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Shear bond strength of experimental methacrylated beta-cyclodextrin-based formulations ☆

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Abstract

Previous studies have shown that methacrylated beta-cyclodextrins (MCDs) can be used as comonomers in resin-based dental composites. These MCDs by virtue of having several polymerizable methacrylate groups and hydrophilic hydroxyl groups, may also promote bonding of dental composites to dentin. This study evaluated MCDs as adhesive comonomers, and optimized comonomer and polymerization initiator concentrations for maximum shear bond strength (SBS). Experimental MCD-based bonding formulations in acetone were prepared by mixing 33 mass fraction % MCDs with (10, 20, 30, 40, or 50) mass fraction % of 2-hydroxyethyl methacrylate (HEMA). The MCD/HEMA-based solutions were activated with varied amounts of camphorquinone (CQ) and ethyl 4-dimethylamino benzoate (4E). Samples for SBS were prepared by bonding a composite resin to acid-etched dentin surfaces of extracted human molars with the experimental bonding solutions. The specimens were immersed in 37 °C water for 24 h and bond strengths were determined in shear mode. With increasing HEMA concentration, the SBS values of MCD-bonding solutions increased to 16 MPa at a composition of 33% MCD, 30% HEMA, and 37% acetone by mass. Also, SBS values of MCD-bonding solutions varied as a function of the CQ and 4E concentrations and passed through a maximum SBS at 21 MPa, which was comparable to that of a commercial control. This preliminary study indicated that nonacidic MCD monomers could be used as an adhesion-promoting comonomer. Additional modification of MCDs having both polymerizable groups and anionic ligand groups, e.g., polymerizable acidic cyclodextrin derivatives should increase the SBS even further.

Keywords: Adhesion; Bond strength; Collagen; Dental adhesive; Dentine bonding agent; Surface treatment; Cyclodextrin methacrylates; Polymerization initiators

1. Introduction

There is continuing need for development of improved materials and methods for bonding preventive and restorative resins and composites to enamel [1], dentin [2,3], and the root surfaces of teeth [4]. In previous studies, molecules and monomers with both organic and multifunctional hydrophilic ligand groups have shown to favorably compete with water for binding to mineral-containing surfaces of dentin, enamel, and calcium-phosphate particles [5,6]. This work led to surface-active monomers that have been effective with calcified tissues [7–10].

Currently, in conventional bonding techniques, dentists acid etch both dentin and enamel to remove weakly bound surface material to infuse appropriate surface-active monomer formulations for bonding resins to surface-decalcified dentin and microporous enamel. Primer and bonding formulations that are in use today contain only one or a few kinds of surface-active comonomers, and these have a very limited number of active groups per molecule for interactions with collagen

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and copolymerization with resins. Although the retention rates of resins with bonding agents have improved over the years [11–13], there is a definite need in clinical dentistry for materials that provide more durable bonding to acid-etched dentin and enamel surfaces. Such materials will permit application of retentive polymeric coatings to protect tooth surfaces susceptible to caries, greater preservation of tooth structures during cavity preparations, better prevention of secondary caries around restorations, and enhancement of esthetics. As the mineral is removed from the dentin surface during removal of weak boundary material, a hydrated network of collagen fibrils remains. Thorough interpenetration and polymerization of collagen-interactive comonomers are needed to form a durable polymer–collagen hybrid layer for long-lasting attachment of dental resins.

Acid-etched and rinsed dentin surfaces are surface demineralized, and consist mostly of retained hydrated Type I collagen fibrils [14] that may be intact, denatured, and/or fragmented [15,16]. For optimal docking and anchoring interactions within this kind of substrate, adhesion-promoting molecules must be capable of competing with water by multiple-bonding interactions with sites on collagen. Because demineralized dental collagen presents such a variety of heterogeneous receptor sites of potential interaction, surface-active comonomer molecules should have a multiplicity of kinds and positions of surface-site interactive ligand groups. The surface-active ingredients must contain groups capable of hydrophilic and hydrophobic interactions. Such diversity might be provided by a family of methacrylated beta-cyclodextrins, MCDs, in which the organophilic polymerizable groups and the hydrophilic hydroxyl groups are located at different positions on the beta-cyclodextrin cores of the individual family members. The 21 potential positions for these group yield a vast diversity of combinations and permutations in the members of a multifunctional MCD family.

The hypothesis of this study is that a formulation comprising a novel MCD family of monomers and a diluent comonomer can promote bonding of a resin-based composite to dentin. Thus, the objectives of this preliminary study were to evaluate MCDs as adhesion-promoting monomers and to optimize compositions of the MCD-based bonding solutions to give maximum shear bond strength (SBS).

2. Materials and methods

The materials used in this study are listed in Table 1. The MCD family was synthesized by reacting beta-cyclodextrin with methacrylic anhydride by a method described previously [17].

2.1. Bonding solution formulations

Three series of bonding solution formulations were prepared as follows:

2.1.1. Formulations with varying 2-hydroxyethyl methacrylate (HEMA) concentrations

Acetone solutions were prepared containing a mass fraction of 33% MCD and a mass fraction of 10%, 20%, 30%, 40%, or 50% HEMA and (57%, 47%, 37%, 27%, or 17%) acetone, respectively. Each solution was activated for visible light photopolymerization by the addition of a mole fraction of 4.8% camphorquinone (CQ) and a mole fraction of 7.76% of ethyl 4-dimethylamino benzoate (4E) with respect to the nonvolatile monomer molecules (MCD + HEMA).

2.1.2. Formulations with equimolar polymerization initiator concentrations

To a mixture containing mass fractions of 33% MCD, 30% HEMA, and 37% acetone were added varied equimolar amounts of the two activators. That is, (0.2, 1.4, 2.6, 3.8, 5.0, 6.2, or 7.4) mol fraction (%) of CQ plus (0.2, 1.4, 2.6, 3.8, 5.0, 6.2, or 7.4) mol fraction (%) of 4E with respect to the nonvolatile monomer molecules (MCD + HEMA). These mixtures are referred to herein as solutions with "equimolar polymerization initiators."

2.1.3. Formulations with constant molar polymerization initiator concentrations

To mixtures containing a combined mass fraction of 33% MCD, 30% HEMA and 37% acetone were added

Table 1
Materials

Chemical	Lot no.	Manufacturer
Methacrylated beta-cyclodextrin	B126-98	Synthesized in PRC laboratory, ADAF, at NIST
2-Hydroxyethyl methacrylate	474-32-03	Esschem Inc., Linwood, PA, USA
Photoinitiators		
Camphorquinone	06724AW	Aldrich Chemical Co. Milwaukee, WI, USA
Ethyl 4-dimethyamino benzoate	15014PN	Aldrich Chemical Co. Milwaukee, WI, USA

the two activators (CQ + 4E) at varied proportions that added up to a combined mole fraction of 7.6% relative to the nonvolatile monomer molecules (MCD + HEMA). Although the sum of the concentrations of the two activators was constant, i.e., mol fraction (%) CQ + mol fraction (%) 4E = 7.6 mol fraction (%), various polymerization initiator proportions were used: (0.3 + 7.3, 1.05 + 6.55, 1.8 + 5.8, 2.55 + 5.05, 3.3 + 4.3, 3.8 + 3.8, 4.05 + 3.55, 4.8 + 2.8, 5.5 + 2.05, or 6.3 + 1.3) mol fraction (%) CQ + mol fraction (%) 4E, respectively. These are referred to as formulations with "constant-molar sum polymerization initiators."

2.2. Shear bond procedure

Flat dentin surfaces were prepared by cutting off, with running water as a coolant, the tops of crowns of caries-free human molars with a low-speed diamond saw (Isomet; Buehler Ltd., Lake Bluff, IL, USA). The teeth were embedded with cold-curing resin in polycarbonate holders, and the dentin surfaces were ground perpendicular to the long axis of the tooth on water-washed #320 grit SiC paper until the occlusal enamel was completely removed. The exposed flat occlusal dentin surfaces were etched with a gel containing 38 mass fraction (%) phosphoric acid (Etch-Rite; Pulpdent Corp., Watertown, MA, USA) for 15 s and rinsed with distilled water. After rinsing, the dentin surface was covered with a moist blotting paper. Two drops (about 40 μL) of the bonding solution were dispensed in a mixing well. Just before applying the bonding solution, the blotting paper was removed. A disposable brush tip was fully saturated with bonding solution and, after assuring that no water puddles were left on the surface, a first coat of the bonding agent was applied to the dentin surface. The solution was agitated for 10 s and a second coat, with the same brush tip saturated a second time from the well, was applied. The surface was gently air dried for 20 s with an air stream emerging from a pipette tip at a 7 cm distance. The entire dentin surface was then light cured for 10 s with the use of an 8 mm tip light source having a 450 mW/cm^2 intensity (Max 100, Caulk Dentsply, Milford, DE, USA). A poly(tetrafluoroethylene)-covered brass ring with an opening, 4 mm in diameter and 1.5 mm deep, was used as a mold for the composite. The ring was held down with the assistance of a polycarbonate holder and the opening was filled with TPH composite (Caulk/Dentsply), which was then irradiated for 1 min with the same light source. The entire assembly was placed in distilled water and stored for 24 h at about 22 °C before being tested. A commercially available bonding solution (Prime One, Mirage Dental Systems, Kansas City, KS, USA) was used as the control.

2.3. Shear bond test

A holding device was used to evaluate the SBS of dentin adhesives. The brass ring holding the dentin-bonded composite was placed against a vertical surface of a nylon block. The ring and the composite were sheared off, at a crosshead speed of 0.5 mm/min, with a flat chisel pressing against the edge of the brass ring. the flat chisel was connected to the platen of a Universal Testing Machine (United Calibration Corporation, Huntington Beach, CA) [17].

2.4. Scanning electron microscopy (SEM)

After storage in water for 24 h, two bonded tooth specimens, one treated with an experimental MCD-based bonding formulation and the other with Prime One as a control, were cut along their long axes to obtain cross sections of the bonded areas. The specimens were immersed in 6 mol/L HCl for 30 s, followed by immersion in 5 mass fraction (%) NaOCl for 10 min. After being thoroughly rinsed with water, the specimens were air dried, sputter-coated with gold, and observed under a scanning electron microscope (JSM-5300, JEOL Ltd, Tokyo, Japan).

2.5. Statistics

Multiple comparisons were made using one-way ANOVA and Tukey's post hoc test. Unless stated otherwise, ± indicates one standard deviation and is assumed to be the estimate of the standard uncertainty.

3. Results

3.1. Formulations with varying 2-hydroxyethyl methacrylate concentrations

Fig. 1 shows the relationship between the SBS and the mol fraction (%) of HEMA in MCD/HEMA-based bonding solutions. The SBS increased significantly ($p < 0.05$) with increasing HEMA concentrations. These experiments, with increasing amounts of HEMA at a polymerization initiator concentration of 4.8 mol fraction (%) CQ and 7.76 mol fraction (%) ethyl 4-dimethylamino benzoate, showed that SBS ranked highest for compositions containing 33 mass fraction (%) MCD, 30 mass fraction (%) HEMA, and 37 mass fraction (%) acetone.

3.2. Formulations with equimolar polymerization initiator concentrations

The composition with a mass fraction of 30% HEMA was chosen for further experiments and was activated

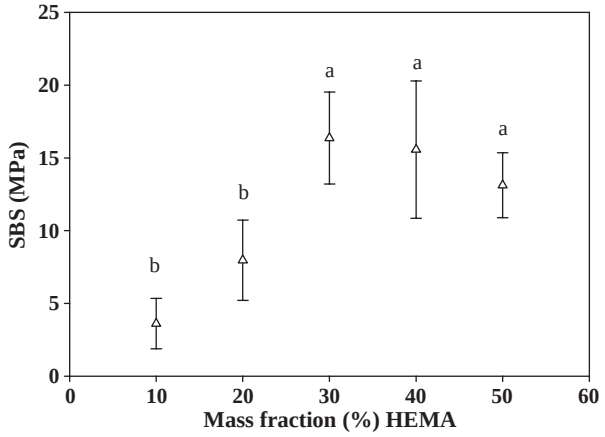

Fig. 1. SBS versus mass fraction (%) HEMA in MCD/HEMA-based bonding solutions. Different letters indicate statistically different groups.

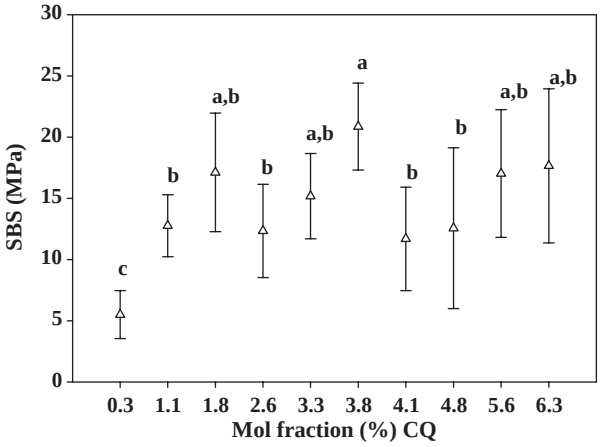

Fig. 3. SBS versus mol fraction (%) CQ in MCD/HEMA-based bonding solutions with "constant molar sum" polymerization initiators. Different letters indicate statistically different groups.

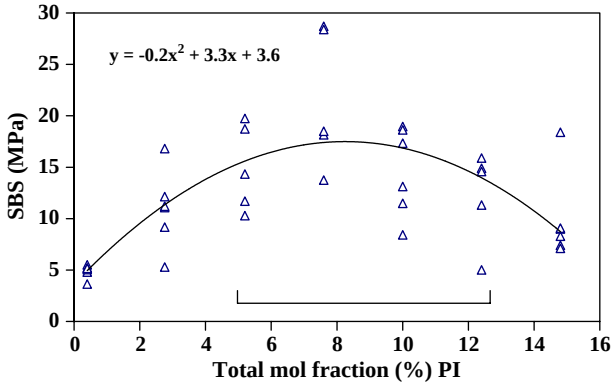

Fig. 2. SBS versus total equimolar concentrations of polymerization initiators (PI) in MCD/HEMA-based bonding solutions.

with varied equimolar concentrations of the two polymerization initiators. SBS values were measured with these "equimolar polymerization initiator" formulations. Fig. 2 shows SBS versus the total mol fraction (%) of polymerization initiators. The mean SBS values increased significantly as the total mol fraction (%) of polymerization initiators increased, passed through a maximum 21 ± 7 MPa corresponding to a photoinitiator (PI) concentration of (3.8 mol% CQ + 3.8 mol% 4E), and then decreased with higher PI concentrations. One-way ANOVA showed that significant differences existed between the groups ($p < 0.05$). The SBS of the control (Prime One) was 30 ± 8 MPa.

3.3. Formulations with constant molar polymerization initiator concentrations

Based on the previous set of experiments (with equimolar polymerization initiator concentrations), it was decided that 3.8 mol fraction (%) CQ + 3.8 mol fraction (%) 4E seemed to give the highest SBS for MCD/HEMA-based bonding solutions. In search of an optimum CQ-to-4E concentration ratio, the mol fraction (%) CQ and mol fraction (%) 4E were varied in such a way as to give a sum of about 7.6 mol fraction (%) of these polymerization initiators in the formulations. Fig. 3 shows the SBS of these "constant molar sum polymerization initiator" formulations. The mean SBS values increased as the mol fraction (%) CQ in the total polymerization initiator increased to a maximum in the same region of 3.8 mol fraction (%) CQ + 3.8 mol fraction (%) 4E as for the equimolar compositions. One-way ANOVA showed that significant differences existed between groups ($p < 0.05$). However, for compositions containing 1.05 mol fraction (%) CQ and above, the mean SBS values were not significantly different.

3.4. Scanning electron micrography

Scanning electron micrographs of the composite–dentin interface treated with experimental MCD-based bonding solution (Fig. 4) and Prime One (control) bonding solution (Fig. 5) showed formation of the hybrid layer and resin tags with lateral branches.

4. Discussion

For the formulations with varying HEMA concentrations, the solutions were each activated with 4.8 mol fraction (%) CQ and 7.76 mol fraction % 4E based on previous work showing that these concentrations of CQ and 4E were required for optimum polymerization because these PI can complex within MCD [18,19].

The mean SBS increased as the mass fraction (%) of HEMA increased (Fig. 1). This lowered the viscosity of the bonding resin and increased its hydrophilicity, which may have improved the potential of the bonding resin to penetrate the dentinal surface collagen. It also resulted

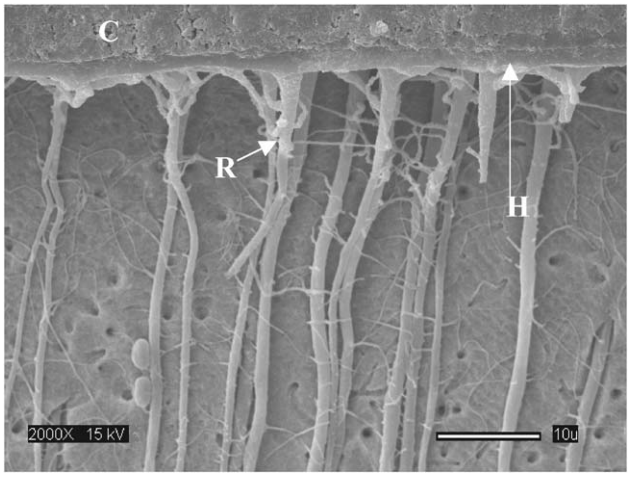

Fig. 4. Scanning electron micrograph (× 2000) of the composite–dentin interface treated with experimental MCD-based bonding solution after 24 h water storage. C, composite; H, hybrid layer; R, resin tags.

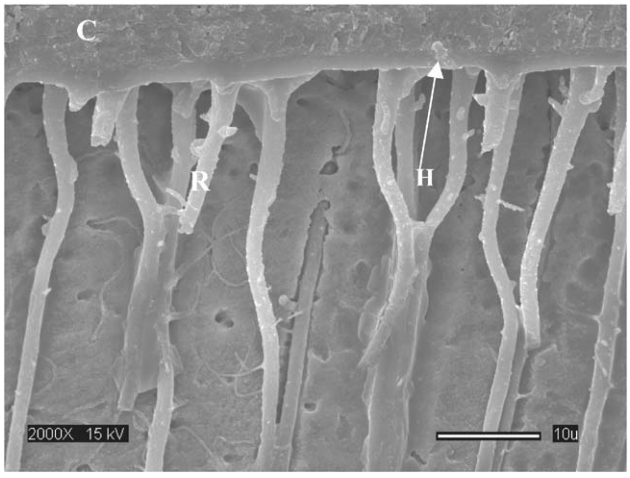

Fig. 5. Scanning electron micrograph (× 2000) of the composite–dentin interface treated with Prime One bonding solution after 24 h water storage. C, composite; H, hybrid layer; R, resin tags.

in a more concentrated bonding solution. Thus, the concomitant decrease in the volatile acetone content may have resulted in an increased adhesive layer thickness, which could have contributed to the higher SBS at acetone concentrations of 37 mass fraction % or less. The latter would be in accordance with the observation that SBS [20] and microtensile bond strength [21,22] increased with the amount of adhesive (i.e., the adhesive layer thickness) in single-bottle bonding solutions.

In the first part of the study, the SBS of the MCD/HEMA-based bonding solution was optimized with respect to HEMA at a composition of 33 mass fraction (%) MCD + 30 mass fraction (%) HEMA + 37 mass fraction (%) acetone. This composition was used to further optimize the SBS with respect to PI concentrations viz., CQ and 4E.

With reference to Fig. 2, although the formulations included in the bracket are not significantly different, the shape of the regression curve shows that the data pass through a maximum at a total mole fraction of 7.6% PI (3.8 mol fraction (%) of each of CQ and 4E). The trend seen in Fig. 2 can be explained as follows: at lower PI concentrations, CQ and 4E are complexed within the cavity of MCD [19] and hence are less available for polymerization. At relatively higher polymerization initiator levels, there may have been sufficient amounts of uncomplexed initiator available to give better polymerization and higher conversion resulting in an increase in the SBS. The SBS after passing through the maximum at 7.6 mol fraction (%) PI, decreased with increasing PI concentrations. This decrease in SBS can be explained with the reported observation that high concentrations of amine used in CQ/amine photopolymerization systems can retard polymerization [23]. Thus, above 3.8 mol fraction (%) 4E, retardation of polymerization may occur lowering the overall methacrylate conversion and reduce the SBS. Also, high concentrations of CQ could produce excess radicals that may lead to shorter polymer chains and/or less cross-links thereby reducing the bond strength.

MCD/HEMA-based bonding solutions with equimolar polymerization initiator compositions showed the maximum mean SBS of 21 ± 7 MPa at a total mole fraction of 7.6% PI (Fig. 2). This polymerization initiator level was chosen and kept constant (constant-molar-sum polymerization initiator), while proportions of CQ and 4E were varied. The mean SBS increased to almost a constant as the mole fraction (%) CQ in the total polymerization initiator increased (Fig. 3). Here again the nominally highest mean SBS was observed for the bonding solution with 3.8 mol fraction (%) CQ and 3.8 mol fraction (%) 4E as for the equimolar compositions. One-way ANOVA showed significant differences that existed between groups ($p < 0.05$). For constant molar sum polymerization initiator compositions containing 1.05 mol fraction (%) CQ and more, the mean SBS values of MCD/HEMA-based solutions were not significantly different except for the bonding solution with 7.6 mol fraction (%) total PI concentration (Fig. 3 at 3.8 mol fraction (%) CQ). The composition with a PI concentration of 1.8 mol fraction (%) CQ and 5.8 mol fraction (%) 4E showed a SBS of 16.9 ± 4 MPa that was statistically comparable with the maximum SBS value observed for the entire series. In a separate experiment, the SBS of MCD/HEMA-based bonding solutions was further optimized at 18.4 ± 5 MPa corresponding to a PI concentration of 1.8 mol fraction (%) CQ and 1.25 mol fraction (%) 4E. The latter PI composition was of interest because of the high bond strength that was achieved with a low amine concentration. This is noteworthy, as high amine concentrations can, apart

from retarding the rate of polymerization, be toxic and mutagenic [24].

The SEM micrograph (Fig. 4) of the composite–dentin interface treated with experimental MCD-based solution was quite similar to that treated with Prime One (Fig. 5). In both SEM micrographs, the coarse texture of the resin tags and lateral branches indicated good wetting and hybridization.

Due to their hydrophilicity, polymerizable acid monomers are normally used in dentin–adhesive formulations [25]. Some of the adhesives currently in use contain acid monomers that are so hydrophilic that water can permeate the dentin–adhesive interface from the underlying bonded dentin. This permeability can lead to incompatibility of composites with the adhesive and quicken degradation of resin–dentin bonds, thus reducing the durability of the adhesive [26]. In this respect, a possible advantage in using MCDs as adhesive comonomers can be seen. MCDs are non acidic monomers containing several organophilic methacrylate groups that theoretically can lead to high cross-link density and together with alcoholic hydroxyl groups can allow these monomers to penetrate hydrated collagen. As a result, MCD monomers are less hydrophilic than acid monomers, and when included in dentin–adhesive formulations may prevent the adverse reaction of water permeating the dentin–adhesive interface and may improve bond durability. The high bond strength to dentin obtained with the MCDs in the above experiments may be attributed to the multiple interactions of the MCD molecules' several hydroxyl groups with the hydrophilic collagen of dentin. Future studies are planned to determine the bond strength as a function of time that would give a measure of the durability of the resin-to-dentin bonds with further-optimized MCD formulations.

5. Conclusions

SBS of MCD-based bonding solutions were affected by the amounts of the comonomer (HEMA) and PI (CQ & 4E). Through optimization of HEMA and PI, dentin SBS as high as that mediated by Prime One was achieved. This preliminary study indicated that MCDs could be used as adhesive co monomers and should be further investigated by modifying them to add just enough number of ionic-terminated ligand groups so as not to render the monomer too hydrophilic, which should increase SBS values with dentin and enamel.

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Disclaimer: Certain commercial materials and equipment are identified in this paper for adequate definition of the experimental procedure. In no instance, does such identification imply recommendation or endorsement by the ADA Foundation, the National Institute of Standards and Technology, or the National Institute of Dental and Craniofacial Research or that the material or equipment is necessarily the best available for the purpose.

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