J Mater Sci: Mater Med (2008) 19:1027–1032
DOI 10.1007/s10856-007-3220-5

Influence of light polymerization modes on degree of conversion and crosslink density of dental composites

Eduardo Moreira da Silva · Laiza Tatiana Poskus ·
José Guilherme Antunes Guimarães · Alexandre de Araújo Lima Barcellos ·
Carlos Eduardo Fellows

Received: 20 July 2006 / Accepted: 22 January 2007 / Published online: 1 August 2007

Abstract This study analyzed the influence of light polymerization modes on crosslink density (CD) and the degree of conversion (DC) of dental composites. A minifilled hybrid and a nanofilled dental composite were photoactivated with two light polymerization modes: Conventional—850 mW/cm^2 for 20 s and Gradual—50 up to 1,000 mW/cm^2 for 10 s + 1,000 mW/cm^2 for 10 s. DC was determined by the use of FT-Raman-spectrometer. A softening test, using Knoop diamond indentation, was carried out at the top and bottom of 2 mm thick dental composite disks, before and after storage in 100% ethanol for 24 h, in order to represent the amount of crosslink density. Data were analyzed by ANOVA and Student–Newman–Keuls' multiple range test ($\alpha = 0.05$). The DC was influenced by light polymerization modes, with Gradual mode presenting lower DC. On bottom surfaces, the nanofilled dental composite was more susceptible to softening by ethanol than minifilled hybrid, and gradual light polymerization of nanofilled dental composite resulted in more softening than when conventional light polymerization was used. The results suggest that nanofilled composites are capable undergoing more plasticization if applied in thick increments.

Introduction

The polymerization reaction of dental composites involves rupture of the C=C bonds of dimethacrylate monomers present in their polymeric matrix and the conversion of intermolecular distances of 0.3–0.4 nm between polymer chains, maintained by Van der Waals attraction forces, into primary C–C covalent bonds with lengths of about 0.15 nm [1]. Moreover, these covalent bonds allow free rotation and a high mobility of polymer chains [1]. The shrinkage generated during this process can lead to gap development, bacterial invasion at the tooth-resin composite interface and post-operative sensitivity [2, 3].

The light intensity and light-polymerization mode can influence the polymerization shrinkage developed by dental composites [4–6]. Photoactivation with higher light intensity leads to a higher degree of conversion. However, greater polymerization shrinkage and greater marginal leakage are developed [7]. Thus, the gradual light polymerization modes were introduced to allow polymerization shrinkage to be reduced by stress relief during resin composite setting [5, 6]. In this mode, the dental composite is initially submitted to a low light intensity followed by final polymerization with high light intensity. While some studies have shown that these light polymerization modes did not reduce the degree of conversion and physical properties of dental composites [8–10], it was also demonstrated that crosslink density could be reduced and a more linear

---

E. M. da Silva · L. T. Poskus · J. G. A. Guimarães ·
A.A. L. Barcellos
Department of Restorative Dentistry, School of Dentistry,
Federal Fluminense University, Rua São Paulo, 28, Niteroi CEP:
24040-110 RJ, Brazil

E. M. da Silva (✉) · L. T. Poskus · J. G. A. Guimarães ·
A.A. L. Barcellos
Universidade Federal Fluminense/Faculdade de Odontologia,
Rua São Paulo, No. 28, Campus Valonguinho, Centro, Niteroi
CEP: 24040-110 RJ, Brazil
e-mail: emsilva@vm.uff.br

C. E. Fellows
Institute of Physics, Federal Fluminense University, Avenida
Litorânea, Niteroi, RJ, Brazil

polymer network formed [8, 11]. This polymer structure is more susceptible to softening in organic solvents.

Dimethacrylate monomers produce a highly crosslinked network after polymerization. Theoretically, in dental composites, a high degree of conversion is associated with better mechanical properties [12]. However, earlier studies have shown that the degree of conversion is not sufficient to characterize the three-dimensional structure of dental composites, and that areas with different concentrations of C=C bonds, present as pendant groups or residual monomer, coexist in the same polymer [8, 11]. This heterogeneity would produce a polymer network with a lower crosslink density [13, 14].

The crosslink density can be indirectly measured by glass transition temperature—*Tg* and by using softening tests [14, 15]. Some studies have used the Wallace indentation (H_w) to evaluate the crosslink density of dental composites and experimental resins, before and after storage in organic solvents, or acids produced by human dental plaque [8, 9, 11, 15, 16]. Recently, Barszczewska-Rybarek et al. [17] developed an equation that relates the crosslink density (q) to degree of conversion (α) to be used as a direct method in polymers prepared by dimethacrylate monomer polymerization.

$$q = \frac{2\alpha - 1}{\alpha}$$

However, this equation can only be used if α is greater than 50%.

The purpose of this study was to investigate the influence of light polymerization mode on the degree of conversion (DC) and crosslink density (CD) of two dental composites with the same polymeric matrix and different types of filler particles. It was hypothesized that irrespective of the light polymerization mode, the degree of conversion would not differ, although the crosslink density would be lower with the gradual mode.

Materials and methods

Two commercially available dental composites, which were chosen in accordance with their different types of filler particles, were tested: a minifilled hybrid (P 60, A3 shade) and a nanofilled dental composite (Supreme, A3B shade). Both materials have the same polymeric matrix (Bis-GMA, Bis-EMA, TEGDMA and UDMA). Their composition are described in Table 1.

All the specimens in this study were photoactivated with a quartz-tungsten-halogen unit (Optilux 501, Kerr, Danbury, CT, USA). Two light polymerization modes were used: Conventional (C)—850 mW/cm^2 for 20 s (17 J/cm^2) and Gradual (G)—50 up to 1,000 mW/cm^2 for 10 s + 1,000 mW/cm^2 for 10 s (≅15.5 J/cm^2). The radiant exposure was calculated as the product of the irradiance of the curing unit, by using a radiometer (model 100, Demetron Inc. Danburry, USA), and the time of irradiation. For the Gradual mode, the radiant exposure was obtained by the sum of mean irradiance over the first 10 s multiplied by 10 s with 10 J/cm^2, corresponding to the radiant exposure in the last 10 s of light exposure.

Degree of conversion—DC (%)

Raman spectra of the uncured and cured specimens of each dental composite were recorded by a Raman spectrometer (Nicolet FT-Raman 950, Thermo Nicolet Inc., Madison, WI, USA) operating with 120 scans at a resolution of 2 cm^{-1}. Increments of each dental composite were compressed between two polyester strips and two glass slides to produce a thin film (approximately 60 μm). Five films of each resin composite were then photoactivated, in accordance with the two light polymerization modes tested, with the light tip in contact with the glass slide. Raman spectra were recorded after 24 h dry storage at 37 °C. The DC was calculated from the ratio between the peaks of the aliphatic C=C bond (1,638 cm^{-1}) to the aromatic C=C bond (1,608 cm^{-1}), obtained from the cured and uncured specimens by the following equation:

$$\mathrm{DC}(\%) = 100 \times [1 - (\mathrm{R}_{\mathrm{cured}}/\mathrm{R}_{\mathrm{uncured}})]$$

where R = peak at 1,638 cm^{-1}/peak at 1,608 cm^{-1}.

Crosslink density (CD)

The amount of crosslink density was indirectly obtained by the softening effect of ethanol. Single increments of both dental composites were applied to an aluminum mold, 5 mm in diameter and 2.2 mm thick, covered with a polyester strip and a glass slide (0.1 mm thick) and photoactivated from the top, in accordance with the two light polymerization modes ($n = 5$). After storage in air at 37 °C for 24 h, the disks were embedded in epoxy resin with the top and bottom sides in contact with glass plates. The disks were polished on both sides with 1200-grit abrasive paper. Disk polishing was controlled with a digital caliper (MPI/E-101, Mitutoyo, Tokyo, Japan) to maintain 2 ± 0.1 mm thickness. The disks were submitted to a microhardness tester (2003, Buehler, Lake Bluff, USA) and five indentations were made on the top and bottom sides, with a Knoop diamond at a 100 g load and 15 s dwell time. The disks were then stored in 100% ethanol for 24 h and the procedure was carried out again.

By analogy with the Wallace indentation hardness that measures the penetration depth of a Vickers diamond under a pre-determined load [9], in the present study, resin

Table 1 Composition of the dental composites used in this study

Denatal composite	Composition
P 60 (A3 shade)	Filler: 61 vol% silica/zirconia filler with mean particle size of 0.6 μm
	Polymeric matrix: Bis-GMA, Bis-EMA, UDMA TEGDMA
Supreme (A3B shade)	Filler: 59.5 vol% combination of aggregated zirconia/silica cluster filler with primary particles size of 5–20 nm, and nonagglomerated 20 nm silica filler.
	Polymeric matrix: Bis-GMA, Bis-EMA, UDMA TEGDMA

composite softening was not based on the Knoop hardness number, but on the Knoop diamond indentation depth (d_k-μm). After Knoop indentation, the diagonal (D_k) corresponding to 172°30′ angle of Knoop diamond (Fig. 1a) was marked on the surface of specimens (Fig. 1b). The internal profile corresponding to the projection of D_k forms two rectangle triangles with sides $D_k/2$, d_k and c; and internal angles: $\alpha = 86°15'$, $\beta = 90°$ and $\lambda = 3°45'$ (Fig. 1c). The d_k was calculated as a function of tan α:

$$\tan\alpha = \frac{\frac{D_K/2}{c}}{\frac{d_K}{c}} \Rightarrow \tan\alpha = \frac{D_K/2}{d_K} \Rightarrow d_K = \frac{D_K/2}{\tan\alpha}$$

Considering the tan α value = 15.26, d_K was obtained by the formula:

$$d_k = \frac{D_K/2}{15.26}$$

A representation of the amount of crosslink density (CD) was indirectly obtained by using the difference between mean d_k values after and before ethanol storage ($\Delta d_k = d_{k\ \mathrm{after}} - d_{k\ \mathrm{before}}$)

Statistical analysis was performed using Statgraphics 5.1 Software (Manugistics, Rockville, MD, USA). The DC data were analyzed by Two-way ANOVA. The d_k and Δd_k data were submitted, separately, to Multifactor ANOVA and Student–Newman–Keuls' multiple range test for multiple comparisons. All statistical analyses were performed at a significant level of $\alpha = 0.05$

Results

The DC (%) values are shown in Fig. 2. Two-way ANOVA did not show a statistically significant influence of the factors resin composite ($p = 0.126$) and light polymerization mode ($p = 0.052$) on the DC. The mean d_k values obtained before and after ethanol storage are summarized in Table 2. The d_k values presented by P 60 were found to be significantly lower than those presented by Supreme ($p < 0.05$). For both resin composites, the d_k values obtained on the top surfaces were significantly lower than those obtained on the bottom surfaces ($p < 0.05$). With respect to light polymerization mode, the dental composites behaved differently. No difference in d_k was observed for P 60 with the two light polymerization modes. For Supreme, a significant difference in d_k values was observed only on the bottom surface, and the C light polymerization mode presented a lower d_k than that presented by the G light polymerization mode ($p < 0.05$). For all experimental groups a significant increase in d_k was observed after ethanol storage ($p < 0.05$), showing that both resin composites were softened by immersion in ethanol, irrespective of light polymerization mode and surface evaluated. Table 3 shows the mean Δd_k. On the top surfaces, the Δd_k presented by

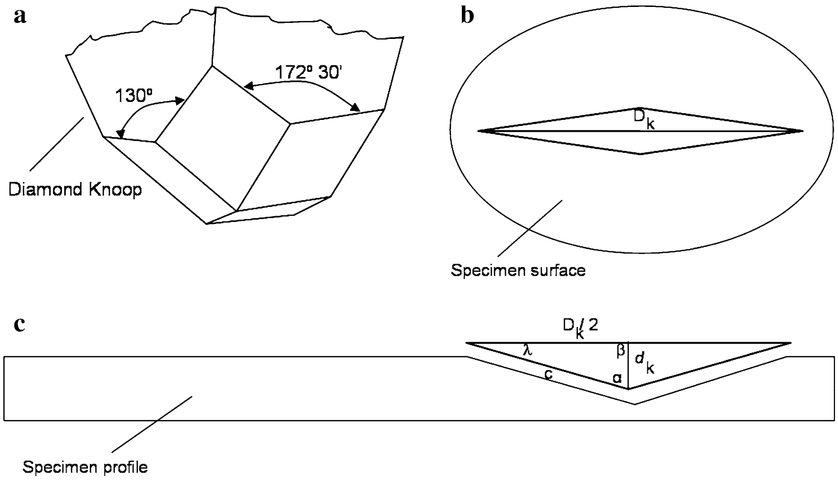

Fig. 1 Schematic representation of the experimental set-up

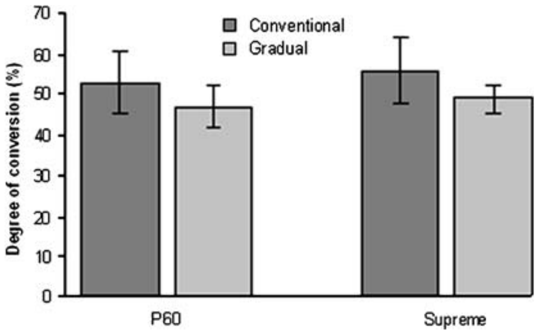

Fig. 2 Degree of conversion (%) of dental composites as a function of light polymerization modes

Table 2 Mean d_k (SD) (μm) before and after ethanol storage

Dental composites	C		G	
	Before	After	Before	After
Top				
P 60	4.20 (0.08)^a	4.48 (0.08)^b	4.28 (0.02)^a	4.59 (0.15)^b
Supreme	4.49 (0.15)^b	4.84 (0.04)^c	4.56 (0.02)^b	4.93 (0.13)^c
Bottom				
P 60	4.51 (0.10)^b	4.77 (0.12)^c	4.44 (0.09)^b	4.76 (0.11)^c
Supreme	4.92 (0.06)^c	5.57 (0.12)^e	5.32 (0.17)^d	6.31 (0.20)^f

Values with the same superscript letters are not statistically different ($\alpha = 0.05$)

Table 3 Mean Δd_k (SD) (μm)

Dental composites	C	G
Top		
P 60	0.29 (0.14)^a	0.30 (0.13)^a
Supreme	0.35 (0.18)^a	0.37 (0.14)^a
Bottom		
P 60	0.26 (0.19)^a	0.32 (0.17)^a
Supreme	0.65 (0.11)^b	0.99 (0.31)^c

Values with the same superscript letters are not statistically different ($\alpha = 0.05$)

Supreme did not differ from that of P 60. On the bottom surface, Supreme specimens were more susceptible to softening than P 60, and the G light polymerization mode resulted in a higher Δd_k value in Supreme than that resulting from the C light polymerization mode ($p < 0.05$).

Discussion

Dental composites are glassy polymers and their polymerization reaction creates densely crosslinked networks. At room temperature, however, the conversion of C=C bonds is not complete, generating a heterogeneous structure with some parts densely crosslinked and others poorly crosslinked [12]. The feature of this final structure is extremely important with regard to polymer permeability by organic solvents. The presence of high crosslink improves the packing density; reduces the hole-free volume between polymer chains and decreases polymer plasticizing [18].

The published studies that used the Knoop Hardness Number as an indirect method to estimate dental composite crosslink density used a 500 g load for specimen indentation [14, 19]. But in all previous studies that used the Wallace indentation (H_w) to assess the crosslink density of dental composite and dental polymers, a load of 0.98 or 1 N was used [8, 9, 11, 15, 16]. This method measures the penetration depth of a Vickers diamond under a pre-determined load, and the greater the penetration depth, the softer is the material [20]. This is really a softening test. In the present study, since the crosslink density was estimated by the Knoop diamond indentation depth instead of Knoop hardness number, a 100 g load, corresponding to 0.98 N was chosen.

Factors such as, the filler particle size and refraction index, restorative material thickness, nature of polymeric matrix and the radiant exposure generated by the light polymerization mode, can influence the DC of dental composites [6, 21]. In the present study, the radiant exposures generated by the two light-polymerization modes (15.5 and 17 J/cm^2) were based on the findings of Emami and Söderholm [22]. These authors showed that small radiant exposures, ranging from 5 to 15 J/cm^2, were sufficient to produce adequate DC at top and bottom surfaces of 2 mm thick specimens of Z250, a dental composite with similar polymeric matrix to P60 and Supreme.

The soft-start polymerization mode was introduced in an attempt to reduce the stress generated during the polymerization reaction of dental composites [23, 24]. This light polymerization mode uses an initial low light intensity followed by high intensity, and can be obtained with different polymerization techniques. In this research field, Watts and Hindi [25] found that shrinkage-strain was lower after irradiation of one dental composite with a two-step polymerization mode, than after a full-intensity mode, and showed that the soft-start effect may also be obtained by a ramped light-intensity. In the present study, Two-way ANOVA showed a p value of 0.052 for the light polymerization mode independent factor. Since this value is superior to the significance level in which the analysis was performed ($\alpha = 0.05$), it should be considered as not significant. However, by rounding, it's reasonable to consider this value as significant, consequently avoiding a Type II statistic error (e.g., not rejecting the null hypothesis when it is really false). From this point of view, the DC presented by G mode could be considered lower than the presented by C mode. Based on the results by Emami and Söderholm [22], this DC result was not expected. In addition, this result disagrees with the study by Silikas et al. [4]. For one specific dental composite (Z100, 3M ESPE), using a gradual polymerization mode, these authors showed a reduction in polymerization shrinkage without reducing the DC. Moreover, Rahiots et al. [24] also showed that although DC was similar, the shrinkage-strain generated during the initial polymerization of a dental composite was lower after the exponential (ramped) mode than after the continuous mode. A reasonable explanation for the disagreement between the DC results of the present study and those of the aforementioned studies can be based on radiant exposure generated by each gradual mode. In the cited studies, the gradual modes generated 24.5 and 40 J/cm^2, respectively. These values are 58 and 158% greater than the radiant exposure used in the present study for G mode (15.5 J/cm^2). On the other hand, the DC generated by the gradual mode in these studies (56.2 and 56.7%) did not differ from those by Emami and Söderholm [22], which ranged from 54.32 to 60.02%. In the present study, the DC was 48% for G mode and 54% for C mode. Confronting these results with those of the aforementioned studies, it is reasonable to speculate that gradual polymerization modes, generating at least 17 J/cm^2 of radiant exposures, would allow a satisfactory DC, allied to a reduced shrinkage-strain.

In the present study, the method used to represent the amount of crosslink density of the dental composites was based on polymeric matrix plasticization. When a polymer is immersed in a suitable solvent (e.g., similar solubility parameter), the solvent enters the polymer network through the intermolecular spaces, forms secondary bonds with the polymer chain, pulls apart the polymer entanglements and reduces the interchain interactions [14]. The reduction in hardness is a consequence of polymer plasticization [26]. In a highly crosslinked polymer, however, the polymer–solvent interaction is not sufficient to overcome the polymer chain primary bonds. Furthermore, the reduced hole-free volume between polymer chains will decrease the solvent uptake and the plasticizing effect [18]. Since the polymeric matrixes of the dental composites used in this study only have difunctional monomers (Bis-GMA, Bis-EMA, TEGDMA and UDMA), which, after polymerization reaction, will form a highly crosslinked network, it is reasonable to considerer the reduction in hardness after ethanol storage (i.e., increase in indentation depth) as an estimate of crosslink density parameter.

Table 2 shows that after ethanol storage, all d_k values were statistically higher than before storage. This finding shows that irrespective of light polymerization mode, both dental composites underwent plasticization. This result is in agreement with some earlier studies [14–16]. While there was a significant difference between the DC obtained by the two light polymerization modes, the data from the Table 3 shows that on the top surfaces the Δd_k means were not statistically different for all the experimental groups. It is possible that the small difference between DC from the two light polymerization modes (around 6%) was insufficient to form different polymer structures on the top surfaces. Based on this, it is safe to assume that the polymer plasticization was similar on the top surfaces of the dental composites, suggesting that the polymeric matrixes presented similar crosslink density. On the other hand, the data in Table 3 show that only the bottom surface of Supreme presented the significantly higher Δd_k. Since both dental composites analyzed in this study have the same polymeric matrix (Bis-GMA, Bis-EMA, UDMA and TEGDMA), this result can be explained by the type of filler particles present in the composition of Supreme (Table 1). The non-agglomerated silica nanoparticles with mean size of 20 nm may have caused a light-scattering effect, reducing the light intensity in the deepest layer of the specimens [27]. From this point of view, it is safe to assume that the deepest layers of Supreme presented a lower DC than the irradiated surfaces. Obviously, this low DC would increase the hole-free volume between polymer chains, thereby increasing the plasticizing effect of ethanol [26]. It is reasonable to conclude that this behavior could be expected in other nanofilled dental composites that present this type of inorganic filler particle in their formulations. In addition, the Δd_k means presented by P60 at the bottom (Table 3) allow one to hypothesize that its polymeric matrix structure did not vary from the top to the bottom surfaces.

It is reasonable to speculate that from the clinical point of view, the higher plasticizing presented by Supreme on the bottom side represents a crucial factor. This dental composite represents a new generation of nanofilled composites indicated for a wide range of anterior and posterior restorations. Although some studies have shown this class of restorative materials to have satisfactory mechanical properties [28–30], their real clinical behavior is not yet completely known. Several studies have shown that the number of bacterial microflora around and beneath composite restorations is greater compared with other restorative materials [31, 32]. Specifically in Class II molar cavities, the distance from occlusal surface to the gingival floor exceeds 2.0 mm [33]. In addition, this region is more susceptible to the action of acids produced by bacterial plaque, specifically acetic acid, which has a solubility parameter close to that of ethanol [15]. This environment could have a degradative effect on the polymer network and thereby diminish the clinical longevity of restorations produced with this type of dental composite.

Conclusions

The results obtained in this in vitro study do not support the experimental hypothesis. The DC was influenced by the light polymerization mode, with Gradual mode presenting lower

DC. The two dental composites presented the same plasticizing effect on the top surfaces, suggesting similar polymeric matrix structures. The higher Δd_k presented by Supreme on the bottom surfaces suggests that, irrespective of the light polymerization mode, nanofilled composites can present a low DC in thicker layers. In addition, the in vitro and in vivo behavior of nanofilled composites, specifically in posterior restorations, must be further investigated.

References

1. A. PEUTZFELDT, *Eur. J. Oral Sci.* **105** (1997) 97
2. I. KREJCI and F. LUTZ, *J. Dent.* **19** (1991) 24
3. J. D. EICK and F. H. WELCH, *Quintessence Int.* **17** (1986) 103
4. N. SILIKAS, G. ELIADES and D. C. WATTS, *Dent. Mater.* **16** (2000) 292
5. C. L. DAVDSON and A. J. FEILZER, *J. Dent.* **25** (1997) 435
6. P. KORAN and R. KURSCHNER, *Am. J. Dent.* **11** (1998) 17
7. B. A. M. VENHOVEN, A. J. DE GEE and C. L. DAVIDSON, *Biomaterials* **14** (1993) 871
8. E. ASMUSSEN and A. PEUTZFELDT, *J. Dent. Res.* **80** (2001) 1570
9. E. ASMUSSEN and A. PEUTZFELDT, *Dent. Mater.* **19** (2003) 466
10. A. MEHL, R. HICKEL and K. H. KUNZELMANN, *J. Dent.* **25** (1997) 321
11. E. ASMUSSEN and A. PEUTZFELDT, *Eur. J. Oral Sci.* **108** (2001) 282
12. I. SIDERIDOU, V. TSERKI and G. PAPANASTASIOU, *Biomaterials* **23** (2002) 1819
13. J. L. FERRACANE, J. C. MITCHEM, J. R. CONDON and R. TODD, *J. Dent. Res.* **76** (1997) 1508
14. M. S. SOH and A. U. J. YAP, *J. Dent.* **32** (2004) 321
15. E. ASMUSSEN, *Scand. J. Dent. Res.* **92** (1984) 257
16. E. ASMUSSEN and A. PEUTZFELDT, *Eur. J. Oral Sci.* **111** (2003) 277
17. I. BARSZCZEWSKA-RYBAREK, M. GIBAS and M. KURCOK, *Polymer* **41** (2000) 3129
18. S. AJITHKUMAR, N. K. PATEL and S. S. KANSARA, *Eur. Polym. J.* **36** (2000) 2387
19. A. U. YAP, M. S. SOH, T. T. HAN and K. S. SIOW, *Oper. Dent.* **29** (2004) 410
20. K. D. JØRGENSEN, *Scand. J. Dent. Res.* **88** (1980) 557
21. I. E. RUYTER and H. ØYSAED, *J. Biomed. Mater. Res.* **21** (1987) 11
22. N. EMAMI and K-JM SÖDERHOLM, *Eur. J. Oral Sci.* **111** (2003) 536
23. R. L. SAKAGUCHI and H. X. BERGE, *J. Dent.* **26** (1998) 695
24. C. RAHIOTIS, A. KAKABOURA, M. LOUKIDIS and G. VOUGIOUKLAKIS, *Eur. J. Oral Sci.* **112** (2004) 89
25. D. C. WATTS and A. AL HINDI, *Dent. Mater.* **15** (1999) 39
26. J. L. FERRACANE, *Dent. Mater.* **22** (2006) 211
27. I. E. RUYTER and H. ØYSAED, *Acta Odontol. Scand.* **40** (1982) 179
28. S. B. MITRA, D. WU and B. N. HOLMES, *J. Am. Dent. Assoc.* **134** (2003) 1382
29. N. SILIKAS, K. KAVVADIA, G. ELIADES and D. WATTS, *Am. J. Dent.* **18** (2005) 95
30. E. C. TEIXEIRA, J. L. THOMPSON, J. R. PIASCIK and J. Y. THOMPSON, *J. Esthet. Restor. Dent.* **17** (2005) 172
31. C. SPLIETH, O. BERNHARDT, A. HEINRICH, H. BERNHARDT and G. MEYER, *Quintessence Int.* **34** (2003) 497
32. M. SVANBERG, I. A. MJOR and D. ORSTAVIK, *J. Dent. Res.* **69** (1990) 861
33. R. B. PRICE, T. DERAND, M. SEDAROUS, P. ANDREOU and R. W. LONEY, *J. Esthet. Dent.* **12** (2000) 320