

## THERMAL ANALYSIS AND STRUCTURAL INVESTIGATION OF DIFFERENT DENTAL COMPOSITE RESINS

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The structural and thermal properties of three different dental composite resins, Filtek™ Supreme XT, Filtek™ Z-250 and TPH<sub>3</sub>® were investigated in this study. The internal structures of uncured and cured resins with blue light-emitting diodes (LEDs) were examined by Micro-Raman spectroscopy. Thermal analysis techniques as DSC, TG and DTG methods were used to investigate the temperature characteristics, as glass transition ( $T_g$ ), degradation, and the thermal stability of the resins. The results showed that the TPH<sub>3</sub>® and Filtek™ Supreme XT presented very similar  $T_g$  values, 48 and 50°C, respectively, while the Filtek™ Z-250 composite resin presented a higher one, 58°C. AFM microscope was utilized in order to analyze the sample morphologies, which possess different fillers. The composed resin Filtek™ Z-250 has a well interconnected more homogeneous morphology, suggesting a better degree of conversion correlated to the glass phase transition temperature. The modes of vibration of interest in the resin were investigated using Raman spectroscopy. It was possible to observe the bands representative for the C=C ( $\sim 1630\text{ cm}^{-1}$ ) and C=O ( $\sim 1700\text{ cm}^{-1}$ ) vibrations were studied with respect to their compositions and polymerization. It was observed that the Filtek™ Z-250 resin presents the best result related to the thermal properties and polymerization after light curing among the other resins.

**Keywords:** AFM, dental resins, Raman, thermal analysis

### Introduction

Dental composite resins were introduced commercially in the mid-1960s for the restoration of anterior teeth. Since their advent composite resins have undergone significant development, which continues to improve the longevity of composite resins restorations [1].

The use of composite resins in posterior teeth has been increasing during the last several years. The renewed interest in this class of materials has been stimulated for several reasons. It was noted that the most important among these is a demand for a more esthetic restoration [2].

Nowadays, visible-light-cured dental composite materials are extensively used in several dentistry applications due to their excellent aesthetics and the improvements in the chemical and mechanical resistance reached in the last years. These materials are composed basically by two phases: a resinous matrix (organic phase), comprising dimethacrylate monomers and/or oligomers, photoinitiator and an inorganic phase, known as filler, generally composed by particulate glass [3]. When the composite resins are irradiated, the radicals generated attack the double bonds of the monomers, creating cross-linked three-dimensional network polymers [4].

The main monomers/oligomers used in the resinous matrix phase are bisphenylglycidyl dimethacrylate (BisGMA), triethylene glycol dimethacrylate (TEGDMA) and urethane dimethacrylate (UDMA). The photoinitiator system is commonly camphorquinone associated with a tertiary amine. Silicate-based glasses, zirconia, alumina, quartz and barium aluminum silicate are used as fillers which normally are surface modified by a coupling agent aiming to improve mechanical properties [5, 6].

The available commercial composites are classified according to their particle size in four categories: traditional composites (8–12  $\mu\text{m}$ ), small particle-filled composite (1–5  $\mu\text{m}$ ), microfilled composite (0.04–0.4  $\mu\text{m}$ ) and hybrid composite (0.6–1.0  $\mu\text{m}$ ) [7]. Recently nanofiller composite (75 nm) and nanohybrid composites were introduced [8].

Few systematic investigations into the effect of particle size and shape have been published in [9–11] and finer particles for a fixed-volume-fraction of filler have been suggested to result in decreased interparticle spacing and reduced wear [12]. With regard to filler geometry, different shapes are very likely present distinct surface area, which again affects the amount of matrix resin in the interfacial region between particles [11].

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Thus, the nanofilled composite resins were introduced as function of the nanotechnology that is used to describe research or products where critical component dimensions are in the range of 0.1 to 100 nanometers (nanometric scale), through several physical and chemical methods [13]. In 2002, the first composite resin with these characteristics was introduced in dentistry [14]. The goal was to use nanotechnology to create a composite that offers the polish retention of a microfill with the strength of a hybrid composite [15].

However, despite of all advantages in using composite materials in dentistry, several problems have been reported including low abrasion resistance, shrinkage during polymerization that causes microleakage and consequently secondary caries and low color stability [16].

The properties of the final restorations are intrinsically related to the polymerization stage and the composition of the material [17, 18].

The Knoop and Vickers hardness test [19–22], the degree of polymerization measured using infrared spectroscopy (IR) [22–24] and other methods that measure leached components in organic solvents [25] or water solution [26] are used to determine the characteristics of dental resins. Thermal analysis techniques, such as differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) are also used to characterize a variety of materials [27–29]. In this study the thermal characteristics of the three dental composite resins, uncured and cured with a blue LED LCU was examined. Techniques, such as Raman spectroscopy and AFM (atomic force microscopy) also have been used.

Thus, the purpose of this study was to evaluate the photo-activation efficiency of the one light curing unit (LCU) based on blue LED by Raman Spectroscopy, AFM, TG and DSC techniques.

## Experimental

### Materials

The dental composite resins used in this study were: Filtek™ Z-250 (3M/ESPE, Dental Products St. Paul, MN), Filtek™ Supreme XT (3M/ESPE, Dental Products St. Paul, MN) and TPH<sub>3</sub>® (Dentsply De Trey GmbH, Konstanz, Germany) at color A<sub>2</sub>. Table 1 summarizes the dental composite resins and the batch number.

### Methods

#### DSC and TG

DSC measurements were performed with a DSC 2910 (TA Instruments). The samples were heated at a constant rate of 10°C min<sup>-1</sup>, from 25 to 300°C under nitrogen flowing at 100 mL min<sup>-1</sup> in order to observe the initial degradation of the different dental composite resins. A mass of ~50 mg of the samples were used in an aluminum sample pan.

TG were performed with a TG 209 (Netzsch), operating in N<sub>2</sub> under a gas flow of 20 mL min<sup>-1</sup> with alumina pan containing ~20 mg of the samples. The runs were single ones and carried out in dynamic conditions at the constant heating rate of 10°C min<sup>-1</sup>. Calibration of the device was performed according to standard procedure available on TA Instruments online help. The TG mass and baseline calibration was conducted with and without  $\alpha$ -alumina standards positioned on the sensors. The temperature calibration was performed using a high purity zinc sample.

#### Raman spectroscopy and AFM

Raman spectra and AFM images were recorded with a confocal Raman microscope (WiTec, model Alpha 300S-CRM 200) equipped with a piezo scanner and 100× microscope objectives (N.A.: 0.90; Nikon, Tokyo, Japan). The spatial resolution is as high as 400 nm in this experiment. Samples were excited with a 514.5 nm air-cooled Ar ion laser (Melles Griot, model 35-LAL – 515-230) with a power of 1 mW incident on the samples. Raman data were also obtained on a monochromator equipped with 1800-groove gratings.

## Results and discussion

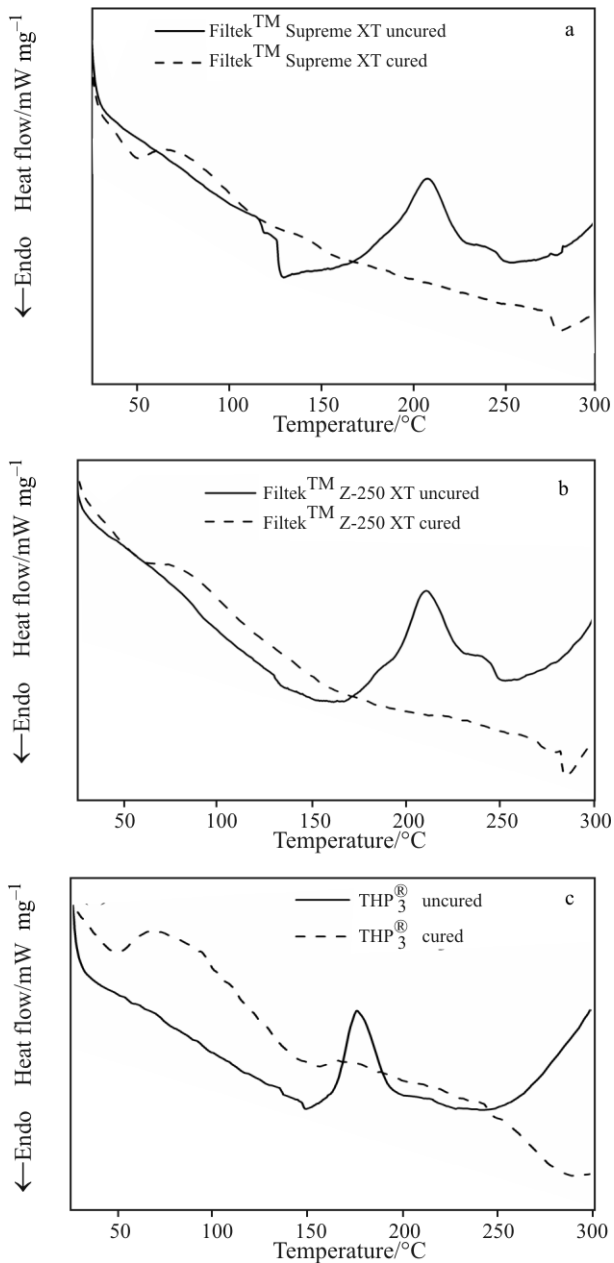
The differences between thermal characteristics of the visible light-cured and uncured composite resins were investigated by DSC, TG and DTG methods. Figure 1 shows the representative DSC curves obtained with the use of the three different composite resins, uncured and cured with the blue LED. The first thermal event that can be seen in the DSC curves of the cured samples is attributed to the glass phase transition ( $T_g$ ) of organic phase. The temperature of  $T_g$  was about 48–58°C (evidenced by the change in the baseline) which is within the range as reported in the literature [30].

Uncured samples present a second thermal event that was an exothermic peak, which occurred in the 150–250°C range and for all cured samples this exothermic events was not observed (Fig. 1).

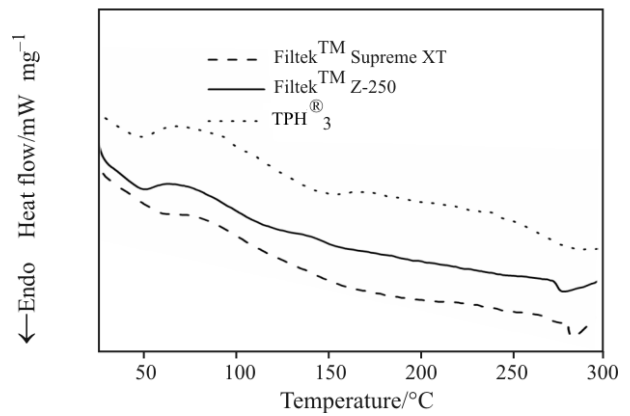
The DSC curves for all cured composite resins are shown in Fig. 2. It can be seen that TPH<sub>3</sub>® and

**Table 1** Dental composite resins used in this study

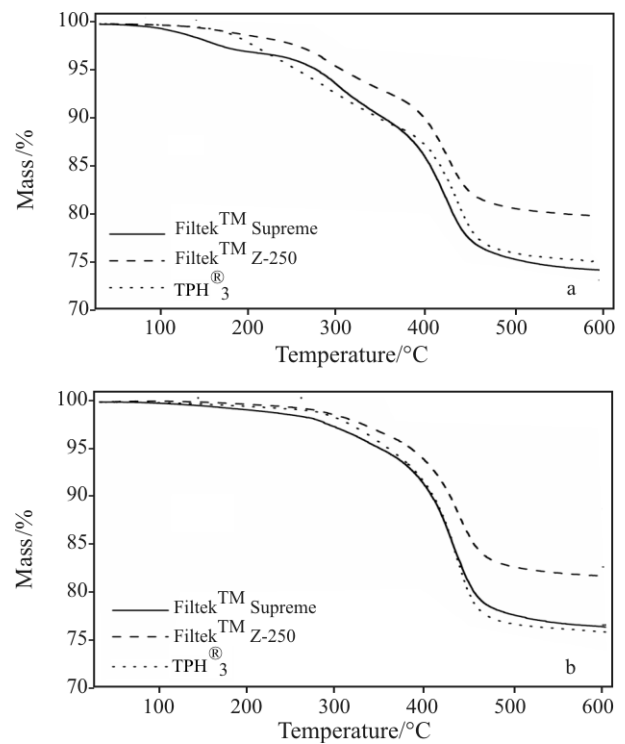
Composite resin	Resinous matrix	Filler type loading/vol%	Batch number
Filtek™ Z-250	<i>Bis</i> -GMA, UDMA, <i>Bis</i> -EMA	Zirconia/silica (60%) 0.19–3.3 μm	1370
Filtek™ Supreme XT	<i>Bis</i> -GMA, UDMA, TEG-DMA, <i>Bis</i> -EMA	Zirconia/silica (59.5%) 0.6–1.4 μm	3910
TPH <sub>3</sub> <sup>®</sup>	<i>Bis</i> -GMA, <i>Bis</i> -EMA Dimethacrylate	Bariumaluminoborosilicate glass, 49.7% Bariumaluminofluorosilicate and highly dispersed silicon dioxide, 24.6%	647011



**Fig. 1** DSC curves for cured and uncured a – Filtek™ Supreme XT, b – Filtek™ Z-250 and c – TPH<sub>3</sub><sup>®</sup> composite resins; 10°C min<sup>-1</sup>



**Fig. 2** Representative DSC curves of cured dental composite resins



**Fig. 3** TG curves of a – uncured and b – cured dental composite resins

Filtek™ Supreme XT presented very similar  $T_g$  values, 48 and 50°C, respectively, while the Filtek™ Z-250 composite resin presented a higher one at 58°C. A lower cross-link density and higher molecular mobility of the network chains cause a lower  $T_g$  temperature. Over time, the faster relaxation of residual stresses is one consequence of lower  $T_g$  of the resin [31].

In Fig. 2 the endothermic curves are shown that occur in a temperature range from 270 to 300°C for all cured samples. It is known that this thermal event represents the decomposition of the dental composite resins [4].

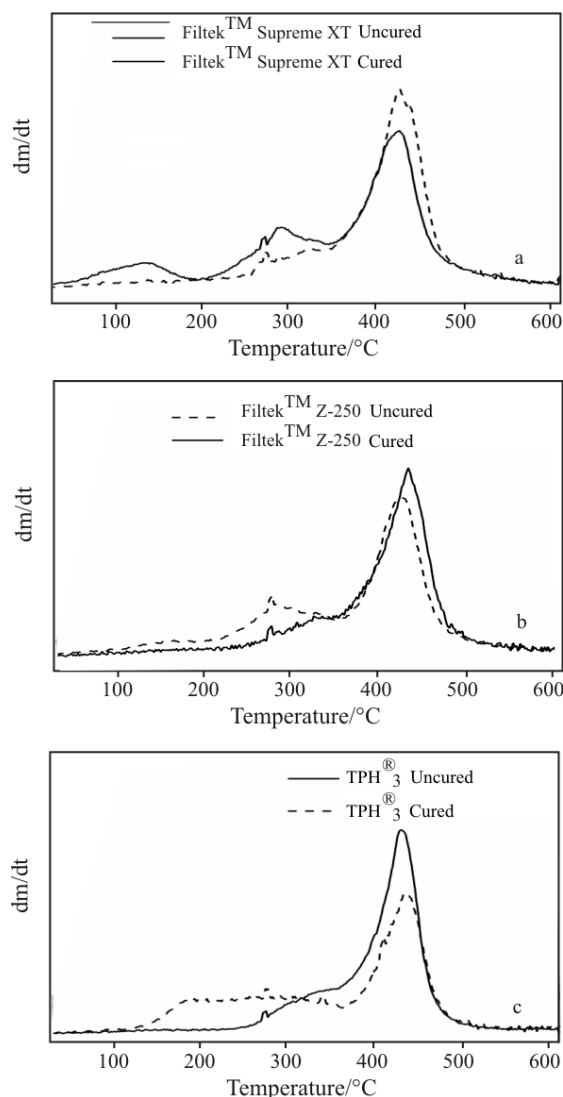
Thermal stability and degradation of the dental composite resins were followed by measuring their TG curves. The results are shown in Fig. 3.

The dental composite resins are filled with about 60–70% of particles (Table 1). From the TG curves (Fig. 3) it can be seen that uncured resins present a residual mass of 73–79%. A 2% enhancement was observed when the dental composite resins were cured with the visible light blue LED. This result was due to the restricted mobility of the polymer chains caused by the presence of the particles.

Figure 4 shows the DTG curves indicating clear differences between cured and uncured dental composite resins. The thermal decomposition temperatures in the first step disappear for the cured samples. These results may be attributed to the visible light-cure that creates the cross-link network polymers and due to the interaction between the polymer chains and inorganic particles. Consequently it prevents the dental composite resins from thermal decomposition by enhancement their thermal stability.

Important thermal events obtained by DSC, TG and DTG methods are summarized in Table 2.

The Filtek™ Z-250 composite resin presents the best thermal stability as shown in TG and DTG curves. This sample has the major residual mass and a major  $T_g$  value (58°C) that suggest a better influence of the fillers and an increased crosslinking provided by the blue LED as related to the other dental composite resins evaluated.



**Fig. 4** DTG curves of cured and uncured dental composite resins

Figure 5 shows the AFM images of the roughness surface and the grain size of the TPH<sub>3</sub> (Fig. 5a), Filtek™ Z-250 (Fig. 5b) and Filtek™ Supreme XT (Fig. 5c) composite resins. Images obtained for the different samples showed that the composite resins exhibit different morphologies. The composed resin

**Table 2** Thermal events for cured composite resins obtained from DSC, TG and DTG curves

Resins	$T_g/\pm 1^\circ\text{C}$	Residual mass/%		Thermal degradation events/ $\pm 2^\circ\text{C}$	
		uncured	cured	uncured	cured
Filtek™ Supreme XT	50	74	76	75	—
				226	258
				362	357
Filtek™ Z-250	58	79	81	127	—
				226	250
				366	356
TPH <sub>3</sub> ®	48	73	75	151	—
				230	259
				378	368

**Table 3** Summary of the Raman shift data

Samples	Intensity Fe/C=C	Pos 1 spurious	Pos 2 fenil	Pos 3 C=C	Pos 4 C=O(1)	Pos 5 C=O(2)	R <sup>2</sup>
Filtek™ Supreme XT	0.58	1560.9	1600.4	1630.6	1698.08	1712.3	0.990
TPH <sub>3</sub> ®	0.60	1574.6	1602.0	1631.1	1704.8	1715.6	0.996
Filtek™ Z-250	0.55	1561.5	1600.4	1630.9	1692.5	1709.7	0.992

R=fitting parameter

Filtek™ Z-250 presents a well interconnected more homogeneous morphology and, suggesting with this one better degree of conversion correlated to the glass phase transition temperature.

Data analysis of the calibration mixtures involved the drawing of a straight baseline between 1500 and 1800 cm<sup>-1</sup> and curve fitting of the bands within this region to the appropriate number of vibrations for the system under consideration. As described by Shin *et al.* [32] the number of bands in this region is assumed to be 5 due to the hydrogen bond influence on the C=O, generating a broadening dublet in this case. Figure 6 shows the data for the three Raman spectra obtained for Filtek™ Supreme XT,

TPH<sub>3</sub>® and Filtek™ Z-250. Table 3 summarizes the data collected from the Raman shift.

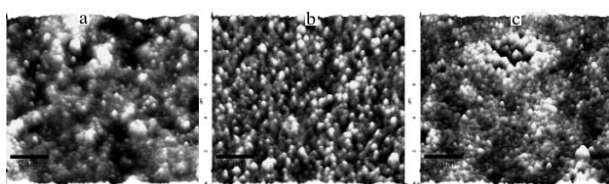
Raman spectroscopy, like infrared spectroscopy, is a vibrational technique and as such is sensitive to the vibrational modes of molecules. In dental composite resins the vibrational bands of interest are typically the C=C double bond, the C=O vibration and the phenyl (O) ring modes of the monomers and crosslinked networks. For highly symmetrical molecules, the quantum mechanical selection rules determine which modes of vibration will be Raman active.

The spectrum of Fig. 6 shows the difference between the different dental composite resins. The band at 1630 cm<sup>-1</sup> of the irradiated sample shows the strongest intensity for composite resin TPH<sub>3</sub>®, suggesting that the associated vibrations are independent of the aliphatic C=C motions of *bis*-GMA.

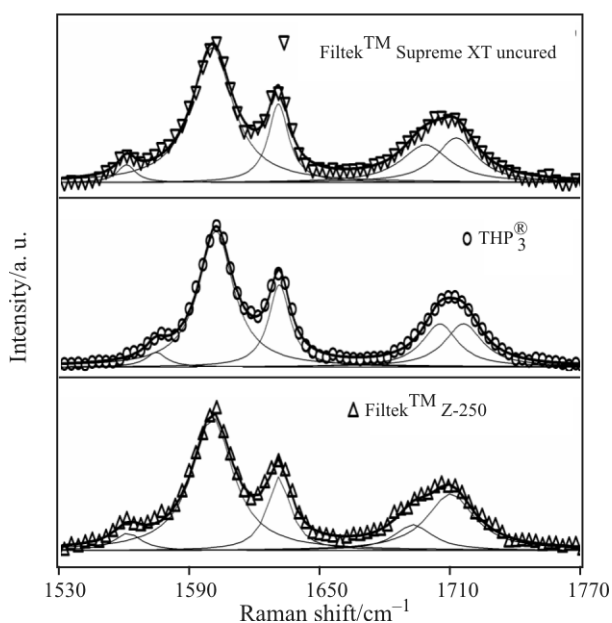
The dental composite resin Filtek™ Z-250 showed the lower intensity Fe/C=C than the others dental composites (Filtek™ Supreme and TPH<sub>3</sub>®). The composite Filtek™ Z-250 presented low number of C=C or residual monomers. The low number of residual monomers may be related to the composition of this material. This fact may be related to the thermal stability of this material. In this sense, Filtek™ Z-250 showed higher thermal stability.

*bis*-GMA, *bis*-EMA and UDMA compose the organic matrix of the Filtek™ Z-250 composite resin. All these monomers present high molecular masses, however different mobilities.

In addition, *bis*-GMA and *bis*-EMA have about the same size in contrast to UDMA and mainly of TEGDMA, which have smaller size and therefore higher concentration of double bonds. This fact may explain the Fe/C=C intensity of the dental composite resin Filtek™ Supreme XT [32].



**Fig. 5** AFM images of the surface of a – TPH<sub>3</sub>®, b – Filtek™ Z-250 and c – Filtek™ Supreme XT resins



**Fig. 6** Raman spectra obtained for Filtek™ Supreme XT, TPH<sub>3</sub>® and Filtek™ Z-250

## Conclusions

Filtek™ Z-250 composite resin presents the best thermal stability as shown in TG and DTG curves. This sample presented the major residual mass and a major *T<sub>g</sub>* value (58°C) that suggest a better influence of the fillers and an increased cross-linking provided by the blue LED as related to the other dental composite res-

ins evaluated. The same resin (Filtek™ Z-250) presents a well interconnected more homogeneous morphology and, suggesting with this one better degree of conversion correlated with the glass phase transition temperature.

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## References

- 1 N. Moszner and U. Salz, *Prog. Polym. Sci.*, 26 (2001) 535.
- 2 K. F. Leinfelder, *J. Am. Dent. Assoc.*, 126 (1995) 663.
- 3 A. Gatti, A. N. S. Rastelli, S. J. L. Ribeiro, Y. Messaddeq and V. S. Bagnato, *J. Therm. Anal. Cal.*, 87 (2007) 631.
- 4 I. E. Ruyter and H. Oeysaed, *Biomed. Mater. Res.*, 21 (1987) 11.
- 5 A. Peutzfeldt, *Eur. J. Oral Sci.*, 105 (1997) 97.
- 6 K. J. Anusavice, *Materiais Dentários*, 10<sup>th</sup> Ed. Phillips' Science of Dental Materials: Guanabara Koogan S.A., 1998, p. 161.
- 7 N. Moszner and S. Klapdohr, *Int. J. Nanotechnol.*, 1 (2004) 130.
- 8 S. Suzuki, K. L. Leinfelder, K. Kaway and Y. Tsuchitani, *Am. J. Dent.*, 8 (1995) 173.
- 9 T. Miyasaka, *Dent. Mater. J.*, 15 (1996) 98.
- 10 T. Miyasaka and T. Yoshida, *Dent. Mater. J.*, 19 (2000) 229.
- 11 K.-J. Söderholm and N. D. Richards, *Gen. Dent.*, 46 (1998) 256.
- 12 R. E. Kirk, D. F. Othmer, J. Kroschwitz and M. Howe-Grant, *Encyclopedia of Chemical Technology*, 4<sup>th</sup> Ed., Wiley, New York 1991. p. 397.
- 13 D. Wu, B.N. Holmes, S. B. Miltra, B. U. Kolb, W. Thompson and N. J. Johnson, *J. Dent. Res.*, 81 (Special Issue A) (2002) A-37.
- 14 F. S. Debastiani and G. C. Lopes, *Clínica: Int. J. Braz. Dent.*, 1 (2005) 11.
- 15 K. J. Anusavice, *Phillips Materiais Dentários*, Translation of Phillips' Science of Dental Materials, 11<sup>th</sup> Ed., Elsevier, Rio de Janeiro 2003, p. 376.
- 16 T. H. Yoon, Y. K. Lee, B. S. Lim and C. W. Kim, *J. Oral Rehabil.*, 29 (2002) 1165.
- 17 N. Silikas, G. Eliades and D. C. Watts, *Dent. Mater.*, 16 (2000) 292.
- 18 D. C. Watts, C. Amer and E. C. Combe, *Br. Dent. J.*, 156 (1984) 209.
- 19 G. Atmadja and R. W. Bryant, *Austral. Dent. J.*, 35 (1990) 213.
- 20 M. L. Swartz, R. W. Phillips and B. Rhodes, *JADA*, 106 (1983) 634.
- 21 J. L. Ferracane, *Dent. Mater.*, 1 (1985) 11.
- 22 A. Peutzfeldt, *Scand. J. Dent. Res.*, 102 (1994) 73.
- 23 S. Imazato, H. Tarumi, K. Kobayashi, H. Hiraguri, K. Oda and Y. Tsuchitani, *Dent. Mater. J.*, 14 (1995) 23.
- 24 C. M. Jan, Y. Nomura, H. Urabe, M. Okazaki and H. Shintani, *J. Appl. Biomater.*, 58 (2001) 42.
- 25 J. L. Ferracane and J. R. Condon, *Dent. Mater.*, 6 (1990) 282.
- 26 J. M. Antonucci and E. E. Toth, *J. Dent. Res.*, 62 (1983) 121.
- 27 P. Dionysopoulos and D. C. Watts, *J. Dent.*, 17 (1989) 140.
- 28 J. Vaidyanathan, T. K. Vaidyanathan, Y. Wang and T. Viswanadhan, *J. Oral Rehab.*, 19 (1992) 49.
- 29 J. M. Antonucci and E. E. Toth, *J. Dent. Res.*, 62 (1983) 121.
- 30 P. Dionysopoulos and D. C. Watts, *J. Dent.*, 17 (1989) 140.
- 31 Y. Nomura, W. Teshima, N. Tanaka, Y. Yoshida, Y. Nahara and M. Okazaki, *J. Biomed. Mater. Res.*, (Appl. Biomater.) 63 (2002) 209.
- 32 W. S. Shin, X. F. Li, B. Schwartz, S. L. Wunder and G. R. Baran, *Dent. Mater.*, 9 (1993) 317.

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