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Tese

Novos compósitos autorreparáveis para restauração dentária

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Novos compósitos autorreparáveis para restauração dentária

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“ A menos que modifiquemos a nossa maneira de pensar, não seremos capazes de resolver os problemas causados pela forma como nos acostumamos a ver o mundo. (Albert Einstein)”

Notas Preliminares

A presente tese foi redigida segundo o Manual de Normas para Dissertações, Teses e Trabalhos Científicos da Universidade Federal de Pelotas de 2019, adotando o Nível de Descrição em Capítulos, descrita no referido manual (https://wp.ufpel.edu.br/sisbi/files/2019/06/Manual.pdf).

Resumo

MOREIRA, Andressa Goicochea. **Novos compósitos autorreparáveis para restauração dentária.** Orientadora: Giana da Silveira Lima. 2020. 74f. Tese (Doutora em odontologia área de concentração Biomateriais e Biologia Oral, ênfase Materiais Odontológicos.) – Faculdade de Odontologia, Universidade Federal de Pelotas, Pelotas, 2020.

A evolução dos materiais dentários facilitou a prática do cirurgião dentista. Os principais objetivos dos tratamentos odontológicos são reestabelecer a saúde bucal e devolver a forma e a função normal dos elementos dentários, propiciando um tratamento longevo, sem prejuízos estéticos e efeitos negativos para os pacientes. Dentro deste contexto, considerando que o uso de resinas compostas tem uma ampla aplicação clínica, e que os distintos procedimentos clínicos nos quais são utilizadas exigem muito das suas propriedades mecânicas e desempenho à longo prazo o desenvolvimento contínuo da qualidade dos compósitos restauradores é um importante. Uma das principais causas de substituição de restaurações com resinas compostas é a fratura. Assim, esse estudo busca contribuir para a evolução destes materiais por meio de uma revisão sistemática da literatura atual e estudo *in vitro.* Os objetivos foram: 1 Revisar sistematicamente a literatura a respeito da existência de sistemas de autorreparo em materiais odontológicos e mapear o atual estágio de desenvolvimento tecnológico desses materiais. 2 Desenvolver e avaliar *in vitro* um novo sistema de autorreparo que combine a utilização de duas cápsulas com monômeros distintos a fim de otimizar o processo de autorreparo e aumentar a resistência mecânica após a trinca ou fratura inicial do compósito. Para o estudo 1, dois revisores realizaram uma pesquisa bibliográfica atualizada até fevereiro de 2020, uma pesquisa eletrônica foi realizada usando as seguintes bases de dados: PubMed (Medline), Embase, Lilacs, Ibecs, Web of Science, Scopus, BBO, Scielo e The Cochrane Library, usando a estratégia de busca desenvolvida para PubMed (Medline) e adaptada para outras bases. Foram incluídos artigos que adicionaram sistemas de autoreparo em materiais odontológicos. Foram analisados dados referentes ao tipo e eficiência do sistema de autoreparo e também sua influência nas propriedades mecânicas dos materiais, 889 registros potencialmente relevantes 12 estudos preencheram todos os critérios de seleção e foram incluídos na análise qualitativa, 5 artigos foram incluídos na meta-analise, análise quantitativa, da eficiência de autorreparo e módulo de elasticidade, 4 artigos para resistência à flexão. No estudo 2, cápsulas de autoreparo foram preparadas por polimerização em emulsão com formaldeído e uréia. Com diferentes composições de líquido autorreparável. As cápsulas foram analisadas quanto à estrutura molecular com espectroscopia no infravermelho por transformada de Fourier (FTIR / ATR), morfologia da superfície avaliada com microscopia eletrônica de varredura (MEV). Resinas experimentais, com e sem a adição de cápsulas de autorreparo foram submetidas aos testes de Grau de conversão (CC), resistência à flexão (σf) e módulo de elasticidade (Ef), Avaliação da tenacidade à fratura (K_{IC}) e eficiência o autorreparo, Microscopia eletrônica de varredura (MEV), análise de rugosidade por microscopia de força atômica (AFM). Como resultado, um novo sistema de autorreparo de resinas compostas foi desenvolvido. Os resultados demonstraram

que as evidências na literatura sugerem que a adição de agentes de autorreparo aos materiais dentários pode melhorar a longevidade dos materiais dentários, sendo capaz de barrar a continuidade da trinca formada. A adição de cápsulas não alterou o desempenho da resina experimental (p> 0,05), e os grupos com cápsulas apresentaram eficiência de autorreparo. O novo sistma de autorreparo apresentou uma eficiência de (22.1 ± 0.08%) na recuperação do K_{IC}. A revisão resumiu uma nova tendência em materiais dentários, os sistemas de autorreparo. Em conclusão, o uso desses materiais em um futuro próximo pode aumentar a longevidade dos materiais dentários. Na resina composta desenvolvida, Todos os materiais testados apresentaram eficiência de autocura. O estudo *in vitro* demonstrou uso de um líquido de autorreparo contendo Bisfenol A glicidilmetacrilato–BisGMA, trietilenoglicol metacrilato–TEGDMA e como iniciadores da reação peróxido de benzoila e dihidroxietil p-toluidina-DHEPT foi eficaz para promover o reparo de trincas no material.

Palavras-chave: Biomateriais, Compósito dentário, Microcápsulas, Líquido cicatrizante polimerizável, Propriedades mecânicas, Recuperação da tenacidade à fratura.

Abstract

MOREIRA, Andressa Goicochea **New self-healing composites for dental restoration.**Advisor: Giana da Silveira Lima. 2020. 74p.Thesis (PhD in Dentistry Biomaterials and Oral Biology, emphasis on Dental Materials.) – Graduate Program in Dentistry.Federal University of Pelotas, Pelotas, 2020.

The evolution of dental materials facilitated the practice of the dental surgeon. The main objectives of dental treatments are to reestablish oral health and restore the normal shape and function of dental elements, providing long-term treatment, without aesthetic damage and negative effects for patients. Within this context, considering that the use of composite resins has a wide clinical application, and that the different clinical procedures where they are used require a lot of their mechanical properties and long-term performance, the continuous development of restorative composites is an important line of research. One of the main causes of replacing restorations with composite resins is fracture. Thus, this study seeks to contribute to the evolution of these materials through a systematic review of the current literature and an in vitro study. The objectives were: 1 To systematically review the literature regarding the existence of self-healing systems in dental materials and to map the current stage of technological development of these materials. 2 To develop and evaluate in vitro a new self-repair system that combines the use of two capsules with different monomers in order to optimize the self-repair process and increase the mechanical strength after the initial fracture of the composite. For study 1, two reviewers conducted a bibliographic search until February 2020, an electronic search was performed using the following databases: PubMed (Medline), Embase, Lilacs, Ibecs, Web of Science, Scopus, BBO, Scielo and The Cochrane Library, using the research strategy developed for PubMed (Medline) and adapted for other databases. Articles that added self-healing systems to dental materials were included. Data regarding the type and efficiency of the self-healing system and its influence on the mechanical properties of the materials were analyzed. 889 potentially relevant records 12 studies met all selection criteria and were included in the qualitative analysis, 5 articles were included in the meta-analysis, quantitative analysis, of the self-repair efficiency and elasticity module, 4 articles for flexural strength. In study 2, self-healing capsules were prepared by emulsion polymerization with formaldehyde and urea. With different compositions of self-repairing liquid. The capsules were analyzed for molecular structure with Fourier transform infrared spectroscopy (FTIR / ATR), surface morphology assessed with scanning electron microscopy (SEM). Experimental resins, with and without the addition of self-healing capsules were subjected to the tests of Degree of conversion (CC), flexural strength (σf) and modulus of elasticity (Ef), Evaluation of fracture toughness (KIC) and self-repair efficiency, Scanning electron microscopy (SEM), roughness analysis by atomic force microscopy (AFM). As a result, a new self-repair system for composite resins was

developed. The results showed that the evidence in the literature suggests that the addition of self-repairing agents to dental materials can improve the longevity of dental materials, being able to block the continuity of the crack formed. The addition of capsules did not alter the performance of the experimental resin ($p > 0.05$), and the groups with capsules showed self-healing efficiency. The new auto repair system, self healing efficiency the (22.1 ± 0.08%) in teh recovery of K_{IC}. The review summarized a new trend in dental materials: self-repair systems. In conclusion, the use of these materials in the near future may increase the longevity of dental materials. In the developed composite resin, All tested materials showed self-healing efficiency. The in vitro study demonstrated the use of a self-repairing liquid containing Bisphenol A glycidylmethacrylate – BisGMA, triethylene glycol methacrylate – TEGDMA and as initiators of the reaction benzoyl peroxide and dihydroxyethyl p-toluidine-DHEPT was effective in promoting the repair of cracks in the material.

Key-words: biomaterials, Self-healing dental composite, Microcapsules, Polymerizable healing liquid, Mechanical properties, Fracture toughness recovery

Sumário

1 Introdução

A restauração dentária é uma forma de fazer com que o dente afetado pela cárie ou que sofreu algum dano em sua estrutura, tenha recuperada sua forma e sua função. Apesar das restaurações de resinas compostas terem demonstrado um desempenho satisfatório em dentes posteriores e anteriores, estudos com longos períodos de acompanhamento apontam as fraturas como principais causas de substituições de restaurações desse tipo (DA ROSA RODOLPHO et al., 2011). A força da mastigação, assim como o biofilme presente na superfície podem afetar a qualidade da restauração, causando defeitos nas margens (FERRACANE, 2013), atuando diretamente na deterioração do material (MELGAR et al., 2017). O ciclo restaurador repetitivo causa um enfraquecimento da estrutura dentária, provocado pela inevitável perda de tecido dental sadio durante o preparo do dente.

A substituição de restaurações é uma prática comum na clínica odontológica, 56% das intervenções realizadas na rotina clínica são em restaurações já existentes (DELIGEORGI; MJÖR; WILSON, 2001). Quando não há dor ou não ocorre falha catastrófica, o critério pra intervenção clinica ainda é motivo para discussões (WILSON et al., 2016). Quando comparado o comportamento de falhas de restaurações em dentes anteriores com as de dentes posteriores, foi observado que ocorre a substituição mais relacionada a motivos estéticos como por exemplo, coloração inadequada, manchas marginais entre outros, nos quais a opinião do paciente tem influência. A longevidade das restaurações de resina composta pode ser prejudicada pela falta de critérios de reintervenção e por um incorreto diagnóstico de cárie secundária (DEMARCO et al., 2017). A degradação significativa de estruturas poliméricas pode ser medida, mas as microfissuras internas não são facilmente detectáveis. Podendo assim gerar falhas catastróficas sem que haja percepção. Se for possível controlar o processo de fratura, provavelmente as falhas iniciais na superficie dos materiais seriam atenuadas, evitando ou postergando a necessidade de reintervenção (ADAMS, 2015).

Considerando que o uso de resinas compostas tem uma ampla aplicação clínica, e que os distintos procedimentos clínicos onde são utilizadas exigem muito

das suas propriedades mecânicas e desempenho a longo prazo, o desenvolvimento contínuo dos compósitos restauradores é importante (FERRACANE, 2011). Nesse sentido, a melhoria das propriedades dos compósitos restauradores, dentre outros fatores, deve abordar uma redução na incidência de pequenos defeitos na matriz polimérica, trincas que levem a fraturas (FERRACANE, 2011). Meios de inibição da propagação de trincas, como por exemplo controle da microestrutura da fase de reforço, partículas inorgânicas e modificação da interface entre a matriz do compósito e as partículas de carga, foram estudados previamente (FERRACANE, 2011; RANDOLPH et al., 2016). A incorporação de cerâmicas como alumina, titânio e zircônia, recobertas com sílica amorfa, como carga, mostrou que os compósitos ganharam reforço mecânico, essas partículas apresentam dureza e tenacidade muito superiores aos vidros silicatos e às nanopartículas de sílica, aumentando o trabalho de fratura em até 40% em relação aos compósitos controles (KAIZER et al., 2016).

Outro meio estudado foi a incorporação de fibras de viro (Nano-fibras) em uma resina composta, onde foi observado que resistência a fratura (KIC) aumentou em comparação com compósitos reforçados com cargas particuladas (nano-hibrida). Possivelmente esse resultado esteja relacionado às propriedades referentes à fibra e à matriz deste material. A resina reforçada com fibra de vidro continha fibras que eram mais longas que o comprimento crítico da fibra e portando foram mais eficazes na transferência de tensão da matriz (ALSHABIB; SILIKAS; WATTS, 2019).

Os compósitos dentários, podem se tornar mais longevos se possuírem a capacidade de autorreparo. A autocura pode ser induzida por stresse mecânico que desencadeie o fenômeno de autorreparo (WU et al., 2016). Os compósitos dentais autorreparáveis podem reparar intrinsecamente a micro-trinca, prolongando significativamente a vida útil do compósito. Durante o processo de autorreparo, moléculas ativas, antimicrobianas e remineralizantes, podem ser adicionados ao sistemas trazendo benefícios podendo promover a remineralização (WU et al., 2019).

Estudos recentes mostraram o desenvolvimento de materiais poliméricos com capacidade de autorreparo, utilizando polímeros com a adição de cápsulas com invólucro encapsulado com líquido (trietilenoglicol metacrilato–TEGDMA, dihidroxietil p-toluidina-DHEPT). Um defeito de propagação de trinca na matriz polimérica pode

romper as cápsulas, liberando um líquido, o qual, em contato com o catalisador (benzoyl peroxide-BPO) presente na matriz polimérica, desencadeia a polimerização do líquido e repara a trinca formada (WU et al., 2019). O desempenho geral desse tipo de autorreparo relatado em compósitos dentários varia de 25% a 80% de taxa de recuperação após a fratura (ALTHAQAFI; SATTERTHWAITE; SILIKAS, 2019).

Apesar do reparo com microcápsulas de TEGDMA parecer ser uma alternativa promissora no desenvolvimento de materiais com menor probabilidade de falha por causa da fratura do material, é importante mencionar que o uso de homo-polímeros de TEGDMA para o reparo apresenta alguns inconvenientes. O fato de o TEGDMA (trietilenoglicol metacrilato) ser uma molécula linear relativamente flexível e de baixo peso molecular, apresenta o inconveniente de aumentar a contração de polimerização. Nesse sentido, TEGDMA é sempre utilizado com outros componentes nas formulações de resinas compostas, como o Bis-GMA (A glycidyl dimethacrylate), que possui um extenso comprimento da cadeia molecular e assim diminui a contração de polimerização. A proporção de cada um dos monômeros em uma formulação resinosa é crítica às propriedades do compósito (GONÇALVES et al., 2009). O melhor resultado entre o aumento do grau de conversão e as taxas de resistência à flexão foi obtido com matriz de resina contendo até 50% molar de BisG-MA e TEGDMA (GONÇALVES et al., 2009).

Portanto o objetivo dessa tese foi revisar sistematicamente a literatura sobre a eficiência de autorreparo em materiais dentários e mapear o atual estágio de desenvolvimento tecnológico desses materiais. Adicionalmente, desenvolver e avaliar um novo sistema de autorreparo que combinasse a utilização de duas microcápsulas com monômeros distintos a fim de otimizar o processo de autorreparo e aumentar a resistência mecânica após a fratura inicial do compósito, eliminando o uso de BPO na matriz do compósito e adicionando o Bis-GMA como parte do líquido no interior das cápsulas.

2 Capitulo 1

Self-healing efficiency in dental materials: A systematic review and meta-analysis[1]

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Keywords: biomaterials, Self-healing dental composite, Microcapsules, Polymerizable healing liquid, Mechanical properties, Fracture toughness recovery.

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Abstract

Objectives: The present study assessed the existence of self-healing systems in dental materials and mapped the present technological development of these materials.

Methods: Two reviewers performed a literature search up to February 2020, an electronic search was carried out using the following databases: PubMed (Medline), Embase, Lilacs, Ibecs, Web of Science, Scopus, BBO, Scielo and The Cochrane Library, using the search strategy developed for PubMed (Medline) and adapted for other databases. It was included articles that added self-healing systems in dental materials. Data regarding type and efficiency of self-healing system, and also their influence in mechanical properties of the materials were analyzed.

Results: It was found 3 self-healing system. The addition of self-healing agents into the materials showed an influence in the self-healing efficiency, flexural strength and modulus of elasticity. Twelve laboratory studies were included; The meta-analysis showed for self-healing efficiency in which the microcapsule presence were effective in promoting self-healing. Also, could be observed that with higher percentage of microcapsules the results were better for self-healing efficiency. For the flexural strength and modulus of elasticity analyzes, it was observed that the control group had better results ($p < 0.005$).

Conclusion: The evidence in literature suggested that the addition of agents of self-healing into the dental materials may improve the longevity of the dental materials being able to block the continuity of the crack formed. All materials tested showed self-healing efficiency. Therefore, more studies are needed to evaluate more properties such as cytocompatibility, shelf life, degradation, degree conversion of these materials. To better understand their influence in the dental materials.

Clinical Significance: This review summarizes a new trend in dental materials, the self-healing systems. The use of these materials in the near future may to increase the longevity of the dental materials.

Keywords: biomaterials, Self-healing dental composite, capsules, Polymerizable healing liquid, Mechanical properties, Fracture toughness recovery.

1 Introduction

In dentistry, a wide range of materials has been used in dentistry and has been well accepted. However, the oral environment can be considered an extreme environment for dental materials. The conditions such as the changes in the temperature, the humidity, cariogenic biofilm, acidic diet, and salivary enzymes are some examples of the challenges that dental materials are exposed to every day. Because of this, the longevity of dental materials is still a problem [1,2].

One of the main causes for the failure of resin restorations is fractures which can arise due to occlusal forces, thermal changes and digestive enzymes in the oral cavity, trauma, cracks, abrasion, tension and or weakening of the materials [3]. Composites have a structure prone to failure when they receive wide variation in thermal and / or mechanical stresses. Significant degradation of polymeric structures can be measured, but internal micro-cracks are not easily detectable. Thus, it can generate catastrophic failures without perception [4].

For these cases, the treatment options are repair or total removal of the material. However, replacement of all restoration material leads to excessive removal of the sound tooth, resulting in weaken the tooth structure, and at worst lead to pulp exposure [4]. Aiming to reduce these drawbacks, the development of dental materials with good mechanical and aesthetic properties and with low polymerization shrinkage [4], greater depth of polymerization and degree of conversion, are the main branches of research in dentistry [5,6].

An alternative to make resin composites more durable is the self-healing ability. Some research has been done recently in this field. Self-healing can be induced by mechanical stress that triggers the phenomenon of self-healing [7,8]. Self-healing dental composites can intrinsically repair the micro-crack, significantly extending the life of the composite [9,10]. During the self-healing process, antimicrobial and remineralizing molecules can be added to the systems, bringing benefits that can promote remineralization and the preve ntion of cavities [11]. Self-healing takes place automatically without any external diagnosis of the problem or human intervention [12].

The present study assessed the efficiency of self-healing in dental material and mapped the present technological development of these materials. The

hypothesis tested is that the efficiency of self-healing in dental material would be promoted due to the addition of self-healing agents.

2 Materials and methods

The PICO was carried out to formulate the question from evidence-based practice: Population: Dental materials; Intervention: presence of self- healing system; Comparison: absence of self-healing system; and Outcome: efficiency self healing. The research question was: Does the presence of self-healing systems in dental materials influence your self-healing efficiency?

2.1 Search strategies

The literature search was carried out by two independent reviewers of studies published during or before February 2020. Nine databases were screened, including PubMed (Medline), Embase, Lilacs, Ibecs, Web of Science, Scopus, BBO, Scielo and The Cochrane Library, using the search strategy developed for PubMed (Medline) (Table 1) and adapted for other databases. In addition, seven patents databases: Espacenet, Google patents, INPI, JPO, PatentScope, Questel Orbit, USPTO. The references cited in the included papers were also checked to identify other potentially relevant articles. After the identification of articles in the databases, the articles were imported into Mendeley to remove duplicates.

2.2 Study selection

Two authors independently assessed the titles and abstracts of all of the documents. For the patents, it was assessed the titles, abstracts and claims. As inclusion criteria: clinical, *in vitro*, in vivo, in situ studies that added self-healing agents in dental materials and assessed the efficiency of self-healing. As exclusion criteria: reviews, editorial letters, case reports, case series and studies published in a language other than English, Portuguese or Spanish. Full copies of all the potentially relevant studies were identified. Those appearing to meet the inclusion criteria or for which there were insufficient data in the title and abstract to make a clear decision were selected for full analysis. The full-text papers were assessed independently and

in duplicate by two authors. Any disagreement regarding the eligibility of the included studies was resolved through discussion and consensus or by a third reviewer. Only papers that fulfilled all of the eligibility criteria were included.

2.3 Data extraction

The data were extracted using a standardized form. If there was some information missing, the authors of the included papers were contacted via e-mail to retrieve any missing data. The following data were tabulated: Author Type, dental material Type, self-healing, self-healing system, size capsules, self-healing evaluation, main findins (Table 2). The characteristics of the included studies, such as selection criteria, control group and mechanical properties included in meta-analysis: Flexural Strength (figure 4) elastic modulus testing (figure 5) and fracture toughness and self-healing, assessmentwere also analyzed (figure 2). In the articles that did not present the complete data of the groups (meanv ± standard deviation), the webplotdigitizer-Web based tool to extract data from plots, images, and maps v4.2 (San Francisco, California, USA) was used to extract the data presented in graphs.

2.4 Assessment of risk of bias

The risk of bias of each included study was evaluated according to the description in the articles of the following parameters for the study quality assessment: materials used according to the manufacturers' instructions, use of bars with similar dimensions, description of sample size calculation, and blinding of the operator of the testing machine. If the authors reported the parameter, the article had a ''Y'' (yes) on that specific parameter; if it was not possible to find the information, the article received an ''N'' (no). Articles that reported one item were classified as having high risk of bias, two or three items as medium risk of bias, and four items as low risk of bias (table 3) [13].

2.5 Statistical analysis

The meta-analysis for flexural strength, elastic modulus and self-healing efficiency variables were performed using Review Manager Software version 5.3 (The Nordic Cochrane Centre, The Cochrane Collaboration, Copenhagen, Denmark). Data on mean difference and standard deviation were obtained from the selected studies. The analysis was carried out using a random-effects model, and pooled-effect estimates were obtained by comparing the mean difference of value. The heterogeneity was assessed by the Q test and quantified with I^2 statistics. Self-healing efficiency analyses were also undertaken using R version 3.6-0 software (R Foundation for Statistical Computing).

3 Results

3.1 Study selection

889 potentially relevant records were identified in all databases, 202 duplicates were removed, leaving 687. An additional study was identified after searching the references of the included articles, 2 articles were excluded due to the language being in Chinese and 6 articles were excluded by do not present self-healing assessment. Three identified patents were excluded because they did not present an evaluation of the self-healing. Figure 1 is a flow chart that summarizes the article selection process according to the PRISMA Declaration. 12 studies met all the selection criteria and were included in the qualitative analysis.

3.2 Descriptive analysis

The research found a total of 12 [7,8,10–12,14–20] articles that met the inclusion criteria of the study (Figure 1) that were used for qualitative analysis (table 2), 5 [17–21]articles were included in the quantitative analysis meta-analysis of self8healing efficiency and flexural strength (σf) [17,18,20,21]and 5 for modulus of elasticity (Ef) [17–21]. All studies were *in vitro* and were published between 2010 and 2020. Three self-healing systems were identified: PUF microcapsules, Silanized silica microcapsules, carbonate precipitation (MICP) bio-Self-healing. The systems were added in the dental materials like dental resin, dental adhesive resin, dental luting cements.

The self-healing method PUF microcapsules consisted of 8 studies, Silanized silica microcapsules methods in 2 studies and carbonate precipitation (MICP) bio-Self-healing in 1 study. The microcapsule system was the most reported, which uses a microcapsule healing mechanism with different self-healing agents and materials that form the capsule crust, the TEGDMA and DHEPT liquid with the polyurea-formaldehyde crust was the most frequent.

3.3 Meta-analysis

The subgroup meta-analysis were performed considering different microcapsule percentage added to dental materials. 5 articles were included in the quantitative analysis of self-healing efficiency (figure 2) and elastic modulus (figure 5) [17–21], 4 articles for flexural strength (figure 4) [17,18,20,21]. Figure 2 and 3 shows the analysis for self-healing efficiency in which the microcapsule presence were effective in promoting self-healing. Also, could be observed that with higher percentage of microcapsules the results were better for self-healing efficiency. For the flexural strength and modulus of elasticity analyzes, it was observed that the control group had better results ($p < 0.05$).

4 Discussion

The hypothesis evaluated was accept once the meta-analysis demonstrated the concentrations of self-healing agents analyzed were effective in promoting self-healing. All revised studies were laboratorial, and in general, they presented a high risk of bias. Meanwhile, the included studies presented substantial heterogeneity, although the heterogeneity found in the meta-analysis is high, the tests used were similar, this high heterogeneity may be due to the low number of articles included and the number of specimens used in the articles, despite the fact that the profiles of the methodological aspects are similar, generating a positive impact in our review.

4.1 Characteristics of self-healing agents

The self-healing capsules studied so far have different sizes, according to the system applied. PUF microcapsules ranged from 11 to 73 µm [14,22,23] while silanized silica microcapsules obtained an average size of 29.46 µm [24]. This variation in sizes can be attributed to the microcapsule PUF mechanism, since the microencapsulation process contains two patways, one due to the effect of pH on the hydrolysis of styrene-maleic anhydride copolymer and the other by the dispersion of droplets in the polymerization process. Through adjustments in the reaction parameters, microcapsules with different sizes and distribution can be obtained from the proposed encapsulation mechanism. In addition, it has been reported that pH regulation at different stages of the process affects the size and distribution of the microcapsules, as it increases the reactivity of the prepolymer and the viscosity of the system leading to coacervation and formation of microcapsules with a wide range of distribution in the sizes [25,26].

Another method reported in the literature is the silanization of microcapsules. In this method, similarly to the previous one, the pH change of sol-gel materials occurs. Thus, it is possible to obtain silica particles with size and shape control, the size of the microcapsule can be determined by agitation speed and surfactants used to make emulsions. The technique is based on the formation of an oxide cage around polar droplets, producing particles equal in size to the droplets. In this technique, by changing the combination of solvent surfactant, different particle sizes can be obtained [24].

In the carbonate precipitation method (MICP), particles with sizes of approximately (±) 0.45 µm were obtained. The formation of CaCO3 crystals in the urease-assisted technique is less dependent on the pH of the environment compared to the MICP-GRAS approaches (bacteria generally recognized as safe). This is mainly due to the absence of microorganisms that require favorable pH and temperature for growth and metabolism.

4.2 Mechanism of action of self-healing

Within the self-healing methods of action, the general performance of the method known as Poly-urea-formaldehyde (PUF) mirocapsules ranged from 25% to 80% recovery rate after fracture [23]. Different formulations were found for both the

wrapping and the content inside the capsules [17,22] the most used materials in the self-healing liquid were triethylene glycol methacrylate – TEGDMA and dihydroxyethyl p-toluidine-DHEPT. The mechanism is based on the rupture of the capsules that is caused by a crack propagation defect in the polymeric matrix. Upon contact with the catalyst (benzoyl peroxide-BPO) present in the polymeric matrix, the polymerization of the liquid and the self-healing of the crack formed are triggered [11,14,21].

Another method reported in the literature more recently was called bio-Self-healing Biomineralization of $CaCO_3$ by urea hydrolysis using bacteria (urease enzyme) or only urease enzyme. It is based on the theory of bioenergetic self-healing (MICP). The oral cavity provides an ideal environment to support microbial metabolism, containing a wide range of bacteria and is therefore the ideal place to use a probiotic treatment. MICP is a biogeochemical process that can occur through two main metabolic pathways: sulfur cycle and nitrogen cycle, the first pathway follows by sulfate dissimilatory, while the second pathway can be achieved through urea hydrolysis, ammonification and dissimilatory reduction of nitrate [10]. In the nitrogen cycle, the biomineralization of $CaCO_3$ is triggered by the catalytic action of urease by bacteria where urea is hydrolyzed. One mole of ammonia and one molar carbamic acid is produced as a result of urea hydrolysis. Hydrolysis of urea elevates Ph by precipitating $CaCO_3$ from an insoluble calcium available in the medium [10,15].

Two studies that used CaCO3 Biomineralization by urea hydrolysis using bacteria (uease enzyme) and only urease enzyme were identified. In these studies, CaCO3 precipitation in a solid matrix (composite resin) was induced. The inoculation of Bifidobacterium longum and B. Licheniformis and the uease enzyme in liquid medium promoted CaCO3 precipitation. Thus, the amount of CACO3 in the matrices was able to initiate the polymerization process and initiate the biosynthesis of CACO3, capable of promoting self-healing, which was evaluated by means of scanning electron microscopy and optical microscopy images [10,15].

The silanization process of the microcapsules (Silanized silica microcapsules) is considered crucial for the capsule rupture when a crack is triggered. Silane agents coupled to the back of the capsule provide this improvement. When a crack is forming and the water enters the microcapsule breaks and releases the self-healing liquid strongtium fluoroaluminosilicate particles which then dissolves the liquid power

aqueous solutions of polyacrylic acids and forms the GIC that repairs the defect. Self-healing in this system is a compomer [27]. Compomers contain a fluoride-releasing silicate that reacts with polyacids to release fluoride. In this system, the polyacid is incorporated to form the glass ionomer cements (GIC) and obtains an autonomous cure of cracks, since groups of functional acids are capable of polymerizing in an acid-base reaction after the resin molecule has taken hold. ± 25% efficiency of self-healing was obtained in 2 studies using these capsules [19].

4.2 Meta-analysis

The percentages of microcapsules used in the study composites, included in the meta-analysis, were evaluated in comparison with the control group 0% microcapsules for the flexural strength and modulus of elasticity tests. The incorporation of self-healing microcapsules led to a reduction in flexural strength and modulus of elasticity, which were superior in the control groups in the meta-analysis performed. This phenomenon can occur due to the fact that smaller loads tend to have a better effect on these properties regarding the strength of the material, composites with wide granulometric distribution showed less degradation of the strength [26]. The evaluated microcapsules have micrometric sizes larger than the charge particles usually added to the polymeric matrix [20,21]. The load force generated during the flexural strength test and modulus of elasticity generates a tension between the interface of the polymeric network and the particle, caused by the difference in the modulus of elasticity. When the particle has a surface smoothness, the force generated on the surface can circumvent it. The same does not occur if the particle has a roughness surface and thus better adhesion with the polymeric matrix, where the fracture penetrates the particle and causes it to break. This can also be a determining factor in flexural strength and modulus of elasticity. Therefore, the combination of size and surface characteristics may have affected the results of the groups with self-healling agents, since the particles found in the literature were relatively large and the capsules had surface roughness [17,21].

In the self-healing efficiency, the presence of the microcapsule was effective in promoting self-healing. It was possible to observe that, with a higher percentage of microcapsules, the results were better for the efficiency of self-healing [17-21]. This

occurred due to the presence of the self-repair liquid present in the capsules, which together with the system initiator triggered the polymerization of the monomers and promoted self-healing; the greater the number of microcapsules in the material matrix, the greater the likelihood that they will break with the formation of cracks, increasing the chance of forming a more consistent polymer film inside the crack and consequently increasing the success of self-healing [17- 21].

4.2 Water aging and cytotoxicity

Studies evaluated the addition of the material in water for 1,2,3,6 and up to 12 months in water, and found that there was no difference in the values of the means for flexural strength and efficiency of the self-healing compared to the same materials stored in an oven with 100% humidity. Indicating that immersion in water did not adversely affect the catalyst reaction of the curing liquid with the initiator in the matrix for polymerization to occur [8,14,18]. Only one study evaluated the cytotoxicity *in vitro*. Cell viability in fibroblast medium without any resin eluents was set as 100%. All five groups of resin specimens with 0%, 5%, 10%, 15% and 20% microcapsules had cell viability similar to that of control 0% [17]. Further studies that prove the viability of the cells are necessary to affirm that the incorporation of microcapsules in the resin did not present results that compromise the cellular viability [23].

In the initial search 3 patents were identified, which were not included in the study because they did not report the efficiency of self-healing. However, the lifting of patents is of paramount importance as they point to a technological prospection of intellectual property. Follow in order number-title-mechanism of self-healing- year -(claim): US9931281B2-Multifunctional self-healing dental composites, methods of synthesis and methods of use- Silanized silica microcapsules, GIC repair technology-2018 (Self-healing, antibacterial, reminerizable dental composites) [28]; US9763858B2-Self-healing dental restorative formulations and related methods-Polyoxymethyleneurea (PMU) microcapsules, DCPD healing agent – 2014 (Self-healing dental composites) [29]; CA2748324C- Composite material with properties of self-healing and release of active ingredients, for biomedical applications- PUF microcapsules-2011 (self-healing dental composites puf microcapsules)[30].

5 Conclusion

This review summarizes a new trend in dental materials, the self-healing systems. The use of these materials in the near future may to increase the longevity of the dental materials. Therefore, more studies are needed to evaluate more properties such as cytocompatibility, shelf life, degradation, degree conversion of these materials. To better understand their influence in the dental materials.

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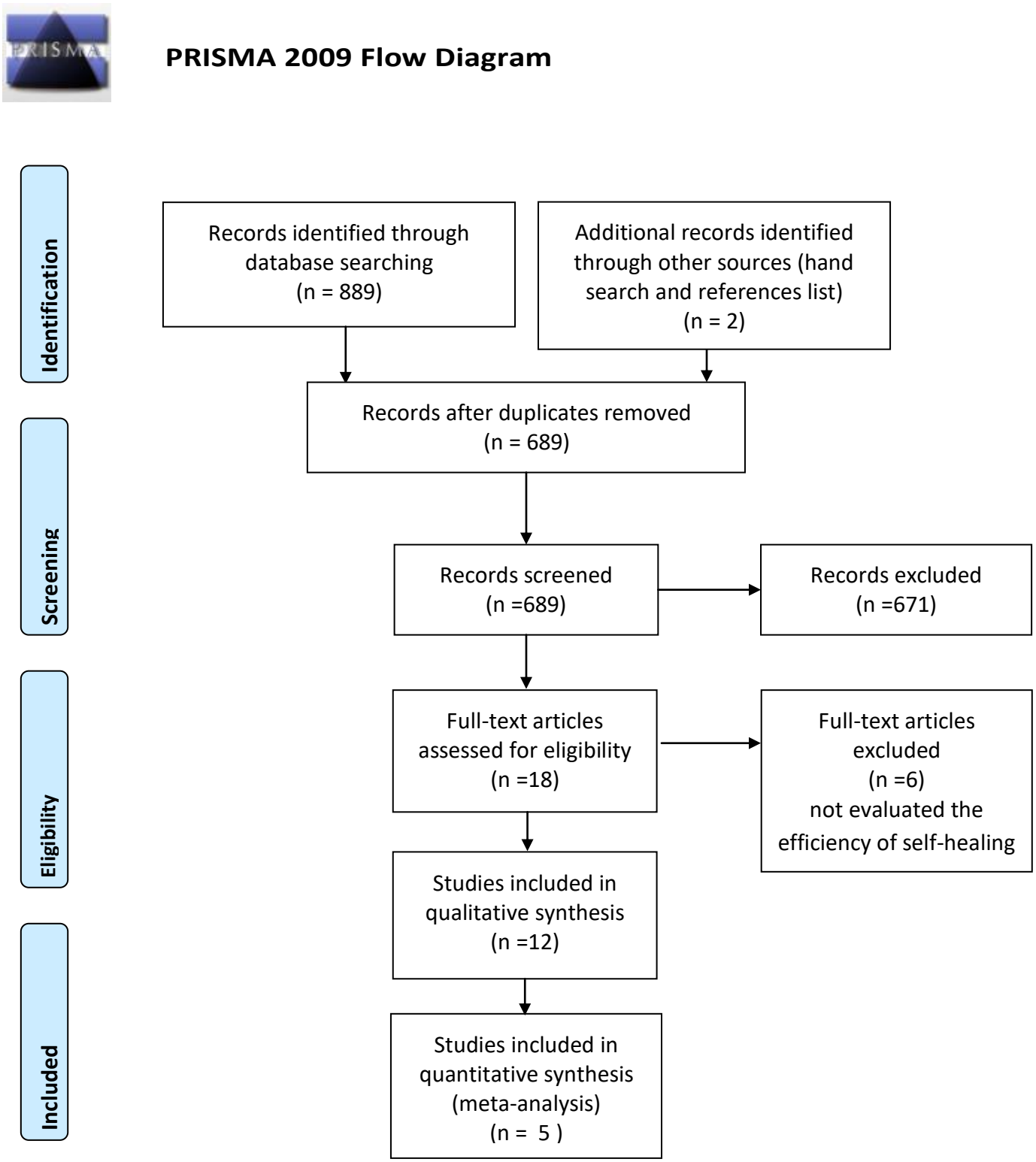

Figure 1. Search flow (as described in the PRISMA statemen

Tables

Table 1 - Search strategy used in PubMed (*MedLine*).

	Search Terms
#1	" Self-healing” OR “Self-sealing” OR “Self-repair”
#2	“Resin composites” OR “Dental composites” OR “Composite Resins” OR “Bisphenol A-Glycidyl Methacrylate” OR “Compomers” OR “Composite”
#3	Search #1 AND #2

Tabela 2- Included studies in the review — self-healing dental composites

Author	Type of dental material	Self-healing system	Size capsules	Self-healing evaluation	Main findings
Wertzberger et al.[7]	Dental resin	Encapsulated dicyclopentadiene spheres and Grubbs' metathesis catalyst.	-	Dynamic mechanical analysis.	The average recovery rate of 57% of the original fracture toughness. The fracture resistance of the self-healing material was statistically similar to the control.
Wu et al.[21]	Dental resin	Encapsulated TEGDMA-DHEPT microcapsules and benzoyl peroxide BPO initiator in the matrix.	70 ± 24 µm	Fracture Toughness and Self-Healing Assessment	The original properties of the composite including flexural strength, elastic modulus and fracture toughness were not adversely affected when microcapsules were incorporated for up to 7.5%. Self-healing was achieved with 65–81% recovery in the virgin fracture toughness.
Wu et al.[18]	Dental resin	Encapsulated TEGDMA-DHEPT microcapsules and benzoyl peroxide BPO initiator in the matrix	70 ± 24 µm	Fracture Toughness and Self-Healing Assessment	The incorporation of 7.5% of microcapsules into the composite did not compromise the flexural strength, elastic modulus and K_{IC}-virgin, compared to that without microcapsules. Recovery of 65–81% was achieved for composites with microcapsule mass fractions at 7.5% and 10% microcapsules
Huyang et al.[19]	Dental resin	silica microcapsules(aqueous solution of polyacrylic acid) and a healing powder (strontium fluoroaluminosilicate particles)	29.46 µm ± 10.28 µm	Fracture Toughness and Self-Healing Assessment	The success of crack healing was confirmed average healing efficiency of SHDCs reached up to 25 %.

Wu et al.[17]	Dental resin	Encapsulated TEGDMA-DHEPT microcapsules and benzoyl peroxide BPO initiator in the matrix	70 ± 24 µm	Fracture Toughness and Self-Healing Assessment	The success of crack healing was confirmed average healing efficiency of SHDCs reached up to 25 %. The flexural strength and elastic modulus of resins containing 0% to 15% microcapsules were not significantly different from each other.
Chen Chen et al.[20]	Dental resin	Encapsulated TEGDMA-DHEPT microcapsules and benzoyl peroxide BPO initiator in the matrix 2-methacryloyloxyethyl phosphorylcholine (MPC)protein-resistant that also can self-repair damage.	73 ± 31 µm	Fracture Toughness and Self-Healing Assessment	The design and development of a protein-repellent dental composite formulation with autonomous crack-healing ability were successfully performed. The flexural strength and elastic modulus of a composite containing 10% microcapsules and 7.5% MPC was not significantly different from controls. High healing efficiency can be 57–71%.
Wu et al.[8]	Luting cement	Encapsulated TEGDMA-DHEPT microcapsules and benzoyl peroxide BPO initiator in the matrix	24 ± 11 µm.	Fracture Toughness and Self-Healing Assessment	The dental luting cement contained fine microcapsules exhibited a self-healing efficiency of 68%-77% recovery, even after being immersed in water for 6 months.
Yahyazadehfara et al.[12]	Dental resin	silica microcapsules(aqueous solution of polyacrylic acid) and a healing powder (strontium fluoroaluminosilicate particles)		Crack growth resistance and healing efficiency testing.	The MA-silane self-healing achieves the best balance of healing efficiency 24.2 ± 3.8% and fracture toughness at 5 wt% loading of microcapsules.
Yue et al.[11]	Dental adhesive	Encapsulated TEGDMA-DHEPT, (NACP; DMAHDM) microcapsules and benzoyl peroxide BPO initiator in the	70 µm	Measurement of fracture toughness KIC and autonomous-healing efficiency	Excellent dentin bond strength, autonomous crack-healing and K_{IC} recovery of 67%, and strong anti-biofilm properties were achieved for the new adhesive resin.

		matrix			
Wu et al. [14]	Dental adhesive	Encapsulated TEGDMA-DHEPT,(NACP; DMAHDM) microcapsules and benzoyl peroxide BPO initiator in the matrix	24 ± 11m	Measurement of fracture toughness K_{IC} and autonomous-healing efficiency	A self-healing efficiency of 67% recovery in K_{IC} was obtained even after 12 months of water immersion, indicating that the self-healing ability was not lost in water-aging.
Seifan et al. [10]	Dental resin	Precipitation of calcium carbonate (CaCO3) minerals (MICP) by bacteria generally recognized as safe (GRAS)		Microscopic Observation Using Optical and Scanning Electron Microscopy	The incorporation of powder healing containing B. licheniformis into composites could initiate the biomineralization of $CaCO_3$ in dental composite throughout the precipitation of $CaCO_3$.
Seifan et al.[15]	Dental resin	Urease breaks down the salivary urea which later binds with calcium to form calcium carbonate (CaCO3).		Microscopic Observation Using Optical and Scanning Electron Microscopy	The healing process and the formation of $CaCO_3$ within dental composites were successfully confirmed.

Table 3. Risk of Bias Considering Aspects Reported in the Materials and Methods Section.

Study	Materials Used According to Manufacturer's Instructions	Bars with Similar Dimensions	Sample Size Calculation	Blinding of the Operator of the Test Machine	Risk of bias
Chen Chen et al.[20]	N	Y	N	N	High
Huyang et al.[19]	N	Y	N	N	High
Seifan et al [10]	N	Y	N	N	High
Seifan et al [15]	N	Y	N	N	High
Wertzberger et al. [7]	N	Y	N	N	High
Wu et al.[8]	N	Y	N	N	High
Wu et al. [14]	Y	Y	N	N	Medium
Wu et al.[21]	N	Y	N	N	High
Wu et al. [18]	N	Y	N	N	High
Wu et al. [17]	N	Y	N	N	High
Yahyazadehfara et al. [12]	N	Y	N	N	High
Yue et al.[11]	Y	Y	N	N	Medium

N=NO / Y=YES

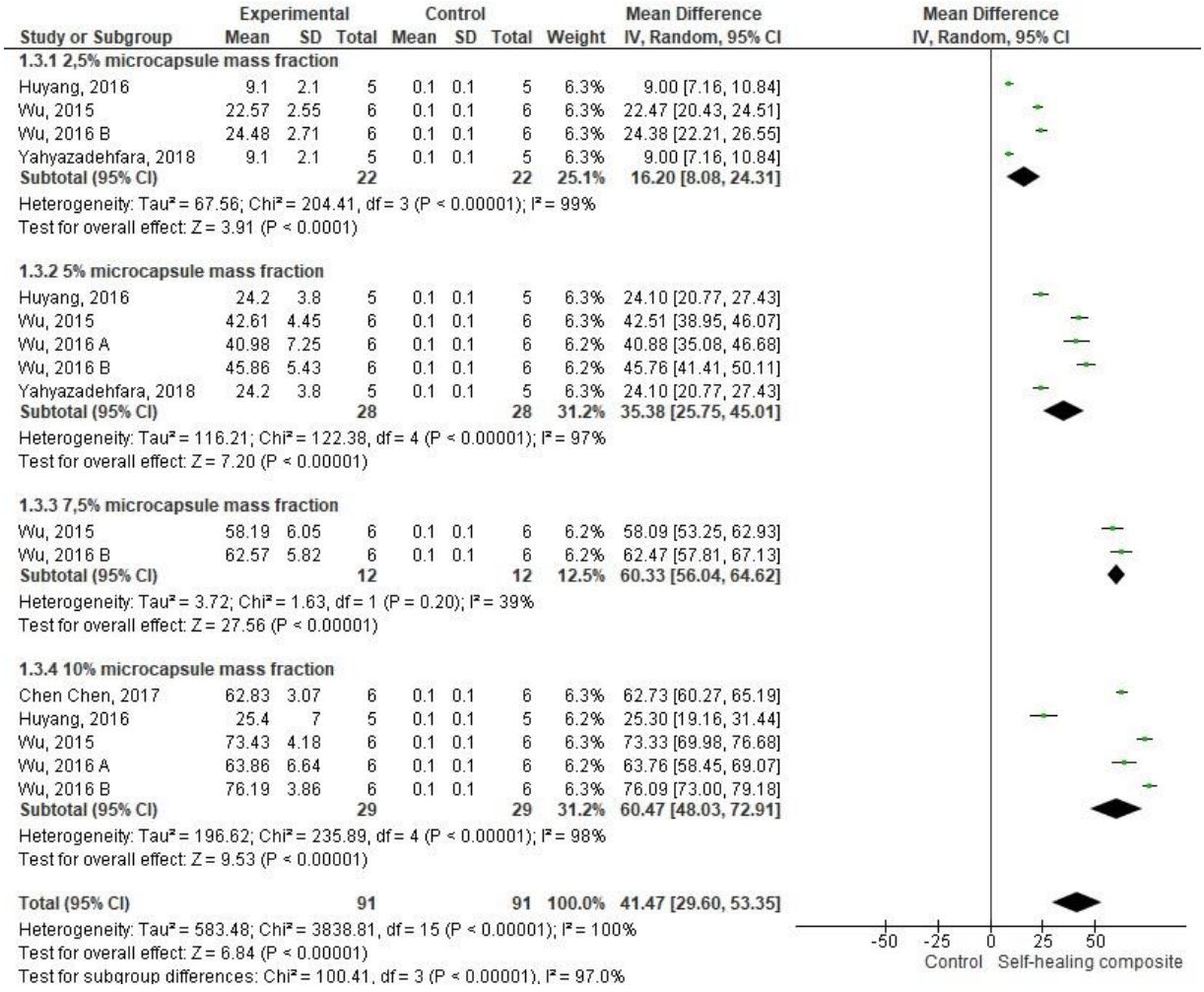

Fig. 2- Forest plot of meta-analysis of self-healing efficiency.The subgroup meta-analysis were performed considering different microcapsule percentage added to dental materials. Self-healing statistically significant difference than control ($p < 0.005$).

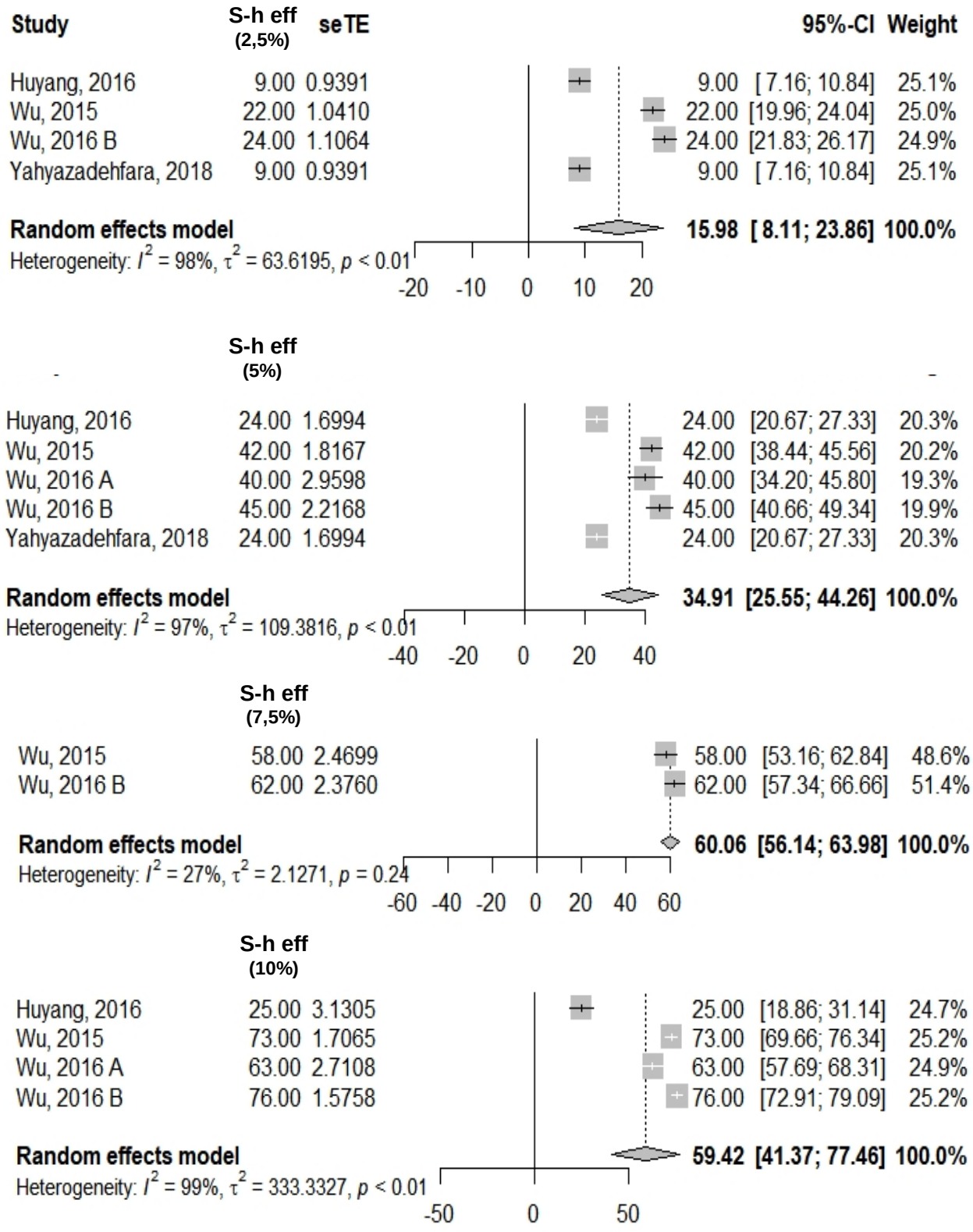

Fig. 2- Forest plot of estimated overall cumulative of self-healing efficiency, **S-h eff.=** self-healing efficienc.

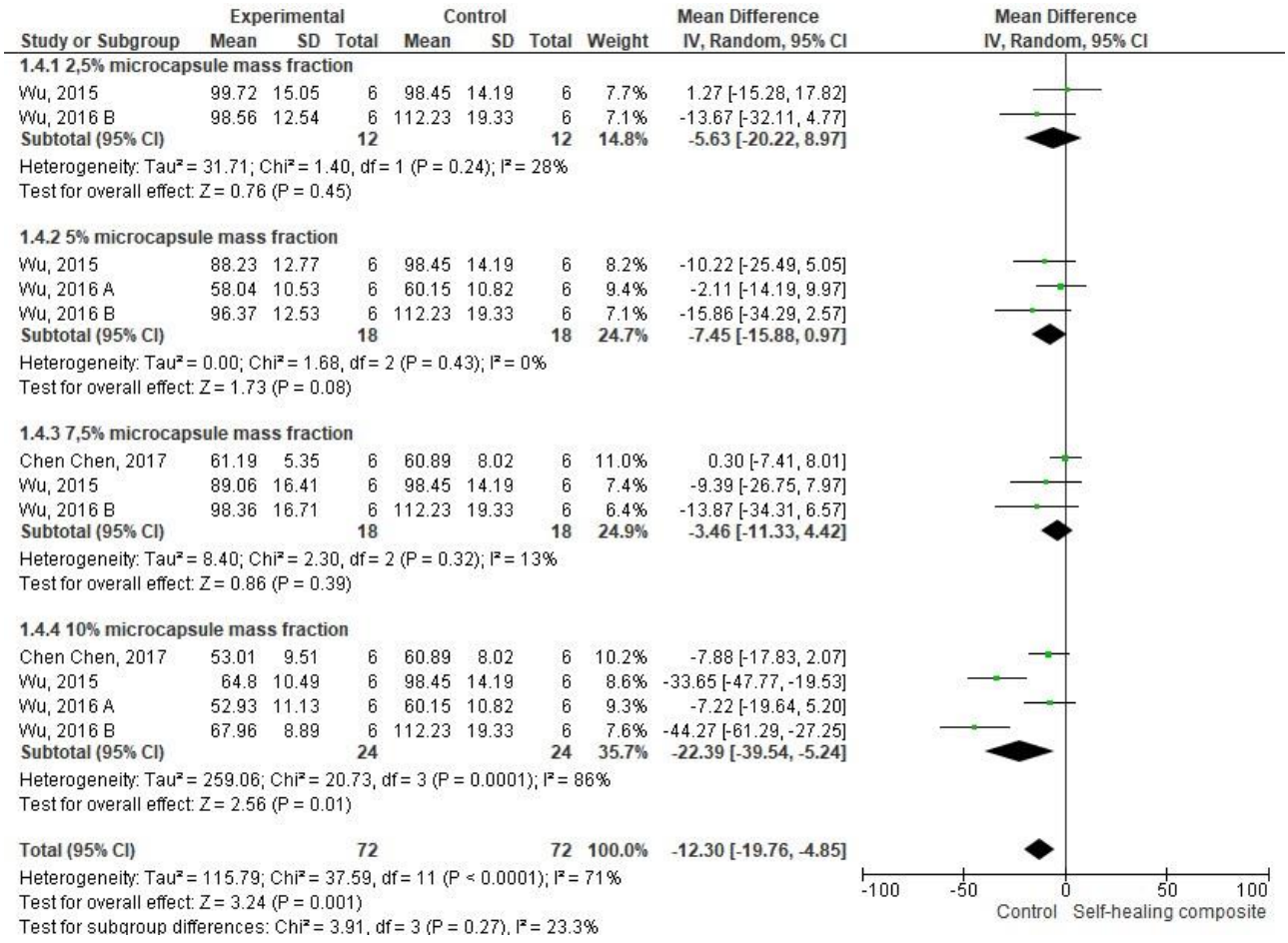

Fig. 4- Forest plot of meta-analysis of flexural strength. The subgroup meta-analysis were performed considering different microcapsule percentage added to dental materials. It was observed that the control group had better results ($p < 0.005$).

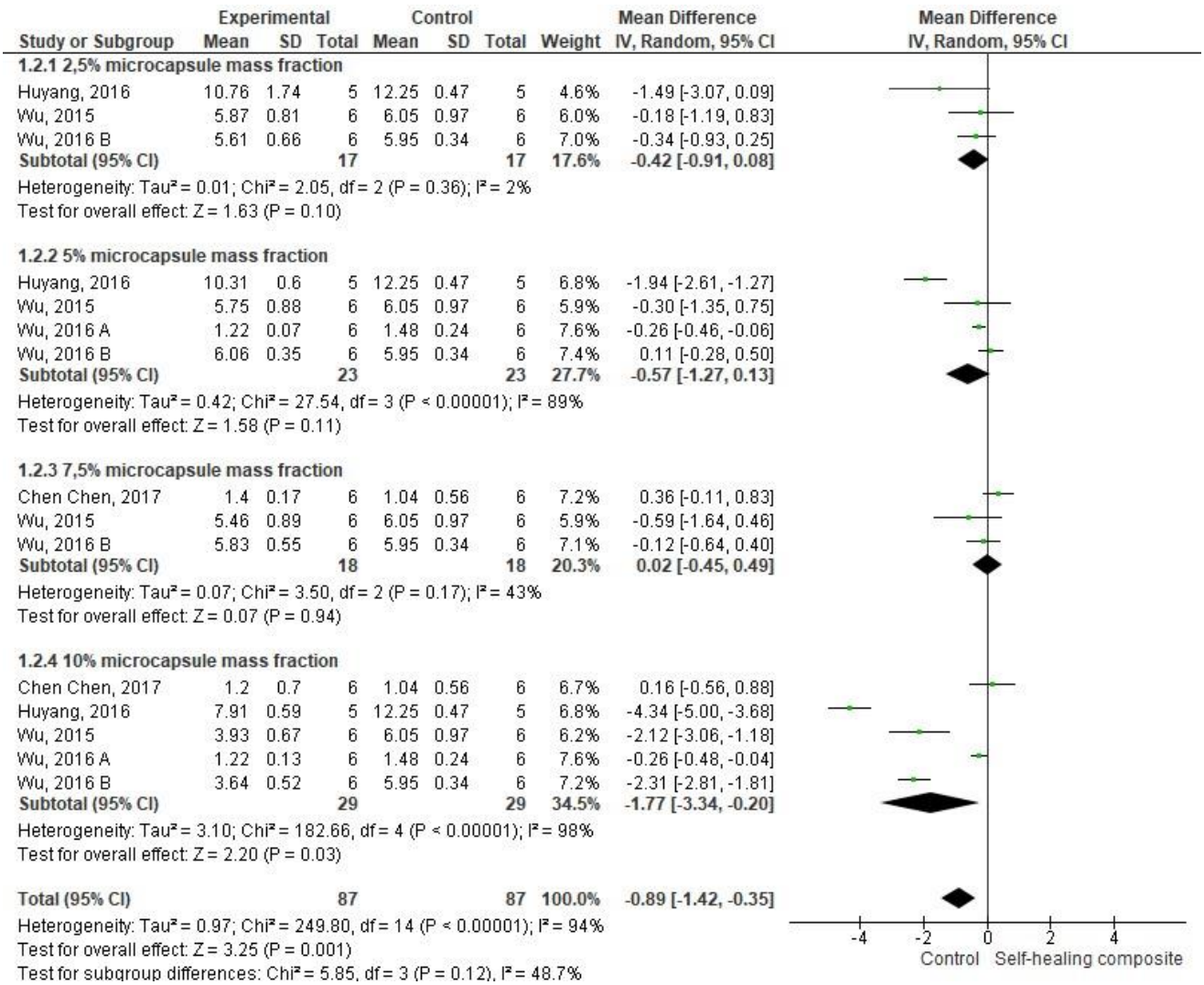

Fig. 5- Forest plot of meta-analysis of elastic modulus. The subgroup meta-analysis were performed considering different microcapsule percentage added to dental materials. It was observed that the control group had better results ($p < 0.005$).

3 Capitulo 2

Novel self-healing system for polymeric materials[1]

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Abstract

Objectives: develop a new self-healing system that combines the use of two capsules with different monomers in order to optimize the self-healing process and increase the mechanical strength after the initial fracture of the composite.

Methods: self-healing capsules were prepared by emulsion polymerization with formaldehyde and urea. With different compositions of self-healing liquid TC_{DHEPT}: triethylene glycol methacrylate – TEGDMA, dihydroxyethyl p-toluidine-DHEPT; BTC_{DHEPT}: Bisphenol A glycidylmethacrylate – BisGMA, triethylene glycol methacrylate – TEGDMA and dihydroxyethyl p-toluidine- DHEPT; BTC_{BPO}: Bisphenol A Glycidylmethacrylate - Bis-GMA, triethylene glycol methacrylate – TEGDMA and benzoyl peroxide – BPO. The capsules were analyzed for molecular structure with Fourier transform infrared spectroscopy (FTIR/ATR), surface morphology evaluated with scanning electron microscopy (SEM). Experimental resins were formulated creating the following groups: Epx resin (ER), ER + BPO, ER + BPO + TC_{DHEPT}, ER+ BTC_{BPO} + BTC_{DHEPT}, Filtek Z350 as a commercial reference (Filtek Z250, 3M ESPE). The composites were submitted to the tests of Degree of conversion (DC), flexural strength (σf) and modulus of elasticity (Ef), Evaluation of fracture toughness (K_{IC}) and self-healing efficiency, roughness analysis by atomic force microscopy (AFM).

Results: The experimental resins showed a higher degree of conversion; the ER+ BTC_{BPO} + BTC_{DHEPT} group presented σf values similar to Filtek Z350; Ef was substantially higher for Filtek Z350. The fracture toughness showed virgenK_{IC} statistically similar between the experimental groups and healed K_{IC} statistically different between the groups ER+ TC_{DHEPT}, ER+ BTC_{BPO} + BTC_{DHEPT}; the self-healing efficiency was higher for ER+ TC_{DHEPT}, AFM (90x90µm) statistically similar between all groups.

Conclusions: A new system for self-healing of composite resins was developed. The results demonstrated that the use of a repair liquid containing BisGMA-TEGDMA was effective to promote the repair of cracks in the material. Studies with material aging after the self-healing process are necessary to demonstrate the effectiveness of this system.

Clinical significance: The efficiency of self-healingr showed that restorative materials can be self-repaired by the new self-healing system, which can prevent fractures of the restoration.

Keywords: biomaterials, Self-healing dental composite, capsules, Polymerizable healing liquid, Mechanical properties, Fracture toughness recovery.

1 Introduction

Dental restoration is a way to make the tooth affected by caries or that has suffered some damage in its structure, return to its shape and its normal function. Although composite resin restorations have shown satisfactory performance on posterior and anterior teeth, studies with more than twenty years of follow-up point to fractures as the main causes of tooth-restorations of this type [1]. The strength of chewing, as well as the biofilm present on the surface, can affect the quality of the restoration, causing defects in the margins[2], acting directly on the deterioration of the material[3]. The repetitive restorative cycle causes a weakening of the tooth structure, caused by the inevitable loss of healthy dental tissue during tooth preparation[4].

Considering that the use of composite resins has a wide clinical application and that the different clinical procedures where they are used demand a lot of their mechanical properties and long-term performance, the continuous development of restorative composites is an important line of research [5]. In this sense, the improvement of the properties of restorative composites, among other factors, must address a reduction in the incidence of fractures [5]. Means for inhibiting crack propagation, such as, control of the microstructure of the reinforcement phase, inorganic particles and modification of the interface between the composite matrix and the filler particles, have been previously studied [6]. The incorporation of ceramics particles such as alumina, titanium and zirconia, covered with amorphous silica as a filler, showed that the composites gained mechanical reinforcement because these particles have much greater hardness and toughness than silicate glass and silica nanoparticles, increasing the fracture work in up to 40%, compared to control composites [7].

Recent studies have shown the development of polymeric materials capable of self-healingr, using polymers with the addition of liquid-encapsulated capsules (triethylene glycol methacrylate – TEGDMA, dihydroxyethyl p-toluidine-DHEPT). A crack propagation defect in the polymeric matrix can break the capsules, releasing a liquid, which, in contact with the catalyst (benzoyl peroxide-BPO) present in the polymeric matrix, triggers the polymerization of the liquid and repairs the formed

crack[8–10]. The overall performance of this type of self-healing reported in dental composites varies from 25% to 80% recovery rate after a fracture[11].

In spite of the fact that the repair with TEGDMA capsules seems to be a promising alternative in the development of materials with less probability of failure due to the fracture of the material [11], it is important to mention that the use of TEGDMA homopolymers for repair has some drawbacks. The fact that TEGDMA (triethylene glycol methacrylate) is a relatively flexible linear molecule and low molecular weight, presents the drawback of increasing the polymerization shrinkage. In this sense, TEGDMA is always used with other components in formulations of composite resins, such as Bis-GMA (A glycidyl dimethacrylate), which has an extensive molecular chain length and thus decreases the polymerization shrinkage. The proportion of each of the monomers in a resin formulation is critical to the properties of the composite [12]. The best result between increasing the degree of conversion and the rates of flexural strength was obtained with a resin matrix containing up to 50 mol% of Bis-GMA and TEGDMA [12].

Therefore, the objective of this study was to develop a new self-healing system that combined the use of two capsules with different monomers in order to optimize the self-healing process and increase the mechanical strength after the initial fracture of the composite, eliminating the use of BPO in the composite matrix and adding Bis-GMA as part of the liquid inside the capsules. The hypothesis tested were: (1) The incorporation of repair capsules in an experimental resin will not affect the chemical-mechanical properties of the material, 2) The incorporation of repair capsules will provide the ability to repair the material after failure.

2 Materials and methods

2.1 Experimental design

A new self-healing system was developed. Self-healing liquid containing capsules with a polyurea formaldehyde (PUF) shell were obtained through emulsion polymerization and added at 7.5wt% concentration into an experimental resin. The materials were evaluated with regards to Degree of conversion (DC), flexural

strength (σf), elastic modulus (Ef) Evaluation of fracture toughness (K_{IC}), self-healing efficiency, and roughness analysis.

2.2 Reagents

Bisphenol-A glycidyl dimethacrylate (Bis-GMA), triethyleneglycol dimethacrylate (TEGDMA), urea, ammonium chloride, and resorcinol were obtained from Esstech Inc. (Essington, PA, USA). Phenyl-bis (2,4,6-trimethyl-benzoyl) phosphineoxide (BAPO), benzoyl peroxide (BPO), formaldehyde, N,N-dihydroxyethyl-p-toluidine(DHEPT), and ethylene-maleic anhydride (EMA) copolymer were obtained from Sigma-Aldrich Chemical Co. (Milwaukee, WI, USA).

2.3 Synthesis of capsules

Prior to the synthesis of the capsules, polymerizable solutions were prepared (Table 1). The self-healing capsules were prepared by emulsion polymerization with formaldehyde and urea[9,13]. 50 ml of water and 13 ml of an aqueous solution containing 2.5% by weight of the ethylene-maleic anhydride copolymer (EMA copolymer) were placed in a glass flask. The EMA solution was used as a surfactant to form two “oil-in-water” emulsions (the “oil” being the different polymerizable solutions previously prepared). The flask was suspended in a water bath in a heating plate and the solution kept under stirring at 300 rpm and immediately afterwards, urea (1.25 g), ammonium chloride (0.125 g) and resorcinol (0.125 g) were added to form capsule lining. Resorcinol was added to the solution to improve the rigidity of the capsules (WU, et al., 2016). After the addition, the pH was adjusted to 3.5 using a ?% sodium hydroxide solution. Then, the stirring rate was increased to 400 rpm and 30 mL of each of the polymerizable solutions, BTC_{DHEPT}, BTC_{BPO} or TC_{DHEPT}, which were added, giving rise to three different stabilized emulsions of BTC_{DHEPT}, BTC_{BPO} or TC_{DHEPT}. After ten minutes of adding the different polymerizable solutions, 3.15g of a 37% aqueous solution of formaldehyde was added to each solution, and then the flasks were sealed with aluminum to prevent evaporation. Polymerization of urea with formaldehyde was carried out isothermally, raising the temperature of the water bath to 55°C, under continuous agitation, for four hours. Within this process, ammonium

chloride catalyzed the reaction of urea with formaldehyde and formed poly urea formaldehyde at the oil-water interface to develop the capsule [9,14]. Thus, the capsules were obtained and immediately afterwards they were washed with water and acetone, filtered in vacuo and dried with air for 24 hours. A sample of the capsules was examined with scanning electron microscopy (SEM) and the capacity of the encapsulation was verified by infrared spectroscopy [9,13].

2.4 Characterization of capsules

To evaluate the molecular structure of the capsules, Fourier transform infrared spectroscopy (FTIR/ATR) was performed (Prestige-21; Shimadzu. Tokyo, Japan), using the 32 scans transmittance setting with a resolution of 4.0cm^{-1} in an absorbance range between 600 and 4000 [15].

The polymerization capacity of encapsulated TEGDMA (TC_{DHEPT}) and Bis-GMA + TEGDMA ($BTC_{DHEPT\ and}$ BTC_{BPO}) was quantified by FTIR (Prestige-21; Shimadzu, Tokyo, Japan) equipped with an ATR device composed of a diamond crystal with 45° mirror angle (Pike Technologies; Madison, WI , USA). To perform the test, a mixture of the TC_{DHEPT} capsules with 0.5% benzoyl peroxide initiator (BPO) (the catalyst) (Sigma-Aldrich) was placed in a silicone mold (6 × 2 × 2 mm) and positioned on the equipment's ATR diamond crystal. In order to evaluate the capsules $BTC_{DHEPT\ and}$ BTC_{BPO}, they were broken by manual spatulation and placed in a silicone mold (6 × 2 × 2 mm) to later be placed in the diamond crystal of the equipment's ATR. FTIR/ATR spectra were performed immediately after mixing and 24 hours post-cure. The degree of conversion (DC) was calculated from the percentage variation in the area of the integrated peak of the methacrylate absorption band = CH2, normalized by the thickness of the sample before and after curing, following a previous study [15].

To analyze the surface morphology of the self-healing capsules, scanning electron microscopy - SEM (SSX-550; Shimadzu, Tokyo, Japan), at 15kV, was used. The capsule diameters were measured using the optical microscope together with image analysis software (ImageJ, NIH, Bethesda). The capsules were spread on a tape adhesive that has been coated with gold dust [16].

2.5 Formulation of experimental resins

Experimental resins were formulated according to the composition shown in Table 2. The organic matrix consists of Bis-GMA and TEGDMA in a 1:1 mass ratio. As a photoinitiator, 1% phenyl-bis oxide (2.4, 6-trimethylbenzoyl) phosphine photoinitiator (BAPO) and 35% of barium boroaluminosilicate glass particles [9]. The speed mixer (FlackTek, Inc Landrum, SC, USA) was used 3500 rpm configuration for 3 min to add the charge particles and capsules. For comparative purposes, a resin was used as a commercial reference (Filtek Z250, 3M ESPE).

2.6 Degree of conversion (DC)

The degree of conversion (DC) was assessed using a FTIR (Prestige21; Shimadzu, Tokyo Japan) equipped with an attenuated total reflectance device (ATR), composed of a diamond crystal, with 45º angled mirrors (PIKE Technologies, USA). The specimens (n=3) of the materials were placed in the diamond cell and spectra were captured during and after the polymerization process, using twelve co-added scans and a $4cm^{-1}$ resolution. Photoactivation was performed, for 20s, using a LED curing unit (valo; Ultradent, South Jordan, Utah, USA) with maximum irradiance operating at the standard power of 1.000 mW/cm² (395-480 nm), which was measured using the MARC Resin Calibrator system (BlueLight Analytics, Halifax, NS, Canada), before the experiment. The distance between the LED tip and the sample was standardized (3 mm). The degree of conversion was calculated considering the intensity of the vibration of the type of stretching of the carbon-carbon double bond (C=C) at the frequency of $1635cm^{-1}$[17].

2.7 Flexural strength and elastic modulus

The flexural strength (σf) and the elastic modulus (Ef) of the materials were evaluated using a three-point flexion test. Based on the ISO 4049 specification (STANDARD, 2000) except for the sample dimensions (10x2x2mm), while the Ef was evaluated according to the procedures established in the specification of the ANSI/ADA Standard specification No. 27 [19] . The materials were inserted in a rectangular matrix and this was covered with polyester strip and glass slide. With the

aid of a metal weight, a pressure was made on the matrix, manually, to avoid the appearance of bubbles. Subsequently, the materials were photoactivated using two light exposures, one at each end of the matrix, for 20s each (n=10). After photoactivation, the bars were removed from the mold, polished with SiC granulation #600 abrasive papers under distilled water irrigation and stored in distilled water in an oven at 37°C. After 24h of storage, the dimensions of the specimens were measured with a digital caliper (Mitutoyo, Tokyo, Japan) and the tests performed with a universal testing machine (DL500, EMIC, São José dos Pinhais, PR). The load was applied in the central region of the bar, with a distance of 8 mm between the points, at a speed of 0.5 mm/min until failure. σf and Ef values were calculated as described in previous [18] studies.

2.8 Evaluation of fracture toughness (K_{IC}) and self-healing efficiency

Fracture toughness (K_{IC}) was determined using the “single-edge notched beam” method. Specimens in the form of bars (n=10) with dimensions of 25mm long × 5mm wide × 2.8mm thick were made in a metallic matrix that has a metallic fragment 2.5mm high and 0.5mm thick in the center. It is possible to make specimens with a 2.5mm deep V-shaped notch. Each surface was photoactivated for 20s at three points on each side of the specimens, totaling 120s of photoactivation for each specimen. Photoactivation was performed using an LED curing unit (valo; Ultradent, South Jordan, Utah, USA). Polyester strips were used on the composite surfaces during photoactivation. The specimens were positioned with the notch opposite to the load application. The specimens were stored in distilled water at 37°C for 24 hours and submitted to the flexion test for three points at a speed of 0.5 mm/min. The fracture toughness was calculated [20]. To test the effectiveness of the self-healing, immediately after fracturing the specimen, the two halves of the specimen were placed inside a silicone mold, to ensure a contact between the fracture faces, allowing the released liquid from the capsule to repair the crack formed. This is similar to the situation in the dental cavity, where the resin with a small fracture would remain in the tooth. The specimens were incubated in a humidifier at 100% relative humidity at 37°C for 24 hours. The notch length of the healed specimen was again measured and made sure it was the same length as the

first “virgin” notch of the same specimen. Then the healed specimen was tested again using the same flexural method, obtaining the healed K_{IC}. The efficiency of autonomous crack-healing (η) was assessed following a previous study: η = K_{IC}-self-healing / K_{IC}-[10,21]virgin. The healed and re-fractured surfaceurface of selected self-healing specimen ER+ BTC_{BPO} + BTC_{DHEPT} were examined via SEM after sputter-coating with gold.

2.9 Roughness analysis by atomic force microscopy (AFM)

Surface roughness measurements (6x2x2) were obtained from three samples per group (Table 1; Filtek Z350, ER, ER + BPO, ER + TC_{DHEPT}, ER + ER+ BTC_{BPO} + BTC_{DHEPT}), using a non-contact mode and PPP-NCL probes (Nanosensors, force constant=48 N/m) in AFM mode (Agilent 5500 Equipment, Agilent Technologies, Santa Clara, CA, USA). When using AFM in “non-contact mode”, the surface characteristics are observed at the nanoscale level and any detected roughness is shown as small grains or particles. The use of this method has many advantages; the most important is the ability to collect 3D surfaces from the analysis and phase type of the data, as well as the number of data on the surface properties and the numerical roughness of the surface. The evaluated parameters were the average surface roughness (Sa) and the average distance between the 5 highest peaks and the 5 values of the main valleys (Sz). AFM micrographs were observed using software probe microscopy data analysis (GwyddionT version 2.33, GNU, Free Software Foundation, Boston, MA, USA). In addition, topographic images were also collected [22].

2. 10 Análise estatística

The equality of the variances and the normal distribution of the errors were checked for all tested response variables. Those that did not satisfy these conditions were parametric assumptions. One-way ANOVA followed by Tukey’s multiple comparisons procedure was used to compare the groups for differences in conversion degree, flexural strength. The analisys of fracture toughness K_{IC} were performed with One-way ANOVA and test T. The elastic modulus data were

submitted to non-parametric Kruskal-Wallis test ($p<0.05$). The conversion degree of the capsules were analysed by test T.Statistical significance was accepted at the $p<0.05$ level.

3 Result

In figure 1, we observe the spectroscopic obtained through FTIR / ATR where it is possible to identify the peaks that correspond to the polymer bonds that form the crust of the capsule, 3300 cm^{-1} NH (Amine), 1710 cm^{-1} C=O (Carbonyl), 1500 cm^{-1} CN (nitrile), which proves that there is no presence of BPO, DHEPT, BisGMA or TEGDMA in the crust of the capsule.

In figure 2, the presence of the band = CH at 1635cm^{-1} indicated that TEGDMA was successfully encapsulated. After polymerization for 24 hours, the reduction in absorbance of this band meant that TEGDMA polymerization occurred. The degree of conversion (Mean ± SD; n = 3), were presented in figure 3, for the TC_{DHEPT} = TEGDMA-DHEPT released was (69.57 ± 1.84%) and BTC_{BPO} + BTC_{DHEPT} = BisGMA-TEGDMA-DHEPT (BTC_{DHEPT}, 7.5%) Bis-GMA–TEGDMA-BPO (BTC_{BPO}, 7.5%) was (60.00 ± 0.83%).

The figure 4A showed capsules crushed with fragments of bark and the healing agent between two glass slides, showing liquid that leaks when the capsule is broken. The SEM image in Fig. 4B showed the outer surface of the capsules. The diameters in two perpendicular directions were measured and calculated for each capsule. The microcapsules were measured and had an average diameter of (118.0 ± 21.0nm; n = 120).

Table 2 shows the values of DC, σf and Ef. The degree of conversion, that of experimental resins was statistically higher than that of commercial resin. With an average of (67.74 ± 2.30%) between the experimental groups and (51.06 ± 1.59%) of the commercial resin. σf showed that the ER+ BTC_{BPO} + BTC_{DHEPT} group presented values statistically similar to those of the group Filtek Z350 ($P <0.001$). The Ef was not significant statistically similar between experimental groups.

The results of K_{IC} fracture toughness are shown in Figure 5 (mean ± sd $MPa^{-m1/2}$; n=10). In Fig. 5-A, virgin K_{IC}, the addition of capsules did not alter the performance of the experimental resin ($p > 0.05$). For Healed K_{IC}, the values of the ER + TC_{DHEPT} group were statistically higher than those of the ER+ BTC_{BPO} + BTC_{DHEPT} group and the other groups showed values=0. The self-healing efficiency is shown in Fig. 5-B. An autocorrection efficiency of (52.5 ± 0.05%) was obtained for the group ER + TC_{DHEPT} and (22.1 ± 0.08%) for ER+ BTC_{BPO} + BTC_{DHEPT} in the recovery of K_{IC}.

In figure 6, we observe the images of atomic force microscopy (AFM) where the peaks and valleys of the surface of the resin specimens are demonstrated. The roughness Sq (quadratic mean) values were extracted from the same software that generated the images in Fig.5. And in table 4 are the values calculated for the 40x40µm and 90x90µm areas. In the 90x90µm area, the Filtek Z350, ER, ER+ BTC_{BPO} + BTC_{DHEPT} groups obtained the highest (means ± sd), in 40x40µm the groups were statistically similar.

The figure 7 shows the polymer film formed after the Evaluation of fracture toughness (KIC) and self-healing efficiency test in the ER + BTC_{BPO} + BTC_{DHEPT} group.

4 Discussion

In this work, a synthesis of capsules containing self-healing liquid with Bis-GMA-TEGDMA-DHEPT and capsules containing Bis-GMA-TEGDMA-BPO was performed and the effect of their incorporation on the physical-chemical properties of experimental composite resins was reported. The performance of the capsules (BTC_{BPO} + BTC_{DHEPT}) was compared with a self-healing system reported in the literature [8,21,23], containing self-healing liquid with TEGDMA-DHEPT (TC_{DHEPT}). Overall, the capsule morphology analyzes of the TC_{DHEPT} and BTC_{BPO} + BTC_{DHEPT} self-healing systems were similar. The Exp resin ER+ BTC_{BPO} + BTC_{DHEPT} DC was similar to the ERTC_{DHEPT} and ER groups, and both were larger than Filtek Z350. ER+ BTC_{BPO} + BTC_{DHEPT} obtained numerical values higher than the ER + TC_{DHEPT} and ER

of (σf). Regarding the fracture toughness (virgin K_{IC}) and the self-healing efficiency, the BTC_{BPO} + BTC_{DHEPT} was 28% lower than the self-healing achieved by the group with TC_{DHEPT}. Therefore, the proposed hypotheses were partially accepted [9].

Figure 4a shows the healing agent when it spills out of the capsules after being pressed between two glass coverslips. Polymeric capsules are often prepared by polymerization in water emulsion, forming an encapsulated poly (urea-formaldehyde) (PUF) with liquid content [9]. In the images, we can see that the TC_{DHEPT} capsules had a higher leakage liquid content, which may be directly related to the self-healing efficiency. The extensive length of the molecular chain, the molecular weight and the viscosity of the Bis-GMA may have interfered with the encapsulation of the self-healing liquid, leaving a smaller content inside the capsules.

Figure 4b shows that, regarding the spheres' morphology, they presented similar spheres sizes (118.0 ± 21.0nm). Proving that the addition of Bis-GMA and BPO in the self-healing liquid did not compromise the formation of the capsule crust and did not directly influence the increase in size and on the surface of the capsule. The self-healing process depends directly on the rupture of the capsules incorporated in the composites, the roughness of the microcapsule crust is of paramount importance for the triggering of self-healing in cracks[9].

The mechanical properties of the composites seem to depend on the mass fraction of the added capsule. Studies report that the flexural strength and elastic modulus of the resin were not adversely affected when the mass fraction of the capsule was ≤ 15%[9]. However, other studies have reported a continuous decrease in flexural strength, elastic modulus and fracture resistance with increased capsule content. One group of studies has shown that these properties are not adversely affected when capsules have been incorporated by up to 7.5wt% [13,24]. For these reasons, this mass fraction of capsules was incorporated as comparative self-healing group ER+TC_{DHEPT} and with the new system with the addition of 7.5wt% of capsules BTC_{BPO} and + BTC_{DHEPT}. The long-term clinical success of dental restorations appears to depend on the mechanical stability of restorative composites [2]. When correlated, parameters of dental materials evaluated *in vitro* with their clinical performance, the results were moderately positive, and fracture toughness is mainly related to clinical fracture and flexion strength with clinical wear[25].

The self-healing mechanism used works basically through the release of the self-healing agents, including methacrylates and initiation system, through the broken capsules. The capsule breaking occurs due to friction between the rough surface of the capsules and the composite during the crack formation within the material. Polymerization of the self-healing agents occurs through the decomposition of the BPO initiator using the DHEPT activator, triggering the polymerization reaction of the methacrylates included in the capsules, recomposing the formed cracks. The thin polymer film newly formed in the polymerized and refracted resin proves the efficiency of self-healing in several studies [10,13,24]. In this work we try to differentiate this method by adding Bis-GMA to the self-healing liquid and instead of placing the BPO in the polymer matrix, we synthesize capsules with the BPO in the ER+ BTC_{BPO} + BTC_{DHEPT} liquid.

Satisfactory polymerization is achieved when BAPO is used. This initiator is capable of promoting polymerization alone, not requiring the addition of a co-initiator [26]. For this reason, it was the initiator chosen for the composite resin, since the benzoyl peroxide added in the matrix of the TC_{DHEPT} self-healing system reacts with the tertiary amine, often used as an accelerator, to generate free radicals. Primers are molecules that have atomic bonds with low dissociation energy and form free radicals under certain conditions, such as temperature, photochemical excitation or oxy-reduction reaction. When the initiator comes into contact with an amine accelerator, such as DHEPT, an oxy-reduction reaction and the generation of free radicals occur, which triggers polymerization, which is why this initiator was added to the liquid in the capsule [27,28]. The same resin base (Tab. 2) was maintained for the new self-healing system.

A composite resin formulated with 50% by weight of Bis-GMA and 50% by weight of TEGDMA + 1 mol% of BAPO (0.011 in 5 grams) reached the maximum rate of polymerization values [Rpmax (s - 1)] and the degree conversion rate was approximately 50% [26]. In this study, the degree of conversion of the experimental resins was statistically similar, being superior to the commercial group Z350, reaching an average above 65%. This increase in values may have occurred by the addition of 1% (0.5 in 5 grams) of BAPO. Each combination of monomers in the experimental composition implies different properties and different molecular

arrangements after polymerization. The resins presented different compositions with the addition of BPO and capsules that differed in their composition in the self-healing liquid. Thus, a higher DC does not necessarily mean better mechanical properties[29]. For flexural strength and elastic modulus when 1 mol% BAPO was used, the values were (90.0 ± 17.0) MPa for σf and (1.1 ± 0.10) GPa for Ef, respectively [26]. We can draw a parallel with the increase in σf with the addition of inorganic particles and self-healing capsules for an average of (104.49 ± 16.96) MPa for the experimental groups: ER, ER + BPO, ER+ TC_{DHEPT}, ER+ BTC_{BPO} + BTC_{DHEPT}. And a slight increase for Ef, with the experimental groups averaging (1.73 ± 0.19)GPa. The ER + ER+ BTC_{BPO} + BTC_{DHEPT} group had an average value of (108.97 ± 16.41) ^{AB} MPa, a result statistically similar to the commercial group Z350, signaling an increase in σf when using ER+ BTC_{BPO} + BTC_{DHEPT} (BTC_{DHEPT} 7.5%; BTC_{BPO} 7.5%) as a system of self-healing. This corroborates to demonstrate that capsules TC_{DHEPT} and ER+ BTC_{BPO} + BTC_{DHEPT} do not impair the chemical and mechanical properties of the composite.

AFM is a technique that maps the topography by lightly touching the surface with an oscillating tip. The amplitude of oscillation changes with the topography of the specimen surface, and the topography image is obtained by monitoring these changes. Sq is a quadratic mean, a statistical measure, used to measure a sample of peaks and valleys, which allows measurements to be made in a small area [30]. AFM operates like this, measuring attractive or repulsive forces between the tip and the specimen. The increase in surface roughness can lead to an increase in the accumulation of biofilm, in the accommodation of food particles, which together with bacterial adhesion can cause changes in optical properties and consequently aesthetic changes that subsequently result in the destruction of the restoration [31].

Virgin K_{IC} fracture toughness was higher for Filtek Z530 and similar among experimental groups, proving that capsules do not interfere with the mechanical properties of the polymer; the curing liquid released was successfully polymerized, capsules of sizes between 10 and 50μm release the liquid after being fractured and broken [13]. We believe that the new self-healing system developed works when pressure is generated to rupture the capsules, of approximate size 180 nm, and these are compressed and release the liquid present inside. Two factors were critical

in fracture toughness and self-healing efficiency in the new self-healing system. The first factor is that the modification of the self-healing liquid by adding Bis-GMA, as seen in figure 4a, BTC_{DHEPT} and BTC_{BPO} obtained a smaller fraction of liquid encapsulated inside, this influenced the amount of liquid polymer film in the crack inside. The second factor is that the association of the two capsule systems BTC_{DHEPT} and BTC_{BPO}, with the placement of the BPO initiator inside the capsule and not in the polymeric matrix[13], made the ER+ BTC_{BPO} + BTC_{DHEPT} system dependent on having an equal fraction of capsules compressed for that the film formed inside the crack obtains a greater healed K_{IC} after resealing of virgin K_{IC}. These combined factors are the possible cause of the 30.4% loss of self-healing efficiency.

It can be seen in figure 7, representative fracture surface of ER+ BTC_{BPO} + BTC_{DHEPT}, demonstrating the efficiency of the new self-healing system in forming polymer films from the released healing liquid that was successfully polymerized to heal the crack.The same was observed for the ER + BPO + TC_{DHEPT} system in previous studies [8,9]. Based on the results, we consider that this study points to the need to evaluate different percentages of ER+ BTC_{BPO} + BTC_{DHEPT} added to the composite resin, in order to stipulate what is the best percentage for the efficiency of the self-healing without affecting the mechanical properties.

5 Conclusion

A new system for self-healing of composite resins was developed. The results demonstrated that the use of a repair containing BisGMA-TEGDMA capsules was effective to promote the repair of cracks in the material. Studies with material aging after the self-healing process are necessary to demonstrate the effectiveness of this system.

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Tables

Table 1- Composition of the capsules self-healing liquid.

Capsules	Experimental Resins		Initiators	
	BisGMA	TEGDMA	DHEPT	BPO
TC_{DHEPT}	-	100%	1%	-
BTC_{DHEPT}	50%	50%	1%	-
BTC_{BPO}	50%	50%	-	1%

Bisfenol A glicidilmetacrilato (BisGMA), trietilenoglicol metacrilato (TEGDMA), dihidroxietil p-toluidina(DHEPT), peróxido de benzoila (BPO).

Table 2 – Composition of experimental resins.

Groups	Experimental resin composition (wt%)				Particles (wt%)	Capsules* (wt%)		
	BisGMA	TEGDMA	BAPO	BPO		TC_{DHEPT}	BTC_{DHEPT}	BTC_{BPO}
ER	50	50	1	-	35	-	-	-
ER + BPO	50	50	1	0.5	35	-	-	-
ER + BPO + TC_{DHEPT}	50	50	1	0.5	35	7.5	-	-
ER+ BTC_{BPO} + BTC_{DHEPT}	50	50	1	-	28.5	-	7.5	7.5

Bisphenol-A glycidyl dimethacrylate (Bis-GMA), triethyleneglycol dimethacrylate (TEGDMA), Phenyl-bis(2,4,6-trimethyl-benzoyl) phosphineoxide (BAPO), benzoyl peroxide (BPO).

* TC_{DHEPT} = trietilenoglicol metacrilato–TEGDMA , dihidroxietil p-toluidina- DHEPT.

BTC= Bisfenol A glicidilmetacrilato–BisGMA, trietilenoglicol metacrilato–TEGDMA , dihidroxietil p-toluidina- DHEPT (BTC_{BPO}, 7.5%) Bisfenol A glicidilmetacrilato – Bis-GMA , trietilenoglicol metacrilato–TEGDMA, peróxido de benzoila–BPO (BTC_{DHEPT}, 7.5%)

Table 3 – Mean values (± standard deviation) of Degree of conversion (DC) composite resins, Flexural strength (σf) of Elastic modulus (Ef).

Groups	DC(%)	σF (MPa)	EF (GPa)
Filtek Z350	51.06 (±1.5)[b]	129.18 (±14.15)[a]	8.75 (±0.71)[a]
ER	65.61 (±3.5)[a]	103.20 (±16.63)[b]	1.60 (±0.11)[c]
ER + BPO	67.88 (±2.7)[a]	104.57 (±20.14)[b]	1.46 (±0.27)[c]
ER + BPO + TC_{DHEPT}	69.47 (±1.5)[a]	101.23 (±14.68)[b]	1.93 (±0.08)[b]
ER+ BTC_{BPO} + BTC_{DHEPT}	67.99 (±1.5)[a]	108.97 (±16.41)[ab]	1.94 (±0.31)[b]

Different letters in the same column indicate significant differences between groups (p<0.001).

Table 4 – Mean values (± standard deviation) of suface quadritc roughness (Sq) in different increases 40x40µm and 90x90µm.

Groups	Sq nm (40x40)	Sq nm (90x90)
Filtek	393.00 (±39.50)[a]	444.00 (±31.48)[a]
ER	418.00 (±72.38)[a]	491.33 (±58.28) [a]
ER + BPO	354.66 (±23.28)[a]	344.00 (±18.52) [bc]
ER + BPO + TC_{DHEPT}	344.66 (±34.58)[a]	297.00 (±23.51) [c]
ER+ BTC_{BPO} + BTC_{DHEPT}	416.33 (±41.58)[a]	423.00 (±19.46) [ab]

Different letters in the same column indicate significant differences between groups (p<0.001

Figures

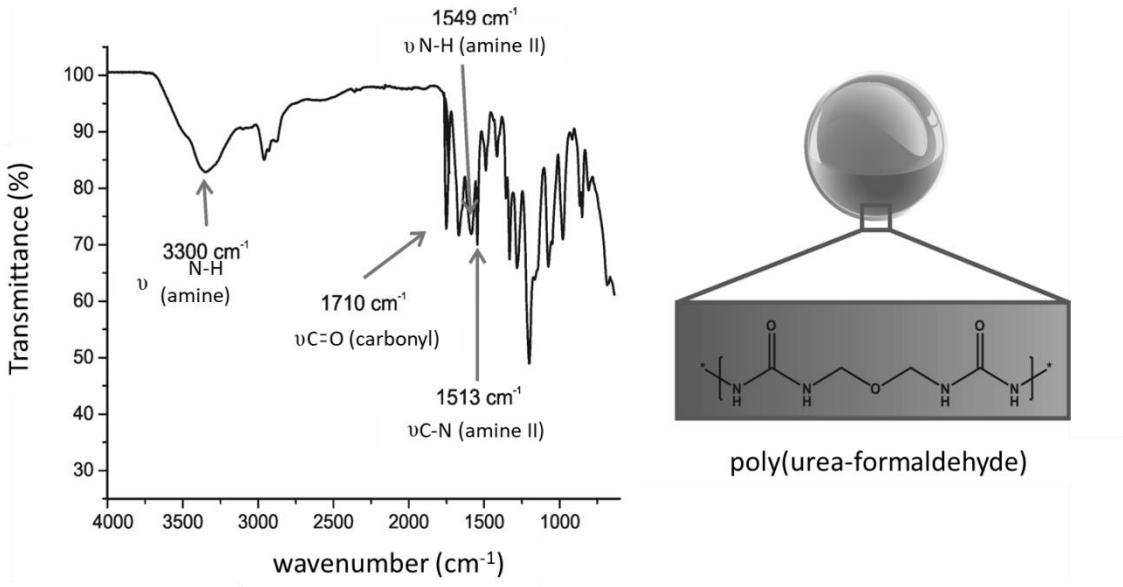

Fig.1– FTIR spectrum of capsules consisting healing liquid inside PUF shells. 3300 cm-1 N-H (Amina), 1710 cm-1 C=O (Carbonila), 1500 cm-1 C-N (nitrila) verified the successful process of encapsulation of capsules.

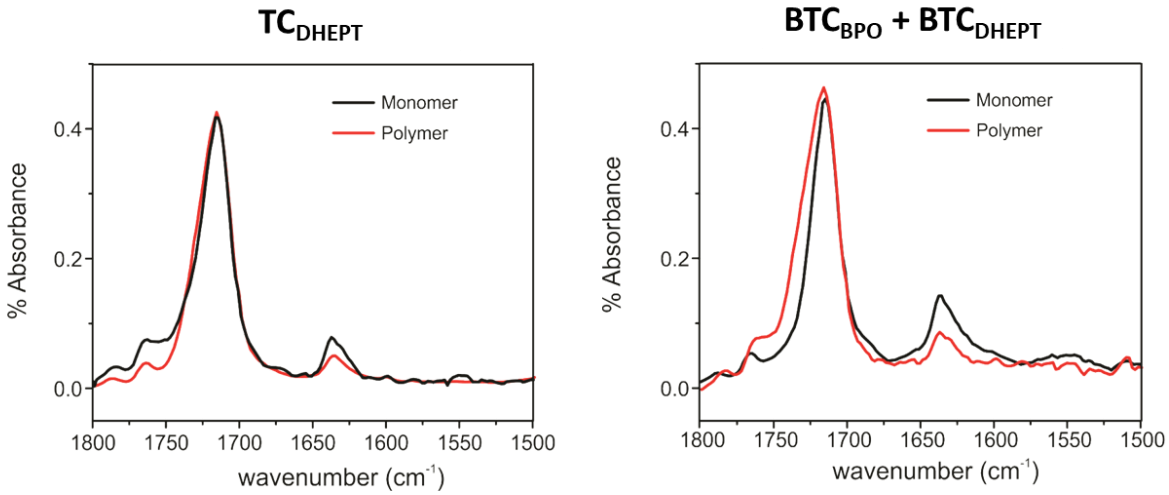

Fig.2– FTIR spectrum of capsules consisting healing liquid inside PUF shells. A mixture of TC_{DHEPT} capsules with 0.5 wt% benzoyl peroxide initiator powder (BPO) (the catalyst), BTC_{BPO} + BTC_{DHEPT}.

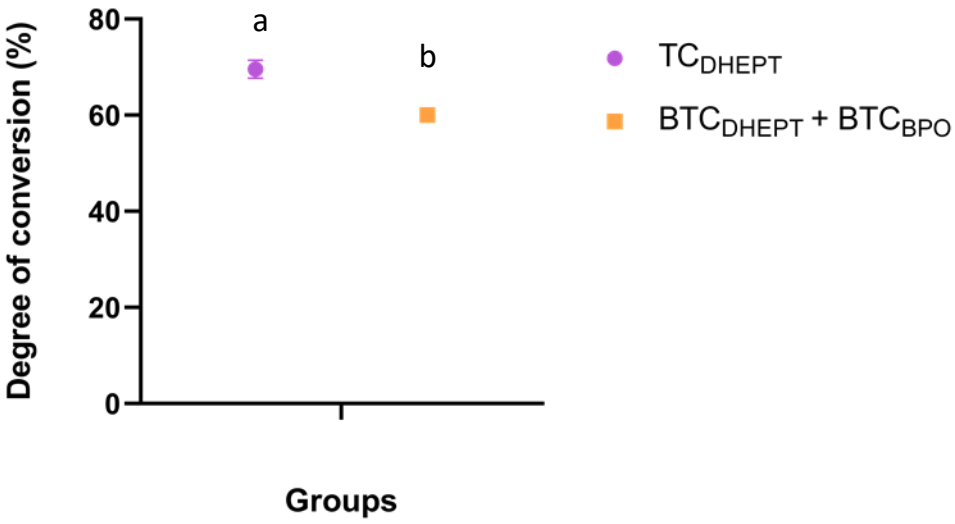

Fig.3– Degree of conversion cápsules (GC) and standard deviation (SD), n = 3. Different letters significant differences between groups (p<0.001).

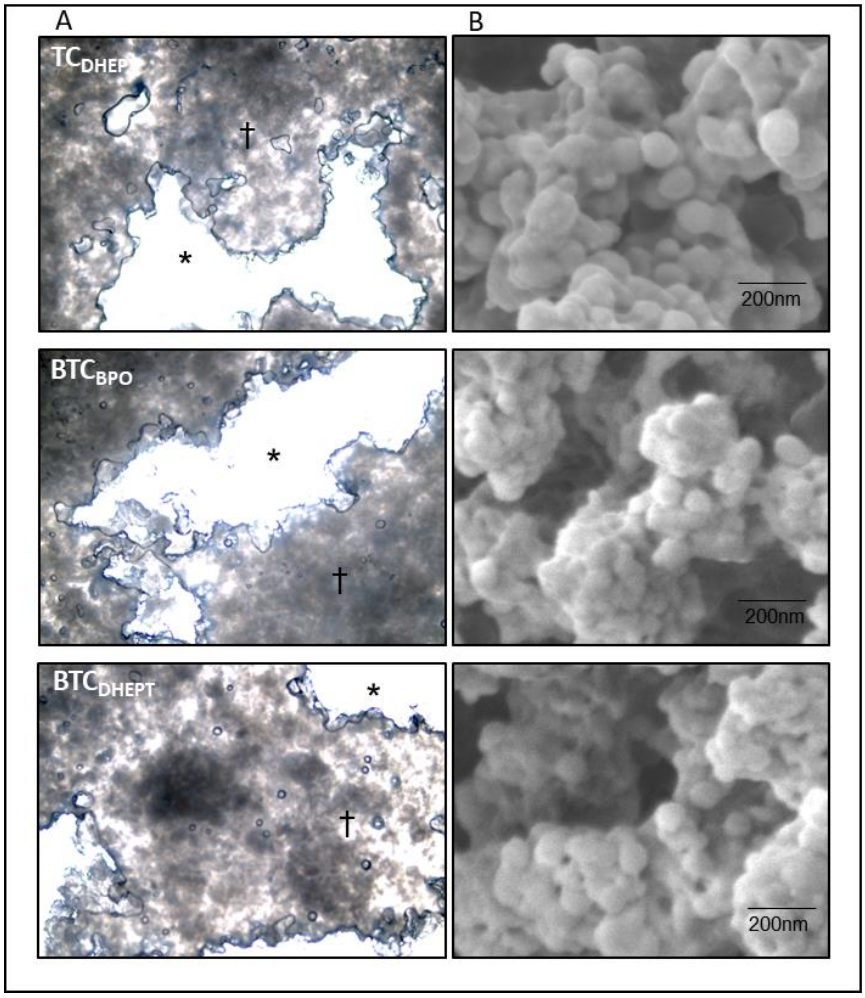

Fig.4– Optical image of crushed capsules showing the released healing liquid films (A) and SEM capsules powders with medical diameters (B). *Realeased healing agent † Crushed shel

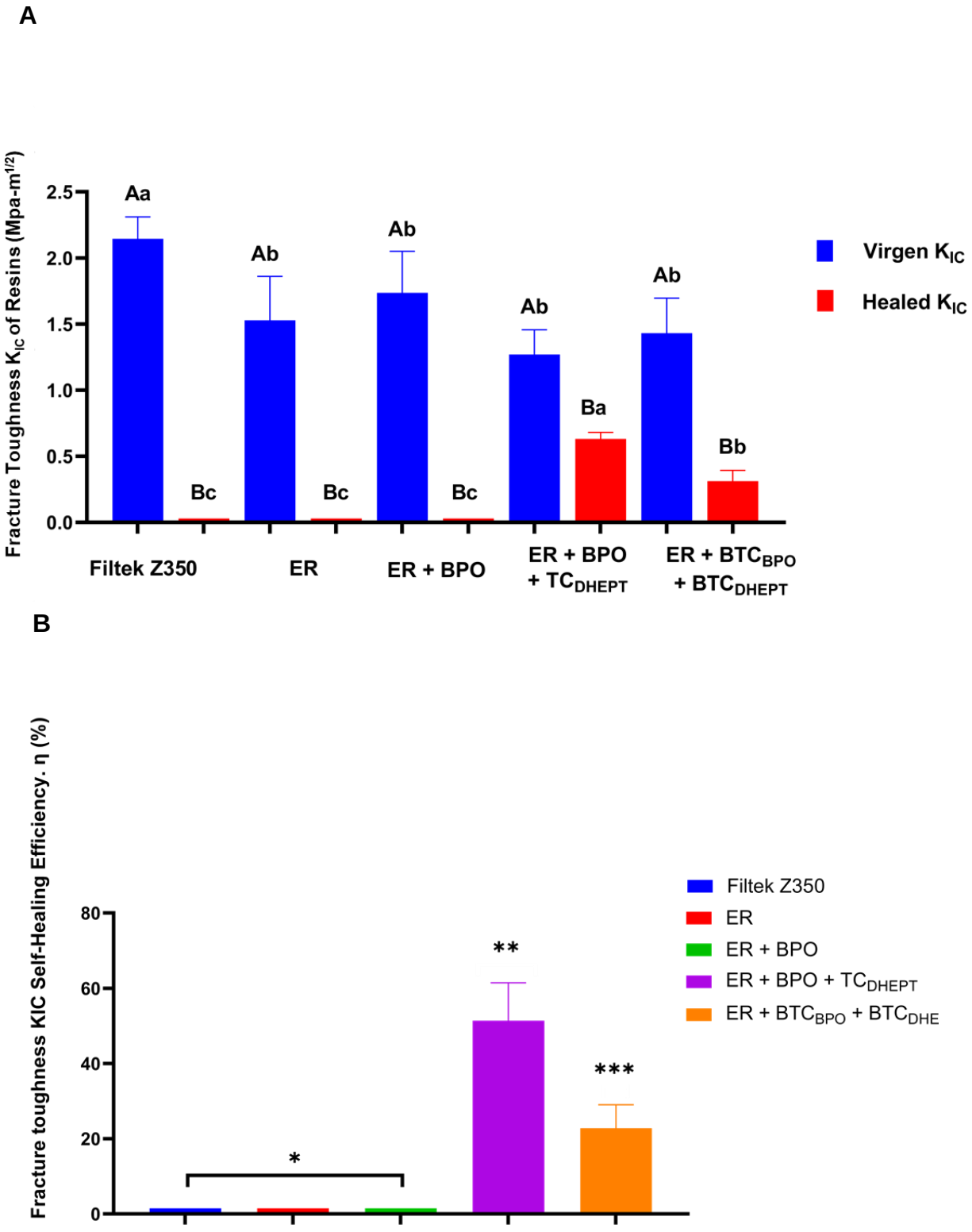

Fig.5 – Self-healing of cracks in resins: (A) Virgin and healed fracture toughness KIC, and (B) autonomous crack-healing efficiency (mean ±sd; n = 10). (A)Uppercase letters indicate comparisons between the same group ($p<0.001$). lowercase letters comparisons between different vingem K_{IC} e Healed K_{IC} ($p<0.001$). (B) different amounts of asterisks indicate statistically significant differences ($p<0.001$).

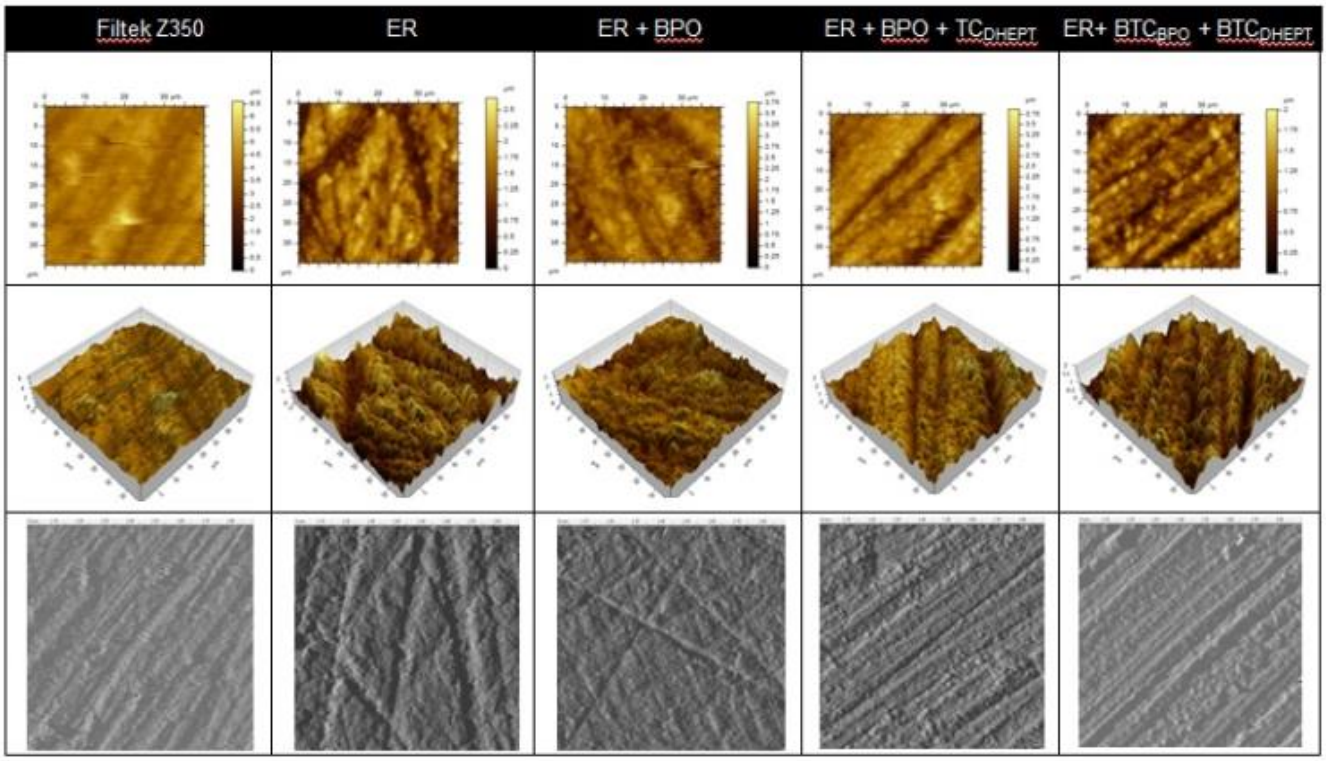

Fig.6– Representative topographic and 3D images of atomic force microscopy (AFM)

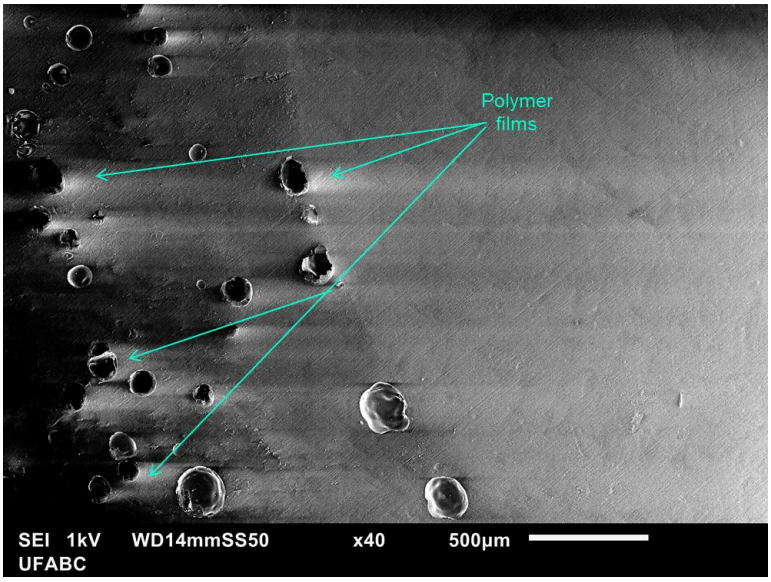

Fig.7– Representative SEM images of the fractured planes from the specimens containing ER+ BTC$_{BPO}$ + BTC$_{DHEPT}$ 15% microcapsules. The healed and re-fractured surface of the resin specimen displaying the presence of released and polymerized healing liquid films.

4 Considerações finais

Evitar a substituição de restaurações deve ser uma prática para os cirurgiões dentistas no que diz respeito à preservação de tecido dental sadio e restaurações com pequenas falhas. Através de revisão sistemática foi possível identificar que o uso de autorreparo é uma realidade promissora e que novos esforços devem ser direcionados a esta temática para identificar os efeitos positivos a longo prazo. Através de estudo laboratorial foi possível concluir que o autorreparo com cápsula de Bis-GMA e TEGDMA é possível e efetivo, devendo novos estudos serem realizados a fim de aprofundar os conhecimentos sobre esse avanço, bem como seu comportamento a longo prazo.

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