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Synthesis and evaluation of modified urethane dimethacrylate resins with reduced water sorption and solubility

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ABSTRACT

Objectives. New aliphatic and aromatic urethane dimethacrylate monomers containing pendant phenyl methoxy or ethyl substituents were synthesized in order to reduce the water sorption and solubility of urethane dimethacrylate systems. Selected properties including flexural strength, flexural modulus, water sorption and solubility, and water contact angle were evaluated. Hoy's solubility parameters were also calculated to rank copolymer hydrophilicity.

Methods. Filled (20%) composite resins were formulated with each of the newly synthesized dimethacrylates as well as the commercially available urethane dimethacrylate monomer, UDMA. Flexural strength, flexural modulus, water sorption and solubility of the urethane composites were evaluated after light-cured specimens were immersed in water for seven days. Water contact angles were measured on the surface of each material. Data were analyzed using ANOVA and Ryan–Einot–Gabriel–Welsch multiple range tests ($\alpha=0.05$).

Results. A significant reduction of nearly 30% and 40% in water uptake was observed with composite polymers containing pendant ethyl and phenyl methoxy groups, respectively, compared to UDMA ($p<0.05$). Urethane copolymers containing pendant ethyl groups also showed a significant reduction in water solubility ($p<0.05$). A positive correlation was found between contact angle and water sorption as well as Hoy's δ_h for hydrogen bonding forces.

Significance. The results of this study indicate that the incorporation of pendant hydrophobic substituents within the monomer backbone may be an effective method in reducing the water sorption and water solubility of urethane based dimethacrylate systems. The use of Hoy's solubility parameters to determine the relative hydrophilicity of a polymer may be limited by its three-dimensional chemical structure.

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1. Introduction

The most preferred dimethacrylate resin monomers for use in dental composite materials today include the aromatic Bis-phenol A derivative, Bis-GMA, and the aliphatic urethane dimethacrylate UDMA [1]. The Bis-GMA monomer contains pendant hydroxyl groups within its molecular backbone. Because of these polar groups, polymers made with this monomer tend to be somewhat hydrophilic and susceptible to increased water sorption [2]. Various methods have been employed in an effort to reduce the hydrophilicity of Bis-GMA based systems. Some of these methods include capping the Bis-GMA hydroxyl groups with more hydrophobic substituents [3], synthesis of novel fluorinated aliphatic and aromatic dimethacrylates [4,5] and the incorporation of methacrylate terminated butadiene terpolymers [6]. Bis-EMA, a non-hydroxylated analogue of Bis-GMA, has also been utilized [7] (Fig. 1). Compared to Bis-GMA, the Bis-EMA monomer is less hydrophilic and exhibits a reduced viscosity [7].

UDMA, 1,6-bis(methacryloyloxy-2-ethoxycarbonylamino)-2,4,4-trimethylhexane, was first introduced as a dental resin in 1974 by Foster and Walker [8] as an alternative monomer to Bis-GMA. It is the reaction product of 2,4,4-trimethylhexamethylene diisocyanate and 2-hydroxyethyl methacrylate (HEMA). Advantages of the UDMA monomer when compared to Bis-GMA include a reduced viscosity, increased filler loading and greater toughness due to the flexibility of the urethane linkages [9,10]. Studies have shown that when evaluating only the monomer systems UDMA based resin composites have improved mechanical properties compared to composites prepared from Bis-GMA [4,11]. Polymers made with the UDMA monomer exhibit similar or slightly less water sorption than those prepared from Bis-GMA [12,13]. However, UDMA polymers show significantly more water uptake than polymers based on non-hydroxylated Bis-GMA analogues such as Bis-EMA [7,12]. Excess water sorption may lead to hydrolytic degradation of the polymer matrix and a reduction in mechanical properties [14]. Chemical erosion may also result in the release of unreacted monomers and degradation by-products into the oral environment [14,15]. In order to improve the mechanical properties of UDMA based polymers, a modified UDMA polymer was prepared which incorporated carboxylic acid side groups [16]. Improved mechanical properties were obtained through increased intermolecular non-covalent crosslinking, however, the addition of polar carboxylic side groups would tend to make the polymer more hydrophilic. Other studies have prepared high molecular weight polyurethane methacrylates in order to improve toughness [17] and reduce polymerization shrinkage [18]. In one of these studies the polyurethane polymer showed a slight decrease in water sorption but a general reduction in mechanical properties when compared to the Bis-GMA based polymer [17].

This study seeks to develop and evaluate novel urethane dimethacrylate monomers that contain various side groups in order to improve the water resistance of the resultant polymers. Therefore, the objective of this investigation was to evaluate the flexural strength, flexural modulus, water contact angle, water sorption and solubility of six experimental

urethane dimethacrylate monomers as well as the commercially available urethane dimethacrylate, UDMA. An additional objective was to calculate Hoy's solubility parameters of the urethane copolymers to determine their relative hydrophilicity.

2. Materials and methods

2.1. Materials and instrumentation

1,6-Hexamethylene diisocyanate, 2,4,4-trimethylhexamethylene diisocyanate (2,4,4-trimethyl diisocyanatohexane), 1,3-bis(isocyanatomethyl) cyclohexane, *m*-tetramethylxylene diisocyanate [1,3-bis(isocyanato-1-methylethyl) benzene], 1,6-hexanediol methacrylate (HDDM), camphorquinone (CQ), 2-(dimethylamino)ethyl methacrylate; butylated hydroxyquinone (BHT), 4-(dimethylamino)pyridine (DMAP), dibutyltin dilaurate, sodium sulfate, 4-(4-nitrobenzyl)pyridine, tetraethylene pentamine, hydroxybutyl methacrylate and deuterated chloroform (CCl_3D) (Sigma-Aldrich, Milwaukee, WI) were used as received. Methacrylic acid (Sigma-Aldrich, Milwaukee, WI) was purified by vacuum distillation. Glycidyl phenyl ether (TCI America, Portland, OR), UDMA and Bis-GMA (Monomer-Polymer & Dajac, Feasterville, PA) and Bis-EMA (Esstech, Essinton, PA) were used as received. Solvents were analytical grade and/or dried over 4A molecular sieves. Infrared spectra were recorded on a Spectrum One PerkinElmer FT-IR spectrophotometer (PerkinElmer, Shelton, Conn) at a resolution of 4 cm^{-1} with 32 scans utilizing NaCl crystals. ^1H NMR spectra were obtained on a Bruker AM 250 MHz spectrometer (Bruker, Billerica, MA) in CCl_3D using tetramethylsilane as an internal standard. Sample concentrations were 60–80 mg/ml.

2.2. Methods

Seven urethane dimethacrylate base monomer resins were evaluated: two aliphatic dimethacrylates (UHP and UTP) contain pendant phenyl methoxy substituents; an aliphatic (UTB) and an aromatic (UXB) urethane dimethacrylate which contain pendant ethyl groups; an aromatic (UXY) and a cyclo-aliphatic (UCY) urethane dimethacrylate (Fig. 2). The commercially available resin monomer (UDMA) was also included as a control.

2.3. General synthesis of UTP urethane monomer containing pendant phenyl methoxy groups (Fig. 3)

2.3.1. Step 1: 3-phenoxy-2-hydroxypropyl methacrylate (PHPM)

A 250 ml three-necked round-bottom reaction flask fitted with a nitrogen inlet adaptor, thermometer, outlet tube stopped with CaCl_2 and fiberglass, water-cooled reflux condenser and a magnetic stirrer was charged with 60 g (0.400 mmol) glycidyl phenyl ether, 36.1 g (0.420 mmol) methacrylic acid, 1.08 g 4-dimethylaminopyridine (DMAP), 0.01 g BHT dissolved in 50 ml dry toluene. The reaction mixture was heated to 70°C and then slowly to 90°C and maintained at this temperature for 8 h. Rapid exotherm was controlled by immersion of the reaction

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