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Optimization of Photopolymerization Process of Dental Composites

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Abstract: The aim of this paper is to perform optimization of photopolymerization process of dental composites in order to obtain maximum hardness. Samples (5 mm diameter; 2, 3 and 4 mm thickness) were made of Universal Composite (UC), Bulk fill Composite (BC) and Flowable Composite (FC). Light curing of specimens was performed with 600, 1000 and 1500 mW/cm^2 light intensity and an irradiation time of 20, 40 and 60 s. Vickers microhardness on the top and bottom surfaces of samples was measured. Optimization was carried out via regression analysis using QStatLab software. Photopolymerization process parameters were calculated using a specially designed MatLab software-based algorithm. For all composites, regression models for hardness on top and bottom surfaces of composite layer were established. Layer thickness as well as hardness on top and bottom surfaces of each composite was calculated for 21 curing modes varying with light intensity and irradiation time. It was established that photopolymerization guidelines only of FC manufacturer guarantee the required hardness, while recommended regimes for UC and BC did not satisfy this requirement. Tables, containing recommended light curing regimes, were developed for three composite types, guaranteeing high hardness of composite restoration. They were designed to facilitate work of dentists in dental offices.

Keywords: light-cured composites; photopolymerization process; microhardness; optimization; regression analysis

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1. Introduction

The introduction of light-cured resin-based composites (RBCs) is a revolutionary step in restorative dentistry because it allows clinicians to determine the beginning of the polymerization process. The reasons for their wide application in everyday practice are the increased aesthetic requirements of patients on the one hand, and on the other—the disadvantages of the amalgam such as low aesthetics, galvanic current flow and corrosion, staining of hard dental tissues, soft tissue tattoos, mercury vapor release and others [1].

Dental composites are essentially a mixture of an organic resin matrix, inorganic filler particles, a coupling agent and a photoinitiator system [2,3]. Depending on the size of the filler particles, RBCs are defined as: macrofilled, microfilled, nanofilled and hybrid [4–7]. However, several manufacturers are now incorporating nano-sized particles into their formulations, resulting in the creation of yet another category, the "nanohybrid" composites. Nanofilled composites have silicon-zirconium particles with a size between 0.005 and 0.01 µm. The small particle size allows good filling of the organic matrix—about 80%. The nanofilled composites present higher mechanical and physical properties to those of microhybrid composites, superior polishability with a gloss comparable to that of the enamel, better wear resistance and transparency [5–8]. Due to their desirable aesthetics, strength and durability, they are increasingly preferred by clinicians as a universal restorative material for both anterior and posterior fillings.

Depending on the viscosity, RBCs are defined as compactable with high viscosity, and flowable with low viscosity. In flowable composites, the percentage of inorganic

filler is lower and rheological modifiers (substances intended mainly to improve handling properties) have been removed from their composition. Their main advantages are high wettability of the tooth surface, providing penetration into any unevenness; ability to form layers with a minimum thickness, which significantly reduces the inclusion or retention of air; high flexibility, so they are less likely to be displaced in areas with high stress concentration; radiopacity and availability in different colors [9]. The disadvantages include a high level of polymerization shrinkage due to the smaller filler amount and lower mechanical properties. Indications for the use of flowable composites are cervical defects, very small occlusal defects as liners in class I and II cavities [10]. In the last decade, universal highly filled flowable composites have been developed, which allow for the restoration of a wide range of of anterior and posterior defects.

One of the main setbacks of RBCs as a direct restorative material is the application technique sensitivity, meaning that the success of composite restorations largely depends on the operator's skills [11]. The implementation of the adhesive protocol involves many steps and there are enough possibilities for error. In addition, the incremental technique is time consuming and contributes to even more inaccuracies. To simplify the procedure, the bulk fill composites are created.

Bulk fill composites are available in flowable and regular (nonflowable) consistency with the possibility of placing layers up to 5 mm (compared to 2 mm for conventional composites), while ensuring an adequate depth of cure. This goal is achieved in various ways, including optimization of the photoinitiator system (new photoinitiators or higher concentration of conventional ones), modification of the fillers (larger size or higher translucency of the particles) or inclusion of various chemicals in the composition [12,13]. The use of bulk fill composites for posterior restorations reduces cusp deflection [14] and polymerization stress [15] while increasing the fracture resistance of the hard tissues and the restoration itself [16]. However, flowable bulk fill composites have lower mechanical properties than non-flowable bulk fill and conventional ones, so they should not be used as a final layer, which is directly exposed to the masticatory forces [17].

The hardness of the materials determines their wear resistance, or their ability to abrade or be abraded from the opposite tooth structures [18,19]. The hardness of RBCs is influenced by several factors, the most important of which are the composition of the organic matrix, the type and amount of inorganic fillers and the degree of monomer-polymer conversion. A positive relationship has been found between the increase in hardness and the increase in the degree of conversion. The microhardness tests are most commonly used for indirect evaluation of the depth of cure and the degree of conversion of dental composites [20–22], because a small change in the degree of conversion can lead to a large hardness change [23].

The amount of light energy reaching the surface and the bottom of the composite restoration depends on many variables, such as the light intensity of the light curing unit (LCU), curing time, distance and angulation of the LCU's tip, composition, thickness, color and opacity of the composite. Therefore, the measured hardness at the top surface of the restoration cannot be accepted as an indicator of the hardness at its bottom. Less than 20% difference between the maximum hardness at the top of the composite and that found at the bottom is suggested as a guideline for adequate curing of the resin composite [24–26]. In addition, a bottom-to-top KHN ratio of 80% has been reported to correspond to a bottom-to-top degree of conversion ratio of 90% [24].

Many researchers have investigated the efficiency of different curing modes for successful polymerization of the resin-based composites expressed mainly by their hardness. Zhu S. and Platt J. [27] established that the polymerization mode and the curing tip distance had a significant effect on the hardness of the composites. Aguiar F.H.B. et al. [28] evaluated the influence of light curing modes and curing time on the microhardness of a hybrid composite. It was found that the increase of the light curing time and usage of appropriate LCU could lead to maximum hardness in polymerization of composites in deep cavities. The research of Spajic J. et al. [29] showed that in the light-cured materials, the material

type had the highest effect on the microhardness, followed by the irradiation time, while the curing mode had the lowest impact. Alkhughairy F.I. [30] investigated the effect of two curing light intensities on the mechanical properties of bulk fill composites. A positive influence of the higher curing light intensity (1200 mW/cm^2) on the microhardness of the bulk fill composites was found.

Despite the daily and routine placement of composite restorations, dentists' level of knowledge about the composite properties and the main factors of the photopolymerization process—light intensity, irradiation time and layer thickness is not high [31,32]. The poor awareness can lead to incorrect curing protocol, which in turn can lead to an incomplete polymerization of the material with all the adverse consequences: reduced hardness and wear resistance, low adhesive bond strength and increased risk of restoration fracture, elution of residual monomers and faster color change. Therefore, there is a need for development of guidance for the curing modes, ensuring effective polymerization of the resin-based composites mostly used in dental practice.

In evaluation the influence of different curing modes on the polymerization process and the composites properties, most of the researchers use different methods of the statistical analysis; independent and paired sample *t*-test, one-way and two-way analysis of variance, multiple comparisons with Tukey test, full factorial ANOVA [27,29,30]. However, these methods allow only the influence and significance of the different parameters of polymerization process as well as the correlation between them to be revealed. Using the regression analysis, the optimal parameters of each process, which guarantee maximal properties of the object or material, can be calculated [33–37].

Therefore, the aim of this paper is to use regression analysis and to perform an optimization of the parameters of photopolymerization process in order to obtain maximum hardness of the dental composites. To the best of our knowledge, this kind of engineering approach is applied here for the first time in order to investigate resin-based composites. Universal nanohybrid, bulk fill and flowable light-cured composites are used in the research. Light curing modes for each composite are developed, which can serve as guidance for successful polymerization in the daily work of dentists.

2. Materials and Methods

2.1. Materials and Samples Preparation

Round samples with diameter of 5 mm and thickness of 2, 3 and 4 mm were prepared of three types of light-cured resin-based composites: Universal nanohybrid Composite (UC) Evetric (Ivoclar Vivadent, Lichtenstein, Germany), nanohybrid Bulk fill Composite (BC) for posterior restorations Filtek One Bulk Fill Restorative (3M Oral Care, St. Paul, MN, USA) and universal nanofilled Flowable Composite (FC) G-aenial Universal Flo (GC, Tokyo, Japan), indicated for restorations of all cavity classes. All composites were of A2 shade, but had a different composition and organic matrix/fillers ratio (Table 1).

The samples were prepared in three polyurethane molds with internal dimeter of 5 mm and thickness of 2, 3, and 4 mm. Glass slides and transparent celluloid strips on the top and bottom of the molds were used that guaranteed smooth surfaces and the same dimensions of all samples in the groups. The polymerization was performed with light curing unit Curing Pen (Eighteeth, Changzhou, China) with 600, 1000 and 1500 mW/cm^2 light intensity and irradiation time of 20, 40 and 60 s [29,31]. LCU's tip was placed parallel and in contact with the glass slide at a distance of 1 mm from the sample. Three specimens were prepared for each combination of parameters. They were stored in a dry dark container at room temperature for 24 h, after which the hardness measurements were performed.

Table 1. Composition of the composites used [38–42].

Composite	Composition		
	Component	**Amount**	**Matrix/Filler Ratio, wt%**
UC Evetric	Matrix: BIS-GMA (Bisphenol A glycydil dimethacrylate) UDMA (Urethane dimethacrylate) Bis-EMA (Bisphenol A polyethethylene glycol dimethacrylate) Fillers: Barium glass, Ytterbium Fluoride (YbF3), Mixed oxides and prepolymers 40 nm–3µm	 3–10% 10–25% 3–10%	19–20/80–81
BC Filtek One Bulk Fill Restorative	Matrix: AUDMA (Aromatic Urethane Dimethacrylate) DDDMA (1,12-Dodecane Dimethycrylate) UDMA (Urethane dimethacrylate) Fillers: Silane Treated Ceramic, Silica, Zirconia and Ytterbium Fluoride	 10–20% <10% 1–10%	23.5/76.5
FC G-aenial Universal Flo	Matrix: UDMA (Urethane dimethacrylate) Bis-EMA (Bisphenol A polyethethylene glycol dimethacrylate) Dimethacrylate component Fillers: Silicon dioxide (16 nm), Strontium glass (200 nm), pigments	 10–20% 5–10% 5–10%	31/69

2.2. Hardness Measurements

The Vickers microhardness was investigated by ZHVµ-S (Zwick/Roell, Ulm-Einsingen, Germany) hardness tester with 50 gr loading for 10 s. Five measurements were performed on the top and bottom surfaces of each specimen and the mean values were recorded.

2.3. Regression Analysis

An optimization of the three parameters of the photopolymerization process, light intensity I, irradiation time t and layer thickness d was caried out. The aim was to obtain a composite layer with a certain thickness, having maximum microhardness on the top surface (HVmax) and microhardness on the bottom surface, 80% of HVmax [24–26], in given intensity values and irradiation times, specific for each LCU.

The governing factors, namely intensity I, irradiation time t and layer thickness d as well as their levels, are listed in Table 2. The factors, measured in natural physical units, are marked with $\widetilde{x}_i$ and have different dimensions. In order to eliminate the experimental plan's dependence from the dimensions, the factors $\widetilde{x}_i$ are transformed into a coded form x_i through dependence

$$x_i = (\widetilde{x}_i - \widetilde{x}_{i,0})/|\widetilde{x}_{i,max} - \widetilde{x}_{i,0}| \quad (1)$$

The objective functions are: Y_1, HV with hardness on the top surface of the composite layer and Y_2, HV hardness on the bottom surface. A planned experiment for the three investigated composites was carried out. The experimental design is shown in Table 3.

Regression analyses of the obtained experimental results for each composite were carried out through QStatLab v 6.1 software. For the objective functions Y_i, i = 1, 2, polynomials from second order were chosen since the governing factors were changed of three levels [33]:

$$Y_k(\{X\}) = a_0 + \sum_{i=1}^{m} a_i x_i + \sum_{i=1}^{m-1} \sum_{j=i-1}^{m} a_{ij} x_i x_j + \sum_{i=1}^{m} a_{ii} x_i^2, k = 1, 2, \quad (2)$$

where $\{X\} = [x_1 x_2]^T \in \Gamma_x$ is the vector of the governing factors, Γ_x is the admissible space of the governing factors and m is their number.

For each of the composites, regression models were created for the objective functions Y_1, hardness on the top surface of the composite layer, and Y_2, hardness on the bottom surface. Using regression models for UC, *Evetric* optimizations were made in nine variations of the governing factors intensity (x_1) and irradiation time (x_2). As a condition for optimization, for each composite the average value of the microhardness on the top surface obtained in the experiment was accepted, and for the microhardness on the bottom surface 80% of the microhardness on the top surface.

Table 2. Governing factors and their levels.

Governing Factors				
Natural $\tilde{x}_i$	**Coded x_i**	**Levels of the Factors**		
		Coded		
		For the first factor		
		−1	−0.1111	1
		For the rest factors		
		−1	0	1
		Natural		
Intensity I [mW/cm^2] $\tilde{x}_1$	x_1	600	1000	1500
Time t [s] $\tilde{x}_2$	x_2	20	40	60
Thickness d [mm] $\tilde{x}_3$	x_3	2	3	4

Table 3. Experimental design.

№	**Composite Type**						**UC**		**BC**		**FC**	
	Governing Factors											
	Coded			**Natural**			Y_1 **HV Top**	Y_2 **HV Bottom**	Y_1 **HV Top**	Y_2 **HV Bottom**	Y_1 **HV Top**	Y_2 **HV Bottom**
	x_1	x_2	x_3	**I, mW/cm^2**	**t, s**	**d, mm**						
1	−1	−1	−1	600	20	2	42.0	33.5	59.1	55.8	42.4	37.9
2	1	−1	−1	1500	20	2	52.4	42.9	61.7	60.2	50.0	46.3
3	−1	1	−1	600	60	2	45.9	41.1	61.8	61.1	47.5	45.5
4	1	1	−1	1500	60	2	57.8	51.3	68.4	67.5	49.9	47.7
5	−1	−1	1	600	20	4	45.0	12.2	57.9	45.4	42.9	13.1
6	1	−1	1	1500	20	4	58.9	26.1	61.7	55.3	45.0	27.0
7	−1	1	1	600	60	4	49.3	32.7	60.3	57.5	45.3	31.7
8	1	1	1	1500	60	4	62.7	45.0	67.2	65.3	48.1	42.6
9	−0.1111	−1	−1	1000	20	2	54.1	42.2	62.2	60.3	47.7	42.3
10	−0.1111	1	1	1000	60	4	56.9	35.8	65.1	61.6	45.8	37.6
11	−1	0	−1	600	40	2	42.4	38.2	63.8	60.3	45.3	43.5
12	1	0	1	1500	40	4	61.7	38.4	65.3	62.5	45.5	36.5
13	−1	−1	0	600	20	3	44.3	22.2	59.2	51.8	46.1	29.9
14	1	1	0	1500	60	3	59.3	48.7	69.1	67.3	51.1	47.1

2.4. Calculation of the Parameters of Photopolymerization Process

The above-mentioned condition for optimization led to incorrect solutions of the equations of regression analysis for some regimes of UC *Evetric*. These incorrect solutions were referred to the photopolymerization parameters, in which the values of the microhardness on the top surface were less than the acceptable ones. Thus, the difference in the microhardness between the top and bottom surfaces was larger than 20%.

For that reason, a *MatLab* software-based algorithm was developed to calculate the microhardness on the top and bottom surfaces as well as the layer thickness, which met the requirement for maximum microhardness and 20% difference.

The regression model for each composite is used as basis of the algorithm in the newly designed program. If UC *Evetric* is taken as an example, the microhardness (at top and bottom, respectively) as a function of the governing factors is:

$$Y_1 = 56.266 + 6.402x_1 + 1.5325x_2 + 2.0025x_3 - 4.458x_1^2, \quad (3)$$

$$Y_2 = 35.936 + 6.118x_1 + 6.459x_2 - 6.991x_3 + 1.189x_1x_3 + 3.089x_2x_3. \quad (4)$$

The following equation expresses the relationship between the two objective functions:

$$0.8Y_1 - Y_2 = 0 \quad (5)$$

The Equation (5) is solved with respect to the thickness x_3:

$$x_3 = x_3(x_1, x_2) \quad (6)$$

or, taking into account (3) and (4):

$$x_3 = \frac{-9.0768 + 0.9964x_1 + 5.233x_2 + 3.5664x_1^2}{8.593 - 1.189x_1 - 3.089x_2}. \quad (7)$$

In the above expression, the coded values of intensity (x_1) and time (x_2) are replaced, and the thickness (coded values) is calculated. The coded coordinates x_1 and x_2 as well as the calculated thickness x_3 are replaced in the expressions for the objective functions Y_1 and Y_2 and the corresponding microhardnesses are calculated. It should be noted that they would be obtained in proportion $1 : 0.8$.

The thickness of the sample in physical coordinates is obtained via the transformation:

$$\widetilde{x}_3 = (\widetilde{x}_{3,max} - \widetilde{x}_{3,0})x_3 + \widetilde{x}_{3,0} \quad (8)$$

where $\widetilde{x}_3$ is the thickness (mm), $\widetilde{x}_{3,max}$ is the maximal thickness (mm), $\widetilde{x}_{3,0}$ is the average level of the thickness (mm).

3. Results

3.1. Microhardness

The mean values of the microhardness measurements on the composite sample top and bottom surfaces are shown in Table 3. BC Filtek One Bulk Fill Restorative is characterized by a highest maximum microhardness of 65+/−4 HV, followed by UC Evetric with 56+/−4 HV, and the lowest microhardness 47+/−4 HV is obtained for FC G-aenial Universal Flo. These values are used as optimization condition in the regression analysis of the investigated composites.

3.2. Universal nanohybrid composite Evetric

The regression models for the objective functions Y_1—hardness on the top surface of the composite layer and Y_2—hardness on the bottom surface of UC *Evetric* are shown in Formulas (3) and (4). Using regression models, nine optimizations are conducted for this composite in different combinations of the parameters intensity (x_1) and irradiation time (x_2) and the results are given in Table 4. In regimes with lower intensity (600 mW/cm^2 and 1000 mW/cm^2/20 s) incorrect solutions are obtained, referring to the lower microhardness values or HV difference between the top and bottom surfaces larger than 20%. With the help of the newly designed program, maximum microhardness on the top surface, 80% microhardness on the bottom surface and the layer thickness (which guarantees it) were calculated for variations of irradiation time and LCU intensity. The results obtained are shown in Table A1 (Appendix A).

Table 4. Optimal regimes for photopolymerization of UC *Evetric* obtained by regression analysis.

№	I mW/cm^2	t s	d mm	HV Top	HV Bottom	Note
1	1500	60	3.10	60.0	48.0	Regimes that meet the requirement of max HV 56 +/−4 on the top surface and HV on the bottom surface ≥ 80%.
2	1500	40	3.05	58.3	41.6	
3	1500	20	2.35	55.3	41.6	
4	1000	60	2.85	57.0	43.0	
5	1000	40	2.15	53.9	41.6	
6	1000	20	Incorrect solution			HV difference between top and bottom surface is larger than 20%.
7	600	60	Incorrect solution			HV values on the top surface are lower than the acceptable 56 +/−4.
8	600	40	Incorrect solution			
9	600	20	Incorrect solution			

The data in Table A1 (Appendix A) can be classified into three groups. The first group includes the curing modes that do not provide the necessary microhardness on the top and bottom surfaces, which is a sign of insufficient polymerization. These are the regimes with an intensity of 600–700 mW/cm^2 for all irradiation times, and an intensity of 800 mW/cm^2 for time 20 and 40 s. The second is the boundary group with two modes: 800 mW/cm^2/60 s and 1000 mW/cm^2/20 s, which provide hardness close to the lower limit. Taking into account the microhardness increase of the composite over time [43], these regimes can be considered acceptable. The third group includes all modes with intensity 1000 mW/cm^2 for time 40 and 60 s, as well as those over 1000 mW/cm^2. They guarantee maximum microhardness on the top surface, and 80% HVmax on the bottom surface at the calculated thickness of the composite layer. In irradiating for a maximum of 60 s, the layer thickness at which 80% HVmax is achieved on the bottom surface is larger than that recommended by the manufacturer—2 mm [39]. Our results show that in this case it is possible to work with a layer thickness of up to 2.39 mm for 1200 mW/cm^2, 2.54 mm for 1300 mW/cm^2 and 3.17 mm for 1500 mW/cm^2. On the other hand, the manufacturer recommends 2 mm composite layer to be polymerized for 20 s with LCU intensities between 500 and 1000 mW/cm^2 and for 10 s with intensities above 1000 mW/cm^2. The results, obtained by us, disprove these recommendations, as observance of the specified parameters would not lead to satisfactory microhardness of the material.

3.3. Nanohybrid Bulk Fill Composite Filtek One Bulk Fill Restorative

For BC Filtek One Bulk Fill Restorative the regression models for the objective functions Y_1 and Y_2 are of the following type:

$$Y_1 = 64.55 + 2.327x_1 + 2.256x_2 - 0.704x_3 - 1.866x_2^2 + 1.003x_1x_2, \quad (9)$$

$$Y_2 = 59.113 + 3.596x_1 + 4.170x_2 - 2.740x_3 + 1.162x_1x_3 + 1.397x_2x_3. \quad (10)$$

The regression models are used for constitution of Equation (5) in order to obtain the thickness x_3:

$$x_3 = \frac{7.473 + 1.7344x_1 + 2.3652x_2 + 1.4928x_2^2 - 0.8024x_1x_2}{2.1768 - 1.162x_1 - 1.397x_2}. \quad (11)$$

The results obtained are shown in Table A2 (Appendix B). Only at I = 600 mW/cm^2 and t = 20 s there is a thickness of 3.86 mm in the range 2–4 mm, where the bottom/top microhardness ratio is equal to 0.8 and the accuracy of the calculated hardness (56.63 HV on top and 45.30 HV on bottom) is guaranteed. For all other "intensity—time" combinations in the table, the calculated limit thickness is larger than the upper limit of the range 2–4 mm. In this composite, for all combinations in the table (except for the first), the bottom/top microhardness ratio is higher or less than 0.8. For the calculated thicknesses larger than 4 mm, i.e., outside the defined range 2–4 mm, the accuracy of the calculated hardness

is not guaranteed, as the regression models are valid only for the intervals in which the governing factors are changed.

Figure 1 illustrates the dependences of the microhardness on the top surface Y_1 and the bottom/top microhardness ratio Y_2/Y_1 as a function of thickness for mode 3 in Table A2 (Appendix B) (I = 600 mW/cm^2 and t = 60 s). For the first mode in Table A2 (Appendix B) the limit thickness is 3.86 mm, while for all others it is over 4 mm. Taking into account the increase of Y_2/Y_1 with thickness decrease (Figure 1), it can be assumed that for the entire thickness interval (2–4 mm) the bottom/top microhardness ratio should be higher than 0.8, which satisfies the requirement.

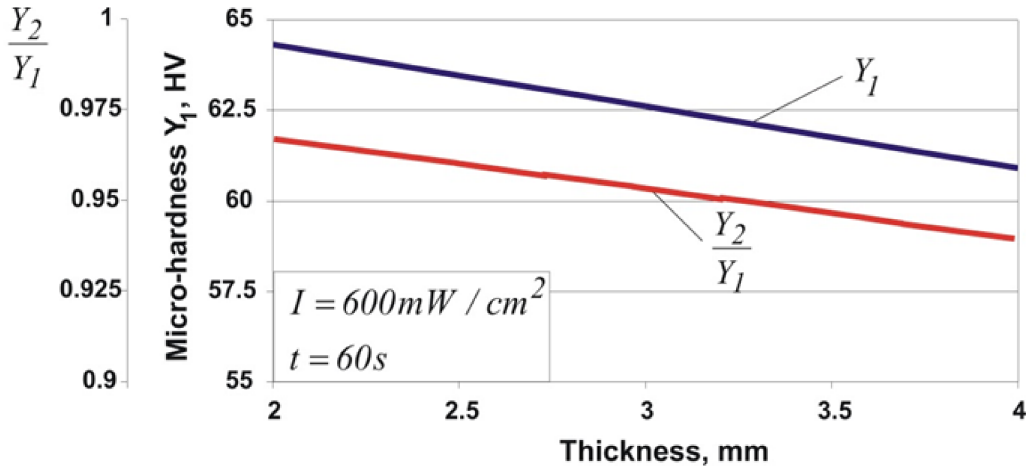

Figure 1. Dependences of the hardness on top surface Y_1 and the bottom/top hardness ratio Y_1/Y_2 as a function of thickness of BC.

The graphs in Figure 2 show the dependence of the microhardness Y_1 on the top surface on the intensity, irradiation time and thickness. It can be clearly seen that for the three thicknesses (2, 3 and 4 mm) the increase of the irradiation time over 40 s is practically unnecessary, as the microhardness on the top surface increases insignificantly. Using Figure 2 and according to the specific conditions, an optimal combination of photopolymerization parameters can be selected to ensure the minimum allowable hardness of 61 HV.

The parameters of photopolymerization of BC Filtek One Bulk Fill Restorative are summarized in Table 5. These parameters provide the minimum allowable hardness 61 HV on the top surface and hardness on the bottom surface—80% of that of the top for layer thickness between 2–4 mm. For comparison, the manufacturer recommends the irradiation time for 4 mm layer to be 40 s with intensity in the range 550–1000 mW/cm^2 and 20 s with intensity above 1000 mW/cm^2 [40,41]. The results of our study show that a satisfactory microhardness cannot be obtained by polymerization for 40 s with intensity of 550–700 mW/cm^2 and for 20 s with an intensity of 1000–1250 mW/cm^2.

Table 5. Optimal parameters of photopolymerization of BC Filtek One Bulk Fill Restorative.

№	Intensity, mW/cm^2	Time, s	Layer Thickness, mm
1	I > 1000	20	2
2	600–1500	40	2
3	I > 1000	20	3
4	600–1500	40	3
5	I > 1250	20	4
6	700–1250	40	4
7	I < 700	60	4

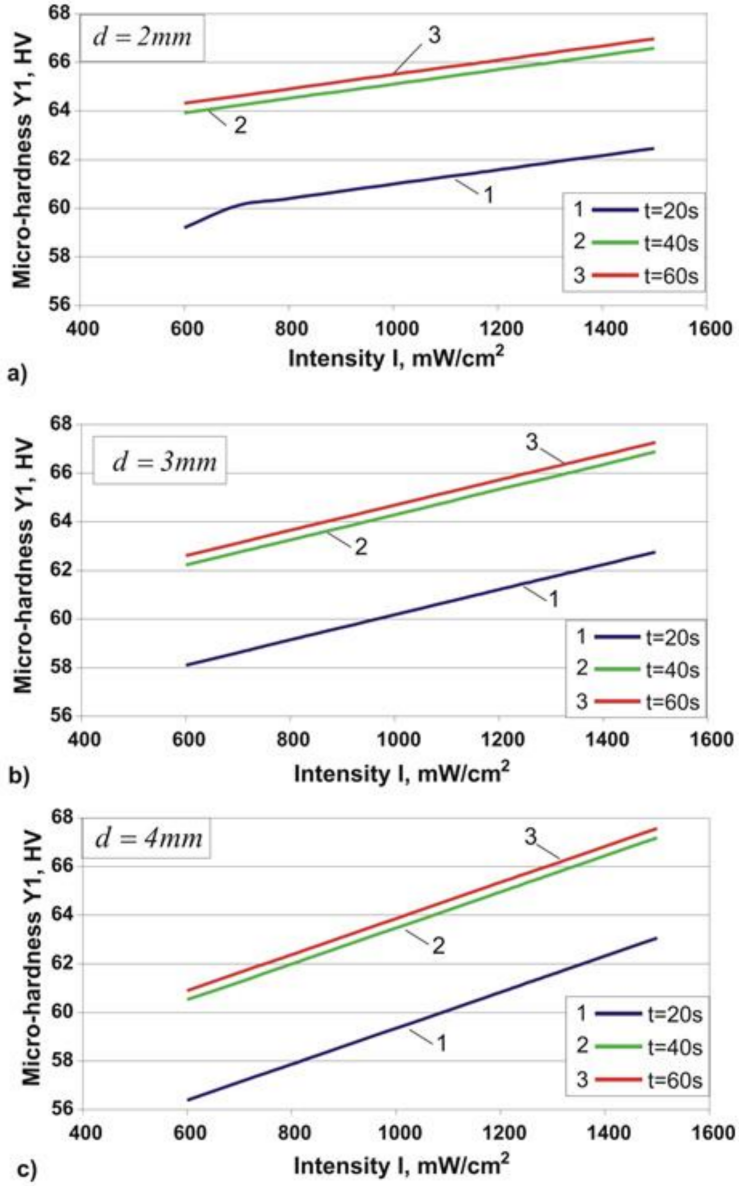

Figure 2. Dependence of the hardness on top surface on the intensity, irradiation time and layer thickness of: (**a**) 2 mm; (**b**) 3 mm and (**c**) 4 mm.

3.4. Universal Nanofilled Flowable Composite G-Aenial Universal Flo

The regression models for the objective functions Y1 and Y2 of FC G-aenial Universal Flo have the following form:

$$Y_1 = 46.762 + 1.715x_1 + 1.054x_2 - 1.326x_3 - 0.766x_1x_3 + 0.730x_1x_2x_3 \quad (12)$$

$$Y_2 = 37.091 + 4.214x_1 + 5.271x_2 - 7.769x_3 + 1.994x_1x_3 + 3.185x_2x_3 \quad (13)$$

They are used to constitute Equation (5) from which the thickness x_3 is expressed:

$$x_3 = \frac{-0.3186 + 2.842x_1 + 4.4278x_2}{6.7082 - 2.6068x_1 - 3.185x_2 + 0.584x_1x_2}. \quad (14)$$

The calculated parameters of photopolymerization for the investigated composite are shown in Table A3 (Appendix C). The data analysis shows that all light curing regimes satisfy the requirement for the surface microhardness. It is noteworthy that two modes lead to lowest hardness on the top surface: regime 1, which is characterized by the lowest

parameters intensity and time, and regime 2 with the highest parameters. The other combinations of parameters provide HVmax in the range 44.46–47.50 HV.

The most probable reason for the reduced surface microhardness at high values of the irradiation time is the large layer thickness (7.63 mm at 1500 mW/cm^2 and 5.37 mm at 1300 mW/cm^2). In these two cases, the volume of the composite to be polymerized is too large and the photopolymerization process cannot proceed completely even at 60 s of irradiation. Therefore in order to ensure maximum microhardness 46–48 HV on the top surface, when working with FC G-aenial Universal Flo the thickness of the layer should not exceed 5 mm.

According to the recommendations of the manufacturer, 1.5 mm layer should be cured for 20 s with LCU intensity of 700 mW/cm^2 and for 10 s with intensity of 1200 mW/cm^2 [42]. The results of our study confirm that if these guidelines are followed, a satisfactory hardness or degree of polymerization of FC G-aenial Universal Flo could be obtained.

4. Discussion

The microhardness of resin-based composites depends mostly on the type and amount of the fillers, as well as the ratio of the monomer-polymer conversion [3,5,23,26]. The fillers of FC G-aenial Universal Flo consists of nano-powders of silicon dioxide and strontium glass with matrix/fillers ratio 31/69 wt% (Table 1). Compared to the other two composites, FC has the lowest filler amount, which defines its lowest hardness. The matrix/filler ratio of BC Filtek One Bulk Fill Restorative is 23.5/76.5 wt%, while that of UC Evetric is 19–20/80–81 wt%. As it can be seen in Table 1, the filler amount of BC is lower than the UC, but its composition is different. The fillers of BC consist only of materials with high hardness: ceramic, silicon dioxide and zirconium particles. While in the composition of the UC fillers in addition to the Ba glass particles, ytterbium fluoride and mixed oxides, prepolimers with lower hardness are included. Therefore, the comparatively high filler content and its composition define the highest hardness of BC Filtek One Bulk Fill Restorative composite.

The conducted optimization shows that for UC Evetric (Table A1, Appendix A) not all light curing modes provide the required microhardness on the top surface. Hence, in this case it is not recommended to use LCUs, operating with intensity below 800 mW/cm^2. In the case of LCU with intensity of 800 mW/cm^2, the required microhardness on the top surface is guaranteed only at irradiation of 60 s. When using LCUs with an intensity in the range of 1000–1500 mW/cm^2, it is possible to work with all irradiation times. It should be taken into account that as the duration of irradiation increases, the thickness of the composite layer and the hardness increase. When the maximum values of intensity and time (1500 mW/cm^2 and 60 s) are used, a layer with thickness of 3 mm having 60 HV microhardness on the top surface, can be successfully polymerized. The recommended light curing regimes of UC Evetric are marked with * in Table A1 (Appendix A).

The situation with BC Filtek One Bulk Fill Restorative is quite different. This composite is intended for posterior restorations [40], and therefore it is characterized by high hardness after polymerization and the ability to be applied in one layer in deep cavities. In our study, we investigated the composite layer thicknesses in the range of 2–4 mm. Regression analysis carried out ensures the accuracy of the results only in this range, i.e., where the bottom/top microhardness ratio is 0.8. According to the results shown in Table A2 (Appendix B), in regimes between mode 2 (600 mW/cm^2 and 40 s) and mode 12 (1000 mW/cm^2 and 60 s) this ratio is equal to or greater than 0.8, and for regimes above mode 12—the ratio is less than 0.8. This means that the modes up to 12th provide a microhardness on the bottom surface higher than 80% of that on the top surface, but the hardness on the top surface is below the minimum allowable 61 HV with the exception of mode 11 (1000 mW/cm^2 and 40 s). In the modes above 12th, the hardness on the bottom surface is within 0.66–0.78 (66–78%) of the hardness on the top surface, which is below the required minimum of 80% [24–26]. The graphs in Figure 2 show that increasing the time above 40 s does not lead to a significant increase in the microhardness of the top surface, therefore in the

photopolymerization of BC *Filtek One Bulk Fill Restorative* it is not necessary to irradiate the obturation for 60 s. Modes that include intensities in the range 1000–1500 mW/cm^2 and irradiation times of 20 and 40 s guarantee microhardness above the minimum allowable for layer thicknesses of 4.71–12.07 mm, but with bottom/top microhardness ratio less than 0.8. Taking into account that a tooth cavity with 7 mm depth is a rare case, and then modes in which the layer thickness is above this value are excluded. The recommended regimes for photopolymerization of BC *Filtek One Bulk Fill Restorative* are marked with * in Table A2 (Appendix B). The layer thickness, greater than the upper limit of the range and the bottom/top microhardness ratio less than 0.8, are achieved in these curing regimes. In these cases, in order to ensure a higher microhardness on the bottom surface ($\geq$80% HVmax), it is necessary to work with a layer thickness less than that indicated in Table A2 (Appendix B). When working with a layer thickness in the range of 2–4 mm, the photopolymerization modes can be selected from Table 5.

Regarding FC G-aenial Universal Flo, it is found that all light curing regimes used in the study, provide the required microhardness on the top surface, but to ensure its maximum value of 46–48 HV, the layer thickness should not exceed 5 mm. Therefore, all modes in Table A3 (Appendix C) can be recommended for successful photopolymerization.

The results of the present study have shown that the instructions for light curing only of the manufacturer of FC G-aenial Universal Flo guarantee the required microhardness of the filling. The recommendations for work with the other two composites, UC Evetric and BC Filtek One Bulk Fill Restorative, do not meet the requirement for high microhardness, which means that a sufficient degree of polymerization can not be achieved. The recommended photopolymerization regimes for the three types of composites, developed in this study, guarantee high microhardness of the fillings.

5. Conclusions

In this study, optimization of the parameters of photopolymerization process of dental composites from three different groups was conducted using regression analysis. To the best of our knowledge, an engineering approach is applied here for the first time in investigation of resin-based composites. For all composites, regression models for the microhardness on the top and bottom surfaces of the composite layer were established. Both the layer thickness and the microhardness on the samples top and bottom surfaces of each composite were calculated for 21 modes of photopolymerization varying with the light intensity and irradiation time. It was established that photopolymerization guidelines only of FC manufacturer guarantee the required hardness, while recommended regimes for UC and BC do not satisfy this requirement. Tables, containing recommended light curing regimes, were developed for three composite types, guaranteeing high hardness of composite restoration. They were designed to facilitate work of dentists in dental offices.

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Appendix A

Table A1. Parameters of photopolymerization of UC *Evetric*.

№	Intensity, mW/cm^2	Time, s	Layer Thickness, mm	Hardness, HV	
				Top	Bottom
1	600	20	2.09	42.05	33.64
2	600	40	2.33	44.07	35.26
3	600	60	2.81	46.56	37.25
4	700	20	1.97	45.00	36.00
5	700	40	2.19	46.97	37.58
6	700	60	2.62	49.36	39.48
7	800	20	1.88	47.57	38.05
8	800	40	2.08	49.49	39.59
9 *	800	60	2.46	51.80	41.44
10 *	1000	20	1.78	51.53	41.22
11 *	1000	40	2.95	53.40	42.72
12 *	1000	60	2.31	55.64	44.51
13 *	1200	20	1.76	53.96	43.17
14 *	1200	40	1.98	55.86	44.69
15 *	1200	60	2.39	58.21	46.57
16 *	1300	20	1.85	54.61	43.69
17 *	1300	40	2.06	56.57	45.26
18 *	1300	60	2.54	59.07	47.26
19 *	1500	20	2.07	54.82	43.85
20 *	1500	40	2.39	56.98	45.59
21 *	1500	60	3.17	60.08	48.06

Note: *—recommended regimes for successful photopolymerization.

Appendix B

Table A2. Parameters of photopolymerization of BC *Filtek One Bulk Fill Restorative*.

№	Intensity, mW/cm^2	Time, s	Layer Thickness, mm	Hardness, HV		Y_2/Y_1
				Top, Y_1	Bottom, Y_2	
1	600	20	3.86	56.63	45.30	0.80
2	600	40	4.72	59.29	48.81	0.82
3	600	60	8.36	53.47	46.27	0.86
4	700	20	4.03	57.08	46.94	0.82
5	700	40	4.99	59.78	49.07	0.82
6	700	60	9.30	53.78	46.33	0.86
7	800	20	4.23	57.58	47.06	0.82
8 *	800	40	5.31	60.35	49.31	0.82
9	800	60	10.58	54.08	46.20	0.85
10	1000	20	4.71	58.78	47.26	0.80
11 *	1000	40	6.16	61.72	49.66	0.80
12	1000	60	15.35	54.61	44.70	0.82
13 *	1200	20	5.34	60.34	47.38	0.78
14 *	1200	40	7.50	63.66	49.73	0.78
15	1200	60	32.66	54.75	36.13	0.66
16 *	1300	20	5.73	61.32	47.39	0.77
17	1300	40	8.51	65.03	49.57	0.76
18	1300	60	91.26	53.28	The results have no physical sense	
19 *	1500	20	6.79	63.89	47.27	0.74
20	1500	40	12.07	69.59	48.39	0.70
21	1500	60	The results have no physical sense			

Note: *—recommended regimes for successful photopolymerization.

Appendix C

Table A3. Parameters of photopolymerization of FC *G-aenial Universal Flo*.

№	Intensity, mW/cm^2	Time, s	Layer Thickness, mm	Hardness, HV	
				Top	Bottom
1	600	20	2.42	43.89	35.11
2	600	40	2.66	45.24	36.19
3	600	60	3.23	45.81	36.65
4	700	20	2.44	44.46	35.57
5	700	40	2.71	45.64	36.51
6	700	60	3.37	46.00	36.80
7	800	20	2.46	45.02	36.02
8	800	40	2.77	46.02	36.82
9	800	60	3.54	46.15	36.92
10	1000	20	2.51	46.09	36.87
11	1000	40	2.91	46.68	37.35
12	1000	60	4.01	46.29	37.03
13	1200	20	2.57	47.06	37.65
14	1200	40	3.11	47.16	37.73
15	1200	60	4.77	46.01	36.81
16	1300	20	2.61	47.50	38.00
17	1300	40	3.24	47.29	37.84
18	1300	60	5.37	45.58	36.46
19	1500	20	2.72	48.22	38.58
20	1500	40	3.61	47.19	37.75
21	1500	60	7.63	43.22	34.58

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