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THE STUDY OF PIT AND FISSURE SEALANTS CONCERNING WATER SORPTION AND SOLUBILITY

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ABSTRACT. Improved dental materials are a requirement in these modern times, because of the highly percent of dental decay found at children. Four commercial pit and fissure sealants have been studied in respect of water sorption and solubility (1, 3, 7 and 14 days).These measurements prove the stability of a material, as well as the adhesion to enamel and the resistance to wear. The materials taking into account are two resin- based sealants - Fotoseal® (Babeş-Bolyai University, Raluca Ripan Chemistry Research Institute), Fissurit FX® (VoCo), one gass-ionomer - Fuji Triage® (GC Fuji) and one compomer - Dyract Seal® (Dentsply). The statistical analysis used a Mixt ANOVA design, with the significance level set at $p \leq 0.01$. Firstly, there were analised the differences between the days of measurement, without taking into account the material type. Secondly, there were examined the differences between materials and finally, the interaction between material type and day of measurement. We also calculated the magnitude of the clinical effect of material type, on each of the days of measurement. Differences in chemical composition determine a modified behavior of these materials. The results showed that Fissurit FX had the lowest values of water sorption and solubility, closely followed by Fotoseal. Dyract Seal had higher values. In the same time, Fuji Triage showed the highest rates for water sorption and a fluctuant behavior concerning solubility, with increased level in the first day of measurement, decreased values in the next days (3, 7) and another small enhancement in the last day of measurement (14).

Keywords: *dental materials, composite resin, glass-ionomers, compomer, water sorption, solubility*

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INTRODUCTION

The chemical composition is closely correlated with the clinical behavior of a dental material. From 1962, since Bowen discovered the resin bis-GMA (2,2-bis(4-(2'-hydroxy-3'methacryloyloxy-propoxy)phenyl)propane), the development of dental composites dedicated to adhesive dentistry grew a lot.

Among the methods used in preventive dentistry, pit and fissure sealing is frequently indicated on both primary and permanent teeth, aiming to block the dental plaque retention in deep, narrow zones on the dental surface and to minimize dental decay initiation. Most pit and fissure sealants are composite resins, having an organic fraction based on bis-GMA, UDMA (urethane dimethacrylate) or TEGDMA (triethylene glycol dimethacrylate) or other dimethacrylates, small inorganic particles of fused silica, quartz, barium, strontium or zirconium silicates as fillers, and a separation interface, silane [1].

Before Bowen's achievement, Buonocore introduced in 1955 the enamel etching technique, with orthophosphoric acid 35-40% [2,3], that allows for mechanical and chemical retention of the composite resins to the dental enamel [4]. The setting is achieved through a polymerization reaction and the result is a polymeric matrix. The polymerization can be initiated by a radiation- UV or visible light, which acts on aromatic ketones, or a chemical reaction between benzoil peroxide (initiator) and tertiary amine (activator), resulting free radicals [1,5]. Dental resins used as pit and fissure sealants have less particles than composites used for fillings, because they need a low viscosity and the capacity to flow and penetrate the small spaces on the dental surfaces. Bis-GMA has a high viscosity, which explain for the addition of a diluent in the form of either methyl methacrylate (MMA), glycol dimethacrylate (GDMA) or triethylene glycol dimethacrylate (TEGDMA).

However, the decreased filler percentage is responsible for polymerization shrinkage and a low elasticity module [6,7].

Glass-ionomer cements, a different group of materials used in preventive dentistry, were introduced in 1972, by Wilson and Kent and they contain polyacrylic acid, itaconic, maleic, mesaconic or other unsaturated acids [8]. The advantages of these materials are physical and chemical bond with the enamel, biocompatibility, fluoride releasing and ease of handling; as disadvantages, their lower retention and resistance to wear in comparison with dental composites, are of clinical relevance [9].

In 1997 a hybrid material was introduced, a composite combined with a polyacid, which was named compomer, containing strontium-alumino-fluoro-phosphor- silicate glass, highly dispersed silicone dioxide, ammonium salt of phosphoric acid modified methacrylate resin, carboxylic acid modified methacrylate resin and diethylenglycol dimethacrylate.

Other hybrid materials are resin-modified glass-ionomer cements, with improved properties than the conventional glass-ionomer cements: photo-polymerization ability, better marginal sealing, better resistance and fluoride release, less material wear and fractures [10,11].

Sorption is the penetration capacity of a liquid within the mass of the composite resins. The results are hydrolytic degradation of the bonding agent, silane, at the interface between matrix and inorganic filler, resulting in particle detachment.

Solubility is the dilution of the unreactive monomer in a solvent, effecting the dimensional stability, mechanical properties and bonding strength [12]. Water sorption and solubility are related with the chemical and dimensional stability of the resin matrix [13]. Degradation induced by water influences the clinical performances of a material and is proportionally reverse with the filler content [14]. Also, the degradation of the organic matrix depends on the conversion degree of C-C double bonds into single bonds. For that, the initiation system of photo-polymerization and the composition of the monomers are important factors [15].

Solubility and water diffusion inside the matrix are lower with the increase of the polymerization rate and density of the matrix.

The aim of this study was to compare the sorption and solubility of a local material, Fotoseal, with a commercial composite (Fissurit FX), a compomer (Dyract Seal) and a glass-ionomer (Fuji Triage). The null hypothesis is that there were no difference among the 1. water sorption and 2. solubility rates of the tested materials.

RESULTS AND DISCUSSION

In order to analyze data, we used a Mixt ANOVA design with two independent variables, the ***material type*** (Fissurit FX, Fotoseal, Dyract Seal and Fuji Triage) and the ***day of measurement*** (Day 1, Day 3, Day 7 and Day 14); the significance level was set at $p \leq 0.01$.

Results for **water sorption** are presented in table 1.

The main effect for *day of measurement* was found to be statistically significant, $F(5.36)=49.047$ (SSE=105.75, $p=0.001$, $\eta^2=.803$, where $\eta^2>0.14$ showes a major clinical effect). Post-hoc Bonferroni comparison showed statistically significant differences between Day 1 compared with Day 7 ($p<0.001$) and Day 14 ($p<0.001$), Day 3 compared with Day 7 ($p<0.001$) and Day 14 ($p<0.001$) and Day 7 compared with Day 14 ($p<0.001$).

There was a significant main effect of *material type*, $F(3. 12)=86.178$ (SSE=360.128, $p=0.001$, $\eta^2=.956$, where $\eta^2>0.14$ showes a major clinical effect), nonsignificant differences were found only between Fotoseal and Fissurit, all other pairwise comparison was found to be significant ($p<0.001$).

Table 1. Water sorption (µg/mm³) as resulted from measurements in day 1, 3, 7 and 14 for the tested materials.

	Material	Mean	Std. Deviation
Day1	Dyractseal	16.515	1.549
	Fissurit	3.576	0.728
	Fotoseal	6.18	1.487
	GC-Fuji	24.84	7.383
Day3	Dyractseal	18.072	1.498
	Fissurit	2.4575	0.957
	Fotoseal	6.642	0.288
	GC-Fuji	25.017	1.645
Day7	Dyractseal	20.477	2.463
	Fissurit	3.075	0.988
	Fotoseal	9.075	1.054
	GC-Fuji	33.8	6.041
Day14	Dyractseal	20.815	0.881
	Fissurit	3.76	0.723
	Fotoseal	8.19	0.391
	GC-Fuji	43.342	6.600

We found a significant *material type x day of measurement interaction*, $F(9.36)=21.568$ (SSE=567.11, $p=0.001$, $\eta^2=.844$, major clinical effect), meaning that the main effect of one variable is not constant regarding the level of the other variable (figure 1).

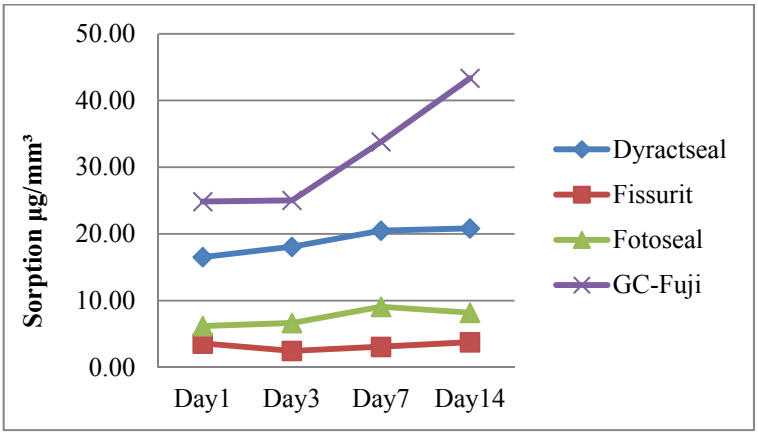

Figure 1. Water sorption for different types of material. Fissurit FX has the lowest water sorption, followed by Fotoseal, Dyract Seal and Fuji Triage.

Data collected on Day 1 showed a significant effect of *material type*, F(3.12)=25.713 (SSE=178.99, p=0.001, η^2=.865, a large clinical effect). At Day 1 we found significant differences between Fissurit and Dyract Seal (p<0.001), Fissurit and Fuji Triage (p<0.001), Fotoseal and Fuji Triage (p<0.001), Fotoseal and Dyract Seal (p<0.001).

Data collected on Day 3 illustrated a significant effect of *material type*, F(3.12)= 288.137 (SSE=17.86, p=0.001, η^2=.986, with a large clinical effect). We found significant differences between Fissurit and Fotoseal (p=0.002), Fissurit and Dyract Seal (p<0.001), Fissurit and Fuji Triage (p<0.001), Fotoseal and Dyract Seal (p<0.001), Fotoseal and Fuji Triage (p<0.001), Dyract Seal and Fuji Triage (p<0.001).

Data collected on Day 7 demonstrated a significant effect of *material type*, F(3.12)= 65.754 (SSE=133.95, p=0.001, η^2=.943, with a major clinical effect). At Day 7 the significant differences were between Fissurit and Dyract Seal (p<0.001), Fissurit and Fuji Triage (p<0.001), Fotoseal and Dyract Seal (p<0.001), Fotoseal and Fuji Triage (p<0.001), Dyract Seal and Fuji Triage (p<0.001). Only between Fissurit and Fotoseal, there were no significant differences.

Data collected on Day 14 showed a significant effect of *material type*, F(3.12)=11.939 (SSE=135.06, p=0.001, η^2=.965), with significant differences between Fissurit and Dyract Seal (p<0.001), Fissurit and Fuji Triage (p<0.001), Fotoseal and Dyract Seal (p<0.001), Fotoseal and Fuji Triage (p<0.001), Dyract Seal and Fuji Triage (p<0.001). As in Day 7, between Fissurit and Fotoseal, there were no significant differences.

Solubility measures were analyzed using the same design (table 2).

Table 2. Solubility for the tested materials (μg/mm³)

	Material	**Mean**	**Std. Deviation**
Day1	Dyractseal	-24.425	0.923
	Fissurit	-5.3875	1.465
	Fotoseal	-14.992	3.071
	GC-Fuji	-35.977	23.150
Day3	Dyractseal	-38.74	2.891
	Fissurit	-9.98	1.560
	Fotoseal	-21.372	1.086
	GC-Fuji	-18.947	11.347
Day7	Dyractseal	-41.8	5.444
	Fissurit	-14.105	0.605
	Fotoseal	-23.747	2.517
	GC-Fuji	-14.345	12.170
Day14	Dyractseal	-42.34	5.594
	Fissurit	-15.782	0.575
	Fotoseal	-27.077	1.061
	GC-Fuji	-16.51	11.861

Main effect for *day of measurement* was found to be statistically significant, F(5.36)=4.895 (SSE=567.11, p=0.006, η^2=.29, a major clinical effect). Post-hoc Bonferroni comparison, showed statistically significant differences between Day 3 compared with Day 14 (p<0.001), Day 7 compared with Day 14 (p<0.001).

There was also a significant main effect of *material type*, F(3.12)=8.242 (SSE=2574.03, p=0.003, η^2=.673, with a major clinical effect), significant differences were found only between Dyract Seal and Fissurit.

More important, we found a significant *material type x day of measurement interaction*, F(9.36)=16.639 (SSE=567.11, p=0.001, η^2=.806, a major clinical effect), meaning that main effect of one variable are not constant across the level of the other variable (figure 2).

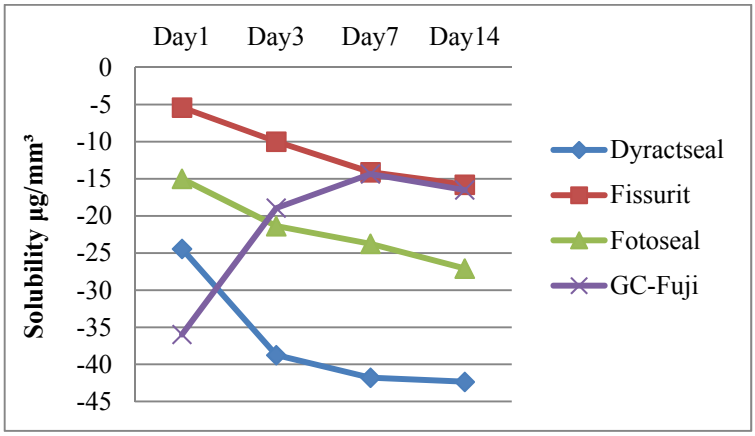

Figure 2. Solubility for different type of materials. Fissurit FX has the lowest value, followed by Fotoseal, Dyract Seal. Fuji Triage has the highest value in Day 1, then the values decrese in Day 3 and Dat 7 and increase slightly in Day 14.

Data collected on Day 1 didn't show a significant effect of *material type*, F(3.12)=4.992 (SSE=1645.17, p=0.018, η^2=.555).

Data collected on Day 3 showed a significant effect of *material type*, F(3.12)=16.452 (SSE=422.23, p=0.001, η^2=.804), with significant differences between Fissurit and Dyract Seal (p<0.001), Fotoseal and Dyract Seal (p=0.008), Dyract Seal and Fuji Triage (p=0.003).

Data collected on Day 7 illustrated a significant effect of *material type*, F(3.12)=14.659 (SSE=553.43, p=0.001, η^2=.786). There were significant differences between Fissurit and Dyract Seal (p=0.001), Fotoseal and Dyract Seal (p=0.001), Dyract Seal and Fuji Triage (p=0.001).

Data collected on Day 14 showed a significant effect of *material type,* $F(3.12)=14.185$ (SSE=520.31, $p=0.001$, $\eta^2=.780$), with significant differences between Fissurit and Dyract Seal ($p=0.001$), Fotoseal and Dyract Seal ($p=0.001$), Dyract Seal and Fuji Triage ($p=0.001$).

The first requisite for an efficient sealant is a viscosity that allows penetration into low-dimension spaces [16]. Chemically-cured sealants have usually no inorganic filler, so, the water sorption and solubility demonstrate very high levels. Photo-cured sealants are with or without inorganic filler added, but they have a low permeation rate and good physical properties, such as low levels of abrasion, heat expansion, water sorption and solubility [17]. In our study. Fissurit FX and Fotoseal, as bis-GMA based materials present lower water sorption and solubility, than Dyract Seal and Fuji Triage.

Also, because of the resin- matrix, Fissurit FX and Fotoseal have high retention rates, but in a clinical moist environment, a glass-ionomer is more suitable [18].

Other requirements for a good sealing material are: short setting time, same thermal conductivity as tooth, good bond strength with the enamel, fluoride-releasing or chemically inert, anti-cariogenic, reduced polymerization shrinkage.

Fluoride containing sealants are of two types. In the first instance, soluble fluoride is added to unpolymerized resin and after the polymerization, the salt dissolves and fluoride ions are released. In this case, the solubility and water sorption are increased. In the second case, an organic fluoride component, chemically bond to the resin, is added and enhances the fluoride release, while maintaining the physical properties of the material [9].

Fissurit FX contains fluoridel (2% NaF), wich is an inorganic component [19,20], as well as, the fluoro-silicate glass, included in Dyract Seal. This affects the physical properties, of water sorption and solubility. Fuji Triage has a high fluoride content, but a low rate of released fluoride [21,22]. For that, it has the highest water sorption and solubility, in the first day, but, also, a low cytotoxic effect.

Besides of the disadvantages, fluoride release is a very important property of glass-ionomers and resin-modified glass-ionomer cements, because fluoride ions reduce the amount of microorganisms and reinforces the structure of enamel. It also determines the clinical selection of the patients who need this type of material [10]. Two reactions occur in the curing of Dyract Seal: quick photo-initiated polymerization and slow acid-base reaction. The last one represents the basis of the continuous release of fluoride ions, an important property of Dyract Seal [23].

Water sorption has not only disadvantages. Because of the increased volume of the material, it contributes to closure of the microscopic gaps resulted from polymerization shrinkage [24].

CONCLUSIONS

It can be concluded that water sorption and solubility levels are depending on material type and time.

1. Resin-based sealants, Fissurit FX and Fotoseal, the local material, demonstrated low values of water sorption and solubility.

2. Fuji-Triage, glass-ionomer based material, showed the highest values of water sorption for each day of measurement and the highest value of solubility in the first day of measurement.

3. Dyract Seal, polyacid modified composite resin, showed intermediate values of water sorption for each day of measurement and just in the first day for solubility. Differences concerning solubility became statistically significant in day 3, 7 and 14.

EXPERIMENTAL SECTION

Materials

Table 3. Materials used in this study: Bis-GMA - 2,2-bis(4-(2'-hydroxy-3'methacryloyloxy-propoxy)phenyl)propane, UDMA- urethane dymethacrylate TEGDMA- triethyleneglycol- dimethacrylate

Material	Class of Material	Organic phase	Inorganic phase	Company
Fissurit FX	Composite resin	-Bis-GMA -UDMA	55%fiiling	VOCO
Fotoseal	Composite resin	-Bis-GMA -UDMA -TEGDMA	-hidroxylapatite with fluorine -alumino- silicate glass -colloidal silica	ICCRR,Cluj-Napoca
Dyract Seal	Compomer	-carboxylic acid modified methacrylate resin -ammonium salt of phos-phoric acid modified methacrylate resin -diethylenglycol dimethacrylate.	-strontium-alumino- fluoro-phosphor- silicate glass, -highly dispersed silicone dioxide	Dentsply
Fuji Triage	Glass-ionomer	-unsaturated polyacid	-high fluoride content	GC America

Bis-GMA and hydroxylapatite from Fotoseal were synthetized in ICCRR, Cluj-Napoca laboratory.

Method

A total of forty specimens were fabricated, ten for each material (n=10), following ISO specifications 4049/2000.

Materials were inserted in a teflon mold, disk-shaped, to obtain samples of 15±1 mm diameter and 1 mm thickness. The sealing material were photo-cured with a LED Woodpecker lamp (Guilin Woodpecker Medical Instrument Co., Ltd), for 30 seconds; after the disks removal, they were polished with sandpaper to gain a smooth and flat surface.

Specimens have been placed in a desiccator DURAN (DURAN Produktions GmbH&Co.KG, Mainz, Germania), at a temperature of 23ºC, until a constant weight was achieved (m1) (Partner 220mg, Partner Corporation, Bucharest). At this constant mass, the volume was calculated, as a result between diameter and thickness. Then, the disks were submerged in glass test tubes (SIMAX, 25ml, Czech Republic), that contained distilled water (10 ml) and they were maintained at 37ºC. In the day 1st, 3rd, 7th and 14th, specimens were removed from water and dried with absorbent paper, then weighed (m2). After which, the samples were reconditioned to constant mass in the desiccator (m3).

Water absorption and solubility were calculated according to the formulas:

$$W = \frac{m2 - m3}{V}$$

$$S = \frac{m1 - m3}{V}$$

$m1$- constant sample weight before immersion in water (μg)
$m2$- sample weight after immersion in water (μg)
$m3$- constant sample weight kept in a desiccator, after immersion in water (μg)
V- sample volume after a constant mass (m1) was obtained (mm3) [25, 26].

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