PER/IADR
Congress, Helsinki, Finland, September 12-15, 2012

שנקר
בית ספר גבוה להנדסה ועיצוב
Shenkar College of Engineering & Design

BJM LAB
B.J.M. Laboratories Ltd.

Final Presentation / Poster Number # 118

Bisphenol-A Free Alternatives For Orthodontic Adhesive Systems

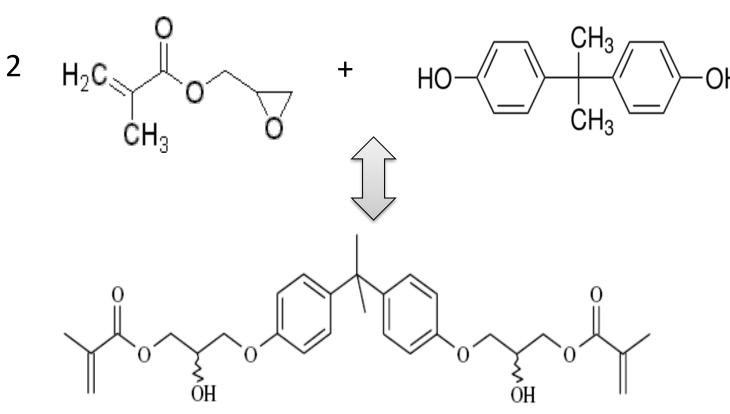
Kira Lizenboim [1, 2], *Irina Suvorov* [1], *Hanna Dodiuk* [2], *Barry Zalsman* [1]

[1]*B.J.M. Laboratories Ltd., Or Yehuda, ISRAEL*
[2]*Shenkar College, Ramat Gan, ISRAEL*

Rationale:

- Bisphenol-A (BPA) is suspected to be an endocrine disrupter (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

Glycidyl Methacrylate



BPA

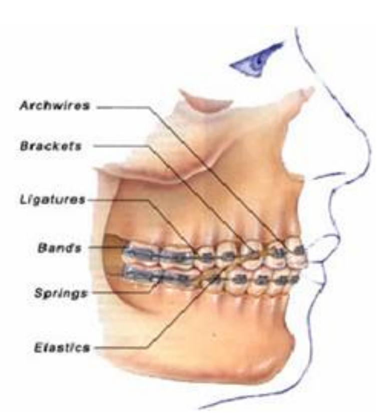
Bis-GMA

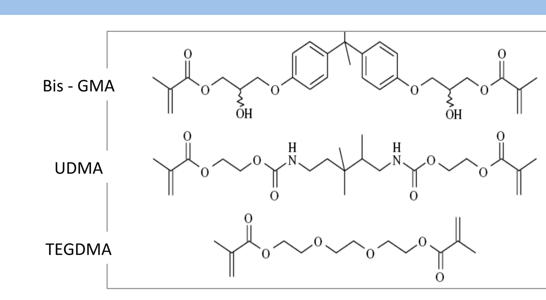
Objectives:

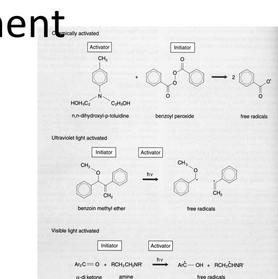
- To evaluate Bisphenol-A free alternatives for potential use in orthodontic adhesive systems:
  - Use of synthetic commercial oligomers
  - Newly synthesized monomers from renewable resources

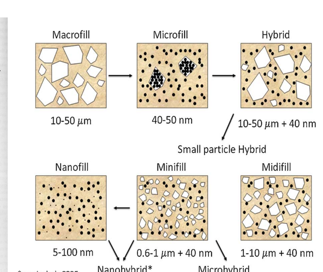
Introduction:

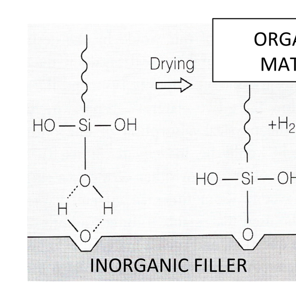
- Orthodontic Adhesive System
  - Key properties:
    - Biocompatibility
    - Excellent bonding to tooth structure
    - Excellent bonding to orthodontic appliances surface
    - Endurance within the aggressive oral environment
    - Dimensional stability
    - Easy handling and Dentist friendly
  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









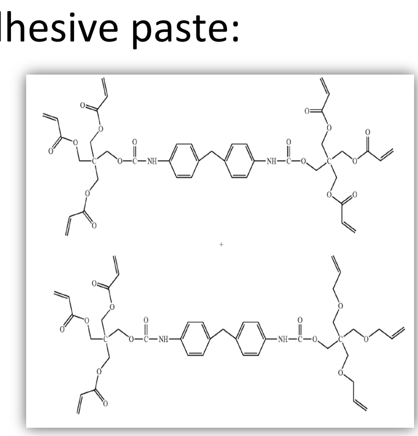


- The orthodontic adhesive system
  - Resin (BPA free)
  - Initiators
  - Fillers
  - Coupling agents (Resin - Filler)

Methods:

Synthetic Alternatives:

- 6 commercial oligomers produced by different manufacturers were studied in the light cure orthodontic adhesive formulations comprising of primer and adhesive paste:
  - Difunctional Polyester Acrylate
  - Difunctional Aliphatic Urethane Acrylate
  - Difunctional Aliphatic Urethane Methacrylate
  - Difunctional Aliphatic Polyester Tri-Urethane Acrylate
  - Urethane Di-Methacrylate
  - Hexafunctional Aromatic Urethane Acrylate (HArUA)

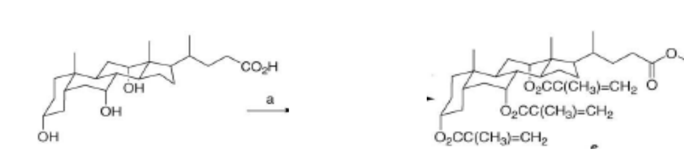


HArUA

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

Renewable 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



Cholic Acid — CAME

Testing Methods:

Nuclear Magnetic Resonance (NMR), FTIR, DSC - verification of the syntesized 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 $p<0.005$.

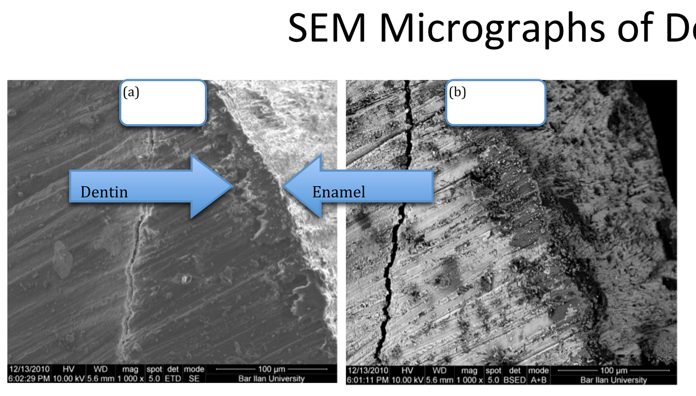
The fractured SBS specimens were examined to determine where failure had occurred. The fractured SBS specimens were examined by Scanning Electron Microscopy (SEM) utilizing two techniques: edge detection technique (EDT) and backscattered electron detection technique (BSED).

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 camphoroquinone and accelerator ethyl-4-dimethylaminobenzoate were added to the composite mixtures
  - Dipentaerythriol Pentacrylate Phosphoric Acid Ester (PENTA) 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 – 17nm, 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-Methacryloxypropyl-tri-methoxy-Silane. Each formulation contained 77wt% of filler.
- In case of orthodontic primer formulations the resins were diluted with ethanol.
- High-Q-Bond Bracket (HQB BR) Light cure bracket adhesive system comprising primer and adhesive paste (made by B.J.M. Laboratories Ltd.) was used as reference. HQB BR contains Bis-GMA and TEGDMA resins and 77wt% glass filler.

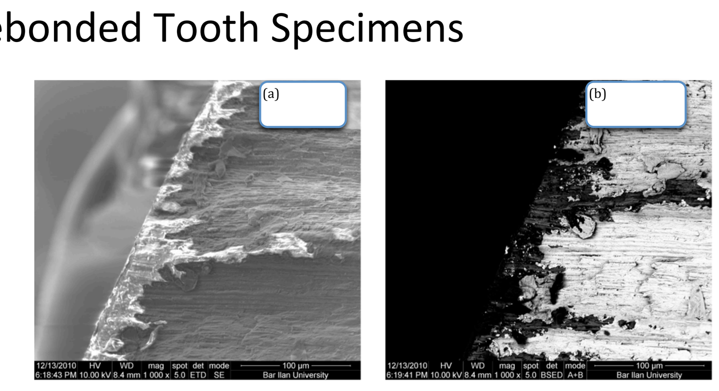
Results:

SEM Micrographs of Debonded Tooth Specimens

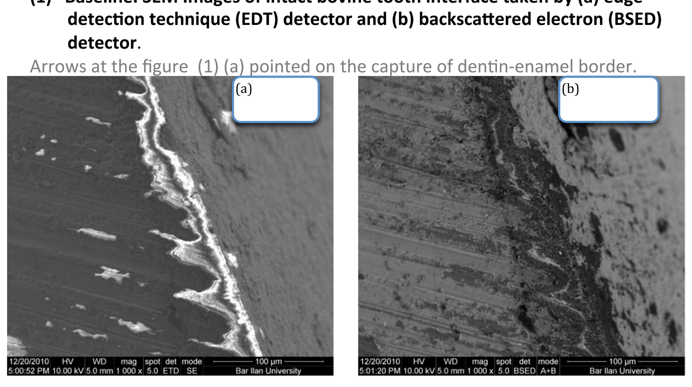


(1) Baseline. SEM Images of intact bovine tooth interface taken by (a) edge detection technique (EDT) detector and (b) backscattered electron (BSED) detector.

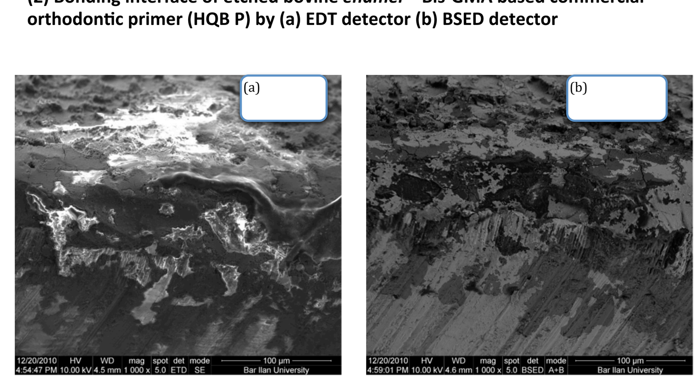
Arrows at the figure (1) (a) pointed on the capture of dentin-enamel border.



(2) Bonding interface of etched bovine *enamel* – Bis-GMA based commercial orthodontic primer (HQB P) by (a) EDT detector (b) BSED detector

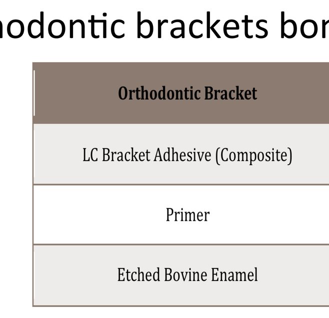


(3) Bonding interface of etched bovine *enamel* - HArUA based orthodontic primer and adhesive paste formulation by (a) EDT detector (b) BSED detector

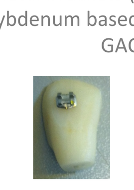


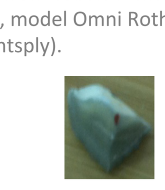
(4) Bonding interface of etched bovine *enamel* - CAME based orthodontic primer and adhesive paste formulation by (a) EDT detector (b) BSED detector

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



Metal brackets (made from cobalt-nickel-molybdenum based alloy, model Omni Roth, by GAC / Dentsply).





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 hours in 37°C oven and afterwards vacuum-desiccated for 24 hours 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.

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

Property	Standard Requirements	CAME based	HArUA based	HQB BR, Bis-GMA Based Reference
Biocompatibility	Material should show no cytotoxicity	N/E	N/E	N/E
Light curing time @ 23°C	Not more than 30 sec	20 sec	20 sec	20 sec
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	62
Water sorption, $\mu g/mm^3$	Maximum 40 $\mu g/mm^3$	40	25	12
Solubility, $\mu g/mm^3$	Maximum 7.5 $\mu g/mm^3$	14	3	7
Flexural strength, MPa	Minimum 50 MPa	88 ± 18^b	168 ± 13^b	207 ± 26^a
Compressive strength, MPa	Minimum 50 MPa	104 ± 19^b	119 ± 16^b	221 ± 14^a
Adhesion (SBS to etched bovine enamel utilizing primer, MPa)	Minimum 15 MPa to etched enamel	14 ± 2^a	19 ± 4^b	38 ± 8^b
Adhesive Remnant Index	Preferably 3 (all adhesive left on the tooth, with distinct impression of the bracket mesh)	2	2	3
Shade (color) stability	Material should be visually homogeneous and match the defined color	√	√	√

Standard deviations are ± (a) 10% and (b) 15%. Values with the different superscript letters (a, b) in the same column are statistically different (p<0.005).

N/E – Not Established in our laboratory.

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/ PENTA/TEGDMA. The filler comprised fumed silica and dental glass of 6μm particle size
- The experimental results showed that Bis-GMA can be substituted by
  - Tri-methacrylated derivative of cholic acid methyl ester (referred to as CAME)
  - Aromatic-urethane hexafunctional oligomer (HArUA)
- Employing both oligomers in a commercial orthodontic adhesive system requires further comprehensive evaluation of their polymerization shrinkage, color stability, cytotoxicity, composition modifications (resin/ diluent ratio, initiators and inhibitors percentage, filler size and load). These subjects are beyond the scope of the present work