UNIVERSIDADE FEDERAL DO RIO GRANDE DO SUL

FACULDADE DE ODONTOLOGIA

PROGRAMA DE PÓS-GRADUAÇÃO EM ODONTOLOGIA

ÁREA DE CONCENTRAÇÃO CLÍNICA ODONTOLÓGICA - MATERIAIS DENTÁRIOS

CIMENTOS RESINOSOS EXPERIMENTAIS FOTOÁTIVÁVEIS E DUAIS CONTENDO HIDROXIETIL ACRILAMIDA

PATRICIA FRANKEN

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LINHA DE PESQUISA: BIOMATERIAIS E TÉCNICAS TERAPÊUTICAS EM ODONTOLOGIA

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RESUMO

O objetivo desse estudo foi desenvolver cimentos resinosos fotoativáveis e de cura dual contendo hidroxietil acrilamida (HEAA) e avaliar suas propriedades físico-químicas e ópticas. Foram formulados três cimentos resinosos fotoativáveis (L) e seis de cura dual (D), contendo somente monômeros metacrilatos Bis-GMA70%/HEMA30% nos grupos controle (L_{HEMA1}; D_{HEMA0}; $D_{HEMA0,25}$; $D_{HEMA0,6}$) e Bis-GMA70%/HEAA30% (L_{HEAA0}; L_{HEAA1}; D_{HEAA0}; $D_{HEAA0,25}$; $D_{HEAA0,6}$) nos grupos experimentais. Entre os cimentos resinosos, diferentes concentrações de amina terciária foram adicionadas: EDAB – 0 ou 1% mol nos fotoativáveis e DHEPT – 0, 0,25 ou 0,6% mol nos duais. Fluoreto de itérbio foi adicionado como carga a 40% em massa. A cinética de polimerização dos cimentos resinosos foi avaliada por calorimetria exploratória diferencial com acessório de fotocalorimetria (n=3). Amolecimento em solvente (ΔKHN, n=5), radiopacidade (n=5), espessura de película (n=3) e estabilidade de cor em água destilada e óleo mineral (n=5) foram avaliados. Resistência coesiva à tração (UTS, n=12) e resistência de união ao microcisalhamento (μSBS, n=12) foram analisadas inicialmente e após 6 meses de armazenamento. Os resultados foram analisados com ANOVA, teste de Tukey e teste t pareado (α=0,05). O grupo L_{HEAA1} não teve diferença estatística do grupo controle em relação à cinética de polimerização, dureza inicial, ΔKHN e estabilidade de cor (p>0,05) . Nos cimentos duais, os grupos com acrilamida apresentaram menor grau de conversão e dureza inicial e maior ΔKHN quando comparados ao grupo $D_{HEMA0.6}$, que obteve maior taxa de polimerização (p<0,05). Não houve diferença estatística em relação à radiopacidade e espessura de película (p>0,05) para todos os cimentos. Em relação a estabilidade de cor em água destilada, os cimentos duais com HEAA obtiveram mudança de coloração superior em relação aos metacrilatos. Propriedades mecânicas imediatas foram inferiores para os grupos com acrilamida ($p<0,05$), porém obtiveram estabilidade hidrolítica longitudinal sem diferença para os grupos L_{HEMA1} e $D_{HEMA0.6}$, dentro de cada modo de ativação ($p<0,05$). A presença do monômero HEAA no cimento resinoso fotoativável L_{HEAA1} não alterou as propriedades físico-químicas e ópticas comparado ao controle, porém com maior estabilidade hidrolítica longitudinal.

Palavras-chave: acrilamidas, hidroxietil metacrilato, cimentos resinosos.

ABSTRACT

The aim of this study was to develop light-cured and dual-cured resin cements containing hydroxyethyl acrylamide (HEAA) and to evaluate their physical-chemical and optical properties. Three light-cured (L) and six dual-cured (D) resin cements were formulated. Methacrylate monomers Bis-GMA70%/HEMA30% were added in the control groups (L_{HEMA1}; D_{HEMA0}; $D_{HEMA0.25}$; $D_{HEMA0.}$6) and Bis-GMA70%/HEAA30% in the experimental groups (L_{HEAA0}; L_{HEAA1}; D_{HEAA0}; $D_{HEAA0.25}$; $D_{HEAA0.6}$). Among resin cements there was differentiation by the tertiary amine concentration: EDAB – 0 or 1% mol in light-cured and DHEPT – 0, 0.25 or 0.6% mol in dual-cured. Ytterbium trifluoride was added as inorganic filler at 40 wt%. The polymerization kinetics of the resin cements were investigated through differential scanning calorimetry with a photocalorimetric accessory, n =3. Softening in solvent (ΔKHN, n =5), radiopacity (n =5), film thickness (n =3) and color stability in distilled water and mineral oil (n=5) were also evaluated. Mechanical properties as ultimate tensile strength (UTS, n =12) and micro-shear bond strength (μSBS, n =12) were analyzed immediately and after 6 months of storage. Results were analyzed by ANOVA, Tukey's test and Student's t test ($\alpha=0.05$). L_{HEAA1} group had no statistical difference from control group regarding polymerization kinetics, initial hardness, ΔKHN and color stability ($p>0.05$). In dual-cured cements, the acrylamide groups presented lower degree of conversion and initial hardness and higher ΔKHN when compared to the $D_{HEMA0.6}$ group, which obtained higher rate of polymerization ($p<0.05$). There was no statistical difference in relation to radiopacity and film thickness ($p>0.05$) for all resin cements. In relation to color stability in distilled water, the dual-cured cements with HEAA obtained a higher color change compared to the methacrylates. Immediate mechanical properties were lower for the acrylamide groups ($p<0.05$), however they got long-term hydrolytic stability without difference for L_{HEMA1} and $D_{HEMA0.6}$ groups within each mode of polymerization ($p<0.05$). The presence of the HEAA monomer in the light-cured resin cement L_{HEAA1} did not altered the physical-chemical and optical properties compared to control, however with longitudinal hydrolytic stability.

Keywords: acrylamides, hydroxyethyl methacrylate**,** resin cements.

SUMÁRIO

1. INTRODUÇÃO

1.1 Cimentos Resinosos

Cimentos resinosos são amplamente utilizados na Odontologia restauradora para cimentação de restaurações indiretas. Apresentam características de similaridade de cor à dentina e ao esmalte, adesão à estrutura dentária (NALCACI et al., 2005; ARRAIS et al., 2007; OEI et al., 2013) e propriedades mecânicas superiores aos demais agentes de cimentação (HOFMANN et al., 2001; TIAN et al., 2014). Características como a resistência à dissolução e uma forte união adesiva do cimento ao dente e ao material restaurador são desejáveis para a longevidade clínica dos cimentos resinosos (PEUMANS et al., 2000; BLATZ et al., 2003). Isso também influenciará positivamente em uma retenção superior e maior resistência à fratura das restaurações (HADDAD et al., 2011).

Os cimentos resinosos podem ser classificados de acordo com o seu mecanismo de ativação dividindo-se em: quimicamente ativáveis, fotoativáveis ou de cura dual (DE SOUZA et al., 2015). Os sistemas quimicamente ativáveis são pouco utilizados clinicamente, pois tem como desvantagens a dificuldade do controle sobre o tempo de trabalho e propriedades mecânicas inferiores (DE SOUZA et al., 2015). Para possibilitar maior controle sobre o tempo de trabalho foram introduzidos sistemas de ativação por meio de energia luminosa. Os sistemas fotoativados dependem do comprimento de onda e da intensidade de luz que atinge o material (ASSMUSSEM e PEUTZFELDT, 2001). A principal vantagem do sistema fotoativável em relação aos cimentos duais é a maior estabilidade de cor (KOISHI et al., 2002; KILINC et al., 2011), sendo principalmente utilizado para cimentação de facetas. Já os cimentos duais são indicados para cimentação de restaurações do tipo onlay, inlay, coroa, ponte fixa cerâmicas e pino intracanal (BACCHI et al., 2014). Assim, quando houver a necessidade de polimerização sob restaurações espessas ou em áreas profundas, onde a luz não consegue penetrar, podemos lançar mão de um sistema de cura dual (HADDAD et al., 2011; MARGHALANI, 2012). O sistema de cura dual irá compensar o efeito atenuador da luz através do seu mecanismo de ativação química (HOFMANN et al., 2001), podendo também ser ativado por luz nas margens da restauração para facilitar a remoção do cimento. É sabido que o mecanismo de ativação química sozinho é menos efetivo que o dual (FONSECA et al., 2004; ARRAIS et al., 2010). A adesão do cimento resinoso à estrutura dental ocorre combinada à técnica adesiva por meio da hibridização com o tecido dentário. A resistência de união dos cimentos resinosos à dentina é influenciada pelo modo de ativação e pelo sistema adesivo utilizado (ARRAIS et al., 2007).

1.2 Composição dos cimentos resinosos

Cimentos resinosos são compostos por partículas inorgânicas revestidas por um agente de união dispersas na matriz resinosa orgânica, que comumente é composta por uma mistura de monômeros metacrilatos. Tais monômeros, quando associados a sistemas ativadores/iniciadores, geram polímeros em uma rede polimérica com ligações cruzadas (VAN LANDUYT et al., 2007), resultando em propriedades mecânicas desejáveis para resistir às forças mastigatórias (ANDRZEJEWSKA, 2001). Cimentos resinosos podem conter monômeros hidrófilos e hidrófobos, sendo que a presença de monômeros hidrófilos pode levar a um aumento de absorção de água ao longo do tempo (YIU et al., 2006).

O monômero Bisfenol A-glicol dimetacrilato (Bis-GMA) possui alta reatividade devido à duas duplas ligações de carbono reativas. Estas duplas ligações de carbono se quebram durante a reação de polimerização, permitindo que o monômero se una a outros na reação (PEUTZFELDT, 1997). Assim como o Bis-GMA, outros dimetacrilatos também dão origem a uma rede polimérica, resultando em efeitos como o aumento da taxa de polimerização, das propriedades mecânicas e da resistência à degradação hidrolítica da matriz polimérica (MOSZNER et al., 2006). Porém, o Bis-GMA apresenta alto peso molecular e dois grupos hidroxila (-OH) que formam pontes de hidrogênio, resultando em um monômero de alta viscosidade, hidrófobo e de baixa solubilidade em água. Por isso, monômeros como o 2-hidroxietil metacrilato (HEMA) com baixo peso molecular e baixa viscosidade (MOSZNER e SALZ, 2007; SIDERIDOU et al., 2002) são necessários. Quando um monômero monofuncional é adicionado a um monômero bifuncional leva a um aumento do grau de conversão (ASMUSSEN et al., 2001). Os monômeros remanescentes que não se converteram durante a reação de polimerização podem ser degradados das cadeias poliméricas e serem lixiviados para o meio bucal (YIU et al., 2006). A adição do monômero metacrilato HEMA no sistema polimérico pode ter um comprometimento da sua estabilidade hidrolítica, pois a hidrólise do grupamento éster ocorre de uma maneira mais acelerada que no Bis-GMA (VAN LANDUYT et al., 2007; YOSHIDA, 2003). A hidrólise pode ocorrer na presença de água, tendo como produto da reação a formação de álcool e ácido carboxilíco e também em sistemas simplificados devido a presença de monômeros ácidos. Não somente o grupo éster pode sofrer hidrólise, mas também fosfatos e grupos carboxílicos presentes em outros monômeros funcionais (VAN LANDUYT et al., 2007). Isso pode resultar na diminuição das propriedades mecânicas e degradação da matriz polimérica. (TAUSCHER et al., 2017).

Além dos monômeros resinosos, as partículas de carga são fundamentais às propriedades mecânicas dos cimentos resinosos. Aumentam a resistência mecânica, reduzem a solubilidade e contração volumétrica de polimerização do cimento resinoso. Entretanto, aumenta a viscosidade do material, o que pode reduzir o escoamento e aumentar a espessura de película (DIAZ-ARNOLD et al., 1999), podendo dificultar o assentamento da peça protética e ocasionar desadaptação marginal (PARAMESWARI et al, 2016). A radiopacidade conferida ao material dentário por partículas inorgânicas também é importante para se obter uma clara localização da interface entre o cimento resinoso e a estrutura dentária. O grau de radiopacidade da molécula é dependente do número atômico, densidade e tamanho dos compostos que constituem o agente radiopaco (FURTOS et al., 2012). O trifluoreto de itérbio possui alto número atômico (z=71) e vem sendo utilizado em materiais comerciais e experimentais, aumentando a radiopacidade, diminuindo a lixiviação das partículas e não alterando o grau de conversão (COLLARES et al., 2010; YOUNG et al., 1996).

1.3 Reação de polimerização dos cimentos fotoativáveis e duais

A reação de polimerização dá-se por meio da Iniciação, Propagação e Terminação. Nos cimentos resinosos fotoativáveis uma pequena quantidade de fotoiniciador é necessária para que ocorra a indução da polimerização (MOSZNER e SALZ, 2007). O sistema canforoquinona/amina (fotoiniciador/co-iniciador) é o mais utilizado nos cimentos ativados pela luz (ELY et al., 2012; VENHOVEN et al., 1996). Nos cimentos de cura dual, dois modos de ativação estão presentes: a fotoativação e a ativação química. Assim, na cura dual a formação do polímero ocorre após a sensibilização do fotoiniciador, ao mesmo tempo que o peróxido de benzoíla reage com a amina terciária, promovendo a ativação química (PFEIFER et al., 2003).

Na etapa de iniciação do sistema fotoiniciador/co-iniciador, os elétrons que estão na órbita mais externa da carbonila (C=O) da canforoquinona se excitam ao absorver um comprimento de onda entre 360 e 510 nm e ocorre uma interação com a amina terciária através da extração de um hidrogênio. Assim, ocorre a transferência de um elétron da amina terciária para a canforoquinona, resultando em um radical amino reativo e um radical cetila inativo. A produção de radicais livres no sistema dual se dá pela oxidação/redução (redox), através de um deslocamento iônico inicial pelo nitrogênio da amina com a ligação com o peróxido de benzoíla. Os radicais livres gerados são transferidos para o monômero que irá reagir com os outros monômeros, na etapa chamada de propagação. (PARK et al., 1999) A terminação ocorre quando os radicais livres reagem e formam uma molécula estável (ANDRZEJEWSKA, 2001). Apesar da correlação direta entre a concentração do co-iniciador e a eficiência da polimerização poder ser considerada, é sabido que pode causar instabilidade de cor devido a eventual formação de produtos oxidativos (JANDA et al., 2004).

1.4 Estabilidade de cor

Cimentos resinosos fotoativáveis geralmente possuem estabilidade de cor da interface adesiva ao longo do tempo, sendo recomendados para a cimentação de restaurações em dentes anteriores (URAL et al., 2016; KILINC et al., 2011; KOISHI et al., 2002). Entretanto, a combinação do sistema iniciador com o ativador nos cimentos resinosos duais gera produtos de oxidação que contribuem para uma maior descoloração (FALKENSAMMER et al., 2013). O problema existente quando cimenta-se restaurações indiretas com cimentos resinosos de cura dual é a descoloração e manchamento das margens da restauração ao longo do tempo, sendo uma das principais razões para efetuar a substituição de restaurações (URAL et al., 2016). A mudança de cor pode ser afetada por fatores intrínsecos relacionados diretamente ao material, como o tipo de carga e fotoiniciador adicionados, composição da matriz resinosa, do sistema de polimerização e a taxa de conversão de ligações duplas de carbono (SCHNEIDER et al., 2008; FALKENSAMMER et al., 2013). Também podendo estar relacionada a fatores extrínsecos que incluem manchas causadas por fumo, comidas e bebidas (SHIOZAWA et al., 2015).

Em estudos *in vitro,* a mudança de cor é geralmente determinada através de um espectrofotômetro e o sistema CIE L*a*b* é um dos sistemas mais comuns de medida de cor. Os dados são transformados em valores quantitativos, determinados pelas coordenadas específicas de cor L*, a* e b*, com os quais calcula-se a mudança de cor (ΔE) (FALKENSAMMER et al., 2013). O ΔE pode ser diretamente afetado pela quantidade de canforoquinona e amina presentes na formulação do cimento (CAMARGO et al., 2015). Além disso, a estrutura química e o modo de polimerização do cimento afetam a estabilidade de cor ao longo do tempo. Cimentos resinosos livres de amina terciária podem alcançar menor mudança de cor independente do modo de ativação (URAL et al., 2016). Alguns sistemas iniciadores como aliltiourea/hidroperóxido de cumeno (T/CH) associado a um co-iniciador como P-octiloxi-fenil-fenil-iodonium hexafluoroantimoniato (OPPI) vêm sendo utilizados com o intuito de melhorar a estabilidade de cor dos cimentos de cura dual, aproximando-se mais com as características ópticas daqueles ativados por luz a fim de serem utilizados também em procedimentos que exigem estética (OEI et al., 2013). A substituição da canforoquinona por iniciadores como o óxido de monoacrilofosfina (TPO) em resinas ativadas por luz também tem demonstrado não interferir no grau de conversão e apresentaram uma melhor estabilidade de cor (ARIKAWA et al., 2009).

1.5 Acrilamidas

As acrilamidas são monômeros com um grupamento amida (RNH-CO) em substituição ao grupo éster (-COOR) presente nos monômeros metacrilatos (ODIAN, 2004). As acrilamidas vêm sendo utilizadas para os desenvolvimento de novos materiais com o intuito de diminuir a hidrólise destes (VAN LANDUYT et al., 2007). Apresentam um composto orgânico carbamida, que é uma amida que possui dois grupos $–NH_2$ ligados a um grupo funcional carbonila (C=O). Isso leva a uma maior estabilidade hidrolítica do que os ésteres devido a baixa reatividade do seu grupo carbonila, mostrando uma melhora em relação aos dimetacrilatos (MOSZNER e SALZ, 2007). A possibilidade de substituição do monômero HEMA por um monômero HEAA com alta reatividade pode resultar em polímeros com alto grau de conversão das ligações duplas de carbono (RODRIGUES et al., 2015; TAUSCHER et al., 2017). Especula-se que seu grupo amida (–NH) pode atuar como co-iniciador através da doação de elétrons e reagindo com a canforoquinona durante o processo de polimerização (RODRIGUES et al., 2015). Há somente um estudo na literatura sobre a adição de N-metil acrilamidas associadas a um monômero uretano dimetacrilto (UDMA) em um cimento resinoso fotoativável, os quais foram avaliados em relação a resistência à flexão e módulo de elasticidade (TAUSCHER et al., 2017). O cimento resinoso fotoativável contendo o monômero N-metil-N-(2-hidroxietil) foi o único que obteve propriedades mecânicas melhores quando comparado ao cimento resinoso contendo HEMA, diferindo da HEAA pela presença de um grupo metila a mais em sua estrutura molecular. Quando maior o espaço entre as cadeias menor a solubilidade e absorção de água, porém há uma diminuição em relação as propriedades mecânicas. Assim, a adição de HEAA a cimentos resinosos experimentais fotoativáveis e duais com diferentes concentrações de amina terciária ainda não foram elucidadas pela literatura, podendo haver uma maior estabilidade hidrolítica da interface adesiva.

OBJETIVO

2.1 Objetivo Geral

Desenvolver cimentos resinosos fotoativáveis e de cura dual contendo hidroxietil acrilamida e avaliar suas propriedades físico-químicas e ópticas.

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Influence of hydroxyethyl acrylamide addition in light- and dual-cured resin cements.

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Abstract

Statement of a problem: Resin cements are frequently used for ceramic restoration and tooth bonding. To enhance hydrolytically stability, the acrylamides have been proposed in literature for longer durability of dental materials.

Purpose: The aim of this study was to develop experimental light-cured and dual-cured resin cements containing N-Hydroxyethyl acrylamide and evaluate the physical-chemical and optical properties.

Material and Methods: Three light-cured (L) and six dual-cured (D) resin cements were formulated. Methacrylate monomers Bis-GMA70%/HEMA30% were added in the control groups (L_{HEMA1}; D_{HEMA0}; $D_{HEMA0.25}$; $D_{HEMA0.}$6) and Bis-GMA70%/HEAA30% in the experimental groups (L_{HEAA0}; L_{HEAA1}; D_{HEAA0}; $D_{HEAA0.25}$; $D_{HEAA0.6}$). Among the light-cured and dual-cured resin cements there was differentiation by the tertiary amine concentration: EDAB – 0 or 1% mol and DHEPT – 0, 0.25 or 0.6% mol, respectively. Ytterbium trifluoride was added as inorganic filler at 40 wt%. The polymerization kinetics of the resin cements were investigated through differential scanning calorimetry with a photocalorimetric accessory, n =3. Softening in solvent (ΔKHN, n =5), radiopacity (n =5), film thickness (n =3) and color stability in distilled water and mineral oil (n=5) were also evaluated. Mechanical properties as ultimate tensile strength (UTS, n =12) and micro-shear bond strength (μSBS, n =12) were analyzed immediately and after 6 months of storage. Results were analyzed by ANOVA, Tukey's test and Student's t test (α=.05).

Results: L_{HEAA1} group had no statistical difference from control group regarding polymerization kinetics, initial hardness, ΔKHN and color stability (*P*>.05). In dual-cured cements, the acrylamide groups presented lower degree of conversion and initial hardness and higher ΔKHN when compared to the $D_{HEMA0.6}$ group, which obtained higher rate of polymerization (*P*<.05). There was no statistical difference in relation to radiopacity and film thickness (*P*>.05) for all resin cements. In relation to color stability in water storage, the dual-cured cements with HEAA obtained a higher color change compared to the methacrylates. Immediate mechanical properties were lower for acrylamide groups (*P*<.05), however they got long-term hydrolytic stability without difference from L_{HEMA1} and $D_{HEMA0.6}$ groups within each mode of polymerization (p<.05).

Conclusions: HEAA alone is not effective in polymerization when there is no tertiary amine present. The addition of HEAA monomer negatively affected the properties of the dual-cured resin cements. The light-cured resin cement L_{HEAA1} did not differed the physical-chemical and optical properties compared to control, however with long-term hydrolytic stability.

Clinical Implications: The success of prosthetic treatment depends on the clinical longevity of resin cements. The results of the study indicate that acrylamides increases mechanical properties over time independently of curing system mode, with good hydrolytic stability.

Keywords: acrylamides, hydroxyethyl methacrylate, resin cements.

INTRODUCTION

Resin cements have become popular in dentistry due to their ability to bond to tooth and to the restoration.[1,2] The mode of activation through light-cured or dual-cured resin cements were the most used in clinical practice.[1,3,4] Examples of their clinical applications include adhesion of laminate veneers, onlays, inlays, crowns, bridges and intra-canal posts.[1] Resin cements are the material of choice because of their excellent esthetics, favorable mechanical properties and strong bond to the tooth structure.[4] The composition of the polymeric matrix can influence the physical, chemical and optical properties of the resin cements.[5-11]

Resin cements are usually based on methacrylate monomers, which the presence of Bisphenol A glycidyl dimethacrylate (Bis-GMA) in the polymeric matrix is known to be responsible for improving the mechanical properties.[12] The monomer 2-Hydroxyethyl methacrylate (HEMA) often present in resin cements composition[13] has a concern about the hydrolytic degradation over time due to presence of ester group.[14,15] The presence of HEMA allows an increasing of the water uptake[16], which may result in a decrease of the mechanical properties and degradation of the polymeric matrix.[13] Also present in the polymeric matrix, the camphorquinone is usually used as initiator in various resin cements and requires an amine co-initiator component, which suffers oxidation over time.[17,18] A dual polymerization usually involves free-radical initiators such as benzoyl peroxide that reacts with a tertiary amine.[19] The amines form byproducts during the polymerization reaction, which may cause a yellowish to brown discolorations[17], affecting the color stability of resin cements.[20,21] Recently, the challenge concern of resin cements is prevent the hydrolytic degradation[14] and find new formulations that could eliminate the tertiary amine as co-initiator[22] that leads to an unfavorable color change.[23] Even the light-cured resin cement has higher color stability than dual-cured cement[24], which its mode of activation will influence the degree of conversion.[25-27]

Potential alternative monomers to HEMA have been studied to improve dental resin properties.[13,26,27] Hydroxyethyl acrylamide (HEAA) have an organic compound carbamide that has two $–NH_2$ groups joined by a carbonyl (C=O) functional group. This amide are more hydrolytically stable than esters considering the lower reactivity of their carbonyl group.[26] It was postulated that the –NH group in acrylamide might act as a tertiary amine co-initiator in the polymerization process.[27] Such co-initiator would reduce the need for those components that contribute with oxidative color changes.[28] Due to carboxylate groups and the similarity to the amino acids that compose collagen fibrils, the acrylamides could facilitate hydrogen bond between collagen and amide groups (N-H).[29]

Only one study so far has tested acrylamides in a light-cured resin cement compared to HEMA.[13] The polymer matrix was composed of urethane dimethacrylate (UDMA) and N-methyl acrylamide, which only flexural strength and flexural modulus of elasticity were evaluated. Furthermore, the dual-cured resin cements with addition of acrylamide have not been attempted before in the literature. The aim of this study was to develop experimental light-cured and dual-cured resin cements containing hydroxyethyl acrylamide and evaluate the physical-chemical and optical properties. The null hypothesis is that the addition of hydroxyethyl acrylamide does not influence resin cement properties.

MATERIALS AND METHODS

Formulation

Three experimental light-cured and six experimental dual-cured resin cements were formulated mixing Bis-GMA (Bis-phenol A diglycidyl dimethacrylate) and HEMA (2-Hydroxyethyl methacrylate); and, Bis-GMA and hydroxyethyl acrylamide (HEAA) in a 70:30 mass ratio (Bis-GMA:HEMA and Bis-GMA:HEAA) (Table1). The initiation system of light-cured resin cements was camphorquinone (1 mol%) and ethyl 4-dhymetyl aminobenzoate (EDAB) (1 mol%). Only in the group L_{HEAA0}, the tertiary amine (EDAB) was not added. The activation/initiation system of dual-cured resin cements was composed by camphorquinone (1 mol%), benzoyl peroxide (1 mol%) and NN-dihydroxyethyl p-toluidine (DHEPT). The tertiary amine DHEPT was added in different concentrations: 0, 0.25 or 0.6 mol%. The inhibitor BHT (butylated hydroxytoluene) was added at 0.01 wt% to all resin cements. All of these components were purchased from Sigma-Aldrich (Aldrich Chemical Co). The dual-cured resin cements were separated in base paste and catalyst paste. Ytterbium trifluoride (Nanostructured & Amorphos Materials) was added as filler at 40 wt% for all luting materials. Initiators and filler were hand mixed with monomers and ultrasonicated for 480 s. To perform resin cements samples photoactivation, except for the polymerization kinetics test, a light-emitting diode unit (Radii Cal., SDI Ltd) was used. An irradiation value of 1200 mW/cm^2 was confirmed with a digital power meter (Ophir Optronics).

Table 1. Composition of light-cured and dual-cured resin cements.

Curing mode	Groups	Bis-GMA[#]	HEMA[#]	HEAA[#]	CQ[*]	EDAB[*]	DHEPT[*]	PB[*]
Light-cured	L_{HEMA}	70%	30%	-	1%	1%	-	-
	L_{HEAA0}	70%	-	30%	1%	-	-	-
	L_{HEAA1}	70%	-	30%	1%	1%	-	-
Dual-cured	D_{HEMA0}	70%	30%	-	1%	-	-	0.6%
	$D_{HEMA0.25}$	70%	30%	-	1%	-	0.25%	0.6%
	$D_{HEMA0.6}$	70%	30%	-	1%	-	0.6 %	0.6%
	D_{HEAA0}	70%	-	30%	1%	-	-	0.6%
	$D_{HEAA0.25}$	70%	-	30%	1%	-	0.25%	0.6%
	$D_{HEAA0.6}$	70%	-	30%	1%	-	0.6 %	0.6%

[*]mol [#]wt; Bis-GMA (Bisphenol A glycidyl dimethacrylate); HEMA (2-Hydroxyethyl methacrylate); HEAA (hydroxyethyl acrylamide); CQ (Camphoroquinone); EDAB (ethyl 4-dhymetyl aminobenzoate); DHEPT (NN-dihydroxyethyl p-toluidine); PB (benzoyl peroxide).

Degree of conversion and polymerization kinetics

The degree of conversion (DC) and polymerization kinetics for each experimental resin cement was evaluated via differential scanning calorimetry (DSC; DSC-Q2000, TA Instrument Co) with a photocalorimetric accessory (PCA). The intensity and wavelength of the PCA was adjusted to 100 mW/cm^2 and 390-500 nm, respectively. Three samples per group (n=3)[27] with approximately 16 mg were polymerized in open aluminum DSC pans and covered with a quartz lid. An additional empty aluminum pan was used as control. The lamp was switched on for 3 to 7 min and heat flow was recorded. The analysis was performed with a nitrogen flow rate of 50 mL/min. Assuming that the value of the heat involved is proportional to the reacted molar amount, the degree of conversion was determined according to the following equation (1):

$$\alpha\ (\text{mol }\%) = 100\ ([M]_0 - [M] / [M]_0) = 100\ Q / (\Delta H_{p,0} / \Delta H_p)\ Q_{tot}$$

where $\Delta H_{p,0}$ (kJ mol^{-1}) corresponds to the heat of polymerization for a total conversion, ΔH_p (kJ mol^{-1}) the heat of polymerization obtained by the apparent area of the curve that corresponds to the total heat of reaction Q_{tot} (J g^{-1}), and Q corresponds to the heat released as partial area under the curve of a time, t. The $\Delta H_{p,0}$ value for a double bond of methacrylate has been reported to be -56 J mol^{-1} , and for acrylamides, - 82.9 J mol^{-1}.[30,31] The rate of polymerization (Rp) is proportional to the heat flow released in the isotherm as a function of irradiation time (t). Thus, Rp (mmol.g^{-1} .s^{-1}) at any point during the reaction can be derived from the heat flow using the $\Delta H_{p,0}$ of the monomer according to the following equation (2):

$$Rp = (dH/dt)\ .\ (M/\ \Delta H_{p,0}\ .\ n)$$

Where dH/dt is the heat flow in J mol^{-1} s^{-1}, M the concentration of the monomer, and n is the number of double bonds per molecule of monomer.

Softening in solvent

Five specimens of each experimental resin cement (n=5) were obtained using a polyvinylsiloxane matrix (5 mm diameter and 1 mm thickness) and photoactivated for 40 s on each side, with exception of group L_{HEAA0} that was photoactivated for 60 s. Subsequently, they were embedded in acrylic resin and polished using 1200-2000 grit silicon carbide sandpapers before Knoop hardness measurements (KHN). Thereafter, they were stored at 37 ºC for 24 hours. The specimens were subjected to a hardness test in which three indentations (10 g/5 s), 100 µm equidistant from each other, were assessed using a digital hardness

Knoop tester (HMV 2, Shimadzu). Hardness was calculated according to a previous study.[32] The initial Knoop hardness number (KHN_1) was recorded, the specimens were subjected to softening in ethanol 70 % at 37 ºC for 2 hours, and the final hardness (KHN_2) was then determined. The percentual hardness reduction (ΔKHN) between KHN_1 and KHN_2 was calculated.

Radiopacity

The resin cements samples (10 mm (± 0.5 mm) diameter and 1 mm (± 0.1 mm) thickness) were radiographed with aluminum stepwedge, which as used as reference based on ISO 4049:2009.[33] The radiographic images were acquired with a phosphorous plate system (VistaScan; Dürr Dental GmbH & Co) and a X-ray machine operating at 70 kV and 8 mA. The exposure time was 0.4 s and focus-to-object distance was 40 cm. All exposed plates were scanned immediately after exposure. The resulting images were transferred in a tiff image files to a personal computer for further analysis with the Image J software (Wayne Rasband., National Institutes of Health). On each image, an area of interest with a size of 25 mm^2 was selected on each specimen and step of aluminum stepwedge image and the reference mean gray values were calculated. Gray values from material were pooled and the mean (SD) gray value of each material was calculated.

Film thickness

The resin cements (n=3) were hand-mixed. The film thickness was determined based on ISO 4049:2009 requirements.[33] Two square glass, having a contact surface area of 200 ± 25 mm^2 and a thickness of 5 mm were used. The combined thickness of the two optically stacked flat glass plates was initially measured using a digital caliper. The upper plate was removed and 0.1 ml of the mixed cement was placed in the center of the lower plate. The upper plate was positioned centrally in the same orientation as in the original measurement. A vertical load of 150 N was applied immediately for 180 s and after that photoactivated for 80 s. The final measurement was made immediately after photoactivation and the subtraction of the thickness of final and initial measurements were made.

Color Stability

The same specimens used in radiopacity have been subjected to color stability analysis. Colour measurements were performed by a spectrophotometer UV-Vis-NIR CARY 5000 (Agilent Technologies) equipped with a diffuse reflectance accessory DRA-1800 Integrating Sphere. The samples were positioned over a standard white background. A dark mask containing a circular slit measuring 4 mm in diameter was placed over the infiltrated surface to set the limits of analysis. The colour of each sample (n = 5) was measured and quantified in terms of three coordinate values (L*, a* and b*), as established by the Commission Internationale de l`Eclariage (CIE). The colour of the resin cements was assessed and recorded under standardized conditions according to CIE L*a*b* system. The overall changes in colour impression (ΔE) were calculated using the following formulas:

$\Delta L = L \text{ (6 months)} - L \text{ (baseline)}$

$\Delta a = a \text{ (6 months)} - a \text{ (baseline)}$

$\Delta b = b \text{ (6 months)} - b \text{ (baseline)}$

$\Delta E = ((\Delta L^2) + (\Delta a^2) + (\Delta b^2))^{1/2}$

Micro-shear bond strength

IPS e.max CAD pre-milled blocks (Ivoclar Vivadent) were used. Sections were prepared from the CAD/CAM blocks using a precision sectioning saw (LowSpeedSaw) with a thickness of 1 mm. Block surfaces were measured with a roughness meter and were flattened under water colling with 600- and 1200-grit silicon carbide sandpaper. The specimens were positioned in a polyvinylchloride cylinder with a dimension of 2.5 cm x 1.7 cm and embebed in an acrilic resin (JET; Classico). The sections from CAD/CAM blocks were randomly divided into nine groups. All the surfaces of ceramic were etched with 10% hydrofluoric acid gel (Condac porcelana 10%., FGM) for 20 s and rinsed with distilled water for 20 s and air-dried. A silane coupling agent (RelyX^{TM} Ceramic Primer., 3M ESPE) was applied on the surface for 20 s andair-blown for 5 s. An adhesive resin was applied (Adhesive, Adper^{TM} Scotchbond^{TM} Multi-Purpose, 3M ESPE) and light-cured for 20 s. The custom-made polyvinylsiloxane matrix was used to produce 12 resin cement cylinders with 1mm of diameter and 1mm of height. Each cylinder was ligth-cured for 40 s. Half of specimens were stored in distilled water at 37^{o}C for 7 days and the other specimens for 6 months. The specimens were tested using a universal testing machine (EZ-SX; Shimadzu) and loaded at a crosshead speed of 1.0 mm/min until fracture occurred with a 0.2mm diameter stainless steel wire placed as close as possible to the bonded interface. Micro-shear bond strength was calculated by dividing the maximum load at failure (N) with the bonding area (mm^2) and recorded in MPa. Mean values and standard deviations were calculated. Failure modes were evaluated 40x under a stereomicroscopy. Failure was assessed as adhesive, cohesive within the resin cement, or mixed.

Ultimate tensile strength test

Twelve samples per group were prepared in a metallic matrix with an hourglass design measuring 8 mm long, 2 mm wide and 1 mm thick, with a cross-sectional area of 1 mm^2 at the constriction. The resin cements were light-cured for 30 s on each side, except for the group L_{HEAA0} that was photoactivated for 40 s on each side. The samples were stored in distilled water at 37^{o}C for 24 h and 6 months before testing. Before being tested they were fixed with a cyanoacrylate adhesive in a metallic device, and the tests were performed in a universal testing machine (EZ-SX; Shimadzu) at a crosshead speed of 1mm/min with values expressed in MPa.

Statistical analysis

The normality of the data was evaluated using the Shapiro-Wilk test. One-way ANOVA and Tukey's post hoc test was performed to evaluate degree of conversion, polymerization rate, radiopacity and film thickness. The difference between KHN1 and KHN2 was assessed by the paired Student's t-test. KHN1, ΔKHN, ΔE were assessed by one-way ANOVA. For micro-shear bond strength and ultimate tensile strength a two-way ANOVA was performed. The failure patterns were evaluated by stereomicroscopy. A level of significance of .05 was considered for all tests.

RESULTS

Figures 1 and 2 shows the degree of conversion and polymerization kinetics of light-cured and dual-cured resin cements, respectively. Among light-cured resin cements, the DC of L_{HEAA1} (35.9%) was not significantly different from control L_{HEMA1} (40.64%) (P=.09). L_{HEAA0} showed the lower value compared to the others light-cured groups (P<.05). The rate of polymerization (Rp) for L_{HEMA1} and L_{HEAA1} groups were comparable (P=.296), but for the L_{HEAAO} group a statistically lower Rp was found (P<.001). For dual-cured resin cements, $D_{HEMA0.6}$ had the highest DC and Rp values (P<.05). Acrylamide groups did not differ significantly between them independently of tertiary amine concentration both for DC and Rp (P>.05).

Maximum degree of conversion (DC max) and polymerization kinetics values, hardness before (KHN_1) and after (KHN_2) immersion in ethanol and the percentage reduction between KHN_1 and KHN_2 (ΔKHN) are shown in Table 2. The group L_{HEAA1} did not differ from control group regarding DC max (P>.05) In dual-cured resin cements, the groups containing HEAA had no statistical difference between them (P>.05), while the methacrylate groups had lower DC max than $D_{HEAA0.6}$ (P=<.05). The groups L_{HEMA1} and L_{HEAA1} had higher KHN1 value than the L_{HEAA0} resin cement (P=.605 and P<.01, respectively). The absence of tertiary amine in light-cured group showed higher degradation (ΔKHN) (P<.05). $D_{HEMA0.6}$ group had the highest value for KNH1 ($D_{HEMA0.6} > D_{HEMA0,25} = D_{HEAA0} = D_{HEAA0.25} = D_{HEAA0.6} > D_{HEMA0}$– P<.05). $D_{HEMA0.6}$ had the lowest degradation for dual-cured groups (ΔKHN) (P<.05). Significant differences between the initial and final hardness values for each group independently of activation mode were observed (P<.001).

Table 2. Mean and standard deviation values of degree of conversion (DC) and polymerization rate (Rp). Hardness of the experimental light-cured and dual-cured resin cements before (KHN1) and after the immersion in solvent (KHN2) and the percentage reduction of Knoop hardness after ethanol immersion (ΔKHN).

Curing mode	Groups	DC max (%)	Rp (mmol.g^{-1}.s^{-1})	KHN1	KHN2	ΔKHN (%)
Light-cured	L_{HEMA1}	41.47 (1.87)^{A}	5.20 (0.59)^{A}	21.66 (1.46)^{Aa}	10.27 (1.38)^{b}	52.02 (8.70)^{A}
	L_{HEAA0}	31.2 (2.51)^{B}	0.30 (0.03)^{B}	2.43 (0.53)^{Ba}	0.84 (0.14)^{b}	64.35 (5.46)^{B}
	L_{HEAA1}	36.52 (2.74)^{AB}	5.73 (0.33)^{A}	22.66 (2.31)^{Aa}	9.10 (1.71)^{b}	59.53 (6.35)^{AB}
Dual-cured	D_{HEMA0}	40.26 (5.91)^{B}	0.44 (0.06)^{C}	8.32 (2.25)^{Ca}	2.72 (1.73)^{b}	68.37 (13.56)^{B}
	$D_{HEMA0.25}$	40.33 (1.63)^{B}	0.65 (0.08)^{B}	15.49 (2.32)^{Ba}	4.8 (1.16)^{b}	69.22 (3.89)^{B}
	$D_{HEMA0.6}$	41.05 (2.28)^{B}	1.30 (0.03)^{A}	21.22 (0.45)^{Aa}	10.3 (0.9)^{b}	51.46 (4.72)^{C}
	D_{HEAA0}	48.42 (0.7)^{AB}	0.66 (0.08)^{BC}	14.56 (1.18)^{Ba}	2.87 (1.05)^{b}	79.92 (8.03)^{A}
	$D_{HEAA0.25}$	48.12 (1.27)^{AB}	0.79 (0.15)^{B}	13.67 (2.08)^{Ba}	2.33 (0.8)^{b}	78.54 (5.01)^{B}
	$D_{HEAA0.6}$	49.4 (3.25)^{A}	0.88 (0.12)^{B}	12.25 (1.04)^{Ba}	3.6 (0.86)^{b}	71.12 (4.78)^{B}

Different capital letters indicate statistically significant difference in the same column ($P<.05$).
Different small letters indicate statistically significant difference in the line within the same test ($P<.05$).

The results of radiopacity and film thickness are shown in Table 3. Both light-and dual-cured showed no statistically difference in all groups ($P>.05$).

Table 3. Mean and standard deviations of radiopacity and film thickness of light- and dual-cured resin cements.

Curing mode	Groups	Radiopacity (mmAl)	Film Thickness (μm)
Light-cured	L_{HEMA1}	0.99 (0.62)^{A}	46.66 (5.77)^{A}
	L_{HEAA0}	1.33 (0.19)^{A}	46.66 (5.77)^{A}
	L_{HEAA1}	1.48 (0.28)^{A}	40.00 (10.00)^{A}
Dual-cured	D_{HEMA0}	1.02 (0.17)^{A}	23.33 (5.77)^{A}
	$D_{HEMA0.25}$	1.08 (0.27)^{A}	36.66 (5.77)^{A}
	$D_{HEMA0.6}$	1.16 (0.62)^{A}	36.66 (11.54)^{A}
	D_{HEAA0}	1.23 (0.35)^{A}	23.33 (5.77)^{A}
	$D_{HEAA0.25}$	1.12 (0.20)^{A}	26.66 (11.54)^{A}
	$D_{HEAA0.6}$	1.11 (0.32)^{A}	33.33 (5.77)^{A}

Different capital letters indicate statistically significant difference in the same column ($P<.05$).

Table 4 presents the results of color stability of the resin cements evaluated after 6 months of storage in distilled water and mineral oil. In the light-activated resin cements groups stored in distilled water, the control group with methacrylate had the lowest color change value, with no statistical difference from L_{HEAA1} group (*P*=.774). In dual-cured cements, $D_{HEMA0.6}$ and all groups containing HEAA showed the greatest changes in colour (*P*<.05). Colour changes in mineral oil storage showed no statistical differences in both resin cements, except for the L_{HEAA1} group (ΔE=6.97, *P*<.05). Based on analysis of changes in lightness (L*), the methacrylate groups proven to lighten up, whereas most acrylamide groups darkened in distilled water. Comparing changes in reddish-green hue (a*) and bluish-yellow hue (b*), the methacrylate groups varied less in mineral oil. In distilled water, all acrylamide groups had greater changes towards the red color. In dual-cured resin cements, the methacrylate and acrylamide groups with higher tertiary amine concentration had greater changes in direction to yellow color. Figure 3 shows the samples of resin cements after 6 months of distilled water and oil mineral storage.

Table 4. Mean and standard deviation of ΔL*, Δa*, Δb* and ΔE of luting materials evaluated after 6 months in distilled water and mineral oil.

Curing mode	Groups	**Distilled water**				**Mineral oil**			
		ΔL*	Δa*	Δb*	ΔE	ΔL*	Δa*	Δb*	ΔE
Light-cured	L_{HEMA1}	1.50	-0.24	-0.41	2.55 (1.41)^{A}	-1.45	0.14	-0.29	1.74 (0.89)^{A}
	L_{HEAA0}	6.59	0.05	1.07	6.74 (2.85)^{B}	-0.29	0.40	-0.89	2.61 (1.37)^{A}
	L_{HEAA1}	-3.24	0.84	0.46	3.49 (1.95)^{AB}	5.80	0.18	0.05	6.97 (1.86)^{B}
Dual-cured	D_{HEMA0}	2.43	1.53	-1.56	4.81 (1.18)^{A}	-3.05	0.16	-1.88	3.69 (1.65)^{A}
	$D_{HEMA0.25}$	1.46	1.19	-0.23	5.22 (1.46)^{AB}	-1.35	0.16	-0.80	4.44 (1.17)^{A}
	$D_{HEMA0.6}$	2.27	1.78	3.32	5.83 (1.63)^{ABC}	-3.09	0.55	-1.93	4.39 (1.64)^{A}
	D_{HEAA0}	-3.49	3.06	-0.19	6.70 (0.61)^{ABC}	-1.73	0.48	1.61	3.73 (1.20)^{A}
	$D_{HEAA0.25}$	-0.33	1.89	0.11	7.49 (1.04)^{BC}	-0.58	0.70	-0.22	5.38 (1.35)^{A}
	$D_{HEAA0.6}$	-2.87	3.89	6.24	8.03 (1.08)^{C}	0.30	0.80	2.80	5.40 (1.02)^{A}

Different capital letters indicate statistically significant difference in the same column (*P*<.05).

The averages and standard deviations for ultimate tensile strength (UTS) and micro-shear bond strength (μSBS) are shown in Table 5. Immediate UTS and μSBS for light-cured resin cements were significantly lower for all acrylamide groups (*P*<.05). There was a statistically significant interaction between storage time and resin cements (*P*<.001 and *P*=.05 for UTS and μSBS, respectively). After 6 months of water storage, the L_{HEAA1} group showed no statistical difference to L_{HEMA1} (*P*>.05) for both tests. Among the dual-cured resin cements, immediate UTS were lower for all acrylamide groups (*P*<.001). $D_{HEMA0.6}$ showed the highest immediate μSBS value (*P*<.05). There was a statistically significant interaction between storage time and resin cements (*P*<.001 for UTS and μSBS). All acrylamide groups had long-term storage UTS and μSBS values higher than initial ones (*P*<.001), except for the D_{HEAA0} in UTS, with no statistical difference from $D_{HEMA0.6}$ group (*P*>.05). Failure mode of light-cured and dual-cured resin cements is shown in Figure 4 and was predominantly adhesive between ceramic and resin cement for all resin cements.

Table 5. Mean and standard deviation values (immediate and after 6 months of water storage) of the UTS test and μSBS test of light- and dual-cured resin cements.

Curing mode	Groups	UTS (24h)	UTS (6m)	μSBS (1w)	μSBS (6m)
Light-cured	L_{HEMA1}	35.93 (6.84)^{Aa}	31.83 (5.76)^{Aa}	15.64 (3.74)^{Aa}	15.25 (7.09)^{Aa}
	L_{HEAA0}	6.25 (2.02)^{Cb}	19.06 (4.85)^{Ba}	7.92(4.78)^{Ba}	8.14 (2.79)^{Ba}
	L_{HEAA1}	15.82 (2.91)^{Bb}	29.00 (8.21)^{Aa}	8.65 (3.91)^{Bb}	13.89 (5.19)^{Aa}
Dual-cured	D_{HEMA0}	30.28 (7.09)^{Ba}	19.05 (2.83)^{Bb}	3.69 (0.88)^{Ca}	4.98 (0.95)^{Ba}
	$D_{HEMA0.25}$	42.90 (5.69)^{Aa}	23.86 (4.34)^{Ab}	6.52 (3.00)^{Ba}	7.24 (1.51)^{Ba}
	$D_{HEMA0.6}$	40.00 (10.30)^{Aa}	26.81 (3.71)^{Ab}	10.83 (4.90)^{Aa}	12.26 (2.5)^{Aa}
	D_{HEAA0}	19.62 (2.96)^{Ca}	22.56 (5.84)^{Aa}	4.26 (0.81)^{Bb}	13.8 (5.25)^{Aa}
	$D_{HEAA0.25}$	19.00 (2.81)^{Cb}	23.67 (6.05)^{Aa}	4.65 (1.52)^{Bb}	17.26 (4.86)^{Aa}
	$D_{HEAA0.6}$	20.81 (7.00)^{Cb}	24.91 (4.54)^{Aa}	4.72 (2.17)^{Bb}	14.90 (3.82)^{Aa}

Different capital letters indicate statistically significant difference in the same column (*P*<.05).
Different small letters indicate statistically significant difference in the line within the same test (*P*<.05).

DISCUSSION

Dental resin cements are composed by resin monomers, initiators/co-initiators, inhibitors and inorganic fillers. Light-cured and dual-cured resin cements containing hydroxyethyl acrylamide (HEAA) with the presence or not of tertiary amine were evaluated. In this work, the polymerization process was affected depending on the chemical component used. Physicochemical and optical properties were evaluated and the addition of HEAA influenced the polymerization behavior, immediate and long-term mechanical properties and color stability of the experimental resin cements. Thus, the null hypothesis must be rejected.

In light-cured resin cements a methacrylate group with absence of ethyl 4-dhymetyl aminobenzoate (EDAB) was not formulated for comparison, as it has been reported in literature, which does not polymerize.[29] The dual-cured groups were formulated considering the less amount of NN-dihydroxyethyl p-toluidine (DHEPT) required for chemical polymerization in acrylamide group. Thus, the corresponding groups with methacrylate and different tertiary amine concentration were formulated as controls. The groups D_{HEMA0} and D_{HEAA0} did not polymerize under chemical conditions, only by light-activation. However, they were submitted to the tests in order to see how the acrylamide group (possibly co-initiator) with free-amine initiator would behave. Since more color stable dual-cured resin cement has been proposed with a self-cure initiator system without tertiary amine already.[22] In dual-cured systems, radical production in the redox system appears to proceed via initial ionic displacement by the nitrogen of the amine on the peroxide linkage.[32] Free radicals are transferred to the monomer, which will react with others monomers, until the formation of a stable molecule.[5] Probably the nitrogen present in HEAA cannot initiate the autopolymerization alone, requiring the presence of an amine co-initiator, however, in lower concentration.

The binary CQ/amine photoinitiator/co-initiator system is the most common combination used in commercially available products that are activated by visible light.[18] Also, a dual polymerization usually involves free-radical initiators such as benzoyl peroxide that reacts with a tertiary amine.[19] Is known that DC was influenced by the CQ:amine ratio.[23] The amount of amine present in resin cements significantly influenced the results. These results are related to the fact that sufficient amine is necessary to act as hydrogen donor for CQ and start the polymerization process.[23] Thus, the absence of EDAB in light-cured groups leads to a reduced DC and Rp and a longer period of time to complete the monomer conversion, corroborating to a previous study.[29] Instead, the methacrylate and acrylamide groups with tertiary amine obtained similarly DC and Rp. Furthermore, decreasing concentrations of tertiary amine (DHEPT) in methacrylate-based dual-cured resin cements, the Rp has been also decreasing from 1.30 to 0.44 mmol.g^{-1}.s^{-1}. The acrylamide groups, however, maintained the Rp independently of amine concentration from 0.88 to 0.66 mmol.g^{-1}.s^{-1}. The results did not reveal a difference in the reactivity between HEMA and HEAA. Nevertheless, from the literature is well known that acrylamides were more reactive than HEMA.[13,29] These studies evaluated the polymerization kinetics of HEAA and N-methyl acrylamides in dental adhesives as monofunctional monomer or in association with another dymethacrylate. Instead, this study has the presence of filler content and did not analyze the homopolymer and co-polymer separately. The filler increases the viscosity of resin cement leading to a lower degree of conversion, probably due to reduced mobility of the monomers in viscous materials.[6] In general, the maximum degree of conversion reached by resin cements is around 60%,[7-9] whereas the resin cements analyzed by DSC-PCA in this study obtained lower values.

Highly cross-linked polymers are more resistant to degradation and solvent uptake, whereas linear polymers present more space and pathways for solvent molecules to diffuse within their structure.[36] The absence or decrease in tertiary amine concentration reduced initial hardness for acrylamide group in light-cured and dual-cured resin cements containing methacrylate monomer. However, despite different concentrations in dual-cured acrylamide groups, there was no difference in the initial hardness, but still are lower than $D_{HEMA0.6}$ group. If ethanol have the capacity to penetrate the polymer network, the efficiency of secondary molecular interactions could be reduced, leading to leaching of unreacted monomers and higher degradation rate.[36] Based on the overall results of this study, it is possible to affirm that with the higher Rp, a greater initial hardness and a lower degradation value of resin cements are forthcoming to appear. Furthermore, a higher degradation in acrylamide groups is probably due to a linear polymer formation and more HEAA monomers converted than Bis-GMA due to high reactivity of HEAA.[29]

Chemical composition, components of the organic matrix and the amount and atomic weight of the filler influences the radiopacity.[37] Ytterbium trifluoride (YbF_3) was added as filler in all resin cements. Due to higher atomic weight (z=71), the element can absorb or reflect more X-rays, leading to an opaque radiographic image.[38] In this study all groups had no statistical difference in radiopacity, since all resin cements received the same amount of filler. The addition of YbF_3 at 40 wt% was due to higher acrylamide viscosity,[13] besides most commercial resin cements have 50-60% of filler content.[4] Some studies also added a lower filler content around 25 wt% and mechanical properties were comparable to the ones obtained with thio-urethane addition to the modified commercial materials.[9,10] It was expected that the low water solubility of YbF_3

could prevent the long-term degradation of dental cements.[39] Also, a higher refractive index could decrease the absorption of emitted light trough the reflection of photons at the surfaces.[40] YbF_3 has a refractive index of approximately 1.5,[40] which allow more light pass trough the resin cement being probably the reason for the resin cements polymerization in amine-free groups D_{HEMA0} and D_{HEAA0}. In addition, the benzoyl peroxide generates radicals that acts as initiator with the possibly interaction of nitrogen from acrylamide.[32] In relation to film thickness, the ISO standards require a thickness no grater than 50 µm for resin-based cements.[35] Besides acrylamides are more viscous than HEMA[13] there was no statistical difference in both types of resin cement. Thus, all resin cements are in accordance to ISO 4049 limits.

Light-cured resins generally have acceptable initial color and color stability after polymerization.[24] Nevertheless, the dual-cured resins have a much darker initial yellow color and a larger color-shift (ΔE*) for a darker shade of yellow after polymerization.[22] Color stability is influenced by intrinsic factors such as composition of resin matrix, conversion rate and type of initiator.[11] Previous studies report $\Delta E \leq 3.3$ as clinically acceptable.[20,22] The color changes (ΔE) in the present study ranged from 2.55 to 6.74 in light-cured resin cements and 4.81 to 8.03 in dual-cured resin cements when stored in distilled water for 6 months. Usually, the storage time of color stability is shorter[28] or in most cases induced by accelerated ageing.[20,22] Accelerated ageing protocol however cannot reliably simulate the clinical situation.[17] In this study, all the samples surfaces were in contact with water during the whole evaluated period, which is considered to be a greater challenge when compared to clinical situation. The mineral oil storage could represent the changes in color considering internal surfaces that are not in contact with water. Only L_{HEMA1} reached the ΔE that is clinically acceptable.

However, L_{HEMA1} and L_{HEAA1} showed no statistical difference and according to previous study, clinicians are more tolerant of shade mismatch in a clinical scenario, than in vitro conditions, which mean acceptability tolerance for 95 % of observers was 4.0 ΔE units.[41] The absence of EDAB in acrylamide light-cured resin cement led to a greater color change due to low monomer conversion and degradation of polymer matrix. Incompletely converted monomer undergoes further oxidation that generates a yellowing of the resin.[23] Leaching of the monomer can occur if significant amounts of unreacted monomers remain in a poorly polymerized resin mass, which leads to porosity and enhanced potential for extrinsic staining.[21] Storage in distilled water showed higher ΔE values compared to mineral oil, which may prevent the effects of water.[42] The $L_{HEAA1,}$ group showed the highest ΔE (6.97) in mineral oil storage, however it can be attributed to increased lightness (ΔL* = 5.8), which became more opaque explaining the greater color variation.

The high initial color and color shift is greatly influenced by the initiator system such as camphorquinone and amine initiator in light curing mode and tertiary aromatic amine and benzoyl peroxide in dual curing mode. Color changes are more evident due to tertiary aromatic amine that are more like to oxidize.[17] The ΔE was dependent on the amount of amine, i.e., the higher the amine content, the higher is yellowing effect.[23] As the amine concentration decreased in dual-cured groups, less color changes were observed. Composites with higher viscosity had higher b* values, i.e. were more yellow than materials with lower viscosity in the baseline color evaluation. Increasing co-monomer viscosity might reduce the efficiency of phoinitiator diffusion through the reaction medium leaving excited but unreacted CQ molecules to return to their original, yellow state.[23] Acrylamide groups in dual-cured resin cements had a considerable color change, probably due to benzoyl peroxide and tertiary amine interaction, where the acrylamide also presents a nitrogen in its molecular structure, which leads to the formation of a radical production in the redox system,[32] leading to a higher color change.

Addition of HEAA in light- and dual-cured resin cements showed lower initial mechanical properties. However, the acrylamide groups increased the mechanical properties after storage. The storage time of this work was 6 months, nevertheless it is expected that 1 year of water storage could lead to a higher degradation in methacrylate groups, which are prone to hydrolytic degradation.[14] A higher water sorption can facilitate the degradation of the polymer matrix and also leads to a decrease of the mechanical properties. HEMA is characterized by low reactivity and lacking hydrolytic stability.[15] A luting composite was formulated based on the monomer N-methyl-N (2-hydroxyethyl) acrylamide, which has an additional methyl group compared to HEAA in this study, being an alternative to increase the initial mechanical properties. The additional methyl group tends to form a cross-linked polymer, instead of a linear polymer, but high hydrophilicity of this monomer may compromise the durability.[13]

Acrylamides seems to have a function in polymerization. The homopolymer HEAA is more reactive than HEMA and played an important role in the earlier stages of polymerization of acrylamide groups and followed by Bis-GMA conversion in the later stages.[29] It can result in unreacted double bonds of dymethacrylate Bis-GMA, which could link to HEAA in later stages of polymerization. In dual-cured resin cements autopolymerization could continues until two weeks, even after light polymerization has been completed and the rate of dual polymerization differs according to the time after mixing and tends to increase with time.[25] It has been speculated that a delay in light activation would enhance the resin cement properties.[26] Thus, the autopolymerization promoters are allowed to react at some extent before being entrapped by the polymeric chains as soon as the photo-activation begins.[27]

The results of the present study suggest that HEAA alone is not effective in polymerization when there is no tertiary amine present. The addition of HEAA monomer negatively affected the properties of the dual-cured resin cements. The light-cured resin cement L_{HEAA1} did not differed the physical-chemical and optical properties compared to control, however with long-term hydrolytic stability. Less degradation of the polymeric matrix is desired for a longer durability of the bond interface between restoration and tooth structure.

CONCLUSIONS

Physicochemical and optical properties of light-cured and dual-cured resin cements were influenced by N-Hydroxyethyl acrylamide addition. The dual polymerization showed lower polymerization kinetics and KHN1, leading to a higher monomer degradation that undergone a significant color change. The L_{HEAA1}, instead, did not differ from control in relation to physicochemical and optical properties, however with long-term hydrolytic stability.

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Figure 1. Degree of conversion and polymerization rate of experimental light-cured resin cements (L_{HEMA1}, L_{HEAA0}, L_{HEAA1}).

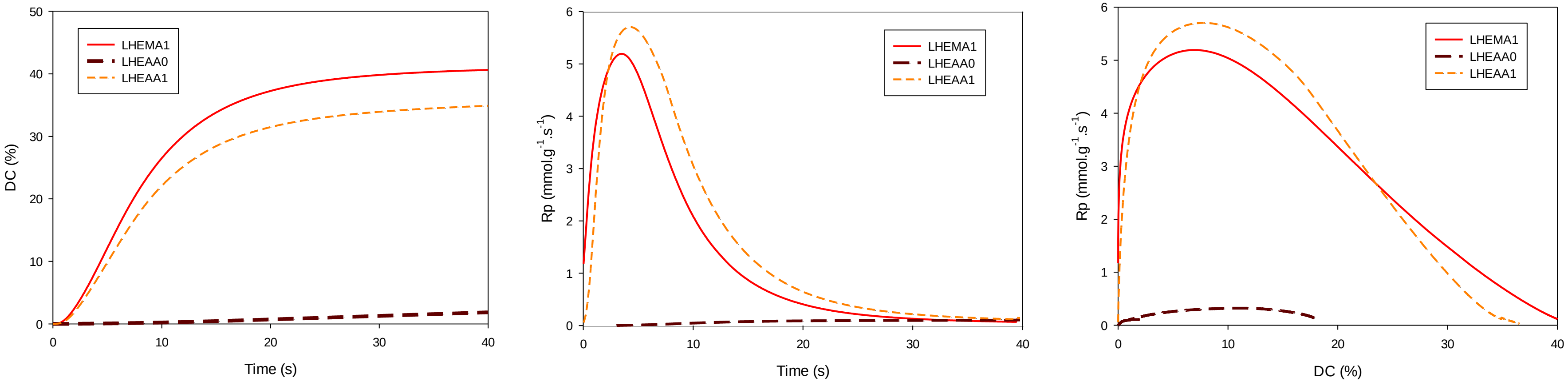


Figure 2. Degree of conversion and polymerization rate of experimental dual-cured resin cements (D_{HEMA0}, $D_{HEMA0.25}$, $D_{HEMA0.6}$, D_{HEAA0}, $D_{HEAA0.25}$, $D_{HEAA0.6}$).

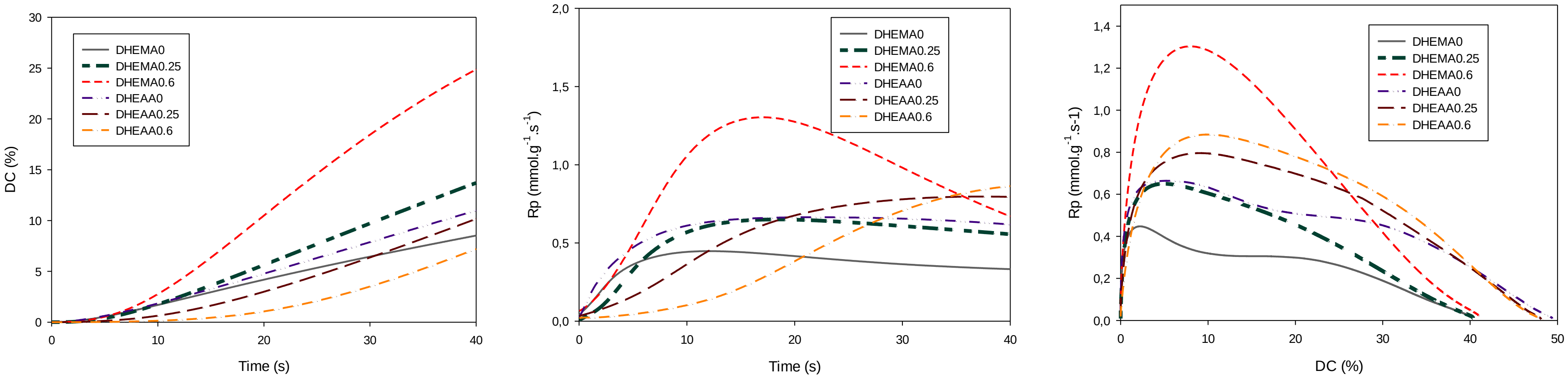


Figure 3. Photographs of light-cured and dual-cured specimens after 6 months of distilled water and mineral oil storage. a) Light-cured resin cements stored in distilled water. b) Light-cured resin cements stored in mineral oil. c) Dual-cured resin cements stored in distilled water. d) Dual-cured resin cements stored in mineral oil.

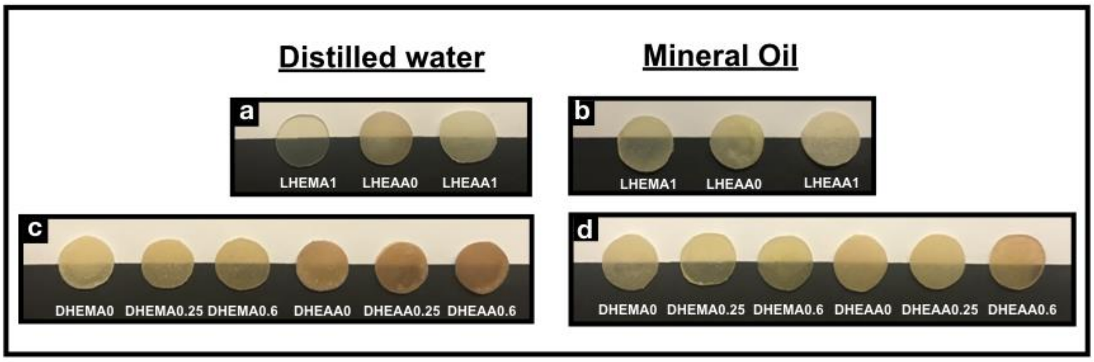
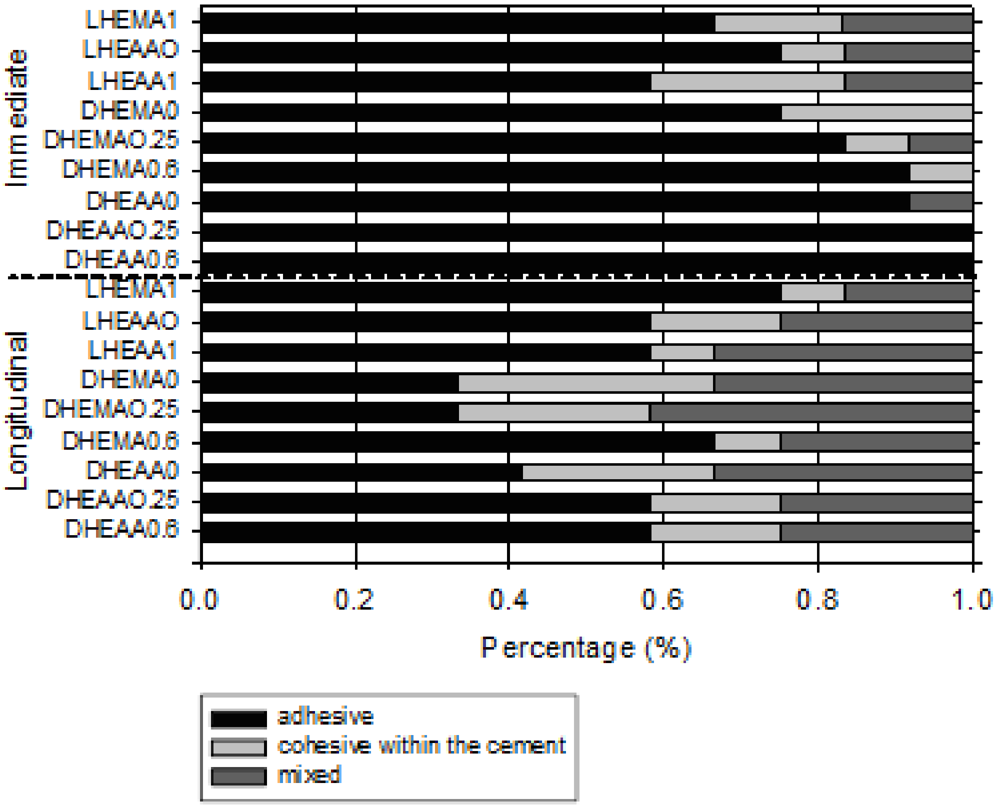


Figure 4. Incidence of failure mode (%) of resin cements analyzed by stereomicroscope.



CONSIDERAÇÕES FINAIS

Os monômeros e concentrações de amina terciária nos cimentos resinosos fotoativáveis e de cura dual propostos nesse estudo foram estipulados levando em conta alguns fatores. O monômero HEMA foi utilizado nos grupos controle devido à similaridade da estrutura química com a HEAA. Nos cimentos de resina fotoativados, não foi formulado um grupo de metacrilato com ausência de 4-dimetil aminobenzoato de etilo (EDAB), pois já foi relatado na literatura que não ocorre a polimerização (RODRIGUES et al., 2015). Os grupos de cura dual foram formulados considerando a menor quantidade de NN-dihidroxietil p-toluidina (DHEPT) necessária para a polimerização química no grupo da acrilamida. Assim, os grupos correspondentes com metacrilato e diferentes concentrações de amina terciária foram formulados como controles. Os grupos D_{HEMA0} e D_{HEAA0} não polimerizaram através da ativação química, somente por fotoativação. No entanto, eles foram submetidos aos testes para observar como o grupo com acrilamida (possivelmente co-iniciador) livre de amina terciária se comportaria.

A cinética dos polímeros testados nesse estudo está relacionada com as propriedades mecânicas dos cimentos resinosos. Os resultados encontrados mostram que os grupos com maior taxa de polimerização apresentam melhores propriedades mecânicas e que não estão diretamente ligadas ao grau de conversão. Os grupos com menor quantidade de amina terciária levam mais tempo para atingir o máximo de conversão. Os cimentos resinosos fotoativáveis e de cura dual com adição de HEAA apresentaram propriedades mecânicas iniciais inferiores aos cimentos resinosos do grupo controle. Contudo, a resistência coesiva à tração e resistência de união ao microcisalhamento longitudinais dos cimentos contendo acrilamida aumentaram após 6 meses de armazenamento em água destilada. É sabido que a HEAA quando associada a um monômero Bis-GMA, por ser mais reativa que o dimetacrilato acaba ligando-se a outros monômeros HEAA, tornando a cadeia polimérica mais linear e com baixas propriedades mecânicas. (RODRIGUES et al., 2015) Uma alternativa para aumentar as propriedades mecânicas iniciais dos cimentos resinosos com HEAA é a adição de um monômero *N,N',N''*-(nitrilotris(ethane-2,1-dyil)tris(2-methylacrylamide). É uma tris (metacrilamida) que resulta em polímeros com aumento da densidade de ligações cruzadas e melhores propriedades mecânicas. (RODRIGUES et al., 2016). Outra alternativa para aumentar o grau de conversão, propriedades mecânicas e diminuição da degradação da matriz polimérica é a adição do sal de difenil iodônio (DPIHFP) nos cimentos fotoativáveis e duais, pois a cura química ocorre mesmo em presença de um sistema ternário (CQ/EDAB/DPIHFP). (AUGUSTO et al., 2017)

Cimentos resinosos de cura dual com maior estabilidade de cor vêm sendo propostos na literatura. (OEI et al., 2013) E a substituição do peróxido de benzoíla por outro componente que não contenha um composto peróxido (R-O-O-R) em sua formulação seria uma alternativa para a formulação de cimentos resinosos duais com monômeros acrilamidas que possuem um nitrogênio na sua estrutura molecular, o qual sofre maior oxidação no sistema de oxirredução. (ODIAN, 2004) Fotoiniciadores do tipo 1 vêm sendo empregados com o objetivo de substituir a canforoquinona de coloração amarelada. (BESSE et al., 2016) Após a irradiação por luz, sofrem uma clivagem de ligação unimolecular para produzir radicais livres e não necessitam de uma amina terciária como co-iniciador da reação de polimerização, diminuindo a formação de produtos oxidativos. Assim, há uma maior estabilidade de cor dos cimentos livres de amina terciária. (URAL et al., 2016)

Dentre os grupos avaliados, o L_{HEAA1} apresentou os melhores resultados quando comparado ao grupo metacrilato fotoativável, porém com maior estabilidade hidrolítica longitudinal. Estudos que avaliem diferentes monômeros acrilamida em formulações alternativas de cimentos resinosos avaliando a estabilidade de cor e hidrolítica, além da resistência de união longitudinal podem complementar e direcionar os achados deste trabalho.

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