



Novel urethane-based polymer for dental applications with decreased monomer leaching



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ABSTRACT

The aim of this study was to synthesize and characterize new multifunctional-urethane-methacrylate monomers to be used as the organic matrix in restorative dental composites, and evaluate the main physical-chemical properties of the resulting material. Bis-GMA (bisphenol-A-diglycidylmethacrylate) and GDMA (glycerol dimethacrylate) were modified by reacting the hydroxyl groups with isocyanate groups of urethane-methacrylate precursors to result in the new monomeric systems U-(bis-GMA)-Mod and U-(GDMA)-Mod, U = Urethane and Mod = Modified. The modifications were characterized by FTIR and ¹H NMR. The final monomeric synthesized system was used to prepare dental resins and composites. The physical-chemical properties were evaluated and compared with those of bis-GMA composites with varying filler contents or unfilled resins. U-(bis-GMA)-Mod and U-(GDMA)-Mod can be used to prepare dental restorative composites, with some foreseeable advantages compared with bis-GMA composites. One significant advantage is that these composites have the potential to be less toxic, once they presented a reduction of 50% in leaching of unreacted monomers extracted by solvent.

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1. Introduction

2,2-bis[*p*-(2'-hydroxy-3'-methacryloxypropoxy)phenyl]propane (bis-GMA) has been largely used to formulate dental composites, and the physical-chemical properties of these materials have been widely studied, including polymerization shrinkage, mechanical properties, degree of conversion, refractive index and amount of leachable components. By means of these studies it was conclusive that bis-GMA is an excellent dental monomer, although so far some of its drawbacks have not been overcome when used as the organic matrix of dental composites [1–2,3,4].

One of the disadvantages of bis-GMA is its relative high viscosity (600–1200 Pa.s) and consequent low mobility, which leads to a relatively low degree of conversion for the homopolymers [5,6], in turn leading to low mechanical properties. The high viscosity also prevents the inclusion of high concentrations of inorganic filler, further jeopardizing several physical-chemical properties. Furthermore, low conversion results in typically higher concentrations of leachable monomer via oral fluids, which can upregulate biofilm formation [7,8], as well as cause allergic reactions in susceptible patients [9,10]. It is also well known that bis-GMA presents a bisphenol-A (BPA) core, and although studies have not been conclusive in regards to the presence of BPA in leachates from this monomer, this presents a potential toxicity concern. Moreover, BPA could be present as impurity during the synthesis of bis-

GMA [11]. Even when TEGDMA is included and conversion increases, the presence of these chemicals in the leachates is still possibly a concern, and many manufacturers are moving to BPA-free formulations.

Low viscosity monomers are usually combined with bis-GMA to improve the degree of conversion, increase the amount of inorganic filler in the composite and also decrease the concentration of leachable components. The most common diluent is TEGDMA (triethylene glycol dimethacrylate). The addition of low-viscosity, low-molecular weight diluent monomers, however, has the disadvantage of increasing polymerization shrinkage [12], which results in the development of internal stresses. An alternative to decrease the elution of monomers from composites is the use of multifunctional monomers, since the higher number of polymerizable groups in the molecule can improve the crosslinking density of the polymeric network [13], which can, in turn, reduce leachable monomers after polymerization.

Since its introduction in the early 1960s, many attempts have been made to modify or replace bis-GMA as the monomer for dental composites. For example, ormocers, branched monomers, new dimethacrylate monomers, dendritic monomers, oligomers and liquid-crystalline monomers have been synthesized [14–15,16,17,18,19,20]. All of these monomers and bis-GMA analogues have advantages and disadvantages compared with bis-GMA. For instance, a 1,6-bis(2'-methacryloxyethoxycarbonylamino)-2,4,4-trimethylhexane (UDMA) has been commonly used to partially replace bis-GMA, with two advantages: lower viscosity and the greater flexibility of the urethane linkage compared with the stiff BPA core of bis-GMA, which can increase the toughness of composites formulated with this monomer [21]. However,

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its great flexibility and the absence of aromatic groups lead to increased cyclization within the polymeric network formed, which in turn contributes to the lower thermal stability compared to bis-GMA [22]. In addition, the odds of greater cyclization and lower molar mass and the presence of low-molecular-weight oligomers prone to leach cause UDMA to present higher water solubility than bis-GMA [23]. In order to reduce the water sorption and water solubility Kerby et al. [24] synthesized UDMA analogue dimethacrylate monomers by adding hydrophobic aromatic groups on its side chain, but the results showed that the final polymer presented significant lower mechanical properties than neat UDMA. UDMA also shows significantly higher polymerization shrinkage than bis-GMA [25].

In addition to that, the refractive index of UDMA ($t = 1.483$) is considered to be low compared with bis-GMA is ($n_D^{25} = 1.548$). Lower refractive indices in the monomer means that the match with the radiopaque glass filler (around 1.55) [26] is impaired, challenging the light transmission in the bulk of the material, thus reducing depth of cure [27].

Mösner et al. synthesized the dimethacrylate (TMX-UDMA) from the reaction between 1,3-bis(1-isocyanato-1-methylethyl)benzene (TMXDI) with hydroxyethylmethacrylate (HEMA). The use of TMXDI is advantageous due to the combination of aromatic features (increasing stiffness and refractive index) with aliphatic features (low tendency to discoloration) [6]. The resulting refractive index for (TMX-UDMA) was $n_D^{25} = 1.509$ [6].

In order to mitigate these disadvantages of dental monomers and mainly to decrease the amount of leachable materials, as well as eliminate the presence of BPA, this work has the purpose of synthesizing a novel organic matrix based on the advantage of using urethane aromatic groups, especially derivative from TMXDI, and multimethacrylate monomers to formulate dental composites and evaluate some properties: degree of conversion (DC, in %), volumetric shrinkage (VS, in %), polymerization stress (PS, in MPa), flexural strength (FS, in MPa), and flexural modulus (FM, in GPa). Water sorption (W_{sp} , $\mu\text{g}/\text{mm}^3$) and solubility (W_{sl} , $\mu\text{g}/\text{mm}^3$) as well as extraction studies in organic solvent were also carried out to determine the amount of leachable components. The null hypothesis is that the composites formulated with the newly synthesized monomers will not show improvement in properties compared to bis-GMA-based controls.

2. Experimental procedures

2.1. Materials

All reagents used in this work were purchased from Sigma-Aldrich (Milwaukee, WI, USA) and used without further purification: 2,6-*tert*-butyl-4-methylphenol (BHT), 2-hydroxyethylmethacrylate (HEMA, 99%), dibutyltin dilaureate (95%), 1,3-bis(1-isocyanato-1-methylethyl)benzene (TMXDI, 97%), 1,3 glycerol dimethacrylate (GDMA), dichloromethane (CH_2Cl_2 , 99%) and deuterated chloroform (CDCl_3 , 99.8 atom % D). The photoinitiator system was camphorquinone (CQ, 97%) and 2-(*N,N*-dimethylamino)ethyl methacrylate (DMAEMA, 99%). The commercial monomers used to prepare the composites were bisphenol-A-diglycidylmethacrylate (bis-GMA), and triethyleneglycoldimethacrylate (TEGDMA, 95%), all obtained from ESSTECH (Essington, PA, USA). Barium glass (V258 2507, SP 345, 5% silane, 0.7 μm) and fumed silica (OX-50, 5% silane, 50 nm) were used as inorganic fillers and were also obtained from ESSTECH.

2.2. Experimental design to synthesize the new monomers and measure physical-chemical properties

Fig. 1 shows the flowchart displaying the rationale to the synthesis of the new monomers and to all physical-chemical measures made with the composite formulation. In this flowchart, it can be seen: the reagents used to synthesize the newly monomers (the goal of this study), the

monomer derivatives from bisphenol-A-diglycidylmethacrylate: U-(bis-GMA)-Mod and the monomer derivative from and glycerol dimethacrylate: U-(GDMA)-Mod. Furthermore, the design shows the measurement performed with the composites and resins fabricated with these monomers and bis-GMA.

2.3. Synthesis of urethane-methacrylate precursors (UMPs)

For the synthesis of the urethane-methacrylate monomers, TMXDI (1 equivalent) dissolved in dichloromethane was placed into a 50 mL flask and catalytic amounts (0.01–0.02 mol fraction %) of dibutyltin dilaureate were added to the reaction mixtures, continuously purged with dry nitrogen to remove oxygen and moisture. Then, HEMA (1 equivalent) was added dropwise to the flask. The reaction temperature was kept at 40 °C while the mixture was vigorously stirred for 8 h. The solvent was removed from the product under vacuum at 45 °C for about 4 h. ^1H NMR was used to confirm the complete elimination of the solvent after the synthesis procedure. This reaction was expected to yield mainly monosubstituted TMXDI (1-(2-methacryloyloxythoxycabonylamino)-3'-1-isocyanato-1-dimethylethyl) benzene and disubstituted TMXDI (1,3-bis-[2-methacryloyloxythoxycabonylamino]1-methylethyl) benzene as well as TMXDI unreacted. The scheme of the synthesis is shown in Fig. 2.

2.4. Synthesis of U-(bis-GMA)-Mod and U-(GDMA)-Mod

In order to obtain the precursors previously mentioned, the UPMs as well as the new mixture U-(bis-GMA)-Mod and U-(GDMA)-Mod, well-known nucleophilic addition reactions were used. These compounds could be easily obtained by the addition reactions between isocyanate (-NCO) groups (highly reactive), which are electrophiles, and the hydroxyl (-OH) groups that are considered good nucleophiles. When the -NCO groups react with -OH groups, the urethane groups ($\text{U} = \text{R}-\text{CO}_2\text{NH}-\text{R}$) are formed.

As previously mentioned, the precursor UPMs are made up of a mixture of 3 compounds which had the percentages calculated by ^1H NMR (it will be discussed later), 1) the [TMXDI] which contains 2 -NCO groups and no methacrylate group (OCN-R-NCO), 2) the [monosubstituted TMXDI] which contains 1 -NCO group and 1 methacrylate group (M-R-NCO) and 3) the [disubstituted TMXDI] with no -NCO left and 2 methacrylate groups (M-R-M). M = methacrylate group and R are all atoms between methacrylates groups and -NCO groups. All structures of UPMs are presented in Fig. 2. These 3 structures were simultaneously reacted with bis-GMA to give the U-(bis-GMA)-Mod or reacted with GDMA to give the U-(GDMA)-Mod.

Therefore, considering the precursors UPMs idealized, we should rationalize a product to U-(bis-GMA)-Mod containing a mixture of 3 different compounds as well, as follows: when UPMs are reacted with bis-GMA (OH_2 -bis-GMA- M_2), which contain 2 -OH groups, and 2 methacrylate groups are formed: A) the new and main compound, the [urethane-tetramethacrylate], which is derived from the reaction between the two -OH groups of bis-GMA and the only -NCO group of *disubstituted* TMXDI (M-R-NCO), as shown schematically: (OH_2 -bis-GMA- M_2 + M-R-NCO \rightarrow U-bis-GMA- M_4); B) [oligomers] the oligomers are derived from the reaction of two -OH groups of bis-GMA (OH_2 -bis-GMA- M_2) with only one -NCO group of *disubstituted* TMXDI (M-R-NCO) or TMXDI (OCN-R-NCO), which contains 2 -NCO groups (it is not possible to make predictions about these oligomers, but their presence in the final product is minor); and C) the [*disubstituted* TMXDI] remaining from UPMs which had no -NCO to be reacted with bis-GMA.

When the UPMs are reacted with GDMA ($\text{OH}-\text{GDMA}-\text{M}_2$), which contain only one -OH groups and 2 methacrylate groups, a mixture of 3 different compounds can also be expected: A) the new and main compound, the [urethane-trimethacrylate], a product derived from the reaction between the only -OH groups of GDMA and the only -NCO group of *disubstituted* TMXDI (M-R-NCO) as shown schematically (M_2 -GDMA-

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