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Influence of hydroxyethyl acrylamide addition to dental adhesive resin

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ABSTRACT

Objective. to determine the physicochemical properties of experimental adhesive resins containing hydroxyethyl acrylamide.

Methods. Three groups of experimental resin were formulated, $G_{HEAA33\%}$ (33.3 wt% HEAA + 66.6 wt% BisGMA), $G_{HEAA50\%}$ (50 wt% HEAA + 50 wt% BisGMA), and $G_{HEAA-FREE}$ (33.3 wt% HEMA + 66.6 wt% of BisGMA). The polymerization process of each adhesive resin group, as well as for the homopolymers, BisGMA, HEMA, HEAA, HEMA* without EDAB, and HEAA* without EDAB, was characterized through differential scanning calorimetry (DSC). Elution of monomers was evaluated by ^{1}H NMR. Dynamic mechanical analysis (DMA) was used to collect the glass transition temperature (T_g), the storage modulus (E') and the reticulation degree (ρ). Flexural strength was calculated by three-point bending test with 0.75 mm/min. Softening in solvent was calculated through hardness before and after immersion in water or ethanol.

Results. $G_{HEAA50\%}$, $G_{HEAA33\%}$, $G_{HEAA-FREE}$ presented higher polymerization rate ($R_{p_{max}} = 13.52$, 12.3 and 5.3 mmol g^{-1} s^{-1}, respectively) than homopolymers HEMA, HEMA* and HEAA*. Group with HEAA presented higher degree of conversion ($G_{HEAA50\%} = 64.07\% > G_{HEAA33\%} = 55.82\% > G_{HEAA-FREE} = 49.02\%$; $p = 0.008$) All groups presented low elution of monomers ($p > 0.05$). The values of E' were higher on $G_{HEAA33\%}$ than $G_{HEAA-FREE}$ ($p = 0.034$). T_g and flexural strength values of $G_{HEAA-FREE}$ were higher than acrylamide groups ($p = 0.022$ and $p < 0.001$, respectively). Hardness varied from 27.05 to 34.78 for water and from 63.27 to 68.51 for ethanol with no difference for ρ values.

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Significance. The addition of HEAA increased the materials reactivity and, consequently, improved the maximum rate of polymerization, degree of conversion and the storage modulus of experimental adhesive resin.

1. Introduction

Dental adhesive systems' bond strength to tooth substrate is related to a wide range of variables, such as the chemical structure [1], polymerization process [2] and interactions between functional monomers [3]. Contemporary adhesives contain hydrophobic and hydrophilic functional monomers – such as acrylates, methacrylates and vinyl esters [3,4] – to achieve polymers with reliable properties [2,5].

Methacrylate monomers, such as 2-hydroxyethyl methacrylate (HEMA), exhibit low reactivity [6], high water sorption [7] and high solubility [1]. In these systems, hydrolysis of the methacrylate ester group can occur, either when these monomers are combined with water from the formulation of commercial adhesive systems or at the adhesive–dentin interface. As a result, polymer properties [8,9] and monomer shelf life [3] are compromised. Low molecular weight and high hydrophilicity of HEMA can also lead to an adhesive layer more prone to water sorption, leading to decreased properties in the formed polymer [9]. Consequently, a decrease in physicochemical properties is observed, affecting the long-term behavior of the adhesive interface [6]. Furthermore, leaching of degraded polymer chains through dentinal tubules can lead to toxicity effects on pulp cells [10].

In order to improve the hydrolysis resistance of adhesive systems, alternatives have been proposed such as HEMA-free adhesive systems [4,11,12] and methacrylates monomers substitution by acrylamides and methacrylamides [3]. Acrylamides and methacrylamides have a more stable amide group (RNH–CO– or –CO–NR$_1$R$_2$) instead of an ester group (–COOR) [13]. Moreover, acrylamides are similar to the amino acids that compose collagen fibrils, with carboxylate groups [14] which could facilitate hydrogen bond between collagen and amide groups (N–H) of acrylamides [15]. Thus, in theory, acrylamide components could also provide hydrolytic stability to the hybrid layer without compromising biocompatibility [16].

Despite the great variety of studies of adhesive systems development regarding different characteristics such as radiopacity [17], anticariogenic potential [18,19], and increased bond strength to dental tissues [1,20], few studies evaluate the development of more hydrolytically stable polymers [12,21,22] and the replacement of HEMA by methacrylamide monomers in adhesive systems are barely studied [23]. Therefore, the purpose of this study is to determine the resultant physicochemical properties – polymerization behavior (degree of conversion and maximum rate or polymerization), residual monomers elution, hardness and the resultant softening, glass transition temperature (T_g), storage modulus, reticulation degree (ρ), and flexural strength – of experimental adhesive resins containing hydroxyethyl acrylamide (HEAA).

2. Materials and methods

2.1. Formulation

Three experimental adhesive resins were produced in order to analyze the influence of HEAA incorporation at adhesive resins: G$_{HEAA33\%}$ (33.3% hydroxyethyl acrylamide—HEAA + 66.6% Bisphenol A glycerolate dimethacrylate-BisGMA), G$_{HEAA50\%}$ (50% HEAA + 50% BisGMA) and G$_{HEAA-FREE}$ (33.3% 2-hydroxyethyl methacrylate—HEMA + 66.6% BisGMA). The photoinitiator:co-initiator system was composed by 0.8 mol% camphorquinone (CQ) and 0.4 mol% ethyl 4-dimethylaminobenzoate (EDAB). The base homopolymers, BisGMA, HEAA, HEMA, HEAA* without EDAB, and HEMA* without EDAB, were characterized by degree of conversion and polymerization kinetics. All components were provided by Sigma-Aldrich (St. Louis, MO, USA). To perform monomer photoactivation, a light-emitting diode unit (Radii Cal, SDI Ltd., AT), at an intensity value of 1200 mW/cm^2, was used.

2.2. Degree of conversion and polymerization kinetics

The degree of conversion and the polymerization kinetics for each experimental adhesive resin and homopolymers were evaluated via differential scanning calorimetry (DSC; DSC-Q2000, TA Instrument Co., DE, USA) 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 (approximately 16 mg) were polymerized in open aluminum DSC pans and covered with a quartz lid. An additional empty aluminum pan was used as a control. The lamp was switched on for 3 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 Eq. (1):

$$\alpha(\text{mol\%}) = 100 \times \frac{[M]_0 - [M]}{[M]_0} = \frac{100Q}{(\Delta H_{p,0}/\Delta H_p)Q_{tot}} \qquad (1)$$

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 for a time, t. The $\Delta H_{p,0}$ value for a double bond of methacrylates has been reported to be −56 J mol^{-1} [24], and for acrylamides, −82.9 J mol^{-1} [25]. The rate of polymerization (R_p) is proportional to the heat flow released in the isotherm as a function of irradiation time (t). Thus, R_p (mmol g^{-1} s^{-1}) at