Sorption and Solubility of Composites Cured with Quartz-tungsten Halogen and Light Emitting Diode Light-curing Units

Luci Regina P. Archegas, DDS, MDS; Danilo B. M. Caldas, DDS, MDS, PhD;
Rodrigo N. Rached, DDS, MDS, PhD; Sergio Vieira, DDS, MDS, PhD;
Evelise M. Souza, DDS, MDS, PhD

Abstract

Aim: The objective of this study was to evaluate the effect of light polymerization on water sorption and solubility of hybrid composites.

Methods and Materials: Three composite resins were used to make discs cured with either quartz-tungsten halogen (QTH) or light emitting diode (LED) curing units. The specimens were stored in a desiccator at 37ºC and weighted to a constant mass, then immersed in deionized water for different periods of time, and reconditioned until achieving a constant mass. Sorption and solubility were calculated and subjected to analysis of variance (ANOVA) and Tukey tests ($p<0.01$).

Results: There were no statistically significant differences between the light sources. Water sorption increased with storage time for all the composites. The lowest sorption was observed for Herculite XRV™, followed by Tetric Ceram™, and Filtek Z250™. Increased storage times reduced the solubility of Filtek Z250™ but did not affect the solubility of Herculite XRV™ and Tetric Ceram™.

Conclusion: Water sorption and solubility of composites are not affected by the type of polymerization when the same intensity and exposure times are used. Thus, the differences found are probably related to the composition of the materials.

Clinical Significance: Water sorption and solubility of composites can lead to a shortened service life. However, these properties are not correlated to the type of polymerization.

Keywords: Water sorption, solubility, composite resins, light-curing units

Introduction

The interaction of dental resin composites with the aqueous oral environment can result in a decrease of their mechanical properties, such as flexural strength,[1,2] modulus of elasticity,[1] tensile strength,[3] and wear resistance.[4] Two different mechanisms occur when a composite is immersed in water: (1) water sorption, which leads to swelling and mass increase and (2) elution of components from filler particles or unreacted monomers which leads to a reduction in mass.[5,6] Water sorption is a diffusion controlled process that takes place largely in the resin matrix.[7-9] However, water may additionally cause debonding of filler particles from the matrix or even cause hydrolytic degradation of filler particles.[10] The phenomena of sorption and solubility may act as precursors to a variety of chemical and physical processes that can lead to deleterious effects on the structure of the polymeric network, which can compromise the clinical performance of the material.[11]

The incomplete polymerization and reduced conversion of monomers can result in increased solubility of the composite material.[5,12] Some studies have demonstrated unreacted monomers are the main components leached from dental composites, and most of these monomers are released within the first days.[12,13] The diluent monomer triethyleneglycol dimethacrylate (TEGDMA) has been identified as the main component leached from dental composites. However, fewer amounts of other monomers, such as bisphenol A glycol dimethacrylate (Bis-GMA) and urethane dimethacrylate (UDMA), can also be released into the water.[13] The leaching of components in composites can affect the initial dimensional change,[8,11] the clinical performance,[5,11] the aesthetic aspect of the restorations,[14] and the biocompatibility of the material.[12,15]

Sorption and solubility of dental composites can be affected by many factors, such as variations in the composition of resin matrix, size and distribution of filler particles, as well as the type of polymerization used.[16] However, there are no studies reported in the literature about the effect of polymerization using light emitting diode (LED) light-curing units on the sorption and solubility of resin composites.

Therefore, the aim of this study was to evaluate the effect of light polymerization on water sorption and solubility of three hybrid composites cured with quartz-tungsten halogen (QTH) and LED light-curing units after different periods of storage in water. The hypothesis tested was composites polymerized with both curing units with the same intensity and exposure time would exhibit the same water sorption and solubility during three periods of storage in water.

Methods and Materials

The methodology used in this study was based upon the ISO 4049 specification.[17] A stainless steel mold was used to create composite discs, 15 ± 0.1 mm in diameter and 1 ± 0.1-mm thick. The three commercial, light-curing resin composites used in the study, as well as their resin matrix composition, type, content, and mean size of fillers (technical profiles), are shown in Table 1. Sixty specimens were made with each composite (A3 shade color). Half of the specimens were irradiated with a QTH light curing unit (Optilux VLC 501, Demetron Research Corp, Danbury, CT, USA) and the other half with a LED light curing unit (LEDemetron I, Demetron Research Corp, Danbury, CT, USA). The mean output intensity of both light sources was 600mW/cm^2, as assessed by the radiometer attached to the respective units. The discs were irradiated with an 11 mm diameter tip positioned on one central and four peripheral points for 20 seconds each, leading to 100 seconds of exposure time for both top and bottom surfaces of each specimen.
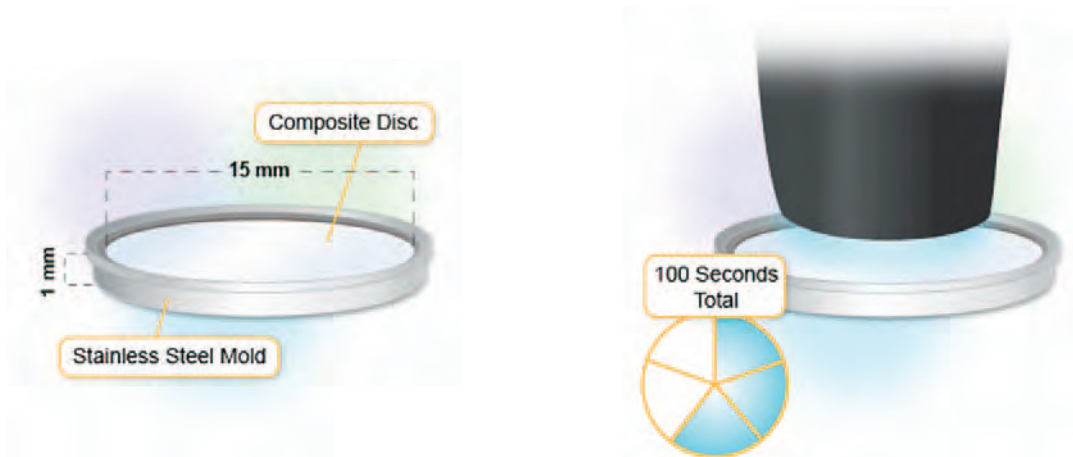
Table 1. Technical profiles of the resin composites evaluated.

Composite	Manufacturer	Batch No.	Polymer	Filler Particle	Filler Size	Filler Content (Volume)	Filler Content (Weight)
Herculite XRV	SDS/Kerr Orange, CA, USA	14546	Bis-GMA TEGDMA	AL-B silicate glass, silica	0.6 μm	59%	79%
Tetric Ceram	Ivoclare AG Schaan, Liechtenstein	G18572	Bis-GMA TEGDMA UDMA	Ba glass, ytterbium trifluoride, Ba AL fluorosilicate glass	0.7 μm	62%	81%
Filtek Z250	3M ESPE St. Paul, MN, USA	4LU	Bis-GMA TEGDMA UDMA Bis-EMA	Zirconia/ silica	0.6 μm	60%	80%

Note:
Bis-GMA = bisphenol A glycol dimethacrylate
TEGDMA = triethyleneglycol dimethacrylate
UDMA = urethane dimethacrylate
Bis-EMA = bisphenol A polyethyleneglycol diether dimethacrylate

The procedures were carried out in a room with controlled temperature (23°C ± 2°C) and relative humidity (50% ± 10%). After removal from the molds, the specimens were transferred to a desiccator containing silica gel maintained at 37°C for 22 hours and then transferred to another desiccator at 23°C ± 2°C for two hours. The specimens were weighted to a precision of 0.0001 g using an analytical balance (Bel Mark U210A, Bel Engineering, Monza, MI, Italy). This cycle was repeated until a constant mass was achieved (m_1). In a pilot study a period of 60 days was determined to be necessary to obtain a constant mass of the composites.

The volume of the specimens was calculated by measuring their diameters at two opposing points on the circumference of the discs with a digital caliper (CD6CS, Mitutoyo, Kanagawa, Japan), their thickness at the center, and at four equally spaced points with a micrometer (103-125, Mitutoyo, Kanagawa, Japan).

The specimens were divided in groups (n=10), placed individually in glass tubes containing 12 mL of deionized water, and stored in an oven at 37°C for 24 hours, seven days, and 28 days. The deionized water was changed weekly for the 28-day period. After each time of storage, the specimens were removed from water, blot dried with an absorbent paper, and waved in the air for 15 seconds. The specimens were

then re-weighted to obtain m_2, reconditioned in a desiccator at 37°C for 22 hours, and again in another desiccator at 23°C ± 2°C for two hours until a constant mass was achieved (m_3).

The values for water sorption (W_{sp}) and solubility (W_{sl}) in $\mu g/mm^3$ were calculated according to the following formula proposed by ISO 4049[17]:

$$W_{sp} = \frac{m_2 - m_3}{V}$$

$$W_{sl} = \frac{m_1 - m_3}{V}$$

Where:
  m_1 is the mass of the specimen, in μg, before immersion in water,
  m_2 is the mass of specimen, in μg, after immersion in water,
  m_3 is the mass of specimen , in μg, after immersion and desiccation,
  V is the volume of the specimen in mm^3.

The SPSS software version 13.0 (SPSS Inc., Chicago, IL, USA) was used for the statistical analysis. A three-way analysis of variance (ANOVA) and Tukey HSD test was carried out at a significance level of 0.01.

Results
Comparing the mean values of sorption and solubility, the ANOVA detected statistically significant differences ($p<0.01$) between composites and storage times.

There were interactions between the composite and light source as well as the composite and storage time for the sorption variable. There were also interactions between the composite and storage times for the solubility variable.

Table 2 shows there were no statistically significant differences between light sources for sorption and solubility effects. Therefore, the sorption and solubility mean values are shown in Table 3, considering only composite and storage time as sources of variation in this study.

Herculite XRV™ exhibited the lowest water sorption values, followed by Tetric Ceram™, and Filtek Z250™ with statistically significant differences among them ($p<0.01$). All the tested materials had an increase in water sorption as a result of the increase of water storage times with statistically significant differences among them. The composite Filtek Z250™ demonstrated higher water sorption after 28 days of storage in water ($p<0.01$).

There were no statistically significant differences in the solubility of Herculite XRV™ and Tetric Ceram™ in the different storage times. However, Filtek Z250™ showed a significant reduced solubility with the increase of storage time in water. The solubility of Herculite XRV™ was significantly lower than Filtek Z250™ in the 24-hour storage time. After 28 days of storage in water, Filtek Z250™ showed significantly lower solubility than Tetric Ceram™ ($p<0.01$).

Discussion
Resin composites indicated as restorative materials must comply with ISO 4049 for a maximum value of 40 $\mu g/mm^3$ for water sorption and 7.5 $\mu g/mm^3$ for water solubility within a seven day period of water storage.[17] The water sorption and solubility values obtained in this study are remarkably lower than ISO guidelines, even for a 28-day storage time. Moreover, because water sorption increased from 24 hours to 28 days suggests a seven day period of storage may be insufficient to evaluate the real values of water sorption in composite resins.[13,18,19]

Table 2. Mean values of sorption and solubility of composites according to light curing units.

Light Source	n	Sorption	Solubility
QTH	90	16 (6) [a]	0.33 (0.36) [a]
LED	89	16 (6) [a]	0.26 (0.41) [a]

Note: Groups with the same superscripted letter were not statistically significantly different ($p>0.01$).

Table 3. Mean values for sorption and solubility of composites after different storage times.

Composite	Storage Time	n	Sorption	Solubility
Herculite XRV	24 hours	20	7.64 (0.40) [a]	0.20 (0.20) [a,b,c]
	7 days	20	15.08 (o.33) [d]	0.10 (0.28) [a,b]
	28 days	20	16.44 (0.34) [e]	0.19 (0.27) [a,b,c]
Tetric Ceram	24 hours	20	8.45 (0.43) [b]	0.45 (0.22) [b,c,d]
	7 days	19	17.60 (0.53) [f]	0.40 (0.40) [b,c,d]
	28 days	20	18.86 (0.68) [g]	0.36 (0.51) [b,c,d]
Filtek Z250	24 hours	20	9.35 (0.47) [c]	0.72 (0.29) [d]
	7 days	20	22.61 (0.47) [h]	0.32 (0.40) [b,c]
	28 days	20	27.95 (0.29) [i]	-0.07 (0.21) [a]

Note: Groups with the same superscripted letters indicate they were not statistically significantly different ($p < 0.01$).

Differences detected for water sorption and solubility results are probably related to the composition of the tested composites. The composites used in this study have a great similarity in the filler particle content by volume (approximately 60%). However, there are some differences regarding the type of filler particles and the monomers used in the resin matrix. Several composites available in the market are composed of a combination of Bis-GMA, UDMA, TEGDMA and, more recently, the bisphenol A polyethyleneglycol diether dimethacrylate (Bis-EMA). The Bis-EMA has been used in the newest composites due to its less hydrophilic characteristic resulting from a molecular structure resembling Bis-GMA but lacking two hydroxyl groups.[20]

Based on the features of the resin monomers, more favorable water sorption results for Filtek Z250™ would be expected but was not observed in the present study. This suggests the relative proportion of each monomer in the matrix should be taken into consideration rather than the composition of the matrix alone. Furthermore, the inorganic components of composites can contribute to the different degrees of water uptake. Although there is not a great amount of water sorption in the filler particles themselves,[9] there may be an accommodation of water in the matrix/filler interface which could cause deleterious effects on bonding over time.[10] Differences observed in water uptake can be attributed to the nature of filler particles and the effectiveness of silanization.[9,21,22] Herculite XRV™ and Tetric Ceram™ composites basically have glass fillers in their composition, and Filtek Z250™ composite has silica-zirconia filler particles which can be responsible for a critical silanization.[21] This fact could explain the higher sorption of Filtek Z250 when compared to the other composites used in the present study. The 28-day storage time for this composite caused a considerable increase in water sorption compared to the other composites. The behavior of Filtek Z250 was the main factor for the detection of interactions between individual composites and their light sources and the same composites' storage times.

The results obtained by Herculite XRV might be related to a higher cross-link density[11,20] and degree of conversion due to the presence of Bis-GMA/TEGDMA copolymer.[23] This combination results in a synergistic effect on the polymerization rate and a better compatibility between the monomers.[23]

The solubility of dental composites reflects the amount of unreacted monomers leached to the water[11,12,22] as well as other low weight molecules, like filler particle compounds[10,14,24] and photo-initiators.[12,15]

In the methodology used in this study and that proposed by ISO, the initial and final dehydration of specimens are crucial in directly affecting the solubility of composites. If the material is not completely dehydrated in the beginning of the process, the solubility values can reflect only the final desiccation of the specimen. A recent study evaluated the solubility of different materials with and without initial dehydration and found values up to eight times higher than those detected for specimens not previously desiccated.[25] Despite the ISO standard suggestion of two to three weeks to obtain a constant mass, a period of 60 days was required in this study, as suggested by the pilot-study. This period of time was the same used by Scarret et al.[4] for the complete dehydration of the specimens before water immersion.

The tested composites demonstrated higher solubility values in the 24-hour storage time which showed the majority of resin components were leached in the beginning of water storage.[12] However, this result differed from other studies in which solubility increased with time.[13,26] In the 24-hour storage the higher solubility of Filtek Z-250™ compared to Herculite XRV™ can be attributed to the differences in their resin matrix composition. Sideridou et al.[20] reported higher solubility of the copolymer Bis-GMA/TEGDMA when compared to UDMA and Bis-EMA copolymers. Additionally, the same authors found a higher degree of conversion with Bis-GMA and TEGDMA resin matrixes.[23] This statement is in accordance to other studies that found a correlation between a reduced degree of conversion to a higher amount of leached components.[5,11,12,15]

Beside the resin matrix components, the inorganic components can also influence the solubility of composites. Söderholm et al.[24] found higher leaching of barium in composites based on UDMA resin immersed in distilled water when compared to composites based on Bis-GMA resin. The barium glass filler particles in the Tetric Ceram composite could cause higher leaching of other inorganic components, especially silicon.[14,24]

The presence of silica/zirconia filler particles in the composite Filtek Z250™ might be the cause of its higher solubility during the first 24 hours in water. Ferracane[12] reported a significantly higher solubility of the composite Z100 in a 48-hour period of immersion in water when compared to other composites as Herculite XRV™. The composite Z100 is the precursor of Filtek Z250™ and has the same type of silica/zirconia filler particles. Filtek Z250™ showed a significant decrease in solubility, reaching negative rates in the 28-day period. As previously discussed, the silica-zirconia filler might not be properly covered by the silane leading to water sorption and an entrapment of water inside the composite.[21] Other studies also showed negative values of solubility of composite restorative materials after long periods of water storage.[13,27]

The extent to which hygroscopic and hydrolytic effects influence the clinical performance of polymer restoratives is yet unknown. However, according to Ferracane[11] water uptake and hydrolytic degradation may affect their mechanical properties, dimensional stability, and biocompatibility leading to a shortened service life of composite restorations.

The performance of dental composites is directly related to the efficiency of their polymerization.[28] In this study the polymerization was carried out with two different light-curing units, one based on a QTH light and the other based on a LED. Both lights were used with the same intensity and time of exposure. Several studies have demonstrated the use of the same energy density (intensity x exposure time), even with different types of light sources, results in similar properties of the composites.[29-31] Another factor that can influence the polymerization efficiency is the emission wavelength of the light curing units.[32] Unlike QTH lights, LEDs produce light in a narrower spectral range, but both are within the absorption wavelength range to activate the camphorquinone (450-500 nm).[32] This is one of the factors that could have contributed to the similar results for sorption and solubility produced by both light curing units, since the composites used in the present study have camphorquinone as the photoinitiator.

The null hypothesis proposed was confirmed since water sorption and solubility of the

composites were not affected by the polymerization with QTH and LED light-curing units.

Conclusions

- Water sorption and solubility of the evaluated composites were not affected by the polymerization using different light sources.
- The water sorption of the composites increased with prolonged storage time.
- Herculite XRV™ exhibited the lowest water sorption among all the tested composites.
- Different storage times in water did not affect solubility of composites, with the exception of Filtek Z250™.

Clinical Significance

Water sorption and solubility of composites can lead to a shortened service life. However, these properties are not correlated to the type of polymerization.

References

1. Oysaed H, Ruyter IE. Composites for use in posterior teeth: Mechanical properties tested under dry and wet conditions. J Biomed Mater Res 1986; 20:261-71.
2. Calais JG, Söderholm K-JM. Influence of filler type and water exposure on flexural strength of experimental composite resins. J Dent Res 1988; 67:836-40.
3. Söderholm K-JM, Roberts MJ. Influence of water exposure on the tensile strength of composites. J Dent Res 1990; 69:1812-6.
4. Scarrett DC, Söderholm K-JM, Ybatich CD. Water and abrasive effects on three-body wear of composites. J Dent Res 1991; 70:1074-81.
5. Pearson GJ, Longman CM. Water sorption and solubility of resin-based materials following inadequate polymerization by a visible-light curing system. J Oral Rehabil 1989; 16:57-61.
6. Yap AUJ, Wee KEC. Effects of cyclic temperature changes on water sorption and solubility of composite restoratives. Oper Dent 2002; 27:147-53.
7. Braden M, Causton EE, Clarke RL. Diffusion of water in composite filling materials. J Dent Res 1976; 55:730-2.
8. Fan PL, Edahl A, Leung RL, Standford JW. Alternative interpretations of water sorption values of composite resins. J Dent Res 1985; 64:78-80.
9. Kalachandra S, Wilson TW. Water sorption and mechanical properties of light-cured proprietary composite tooth restorative materials. Biomaterials 1992; 13:105-9.
10. Söderholm KJ, Zigan M, Ragan M, Fischlschweiger W, Bergman M. Hydrolytic degradation of dental composites. J Dent Res 1984; 63:1248-54.
11. Ferracane JL. Hygroscopic and hydrolytic effects in dental polymer networks. Dent Mater. 2006; 22:211-22.
12. Ferracane JL. Elution of leachable components from composites. J Oral Rehabil 1994; 21:441-52.
13. Örtengren U, Wellendorf H, Karlsson S, Ruyter IE. Water sorption and solubility of dental composites and identification of monomers released in an aqueous environment. J Oral Rehabil 2001; 28:1106-15.
14. Söderholm K-JM. Leaking of fillers in dental composites. J Dent Res 1983; 62:126-30.
15. Lygre H, Hol PJ, Solheim E, Moe G. Organic leachables from polymer-based dental filling materials. Eur J Oral Sci 1999; 107:378-83.
16. von Fraunhofer JA, Curtis Jr P. Physical and mechanical properties of anterior and posterior composite restorative materials. Dent Mater 1989; 5:365-8.
17. International Organization for Standardization. ISO 4049: Dentistry polymer – based filling, restorative and luting materials. Switzerland, 2000.
18. Martin N, Jedynakiewicz N. Measurement of water sorption in dental composites. Biomaterials 1998; 19:77-83.
19. Sakagushi RL. Review of the current status and challenges for dental posterior restorative composites: clinical, chemistry, and physical behavior considerations. Summary of discussion from the Portland Composites Symposium (POCOS) June 17-19, 2004, Oregon Health and Science University, Portland, Oregon. Dent Mater 2005; 21:3-6.

20. Sideridou I, Terski V, Papanastasiou G. Study of water sorption, solubility and modulus of elasticity of light-cured dimethacrylate-based dental resins. Biomaterials 2003; 24:655-65.
21. Mohsen NM, Craig RG. Hydrolytic stability of silanated zirconia-silica-urethane dimethacrylate composites. J Oral Rehabil 1995; 22:213-20.
22. Toledano M, Osorio R, Osorio E, Fuentes V, Prati C, Garcia-Godoy F. Sorption and solubility of resin-based restorative dental materials. J Dent 2003; 31:43-50.
23. Sideridou I, Tserki V, Papanastasiou G. Effect of chemical structure on degree of conversion in light-cured dimethacrylate-based dental resins. Biomaterials 2002; 23:1819-29.
24. Söderholm K-JM, Mukherjee R, Longmate J. Filler leachability of composites stored in distilled water or artificial saliva. J Dent Res 1996; 75:1692-9.
25. Mortier E, Gerdolle DA, Dahoun A, Panighi MM. Influence of initial water content on the subsequent water sorption and solubility behavior in restorative polymers. Am J Dent 2005; 18:177-81.
26. Palin WM, Fleming GJP, Burke FJT, Marquis PM, Randall RC. The influence of short and medium-term water immersion on the hydrolytic stability of novel low-shrink dental composites. Dent Mater 2005; 21:852-63.
27. Martin N, Jedynakiewicz NM, Fisher AC. Hygroscopic expansion and solubility of composite restoratives. Dent Mater 2003; 19:77-86.
28. Emami N, Söderholm K-JM. How light irradiance and curing time affect monomer conversion in light-cured resin composites. Eur J Oral Sci 2003; 111:536-42.
29. Mills RW, Uhl A, Blackwell GB, Jandt KD. High power light emitting diode (LED) arrays versus halogen light polymerization of oral biomaterials: Barcol hardness, compressive strength and radiometric properties. Biomaterials 2002; 23:2955-63.
30. Moon HJ, Lee YK, Lim BS, Kim CW. Effects of various light curing methods on the leachability of uncured substances and hardness of a composite resin. J Oral Reabil 2004; 31:258-64.
31. Vandewalle KS, Roberts HW, Tiba A and Charlton DG. Thermal emission and curing efficiency of LED and halogen curing lights. Oper Dent 2005; 30:257-64.
32. Leonard DL, Charlton DG, Roberts HW, Cohen ME. Polymerization efficiency of LED curing lights. J Esthet Restor Dent 2002; 14:286-95.

About the Authors

Luci Regina P. Archegas, DDS, MDS

Dr. Archegas is a PhD student in the Department of Restorative Dentistry of the School of Dentistry at the Pontifical Catholic University of Parana where she received her Masters in Dental Science degree. She currently serves as a faculty member at the Technological School at the Federal University of Parana in Curitiba, PR, Brazil.

e-mail: luci.archegas@ufpr.br

Danilo B. M. Caldas, DDS, MDS, PhD

Dr. Caldas is an Adjunct Professor of Restorative Dentistry of the School of Dentistry at the Pontifical Catholic University of Parana in Curitiba, PR, Brazil.

e-mail: danilocaldas@hotmail.com

Rodrigo N. Rached, DDS, MDS, PhD

Dr. Rached is an Adjunct Professor of Dental Materials of the School of Dentistry at the Pontifical Catholic University of Parana in Curitiba, PR, Brazil.

e-mail: ronura@yahoo.com

Sergio Vieira, DDS, MDS, PhD

Dr. Vieira is a Professor of Restorative Dentistry and Chair of the Graduate Program of the School of Dentistry at the Pontifical Catholic University of Parana in Curitiba, PR, Brazil.

e-mail: s.vieira@pucpr.br

Evelise M. Souza, DDS, MDS, PhD

Dr. Souza is an Adjunct Professor of Restorative Dentistry of the School of Dentistry at the Pontifical Catholic University of Parana in Curitiba, PR, Brazil.

e-mail: evesouza@yahoo.com