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Bisphenol-A free dental polymeric materials

K. Lizenboim^{a,b*}, H. Dodiuk^b, N. Iuster^b, T. Kidan^b, I. Suvorov^a, S. Kenig^b and B. Zalsman^a

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Bisphenol-A (BPA) is suspected to be an endocrine disrupter. Current polymeric dental materials are based on BPA derivatives, for example, Bisphenol-A diglycidylether methacrylate (Bis-GMA) which may leach out unreacted monomers and their degradation products. Consequently, the objective of the present work was to study the properties of BPA-free alternatives, for potential use in dental polymers and composites.

Experimental results indicated that BPA-free monomers from natural and commercial sources can replace Bis-GMA with adequate physical and mechanical properties of the final dental polymeric adhesives and composites.

Keywords: Bisphenol-A Free; natural resources; dental adhesives; dental composites

1. Introduction

Dental restorations are designed to repair a damaged tooth. The main restorative dental materials are ceramics, metals, polymers, and composites. An ideal dental material is characterized by biocompatibility, long lasting bonding to tooth structure, matching natural tooth color, and above all, endurance in the aggressive conditions of the oral environment.

Most of the R&D activities in dental materials are related to replacement of amalgam with polymer composites and development of improved dental adhesives. The main challenge for dental adhesives is to provide an equally effective bond to two hard tissues of different nature – dentin and enamel. As for dental composites, recently, the most important changes have been related to the reinforcing fillers due to nanotechnology developments. Current efforts are focused on the polymeric matrix with the objectives to reduce polymerization shrinkage and polymerization stresses, and the development of self-adhering adhesives to the tooth structure.

Dental composites usually consist of methacrylate-based resin matrix and 70–75 wt.% glass or ceramic fillers [1]. The organic matrix is typically a blend of two or more different dimethacrylate monomers, of which the most common are 2,2-bis [4-(2-hydroxy-3-methacryloxypropoxy)phenyl] propane (Bis-GMA) and triethylene glycol dimethacrylate (TEGDMA) (Figure 1) [2]. These composite materials have the required mechanical properties, the esthetic quality, are easy to handle during application, and are able to bond to the enamel surface.

As stated above, commercially available composite restorative materials contain Bis-GMA. It has a relatively low degree of double bond conversion and has been shown in *in vitro* experiments to release a variety of cytotoxic, estrogenic monomers, and monomer degradation

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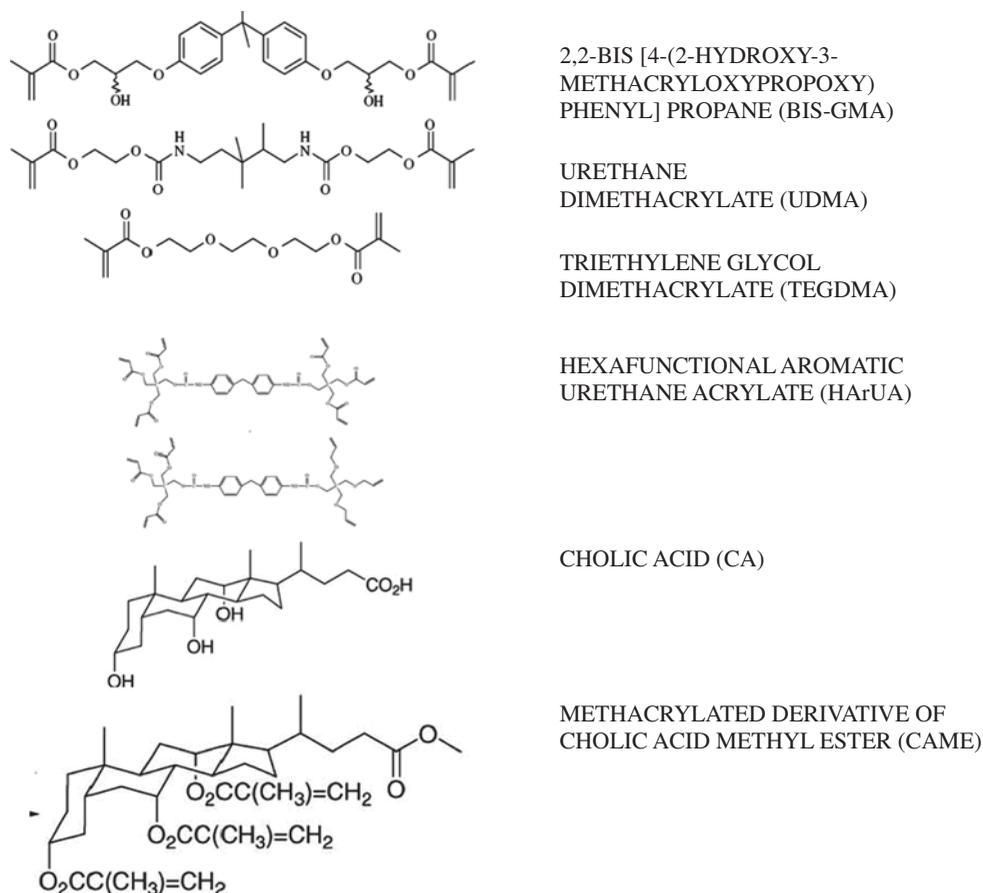


Figure 1. Structures of monomers used in dental composite formulations.

products [3,4]. Bisphenol-A (BPA) is one of these materials, as it is used to synthesize Bis-GMA (Figure 1). BPA mimics the estrogen hormone known to be an endocrine disruptor. The growing international concern regarding the presence of BPA in commercial products has led to many studies of its effect on human health. This topic is still controversial.

Consequently, the objective of the present study was to investigate alternative monomers for Bis-GMA having low viscosity prior to cure, low polymerization shrinkage to insure good adhesion to both enamel and the glass/ceramic fillers, high mechanical properties (especially compressive strength, fracture toughness and fatigue endurance), surface hardness, abrasion resistance, low water uptake, low coefficient of thermal expansion, ease of handling in the oral environment, good adhesion, and the ability to match colors for the esthetics reasons of the patient's teeth [5].

A variety of resins and monomers were evaluated as potential replacement for Bis-GMA, among them urethane dimethacrylates and bile acids.

Various dimethacrylates resin derivatives have been explored through the years in attempts to reduce viscosity and to increase the degree of conversion. Urethane dimethacrylate (UDMA) (Figure 1) has been used as a cross-linker in restorative composites together with Bis-GMA. It was suggested to use UDMA as a substitute for Bis-GMA in restorative composites, based on similar mechanical and optical properties but lower cytotoxicity [6].

Bile acids are produced in the liver from cholesterol. They are amphiphilic substances, that is, possess both hydrophilic and lipophilic characteristics. Compounds derived from natural bile acids are expected to be safe and nontoxic when used in biomedical and pharmaceutical fields [7]. Biocompatible by nature, they are generally recognized as safe by the American Food and Drug Administration. Various polymers have been made from derivatives of bile acids for potential biomedical applications [4].

Cholic acid (CA) or 3 α ,7 α ,12 α -trihydroxy-5 β -cholan-24-oic acid (Figure 1), one of the most commonly occurring bile acids, contains three hydroxyl groups and a carboxylic acid group [7–8]. CA can be synthesized by adding multiple methacrylate groups by the use of methacrylic acid, methacryloyl chloride, and methacryloyl anhydride as the acrylating agents. The presence of polar groups and their rigid steroid backbone, which contains only cyclic carbon–carbon single bonds, impart the characteristics required for the organic resins for dental composites, for example, adhesion and higher mechanical properties. In addition, the high molecular weights of the bile acids reduce polymerization shrinkage. The possibility to add multiple double bonds (methacrylates) may ease their incorporation into the polymer matrix and avoid postpolymerization leakage. Their biological origin resolves the biocompatibility concerns, even in cases of incomplete polymerization or degradation products [4].

Cross-linked methacrylate monomers derived from bile acids have been proposed for composite dental fillings [9].

In oral environment, restorations are subjected to stresses from the chewing action. Thus, it is important to introduce appropriate tests concepts relevant to the performance of restorative dental materials in service [10–11]. Since most of masticatory forces are compressive and flexural, those modes of loading are tested. Generally, acrylic resin materials exhibit endurance for plastic deformation under masticatory loads [12]. In addition, the humid oral environment that may lead to hydrolytic degradation requires that water sorption should be included in the set of tests used for characterization of dental materials. Furthermore, water causes plasticization, lowering of the glass transition temperature (T_g) and decrease of the mechanical properties of dental acrylates. Exposure to water for prolonged durations may lead to irreversible changes, resulting in crazing, cracking, and matrix chemical degradation [13].

The extent of polymerization in resin composites is defined in terms of the conversion degree of monomers double bonds into single bonds. The degree of conversion (DC) and polymerization shrinkage of the resin are closely related. An ideal dental composite would show an optimal degree of conversion and minimal polymerization shrinkage. These seem to be contradictors attributes, as an increase in monomer conversion leads to high polymerization shrinkage. Thus, linear and volumetric shrinkages of dental cements and composites are of great interest, since they may have a significant effect on the ultimate clinical outcome.

The ultimate goal in dental materials is to produce a strong and durable bonded interface. Characterization of the interface after application, during service, and following failure remains a challenge [14], as the microstructure of the interface changes with time due to water effects, intraoral enzymes, thermal cycling, mechanical cycling, and other intraoral factors.

2. Experimental

2.1. Materials

2.1.1. Bile acids

The synthesis of bile acid derivatives and their incorporation into dental materials as a Bis-GMA replacement is relatively new in dental composites [4,7]. Thus, special attention was

directed to the synthesis of the trimethacrylate monomer of cholic acid (CAME) and to the characterization using NMR (Figure 1) [15].

Subsequently, the CAME derivative was evaluated as Bis-GMA replacement with respect to its rheological properties for fillings, the mechanical and adhesive characteristics.

2.1.2. Oligomers as Bis-GMA replacements

Seven commercial oligomers were studied as core resins for dental composites, and compared with the conventional Bis-GMA-based dual-cure core composite material (Q-Core by B.J.M Laboratories Ltd.) [15]. The following oligomers were studied:

Oligomers by Sartomer LLC, Pennsylvania, USA: Ethoxylated (4) Bisphenol-A dimethacrylate (EBAD), Difunctional Polyester Acrylate, Hexafunctional Aromatic Urethane Acrylate (HArUA)

Oligomers by Rahn AG, Switzerland: Difunctional Aliphatic Urethane Acrylate, Difunctional Aliphatic Urethane Methacrylate, Difunctional Aliphatic Polyester Tri-Urethane Acrylate

Oligomer by Esstech Inc., Pennsylvania, USA: Urethane Di-Methacrylate.

Two of the most promising oligomers (HArUA, EBAD) were selected for further study. Along with the bile acid derivative (CAME) they were studied as replacement for Bis-GMA in the dental light-cure composite formulations.

2.1.3. Preparation of orthodontic adhesive formulation

Bis-GMA-based reference orthodontic formulation for metallic bracket adhesive system (HQB BR, B.J.M Laboratories Ltd.) is comprised of primer and adhesive paste, as shown in Table 1. In the studied formulations, the Bis-GMA was replaced with the BPA-free oligomers HArUA and tri-methacrylated derivative of cholic acid methyl ester (CAME). TEGDMA was used as a diluent. Dipentaerythriol Pentacrylate Phosphoric Acid Ester (PENTA) was used as an adhesion promoter.

The photoinitiator used was camphoroquinone (CQ) and the accelerator was ethyl-4-dimethylaminobenzoate (EDB).

In case of orthodontic adhesive paste formulations filler was introduced into the resins. Each formulation contained 77 wt.% of filler. The filler comprised 3 wt.% untreated fumed silica (average single particle size – 17 nm, aggregate size 200–300 nm) (Cab-O-Sil) (by CABOT Corporation, USA) and 97 wt.% X-ray-opaque, barium-aluminum-borosilicate glass powder (Opaque Powder) (by SCHOTT Electronic Packaging GmbH, Germany) having a refractive index similar to the composite resin matrix (1.53) and an average particle size of 6 μm and treated with γ -methacryloxypropyltrimethoxy silane. For comparison purposes, the ratios [wt.%] of all additives and fillers in the mixture were kept the same.

In case of orthodontic primer formulations the resins were diluted with ethanol.

2.1.4. Preparation of light-cure composite

In the first stage of the work five different formulations (1-F1, 2-F1, 3-F1, 4-F1 and 5-F1), based on the three different oligomers, were investigated, as shown in Tables 2 and 3. The formulations were prepared in different ratios of resin/Bis-GMA/TEGDMA (1–2) and afterward in different ratios of only resin/TEGDMA, without Bis-GMA (3–5). Photoinitiator camphoroquinone (CQ) (0.33 wt.%) and accelerator ethyl-4-dimethylaminobenzoate (EDB)

Table 1. Composition of orthodontic adhesive (based on the ratios used in reference orthodontic adhesive bracket composition, comprising primer and adhesive paste).

Orthodontic adhesive paste			
Component	Quantity (wt.%)		
<i>Resin:</i>	23		
<i>Resins blend:</i>	99.4		
Basic monomer	Bis-GMA		65.4
Diluent	TEGDMA		28.0
Adhesion Promoter	PENTA		6.0
<i>Initiators and inhibitors:</i>	0.6		
Photoinitiator	CQ		0.33
Accelerator	EDB		0.27
<i>Total resin parts:</i>	100.0		
<i>Filler:</i>	77		
Filler	Opaque powder		95
Filler	Cab-O-Sil		5
<i>Total filler parts:</i>	100.0		
<i>Total:</i>	100.0		
Orthodontic primer			
<i>Resin:</i>	90		
<i>Resins blend:</i>	99.4		
Basic monomer	Bis-GMA		65.4
Diluent	TEGDMA		28.0
Adhesion Promoter	PENTA		6.0
<i>Initiators and inhibitors:</i>	0.6		
Photoinitiator	CQ		0.33
Accelerator	EDB		0.27
<i>Total resin parts:</i>	100.0		
<i>Solvent:</i>	10		
Diluent	Ethanol		100.0
<i>Total solvent parts:</i>	100.0		
<i>Total:</i>	100.0		

(0.27 wt.%) were added to the composite mixture. Glass filler (75 wt.%) was introduced into the resin mixtures.

The fillers were composed of barium-aluminum-borosilicate glass powder for dental composite (Opaque Powder) having a refractive index similar to the composite resin matrix (1.53) and four different particle sizes (0.4 μm , 1.5 μm , 6 μm and 180 nm). The filler content of the composites comprised of 3 wt.% untreated fumed silica (single average particle size – 17 nm, aggregate size 200–300 nm) (Cab-O-Sil) and of 97 wt.% Opaque Powder treated with γ -methacryloxypropyltrimethoxy silane. Five mixtures containing new glass fillers were formulated. Table 2 summarizes the different filler contents of formulations F1–F5. The mixtures vary in $\mu\text{m}/\text{nm}$ particle ratio and contain the same 3 wt.% Cab-O-Sil.

The above glass mixtures were incorporated in the various resin matrices based on Bis-GMA, HARUA, and CAME monomers. TEGDMA was used as a diluent. Each formulation contained 75 wt.% of filler.

Table 3 describes the light-cured compositions. The light-cure dental composite restorative material (ProFil by Silmet Ltd., Israel) was used as reference. ProFil contains Bis-GMA (70 wt.%) and TEGDMA (30 wt.%) oligomers, photoinitiator CQ, and accelerator EDB, and

Table 2. Fillers Compositions.

Filler composition	Micrometer particles (wt.%)			Nano particles (wt.%)		Total
	Opaque powder (6 μm)	Opaque powder (1.5 μm)	Opaque powder (0.4 μm)	Opaque powder (180 nm)	Cab7-O-Sil (17 nm)	
F1	97	0	0	0	3	100
F2	55	28	0	14 (0% silane)	3	100
F3	55	28	0	14 (6% silane)	3	100
F4	55	28	0	14 (13% silane)	3	100
F5	43.4	32.6	21.6	0	2.4	100

Table 3. Compositions and mechanical properties¹ of selected light-cure composites.

Mixture number	Oligomers mixture number	Oligomers mixture description	Filler composition	Compressive strength (MPa)	Flexural strength (MPa)
1-F1	1	HArUA: TEGDMA: Bis-GMA	F1	202 \pm 18 ^a	189 \pm 33 ^b
1-F2	1	HArUA: TEGDMA: Bis-GMA	F2	257 \pm 22 ^a	162 \pm 23 ^b
1-F3	1	HArUA: TEGDMA: Bis-GMA	F3	236 \pm 10 ^a	220 \pm 21 ^a
1-F4	1	HArUA: TEGDMA: Bis-GMA	F4	135 \pm 40 ^b	212 \pm 35 ^b
1-F5	1	HArUA: TEGDMA: Bis-GMA	F5	260 \pm 21 ^a	239 \pm 31 ^a
2-F1	2	EBAD: TEGDMA: Bis-GMA	F1	180 \pm 38 ^b	182 \pm 8 ^a
3-F1	3	HArUA: TEGDMA = 70:30	F1	149 \pm 29 ^b	177 \pm 20 ^a
3-F5	3	HArUA: TEGDMA = 70:30	F5	272 \pm 28 ^a	239 \pm 31 ^a
4-F1	4	HArUA: TEGDMA = 80:20	F1	167 \pm 40 ^c	221 \pm 14 ^a
4-F4	4	HArUA: TEGDMA = 80:20	F4	181 \pm 19 ^a	161 \pm 28 ^b
4-F5	4	HArUA: TEGDMA = 80:20	F5	294 \pm 21 ^a	227 \pm 13 ^a
5-F1	5	CAME: TEGDMA = 60:40	F1	70 \pm 8 ^a	110 \pm 11 ^a
5-F5	5	CAME: TEGDMA = 60:40	F5	130 \pm 9 ^a	64 \pm 12 ^b
ProFil (Ref.)		Bis-GMA: TEGDMA = 70:30		223 \pm 33 ^a	274 \pm 52 ^b

¹Standard deviations are (a) \pm 10%, (b) \pm 15%, and (c) \pm 20%. Values with the different superscript letters (a, b, c) in the same column are statistically different ($p < 0.05$).

75 wt.% glass filler. In case of ProFil the filler comprised fumed silica and dental glass powder (Opaque Powder).

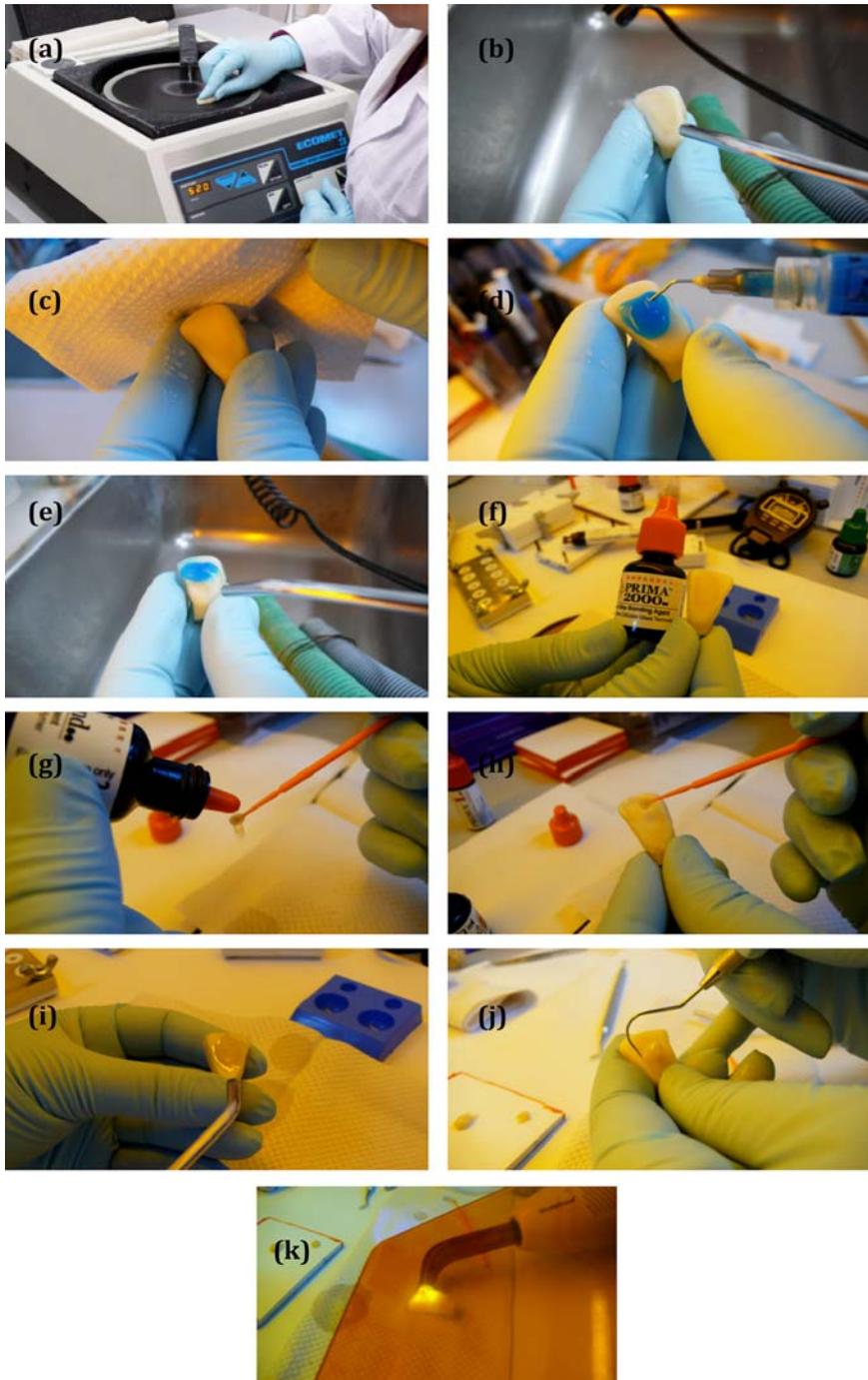


Figure 2. Illustration of the shear bond strength sample preparation process. (a) Substrate surface preparation by grinding teeth using water cooled abrasive wheel; (b) rinsing by water; (c) blot-drying with a tissue; (d) surface etching by 37% phosphoric acid gel; (e) rinsing by water and air-drying; (f–i) primer applying and air-drying; (j) bonding of the gelatin capsule filled with light-cure composite; (k) light curing with dental LED lamp.

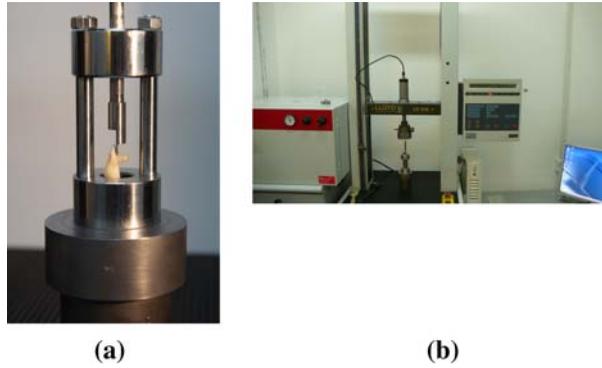
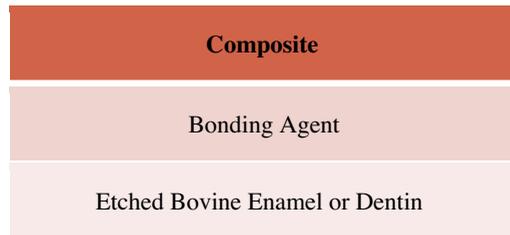


Figure 3. Shear bond strength testing devices: (a) Bencor Multi-T testing device and (b) mechanical tester (Lloyd Testing Machine, Model LR 10K) equipped with a load cell of 500 N and a chisel-shaped rod (Bencor Multi-T testing device).



(a)



(b)

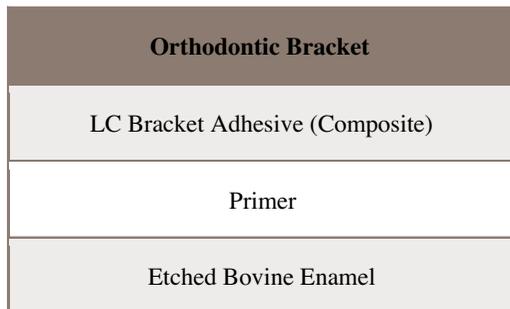


Figure 4. Structure of the various adhesive joints prepared utilizing two adhesive techniques: (a) gelatin capsule technique and (b) orthodontic brackets bonding.

2.2. Characterization methods

Compressive, flexural, shear bond strength, water sorption, solubility, light curing time, degree of conversion, and volumetric shrinkage tests were carried out and the results are presented in Tables 3 and 4.

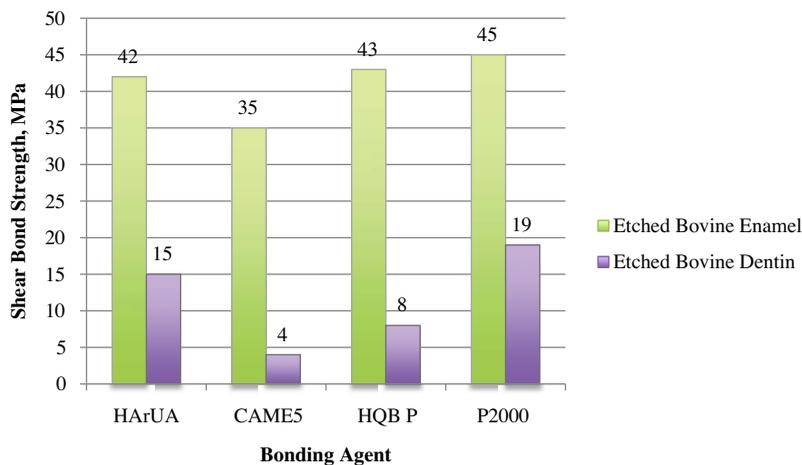


Figure 5. Shear bond strength (Standard deviation is $\pm 10\%$.) of orthodontic primers used as bonding agent and light-cure composite bonded to bovine enamel and dentin (Utilizing Gel Cap Bonding Technique).

Shear bond strength of the metal bracket (cobalt-nickel-molybdenum-based alloy) to bovine enamel substrate was studied according to ISO standard ISO/TS 11,405 [16]. Flat surfaces were prepared on the buccal surface of bovine teeth by grinding teeth using water cooled abrasive wheel (Metaserv 2000 Grinder/Polisher, Buehler Ltd.) 180 grit, and then with 600 grit to reach the dentin surface or 600 grit to reach the enamel surface.

The substrate surfaces were rinsed with water for 10 s and blot-dried with a tissue.

The orthodontic primer, orthodontic adhesive paste and/or light cure composite formulations were applied on the etched (by 37% phosphoric acid gel) tooth surface utilizing two techniques:

- (1) After applying the primer, metal brackets (made from cobalt-nickel-molybdenum-based alloy, model Omni Roth, by GAC/Dentsply) were bonded to the enamel surfaces utilizing an orthodontic adhesive paste and then cured with a dental LED lamp.
- (2) After applying the primer, cylinders of light-cure composite were bonded to the dentin/enamel surfaces, using the gelatin capsule technique in which a resin cylinder 3.5 mm in diameter was prepared by loading composite in gelatin capsules and then applied to the primed tooth surface and cured with a dental LED lamp. In this case, the orthodontic primer was tested as an adhesive. Prima 2000 (B.J.M Laboratories – P2000) was used as reference. Compatibility of the commercial light cure composite (ProFil by Slimet Ltd., Israel) with the experimental adhesives was evaluated with respect to adhesive strength [16].

The specimens were stored for an hour at ambient temperature and then immersed in distilled water at 37 °C for 24 h. Following conditioning, the samples were mounted on a 2 cm stainless steel rings with self-curing acrylic.

Mechanical loading was performed using a mechanical tester (Lloyd Testing Machine, Model LR 10K, Serial No. 9211) equipped with a load cell of 500 N and a chisel-shaped rod (Bencor Multi-T Testing Device) to deliver the shearing force. The specimens were aligned with the shearing rod parallel to the bonding site (Figures 2–4). Each bonded cylinder/bracket

Table 4. Mechanical and shear bond strength (SBS) properties¹ of adhesively bonded metal to bovine enamel.

Property	Standard requirements	CAME based	HArUA based	HQB BR
Flexural strength (MPa)	Minimum 50 MPa	88 ± 18 ^b	168 ± 13 ^a	207 ± 26 ^a
Compressive strength (MPa)	Minimum 50 MPa	104 ± 19 ^b	119 ± 16 ^a	221 ± 14 ^a
SBS to etched bovine enamel (MPa)	Minimum 15 MPa to etched bovine enamel	14 ± 2 ^a	19 ± 4 ^b	38 ± 8 ^b

¹Standard deviations are (a) 10% and ± (b) 15%. Values with different superscript letters (a, b) in the same column are statistically different ($p < 0.05$).

was loaded continuously at a rate of 5 mm per minute until fracture occurred. The fractured specimens were examined to determine where failure had occurred. The fractured specimens were examined by scanning electron microscopy (SEM) utilizing two techniques: edge detection technique (EDT) and backscattered electron detection technique (BSED). The teeth specimens were sectioned using a diamond-wafering blade through the restoration from facial to lingual. The specimens for the SEM were dried for 24 h in 37 °C oven and afterwards vacuum-desiccated for 24 h followed by coating with gold at 15 mA for 2 min prior to visualization in an Inspect FEI Model F50 Scanning Electron Microscope at 5 and 10 kV acceleration voltage and 5 and 10 mm working distance [15].

Compression, flexural, water sorption, and solubility specimens were prepared using Teflon® molds according to relevant ISO standards: ISO 4049, ISO 9917 [5,16].

FT-IR spectroscopy analysis was carried out to determine the degree of conversion of the Bis-GMA-free matrices containing the new fillers [17]. The change in the ratio of double bonds (C=C) of the reactive methacrylate groups compared to unchanged standard groups was followed. The degree of conversion was determined from the ratio between the absorbance peaks of the C=C bonds in the monomer and the polymer. The following formula was used for the calculations:

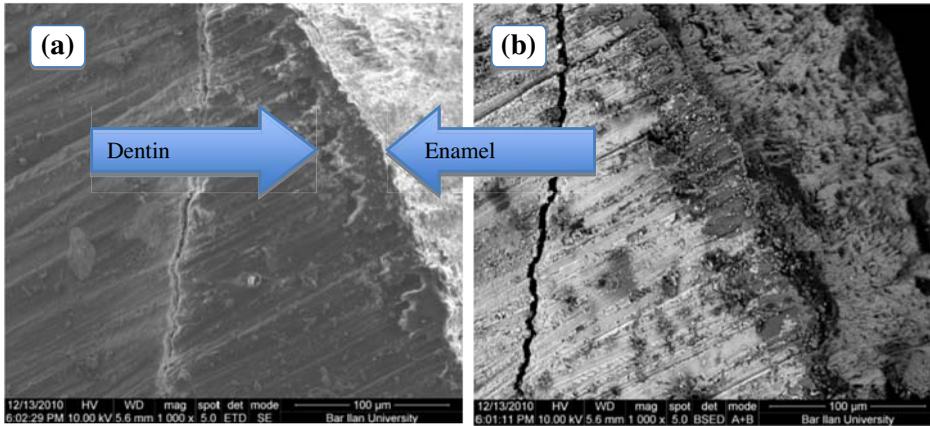
$$DC = 100 \cdot \left[1 - \frac{[A(C=C)/A(C=O)]_{\text{polymer}}}{[A(C=C)/A(C=O)]_{\text{monomer}}} \right]$$

The light-curing time was measured according to the following procedure: a spheroidal mass of 30 mg composite was irradiated by dental LED lamp for duration from 10 s to a maximum of 60 s with the 10 s steps. Material was inspected visually and checked by dental spatula to see whether it was physically homogeneous and hard (polymerized). The entire procedure was repeated twice, using a new sample for each test. Results of all three tests were monitored by a timer with 1 s resolution.

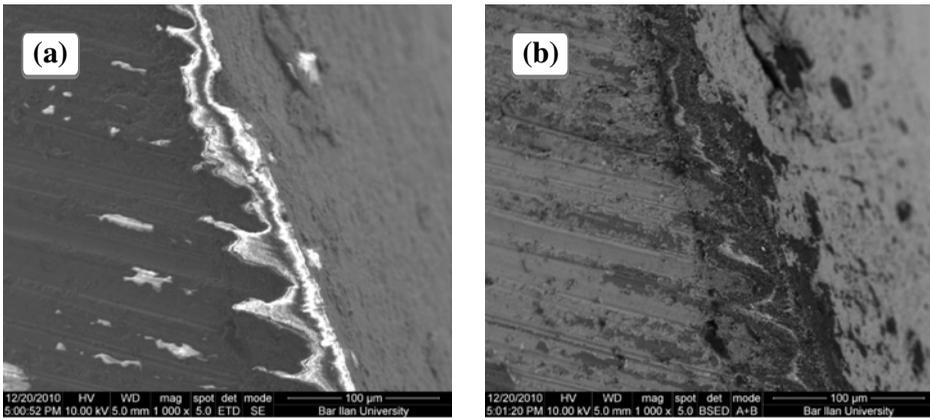
Intensity of the dental LED lamp was calibrated prior to testing.

Volumetric shrinkage of the light cure composites was evaluated utilizing Archimedes principle [18].

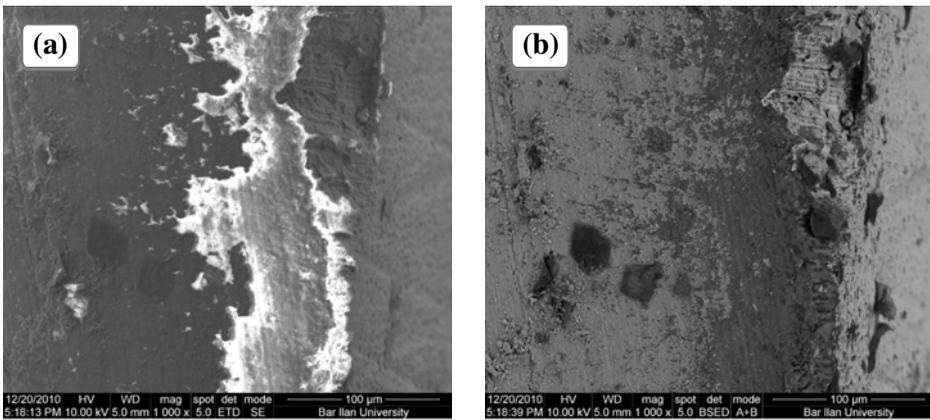
All data were statistically analyzed by the analysis of variance (ANOVA) method, at a significance level set at $p < 0.005$ to ensure the statistical significance of the results.



(1) Baseline. SEM Images of intact bovine tooth interface taken by (a) edge detection technique (EDT) detector and (b) backscattered electron (BSED) detector

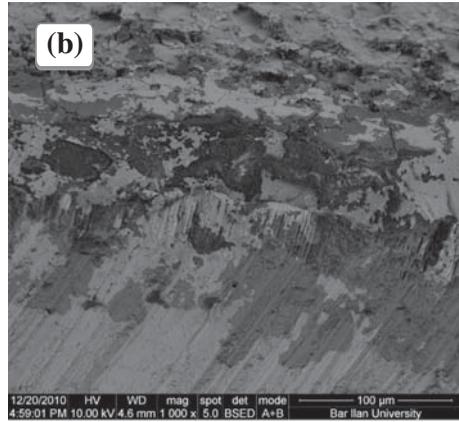
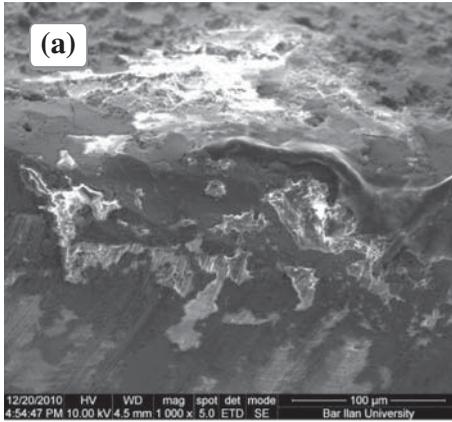


(2) Bonding interface of etched bovine *enamel* - HARUA based bonding agent by (a) EDT detector (b) BSED detector

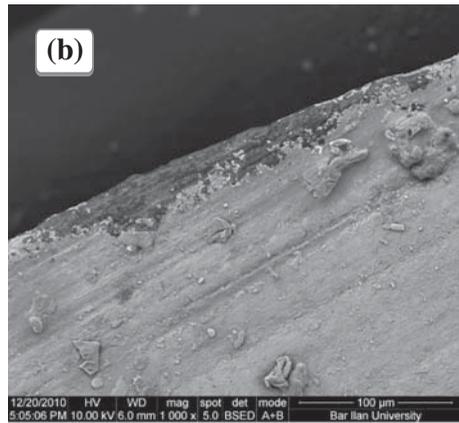
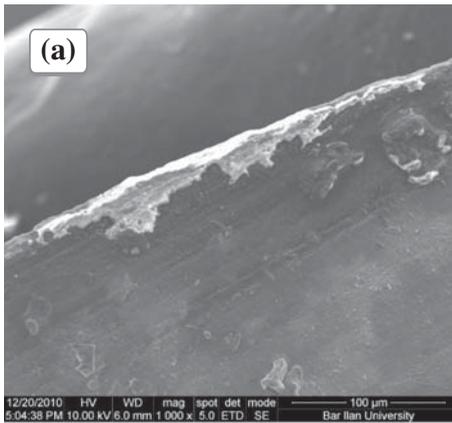


(3) Bonding interface of etched bovine *dentin* - HARUA based bonding agent by (a) EDT detector (b) BSED detector

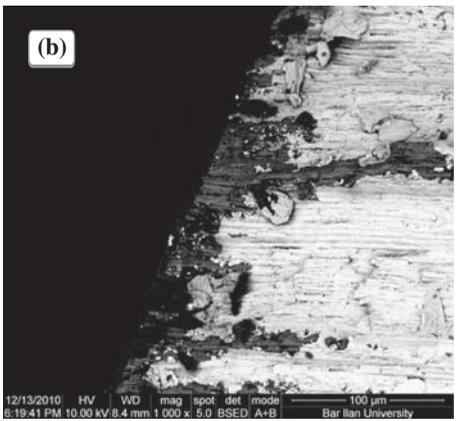
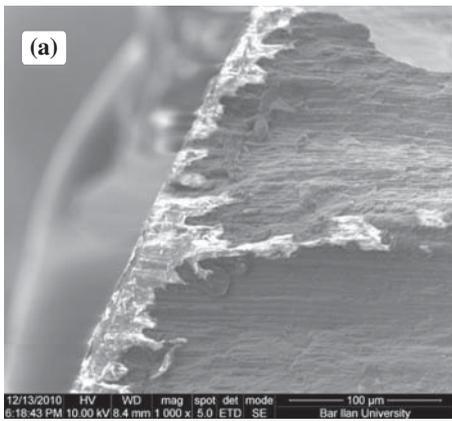
Figures 6. SEM micrographs of debonded tooth specimens.



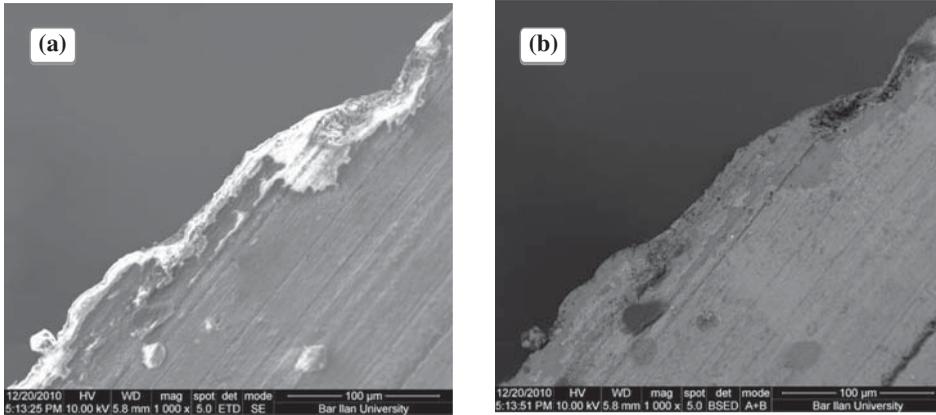
(4) Bonding interface of etched bovine *enamel* - CAME5 based bonding agent by (a) EDT detector (b) BSED detector



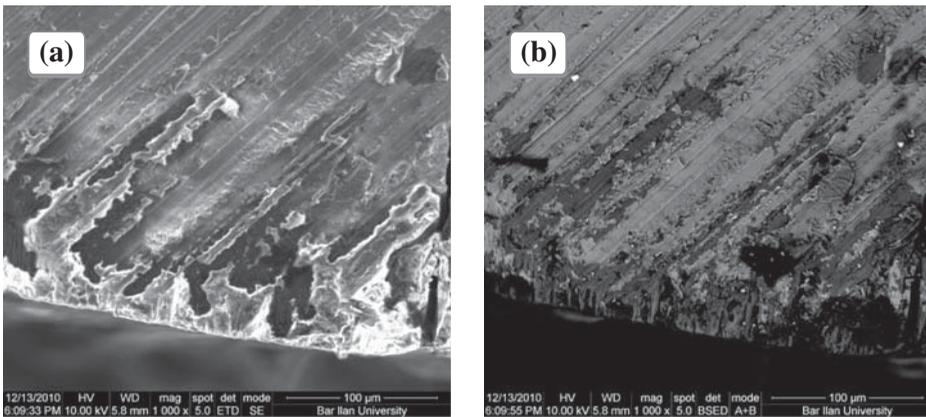
(5) Bonding interface of etched bovine *dentin* - CAME5 based bonding agent by (a) EDT detector (b) BSED detector



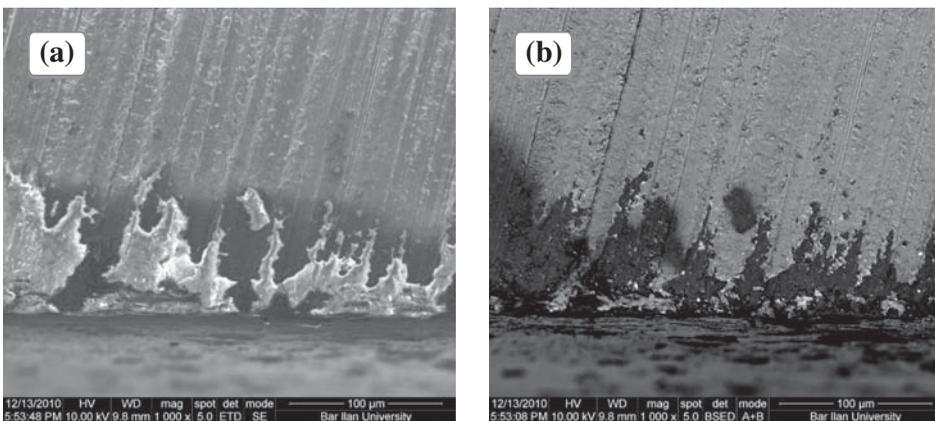
(6) Bonding interface of etched bovine *enamel* - Bis-GMA based commercial orthodontic primer (HQB P) (tested as bonding agent) by (a) EDT detector (b) BSED detector



(7) Bonding interface of etched bovine *dentin* – Bis-GMA based commercial orthodontic primer (HQB P) (tested as bonding agent) by (a) EDT detector (b) BSED detector



(8) Bonding interface of etched bovine *enamel* – Bis-GMA based commercial bonding agent (P2000) by (a) EDT detector (b) BSED detector



(9) Bonding interface of etched bovine *dentin* – Bis-GMA based commercial bonding agent (P2000) by (a) EDT detector (b) BSED detector

3. Results and discussion

3.1. Orthodontic adhesives

The adhesion properties were studied for joints made of the tooth enamel and the metal brackets. Accordingly, metal brackets were bonded to uncut etched surface of bovine enamel utilizing the two selected adhesive paste systems (CAME and HARUA based), using a primer. The bracket adhesive system containing Bis-GMA was used as a reference. Shear bond strength (SBS) results are presented in Table 4.

As can be seen in Table 4 the reference bracket adhesive system exhibited a high level more than 200 MPa compression and flexural strengths and SBS values of more than 30 MPa. As shown both oligomers (CAME and HARUA) exceed the required minimum strength values in both mechanical tests. The bond failure in all cases was cohesive, in the adhesive, as determined visually.

In the next stage of the investigation, the orthodontic primer was used as an adhesive utilizing the gel cap bonding technique. Light-cure composite (ProFil by Silmet Ltd., Israel) was applied to the gel capsules and bonded to the etched enamel and dentin surfaces with each of the studied liquid adhesives (referred above as orthodontic primers) including bracket adhesive primer (HQB P) and liquid adhesive (Prima 2000 by B.J.M Laboratories), which was used as reference.

The reference (Prima 2000) exhibited an average SBS value of 45 MPa to enamel and 19 MPa to dentin. The bracket adhesive primer also exhibited high SBS of 43 MPa to enamel, but low adhesion to dentin (8 MPa). Figure 5 indicates that both oligomers demonstrated good strength values, close to those demonstrated by the reference.

Figure 6 (2–9) show the SEM images of the fractured surfaces. As can be seen penetration of the adhesives into tooth tissues is evident compared to the intact tooth structure presented in Figure 6 (1).

Images obtained by BSED detector contain valuable information about the topography and composition due to the differences in chemical structure and density of tooth enamel and dentin, and the studied adhesive compositions as well.

HARUA-(aromatic-urethane hexafunctional oligomer) based formulation showed large penetration depth into dentin and enamel and a continuous adhesive layer on the debonded surfaces. These observations correlate well with the adhesive strength results.

The CAME-based formulation showed acceptable penetration depth into tooth tissues. The structure and depth of the adhesive layer are similar to those obtained by the commercial Bis-GMA-based primer (HQB P). The adhesive strength correlates well with SEM observations.

3.2. Light-cure composites

The objective in the case of light-cure composites was to replace the Bis-GMA resin and maintain the key properties, while changing as little as possible the composition (resin/TEGDMA ratio and filler content). The minimal requirements as specified in the relevant standards for dental applications are 50 MPa compressive strength and 50 MPa flexural strength.

Table 3 depicts the mechanical properties of the 6 Bis-GMA containing and 7 Bis-GMA-free light-cure composite formulations. The formulations were prepared in different ratios of resin/Bis-GMA/TEGDMA (1–2) and resin/TEGDMA without Bis-GMA (3–5). The filler comprised fumed silica and Opaque Powder (F1–F5).

Results indicated that the oligomers were adequate candidates for Bis-GMA replacement. The studied oligomers/monomers demonstrated miscibility with TEGDMA and other components. The resultant rheological behavior of the formulations was satisfactory (assessed by the ability to flow the paste out of a syringe).

Table 5. Physical properties of Bisphenol-A free dental composites.

Property	Standard requirements	CAME based (5-F5)	HArUA based (4-F5)
Biocompatibility	Material should show no cytotoxicity	N/E ¹	N/E
Light curing time at 23 °C	No more than 30 s	20 s	20 s
Degree of conversion (%)	Degree of conversion should reach at least 50% 5 min after the start of irradiation by a visible light-curing lamp	44	45
Water sorption ($\mu\text{g}/\text{mm}^3$)	Maximum 40 $\mu\text{g}/\text{mm}^3$	40	23
Solubility ($\mu\text{g}/\text{mm}^3$)	Maximum 7.5 $\mu\text{g}/\text{mm}^3$	14	2
Flexural strength (MPa)	Minimum 50 MPa	64	227
Compressive strength (MPa)	Minimum 50 MPa	130	249
Radiopacity (% Al)	Minimum 100% Aluminum	✓	✓
Adhesion (SBS to etched bovine enamel, MPa)	Minimum 15 MPa to etched enamel using a bonding agent	33	38
Volumetric shrinkage (%)	Maximum 7%	2.4	0.1
Wear resistance	Maximum material height loss of 10 μm per 156,000 3-body wear cycles	N/E	N/E
Handling property: viscosity vs. shear rate	While the viscosity decreases under an increasing shear rate, once the force is removed, the viscosity should return to the higher viscosity	✓	✓
Shade (color) stability	Material should be visually homogeneous and match the defined color	✓	✓

¹N/E – Not Established in our laboratory.

Overall, the mechanical properties of the bile acid derived matrix (CAME) reached the minimum required by the standards. Ethoxylated Bisphenol-A Oligomer (EBAD) demonstrated high mechanical properties. However, the presence of Bisphenol-A as a coreactant excluded it as a potential replacement.

Suitable results were obtained using HArUA. Its mechanical and adhesive properties excelled in all formulations. This was attributed to the highly cross-linked network due to its high functionality and aromatic structure.

Table 3 displays results of compressive and flexural strengths of the HArUA and CAME-based matrices filled with glass mixture of micro and nano-particles (5 μm , 1.5 μm , 0.4 μm , and 180 nm).

The ProFil reference exhibited average values of 223 MPa, for compressive and 274 MPa for flexural strength. Table 3 indicates that the compositions containing the oligomers exceed the required minimum values. High strengths were obtained for formulations containing F2, F3, and F4 filler compositions (microsized filler and a constant percentage of nanoparticles). The best strength balance was demonstrated for formulation F5 (containing mainly micro-sized filler and fumed silica).

Favorable compressive strength results were attained for the Bis-GMA-free composite containing HArUA as matrix and micro-sized filler mixture F5.

Another aspect that was studied was related to the handling characteristics. HArUA matrix was much easier to handle and to flow out of the syringe than the CAME-based matrix. This observation can be attributed to the compatibility of the filler's composition to the urethane matrix. All compositions showed acceptable short time conversion degree, followed by post-cure within the oral environment.

As shown in Table 5, in the case of CAME containing formulation (5-F5), water sorption meets the standard's requirement, but the solubility is out of range. This may be due to excess of hydroxyl groups that makes it soluble in water. However, water sorption and solubility of HARUA containing formulation (4-F5) are very low and meet the standard's requirement.

Mechanical properties of CAME containing formulation reached the minimum required by the standards. However, HARUA containing composite exceeded the required minimum values and makes it a potential attractive candidate for Bis-GMA replacement.

The studied composites showed excellent compatibility with commercial bonding agent demonstrating high shear bond strength values.

Both composites demonstrated acceptable volumetric shrinkage after 24 h conditioning in water at 37 °C. Favorable volumetric shrinkage result was attained for CAME containing formulation.

The study indicated that the CAME derivative and HARUA could replace Bis-GMA in light-cure dental composite restorative materials. Physical, mechanical, and adhesive properties of HARUA excelled in all formulations.

4. Conclusion

The main objective of the work was to formulate alternatives for Bis-GMA in dental composites and adhesives. Consequently, a novel monomer from natural resources was synthesized (CAME) and commercial oligomers were investigated as dental matrices, with addition of novel barium-aluminum-borosilicate glass fillers having different particle sizes. The experimental results showed that Bis-GMA could be substituted by the tri-methacrylated derivative of cholic acid methyl ester (CAME) and aromatic-urethane hexafunctional oligomer (HARUA).

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