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X-ray photoelectron spectroscopic study of composite glass fillers

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Modern dental practice has become very dependent on its materials, such that a great challenge in restorative stomatology is choosing the right combinations of materials. Dental composites consisting of a polymerisable matrix and glass filler particles attracted a large interest. In this study are investigated by X-ray Photoelectron Spectroscopy (XPS) four composite materials obtained from about 1/4 organic phase and 3/4 inorganic phase in form of oxide glass powder. C 1s core level spectra were analysed in order to get information on functional groups. The O 1s core level peaks for all samples show that the environments around the oxygen atoms are similar and according to binding energy values they denote non-bridging oxygens in the investigated composites.

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1. Introduction

With the advancement of modern materials science, many times a single material does not possess the desired properties for certain applications. For example, some materials have desired bulk properties (chemical, mechanical, electrical, etc.) but their surface properties are inadequate. In these cases, a combination of two or more materials or a modification of the bulk material is requested. Recent progress in the synthesis, characterization, and biological compatibility of biomedical implant materials focus particular attention. The synthesis and control of biomaterials can provide access to new levels of material properties and device characteristics that were previously unattainable. Investigations of novel materials whose microstructure can be engineered have been intensified, especially in the last two decades. Surface modification is basically a process in which the surface of a material is chemically, physically, or mechanically altered so that the surface properties are changed from that of the original bulk. Materials surfaces are commonly modified by techniques involving, for example, deposition of some additional material as a thin coating or implantation of energetic ions to alter the local atomic bonding.

In addition, functionally graded structures can be engineered to provide a more viable transition from the bulk to the surface. The novel materials whose microstructure can be engineered can exhibit enhanced mechanical, electrical, magnetic, and/or optical properties compared to their conventional micrometer-scale, or larger, counterparts [1].

The composites in contemporary dentistry have improved substantially in regard to these issues. Photoactivated composites are used in restorative dentistry, as well as to fabricate large restorations such as crowns and fixed partial dentures [2]. Modern dental practice has become very dependent on its materials, such that a great challenge in restorative stomatology is choosing the right combinations of materials. Dental composites consisting of a polymerisable matrix and glass filler particles attracted a large interest [3].

A key issue in most applications of biomaterials is the way in which a given material influences and is influenced by the biological response that results from the contact between the biomaterial and the biological system, particularly at the thin surface layers. It is widely accepted [4] that the surface of the material has a critical influence on the biological response. In recent years there has been a considerable increase in the use of the various surface analytical methodologies, including X-ray induced photoelectron spectroscopy (XPS) [5, 6]. The XPS technique, in particular, provides information on the first tens Angstroms of the sample surface and it is a key tool in understanding the chemistry and physics taking place on surfaces and at interfaces.

The aim of the study is to investigate by XPS four composite materials obtained from about 1/4 organic phase and 3/4 inorganic phase in form of oxide glass powder. Elemental chemical composition on samples surface is determined and compared with reference data. C 1s and O 1s core level spectra are analysed in order to get information on functional groups and on electronic charge density around the most abundant elements in these samples.

2. Experimental procedure

The samples were prepared by inorganic phase dispersion in the monomers mixture. Samples solidification was induced by photopolymerisation using a

XL3000 - 3M Dental Products lamp of 14 W. Powder of boro-silicate glasses with ZnO is the inorganic phase. The organic phase consists of a monomer mixture containing in sample (I) isophorene-di(carbamoiloxy-4butyl acrylate) and triethyleneglycole dimethacrylate (TEGDMA), in sample (II) polyethylene oxide di(urethane ethylmethacrylate) and TEGDMA, in sample (III) and (IV) the organic phase also contains Bis-GMA related to sample (II) and (I), respectively. Dimethylaminoethylene methacrylate was introduced as accelerator of polymerisation and camphorequinone as photosensibiliser.

The X-ray diffraction analysis was carried out by means of standard DRON powder diffractometer.

XPS measurements were performed using a PHI 5600ci Multi Technique system with monochromatised Al Kα radiation from a 250 W X-ray source (hν = 1486.6 eV). During the measurements the pressure in the analysis chamber was in the 10^{-9} Torr range. Low energy electron beam was used to achieve charge neutrality at the sample surface. High resolution core level scans were acquired for the C 1s, Si 2p, N 1s, F1s, Zn 2p and O1s photoelectron peaks. The absolute binding energies of the photoelectron spectra were determined by referencing to the C 1s transition at 284.6 eV. The position and full width at half maximum of photoelectron peaks were estimated using spectra simulation based on summation of lorentzian and gaussian functions.

3. Results and discussion

The prevalent inorganic phase of the investigated composites is glass powder with ZnO. X-ray powder diffraction analysis proves the vitreous state of the inorganic phase. The diffraction pattern (Fig. 1) consists of a single broad peak around 2θ = 32° and do not reveal any crystalline phase.

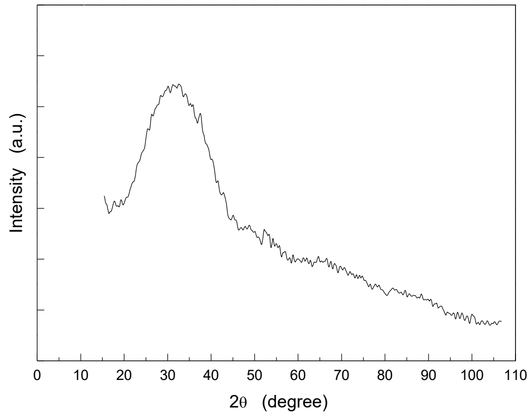

Fig. 1. X-ray diffraction pattern recorded from inorganic component of the investigated composites .

The survey XPS spectra (Fig. 2) evidence photoelectron peaks of all entering elements. Fluorine and zinc were measured in small amounts at baseline.The XPS wide-scan spectra were used, by estimating of the area under photoelectron peaks, for elemental chemical analysis (Electron Spectroscopy for Chemical Analysis-ESCA) on samples fracture. The results are summarised in Table 1. The most abundant elements are carbon (toward 60 at %) and oxygen (around 30 at %), while silicon is between 6.9 and 8.5 at %.

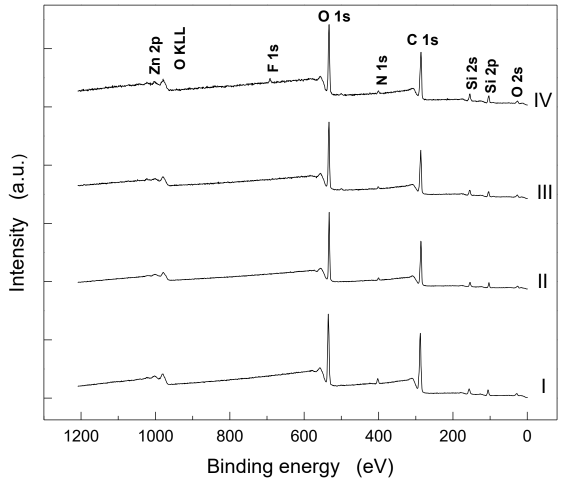

Fig. 2. XPS survey spectra of the four investigated compositions.

Boron oxide was added to inorganic glass phase in order to decrease the melting temperature of silicate glasses. The very low content of boron on the surface of the fractured samples was under accuracy limits.

Table 1. Elemental composition (at %) of samples.

Sample	C1s	N1s	O1s	F1s	Si2p	Zn2p
I	58.0	3.1	30.4	0.2	7.8	0.4
II	56.1	1.9	32.8	0.2	8.5	0.4
III	57.8	1.9	32.4		6.9	0.9
IV	57.9	2.1	29.6	1.2	8.5	0.7

The C:O, C:Si and C:Zn ratios are often used to characterise the properties of dental fillers, because these ratios changes during the aging process of the investigated composites [2]. According to the elemental composition determined from ESCA we calculated C:O, C:Si and C:Zn ratios which are summarised in Table 2 along with the values reported for other polymer-ceramic dental composites.

Table 2. Atomic % ratios C:O, C:Si and C:Zn for dental filler composites.

Sample	C:O	C:Si	C:Zn
I	1.64	7.4	145
II	1.71	6.6	140
III	1.95	8.4	64
IV	2.0	6.8	83
Ref. [2]	3.0	6.0	86

The overall C 1s photoelectron peaks (Fig. 3) can be fitted in the range 283-289 eV by a superposition of four peaks. The main peak, around 284.6 eV, is attributed to C-C and C-H bindings, while other three peaks are assigned to C-O (around 286.2eV), C=O (around 287.5 eV) and O-C=O (around 288.8 eV) respectively [6, 7].

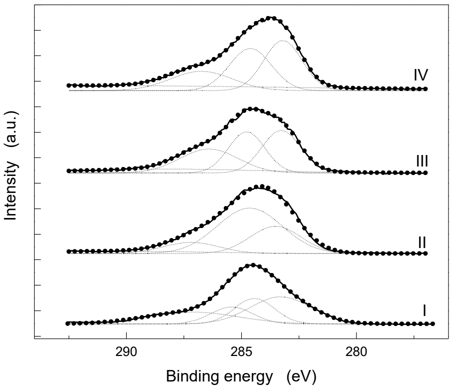

Fig. 3. C 1s core level experimental (solid line) and simulated (short dots) photoelectron spectra of the four investigated compositions.

According to these fits (Table 3) the Bis-GMA addition has a larger effect on sample II than on sample I.

Table 3. Components of C 1s peak fits (%).

Sample	C-C,C-H	-C-OH	-C=O	-COOH
I	37	23	16	24
II	26	55	12	7
III	31	29	27	13
IV	27	25	17	31

O1s high resolution spectra (Fig. 4) are analysed in order to get information on electronic charge density and implicitly on the environment around the next abundant element in the investigated samples.

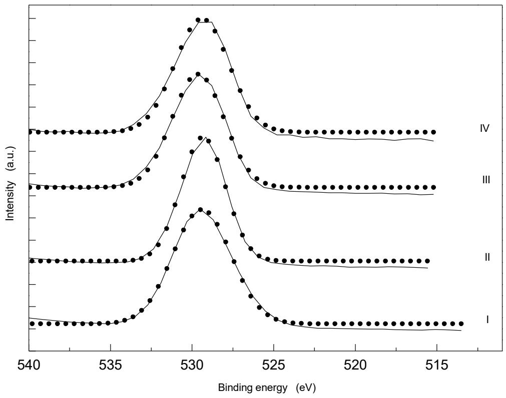

Fig. 4. O 1s core level experimental (solid line) and simulated (short dots) photoelectron spectra of the four investigated compositions.

Binding energies corresponding to O 1s photopeaks are in the range reported for silicate glasses [8, 9]. In the XPS studies of oxide glasses, the binding energy of O 1s electrons in oxygens bonded to different cations seems to be the most informative measurement with respect to the structure of the glass [10-12]. This binding energy is a measure of the extent to which electrons are localized on the oxygen or in the internuclear region and hence of the constraints on the network, as reflected by the physical properties. This increase in electron density at the oxygen atoms means that the electron binding energies are reduced and this is reflected in the photoelectron spectrum, giving rise to non-bridging oxygen peak. According to the classical model of silicate glasses, the influence of the network modifier cations on the local structure consists in the compensation of the negative charges and is responsible for the disruption of the oxygen bridges in the silica network [13]. In the investigated composites the modifier cation entering the silicate glass is the zinc, having the ionic radius almost two times larger than the silicon and the cation field strength is only 3.65 Å^{-2} in comparison to 25 Å^{-2} corresponding to silicon. In our samples the O 1s peak is well simulated with a single peak (Fig. 4). This would indicate that electrons on the oxygen atoms in the different configuration have similar binding energies. Both binding energy and line width are less influenced by composition changes in I-IV samples.

The O 1s core level peaks for all samples are symmetric, indicating that the environments around the oxygen atoms are undistinguishable.

Table 4. Core level electron binding energies (BE) and full-width at half-maximum (FWHM) for O 1s photoelectron peaks.

Sample	I	II	III	IV
BE (eV)	529.4	529.3	529.6	529.4
FWHM (eV)	3.5	2.8	3.2	3.3

The binding energies of O 1s core level photoelectrons (Table 4) are comprised between 529.3 and 529.6 eV and are lower than the values reported for bridging oxygens in glasses [14-16] showing that in these samples the oxygen atoms are non bridging oxygens. One also remarks a narrowing of O 1s core level photoelectron peak for sample II that points out more order around oxygen atoms in this composite as compared with other three compositions.

4. Conclusions

Content of fluorine, cariostatic element, ranges in investigated samples from 0 to 1,2 atomic percent. Peak fitting of C 1s core level spectra allow evaluating the relative ratio between the functional groups. The composite based on isophorene-di(carbamoiloxy-4butyl acrylate) is less affected by Bis-GMA addition than the composite based on polyethilen oxide di(urethane ethylmethacrylate). The binding energy of O 1s photoelectrons and the symmetric O 1s core level peaks indicate that oxygen atoms in the different samples are non bridging and the environments around the oxygen atoms are undistinguishable.

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References

[1] S. A. Catledge, M. Fries, Y. K. Vohra, Encyclopedia of Nanoscience and Nanotechnology, Ed. H.S. Nalwa, American Scientific Publishers 2003, vol. X, p.1–22.
[2] K. A. Schulze, J. Tinschert, S. J. Marshall, G. W. Marshall, Int. J. Prosthodontics **16**(4), 355 (2003)
[3] 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).
[4] J. A. Gardella Jr., N. I. H. de Gatrica, J. Elecron Spectrosc. Relat. Phenom. **81**, 227 (1996)
[5] G. Polzonetti, G. Iucci, A. Frontini, G. Infante, C. Furlani, L. Avigliano, D. Del Principe, G. Palumbo, N. Rosato, Biomaterials **21**, 1531 (2000).
[6] J. Xie, N. Zhang, M. Guers.V. K. Varadan, Smart Mater. Struct. **11**, 575 (2002).
[7] J. C. Vickermann, Surface analysis – The principal Techniques, Chichester, Wiley, 1997.
[8] P. C. Soares, P. A. P. Nascente, E. D. Zanotto, Phys. Chem. Glasses, **43**(3), 143 (2002).
[9] S. Andersson , P.A. Bruhwiler, A. Sandell, M. Frank, J. Libuda, A. Giertz, B. Brena, A.J. Maxwell, M. Baumer, H.-J. Freund, N. Martensson, Surface Science **442**, L964 (1999).
[10] A. Mekki, Arab. J. Sci. Eng. **28**, (1A), 74 (2003).
[11] G. D. Khattak, N. Tabet, M. A. Salim, J. Electron Spectros. Relat. Phenom. **133**, 103 (2003).
[12] G. D. Khattak, N. Tabet, L.E. Wenger , Phys. Rev. B **72**, 104203 (2005).
[13] E. Muller, K. Heide, E.D. Zanutto, Zeitschrift fur Kristallographie **200**, 287 (1992).
[14] V. Dimitrov, T. Komatsu, J. Solid State Chem. **163**, 100 (2002).
[15] V. Simon, D. Eniu, A. Takács, K. Magyari, M. Neumann, S. Simon, J. Non-Cryst. Solids **351**, 2365 (2005).
[16] V. Simon, M. Todea, A.F. Takács, M. Neumann, S. Simon, Solid State Commun. **141**, 42 (2007).

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