High-Performance Dental Adhesives Containing an Ether-Based Monomer

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Abstract

Dental adhesives are vital for the success of dental restorations. The objective of this study is to make strong and durable dental adhesives that are free from 2 symbolic methacrylate-based dental resins—2-bis[4-(2-hydroxy-3-methacryl-oxypropoxy)-phenyl]propane (Bis-GMA) and 2-hydroxyethyl-methacrylate (HEMA)-and have equivalent/improved bonding strength and durability. We formulated, prepared, and evaluated 2 dental adhesives using mixtures of a hydrolytically stable ether-based monomer, triethylene glycol divinylbenzyl ether (TEG-DVBE), with urethane dimethacrylate (UDMA) or pyromellitic glycerol dimethacrylate. These adhesives were composed of equimolar ester-/ether-based vinyl functional groups. They were compared with Bis-GMA/HEMA-based commercial and experimental dental adhesives in terms of shear bond strength and microtensile bond strength (µTBS) to human dentin and the µTBS bond stability under extended thermocycling challenges. In addition, the resins' infiltration to dentin tubules, mechanical performance, and chemical properties were assessed by scanning electron microscopy, ISO standard flexural strength and modulus measurements, contact angle measurements, and water sorption/solubility measurements. The hybrid TEG-DVBE-containing dental adhesives generated equivalent shear bond strength and µTBS in comparison with the controls. Significantly, these adhesives outperformed the controls after being challenged by 10,000 thermocycles between 5 °C and 55 °C. Water contact angle measurements suggested that the hybrid dental adhesives were relatively more hydrophobic than the Bis-GMA/HEMA controls. However, both TEG-DVBE-containing adhesives developed more and deeper resin tags in dentin tubules and formed thicker hybrid layers at the composite-dentin interface. Furthermore, the water solubility of UDMA/TEG-DVBE resins was reduced approximately 89% in comparison with the Bis-GMA/HEMA controls. The relatively hydrophobic adhesives that achieved equivalent/enhanced bonding performance suggest great potentials in developing dental restoration with extended service life. Furthermore, the TEG-DVBE-containing materials may find wider dental applications and broader utility in medical device development.

Keywords: ether-based resin, tensile bond strength, dentin infiltration, dental restoration, medical device, bonding agent

Introduction

Dental adhesives bond restorative composites to teeth and provide protection against cariogenic demineralization and collagen breakdown (Ferracane 2011; Campoccia et al. 2013; Turco et al. 2016; Nagarkar et al. 2019). Methacrylate-based resins are the most popular contemporary dental adhesives for direct restorations (De Munck et al. 2005; Nishitani et al. 2006; van Dijken et al. 2007). They typically employ 2-bis[4-(2-hydroxy-3-methacryl-oxypropoxy)-phenyl]-propane (Bis-GMA) as a base monomer and the low-viscosity 2-hydroxyethyl-methacrylate (HEMA) as a diluent monomer to enhance the material's handling properties and achieve suitable dentin infiltration (Spencer et al. 2000). However, adhesives' durability and tooth protection capability are frequently compromised by the failure of tooth/restoration interface (Hashimoto et al. 2003; Wang et al. 2007). These failures are attributed to the hydrolysisprone ester functional groups in the resin's constituent monomers, especially when challenged by enzymes and cariogenic bacteria, moderate dentin infiltration capability, and high water sorption of the resin network (Armstrong et al. 2001; Sideridou et al. 2003; Yiu et al. 2004; Huang et al. 2018). In addition, leaching of the unreacted HEMA (Massaro et al. 2019) and degradation products of Bis-GMA, such as bisphenol A (Moreira et al. 2017), also draw human health concerns. The eluted methacrylate monomers may cause acute cytotoxicity and have the potential to modify cellular regulation at much lower concentrations chronically (Putzeys et al. 2019). Combined durability and toxicity concerns necessitate the development of Bis-GMA-/HEMA-free, longer-lasting dental adhesives.

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New monomers and polymerization mechanisms have been suggested to replace the hydrolysable Bis-GMA (Ge et al. 2014; Gonzalez-Bonet et al. 2015; Podgorski et al. 2015; Yang et al. 2016) and reduce leaching of HEMA (Song et al. 2019). Specifically, for dental adhesives, a relatively hydrophobic resin network is desirable. A hydrophobic resin network is less likely to absorb water and, hypothetically, can reduce enzymecatalyzed hydrolysis of collagen at the composite/tooth interface. Consequently, restoration may have better durability in oral environments (Hosaka et al. 2009; Sadek et al. 2010). Obtaining good dentin infiltration has been a bottleneck in converting a relatively hydrophobic resin into a high-performance dental adhesive. Triethylene glycol divinylbenzyl ether (TEG-DVBE) is a hydrolytically stable ether-based monomer (Gonzalez-Bonet et al. 2015). This compound has a dumbbellshaped amphiphilic structure with a hydrophilic core and 2 hydrophobic vinyl-benzyl groups. TEG-DVBE and UDMA may form interspecies H-bonding in which UDMA is an H-donor and TEG-DVBE is an H-acceptor (Ryu et al. 2018). Such interspecies H-bonding indicates the formation of UDMA/TEG-DVBE clusters. In addition, the rapid compositioncontrolled copolymerization mechanism of equimolar UDMA/ TEG-DVBE showed no diffusion limitation of high-viscosity UDMA, which also suggested that the UDMA and TEG-DVBE were polymerized together as clusters and maintained the feeding molar ratio of monomers as the degree of vinyl conversion (DC) increased (Yang et al. 2016). Although the exact structure of these clusters is still under investigation, the flexible dumbbell-shaped TEG-DVBE and the corresponding clusters contain organophilic and hydrophilic moieties that can change their spatial configurations to present outward-facing aspects with lower interfacial energy in hydrophobic or hydrophilic environments (Asmussen et al. 1991; Sun et al. 2008). Hypothetically, such flexible and amphiphilic clusters may have better dentin infiltration than the rigid and hydrophilic resin mixtures, such as Bis-GMA/HEMA.

Given the amphiphilic structure of TEG-DVBE and its cluster-forming capability with H-donors, we hypothesize that the relatively hydrophobic (cf. Bis-GMA/HEMA adhesives) TEG-DVBE-containing monomer mixtures may yield compatible dental adhesives that contain equimolar ester-based vinyl functional groups and hydrolytically stable ether-based vinyl functional groups. We formulated and evaluated 2 TEG-DVBE-containing monomer mixtures: TEG-DVBE with UDMA or pyromellitic glycerol dimethacrylate (PMGDM). UDMA and PMGDM may form H-bonding with TEG-DVBE as H-donors. UDMA is one of the most popular substitutes of Bis-GMA as a base monomer (Papakonstantinou et al. 2013). PMGDM contains 2 carboxylic acid groups. These carboxylic acid groups are important for making adhesives/composites with remineralization capability (Zhang et al. 2016). These TEG-DVBE-containing dental adhesives were compared with 1 experimental control (Bis-GMA/HEMA) and 1 commercial control (Adper Scotchbond Multi-Purpose Adhesive). The adhesives' bonding performance was compared on the basis of shear bond strength (SBS) and microtensile bond strength (μTBS) measurements. Moreover, the stability of μTBS upon thermocycling challenge was evaluated. A battery of morphologic, mechanical, and chemical measurements, including dentin infiltration, mechanical strength, and water sorption/solubility, were utilized to gain better understanding on the adhesives' bonding performance.

Results and Discussion

Equivalent Bonding Strength (SBS and μ TBS) and Improved Bond Stability under Extended Thermal Cycling

We hypothesize that the relative hydrophobic TEG-DVBEcontaining adhesives may achieve strong and durable bonding that is at least equivalent to the Bis-GMA/HEMA-based controls. Considering the complication of geometrical, mechanical, materials, and operational variables in the bonding test (Ferracane et al. 2009; Scherrer et al. 2010; Soderholm 2010), we selected 2 popular dental bonding tests—SBS (Fig. 1A) and μ TBS (Fig. 1B) tests (refer to the Appendix for details)—to evaluate and compare the bonding strength. In addition, the μ TBS combined with extended thermal cycling was used to distinguish the bonding stability of the Bis-GMA- and HEMAfree adhesives from the controls. For SBS tests, mixed failures were observed on each fractured tooth/composite interface (Appendix Fig. 1). For μ TBS tests, only cohesive and adhesive failures were observed. There was no pretest failure.

The 2 Bis-GMA- and HEMA-free dental adhesives achieved equivalent SBS to the commercial control but exceeded the SBS of the experimental control (Fig. 2A). Also, all 4 dental adhesives indicated that their μ TBS values were equivalent before being challenged by thermal cycling (Fig. 2B). In the SBS and μ TBS tests, the primers and resin composites were ester-based resins. The hydrolytically stable etherbased TEG-DVBE is introduced for the first time in dental adhesives as a diluent monomer. The equivalent SBS and μ TBS suggest that the usage of TEG-DVBE in adhesives does not compromise their bonding strength and the TEG-DVBEcontaining additives are compatible with methacrylate-based primers and composites.

Thermal cycling has been used to accelerate the fatigue of bonding. Alternating temperature between 5 °C and 55 °C simulates the extreme cold and warm oral environments. Such large temperature fluctuation also induces shrinking and swelling of materials. In general, dental adhesives have a larger volume variation in response to temperature changes due to their low filler content in comparison with composites and dentin. Consequently, the bonding failures are more likely to take place within the dental adhesives or at the dentin/adhesive interface. We used Filtek Z250 Universal Restorative Dental Composite from 3M as the composite for all the μ TBS evaluations, which warrant cohesive/adhesive failures. There was no pretest failure after teeth sectioning or after thermal cycling. As illustrated in Figure 2, after 10,000 thermal cycles, the average μ TBS (mean \pm SD) of Scotchbond and Bis-GMA/HEMA (B/H) adhesives



Figure 1. Bonding procedures and methods of bonding strength tests: (A) procedures of tooth embedding and 3-step bonding procedures, (B) setup and procedures for shear bond strength evaluation, and (C) setup and procedures for microtensile bond strength evaluation.

drops significantly from 30.3 ± 16.0 MPa to 13.4 ± 8.0 MPa and from 39.3 ± 12.3 MPa to 22.8 ± 14.0 MPa, respectively. In contrast, new adhesives maintain their bonding strength, and their µTBS values after thermal cycling are significantly higher than those of the controls (*P* < 0.05). The observed improvement in µTBS durability signifies the impact of the TEG-DVBE-containing resin chemistry on adhesive performance.



Figure 2. Performance of dental adhesives: (A) shear bond strength (SBS) and (B) microtensile

bond strength (μ TBS) and bonding durability after 10,000 thermal cycles. Scotchbond and experimental B/H adhesives are used as controls. The number of beams tested for each μ TBS

evaluation is listed, and the number is 15 for the μ TBS evaluation before thermal cycling. Asterisks indicate statistically significant differences (P < 0.05). Significant differences are also

Mechanical Properties of the Resins

The elastic modulus and flexural strength of adhesives indicate rigidity and strength of resin networks and provide supplementary information on the bonding performance (Sun et al. 2011; Sun et al. 2017). Appendix Table 2 shows these mechani-

cal properties. At the same DC, the B/H controls are significantly stronger and more rigid than the TEG-DVBE-containing adhesives, UDMA/TEG-DVBE (U/V) and PMGDM/TEG-DVBE (P/V). The relatively lower flexural strength in comparison with the B/H controls indicates that other factors are vital for the equivalent bonding performance of the Bis-GAM/ HEMA-free adhesives. Considering the dumbbell-shaped amphiphilic chemical structure of TEG-DVBE and its

indicated by letters *a* and *b*, and the average values follow this order: a < b. B/H, Bis-GMA/HEMA; P/V, PMGDM/TEG-DVBE; U/V, UDMA/TEG-DVBE. Bis-GMA, 2-bis[4-(2-hydroxy-3-methacryl-oxypropoxy)-phenyl]-propane; HEMA, 2-hydroxyethyl-methacrylate; PMGDM, pyromellitic glycerol dimethacrylate; TEG-DVBE, triethylene glycol divinylbenzyl ether; UDMA, urethane dimethacrylate.

cluster-forming capability, we focus on the dentin infiltration and hybrid layers.

Enhanced Dentin Infiltration of TEG-DVBE-Containing Adhesives

Figure 3 shows scanning electron microscopy (SEM) images of resin/dentin interfaces. The experimental and commercial



Figure 3. Morphologic observation of dentin-adhesive composite interfaces by scanning electron microscopy (SEM). Restorations with B/H (A), U/V (B), and P/V (C) adhesives. The number of resin tags in the white rectangle is counted and labeled. The blue rectangles highlight the location of panels **D–F**. The hybrid layers are highlighted in panels **G–I** by white arrows. B/H, Bis-GMA/ HEMA; P/V, PMGDM/TEG-DVBE; U/V, UDMA/TEG-DVBE. Bis-GMA, 2-bis[4-(2-hydroxy-3-methacryl-oxypropoxy)-phenyl]-propane; HEMA, 2-hydroxyethyl-methacrylate; PMGDM, pyromellitic glycerol dimethacrylate; TEG-DVBE, triethylene glycol divinylbenzyl ether; UDMA, urethane dimethacrylate.

controls showed the identical interface morphologies due to the same resin chemistry. Thus, the experimental B/H resin was used to represent both controls. We applied these adhesives on the same teeth for SEM observation to circumvent the potential complications due to morphologic and biological variations of teeth. In general, resin tags are found in dentin tubules, and all adhesives formed hybrid layers (Fig. 3A–F). In-depth analysis suggested that TEG-DVBE-containing adhesives have much better dentin infiltration in comparison with the controls. Specifically, the U/V and P/V went deeper into the dentin tubules, and more resin tags were found. In addition, the U/V and P/V formed thicker hybrid layers. The number of resin tags in U/V (220; Fig. 3B) and P/V (178; Fig. 3C) adhesives was dramatically higher than that in B/H adhesives (4; Fig. 3A). Additionally, resin tags of B/H adhesives extended up to 100 µm in dentin from the resin/dentin interface. The maximum B/H infiltration depth was approximately two-thirds of the average infiltration depth detected in U/V and P/V adhesives. Such improved infiltration depth indicates that U/V and P/V penetrate deeper into dentin tubules.

The hybrid layers formed by TEG-DVBE-containing adhesives were approximately 55% thicker than those seen in control adhesives. The mean thickness of the hybrid layer of Scotchbond and B/H adhesive is $1.37 \pm 0.27 \mu m$ and $1.38 \pm 0.28 \mu m$ (Fig. 3G), respectively, while that for U/V (Fig. 3H) and P/V (Fig. 3I) is $2.11 \pm 0.22 \mu m$ and $2.17 \pm 0.11 \mu m$,

respectively. The calculated thickness of hybrid layers represents an average value of 10 locations for each adhesive.

The different thickness of hybrid layers is the result of physical entanglement and molecular forces between the resin and the exposed collagen. The change in hybrid layer thickness is hypothetically triggered by intermolecular forces which may also swell polymers in good solvents. A bold suggestion to be proved: the increased hybrid layer thickness may be an indication of enhanced resin-collagen compatibility, which agrees with the trend of resins' dentin infiltration.

Understanding the Improved Dentin Infiltration of TEG-DVBE-Containing Adhesives

Adhesive spreading on dentin surfaces, as assessed by contact angle (CA) measurements, was utilized to study dentin wettability of adhesives and understand the deep dentin infiltration of TEG-DVBEcontaining adhesives. Appendix Table 3 summarizes the results of these measurements in 3 sections: 1) water contact angles on cured adhesives, 2) adhesive contact angles on acid-etched dentin, and

adhesive contact angles on acid-etched and primed dentin.
The water CA results indicate that the hydrophilicity of

the 4 adhesives ranks in the following order: Scotchbond > B/H > P/V > U/V. Clearly, this order is different from dentin infiltration depth. The established order of the dentin infiltration depth, Scotchbond = B/H < P/V = U/V, is simplified on the basis of resin chemistry to B/H adhesives < Bis-GMA-and HEMA-free adhesives. Although the water CAs of B/H and P/V were close (only 2.6-degree difference), their dentin infiltration was dramatically different. Moreover, TEG-DVBE-containing P/V and U/V adhesives had the same hybrid layer thickness, but their water CAs are 6.8 degrees apart.

We also assessed adhesive spreading on 2 conditioned dentin surfaces—acid-etched dentin and primed dentin—using dynamic CA measurement. After acid etching, the smear layer was removed, and the collagen was exposed. The primer step resulted in an additional layer of primer, composed of NTG-GMA, PMGDM, and HEMA, on the dentin surface. We applied these 2 conditioned dentin substrates to evaluate the adhesives' interactions with exposed collagen and primercoated surfaces. Specifically, the primed dentin duplicates the exact conditions in applying dental adhesives for SBS and μ TBS tests. For all the CA measurements (2 measurements × 3 teeth) on conditional dentin substrate, different resin compositions were evaluated and compared on the same substrate (conditioned dentin) to minimize the impact of biological and morphologic variation of dentin.

Three parameters are highlighted in Appendix Table 3. They illustrate the trends discovered by the CA measurements. These parameters are initial CA, stabilized CA, and the maximum rate of CA changes (R_{max}) during the initial 15 s of interaction between adhesives and the substrates (Fig. 4A, B). The initial CA captures the moment when resin first interacted with the substrates. The stabilized CA indicated the end of resin infiltration. The R_{max}, calculated from the slope of linear regression of the initial CAs as a function of time, represents the spreading kinetics during the initial moments, such as spreading acceleration and culmination. The main driving force for adhesives' infiltration into dentin is capillary action of dentin tubules (Menzies and Jones 2010; Gittens et al. 2014). Figure 4C illustrates the correlation between the adhesive/dentin infiltration and capillary action. Briefly, materials that have better infiltration have a stronger capillary action. As a result, faster \boldsymbol{R}_{\max} and deeper resin tags take place.

CA measurement is very sensitive to surface morphology and its chemical composition (Sun et al. 2010; Ding et al. 2011). Even a small amount of a chemical in the adhesives can greatly affect the CA value. Therefore, we discuss only the CA results of the 3 experimental adhesives whose chemical components are defined. Due to the chemical and morphologic complexity of the conditioned dentin substrates, values of the initial CA and stabilized CA are used as references to improve our understanding of R_{max} instead of comparing different adhesives. The R_{max} evaluates the dynamic and temporal CA changes due to capillary action, which consequently avoids the aforementioned limitations in static CA measurement. On both conditioned dentin substrates, the R_{max} values of B/H-free adhesives (approximately 0.4 and 0.6 deg/s for P/V and U/V adhesives, respectively) are significantly higher than

the B/H adhesive (<0.2 deg/s), which agrees well with the longer resin tags observed by SEM. In addition, the values of R_{max} are consistent on both dentin substrates and independent of the treatments to the dentin. The R_{max} values of B/H-free adhesives are the same, although the initial CA on acid-etched surface is significantly higher than that on the primed substrate. The R_{max}



Figure 4. Contact angle (CA) evaluation of adhesive spreading on acid-etched dentin (**A**) and etched and primed dentin (**B**) substrates. Three parameters for understanding the adhesives' infiltration into dentin are labeled as initial CA, stabilized CA, and maximum rate of CA changes (R_{max}). Time interval between adjacent data points is 5 s for R_{max} evaluation. (**C**) The correlation of capillary action and dentin infiltration. B/H, Bis-GMA/HEMA; P/V, PMGDM/TEG-DVBE; U/V, UDMA/TEG-DVBE. Bis-GMA, 2-bis[4-(2-hydroxy-3-methacryl-oxypropoxy)-phenyl]-propane; HEMA, 2-hydroxyethyl-methacrylate; PMGDM, pyromellitic glycerol dimethacrylate; TEG-DVBE, triethylene glycol divinylbenzyl ether; UDMA, urethane dimethacrylate.



Figure 5. Water sorption as a function of time (**A**) and water solubility (**B**) of 4 dental adhesives evaluated. Significant differences are also indicated by letters *a* and *b*, and the average values follow this order: a < b < c < d. B/H, Bis-GMA/HEMA; P/V, PMGDM/TEG-DVBE; U/V, UDMA/TEG-DVBE. Bis-GMA, 2-bis[4-(2-hydroxy-3-methacryl-oxypropoxy)-phenyl]-propane; HEMA, 2-hydroxyethyl-methacrylate; PMGDM, pyromellitic glycerol dimethacrylate; TEG-DVBE, triethylene glycol divinylbenzyl ether; UDMA, urethane dimethacrylate.

of P/V adhesives is 0.6 ± 0.1 deg/s and 0.6 ± 0.1 deg/s on etched and primed dentin substrates, respectively, while the corresponding initial CA on etched dentin, 21.8 ± 0.5 degrees, is significantly higher than the primed dentin, 13.9 ± 1.7 degrees. Furthermore, on primed dentins, the B/H and U/V adhesives have the same initial CA and stabilized CA, but the

 R_{max} of U/V adhesives, 0.4 ± 0.1 deg/s, is 2 times faster than the R_{max} of B/H adhesives, 0.2 ± 0.1 deg/s. The greater R_{max} indicates a stronger capillary action, which agrees well with the trend in resin tag observed under SEM.

Understanding the Bonding Stability under Extended Thermal Cycling

In response to alternating cold and warm environments, the adhesives shrink and swell, respectively. Materials with greater volume changes are more likely to fail quicker. Theoretically, low water sorption is desirable to reduce the fatigue caused by volume changes (Wang et al. 2018). Figure 5A shows the temporal water sorption of these 4 adhesives over 2 wk of aqueous immersion. For all the adhesives, the water sorption reached its peak in 2 d and then plateaued. At the end of 2 wk, the water sorption values of Scotchbond, B/H, U/V, and P/V are 7.0% \pm 0.0%, 6.4% \pm 0.2%, 3.1% \pm 0.3%, and 4.8% \pm 0.1%, respectively. The TEG-DVBE-containing adhesives absorb much less water than the B/H controls at the same DC. Specifically, U/V-adhesive reduced water sorption >50% in comparison with the B/H controls.

Another parameter to understand µTBS stability is the water solubility of cured adhesives, which is the weight loss at the end of the water sorption test (Fig. 5B). The experimental control had the largest weight loss $(2.4\% \pm 0.1\%)$, which is more than twice that of Scotchbond $(1.1\% \pm 0.1\%)$. The difference may be attributed to the unknown composition of Scotchbond. These significant weight losses also cause a slight decrease of water sorption after 1 and 2 d (Fig. 5A). Again, the TEG-DVBE-containing resins outperformed the controls. Specifically, the weight loss of U/V is less than one-fourth of Scotchbond's and approximately one-ninth of B/H's. Such significantly reduced weight loss suggests less leachability in terms of unpolymerized resins and degradation products. The high weight loss is partially attributed to the low cross-linking capacity of HEMA. In comparison, Bis-GMA/TEGDMA (mixture of 70/30 by mass) has a lower weight loss than B/H but still 2 times higher than U/V (Wang et al. 2018).

Versatile Applications of TEG-DVBE-Containing Resins

The success of prior and current dental adhesive methodologies is limited, at least in part due to the partitioning or phase separations of the components as they diffuse into substrates. These phase separations result from the different solubility of the monomers, initiators, promoters, and other material components as they interact with the hydrated, hydrophilic tooth surface layers. These components need to stay together to achieve the optimal interactions with the substrate, polymerization, cross-linking, and durability of the adhesive bonding. Consequently, most of the dental adhesives are relatively hydrophilic, which unavoidably leads to high water sorption. The TEG-DVBE-containing dental adhesives may be an ideal example on how to use relatively hydrophobic monomers and their polymers to minimize the subsequent water sorption. The dumbbell-shaped amphiphilic structure and hydrolytically stable ether functional groups are beneficial. When mixing with UMDA or PMGDM, the monomer mixtures infiltrate well into dentin, and their copolymers have significantly lower water sorption/solubility. These 2 phenomena are essential to achieve strong and durable bonding for the B/H-free adhesives. Previous studies of UDMA/TEG-DVBE resin have shown that these 2 monomers form clusters through H-bonding (Ryu et al. 2018). These clusters contain monomers with distinct viscosity. In the composition-controlled copolymerization of UDMA/ TEG-DVBE, the molar ratio of the feeding monomers is preserved in copolymers, and the 2 monomers are converted at the same rate without showing diffusion limitation, which generally causes low DC of high-viscosity monomers (Stansbury and Dickens 2001; Yang et al. 2016). In addition, when formulated with fillers, these resins yielded high-performance resin composites (Wang et al. 2018). The same resin composition achieves effective performance as either dental adhesives or resin composites, which differentiates them from the conventional ester-based Bis-GMA/TEGDMA resins. Such methacrylate resins generally used different diluting monomers to achieve the needed performance, such as HEMA in adhesives and triethylene glycol dimethacrylate in composites.

Conclusion

Two Bis-GMA- and HEMA-free dental adhesives with a hydrolytically stable ether-based resin, TEG-DVBE, as the diluent monomer were successfully prepared and evaluated. The bonding strength of the TEG-DVBE-containing adhesives to dentin and resin composites was equivalent to the experimental and commercial controls. Moreover, the bonding stability of these B/H-free adhesives exceeded stability of controls under extended challenges by thermocycling. The superior adhesive performance correlated well with the good mechanical performance, enhanced dentin infiltration, and significantly improved water sorption/solubility of TEG-DVBE-containing resin networks. The success of these hybrid ether/ester resins as dental adhesives opens avenues for applying these materials in wider dental applications and in medical devices.

Author Contributions

S. Yamauchi, X. Wang, J. Sun, contributed to conception, design, data acquisition, analysis, and interpretation, drafted and critically revised the manuscript; H. Egusa, contributed to conception and data analysis, critically revised the manuscript. All authors gave final approval and agree to be accountable for all aspects of the work.

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