JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 11, November 2007, p. 3415 - 3418

Effect of coupling agents on the local mechanical properties of bioactive dental composites

M. MOLDOVAN*, C. PREJMEREAN, A. COLCERIU, C. TAMAS, G. FURTOS, D. PRODAN, M. TRIF, C. ALB[a], S. NEAMT[a], V. POPESCU[b]
Raluca Ripan Chemistry Research Institute, 400294 Cluj-Napoca, Romania
[a]*Dental Medecine"Iuliu Hatieganu", University of Medicine and Pharmacy, Cluj-Napoca, Romania*
[b]*Technical University of Cluj-Napoca, Romania*

Recent studies have shown that composite resins with non-impregnated filler have a higher probability of elution-in-water and water-uptake than the resins with a silane coupling agent-impregnated filler. This coupling agent may induce an interaction between matrix and filler and it may protect the surface of the filler against elution in water. The purpose of the present study was to evaluate the efficiency of two silane-coupling agents: A171 [3-(trimethoxysilyl) propyl silane] and A-174 [γ-metacriloyloxypropyl-trymethoxysilane] in creating a different polymer/inorganic surface link, by determining the mechanical properties of the new composites (ISO 4049). The quantity of active double bonds attached to the nanofiller particles surfaces was determined through FTIR spectroscopy of the silane-coupling agent coated on the synthesized powders. A Philips XL 30 SEM scanning electronic microscope was used for the determination of particles morphology. A relative homogeneous microstructure with different particles' size and shape was observed in the microphotographs in all cases.

(Received March 23, 2007; accepted November 1, 2007)

Keywords: Dental composites, Mechanical properties, Silane treatment, IR spectroscopy

1. Introduction

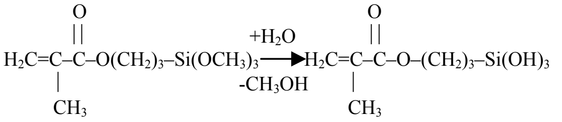
Recent studies have shown that composite resins with non-impregnated filler have a higher probability of elution-in-water and water-uptake than the resins with a silane coupling agent-impregnated filler. This coupling agent may induce an interaction between matrix and filler and it may protect the surface of the filler against elution in water. [1-7]. Other studies have disputed the idea, showing that this protection is almost inefficient and that water microleakage through the silane-coupling agent is quite probable. Regarding the behavior in water, it is important to know that the surface of the filler has a high hydrophilicity and that the accumulation of water molecules at the interface facilitates the reaction of hydrolysis. A lot of today knowledge about composite resins can be largely attributed to the study of model composite systems in which compositions can be carefully controlled [8-9]. Studies made by Bowen [10], Hirasawa [11-13] and Soderholm [14-15] have clearly demonstrated the important role of filler content and coupling agent in determining the composites properties. Thus, the chemical structure of the filler becomes extremely important not only because of the strength and durability of the particles, but also because of the interaction with the resin in the composite material.

A dental resin reinforced with bioactive filling based on hydroxyapatite (HAP) crystals seems, a favorable restorative material for human tissues.

The use of HAP in restorative dentistry offers several promising advantages including intrinsic radioopaque response, enhanced polishability and improved wear performance**.** [16-19]. The synergy between the organic polymer matrix and the usual inorganic reinforced filler is mainly mediated by the interfacial phase. Coupling agents are generally applied to the fillers in order to improve the strength properties of inorganic filler-resin composites**.** The structure and properties of surface (boundary, interfacial) layers at the interface with a solid are important factors determining the properties of bioactive dental composites. A boundary or surface layer of a solid material can be considered as a layer whose properties vary under the action of the surface force field, and they differ from the properties of the same material in bulk. The hydrolytic stability of the polymer/inorganic filler interface leads to creating some polymeric composites with improved mechanical properties [20-23]. The purpose of the present study was to evaluate the efficiency of two silane-coupling agents: A171 [3-(trimethoxysilyl) propyl silane] and A-174 [γ-metacriloyloxypropyl-trymethoxysilane] in creating a different polymer/inorganic surface bond, by determining the mechanical properties of the new composites (ISO 4049).

2. Experimental procedure

The organic phase consists of a mixture of dimethacrylate monomers: Bis-GMA (synthesized in our laboratory)/ TEGDMA (Aldrich) in 65/35 ratio with camphorquinone (Merck)/N,N dimethyl amino methyl methacrylate (Aldrich) as initiator/activator system. The inorganic phase consists of silanizated fillers based on a mixture between hydroxyapatite (HAP), SiO_2 and some nanofillers (N1, N2, N3) obtained through the sol-gel method in our laboratory. The above mentioned nanofiller was: N1- nanoparticles based on colloidal silica and zirconium oxide (SiO_2- ZrO_2); N2- nanoparticles of Al_2O_3-ZrO2; N3- nanoparticles of $La_2Zr_2O_7$. Silanation was made from an acidulated ethanol-water solution of the silane A171- [3- (trimethoxysilyl)propyl silane] (Aldrich) and A174 [γ-metacriloyloxypropyl-trymethoxysilane] (Aldrich). For silanation of nanofiller particles, the process started by subjecting the A174 and A171 coupling agents to a hydrolysis reaction, which yielded a stable silanol.



$$H_2C=\underset{\underset{CH_3}{|}}{C}-\overset{\overset{O}{||}}{C}-O(CH_2)_3-Si(OCH_3)_3 \xrightarrow[-CH_3OH]{+H_2O} H_2C=\underset{\underset{CH_3}{|}}{C}-\overset{\overset{O}{||}}{C}-O-(CH_2)_3-Si(OH)_3$$

The ratio of ethanol to water was 90/10. The solution was acidulated at pH 3.5-4 using acetic acid to provide the hydrolysis of methoxy groups of the silane to silanol groups. The amount of silane coupling agent (X) used for the filler treatment was determined using the equation proposed by Arkles:

$$X=A\times f/\omega$$

where X is the amount of coupling agent in grams (g) needed to obtain minimum uniform coverage, f is the amount of filler (g), A is the surface area of the nanofiller (m^2/g) and ω is the wetting specific surface of silane (m^2/g., ω is 314 m^2/g for silane A 174 and A 171). The **IR spectra** were registered on a FTIR Spectrophotometer, JASCO– 610 and evaluated the bond of silanes to inorganic fillers. Information upon the **silane-coupling agent** is obtained from the KBr pills in domain analysis 400-4000cm^{-1}. The morphplogy of the particles was studied with a Philips XL 30 ESEM scanning electronic microscope. The composites (C_{11}-C_{41}) were prepared as a paste (Table 1), by dispersing in the organic phase the silanizated bioactive inorganic fillers with A171 silane, respectively (C_{12}-C_{42}) obtained with bioactive inorganic fillers silanizated with A174 silane comparatively with unsilanizated fillers (C_5^*).

Table 1. The chemical composition of the composites [wt%].

Composites	Organic phase	Inorganic phase				
		HAP	N_1	N_2	N_3	SiO_2
C_{11} –C_{12}	22	20	40	-	-	18
C_{21}-C_{22}	25	20	-	40	-	15
C_{31}-C_{32}	23	20	-		40	17
C_{41}-C_{42}	30	40				30
C_5^*	40	20	20			20

Characterization of the composites. The tests for the mechanical properties such as compressive strength (CS), diametral tensile strength (DTS) and flexural strength (FS) were performed with a universal mechanical testing instrument from the LOYD Company, at 23 °C. The samples, were obtained in Teflon moulds (6 mm diameter and 3 mm) thick for DTS; (3mm diameter and 6 mm) thick for CS; (2×2×25 mm) for FS where the composite resins were polymerized with a 3M XL 2500 Lamp for 40 sec, from several directions. After the polymerization process, the samples were kept into distilled water at a temperature of 37±1 °C for 24h. The compressive strength was calculated from the equation:

$$CS = 9,81F/0,785d^2$$

where **F** is the load at fracture and **d** the cylinder diameter. The diametral tensile strength was determined from relationship:

$$DTS = 2F/ \pi dt$$

where **d** is the diameter and **t** the thickness of the cylinder. The flexural strength in three-point bending was obtained using the expression

$$FS = 3Fl / 2bh^2$$

where **l** is the distance between the two supports, **b** the width and **d** the depth of the specimen.

3. Results and discussion

The FTIR analyse showed the presence of the coupling agent on the HAP and nanofiller surface. This was confirmed by the carboxylate anion antisymmetric and symmetric vibrations at 1610-1550cm^{-1} and 1400-1300 cm^{-1}; in addition the carbonyl stretching vibration at 1715-1690 cm^{-1} and the C=C aliphatic absorption around 1640 cm^{-1}. (Fig. 1).

Important modifications in the 800-1200 cm^{-1} domain showed the formation of some new types of Si–O bonds after the filler's silanization, corresponding to Si-O-CH_3 asymmetric and symmetric stretch bands at 1088 cm^{-1} and 817 cm^{-1}. The absorbances are normalized to C=C band at 1638cm^{-1}, with reduced absorbance in the asymmetric CH_3 and CH_2 domain stretch region in 2800-3000 cm^{-1}. The broad band from 3800 cm^{-1} to 3000 cm^{-1} with maximum at aprox 3450 cm^{-1} is attributed to stretching of OH of Si-OH groups that are hydrogen bonded plausibly to O=C groups (Si-OH…O=C). Part of the 3450 cm^{-1} band may also arise from Si-OH hydrogen bonded to Si-OH groups and from water hydrogen bonded to itself and to the Si-OH groups. The infrared spectra of ZrO_2 gave a strong absorbtion at 1600-1610, 1350-1360, 1120-1110 cm^{-1} and a less band at 2350-2360 cm^{-1}. The infrared spectra of La_2O_3 gave a strong absorbtion at 1380-1400, 1590-1610, and 3400-3500 cm^{-1} .Therefore the strong bands observed at 1350-1335, 1590-1625 and 3500-3600 cm^{-1} in $La_2Zr_2O_7$ could be due to Zr-O, La-O vibrations, while the less intense band at 2940-2950 cm^{-1} could be due to Zr-O vibration only. A scanning electron microscopy (SEM) was used to observe the surface microstructure of synthetized nanofillers. As for the N1 powder, the SEM revealed the presence of the nanoparticles in an agglomerated structure dispersed throughout the SiO_2 and ZrO_2 crystals (Fig. 2).

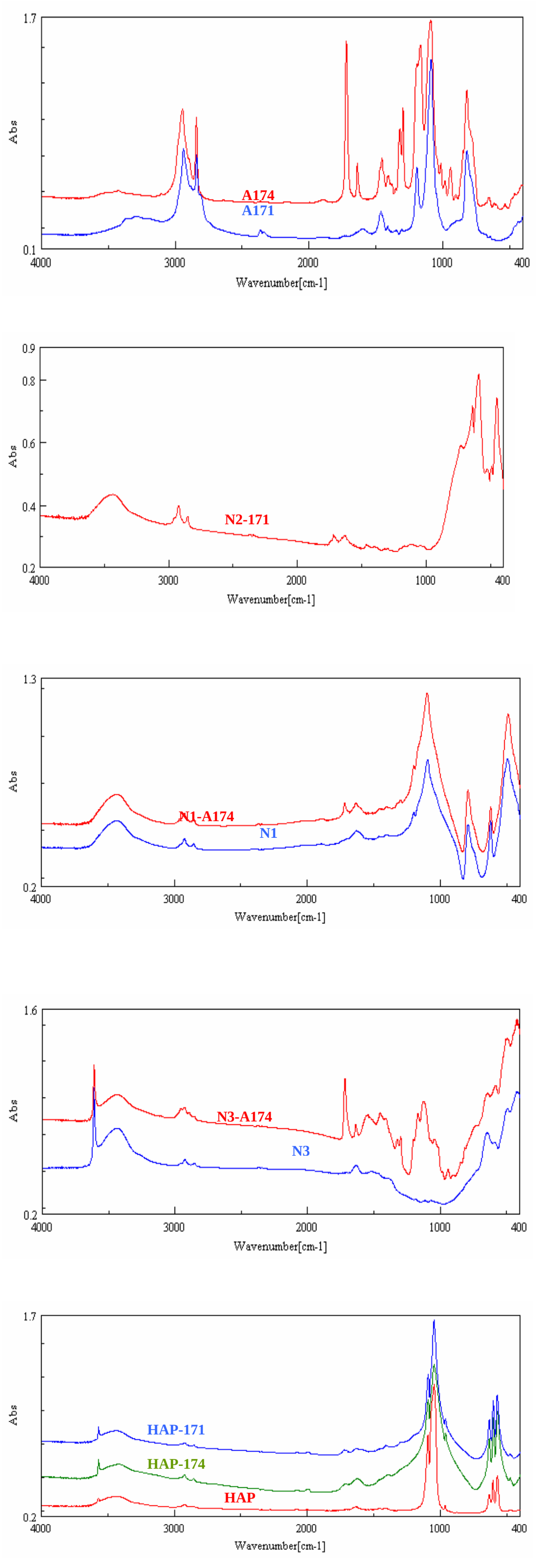


Fig. 1. IR spectra for N1, N2, N3, HAP silanated and unsilanated.

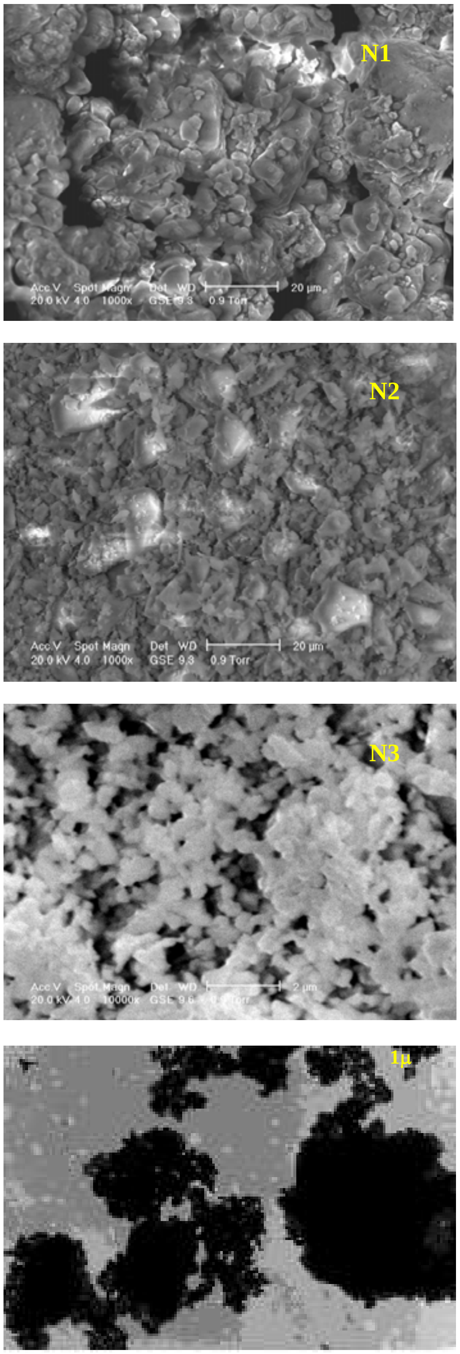


Fig. 2. SEM image for N1, N2, N3, and SiO_2.

In the case of the N3 powder a homogenous structure of the nanoparticles was found. Fig. 2 shows the habit of the precipitated SiO_2 particles. The needle-like nanoparticles of 50-100 nm lengths had a high specific surface area of ~ 150 m^2/g while the microscopic 1-5 μm had only ~ 5 m^2/g. The values for mechanical properties (DTS, CS, FS) of the studied composites are shown in Fig. 3.

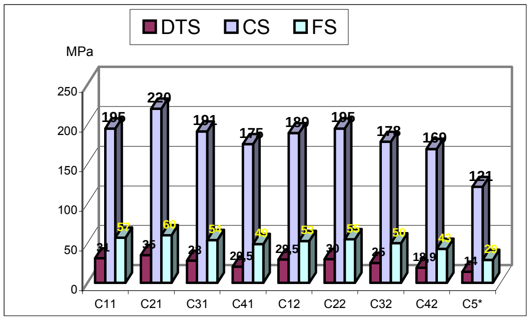


Fig. 3. The values for mechanical properties.

Generally, sequential additions of filler to resin matrix produced minor changes in tensile strength. In the case of C5* sample (unsilanized) all mechanical properties are weaker. The best results were obtained for the C_{21} composite obtained with N2 filler based on nanoparticles of Al_2O_3-Z_rO_2. In order to make a strong polymer-bioactive composite (polymer matrix containing HAP, nanoparticles and silica), the filler particles must be bonded to the resin. This bonding is achieved with a so-called "coupling agent." The most efficient coupling agent for methacrylates (BisGMA, TEGDMA) was considerated A-174. The coupling silane molecule can bond at one end to the bioactive filler and at the other end to the resin matrix. Filler particles with silane transfer stress between filler and matrix. The coupling agent makes it possible to transfer stress from the weaker resin matrix to the filler. Without a coupling agent, the composite would become weaker in tension and filler particles would easily be plucked out from the surface during mastication.

4. Conclusions

The results of the study proved the importance of the relationship between composition, coupling agents and mechanical properties on some composite made by dispersing bioactive fillers in Bis-GMA/TEGDMA resin matrix. The IR spectra recorded for silanized N1 nanoparticles with A174 silane showed the characteristic bands of A174 silane –filler. The values of the flexural strength, compressive strength and diametral tensile strength were determined. The highest values have been registered for the light-cured composite C21 that has the inorganic filler based on 20%, HAP, 15% colloidal silica and 40% N2. These results may be explained by higher degrees of interfacial bond for A171 silane to the above-mentioned inorganic filler in Bis-GMA/TEGDMA resin matrix and a more homogenous dispersion of the nanoparticles in the organic matrix. These changes in morphology of the silicate matrix can be manipulated by the selection of sol-gel catalyst with dramatic effect on the physical properties of the nanocomposites. [24].

The results of our experimental studies have shown the superiority of nanofilling systems that we have obtained, as compared to the currently used or less hard fillers, allowing a better finishing of the composite.

Acknowledgement

This work was supported by MATNANTECH PROGRAM Project CEEX-30/2005.

References

[1] N. M. Mohsen. R. G. Craig Journal of Oral Rehabilitation **22**, 213 (1995).
[2] K. K. Rao, T Banu, M. Vithal, G. Y. S. K. Swamy, K. R. Kumar, Materials Letter **54**, 205 (2002).
[3] G. Willems, P. Lambrechts, M. Braem, J. P. Celis, G. Vanherle, Dent. Mater. **8**, 301 (1992).
[4] R. Labella, M. Braden, S. Deb, Biomaterials **15**, 1197 (1994).
[5] Y. Yoshida, K. Nagakane, R. Fukuda, M. Itoh, M. Okazaki, H. Shintani, S. Inoue, P. Lambrechts, G. Vanherle,B. Van Meerbeek, J. Dent. Res. **83**, 454 (2004).
[6] S. Daniel, S. Deepak, Emmanuel P. Giannelis, Mater. Sci, **6**, 205 (2002).
[7] A. Okada, M. Kawasumi, T. Kurauchi, O. Kamigaito, Polym Prepr **28**, 447 (1987).
[8] A. Usuki, M. Kawasumi, Y. Kojima, A. Okada, T. Kurauchi, O. Kamigaito, J Mater Res. **8**(5), 1174 (1993).
[9] K. Yano, A. Usuki, A. Okada, T. Kurauchi, O. Kamigaito, J Poly Sci (Part A), **31**, 2493 (1993).
[10] R. L. Bowen, J. Am. Dent. Assoc. **69**, 481-495 (1964).
[11] T. Hirasawa, in Reports of the Research Institute of Dental Materials **2**, 443 (1963).
[12] T. Hirasawa in Reports of the Research Institute of Dental Materials **2**, 629 (1965).
[13] T. Hirasawa in Reports of the Research Institute of Dental Materials **2**, 644 (1965).
[14] K. J. M. Söderholm Acta Odontol. Scand. **40**, 145 (1982).
[15] K. J. M. Söderholm, J.Dent.Res. **63**, 1321 (1984).
[16] M. W. Beatty, M. L. Swartz, B. K. More, R. W. Phillips, T. A. Roberts, J. Biomed Mater Res **40**, 12 (1998).
[17] M. W. Raney, S. E. Berger, J. G. Marsden, Composite Materials 6, E .P. Pleueddemann, ed., Academic Press., NY (1974).
[18] E. P. Plueddemann, L. H. Lee, ed., Plenum Press, NY(1991) pp. 279-290.
[19] T. M. Che, G. M. Brauer, J. Dent. Res. **61**(12), 1439-1443 (1982).
[20] S. Venz, J. M. Antonucci, J. Dent. Res. **65**, 191, Abst. No. 191 (1986).
[21] K. J. M. Söderhol, S-W. Shang, J. Dent. Res **72**, 1050-1054 (1993).
[22] S. H. Dickens, J. M. Antonucci, B. O. Fowler, Polymer Preprints **43**(2), 747-748 (2002).
[23] J. M. Antonucci, B. O. Fowler, S. H. Dickens, N. D. Richards, Polymer Preprints **43**(2), 633-634 (2002).
[24] M. K. Harrup, A. K. Wertsching, F. F. Stewart, Amer. Chem. Soc. PMSE Preprints **82**, 307 (2000).

---

*Corresponding author: mmarioara2004@yahoo.com