Bisphenol-A Free Alternatives For Orthodontic Adhesive Systems

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Rationale:
- Bisphenol-A (BPA) is suspected to be an endocrine disruptor (resembling Estrogen hormone)
- Current polymeric dental materials are based on BPA derivatives, e.g. Bisphenol-A Diglycidylether Methacrylate (Bis-GMA) which may leach out unreacted monomers and its degradation products
- The growing international concern regarding the presence of BPA in commercial products has led to many studies of its effect on human health
- However, this topic is still controversial because regulators think that the methods used in many of those studies haven’t been fully validated

Objectives:
- To evaluate Bisphenol-A free alternatives for potential use in orthodontic adhesive systems:
  - Use of synthetic commercial oligomers
  - Newly synthesized monomers from renewable resources

Introduction:

Orthodontic Adhesive System

Key properties:
- Biocompatibility
- Excellent bonding to tooth structure
- Excellent bonding to orthodontic appliances surface
- Endurance within the aggressive oral environment
- Dimensional stability
- Easy handling and Dentist friendly
- Matching natural tooth color

Synthetic Alternatives:
- 6 commercial oligomers produced by different manufacturers were studied in the light orthodontic adhesive formulations comprising of primer and adhesive paste:
  - Bisphenol Polyacrylate
  - Bisphenol Aliphatic Urethane Acrylate
  - Bisphenol Aliphatic Urethane Methacrylate
  - Bisphenol Aliphatic Polyurethane Tri-urethane Acrylate
  - Urethane Di-Methacrylate
  - Hexfunctional Aromatic Urethane Acrylate

Physical, mechanical and adhesive properties of HArUA excelled in all formulations.

Methods:

Synthetic Resource Monomer:
- Bile Acid (Cholic Acid)
  - Synthesis of a tri-methacrylate monomer of cholic acid was carried out and verified by different methods as methacrylated derivative of cholic acid methyl ester (CAME)
- The cholic acid derivative (CAME) were evaluated as Bis-GMA replacement

Testing Methods:
- Nuclear Magnetic Resonance (NMR), FTIR, DSC - verification of the synthesized cholic acid derivative;
- Compressive, Flexural, Shear Bond Strength (SBS), Water Sorption, Solubility, Light Curing Time - Degree of Conversion, Flow Properties - verification of adhesive formulations.
- All data was statistically analyzed by the analysis of variance (ANOVA) method, at a significance level set at p<0.005.

Preparation of Orthodontic Adhesive Formulations:
- Various orthodontic adhesive paste formulations were based on the two selected oligomers:
  - Different ratios of Resin/Bis-GMA / TEGDMA
  - Photoinitiator camphorquinone and acceleratotr ethyl-4-dimethylaminobenzene were added to the composite mixtures
  - Dipenténylphosphatoyl Phosphoric Acid Ester (PDMAE) was used as an adhesion promoter

- The Filler comprised fumed silica (Cab-O-Sil) and barium-aluminum-borosilicate glass powder (Dental Glass)
- The Filler content of orthodontic adhesive paste formulations comprised of 3% untreated fumed silica (single particle size ~17 nm, aggregate size 200-300nm) [Cab-O-Sil] and of 97% Dental Glass having a refractive index similar to the composite resin matrix [1.53] and treated with γ-Methacryloxypropil tri-methoxy-Silane. Each formulation contained 7.74% of fillers.
- In case of orthodontic primer formulations the resins were diluted with ethanol.
- High-Q-Bond Bracket (HOBB BR) Light cure bracket adhesive system comprising primer and adhesive paste (made by B.J.M. Laboratories ltd.) was used as reference. HOBB BR contains Bis-GMA and TEGDMA resins and 77%-v glass filler.

Results:

SEM Micrographs of Debonded Tooth Specimens

Structure of the adhesive point prepared utilizing adhesive technique of orthodontic brackets bonding

Physical Properties of Investigated Bisphenol-A Free Light Cure Orthodontic Adhesive Formulations

<table>
<thead>
<tr>
<th></th>
<th>Bisphenol Polyacrylate</th>
<th>Bisphenol Aliphatic Urethane Acrylate</th>
<th>Bisphenol Aliphatic Urethane Methacrylate</th>
<th>Bisphenol Aliphatic Polyurethane Triurethane Acrylate</th>
<th>Urethane Di-Methacrylate</th>
<th>Hexfunctional Aromatic Urethane Acrylate (HArUA)</th>
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</thead>
<tbody>
<tr>
<td>Degree of Conversion</td>
<td>75%±2</td>
<td>76%±2</td>
<td>76%±1</td>
<td>76%±1</td>
<td>76%±1</td>
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<td>Compressive strength</td>
<td>34.9±4</td>
<td>32.8±4</td>
<td>30.8±4</td>
<td>32.8±4</td>
<td>34.9±4</td>
<td>35.1±5</td>
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<td>Biocompatibility</td>
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<td>≥95%</td>
<td>≥95%</td>
<td>≥95%</td>
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Conclusions:

- The objective was to replace the Bis-GMA resin
- Maintain its key properties
- Changing as little as possible the composition (Resin/TEGDMA ratios, initiators and filler)
- In the two systems Bis-GMA was replaced by each of the two selected oligomers in both primer and adhesive components. Adhesive formulations were prepared in constant ratios of resin/Resin/PENTA/TEGDMA. The filler comprised fumed silica and dental glass of 6.8% particle size
- The experimental results showed that Bis-GMA can be substituted by
  - Aromatic-urethane hexahyrdicolic oligomer (HArUA)
- Employing both oligomers in a commercial orthodontic adhesive system requires further comprehensive evaluation of their polymerization shrinkage, color stability, cytotoxicity, composition modifications (molar dilution ratio, initiators and inhibitors percentage, filler size and load). These subjects are beyond the scope of the present work