Microscopic and spectroscopic analysis of interface formation in dental restoration using Zr/Si composite

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The purpose of this study is to evaluate the adherence quality and interface formation upon using a Zirconia-Silica based composite in premolar restoration, by SEM microscopy and FTIR spectroscopy. The SEM image and the quantitative chemical analyses revealed a good biocompatibility of the composite and a successful medical procedure, as the micrograph indicate no gap between the tooth structure and the composite. Moreover, as a result of silanisation, 11% of silica content from Zr-Si composite was diffused in the natural tissue, revealing a good adherence of the biocomposite to the natural tissue. The ATR FTIR spectra confirmed the presence of the inorganic components of the filler along with the dentin organic components in specimens containing the junction between the composite and dentin. The results of this investigation demonstrate that complementary FTIR spectroscopy and SEM-EDS allowed for a quick and accurate identification of the performance of restorative materials and evaluation of their remineralization capability toward the natural tissue.

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1. Introduction

Resin based materials are widely used as direct restorative materials. Composite resins consist of a heterogeneous blend of organic resins and inorganic fillers with excellent esthetic and physical properties. These have enabled the dental profession to advance tremendously in cosmetic dentistry. The performance and service life of glass or ceramic -filled polymeric composites depend on the nature of their resin, filler and interfacial phases as well as the efficacy of the polymerization process. The surface of the composite filling contains both resin matrix and filler particles. Therefore, if there is a mismatch between the filler hardness and surface roughness of the composite and that of enamel, there is a danger that the enamel will be worn down. During mastication, composite filler particles may scratch and abrade the antagonistic enamel. The vertical dimension will thus decrease if premolar and molar regions are treated with such a restorative material. Therefore, the surface texture and the particle size, shape, size distribution, and hardness play important roles in determining the biological strength of composite restorations [1,2]. A smooth surface provides reduced frictional wear at the occlusal contact areas. This smoothness will benefit the composite wear as well as the antagonistic enamel wear. To meet smoothness requirements, the intrinsic surface roughness of resin composites must be equal to or less than the average roughness value of enamel-to-enamel occlusal contact areas.

The synergy that exists between the organic polymer matrix and the usually inorganic reinforcing filler phase is principally mediated by the interfacial/interphasial phase [2,3]. In the case of silica-based fillers, the later phase develops as a result of the dual reactivity of a silane coupling agent, a bifunctional molecule capable of reacting with the silanol groups of glass or ceramic fillers via its silane functional group to form Si-O-Si bonds to filler surfaces, and also with the resin phase [4]. Generally the new dental composites consist of a paste created by combining a mixture of cross-linking agents with up to 80 wt % silane-coated glass or ceramic particles (the filler) whose sizes range from 0.04 to 4 μm. Silane is a coupling agent used to promote adhesion on the surface of minerals such as glass or ceramic and also on the surface of organic polymers such as epoxy, polyester or metacrylate resins. In spite of the large number of dental composite materials appeared during the past 15 years, they are all combinations of silane-coated inorganic filler particles. Usually the filler particles are either barium silicate glass, quartz or zirconium silicate, often combined with very small-sized particles of colloidal silica.

The gap formation between filling materials and tooth structure has been a major dental problem that is responsible for cases of secondary or recurrent caries, discoloration as well as pulpal inflammation and re-infection. The dental practitioner must carefully evaluate the probable abrasive effects of using certain restorative materials like porcelain or resin composites to oppose existing tooth structure. The objective of this study is to evaluate the adherence quality and interface formation upon using a Zirconia-Silica based composite in premolar restoration, by SEM microscopy and FTIR spectroscopy. Scanning electron microscopy analyses combined with local quantitative chemical analyses based upon the X-rays characteristic spectrum (EDS) for the composition elements allow the observation of the details of the surfaces morphology concomitant with the elemental analyses in situ, at the interface between the composite and natural tissue (dentine) [5,10,13]. The study of sound enamel using X-ray microtomography (XMT) was performed previously to assess quantitative mineral distribution in occlusal pit and fissure of the teeth. These sites of the teeth are the most susceptible for primary carious lesions. Hence is essential meaning such of examinations for dentistry.

On the other hand, ATR-FTIR spectroscopy allowed for a quick differential identification of typical dental materials produced from organic compounds for inorganic restorations and of tooth structure-resembling hydroxyapatite and its contaminate forms with fluoride and carbonate ions. For the purpose of assessing mineral properties of calcified tissues i.e. bone and tooth, crystal structure studies of human dental apatite as a function of age - the vibrational spectroscopy, based on Fourier techniques is required [6,7]. Thus, the researchers used these methods to carry out comparisons of dental tissues including enamel and dentin and to examine the hydroxyapatite single crystallites. The chemical composition of apatite is significant because of the consequences, which ensue from different chemical and physical properties [8]. Moreover, the application of near-infrared spectroscopy was also reported as a useful tool for the characterization of minerals, especially combined with hydroxyl groups or water bonded in the structure [9,11,12].

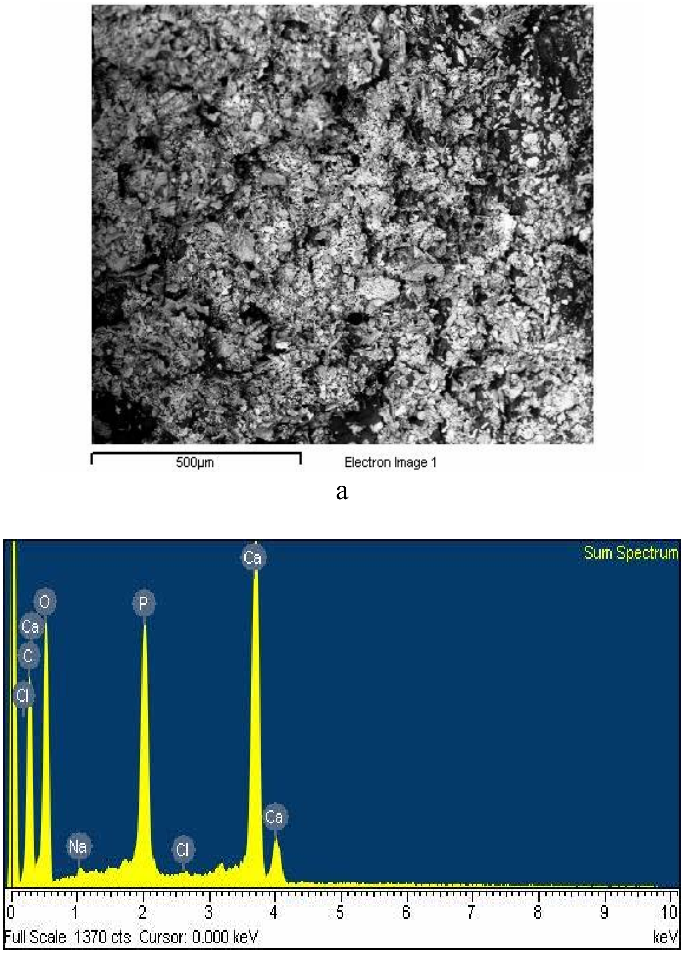
2. Materials and methods

Zirconia-Silica based composite commercially available as Valux ^{TM} Plus was used as restorative material in the case of a permanent premolar with the cavities dimension 4mm in length, 3 mm in width and 2 mm in depth. It is a visible-light activated, radiopaque, restorative composite. The inorganic filler (zirconia-silica) loading is 71% by volume with a particle size range of 3.5 to 0.01 micron. Valux Plus also contains BIS-GMA (bisphenol-*a*-glycidyl methacrylate) and TEGMA (triethylene-glycol dimethacrylate) resins. Upon restoration, the premolar was extracted for orthodontic reason and stored in sodium chloride solution at 0.9 wt. %. In the first step, a longitudinal section containing the interface between the composite and the natural tissue was prepared by polishing the surface using a water-cooled polishing machine at 10,000 rpm. Dentine specimens were also prepared from the central area of the damaged region (the interior of the dental decay) and from the healthy dentine as well. The specimens were kept in artificial saliva at 37º C.

The surface morphology of the specimens were investigated using a scanning electronic microscope type 5600 LV JEOL equipped with an X-rays spectrometer type Oxford Instrument, with the following characteristics: resolution 3.5 nm with secondary electrons; enlargement 300,000x; local quantitative chemical analyses based upon the X-rays characteristic spectrum (EDS) for the elements listed between boron and uranium, with the detection limit of 0.01%. Each specimen surface was also investigated by FTIR spectroscopy using an Elmer-Perkin BXII spectrometer, equipped with an ATR Miracle device (single reflection ATR with ZnSe crystal). The spectra were collected in the range 400 to 4000 wave numbers [cm^{-1}], with the spectral resolution 2 cm^{-1}.

3. Results and discussions

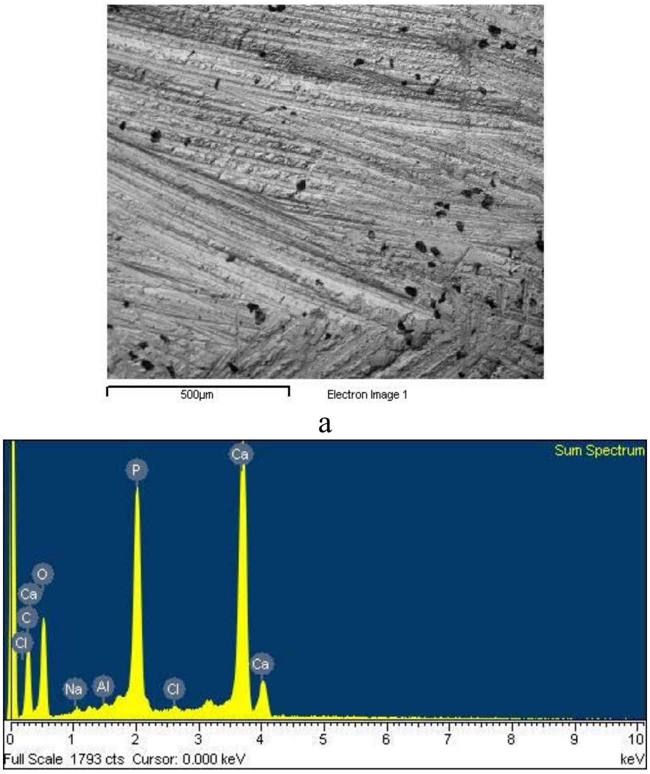
The morphology and microstructure of the different specimens observed by SEM are presented in fig. 1-3, along with the local elemental analysis. Beside the relevant optical aspect of the recorded images, large differences regarding the calcium and phosphorus content in each specimen is revealed. The first specimen containing damaged dentine shows 20% calcium and 7.2 % phosphorus (weight percent), while in the healthy dentine the content is 30% and 12% respectively. According to the literature [14], a ratio of Ca/P ≥ 2.0 indicate a predominant content of tetracalcium phosphate, whereas a value between 1.5 and 2.0 of this ratio is characteristic to hydroxyapatite. The most relevant information is related to the fig. 3. Both the SEM image and the quantitative chemical analyses presented in this figure revealed a good biocompatibility of the composite and a successful medical procedure, as the micrograph indicate no gap between the tooth structure and the composite. Moreover, as a result of silanisation, 11% of silica content from Zr-Si composite was diffused in the natural tissue, revealing a good adherence of the biocomposite to the natural tissue. The placement of a low –viscosity and adhesive bonding resin before the restorative resin material readily wets tooth surface and allows flow of material into the micro pores created by the etching process. It has been well documented in the literature that a common mechanical failure in most composites is the filler/polymer interface, especially if the interfacial interaction of the two phases is poor [15-17]. To enhance the integrity of glass-filled composite, the mineral filler surface is commonly treated with coupling agents, such as organofunctional silanes [16]. This improves the composite's mechanical properties by promoting the adhesion between mineral substrate and polymer matrix. In this way, the siliceous filler can be bonded to the polymer matrix, and thereby, reinforce the weaker organic phase of the composite and provide a mechanism for stress transfer from the lower modulus matrix to higher modulus filler phase.



a

b

Fig.1. a) The surface morphology of a specimen prepared from damaged dentine of a premolar - the interior region of the dental decay. Magnification X 100. b) The corresponding EDS spectrum with local quantitative elemental analyses.



a

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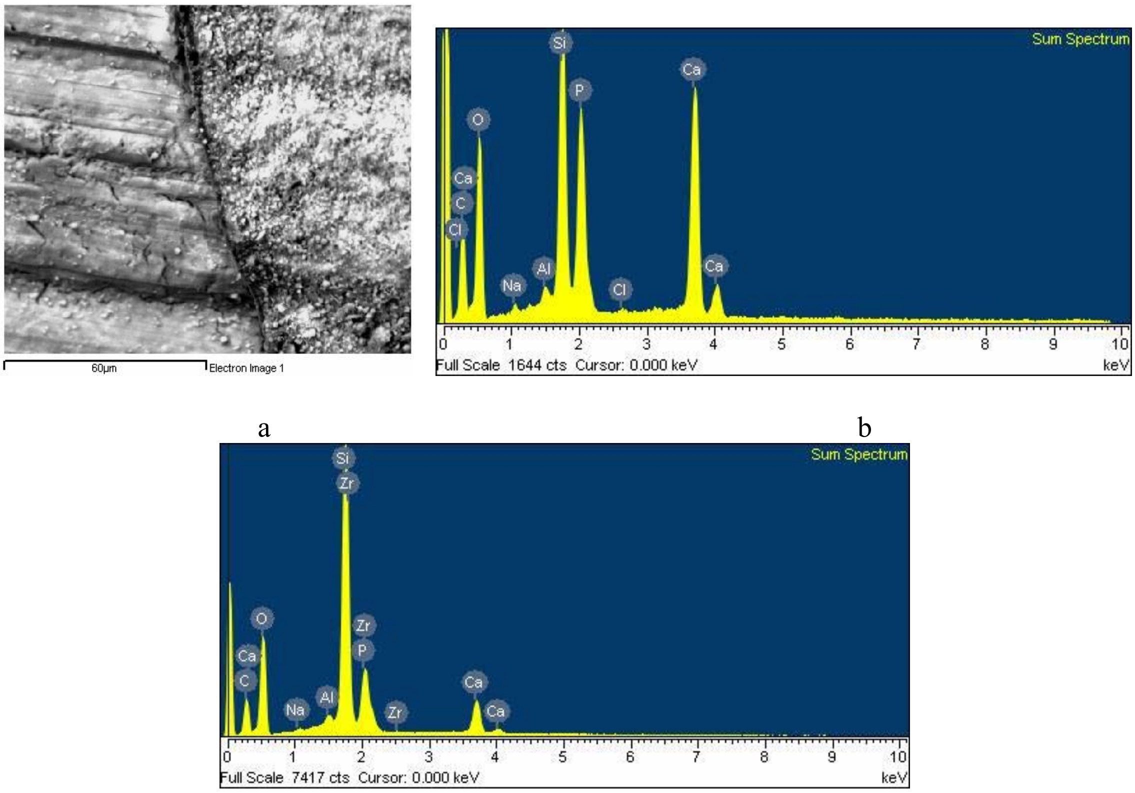
Fig. 2. a) The surface morphology of a specimen prepared from healthy dentine of a premolar. Magnification X 100. b) The corresponding EDS spectrum.



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a b

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Fig.3. a) The surface morphology of the specimen corresponding to the interface (junction) between the composite and the natural tissue: right side- dentine, left side- Zr-Si composite. Magnification X 300. b) The corresponding EDS spectrum of left side and (c) right side of the junction, respectively.

In order to sustain the chemical and structural properties of the dental composite in contact with the natural tooth, the characteristics of the ATR-FTIR spectra of the specimens were investigated and presented in fig. 4-6.

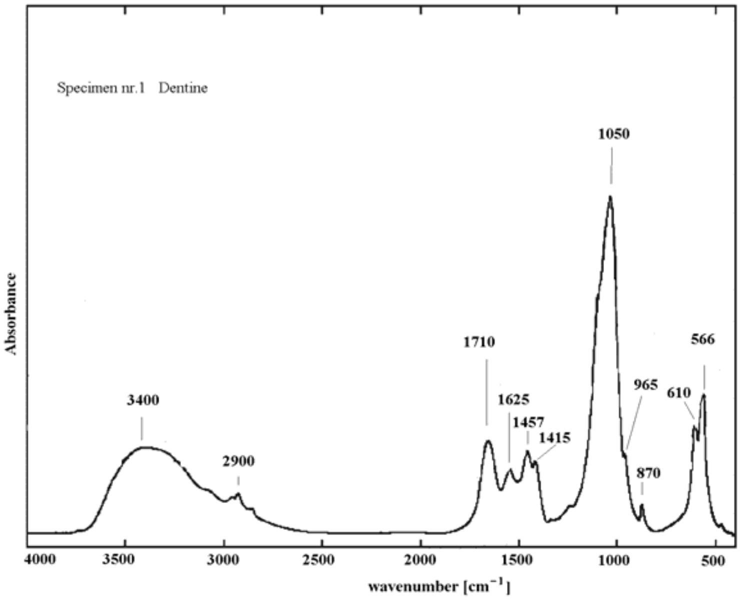

Fig.4. ATR FTIR spectrum of the specimen containing the natural tissue (dentine).

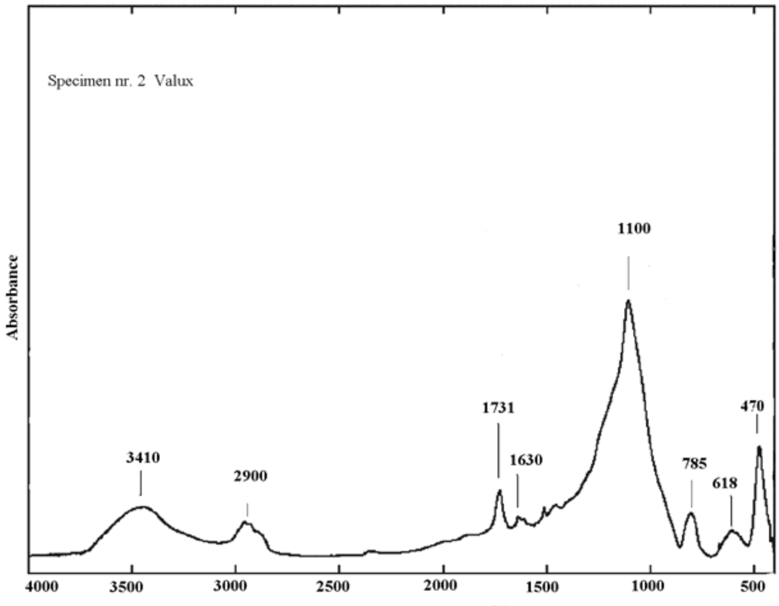

Fig.5. ATR FTIR spectrum of the specimen containing Valux ^{TM} Plus (Zr-Si composite).

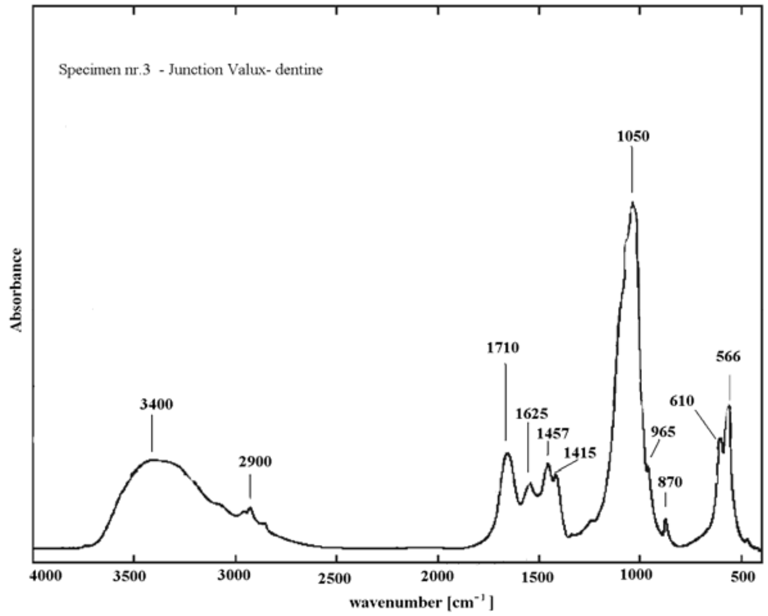

Fig. 6. ATR FTIR spectrum of the specimen containing the Zn-Si filler in contact with the natural tooth (junction).

In fig. 4, the characteristic fingerprints of dentine are assigned to phosphate ion located at 560 cm^{-1} (υ_4- asymmetric bending mode of PO_4^{3-}), 962 cm^{-1}(υ_1- stretching mode) and a very strong broad band at 1028 cm^{-1}(υ_3- asymmetric stretching mode) consisting of at least three submodes.

The peaks assigned to the B-type carbonate substitution (carbonate for phosphate ion) are observed at 872 cm^{-1}(υ_2 CO_3 mode) and between 1405- 1450 cm^{-1}(υ_3 CO_3 mode). The weak bands in these regions are attributed to CO_3^{2-} replacing PO_4^{3-} ions without an adjacent OH^- ion. These results confirms the presence of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) which constitutes 70-75% of dentine. The organic phase in dentin (mainly collagen) is related to amide II band at 1540 cm^{-1} (-CO-NH- vibrations) and strong amide I at 1640 cm^{-1} (-CO-NH_2 vibrations), whereas a broad water band is related to 2500-3700 cm^{-1} interval [11,18]. In fig. 5 are displayed the finger prints of Zn-Si biocomposite emphasizing a strong absorption band at 1100 cm^{-1}, assigned to SiO_4 asymmetric stretching. The IR bands at 785 and 618 cm^{-1} could be assigned to Zr-O stretching vibrations, while the intense band at 470 cm^{-1} is the superposition result of stretching Zr-O and deformation Si-O-S vibrations [19]. The organic matrix i.e. Bis-GMA exhibited strong absorption band at 1731 cm^{-1} corresponding to the ester group (-$COOCH_3$) and 1630 cm^{-1} corresponding to C=C bonds in amide I. In the high wavelength region, the C-H stretch is represented by the broad band at 2900 cm^{-1} and NH stretch at 3410 cm^{-1}.

The junction region presents FTIR characteristics of both the natural tissue and the biocomposite as shown in fig.6. The most intense band in this case (1050 cm^{-1}) represents the superposition of PO_4^{3-} and SiO_4 asymmetric stretching, with a less resolved shoulder at 965 cm^{-1} which might be due to Si-O-Zr asymmetric stretching vibration, confirming bonding of zirconia particles with silanol group. In the low wavelength spectral region, the bands at 870, 610 and 566 cm^{-1} are assigned to CO_3^{2-} vibration mode, Zr-O stretching vibrations and PO_4^{3-} bending vibrations respectively, similar to that of previous specimens. The carbonate ions are also represented by additional bands at 1457 and 1415 cm^{-1}. In the same time, the fingerprint of organic matrix Bis-GMA is low shifted to 1710 cm^{-1} as well as the organic phase in dentin at 1625 cm^{-1} (amide I). As a result of remineralization initiated by the restorative composite in contact with the natural tissue, evident spectral differences between intensity of absorption bands due to phosphate and carbonate ions are observed when compare the spectra in fig.4 and fig.5.

4. Conclusions

The results of this investigation demonstrate that complementary FTIR spectroscopy and SEM-EDS allowed for a quick and accurate identification of the performance of restorative materials and evaluation of their remineralization capability toward the natural tissue. The analysis confirmed the presence of the inorganic components of the filler along with the dentin organic components in specimens containing the junction between the composite and dentin. From our study as well as the recent literature reviewed it appears that investigators uniformly confirm the benefits of ATR FTIR spectroscopy concerning the identification of chemical functional groups in order to evaluate adhesive infiltration in the natural tissue. However, the action of these new materials on dentinal tissue is not well known and must be analyzed under different aspects, in order to be properly used by professionals so that they can make the best of properties during clinical applications.

References

[1] J. M. Antonucci, S. H. Dickens, B. O. Fowler, H.H.K. Xu, W. G. McDonough, J. Res. Natl. Inst. Stand. Technol.**110**, 541 (2005).
[2] S. M. Masudi, N. Roslin, S. Sulaiman, Microsc. Microanal. 9,supl. 3, 364 (2003).
[3] A. Carden, M.D. Morris, J. Biomed. Opt. **5**, 259 (2000).
[4] R. H. Halvorson, R. L. Erickson, C.L. Davidson, Dent. Mater.**19**, 327 (2003).
[5] J. Perdigao, E.J. Swift, Int. Dent.J. **44**, 349 (1994).
[6] I. D. Ana, S. Matsuya, M. Otha, K. Ishikawa, Biomaterials **24**, 3061 (2003).
[7] H. Fong, S.H. Dickens, D. M. Flaim, Dent. Mater. **21**, 520 (2005).
[8] S.E.P. Dowker, J.C. Elliott, G.R. Wilson, P. Cloetens, Eur. J. Oral Sci. **114**, 353,(2006).
[9] R. L. Frost, K. L. Erickson, Spectrochim. Acta A Mol. Biomol. Spectrosc. **61**, 45 (2005).
[10] A. Franz, F. KÄonig, M. Anglmayer, X. Rausch-Fan, G. Gille, W.-D. Rausch,T. Lucas, W. Sperr, A. Schedle, Dent. Mater. **19**, 382 (2003).
[11] Th. Leventouri, A. Antonakos, A. Kyriacou, R. Venturelli, E. Liarokapis, V. Perdikatsis**,** Int. J. Biomat. doi:10.1155/2009/698547 (2009).
[12] M. Kakei, H. Nakahara, M. Kumegawa, M. Yoshikawa, S. Kunii, Biochim. Biophys. Acta **1524**, 189 (2000).
[13] G. Willems, P. Lambrechts, M. Braem, M. Vuylsteke-Wauters , G. Vanherle, J. Dent.Res **70**, 1299 (1991).
[14] C-Pin Lin, B-Sh. Lee, F-Huei Lin, S-Heng Kok, W-Hong Lan, J. Endodontics **27**(6), 389 (2001).
[15] D. Skrtic, J. M. Antonucci, E. D. Eanes, R. T. Brunworth1, J. Biomed Mater Res **59**, 597 (2002).
[16] E. P. Plueddeman in Silane coupling agents, New York Plenum Press,167–205 (1982)
[17] A. Popovici, O. Fodor, M. Moldovan, A. Roman, D. Borzea, Optoelectronics Adv. Mater. – Rapid Comm. **2**(12) 891- 894 (2008).
[18] N. Martin, N.M. Jedynakiewicz, A.C. Fisher, Dent. Mater. **19**, 77 (2003).
[19] C. Tamas, M. Moldovan, C. Prejmerean, A. Colceriu, G. Furtos, L. Vezsenyi, D. Prodan, R. Grecu,V. Simon, J. Optoelectronics Adv. Mater. **7**(6), 2849 (2005).

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