UNIVERSIDADE DE SÃO PAULO
FACULDADE DE ODONTOLOGIA DE BAURU

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# Influence of the incorporation of functionalized $TiO_2$ nanotubes on the properties of resins for 3D printing

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Orientador: Prof. Dr. Adilson Yoshio Furuse

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“If I have seen further, it is by standing upon the shoulders of giants”

**Sir Isaac Newton**

**ABSTRACT**

**Influence of the incorporation of functionalized TiO2 nanotubes on the properties of resins for 3D printing**

**Introduction:** Since it is a highly versatile manufacturing method that can be applied to metals, ceramics and polymers, additive manufacturing, also known as 3D printing, is rapidly gaining space in dentistry, however, there is still a great potential for improvement of the materials. **Objective:** The objective of this study was to evaluate the influence of the addition of functionalized $TiO_2$ nanostructures on physicochemical and mechanical properties of resins for 3D printing. **Material and methods:** Two commercially available resins where be used: Cosmos TEMP – Yller Biomaterials, Smart Print Bio Temp - Smart Dent. $TiO_2$ nanostructures of were functionalized with 3-Aminopropyl Trimethoxysilane (APTMS) or 3-Trimethoxysilyl-Propyl-Methacrylate (TMSPM) silanes. The incorporation of nanostructures of $TiO_2$ into resins was made by mechanical mixing, in mass proportions of 0.3wt% and 0.9wt%. Resins without nanotubes were used as control. With the specimens divided into groups according to the resin and the concentration of nanostructures incorporated, the flexural strength, modulus of elasticity, water solubility and sorption and color stability were evaluated. The results were analyzed using the two-way ANOVA and Tukey tests, adopting a significance level of 5%. **Results:** For the flexural strength and Young's modulus, significant differences were found between the resins used, between the presence of nanotubes and the functionalizations ($p < 0.05$). The interaction effect between resin and functionalization was also significant ($p < 0.05$). For solubility, the lowest values were observed for Smart Print Bio Temp resin with the addition of 0.9wt% of APTMS-functionalized nanotubes and the highest for Cosmos Temp resin without nanotubes. For color stability using the CIE-Lab formula after aging, significant differences were observed for resin and addition of functionalized nanotubes ($p < 0.05$). The interaction effect between resin and addition of nanotubes was also significant ($p < 0.05$). The color stability $\Delta E00$ addressed by CIED2000 showed the same trend. **Conclusion:** Flexural strength, modulus of elasticity, water sorption and color stability of resins for 3D printing were influenced by the addition of $TiO_2$ nanotubes functionalized with APTMS and TMSPM in the concentrations of 0.3wt% and 0.9wt%. Functionalized nanotube additives may be used to improve resinous materials used for additive manufacturing.

Keywords: 3D printing. Polymers. Nanostructures.

# RESUMO

## Influência da incorporação de nanotubos funcionalizados de $TiO_2$ nas propriedades de resinas para impressão 3D.

**Introdução:** Por ser um método de fabricação altamente versátil que pode ser aplicado em metais, cerâmicas e polímeros, a manufatura aditiva, também conhecida como impressão 3D, vem ganhando espaço rapidamente na odontologia, porém, ainda há um grande potencial de aprimoramento dos materiais. **Objetivo:** O objetivo deste estudo foi avaliar a influência da adição de nanoestruturas de $TiO_2$ funcionalizadas nas propriedades físico-químicas e mecânicas de resinas para impressão 3D. **Material e métodos:** Duas resinas comercialmente disponíveis: Cosmos TEMP - Yller Biomaterials, Smart Print Bio Temp - Smart Dent foram utilizadas. As nanoestruturas de TiO2 foram funcionalizadas com 3-Aminopropil Trimetoxissilano (APTMS) ou 3-Trimetoxissilil-Propil-Metacrilato (TMSPM). A incorporação das nanoestruturas de TiO2 nas resinas foi feita por mistura mecânica, nas proporções de massa de 0,3% e 0,9%. Resinas sem nanotubos foram utilizadas como controle. Com os corpos-de-prova divididos em grupos de acordo com a resina e a concentração de nanoestruturas incorporadas, foram avaliados a resistência à flexão, módulo de elasticidade, solubilidade e sorção de água e estabilidade de cor. Os resultados foram analisados pelos testes ANOVA de dois fatores e Tukey, adotando-se nível de significância de 5%. **Resultados:** Para a resistência à flexão e modulo de elasticidade, diferenças significantes foram encontradas entre as resinas utilizadas, entre a presença de nanotubos e as funcionalizações ($p < 0.05$). O efeito de interação entre a resina utilizada e adição de nanotubos também foi significante ($p < 0.05$). Para solubilidade, os menores valores foram observados para a resina Smart Print Bio Temp com adição de 0,9% em peso de nanotubos funcionalizados com APTMS e os maiores para a resina Cosmos Temp sem nanotubos. Para a estabilidade de cor após envelhecimento utilizando a formula CIE-Lab, diferenças significantes foram observadas para a resina e a adição de nanotubos funcionalizados ($p < 0.05$). O efeito de interação entre resina e adição de nanotubos também foi significante ($p < 0.05$). A estabilidade de cor $\Delta E00$ avaliada por CIED2000 apresentou a mesma tendência. **Conclusion:** Resistência à flexão, modulo de elasticidade, sorção de água e estabilidade de cor de resinas para impressão 3D foram influênciadas pela adição de nanotubos de $TiO_2$ funcionalizados com APTMS e TMSPM nas concentrações de 0,3% e 0,9% em peso. Aditivos de nanotubos funcionalizados podem ser utilizados para aprimorar materiais resinosos para manufatura aditiva.

Palavras-chave: Impressão 3D. Polímeros. Nanoestruturas.

**LIST OF ABBREVIATIONS AND ACRONYMS**

| | |
|---|---|
| APTMS | 3-Aminopropyl Trimethoxysilane Silane |
| TMSPM | 3-Trimethoxysilyl Propyl Methacrylate |
| TiO2 | Titanium dioxide |
| SLS | Selective laser sintering |
| SLA | Stereolithography |
| SLM | Selective Laser Melting |
| DLP | Digital Light Processing |
| LED | Light-emitting Diode |
| TiOnts | Titanium dioxide nanotubes |

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# 1 Introduction

# 1 **INTRODUCTION**

3D printing is becoming a powerful and revolutionary technological tool in Dentistry due to the precision in the manufacture of individualized parts associated with the speed and little waste created (Alharbi et al., 2016; Jamróz et al., 2018). Currently, most computer aided manufacturing (CAM) systems are based on subtractive techniques, in which a cutting tool, following the computer's instructions, trims the material until the desired design is obtained (Davidowitz e Kotick, 2011). In contrast, the additive manufacturing process consists of depositing material layer by layer, which reduces waste by up to 40%, allowing the manufacture of objects regardless of dimensional complexity, with details finer than the size of a drill (Azari e Nikzad, 2009). Therefore, studies that evaluate the processing by additive manufacturing and the materials used for this need to be carried out.

Several additive manufacturing techniques can be used in dentistry, including selective laser sintering (SLS), selective laser fusion (SLM), stereolithography (SLA) and digital light processing (DLP) (Van Noort, 2012; Abduo et al., 2014). Currently, most used processes in dentistry are SLA and DLP, which are based on the decomposition of digital three-dimensional models in transverse layers and the construction of objects occurs through the stacking of thin layers of resinous material followed by their laser light curing (SLA) or LED light (DLP) (Nayar et al., 2015; Alharbi et al., 2017). Both techniques can serve as processing methods for temporary restorations, for aesthetic, phonetic and occlusal evaluation before the final restorations are made (Maeda et al., 1994; Inokoshi et al., 2012; Sancho-Puchades et al., 2015). In addition, these techniques have been used for the manufacture of complete dentures, surgical guides, occlusal plates and anatomical models (Chen e Yakovlev, 2010; Stansbury e Idacavage, 2016; Chen et al., 2019; Gad e Abualsaud, 2019). This intraoral use, although quite promising, is still less common in Restorative Dentistry due to limitations related to the resistance of resins used for temporary restorations (Tahayeri et al., 2018).

Factors such as manufacturing parameters, photopolymerization process and the properties of the polymer can influence the properties of 3D-printed materials obtained by both SLA or DLP techniques, (Fuh et al., 1999; Curtis et al., 2003; Chockalingam et al., 2006; Puebla et al., 2012; Abduo et al., 2014). Therefore, more research is needed in the improvement of materials for printing, aiming at the production of restorative materials suitable for long-term use with good clinical performance. The future of using additive manufacturing or 3D printing for making restorations depends on the improvement and development of materials with better mechanical, biological and aesthetic properties associated with an affordable cost. Although restorations made using the additive manufacturing technique can offer some advantages over milled ones, their properties have not been sufficiently investigated. Especially when it comes to the factors that could influence these properties.

Research in the field of dental materials development has explored ways in which resins can be modified to improve the performance of manufactured restorations (Puebla et al., 2012). There is evidence that restorative composites started to present better physical, mechanical, electrical and biological properties with the addition of nanometric or nano-agglomerated filler particles to the resin matrix (Kim et al., 2002; Moszner e Klapdohr, 2004; Mota et al., 2006; Zhang e Webster, 2009; Anusavice et al., 2012). The type and quantity of charge particles are factors that determine and influence properties such as mechanical strength, resistance to abrasion (Chung e Greener, 1990; Ruddell et al., 2002).

In this context, $TiO_2$ nanostructures have interesting properties such as photocatalytic activity - related to the formation of electron pairs after irradiation with light, (Diebold, 2003) high density of surface sites - increasing its performance and interaction with the medium (Carp et al., 2004; Chen e Mao, 2007), antimicrobial activity, excellent mechanical properties, in addition to being chemically inert (Xia et al., 2008; Roy et al., 2011; Sun et al., 2011; Poosti et al., 2012; Arruda et al., 2015). These nanostructures can be obtained in different morphologies, among them: nanoparticles, nanotubes, nanowires, nanobonds, nano needles, nano sheets and nanospheres (Simons e Dachille, 1967; Devan et al., 2012; Cheng et al., 2013; Ramos-Tonello et al., 2017).

However, $TiO_2$ nanostructures have a tendency to agglomerate after being incorporated into the resin matrix (generating losses in its mechanical properties) (NavíO et al., 1999). To avoid this, $TiO_2$ particles can be functionalized by several bifunctional molecules, the chemical functionalization process aims to improve the interaction of the oxide with the environment, that is, to minimize the nano-agglomerates and to promote a better distribution of the particles throughout the resinous matrix. The surface of these oxides is mainly terminated by -OH groups, easily bonded to carboxylic acids, esters, acid chlorides and carboxylate salts - capable of covalent bonds with metals (Frankamp et al., 2006; De Palma et al., 2007; Chen e Yakovlev, 2010; Trino et al., 2018). Studies show that APTMS (3-aminopropyl trimethoxysilane) it acts by modifying the surface of the oxides - silane hydrolysis in silanols, followed by condensation between silanols and hydroxyls. Forming covalent bonds between the different molecular groups of silane and -OH on the surface of the nanoparticles (Fig. 1.1).

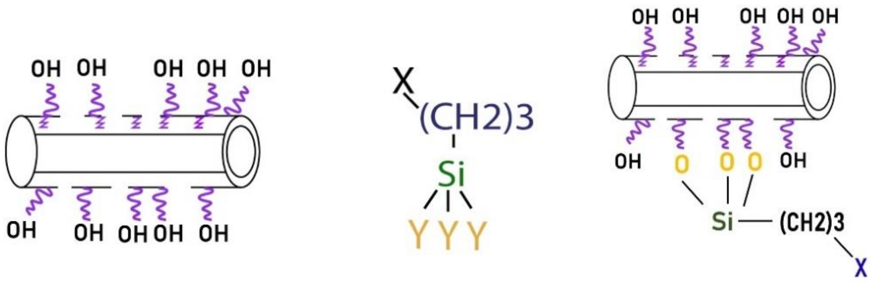


Fig. 1.1 - Functionalization of TiONts with organosilane. The $TiO_2$ have -OH terminations that can react with silanes to form a functionalized nanostructure. The bifunctional molecule has two ends, one of which (Y in the scheme) binds to the hydroxyls of the nanotube and the other (X) has the potential to bind to other materials such as resinous materials. Adapted from Huang et al, Journal Material Chemistry B 2014, 8616-25.

Another bifunctional compound that has double reactivity is 3-Trimethoxysilylpropeil-Methacrylate (TMSPM). The TMSPM presents a polymerizable and a hydrolyzable group, making chemical bonds to the matrix. Its action as a coupling compound is commonly used to interconnect organic and inorganic components, an excellent property in the composition of hybrid materials such as composite resin (Levy e Zayat, 2015).

Therefore, it is hypothesized that functionalized $TiO_2$ nanostructures could improve the properties of resins designed for 3d printing. Thus, the aim of the present study was to analyze the influence of the incorporation of different amounts of $TiO_2$ nanotubes functionalized with either APTMS or TMSPM on the properties of a resin for 3D printing. For this purpose, this study will be presented as an article to be further submitted to a peer-reviewed magazine.

# 2 Article

# 2 **ARTICLE**

The article presented in this Dissertation was written according to The Journal of Prosthetic Dentistry instructions and guidelines for article submission. For the sake of simplifying the evaluation, pictures and tables were inserted through the text, close to first mention, instead of adding them at the end of the text as recommended by the magazine's guidelines for authors.

$TiO_2$ nanotubes as additives for 3D printing resins

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**Abstract**

**Statement of the problem:** 3D printing materials present properties that are incompatible with intraoral use for medium and long term and lack regulatory approval. The photo-catalytic properties of titanium dioxide nanoparticles can lead to enhancement of resin properties due to its capability to absorb light and generate free radicals without consuming themselves.

**Objective:** to evaluate the performance of commercially available resins for 3D-printed temporary restorations with the addition of functionalized $TiO_2$ nanotubes.

**Materials and methods:** Specimens were 3D-printed using commercially available printable resins: Cosmos Temp - Yller Biomaterials (CT) and Smart Print Bio Temp - Smart Dent (SP) with the addition of 0.3 and 0.9% by weight of $TiO_2$ nanotubes in a Elegoo Mars LCD MSLA 3D printer. Flexural strength and Young's modulus were measured using a 3-point bending test, Spectrophotometry was used to evaluate ΔE and ΔE00 after accelerated artificial aging, and water sorption and solubility were evaluated using a precision scale. Results were analyzed using the two-way ANOVA and Tukey tests, adopting a significance level of 5%.

**Results:** Specimens printed with SP containing 0.9wt% of TMSPM-functionalized nanotubes showed the highest values of flexural strength and elastic modulus ($p < 0.05$). The lowest water sorption was observed for CT containing 0.3wt% APTMS -functionalized nanotubes, while the lowest solubility was observed for SP containing 0.9wt% of APTMS-functionalized nanotubes. ΔE showed lowest values for CT containing 0.9wt% of APTMS-functionalized nanotubes. ΔE00 confirmed the color stability results showed by ΔE.

**Conclusions:** results suggest that the addition of functionalized $TiO_2$ nanotubes has the potential to improve the assessed physical and mechanical properties of the 3D printable provisional restorative materials.

**Clinical Implications:**

These results provide a useful account of how we can improve materials for 3D printing in order to broaden their indications.

## INTRODUCTION

Stereolithography (SLA) and Digital Light Processing (DLP) are two manufacturing approaches that produce objects through layer deposition of light curable liquid polymers; these technologies are commonly called 3D printing or additive manufacturing.[1] The use of additive manufacturing in the fabrication of surgical guides, diagnostic models and occlusal splints has been reported in the literature for some years[2,3,4,5] since the technique is relatively fast, has accuracy in creating complex shapes with relatively smooth surfaces, and generates little waste[1]. However, its uses are limited by the properties of the polymers employed and most of these examples have generally used polymers that have little potential for intraoral clinical application due to lack of regulatory approval, and incompatibility of their properties with medium to long-term dental applications.[6,18]

A key aspect of $TiO_2$ nanoparticles is that it presents unique photo-catalytic activities. Traditionally used as a pigment additive in dental composites the $TiO_2$ nanoparticles are inexpensive, chemically stable, have excellent mechanical properties, high refractive index, antimicrobial properties and potential to act as a photoinitiator due to the capacity to utilize energy from light irradiation and produce free radicals.[7,8,9,10,11] Taking advantage of this property can lead to a significant improvement in resin performance and provide flexibility in controlling the structure and functionality of the resin network, thus creating new materials capable of meeting complex requirements for functionality and durability[8,12].

However, $TiO_2$ nanostructures have a tendency to agglomerate after being incorporated into the resin matrix (generating losses in its mechanical properties).[13] To avoid this, $TiO_2$ particles can be functionalized by several bifunctional molecules. The chemical functionalization process aims to improve the interaction of the oxide with the environment, that is, to minimize the nano-agglomerates and to promote a better distribution of the particles throughout the resinous matrix. The surface of these oxides is terminated mainly by -OH groups, easily bonded to carboxylic acids, esters, acid chlorides and carboxylate salts - capable of covalent bonds with metals. [14,15,16,17]

Studies show that 3-aminopropyl trimethoxysilane (APTMS) acts by modifying the surface of the oxides, forming covalent bonds between the different molecular groups of silane and -OH on the surface of the nanoparticles. Another bifunctional compound that has dual reactivity is 3-Trimethoxysilylpropeil-Methacrylate (TMSPM) which demonstrates the action of coupling compound and is commonly used to interconnect organic and inorganic components, excellent property in the composition of hybrid materials such as composite resin.[19]

There is evidence that the $TiO_2$ nanoparticles peak their photocatalysis effect when irradiated with UV light[9]. At the same time, both SLA and DLP additive manufacturing approaches are based on liquid polymers that are light polymerized with UV lights. Therefore, it is hypothesized that functionalized $TiO_2$ nanostructures could improve the properties of resins designed for 3d printing. Thus, the aim of the present study was to analyze the influence of the incorporation of different amounts of $TiO_2$ nanotubes functionalized with either APTMS or TMSPM on the properties of a resin for 3D printing. The null hypotheses evaluated were: 1) there would be no difference between evaluated resins; and 2) there would be no differences on flexural strength, elastic modulus, water sorption, water solubility and color stability when different amounts of functionalized $TiO_2$ nanotubes were added to the resins.

## MATERIALS AND METHODS

### Study design

This in vitro study involved two factors: 3D printing resins, in two levels (Cosmos Temp and Smart Print Bio Temp) and addition of $TiO_2$ nanotubes, in five levels (control – no nanotubes, 0.3wt% of APTMS-functionalized $TiO_2$ nanotubes, 0.9wt% of APTMS-functionalized $TiO_2$ nanotubes, 0.3wt% of TMSPM-functionalized $TiO_2$ nanotubes, and 0.9wt% of TMSPM-functionalized $TiO_2$ nanotubes). The response variables were flexural strength, water sorption and solubility, and color stability.

### 3D CAD designs and 3D printing

Samples were designed using an CAD software (Meshmixer). Prior to 3D printing, the designs were then saved as .STL files and exported into the 3D printing software (Chitubox 1.8.1). For all printed specimens no supports were used.

Printing parameters of samples were determined by evaluating different settings (bottom layer count, exposure time and bottom exposure time) and comparing the width, length and thickness achieved using the resins without addition of nanotubes versus the set dimensions of CAD designs. The starting point of settings were provided by the manufacturers and the altered settings were exposure time and bottom exposure time. The parameters used in the printing of specimens are described in Table 1.

Table 1. Parameters used in the printing of specimens

| Resin material | Exposure time | Bottom exposure time | Bottom layers | Layer thickness | Off time |
|---|---|---|---|---|---|
| **Cosmos Temp** | 11s | 80s | 5 | 0,05mm | 5s |
| **Smart Print Bio Temp** | 9 s | 70s | 12 | 0,05 mm | 5s |

After the printing parameters were established for each resin the $TiO_2$ nanotubes functionalized with two different bifunctional compounds were added in two different concentration rates 0.3 and 0.9% by weight. The experimental groups are described in Table 2.

After printing, all specimens were washed in PA isopropyl alcohol for 10 minutes, dried and then taken to a UV light curing chamber (72 W), the groups containing the resin CT was post-cured for 10 minutes and the groups containing the resin SP was post-cured for 2 minutes, as the manufacturers recommend.

Table 2. Different experimental groups with concentration of nanotubes and proposed functionalizations

| Resin material (Code used in the study) | $TiO_2$ nanotubes (wt%) | Functionalization |
|---|---|---|
| **Cosmos Temp (CT)** | 0 | None |
| **Smart Print Bio Temp (SP)** | 0 | None |
| **Cosmos Temp (CT 0.3 APTMS)** | 0.3 | APTMS |
| **Smart Print Bio Temp (SP 0.3 APTMS)** | 0.3 | APTMS |
| **Cosmos Temp (CT 0.9 APTMS)** | 0.9 | APTMS |
| **Smart Print Bio Temp (SP 0.9 APTMS)** | 0.9 | APTMS |
| **Cosmos Temp (CT 0.3 TMSPM)** | 0.3 | TMSPM |
| **Smart Print Bio Temp (SP 0.3 TMSPM)** | 0.3 | TMSPM |
| **Cosmos Temp (CT 0.9 TMSPM)** | 0.9 | TMSPM |
| **Smart Print Bio Temp (SP 0.9 TMSPM)** | 0.9 | TMSPM |

**Flexural strength and Young's Modulus**

The flexural strength was determined with a 3-point bending test using an Instron universal testing machine (Instron, Norwood, Massachusetts, United States) with 50N connected load cell and constant test speed of 0.5 mm / min. Resin bars for 3D printing in the dimensions of 2 x 2 x 25 mm were made by additive manufacture for each experimental group (n = 10). The samples remained in distilled water and a controlled temperature of 37° C for 24 hours before testing. The specimens were placed in a flexing device with a distance of 12 mm between the lower cylindrical supports and the load was applied to the center by the upper metal rod. The flexural strength and Young's Modulus values were calculated by the software of the universal testing machine (Bluehill Universal).

**Water Sorption (S) and Solubility (SL)**

Ten specimens from each experimental group manufactured by additive manufacturing were weighed on a precision scale (0.1 mg) until a constant mass (M0) was obtained. Then the specimens were dehydrated in a desiccator containing silica and calcium chloride for 22 hours at 37 ° C and then stored in another container with silica for a period of 2 hours at 23 ° C. After the dehydration cycle, the specimens were weighed on a precision scale until a constant mass was obtained (M1). The volume of the specimens (V) was calculated in $mm^3$, by measuring the thickness and diameter of each specimen with a digital caliper calibrated to 0.001mm accuracy (Mitutoyo Sul Americana). In the second stage, the specimens were placed in individual flasks containing 5 ml of distilled water and kept at 37 ° C for 7 days. The water was not changed during this period. After removing the water, the specimens were dried on absorbent paper and weighed again (M2). A new dehydration cycle was conducted, as previously described, to obtain the final mass (M3). Water sorption (S) and solubility (SL) were calculated using the equations 1 and 2, respectively:

$$S = \frac{M2 - M3}{V} \quad (1)$$

$$SL = \frac{M1 - M3}{V} \quad (2)$$

, where M1 is the initial mass of the dry specimen before immersion in distilled water, M2 is the mass of the saturated specimen after immersion in distilled water for 7 days, M3 is the final mass of the specimen after desiccation and V is the specimen volume.

**Color stability (ΔE and ΔE00)**

Ten resin disks in the dimensions of 10 mm in diameter and 2 mm in height from each experimental group manufactured by additive manufacturing were polished with decreasing grit polishing disks (Diamond Master - FGM) by a single operator by using a dental handpiece (Kavo Dental). The color change was assessed at different time points by using a CIE-Lab-based colorimeter (Easyshade Advance; Vita Zahnfabrik). Before measurements, the spectrophotometer was calibrated according to the manufacturer's instructions. An initial measurement was performed 7 days after polishing; a second measurement after artificial aging (P2) consisting of 24 hours of distilled water storage at 60° C.[18,20,21] Between the polishing and P1, all specimens were kept dry and stored at 37° C in the absence of light. Three consecutive measurements were made in the center of each specimen and the average of them was calculated.

The ΔE was calculated based on the equation 3:

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (3)$$

, where ΔL *, Δa and Δb * represent the differences between the readings of the color parameters obtained from the specimens at the different evaluated moments.

Additionally, the CIEDE2000 color change (ΔE00) was measured using the equation 4:

$$\left[\left(\frac{\Delta L}{K_L \times S_L}\right) + \left(\frac{\Delta C}{K_C \times S_C}\right)^2 + \left(\frac{\Delta H}{K_H \times S_H}\right)^2 + R_T \times \left(\frac{\Delta C}{K_C \times S_C}\right) \times \left(\frac{\Delta H}{K_H \times S_H}\right)\right]^{0,5} \quad (4)$$

, where ΔL', AC' and AH 'represent luminosity, chroma and hue, respectively. RT refers to the difference between chroma and hue in the blue region. SL, SC and SH are weighting functions that adjust the total color difference within the coordinates L *, a * and b * and KL, KC and KH are functions to be adjusted according to different parameters of visualization for experimental conditions, in the case of this study they were set to 1.[22]

**Data analyses**

Normal distribution was confirmed using the Shapiro-Wilk test. Data were analyzed with two-way ANOVA and the Tukey's HSD multiple comparison, considering resins and addition of nanotubes as independent variables. A global level of significance of 5% was adopted.

## RESULTS

Mean values and standard deviations of flexural strength and Young's modulus are presented in Table 3. For flexural strength significant differences were found between the resins, with higher overall results being observed by SP ($p = 0.000000$). While the addition of nanotubes was not significant ($p = 0.888$), and the interaction effect between resins and addition of nanotubes was found to be significant ($p = 0.000004$). Thus, as shown on Figure 1, due to the significant interaction the influence of the addition of nanotubes was material-dependent and higher flexural strength values were observed for SP when TMSPM-functionalized nanotubes were added at 0.9wt% [98.51 (7.65)$^{D}$] and 0.3wt% [90.83 (11.17)$^{CD}$]. For SP the addition of APTMS-functionalized nanotubes at 0.3wt% [76.78 (16.64)$^{BC}$] and 0.9wt% [81.63 (10.69)$^{C}$] showed similar results to the control [85.33 (20.38)$^{CD}$]. On the other hand, for CT the addition of nanotubes did not influence the flexural strength ($p > 0.05$). For the Young's modulus significant differences were found for resins ($p = 0.000000$) and the addition of nanotubes ($p = 0.036864$). The interaction effect between resins and addition of nanotubes was also significant ($p = 0.002322$). The higher overall values were observed for SP ($p < 0.05$).

Table 3. Mean values and standard deviations of flexural strength and Young's modulus for evaluated groups. Different uppercase and lowercase letters indicate statistically significant differences in the same column ($p < 0.05$).

| Experimental Group | Flexural strength | Young's modulus |
|---|---|---|
| **CT** | 54.95 (4.78)$^{A}$ | 112.31 (22.40)$^{ab}$ |
| **SP** | 85.33 (20.38)$^{CD}$ | 203.63 (26.59)$^{c}$ |
| **CT 0.3 APTMS** | 64.48 (11.64)$^{AB}$ | 141.99 (31.53)$^{ab}$ |
| **SP 0.3 APTMS** | 76.78 (16.64)$^{BC}$ | 196.82 (32.90)$^{c}$ |
| **CT 0.9 APTMS** | 63.64 (10.62)$^{AB}$ | 147.56 (25.00)$^{b}$ |
| **SP 0.9 APTMS** | 81.63 (10.69)$^{C}$ | 213.69 (32.46)$^{c}$ |
| **CT 0.3 TMSPM** | 51.62 (2.48)$^{A}$ | 106.00 (15.96)$^{a}$ |
| **SP 0.3 TMSPM** | 90.83 (11.17)$^{CD}$ | 219.39 (29.75)$^{c}$ |
| **CT 0.9 TMSPM** | 48.32 (8.26)$^{A}$ | 105.83 (16.23)$^{a}$ |
| **SP 0.9 TMSPM** | 98.51 (7.65)$^{D}$ | 209.92 (21.23)$^{c}$ |

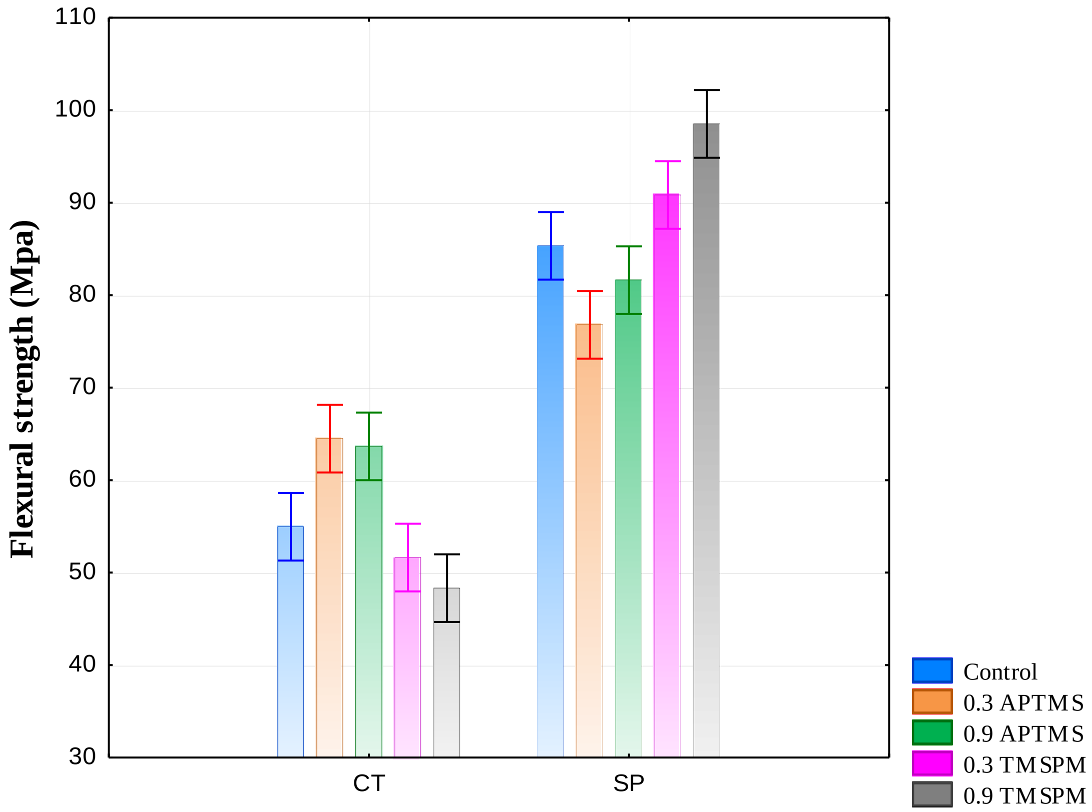


Figure 1. Mean values of flexural strength for evaluated groups.

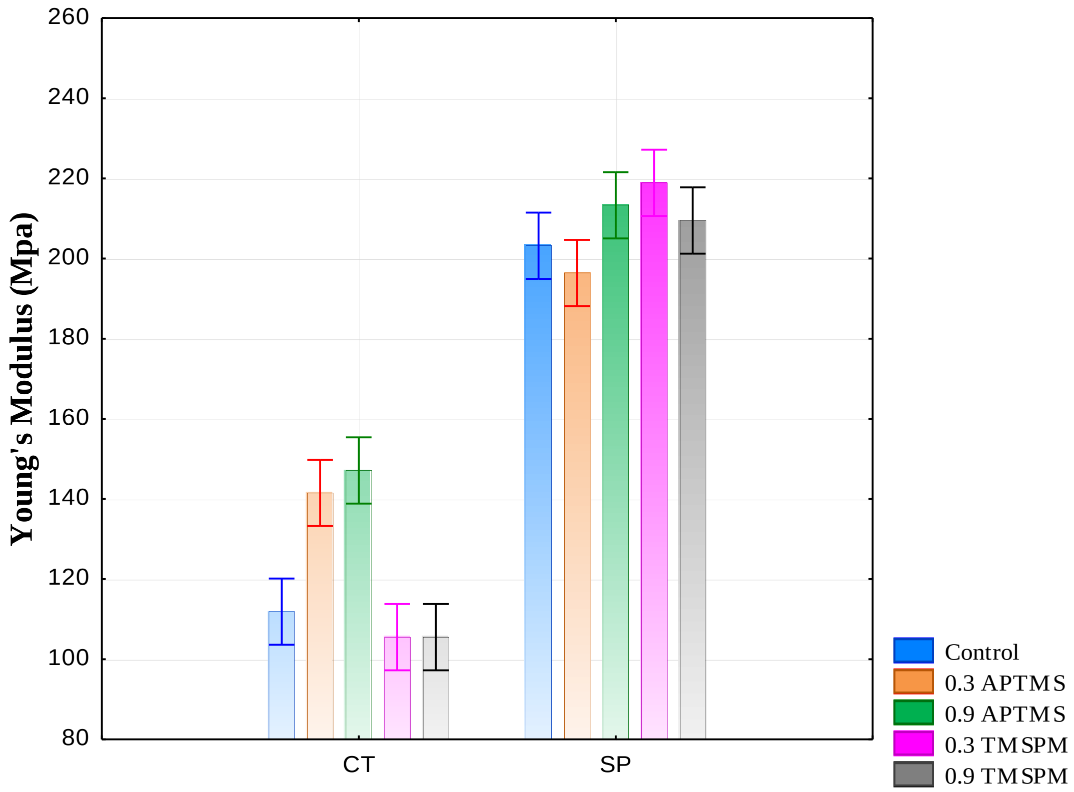


Figure 2. Mean values of Young’s Modulus for evaluated groups.

The results for water sorption and solubility are shown in Table 4 and Figures 3-4. For water sorption significant differences were found for resins ($p = 0.000002$) and addition of nanotubes ($p = 0.000015$). The interaction effect between resins and addition of nanotubes was also significant ($p = 0.000531$). Higher overall water sorption was observed for SP. The lowest values of water sorption were observed for CT 0.3 APTMS [6.15 (0.11)$^{A}$], while the higher values were observed for CT without any addition of nanotubes [12.04 (0.39)$^{C}$]. SP was not influenced by the addition of nanotubes.

For solubility significant differences were found for resin ($p = 0.000000$), and the addition of nanotubes ($p = 0.049997$). The interaction effect was not significant ($p = 0.616398$). The lowest values were observed for SP 0.9 APTMS and the biggest for the CT group without any addition of nanotubes.

Table 4. Mean values and standard deviations of water sorption and solubility (both in µg/mm$^3$) for evaluated groups. Different uppercase and lowercase letters indicate statistically significant differences in the same column ($p < 0.05$).

| Experimental Group | Water sorption | Solubility |
|---|---|---|
| **CT** | 12.04 (0.39)$^{C}$ | -1.79 (3.27)$^{c}$ |
| **SP** | 10.72 (0.27)$^{C}$ | -4.77 (1.44)$^{ab}$ |
| **CT 0.3 APTMS** | 6.15 (0.11)$^{A}$ | -2.11 (1.32)$^{c}$ |
| **SP 0.3 APTMS** | 10.52 (0.08)$^{C}$ | -5.97 (1.91)$^{a}$ |
| **CT 0.9 APTMS** | 7.23 (0.15)$^{AB}$ | -2.96 (0.99)$^{bc}$ |
| **SP 0.9 APTMS** | 9.79 (0.05)$^{BC}$ | -6.20 (0.70)$^{a}$ |
| **CT 0.3 TMSPM** | 9.55 (0.22)$^{BC}$ | -2.15 (0.45)$^{c}$ |
| **SP 0.3 TMSPM** | 11.03 (0.22)$^{C}$ | -5.03 (2.48)$^{ab}$ |
| **CT 0.9 TMSPM** | 7.10 (0.22)$^{AB}$ | -2.04 (1.25)$^{c}$ |
| **SP 0.9 TMSPM** | 10.78 (0.09)$^{C}$ | -4.20 (0.98)$^{abc}$ |

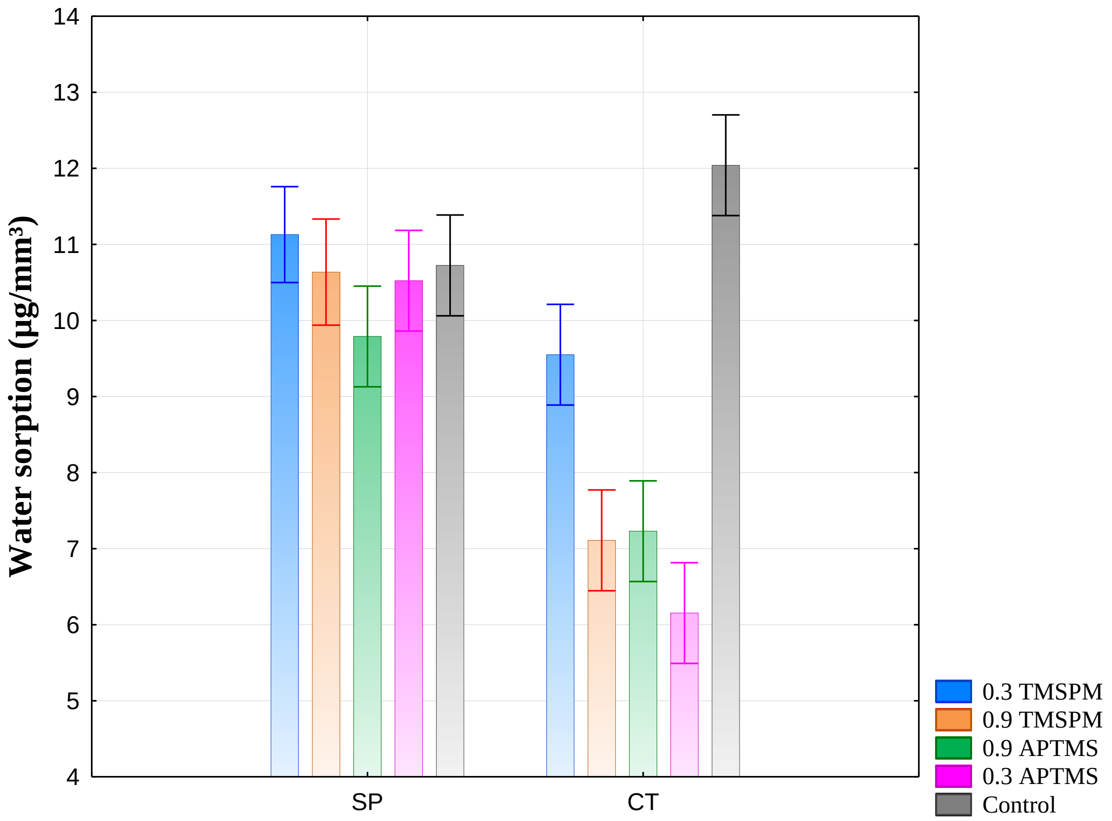


Figure 3. Mean values of water sorption for evaluated groups.

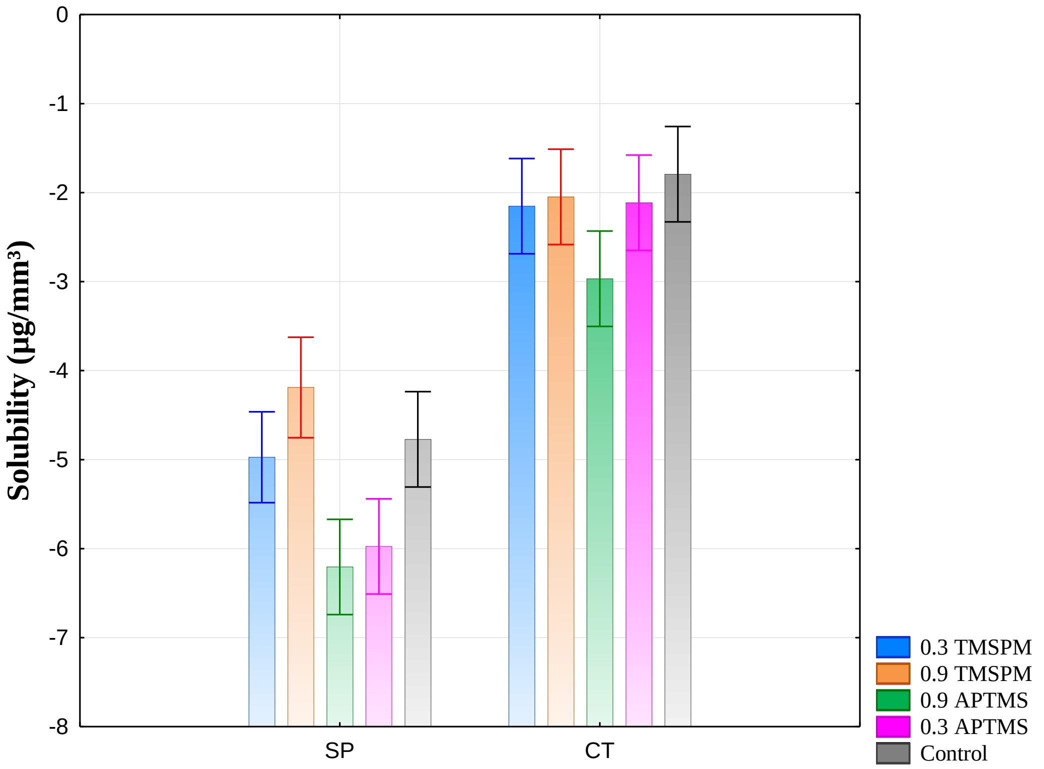


Figure 4. Mean values of solubility for evaluated groups.

The results for ΔE and ΔE00 are shown in Table 5 and Figures 5-6. For color stability using the CIE-Lab formula (ΔE), significant differences were observed for resins (p=0.000000) and addition of nanotubes (p=0.000000). The interaction effect between resins and addition of nanotubes was also significant (p=0.000274). The lowest value of ΔE was observed for the group CT 0.9 APTMS [(0.71 (0.18)$^{A}$], while the highest value was observed for the group SP without the addition of nanotubes [2.46 (0.75)$^{E}$]. For ΔE00, evaluated by the CIEDE2000 formula, the same trend was observed and significant differences were observed for resins (p = 0.000000) and addition of nanotubes (p = 0.000003). The interaction effect between resins and addition of nanotubes was also significant (p = 0.001003). The lowest value was observed for the group CT 0.9 APTMS as well as in the calculation of ΔE. While the highest values were observed for the group SP 0.3 TMSPM.

Table 5. Mean values and standard deviations of ΔE and ΔE00 for evaluated groups. Different uppercase and lowercase letters indicate statistically significant differences in the same column ($p < 0.05$).

| Experimental Group | ΔE | ΔE00 |
|---|---|---|
| **CT** | 1.44 (0.39)$^{BCD}$ | 1.07 (0.35)$^{b}$ |
| **SP** | 2.46 (0.75)$^{E}$ | 1.74 (0.46)$^{c}$ |
| **CT 0.3 APTMS** | 1.14 (0.51)$^{ABC}$ | 0.93 (0.46)$^{ab}$ |
| **SP 0.3 APTMS** | 1.66 (0.38)$^{CD}$ | 1.22 (0.30)$^{b}$ |
| **CT 0.9 APTMS** | 0.71 (0.18)$^{A}$ | 0.55 (0.14)$^{a}$ |
| **SP 0.9 APTMS** | 1.17 (0.33)$^{ABC}$ | 1.09 (0.29)$^{b}$ |
| **CT 0.3 TMSPM** | 1.01 (0.30)$^{AB}$ | 0.95 (0.16)$^{ab}$ |
| **SP 0.3 TMSPM** | 1.92 (0.46)$^{DE}$ | 1.83 (0.33)$^{c}$ |
| **CT 0.9 TMSPM** | 1.35 (0.45) $^{BCD}$ | 1.17 (0.57)$^{b}$ |
| **SP 0.9 TMSPM** | 1.17 (0.25)$^{ABC}$ | 1.12 (0.17)$^{b}$ |

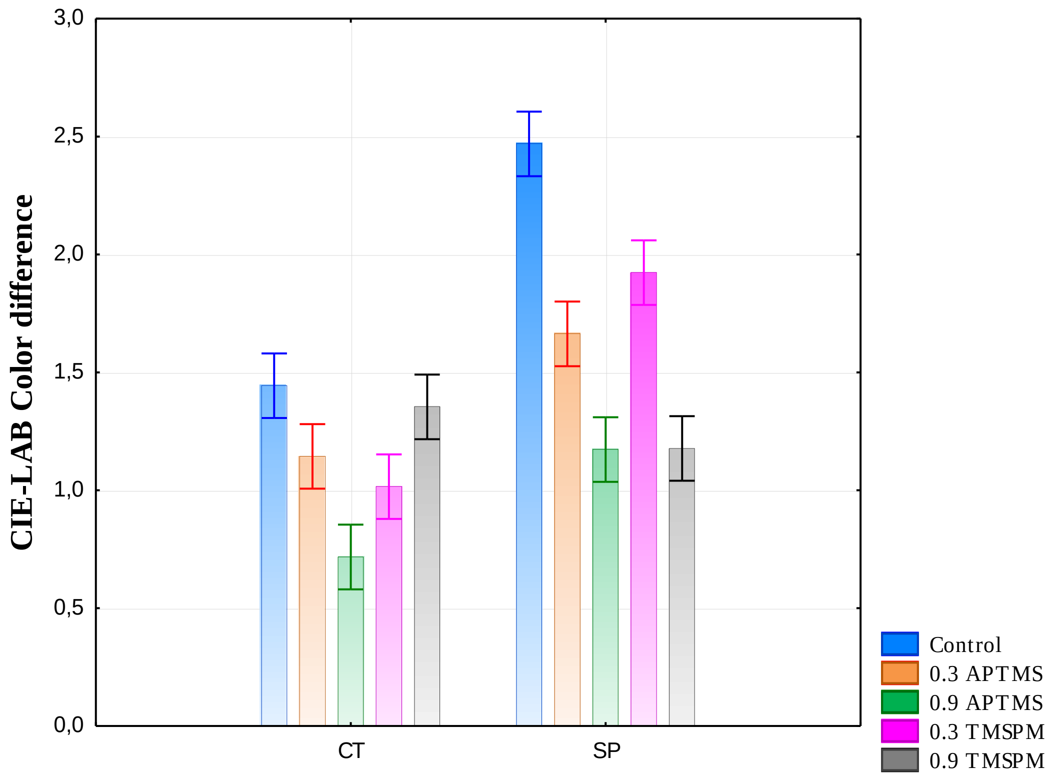


Figure 5. Mean values of ΔE for evaluated groups.

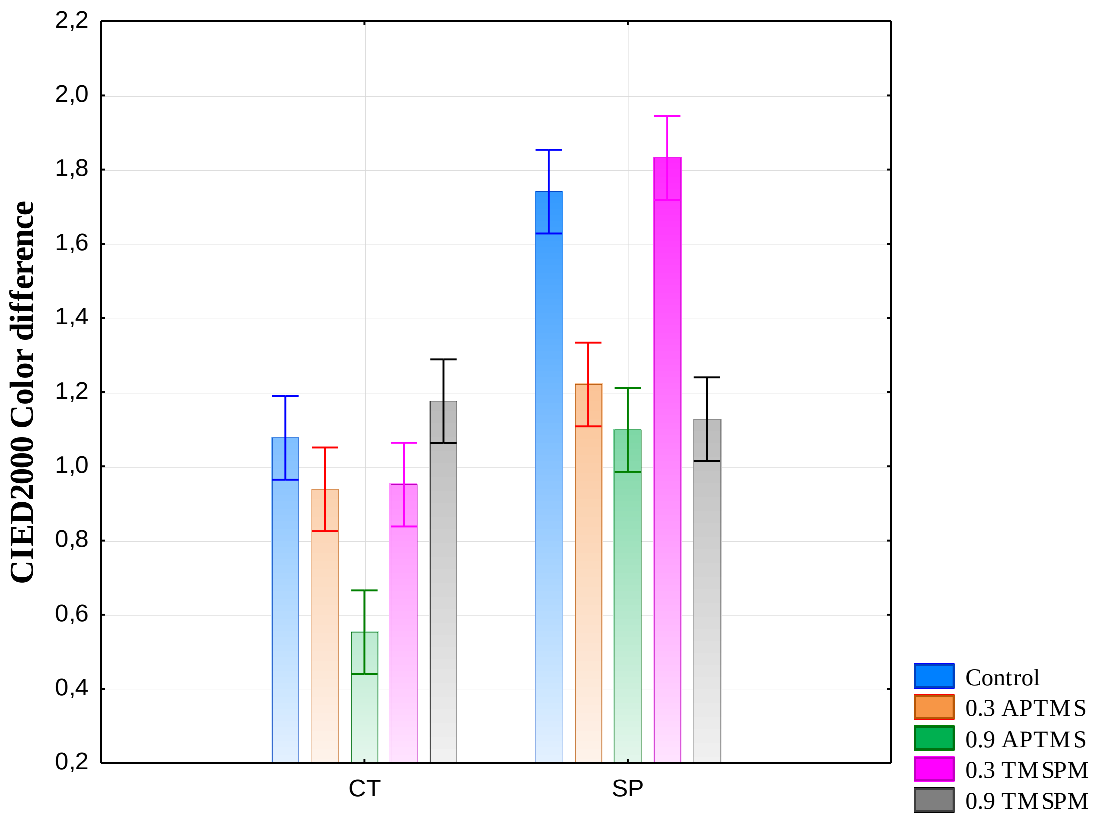


Figure 6. Mean values of ΔE00 for evaluated groups.

**Discussion**

Several reports have shown that 3D printing has great potential in the field of clinical dentistry with the possibility of revolutionizing the manufacture of provisional restorations. For provisional restorations to be made by 3D printing materials should have excellent properties, such as stable chemical properties, good physical and mechanical properties, be easy to polish and non-toxic. Thus in the present study, functionalized $TiO_2$ nanotubes were added to commercially available 3D printing resins to enhance their properties. Based on data from this study, both null hypotheses were rejected as there were significant differences between resins, and all evaluated properties were influenced when different amounts of functionalized $TiO_2$ nanotubes were added to the resins. For the flexural strength the highest values were observed in the groups that contained the SP resin modified by the addition of 0.9wt% of TMSPM-functionalized nanotubes. A possible explanation for this might be that the composition of the resin reacts favorably to the compound 3-Trimethoxysilylpropeil-Methacrylate (TMSPM). However, it is important to keep in mind the composition of the material is not disclosed by the manufacturer. For Young's modulus, the same trend was observed with the highest values being observed for the groups containing the SP resin, however, in this case a material dependent effect was observed.

For water sorption the highest values were observed for the group containing the resin CT without any addition of $TiO_2$ nanotubes, nevertheless the group containing the same resin with the addition of 0.3% by weight of nanotubes functionalized with APTMS showed the lowest values. Increased water sorption has been shown to result in degradation of the filler-matrix interface and act as a plasticizer within the polymer matrix of resin-based materials.[23] Thus, the effect of decreasing water sorption shown by the addition of nanotubes on the CT resin is interesting. As for the solubility, all groups expressed negative values, which is surprising since it is expected that the resin would endure some degree of dissolution after water storage. It seems possible that these results are due to an interaction between the polar solvent and the polymer where part of the absorbed water is firmly bound to the resin matrix and cannot be reversely extracted, or a sequestration in microcavities present in the resin matrix or even sites created by poor filler/matrix interfacial adhesion.[24,25]

The color stability evaluation also confirmed the hypothesis that $TiO_2$ nanotubes could be used to improve the properties of resins for 3D printing. It should be noted that according to the results of the present study the 3D-printed resins evaluated showed some color stability with $\Delta E$ values bellow 3.3. On the other hand, it has been previously reported that 3D printing are less color stable after aging than the other suitable for provisional restoration materials like polymethyl methacrylate (PMMA) and bis-acrylic resins and information about their optical properties are scarce[18]. When the CIE-Lab formula was employed the group containing the resin CT with the addition of 0.9wt% of nanotubes functionalized with APTMS demonstrated the best color stability with the lower values of ΔE, while the group containing the resin SP without addition of functionalized nanotubes had the worst color stability after aging expressed by the highest values of ΔE. However, when the CIEDE2000 formula was employed, the group containing the resin CT with the addition of 0.9wt% of nanotubes functionalized with APTMS demonstrated the best color stability with the lower values of ΔE, confirming the results of CIE-Lab, while the resin containing the resin SP with the addition of 0.3wt% of nanotubes functionalized with TMSPM had the worst color stability after aging expressed by the highest values of ΔE00. Overall this property is influenced by a myriad of factors including degree of conversion, polarity of monomers, amount of crosslinking, initiator system, particle size and distribution, water sorption, monomer conversion, pigment stability and in the case of additive manufacturing post-curing and even mixing of the product prior to use.[18,26,27,28] Considering thresholds of ΔE = 1.2 and ΔE00 = 0.8 for perception and ΔE = 2.7 and ΔE00 = 1.8 for acceptability of color changes[29] is interesting to notice that 5 out of 10 groups showed perceptible color change based on the value of ΔE, including the groups containing the commercially available resins without the addition of $TiO_2$ nanotubes, while all the groups showed perceptible color change based on the value of ΔE00 except for the group containing the resin CT with the addition of 0.9 by weight of $TiO_2$ nanotubes functionalized with APTMS.

Before the study could be conducted, a pilot study was conducted to determine printing parameters of samples before the present study started. In the pilot study different settings such as bottom layer count, exposure time and bottom exposure time were evaluated. After 3D printing, the dimensions of the samples were compared to the dimensions of the CAD designs. The first pilot study was conducted due to the fact that different printers can have different light intensities.[6]

A great number of reports suggest that polymer nanocomposites present new and improved properties. (Kim *et al.*, 2002; Mota *et al.*, 2006; Xia *et al.*, 2008; Zhang e Webster, 2009) In accordance to the literature, these finds suggest that the concern regarding the physical and esthetic properties of using 3D printing in the manufacture of temporary restorations can be overcome with the addition of $TiO_2$ nanotubes and this opens new perspectives of research for greater applicability of this technology in the manufacture of restorations since the properties of nanocomposites change depending on the type, size, concentration and shape of the nanoparticles added A note of caution is due here since if the $TiO_2$ nanotubes content exceed a critical value in the resin matrix, defects such as voids and incomplete polymerization of the resin can be observed, since the excessive absorption of UV light can impair the photopolymerization process and the facility to aggregate that nanomaterials have can cause degradation of the resin matrix. Still there are several questions unanswered takin in consideration properties like surface roughness, cell viability and clinical protocols.

**Conclusion**

Based on the findings of this in vitro study, the following conclusions were drawn:

1 – The addition of functionalized $TiO_2$ nanotubes did not compromise flexural strength or Young's modulus of the commercially available resins.

2 – The addition of 0.3% by weight of $TiO_2$ nanotubes functionalized with APTMS reduced the water sorption of the resin CT.

3 – The addition of 0.9% by weight of $TiO_2$ nanotubes functionalized with APTMS improved the color stability of the resin CT using two evaluation methods.

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# 3 Discussion

## 3 **DISCUSSION**

3D printing has great potential in the field of clinical dentistry with the ability to satisfy the demand for patient-personalized models. A wide variety of materials can be used to produce surgical guides, crowns, dentures and provisional restorations but mostly uses the active polymerization of photo-sensitive resins. The mechanical strength of the parts produced by these techniques strongly depends on the properties exhibited by the monomers used, as composition can prioritize the use of acrylates that are faster to cure or methacrylates that have better mechanical and biological properties. (Stansbury e Idacavage, 2016) In the case of provisional restorations materials should be chemically stable, present good physical and mechanical properties, be easy to polish and non-toxic. In this study, we introduced functionalized $TiO_2$ nanotubes to enhance the properties of the commercially available resins for provisional restorations. Based on data from the present study, all null hypotheses were rejected.

For the flexural strength several reports have shown that the building orientation affects the manner the object is layered and the number of layers to be printed resulting in different values of accuracy and mechanical properties. It is known that vertically printed specimens with the layers oriented perpendicular to load direction have better mechanical properties than horizontally printed specimens.(Alharbi *et al.*, 2016) Additionally, there is evidence that position on the building plate can also affect mechanical properties when it comes to SLA based printers but are unlikely to influence DLP based printers. The current study found that the highest values were observed in the groups that contained the SP resin, however, with the addition of 0.9% by weight of nanotubes functionalized with TMSPM there was a significant increase in the values, a possible explanation for this might be that the composition of the resin reacts favorably to the compound 3-Trimethoxysilylpropeil-Methacrylate (TMSPM) but it is important to keep in mind the possible bias in these statements since the composition of the material is not disclosed. For Young's modulus, the same trend was observed with the highest values being observed for the groups containing the SP resin, however, in this case a material dependent effect was observed.

If now we turn to the water sorption there's evidence that 3D printed resin tended to have higher rates than that polycarbonate or dispersed-filled composite blocks for CAD/CAM milling but lower than pre-fabricated PMMA material, (Shin *et al.*, 2020) interestingly, since water sorption has been shown to result in degradation of the filler-matrix interface and act as a plasticizer within the polymer matrix.[23]. In this study the highest values were observed for the group containing the resin CT without any addition of $TiO_2$ nanotubes, nevertheless the group containing the same resin with the addition of 0.3% by weight of nanotubes functionalized with APTMS showed the lowest values. As for the solubility all groups expressed negative values, which is surprising since it is expected that the resin would endure some degree of dissolution after water storage, It seems possible that these results are due to an interaction between the polar solvent and the polymer where part of the absorbed water is firmly bound to the resin matrix and cannot be reversely extracted, or a sequestration in microcavities present in the resin matrix or even sites created by poor filler/matrix interfacial adhesion. (Söderholm, 1984; Ferracane e Condon, 1990) These results differ from other reports in literature as Shin et al. observed higher values of solubility, however by the time of our experiment we were unaware of the difficulty of extracting the water during the process of desiccation and performed cycles of 24h unlike Shin et al. who performed desiccation until no mass alteration was observed. However, this difference also may be attributed to different compositions in the materials.

As for color stability the 3D-printed resin were less color stable after aging than the other suitable for provisional restoration materials like polymethyl methacrylate (PMMA), bis-acrylic resins and CAD/CAM resins and information about their optical properties are scarce. (Scotti *et al.*, 2020; Shin *et al.*, 2020) Color stability also differed between the two types of 3D printing resins used in this study and the differences in the composition of the resins are theorized to be the reason. When the CIE-Lab formula was employed the group containing the resin CT with the addition of 0.9% by weight of nanotubes functionalized with APTMS demonstrated the best color stability with the lower values of ΔE, while the group containing the resin SP without addition of functionalized nanotubes had the worst color stability after aging expressed by the highest values of ΔE. However, when the CIEDE2000 formula was employed, the group containing the resin CT with the addition of 0.9% by weight of nanotubes functionalized with APTMS demonstrated the best color stability with the lower values of ΔE, confirming the results of CIE-Lab, while the resin containing the resin SP with the addition of 0.3% by weight of nanotubes functionalized with TMSPM had the worst color stability after aging expressed by the highest values of ΔE00. Overall, this property is influenced by a myriad of factors including degree of conversion, polarity of monomers, amount of crosslinking, initiator system, particle size and distribution, water sorption, monomer conversion, pigment stability and in the case of additive manufacturing post-curing and even mixing of the product prior to use. (Powers *et al.*, 1978; Paravina *et al.*, 2005; Kim *et al.*, 2020; Scotti *et al.*, 2020) Considering thresholds of ΔE = 1.2 and ΔE00 = 0.8 for perception and ΔE = 2.7 and ΔE00 =

1.8 for acceptability of color changes (Paravina *et al.*, 2015) is interesting to notice that 5 out of 10 groups showed perceptible color change based on the value of ΔE, including the groups containing the commercially available resins without the addition of $TiO_2$ nanotubes, while all the groups showed perceptible color change based on the value of ΔE00 except for the group containing the resin CT with the addition of 0.9 by weight of $TiO_2$ nanotubes functionalized with APTMS.

The findings suggest that the concern regarding the physical and aesthetic properties of using 3D printing in the manufacture of provisional restorations can be overcome with the addition of $TiO_2$ nanotubes, however a note of caution is due here since the content of functionalized $TiO_2$ nanotubes cannot exceed critical concentration in the resin matrix, otherwise defects, voids and incomplete polymerization can happen and harm the properties of interest in the material. Despite these promising results, questions remain and further research should be undertaken to investigate the influence of the addition of $TiO_2$ functionalized nanotubes in the surface roughness and cell viability of 3D printing resins.

# 4 Final considerations

# 4 FINAL CONSIDERATIONS

The commercially available resins did not had benefit in the flexural strength or Young's modulus after the addition of functionalized nanotubes, but the addition of 0.3% by weight of $TiO_2$ nanotubes functionalized with APTMS reduced water sorption, and the addition of 0.9% by weight of $TiO_2$ functionalized with APTMS improved color stability of the resin CT using two evaluation methods.

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