is not guarantee for contraction stress reduction, thus confirming that this subject is complex since it depends on several intrinsic factors related to the material's composition. Therefore, and taking into consideration that bulk-fill materials are considerably new in dentistry, additional studies must be conducted regarding their usage, but from current literature, it seems that they may be satisfactorily used to reduce stress.

Taking all the meta-analyses performed within the "composition category" together, the use of alternative monomers/molecules demonstrated the highest mean difference (5.96), followed by the use of thio-urethane oligomers (mean difference = 5.35); consequently, these foregoing strategies were the most effective approaches related to the modification of the material composition. By contrast, the incorporation of alternative fillers exhibited the lowest mean difference of this review (0.06). Once again, these results should be interpreted with caution since heterogeneity was also high for all analyses performed.

CONCLUSION

Although the studies presented heterogeneity, the findings of the present systematic review and meta-analyses revealed the existence of several strategies that may positively reduce/control contraction stress of resin-based restorative materials. From the simple modification of the material's placing technique/photo-activation protocol to the modification of the material's composition, it seems that the latter main strategy contributes more to minimize stress development than the former. Indeed, the stress decreasing technology used for the formulation of low-shrinkage and bulk-fill materials has optimized the conventional chemistry of current dental materials, showing promising application for reducing/controlling stress development. Worth mentioning, there are other formulations that have not been yet translated to commercial materials such as the thiol-ene, thio-urethane, tetraoxaspiroalkane, or trithiocarbonate systems; therefore, it can be expected further improvements in the formulation of new stress decreasing restorative materials.

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Ye S, Cramer NB, Smith IR, Voigt KR, Bowman CN (2011). Reaction Kinetics and Reduced Shrinkage Stress of Thiol-Yne-Methacrylate and Thiol-Yne-Acrylate Ternary Systems. *Macromolecules* 44:9084-9090.

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Zanchi CH, de Carvalho RV, Rodrigues Junior SA, Demarco FF, Burnett Junior LH (2006). Shrinkage stress of three composites under different polymerization methods. *Braz Oral Res* 20:137-142.

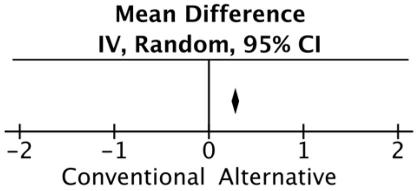
Zorzin J, Maier E, Harre S, Fey T, Belli R, Lohbauer U, *et al.* (2015). Bulk-fill resin composites: polymerization properties and extended light curing. *Dent Mater* 31:293-301.

Tables

Table 1. Search strategy used in PubMed (MEDLINE)

	Search terms
#4	Search #1 AND #2 AND #3
#3	reduction OR reduce OR reduc$
#2	Composite Resins OR Resins, Composite OR Dental Resins OR Dental Resin OR Resin, Dental OR Resins, Dental
#1	Dental Stress Analysis[MeSH Term] OR Analysis, Dental Stress OR Stress Analysis, Dental OR Analyses, Dental Stress OR Dental Stress Analyses OR Stress Analyses, Dental OR shrinkage stress OR polymerization shrinkage stress OR contraction stress

Table 2. Studies that reduced contraction stress by using an alternative technique/additional step of placing the material, by modifying the irradiant intensity/energy used to photo-activate the material, or by using alternative light-curing unit/source. The specific strategy used to reduce stress, as well as the stress reduction range and results for the meta-analyses are also presented.

General strategy	Study	Specific strategy used to reduce stress	Stress reduction (% range)	Meta-analyses results
Use of alternative technique or additional step for placing the material	Alster 1992	Increasing the concentration of porosity in the material from 38 to 114%	17 – 42	 **Mean Difference**: 0.29 [0.24, 0.33] **Heterogeneity:** Tau^2=0.01; Chi^2=2953.78, df=44 (p<0.01); I^2=99% **Test for overall effect:** Z=13.17 (p<0.01)
	Braga 2002b	Curing the material using the self-cure mode instead of the dual-cure mode	24 – 38	
	Braga 2003	Using a pre-cured liner (flowable composite or unfilled resin) below the restorative material	2 – 41	
	Calheiros 2014	Pre-heating the material to 40 or 60°C and lowering light-activation exposure to 5s	54 – 70	
	Choi 2000	Applying an increased thickness of low-stiffness adhesive between tooth and the restorative material (exceeding 100 µm)	17 – 37	
	Cunha 2006	Using a flowable composite liner between tooth and the restorative material	16 – 40	
	Cunha 2006	Using three adhesive coats instead of one between tooth and the restorative material	2 – 18	
	Faria-e-Silva 2011	Delaying the photo-activation of the material (5 min)	14 – 25	
	Ishikiriama 2013	Reducing the volume of the material from three to five times	16 – 40	
	Lee 2007	Reducing the thickness of the material from 2.0 to 1.0/0.5 mm	16 – 53	
	Watts 2014	Increasing the material's temperature to 37°C during polymerization	6 – 16	

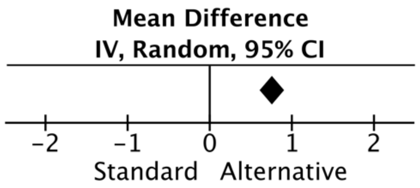
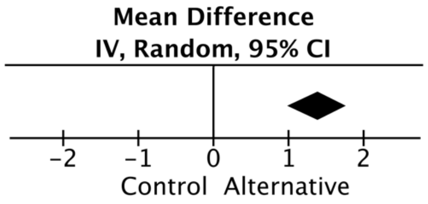
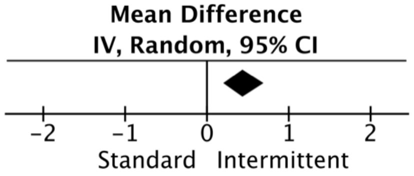
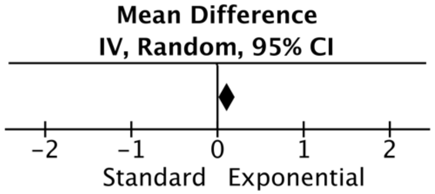
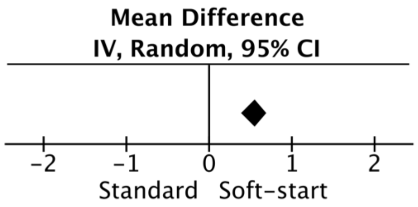
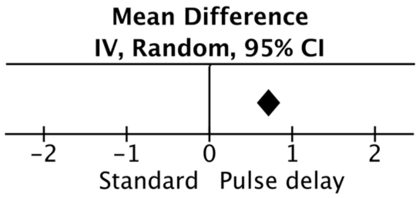
Modification of the irradiation intensity/ energy used to photo-activate the material	Bouschlicher 2000	Halving the irradiation intensity (from 800 to 400 mW/cm^2) and doubling the exposure duration	15	 **Mean Difference**: 0.77 [0.63, 0.91] **Heterogeneity:** Tau^2=0.08; Chi^2=509.91, df=25 ($p<0.01$); I^2=95% **Test for overall effect:** Z=10.94 ($p<0.01$)
	Calheiros 2004	Halving the irradiation energy (from 27 to 13.5 J/cm^2)	26 – 52	
	Calheiros 2006	Halving the irradiation energy (from 24 to 12 or 12 to 6 J/cm^2)	11 – 51	
	Calheiros 2008	Halving the irradiation energy (from 24 to 12, 12 to 6, or 6 to 3 J/cm^2)	37 – 75	
	Ilie 2007	Halving the irradiation energy (from 32 to 16 or 16 to 8 J/cm^2 for the Mini LED light curing unit or from 72 to 36 or 36 to 18 J/cm^2 for the Bluephase unit)	8 – 34	
	Tauböck 2014	Reducing and increasing three times the irradiation energy and the exposure duration, respectively	6 – 14	
	Witzel 2005	Reducing and increasing three times the irradiation energy and the exposure duration, respectively	6	
	Wydra 2014	Halving the irradiation intensity (from 24 to 12, 12 to 6, or 6 to 3 J/cm^2)	4 – 10	
Use of alternative light-curing unit/source	Delfino 2009	Photo-activating the material with argon ion laser at 250 mW for 10s	19 – 72	 **Mean Difference**: 1.39 [1.00, 1.77] **Heterogeneity:** Tau^2=0.32; Chi^2=132.42, df=9 ($p<0.01$); I^2=93% **Test for overall effect:** Z=7.04 ($p<0.01$)
	Zanchi 2006	Photo-activating with a light emitting diode (LED) curing unit	10 – 78	

Table 3. Studies that reduced contraction stress by using an alternative photo-activation mode, and information about the photo-activation protocols used, light-curing source, the stress reduction range (%), and results for the meta-analyses.

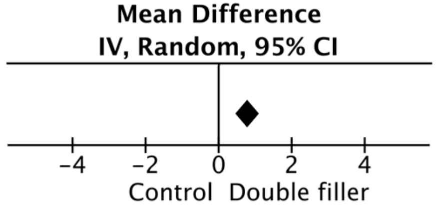
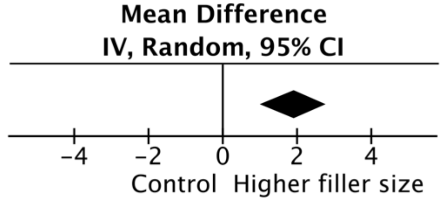
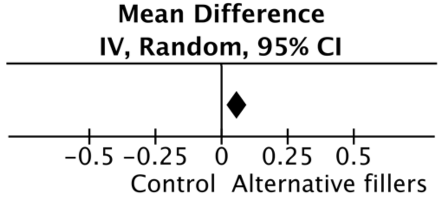
Alternative photo-activation mode	Study	Photo-activation protocol and light-curing unit/source used	Stress reduction (% range)	Meta-analyses results
Intermittent light (Pulsed curing)	Cunha 2006	Cycles of 4 s (2 s light on and 2 s light off) for 80 s at 600 mW/cm^2 using an adapted Optilux 150 (Demetron Research Corp., Orange, CA, USA)	11	 **Mean Difference**: 0.46 [0.21, 0.70] **Heterogeneity:** Tau^2=0.0; Chi^2=0.15, df=1 (p=0.70); I^2=0% **Test for overall effect:** Z=3.59 (p<0.01)
	Ilie 2007	Emission of 10 pulses in 12 s using the pulse program of the curing unit MiniLED (Satelec, Bordeaux, France)	18	
Exponential (Ramped curing)	Bouschlicher 2000	Emission of 150 mW/cm^2 with a logarithmic increase to 800 mW/cm^2 in 15 s + 800 mW/cm^2 for 25 s, using Elipar^{TM} Trilight (3M ESPE Dental AG, Seefeld, Germany)	33	 **Mean Difference**: 0.11 [0.02, 0.21] **Heterogeneity:** Tau^2=0.01; Chi^2=44.43, df=6 (p<0.01); I^2=86% **Test for overall effect:** Z=2.30 (p=0.02)
	Charton 2007a	Emission of 150 mW/cm^2 with a logarithmic increase to 800 mW/cm^2 in 15 s + 800 mW/cm^2 for 45 s, using Elipar^{TM} Trilight (3M ESPE, Germany)	1 – 7	
	Ernst 2003	Emission of 150 mW/cm^2 with a logarithmic increase to 800 mW/cm^2 in 15 s + 800 mW/cm^2 for 25 s, using Elipar® Trilight (3M ESPE, Germany)	2 – 7	
	Ilie 2007	Emission of a ramped light intensity for 10 s + additional 10 s at maximum intensity using the MiniLED (Satelec, France)	27	

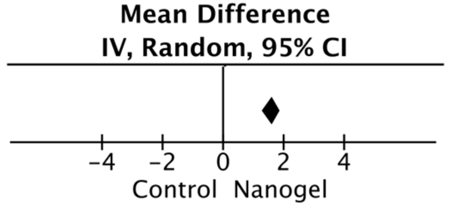
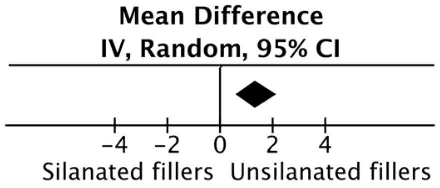
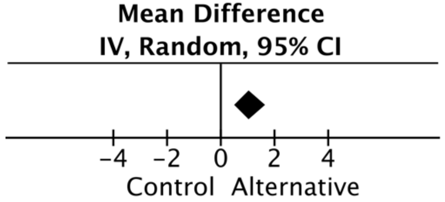
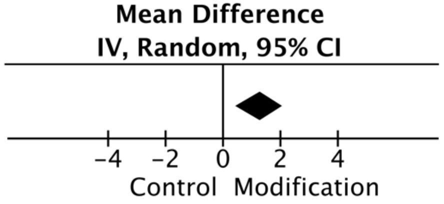
Soft-start	Bouschlicher 2000	Emission of 100 mW/cm^2 for 10 s + 800 mW/cm^2 for 30 s using Elipar^{TM} Highlight (3M ESPE, St. Paul, MN, USA)	10	 **Mean Difference**: 0.55 [0.40, 0.70] **Heterogeneity:** Tau^2=0.06; Chi^2=441.35, df=13 ($p<0.01$); I^2=97% **Test for overall effect:** Z=7.20 ($p<0.01$)
	Cunha 2006	Emission of 150 mW/cm^2 for 10 s + 800 mW/cm^2 for 30 s using a XL 2500 curing unit (3M ESPE, USA)	2	
	Cunha 2007	Emission of 150 mW/cm^2 for 10 s + 550 mW/cm^2 for 27 s using the VIP light-curing unit (Variable Intensity Polymerizer, Bisco, Schaumburg, IL, USA)	1	
	Lu 2005b	Emission of 100 mW/cm^2 for 5 s + 450 mW/cm^2 for 60 s using the VIP light-curing unit	14	
	Tauböck 2014	Emission of 300 mW/cm^2 for 15 s + 900 mW/cm^2 for 25 s using a light-emitting diode (LED) light-curing unit (Bluephase, Ivoclar Vivadent, Schaan, Liechtenstein)	3 – 10	
	Zanchi 2006	Emission of 166 mW/cm^2 for 20 s + 507 mW/cm^2 for 40 s using a XL3000 curing unit (3M ESPE, USA)	18 – 50	
Pulse delay	Cunha 2007	Emission of 80 mW/cm^2 for 5 s + 3 min of hiatus + 550 mW/cm^2 for 29 s using the VIP light-curing unit	23	 **Mean Difference**: 0.73 [0.59, 0.87] **Heterogeneity:** Tau^2=0.06; Chi^2=446.52, df=26 ($p<0.01$); I^2=94% **Test for overall effect:** Z=10.32 ($p<0.01$)
		Emission of 150 mW/cm^2 for 5 s + 3 min of hiatus + 550 mW/cm^2 for 28 s using the VIP light-curing unit	10	
	Cunha 2008	Emission of 80 mW/cm^2 for 5 s + 3 min of hiatus + 550 mW/cm^2 for 29 s using the VIP light-curing unit	38	
		Emission of 150 mW/cm^2 for 5 s + 3 min of hiatus + 550 mW/cm^2 for 28 s using the VIP light-curing unit	14	
	Ishikiriama 2012	Emission of 100 mW/cm^2 for 5 s + 40 s of hiatus + 600 mW/cm^2 for 20 s using the VIP light-curing unit	2 – 26	
	Lim 2002	Emission of 60 mW/cm^2 for 5 s + 2 min of hiatus + 330 mW/cm^2 for 60 s using the VIP light-curing unit	19 – 30	

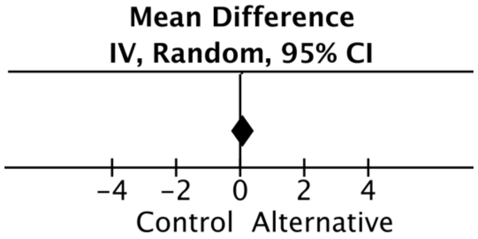
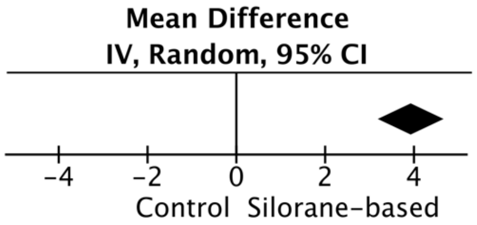
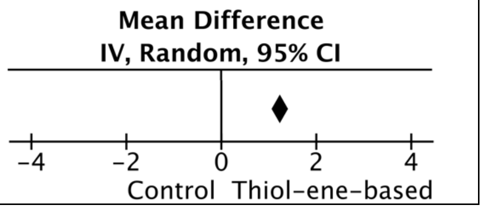
	Lopes 2008	Emission of 200 mW/cm^2 for 3 s + 3 min of hiatus + 600 mW/cm^2 for 59 s using the VIP light-curing unit	4 – 11	
	Lu 2005b	Emission of 100 mW/cm^2 for 5 s + 2 min of hiatus + 450 mW/cm^2 for 60 s using the VIP light-curing unit	19	
	Pfeifer 2006	Emission of 100 mW/cm^2 for 5 s + 1 or 3 min of hiatus + 500 mW/cm^2 for 39 s using the VIP light-curing unit	8 – 23	
		Emission of 500 mW/cm^2 for 1 s + 1 or 3 min of hiatus + 500 mW/cm^2 for 39 s using the VIP light-curing unit	12 – 33	
	Tauböck 2014	Emission of 300 mW/cm^2 for 3 s + 3 min of hiatus + 900 mW/cm^2 for 29 s using the LED light-curing unit	10 – 32	
	Witzel 2005	Emission of 600 mW/cm^2 for 1 s + 1 or 3 min of hiatus + 600 mW/cm^2 for 39 s using the VIP light-curing unit	28	

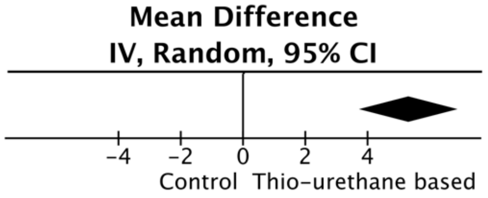
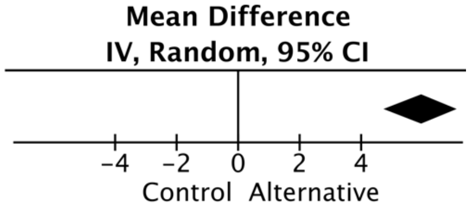
hiatus: delay time without light-activation.

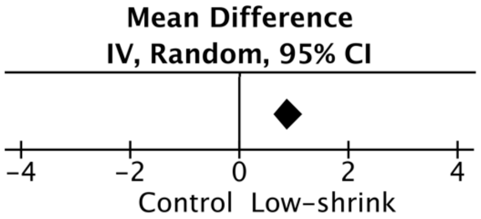
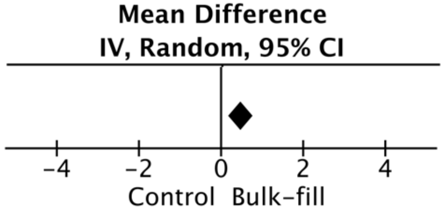
Table 4. Studies that reduced contraction stress by modifying the chemical composition of the material allocated by modified part, the strategies and main mechanisms used, as well as the stress reduction range and results for the meta-analyses.

Part of the material modified	Strategy used to reduce stress	Study	Main mechanism proposed	Stress reduction (% range)	Meta-analyses results
Filler phase	**Increasing the content of fillers**	Gonçalves 2010a	The higher the concentration of fillers, the lower the content of resin matrix prone to shrink, thereby developing lower contraction stress	22 – 26	 **Mean Difference**: 0.80 [0.48, 1.13] **Heterogeneity:** Tau^2=0.15; Chi^2=33.07, df=6 (p<0.01); I^2=0% **Test for overall effect:** Z=4.84 (p<0.01)
		Gonçalves 2011		6 – 14	
	Increasing the size of spherical fillers	Satterthwaite 2012	Smaller fillers also increase the surface area of the dispersed phase, thus increasing the fillers constraint upon the resin matrix, increasing stress; Filler particles, themselves constrained by the resin matrix, undergo translation and rotational movement, thereby relaxing stress within the material; this effect seemed to increase with increasing sphericity of the dispersed phase;	21 – 48	 **Mean Difference**: 1.91 [1.02, 2.80] **Heterogeneity:** Tau^2=1.13; Chi^2=66.81, df=5 (p<0.01); I^2=93% **Test for overall effect:** Z=4.20 (p<0.01)
	Increasing the size of irregular fillers			10 – 17	
	Incorporation of alternative fillers	Ferracane 2003	The incorporation of high-density polyethylene spheres facilitate plastic deformation during stress buildup derived from polymerization contraction	7 – 29	 **Mean Difference**: 0.06 [0.02, 0.10] **Heterogeneity:** Tau^2=0.00; Chi^2=89.68, df=13 (p<0.01); I^2=86% **Test for overall effect:** Z=2.98 (p<0.01)
		Garoushi 2008	The incorporation of short E-glass fiber fillers into the resin matrix increases stress transfer from polymer matrix to fibers	4.5	
		Szaloki 2013	Reactive polymeric nanoparticles can absorb stress	2 – 18	

	Incorporation of nanogels	Liu 2012	Nanogels are internally crosslinked and cyclized single or multi-chain polymeric particles that induce delayed production of modulus and vitrification, which in turn decreases the resultant stress developed by the nanogel-modified composition	2 – 59	 **Mean Difference**: 1.61 [1.33, 1.89] **Heterogeneity:** Tau^2=0.41; Chi^2=465.05, df=21 (p<0.01); I^2=95% **Test for overall effect:** Z=11.11(p<0.01)
		Moraes 2011		27 – 45	
Resin-filler interface	**Use of non-bonded/ unsilanized fillers**	Condon 1998	The absence of chemical bond between the fillers and the resin matrix may increase the stress-relieving capability of the material	10 – 31	 **Mean Difference**: 1.40 [0.59, 2.20] **Heterogeneity:** Tau^2=1.12; Chi^2=55.76, df=7 (p<0.01); I^2=87% **Test for overall effect:** Z=3.39 (p<0.01)
		Condon 2002		12 – 27	
	Use of alternative functionalization system	Condon 1998	The use of non-functional *versus* functional silane may contribute to reduce interaction between resin and fillers, thus facilitating pre-gelation and stress reduction	9 – 46	 **Mean Difference**: 1.11 [0.55, 1.66] **Heterogeneity:** Tau^2=0.34; Chi^2=85.99, df=5 (p<0.01); I^2=94% **Test for overall effect:** Z=3.92 (p<0.01)
		Ye 2012	The use of flexible hyperbranched oligomer as an interfacial layer between resin matrix and glass filler provides higher compliance and enough mobility for the system, thus reducing stress	33	
Resin matrix	**Modification of the composition ratio of conventional formulations**	Braga 2002a	The increase in inhibitor (BHT) concentration decreases the reaction speed (curing rate), thus extending the pre-gel phase with consequent stress delay	2 – 39	
		Charton 2007b	The decrease in the ratio of TEGDMA from 50 to 30 wt.% reduces polymerization shrinkage, thus reducing stress	46	

		Gonçalves 2010b	Halving TEGDMA concentration directly decreases polymerization shrinkage, thus reducing stress	16 – 42	**Mean Difference**: 1.28 [0.45, 2.12] **Heterogeneity:** Tau^2=4.11; Chi^2=6270.41, df=22 ($p<0.01$); I^2=100% **Test for overall effect:** Z=3.01 ($p<0.01$)
		Gonçalves 2011		32 – 36	
	Use of alternative photo-initiators	Oliveira 2012	The use of PPD as photoinitiator produces a slower polymerization reaction when compared to CQ-based systems, allowing more stress relaxation	0.3 – 5	 **Mean Difference**: 0.10 [-0.25, 0.45] **Heterogeneity:** Tau^2=0.23; Chi^2=116.98, df=7 ($p<0.01$); I^2=94% **Test for overall effect:** Z=0.57 ($p=0.57$)
		Palin 2014	The use of MAPO as photoinitiator delays diffusion-controlled propagation step during polymerization and increases the reaction temperature, thus allowing higher reaction mobility and greater stress relief by delaying the onset of vitrification when compared to CQ-based systems	7 – 24	
	Use of silorane-based monomers	Eick 2007	The incorporation of TOSU, which is a spiroorthocarbonate monomer that polymerize via cationic polymerization, reduced stress probably due to lower shrinkage and factors such as lower elastic modulus, higher gel point, and lower glass transition temperatures	82 – 97	 **Mean Difference**: 2.86 [2.39, 3.32] **Heterogeneity:** Tau^2=0.84; Chi^2=1776.22, df=17 ($p<0.01$); I^2=99% **Test for overall effect:** Z=12.10 ($p<0.01$)
		Gao 2012	The cationic ring-opening reaction generates lower polymerization shrinkage, thereby reducing stress development. Moreover, siloranes-based materials have improved ability to flow during the initial curing stage before reaching the gel point, thus possessing the largest potential for stress relief	45	
		Ilie 2011		32	
		Li 2012		24	
		Marchesi 2010		16 – 22	
		Min 2010		57 – 69	
		Oliveira 2012		3 – 14	
		Xiong 2011*		47	
		Yamasaki 2013		38	
	Use of thiol-ene-based monomers	Boulden 2011	Thiol-ene-based systems polymerize via a step-growth mechanism, rather than the chain-growth mechanism characteristic of dimethacrylate-based resins, resulting in reduced polymerization shrinkage, a delayed gel point since most of the shrinkage occurs prior to gelation, and	22 – 35	
		Beigi Burujeny 2015		45 -74	
		Carioscia 2005		89 – 94	
		Carioscia 2007		90	
		Cramer 2010a		37 – 74	
		Cramer 2010b		61	
		Lu 2005a*		86	

		Schreck 2011*	enhanced control of the polymerization; all of these factors together lead to stress reduction	39 – 53	**Mean Difference**: 1.25 [1.06, 1.44] **Heterogeneity:** Tau^2=0.16; Chi^2=11158.56, df=17 (p<0.01); I^2=100% **Test for overall effect:** Z=13.06 (p<0.01)
		Ye 2011		14 – 21	
	Use of thio-urethane oligomers	Bacchi 2014	The presence of thio-urethane oligomers within methacrylate-based resins allow chain transfer reactions from the pendant thiols on the thio-urethane structure to the surrounding methacrylate matrix, delaying gelation/vitrification, which in turn reduce stress development at the later stages of polymerization	23 – 66	 **Mean Difference**: 5.35 [3.77, 6.92] **Heterogeneity:** Tau^2=5.44; Chi^2=62.29, df=9 (p<0.01); I^2=86% **Test for overall effect:** Z=6.65 (p<0.01)
		Bacchi 2015		10 – 86	
	Use of alternative monomers/ molecules	Chappelow 2008	The use of monomers based on tetraoxaspiroalkanes, which polymerize via cationic reaction, reduces elastic modulus, glass transition temperatures, as well as the polymerization rate of the reaction, thus increasing gel point and stress relaxation	48 – 99	 **Mean Difference**: 5.96 [4.75, 7.17] **Heterogeneity:** Tau^2=3.64; Chi^2=3127.58, df=9 (p<0.01); I^2=100% **Test for overall effect:** Z=9.65 (p<0.01)
		Eick 2007		79 – 97	
		Leung 2012	The incorporation of 1.5 to 2 wt.% of trithiocarbonate-based monomers into a dimethacrylate-based network allowed a reversible AFCT reaction to occur, thus promoting network rearrangement and stress relaxation	25 – 54	
		Park 2012a	The use of an allyl sulfide-based system allowed the AFCT reaction to occur, thus relieving stress via network rearrangement	34 – 96	
		Park 2012b	TTCDMA is capable of undergoing AFCT reaction, which allows stress relaxation	65	
		Wilder 2005	The incorporation of DBS (up to 3.13 wt.%) is capable of inducing physical gelation by forming self-assembled networks, causing the decrease in conversion, thus reducing stress	26	

	Use of low-shrink compositions	Aleixo 2014	The presence of TCD-DI-HEA combines low polymerization shrinkage with low viscosity, thus reducing stress development	76	 **Mean Difference**: 0.89 [0.64, 1.15] **Heterogeneity:** Tau^2=0.30; Chi^2=1245.38, df=19 (p<0.01); I^2=98% **Test for overall effect:** Z=6.81 (p<0.01)
		Boaro 2010		4 – 21	
		Cadenaro 2008	The resin characteristics of low-shrink composites associated with a low resin matrix volume can be used to reduce stress	39 – 41	
		Ernst 2004	Increasing filler load or using less reactive solvents produce less stress	14 – 46	
		Gao 2012	The presence of TCD-DI-HEA allows a slow cure rate with long gel and vitrification times; it also reduces conversion and the crosslinking of the network, thus reducing elastic modulus, ad consequently, stress	45	
		Marchesi 2010		21 – 48	
		Watts 2014	The monomers DX-511 in Kalore and TCD-DI-HEA in Venus Diamond bring a low-shrinking ability, thus reducing stress	16 – 19	
		Yamasaki 2013	The presence of DX-511 in Kalore decreases the concentration of reactive groups for reaction, and the presence of *dimer acid derivative* in N'Durance, induces heterogeneity in the material; both strategies allow stress reduction	14 – 36	
	Use of bulk-fill technology	El-Damanhoury 2014	Bulk-fill materials are similar to conventional dimethacrylate-based materials, although they have been optimized with regards to their resin matrix and initiator chemistry as well as filler technology, which result in distinct properties that directly influence stress development; in special, stress is considerably reduced when materials with low elastic modulus are used	9 – 32	 **Mean Difference**: 0.50 [0.19, 0.81] **Heterogeneity:** Tau^2=0.41; Chi^2=2937.14, df=17 (p<0.01); I^2=99% **Test for overall effect:** Z=3.15 (p<0.01)
		Ilie 2011		79	
		Kim 2015		0.8 – 52	
		Tauböck 2014		48 – 51	
		Zorzin 2015		13	

BHT: butylated hydroxytoluene; TEGDMA: tryethyleneglycol dimethacrylate; PPD: 1-Phenyl-1,2-propanedione; CQ: camphorquinone; MAPO: monoacylphosphine oxide; TOSU: 3,9-Diethyl-3,9-bis(trimethylsilylpropyloxy-methyl)-1,5,7,11-tetraoxaspiro[5.5]undecane; AFCT: addition-fragmentation chain transfer; TTCDMA: trithiocarbonate dimethacrylate; DBS: dibenzylidene sorbitol; TCD-DI-HEA: Bis-[acryloyloxymethyl] tricyclo[5.2.1.02,6]decane.

Figures

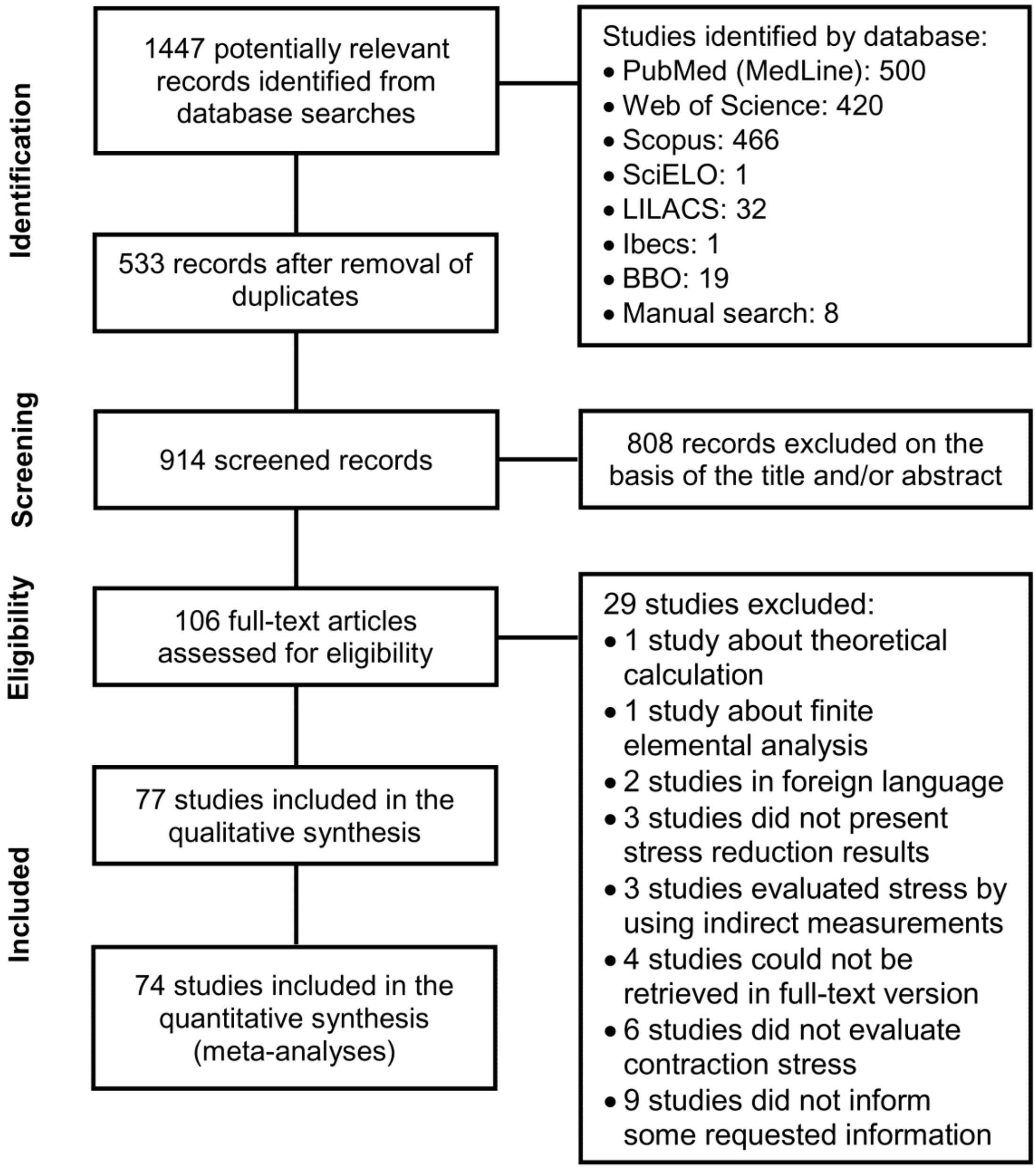


Figure 1. Search flow (as described in the PRISMA statement) (Moher et al., 2009).

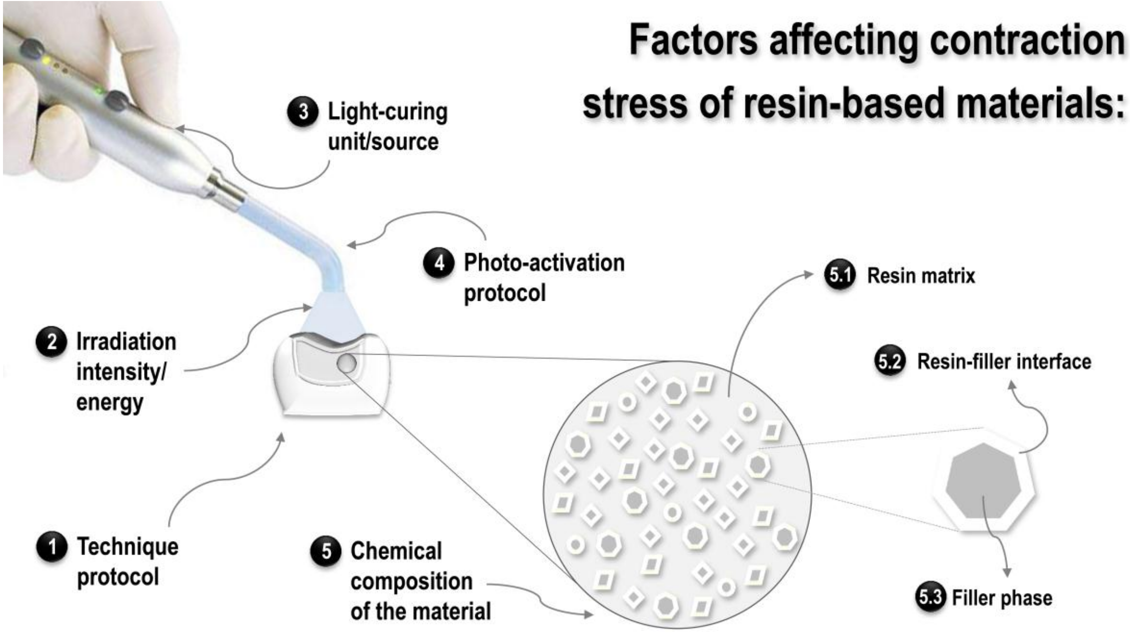


Figure 2. Factors that may affect contraction stress development of resin-based materials.

Appendice. Quality assessment and risk of bias (according to Downs and Black, 1998).

Study	Informed number of specimens	Informed mean ± SD values	Used a clear control	Informed specimen dimension	Monitored stress kinetic	Informed about testing compliance	Risk of bias
Aleixo 2014	Yes	Yes	Yes	Yes	No	No	Medium
Alster 1992	Yes	Yes	Yes	Yes	Yes	No	Low
Bacchi 2014	Yes	No	Yes	No	Yes	Yes	Medium
Bacchi 2015	Yes	No	Yes	Yes	Yes	Yes	Low
Boaro 2010	Yes	Yes	No	Yes	Yes	Yes	Low
Boulden 2011	Yes	Yes	Yes	Yes	Yes	Yes	Low
Bouschlicher 2000	Yes	Yes	Yes	Yes	Yes	Yes	Low
Braga 2002a	Yes	Yes	No	No	Yes	Yes	Medium
Braga 2002b	Yes	Yes	No	Yes	Yes	Yes	Low
Braga 2003	Yes	Yes	No	Yes	Yes	Yes	Low
Burujeny 2015	No	Yes	Yes	No	Yes	No	Medium
Cadenaro 2008	Yes	Yes	No	Yes	Yes	Yes	Low
Cadenaro 2009	Yes	Yes	Yes	Yes	Yes	Yes	Low
Calheiros 2004	Yes	Yes	No	Yes	Yes	Yes	Low
Calheiros 2006	Yes	Yes	No	Yes	Yes	Yes	Low
Calheiros 2008	Yes	Yes	No	Yes	Yes	Yes	Low
Calheiros 2014	Yes	Yes	Yes	Yes	Yes	Yes	Low
Carioscia 2005	Yes	Yes	Yes	Yes	Yes	Yes	Low
Carioscia 2007	Yes	Yes	Yes	Yes	Yes	Yes	Low
Chappelow 2008	Yes	Yes	Yes	Yes	Yes	Yes	Low
Charton 2007a	Yes	Yes	Yes	Yes	Yes	Yes	Low
Charton 2007b	Yes	Yes	No	Yes	Yes	Yes	Low
Choi 2000	Yes	Yes	Yes	Yes	Yes	Yes	Low
Condon 1998	Yes	Yes	Yes	Yes	Yes	Yes	Low
Condon 2002	Yes	Yes	Yes	Yes	Yes	Yes	Low
Cramer 2010a	Yes	Yes	Yes	Yes	Yes	Yes	Low
Cramer 2010b	Yes	Yes	Yes	Yes	Yes	Yes	Low
Cunha 2006	Yes	Yes	Yes	Yes	Yes	No	Low
Cunha 2007	Yes	Yes	Yes	Yes	Yes	Yes	Low
Cunha 2008	Yes	Yes	Yes	Yes	Yes	Yes	Low
Delfino 2009	Yes	Yes	Yes	Yes	Yes	Yes	Low
Eick 2007	Yes	Yes	Yes	Yes	Yes	Yes	Low
El-Damanhoury 2014	Yes	Yes	Yes	Yes	Yes	Yes	Low
Ernst 2003	Yes	No	No	Yes	Yes	No	Medium
Ernst 2004	Yes	Yes	No	No	Yes	No	Medium
Faria-e-Silva 2011	Yes	Yes	Yes	Yes	Yes	Yes	Low
Ferracane 2003	Yes	Yes	Yes	Yes	Yes	Yes	Low
Gao 2012	Yes	Yes	No	Yes	Yes	Yes	Low

Garoushi 2008	Yes	Yes	Yes	Yes	Yes	Yes	Low
Gonçalves 2010a	Yes	Yes	No	Yes	Yes	Yes	Low
Gonçalves 2010b	Yes	Yes	No	Yes	Yes	Yes	Low
Gonçalves 2011	Yes	Yes	No	Yes	Yes	Yes	Low
Ilie 2007	Yes	Yes	No	Yes	Yes	Yes	Low
Ilie 2011	Yes	Yes	No	Yes	Yes	Yes	Low
Ishikiriama 2011	Yes	Yes	No	Yes	Yes	No	Medium
Ishikiriama 2012	Yes	Yes	Yes	Yes	Yes	No	Low
Kim 2015	Yes	Yes	Yes	Yes	Yes	Yes	Low
Lee 2007	Yes	Yes	No	Yes	Yes	Yes	Low
Leung 2012	Yes	Yes	Yes	Yes	Yes	Yes	Low
Li 2012	Yes	Yes	No	Yes	Yes	No	Medium
Lim 2002	Yes	Yes	No	Yes	Yes	Yes	Low
Liu 2012	Yes	Yes	Yes	Yes	Yes	Yes	Low
Lopes 2008	Yes	Yes	No	Yes	Yes	No	Medium
Lu 2005a	No	No	Yes	Yes	No	Yes	Medium
Lu 2005b	Yes	Yes	Yes	Yes	Yes	Yes	Low
Marchesi 2010	Yes	Yes	No	Yes	Yes	Yes	Low
Min 2010	Yes	Yes	Yes	Yes	Yes	Yes	Low
Moraes 2011	Yes	No	Yes	Yes	Yes	Yes	Low
Oliveira 2012	Yes	Yes	Yes	Yes	No	No	Medium
Palin 2014	Yes	Yes	Yes	Yes	Yes	Yes	Low
Park 2012a	Yes	Yes	Yes	Yes	Yes	Yes	Low
Park 2012b	Yes	Yes	Yes	No	Yes	Yes	Low
Pfeifer 2006	Yes	Yes	No	Yes	Yes	Yes	Low
Satterhwaite 2012	Yes	Yes	No	Yes	Yes	Yes	Low
Schreck 2011	No	Yes	Yes	Yes	Yes	Yes	Low
Szaloki 2013	Yes	Yes	Yes	Yes	No	No	Medium
Tauböck 2014	Yes	Yes	No	Yes	Yes	Yes	Low
Watts 2014	Yes	Yes	Yes	Yes	Yes	Yes	Low
Wilder 2005	Yes	Yes	Yes	Yes	Yes	Yes	Low
Witzel 2005	Yes	Yes	Yes	Yes	Yes	Yes	Low
Wydra 2014	Yes	Yes	No	Yes	Yes	Yes	Low
Xiong 2011	No	Yes	No	Yes	Yes	Yes	Medium
Yamasaki 2013	Yes	Yes	Yes	Yes	Yes	Yes	Low
Ye 2011	Yes	Yes	No	Yes	No	Yes	Medium
Ye 2012	Yes	Yes	Yes	Yes	Yes	Yes	Low
Zanchi 2006	Yes	Yes	Yes	Yes	Yes	No	Low
Zorzin 2015	Yes	Yes	No	Yes	Yes	Yes	Low

SD: standard deviation.

5 Artigo 2

Application of novel elastomeric urethanes as stress-reducing agents for resin-based dental materials[§]

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Key words: Exothane™ elastomers, urethane dimethacrylate, degree of conversion, rate of polymerization, contraction stress, infrared spectroscopy (FTIR).

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Abstract

Objective. The aim of this study was to evaluate polymerization kinetics (degree of conversion/DC and rate of polymerization/RP) and contraction stress (CS) of urethane-based dimethacrylates (Exothanes™) containing different initiation systems.

Methods. Experimental resins were prepared by mixing one type of Exothane (8, 9, 10, 24, or 32) with different initiation systems: unitary (camphorquinone/CQ); binary (CQ and ethyl 4-dimethylamino benzoate/EDAB); and ternary (CQ, EDAB and diphenyliodoniun hexafluorphosphate/DPI). Urethane dimethacrylate (UDMA) was used as control. DC and RP of the resins were determined using Fourier Transform infrared (FTIR) spectroscopy (n=3). CS was determined using a low-compliance mechanical testing system (n=5). Data were analyzed using two-way ANOVA and Tukey ($\alpha = 0.05$) and linear regression analyses.

Results. Exothanes 8, 9, and 32 achieved higher DC than the other Exothanes and UDMA ($p \leq 0.010$), as well as an overall higher RP. Initiation system did not significantly influence polymerization kinetics, except for Exothane 24 which exhibited higher DC and RP when combined with the tertiary system ($p \leq 0.001$). All Exothane-based resins produced lower CS than UDMA ($p < 0.001$). UDMA and Exothanes 9 and 24 resulted in higher CS when combined with the binary initiator system. No statistically significant correlation was found between CS and DC or RP ($R2 \leq 0.333$, $p = 0.282$).

Significance. Exothanes demonstrated potential to be used as stress-reducing agents in resin-based materials, with similar or even superior polymerization efficacy compared to UDMA.

1. Introduction

Currently, dental restorations can be satisfactorily performed with the use of resin composites, which are user-friendly, environmentally safe and cost-effective when compared to other restorative materials (e.g., ceramics, amalgam). According to longitudinal evaluations, composite restorations may last as much as amalgam restorations, thus becoming the material of choice for restoring teeth with low to moderate destruction [1, 2]. Nevertheless, these restorations still fail due to bulk fracture and secondary caries [3, 4].

Stress development at the tooth/restoration interface is a common phenomenon caused by polymerization shrinkage (contraction) of the material under wall-constrained circumstances, which may jeopardize the longevity of the restoration [5]. Indeed, innumerous studies have reported negative effects such as cuspal deflection, de-bonding of the restoration, microleakage, and post-operatory hypersensitivity, after polymerizing composite resins into tooth cavities [6, 7], especially those cavities with high ratio between bonded and non-bonded surfaces (i.e., high “configuration factor”/C-factor) [8]. Despite of those negative effects, contraction stress can be significantly reduced upon proper insertion techniques and/or photo-activation protocols; nonetheless, these strategies may be sometimes difficult to control as well as time-consuming, so alternative strategies have been investigated.

Contraction stress magnitude can be accomplished also by modifying the chemical composition of the material, including but not limited to the replacement of conventional monomers (e.g., dimethacrylates) by low-shrink monomers such as the siloranes [9], or even by using modified dimethacrylates (e.g., DX-511, dimer acid derivatives) [10]. Unfortunately, while some of these modifications truly contributed for significant contraction stress reduction [10, 11], others have not worked as the expected [9], and this is probably because stress development is not only a matter of the polymerization shrinkage process, but it is also dependent on modulus development and polymerization kinetics parameters [5].

Stress magnitude is also directly affected by the overall compliance of the system [12]. Compliance is the inverse of stiffness, which means that if the system (i.e., the substrate receiving the material and the material itself) allows stress relaxation to occur during polymerization of the material and especially before gelation/vitrification, it is considered a highly compliant system; conversely, if the system is not able to undergo plastic deformation under the shrinkage forces, it is considered a low compliance system [7]. Considering the aforementioned idea, some recent studies have reported on effective contraction stress reduction upon the incorporation of multifunctional monomers (e.g., thiol- and ene-based systems) capable of undergoing addition-fragmentation chain transfer during polymerization [13-21]. Those monomers facilitate stress relaxation by rearranging the network system during polymerization and by delaying the vitrification stage, thus enhancing the overall compliance of the system.

Recently, a new group of urethane-based dimethacrylates having at least one terminal isocyanato acrylic pendent radical (Exothane™ Elastomers, Esstech) became available [22]. These monomers have the potential of acquiring high conversion values and lower polymerization shrinkage when compared to dimethacrylates such as Bis-GMA, TEGDMA, and UDMA [22]. Worth mentioning, their flexible/elastic characteristics make them potential “stress-reducing”. However, there are several types of Exothanes available in the market, and, from the best of our knowledge, no study had evaluated their effect on contraction stress development of resin-based dental materials.

The present study reported on the contraction stress development of different Exothanes. Additionally, considering that the type of photoinitiators used to initiate and propagate the polymerization reaction may directly affect monomer conversion [23], the present study also investigated the effects of distinct initiation systems on the polymerization kinetic as well as on contraction stress developed by the Exothanes. Three hypotheses were formulated: (1) the Exothanes would present improved polymerization performance when compared to UDMA (control); (2) the Exothanes would develop less contraction stress when compared to the control; and (3) the type of initiation system would influence both the polymerization performance and the contraction stress developed by the Exothanes.

2. Materials and methods

2.1. Reagents

Exothanes (8, 9, 10, 24, and 32), UDMA, and camphorquinone (CQ) were obtained from Esstech Inc. (Essington, PA, USA). Ethyl 4-dimethylamino benzoate (EDAB) was purchased from Fluka (Milwaukee, WI, USA) and diphenyliodoniun hexafluorphosphate (DPI) was obtained from Sigma-Aldrich (St Louis, MO, USA). All the reagents were used as received, without further purification.

2.2. Experimental resins formulation

Experimental resins were prepared mixing one type of the Exothanes or UDMA (control) with different combinations of CQ, EDAB, and DPI (0.5 wt.%, 1.0 wt.%, and 1.0 wt.%, respectively), comprising resins containing unitary (only with CQ), binary (with CQ and EDAB), or ternary (with CQ, EDAB, and DPI) initiation systems. All resins were homogenously mixed by stirring overnight and by ultrasound immersion for 15 minutes.

2.3. Polymerization reaction analysis

The polymerization kinetic (here assessed by means of degree of conversion/DC and rate of polymerization/RP analyses) of all resins were evaluated in triplicate using real time Fourier Transform infrared spectroscopy (RT-FTIR) with a Shimadzu Prestige21 spectrometer equipped with an attenuated total reflectance device, composed of a diamond crystal. The IRsolution program (Shimadzu, Columbia, MD, USA) was used in the monitoring scan mode, using the Happ-Genzel appodization, within the range of 1750 and 1550 cm^{-1}, resolution of 8 cm^{-1} and mirror speed of 2.8 mm/s. One scan per second was acquired during light-activation (30s) using a light-emitting diode (LED) light-curing unit (Radii, SDI, Bayswater, VIC, Australia) with irradiance of 900 mW/cm^{2}, at a controlled room temperature of 23ºC (±2ºC) and 60% (±5%) relative humidity. DC was calculated as previously described [24] and data was plotted with curve fitting performed by Hill 1 parameter non-linear regression. The RP was calculated as the DC at time t subtracted from DC at time t – 1 [25]. The coefficient of determination was greater than 0.97 for all curves.

2.4. Contraction stress analysis

Each resin was evaluated in quintuplicate according to a previous study [6]. Briefly, glass rods (5 mm diameter × 13 or 28 mm in length) were used as bonding substrates, and one of their flat surfaces was roughed with #180-grit sandpaper and coated with silane (Silano, Biodinamica, Ibiporã, PR, Brazil). The opposite surface of the shorter rod was polished with decreasing sandpaper's grits (#600-, #1200-, #1500-, #2000-, and #2500-grit) in order to facilitate light transmission through the rod. While the 28 mm-long rod was attached to the upper fixture connected to a universal testing machine (Instron 5565, Canton, MA, USA), the 13-mm rod was fixed to a stainless steel attachment, which allowed the close contact between the LED and the polished surface of the rod. Each resin was inserted between the two silanized glass surfaces, which were distant from each other by 1 mm. Specimen height (1 mm) was kept constant by using an extensometer (model 2630-101, Instron) at resolution of 0.1 µm. Each sample was photo-activated for 40s and the contraction force was monitored for 10 min; the maximum nominal stress was calculated by dividing the maximum contraction force by the cross-sectional area of the rods.

3.5. Statistical analysis

The DC and CS data obtained in the study were analyzed with the statistical program SigmaPlot version 12 (Systat Software Inc., San Jose, CA, USA) using two way analysis of variance and Tukey test for multiple comparisons (α=5%). Linear regression models were also performed to analyze the relationship between DC and CS, maximum R_P and CS, or DC at maximum R_P and CS.

3. Results

3.1. Polymerization kinetics

According to results shown in Figure 1 and Table 1, Exothane 32 displayed the highest R_P^{max} and DC, reaching full monomer-conversion after only 10 s from the beginning of light-activation. While Exothanes 8 and 9 exhibited similar RPmax and DC values ($p=0.161$) compared to Exothane 32, Exothanes 10 and 24 were the least effective, showing DC values ranging from 19 to 52%, which were significantly lower than the other Exothanes ($p<0.001$). UDMA resulted in intermediary DC values, ranging from 59 to 61%. Overall, the R_P^{max} of UDMA was lower ($p\leq0.01$) when compared to Exothanes 8, 9, and 32, but similar ($p=0.243$) compared to Exothanes 10 and 24; the exceptions were Exothanes 10 and 24 containing only CQ, which DC values were significantly lower than UDMA ($p\leq0.01$). Regarding the DC values reached at R_P^{max}, the order of the highest to the lowest DC is as follows: Exothane 9 > Exothane 8 > Exothane 32 > Exothane 10 > Exothane 24 > UDMA (Table 1).

Regarding to the initiation system factor, while it did not affect the overall polymerization performance of UDMA and Exothanes 9, 10, and 32, the binary and ternary systems improved, respectively, the final DC of Exothanes 8 ($p\leq0.05$) and 24 ($p\leq0.01$) relative to the unitary system (Table 1). CQ alone was capable to initiate the polymerization reaction for all Exothane- and UDMA-based resin blends.

3.2. Contraction stress (CS)

According to the statistical analysis, the factors “resin monomer” and “initiation system” interacted significantly to define CS response ($p \leq 0.001$) (Table 2). Regardless of the initiation system, UDMA produced the highest CS levels of the study, which ranged from 3.6 to 6.2 MPa. All Exothanes resulted in significantly lower CS than UDMA ($p<0.001$), and most of them displayed CS values inferior to 1.0 MPa (Exothanes 8, 10, and 32). Exothanes 9 and 24 presented an overall higher CS than the others, except for Exothane 24 combined with the unitary initiation system, which produced a CS value of 0.2 MPa and similar to Exothanes 8, 10, and 32 ($p=0.958$). The type of initiation system did not affect CS for Exothanes 8, 10, and 32 ($p \geq 0.078$), whereas CS was significantly higher for the other monomers when combined with the binary initiator system ($p \leq 0.006$).

3.3. Linear regression models

According to results shown in Figure 2, DC, R_P^{max}, and DC at R_P^{max} were not correlated to CS ($R^2 \leq 0.333$, $p=0.282$) at any of the linear regression models investigated. For example, UDMA produced the highest CS of the study, although it presented intermediary DC and R_P^{max} values and low DC at R_P^{max}. Exothane 32, which presented the highest DC and R_P^{max} values, generated intermediary DC at R_P^{max} as well as the lowest CS. Lastly, Exothane 24, which exhibited low DC, R_P^{max}, and DC at R_P^{max}, originated high CS values.

4. **Discussion**

Elastomers are viscoelastic polymeric materials used for various applications such as the fabrication of tires and tubes, hoses, chemicals, oil seals, O-rings, toes, and soles [26]. In dentistry, they have been applied as impression materials, and more recently for the formulation of experimental resin adhesives [27]. The Exothanes investigated here are elastomers in nature and they are also derived from UDMA, making them dimethacrylates; surprisingly, they have never been characterized before by means of their polymerization and contraction stress behavior, thereby becoming the purpose of the present study.

Five different Exothanes were tested and all of them exhibited distinct polymerization profiles (Figure 1 and Table 1). Chemically speaking, several factors may affect the polymerization reaction of dimethacrylates, including but not limited to their viscosity, degree of functionality (i.e., the number of double bond terminations per molecule), and the chain extender length between the two unsaturations [28]. Unfortunately, there is no available information regarding structural formula and molecular weight of the Exothanes, as this information is not provided by the manufacturer; this fact precludes the proper determination of which characteristics, specific for each Exothane, are influencing their polymerization reaction. The only exception is Exothane 9, which was previously marketed as an extended UDMA having a PEG 400 (i.e., polyethylene glycol 400) portion [22]. The molecular structure of Exothane 9 is shown in Figure 3, and it is basically the combination of two UDMA molecules with a PEG 400 molecule in the center. Comparing the results of Exothane 9 with that from UDMA, it is possible to note that the former resulted in considerably higher monomer conversion and faster polymerization reaction than the latter (Figure 1 and Table 1). This is probably explained by the longer chain backbone of Exothane 9 when compared to UDMA, providing greater flexibility and mobility for the system [28]. In addition, vitrification is not usually detected in the polymerization of methacrylates presenting a long flexible chain, which means that the system may acquire almost 100% conversion [29]. Indeed, this was not only observed for Exothane 9 but also for Exothanes 8 and 32, and more specifically for the latter, which exhibited full monomer conversion after approximately 10 s of light-activation (Figure 1). Therefore, it can be inferred that Exothanes 8 and 32 have some structural similarities to Exothane 9, probably related to the chain extender length. However, some peculiar differences can be also suggested: first, Exothane 8 displayed a considerably slower polymerization reaction than Exothanes 9 and 32 (note the former's lower R_P^{max} shown in Figure 1), which may be probably associated to the greater viscosity of Exothane 8 compared to Exothanes 9 and 32 (Table 3); second, Exothane 32 demonstrated a rate of polymerization similar to Exothane 9, but its ability to achieve full conversion may suggest that other features may be influencing its polymerization kinetic. Nevertheless, as stated earlier, it is impossible to confirm these inferences using only the methodologies presented here, thereby indicating that future studies should be conducted using chemical analyses capable of revealing the chemical composition and/or structure of these Exothanes (e.g., CHN analysis, atomic spectroscopy).

Differently from Exothanes 8, 9, and 32, the Exothanes 10 and 24 resulted in the least effective polymerization of the study, in special for Exothane 24 (Table 1). Once again, it is difficult to explain the exact reasons for their reduced performance, although some speculations can be suggested. For example, viscosity plays an important role in the polymerization of methacrylate-based monomers since it may affect the mobility of the system [28, 30]. Indeed, the greater the viscosity of the resin, the lower its reactivity. According to information given by Esstech™, Exothane 10 is very viscous at room temperature (Table 3), fact that may explain its slow polymerization kinetics (Figure 1 and Table 1). On the other hand, Exothane 24 is not as viscous (Table 3), so its low reactivity may be attributed to a different factor rather than viscosity. According to Esstech™, Exothane 24 is a tetra-functional monomer capable to increase crosslinking. Although its higher functionality could enhance system reactivity, without the flexibility granted by a long chain backbone, the molecule will present reduced mobility, thus reducing the overall reactivity of the system [29]. With low mobility and low reactivity, vitrification is prone to occur at early stages of polymerization, decreasing the monomer conversion; this was indeed observed with Exothane 24. Consequently, it can be suggested that Exothane 24 has a shorter molecule compared to the others, thereby explaining its relatively low rate of polymerization shown in Figure 1.

Another aspect related to the polymerization of Exothanes that should be mentioned is the degree of conversion reached by each resin at the moment of its maximum rate of polymerization (DC_{Rpmax}). Overall, all Exothanes reached higher DC values than UDMA at the peak of the reaction rate (Table 1). Within the Exothanes category, however, three different patterns were observed: Exothanes 8 and 9 reached high DC values (≥ 63%) at their R_P^{max}, which were also further completed; Exothanes 10 and 24 showed low DC values (≤ 33%) at their R_P^{max}, with a slightly or moderately increase of conversion after that point; lastly, Exothane 32 reached intermediary DC values (from 31 to 40%) at the R_P^{max}, although with a significant increase (full conversion of monomers) after the reaction decreased its velocity. Generally speaking, the polymerization reaction of dimethacrylate monomers can be characterized by a first stage in which the velocity of the reaction increases until it reaches the maximum rate of polymerization (acceleration), and also by a second stage in which the reaction slows down and both propagation and termination become diffusion controlled (deceleration) [31]. During the first stage, monomers present full mobility, which means they can freely polymerize and rearrange within the system; conversely, during the second stage, vitrification takes place, thus progressively reducing monomer mobility [32]. Exothanes displayed different polymerization profile, with Exothane 32 being the only one that did not demonstrate a vitrification behavior, reaching full conversion of monomers. One possible explanation is the very low modulus of Exothane 32 (Table 3), which leads to a rubbery behavior [28], thus maintaining monomers mobility and reactivity until the end of the reaction. Therefore, and taking all the findings presented up to here together, the first hypothesis of the study can be partially accepted.

Another purpose of the present study was to investigate the effects of the Exothanes regarding CS development. In theory, the elastomeric nature of Exothanes brings the idea that they are flexible, which would contribute to increase the compliance of the system, and consequently, to reduce stress development. CS is a very complex phenomenon since it strongly depends on the interplay among resin viscosity, volume shrinkage, rate of polymerization, degree of conversion, elastic modulus development, and network formation [5]. However, and according to the linear regression analyses performed here, DC and RP demonstrated a poor relationship with CS (Figure 2), denoting that these characteristics do not have a strong influence on the urethane-based resins investigated. One could note that in light of the elastomeric nature of the Exothanes, maybe other factors such as elastic modulus and volumetric shrinkage may have played a more important role on the CS phenomenon. UDMA produced the highest levels of stress (Table 2), probably due to its high modulus and volumetric shrinkage (Table 3). On the other hand, the Exothanes have considerably lower modulus and volumetric shrinkage when compared to UDMA, although with some exceptions: Exothanes 9 and 24 have, respectively, a close volumetric shrinkage and elastic modulus to UDMA. Surprisingly, both Exothanes 9 and 24 resulted in overall higher stress than the other Exothanes, thus indicating that for Exothane-based resins, those foregoing properties seem to have a more significant influence on the development of CS.

Despite the present results can be satisfactorily explained by means of the elastic modulus and volumetric shrinkage of each monomer investigated, it is known that most of the deleterious stress is originated only after the polymer network reaches the gel point. Prior to gelation, the system is able to rearrange itself, relieving stress. Conversely, at the moment the system reaches the gel point, i.e., during gelation and vitrification, modulus development and volumetric shrinkage will result in measurable CS values [31]. A fast or delayed gel point may be coarsely predicted by analyzing the DC achieved by the resin at its R_P^{max}, which can be observed in Table

1. UDMA showed the lowest conversion of monomers at the R_P^{max} (approximately 20% of its total conversion); consequently, most of its conversion occurred after gelation and vitrification stages, which in association with high elastic modulus and volumetric shrinkage, resulted in the highest levels of stress of the study. Exothane 8, on the other hand, reached almost 80% of its total conversion before the gel point, and considering its low modulus and volumetric shrinkage, it produced low levels of stress. Worth mentioning, although Exothanes 9 and 24 have reached more than 80% (except for Exothane 24 combined with the tertiary initiation system, which was around 40%) of their total conversion before gelation/vitrification, the high volumetric shrinkage of Exothane 9 as well as the high elastic modulus of Exothane 24 may have contributed to increase CS when compared to the other Exothanes (Table 2). However, CS developed by Exothanes 9 and 24 was still inferior to that originated by UDMA. Therefore, it can be noted that prolonging the gel point may be beneficial to diminish the negative effects that modulus development and volumetric shrinkage have on the CS phenomenon. Lastly, for Exothanes 10 and 32, which have reached intermediary levels of total conversion before the gel point (e.g., from 31 to 63%), their low elastic modulus and volumetric shrinkage allowed them to produce low levels of stress, similarly to Exothane 8. According to all CS results presented up to here, the second hypothesis of this study can be totally accepted.

According to several previous reports in the literature, the type of photoinitiators used to initiate and propagate the polymerization reaction of resin-based materials influence polymerization [23, 33, 34] as well as CS development [11, 35]. Three different initiation systems were chosen in this study: one containing only the photoinitiator (CQ, unitary system), one containing both photoinitiator and coinitiator (CQ+EDAB, binary system), and one containing photoinitiator, coinitiator, and a catalyst (CQ+EDAB+DPI, ternary system). The binary system was considered here as the control since the combination of CQ with an amine-based coinitiator such as EDAB has been thoroughly used in the formulation of light-sensitive dental materials [24, 36]. However, the unitary system was also tested because the amine groups present in urethane-based monomers (Figure 3) may work as coinitiators for CQ. Important to say, CQ is a type II photoinitiator, which means the presence of a coinitiator (electron acceptor) is mandatory to promote an efficient polymerization reaction [23, 33, 34]. As shown in Figure 1 and Table 1, the presence of the unitary system allowed the resins to polymerize, thus confirming that all urethane-based monomers tested (i.e., UDMA and the Exothanes) worked as coinitiators of the reaction, resulting in similar polymerization performance when compared to the binary system. The only exception was Exothane 8, which despite showing satisfactory degree of conversion (around 80%), produced lower DC than the binary system, probably explained by its slower rate of polymerization (Figure 1 and Table 1). Although this was not the primary purpose of the present study, the fact that CQ alone may be used to start the polymerization reaction of urethane-based compositions is important since most of the coinitiators used in dentistry are cytotoxic [37-39] and/or may bring chemical instability in acidic materials such as self-etch adhesives/cements [40-42].

Regarding to the tertiary initiation system tested, it was designed in the present study because according to Ogliari et al. [24], oniun salt derivatives such as DPI can increase the DC of dimethacrylates. Indeed, it was demonstrated that DPI may work as coinitiator and catalyst of the reaction. Chemically speaking, DPI reacts with CQ forming an exciplex, which will further react with EDAB, giving a radical amine; this radical initiates the polymerization, and the DPI is thereby regenerated, enabling the onium salt to form another exciplex with a new photo-activated CQ. Consequently, reaction kinetics is improved. Surprisingly, the presence of DPI did not result in better polymerization when compared to the other initiation systems, except for Exothane 24 (Figure 1). The most reasonable explanation for this fact is that the resins containing the tertiary initiation system reached the saturation level of coinitiator moieties (e.g., amino groups found within the structure of monomers; amino groups found in EDAB; diphenyliodine radicals originated from DPI), thus maintaining the polymerization efficacy similar to the systems containing lower amount of coinitiators. For Exothane 24, however, the presence of the tertiary system increased the polymerization kinetic, resulting in both higher DC and higher rate of polymerization than the counterparts formulated with the unitary or binary systems (Figure 1). Again, it can be speculated that the tetra-functional nature of Exothane 24 may have hampered the reactivity and mobility of the system; nonetheless, DPI acted as a catalyst, thus increasing the kinetic of reaction, and consequently the polymerization performance of the resin [24, 33].

Finally, and according to data shown in Table 2, although the type of initiation system did not affect the CS results for Exothanes 8, 10, and 32, the unitary system produced considerably lower CS for UDMA, Exothanes 9 and 24 than the counterparts containing the binary system. The same was also observed for Exothanes 9 and 24 containing the tertiary system. According to Ye et al. [43], the presence of distinct photoinitiators may produce differences in polymer crosslink density, which in turn may affect elastic modulus within the material; the presence of the unitary or ternary systems in the previous Exothanes may have contributed to change modulus development, thus contributing to decrease CS. Therefore, it can be stated that overall, EDAB and DPI were not essential to improve the polymerization of the resins investigated, and sometimes their presence was associated to higher stress development, thus partially accepting the third hypothesis of this study.

5. Conclusion

In summary, some Exothanes (e.g., Exothanes 8, 9, and 32) demonstrated considerably higher degree of conversion and a moderate to fast polymerization reaction when compared to UDMA. All Exothanes produced less contraction stress than UDMA, regardless of the initiation system used. However, one additional point that should be also considered is that the present results were obtained using a low compliant system during the contraction stress testing, which may imply that different results may be expected upon testing with a more compliant system [7]. Notwithstanding, the Exothanes demonstrated a highly compliant behavior, thereby highlighting their potential application as stress-reducing agents for dental materials application. Furthermore, the urethane-based monomers tested acted in the coinitiation of CQ, showing an utmost importance for the development of more compatible/stable light-sensitive dental materials.

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Tables

Table 1. Mean (standard deviation) of the maximum degree of conversion (DC_{max}), maximum rate of polymerization (R_P^{max}), and degree of conversion at maximum rate of polymerization (DC_{Rpmax}) obtained for the resins containing different initiation systems.

Resins	**Initiation system**								
	Unitary (CQ)			**Binary (CQ+EDAB)**			**Ternary (CQ+EDAB+DPI)**		
	DC_{max} (%)	**R_P^{max} (%/s)**	**DC_{Rpmax} (%)**	**DC_{max} (%)**	**R_P^{max} (%/s)**	**DC_{Rpmax} (%)**	**DC_{max} (%)**	**R_P^{max} (%/s)**	**DC_{Rpmax} (%)**
UDMA	59.6 (2.7) ^{c}	2.5 (0.3) ^{c}	12.1 (1.2) ^{e}	61.2 (6.1) ^{b}	2.8 (0.4) ^{d}	14.6 (1.1) ^{e}	59.0 (2.3) ^{b}	2.7 (0.2) ^{d}	13.5 (1.6) ^{f}
E8	80.4 (15.5) ^{b}	2.6 (0.9) ^{c}	63.0 (2.1) ^{b}	99.0 (1.0) ^{a}	3.5 (0.2) ^{c}	77.3 (3.1) ^{b}	90.6 (6.9) ^{a}	2.4 (0.3) ^{d}	65.8 (5.1) ^{b}
E9	89.0 (3.8) ^{ab}	3.9 (0.2) ^{b}	71.7 (3.2) ^{a}	95.1 (8.4) ^{a}	6.8 (0.7) ^{a}	82.6 (3.2) ^{a}	92.0 (5.5) ^{a}	7.4 (0.2) ^{b}	80.0 (3.3) ^{a}
E10	40.0 (6.0) ^{d}	0.9 (0.3) ^{d}	13.3 (1.1) ^{de}	52.1 (2.4) ^{b}	1.6 (0.1) ^{e}	32.9 (2.1) ^{c}	52.1 (17.8) ^{b}	1.7 (0.3) ^{e}	25.3 (2.1) ^{d}
E24	19.0 (1.3) ^{e}	0.6 (0.2) ^{d}	15.4 (1.1) ^{d}	26.8 (2.9) ^{c}	1.0 (0.1) ^{f}	23.1 (2.5) ^{d}	47.5 (27.7) ^{b}	3.6 (0.2) ^{c}	18.7 (1.2) ^{e}
E32	100.0 (0) ^{a}	5.9 (0.4) ^{a}	40.2 (1.8) ^{c}	100.0 (0) ^{a}	4.7 (0.2) ^{b}	30.5 (3.1) ^{c}	100.0 (0) ^{a}	8.2 (0.3) ^{a}	38.7 (2.1) ^{c}

CQ: camphorquinone; EDAB: ethyl 4-dimethylamino benzoate; DPI: diphenyliodoniun hexafluorphosphate; UDMA: urethane dimethacrylate; E8, E9, E10, E24, and E32: Exothanes 8, 9, 10, 24, and 32, respectively.

Distinct superscript letters within the same column indicate statistically significant differences among the resins ($p<0.05$).

Table 2. Contraction stress means (standard deviation) for all resins investigated.

Resin blends	Initiation system		
	Unitary (CQ)	**Binary (CQ+EDAB)**	**Ternary (CQ+EDAB+DPI)**
UDMA	3.6 (0.2) $^{A\,b}$	5.9 (1.1) $^{A\,a}$	6.2 (0.6) $^{A\,a}$
E8	0.3 (0.1) $^{C\,a}$	0.6 (0.1) $^{D\,a}$	0.6 (0.1) $^{D\,a}$
E9	1.1 (0.2) $^{B\,b}$	1.8 (0.2) $^{C\,a}$	1.2 (0.3) $^{C\,b}$
E10	0.2 (0.1) $^{C\,a}$	0.7 (0.1) $^{D\,a}$	0.6 (0.1) $^{D\,a}$
E24	0.2 (0.1) $^{C\,c}$	3.6 (0.5) $^{B\,a}$	2.9 (0.2) $^{B\,b}$
E32	0.3 (0.1) $^{C\,a}$	0.5 (0.1) $^{D\,a}$	0.4 (0.1) $^{D\,a}$

CQ: camphorquinone; EDAB: ethyl 4-dimethylamino benzoate; DPI: diphenyliodoniun hexafluorphosphate; UDMA: urethane dimethacrylate; E8, E9, E10, E24, and E32: Exothanes 8, 9, 10, 24, and 32, respectively.

Distinct uppercase and lowercase superscripts within the same column and the same row indicate, respectively, statistically significant differences among the resins ($p<0.05$).

Table 3. Selected properties of monomers tested in the study.

Monomer	Selected properties [*]		
	Viscosity (PaS)	**Modulus (GPa)**	**Volumetric shrinkage (%)**
UDMA	8.5	0.7	5.8
E8	30.1	0.08	3.3
E9	1.8	0.1	5.3
E10	70.0	0.3	3.2
E24	3.8	0.8	4.2
E32	5.9	0.008	3.1

UDMA: urethane dimethacrylate; E8, E9, E10, E24, and E32: Exothanes 8, 9, 10, 24, and 32, respectively.

[*] Data obtained from Esstech™ website (http://catalog.esstechinc.com/viewitems/all-categories/esstech-specialty-chemicals-exothane?2015).

Figures

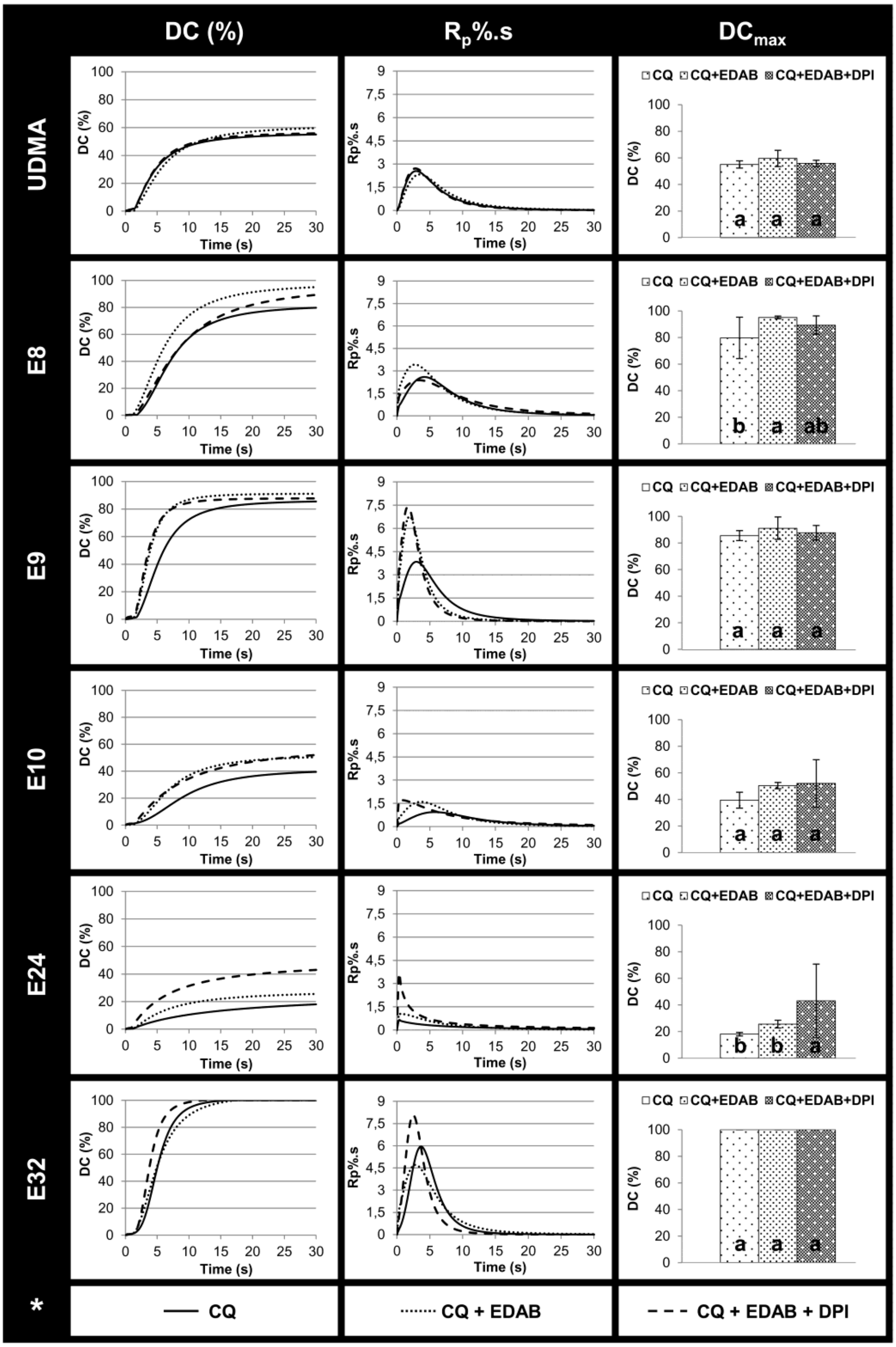

Figure 1. Graphs showing the kinetic of polymerization (degree of conversion/DC at every second of polymerization), rate of polymerization (R_P%.s), and maximum DC (DC_{max}) for all resins containing distinct initiation systems (unitary: CQ; binary: CQ + EDAB; ternary: CQ + EDAB + DPI).

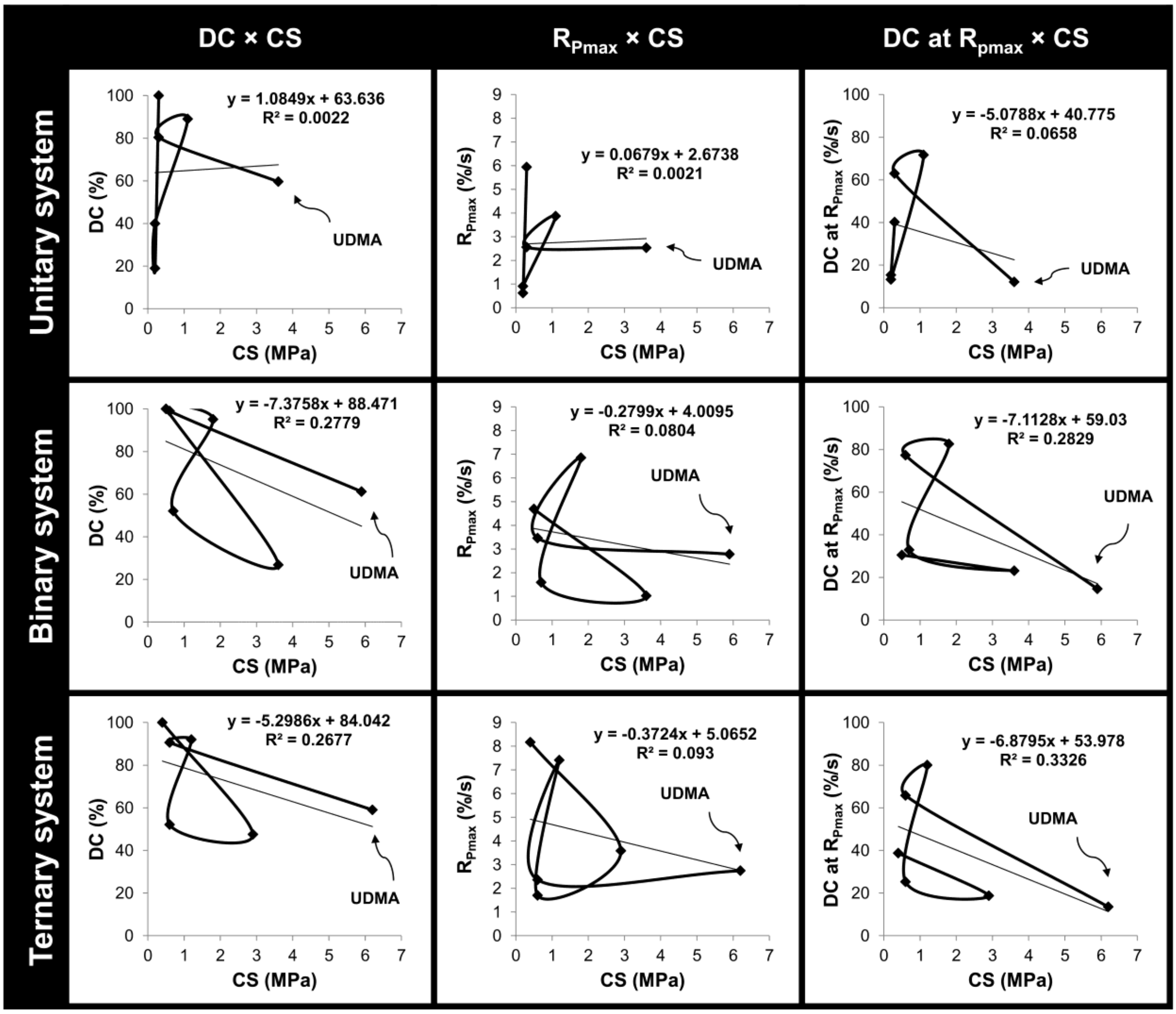

Figure 2. Linear regression analyses between maximum degree of conversion (DC) and contraction stress (CS), maximum rate of polymerization (R_P^{max}) and CS, and DC at R_P^{max} and CS for all groups investigated.

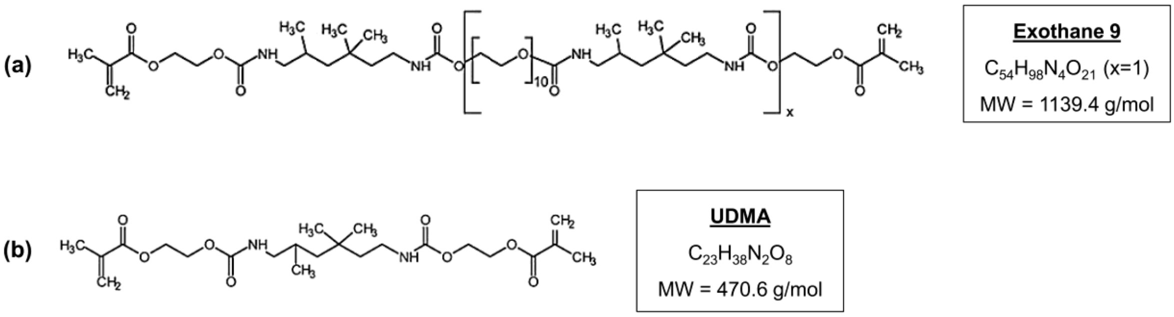

Figure 3. Molecular structure, formula, and weight for Exothane 9 and UDMA.

6 Artigo 3

Effects of poly(ε-caprolactone) fibers as stress-reducing agents for dental materials applications[§]

Short title. Electrospun fibers as stress-reducing agents

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Key words: electrospinning, FTIR, hardness, scanning electron microscopy.

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Abstract

Objectives: The aim of this study was to synthesize poly(ε-caprolactone)/PCL fibers via electrospinning and to investigate their effect on selected properties and contraction stress/CS development of experimental resin blends.

Methods: Electrospun PCL fiber mats were immersed into an unfilled resin, light-activated, and then cryomilled to obtain micron-sized fiber-modified fillers. The fillers were incorporated into an experimental resin blend constituted of Bis-GMA/HEMA (60:40 wt.%) at different concentrations: 0 (control), 5, 10, 15, and 20 wt.%. Degree of conversion/DC, hardness/KHN, flexural strength/FS, flexural modulus/FM, and CS analyses were performed. Scanning electron microscopy/SEM analysis was also conducted to determine fibers and fillers morphology. Data were analyzed using ANOVA and Tukey, as well as linear regression analyses ($p<0.05$).

Results: The PCL fibers demonstrated a heterogeneous diameter distribution, with an average size of 333±322 nm. The obtained fillers were irregular in shape and clearly demonstrated the presence of short fibers embedded within their matrix. The fiber-containing resin blends exhibited similar DC, KHN, FS, and FM values when compared to the fiber-free control group ($p\geq0.210$). CS was significantly reduced upon the incorporation of the fiber-modified fillers, with the greater the content of fillers, the lower the stress produced ($p<0.001$, $R^2=0.9275$). SEM images of fractured specimens showed a more irregular/heterogeneous cross-sectional surface for the fiber-containing resins compared to their fiber-free counterpart.

Conclusion: The strategy proposed here (i.e., incorporation of fiber-modified fillers into an unfilled resin) demonstrated effectiveness to control/minimize stress development without jeopardizing important physic-mechanical properties of the material.

Clinical significance: Based on the well-known application of electrospun fibers as carriers of several bioactive compounds, fiber-modified fillers bring potential application for the development of new dental materials with improved biological properties as well as less contraction stress production.

1. Introduction

For most of the resin-based materials currently used in restorative dentistry, contraction stress is still an undesirably and frequent consequence, especially in cases where the material is applied under confined circumstances such as root canals or tooth cavities showing high C-factor. Indeed, problems like tooth structure deformation, microcrack propagation, as well as adhesive failure may occur, thereby compromising the restorative treatment.[1] In light of this, several efforts have been made in order to minimize and/or control stress development at the tooth/restorative interface. One approach intended to reduce the volumetric shrinkage suffered by the material during its polymerization since it is considered one of the major influencing causes for contraction stress development.[2] This was the case of the well-known silorane-based materials, which are hybrid compounds containing siloxane and oxirane functional groups.[3] Nevertheless, although they do shrink less when compared to conventionally used methacrylate-based monomers,[4, 5] siloranes may still produce as much stress as the latter monomers.[6, 7] Moreover, and according to a recent randomized clinical trial,[8] silorane-based restorations did not show any advantage over methacrylate-based restorations. Alternative strategies rather than just reducing volumetric shrinkage were also investigated. The SDR™ technology (i.e., stress decreasing resin), for example, is one of the most recent approaches. Chemically speaking, this technology has optimized both the organic matrix (i.e., by using alternative/modified monomers and initiators) and the filler phase of the material,[9, 10] thus resulting in considerably less stress development when compared to conventional materials that do not use the SDR™ chemistry.[9, 11, 12] Worth mentioning, the so-called bulk-fill resin-based composites are examples of the SDR™ technology, and they have demonstrated satisfactory clinical results.[13, 14]

One of the most important concerns about pursuing/developing new formulations for resin-based restoratives is to preserve the characteristics and properties that do not need to be modified. Sometimes, even though considerable stress reduction can be obtained upon the modification or incorporation of new compounds within the material, other important properties may be compromised, especially those related to the material's strength. For example, depending on the material, both silorane-based and bulk-fill composites demonstrated significant reduction of flexural strength, flexural modulus, and hardness when compared to conventional composites.[11, 15] Therefore, the development of restorative materials that reduce and/or eliminate the occurrence of contraction stress without jeopardizing important physic-mechanical properties is paramount to translate higher durability for the restorative treatment. Remarkably, another technology that has been recently incorporated to dentistry is the fabrication and application of electrospun nanofibers as bioactive additives of dental materials.[16-18] Nanofibers can be defined as very thin filaments situated below the range of 500 nm, which usually present low density and high area/volume ratio.[19] In addition, nanofibers have high flexibility, toughness, and strength characteristics,[20] which make them very unique structures. Important to mention, electrospinning, which is a cost-effective and straightforward processing technique, can turn polymer solutions into fibers in a very easy way, thus becoming the fairest approach to fabricate fibers.

During the last few years, electrospun fibers have been mostly used as vehicle for drug-delivery systems[16-18] or to reinforce the structure of composite materials.[21, 22] Nonetheless, from the best of our knowledge, there is a lack of information regarding the effect of fibers on contraction stress development for resin-based materials. Interestingly, one previous report has demonstrated that the use of short E-glass fiber fillers reduced stress development of composite resins;[23] indeed, it was stated that the fiber fillers allowed stress transfer from polymer matrix to fibers. This stress reduction mechanism could perhaps be used to decrease the negative effects of stress suffered by resin-based dental materials. Therefore, the purpose of this study was first to synthesize polymer-based fibers via electrospinning, and second to investigate their effect on selected properties and contraction stress development of experimental resin blends. Two hypotheses were formulated: the incorporation of fibers into resin blends (1) would not decrease the overall strength of the resins and (2) would reduce contraction stress when compared to a nanofiber-free resin blend.

2. Materials and Methods

2.1. Reagents

Poly(ε-caprolactone) pellets (PCL, M_W=80,000), 1,1,1,3,3,3-hexafluoro-2-propanol (HFP), camphorquinone (CQ, Batch #09003AQ), and 2-(dimethylamino) ethyl methacrylate (DMAEMA, Batch #SHBC0036V) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Bisphenol A bis(2-hydroxy-3-methacryloxypropyl) ether (Bis-GMA, Batch #786-28-02) and 2-hydroxyethyl methacrylate (HEMA, Batch # 772-

37) were purchased from Esstech Inc. (Essington, PA, USA). All reagents were used as-received.

2.2. Fabrication of fibers via electrospinning

PCL was dissolved in HFP to obtain a 10 wt.% polymer solution (100 mg/mL), which was stirred overnight. The solution was then loaded into a plastic syringe (5 mL, Becton, Dickson and Company, Franklin Lakes, NJ, USA) fitted with a 27G metallic blunt-tip (CML Supply, Lexington, KY, USA) and electrospun using an electrospinning system consisted of a high-voltage source (ES50P-10W/DAM, Gamma High-VoltageResearch Inc., Ormond Beach, FL, USA), a syringe pump (Legato200, KD Scientific Apparatus, Holliston, MA, USA), and a grounded stainless steel collecting drum connected to a high-speed mechanical stirrer (BDC6015, Caframo, Wiarton, ON, Canada).[18, 24, 25] Processing parameters were as follows: rotating mandrel with 120 rpm of speed, fixed spinning distance of 18 cm, flow rate of 1.5 mL/h, and 15 kV of electric voltage. The obtained mat (i.e., piece of fibers) was collected at room temperature and then dried under vacuum for at least 48h to complete removal of any remaining solvent.[24]

2.3. Fibers characterization and filler preparation

The electrospun mat was observed under a field-emission scanning electron microscope (FE-SEM, Model JSM-6701F, JEOL, Tokyo, Japan) to evaluate the morphology and overall architecture of fibers. Briefly, samples taken from the mat were mounted on an Al stub and sputter-coated with Au-Pd prior to imaging. Image J software (National Institutes of Health, Bethesda, MD, USA) was used to calculate the diameter of 50 single-fibers per image obtained from the FE-SEM analyses (3 images in total) at the same magnification (5000×); the fiber diameter was then averaged and reported as mean ± SD.

In order to incorporate the fibers into experimental resin-based materials, the electrospun mat was processed to result in a powder (microfillers composed of fibers), as previously described.[26] In brief, the mat was cut into pieces (30 × 30 mm^2) and immersed into a resin blend constituted of 60 wt.% of Bis-GMA, 40 wt.% of HEMA, and 0.4/0.8 wt.% of CQ/DMAEMA. Each soaked piece was then cautiously removed and placed in-between two Mylar sheet and two glass plates, and light finger pressure was applied to remove any resin excess as well as air bubbles. The samples were light-cured for 2 min each side into a TRIAD 2000 chamber (Dentsply International, Inc., York, PA, USA); the final resin/mat composites had a fibers' content of approximately 25 wt.%. Next, all the resin/mat composites were subjected to a cryomilling process using a cryogenic impact mill (model Spex CertiPrep 6750, Spex CertiPrep, Metuchen, NJ, USA) to obtain a fine micron-sized powder. The samples were precooled for 2 min and then milled for 15 min, which consisted of alternating cycles of 1 min of milling time separated by cooling intervals of 1 min. Liquid nitrogen surrounding the milling chamber was used to ensure complete cooling during cycles. Finally, the resultant powder/filler was imaged under the FE-SEM to determine morphology and particle distribution of the milled samples.[26]

2.4. Preparation of experimental resin blends modified with fibers

A stock resin blend was prepared as mentioned before (60/40 wt.% ratio of Bis-GMA/HEMA + 0.4/0.8 wt.% ratio of CQ/DMAEMA) and then divided into five groups according to the concentration of fillers added: 0 (control), 5, 10, 15, and 20 wt.%. The experimental resin blends were stirred overnight to ensure proper filler distribution within the resin matrix.

2.5. Degree of conversion

The degree of conversion (DC) for the formulated resin blends was evaluated using a Fourier Transform infrared spectroscopy (model 4100, JASCO International Co., Tokyo, Japan) in attenuated total reflection (ATR) mode. Uncured specimens (6 mm in diameter × 0.25 mm in thickness, n=5) were prepared and measured, followed by their light-activation for 20 s using a light-emitting diode light curing system (DEMI LED, Kerr, Orange, CA, USA), and they were then measured again (cured state). The light irradiance was >900 mW/cm2 and it was measured periodically using the Managing Accurate Resin Curing (MARC®-RC) calibrator (BlueLight Analytics Inc., Halifax, Nova Scotia, Canada). The absorbance bands at 1637 cm^{-1} (methacrylate group, C=C) and 1607 cm^{-1} (ester group, C=O) were used to calculate the DC (expressed in %) according to the following equation:[27]

$$\mathrm{DC} = 1 - \frac{\text{cured (area under 1637/area under 1607)}}{\text{uncured (area under 1637/area under 1607)}} \times 100$$

2.6. Hardness

Disk-shaped specimens (4 mm in diameter × 2 mm in thickness, n=5) were prepared using elastomeric molds. The specimens were light-activated for 20 s on both the top and bottom surfaces, stored at 37°C for 24 h, polished with diamond paste (METADI, 0.25 micron, Buehler, Lake Bluff, IL, USA), and sonicated for 5 min in distilled water. Next, they were subjected to hardness testing (M-400, LECO

Corporation, St. Joseph, MI, USA) using a Knoop diamond indenter, 50 kg of load, and 15 s of dwell time. Five readings with a minimum of 100 microns between indentations were obtained from each specimen. The diagonal lengths were measured immediately after each indentation, and the values were converted to Knoop Hardness Number (KHN).

2.7. Flexural strength/modulus and FE-SEM analysis

Bar-shaped specimens (25 mm in length × 2 mm in width × 2 mm in thickness) were prepared for each group (n=5) according to ISO 4049:2009.[28] Each specimen was light-cured for 20 s in four overlapping irradiation zones, on both the top and bottom surfaces. The specimens were then wet-finished with 320-grit silicon carbide abrasive paper and stored in distilled water at 37°C for 24 h. The specimens were tested using three-point bend flexural strength (FS) testing (MTS Sintech Renew 1123, MTS Systems Corporation, Eden Prairie, MN, USA) at a crosshead speed of 1 mm/min. The FS was then calculated using the following equation and expressed in MPa:

$FS = 3Fl/2bh2$

Where F is the maximum load exerted on the specimen in Newton, l is the distance between the supports in mm, b is the width of the specimen in mm, and h is the thickness of the specimen in mm.

The flexural modulus (FM) of each specimen was obtained directly through the software of the MTS testing machine and the data was converted to GPa.

Selected fractured samples from the FS test were separated and observed using FE-SEM. The samples were mounted in Al stubs, sputter-coated with Au-Pd and imaged at distinct magnifications (60, 250, and 1000×) for qualitative analysis of the fractured surfaces.

2.8. Contraction stress

Contraction stress (CS) was measured using a universal testing machine (Instron 5565, Canton, MA, USA) and glass rods (diameter, 5 mm; 13 or 28 mm in length) as bonding substrates for the resin blends.[2, 5] For adhesion purpose, one of the flat surfaces of each rod was roughed with #180-grit sandpaper and coated with silane (Silano, Biodinamica, Ibiporã, PR, Brazil); the opposite surface of the shorter rod was polished with decreasing sandpaper's grits (#600-, #1200-, #1500-, #2000-, and #2500-grit) in order to facilitate light transmission through the rod. While the 28 mm-long rod was attached to the upper fixture connected to a universal testing machine, the 13-mm rod was fixed to a stainless steel attachment, which allowed the close contact between the LED and the polished surface of the rod. Each resin blend was inserted between the two silanized surfaces, which were 1 mm far apart by using an extensometer (model 2630-101, Instron) at resolution of 0.1 µm. The samples (n=5) were light-activated for 40s and the CS developed was monitored for 10 min; the maximum nominal stress was calculated by dividing the maximum contraction force by the cross-sectional area of the rods.

2.9. Statistical analysis

All data obtained in the study were analyzed with the statistical program SigmaPlot (version 12, Systat Software Inc., San Jose, CA, USA) and using One-Way Analysis of Variance and the Tukey's test for multiple comparisons. The level of significance was set at $p<0.05$. Linear regression models were used to determine the relationship between each property investigated and the concentration of fillers added in the resin blends.

3. Results

3.1. Fibers morphology

The PCL fibers synthesized in this study were smooth and free of beads/defects, and they demonstrated a heterogeneous diameter distribution, ranging from 58 to 1,582 nm (Figure 1). Fibers exhibited an average diameter size of 333 nm and were more frequently situated below the 400 nm range.

3.2. Fillers morphology

As shown in Figure 2, the PCL-mats were transformed into a micron-sized powder which demonstrated the presence of PCL fibers entrapped within the organic matrix.

3.3. Degree of conversion

The DC values obtained for each group investigated are shown in Table 1. According to the statistical analysis, the groups did not differ from each other ($p\geq0.210$), ranging from 65.0 to 66.4% (Table 1). DC and filler content were not strongly related to each other ($R^2=0.6333$).

3.4. Hardness

The KHN values obtained are demonstrated in Table 1. The groups were not statistically different from each other ($p\geq0.867$), although a strong correlation was observed between KHN values and the concentration of fillers incorporated to the resin (R^2=0.9586), with the greater the filler content, the lower its hardness.

3.5. Flexural strength and flexural modulus

According to results displayed in Table 1, all groups tested exhibited similar FS and FM values (p≥0.708), regardless of the filler content. Both FS and FM demonstrated a strong relationship with the content of fillers added to the resin (R^2≥0.9412), with the greater the filler content, the greater the strength of the resins. Regarding to the fractured samples, Figure 3 shows a set of SEM images of the control group (fiber-free, images a–c) and the group containing 20 wt.% of fillers (fiber-containing, images d–f). While the control group produced a more uniform cross-sectional surface (moderately smooth), the fiber-containing group presented a more irregular cross-sectional surface, clearly rougher than its fiber-free counterpart.

3.6. Contraction stress

Table 1 also shows the CS results obtained in the study. According to the statistical analysis, the presence of fiber-containing fillers contributed to significantly reduce CS for the resins investigated. The control produced the highest level of stress (5.1±0.3 MPa), which was higher than the fiber-containing groups (p<0.001). The CS values were also strongly correlated to the content of fillers (R^2=0.9275), with the greater the filler content, the lower the stress produced. The incorporation of 5, 10, 15, and 20 wt.% of fillers resulted in approximately 24, 32, 42, and 50% of stress reduction when compared to the fiber-free group (control).

Discussion

The application of micron/nano-sized fibers in dentistry as a strategy to enhance the bioactivity of dental materials has recently started to be pursued by researchers all over the world. Interestingly, fibers are very unique structures that present high specific surface area, as well as flexibility and directional strength. These foregoing characteristics may perhaps be used to control the contraction stress phenomenon suffered by resin-based restorative materials, especially due to the fact that the compliance of the system may increase upon the incorporation of more flexible and "spacious" structures,[29, 30] thereby reducing the negative effects of stress development at the tooth/restorative interface. Considering that there is a lack of studies investigating the effect of fibers on contraction stress development of resin-based materials, this became the purpose of the present study.

PCL was chosen here as polymer source for the fabrication of fibers due to its extensive and successful application for the development of diverse biomaterials.[31] Indeed, PCL is a synthetic polymer with well-known high hydrophobicity[16] and flexible mechanical properties;[32, 33] it was also revealed to be non-cytotoxic to several human-body cells and tissues.[16, 34, 35] According to the SEM images shown in Figure 1, the electrospun fibers obtained in this study demonstrated satisfactory morphology and a predominantly nano-sized diameter distribution; this is important to obtain the best from the structure of the fiber. Although electrospinning can be considered an outstanding method to obtain fine fibers with distinct intrinsic properties, the incorporation of fibers into resin-based materials is not as simple as it can be expected since they are very thin and tremendously longer than conventional filler particles used to reinforce dental materials. Additionally, fibers are continuously collected during their fabrication process, thus resulting in a mat comprised of several continuous fibers entrapped among each other; this fact, however, makes it difficult to incorporate the fibers into the material. There are at least two possible strategies available to successfully incorporate electrospun fibers into resin-based materials: one approach is to fabricate short electrospun fibers with well-defined length in the micrometer or millimeter range;[36-39] and the other approach is to process the electrospun fiber mats into a powder.[26, 40] While the former strategy uses a modified electrospinning system, but still dependent on several environmental (e.g., temperature, relative humidity) and technical (e.g., polymer concentration, viscosity/conductivity of the solution, voltage, flow rate, among others) factors to result in effective fibers, the latter strategy is a simpler and more predictable method; the present study used the second strategy to reduce the size of fibers that were then incorporated into the experimental resin blends.

According to Figure 2, a micron-sized powder was obtained via the cryomilling process, and the presence of the fibers could be easily detected within the organic matrix of the fillers. Chemically speaking, the processed fillers were nothing less than polymers, i.e., PCL-based fibers entrapped within Bis-GMA/HEMA prepolimerized particles. Usually, fillers used in dentistry have an inorganic nature (e.g., quartz, silica, glass), which enables them to positively reinforce the material.[41, 42] Conversely, the use of polymeric fillers was revealed to negatively affect important mechanical properties of experimental composites, such as flexural modulus, flexural strength, and fracture toughness.[29] Notably, the incorporation of up to 20 wt.% of the polymeric fillers tested here did not alter degree of conversion, hardness, flexural strength, and flexural modulus of the resin blends (Table 1). First, it can be suggested that the polymeric fillers were homogeneously distributed within the organic matrix of the resins, thus keeping the properties unchanged. Second, and according to Szaloki et al.,[43] polymeric fillers may swell if incorporated into unfilled resins, i.e., they may get embedded within the organic matrix of the material, thus increasing viscosity and the cross-linking density of the system. This may perhaps explain the slight but progressive increase in mechanical properties observed upon the incorporation of greater amount of fillers (from 2.9 to 11.3% for FS and from 4.5 to 13.6% for FM). Moreover, the incorporation of fibers may increase the crystallinity level of the material, thus improving its mechanical strength.[21]

Another aspect that must have contributed to slightly increase the mechanical strength of the fiber-containing resin blends is their resultant heterogeneous bulk structure when compared to the more homogeneous structure of the fiber-free resin (Figure 3). It is noticeable that the rougher cross-sectional surface of the former demanded higher energy consumption to break than the less irregular cross-sectional surface of the latter.[21, 44] It is also reasonable to assume that the increase in heterogeneity of a bulk structure may directly enhance its cohesiveness, thus producing higher strength characteristics. Furthermore, it is known that surface treatment (i.e., functionalization) of filler particles may improve their interaction with the organic matrix, thereby enhancing mechanical properties.[42, 45] Nevertheless, the polymeric fillers used here were not functionalized, so it can be expected additional improvements upon the incorporation of functionalized-polymeric fillers into the resin blends investigated. Taking the findings presented up to here together, the first hypothesis of the study can be accepted.

The positive effect of the fiber-containing fillers on contraction stress reduction (Table 1) may be explained by different reasons. First, it has been revealed that the higher the concentration of fillers, the lower the amount of organic matrix prone to shrink, thereby reducing stress development;[46, 47] this effect is also increased since the fillers were added in a prepolimerized state, so no additional polymerization shrinkage was observed due to the polymeric nature of the fillers. Second, the use of less stiff fillers as used here instead of inorganic fillers reduces the overall modulus development of the system, thus contributing to improve plastic deformation during stress buildup derived from polymerization shrinkage,[29] as well as stress absorption ability as demonstrated elsewhere.[43] Third, fibers were revealed to increase the stress transfer ability of experimental resin blends,[23] which may have also occurred here. Fourth, the use of high compliant compounds such as nanogels or polymer-modified glass fillers provided higher compliance and mobility for the system, thus resulting in stress reduction;[30, 48, 49] indeed, the polymeric nature of fibers used in this study associated to their high area/volume aspect ratio have probably improved the overall compliance of the fiber-modified resin blends, delaying the production of modulus and vitrification, and consequently, allowing the system to relieve stress. Lastly, the absence of chemical bond between the fillers and the resin matrix, as stated before, may have also contributed to increase the stress-relieving capability of the resins.[50, 51]

Although several factors have reasonably contributed to reduce contraction stress development in the present study, the study design and methodology used here do not allow the extrapolation of these findings to composite materials. According to Szaloki et al.,[43] the incorporation of polymeric nanoparticles resulted in considerably more stress when incorporated into composite materials (i.e., containing both inorganic fillers and organic components) compared to unfilled resins. Consequently, the fiber-containing fillers prepared in the present study may be less effective in reducing stress if incorporated into compositions containing inorganic compounds, thus indicating a limitation of the present study. However, this must be investigated by further studies. Moreover, the stress reduction potential of functionalized *versus* non-functionalized fibers or fiber-containing fillers should be also evaluated, since it was not investigated here. Despite these limitations, the second hypothesis of this study can be accepted since the incorporation of fiber-containing fillers was an effective strategy to reduce contraction stress development by a model resin blend typically used for the formulation of dental materials.

In conclusion, the strategy proposed here demonstrated effectiveness to control and minimize stress development without jeopardizing important physic-mechanical properties of the material. Worth mentioning, there are several recent strategies that proposed to modify the composition of dental restorative materials in order to produce stress reducing formulations, thus denoting that this subject is actual and important for clinical practice dentistry. Furthermore, and taking into consideration that fibers can be loaded with several options of nanoparticles/minerals, antibiotics, growth factors, among others,[16-18] the present findings bring potential application for the development of new materials with improved biological properties and lower production of stress.

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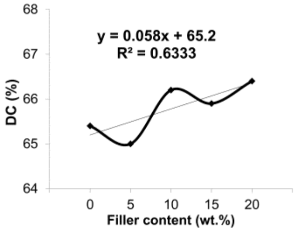
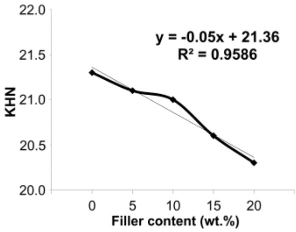
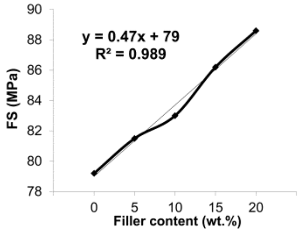
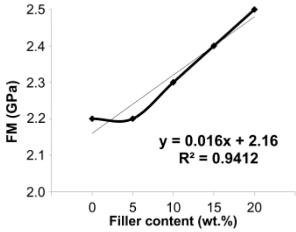
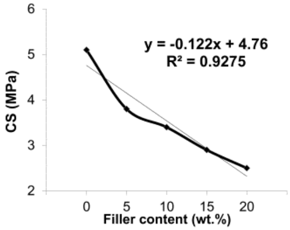
Table 1. Mean (±standard deviation/SD) of the degree of conversion/DC, hardness/KHN, flexural strength/FS, flexural modulus/FM, and contraction stress/CS, as well as linear regression results of groups investigated in the study.

Filler content (wt.%)	**DC (%)**	**KHN**	**FS (MPa)**	**FM (GPa)**	**CS (MPa)**
0	65.4 (±0.9) a	21.3 (±2.1) a	79.2 (±17.2) a	2.2 (±0.1) a	5.1 (±0.3) a
5	65.0 (±0.7) a	21.1 (±1.9) a	81.5 (±10.7) a	2.2 (±0.1) a	3.8 (±0.2) b
10	66.2 (±0.5) a	21.0 (±1.8) a	83.0 (±11.2) a	2.3 (±0.2) a	3.4 (±0.4) bc
15	65.9 (±0.9) a	20.6 (±2.1) a	86.2 (±14.3) a	2.4 (±0.1) a	2.9 (±0.4) cd
20	66.4 (±0.9) a	20.3 (±2.3) a	88.6 (±11.9) a	2.5 (±0.3) a	2.5 (±0.3) d
Linear regression analysis					

Similar letter after mean (±SD) in a same column indicates absence of statistical significant differences among the resin blends tested (p≥0.05).

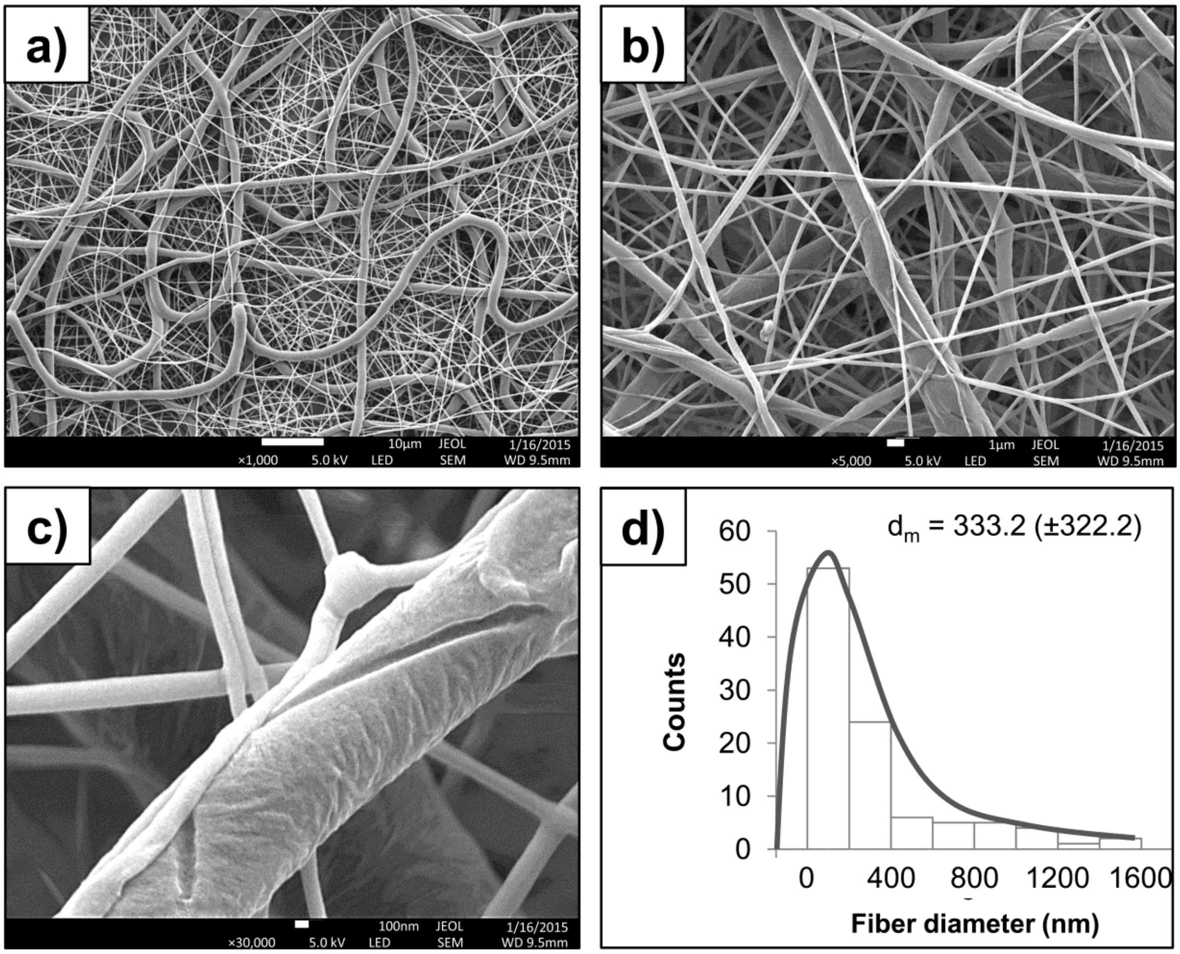


Figure 1. Representative SEM micrographs of the PCL electrospun mat at different magnifications: 1,000× (a), 5,000× (b), and 30,000× (c). Mean fiber diameter and fiber diameter distribution of the PCL electrospun mat (d).

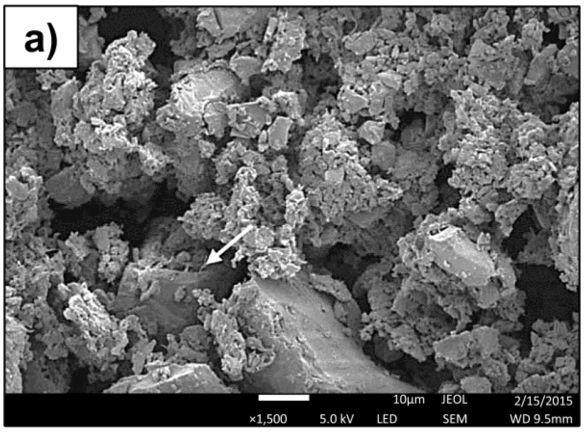


Figure 2. Representative SEM micrographs of cryomilled samples (15 minutes) containing electrospun PCL fibers at different magnifications: 1,500× (a) and 5,000×(b).

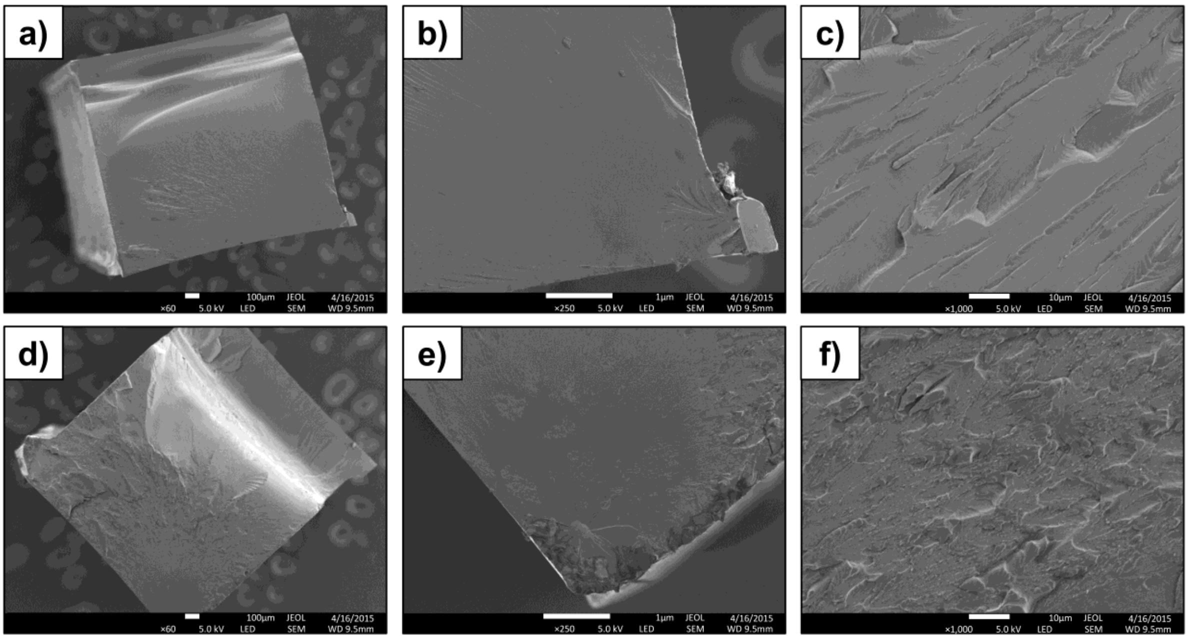


Figure 3. SEM micrographs showing the cross-sectional surface for fiber-free (a, b, c) and 20 wt.% fiber-containing (d, e, f) fractured specimens. Images were given at different magnifications: 60× (a, d), 250× (b, e) and 1,000× (c, f).

7 Considerações finais

Após análise conjunta de todos os dados obtidos no presente estudo é possível concluir que existem várias alternativas para se reduzir o fenômeno de tensão de contração desencadeado por materiais resinosos. Dentre as alternativas, e considerando-se a revisão sistemática realizada, parece que a modificação da composição química do material é aquela que resulta em mais promissores resultados, e tendo a utilização de monômeros alternativos como a estratégia mais efetiva. Confirmando esse achado, as duas estratégias investigadas nesse estudo, isto é, utilização de monômeros elastoméricos (exotanos) ou nanofibras poliméricas, reduziram a tensão de contração de resinas experimentais, demonstrando assim potencial aplicação no desenvolvimento de novos materiais com reduzida tensão de contração.

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