



# Surface free energy and roughness of flowable dental composites

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*Purpose:* The surface properties like roughness, wettability and surface free energy are important for utility properties of traditional and flowable dental restorative composites, due to their role in plaque formation, discoloration, mechanical wear or adhesion and bonding. The goal of our work was to assess the surface free energy (SFE) and the surface roughness (Ra) of three commercial flowable dental composites: everX Flow (bulk), everX Flow (dentin) and Flow-Art. *Methods:* Surface roughness, contact angle and surface free energy were determined for tested composites. Two surface states (control and roughened) were compared. Roughness was measured with the use of the 3D optical profilometer. The contact angle (CA) was determined through the sessile drop method with the use of four different probing liquids. This enabled to apply two surface free energy approaches (Owens–Wendt (O–W) and van Oss–Chaudhury–Good (LWAB)). Additionally, Zisman’s approach ( $\gamma_c$ ) was used. *Results:* The water contact angle values were similar for Flow-Art ( $67.56 \pm 1.49^\circ$ ) and everX Flow (bulk) ( $68.94 \pm 2.72^\circ$ ) compared to higher value for everX Flow (dentin) ( $74.39 \pm 2.05^\circ$ ). SFE was in the range from 43 to 50 mJ/m<sup>2</sup> for O–W and from 47 to 62 mJ/m<sup>2</sup> for LWAB. The  $\gamma_c$  was from 37 to 45 mJ/m<sup>2</sup>. *Conclusions:* Roughening composites’ surface influenced on increasing the CA value. All approaches of surface free energy calculations provide useful data for predicting interactions between flowable composites and dental tissues. Tested composites showed good wetting for initial state of surface after polymerization. These influence on better adhesion of the material to the bonding system during dental restoration.

*Key words:* flowable dental composite, surface free energy, wettability, roughness

## 1. Introduction

Dental flowable resin composites are a tooth-colored restorative material with a lower viscosity than conventional resin composites. This facilitates the application of the restorative material into complex cavity spaces and its good adaptation. These limit marginal gap defects within a restoration and time of application [1]. Lower viscosity of flowable composites compared to conventional composites results from reducing filler content to 37–65% (volume) and/or by integrating less viscous monomers [2]. In comparison with conventional dental resin the bulk-fill composites have less or the same polymerization shrinkage, polymerization

stress and marginal gaps [3], [4]. The good functionality of the flowable resin composites is determined by several factors such as the filler percentage and the viscosity, the composition of the monomers and other components, the polymerization shrinkage, the thermomechanical tolerance and physicochemical parameters of the materials, the color stability and overall wear resistance [2]. Also surface properties, e.g., roughness, surface energy and wetting play an important role in dental restorative composites performance, due to their impact on plaque formation in the oral cavity environment, discoloration, mechanical wear, adhesion and bonding [5].

Adhesion enables attachment of restoration material to dentin and enamel and is improved by using

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different bonding systems. Adhesive systems are composed of monomers with hydrophilic and hydrophobic groups. The hydrophilic groups enhance the wettability to the dental hard tissues and the hydrophobic groups interact with the restorative material. The combination of hydrophilic and hydrophobic interactions in adhesive systems makes it possible to create a bridge over the gap between the hydrophilic tooth tissue and hydrophobic restorative composite [6], [7]. Adhesion may be also enhanced by increasing the surface free energy value [8], [9]. In dependence of the surface free energy components, the joined surfaces will connect with dispersive interactions or acid-based interactions [8], [10]. Values of surface energy of bonded materials can be used to determine the work of adhesion as an indirect method of adhesion estimation [8]. The most popular method to determine the surface free energy is contact angle measurement. The contact angle (CA) expresses the wetting of the solid by the liquid phase. It is used to indicate the interfacial tension. The wetting of a solid by a liquid is related to the surface free energy of the solid and the surface tension of the liquid [11]. The surface free energy (SFE) shows the difference between an atom on the solid surface and an atom in the interior. In the interior of a material, atoms are in equilibrium and the interatomic forces between nearby atoms in the crystal structure are in equilibrium. At the outer layer of material, there are no interatomic interactions on the external surface of the atoms [12], [7].

Studies that evaluated the surface characterization of flowable dental composites focused on ability of a material to reflect direct light, the aesthetic appearance, color stability, the roughness and influence of finishing and polishing techniques on materials' performance [13], [14].

EverX Flow was tested in a few areas of application, like fracture or wear [15], [16]. There are pilot clinical applications of everX Flow to reinforce direct composite bridges [17] and application in bilayer structure system of anterior composite crown restorations [18]. The use of these materials in combination with other dental materials [19]–[21] shows the importance of the adhesive properties of flowable composites.

Ability of flowable composites to fill deep tooth cavities indicates their good wettability but there are limited published studies reporting values of the contact angle for new-generation flowable resin composites for dental restorations. Studies that evaluated contact angle and surface free energy for dental flowable composites reported moderate wettability ( $78.62^\circ$  for Flow-Art) and SFE at the level of  $49.33 \text{ mJ/m}^2$  [22].

Available in the literature data of the surface free energy and roughness have been focused on dental

ceramic [9], dental cements [23] and universal dental restorative materials [24]. Also, works on the evaluation of the roughness and wettability of some bulk fill materials are available, but recently properties of flowable composites have been improved due to nanotechnology and greater filler content, thus further studies are needed to analyze these rapidly developing composites [25]. Determination of surface energy states and wettability of new-generation dental materials becomes an important issue that gives the possibility to assess the level of adhesion. The objective of this investigation was to estimate the relationship between surface free energy (SFE) and the surface roughness of three commercial flowable dental composites.

Wettability and surface free energy for two surface states, as delivered and after roughening, were compared to estimate the influence of roughness on wettability and surface free energy. In the contact angle measurement, other probing liquids (with different physicochemical properties) were used in addition to water. This enabled the researchers to use different surface free energy models and to compare the influence of number of SFE parameters and type of probing liquids on obtained SFE values. It can provide further information on the materials' surface and give some insight into the necessity of proper choosing test liquids. The null hypothesis was that roughening the surface of flow composites will not affect wettability and surface free energy. Fundamental knowledge related to the influence of surface roughness on flowable composites surface wettability, and the different associated wetting regimes, can improve understanding the role of wettability on adhesion and the biological outcome.

## 2. Materials and methods

### 2.1. Materials

Samples were prepared from the following flowable dental composites: everX Flow (GC Corporation, Japan) in two shades: the bulk shade for deep cavities (depth of cure – 5.5 mm) and the dentin shade for aesthetic results (depth of cure – 2 mm) and Flow-Art (Arkona, Poland). Flow-Art is used in deep cavities up to crown modeling. The bulk shade has a higher transparency/translucency, so it can conduct and scatter the irradiated light to every corner of the cavity. This behavior is important in deep cavities reaching the root canals, which are difficult to irradiate. Flow-Art resin matrix is composed of Bis-GMA and methacrylate

monomers (TEGDMA, UDMA). The filler material is barium-aluminum-silicon glass with content of 61% (w/w) [26]. EverX Flow is composed of matrix resin (Bis-MEPP, TEGDMA, UDMA) and 70% (w/w) of the filler (barium glass and glass fiber) [27].

All samples were prepared according to the manufacturers' instructions. The samples were prepared in the shape of cuboids with dimensions 10.0 × 10.0 × 15.0 mm in mold made of polytetrafluoroethylene. Composites were applied into the mold in 2 mm layers. Each layer of composite was irradiated for 10 seconds using a polymerization lamp with High Power LED, prior to the application of next layer. For each sample, the upper surface was covered by a glass slide to avoid the influence of oxygen inhibition layer on results.

Samples were tested after polymerization (control group – C) and after surface treatment (sandblasted group – S). For the sandblasting group, specimens were blasted with 135–180 μm aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) (Sand Fengda® BD-60, Ningbo Bida Machinery Manufacture, China) by a sandblasting device (air eraser, DB-178, Ningbo Bida Machinery Manufacture, China) at a distance of 100 mm with a pressure 0.2–0.4 MPa for 5 s. In this work, sandblasting was used to increase the surface roughness. Roughness increase is related with an enhancement of surface wettability, which influence on the bond strength of dental restorative materials [28].

## 2.2. Methods

Roughness measurement was conducted by the 3D optical profilometer Keyence VR-6200 (Keyence, Itasca, U.S.A). Roughness parameters were measured along the line ( $Ra$ ,  $Rz$ ) according to EN ISO 21920-2:2022 and across the surface ( $Sa$ ,  $Sz$ ) according to EN ISO 25178-2:2021.  $Ra$  is referred to the arithmetic mean roughness (arithmetic mean height of a line) and  $Rz$  is referred to the maximum roughness [29]. The extension of  $Ra$  to a surface is  $Sa$ . It expresses the difference in height of each point compared to the arithmetical mean of the surface.  $Sz$  is defined as the sum of the largest peak height value and the largest pit depth value within the defined area [30].

Contact angle measurements were carried out using the sessile drop method. The optical goniometer (Advex Instrument, Czech Republic) with colorful 2 Mpix (1600 × 1200) UVC camera, high-resolution glass objective lens and compatible software SeeSystem6.3 were used. Four probe liquids with defined values of surface tension (program data) were used in the tests for contact

angle examinations: diiodomethane and a-bromonaphthalene (Sigma-Aldrich, USA), glycerol (Chempur, Poland), distilled water (Biomus, Poland). Contact angles were measured at room temperature (23 ± 1 °C) and 50 ± 5% RH. Each surface of samples was cleaned in 99.8% V/V ethanol (Avantor Performance Materials, Poland). A liquid drop of 0.5 μl volume was dropped perpendicularly to the material's surface, with the use of micropipette Vitrum (VITRUM, Czech Republic), and the drop profile image was captured by SeeSystem software. The value of contact angle was calculated from the drop profile image based on the analysis of height and width of the drop. The final contact angle for analysis was an average of ten measured values for each liquid and surface.

The surface free energy of tested composites was calculated using two approaches: the Owens–Wendt's (O–W) method and van Oss–Chaudhury–Good's (LWAB) method. Additionally, Zisman's approach was used to obtain values of the critical surface tension.

The Owens–Wendt's model considers the geometric meaning of the polar and dispersive parts of the liquid's surface tension and the solid's surface energy [31]. According to this method, the surface free energy ( $\gamma_s$ ) is a sum of two components: the long-range dispersion (Lifshitz – van der Waals) ( $\gamma_s^d$ ) and the short-range polar (hydrogen bonding) ( $\gamma_s^p$ ) (1):

$$\gamma_s = \gamma_s^d + \gamma_s^p. \quad (1)$$

Two probe liquids (polar and nonpolar) are used to measure the contact angle and determine the polar and the nonpolar components of the SFE. Usually, the tests are carried out with distilled water as polar liquid and diiodomethane as nonpolar liquid. Polar and dispersive components of solid's SFE are calculated from the formula (2) by forming a system of equations (one with data for a polar liquid and the second with data for a nonpolar liquid).

$$\frac{1}{2}(1 + \cos \theta)\gamma_L = \sqrt{(\gamma_s^d \gamma_L^d)} + \sqrt{(\gamma_s^p \gamma_L^p)}, \quad (2)$$

where:  $\gamma_s$  – surface free energy of tested material,  $\gamma_s^d$  – SFE dispersive component of tested material,  $\gamma_s^p$  – SFE polar component of tested material,  $\gamma_L$  – surface free energy of probe liquid,  $\gamma_L^d$  – SFE dispersive component of probe liquid,  $\gamma_L^p$  – SFE polar component of probe liquid and  $\theta$  – contact angle.

SFE according to this model was calculated for two different pairs of liquids: (1) distilled water and diiodomethane; (2) distilled water and a-bromonaphthalene.

In the van Oss–Chaudhury–Good's approach [32], the surface free energy of a solid ( $\gamma_s$ ) is the sum of apolar Lifshitz–van der Waals ( $\gamma_s^{LW}$ ) and polar acid–base interactions ( $\gamma_s^{AB}$ ), the latter divided into two parts, acid ( $\gamma_s^+$ ) and basic ( $\gamma_s^-$ ) (3):

$$\gamma_s = \gamma_s^{LW} + \gamma_s^{AB} = \gamma_s^{LW} + 2\sqrt{\gamma_s^+ \gamma_s^-}, \quad (3)$$

where  $\gamma_s^+$ ,  $\gamma_s^-$  represent the polar components (acid–base).

The different components of the solid and the liquid surface free energies, and the contact angle are related by Eq. (4).

$$\frac{1}{2}(1 + \cos\theta)\gamma_L = \sqrt{(\gamma_s^{LW} \gamma_L^{LW})} + \sqrt{(\gamma_s^+ \gamma_L^-)} + \sqrt{(\gamma_s^- \gamma_L^+)}. \quad (4)$$

Three parameters  $\gamma_s^{LW}$ ,  $\gamma_s^+$ ,  $\gamma_s^-$  must be found to solve this equation. Therefore, the contact angle measurement must be conducted with three different measurement liquids (non-polar and two polar). SFE calculations according to this model were performed for two triple of measuring fluids: (1) distilled water, diiodomethane and glycerol; (2) distilled water, a-bromonaphthalene and glycerol.

The Zisman's method is used to determine the critical surface energy ( $\gamma_C$ ). The critical surface energy is the surface tension of the liquid needed to completely wet the solid. In a contact angle measurement, numerous liquids from a given homologous series are used. Based on contact angle values, a plot is generated having the surface tension of the liquid ( $x$ -axis) and  $\cos\theta$  ( $y$ -axis). Measurement points are fitted to straight line and extrapolated to point  $\cos\theta = 1$ . It gives the critical surface tension value for the surface [33]. The equation of the straight line (5) can be determined in a defined coordinate system in which  $b$  is the directional coefficient of the line.

$$\cos\theta = 1 + b(\gamma_C + \gamma_L). \quad (5)$$

Using Young's equation and Eq. (5), for the tested material, the relationship between surface free energy and critical surface energy is given (6).

$$\gamma_s = \frac{(b \cdot \gamma_C + 1)^2}{4b}. \quad (6)$$

Statistical analysis was performed based on the Student's  $t$ -test for non-ferrous samples separately for materials before and after roughening, and the Student's  $t$ -test for the dependent samples to check whether the roughening operation indicates significant differences between the mean values for each of the analyzed materials. The Statistica software (TIBCO Software Inc., U.S.A.) was used. The accepted level of significance was  $p = 0.05$ . At the beginning, the basic assumptions of the Student's  $t$ -test were checked, i.e., equality of groups (both samples contain  $n = 10$  observations each), normality of distribution conducted with the use of Shapiro–Wilk  $U$ -test and homogeneity of variance (Levene's test).

### 3. Results

Parameters of surface roughness were measured from average line and on the area (Table 1). For all tested composites, the increase of roughness parameters were observed after sandblasting. The highest mean roughness, both for initial state and sandblasted state of the surface was noticed for everX Flow (dentin).

The values of contact angle measured with the use of four probe liquids were presented in Table 2. In Figure 1, the exemplary shape of water drops on the flow composites' surfaces for control group and sandblasted group were shown. The wettability of tested flow composites for two states of surface was compared in Fig. 2. The water contact angle measurements showed that all the surfaces are moderately wettable surfaces ( $68.91 \pm 4.16^\circ$  for everX Flow (bulk),  $74.34 \pm 3.12^\circ$  for everX Flow (dentin) and  $67.44 \pm 2.20^\circ$  for Flow-Art).

Table 1. Roughness parameters for initial and sandblasted surface of tested composites.  
 $Ra$  – the arithmetical mean height of line,  $Rz$  – maximum profile height of line,  
 $Sa$  – the arithmetical mean height of the surface,  $Sz$  – maximum height of the surface

Material	Surface	$Ra$ [ $\mu\text{m}$ ]	$Rz$ [ $\mu\text{m}$ ]	$Sa$ [ $\mu\text{m}$ ]	$Sz$ [ $\mu\text{m}$ ]
everX Flow (bulk)	C	1.142	6.188	1.186	26.090
	S	2.356	16.309	3.844	36.920
everX Flow (dentin)	C	4.236	20.404	6.432	40.520
	S	4.679	21.578	5.280	63.410
Flow-Art	C	1.682	9.304	1.986	29.700
	S	2.595	17.067	2.786	35.100

Table 2. The values of contact angles ( $\theta$ ) for four probe liquids for control (C) and sandblasted surfaces (S). Mean values (standard deviation)

Material	Surface	$\theta$ [°]			
		water (W)	diiodomethane (D)	glycerol (G)	a-bromonaphthalene (B)
everX Flow (bulk)	C	68.94 (2.72)	39.62 (2.35)	75.77 (3.42)	23.06 (2.75)
	S	81.75 (2.41)	24.79 (4.16)	65.62 (4.11)	14.66 (2.21)
everX Flow (dentin)	C	74.39 (2.05)	46.26 (2.04)	93.74 (3.82)	30.16 (3.47)
	S	96.59 (1.79)	31.87 (2.03)	104.42 (5.69)	11.20 (1.37)
Flow-Art	C	67.56 (1.49)	35.16 (2.78)	70.92 (3.82)	21.59 (2.08)
	S	90.50 (1.98)	21.71 (1.32)	85.08 (1.13)	10.02 (0.47)

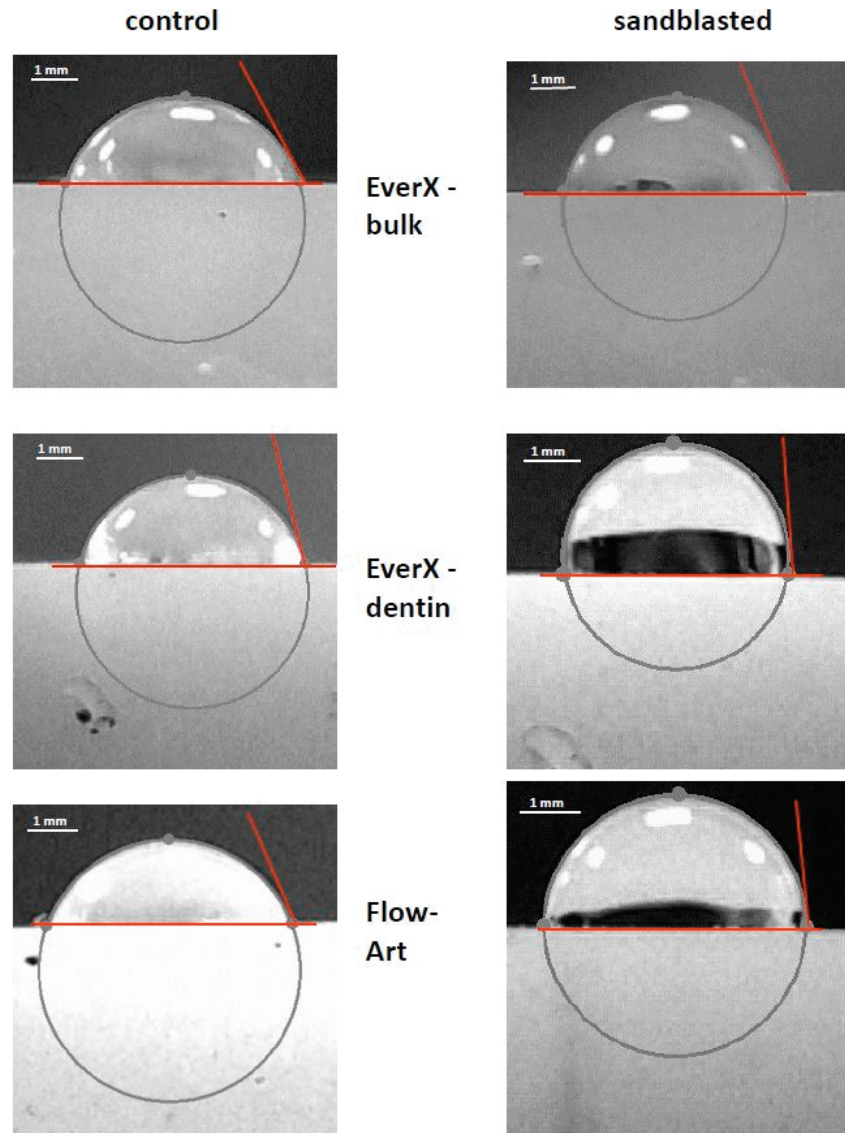


Fig. 1. The shape of water drops on the flow composites' surfaces for control group and sandblasted group

The wettability of everX Flow (bulk) and Flow-Art are very similar (no statistical significant difference between mean values,  $p = 0.17$ ). After roughening, differences in contact angle values between all materials can be seen ( $p \leq 0.05$ ). Considering only the water contact angle, roughening materials' surface influenced an

increase of the contact angle value for each material ( $p \leq 0.05$ ). The character of the everX Flow (bulk) and Flow-Art surface became more hydrophobic. Comparison of the effect of roughness change on the contact angle values did not show a proportional relationship between these parameters.

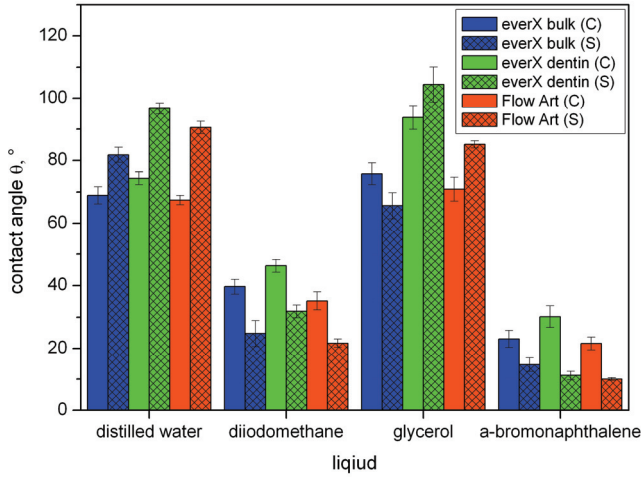


Fig. 2. The values of contact angle for four probes liquids

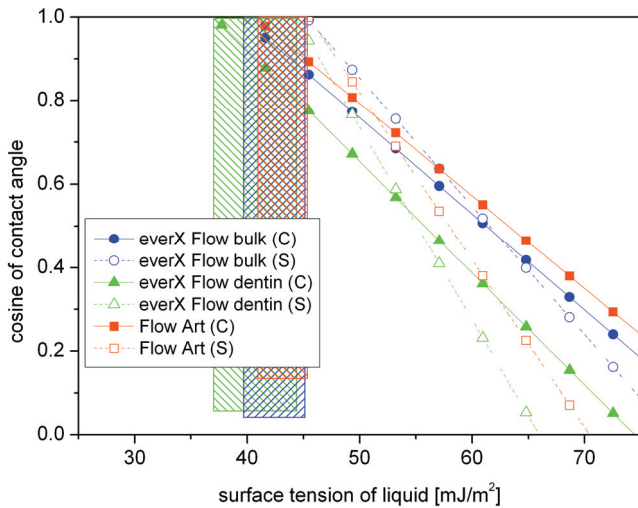


Fig. 3. Comparison of the surface state influence on the critical surface free energy flowable dental materials obtained by Zisman's method. The hatched area shows the difference of  $\gamma_C$  between samples in the initial control state (C) and after sandblasted (S)

The surface free energy is a sum of the polar and dispersive components of surface tension. According to the Owens–Wendt's calculations, tested materials

showed a low total SFE (Tables 3 and 4). Composites' surface after roughening presented similar values of  $\gamma_S$  when compared to composites without any treatment. Differences in SFE values before and after roughening are statistically significant for Flow-Art material (both pairs of probe liquids), at the assumed significance level of 0.05. There are no statistically significant differences before and after roughening for everX Flow (bulk) and everX Flow (dentin) for OW model calculated for water and diiodomethane as probe liquids ( $p > 0.05$ ). However, increase of the dispersive component ( $\gamma_S^d$ ) values and reduction of polar component ( $\gamma_S^p$ ) values were observed after sandblasting of the surface. Van Oss–Chaudhury–Good's model based on the results of the measurement of the contact angle using three liquids, showed much higher values of the total SFE ( $\gamma_S$ ) for everX Flow (dentin) and similar values for the other two materials (Tables 5 and 6) compared to Owens–Wendt's model. Differences in values of  $\gamma_S$  between treated and untreated materials' surfaces are statistically significant between everX Flow (dentin) and everX Flow (bulk) ( $p \leq 0.05$ ) and Flow-Art and everX Flow (bulk) ( $p \leq 0.05$ ). The difference between SFE values for Flow-Art and everX Flow (dentin) is not statistically significant. Large differences can be noted for polar components of SFE resulting from a decrease after the roughening process. Both methods of SFE calculations showed that a polar component was low with a dispersive component as a greater part of SFE.

Comparison of the SFE values according to Owens–Wendt's model calculated with the use of two pairs of probe liquids (Tables 3 and 4) showed that before the roughening process, statistically significant differences can be observed only for the everX Flow (bulk) ( $p \leq 0.05$ ), the other materials seem to be similar, regardless of the pair of probe liquids adopted. On the other hand, after roughening, the situation was reversed. The everX Flow (dentin) and Flow-Art mate-

Table 3. Surface free-energy ( $\gamma_S$ ) and its components ( $\gamma_S^d$  – Lifshitz–van der Waals surface tension component,  $\gamma_S^p$  – Lewis acid–base interaction) according to Owens–Wendt's model (water and diiodomethane as probe liquids).

Mean values (standard deviation)

Material	Surface	$\gamma_C$ [mJ/m <sup>2</sup> ]	$\gamma_S^d$ [mJ/m <sup>2</sup> ]	$\gamma_S^p$ [mJ/m <sup>2</sup> ]
everX Flow (bulk)	C	47.70 (1.28)	39.78 (1.17)	7.92 (1.40)
	S	48.12 (0.94)	46.13 (1.44)	1.99 (0.73)
everX Flow (dentin)	C	42.73 (1.56)	36.32 (1.11)	6.41 (0.72)
	S	43.48 (0.84)	43.41 (0.88)	0.07 (0.07)
Flow-Art	C	49.83 (1.16)	41.92 (1.27)	7.91 (0.78)
	S	47.59 (0.40)	47.25 (0.43)	0.34 (0.20)

rials were characterized by statistically significant differences, while the everX Flow (bulk) material seemed to be similar regardless of the adopted liquids.

Comparison of the SFE values according to van Oss–Chaudhury–Good’s model calculated with the use of different probe liquids (Tables 5 and 6) before the

Table 4. Surface free-energy ( $\gamma_s$ ) and its components ( $\gamma_s^d$  – Lifshitz–van der Waals surface tension component,  $\gamma_s^p$  – Lewis acid-base interaction) according to Owens–Wendt’s model (water and a-bromonaphthalene as probe liquids).

Mean values (standard deviation)

Material	Surface	$\gamma_c$ [mJ/m <sup>2</sup> ]	$\gamma_s^d$ [mJ/m <sup>2</sup> ]	$\gamma_s^p$ [mJ/m <sup>2</sup> ]
everX Flow (bulk)	C	48.47 (1.64)	40.89 (0.77)	7.58 (1.11)
	S	45.36 (0.69)	42.94 (0.43)	2.43 (0.67)
everX Flow (dentin)	C	44.39 (1.13)	38.54 (1.24)	5.84 (0.96)
	S	43.61 (0.21)	43.55 (0.21)	0.06 (0.06)
Flow-Art	C	49.39 (1.03)	41.32 (0.57)	8.07 (0.59)
	S	44.28 (0.23)	43.72 (0.06)	0.56 (0.25)

Table 5. Surface free-energy and its components ( $\gamma_s^{LW}$  – Lifshitz–van der Waals surface tension component,  $\gamma_s^{AB}$  – Lewis acid-base interaction,  $\gamma_s^+$  – Lewis-acid and  $\gamma_s^-$  – Lewis-base) according to van Oss–Chaudhury–Good’s model (water, diiodomethane and glycerol as probe liquids). Mean values (standard deviation)

Material	Surface	$\gamma_s$ [mJ/m <sup>2</sup> ]	$\gamma_s^{LW}$ [mJ/m <sup>2</sup> ]	$\gamma_s^{AB}$ [mJ/m <sup>2</sup> ]	$\gamma_s^+$ [mJ/m <sup>2</sup> ]	$\gamma_s^-$ [mJ/m <sup>2</sup> ]
everX Flow (bulk)	C	48.09 (3.57)	39.78 (1.17)	8.30 (3.46)	0.80 (0.53)	23.34 (4.27)
	S	47.62 (1.40)	46.13 (1.44)	1.49 (0.92)	0.24 (0.15)	3.16 (2.71)
everX Flow (dentin)	C	62.10 (8.45)	36.32 (1.11)	25.78 (7.59)	5.01 (1.85)	38.58 (6.78)
	S	59.84 (7.44)	43.41 (0.88)	16.43 (6.90)	7.42 (3.21)	9.15 (3.89)
Flow-Art	C	47.52 (4.88)	41.92 (1.27)	5.59 (3.86)	0.48 (0.41)	20.75 (3.39)
	S	52.25 (1.12)	47.25 (0.43)	4.99 (0.93)	1.53 (0.25)	4.15 (1.12)

Table 6. Surface free-energy and its components ( $\gamma_s^{LW}$  – Lifshitz–van der Waals surface tension component,  $\gamma_s^{AB}$  – Lewis acid-base interaction,  $\gamma_s^+$  – Lewis-acid and  $\gamma_s^-$  – Lewis-base) according to van Oss–Chaudhury–Good’s model (water, a-bromonaphthalene and glycerol as probe liquids). Mean values (standard deviation)

Material	Surface	$\gamma_s$ [mJ/m <sup>2</sup> ]	$\gamma_s^{LW}$ [mJ/m <sup>2</sup> ]	$\gamma_s^{AB}$ [mJ/m <sup>2</sup> ]	$\gamma_s^+$ [mJ/m <sup>2</sup> ]	$\gamma_s^-$ [mJ/m <sup>2</sup> ]
everX Flow (bulk)	C	49.80 (4.26)	40.89 (0.77)	8.91 (3.80)	0.92 (0.64)	23.15 (4.09)
	S	44.75 (0.74)	42.94 (0.43)	1.81 (0.67)	0.38 (0.20)	3.32 (2.74)
everX Flow (dentin)	C	65.60 (7.89)	38.54 (1.24)	27.06 (7.41)	5.58 (1.88)	33.16 (6.88)
	S	59.99 (6.68)	43.55 (0.21)	16.44 (6.77)	7.43 (3.01)	9.14 (3.93)
Flow-Art	C	46.50 (3.49)	41.32 (0.57)	5.18 (3.53)	0.40 (0.34)	20.85 (4.02)
	S	48.08 (0.78)	43.72 (0.06)	4.35 (0.82)	1.10 (0.18)	4.38 (1.16)

Table 7. Critical surface energy ( $\gamma_c$ ) of dental flowable composites and coefficient of determination linear regression

Material	Surface	$\gamma_c$ mJ/m <sup>2</sup> ]	$R^2$
evreX Flow (bulk)	C	39.46	0.91
	S	45.22	0.99
evreX Flow (dentin)	C	37.04	0.81
	S	44.24	0.92
Flow-Art	C	40.63	0.93
	S	45.46	0.96

roughening process showed statistically significant differences only for the everX Flow (bulk) ( $p \leq 0.05$ ), the other materials seem to be similar, regardless of the probe liquids adopted. After roughening, the situation was reversed. The everX Flow (dentin) and Flow-Art were characterized by statistically significant differences ( $p \leq 0.05$ ) for the adopted liquids, while everX Flow (bulk) seemed to be similar regardless of the adopted probe liquid.

The critical surface energy ( $\gamma_c$ ) was determined by Zisman's method (Fig. 3), values of energy were presented in Table 7. Initial values of the critical surface energy are similar for all samples. After sandblasting, the increase of critical energy was observed for all materials.

## 4. Discussion

In this paper, an experimental study focused on the comparison of roughness, wettability and surface free energy of three commercial dental flowable composites: everX Flow in two shades and Flow-Art is presented. The surface of composites was tested in two states, after polymerization in the form as initial state and after roughening. EverX Flow (bulk) and Flow-Art showed similar roughness parameters both in the initial and sandblasted state. EverX Flow (dentin) showed more than twice higher roughness in the initial state in comparison with other materials. A similar trend was observed for contact angle values, with higher values for everX Flow (dentin) and lower for the other two. The surface free energy was calculated according to van Oss–Chaudhury–Good's approach and Owens–Wendt's approach, what gives possibility to better estimate SFE of tested materials, while verifying all approaches. Average values of SFE from two approaches agreed very well for flowable composites dedicated for deep cavities (everX Flow (bulk) and Flow-Art). For dentin shade composite (everX Flow (dentin)), the average value of SFE differed between approaches, mainly due to different values of polar component. The combination of three probe liquids in LWAB approach and two liquids in O–W approach did not affect obtained SFE values.

Increase of surface roughness after sandblasting did not affect the significant change of the surface free energy calculated according to both approaches. However, comparison of separated components of the surface free energy showed a slight increase of dispersive component and significant decrease of polar component. For both surface states (initial and sandblasted),

the dispersive component has the predominant share in the surface free energy value. It indicates that tested materials have higher ability to interact on dispersive way and a higher adhesive affinity for non-polar substances [22]. The polar part of the SFE according to LWAB approach is separated into an acid ( $\gamma_s^+$ ) and a base component ( $\gamma_s^-$ ). For tested composites the base component dominated over the acid component. The base component of SFE energy may improve interactions between resin and more acidic surface. The character of dental tissue surface depends on dental adhesive systems used in restorative procedures. For example, adhesive-treated dentin has an acidic character [34], so a dental resin contacts with an acidic surface. Higher value of the base component of the surface free energy has influence on increasing interactions between dentin acidic surface and composite. On the other hand, acidic treated tissue may contribute to problems with resin polymerization at the interface. It results from reaction between the aromatic tertiary amine from the composite and acidic adhesive monomer. However, some accelerators, e.g., aromatic sulfinic-acid sodium salts have been incorporated into adhesives to improve polymerization in the presence of acidic monomers [35]. For practical reasons, when applying dental resin to dentine, it appears to be advantageous to use a resin composite compatible with the adhesive system.

Contact angle and surface free energy values were utilized in many studies for dental biomaterials as factors used in estimating adhesion and bonding to dental tissues [22]. Our results for the initial state of surface showed more hydrophilic surface but surface roughening influenced on achieving more hydrophobic character of the surface. It should be considered during composite application, which should have good wettability to ensure adhesion to the dental tissues.

Comparison of obtained result for dental flow composites is difficult due to the limited number of publications estimating wettability and surface free energy for this types of composites. The values of surface free energy and its components determined by the O–W method were reported for Flow-Art composite [22]. The water contact angle was  $78.62 \pm 2.48^\circ$  and diiodomethane contact angle was  $23.55 \pm 1.64^\circ$ . These values are in good agreement with our results:  $67.56 \pm 1.49^\circ$  (water) and  $35.16 \pm 2.78^\circ$  (diiodomethane) for the control surface and  $90.50 \pm 1.98^\circ$  (water) and  $21.71 \pm 1.32^\circ$  (diiodomethane) for the sandblasted surface.

Comparison of roughness and wettability ( $R_a$ ,  $\mu\text{m}/\text{CA},^\circ$ ) of eight different dental materials' surfaces referred in [12], [36] for amalgam ( $0.40 \mu\text{m}/81^\circ$ ), Chromasit ( $0.26 \mu\text{m}/73^\circ$ ), Co-Cr alloy ( $0.53 \mu\text{m}/100^\circ$ ), IPS



InLine ceramic ( $0.40 \mu\text{m}/68^\circ$ ), resin-based composite ( $0.39 \mu\text{m}/76^\circ$ ), Au-Pt alloy ( $0.57 \mu\text{m}/90^\circ$ ), TPZ ceramic ( $0.23 \mu\text{m}/41^\circ$ ), and tooth ( $0.5 \mu\text{m}/71^\circ$ ) can be supplemented with the results of flowable materials (average of everX Flow (bulk) ( $1.14 \mu\text{m}/69^\circ$ )). Different commercial bulk-fill composite materials were used in the work [37] to evaluate the bacterial adhesion and related surface properties like SFE, CA and  $R_a$ . The values of SFE (mN/m) were from 23.5 (for Beautiful Bulk Restoration) to 39.9 (for Sonic Fill) and are related to our values of  $\gamma_s$  ( $42.73$  to  $49.83 \text{ mJ/m}^2$ ) and water contact angle ( $68^\circ$  to  $90^\circ$ ).

The control (initial) surface roughness of our samples resulted from the roughness of the mold used for their polymerization. For this reason, discrepancies in control values are observed. Roughening resulted in the increase of the critical surface energy ( $\gamma_c$ ) value for everX Flow (bulk) by 13%, for everX Flow (dentin) by 16% and for Flow-Art by 11%, respectively. Comparing the critical energy values of flowable materials obtained in the range of  $37$ – $45 \text{ mJ/m}^2$  with the values of composite materials used in dentistry like Villacryl SP –  $44 \text{ mJ/m}^2$ , Villacryl H Plus –  $46 \text{ mJ/m}^2$ , Vip Esthetic V2 –  $27 \text{ mJ/m}^2$  and tooth tissues (swine model) – enamel pig's tooth –  $21 \text{ mJ/m}^2$  and root tissue  $39$  –  $\text{mJ/m}^2$  determined in [38] shows their similarity. The values of obtained critical surface tension are close to values reported by Baier corresponding to the range of good tissue bioadhesion (above  $40 \text{ mJ/m}^2$ ) [39].

Observed differences in wettability and surface free energy between flow composites dedicated for the deep cavities and for aesthetic results indicate better bonding capability for everX Flow (bulk) and Flow-Art compared to everX Flow (dentin). However, the limitations associated with the assessment of only selected surface parameters such as wettability, surface free energy and roughness must be taken into account. In aim to extensive understanding the problem of influence of roughening on wettability and adhesion of flow composites, research should be performed on a wider group of dental materials. Future studies should consider adhesion force estimation between the material and a tissue in relation to the surface free energy.

## 5. Conclusions

Two common approaches for SFE estimation have been reviewed. The use of new-generation flowable dental composite materials in clinical practice is becoming more popular. There are studies comparing tra-

ditional dental composites with flow composites [40], [41], but there are no data available on surface properties which characterize wettability and surface free energy. Tested composites showed good wetting for initial state of surface after polymerization what is required for tooth restorations. Wettability and surface free energy for materials in initial state was statistically different for two types of everX Flow and between Flow-Art and everX Flow (dentin). This shows that the energetic state of the surface layer and the related adhesion are different in the case of flow composites intended for deep cavities and aesthetic purposes. Increase of roughness influences decrease of wettability and increase of surface free energy for all materials being tested, what is the basis for the rejection of the null hypothesis. Importantly, this resulted from the decrease in the polar energy component and the dominant share of the dispersive component. This indicates a higher ability to interact on dispersive than acid-base way and better adhesion under conditions of interaction with non-polar substances. Presented results of contact angle measurements and SFE calculation for new-generation flowable dental composites complements available literature data which focus on strength and fracture toughness, wear-resistance, and polymerization shrinkage. From a practical aspect, contact angle measurements procedure using four probe liquids gives some new insights into demands of proper choosing sets of liquids implemented in surface free energy calculations, as well as SFE approaches.

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## References

- [1] BEHL S., RAJU, RAJAN G., ELLAKWA A., FARRAR P., PRUSTYA B.G., *Physical and mechanical characterization of flowable dental composites reinforced with short aspect ratio micro-sized S-Glass fibre*, Mater. Sci. Eng. C, 2020, 111, 110771, DOI: 10.1016/j.msec.2020.110771.
- [2] VOUVODI E.C., *Overviews on the progress of flowable dental polymeric composites: their composition, polymerization process, flowability and radiopacity aspects*, Polymers, 2022, 14, 418, DOI: 10.3390/polym14194182.
- [3] KHORAMIAN TUSI S., HAMDOLLAHPUR H., MOHAMMADI SAVADROODBARI M., SHEIKH FATHOLLAHI M., *Comparison of Polymerization Shrinkage of a New Bulk-fill Flowable Composite with Other Composites: An in Vitro Study*, Clin. Exp. Dent. Res., 2022, 8, 1605–1613, DOI: 10.1002/cre2.656.

- [4] DA SILVA PEREIRA R.A., DE BRAGANÇA G.F., VILELA A., DE DEUS R.A., MIRANDA R.R., VERÍSSIMO C., SOARES C.J., *Post-gel and total shrinkage stress of conventional and bulk-fill resin composites in endodontically-treated molars*, *Oper. Dent.*, 2020, 45 (5), E217–E226, DOI: 10.2341/19-187-L.
- [5] IMTIAZ T., GANESH S.B., JAYALAKSHMI S., *Surface roughness changes of two composite resin restorative materials after thermocycling*, *J. Adv. Pharm. Tech. Res.*, 2022, 13, 466–469, DOI: 10.4103/japtr.japtr\_255\_22.
- [6] SOFAN E., SOFAN A., PALAIA G., TENORE G., ROMEO U., MIGLIAU G., *Classification review of dental adhesive systems: from the IV generation to the universal type*, *Ann. Stomatol. (Roma)*, 2017, 8 (1), 1–17, DOI: 10.11138/ads/2017.8.1.001.
- [7] ZHAO Z., WANG Q., ZHAO J., ZHAO B., MA Z., ZHANG, *Adhesion of Teeth*, *Front. Mater. C*, 2021, 7, 615225, DOI: 10.3389/fmats.2020.615225.
- [8] OKULUS Z., STRZEMIECKA B., CZARNECKA B., BUCHWALD T., VOELKEL A., *Surface energy of bovine dentin and enamel by means of inverse gas chromatography*, *Mater. Sci. Eng. C*, 2015, 49, 382–389, DOI: 10.1016/j.msec.2015.01.038.
- [9] RAMAKRISHNAIAH R., ALKHERAIF A.A., DIVAKAR D.D., MATINLINNA J.P., VALLITTU P.K., *The effect of hydrofluoric acid etching duration on the surface micromorphology, roughness, and wettability of dental ceramics*, *Int. J. Mol. Sci.*, 2016, 17, 822, DOI: 10.3390/ijms17060822.
- [10] COMBE E.C., OWEN B.A., HODGES J.S., *A protocol for determining the surface free energy of dental materials*, *Dent. Mater.*, 2004, 20, 262–268, DOI: 10.1016/S0109-5641(03)00102-7.
- [11] TSUJIMOTO A., IWASA M., SHIMAMURA Y., MURAYAMA R., TAKAMIZAWA T., MIYAZAKI M., *Enamel bonding of single-step self-etch adhesives: Influence of surface energy characteristics*, *J. Dent.*, 2010, 38 (2), 123–130, DOI: 10.1016/j.jdent.2009.09.011.
- [12] KOZMOS M., VIRANT P., ROJKO F., ABRAM A., RUDOLF R., RASPOR P., ZORE A., BOHINC K., *Bacterial adhesion of *Streptococcus mutans* to dental material surfaces*, *Molecules*, 2021, 26, 1152, DOI: 10.3390/molecules26041152.
- [13] JIN J., TAKAHASHI R., HICKEL R., KUNZELMANN K.-H., *Surface properties of universal and flowable nanohybrid composites after simulated tooth brushing*, *Am. J. Dent.*, 2014, 27 (3), 149–154.
- [14] LAI G., ZHAO L., WANG J., KUNZELMANN K.-H., *Surface properties and color stability of dental flowable composites influenced by simulated toothbrushing*, *Dent. Mater. J.*, 2018, 37 (5), 717–724, DOI: 10.4012/dmj.2017-233.
- [15] BIJELIC-DONOVA J., GAROUSHI S., LASSILA L.V., ROCCA G.T., VALLITTU P.K., *Crack propagation and toughening mechanism of bilayered short-fiber reinforced resin composite structure – Evaluation up to six months storage in water*, *Dent. Mater. J.*, 2022, 30, 41 (4), 580–588, DOI: 10.4012/dmj.2021-321.
- [16] LASSILA L., NOVOTNY R., SÄILYNOJA E., VALLITTU P.K., GAROUSHI S., *Wear behavior at margins of direct composite with CAD/CAM composite and enamel*, *Clin. Oral. Invest.*, 2023, 27, 2419–2426, DOI: 10.1007/s00784-023-04883-w.
- [17] SZABÓ V.T., SZABÓ B., BARCSAYNÉ-TÁTRAI N., MÉSZÁROS C., BRAUNITZER G., SZABÓ B.P., LASSILA L., GAROUSHI S., FRÁTER M., *Fatigue resistance of dissected lower first molars restored with direct fiber-reinforced bridges – an in vitro pilot study*, *Polymers*, 2023, 15, 1343, DOI: 10.3390/polym15061343.
- [18] LASSILA L., HAAPSAARI A., VALLITTU P.K., GAROUSHI S., *Fracture Resistance of Anterior Crowns Reinforced by Short-Fiber Composite*, *Polymers*, 2022, 14, 1809, DOI: 10.3390/polym14091809.
- [19] OTERO C.A., BIJELIC-DONOVA J., SARATTI C.M., VALLITTU P.K., BELLA E., KREJCI I., ROCCA G.T., *The influence of FRC base and bonded CAD/CAM resin composite endocrowns on fatigue behavior of cracked endodontically-treated molars*, *J. Mech. Beh. Biomed. Mat.*, 2021, 121, 104647, DOI: 10.1016/j.jmbbm.2021.104647.
- [20] FRÁTER M., SÁRY T., VINCZE-BANDI E., VOLOM A., BRAUNITZER G., SZABÓ B., GAROUSHI S., FORSTER A., *Fracture behavior of short fiber-reinforced direct restorations in large MOD cavities*, *Polymers*, 2021, 13, 2040, DOI: 10.3390/polym13132040.
- [21] SUNI A.O., LASSILA L.V.J., TUOKKO J.K., GAROUSHI S., VALLITTU P.K., *Adhesion of individually formed fiber post adhesively luted with flowable short fiber composite*, *Biomater. Invest. Den.*, 2023, 10 (1), DOI: 10.1080/26415275.2023.2209593.
- [22] SOWA M., PRZEKORA A., PALKA K., *Microstructure and surface free energy of light-cured dental composites after their modification with liquid rubber*, *Engineering of Biomaterials*, 2022, 25 (164), 9–15, DOI: 10.34821/eng.biomat.164.2022.9-15.
- [23] BRAJKOVIC D., ANTONIJEVIC D., MILOVANOVIC P., KISIC D., ZELIC K., DJURIC M., RAKOCEVIC Z., *Surface characterization of the cement for retention of implant supported dental prostheses: In vitro evaluation of cement roughness and surface free energy*, *App. Surf. Sci.*, 2014, 311, 131–138, DOI: 10.1016/j.apsusc.2014.05.027.
- [24] ISHII R., TAKAMIZAWA T., TSUJIMOTO A., SUZUKI S., IMAI A., BARKMEIER W.W., LATTA M.A., MIYAZAKI M., *Effects of finishing and polishing methods on the surface roughness and surface free energy of bulk-fill resin composites*, *Oper. Dent.*, 2020, 45 (2), E91-E104, DOI: 10.2341/18-246-L.
- [25] SHEKHAR S., SUPRABHA B.S., SHENOY R., NATARAJAN S., RAO A., *Comparative Evaluation of Surface Roughness and Wettability of an alkasite with nano bulk-fill and nanofilled resin composite restorative materials: In vitro Study*, *Contemp. Clin. Dent.*, 2022, 13 (4), 337–343. DOI:10.4103/ccd.ccd\_95\_21.
- [26] <https://arkonadent.com/kontakt/>, access data: 2023-03-02.
- [27] [https://www.gcamerica.com/products/operator/everx\\_flow/everx\\_flow\\_world\\_of\\_proof\\_study.pdf](https://www.gcamerica.com/products/operator/everx_flow/everx_flow_world_of_proof_study.pdf), access data: 2023-03-02.
- [28] NISHIGAWA G., MARUO Y., IRIE M., MAEDA N., YOSHIHARA K., NAGAOKA N., MATSUMOTO T., MINAGI S., *Various effects of sandblasting of dental restorative materials*, *Plos One*, 2016, 14, 11 (1), 0147077, DOI: 10.1371/journal.pone.0147077.
- [29] EN ISO 21920-2:2022. *Geometrical product specifications (GPS) – Surface texture: Profile – Part 2: Terms, definitions and surface texture parameters.*
- [30] EN ISO 25178-2:2021. *Geometrical product specifications (GPS) – Surface texture: Areal – Part 2: Terms, definitions and surface texture parameters.*
- [31] OWENS D.K., WENDT R.C., *Estimation of the surface free energy of polymers*, *J. Appl. Polym. Sci.*, 1969, 13, 1741–1747, DOI: 10.1002/app.1969.070130815.
- [32] OSS C.J., CHAUDHURY M.K., GOOD R.J., *Interfacial Lifshitz – van der Waals and polar interactions in macroscopic systems*, *Chem. Rev.*, 1988, 8, 927–941, DOI: 10.1021/cr00088a006.
- [33] SIBONI S., VOLPE C.D., MANIGLIO D., BRUGNARA M., *The solid surface free energy calculation II. The limits of the Zisman and of the “equation-of-state” approaches*, *J. Colloid Interface Sci.*, 2004, 271 (2), 454–472, DOI: 10.1016/j.jcis.2003.09.050.
- [34] ASMUSSEN E., PEUTZFELDT A., *Resin composites: Strength of the bond to dentin versus surface energy parameters*,

- Dent. Mat., 2005, 21 (11), 1039–1043, DOI: 10.1016/j.dental.2004.12.004.
- [35] OYAMA K., TSUJIMOTO A., OTSUKA E., SHIMIZU Y., SHIRATSUCHI K., TSUBOTA K., TAKAMIZAWA T., MIYAZAKI M., *Influence of oxygen inhibition on the surface free energy and enamel bond strength of self-etch adhesives*, Dent. Mater. J., 2012, 31 (1), 26–31, DOI: 10.4012/dmj.2011-162.
- [36] SZCZESIO-WŁODARCZYK A., KOPACZ K., SZYMKOWSKA-JÓZWIK M.I., SOKOŁOWSKI, J., BOCIONG K., *An Evaluation of the Hydrolytic Stability of Selected Experimental Dental Matrices and Composites*, Materials, 2022, 15, 5055, DOI: 10.3390/ma15145055.
- [37] BILGILI D., DÜNDAR A., BARUTÇUGIL C., TAYFUN D., ÖZYURT Ö.K., *Surface properties and bacterial adhesion of bulk-fill composite resins*, J. Dent., 2020, 95, 103317, DOI: 10.1016/j.jdent.2020.103317.
- [38] LIBER-KNEČ A., ŁAGAN S., *Surface testing of dental biomaterials-determination of contact angle and surface free energy*, Materials, 2021, 14 (11), DOI: 10.3390/ma14112716.
- [39] BAIER R.E., *Correlations of materials surface properties with biological responses*, J. Surf. Eng. Mater. Adv. Technol., 2015, 5, 42–51, DOI: 10.4236/jsemt.2015.51005.
- [40] MEENAKUMARI C., BHAT K.M., BANSAL R., SINGH N., *Evaluation of mechanical properties of newer nanoposterior restorative resin composites: An in vitro study*, Contemp. Clin. Dent., 2018, 9 (1), 142–S146, DOI: 10.4103/ccd.ccd\_160\_18.
- [41] RANKA S., RAO A.S., SHAH U., SOLANKI D., PAWAR A.M., REDA R., ZANZA A., TESTARELLI L., *Comparative evaluation of two different fiber-reinforced composite materials in Class I post-endodontic restorations in molars – A randomized clinical study*, Materials, 2022, 15, 7858, DOI: 10.3390/ma15217858.