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In vitro degradation of composite resins for dental restorations

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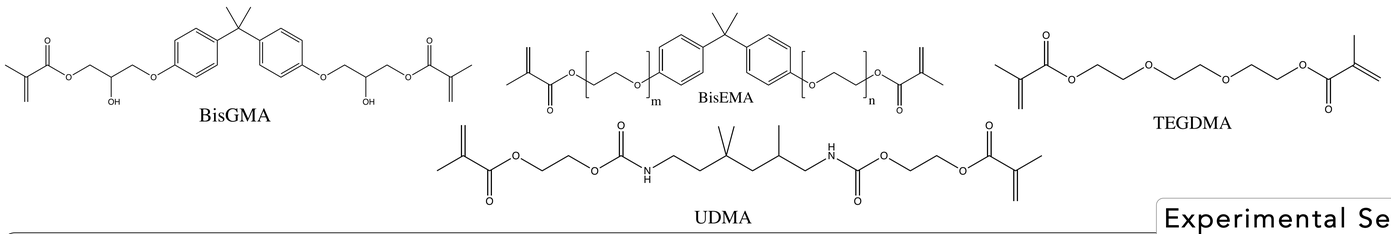
Introduction

Composite resins for dental restorations consist of (BPA-based) monomers, (photo-)initiators and other additives. Common monomers with a BPA core are BisGMA and BisEMA. Commonly used alternatives without BPA core are TEGDMA and UDMA.
During polymerization, the degree of conversion of monomers is around 50-70%, leading to leaching of unreacted monomers. Additive leaching can occur over time due to degradation of the composite restoration.

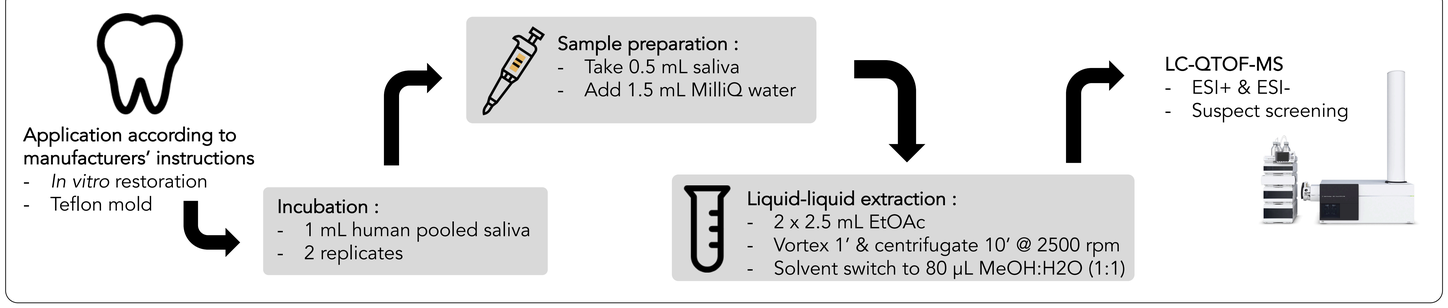
Aim: Identify leaching monomers and degradation products from *in vitro* saliva degradation



Tested materials

Composite	Material Type	Manufacturer	Chemicals present according to information present on Materials Safety Data Sheets (MSDS)
C1: Gradia Direct Posterior	Composite	GC Europe	UDMA (20-25%), bismethacrylate* (1-5%), dimethacrylate* (1-5%)
C2: G-**ænial** Posterior	Composite	GC Europe	UDMA (10-20%), Dimethacrylate (5-10%), Silicon dioxide (1-5%), Fluoro Alumino-silicate glass (45-50%), Composite filler (30-35%), Pigment (< 1%), Photo initiator (< 1%)
C3: Filtek Supreme XTE	Composite	3M	UDMA (1-10%), BisEMA-6 (1-10%), BisGMA (1-10%), PEGDMA (< 5%), TEGDMA (< 1%), Silane treated silica (1-10%), Silane treated ceramic (60-80%), Silane treated zirconia (1-5%)
C4: Ceram.X Universal	Composite	Dentsply Sirona	BisEMA (3-<10%), Urethane modified Bis-GMA dimethacrylate resin (3-<10%), TEGDMA, 3-<10%, Ytterbium trifluoride (1-<2.5%), 2,6-di-tert-butyl-p-cresol (0.1-<0.3%)
C5: Solitaire 2	Composite	Kulzer	BisGA (5-10%), TEGDMA (5-10%), 2,2-dimethoxy-1,2-diphenylethan-1-one (<1%)
C6: Scotchbond Universal	Adhesive	3M	HEMA (15-25%), BisGMA (15-25%), 2-propenoic acid, 2-methyl-, reaction products with 1,10-decanediol and phosphorous oxide (10-20%), Camphorquinone (< 2%), EDMAB (< 2%), DMAEMA (< 1%)
C7: Clearfil SE Bond 2	Adhesive	Kuraray Dental	Bond: BisGMA (25-45%), HEMA (20-40%); Primer: HEMA (20-40%), 10-methacryloyloxydecyl dihydrogen phosphate, hydrophobic aliphatic dimethacrylate, dl-camphorquinone
C8: Fissurit FX	Sealant	VOCO	TEGDMA (10-25%), BisGMA (5-10%), sodium fluoride (< 2.5%)
C9: AH Plus Jet	Root Canal Sealer	Dentsply Sirona	BADGE (25-50%), BFDGE (≥ 2.5 – < 10%)

Experimental Setup



Suspect Screening: Results

Compound	Formula	RT (min)	MS2 product ions	Saliva degradation									Specificity
				C1	C2	C3	C4	C5	C6	C7	C8	C9	
BADGE	C21 H24 O4	6.95	191.1022; 161.0907; 135.0790									X	BADGE
BADGE.H2O	C21 H26 O5	5.87	Not Acquired									X	BADGE
BADGE.H2O.HCl	C21 H27 Cl O5	5.94	Not Acquired									X	BADGE
BFDGE.H2O	C19 H22 O5	5.50	Not Acquired									X	BFDGE
BFDGE.H2O.HCl	C19 H23 Cl O5	5.66	Not Acquired									X	BFDGE
BFDGE.2H2O	C19 H24 O6	4.85	181.0836; 133.0627; 105.0681									X	BFDGE
BHM	C16 H24 O3	7.27	161.1273; 133.0970; 91.0518	X	X								BHM
∑ BisEMA	Not Applicable (group)	9-10	Not Applicable (group)		X	X	X				X		BisEMA
∑ BisEMA-H	Not Applicable (group)	7.5-7.8	Not Applicable (group)		X	X	X				X		BisEMA
∑ BisE	Not Applicable (group)	5.8-6.5	Not Applicable (group)		X	X	X				X		BisEMA
BisGA	C27 H32 O8	6.84	Not Acquired					X					BisGA
BisGA-H	C24 H30 O7	5.87	Not Acquired					X					BisGA
BisGMA	C29 H36 O8	7.99	277.1385; 209.1130; 143.0672			X	X		X	X	X		BisGMA
BisGMA-H	C25 H32 O7	6.39	277.1396; 209.1139; 143.0678			X	X		X	X	X		BisGMA
BisGMA-M	C31 H40 O9	9.75	Not Acquired						X				BisGMA
BisHPPP	C21 H28 O6	5.09	209.1142; 135.0787; 107.0483			X	X	X	X	X	X	X	BADGE, BisGA, BisGMA
DDDMA	C18 H30 O4	10.61	225.1797; 83.0837; 55.0531						X				DDDMA
DDMMA	C14 H26 O3	7.69	87.0426; 83.0843; 55.0538						X				DDDMA
Decanediol	C10 H22 O2	5.23	83.0845; 69.0696; 55.0542						X				DDDMA
DEG	C4 H10 O3	1.90	91.0503; 65.0373						X				DEGDMA
DEGMMA	C8 H14 O4	4.25	113.0576; 69.0324						X				DEGDMA
DMAB	C9 H11 N O2	4.12	120.0798; 77.0381; 51.0228		X		X		X	X	X		EDMAB
DMAEMA	C8 H15 N O2	5.32	Not Acquired						X				DMAEMA
DMPA	C16 H16 O3	6.38	Not Acquired					X					DMPA
EDMAB	C11 H15 N O2	6.20	179.0917; 134.0579; 77.0374		X		X		X	X	X		EDMAB
HMBP	C14 H12 O3	6.91	151.0355; 105.0311; 77.0370				X	X					HMBP
MMHM	C10 H16 O4	5.73	N.A.	X	X			X			X		MMHM
TCDDMDMA	C20 H28 O4	10.12	247.1640; 161.1290; 133.0979	X	X								TCDDMDMA
TCDDMMMA	C16 H24 O3	7.27	179.1376; 161.1273; 133.0970	X	X								TCDDMDMA
TCDDM	C12 H20 O2	5.28	116.1062; 77.0399; 55.0552	X	X								TCDDMDMA
TEEGDMA	C16 H26 O7	5.53	113.0575; 69.0327			X	X	X			X		TEEGDMA
TEEGMMA	C12 H22 O6	4.48	N.A.			X	X	X			X		TEEGDMA
TEGDMA	C14 H22 O6	5.51	113.0586; 69.0330			X	X	X	X		X		TEGDMA
TEGMMA	C10 H18 O5	4.37	113.0585; 69.0328			X	X	X	X		X		TEGDMA
TEG	C6 H14 O4	2.84	133.0816; 89.0580			X	X	X	X		X		TEGDMA
UDMA	C23 H38 N2 O8	6.62	385.2305; 113.0585; 69.0330	X	X	X		X			X		UDMA
UDMA-D1	C19 H34 N2 O7	5.44	273.1780; 113.0584; 69.0332	X	X	X		X			X		UDMA
UDMA-D2	C15 H30 N2 O6	4.69	273.1768; 255.1649; 168.1339	X	X	X		X			X		UDMA

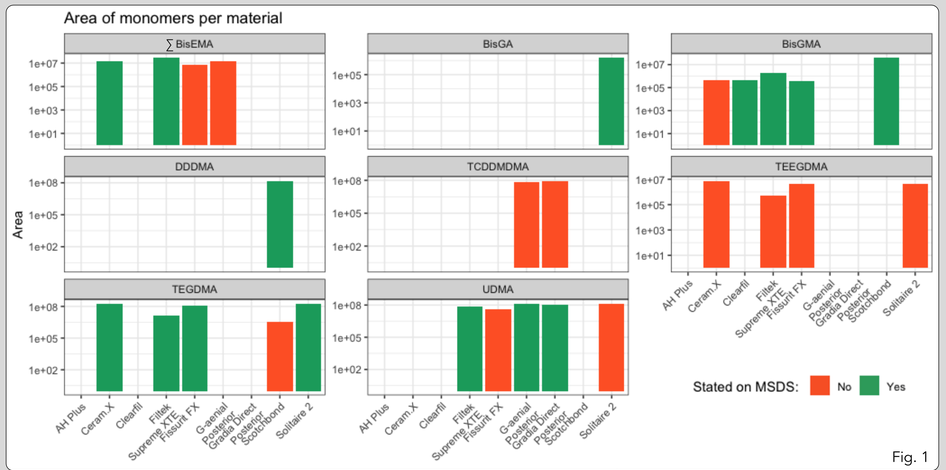


Fig. 1

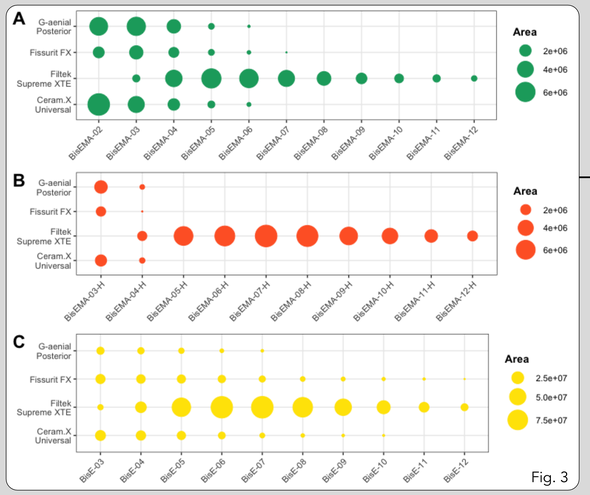


Fig. 3

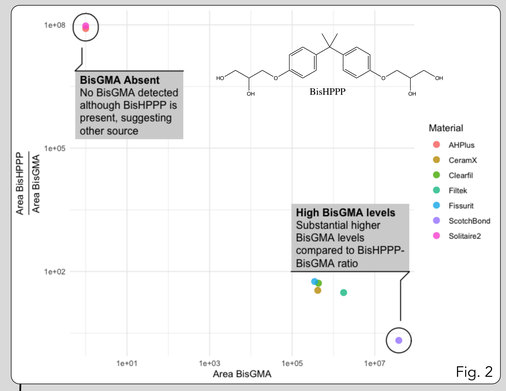


Fig. 2

Ratio between monomers and their degradation product(s) in saliva can be used to identify abnormalities

- BisGMA absent in AH Plus & Solitaire 2: BisHPPP can also be formed from BADGE and BisGA
- Release of BisGMA higher in Scotchbond compared to other adhesive or composites

Information on safety data sheets not complete

- Fig. 1 shows the area of all identified monomers which are not listed on the SDS (log_{10} scale).
- Not all monomers are listed on MSDS (colored in red), leading to possible bias in safety assessment
- Difficult to compare release of monomers (and degradation products) as manufacturers only give rough values on composition

Differences in BisEMA profiles

Fig. 3 shows area of the different oligomers of BisEMA (green) and degradation products BisEMA-H (red) and BisE (yellow) per material.

Leaching of unreacted BisEMA monomers (green) does not reveal full profile per material

- Degradation products BisE (yellow) reveal use of longer oligomers in e.g. Fissurit FX
- Intermediate monomethacrylates (red) useful for additional confirmation only
- Use of BisEMA not listed for Fissurit, but shows highest leaching for all oligomers of parent and degradation products

Conclusions

- HRMS reveals the true usage of different monomers and additives in composites for dental restorations.
- Different monomers, photo initiators and their degradation products were identified in the tested materials, often not listed on MSDS.
- Observed degradation products resulted from ester hydrolysis reactions, leading to e.g. removal of (meth)acrylic acid moieties in monomers.
- Although LC-MS can detect most monomers and their degradation products, complementary use of GC-(HR)MS is useful for smaller monomers remaining undetected (e.g. HEMA).