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Material Performance

# Effect of drinks on the surface properties of dental resin composites

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**Abstract**

The aim of this study was to evaluate the effect of different drinks on the surface properties of the commercial resin composite Charisma cured by a light emitting diode (LED). Hardness, adsorption of components on the surface and porosity were analyzed through nano-indentation, polarized laser-induced fluorescence (PLF) and adsorption/desorption nitrogen isotherm methods, respectively. Specimens with a degree of cure of 70%, immersed for 24 h and 168 h in a sports drink, yogurt, soft drink and wine, showed changes on the specimen surfaces through PLF. These changes suggested that a very thin layer of drink components was adsorbed on the specimens, which were detected through polarization laser-induced fluorescence. This showed the influence of each drink and the time factors on the behavior of all specimens tested. Average pore sizes were of the same magnitude and the hardness values remained the same after specimens were immersed in the drinks, except for specimens immersed in yogurt, which showed higher hardness values than the control group, and the porosity could not be measured due to the small pore size and the low sensitivity of the analysis method. However, the hardness value for enamel was 10 times higher than that for the resin specimens and dentin.


*Keywords:* Resin composites; Nano-indentation; Porosity; Fluorescence

## 1. Introduction

Resin composites are a class of materials which have been used in dentistry for 50 years and new components are continually being developed to improve their mechanical and chemical properties. They are used as restorative materials when a tooth has caries disease or has been fractured. Dental resin composites are constituted mainly by an inorganic phase (60–80%) and an organic phase of methacrylate based resin. Composites can be

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classified by the size and distribution of the inorganic particles as macroparticles, with 75 wt% of the particles having dimensions between 1 and 3 μm, and microparticles in the range of 0.04–0.2 μm. Resin composites with 80–90 wt% of the inorganic phase with particle dimensions around 1 μm, and the other part comprised of microparticles, are denominated hybrid resins [1].

In a water environment, in the case of a hydrophilic matrix, water sorption occurs in these materials, resulting in a whiter and more opaque shade. For a hydrophobic matrix, there is less water sorption and only a small impact on the color is seen. Even the composition of the filler may have an influence on the discoloration. In contrast to exogenous discolorations caused by adsorption of dyes or plaque that can be easily removed by polishing, endogenous discolorations are irreversible. Also, the photo initiator system and the other components of a filling resin may influence the curing characteristics, the strength of the materials and color stability [2–4].

Resin composites must have good adaptation to the dental structure, dimensional stability and resistance to occlusion stress, allowing a simple technique for durable restoration, and acceptable aesthetics in terms of color. Many factors, such as resin composition, specimen geometry, concentration of the photo initiator, intensity and exposure time of the light beam and temperature of the curing process, are related to the degree of cure.

Nano-indentation is a depth-sensing technique that can accurately characterize the mechanical properties of almost all types of solid materials on a small scale. In addition, nano-indentation can continuously record the penetration depth of the specimen during dynamic loading and unloading at the indentation tip, while providing information on the degree of energy absorbed, the Young's modulus and hardness of the specimens [5].

Many important liquid–solid interfacial processes take place in liquid films flowing on solid substrates. These interactions depend on solid surface structure and roughness, as well as on the chemical constitution of the solid substrate and the flowing liquid film. Steady-state fluorescence depolarization was recently applied to study the interfacial molecular interaction of fast flowing thin liquid films, flowing without boundaries on solid substrates. These specific wettings were attributed to the dynamic relationship of the contact angle to the static interfacial tension between solid and liquid, caused by the magnitude and direction of transient interactions between liquid flow and solid.

A previous paper [6] has reported that the degree of conversion for Charisma resin composite specimens after curing for 40 s using light emitting diode (LED) was 70%, as observed by Raman spectroscopy, and the spectroscopy results showed no changes that can be attributed to reactions between the components of the drinks and the specimen surface. The color change parameters were investigated by measuring the CIE-lab-values after immersed in distilled water, a sports drink, yogurt, a soft drink based on cola and red wine for 24 and 168 h at 37 °C. The color change parameters ($L^*$, $a^*$ and $b^*$) were significantly affected when the specimens were immersed in wine or yogurt.

In this study, complementary analyses using the polarized laser-induced fluorescence (PLF) technique, hardness test and porosity analysis were used to evaluate changes in the resin specimen surface after immersion in commercial drinks.

## 2. Materials and methods

### 2.1. Materials

A hybrid resin was used, called Charisma (Heraeus Kulzer, Hanau, Germany), A2 shade, with a predominance of inorganic particles with a dimension of 1 μm and 30% of the particles with sizes between 0.01 and 0.04 μm, according to the manufacturer's catalog. The light source used for the photo polymerization of the resin was Elipar free light (3M ESPE Dental Products, Minnesota, USA). The specimens were prepared in steel molds with specific dimensions according to each method to be used, and after cure polishing with a sequence of abrasive papers (240, 400, 600 and 1200 grit). The storage environment was different drinks used in everyday diets, and distillated water as the control. The drinks were a sports drink (Gatorade®-citric fruits), a yogurt obtained from lactobacillus (Yo-mix™ cultures), a soft drink based on cola (Coca-Cola Company®) and a red wine (Cordier Le Merlot, 2000).

### 2.2. Methods

#### 2.2.1. Scanning electron microscopy (SEM)

The specimens were covered with a thin gold layer in a D2 metalizer of the diode sputtering system, made by International Scientific Instruments (ISI).

The specimen surface was analyzed by SEM, using a Phillips XL 30 microscope with a tungsten electron source and a secondary electron detector.

### 2.2.2. PLF-flow-induced (PLF-FI)

PLF-FI was used to determine the alterations in the dynamic interfacial tension between solid and liquid due to immersion in drinks. For this, specimens with 20 mm long, 20 mm high and 1 mm thick were used. The apparatus employed to study the PLF-FI of thin liquid films flowing on solid surfaces (Fig. 1) was developed recently by Quintella et al. [7]. The experiment consists of pumping a liquid at a high flow rate through a thin slit nozzle; the liquid impinges on the solid surface at an angle of 10° with respect to the vertical, generating a thin liquid film flowing without boundaries on the solid surface. Fluorescence was induced by focusing the laser on a small spot. PLF was bi-dimensionally mapped by varying the vertical and horizontal positions of the sample relative to the laser spot within the liquid flow. Depending on the adhesion yielded by the dynamic interfacial tension, the pattern can have different formation times, hence occurring at different downstream positions. The average polarization was calculated by averaging the polarization maps obtained for the flow on each sample.

The liquid employed was monoethylene glycol from Merck (MEG) (99.5% purity). A constant

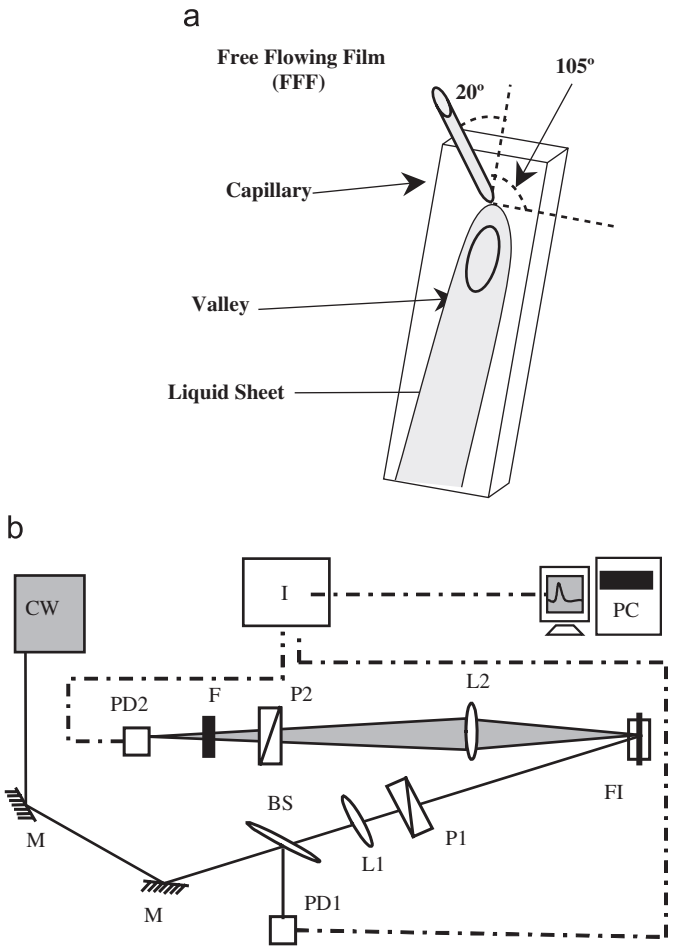


Fig. 1. (a) Scheme of the free flowing film (FFF), generated by a free liquid jet impinging on a solid surface, for PLF-FI [Reproduced by permission of Journal of Colloid and Interface Science 281 (2005) pp. 201–208 [doi:10.1016/j.jcis.2004.08.085]. © Elsevier]. (b) Experimental setup for polarized laser-induced fluorescence within liquid-induced flows (PLF-FI) to detect fluorescence depolarization. CW—laser, M—mirrors, L1, L2—lenses, P1, P2—Glan-Thompson Polarizer, PD1, PD2—photodiodes, I—interface, PC-Personal computer, FI—liquid flow, F—color filter, BS—beam splitter. [Reproduced by permission of Química Nova, 2005, vol. 28, no 2, 227–339. © Sociedade Brasileira de Química].

temperature bath kept the liquid flow at (21.0 ± 0.5) °C. Rhodamine 6G (Lambdaphysik, 99.99% purity) was used as the fluorescent probe at a concentration of $1.9 \times 10^{-3}$ mol $L^{-1}$.

During their excited-state lifetime, the photoselected probes may or not rotate, depending on the mobility of neighboring molecules and their chemical environment. With a greater interaction between the solid surface and the flowing liquid, there is increased wetting efficiency. Surface drag propagates through adjacent liquid flow layers decreasing slipping. Microturbulence can then develop, generating misaligned molecular domains at the interface and decreasing both the polarization and anisotropy imposed by the high rate of the liquid flow. Fluorescence depolarization data can be interpreted as a bi-dimensional phenomenon in terms of polarization ($P$), using Eq. (1), where $I_{\parallel}$ and $I_{\perp}$ denote the parallel and perpendicular fluorescence components, respectively [7].

$$P = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp}). \quad (1)$$

### 2.2.3. Adsorption/desorption nitrogen method

Cylindrical stainless steel molds, 6 mm in diameter and 1 mm high, were used to obtain the cured specimens. Quantochrome Autosorb was used to take the adsorption/desorption nitrogen isotherms, which can be used to calculate the average pore size and volume distribution.

### 2.2.4. Nano-indentation

The nano-indentation test is based on the resistance to penetration of the material. A nano-indenter from MTS with a diamond pyramid as the indenter (Berkovich) and applied loads from 1 mg to 40 g was used.

Data were obtained from resin specimens, enamel and dentin. Human canine teeth were sectioned into thin slices with a diamond disc and embedded into phenolic resin. At least 10 samples were analyzed.

## 3. Results and discussion

Fig. 2 shows the micrograph of the Charisma specimen surface, with a predominance of inorganic compounds with dimensions around 1 μm. The value of 20% of organic phase was estimated from a thermogravimetric (TG) curve, considering that the inorganic phase was maintained as the residual fraction. This value is in agreement with the information supplied by the manufacturer.

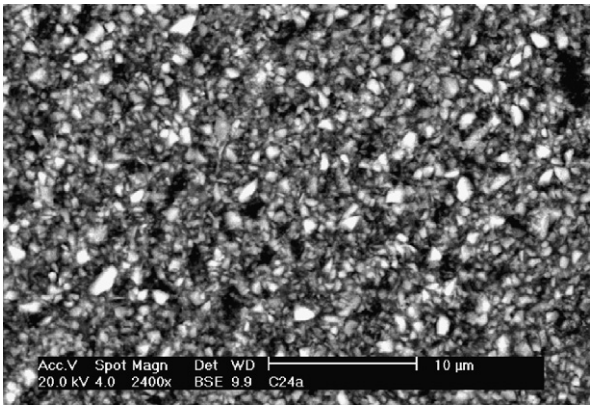


Fig. 2. SEM micrograph for Charisma specimen surface.

Table 1
Average polarization for the liquid flow on specimens

| Drink | Average polarization (%) | | | |
|---|---|---|---|---|
| | 24 h | | 168 h | |
| | Average | SD | Average | SD |
| Control | 5.1 | 0.1 | 5.1 | 0.1 |
| Sports drink | 3.5 | 0.2 | 0.8 | 0.1 |
| Yogurt | 1.2 | 0.1 | 1.1 | 0.1 |
| Soft drink | 4.0 | 0.2 | 3.5 | 0.2 |
| Wine | 3.3 | 0.1 | 0.9 | <0.1 |

Table 1 shows the averaged polarization of the liquid flow on each specimen surface. The polarization increases when the adhesion or wet ability decreases.

The average polarization was 5.1% for the control specimen and was lower for all drinks, suggesting a change in the specimen surface due to the occurrence of an interaction between the resin components and polar liquid. However, it was more pronounced for the specimen immersed in yogurt, which had decreased to 1.2% after 24 h immersion and with further immersion decreased to 1.1%.

The average polarization for specimens immersed for 24 h in the soft drink, sports drink and wine showed small changes, indicating a weaker interaction with the resin surface for a short immersion time. Nevertheless, after 168 h of immersion, the value for the sports drink and wine decreased to 0.8%. Thus, for longer immersion times, the sports drink and wine increase the interactions more than the soft drink.

As discussed in the previous paper [6], the Raman spectroscopy results showed no changes that can

be attributed to reactions between the components of the drinks and the specimen surfaces. The dynamic interfacial tension monitored through average polarization results was clearly changed, suggesting that a very thin layer of drink components was adsorbed on the specimens, which can be detected through PLF. Previous results with this experimental technique also showed that it is much more sensitive to small surface alterations than other techniques, such as static contact angle [8].

The adsorption and desorption gas volume versus initial and relative pressure isotherm curves were coincident for all experiments, with the same behavior for all conditions studied, which can be used to determine surface area, and pore size and distribution. For specimens immersed for 24 h and 168 h in the drinks, the mesopores calculated by the BJH mathematical treatment were of the same order of magnitude, from 15 to 100 A (0.0015–0.01 μm). However, pore intensity of the specimen surfaces increased with immersion time interval in the different drinks, changing from $0.7 \times 10^{-4}$ to $1.4 \times 10^{-4}$ ($cm^3\,g\,A^{-1}$) for 24 h and 168 h, respectively, for pores with dimensions of 30 A, as shown in Fig. 3.

For the resin specimens immersed in yogurt, the adsorption/desorption versus pressure curves showed negative values due to the small pore sizes being out of the detection limit of the equipment, due to the effectiveness of calcium lactate present in milk and it derivates in reducing the intra-oral demineralization of enamel [9,10] and, in the case of a restorative material like a resin composite, some deposition of the drink component must occur.

None of the conditions studied showed an effective change in average pore size, in contrast to highly alkaline or very low ($pH < 2.0$) acidity media, as discussed by Prakki et al. [11] which accelerate dental composite hydrolysis and quickly produce microstructural damage.

Nano-indentation is a sensitive method to detect material hardness, which permits the evaluation of hardness at different specimen depths as a function of applied load. Fig. 4a shows Charisma resin hardness after 168 h of immersion in drinks with different applied loads. As for the general behavior of polymers, the hardness values for the Charisma resin changed with applied load until reaching a constant value [5,12–14].

The low hardness values when applied load values are low, and the increase in hardness with an

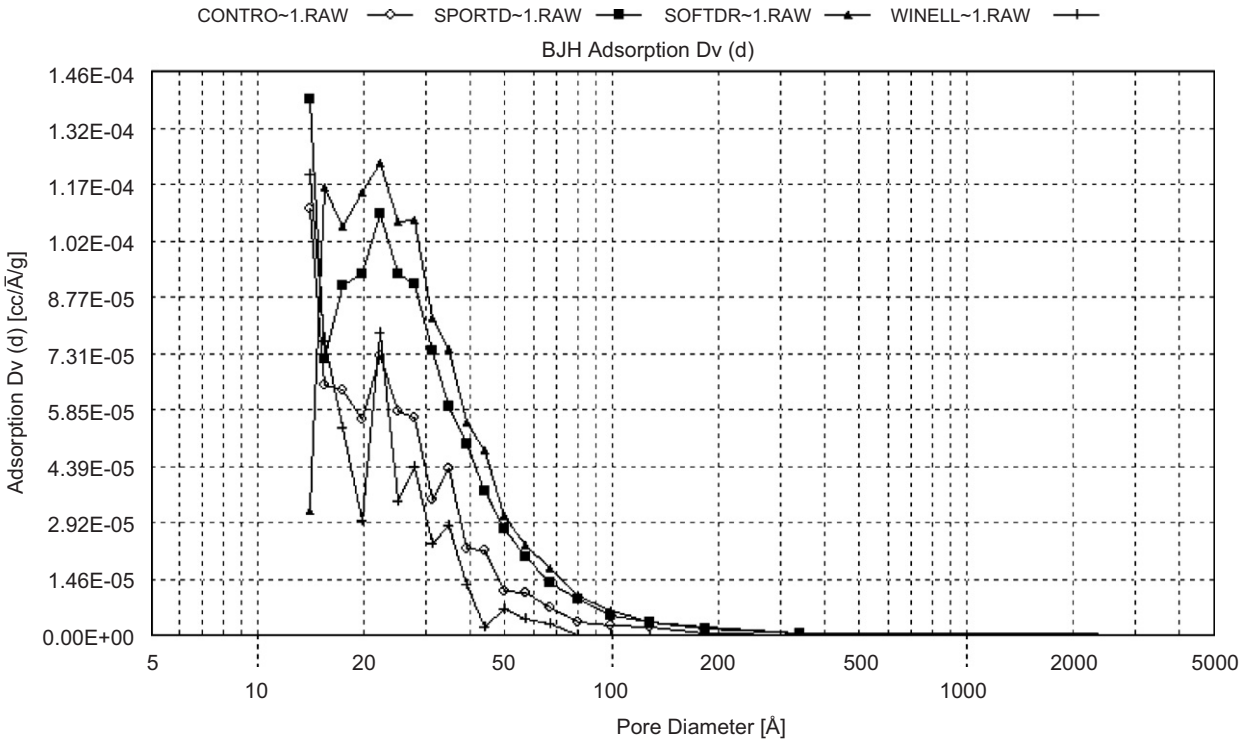


Fig. 3. Pore volume distribution as a function of pore diameter of the resin immersed in different drinks.

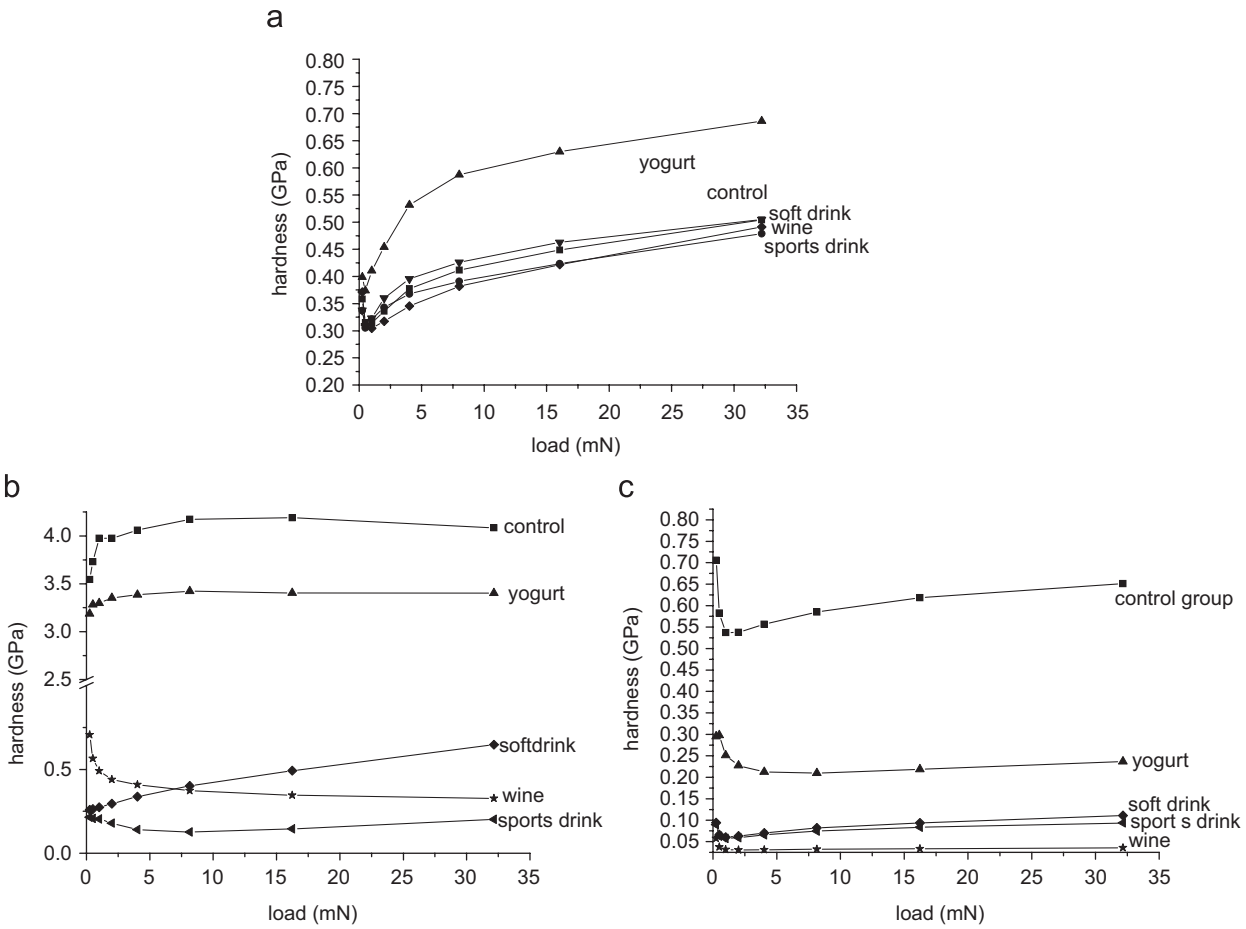


Fig. 4. Hardness values as a function of applied load for specimens immersed for 168 h in drinks obtained by nano-indentation analysis: (a) Charisma specimens, (b) enamel and (c) dentin.

increase in applied load, up to a constant value which is characteristic of polymeric materials, in contrast to metallic materials where hardness is not dependent on applied load. This is probably due to the superficial roughness and plastic deformation of the polymer materials. This characteristic curve was observed for the resin composite control group, due to the presence of an organic phase in the resin composition. In comparison with the control group, Fig. 4a shows slightly lower hardness versus load curves for specimens immersed in the wine, sports drink and soft drink over 168 h, related to changes in the superficial roughness. The specimens immersed in yogurt showed higher hardness values than the control group, probably due to calcium deposition from the milk derivates, as described in the Refs. [9,10]. For enamel, the hardness values remain constant in relation to applied load, and in some cases are around 10 times higher than those of the resin specimens, as shown in Fig. 4b. For yogurt, these values were 10% lower compared with enamel maintained in distillated water. An analogous behavior was observed for the dentin specimens (Fig. 4c). For an applied load of 1 mN, the hardness values for the enamel, dentin and Charisma resin specimens were 3.85, 0.54 and 0.50, respectively. These results can be attributed to the ductile characteristic of dentin and resin in contrast to the fragile characteristic of enamel.

## 4. Conclusions

PLF showed the adsorption of components on resin specimen surfaces, through changes in the liquid flux. However, the components of this thin layer did not react with the resin, as discussed in a previous study reporting Raman spectroscopy results.

The appearance of pores on the surface of the resin specimens, in the order of 100 A, after specimen immersion in the drinks, did not influence the hardness of material. The effect of drinks on the enamel was greater than that on the resin.

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