TEGDMA and UDMA monomers released from composite dental material polymerized with diode and halogen lamps

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Abstract

Background. More than 35 substances released from composite fillings have been identified. Among these, basic monomers and the so-called co-monomers are most often reported. The substances released from polymer-based materials demonstrate allergenic, cytotoxic, genotoxic, mutagenic, embryotoxic, teratogenic, and estrogenic properties.

Objectives. The aim of this study was to measure the amounts of triethylene glycol dimethacrylate (TEGDMA) and urethane dimethacrylate (UDMA) monomers released from composite dental fillings to citrate-phosphate buffer with the pH of 4, 6, 8 after 24 h and 6 months from the polymerization.

Material and methods. Ten samples for each polymerization method had been made from the composite material (Filtek Supreme XT, 3M ESPE, St. Paul, USA), which underwent polymerization using the following lamps: halogen lamp (Translux CL, Heraeus Kulzer, Hanau, Germany) (sample H) and diode lamp (Elipar Freelight 2, 3M ESPE), with soft start function (group DS) and without that function (group DWS).

Results. It has been demonstrated that the type of light-curing units has a significant impact on the amount of TEGDMA and UDMA released. The amount of UDMA and TEGDMA monomers released from composite fillings differed significantly depending on the source of polymerization applied, as well as the pH of the solution and sample storage time.

Conclusions. Elution of the monomers from composite material polymerized using halogen lamp was significantly greater as compared to curing with diode lamps.

Key words: light curing units, triethylene glycol dimethacrylate, urethane dimethacrylate, fluorescence spectrometry

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Introduction

In the oral cavity, chemical compounds from composite dental fillings can be released. Various factors contribute to this process, including a low degree of monomer conversion (DC%) of the polymer matrix (the reported DC% varies between 35 and 77%),^{1,2} washing out with such fluids as saliva, gingival crevicular fluid, drinks consumed, an adequate light activation technique, the processes of enzymatic degradation of the material, the quality of light-curing unit used, the regime of restorative procedure, or wearing dental prostheses. The substances released from polymer-based materials demonstrate allergenic, cytotoxic, genotoxic, mutagenic, embryotoxic, teratogenic, and estrogenic properties.^{3–11}

More than 35 substances released from composite fillings have been identified. Among these, basic monomers and the so-called co-monomers are most often reported. Substantial cytotoxic potential is observed in the basic monomers, such as bisphenol A-glycidyl methacrylate (Bis-GMA) and urethane dimethacrylate (UDMA), which inhibit cell growth in vitro, at the concentration of 0.1 mM.³ Among the co-monomers, diethyleneglycol dimethacrylate (DEGDMA) and triethyleneglycol dimethacrylate (TEGDMA) exhibit the worst biocompatibility. It has been demonstrated that monomers also have sensitizing properties. Among the most allergenic ones, there are 2-hydroxyethyl methacrylate (HEMA), ethyleneglycol dimethacrylate (EGDMA) and TEGDMA. Authors describe allergic reactions on the oral mucosal membrane of patients; however, dentists are more prone to contact allergies.³ The frequency of occurrence of allergy to methacrylates among dentists and their personnel varies between 1.3 and 14%.¹² Often, apart from skin lesions, asthma and sinusitis occur. Latex gloves do not protect against monomers, which penetrate through them within 1 min.¹² Some substances released from composite fillings may bind with estrogen receptors, mimicking natural hormones. They are called xeno-estrogens. Among them, there are: bisphenol A (BPA), bisphenol A-glycidyl methacrylate (Bis-GMA), bisphenol A-dimethacrylate (Bis-DMA), and TEGDMA.¹³ Monomers have a damaging effect on cell genetic material; they disturb the regulation of cell growth cycle as well as the oxidation-reduction balance that may activate reactions leading to apoptosis.^{3,7,14}

The type of light source used for photopolymerization has a considerable influence on the amount of monomers released from composite resin materials. Light-curing units used in dentistry include conventional quartz-tungsten-halogen (QTH, still in use), light-emitting diode (LED), plasma arc (PAC) lamps, and argon laser. The following parameters differentiate them: the light source and optic elements, the amount of thermal energy emitted, the efficiency of material polymerization and the intensity of curing, the performance efficiency, the existence of voltage stabilization system.¹⁵

The main feature which distinguishes LED lamps from halogen light-curing units is the source of light. A halogen lamp produces light by heating a metal filament wire to a high temperature until it glows. The spectrum of emitted waves is in the broad range of 360–560 nm, while the luminous intensity peak is in the range of 400–500 nm. Producers install special systems of filters to eliminate the useless radiation of ultraviolet or infrared ranges. Also, the elements of optical system and the bulb itself are subject of gradual degradation. As a result of those processes, the amount of emitted light is insufficient. It is assumed that halogen lamps function with 100% efficiency for some 50 h, which directly influences the increased presence of residual monomers, that is, their low level of conversion.¹⁶

In diode lamps, the sources of light emission are semiconductor p-n junctions or diodes (precisely light-emitting diodes, LEDs). The semiconductor used there is gallium nitride (GaN). The conduction of that compound is associated with the number of electrons and holes in the valence band of its atoms. The selection of specific semiconductor depends upon the selected range of emitted waves. The average spectra of diode lamps vary from 440 to 495 nm. The efficiency of LED lamps is approx. 10 times higher than that of halogen lamps, as the length of the emitted wave is better adjusted to the photoinitiators used in light-cured materials.¹⁷ In the majority of composite materials, camphorquinone is the photoinitiator. It is activated by light of a wavelength of 468 nm. Better selectivity of diode lamps contributes to the reduction of the light intensity by 40–70% in the course of polymerization of dental materials in comparison with halogen lamps.¹⁷ Due to the narrow radiation spectrum, producers eliminated the need of applying filter systems in those lamps. As a result, they can function with 100% efficiency for some 10,000 h.¹⁷ However, not all dental materials may be cured with diode lamps. The above applies to materials in which the initiators or co-initiators of polymerization react to waves whose lengths are outside the emission range of LEDs.

The aim of the study was to assess the amount of TEGDMA and UDMA monomers released from composite dental filling materials to the solution, depending upon the light-curing units used for polymerization – halogen or diode ones, with and without the soft start function.

Material and methods

From Filtek Supreme XT composite material (3M ESPE, St. Paul, USA; dentinal shades A3D, A4D, B3D), 4 groups of 10 samples were prepared using standardized molds (the diameter of 15 ± 1 mm and the thickness of 0.5 ± 0.1 mm). The samples were polymerized using halogen (Translux LC, Heraeus Kulzer, Hanau, Germany – group H) and diode (Elipar FreeLight 2, 3M ESPE) light-curing units. A diode lamp was used with a soft start function (group DS) and the continuous light mode (group DWS). Soft start

polymerization means that irradiation is initiated with light of lower intensity and continued with higher irradiation compared to that in the continuous method. In the Elipar FreeLight 2 lamp, the intensity increases exponentially. The curing time was 40 s for all lamps. The control group consisted of 10 non-polymerized samples (group N). All samples were stored in Eppendorf tubes with 1 mL of citrate-phosphate buffer (No. P 4809, Perkin Elmer Inc., Waltham, USA) with different pH levels (4, 6 and 8) for 24 h and 6 months, at 36.6°C.^{18,19} After 24 h and 6 months, the polymerized and non-polymerized materials were removed from the buffer. The samples examined after 24 h and 6 months (10 in each group) were separate collections of research material. The quantitative analysis of the residual monomer leached into solutions was carried out using a fluorescent spectrometer LS45 (Perkin Elmer Inc.), with a 0.6 mL quartz cuvette. The absorbance measurements of the samples were taken in reference to a buffer with corresponding pH. The optimum values of excitation (ex) and emission (em) for model substance (TEGDMA No. 90412 and UDMA No. 436909, Perkin Elmer Inc.) were determined using a spectrophotometer (Shimadzu UV-160A, Kyoto, Japan). The values recorded were as follows: for TEGDMA $\lambda_{\text{ex}} = 223$ nm and $\lambda_{\text{em}} = 290$ nm, and for UDMA $\lambda_{\text{ex}} = 219$ nm and $\lambda_{\text{em}} = 285$ nm.

Statistical analysis of the data was performed using STATISTICA software v. 8.0 (StatSoft Inc., Tulsa, USA). Values in all groups were checked for normal distribution, applying the normality of the Shapiro-Wilk and Kolmogorov tests. If the distribution remained normal in both dependency tests, the data was analyzed using tests of 2 or multiple averages. In other cases, the Mann-Whitney U and the Kruskal-Wallis tests were used. If more than 1 sample has demonstrated differences in the tests (multiple averages or Kruskal-Wallis tests), post-hoc tests were performed. Statistical significance was set at $p \leq 0.05$.

Results

The mean concentrations of UDMA and TEGDMA monomers released into the citrate-phosphate buffer of different pH (4, 6, 8) after 24 h and 6 months, and a kind of distribution are presented in Tables 1 and 2. Between 24 h and 6 months, the mean concentrations of UDMA and TEGDMA significantly increased ($p < 0.001$) within all the groups, irrespective of the pH of the buffer (Table 3).

After 24 h, non-polymerized samples (N) released significantly more UDMA than samples polymerized using a diode lamp (DS and DWS) at pH 4 and samples cured using a diode lamp without the soft start function (DWS) in the solutions having pH 6 and 8. The release of UDMA occurred at a significant lower rate in samples cured with a diode lamp (DS and DWS) when compared with samples cured using a halogen lamp (H) in the solutions of pH 4 and 6. In the buffer pH 8 with the same residence time, there was significantly less ($p < 0.05$) UDMA when samples were cured with a diode lamp without the soft start function (DWS) compared with the samples polymerized using a halogen lamp (H).

After 6 months, no significant differences were found in the release of UDMA to the buffer pH 4 in all groups. In the buffer pH 6, the release of that monomer occurred to be significantly higher in uncured samples (N). However, when the pH of the buffer was 8, a reverse situation was noted – a significantly lower concentration of UDMA in group N as compared to other groups. In the buffer pH 8, a significantly higher release of that monomer was observed in the DWS group than in the N, DS and H groups ($p < 0.001$). In the H group, the amount of UDMA in the buffer was significantly lower when compared with the DS group ($p < 0.05$). The results are shown in Table 4.

After 24 h, in all groups, the mean concentration of UDMA in the buffer pH 4 was significantly higher than

Table 1. The amount of UDMA ($\mu\text{g/g}$) released from composite material into citrate-phosphate buffer at different pH level after 24 h and 6 months

Type of sample	Number of measurements	24 h (pH 4 / pH 6 / pH 8)				6 months (pH 4 / pH 6 / pH 8)			
		mean ($\mu\text{g/g}$)	standard deviation	standard normal distribution		mean ($\mu\text{g/g}$)	standard deviation	standard normal distribution	
				Shapiro-Wilk test	Kolmogorov test			Shapiro-Wilk test	Kolmogorov test
N	10/	94.78/	24.81/	+/	+/	163.37/	32.85/	+/	+/
	10/	12.09/	4.07/	+/	+/	161.57/	75.31/	+/	+/
	10	8.65	1.01	–	+	17.33	3.90	+	+
DS	10/	60.03/	9.25/	–/	+/	364.96/	247.65/	–/	+/
	10/	8.94/	1.74/	–/	+/	118.52/	38.16/	+/	+/
	10	7.64	1.15	+	+	100.33	15.30	+	+
DBS	10/	62.73/	8.91/	+/	+/	349.66/	260.23/	–/	–/
	10/	7.83/	1.14/	+/	+/	95.12/	38.07/	+/	+/
	10	7.28	1.26	+	+	142.92	38.49	+	+
H	10/	86.78/	25.51/	–/	+/	392.37/	333.16/	–/	+/
	10/	12.11/	2.32/	+/	+/	115.00/	19.52/	+/	+/
	10	8.99	1.26	+	+	81.97	8.28	+	+

N – group of samples non-polymerized; DS – group of samples polymerized using diode light-curing unit with soft start function; DBS – group of samples polymerized using diode light-curing unit without soft start function; H – group of samples polymerized using halogen light-curing unit.

Table 2. The amount of TEGDMA ($\mu\text{g/g}$) released from composite material into citrate-phosphate buffer at different pH level after 24 h and 6 months

Type of sample	Number of measurements	24 h (pH 4 / pH 6 / pH 8)				6 months (pH 4 / pH 6 / pH 8)			
		mean [$\mu\text{g/g}$]	standard deviation	standard normal distribution		mean [$\mu\text{g/g}$]	standard deviation	standard normal distribution	
				Shapiro-Wilk test	Kolmogorov test			Shapiro-Wilk test	Kolmogorov test
N	10/	93.25/	21.94/	+/	+/	164.78/	25.37/	+/	+/
	10/	81.80/	25.63/	+/	+/	1002.26/	450.30/	+/	+/
	10	73.79	11.34	–	+	151.77	39.27	+	+
DS	10/	60.62/	9.55/	+/	+/	336.48/	244.28/	–/	+/
	10/	57.54/	8.48/	+/	+/	724.74/	205.49/	–/	+/
	10	62.69	6.17	+	+	868.31	134.20	+	+
DBS	10/	62.16/	7.63/	+/	+/	315.65/	265.82/	–/	–/
	10/	49.65/	7.33/	+/	+/	632.66/	217.71/	+/	+/
	10	60.17	9.30	+	+	1250.57	337.96	+	+
H	10/	79.84/	19.03/	+/	+/	404.61/	393.20/	–/	+/
	10/	73.32/	12.89/	+/	+/	704.31/	135.78/	+/	+/
	10	74.82	7.86	+	+	712.55	74.55	+	+

N – group of samples non-polymerized; DS – group of samples polymerized using diode light-curing unit with soft start function; DBS – group of samples polymerized using diode light-curing unit without soft start function; H – group of samples polymerized using halogen light-curing unit.

Table 3. UDMA or TEGDMA monomers released from composite material, depending on the sample residence time in citrate-phosphate buffer – pH 4, pH 6, pH 8

Type of sample pH 4 / pH 6 / pH 8	UDMA 24 h–6 months t DA	UDMA 24 h–6 months t UM-W	TEGDMA 24 h–6 months t DA	TEGDMA 24 h–6 months t UM-W
N	a/a/–	–/–/a	a/a/–	–/–/a
DS	–/–/a	a/a/–	–/–/a	a/a/–
DBS	–/a/a	a/–/–	–/a/a	a/–/–
H	–/a/a	a/–/–	–/a/a	a/–/–

N – group of samples non-polymerized; DS – group of samples polymerized using diode light-curing unit with soft start function; DBS – group of samples polymerized using diode light-curing unit without soft start function; H – group of samples polymerized using halogen light-curing unit; a – $p < 0.001$; t DA – double average test; t UM-W – U Mann-Whitney test.

Table 4. UDMA monomer released from composite material into citrate-phosphate buffer (pH 4, pH 6, pH 8), depending upon polymerization light-curing unit used, after 24 h and 6 months

UDMA pH 4 / pH 6 / pH 8	24 h t K-W / t K-W / t K-W				6 months t K-W / t MA / t MA			
Type of sample ▶	N	DS	DBS	H	N	DS	DBS	H
R or X ▶	30.00/ 27.10/ 26.10	10.80/ 15.80/ 15.90	14.10/ 10.30/ 12.50	27.10/ 28.80/ 27.50	13.10/ 161.57/ 17.33	23.30/ 118.52/ 100.33	25.10/ 95.12/ 142.92	20.50/ 115.00/ 81.97
Type of sample ▶ ▼	N	DS	DBS	H	N	DS	DBS	H
N		$p < 0.001$ / $p = 0.0920$ / $p = 0.1532$	$p < 0.01$ / $p < 0.01$ / $p < 0.05$	$p = 1.0000$ / –/– –		–/ $p < 0.05$ / –	–/ $p < 0.01$ / –	–/–/–
DS	–/– –		–/– –/ $p = 1.0000$	–/– –/ –	$p = 0.1532$ –/ $p < 0.001$		–/ $p = 0.1381$ / –	$p = 1.0000$ / $p < 0.05$ / $p < 0.05$
DBS	–/– –	$p = 1.0000$ / –/ –		–/– –/ –	$p = 0.0652$ –/ $p < 0.001$	$p = 1.0000$ –/ $p < 0.001$		$p = 1.0000$ / $p = 0.4344$ / $p < 0.001$
H	–/ $p = 1.0000$ / $p = 1.0000$	$p < 0.01$ / $p < 0.05$ / $p = 0.0795$	$p < 0.05$ / $p < 0.01$ / $p < 0.05$		$p = 0.4708$ –/ $p < 0.001$	–/ –/ –	–/ $p = 0.1769$ / –	

N – group of samples non-polymerized; DS – group of samples polymerized using diode light-curing unit with soft start function; DBS – group of samples polymerized using diode light-curing unit without soft start function; H – group of samples polymerized using halogen light-curing unit; R – average t MA; X – average t K-W; t MA – multiple average test; t K-W – Kruskal-Wallis test.

Table 5. UDMA monomer released into citrate-phosphate buffer, depending on pH, after 24 h and 6 months

UDMA Sample N / DS / DBS / H		24 h t K-W / t K-W / t MA / t K-W			6 months t MA / t K-W / t K-W / t K-W		
pH value ▶		4	6	8	4	6	8
R or X ▶		25.50/ 25.50/ 62.74/ 25.50	13.00/ 13.20/ 7.83/ 14.50	8.00/ 7.80/ 7.28/ 6.50	163.37/ 25.30/ 24.30/ 25.10	161.57/ 12.30/ 7.90/ 15.10	17.33/ 8.90/ 14.30/ 6.30
pH value ▶ ▼		4	6	8	4	6	8
4			p < 0.01/ p < 0.01/ p < 0.001/ p < 0.01	p < 0.001/ p < 0.001/ p < 0.001/ p < 0.001		p = 0.4665/ p < 0.01/ p < 0.001/ p < 0.05	p < 0.001/ p < 0.001/ p < 0.05/ p < 0.001
6				p = 0.3061/ p = 0.2553/ p = 0.4080/ p = 0.0632			p < 0.001/ p = 0.2553/ –/ p < 0.05
8						–/ –/ p = 0.1561/ –	

N – group of samples non-polymerized; DS – group of samples polymerized using diode light-curing unit with soft start function; DBS – group of samples polymerized using diode light-curing unit without soft start function; H – group of samples polymerized using halogen light-curing unit; R – average t MA; X – average t K-W; t MA – multiple average test; t K-W – Kruskal-Wallis test.

in buffers pH 6 and 8. On the other hand, for non-polymerized samples after 6 months, a significantly lower UDMA was noted when the pH of the buffer was 8 as compared to the solutions with lower pH values ($p < 0.01$) (Table 5).

The release of TEGDMA after 24 h was significantly higher in the non-polymerized group (N) in the buffer pH 4. At that time, no significant differences occurred in the release of this monomer from the samples cured using a diode lamp (DS and DWS) for all pH values. Regardless of the pH of the solution, the release of TEGDMA after 24 h was significantly lower when samples were cured with a diode lamp (DS and DWS) in relation to the samples cured with a halogen lamp (H). After 6 months, no significant differences were disclosed in the amount of TEGDMA released to the buffers pH 4 and 6 for all examined samples. However, when the pH of the solution was 8, a significantly lower concentration of this monomer was noted in the case of non-polymerized samples as compared with the polymerized ones, whatever the lamp type was ($p < 0.001$). Samples polymerized using a diode lamp without the soft start function (DWS) released significantly ($p < 0.001$) more TEGDMA to the buffer in comparison with the remaining samples. The results are shown in Table 6.

After 24 h, the release of TEGDMA from non-polymerized samples (N) to the buffer with pH 8 was significantly ($p < 0.05$) diminished in comparison with the solution of pH 4.

After 6 months, the mean concentration of TEGDMA released from samples N was significantly lower in solutions pH 4 and 8 in comparison with those of pH 6 ($p < 0.001$).

The highest amount of TEGDMA was released in the DBS group in solutions of pH 8. The results are presented in Table 7.

Discussion

The quantitative and qualitative assessment of residual monomers released from composite fillings to external environment has been a subject of investigations by many authors.^{1,18–25} The willingness to examine thoroughly what happens with the composite filling used, to what degree it is degraded and what influence the chemical compounds released from fillings have upon the human organism compelled the search for ever more accurate analytic methods. For the analysis of released monomers, the authors applied gas and liquid chromatography as well as fluorescence spectrophotometry. An intermediate method for examining the condition of fillings after curing, attesting to the degree of conversion of materials exposed to curing, is Raman or Fourier spectrometry.^{26–30} These methods consist of a comparative analysis of double carbon bonds occurring in polymerized and non-polymerized material.

Polydorou et al. studied the release of Bis-GMA, UDMA and TEGDMA from Filtek Supreme XT restorative composite.¹ The cured and uncured samples were stored in 75% ethanol solution for 24 h, 7 days, 28 days, and 12 months. Elipar Highlight (3M ESPE) halogen lamp was used in the study, and the following polymerization time was applied: 0, 20, 40, and 80 s. Liquid chromatography-mass spectrometry was used for quantitative and qualitative analysis.

Table 6. TEGDMA monomer released from composite material into citrate-phosphate buffer (pH 4, pH 6, pH 8), depending upon polymerization light-curing unit used, after 24 h and after 6 months

TEGDMA pH 4 / pH / pH 8	24 h t MA / t MA / t K-W				6 months t K-W / t K-W / t MA			
Type of sample ▶	N	DS	DBS	H	N	DS	DBS	H
R or X ▶	93.25/ 81.81/ 26.30	60.62/ 57.54/ 15.40	62.16/ 49.65/ 11.60	79.84/ 73.32/ 28.70	19.20/ 27.20/ 151.77	20.20/ 20.10/ 868.31	20.80/ 16.50/ 1250.57	21.80/ 19.20/ 712.55
Type of sample ▼	N	DS	DBS	H	N	DS	DBS	H
N		p < 0.001/ p < 0.001/ p = 0.1112	p < 0.001/ p < 0.001/ p < 0.05	p < 0.05/ p = 0.1129/ –		–/ p = 0.5234/ –	–/ p = 0.1221/ –	–/ p = 0.2555/ –
DS	–/ –/ –		–/ p = 0.1297/ p = 1.000	–/ –/ –	p = 1.0000/ –/ p < 0.001		–/ p = 1.000/ –	–/ p = 1.000/ p < 0.05
DBS	–/ –/ –	p = 0.4146/ –/ –		–/ –/ –	p = 1.0000/ –/ p < 0.001	p = 1.0000/ –/ p < 0.001		–/ –/ p < 0.001
H	–/ –/ p = 1.000	p < 0.01/ p < 0.05/ p < 0.05	p < 0.01/ p < 0.001/ p < 0.01	–/ –/ –	p = 1.0000/ –/ p < 0.001	p = 1.0000/ –/ –	p = 1.0000/ –/ –	

N – group of non-polymerized sample; DS – group of sample polymerized using diode light-curing unit with soft start function; DBS – group of sample polymerized using diode light-curing unit without soft start function; H – group of sample polymerized using halogen light-curing unit; R – average t MA; X – average t K-W; t MA – multiple average test; t K-W – Kruskal-Wallis test.

Table 7. TEGDMA monomer released into citrate-phosphate buffer, depending on pH, after 24 h and 6 months

TEGDMA Sample N / DS / DBS / H	24 h t K-W / t MA / t MA / t MA			6 months t MA / t K-W / t K-W / t K-W		
pH value ▶	4	6	8	4	6	8
R or X ▶	19.50/ 60.62/ 62.16/ 79.34	16.00/ 57.54/ 49.65/ 73.32	11.00/ 62.70/ 60.17/ 74.82	164.78/ 6.90/ 7.50/ 9.20	1002.26/ 17.30/ 13.50/ 18.10	151.77/ 22.30/ 25.50/ 19.20
pH value ▼	4	6	8	4	6	8
4		p = 0.5610/ p = 0.2037/ p < 0.01/ p = 0.1538	p < 0.05/ –/ p = 0.2949/ p = 0.2155			p = 0.4561/ –/ –/ –
6			p = 0.3061/ –/ –/ –	p < 0.001/ p < 0.05/ p = 0.1913/ p < 0.05		p < 0.001/ –/ –/ –
8	–/ p = 0.2884/ –/ –	–/ p = 0.855/ p < 0.01/ p = 0.4060		–/ p < 0.001/ p < 0.001/ p < 0.05	–/ p = 0.3061/ p < 0.01/ p = 1.0000	

N – group of non-polymerized sample; DS – group of sample polymerized using diode light-curing unit with soft start function; DBS – group of sample polymerized using diode light-curing unit without soft start function; H – group of sample polymerized using halogen light-curing unit; R – average t MA; X – average t K-W; t MA – multiple average test; t K-W – Kruskal-Wallis test.

The release of monomers got significantly reduced with the extension of curing time.¹ The results of this study are in agreement with our report on monomers released from polymerized samples (40 s) and non-polymerized ones (0 s) made of the Filtek Supreme XT material, after 24 h of residence in citrate-phosphate buffer, whatever the

pH level was, and after 6 months, when the pH of the buffer amounted to 6. The release of monomers, in accordance with above-mentioned Polydorou et al., also significantly differed in time. The amounts of free TEGDMA dropped, whereas those of the Bis-GMA monomer remained at a similar level.¹ This part of their results was different

from our study. This may be ascribed to a shorter observation time (6 months) as well as sample storage conditions (citrate-phosphate buffer with different pH levels: 4, 6, 8). The results of the release of the 3 monomers were presented by the authors quoted in the form of logarithmic function, which is why they prove difficult to refer to the results of this study.

Örtengren et al. analyzed the influence of the solution pH value and of time upon the release of monomers from the Z-100 composite material.¹⁸ The samples were stored in citrate-phosphate buffer with different pH levels (4, 6, 8) for 24 h and for 6 months. For the sake of comparison, 2 methods were applied for the sample analysis: gas chromatography and fluorescence spectrophotometry. The highest levels of organic substances release were noted in the case of methacrylic acid, TEGDMA and camphoroquinone. The authors of this study applied identical conditions for sample storage (citrate-phosphate buffer, with the pH values of 4, 6, 8, sample storage time: 24 h and 6 months). Örtengren et al., in the case of 24 h storage, obtained the following results concerning TEGDMA eluted to the medium: at the pH of 4 – 100 µg/g, at the pH of 8 – 87 µg/g of sample (by fluorescence spectrophotometry).¹⁸ After 6 months, the amount of TEGDMA increased significantly at the pH of 4 – 230 µg/g and at the pH of 6 – 320 µg/g of sample. In the analysis by means of gas chromatography, which, in accordance with the authors quoted, proved to be more accurate after 24 h and after 6 months of storage, a significantly lower level of TEGDMA has been noted at the pH of 8 in comparison with other pH values (4 and 6). Applying the other analytical method, the lowest values of monomer release were obtained at the pH of 6 after 24 h and at the pH of 4 after 6 months of storage.¹⁸ The authors of this study applied the fluorescence spectrophotometry method and obtained similar results after 24 h of storage (the best convergence for samples cured using a halogen lamp), but in the case where the pH of the buffer amounted to 8, the average concentration of TEGDMA was higher than at the pH of 4 and 6. After 6 months of storage, the amount of released TEGDMA was higher than in the results obtained by Örtengren et al., using fluorescence spectrophotometry. One should also add that it increased with increasing pH of the buffer.

Örtengren et al. analyzed water adsorption and solubility of the samples, made of 6 composite materials, in aqueous solution. The analysis of monomers was carried out with liquid chromatography. The sample storage time amounted to 4, 24 h as well as 7, 60 and 180 days. They showed that composite materials containing hydrophilic monomers demonstrate higher sorption of water. The composite mass increased via chemical reaction between the filling and water. The monomer released in biggest quantities was TEGDMA, with the highest concentration after 7 days.²³

Using the gas chromatography method, Moharamzadeh et al. analyzed the influence of various extraction solutions upon the release of TEGDMA, UDMA and Bis-GMA.²⁰ The extraction solutions used were: distilled water,

isotonic salt solution, artificial saliva as well as Dulbecco medium, without serum and with 10% fetal calf serum. The results were indicative of a significant influence of the solution in which cured composite samples were stored on the release of monomers. The highest concentration of TEGDMA monomer was noted in the Dulbecco medium with serum. In other solutions, the concentration of this monomer was similar. The release of UDMA and Bis-GMA to the studied solutions was not observed. On the basis of results, the authors found that TEGDMA is leached in high quantities to aqueous solutions.

Sideridou and Achilias analyzed, by means of liquid chromatography, the influence of sample curing time and their storage time upon the release of Bis-GMA, ethoxylated bisphenol A glycol dimethacrylate (Bis-EMA), UDMA, and TEGDMA.²⁴ The samples were stored in 75% ethanol, at 37°C, for 3, 6, 24 h, and 3, 6 or 30 days. The curing time amounted to 60, 80 and 100 s. The authors found an increase of Bis-GMA monomer up to 3 days. After that time, the release was maintained at a stable level. The amount of Bis-EMA monomer released was much higher than that of Bis-GMA monomer throughout the study period (up to 30 days). On the other hand, the release of TEGDMA and UDMA monomers was at a similar level, and much lower in comparison with the above-mentioned monomers. The authors found that the amount of eluted monomers depends upon the chemical structure of the examined compound and sample storage time.²⁴

Carvalho et al. investigated the effect of light sources (LED and QTH curing units) and curing mode techniques on sorption, solubility and biaxial flexural strength of a composite resin.³¹ In their opinion, tested curing units produced no influence on sorption, solubility or biaxial flexural strength of tested composite resins. They observed that ethanol storage media caused more damage on a composite resin than water storage media.³¹

Summarizing the above results, it should be stressed that the proper installation and polymerization of the composite material with a diode curing unit reduces the monomer concentration and its negative influence on the dental pulp, surrounding tissues as well as entire organism.

Conclusions

The amount of UDMA and TEGDMA monomers released from composite fillings differed significantly, depending on the source of polymerization applied as well as the pH of the solution and sample storage time. The degree of material polymerization depends on the lamp used; significantly more monomers are released from samples polymerized with halogen lamps in comparison with those cured using a diode lamp.

The use of soft start function in a diode lamp did not influence significantly the amount of monomers released from composite samples.

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