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***INFLUÊNCIA DA ADIÇÃO DE Bis-EMA SOBRE
PROPRIEDADES FÍSICAS DE CIMENTOS RESINOSOS
EXPERIMENTAIS BASEADOS EM Bis-GMA E TEGDMA***

Dissertação apresentada à Faculdade de Odontologia de Piracicaba, da Universidade Estadual de Campinas, para obtenção do Título de Mestre em Materiais Dentários.

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RESUMO

O objetivo deste estudo foi investigar a influência da adição de Bis-EMA sobre propriedades físicas e mecânicas de cimentos resinosos experimentais à base de Bis-GMA/TEGDMA. A partir da mistura de Bis-GMA e TEGDMA na proporção de 50:50 em peso (R_{01}), o monômero Bis-EMA foi gradualmente incorporado à mistura, 10% em peso por vez, definindo onze formulações adicionais com as seguintes proporções entre Bis-GMA/TEGDMA/Bis-EMA: 50/40/10 (R_{02}), 50/30/20 (R_{03}), 50/20/30 (R_{04}), 50/10/40 (R_{05}), 50/0/50 (R_{06}), 40/10/50 (R_{07}), 30/10/60 (R_{08}), 20/10/70 (R_{09}), 10/10/80 (R_{10}), 0/10/90 (R_{11}) e 0/0/100 (R_{12}). Canforoquinona (0,4%), N,N-dimetil-p-toluidina (0,8%) e hidroquinona (0,2%) foram dissolvidas em cada mistura, às quais foram adicionados 60% em peso de partículas de vidro silanizadas. O grau de conversão foi avaliado por espectroscopia infravermelha em tempo real. A resistência flexural e módulo de elasticidade foram analisados em teste de flexão de três pontos. A espessura de película foi mensurada colocando os materiais entre placas de vidro polidas. A dureza Knoop foi determinada em um microdurômetro, com carga de 50g por 15s. A sorção de água e a solubilidade foram avaliadas por meio de alteração de peso das amostras após imersão em água destilada por sete dias. Os dados foram separadamente submetidos à Análise de Variância e teste de Tukey ($\alpha = 0,05$). As médias para grau de conversão (%) variaram entre 49,8 (R_{10}) e 65,0 (R_{06}). A substituição de TEGDMA por Bis-EMA aumentou a conversão de ligações duplas, enquanto a substituição de Bis-GMA por Bis-EMA não apresentou influência significativa. No teste de flexão, as médias (MPa) variaram entre 104 (R_{10}) e 131 (R_{02}), mas nenhuma diferença significativa entre os grupos foi detectada. Para o módulo de elasticidade, enquanto a substituição de TEGDMA por Bis-EMA não apresentou influência significativa, a substituição de Bis-GMA por Bis-EMA diminuiu significativamente os valores, com médias (GPa) variando entre 5,41 (R_{09}) e 9,59 (R_{04}). As médias de espessura de película (μm) variaram entre 29,3 (R_{01}) e 66,7 (R_{06}), com a substituição de TEGDMA por Bis-EMA gradualmente aumentando os valores, e R_{04-06} apresentando películas significativamente mais espessas. Médias para dureza (kg/mm^2) variaram entre 35,5 (R_{01}) e 47,9 (R_{05}), com a substituição de TEGDMA por Bis-EMA aumentando gradualmente a dureza, exceto para

R₀₆, enquanto a substituição de Bis-GMA por Bis-EMA não apresentou efeito significativo. Uma gradual diminuição na sorção de água foi verificada à medida que TEGDMA e Bis-GMA foram sendo substituídos por Bis-EMA, com médias ($\mu\text{g}/\text{mm}^3$) variando entre 48,96 (R₀₁) e 15,68 (R₁₂). Médias para solubilidade variaram entre 4,55 (R₀₄) e 9,77 (R₀₂), sem diferença significativa observada entre os grupos. Em geral, os achados do presente estudo mostram que, dependendo da quantidade de Bis-EMA substituindo Bis-GMA e/ou TEGDMA, maior conversão de monômeros ou menor módulo de elasticidade foram detectados. Por outro lado, a substituição de TEGDMA por Bis-EMA aumentou a dureza e diminuiu a sorção de água, embora um aumento na espessura de película tenha sido detectado para algumas misturas. Além disso, a substituição de Bis-GMA por Bis-EMA apresentou influência significativa na diminuição da sorção de água.

Palavras-chave: cimentos resinosos, dureza, espessura de película, grau de conversão, metacrilatos, módulo de elasticidade, resistência à flexão, solubilidade, sorção de água.

ABSTRACT

The aim of this study was to investigate the influence of Bis-EMA addition on physical and mechanical properties of experimental resin luting agents based on Bis-GMA/TEGDMA. Starting from a 50:50 wt:wt ratio blend of Bis-GMA and TEGDMA (R₀₁), the Bis-EMA monomer was gradually added to the mixture, 10wt% at a time, defining eleven additional formulations with the following Bis-GMA/TEGDMA/Bis-EMA ratios: 50/40/10 (R₀₂), 50/30/20 (R₀₃), 50/20/30 (R₀₄), 50/10/40 (R₀₅), 50/0/50 (R₀₆), 40/10/50 (R₀₇), 30/10/60 (R₀₈), 20/10/70 (R₀₉), 10/10/80 (R₁₀), 0/10/90 (R₁₁) and 0/0/100 (R₁₂). Camphorquinone (0.4%), N,N-dimethyl-p-toluidine (0.8%) and hydroquinone (0.2%) were dissolved in each mixture, which were loaded to a constant 60wt% with silanated glass fillers. Degree of conversion was assessed by real-time infrared spectroscopy. Flexural strength and elastic modulus were determined in a three-point bending test. Film thickness was measured by placing the materials between optically flat glass plates. Knoop hardness evaluation was carried out through an indenter, with a load of 50g for 15s. Water sorption and solubility were assessed by weight alteration of samples after storage in distilled water for seven days. Data were separately submitted to Analysis of Variance and Tukey's test ($\alpha = 0.05$). Means for degree of conversion (%) varied between 49.8 (R₁₀) and 65.0 (R₀₆). Replacing TEGDMA with Bis-EMA caused an increase in conversion of double bonds, while the substitution of Bis-GMA by Bis-EMA had no significant influence. Means for flexural strength (MPa) varied between 104 (R₁₀) and 131 (R₀₂), but no significant difference among groups was detected. For the elastic modulus, while replacing TEGDMA with Bis-EMA had no significant influence, the replacement of Bis-GMA by Bis-EMA significantly decreased the values, with means (GPa) varying between 5.41 (R₀₉) and 9.59 (R₀₄). Film thickness means (μm) varied between 29.3 (R₀₁) and 66.7 (R₀₆), with the substitution of TEGDMA by Bis-EMA gradually increasing the film values, and R₀₄₋₀₆ showing significantly thicker films. Hardness means (KHN, kg/mm^2) varied between 35.5 (R₀₁) and 47.9 (R₀₅), with the replacement of TEGDMA by Bis-EMA gradually increasing hardness, except for R₀₆, while replacing Bis-GMA with Bis-EMA had no significant effect. A gradual decrease in water sorption was detected as TEGDMA and Bis-GMA were

gradually replaced by Bis-EMA, with means ($\mu\text{g}/\text{mm}^3$) varying between 48.96 (R_{01}) and 15.68 (R_{12}). Solubility means ($\mu\text{g}/\text{mm}^3$) varied between 4.55 (R_{04}) and 9.77 (R_{02}), with no significant differences detected among groups. In general, the present findings show that, depending on the amount of Bis-EMA replacing Bis-GMA and/or TEGDMA, increased monomer conversion or decreased elastic modulus were detected. On the other hand, replacing TEGDMA with Bis-EMA increased hardness and decreased water sorption, although an increase in film thickness has been detected for some mixtures. Also, the substitution of Bis-GMA by Bis-EMA had a significant influence on decreasing water sorption.

Key words: degree of conversion, elastic modulus, film thickness, flexural strength, hardness, methacrylates, resin cements, solubility, water sorption.

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INTRODUÇÃO

Compósitos resinosos estão cada vez mais populares na Odontologia devido a características como boa estética, facilidade de manipulação e potencial união às estruturas dentais. Estes materiais apresentam ampla gama de aplicações, abrangendo restauradores diretos e indiretos, agentes de cimentação, selantes de fósulas e fissuras, entre outros. As formulações são, em geral, compostas por mistura de monômeros dimetacrilatos, os quais possibilitam a formação, geralmente por meio de reação de polimerização por adição, de redes poliméricas tridimensionais rígidas, com formação de ligações cruzadas (Achilias & Sideridou, 2004; Asmussen & Peutzfeldt, 2001; Elliott, *et al.*, 2001; Jones & Rizkalla, 1996). A matriz resinosa é carregada com partículas de cerâmica e/ou de vidro, de maneira a melhorar as propriedades mecânicas e físicas do material, como resistência ao desgaste, dureza, translucidez e radiopacidade (Rosenstiel, *et al.*, 1998; Rueggeberg, 2002).

Compósitos utilizados para procedimentos restauradores diretos apresentam quantidade de carga de até 85% em peso (Fortin & Vargas, 1999). Por outro lado, a agentes de cimentação, que permitem a união entre elementos protéticos e a estrutura dentária de suporte, são incorporadas partículas de carga à quantidade máxima de 70% em peso (Rosenstiel *et al.*, 1998), com o objetivo de propiciar menor viscosidade e adequado escoamento durante a cimentação, além de mínima espessura de película. Além disso, os cimentos devem preencher critérios adicionais, como tempo de trabalho adequado, curto tempo de presa, baixa sorção de água e solubilidade, alta resistência à compressão e à flexão.

O bisfenol A glidicil dimetacrilato (Bis-GMA, Figura 1) é o componente mais comumente utilizado na matriz orgânica de materiais resinosos, apresentando alto peso molecular e baixa contração de polimerização (Rueggeberg, 2002). No entanto, devido à

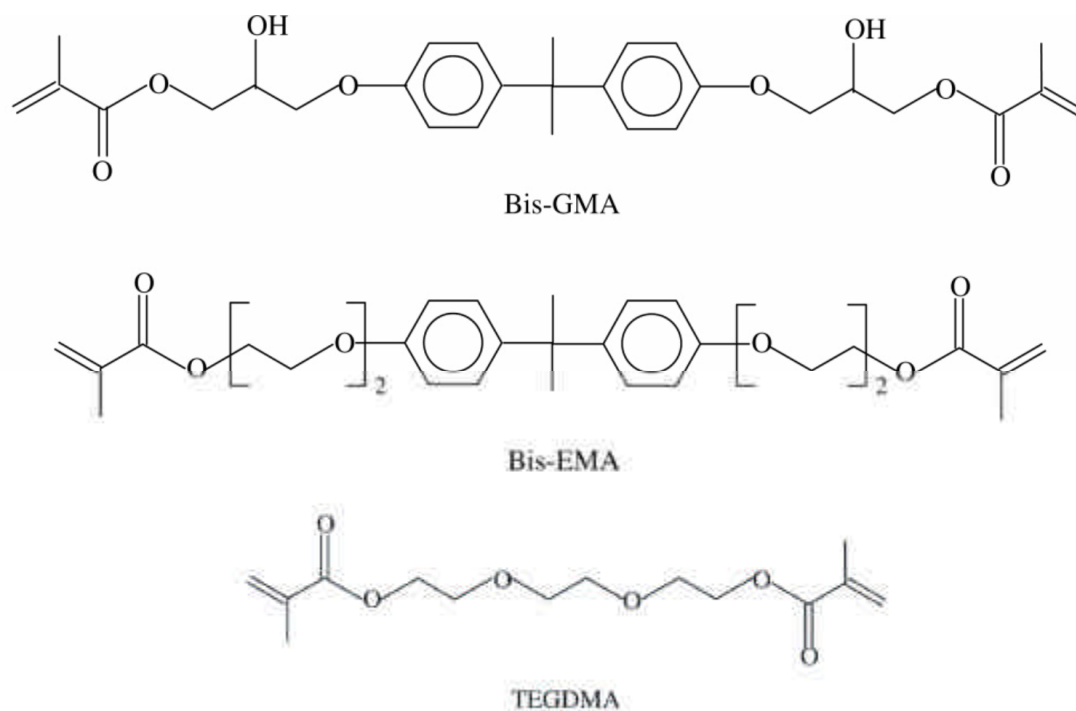


Figura 1. Estrutura química dos monômeros Bis-GMA, Bis-EMA e TEGDMA.

alta viscosidade desse monômero, a matriz orgânica necessita ser diluída com monômeros mais fluidos. Este procedimento é normalmente realizado utilizando-se o trietileno glicol dimetacrilato (TEGDMA, Figura 1), que é um monômero mais flexível e de menor peso molecular. O processo de diluição melhora as características de manipulação do compósito e permite a incorporação de maior quantidade de carga (Dulik, *et al.*, 1981), ainda assim provendo adequado escoamento e mínima espessura de película, no caso de cimentos. Entretanto, tal diluição ocasiona determinadas limitações, uma vez que o TEGDMA aumenta a absorção de água e principalmente a contração de polimerização do material (Dulik *et al.*, 1981; Anseth, *et al.*, 1996; Dermann, *et al.*, 1982).

Mais recentemente, o bisfenol A glicidil dimetacrilato etoxilado (Bis-EMA, Figura 1) tem sido investigado e utilizado como componente alternativo para compósitos odontológicos (Achilias & Sideridou, 2004; Sideridou, *et al.*, 2004a; Sideridou, *et al.*, 2004b; Sideridou, *et al.*, 2002; Sideridou, *et al.*, 2003). Este monômero é estruturalmente

semelhante ao Bis-GMA, com um grupamento fenil central rígido, sem, entretanto, apresentar os dois radicais hidroxil pendentes, que por sua vez são responsáveis pela sorção de água e principalmente pela alta viscosidade do Bis-GMA, devido às fortes pontes de hidrogênio que formam com os radicais carbonil (Kalachandra & Kusy, 1991; Kalachandra, *et al.*, 1997a). Dessa forma, o Bis-EMA poderia minimizar ou mesmo eliminar o uso do TEGDMA como diluente.

Diversos pesquisadores demonstraram que a seleção dos monômeros que compõem a matriz orgânica pode afetar significativamente propriedades do compósito (Asmussen & Peutzfeldt, 2001; Dulik *et al.*, 1981; Anseth *et al.*, 1996; Dermann *et al.*, 1982; Sideridou *et al.*, 2004a; Sideridou *et al.*, 2004b; Sideridou *et al.*, 2002; Sideridou *et al.*, 2003; Asmussen & Peutzfeldt, 1998; Ferracane & Greener, 1986; Ito, *et al.*, 2005; Kawai, *et al.*, 1998; Musanje & Ferracane, 2004), como reatividade, viscosidade, grau de conversão, contração de polimerização, sorção de água, entre outras. Isto ocorre porque os diversos monômeros utilizados apresentam diferente peso molecular, diferente flexibilidade de cadeia e distinta afinidade por água. Entretanto, tais estudos tendem a se concentrar nas características de compósitos utilizados como restauradores diretos, deixando de lado propriedades mais relacionadas a agentes de cimentação, como espessura de película e viscosidade. Além disso, não há relato na literatura sobre a gradual incorporação de Bis-EMA a compósitos baseados em Bis-GMA e TEGDMA sobre propriedades físicas e mecânicas desses materiais.

Dessa maneira, o objetivo do presente estudo foi investigar a influência da adição gradual do monômero Bis-EMA, em substituição aos monômeros Bis-GMA e/ou TEGDMA, sobre propriedades físicas e mecânicas de cimentos resinosos experimentais. Na primeira parte desta investigação (Capítulo 1), grau de conversão, resistência à flexão e módulo de elasticidade foram avaliados, enquanto a segunda parte do estudo (Capítulo 2) teve como foco a investigação de espessura de película, dureza, sorção e solubilidade em água.

O presente trabalho é apresentado no formato alternativo de dissertação de acordo com as normas estabelecidas pela deliberação 002/06 da Comissão Central de Pós-Graduação da Universidade Estadual de Campinas. Os artigos referentes aos Capítulos 1 e 2 foram submetidos aos periódicos *Journal of Biomedical Materials Research Part B: Applied Biomaterials* e *Dental Materials*, respectivamente.

CAPÍTULO 1

Influence of Bis-EMA4 on degree of conversion, flexural strength and elastic modulus of experimental resin luting agents

INTRODUCTION

Resin-based composite materials are widely used in dentistry due to their advantageous characteristics such as aesthetics, easy handling and ability to bond to tooth structure. Formulations are usually mixtures of dimethacrylate monomers, which are able to produce, through free radical polymerization, cross-linked, rigid three-dimensional polymer networks. The resin phase is loaded with ceramic and/or glass filler particles, in order to improve the mechanical and physical properties, as well as to attain necessary radiopacity to the final composite.

Resin composites used for restorative purposes are generally loaded in excess of 80wt%, to reduce the amount of resin, increase the wear resistance and create a particular handling property [1]. On the other hand, luting agents provide the link between a fixed prosthesis and the supporting tooth structure. Unlike direct restoratives, cements are filled up to a maximum of 70wt% [2], in order to provide adequate viscosity and flow during cementation and also a resulting minimal film thickness. Also, these materials should fulfill additional criteria in order to be applicable in common practice, such as long working time, rapid set, low solubility, high compressive strength and biocompatibility [2].

The bisphenol A glycol dimethacrylate (Bis-GMA) is the most common monomer in the resin phase of luting cements, presenting high molecular weight and low polymerization shrinkage [3]. Nonetheless, due to the high viscosity of Bis-GMA, the organic phase is usually diluted with triethylene glycol dimethacrylate (TEGDMA), which is a more flexible monomer, with lower molecular weight. Such a dilution enhances the handling of the final cement and permits the use of high amount of filler, also providing

adequate flow and an optimal film thickness. Nonetheless, the dilution process also creates some shortcomings, as TEGDMA has been shown to increase the water sorption as well the polymerization shrinkage of the final material [4-6].

More recently, the ethoxylated bisphenol A glycol dimethacrylate (Bis-EMA) has been investigated as an alternative monomer in dental composite formulations [7-11]. This monomer presents lower bulk viscosity than Bis-GMA, and therefore could minimize or eliminate the use of diluents. Bis-EMA is structurally analogous to Bis-GMA, with a stiff central phenyl ring core, without, however, the two pendant hydroxyl groups, which are responsible for the higher water sorption and mainly for the extremely high viscosity of Bis-GMA, due to the strong hydrogen bonding with carbonyl groups [12,13].

Several investigators have reported that the selection of the monomers composing the organic matrix strongly affects the final properties of the composite, such as its reactivity, viscosity, degree of conversion, polymerization shrinkage and water sorption [4-6,8-12,14-23]. This occurs because distinct monomers present different molecular weight and flexibility, as well different hydrophilicity. However, the aforementioned studies tend to concentrate on characteristics of composites for filling purposes, thereby usually neglecting properties that are more closely related to luting cements. Furthermore, literature lacks of investigation on the influence of gradual addition of Bis-EMA to Bis-GMA/TEGDMA-based composites on properties of the final material.

Therefore, the overall aim of this study was to investigate mechanical and physical properties of experimental resin luting agents in which Bis-EMA gradually replaced Bis-GMA and/or TEGDMA. In the first part of this investigation, the degree of conversion, flexural strength and elastic modulus of the different luting agents were evaluated.

MATERIALS AND METHODS

Formulation of the luting agents

Twelve formulations of luting materials based on Bis-GMA, TEGDMA and/or Bis-EMA (Esstech Inc., Essington, Pennsylvania, USA) were tested. Figure 1 shows the chemical structure of these monomers. The composition of all cements is listed in Table 1. Starting from a 50:50 wt:wt ratio blend of Bis-GMA and TEGDMA (R₀₁), in the first series (R₀₂₋₀₆), different mixtures were produced in which TEGDMA was successively substituted by Bis-EMA, 10wt% at a time. In the next series (R₀₇₋₁₁), a constant 10wt% of TEGDMA was used, and Bis-GMA was successively substituted by Bis-EMA, 10wt% at a time. R₁₂ was composed by 100% Bis-EMA.

In order to make photo-curing materials, 0.4wt% of camphorquinone (Esstech Inc.) and 0.8wt% of N,N-dimethyl-p-toluidine (Aldrich Chemical Co., Milwaukee, WI, USA) were dissolved in each mixture. In addition, 0.2wt% of hydroquinone (Aldrich Chemical Co.) was used as a radical scavenger. All chemicals were used as received, without further purification. Materials were loaded with silanated strontium glass fillers (Esstech Inc.), 0.7 and 2 μ m in size, to a constant content of 60wt% (1:1 of each size).

Degree of conversion

Degree of conversion (DC) was assessed by real-time Fourier transformed infrared spectroscopy (Prestige21 spectrometer, Shimadzu, Tokyo, Japan), using a horizontal attenuated total reflection (ATR) accessory. For irradiance procedures, an apparatus allowed positioning the halogen curing unit (XL3000 – 3M ESPE, St. Paul, MN, USA) with a 5mm standard distance between the light guide tip and the sample. A 1mm-thick layer of each uncured luting agent was placed onto the ZnSe ATR crystal. Light-activation was carried out for 200s, and the polymerization reaction was monitored throughout this time. Curing unit irradiance was 700mW/cm², between 400 and 500nm, which was assessed with a digital power meter (Ophir Optronics, Danvers, MA, USA) and a computer-controlled spectrometer (USB 2000, Ocean Optics, Dunedin, FL, USA), respectively.

The software IRsolution (Shimadzu), operating in the scanning mode, was used to analyze the real-time conversion of the luting agents, at a rate of 1 scan/s. Infrared spectra in the range between 1800cm⁻¹ and 1500cm⁻¹ were collected in the absorbance mode, at a

pre-set resolution of 8cm⁻¹. Spectra for the uncured luting agents were also obtained. Monomer conversion was determined by standard methods that utilize changes in the ratios of aliphatic-to-aromatic carbon-carbon double bonds absorption peaks in the uncured and cured states. The baseline parameters and the formula used to calculate DC were previously described [24]. Three specimens were tested for each material.

Flexural strength

Flexural test was conducted in accordance with ISO 4049 specification [25]. Five rectangular bar-shaped specimens (25mm x 2mm x 2mm) were prepared for each material by placing the luting agents into a stainless steel mold held between two glass microscopic slides. After light-activation procedures, the specimens were removed from the mold and stored in distilled water, at 37°C, in the dark. After 24h, the height and width of the specimens were measured, using a digital caliper (Mitutoyo, Tokyo, Japan, 0.01mm accuracy), and the samples were subjected to a three-point bending test in a universal testing machine (DL500 – EMIC, São José dos Pinhais, PR, Brazil), at a cross-head speed of 0.5mm/min until failure. Flexural strength (F) was determined as follows:

$$F = 3P_f L / 2WH^2$$

where P_f is the measured maximum load (in N) at the time of specimen fracture, L is the distance between the supports on the tension surface (20mm), W is the mean specimen width, and H is the mean height of the specimen between the tension and compression surfaces.

Elastic modulus

A chart plotter recorded the stress-deformation profile during the flexural test. The elastic modulus (E) was calculated from the linear-elastic range, between bending force and specimen displacement before fracture, as follows:

$$E = (\Delta F / \Delta y) \times (L^3 / 4WH^3)$$

where $\Delta F / \Delta y$ is the change in force (ΔF) per unit change in deflection of the center of the specimen (Δy).

Statistical analysis

Data from each evaluation were separately analyzed using one-way ANOVA, followed by Tukey's post hoc test, at $\alpha = 0.05$.

RESULTS

Results for DC, flexural strength and elastic modulus are shown in Table 2. For DC, as depicted in Figure 2, replacing TEGDMA with Bis-EMA caused an increase in conversion of double bonds. In fact, luting agents containing 50wt% of Bis-GMA and 30, 40 or 50wt% of Bis-EMA showed the highest DC mean values among all groups. Conversely, the substitution of Bis-GMA by Bis-EMA had no significant effect on conversion of monomers: R₀₇₋₁₂ showed similar outcomes compared with R₀₁₋₀₃.

In the 3-point bending test, as shown in Figure 3, flexural strength mean values greater than 100MPa were observed for all materials, but no significant differences among them were detected. Conversely, in the elastic modulus assessment, significant differences were observed. When replacing TEGDMA with Bis-EMA, using a constant 50wt% of Bis-GMA, no significant influence on elastic modulus was observed. On the other hand, when replacing Bis-GMA with Bis-EMA, a significant decrease was detected, as shown in Figure 4. In general, R₀₆₋₁₂ showed significantly lower elastic modulus values in comparison to R₀₁₋₀₅, except for R₀₂.

DISCUSSION

Degree of conversion

The DC plays a major influence on the properties of a polymer. High DC produces a material with good mechanical properties and a minimum of unreacted, leachable components. It has been demonstrated that composites with the poorest cure showed the most substantial and long-term reductions in hardness after storage in water, and also that enhancing the cure of a polymer results in improving its fracture toughness [26]. In addition, any unreacted functional groups that remain in the resin can act as plasticizers, reducing the mechanical strength of the material and increasing the swelling [27]. Furthermore, monomers trapped into the restoration may reduce the clinical serviceability of composites through oxidation and hydrolytic degradation processes, which may be clinically manifested in forms such as discoloration of the fillings and accelerated wear.

The present outcomes show that replacing TEGDMA with Bis-EMA caused an increase in conversion of double bonds for R₀₄₋₀₆. Indeed, these materials contained 50wt% of Bis-GMA and 30, 40 or 50wt% of Bis-EMA, respectively, and showed the highest means for DC among all groups. Nonetheless, this result is in contrast with previous ones found in literature. Regarding the nature of the monomer, several authors have reported that increasing amounts of TEGDMA will result in increased conversion [28-31]. In addition, Achilias and Sideridou [7] described greater reaction rate values and higher final double bond conversion for TEGDMA in comparison to Bis-EMA, suggesting that the aliphatic chain of TEGDMA could more easily move in space and thus to react to a greater extent than Bis-EMA, which is more viscous and includes aromatic rings in the C–C chain. Furthermore, during the formulation of the luting agents, the gradual addition of Bis-EMA noticeably increased the viscosity of the materials, and this subject will be focused on the next part of this study. Indeed, previous authors [23,32,33] have showed that high resin viscosity restricts the mobility of reactive species and lessens the frequency and possibility of the chance encounters, leading to a decrease in the propagation of polymerization.

In spite of that, a previous study suggests an explanation for the findings of the present study. According to Emami and Söderholm [34], there is a theoretical aliphatic-to-aromatic proportion rate that should be taken into account in order to analyze the DC from different resin formulations. In the present study, the first series of composites (R_{01-03}) presented high amounts of TEGDMA and, therefore, almost all aromatic groups presented in the resin were from the Bis-GMA content. On the other hand, in the series in which Bis-EMA replaced TEGDMA to a significant content (R_{04-06}), there is an increasing aromatic contribution from Bis-EMA. In other words, in R_{04-06} , the aromatic resin content by weight was higher compared with R_{01-03} and, in turn, fewer aliphatic groups compared with aromatic groups are available for the former ones. Thereby, despite a lower final conversion value for R_{01-03} , probably more aliphatic bonds had reacted in these materials in comparison to R_{04-06} . However, lower maximum conversion values are noticed, and this occurs is due to the increased initial concentration of double bonds in the resin. In fact, Anseth et al. [4] reported that, within certain limits, increasing the molecular weight of the monomer resin, and thereby decreasing the concentration of double bonds in the system, is an effective approach to increase conversion and to reduce the polymerization shrinkage, while maintaining the mechanical strength of the polymer.

Nevertheless, other explanations might be associated with the present results. For example, when compared to Bis-GMA and Bis-EMA, TEGDMA has smaller size and therefore higher concentration of double bonds; so the latter at equal degrees of conversion will probably exhibit higher density of cross-linking, which might limit further mobility of reacting species during polymerization and restrict additional conversion. Also, it has been suggested the refractive indices of the different dimethacrylates composing the material should match those of the reinforcing fillers [10], in order to allow adequate in-depth conversion to the composite by minimizing light-scattering and absorption effects, thus enhancing polymerization. From this standpoint, Sideridou et al. [10] indicated Bis-GMA and Bis-EMA as more suitable monomers for use in dental composites. Moreover, in the current study, the luting agents were rendered light-curable by the addition of 0.4wt% of camphorquinone, and the usage of a constant concentration by weight, rather than by mol percentage, did not take into account differences related to the resin formulation, such as

the concentration of double bonds in the system. Therefore, it can be speculated that mixtures with less content of double bonds would be benefited in terms of photo-initiator available for free-radical formation and propagation of polymerization.

On the other hand, the substitution of Bis-GMA by Bis-EMA had no significant effect on conversion of monomers, with R₀₇₋₁₂ showing similar outcomes to R₀₁₋₀₃. The lack of the pendant hydroxyl groups in the molecular structure of Bis-EMA gives this material a low viscosity, and thus one could expect a higher degree of conversion in comparison to Bis-GMA. Again, the previous explanations might be probably related to this result, since the replacement of Bis-GMA with Bis-EMA kept constant the aliphatic-to-aromatic proportion rate in the composite.

Flexural strength

Previous investigators have described a positive correlation between the strength of the bond to dentin and the flexural strength of the resin composite [35,36], indicating the flexural strength to serve as a selecting criterion in the search for high bonding potential of composite materials. Other investigators have reported that the monomers composing the resin phase of the composite can interfere with the flexibility of the resulting polymer [16,26,29]. Nonetheless, the present results show no significant differences among materials regarding flexural strength, i.e., the addition of Bis-EMA in substitution to either TEGDMA or Bis-GMA had no significant influence on the flexural properties of the luting agents, even though significant differences were detected for DC and elastic modulus. Nonetheless, it is worth to mention that, according to the ISO 4049 specification, resin luting agents must show flexural strengths higher than 50MPa, and all luting materials tested here present mean values higher than 100MPa.

In fact, literature presents conflicting findings regarding the relationship between flexural and other physical/mechanical properties. Ferracane et al. [26] observed that the flexural strength of the composites generally increased with DC, while other studies reported no significant correlation between DC and flexural properties [17,28,29]. Such outcomes are probably related to the fact that, according to Karmaker et al. [37], the

flexural strength of composites is controlled mainly by the stiffness/flexibility of their organic matrices. TEGDMA has an aliphatic flexible structure, while Bis-GMA and Bis-EMA present aromatic groups and hence are stiffer monomers. However, the presence of hydroxyl groups, and the resulting potential for hydrogen bonding, renders the Bis-GMA much more viscous than Bis-EMA. In spite of that, no significant differences in flexural properties were detected even when the luting agent was composed of only Bis-EMA. These findings suggest that other characteristics should be taken into account when evaluating flexural strength of polymers, such as the degree of cross-linking of the network, the filler concentration and the bonding between filler and resin matrix.

Elastic modulus

It has been suggested that luting agents should have a modulus of elasticity value between that of the dentin and of the indirect restorative material [38], in order to allow effective stress transfer from the restorative to the supporting tooth structure. Nonetheless, previous authors [39,40] reported that the magnitude of the elastic modulus is directly related to the resulting shrinkage stress during constrained polymerization. That is, materials with lower elastic modulus in general produce lower stress generation at the tooth-filling interface. Such a relationship has been described elsewhere [39]. During polymerization, there is a stage at which an insoluble network is formed within the resin phase, referred to as the gel point. At this point, the elastic modulus of the composite has substantially increased, and the composite's elastic limit has reached a level that does not allow enough plastic deformation to compensate for the reduction in volume. Beyond this stage, additional contraction may generate significant stress within the composite. In the clinical situation, most of the adhesive restorations do not allow for free curing contraction of the luting cement. Under restrained conditions, the setting stresses may be detrimental to the integrity of the adhesive joint [41], since they may exceed the cohesive or the bond strength to tooth structure, placing restoration longevity at risk.

According to the present outcomes, when replacing TEGDMA with Bis-EMA, and using a constant 50wt% of Bis-GMA, no significant influence on elastic modulus was

observed. TEGDMA has an aliphatic flexible structure, while Bis-GMA and Bis-EMA present aromatic groups and, hence, stiffer structures. In spite of that, the current outcomes indicate that the mixture of either TEGDMA or Bis-EMA with 50wt% of Bis-GMA did not decrease the elastic modulus, even though TEGDMA being more flexible and less viscous than Bis-EMA. This corroborates with the findings from the flexural test, which showed no significant differences between Bis-GMA/TEGDMA and Bis-GMA/Bis-EMA blends.

However, the above findings do not corroborate with those from Jones and Rizkalla [42], which reported a trend toward decreased elastic modulus with increasing proportions of TEGDMA. On the other hand, Sideridou et al. [11] reported that copolymers prepared from mixtures of Bis-GMA and Bis-EMA showed Young's modulus values slightly lower than Bis-GMA/TEGDMA blends, indicating that Bis-EMA act as internal plasticizers of the polymer network. The most probable explanation for the different results observed in the current study is related to the high concentration of Bis-GMA used in R₀₁₋₀₆, which probably hindered an effective plasticizing effect of the diluent monomers and thereby their capability in reducing the modulus of elasticity.

Another possible explanation for the similar findings observed for TEGDMA and Bis-EMA lays on the fact that the former, having smaller size and therefore higher concentration of double bonds than the latter, favors the formation of highly cross-linked polymers, i.e., tighter networks [4], and the degree of cross-linking is closely related to elastic modulus [39]. Also, both Bis-EMA and TEGDMA are non-viscous liquids with a glass transition temperature (T_g) much lower than that of Bis-GMA [10]. The T_g is a measure of chain flexibility of monomers, which depends upon the nature and the size of the groups in the chain. Large and polar groups, which are responsible for intra and intermolecular interactions, decrease the flexibility of the chain and increase the T_g value. Therefore, the low T_g values of TEGDMA and Bis-EMA might be related to the their similar plasticizing effect on Bis-GMA observed here.

On the other hand, when replacing Bis-GMA with Bis-EMA, a significant decrease in the modulus of elasticity was detected. In general, R₀₆₋₁₂ showed significantly lower elastic modulus than R₀₁₋₀₅. Although Bis-GMA and Bis-EMA have about the same size, this finding is related to the lower viscosity and lower T_g of Bis-EMA [10]. Replacing Bis-

GMA with Bis-EMA reduces the close molecular packing caused by the strong specific interactions that originate from the polar hydroxyl and carbonyl groups in Bis-GMA, hence decreasing the density of the molecule [11]. Corroborating this outcome, Sideridou et al. [11] reported that copolymers prepared from mixtures of Bis-GMA/TEGDMA showed significantly high values for the Young's modulus, and linked this behavior to the formation of hydrogen bonds between the –OH– groups of Bis-GMA and >C=O or –O– groups of TEGDMA. Also, Karmaker et al. [37] observed Tg to increase with the increase of Bis-GMA concentration, and Jones and Rizkalla [42] reported a trend toward increased elastic modulus with higher proportions of Bis-GMA. Furthermore, Jones & Rizkalla [42] showed that mixtures of TEGDMA with ethoxylated bisphenol A dimethacrylate (EBAD) blends had much lower elastic moduli than Bis-GMA/TEGDMA blends, which is in line with the current results.

CONCLUSIONS

The present results show that, depending on the amount of Bis-EMA replacing Bis-GMA and/or TEGDMA, increased monomer conversion or decreased elastic modulus were detected. This implies that, within certain limits, the incorporation of Bis-EMA to Bis-GMA/TEGDMA blends may present beneficial effects with regard to properties of the resulting composite. On the other hand, no significant influence was observed for flexural strength.

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Table 1. Composition of the experimental resin luting agents.

Material	Monomers (wt%)		
	Bis-GMA	TEGDMA	Bis-EMA
R ₀₁	50	50	0
R ₀₂	50	40	10
R ₀₃	50	30	20
R ₀₄	50	20	30
R ₀₅	50	10	40
R ₀₆	50	0	50
R ₀₇	40	10	50
R ₀₈	30	10	60
R ₀₉	20	10	70
R ₁₀	10	10	80
R ₁₁	0	10	90
R ₁₂	0	0	100

Additional composition: 0.4wt% of camphorquinone, 0.8wt% of N,N-dimethyl-p-toluidine, 0.2wt% of hydroquinone, 60wt% of glass filler particles (0.7 and 2 μ m).

Table 2. Means (standard deviation) for degree of conversion (%), flexural strength (MPa) and elastic modulus (GPa).

	Degree of conversion	Flexural strength	Elastic modulus
R ₀₁	51.5 (1.8) ^c	110 (15) ^a	8.61 (0.6) ^{ab}
R ₀₂	55.6 (2.5) ^{bc}	131 (15) ^a	7.77 (0.7) ^{bc}
R ₀₃	53.2 (2.3) ^c	124 (31) ^a	8.40 (0.8) ^{ab}
R ₀₄	62.8 (1.6) ^a	114 (17) ^a	9.59 (0.7) ^a
R ₀₅	60.3 (2.1) ^{ab}	110 (21) ^a	8.63 (0.7) ^{ab}
R ₀₆	65.0 (2.5) ^a	110 (11) ^a	6.35 (0.5) ^{cd}
R ₀₇	56.0 (1.3) ^{bc}	110 (16) ^a	6.57 (1.0) ^{cd}
R ₀₈	52.0 (1.9) ^c	115 (19) ^a	6.52 (0.4) ^{cd}
R ₀₉	55.7 (1.5) ^{bc}	119 (16) ^a	5.41 (0.6) ^d
R ₁₀	49.8 (1.9) ^c	104 (12) ^a	5.86 (0.4) ^d
R ₁₁	50.6 (2.2) ^c	105 (14) ^a	6.03 (0.6) ^d
R ₁₂	49.9 (2.0) ^c	126 (33) ^a	5.98 (0.8) ^d

Means followed by the same superscripted letter in the column were not significantly different at $\alpha = 0.05$.

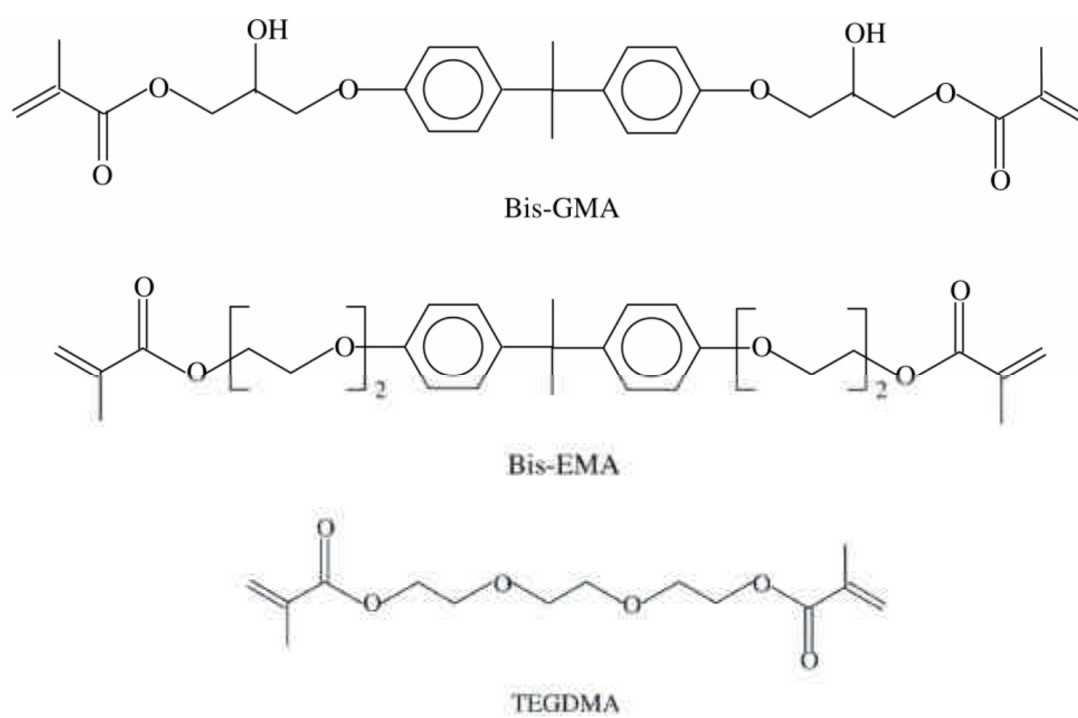


Figure 1. Chemical structure of the monomers tested in the study.

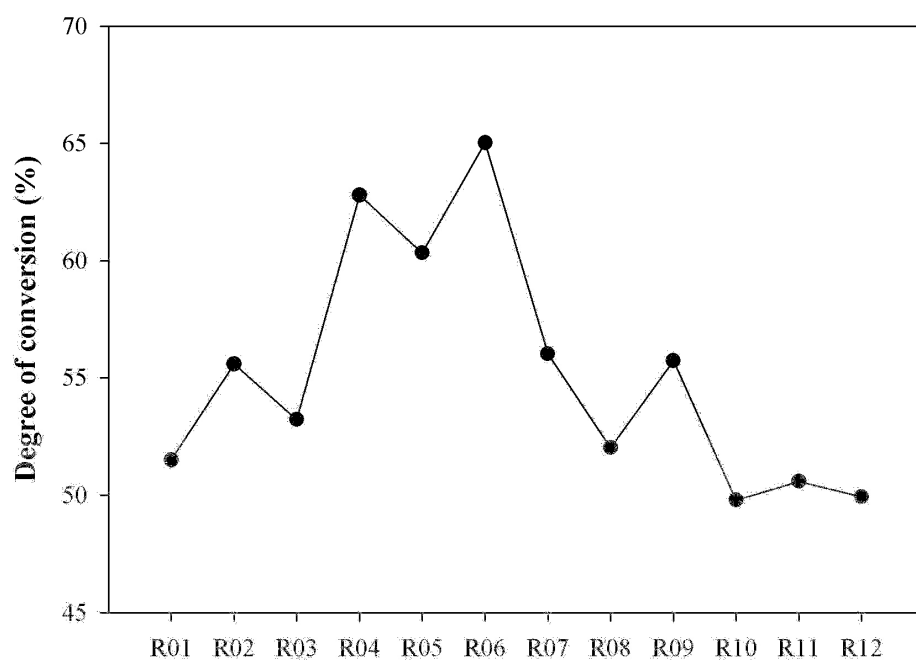


Figure 2. Comparison of degree of conversion results for all luting agents.

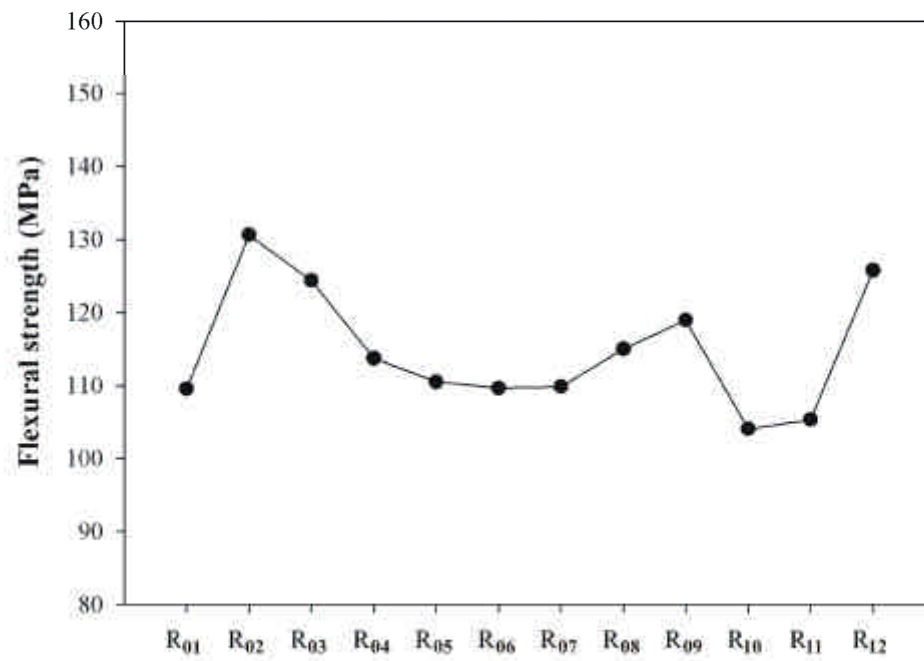


Figure 3. Comparison of flexural strength results for all luting agents.

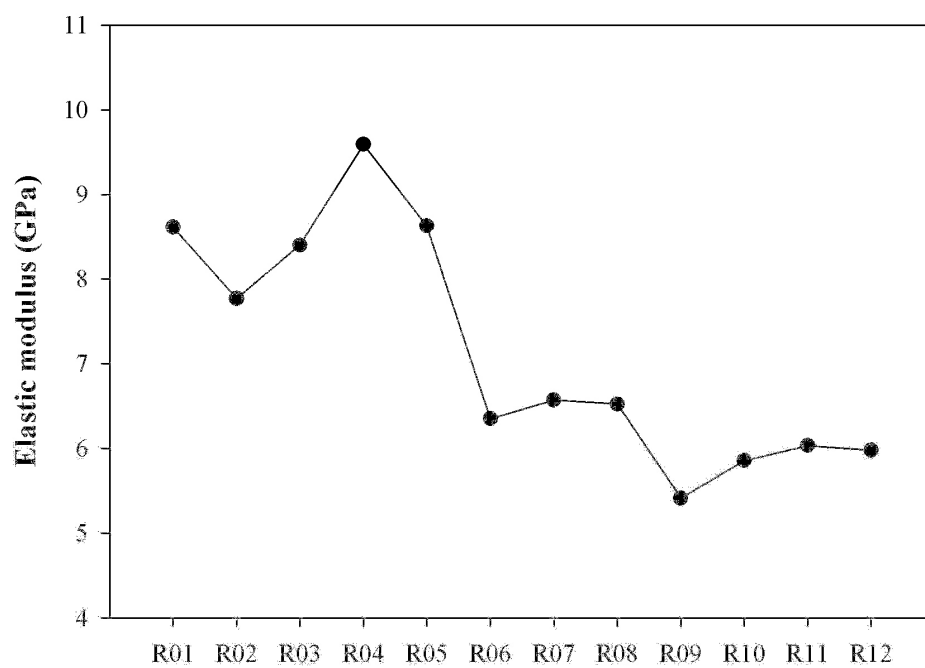


Figure 4. Comparison of elastic modulus results for all luting agents.

CAPÍTULO 2

Effect of Bis-EMA4 on physical properties of experimental resin luting agents

INTRODUCTION

Resin-based luting agents are increasingly popular in restorative dentistry. They provide an adhesive link between a fixed prosthesis and the supporting tooth structure. Unlike direct restoratives, cements are filled up to a maximum of 70wt% [1], thereby providing low viscosity, adequate flow during cementation and a resulting minimal film thickness to the material.

Recent studies have investigated the use of ethoxylated bisphenol A glycol dimethacrylate (Bis-EMA) monomer in dental composite formulations [2-4]. This monomer is structurally analogous to bisphenol A glycol dimethacrylate (Bis-GMA); however, without the two pendant hydroxyl groups (Figure 1), therefore presenting lower bulk viscosity as well lower hydrophilicity. The addition of Bis-EMA to composite formulations could minimize or eliminate the use of diluents, such as triethylene glycol dimethacrylate (TEGDMA), thereby overcoming shortcomings of the dilution process, such as higher water sorption and increased polymerization shrinkage [5-7].

It is well-recognized that the selection of the monomers composing the organic matrix interferes with the final properties of the composite [2-14]. Therefore, the aim of the present study was to investigate selected properties of experimental resin luting agents in which Bis-EMA4 gradually replaced Bis-GMA and/or TEGDMA. This investigation is focused on the evaluation of film thickness, hardness and water sorption/solubility of experimental resin luting agents in which Bis-EMA4 gradually replaced Bis-GMA and/or TEGDMA.

MATERIALS AND METHODS

Formulation of the luting agents

Twelve formulations of luting materials based on Bis-GMA, TEGDMA and/or Bis-EMA4 (Esstech Inc., Essington, PA, USA) were tested. Figure 1 shows the molecular structure of each monomer. The composition of all cements is shown in Figure 2. Starting from a 50:50 wt:wt ratio blend of Bis-GMA and TEGDMA, in the first five series different mixtures were produced in which TEGDMA was successively replaced by Bis-EMA4, 10wt% at a time. In the next six series, a constant 10wt% of TEGDMA was used, and Bis-GMA was successively replaced by Bis-EMA4, 10wt% at a time. Each material was labeled as $R_{(G/T/E)}$, where R=resin, G=Bis-GMA wt%, T=TEGDMA wt% and E=Bis-EMA4 wt%. The percentage values are relative to the monomer fraction in the organic phase.

In order to make photo-curing materials, 0.4wt% of camphorquinone (Esstech Inc.) and 0.8wt% of N,N-dimethyl-p-toluidine (Aldrich Chemical Co., Milwaukee, WI, USA) were dissolved in each mixture. In addition, 0.2wt% of hydroquinone (Aldrich Chemical Co.) was used as a radical scavenger. All chemicals were used as received, without further purification. Materials were loaded with silanated strontium glass fillers (Esstech Inc.), 0.7 and 2 μ m in size, to a constant content of 60wt% (1:1 of each size).

Film thickness

Film thickness was assessed according to ISO 4049 specification. [15]. Two optically flat, square glass plates, each 5mm thick and having a contact surface area of 200mm², were used. The combined thickness of the glass plates stacked in contact was measured with a digital caliper (reading A), accurate to 0.01mm (Mitutoyo, Tokyo, Japan). Then, 0.05ml of each luting material was placed centrally between the plates, and a constant load of 150N was carefully applied vertically and centrally via the top plate, for 180s, using a custom loading device. After this period, the loading system was released and light irradiation was performed for 80s (XL2500 – 3M ESPE, St. Paul, MN, USA,

700mW/cm²), in order to stabilize the specimen. The combined thickness of the two glass plates and the cement film was measured (reading B). Film thickness (μm) was recorded as the difference between reading B and reading A. For each material, five determinations were carried out.

Knoop hardness

The materials were placed into cylinder-shaped elastomer molds (5.5mm inner diameter x 1mm thick). A transparent polyester strip and a glass slide were placed against the bottom and top layers, and hand pressure was applied prior to 40s of light-activation on each layer. The specimens were then stored in light-proof containers at 37°C, for 24h. The specimens were then embedded in epoxy resin (Buehler, Lake Bluff, IL, USA) and wet-ground in an automatic polisher (APL-4, Arotec, Cotia, SP, Brazil) with 400-, 600- and 1200-grit SiC papers. A final polishing using 0.3μm alumina paste (Arotec) was carried out. After cleaning with air/water spray for 1min, five readings were performed on each sample through a microindenter (HMV-2, Shimadzu, Tokyo, Japan), under a load of 50g and a dwell time of 15s. The Knoop hardness number (KHN) for each specimen was recorded as the average of the five indentations.

Water sorption/solubility

Water sorption and solubility were tested according to ISO 4049 specification [15], except for the dimension of the specimens. For each material, five cylindrical samples were obtained using an elastomer mold (5.5mm inner diameter x 1mm thick). After light-activation for 40s on each side, both the thickness and diameter of samples were measured with a digital caliper, and the volume (V , in mm³) was calculated. Samples were stored in a desiccator at 37°C, and repeatedly weighed after 24h intervals using an analytical digital balance (AG-200, Gehaka, São Paulo, SP, Brazil) accurate to 0.1mg, until a constant mass (m_1) was obtained.

Samples were then individually placed in sealed plastic vials, immersed in 3mL of distilled water and stored at 37°C, for 7 days. Afterwards, the surface water of the specimens was removed by blotting with absorbent paper and waving the specimen in the air for 15s. Weighing procedures were repeated, whereby m_2 was recorded. Then, the specimens were placed again in the desiccator, at 37°C, and reweighed until a constant mass (m_3) was obtained. Water sorption (W_{sp}) and solubility (W_{sl}), given in $\mu\text{g}/\text{mm}^3$, were calculated as follows:

$$W_{sp} = (m_2 - m_3) / V$$

$$W_{sl} = (m_1 - m_3) / V$$

Statistical analysis

Data from each evaluation were separately submitted to ANOVA, followed by post-hoc Tukey test ($\alpha=0.05$). Additionally, a non-linear regression analysis was carried out in order to investigate the relationship between the gradual addition of Bis-EMA4, in substitution to either TEGDMA or Bis-GMA, and each physical property.

RESULTS

Table 1 shows the results for film thickness. During the mixing procedures, using a constant 50wt% of Bis-GMA, the addition of Bis-EMA4 increased the apparent viscosity of the luting materials. As a result, $R_{50/20/30}$, $R_{50/10/40}$ and $R_{50/0/50}$ showed significantly thicker films than $R_{50/50/0}$, $R_{50/40/10}$ and $R_{20/10/70}$ ($p<0.05$). Indeed, the non-linear regression model (Figure 3) was found to be significant ($R^2=0.999$; $p=0.002$), showing that the replacement of TEGDMA with Bis-EMA4 increased the film values, according to a sigmoid behavior, with a plateau of $66.7\mu\text{m}$ for $R_{50/0/50}$. On the other hand, when Bis-EMA4 substituted Bis-GMA, no significant increase in thickness was detected, despite the slight decay trend identified by the polynomial equation model in Figure 3 ($R^2=0.676$; $p=0.045$).

Hardness data are shown in Table 1. As depicted in Figure 4, a significant non-linear Gaussian relationship was detected between the substitution of TEGDMA and the

increase in hardness ($R^2=0.974$; $p=0.039$). $R_{50/20/30}$, $R_{50/10/40}$ and $R_{50/0/50}$ showed the highest hardness values among all groups ($p<0.05$). However, for luting materials in which Bis-EMA4 replaced Bis-GMA, no significant differences in hardness were detected, despite the significant relationship observed between increased hardness and the substitution of Bis-GMA ($R^2=0.984$; $p=0.002$), according to an exponential growth equation model of non-linear regression analysis.

Results for water sorption and solubility are also shown in Table 1. A continuous decrease in water uptake was observed when TEGDMA was substituted by Bis-EMA4, with a significant linear equation ($R^2=0.716$; $p=0.033$) detected (Figure 5). As a matter of fact, the decrease in water uptake still continued to take place when Bis-GMA was substituted by Bis-EMA4 ($R^2=0.904$; $p=0.030$), with an exponential non-linear decay behavior (Figure 5). For all groups, $R_{50/0/50}$ showed the highest sorption values ($p<0.05$), which were similar only to $R_{50/40/10}$. On the other hand, $R_{0/10/90}$ and $R_{0/0/100}$ displayed the lowest values ($p<0.05$). Unlike the sorption analysis, no significant differences regarding solubility were observed among the tested groups. The non-linear regression analysis was unable to detect any trends in alteration.

DISCUSSION

Film thickness

The increase in film thickness observed when TEGDMA was substituted by Bis-EMA4 is in accordance with previous studies [7,13,14], which showed the fluidity of a composite to be strongly dependent upon its resin components. This might be attributed to the higher viscosity of Bis-EMA4 (0.9Pa.s) [2] compared with TEGDMA (0.011Pa.s) [2]. In fact, $R_{50/20/30}$, $R_{50/10/40}$ and $R_{50/0/50}$ formed significantly thicker films compared to all remaining materials. This is probably related to the fact that Bis-GMA and Bis-EMA4 have a rigid molecular structure from the presence of phenyl groups, while TEGDMA has three oxyethylene units as a chain extender. Also, the presence of pendant hydroxyl groups in

Bis-GMA is the main reason for its viscosity, due to the strong hydrogen bonding with carbonyl groups [12,16].

The present results also showed that, when mixing at least 30wt% of TEGDMA with 50wt% of Bis-GMA, no significant influence on film thickness was detected. For amounts of less than 30wt% of TEGDMA, a significant sigmoid non-linear relationship was detected between the addition of Bis-EMA4 and the increase in film thickness (Figure 3). Despite both TEGDMA and Bis-EMA4 present lower viscosity than Bis-GMA, this result indicates that the dilution ability of TEGDMA is higher than that of Bis-EMA4, as explained by both the higher molecular weight and the higher structure stiffness of the Bis-EMA4 molecule.

On the other hand, when Bis-EMA4 substituted Bis-GMA, no significant difference in film thickness was detected, despite the slight trend toward decreased film thickness identified by the polynomial equation model (Figure 3). Surprisingly, substitution of the polar Bis-GMA by a more apolar structure did not improve resin flow. A hypothesis for this result is a possible capacity of the Bis-EMA4, even in a concentration of 50wt%, to act efficiently in disrupting the intermolecular polar forces attributed to Bis-GMA.

Knoop hardness

According to the present results, and as shown in Figure 4, the substitution of TEGDMA by Bis-EMA4 gradually increased the hardness means. This might be related to an increase in the degree of conversion as a function of the differences in the flexibility of the molecular structure and characteristics of the polymerization kinetics of Bis-EMA4 and TEGDMA, mainly their maximum rate of polymerization [9]. Also, this could be a result of replacing the flexible monomer, TEGDMA, with the stiffer Bis-EMA4 in the polymer, stiffening the network structure. Nonetheless, the increase in hardness followed a non-linear Gaussian equation model, with a reduction in hardness for $R_{50/0/50}$. This result might be related to the high viscosity of this material, which could have interfered with the monomer mobility in the environment, decreasing the reaction rate parameters and leading to lower double-bond conversion. In fact, this outcome corroborates with the results of the

film thickness analysis, which showed thick films for R_{50/0/50}, suggesting a high material viscosity.

In general, the current results showed that luting materials with high amounts of Bis-GMA presented the highest values for hardness, while composites with high amounts of TEGDMA showed lower values. Previous studies confirm hardness to be higher for Bis-GMA-rich composites [17,18]. Indeed, Sankarapandian et al. [18] reported that the presence of hydroxyl side chain groups in a polymer is related to its hardness value, and suggest that this is due to the formation of intermolecular hydrogen bonding, stiffening the network. In addition, the bulky aromatic rings of Bis-GMA hinder the mobility of monomers and polymer chains, enhancing the three-dimensional microstructure of the composite and improving its mechanical strength [18].

On the other hand, for the experimental luting materials in which Bis-EMA4 replaced Bis-GMA, no significant influence on hardness was detected, despite the relatively lower molecular stiffness of Bis-EMA4. This might be related to the reduction in the viscosity of the monomer system and, thus, to a higher degree of conversion. As a matter of fact, a trend toward decreased film thickness was observed when Bis-EMA4 replaced Bis-GMA in the comonomer.

Water sorption/solubility

As shown in Figure 4, a continuous decrease in water sorption was detected with the replacement of TEGDMA by Bis-EMA4. Likewise, this trend was observed when Bis-GMA was successively replaced by Bis-EMA4. This result can be explained by the chemical structure of the monomers composing the resin phase. The hydrophilic nature of a polymer is, in large part, a function of the chemistry of its components [11,12,19], especially with regard to the potential for hydrogen bonding and polar interactions [4,10]. TEGDMA has an aliphatic chain composed of ether linkages, which are hydrophilic, and Bis-GMA has an aromatic chain with polar hydroxyl groups. On the other hand, despite Bis-EMA4 being an aromatic dimethacrylate like Bis-GMA, the former has ether linkages in its molecular structure, but the hydroxyl groups, which form strong hydrogen bonds with

water molecules, are not present. Indeed, previous studies showed water sorption to be greater for Bis-GMA/TEGDMA-based resins compared with Bis-EMA-based materials [4,18].

Nonetheless, the explanation for the present outcomes does not solely rely on the chemical nature of the monomers. In general, polymers derived from TEGDMA present a much denser network than Bis-GMA and Bis-EMA4 derivatives [4]. Previous investigators have showed that the more densely cross-linked the network, the more heterogeneous is its structure [20,21]. Therefore, the high heterogeneity of TEGDMA polymers might favor moisture sorption, as the space available between the polymer clusters is larger, potentially accommodating high amounts of water [4,19].

Although most of the unreacted groups are not capable of being leached, as they are part of molecules that have reacted on only one end and are covalently bonded to the main polymer chain, the release of double unreacted units or oligomer chains, as well of polymerization promoters, may occur in an aqueous environment. Despite the differences described for water sorption, no significant differences were observed in the solubility analysis. A possible explanation for this is the time of immersion of the specimens. The ISO 4049 specification indicate that water sorption and solubility have to be calculated after 7 days immersion in water. Nevertheless, this period might be insufficient to permit the complete release of leachable species in the environment [4], as the access of water in a polymeric network is dependent upon the diffusion coefficient of water through the composite [22], which is also dictated by the formulation of the material

CONCLUSION

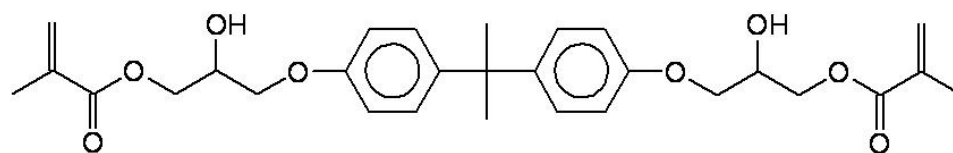
Within the limitations of the present study, Bis-EMA4 demonstrated to be a useful alternative in the development of resin-based luting agents.

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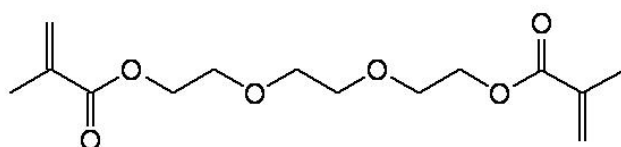
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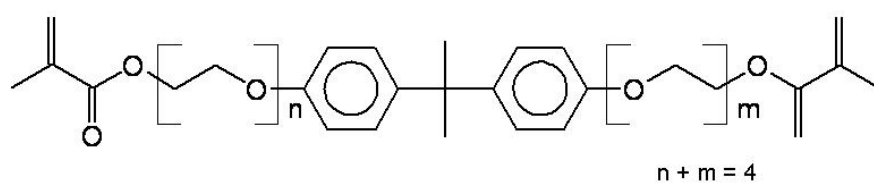
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Bis-GMA



TEGDMA



Bis-EMA4

Fig. 1 – Molecular structure of the monomers used in the study.

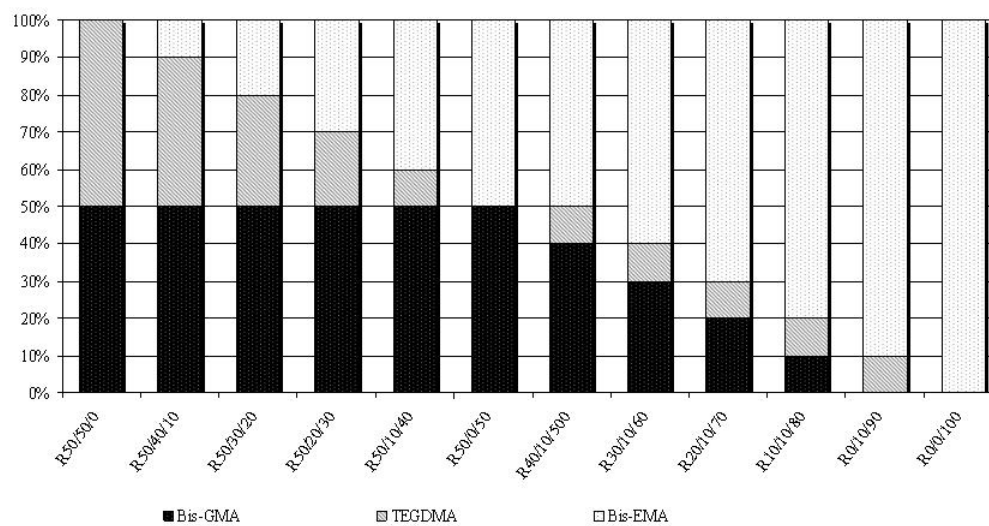


Fig. 2 – Organic matrix components (wt%) of the experimental resin luting agents.

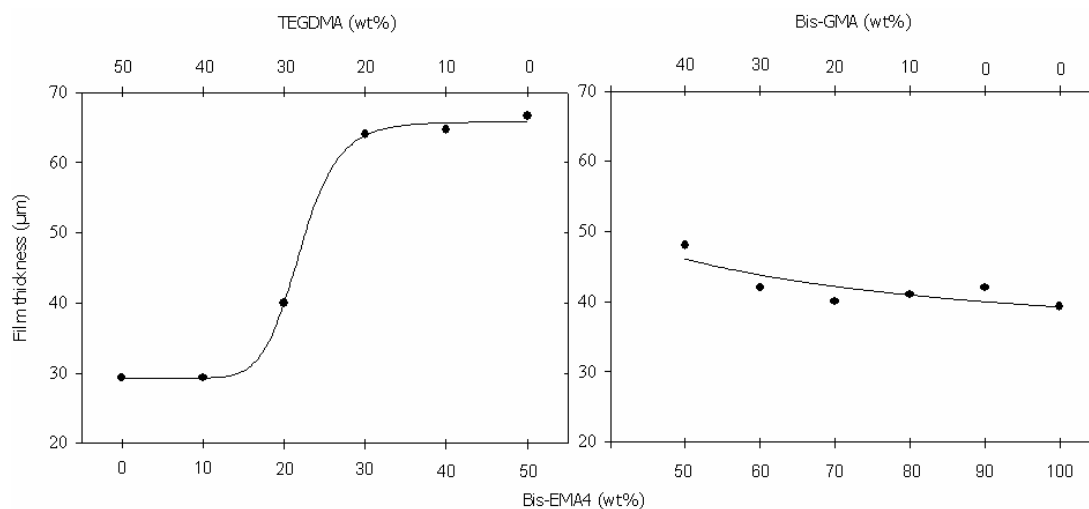


Fig. 3 – Non-linear regression model for film thickness. A significant relationship between the replacement of TEGDMA with Bis-EMA4 and the increase in thickness was detected ($R^2=0.999$; $p=0.002$), according to a sigmoid behavior. When Bis-EMA4 substituted Bis-GMA, only a slight decay trend was identified by a polynomial equation model ($R^2=0.676$; $p=0.045$).

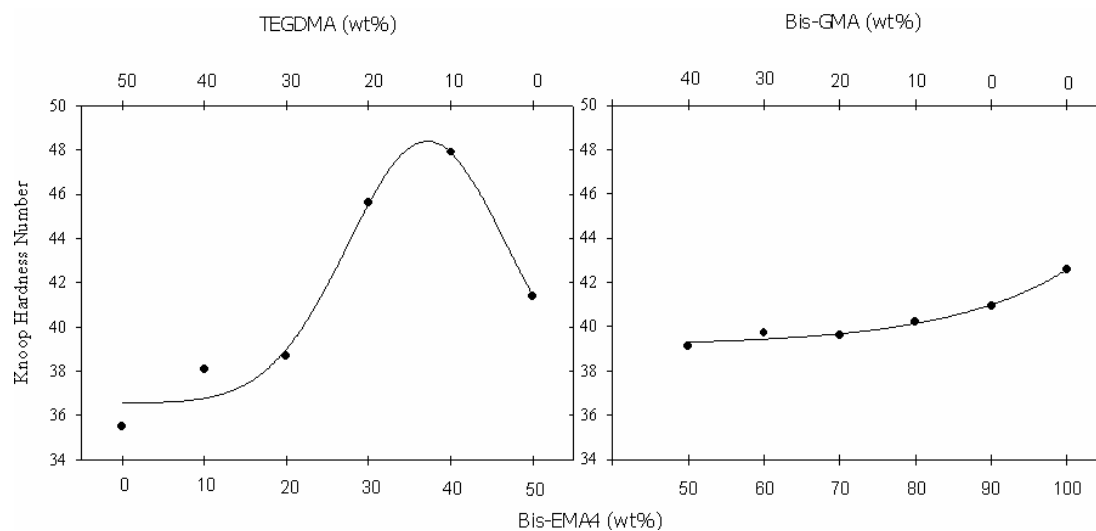


Fig. 4 – Non-linear regression model for hardness. A significant Gaussian relationship was detected between the substitution of TEGDMA by Bis-EMA4 and the increase in hardness ($R^2=0.974$; $p=0.039$). A significant relationship was also observed between increased hardness and the substitution of Bis-GMA by Bis-EMA4 ($R^2=0.984$; $p=0.002$), according to an exponential growth equation model.

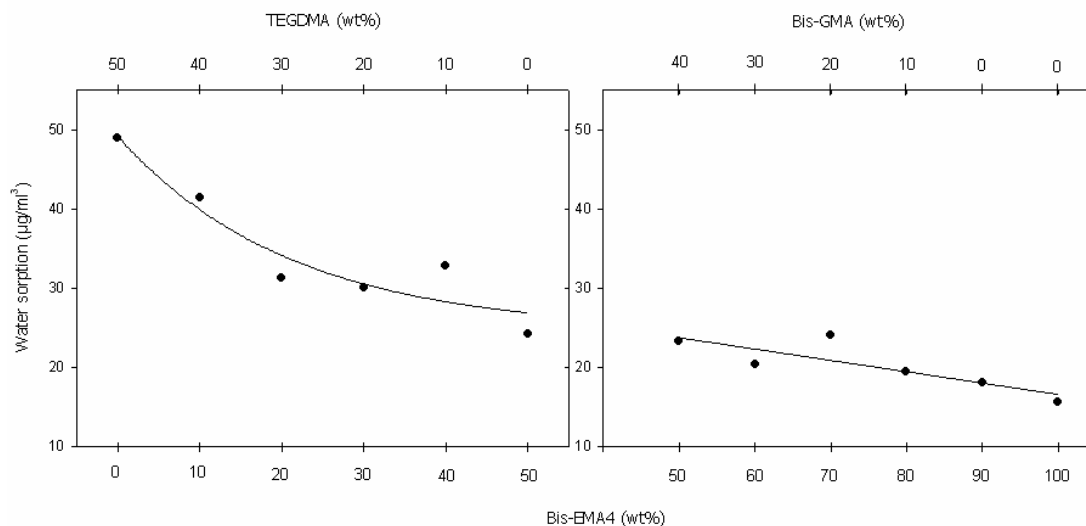


Fig. 5 – Regression model for water sorption. A continuous decrease in water uptake was observed when TEGDMA was substituted by Bis-EMA4, according to a significant linear equation ($R^2=0.716$; $p=0.033$). The decrease in water sorption still continued to take place when Bis-GMA was substituted by Bis-EMA4, with a significant exponential non-linear decay behavior ($R^2=0.904$; $p=0.030$).

CONSIDERAÇÕES GERAIS

Com o objetivo de investigar a influência da incorporação de Bis-EMA sobre propriedades de agentes de cimentação resinosos, o primeiro passo deste estudo foi avaliar o grau de conversão dos materiais. Os resultados mostraram que a substituição de TEGDMA ocasionou significativo aumento na conversão de ligações duplas. Embora algumas explicações para este resultado tenham sido sugeridas no Capítulo 1, este resultado mostrou, inicialmente, efeito positivo na substituição de TEGDMA, uma vez que a conversão de monômeros está intimamente relacionada a propriedades como dureza e solubilidade, além de influenciar a biocompatibilidade do material. Por outro lado a substituição do Bis-GMA não apresentou efeito significativo no grau de conversão.

No teste de resistência à flexão, nenhuma influência significativa da incorporação de Bis-EMA foi verificada. Todos os materiais apresentaram valores médios maiores que 100MPa, sendo estes superiores aos valor recomendado pela especificação 4049 da ISO. Dessa forma, a incorporação do monômero Bis-EMA, embora não tenha aprimorado as características de flexão dos cimentos, demonstrou novamente não influenciar negativamente esses materiais. Por outro lado, no mesmo ensaio, durante a avaliação do módulo de elasticidade, diferenças significativas foram verificadas. Embora a substituição de TEGDMA não tenha apresentado influência significativa, provavelmente devido à alta quantidade de Bis-GMA presente nas misturas R₀₁₋₀₆, a substituição de Bis-GMA reduziu significativamente o módulo de elasticidade. Como salientado no Capítulo 1, a avaliação do módulo de elasticidade pode indicar importantes características do compósito, como densidade de ligações cruzadas e tensão de contração de polimerização. De forma geral, um baixo valor para o módulo de elasticidade significa menor tensão de contração sendo gerada. Assim, efeito positivo da incorporação de Bis-EMA em substituição ao Bis-GMA foi evidenciado.

Durante a mistura de monômeros e formulação dos materiais, verificou-se que, quando a concentração de Bis-GMA era mantida constante em 50%, a gradual incorporação de Bis-EMA aumentou gradualmente a viscosidade dos materiais. De fato, durante a avaliação de espessura de película, os agentes que continham misturas de 50% de Bis-GMA

com altas concentrações de Bis-EMA (30, 40 e 50%) foram os únicos a ultrapassar o valor limite de 50µm estipulado pela especificação 4049 da ISO. Este resultado implica que, apesar da influência benéfica da incorporação de Bis-EMA sobre determinadas propriedades, tal adição deve ser feita com cuidado quando grande quantidade de Bis-GMA compõe a matriz orgânica. A viscosidade do sistema está relacionada a características de manipulação e escoamento do mesmo, e pode interferir na reatividade do meio e, assim, na conversão de ligações duplas. Em contrapartida, quando o Bis-GMA passou a ser substituído por Bis-EMA, nenhum efeito significativo na espessura de película foi evidenciado, bem como nenhuma influência significativa sobre a viscosidade das misturas foi detectada.

Por outro lado, os resultados do teste de dureza mostraram que compósitos com grandes quantidades de Bis-EMA e/ou Bis-GMA apresentaram valores significativamente maiores quando comparados a misturas com grande quantidade de TEGDMA. A dureza é uma propriedade comumente relacionada à resistência ao desgaste e à tenacidade do material. Este resultado, em conjunto principalmente com o do grau de conversão, reafirma que a adição de Bis-EMA, principalmente em substituição ao TEGDMA, pode influenciar de maneira positiva as propriedades do compósito.

Por outro lado, a avaliação que apresentou influência mais destacada da substituição tanto de TEGDMA quanto de Bis-GMA foi a de sorção de água. Os resultados mostraram diminuição gradual e significativa da quantidade de água absorvida à medida que o Bis-EMA era incorporado, ou seja, materiais contendo maiores quantidades de Bis-EMA apresentaram menor quantidade de água absorvida. Considerando que os efeitos deletérios da água na rede polimérica são bem conhecidos, com potencial para alteração química e estrutural da mesma, materiais que permitam menor acesso à umidade potencialmente apresentariam maior longevidade clínica. Dessa forma, pode se considerar que a incorporação de Bis-EMA apresenta promissora influência relacionada à estabilidade hídrica dos mesmos.

Apesar dos dados obtidos para a avaliação da sorção de água, a solubilidade dos materiais não foi influenciada pela substituição de TEGDMA ou Bis-GMA. Como sugerido no Capítulo 2, este resultado provavelmente está mais relacionado ao curto tempo de

imersão das amostras em água do que propriamente à composição da matriz orgânica dos compósitos. Dessa forma, em avaliações futuras, tempos maiores de imersão, assim como o efeito de outros solventes na rede polimérica, são fatores que necessitam investigação mais profunda. No entanto, de maneira geral, o presente estudo mostra que a incorporação de Bis-EMA a compósitos baseados em Bis-GMA e TEGDMA apresenta grande potencialidade em relação à melhoria de propriedades físicas e mecânicas dos mesmos, sendo este um dos primeiros passos a serem considerados para uma mais ampla utilização deste monômero em formulações comerciais de compósitos resinosos odontológicos.

CONCLUSÃO

Dentro das limitações do presente estudo, as seguintes conclusões podem ser definidas:

1. Quanto à substituição de TEGDMA por Bis-EMA:

- promoveu aumento significativo no grau de conversão de monômeros;
- não influenciou significativamente a resistência à flexão dos materiais;
- não apresentou influência significativa sobre o módulo de elasticidade;
- ocasionou aumento significativo na espessura de película dos cimentos;
- aumentou significativamente a dureza dos materiais;
- proporcionou contínua e significativa diminuição na sorção de água;
- não influenciou a solubilidade em água dos compósitos.

2. Quanto à substituição de Bis-GMA por Bis-EMA:

- não apresentou influência significativa no grau de conversão de monômeros;
- não influenciou significativamente a resistência à flexão dos materiais;
- reduziu significativamente o módulo de elasticidade dos compósitos;

- não influenciou significativamente a espessura de película;
- não ocasionou influência significativa na dureza dos cimentos;
- proporcionou contínua e significativa diminuição na sorção de água;
- não influenciou a solubilidade em água dos materiais.

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APÊNDICE 1

METODOLOGIA ILUSTRADA



Fig. 1 – Monômeros utilizados no estudo: Bis-GMA, TEGDMA e Bis-EMA.



Fig. 2 – Demais reagentes: canforoquinona, dimetil-p-toluidina, cargas silanizadas de vidro de estrôncio (0,7 e 2µm).

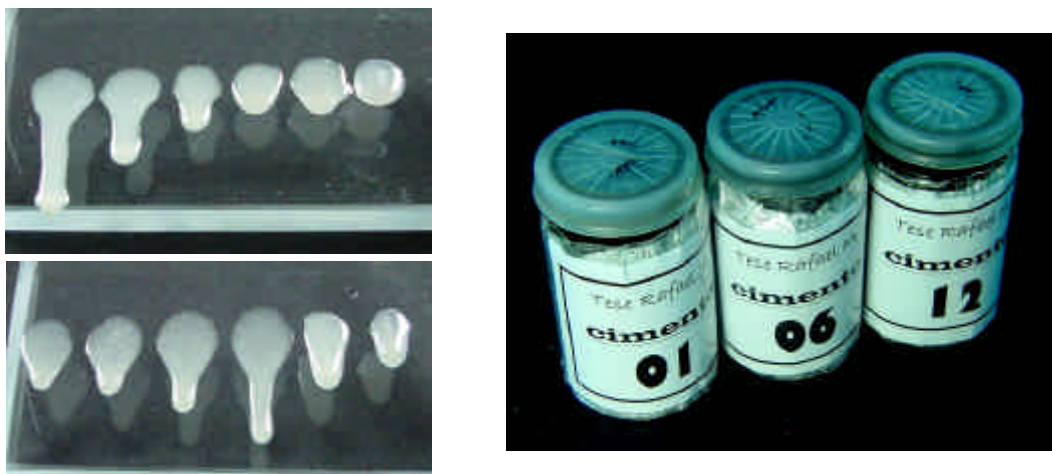


Fig. 3 – Viscosidade das diferentes misturas (R₀₁ a R₀₆) e (R₀₇ a R₁₂). Ao lado, detalhe dos frascos utilizados para identificação e armazenamento dos cimentos.

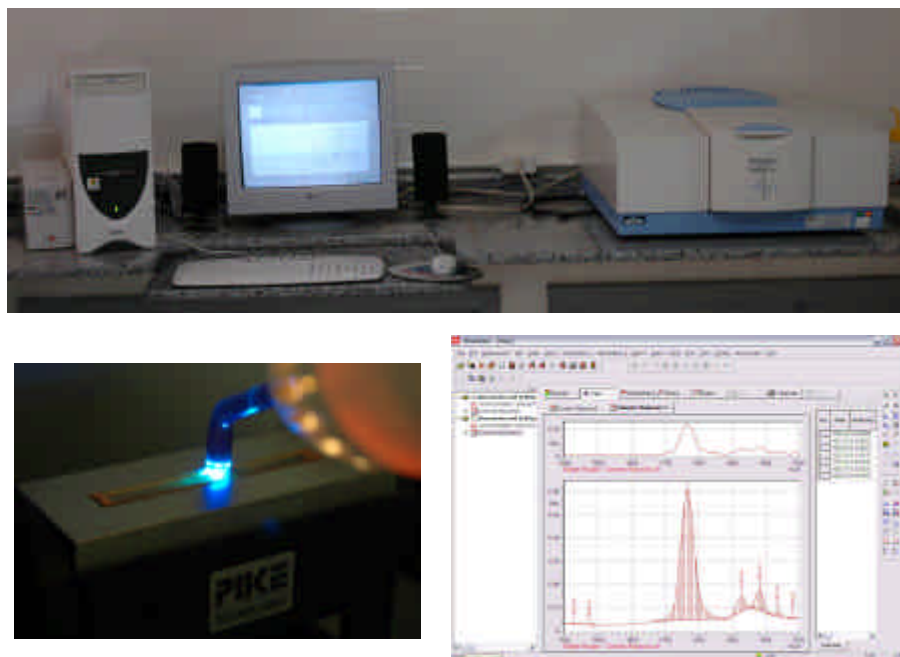


Fig. 4 – Equipamento utilizado para análise do grau de conversão. Em detalhe, dispositivo para ativação das amostras e o software IRSolution em

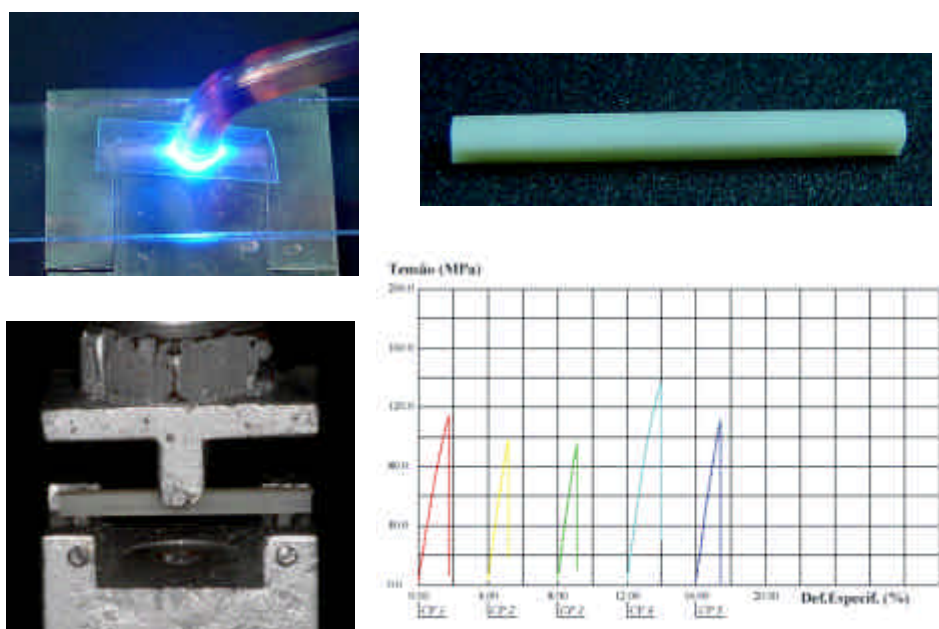


Fig. 5 – Confeção de amostras para teste de resistência à flexão. Em detalhe, dispositivo de 3 pontos e gráfico (tensão x deformação) para obtenção do módulo de elasticidade.

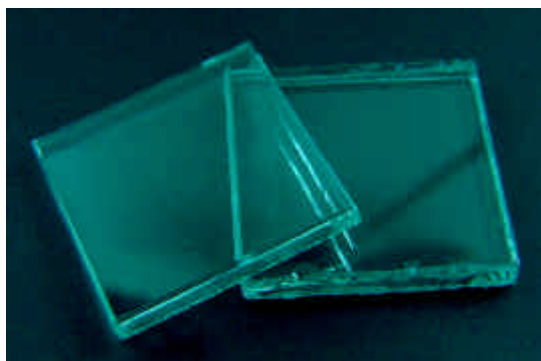


Fig. 6 – Placas de vidro utilizadas para avaliação da espessura de película. Ao lado, mensuração das placas em contato.

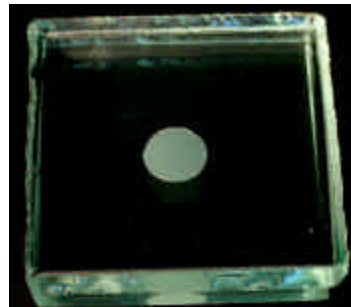


Fig. 7 – Padronização do volume de cimento a ser dispensado entre as placas de vidro.

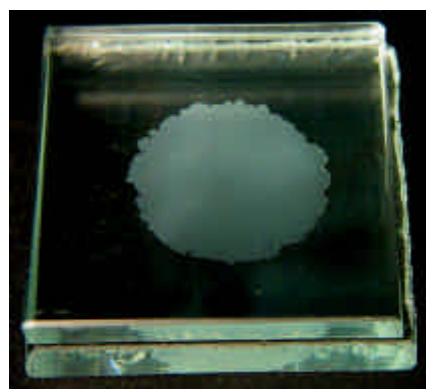
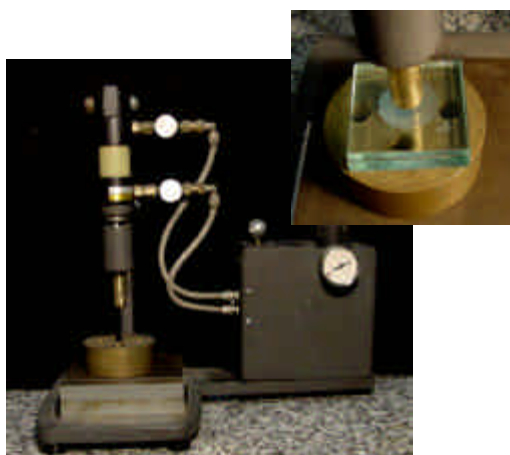


Fig. 8 – Dispositivo utilizado para aplicação de carga constante. Ao lado, película de cimento obtida ao final do teste.



Fig. 9 – Amostras do teste de flexão sendo incluídas em resina epóxi para posterior polimento em politriz automática com lixas d'água (granulação 400, 600 e 1200) e pasta de alumina (0,3 μ m).

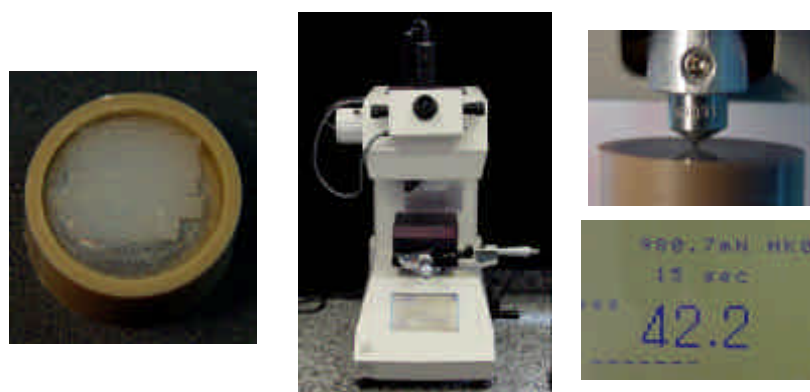


Fig. 10 – Amostras levadas ao microdurômetro. Ao lado, penetração sendo realizada e número de dureza calculado pelo software do equipamento.

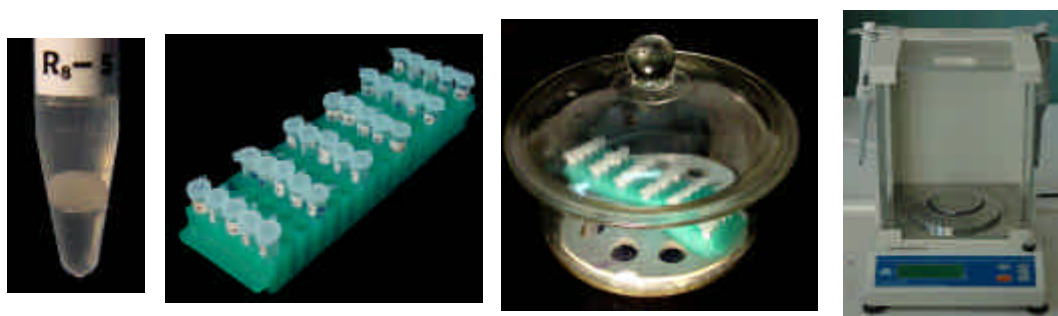


Fig. 11 – Espécimes para sorção e solubilidade sendo armazenados em dessecador. Ao lado, balança analítica digital utilizada para pesagem das amostras.

APÊNDICE 2

ANÁLISE ESTATÍSTICA DETALHADA

One Way Analysis of Variance sexta-feira, novembro 24, 2006, 19:08:15

Data source: Degree of conversion

Normality Test: Passed (P = 0,554)

Equal Variance Test: Passed (P = 0,919)

Group Name	N	Missing	Mean	Std Dev	SEM
R01	3	0	51,500	1,808	1,044
R02	3	0	55,600	2,456	1,418
R03	3	0	53,233	2,303	1,330
R04	3	0	62,800	1,572	0,907
R05	3	0	60,333	2,101	1,213
R06	3	0	65,033	2,468	1,425
R07	3	0	56,033	1,258	0,726
R08	3	0	52,033	1,856	1,071
R09	3	0	55,733	1,501	0,867
R10	3	0	49,827	1,856	1,071
R11	3	0	50,600	2,193	1,266
R12	3	0	49,933	2,013	1,162

Source of Variation	DF	SS	MS	F	P
Between Groups	11	1213,357	110,305	28,064	<0,001
Residual	24	94,333	3,931		
Total	35	1307,690			

The differences in the mean values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0,001).

Power of performed test with alpha = 0,050: 1,000

All Pairwise Multiple Comparison Procedures (Tukey Test):

Comparisons for factor:

Comparison	Diff of Means	p	q	P	P<0,050
R06 vs. R10	22,067	12	19,278	<0,001	Yes
R06 vs. R12	15,100	12	13,192	<0,001	Yes
R06 vs. R11	14,433	12	12,610	<0,001	Yes
R06 vs. R01	13,533	12	11,823	<0,001	Yes
R06 vs. R08	13,000	12	11,357	<0,001	Yes
R06 vs. R03	11,800	12	10,309	<0,001	Yes
R06 vs. R02	9,433	12	8,241	<0,001	Yes
R06 vs. R09	9,300	12	8,125	<0,001	Yes

R06 vs. R07	9,000	12	7,863	<0,001	Yes
R06 vs. R05	4,700	12	4,106	0,201	No
R06 vs. R04	2,233	12	1,951	0,957	Do Not Test
R04 vs. R10	19,833	12	17,327	<0,001	Yes
R04 vs. R12	12,867	12	11,241	<0,001	Yes
R04 vs. R11	12,200	12	10,658	<0,001	Yes
R04 vs. R01	11,300	12	9,872	<0,001	Yes
R04 vs. R08	10,767	12	9,406	<0,001	Yes
R04 vs. R03	9,567	12	8,358	<0,001	Yes
R04 vs. R02	7,200	12	6,290	0,007	Yes
R04 vs. R09	7,067	12	6,174	0,009	Yes
R04 vs. R07	6,767	12	5,912	0,014	Yes
R04 vs. R05	2,467	12	2,155	0,919	Do Not Test
R05 vs. R10	17,367	12	15,172	<0,001	Yes
R05 vs. R12	10,400	12	9,086	<0,001	Yes
R05 vs. R11	9,733	12	8,503	<0,001	Yes
R05 vs. R01	8,833	12	7,717	<0,001	Yes
R05 vs. R08	8,300	12	7,251	0,002	Yes
R05 vs. R03	7,100	12	6,203	0,009	Yes
R05 vs. R02	4,733	12	4,135	0,194	No
R05 vs. R09	4,600	12	4,019	0,224	Do Not Test
R05 vs. R07	4,300	12	3,757	0,304	Do Not Test
R07 vs. R10	13,067	12	11,416	<0,001	Yes
R07 vs. R12	6,100	12	5,329	0,035	Yes
R07 vs. R11	5,433	12	4,747	0,085	No
R07 vs. R01	4,533	12	3,961	0,241	Do Not Test
R07 vs. R08	4,000	12	3,495	0,401	Do Not Test
R07 vs. R03	2,800	12	2,446	0,838	Do Not Test
R07 vs. R02	0,433	12	0,379	1,000	Do Not Test
R07 vs. R09	0,300	12	0,262	1,000	Do Not Test
R09 vs. R10	12,767	12	11,154	<0,001	No
R09 vs. R12	5,800	12	5,067	0,053	No
R09 vs. R11	5,133	12	4,485	0,122	Do Not Test
R09 vs. R01	4,233	12	3,698	0,325	Do Not Test
R09 vs. R08	3,700	12	3,232	0,511	Do Not Test
R09 vs. R03	2,500	12	2,184	0,913	Do Not Test
R09 vs. R02	0,133	12	0,116	1,000	Do Not Test
R02 vs. R10	12,633	12	11,037	<0,001	No
R02 vs. R12	5,667	12	4,951	0,063	Do Not Test
R02 vs. R11	5,000	12	4,368	0,143	Do Not Test
R02 vs. R01	4,100	12	3,582	0,367	Do Not Test
R02 vs. R08	3,567	12	3,116	0,562	Do Not Test
R02 vs. R03	2,367	12	2,068	0,937	Do Not Test
R03 vs. R10	10,267	12	8,969	<0,001	No
R03 vs. R12	3,300	12	2,883	0,666	Do Not Test

R03 vs. R11	2,633	12	2,301	0,883	Do Not Test
R03 vs. R01	1,733	12	1,514	0,993	Do Not Test
R03 vs. R08	1,200	12	1,048	1,000	Do Not Test
R08 vs. R10	9,067	12	7,921	<0,001	No
R08 vs. R12	2,100	12	1,835	0,972	Do Not Test
R08 vs. R11	1,433	12	1,252	0,999	Do Not Test
R08 vs. R01	0,533	12	0,466	1,000	Do Not Test
R01 vs. R10	8,533	12	7,455	0,001	No
R01 vs. R12	1,567	12	1,369	0,997	Do Not Test
R01 vs. R11	0,900	12	0,786	1,000	Do Not Test
R11 vs. R10	7,633	12	6,669	0,004	No
R11 vs. R12	0,667	12	0,582	1,000	Do Not Test
R12 vs. R10	6,967	12	6,086	0,010	No

One Way Analysis of Variance

terça-feira, novembro 28, 2006, 00:07:00

Data source: Flexural strength

Normality Test: Passed (P = 0,355)

Equal Variance Test: Passed (P = 0,590)

Group Name	N	Missing	Mean	Std Dev	SEM
R01	5	0	109,543	14,821	6,628
R02	5	0	130,610	15,420	6,896
R03	5	0	124,367	30,452	13,619
R04	5	0	113,715	17,478	7,817
R05	5	0	110,477	21,050	9,414
R06	5	0	109,626	10,962	4,902
R07	5	0	109,842	15,978	7,145
R08	5	0	115,003	19,414	8,682
R09	5	0	118,928	15,816	7,073
R10	5	0	104,065	12,490	5,586
R11	5	0	105,317	14,224	6,361
R12	5	0	125,776	32,633	14,594

Source of Variation	DF	SS	MS	F	P
Between Groups	11	3915,218	355,929	0,937	0,514
Residual	48	18236,546	379,928		
Total	59	22151,763			

The differences in the mean values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference ($P = 0,514$).

Power of performed test with $\alpha = 0,050$: 0,050

The power of the performed test (0,050) is below the desired power of 0,800. Less than desired power indicates you are more likely to not detect a difference when one actually exists. Be cautious in over-interpreting the lack of difference found here.

One Way Analysis of Variance

sexta-feira, novembro 24, 2006, 16:08:50

Data source: Elastic modulus

Normality Test: Passed ($P = 0,228$)

Equal Variance Test: Passed ($P = 0,902$)

Group Name	N	Missing	Mean	Std Dev	SEM
R01	5	0	8,613	0,581	0,260
R02	5	0	7,771	0,703	0,314
R03	5	0	8,401	0,790	0,353
R04	5	0	9,593	0,666	0,298
R05	5	0	8,630	0,675	0,302
R06	5	0	6,352	0,505	0,226
R07	5	0	6,571	1,012	0,453
R08	5	0	6,524	0,379	0,170
R09	5	0	5,412	0,555	0,248
R10	5	0	5,858	0,425	0,190
R11	5	0	6,034	0,589	0,263
R12	5	0	5,979	0,798	0,357

Source of Variation	DF	SS	MS	F	P
Between Groups	11	104,598	9,509	21,735	<0,001
Residual	48	20,999	0,437		
Total	59	125,597			

The differences in the mean values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference ($P = <0,001$).

Power of performed test with $\alpha = 0,050$: 1,000

All Pairwise Multiple Comparison Procedures (Tukey Test):

Comparisons for factor:

Comparison	Diff of Means	p	q	P	P<0,050
R04 vs. R09	4,180	12	14,133	<0,001	Yes
R04 vs. R10	3,735	12	12,627	<0,001	Yes
R04 vs. R12	3,613	12	12,216	<0,001	Yes
R04 vs. R11	3,559	12	12,032	<0,001	Yes
R04 vs. R06	3,241	12	10,955	<0,001	Yes
R04 vs. R08	3,069	12	10,374	<0,001	Yes
R04 vs. R07	3,022	12	10,215	<0,001	Yes
R04 vs. R02	1,822	12	6,159	0,004	Yes
R04 vs. R03	1,192	12	4,028	0,193	No
R04 vs. R01	0,979	12	3,311	0,464	Do Not Test
R04 vs. R05	0,963	12	3,255	0,490	Do Not Test
R05 vs. R09	3,218	12	10,878	<0,001	Yes
R05 vs. R10	2,772	12	9,372	<0,001	Yes
R05 vs. R12	2,651	12	8,961	<0,001	Yes
R05 vs. R11	2,596	12	8,777	<0,001	Yes
R05 vs. R06	2,278	12	7,700	<0,001	Yes
R05 vs. R08	2,106	12	7,119	<0,001	Yes
R05 vs. R07	2,059	12	6,961	<0,001	Yes
R05 vs. R02	0,859	12	2,905	0,656	No
R05 vs. R03	0,229	12	0,774	1,000	Do Not Test
R05 vs. R01	0,0165	12	0,0559	1,000	Do Not Test
R01 vs. R09	3,201	12	10,822	<0,001	Yes
R01 vs. R10	2,756	12	9,316	<0,001	Yes
R01 vs. R12	2,634	12	8,905	<0,001	Yes
R01 vs. R11	2,580	12	8,722	<0,001	Yes
R01 vs. R06	2,261	12	7,645	<0,001	Yes
R01 vs. R08	2,089	12	7,064	<0,001	Yes
R01 vs. R07	2,042	12	6,905	<0,001	Yes
R01 vs. R02	0,843	12	2,849	0,682	Do Not Test
R01 vs. R03	0,212	12	0,718	1,000	Do Not Test
R03 vs. R09	2,989	12	10,105	<0,001	Yes
R03 vs. R10	2,543	12	8,599	<0,001	Yes
R03 vs. R12	2,422	12	8,187	<0,001	Yes
R03 vs. R11	2,368	12	8,004	<0,001	Yes
R03 vs. R06	2,049	12	6,927	<0,001	Yes
R03 vs. R08	1,877	12	6,346	0,003	Yes
R03 vs. R07	1,830	12	6,187	0,004	Yes
R03 vs. R02	0,630	12	2,131	0,931	Do Not Test
R02 vs. R09	2,359	12	7,973	<0,001	Yes
R02 vs. R10	1,913	12	6,468	0,002	Yes
R02 vs. R12	1,791	12	6,056	0,005	Yes

R02 vs. R11	1,737	12	5,873	0,007	Yes
R02 vs. R06	1,419	12	4,796	0,056	No
R02 vs. R08	1,247	12	4,215	0,147	Do Not Test
R02 vs. R07	1,200	12	4,056	0,186	Do Not Test
R07 vs. R09	1,159	12	3,918	0,225	No
R07 vs. R10	0,713	12	2,412	0,857	Do Not Test
R07 vs. R12	0,592	12	2,000	0,955	Do Not Test
R07 vs. R11	0,537	12	1,817	0,977	Do Not Test
R07 vs. R06	0,219	12	0,740	1,000	Do Not Test
R07 vs. R08	0,0470	12	0,159	1,000	Do Not Test
R08 vs. R09	1,112	12	3,759	0,278	Do Not Test
R08 vs. R10	0,666	12	2,253	0,903	Do Not Test
R08 vs. R12	0,545	12	1,842	0,975	Do Not Test
R08 vs. R11	0,490	12	1,658	0,989	Do Not Test
R08 vs. R06	0,172	12	0,581	1,000	Do Not Test
R06 vs. R09	0,940	12	3,178	0,526	Do Not Test
R06 vs. R10	0,495	12	1,672	0,988	Do Not Test
R06 vs. R12	0,373	12	1,261	0,999	Do Not Test
R06 vs. R11	0,319	12	1,077	1,000	Do Not Test
R11 vs. R09	0,621	12	2,101	0,937	Do Not Test
R11 vs. R10	0,176	12	0,595	1,000	Do Not Test
R11 vs. R12	0,0543	12	0,184	1,000	Do Not Test
R12 vs. R09	0,567	12	1,917	0,966	Do Not Test
R12 vs. R10	0,122	12	0,411	1,000	Do Not Test
R10 vs. R09	0,445	12	1,506	0,995	Do Not Test

One Way Analysis of Variance

Friday, May 12, 2006, 12:21:30

Data source: Film thickness

Normality Test: Passed(P = 0.229)

Equal Variance Test: Passed (P = 0.145)

Group	N	Missing
R1	5	0
R2	5	0
R3	5	0
R4	5	0
R5	5	0
R6	5	0
R7	5	0
R8	5	0

R9	5	0
R10	5	0
R11	5	0
R12	5	0

	Group Mean	Std Dev	SEM
R1	36.000	8.654	3.870
R2	28.000	6.515	2.914
R3	40.000	11.287	5.048
R4	64.000	8.625	3.857
R5	66.660	18.580	8.309
R6	64.680	16.599	7.423
R7	48.000	5.603	2.506
R8	42.020	4.480	2.003
R9	34.680	13.267	5.933
R10	45.360	15.016	6.715
R11	42.000	9.589	4.288
R12	39.320	10.090	4.512

Power of performed test with alpha = 0.050: 1.000

Source of Variation	DF	SS	MS	F	P
Between Treatments	1188	43.281	803.935	6.081	<0.001
Residual	4863	46.216	132.213		
Total	5915	189.497			

The differences in the mean values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference ($P = <0.001$).

All Pairwise Multiple Comparison Procedures (Tukey Test):

Comparisons for factor:

Comparison	Diff of Means	p	q	P<0.05
R5 vs. R2	38.660	12	7.518	Yes
R5 vs. R9	31.980	12	6.219	Yes
R5 vs. R1	30.660	12	5.962	Yes
R5 vs. R12	27.340	12	5.317	Yes
R5 vs. R3	26.660	12	5.185	Yes
R5 vs. R11	24.660	12	4.796	No
R5 vs. R8	24.640	12	4.792	No
R5 vs. R10	21.300	12	4.142	No
R5 vs. R7	18.660	12	3.629	No
R5 vs. R4	2.660	12	0.517	No
R5 vs. R6	1.980	12	0.385	No
R6 vs. R2	36.680	12	7.133	Yes

R6 vs. R9	30.000	12	5.834	Yes
R6 vs. R1	28.680	12	5.577	Yes
R6 vs. R12	25.360	12	4.932	Yes
R6 vs. R3	24.680	12	4.799	No
R6 vs. R11	22.680	12	4.411	No
R6 vs. R8	22.660	12	4.407	No
R6 vs. R10	19.320	12	3.757	No
R6 vs. R7	16.680	12	3.244	No
R6 vs. R4	0.680	12	0.132	No
R4 vs. R2	36.000	12	7.001	Yes
R4 vs. R9	29.320	12	5.702	Yes
R4 vs. R1	28.000	12	5.445	Yes
R4 vs. R12	24.680	12	4.799	No
R4 vs. R3	24.000	12	4.667	No
R4 vs. R11	22.000	12	4.278	No
R4 vs. R8	21.980	12	4.274	No
R4 vs. R10	18.640	12	3.625	No
R4 vs. R7	16.000	12	3.111	No
R7 vs. R2	20.000	12	3.889	No
R7 vs. R9	13.320	12	2.590	No
R7 vs. R1	12.000	12	2.334	No
R7 vs. R12	8.680	12	1.688	No
R7 vs. R3	8.000	12	1.556	No
R7 vs. R11	6.000	12	1.167	No
R7 vs. R8	5.980	12	1.163	No
R7 vs. R10	2.640	12	0.513	No
R10 vs. R2	17.360	12	3.376	No
R10 vs. R9	10.680	12	2.077	No
R10 vs. R1	9.360	12	1.820	No
R10 vs. R12	6.040	12	1.175	No
R10 vs. R3	5.360	12	1.042	No
R10 vs. R11	3.360	12	0.653	No
R10 vs. R8	3.340	12	0.650	No
R8 vs. R2	14.020	12	2.726	No
R8 vs. R9	7.340	12	1.427	No
R8 vs. R1	6.020	12	1.171	No
R8 vs. R12	2.700	12	0.525	No
R8 vs. R3	2.020	12	0.393	No
R8 vs. R11	0.0200	12	0.00389	No
R11 vs. R2	14.000	12	2.723	No
R11 vs. R9	7.320	12	1.424	No
R11 vs. R1	6.000	12	1.167	No
R11 vs. R12	2.680	12	0.521	No
R11 vs. R3	2.000	12	0.389	No
R3 vs. R2	12.000	12	2.334	No

R3 vs. R9	5.320	12	1.035	No
R3 vs. R1	4.000	12	0.778	No
R3 vs. R12	0.680	12	0.132	No
R12 vs. R2	11.320	12	2.201	No
R12 vs. R9	4.640	12	0.902	No
R12 vs. R1	3.320	12	0.646	No
R1 vs. R2	8.000	12	1.556	No
R1 vs. R9	1.320	12	0.257	No
R9 vs. R2	6.680	12	1.299	No

One Way Analysis of Variance

Saturday, October 14, 2006, 20:16:14

Data source: Hardness

Normality Test: Passed (P = 0.246)

Equal Variance Test: Passed (P = 0.715)

Group	N	Missing
R01	5	0
R02	5	0
R03	5	0
R04	5	0
R05	5	0
R06	5	0
R07	5	0
R08	5	0
R09	5	0
R10	5	0
R11	5	0
R12	5	0

Group	Mean	Std Dev	SEM
R01	35.464	1.211	0.542
R02	38.080	1.506	0.673
R03	38.696	1.905	0.852
R04	45.540	1.028	0.460
R05	47.908	3.465	1.549
R06	41.428	1.621	0.725
R07	39.084	1.213	0.543
R08	39.692	1.206	0.540
R09	39.644	2.999	1.341
R10	40.160	2.108	0.943
R11	40.908	0.979	0.438

R12 42.568 2.036 0.911

Power of performed test with alpha = 0.050: 1.000

Source of Variation	DF	SS	MS	F	P
Between Treatments	11	1613.621	55.784	15.036	<0.001
Residual	48	178.085	3.710		
Total	59	791.706			

The differences in the mean values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001).

All Pairwise Multiple Comparison Procedures (Tukey Test):

Comparisons for factor:

Comparison	Diff of Means	p	q	P<0.05
R05 vs. R01	12.444	12	14.446	Yes
R05 vs. R02	9.828	12	11.409	Yes
R05 vs. R03	9.212	12	10.694	Yes
R05 vs. R07	8.824	12	10.244	Yes
R05 vs. R09	8.264	12	9.594	Yes
R05 vs. R08	8.216	12	9.538	Yes
R05 vs. R10	7.748	12	8.995	Yes
R05 vs. R11	7.000	12	8.126	Yes
R05 vs. R06	6.480	12	7.523	Yes
R05 vs. R12	5.340	12	6.199	Yes
R05 vs. R04	2.368	12	2.749	No
R04 vs. R01	10.076	12	11.697	Yes
R04 vs. R02	7.460	12	8.660	Yes
R04 vs. R03	6.844	12	7.945	Yes
R04 vs. R07	6.456	12	7.495	Yes
R04 vs. R09	5.896	12	6.845	Yes
R04 vs. R08	5.848	12	6.789	Yes
R04 vs. R10	5.380	12	6.246	Yes
R04 vs. R11	4.632	12	5.377	Yes
R04 vs. R06	4.112	12	4.774	No
R04 vs. R12	2.972	12	3.450	No
R12 vs. R01	7.104	12	8.247	Yes
R12 vs. R02	4.488	12	5.210	Yes
R12 vs. R03	3.872	12	4.495	No
R12 vs. R07	3.484	12	4.045	No
R12 vs. R09	2.924	12	3.394	No
R12 vs. R08	2.876	12	3.339	No
R12 vs. R10	2.408	12	2.795	No
R12 vs. R11	1.660	12	1.927	No

R12 vs. R06	1.140	12	1.323	No
R06 vs. R01	5.964	12	6.924	Yes
R06 vs. R02	3.348	12	3.887	No
R06 vs. R03	2.732	12	3.172	No
R06 vs. R07	2.344	12	2.721	No
R06 vs. R09	1.784	12	2.071	No
R06 vs. R08	1.736	12	2.015	No
R06 vs. R10	1.268	12	1.472	No
R06 vs. R11	0.520	12	0.604	No
R11 vs. R01	5.444	12	6.320	Yes
R11 vs. R02	2.828	12	3.283	No
R11 vs. R03	2.212	12	2.568	No
R11 vs. R07	1.824	12	2.117	No
R11 vs. R09	1.264	12	1.467	No
R11 vs. R08	1.216	12	1.412	No
R11 vs. R10	0.748	12	0.868	No
R10 vs. R01	4.696	12	5.452	Yes
R10 vs. R02	2.080	12	2.415	No
R10 vs. R03	1.464	12	1.700	No
R10 vs. R07	1.076	12	1.249	No
R10 vs. R09	0.516	12	0.599	No
R10 vs. R08	0.468	12	0.543	No
R08 vs. R01	4.228	12	4.908	Yes
R08 vs. R02	1.612	12	1.871	No
R08 vs. R03	0.996	12	1.156	No
R08 vs. R07	0.608	12	0.706	No
R08 vs. R09	0.0480	12	0.0557	No
R09 vs. R01	4.180	12	4.853	Yes
R09 vs. R02	1.564	12	1.816	No
R09 vs. R03	0.948	12	1.101	No
R09 vs. R07	0.560	12	0.650	No
R07 vs. R01	3.620	12	4.202	No
R07 vs. R02	1.004	12	1.166	No
R07 vs. R03	0.388	12	0.450	No
R03 vs. R01	3.232	12	3.752	No
R03 vs. R02	0.616	12	0.715	No
R02 vs. R01	2.616	12	3.037	No

One Way Analysis of Variance

domingo, setembro 17, 2006, 00:38:56

Data source: Water sorption

Normality Test: Passed (P = 0,076)

Equal Variance Test: Passed (P = 0,959)

Group Name	N	Missing	Mean	Std Dev	SEM
R01	5	0	0,0490	0,00675	0,00302
R02	5	0	0,0414	0,00353	0,00158
R03	5	0	0,0313	0,00549	0,00245
R04	5	0	0,0301	0,00598	0,00267
R05	5	0	0,0328	0,00367	0,00164
R06	5	0	0,0242	0,00528	0,00236
R07	5	0	0,0234	0,00549	0,00245
R08	5	0	0,0204	0,00482	0,00216
R09	5	0	0,0240	0,00311	0,00139
R10	5	0	0,0195	0,00395	0,00177
R11	5	0	0,0180	0,00615	0,00275
R12	5	0	0,0157	0,00491	0,00220

Source of Variation	DF	SS	MS	F	P
Between Groups	11	0,00544	0,000495	19,409	<0,001
Residual	48	0,00122	0,0000255		
Total	59	0,00667			

The differences in the mean values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0,001).

Power of performed test with alpha = 0,050: 1,000

All Pairwise Multiple Comparison Procedures (Tukey Test):

Comparisons for factor:

Comparison	Diff of Means	p	q	P	P<0,050
R01 vs. R12	0,0333	12	14,744	<0,001	Yes
R01 vs. R11	0,0309	12	13,704	<0,001	Yes
R01 vs. R10	0,0295	12	13,057	<0,001	Yes
R01 vs. R08	0,0285	12	12,640	<0,001	Yes
R01 vs. R07	0,0256	12	11,344	<0,001	Yes
R01 vs. R09	0,0250	12	11,062	<0,001	Yes
R01 vs. R06	0,0248	12	10,985	<0,001	Yes
R01 vs. R04	0,0189	12	8,349	<0,001	Yes
R01 vs. R03	0,0176	12	7,809	<0,001	Yes
R01 vs. R05	0,0162	12	7,165	<0,001	Yes
R01 vs. R02	0,00755	12	3,345	0,448	No
R02 vs. R12	0,0257	12	11,399	<0,001	Yes
R02 vs. R11	0,0234	12	10,359	<0,001	Yes

R02 vs. R10	0,0219	12	9,712	<0,001	Yes
R02 vs. R08	0,0210	12	9,296	<0,001	Yes
R02 vs. R07	0,0181	12	7,999	<0,001	Yes
R02 vs. R09	0,0174	12	7,718	<0,001	Yes
R02 vs. R06	0,0173	12	7,641	<0,001	Yes
R02 vs. R04	0,0113	12	5,005	0,038	Yes
R02 vs. R03	0,0101	12	4,464	0,099	No
R02 vs. R05	0,00863	12	3,820	0,257	Do Not Test
R05 vs. R12	0,0171	12	7,579	<0,001	Yes
R05 vs. R11	0,0148	12	6,539	0,002	Yes
R05 vs. R10	0,0133	12	5,891	0,007	Yes
R05 vs. R08	0,0124	12	5,475	0,015	Yes
R05 vs. R07	0,00944	12	4,179	0,155	No
R05 vs. R09	0,00880	12	3,897	0,232	Do Not Test
R05 vs. R06	0,00863	12	3,820	0,257	Do Not Test
R05 vs. R04	0,00267	12	1,184	0,999	Do Not Test
R05 vs. R03	0,00145	12	0,643	1,000	Do Not Test
R03 vs. R12	0,0157	12	6,935	<0,001	Yes
R03 vs. R11	0,0133	12	5,895	0,006	Yes
R03 vs. R10	0,0118	12	5,248	0,024	Yes
R03 vs. R08	0,0109	12	4,832	0,052	No
R03 vs. R07	0,00798	12	3,535	0,365	Do Not Test
R03 vs. R09	0,00735	12	3,254	0,490	Do Not Test
R03 vs. R06	0,00717	12	3,177	0,526	Do Not Test
R03 vs. R04	0,00122	12	0,541	1,000	Do Not Test
R04 vs. R12	0,0144	12	6,395	0,002	Yes
R04 vs. R11	0,0121	12	5,355	0,019	Yes
R04 vs. R10	0,0106	12	4,707	0,065	No
R04 vs. R08	0,00969	12	4,291	0,130	Do Not Test
R04 vs. R07	0,00676	12	2,995	0,613	Do Not Test
R04 vs. R09	0,00613	12	2,713	0,742	Do Not Test
R04 vs. R06	0,00595	12	2,636	0,774	Do Not Test
R06 vs. R12	0,00849	12	3,758	0,278	No
R06 vs. R11	0,00614	12	2,718	0,740	Do Not Test
R06 vs. R10	0,00468	12	2,071	0,943	Do Not Test
R06 vs. R08	0,00374	12	1,655	0,989	Do Not Test
R06 vs. R07	0,000809	12	0,358	1,000	Do Not Test
R06 vs. R09	0,000174	12	0,0769	1,000	Do Not Test
R09 vs. R12	0,00831	12	3,682	0,307	Do Not Test
R09 vs. R11	0,00596	12	2,641	0,772	Do Not Test
R09 vs. R10	0,00450	12	1,994	0,956	Do Not Test
R09 vs. R08	0,00356	12	1,578	0,992	Do Not Test
R09 vs. R07	0,000636	12	0,282	1,000	Do Not Test
R07 vs. R12	0,00768	12	3,400	0,423	Do Not Test
R07 vs. R11	0,00533	12	2,360	0,873	Do Not Test

R07 vs. R10	0,00387	12	1,713	0,986	Do Not Test
R07 vs. R08	0,00293	12	1,296	0,999	Do Not Test
R08 vs. R12	0,00475	12	2,104	0,937	Do Not Test
R08 vs. R11	0,00240	12	1,064	1,000	Do Not Test
R08 vs. R10	0,000940	12	0,416	1,000	Do Not Test
R10 vs. R12	0,00381	12	1,687	0,987	Do Not Test
R10 vs. R11	0,00146	12	0,647	1,000	Do Not Test
R11 vs. R12	0,00235	12	1,040	1,000	Do Not Test

One Way Analysis of Variance

domingo, setembro 17, 2006, 00:41:38

Data source: Solubility

Normality Test: Passed (P = 0,669)

Equal Variance Test: Passed (P = 0,920)

Group Name	N	Missing	Mean	Std Dev	SEM
R01	5	0	0,00585	0,00294	0,00131
R02	5	0	0,00977	0,00432	0,00193
R03	5	0	0,00562	0,00402	0,00180
R04	5	0	0,00455	0,00159	0,000711
R05	5	0	0,00827	0,00431	0,00193
R06	5	0	0,00785	0,00361	0,00161
R07	5	0	0,00686	0,00294	0,00132
R08	5	0	0,00608	0,00300	0,00134
R09	5	0	0,00835	0,00432	0,00193
R10	5	0	0,00572	0,00202	0,000901
R11	5	0	0,00696	0,00329	0,00147
R12	5	0	0,00986	0,00442	0,00198

Source of Variation	DF	SS	MS	F	P
Between Groups	11	0,000157	0,0000143	1,159	0,340
Residual	48	0,000593	0,0000123		
Total	59	0,000750			

The differences in the mean values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0,340).

Power of performed test with alpha = 0,050: 0,096

ANEXO



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