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Structure–properties relationships in dental adhesives: Effect of initiator, matrix monomer structure, and nano-filler incorporation

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ABSTRACT

Objectives. This is a confirmatory study to evaluate the effect of photoinitiator type and concentration, matrix monomer chemical structure, and nanoparticle incorporation on the physical and mechanical properties of an experimental dentin bonding agent.

Materials and methods. Different concentrations of camphorquinone-amine (CQ-A) system, butanedione (BD), and phenylpropanedione (PPD), as photoinitiator, BTDMA, as a comonomer containing carboxylic acid groups, and silica nanoparticles as reinforcing inorganic filler were incorporated into a methacrylate base experimental dental adhesive. The effect of these ingredients, as independent variables, on the shrinkage kinetics, flexural strength and modulus, and microshear bond strength of the adhesives were then investigated. The results were analyzed using one-way ANOVA and Tukey's post-hoc test at the significance level of 0.05.

Results. The results indicate that the efficiency of CQ-A initiator system is diminished in the presence of the acidic monomer BTDMA while the photopolymerization is efficiently progressed with BD as initiator. PPD shows the lowest efficiency in the photopolymerization of the adhesives. BTDMA as a monomer with the capability of interaction with tooth structure provides adhesive with improved microshear bond strength to dentin. Incorporation of silica nanoparticles at low concentrations enhances the flexural and microshear strength of the dentin bonding agent.

Significance. Understanding the structure–property relationship in dental adhesives may help the material selection in clinical dentistry. The study elucidates the relationship between monomer structure, initiator type, and nanofiller and physical and mechanical properties in dental adhesives.

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1. Introduction

The main role of dental adhesives is creation of a good adhesion between the restorative composites and dental structure in order to avoid sensitivity after restoration, color change, and micro leakage [1–4]. Due to the dynamic nature of dentin, adhesion to this wet substrate is more complicated than enamel [5,6]. The bonding mechanism of dentin adhesives is based on the penetration of amphiphilic molecules into the acid-etched dentin, which subsequently results in a hybrid layer of polymerized resin and collagen fibrils and strengthening of adhesion to dentin [7,8]. The adhesive layer at the resin–dentin interface has the lowest elastic modulus [4,9]. Defects or cracks may occur at the low-modulus adhesive layer when the occlusal load exceeds its inherent strength leading to the failure of restoration [8,10,11]. Adhesives ingredients have important role in their adhesive and cohesive properties. Monomers are the main components in dental adhesives which affect the properties and hydrolytic stability of dental adhesives in wet tooth structure and the formed hybrid layer [12–17]. Bifunctional monomers containing carboxylic acid or phosphate groups in their structure are able to provide ionic bond to the tooth structure while their methacrylate functionalities create covalent bonds with the resin monomers of the restorative composites [4,18]. It has also been reported that the incorporation of fillers into the adhesives would increase the mechanical properties of the adhesive layer and adhesion strength [8,19,20]. Polymerization initiators are responsible for setting process in the adhesives. The degree of polymerization conversion, rate of polymerization, and, consequently, the mechanical and adhesion properties of the bonding agents are affected by the type and concentration of the applied initiator system [1,21–24]. The phase separation of the hydrophilic/hydrophobic adhesive monomers and solvents and the partitioning of the photoinitiator/activator in the phases should also be considered in the initiator selection [22,25,26].

Therefore, in this study the effects of the structural adhesive components are studied. The effect of incorporation of BTDMA, a dimethacrylate monomer based on BTDA (3,3′,4,4′-benzophenone tetracarboxylic dianhydride), containing carboxylic acid functionalities [27], as a functional monomer, and three photoinitiators, camphorquinone-amine (CQ-A), butanedione (BD), and phenylpropanedione (PPD) on the shrinkage behavior of an experimental dentin bonding system is investigated. In addition, the effect of the incorporation of silica nanoparticles and BTDMA on the adhesion strength and mechanical properties of the dentin adhesive are studied.

2. Materials and methods

2.1. Materials

Table 1 – Formulation of the base experimental adhesives used in this study.

Materials	% weight
Bis-[4-(2-hydroxy-3-methacryloy loxyproxy) phenyl] propane (Bis-GMA)	14
2-Hydroxy ethyl methacylate (HEMA)	26
1,6-Bis-[2-methacryloxyethoxycarbonylamino]-2,4,4 -trimethylhexane (UDMA)	12
2-Ethyl-2-(hydroxymethyl)-1,3-propandiol trimethacrylate (TMPTMA)	8
Ethanol	40

Photoinitiators were added to the adhesive, in dark, after mixing all other ingredients.

2-Hydroxyethyl methacrylate (HEMA), 2-ethyl-2-(hydroxymethyl)-1,3-propandiol trimethacrylate (TMPTMA), N, N-dimethylformamide (DMF), hydroquinone (HQ), and ethanol were purchased from Merck (Germany). N, N-dimethyl aminoethyl methacrylate (DMAEMA) was obtained from Fluka (Germany). 1,6-Bis-[2-methacryloxyethoxycarbonylamino]-2,4,4-trimethylhexane (UDMA), 2,2-bis-[4-(2-hydroxy-3-methacryloxypropoxy)-phenyl] propane (Bis-GMA), and amorphous fumed silica with the primary particle size of 12 nm in diameter and surface area of 200 $m^2 g^{-1}$ (Aerosil® 200) were supplied by Evonik (Germany). Camphorquinone (CQ), 2,3 butanedione (BD), phenylpropanedione (PPD), 3-(trimethoxysilyl)propyl methacrylate(γ-MPS), and acetic acid were purchased from Sigma-Aldrich (Germany). POINT 4, a commercially available dental composite, and the 37.5% phosphoric acid gel (Kerr Gel Etchant) were obtained from Kerr (USA). BTDMA was synthesized in our laboratory via the reaction of 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA, Aldrich) and HEMA (Merck).

2.2. Methods

2.2.1. Synthesis of BTDMA monomer and preparation of dentin bonding

Synthesis of BTDMA monomer that consist of both carboxylic acid and methacrylate groups was performed through the reaction of BTDA and HEMA in DMF as reaction media according to the method reported in Ref. [28]. The base experimental dentin bonding was prepared according to Table 1 and other ingredients were then incorporated into the base in phr (part per hundred resin) as described in the text.

2.2.2. Silanization of the silica nanoparticles

The surface of nanoparticles was treated with γ-MPS to improve their wetting property. γ-MPS was prehydrolyzed for one hour in an aqueous solution of 70 wt.% ethanol and 30 wt.% deionized water (pH of the solution was adjusted to 3–4 adding a few droplets of acetic acid). The nanoparticles were added to the solution and left for 24 h. The treated fillers were centrifuged and washed several times with the same solution to remove the unreacted γ-MPS and dried at room temperature. The silanized particles were then ball milled to break the agglomerates formed during silanization [29]. TGA thermogram (TGA, PL instruments, UK; heating rate = 10 °C min^{-1}, atmosphere = N_2) of the silanized nanoparticles reveals 8 wt% silanization of the particles (Fig. 1). The nanoparticles were incorporated into the adhesives and

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