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Effect Of Light Curing On The Inorganic And Organic Composition Of A Composite Resin–Based Dental Material: A Chromatographic And Spectroscopic Analysis

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Abstract

Background In the backdrop of a global phase-down of dental amalgams, composite resins have emerged as promising alternatives, but their complex composition raises questions about safety. This study aims to elucidate extractables and determine the extent of polymerization of Bisphenol A (BPA)–derived monomers from a commercially available composite resin–based dental material.

Methods Differences in inorganic and organic composition between pre-cured and post-cured samples were analyzed. Thermogravimetric analysis assessed the thermolability of pre-cured samples. Inductively Coupled Plasma Mass Spectroscopy and ion chromatography were used for analysis of cationic and anionic composition. Gas chromatography–mass spectrometry was employed for analysis of organic resins.

Results The study revealed a 25.12% weight loss in pre-cured samples during calcination at 500°C, indicating thermal degradation of volatile components. Inorganic composition alterations were observed, with reductions in cations and anions in both pre and post-cured samples. GC–MS analysis showed the presence of UDMA, Bis–GMA, and Bis–EMA in pre-cured samples, while post-cured samples exhibited effective polymerization, containing only UDMA.

Conclusion The study concludes that pre-cured samples contain Bis–GMA and Bis–EMA, and the novel laser sintering and light curing processes under high temperature and pressure results in effective polymerization of free monomers, maintaining clinically meaningful amounts of inorganic fillers.

Keywords Composite resin, curing, polymerization, Bis–GMA, Bis–EMA, chromatography, spectroscopy, gravimetry

Background

Concerns regarding the environmental and health impact of mercury and the consequent advocacy for a global phase-down of dental amalgam by the World health organization (WHO) has augmented the use resin-based dental materials in restorative dentistry [1–3]. In line with the recommendations of the Minamata Convention (Annex A, Part II), promoting research and development of quality mercury-free materials has been a priority [4–5]. In this backdrop, composite resins have emerged as clinically promising restorative alternatives to dental amalgam [5–7].

Resin-based dental materials are essentially a siloxane-coupled mixture of a polymer matrix with an inorganic filler, and the former could comprise of methacrylate monomers with or without a Bisphenol A (BPA) backbone [8]. While monomers such as triethylene glycol dimethacrylate (TEGDMA) or urethane dimethacrylate (UDMA) lack the BPA backbone, others such as Bisphenol A glycidyl methacrylate (BisGMA) and Bisphenol A ethoxylate methacrylate (BisEMA) are derived from BPA, a known endocrine disruptor [8–10]. The weak estrogenic activity of BPA is a healthcare concern, and this estrogen-mimicry is known to adversely affect several biological processes including metabolism, and the normalcy of thyroid and androgen-related endocrinal functioning [10–11].

While BPA-mediated toxicity in animal models occurs at doses far exceeding the typical levels of human exposure, endocrinal disruptions are known to occur even at low doses [12–13]. Although the exact health impact of BPA in humans is still a topic of ongoing research, steps to limit exposure to BPA, especially in products that come into contact with oral milieu is an important clinical priority [13–15]. In these contexts, ensuring optimal polymerization of BPA-derived monomers such as BisGMA and BisEMA are important steps to avoid their potential degradation into BPA.

Available data indicates that the degree of conversion of monomers to polymers in resin-based dental materials may range between 35 to 77% [16]. Such incomplete conversions lead to a possibility of leaching unpolymerized monomers into systemic circulation. Furthermore, enzymatic and/ or bacterial action along with thermal and mechanical stressors of the oral milieu could release the degradation products for systemic uptake and associated consequences for endocrinal disruption, gene-level changes, induction of apoptosis and release of pro-inflammatory cytokines [17–18].

Along with this, the premise of “trade-secret” could lead to non-disclosure of the full composition of resin matrices, which may contain undisclosed photo initiators and stabilizing agents that can leach over time [19]. Thus, reliance on material safety data sheets (MSDS) for composition information becomes challenging in routine clinical practice. In the backdrop of these considerations, the study presented herein aimed to elucidate extractables and determine the extent of a novel laser sintering polymerization process of BPA-derived monomers from a commercially available composite resin-based dental material (Edelweiss Dentistry products; Edelweiss).

Materials and Methods

This study analyzed the differences in inorganic and organic composition between pre-cured (SE1) and post-cured (SP1) samples of a commercially available composite resin-based dental material (Edelweiss Dentistry Product; Edelweiss). The pre-cured sample in a gel form and a post-cured sample (in a powder form) were sent for analysis of inorganic and organic composition to International Center of Clean Water, Indian Institute of technology (IIT), Madras.

A thermogravimetric (TGA) analysis was performed to characterize the thermolability of pre-cured samples. An elemental analysis of cations such as Aluminum, Zinc, Barium, and Silicon in SP1 and SP2 were performed using inductively coupled plasma mass spectroscopy (ICPMS) and ion chromatography (IC) was used for detecting anions such as fluorides. Furthermore, this study also analyzed the presence of organic resins such as UDMA, BisGMA and BisEMA in pre and post-cured samples using gas chromatography/mass spectrometry (GCMS).

Characterization of Thermolability

Thermogravimetric analysis (TGA) was undertaken to elucidate the thermo-lability of pre-cured samples. Specifically, the pre-cured sample was weighed and placed within a sample pan and was loaded into the thermogravimetric analyzer. The pre-cured sample was then subjected to a gradual temperature ramp and was calcined up to 500°C in atmospheric air.

Analysis of Inorganic Composition

For the purpose of analyzing the inorganic composition, samples were digested in nitric acid media at 200°C under hydrothermal conditions for 120 minutes. These digested samples were subjected to Inductively Coupled Plasma Mass Spectroscopy (ICPMS; PerkinElmer, NexION 300X) for analyzing the cationic composition of the samples. The anionic composition of the samples was analyzed using ion chromatography (883 Basic IC plus model). Specifically, these chromatographic analyses were performed in an aqueous solution using Metrosep A Supp 5 – 250/4.0 column. Polyvinyl alcohol with quaternary ammonium groups used as carrier materials. Sodium carbonate (3.2×10^{-3} M) and sodium bicarbonate (1×10^{-3} M) mixture were used in a 1:1 ratio for anion sample detection. In addition, 100×10^{-3} M H₂SO₄ and deionized water were used as suppressor eluents for cleaning the column.

Analysis of Organic Resins

Gas chromatography–mass spectrometry (GC–MS) was employed for the quantitative analysis of organic resins, namely UDMA, Bis–GMA, and BisEMA, in both pre-cured and post-cured samples. The analytical parameters for GC involved an HP5MS column with dimensions 30m x 0.250mm, maintained at a constant temperature of 300°C. Helium pressure was set at 100 KPa, and a 1 microliter injection volume was utilized with a splitless injection mode for the initial minute. The temperature program involved an initial temperature of 120°C, ramped at 10°C/min to a final temperature of 300°C. The transfer line was heated to 300°C. This experimental setup adheres to standard protocols for GC–MS analysis, facilitating the separation and identification of volatile and semi-volatile compounds present in pre and post-cured samples. The mass spectrometry (MS) analysis was conducted with electron energy of 70 eV (E1), a temperature set at 200°C, a solvent cut time of 3 minutes, and a scan range of 40–800 m/z. Concurrently, the solvent peak was determined using gas chromatography coupled with a flame ionization detector. The signals from pre-cured and post-cured samples were integrated and corrected with the blank. The mass spectra of the organic compounds were extracted and characterized using the NIST17.L library of mass spectra.

Results

Results of the thermogravimetric analysis revealed a weight loss of 25.12% when precured samples were calcined up to 500°C in an air atmosphere. Using this data along with data from by ICPMS (for cations) and ion chromatography (for anions), the relative elemental composition of the pre and post-cured samples were deduced (Table 1). The percentage differences indicate notable changes in elemental composition between pre-curing and post-curing samples and the consistent reductions across various elements suggest a systematic shift in the material's inorganic composition during the curing process. Figures 1 and 2 present the gas chromatograms pre-cured and post-cured samples, respectively. The mass spectroscopic signals of pre-cured and post-cured samples are presented as figures 3 and 4, respectively. Table 2 summarizes the results of the combined GC–MS interpretations for the presence of unpolymerized monomers in the pre and post-cured samples. Overall, the results indicate that the process of light curing at high temperature and pressure alters the inorganic and organic composition of the samples tested herein with the absence

of Bis-GMA and Bis-EMA in post-cured samples. However, both pre-cured and post-cured samples showed the presence of UDMA.

Table 1: Relative elemental composition of the cured samples (SP2)

Sample Cohort	Aluminum*		Zinc*		Barium*		Silicon*		Fluoride**	
	mg/L	% (w/w)	mg/L	% (w/w)	mg/L	% (w/w)	mg/L	% (w/w)	mg/L	% (w/w)
Pre-curing	550.44	53.8	165.64	16.2	9.42	0.92	13.30	1.53	95.41	9.3
Post-curing	446.78	50.7	133.58	15.2	7.72	0.88	10.82	1.47	90.61	8.9
% Difference	18.83	5.76	19.36	6.17	18.05	4.35	18.65	3.92	5.03	4.30

* assessed using Inductively Coupled Plasma Mass Spectroscopy;
 ** assessed using ion chromatography.

Table 2: RT values and m/z fragmentation values of SE1 and SP1 from GCMS

RT values of pre-cured sample (in mins)	RT values of post-cured sample (in mins)	Relative RT values matched to standard resins	m/z values	Compound name
20.393	Not Observed	Bis-EMA (RT 20.447)	113	Spiro[bicyclo[2.2.1]heptane-2,2'-[1,3]dioxolane]-3-one, 1,7,7-trimethyl-
20.393	Not Observed	Bis-GMA (RT 20.447)	113	Spiro[bicyclo[2.2.1]heptane-2,2'-[1,3]dioxolane]-3-one, 1,7,7-trimethyl-
22.115	22.115	UDMA (RT 22.250)	113	2-Propenoic acid, 2-methyl-, oxybis (2,1-ethanedioxy-2,1-ethanediyl) ester
Not observed	19.6124	UDMA (RT 19.800)	57, 316	Tris(2,4-di-tert-butylphenyl) phosphate
Not observed	20.9311	UDMA (RT 20.732)	113	Spiro[bicyclo[2.2.1]heptane-2,2'-[1,3]dioxolane]-3-one, 1,7,7-trimethyl-
Not observed	21.9269	UDMA (RT 21.790)	73	Bisphenol G, bis(tertbutyldimethylsilyl) ether

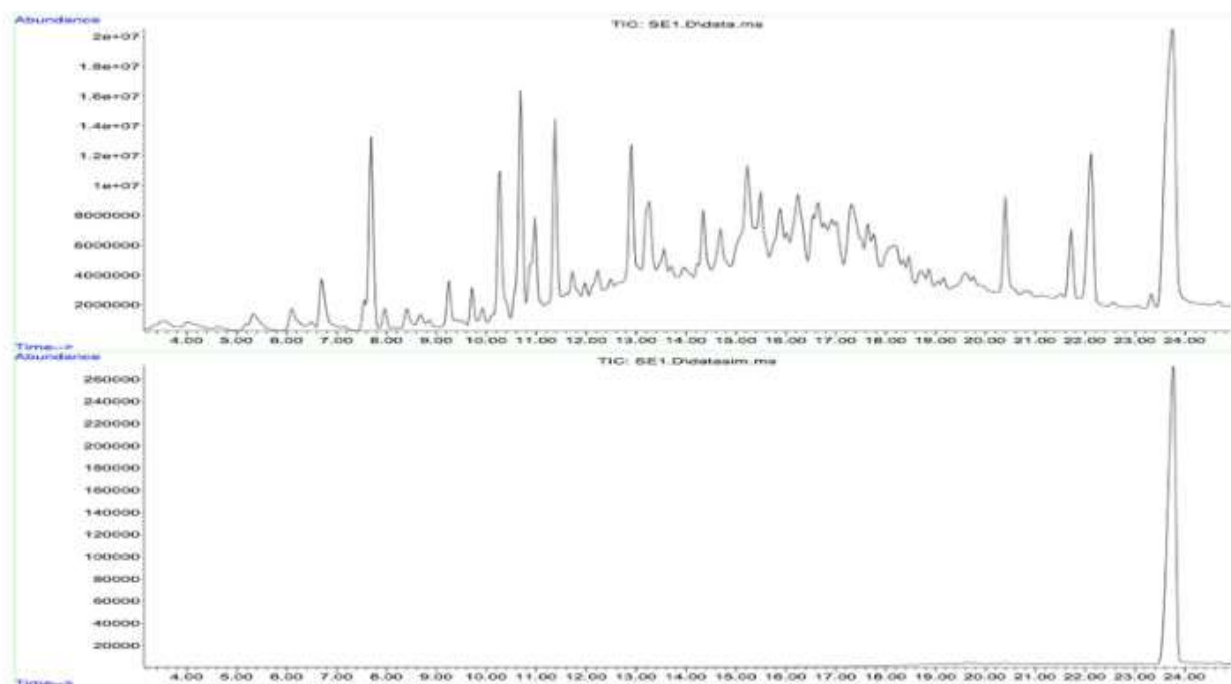


Figure 1: Gas Chromatogram of pre-cured sample.

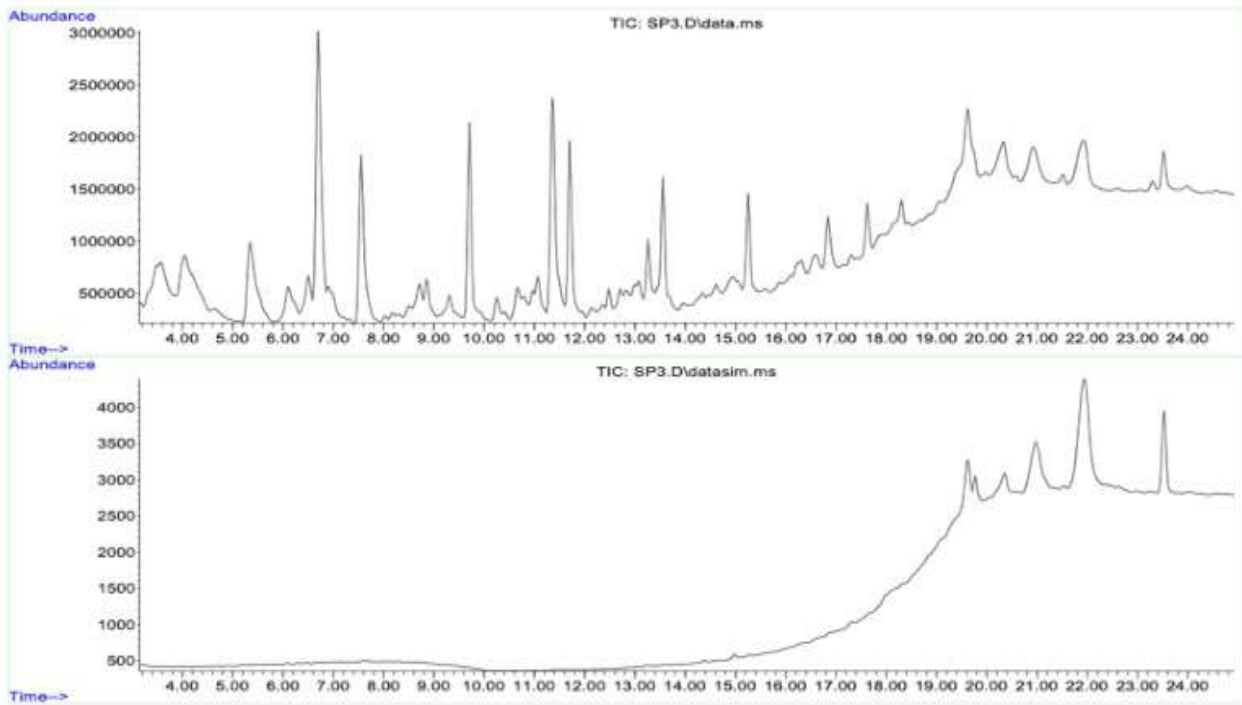


Figure 2: Gas Chromatogram of post-cured sample.

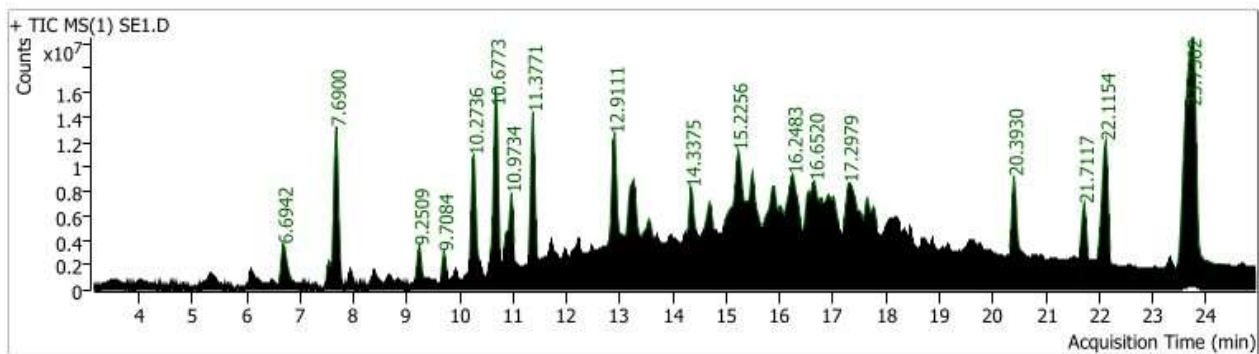


Figure 3: GCMS spectral data recorded for pre-cured sample.

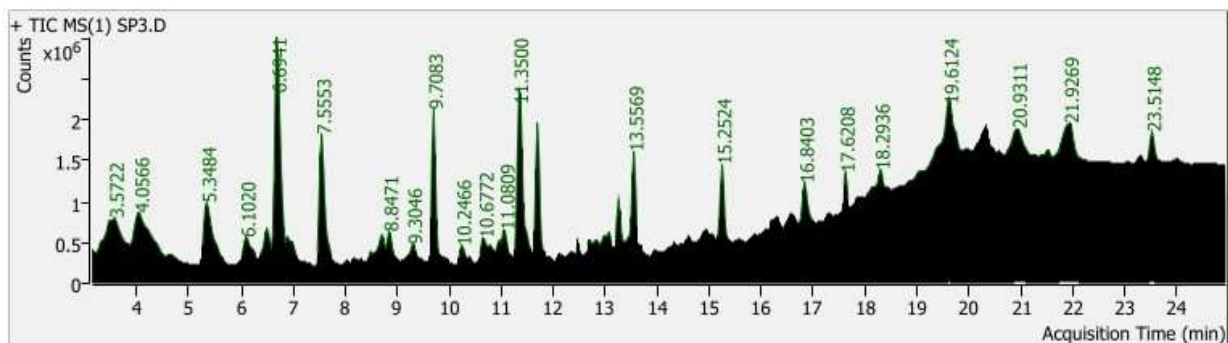


Figure 4: GCMS spectral data recorded for post-cured sample.

Discussion

In agreement with the manufacturer’s specifications, the pre-cured composite resin-based dental material analyzed in the current study features a high content of inorganic fillers (table 1) and methacrylates such as UDMA, BisGMA and BisEMA (table 2). Furthermore, results of the gravimetric

analysis indicated a 25.12% weight loss during the calcination of pre-cured samples up to 500°C. This suggests the presence of volatile components within the pre-cured sample that are susceptible to thermal degradation. The specific temperature at which this weight loss occurs, in this case, up to 500°C, is particularly informative, as it indicates the material's response to conditions that might be encountered during clinical procedures or other thermal stress situations.

In contrast to many of current resin based CAD/CAM blocks that are produced through a chemical curing between a base and a catalyst, the EDP-derived CAD/ CAM blocks are produced as a result of a unique and patented laser sintering and light curing under high temperature and pressure [20–21]. Results of the current study indicate this process of light curing alters the inorganic composition of composite resin-based dental material analyzed herein. The reductions in inorganic compositions were < 7% w/w (table 1) for both cations (aluminum, zinc, barium and silicon) and anions (fluoride).

Another claim from the manufacturer of the composite resin-based dental material analyzed herein is that CAD/CAM blocks produced as a result of light curing under high temperature and pressure may result in complete polymerization of free monomers. In general agreement with this claim, results of GC-MS analysis indicate that the pre-cured samples contain UDMA, Bis-GMA and Bis-EMA. However, post-cured samples contain only UDMA but not Bis-GMA and Bis-EMA. While the former is devoid of a BPA back bone, the latter (Bis-GMA and Bis-EMA) have a BPA backbone [8–10]. Available data indicates that the degree of conversion of monomers to polymers in resin-based dental materials may range between 35 to 77% [16]. Such incomplete conversions lead to a possibility of leaching unpolymerized monomers into systemic circulation. Results of the current study provide for a qualitative assessment of the degree of polymerization and the results of GC-MS analysis indicate the absence of Bis-GMA and Bis-EMA in the post-cured samples. While the lack of quantitative estimations of these monomers may be a limitation of the current study, another in vivo toxicology study, noted that CAD/CAM blocks prepared using the composite resin-based dental material analyzed herein was not associated with any morphological deformities in zebrafish embryos and larvae at 48 and 72 hours post-fertilization (unpublished observation; manuscript in preparation).

In the broader context of safety of dental materials, the findings of this study hold significant implications for both dental practitioners and patients. The identification of alterations in inorganic composition and the effective polymerization of free monomers during the light curing process at high temperature and pressure underscore the importance of understanding the dynamic transformations that dental materials undergo during processes of exposure to high temperatures and other manipulations in clinical dentistry.

Conclusions

Taken together, these results indicate that pre-cured samples of composite resin-based dental material analyzed herein contains monomers such as Bis-GMA and Bis-EMA and the process of light curing under high temperature and pressure may result in effective polymerization of free monomers along with maintaining clinically meaningful amounts of inorganic fillers.

List of Abbreviations

TGA: Thermogravimetric analysis; ICPMS: Inductively Coupled Plasma Mass Spectroscopy; IC: ion chromatography; GC-MS: Gas chromatography-mass spectrometry; UDMA: Urethane dimethacrylate; BisGMA: Bisphenol A glycidyl methacrylate; BisEMA: Bisphenol A ethoxylate methacrylate; BPA: Bisphenol A; MSDS: Material safety data sheets.

Ethics approval and consent to participate

Not Applicable

Consent for publication

Not Applicable

Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no competing interests

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Nil

Authors' contributions

Conceptualization: S.L. and D.G.; **Data curation:** V.S.V. ; **Formal analysis:** S.L. and J.K.; **Investigation:** S.L.; **Methodology:** D.M.; **Project administration:** D.M; **Supervision:** D.G.; **Writing–original draft:** S.L and D.M; **Writing–review & editing:** D.G and J.K.

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