# Optical stability and fluoride release of resin-based sealants

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The purpose of this in vitro study was to appraise the resin-based sealants for colour stability and fluoride release, as indicators for material structure alteration. For colour stability, Fotoseal® and Fissurit FX® samples were immersed in: orange juice, non-carbonated drink, carbonated drink and distilled water, and we estimated the variation of the CIE lab parameters. The concentration of fluorine anions was determined by potentiometric method. Fotoseal® express the largest variations of colour parameters, in carbonated drink and orange juice and release less fluoride. In conclusion, colour changes reveal structural outcomes in material resin matrix.

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## 1. Introduction

Sealing materials have a lower spectral transmission and are used in areas where the appreciation of chromatic characteristics is difficult. These products provide strong, durable bonds and have superior light transmission even when exposed to chemicals, heat and other adverse environmental conditions. Dental caries remains the major public health problem in dentistry and according to literature, shows an increase in global prevalence, despite progress of preventive methods [1]. Public health programs are well known strategies to control dental decay prevalence, especially in children, and among other actions (dental health education, fluoride toothpaste, fluoride gels for professional or individual use) the application of pit and fissure sealants is generally used because the first two years after molar teeth start erupting, they're still immature and if the biofilm control isn't efficient, occlusal surfaces exert high risk for decay [2].

Dental materials recommended as dental sealants are from various classes, but commonly resin-based sealants are used to protect pits and fissures, due to theirs higher retention rate [3].

In the oral environment, resin materials used as sealants are submitted to physical stresses and chemical process. Dental sealant chemical composition may be affected by the exogenous substances taken in the diet, which contain a variety of acids such as tartaric acid present in grape juice and phosphoric acid in cola beverages [4]. Interaction, duration of exposure and chemical composition are important to determine the relations between molecule and dental material polymeric network [5].

Resin-based materials are susceptible to degradation, mainly those with no or low inorganic filler content [6,7] such as sealants. The early effect of degradation is an increased surface roughness, which raise biofilm accumulation and colour change due to stain penetration into the polymeric matrix [7, 8]. In the chemical composition of the sealing materials, the introduction of the fluoride ion (F -) delimited the fourth generation of sealants, the first three being different in the way of initiating the polymerization (UV, chemical and visible light). In resin-based sealant, fluoride can be introduced by two methods: addition of fluorinated salt or anion exchange with an organic fluoride compound [9,10]. Fluoride release sealants protect the enamel adjacent to the cracks, demineralized after conditioning with phosphoric acid, better than conventional ones, even if they tend to be more viscous [11].

The *novelty* of the study consists in the optical stability assessment for materials use in dental sealants since these properties are evaluated mainly for restorative materials.

In view of the fact that information on the colour changes of pit and fissure sealants are limited, the purpose of this study was to examine the changes in dental sealants colour, in order to asses' structural variations.

## 2. Experimental

For this in vitro study we evaluate 2 resin based dental sealants, with different filler amount (Table 1).

*Table 1. Dental sealants composition*

| Material | Organic phase | Inorganic phase | Company |
|---|---|---|---|
| **Fissurit FX** | Bis-GMA -UDMA | 55% | VOCO |
| **Fotoseal** | Bis-GMA -UDMA -TEGDMA | 40% | ICCRR, Cluj-Napoca |

### 2.1. Colour assessments

40 discs for every dental sealant were made (12 mm diameter and 1 mm thick), using a prefabricated device (Porcelain Sempler, Smile Line, Switzerland). The sealant was applied into this pattern using specific applicators. After 60 seconds photo polymerization, using a LED dental lamp (Woodpecker), the disc was removed from the pattern and photo polymerized on the opposite surface for another 30 seconds. The discs were measured with an electronic chisel in order to respect the thickness; if necessary, polished was perform with abrasive paper. After that, the specimens were introduced into ultrasonic bath, with distilled water, for 5 minutes, to remove all impurities.

To evaluate colour stability, specimens of each sealant (n=10) were distributed in subgroups (n=4) assigned according to used beverages (orange juice, non-carbonated soft drink, Coca-Cola® carbonated drink, and distilled water).

We selected beverages which are popular among teenagers and young people in Romania: orange juice (freshly made from orange), non-carbonated soft drink orange flavour (Tymbark®), carbonated soft drink (Coca-Cola®, The Coca-Cola Company). Beverages were maintained at 4°C during the study period (14 days) and at room temperature, before placing specimens. Each specimen was individually immersed in a container with 5 ml of beverage at room temperature for one hour daily. Specimens were washed with distilled water and stored again in distilled water at 37°C until used. As a control group, specimens were individually immersed in vessels with distilled water for 24 h per day, spending one hour at room temperature. Containers were sealed during immersion to prevent the evaporation, and all solutions were renewed daily.

For colour evaluation, a spectrophotometer (Vita EasyShade® V, Vita Zahnfabrik, Bad Säckingen, Germany) was used; and according to the CIE lab system, we assessed the colour parameters: L* (brightness), a* (chromatic on the red-green axis), b* (chromatic on the yellow-blue axis). Measurement were done by one examiner, to decrease inter-human variation, with the right angle, according to the Commission Internationale del' Eclairage (CIE lab) [12]. In order to reduce the effect of external light, colour measurements were made at midday, in the same place, every time. The instrument was automatically calibrated, using an integrated calibration plate, on the base station, after each determination. For every sample, at each assessment, we recorded three values to allow a better appraisal. The evaluations were made at the beginning of the study, after 1, 7 and 14 day, respectively.

The variation of the colour parameters L*, a*, b* was calculated as the difference between the initial values and values recorded at 24h (ΔL1*, Δa1*, Δb1*), 7 days (ΔL2*, Δa2*, Δb2*) and 14 days (ΔL3*, Δa3*, Δb3*), for each of the tested materials. The colour difference ΔEab* between the initial and recorded parameters at 24h (ΔE1*), 7 days (ΔE2*) and 14 days (ΔE3 *) was calculated using the formula: ΔE = [(ΔL*)2 + (Δa*)2 + (Δb*)2]1/2. The aim of this study was to evaluate dental sealants colour changes related to specific beverage.

### 2.2. Fluoride release

Fluoride decreases the number of bacteria, by inhibiting bacterial metabolism and favours remineralization of enamel from incipient carious lesions, by replacing hydroxyapatite groups with those of Fluor apatite, more resistant to acid attack [9,11]. The concentration of fluorine anions in each material was determined by potentiometric method, with fluoride ion selective electrode, electrochemical sensors that transform ions concentration in a solution into electric potential. From each sealing material, 10 samples were obtained in disk configuration (n = 10), measuring 15 mm in diameter and 1 mm in thickness, in Teflon moulds by exposure to visible radiation generated by a LED dental lamp (LED. D Woodpecker) for 20 seconds at five points on the surface of the disk. Samples were introduced for 24 hours in 5 ml concentrated solution of TISAB III (Total ionic strength adjustment buffer), (HI 4010-06, Hanna Instruments, USA) and 45 ml distilled water (Simplicity UV, Water Purification System Millipore, USA), in polyethylene containers and kept in a thermostatic bath at 37°C. They were then removed and the concentration of fluoride anions (mV), released from the samples, in the respective solution, was measured with the selective fluoride ion electrode (Combination Fluoride Electrodes HI 4110, Hanna instruments), at 21°C. After every single measurement, the samples from each material were placed in the same storage container, made of polyethylene and kept in a thermostatic bath at 37°C, until the next measurement. The present study aims to assess which of these sealants has a more intense optical stability, and release a larger fluoride quantity over time.

### 2.3. Statistics

The ANOVA test for repeated measurements ($\alpha$ = 0.05) was used to analyse the influence of the immersion time, the nature of solution and the type of dental sealant on colour parameters variation. Multiple comparisons were adjusted using the Bonferroni method. Data were processed using a specific program (IBM SPSS Statistics v20.0.0, Chicago, Ill).

## 3. Results

Sealing materials create a mechanical barrier and transform occlusal surfaces negative details in plane areas, a measure that prevent colonization of caries-related bacterial species on enamel surface (Fig. 1).

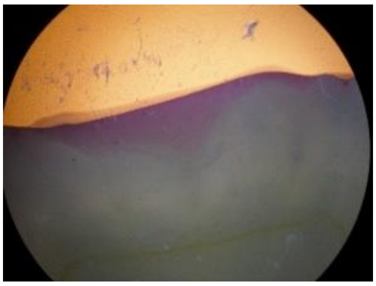

*Fig. 1. U-shaped appearance of occlusal fissures. The sealing material makes the occlusal surface less retentive (Fotoseal®) (color online)*

### 3.1. Colour assessments

Colour changes occurred even after 24 hours for resin-based sealants used in our study, according to selected solution encoded as follow: orange juice (OJ), non- carbonated soft drink (NCD), carbonated drink (CD) and distilled water (DW) (Fig. 2).

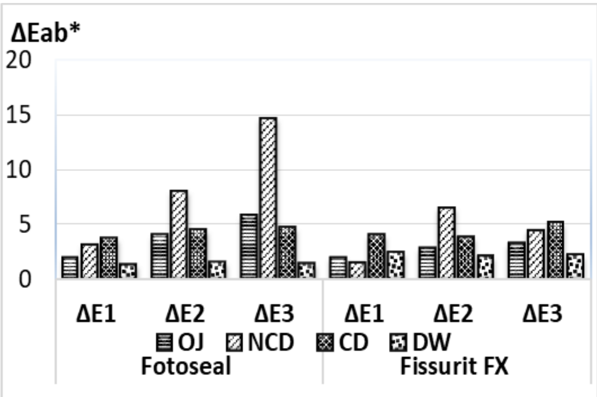


*Fig. 2. ΔEab * variation for evaluated sealant at 1-ΔE1, 7-ΔE2 and 14-ΔE3 days*

There are statistically significant differences between Fotoseal and Fissurit FX, at 1, 7 respectively 14 days, for samples exposed to NCD ($p<0.05$).

Regarding the variation of brightness, L* parameter, for both evaluated materials express dissimilarities (Fig. 3).

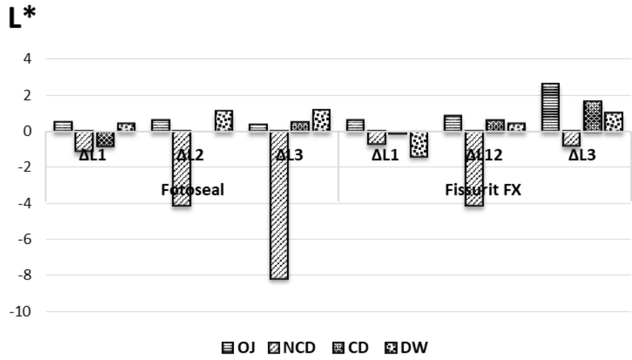


*Fig. 3. ΔL * variation for evaluated sealant at 1-ΔL1, 7-ΔL2 and 14-ΔL3 days*

For ΔL, with the exception of values measured after 14 days for NCD ($p<0.001$), no variances with statistically significant differences were observed. Brightness varied by increase in OJ, CD and DW and decrease in NCD.

Considering the variation of a*parameter, the main differences were presented by Fotoseal® (Fig. 4).

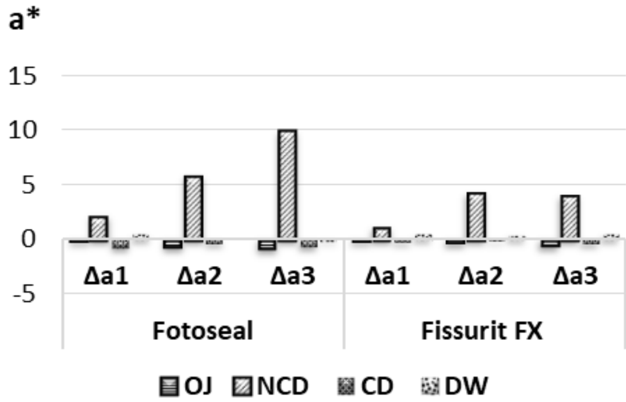


*Fig. 4. Δa* variation for evaluated sealant at 1-Δa1, 7-Δa2 and 14-Δa3 days*

There were statistically significant differences between materials at all 3-time intervals, only for samples immersed in NCD ($p<0.001$) (Fig. 3). For all 2 materials, in OJ and CD the Δa*values became negative (the colour turned to green) and in NCD the Δa* values became positive (the colour turned to red).

Regarding the dissimilarity of parameter b*, the largest variations were presented by the material Fotoseal® (Fig. 5).

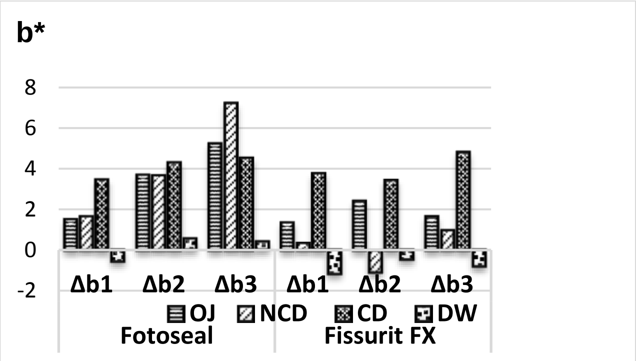


*Fig. 5. Δb* variation for evaluated sealant at 1-Δb1, 7-Δb2 and 14-Δb3 days*

Significant differences were observed between materials after immersion in OJ (at 7 days interval) and NCD (at 7- and 14-days interval) ($p < 0.001$) (Fig.4). For all materials, Δb* had positive values (the colour turned to yellow), except for immersion in flat water, where the Δb* values are negative (the colour turned to blue).

SEM images reveal discontinuities in material structure, in accordance with beverage characteristics (Fig. 6).

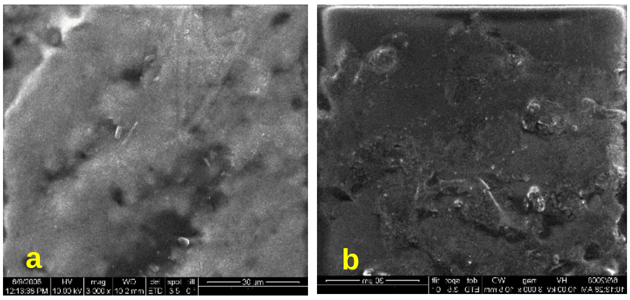


*Fig. 6. SEM images for Fotoseal® immersed in CD (a) and DW (b) Fluoride release*

Previous to fluoride ion exchange evaluation, the electrode was calibrated using a series of standard solutions of concentrations ranging from $10^{-5}$ to $10^{-2}$mol / L F. The concentration of fluoride anions in each resin-based sealant was transformed into parts per million (ppm). We notice for both evaluated materials, that the largest amount of fluoride reside after day 1 and decrease progressively until day 4 (Fig.7).

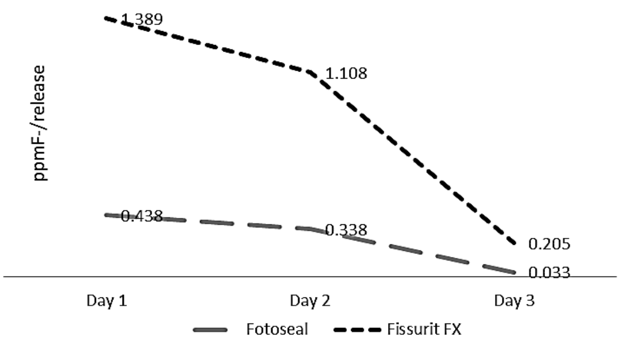


*Fig. 7. Fluoride release-quantitative evaluation*

### 4. Discussions

Pit and fissure sealants are recommended for occlusal surfaces decay prevention. Intended for this particular reason, resin-based materials are preferred, because of mechanical resistance and durability over time. All these attributes can be achieved if the sealants are applied in respect with the manufacturer protocol, in dry field, and the follow up at six-month intervals is respected [3]. Dental sealants may experience colour changes, within a clinically acceptable range; however, the material should be evaluated during regular examination appointments for colour stability and/or surface defects [8].

The optical attributes of a material are above all related with the chromatic properties: hue, brightness, saturation, translucency and opacity [12, 13]. These can be influenced by coloured solutions, natural or artificial, thus affecting chromatic stability of the material. In contrast to the composite materials used for restorations, found in a wide variety of shades and opacities, to play as better the natural appearance of teeth, resin-based sealing materials are often found in a single hue. This is because sealants are employed in the fissures of the posterior teeth and did not affect dental or facial aesthetics [8, 10].

The chromatic stability of dental sealants is not an important factor, from aesthetic point of view, since they are used in the posterior area, but the changes in material colour, associated with marginal microleakage can generate changes in dental sealant structure with subsequent consequences on mechanical properties. For this reason, our study aimed to add information regarding the possible alterations of sealants colour, in oral environment, when exposed to chromatic agents from beverages. Resin based materials are investigated for staining frequently for coffee or red wine [14]. In our study, since the children benefit mainly from dental sealants, we chose products that could be easily found in children diet.

Materials used in this study are resin-based with organic and inorganic filler: Fissurit FX® comprise 55% filler; Fotoseal® has a smaller amount of filler 40%. We assume that this element plays an important role in colour differences between evaluated products. Inorganic and organic fillers exert a direct influence on resin-based material chromatic changes; the highest organic filler amount, the lowest chromatic changes. The explanation resides in direct association between organic component and material colour stability [11, 13]. With increased fillers, the colour stability would be expected to be higher, due to the lower percentage of the resin matrix. As a result of an inadequate resin polymerisation, the resin-based materials easily absorb stains and the colour may change [14, 15]. Hydrophilic stains are readily soluble in aqueous solutions and penetrate easily into materials [16]. Hydrophobic resin composites exhibit superior colour stability and resistance to colour change [15, 17]. In our study, both products show some colour instability even when stored in distilled water.

Colour alteration in resin based dental sealants certified the structural transformations in the material as a result of various factors: alters of the surface morphology, extrinsic staining, chemical differences of resin components (polymeric structure, photo-initiator system). As a result of resin-based composites degradation, micro-flaws or gaps in the matrix/filler interface allow micro-passageways through which stains can penetrate easily [16,17]. Adequate adhesion at the interface between enamel and resin- based sealant material is crucial for achieving good clinical performance [18]. The filler characteristics as well as their integration in the composite properties are key factors for adequate adhesion [19].

Light cured unfilled resins are shown in the literature to have greater colour stability than conventional composites and that could be explained by the presence of the silane surrounding the composite particles, since silanes have high water absorption levels [20]. In line with this, we can use dental sealant colour change as indicator for external or internal changes taking place in material structure [21].

The greater colour change detected in alkaline or acidic media may be related to the degradation of different components leading to subsurface damage [21]. This was followed by leaching out of hydrolysed components creating voids allowing diffusion of different stains [21, 22]. This structural change may create components with different refractive indexes affecting the pattern of light reflection [23, 24]. The application of different colorimetric measurements, such as the CIE L*a*b* is regarded as representing better visual perception in dentistry [25].

The addition of fluoride to pit and fissure sealants was considered more than 25 years ago [26]. The fluoride containing sealant did not have better retention when compared to the conventional [26]; their bioactive properties present interest especially in constant fluoride release for a prolonged period of time and the ability to function as a reservoir of fluoride ion for enamel and to promote Fluor apatite formation [27]. For dental sealants evaluated in this in vitro study the fluorinated salt is added to the un-polymerized resin, and after the polymerization, the salt is dissolved and the fluoride ions are released. The organic compound releases fluoride ions, while maintaining the physical properties of the material [28]. Hydroxyl and chloride ions in enamel replace the fluoride ion in the sealing material. Thus, the released fluoride will be included in the hard structures of the tooth and will favour the remineralization process of the demineralized enamel. Fluoride is released in large quantities on the first day, decreases sharply in the next 24 hours and then slowly, up to 30 days [29]. The level of fluoride emission does not depend on the concentration of this ion in the material, but on its external diffusion and the hydrophilicity of the material, because the ions are released from the fraction of the material, which absorbs water [30]. Fissurit FX and Fotoseal sealants are more stable in relation to water sorption and therefore the amount of fluoride anions released is lower. Fotoseal releases less fluoride compared to Fissurit FX. The fluoride exchange permitted us to assume a biodynamic comportment for assessed sealants [29, 30]. The fact that the evaluated resin-based dental sealants release the greatest amount of fluoride in the first 24 hours confirms the results of the literature studies [31].

## 5. Conclusions

Within the limitations of the present study, it appears that the colour stability varied among evaluated resin based dental sealants. Knowing this phenomenon is vital as this could be the earliest indicator for the initiation of secondary caries. The clinical significance of these colour changes must be closely correlated with structural alterations of the sealing material, because the sealing materials are used on the lateral teeth and have no aesthetic but only prophylactic purpose.

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