"BABEŞ BOLYAI" UNIVERSITY CLUJ–NAPOCA
FACULTY OF CHEMISTRY AND CHEMICAL ENGINEERING

PhD THESIS

NEW COMPOSITE MATERIALS WITH MULTIPLE FUNCTIONALITIES USED IN MEDICINE

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2010

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INTRODUCTION

The approach of dental materials, intensely investigated in the last years, continues to represent a very interesting subject mainly stimulated by the introduction of polymerisable composites with superior performances when compared to amalgam materials, such as esthetic features, thermal conductivity, hardness and resistance [1-7]. The new class of materials used for the restoration of the dental anatomy and imposed after 1970 was based on acrylic / methacrylic polymer structures combined with inorganic fillers characterized by appropriate properties (rapid photopolymerisation, good mechanical resistance, hardness, elasticity, reduced fragility, low water absorption, texture similar to the tooth structure, etc.)

Progress they are currently registered materials science on the one hand, the second polymer and those recorded in the medical field, make composite materials at borders so many disciplines, is always a challenge to their approach to achieve specific performance special. A number of investigations are currently in nanotechnology to develop the next generation of dental composites.

The approaches used include: *1) modifications of filler particles for controlled surface topography at the particle-resin interface, 2) nanoscale computational modeling of complex chemistries at the hydrophobic-hydrophilic interface of tooth and composite resin, 3) use of nanostructured components spiked into traditional dental materials to minimize shrinkage stress and/or maximize phase integrations, 4) layering nanostructured materials within a composite to mimic the shock-absorbing transition zones in natural teeth, and 5) incorporation of nanofibers dispersed through the resin for fibrous reinforcement.*

Modern dentistry includes items related to the scope of dental restorations and dentin hypersensitivity, which in turn correlates with the degree of infiltration of plaque in the dentin tubules. Over 35% of the population suffers from dentin sensitivity. In this context biological integration of dentin adhesives is a condition sine qua non of therapeutic success of dental fillings.

Dental restorations, in particular lesions such as micro fissure, caries were made over time in a number of different steps and materials becoming more efficient. Restoration of tooth injury involves: surface adherent cleaning, conditioning adherent surface (acid etching, washing, drying), applying the adhesive and finally composite application. The most common therapeutic solutions in such cases have supported and will support the improvements over time. In this respect, the trajectories of modern therapeutic solution to improve adhesion of dentin hypersensitivity composite restoration applied to the dentin, through the application of dentin adhesives in order to mitigate it.

The aim of the present thesis consisted of obtaining new inorganic fillers with metal oxides, non-metallic transformed in glasses and nanofillers, dimethacrylate monomers and form new composite materials and adhesives used in dentistry.

Determination of physico-chemical, mechanical and biological properties of restorative materials is an obligatory step in estimating their ability to cope successfully in clinical conditions. To this end I proposed experimental characterization of composite materials and adhesives for having more parameters as required by landmark regulations to international standards.

The experimental work carried out was intended to provide:

- synthesis and characterization of new inorganic fillers with metal oxides, non-metallic transformed in glasses and nanofillers;
- synthesis and characterization of urethane dimethacrylate monomers with carboxyl groups and phosphate, with superior properties in terms of adhesion to dentin tissues;
- formulation and characterization of new nanocomposites and adhesives used in direct dental restorations;
- study on the interaction of composite materials and adhesives to dental hard tissues.

The thesis is structured on three parts: "the literature overview", "personal contributions" and "experimental part" and a chapter of "conclusions" and "references".

The first part consists of two major chapters resuming: development issues and the importance of composite materials with multiple functionalities used in dentistry, and the structure and composition of composite materials and adhesives used in dentistry.

Part two is structured in four chapters and presents personal contributions on:

- synthesis of inorganic fillers used in formulation of adhesives and composites used in dentistry;
- synthesis of $La_2Zr_2O_7$, HA, HA-ZnO, HA-ZrO_2, HA-SiO_2 nanofillers used as inorganic phase in formulation of adhesives and composites;
- synthesis and characterization of urethane dimethacrylates with carboxyl groups of oligomers type, acid monomers with phosphate groups and $(Bis\text{-}GMA)_{0\text{-}2}$ superiors oligomers used as organic phase in the formulation of composite materials and adhesive systems;
- formulation of composite matarials and dental adhesives used in dentistry;
- characterization of the obtained composite and adhesives materials through physico-chemical methods;
- study on the interaction of composite materials and adhesive systems to dental hard tissues.

I should be mentioned the fact that the results were obtained at „Babes Bolyai" University-„Raluca Ripan" Chemistry Research Institute Cluj-Napoca (Dr.C.S.I. Marioara Moldovan), Petru Poni Institute of Macromolecular Chemistry Iaşi (Dr. Tinca Buruiana), Technical University Cluj-Napoca (Prof.Dr. Violeta Popescu), Iuliu Hațieganu University of Medicine and Pharmacy Cluj-Napoca, Faculty of Dental Medicine (Conf.Dr. Codruța Nicola), National Institute for Research and Development of Isotopic and Molecular Technologies Cluj Napoca (CSI Emil Indrea) şi S.C. Metav Research and Development S.A. (Vasile Eugeniu).

The research was funded by the Romanian Ministery of Education and Research (CEEX 30 (2005- 2008) and TD- 253 (2007-2008)).

II. PERSONAL CONTRIBUTIONS

II.1. SYNTHESIS OF INORGANIC FILLERS USED IN FORMULATION OF ADHESIVES AND COMPOSITES USED IN DENTISTRY

II.1.1. GLASS SYNTHESIS

Motivation for choosing to study these two types of glass, barium and strontium, one is their applicability in dentistry, by confer important radiopaque properties to the dental materials for restoration. Glass synthesis in laboratory conditions with appropriate characteristics for their intended purpose has been achieved by the conventional method of melting, placing emphasis on the choice of oxides introduced into the melt and the preparation of mixtures of materials. To obtain vitreous fillers I had in mind the following considerations:

- achievement of several glasses with different chemical composition, including addition oxides and oxide glass formers with radioopaque effects in sufficient quantities to give a radiopaque filling sound;
- achieve a variety of glasses was made in order to choose the composition with characteristics most suitable for providing a range of filling materials as complex oxides;

- use of network modifiers oxides with no toxicity, having regard to medical use of these materials;
- developing and perfecting methods of analysis and control.

For characterization of barium and strontium glasses (S1, S2) we consider first the features of interest in terms of the scope. Thus, the glass has been characterized, by determining them the specific surface and size distribution. Glasses structure was investigated by X-ray diffraction method, IR spectroscopy and electron microscopy. The silane coupling agent deposited on the glass particles was investigated by IR spectroscopy.

Glass powder surface area of barium and strontium was determined by BET method and have obtained values of 3.45 m^2/g for glass S1 and 2.85 m^2/g for S2 glass. Glass density is 2.55 g/cm^2 for S1 and is 2.80 g/cm2 for S2 glass. X-ray diffraction spectra gives a typical amorphous structure, specific to the glasses, with variable intensity, indicating the presence of local ordering.

II.1.3. SYNTHESIS OF $La_2Zr_2O_7$, HA, HA-ZnO, HA-ZrO_2, HA-SiO_2 NANOFILLERS THROUGH SOL-EMULSION-GEL METHOD

We synthesized 5 nanofillers: oxizd based on lanthanum and zirconium ($La_2Zr_2O_7$), hydroxyapatite (HA) and combinations of hydroxiapatite with various oxides (HA-ZnO, HA-ZrO_2, HA-SiO_2). Nanofillers obtained were characterized by: particle size distribution, electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction and IR spectroscopy. All nanofillers were characterized before and after heat treatment applied.

II.1.4.2. Investigation of nanofillers structure through X ray diffraction method

X-ray diffraction was performed with a Bruker D8 Advance powder difractometru for working at 40 kV and 40mA, using CuKα wavelength, with a monochrome germanium in the incident beam.

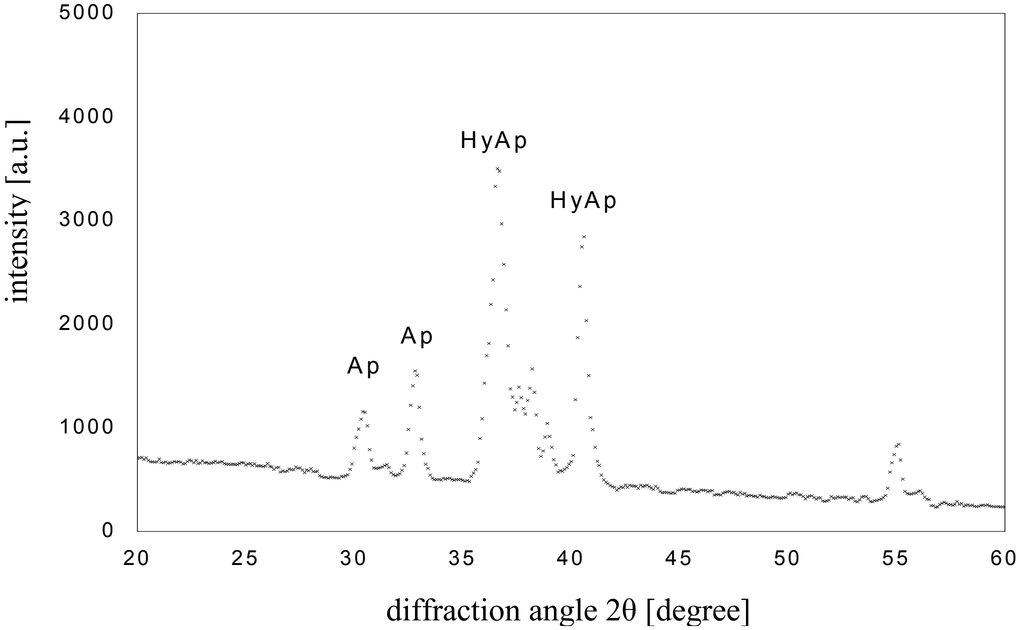


Figure1. IR spectrum for hydroxyapatite heat treated (900 ° C)

The X-ray diffraction spectrum for HA powder heat treated at 900 ° C are identified crystalline phase is observed and the main component of the system, which is hydroxyapatite (HA), but appears a component of apatite (Ap).

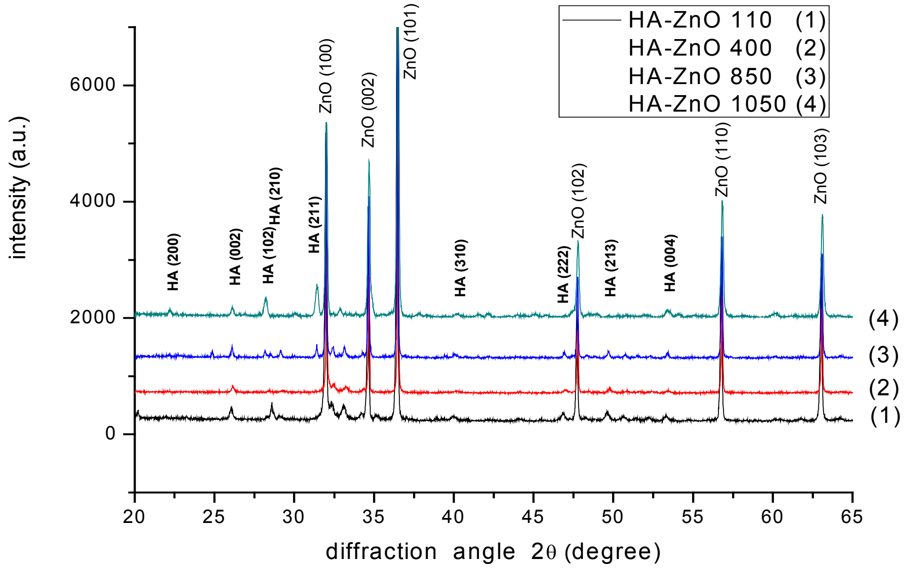


Figure 2. FT-IR spectrum for HA-ZnO powder

The diffraction peaks positions are evidenced by oxidic compounds formed during the technological process. Sizes of crystallites estimated bandwidth of diffraction is about 20 to 30 nm. The diffraction spectra shown at various temperatures of heat treatment, compound system is hydroxyapatite (HA), but there is a major component of apatite (Ap).

Spectra shows that the sample obtained in our synthesis conditions, contains an important component of crystalline ZnO with hexagonal structure, ICDD PDF number 89-7102, a = b = 0.32495 nm, c = 0.52069 nm, space group hexagonal system P63mc (186) with Zn and O atoms in special Wyckoff positions.

II.1.4.3. Investigation, through FT-IR spectroscopy, of the synthesized nanofillers

Powders of HA and HA-oxides were characterized using FTIR spectrophotometer JASCO - 610, in the 400-4000 cm-1 using the KBr pellet technique .

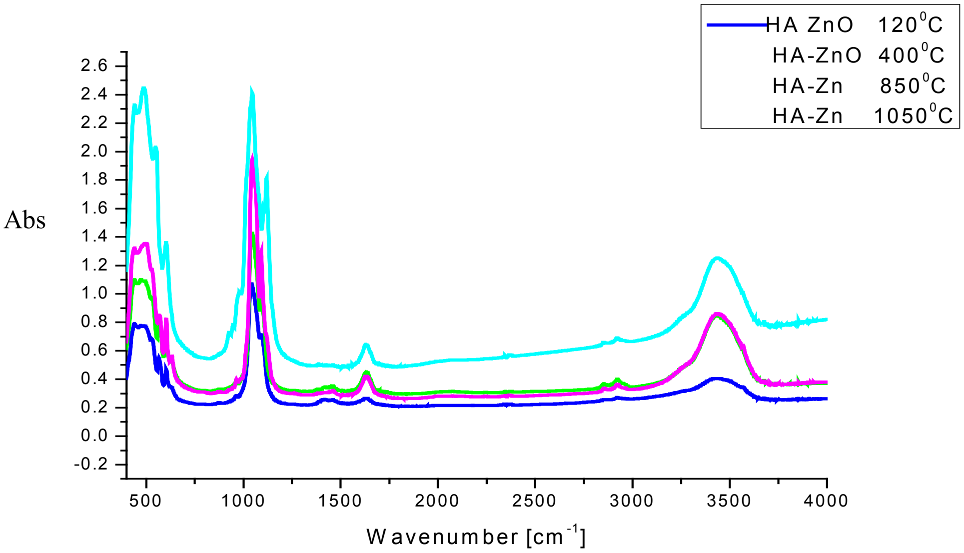
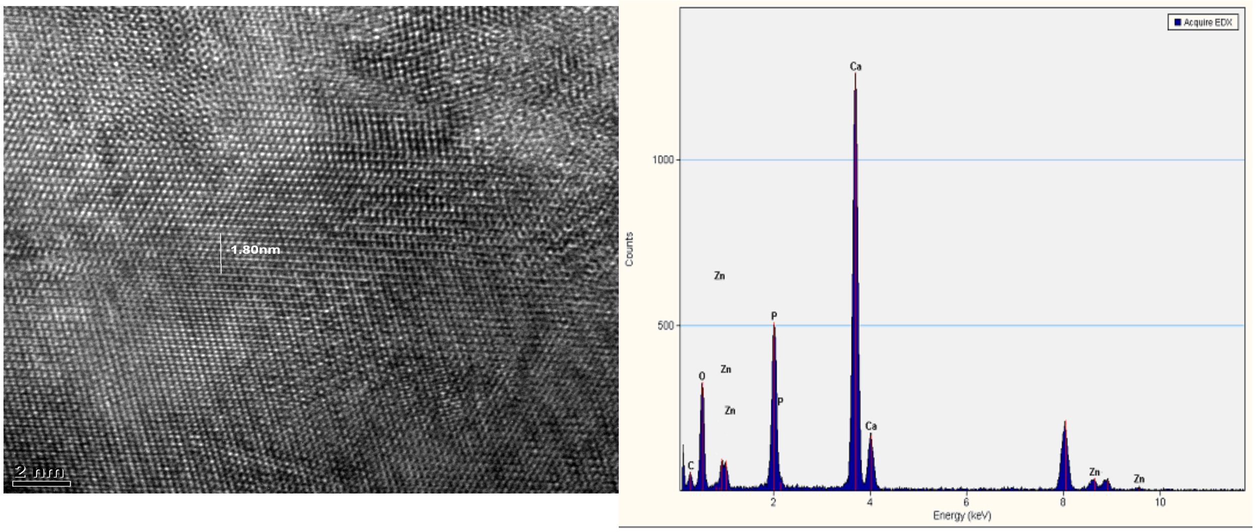


Figure 3. FT- IR spectra for HA-ZnO powder

In all spectra appear the characteristic bands of hydroxyapatite. Weak and sharp band at 3572 cm^{-1} attributed to OH free valence vibration and broad band and increased from 3432 cm^{-1} is attributed to OH-linked through hydrogen bonds. The two characteristic bands at 1090 cm^{-1} and 1050 cm^{-1} correspond to asymmetric valence vibration of the bond P-O and sharper band at 964 cm^{-1} corresponds to symmetric valence vibration P-O. Sharp and less intense bands at 632 cm^{-1}, 605 cm^{-1}, 570 cm^{-1} we attribute to deformation vibration of the bond P-O-P from PO_4^{3-}. ion. The spectra presented bands at 530 cm^{-1}, 480 cm^{-1}, 440 cm^{-1} we attribute to zinc oxide, after treatment at 1050 ° C these bands are more evident.

II.1.4.4. Microstructural characterization of nanofillers by transmission electron microscopy

Elctronic microscopy study was performed by transmission electron microscopy with high resolution (HRTEM) of type TECNAI F30 G^2 linear resolution of 1Å and spot resolution of 1,4 Å. The samples consist of small quantities of powder immersed in absolute alcohol, the suspension was homogenized by ultrasonic.



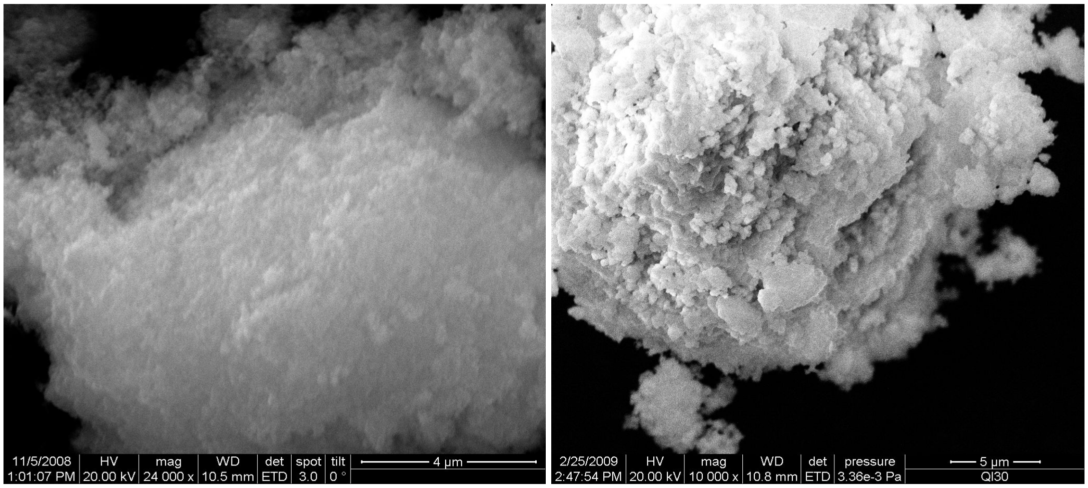
a *b*

Figure 4. Electron transmission microscopy image in high resolution (a) and X-ray spectrum of energy dispersion (b) HA-ZnO sample heat treated at 1050 ° C

Electron transmission microscopy image in high resolution (HRTEM) *figure 4a* highlight the crystallized nanoparticles with diameters in the 1-3 nm. Spectrum in the energy dispersive X-ray (EDAX) *figure 4b,* associated with the selected microregion from *figure 4a*, shows the presence in the sample of Ca, P, Zn and O.

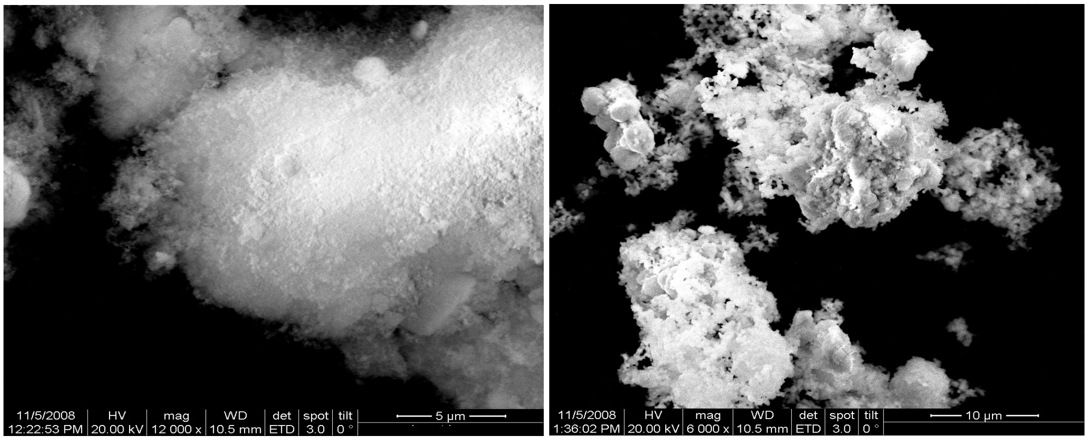
II.1.4.5. Investigation of the nanofillers structure through electron microscopy

Investigation of nanoparticles HA and HA-oxides was achieved using electron microscope Inspect FEI Company's product.



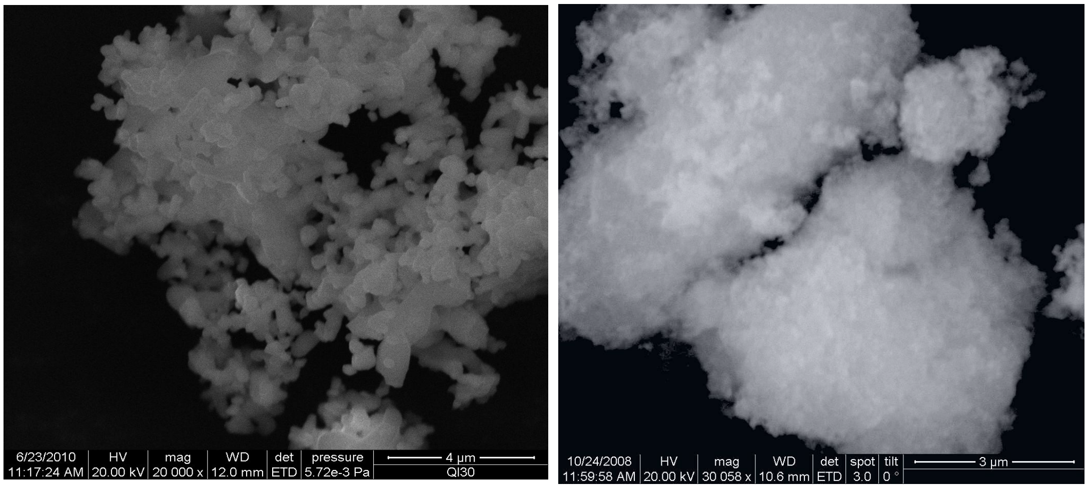
a *b*

Figure 5. SEM image for HA dried at 120 °C (a) and heat treated at 1050 °C (b)



a *b*

Figure 6. SEM image for HA HA-ZrO_2 *dried at 120 °C (a) and heat treated at 1050 °C (b)*



a *b*

Figure 7. SEM image for HA-ZnO heat treated at 1050 °C *(a) and HA-*SiO_2 *heat treated at 900* °C *(b)*

In this study, performed by SEM have revealed agglomeration of particles in a wider area, particle size is greater than 1 micron. Can see the influence of heat treatment on powder obtained thus increasing its lead to formation of larger crystals of different shapes.

HA powder dried at 120 °C (*figure 5 a*) looks like a very loose mass consisting of agglomerations of sub-micron particle sizes, shapes and contours undefined. Same powder, after heat treatment for 1 hour at 1050 °C (*figure 5 b*) change their appearance and size of particles, they become larger and hydroxiapatite specific crystalline form.

SEM images obtained for HA-ZrO_2 powder dried at 120 °C showed a bulky mass gatherings of sub-micron sized particles (*figure 6 a*). After 1 hour heat treatment at 1050 °C, senses a decrease in the volume of powder mass, particles with well-drawn shapes, faces and edges with specific crystalline structure of HA, surrounded by "hallow" of fine particles, which we consider as ZrO_2 microparticles, for which the temperature of 1050 °C applied during the heat treatment was not sufficiently to affecting the zirconium oxide structure and transform in a crystalline structure (*figure 6 b*). HA-ZnO system at low temperatures prevail spherical, and by heat treatment at higher temperatures prevail elongated shape (*figure 7 a*) with an average grain size below 50 nm. HA-SiO_2 system (*figure 7 b*) revealed that agglomerations are more and an average particle size is between 0.02 to 0.04 mm. Using smaller particles creates the possibility of minimizing the space between particles as is and remove them from abrasion.

II.2. SYNTHESIS AND CHARACTERIZATION OF ORGANIC PHASE USED IN THE FORMULATION OF COMPOSITE MATERIALS AND ADHESIVE SYSTEMS USED IN DENTISTRY

In agreement with literature data, the approach of monomers with adhesive properties and specific applications in areas covered are based on the elucidation of their mechanisms of action compared with other ingredients commonly used in dental formulations, which implies knowledge structure correlations structure - properties - biobehavior. There are two main orientations regarding correlation of adhesive properties with chemical structure:

- correlations based on the work of independent contributions of carboxyl or phosphate functions grouped around the photopolymerizable acrylic structure;
- correlation of adhesive action with physico-chemical and biological parameters defined in the formulation of dental materials with variable composition.

II.2.1. Synthesis of urethane dimethacrilates with carboxyl groups of oligomer type

Range of acrylic monomers with urethane structure and affinity to dentin have synthesized a number of 3 dimethacrylates with carboxyl groups introduced through bifunctional specific derivates, able to participate in polyaddition reactions. An extension of research on urethane oligomers is expected to provide a plurality of properties generated by the existing chain functions: sequence hydrophilic and biocompatible introduced by polyethylene glycol (PEG), urethane groups related to peptide structure introduced by an aliphatic diisocyanate, or adhesive carboxyl groups.

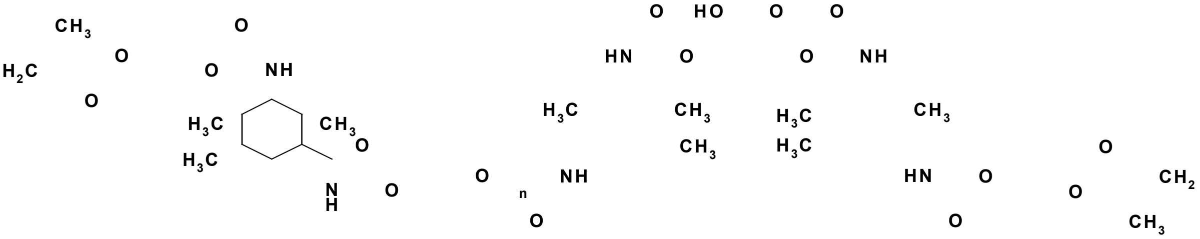


Figure 8. Urethane dimethacrylate with carboxyl groups of oligomer type AdO-1

II.2.3. Synthesis of acid monomer with phosphate groups

Starting from the concept of directed modification of the resins properties, was taken in study the esterification reaction of HEMA with polyphosphoric acid (PA) to establish appropriate conditions that lead to unsaturated ester by phosphate type, avoiding unwanted complications related to polymerization of acrylic function.

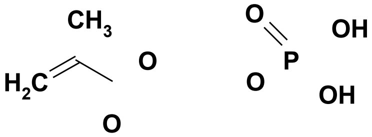


Figure 9. Acid monomer with phosphate groups Ad-P1

I.2.5. Synthesis of (Bis-GMA)$_{0-2}$ superior olygomers

Polymer matrix although it varies depending on the composite it is represented mainly by diacrylates. One of the first polymer proposed as restoration material in the treatment of cavities is obtained from 2,2-bis(3-(2'-hydroxy-3'methacryloyl-oxypropoxy)phenyl)propane (Bis-GMA). With the development of composite biomaterials, it's trying to improve the Bis-GMA characteristics by obtaining of monomers with lower viscosity by converting secondary hydroxyl groups of Bis-GMA in metacryloxy groups. Bis-GMA used with other compounds included in dental adhesives or in composites leads to the desired physical properties, but they show considerable shrinkage and poor adhesion to the tooth. In this study we synthesized 2,2-bis[p-(2'-hydroxy-3'-metacyiloxypropoxy)phenil]-propane (Bis-GMA$_{0-2}$). This product we characterized by IR spectroscopy and high performance liquid cromatography (HPLC).

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Figure 10. Bis-GMA$_{0-2}$onomer

II.3. FORMULATION OF COMPOSITE MATARIALS AND DENTAL ADHESIVES USED IN DENTISTRY

To approach the studies by determining the physico-chemical properties and biocompatibility of composite materials and adhesive systems for dentistry, I realized these materials in the form of photopolymeryzable paste based on organic ingredients and silanizate hybrid inorganic fillers consisting of radioopaque barium glass (S1), strontium glass (S2), quartz, colloidal silica, nanoparticles $La_2Zr_2O_7$ (N1), HA (N2), HA-ZnO (N3), HA-ZrO_2 (N4) and HA-SiO_2 (N5). I prepared 15 composite with photochemical initiation and 14 adhesive systems in three, two and one step of application.

II.4.1. Determination of water absorption and water solubility of dental composites and adhesives (according to ISO 4049)

Water absorption represent the total amount of water uptaken by a material immersed in water and determines the increasing of the material's volume of due to water uptake in the polymer matrix of the composite / adhesive [204]. It is expressed through the decrease of the cylinder epruvettes after 1, 7 and 28 days of immersion in distilled water and artificial saliva at 37 °C. It was shown that, in a certain way the water uptake is positive, equilibrating the polymerisation shrinkage and reducing that way the marginal percolation [206]. An increased of water uptake leads to weaker bonds inside the polymer matrix leading to the separation of the filler from the polymer matrix, hydrolytically degrading the filler, finally leading to the decrease of the mechanic resistance and of the weare resistance of the obtuorations.

The value of the water and artificial saliva absorption can be estimated as follows:

$$\mathbf{W_{sp} = (m_2 - m_3)/V}$$

unde: $\mathbf{m_2}$ – the mass of the sample following the 24 hours,7 days and 28 days immersion (in μg)
$\mathbf{m_3}$ – the mass of the reconditioned sample (in μg)
V – the sample's volume (în mm^3)

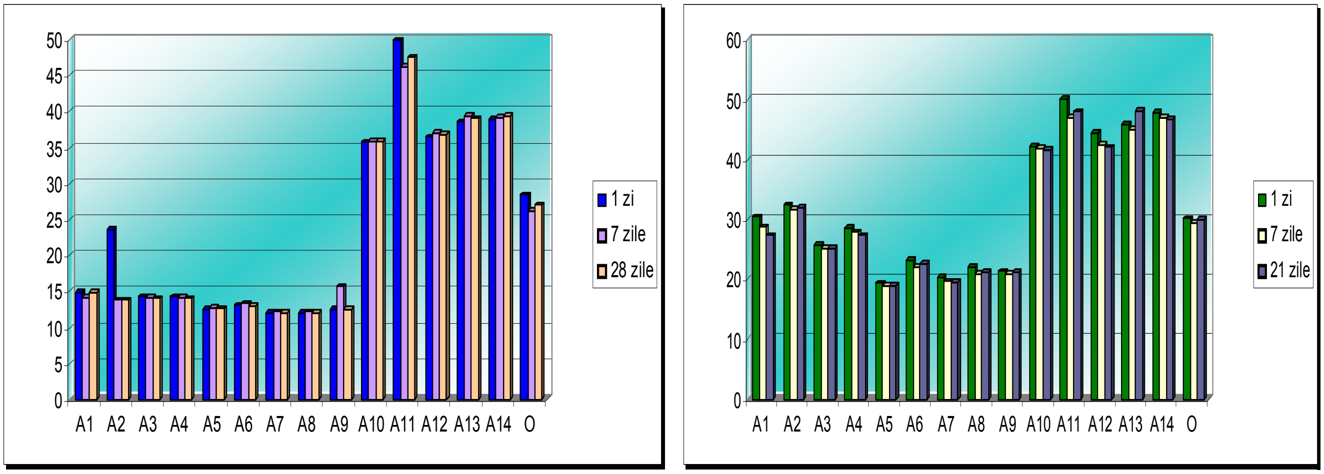


Figure 11. Values for water absorption in water and artificial saliva of investigated adhesive systems

Samples immersed in artificial saliva showed higher values of absorption and solubility compared to those kept in water. The lowest values were recorded for two-step adhesive systems application (A5, A7, A8, A9), compared with a single step application (A11, A13, A14) have the highest values of water absorption.

II.4.2. Hydrolytic degradation of composite materials

Hydrolytic degradation of experimental composite materials based on urethane monomers / oligomers was studied after 33 days of immersion in water, artificial saliva and 50 % alcohol solution (ethilic alcohol) and was investigated by FTIR spectroscopy. Sample size is 15 mm diameter and 1mm thickness.

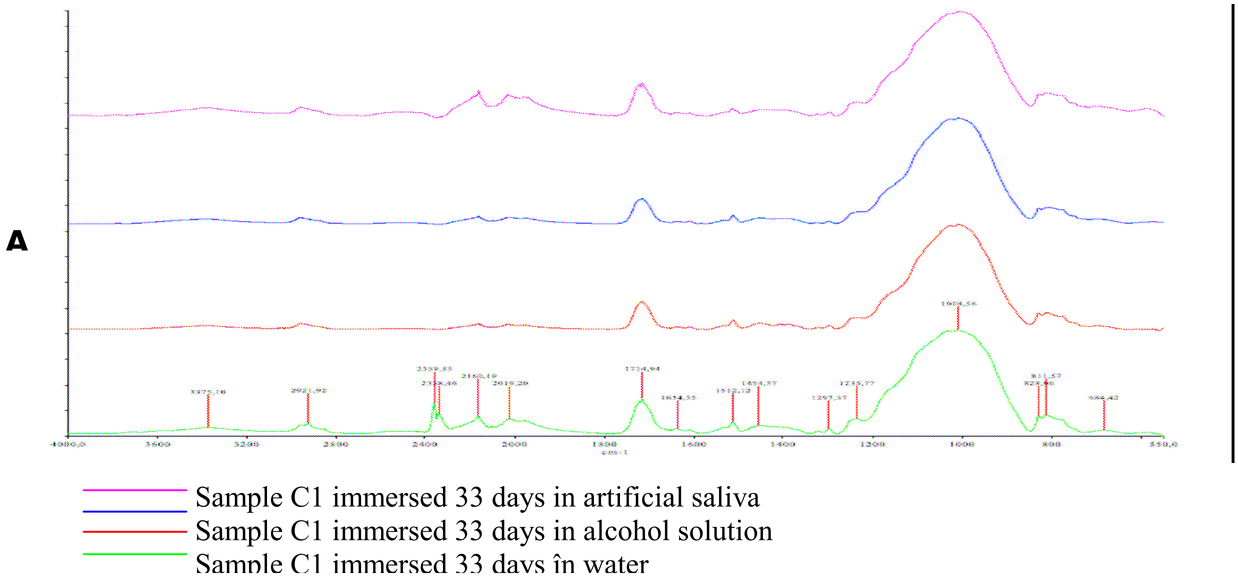


Figure 12. FT-IR spectra of the C1 composite

In all spectra we observe bands at 1608 cm^{-1} due to stretching vibrations $\nu(C{=}C)_{as}$ aliphatic, at 1583 cm^{-1} due to stretching vibrations $\nu(C = C)_s$ aliphatic and 1508 cm^{-1} correspond to valence vibrations $\nu(C{=}C)$ of benzene rings disubstituite. It highlights the characteristic bands for Si-O-Si and Si-O-CH_2 bonds in the 1190 -1140 cm^{-1} domain. We also have the band at 2160 cm^{-1} in all spectra and we have assigned to a stretching vibration of Si-H functional group and the band at 825 cm^{-1} is attributed to deformation vibration of the same functional group, that confirm once again the presence of Si-H bond. Increase in band intensity at 2160 cm^{-1} for C1 composite immersed in artificial saliva can also assign the formation of strong hydrogen bridges caused by a larger number of OH groups from saliva by composition (carbohydrates, proteins, glycoprotein's) compared with the number of OH groups from water, respectively alcohol solution.

II.4.3. Investigating resistance to wear by abrasion of composite materials

Abrasive wear of composite materials is the loss of material removal and adjustment due to contact with one or more materials. When two solid materials are in contact, they touch the highest peaks of their rough.

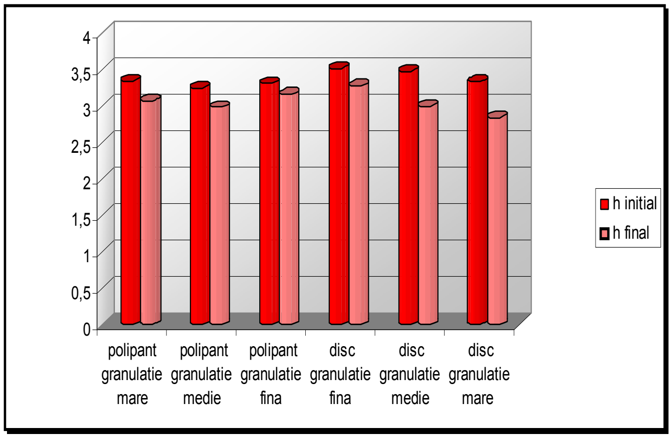


Figure 13. Graphic representation of C1 light cured with Optilux lamp, after treatment with different disks

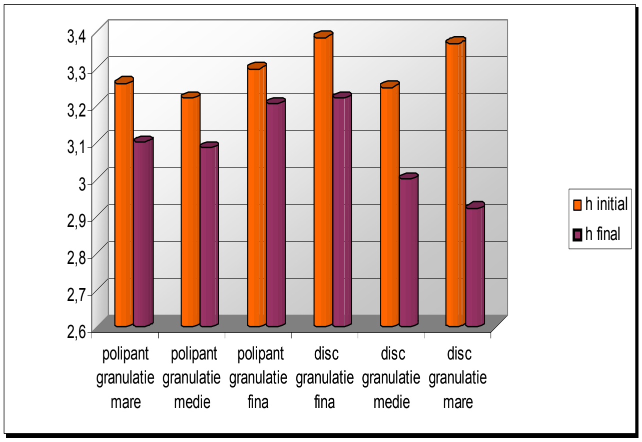


Figure 14. Graphic representation of C1 light cured with *LED Bluephase G2 lamp,* after treatment with different disks

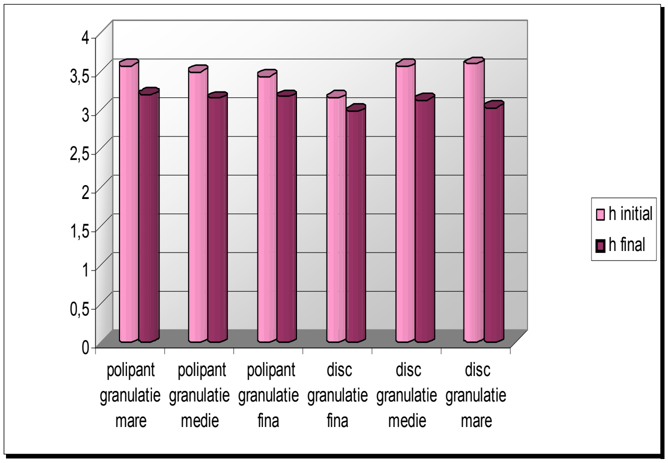


Figure 13. Graphic representation of C6 light cured with Optilux lamp, after treatment with different disks

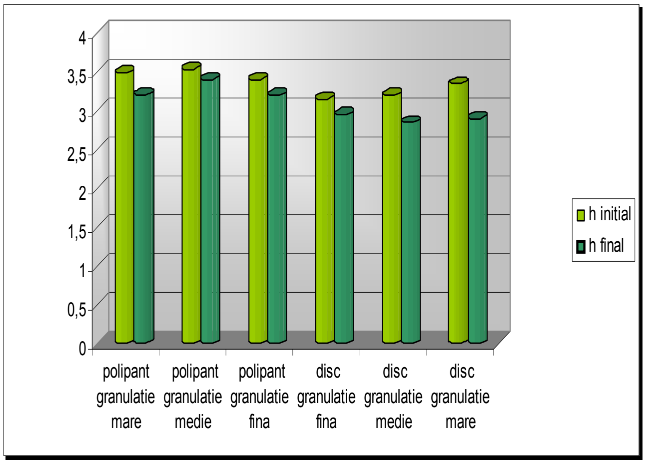


Figure 14. Graphic representation of C6 light cured with *LED Bluephase G2 lamp,* after treatment with different disks

In the study to determine the wear materials were chosen 4 composite with different inorganic composition in filling degree between 75-80 % and we used different wear discs. Wear differences between the composites investigated are not large, indicating that slight variation in filler particle size and chemical composition differences of the fillers does not affect in vitro wear of these composite materials. There was a reduction in the height of samples, after polishing with six discs. Minimum mass loss was observed in C6 composite polymerized with two lamps (Optilux 501 and Bluephase G2) and finished with fine granulation polypanth. All composites tested showed similar degrees of wear after polymerization with Optilux 501.

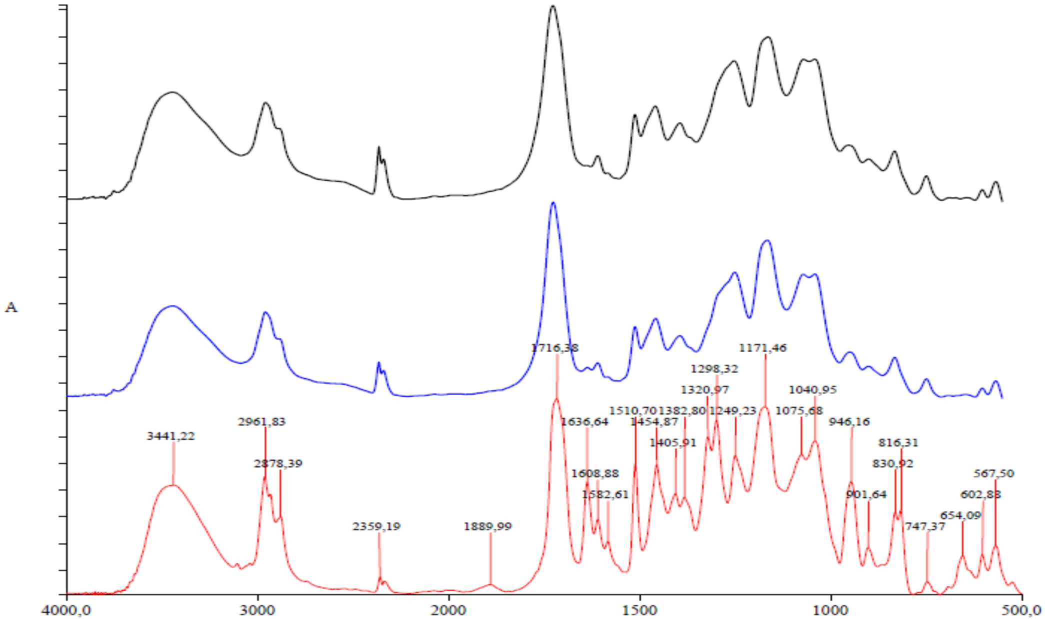
II.4.5. Determination of residual double bonds and degree of conversion of adhesives

To determine the residual double bonds of the adhesive systems we used a FTIR spectroscope Spectrum BX2. We used pellet method in potassium bromide (for polymerized adhesive) and between potassium bromide windows (for un-polymerized adhesive).

For adhesives having internal standard, the percentage of unreacted aliphatic C=C bonds remaining throughout the polymerization reaction is obtained by the equation:

$$(\% \, C{=}C) = \frac{[\text{Abs (aliphatic) /Abs (aromatic)}]\text{polymer}}{[\text{Abs (aliphatic) / Abs (aromatic)}]\text{monomer}} \times 100$$

where: Abs – area of absorption band
C=C aliphatic band peak at 1635 cm^{-1}
C=C aromatic band peak at1610 cm^{-1}
DC is determined by subtracting the residual percentage of aliphatic C=C from 100% (*DC%*=100-(*%C=C*)).



A8 II polymer
A8 I polymer
A8 monomer

Figura 17. FT- IR spectrum for A8 adhesive

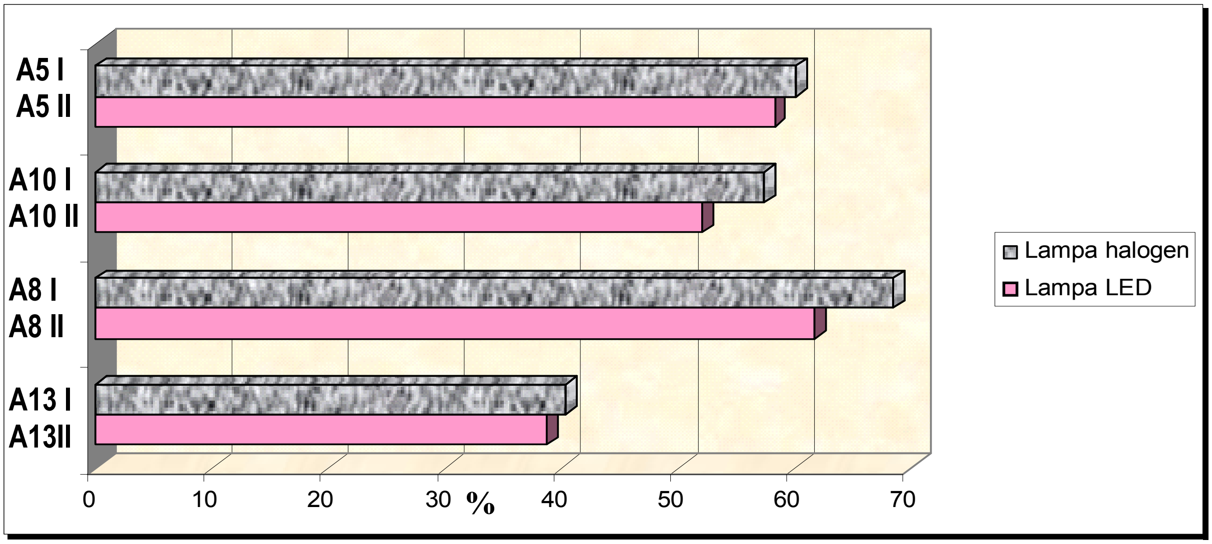


Figura 18.Graphyc representation of residual double bonds values of experimental adhesives

The results obtained reveald a small percentage of residual double bonds and a high conversion of 61.37 % for experimental adhesive A5 in two steps of application based on urethane monomer AdO-1 and light cured with LED dental lamp, respectively 59.69 % for the same adhesive light cured with Optilux lamp. Close values were obtained for A8 adhesive in two steps of application, in whose composition is present only Bis-GMA monomer, namely 47.92 % (LED lamp) and 42.64 % (Optilux lamp). Lower values were obtained for adhesives in a single step of application A10 and A13, values between 31.59 - 41.7 6%.

II.4.6. Adhesion testing of composites and adhesives to shear bond strength

Strength of composite restorations in the oral cavity depends not only on their physical properties, but also the ability to have a good adhesion to dental hard tissues. The adhesion depends on properties of adhesive used, the ability to achieve strong adhesive bonding between the composite material and dental hard tissues. Also, the adhesion strength of composites to dental hard tissues depends on the physical properties of adhesives used.

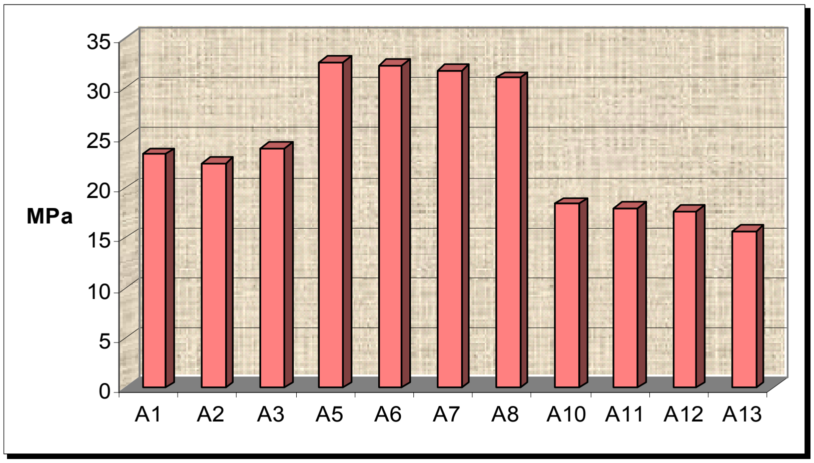


Figure 19. Adhesion values obtained for experimental adhesives

Values obtained are relevant for this type of testing, and the best value was obtained for adhesive A5. Adhesions testing of the experimental materials to dentin by shear forces were used C6 experimental composite in which composition are urethane monomer AdO-1 and experimental adhesives. Best values were obtained for adhesive A6, A7, A8, and the lowest value was obtained for adhesive A13.

II.4.7. Investigation by electron microscopy of the hybrid layer formation

Base adhesive connection formed between composite resin and dentin is forming a hybrid layer. It is formed by penetration of resin monomers into demineralized collagen network, and their polymerization" in situ". This forms a micromechanic bond between the composite resin and dentin adhesives in the case of average autoengrave even formed a chemical bond [226]. In this study we evaluate the hybrid layer formed by scanning electron microscopy examination. We used five adhesives with experimental composite materials and selected based on appearance and physical-chemical properties obtained.

Group.	**No. teeth**	**Composite**	**Adhesive system**
1	4	C1	Adhesive system in 3 steps (A3)
2	4	C4	Adhesive system in 2 steps (A7)
3	4	C6	Adhesive system in 2 steps (A5)
4	4	C6	Adhesive system in 1 step (A10)
5	4	Restacril	Adhesive system in 1 step (A12)

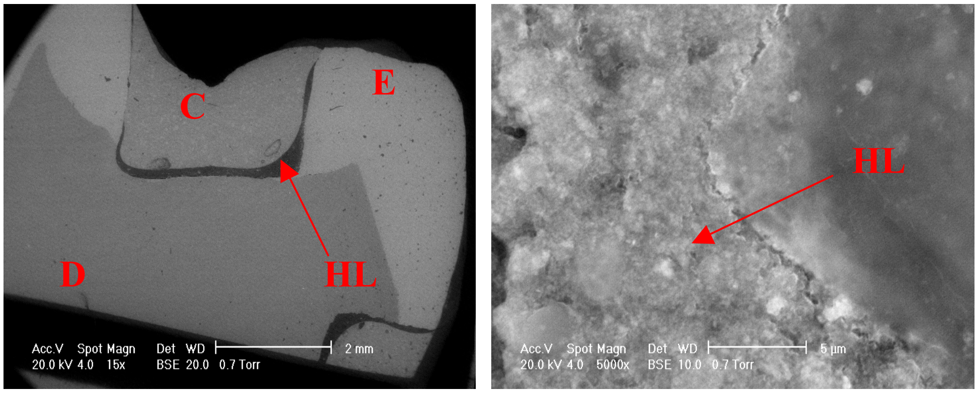


Figure 20. SEM images of a sectioned tooth and emphasizing the hybrid layer formation

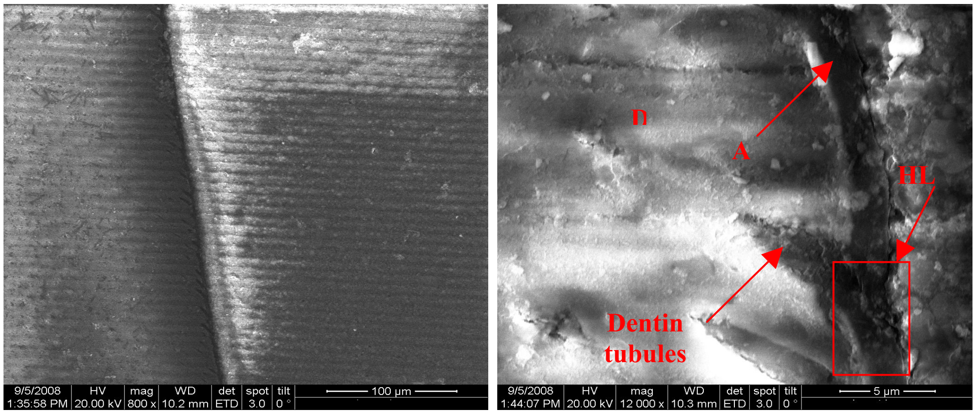


Figure 21. Restoration with C6 composite and A5 adhesive C6 light cured with LED lamp
HL- hybrid layer, A- adhesive, D-dentin

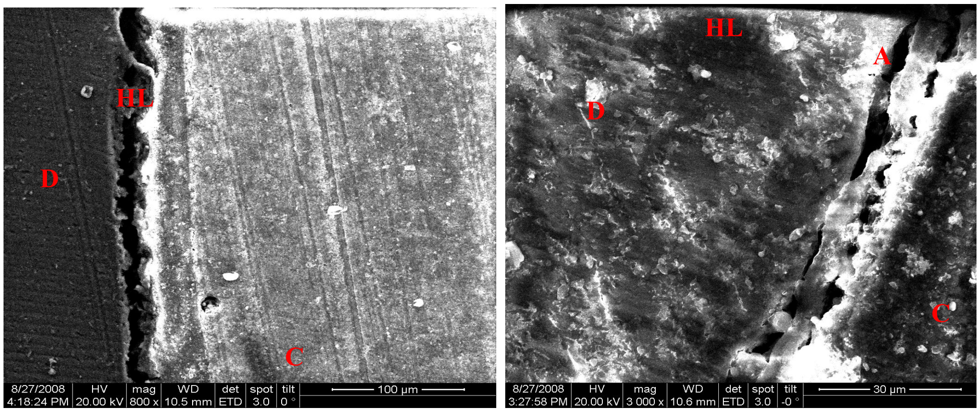


Figure 22. Restoration with Restacril composite and A12 adhesive
HL- hybrid layer, C-Composite, D-dentin

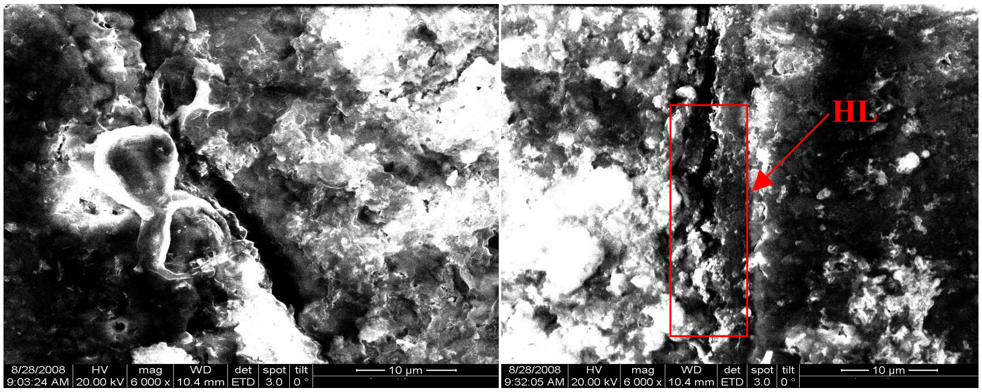


Figure 23. Restoration with C6 composite and A10 adhesive
HL- hybrid layer

On microscopy images was observed that the adhesive film has a thickness of less than 10 microns, making it possible to use adhesive in indirect restorations. It was noted also the high degree of homogeneity of nanoadeziv polymerized layer (figure 20, fFigure 21, figure 22). Formation of a homogeneous hybrid layer means closure of any ways of communication between the pulp board and outer, thus realizing a wound sealing dentin.

II.4.8. Evaluation of marginal microinfiltration adhesive materials

This study wants to evaluate the marginal microinfiltration at the enamel and cement level in class II cavities using four experimental adhesive systems with inorganic filler based on hydroxyapatite and HA-SiO_2.

Microinfiltration marginal rating was made for both cervical limit cavities in enamel and cement, using an ordinary scale (0-3) recorded the maximum score of 6 results for each tooth. Comparing the results for microinfiltration in enamel with those obtained in cement, we found for groups I and II statistically significantly better values in enamel than in cement.

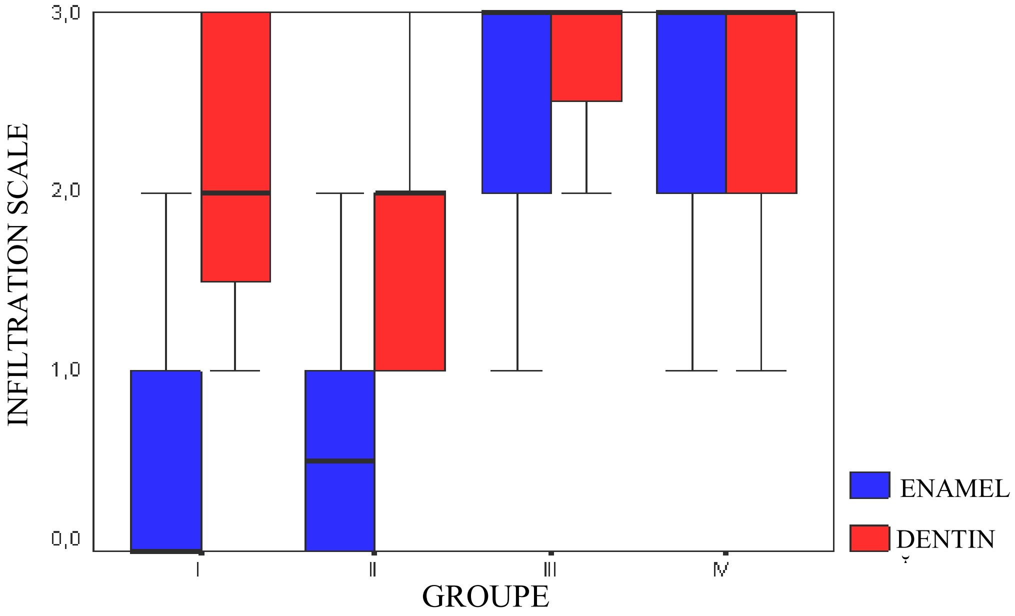


Figure 24. Graphical representation of the results for marginal microinfiltrations

Adhesive systems in three steps, involving etching and washing are a statistically significant difference in the tightness of the closure of marginal enamel against cement. Etching and washing systems offer better marginal sealing at the enamel to autoengraven systems. At the cement level all the adhesive systems with ethanol solvent have similar performance. The presence of water as a solvent in the primer, along with ethanol significantly enhances the adhesion to the wet cement substrate, even if it is an adhesive system in three steps.

CONCLUSIONS

1. Research and application of a new class of materials used to restore dental anatomy, based on acrylic / methacrylic polymer structures combined with inorganic fillers are characterized by a set of favorable properties. Composite materials and adhesive dynamics have known a rapid development over time.

2. Literature study was focused on issues concerning the development of composite and adhesive materials used in dentistry with multiple functionalities.

3. One of the objectives in the study was to obtain the multifunctional monomers with compositional variety, structural homogeneity, which form high polymers reticulate, resistant, rigid, durable and an reduced polymerization shrinkage.

4. It revealed new trends exist in the field of dental materials, the inorganic fillers used namely decreasing particle size while increasing the degree of including it in the composite mixture and use of nanoscale fillers.

5. Known the importance of compatibility at the interfaces, to inorganic fillers - polymer matrix bond, in obtaining composites with adequate properties, the paper presents the current mode of making such connections through silane coupling agents.

6. Studies made in this thesis focused on four main directions, aimed at finally getting new dental composites and new next generation dentin adhesives with improved properties.
Thus, the main directions that research was directed are:

- synthesis of micro and nano-sized powders to be used as fillers in new composites and adhesive systems.
  We made 6 glasses vitroase having in their composition biocompatible chemical compounds which were set parameters of synthesis in our laboratory and ***5*** new biocompatible nanofillers of: ***$La_2Zr_2O_7$, hydroxyapatite (HA)*** and 3 types of nanofillers based on HA and different oxides: ***HA-ZnO; HA-ZrO_2; HA-SiO_2***.
- synthesis of urethane-dimethacrylate monomers with carboxyl groups and phosphate, with superior properties regarding the adhesion of dentin tissues;
- formulation of a new ***15 experimental composite*** and ***14 experimental adhesive systems*** from the last generation used in dentistry;
- characterization of fillers, monomers, composites and adhesives using modern methods and multiple physical and chemical analysis.

7. Inorganic fillers obtained were characterized by: BET specific surface, size distribution of particle size, density, electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction and IR spectroscopy. All nanofillers were characterized before and after heat treatment applied.

8. The glass powder specific surface and those of mixed oxide has values between 2.56 m^2/g and 71.33 m^2/g and density values fillers range from 2.15 to 2.90 g/cm^2. Granulometric composition of investigated materials varies in a a wide range depending on technological parameters.

9. Peaks positions by X-ray diffraction are attributed oxidic compounds formed. Dimensions of crystallites estimated from X-ray diffraction bands are approximately 20-30 nm. For both S1 and S2 glass analyzed $I_{2\theta}$ scattering curves gives a typical amorphous structure, variable intensity, indicating the presence of local ordering. The diffraction spectrum of synthesized nanofiller, the main systems compound is hydroxyapatite (HA), but there is also a major component of apatite (Ap).Content of β-TCP phase, which is unstable and very bioresorbable in human bodies, was identified for HA and other HA-oxide powders. Increase temperature to 80 °C had a positive effect on the disappearance of impure phase.

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10. IR spectral analysis of glass fillers silanizated and unsilanizated indicates the appearance of intense absorption maximum in 1017 - 1048 cm^{-1} domain, corresponding bond vibrations $\nu_{(Si\text{-}O\text{-}Si).}$ Absorption at 792, 754, 540 cm^{-1} due to bond vibrations $\nu_{(Si\text{-}O\text{-}Al)}$, while those in the field of 453 - 464 cm^{-1} are attributed to bond vibrations $\nu_{(M\text{-}O)}$.

11. Compatibility between organic and inorganic phase was achieved by deposing on the fillers surface a silane coupling agent. The presence and bonding of silane was highlighted by a study compared FT-IR spectrophotometer on filler unsilanizated and silanizated. The absorption bands characteristic silane, presented in the IR spectrum, confirms that silane is deposited on the filler and is chemically bonded.

12. IR spectra of the fillers included in KBr pellets, recorded in 400 - 4000 cm^{-1} domain revealed characteristic bands of hydroxyapatite. Sharp and less intense bands at 632 cm^{-1}, 605 cm^{-1}, 570 cm^{-1} attribute to the deformation bond vibration $\delta_{(P\text{-}O\text{-}P)}$ from PO_4^{3-} ion.. In general, metal oxides containing groups M=O vibration band are between 1100 - 825 cm^{-1}.

13. By transmission electron microscopy image in bright field (TEMBF) presents a set of micro and nanaoparticles of hydroxyapatite, zirconium oxide, zinc oxide and silicon oxide and shows nanostructured particles of CaO and 0.1 – 0.3 mm large particles of hydroxyapatite.

14. Electron transmission microscopy image in high resolution (HRTEM) highlight the crystallized nanoparticles with diameters in the 1-3 nm. Spectrum in the energy dispersive X-ray (EDAX), associated with the selected microregion, shows the presence in the sample of Ca, P, Zn and O.

15. SEM images for S1 and S2 glasses reveal amorphous mass, relatively homogeneous irregularly shaped particles with rounded corners, with the majority of particle size greater than 1 micron. The S2 glass particles have sizes predominantly higher than those of glass S1 explained by the fact that S2 glass hardness is higher than S1.

16. In the case of nanofillers were revealed agglomeration of particles and can see the influence of heat treatment on the powders obtained, and increasing temperatures lead to formation of larger crystals of different shapes. The structural characteristics of HA and HA-oxides were affected by the precursor synthesis, pH, reaction temperature and heat treatment process including aging fillers.

17. Range of acrylic monomers with urethane structure and affinity to dentin have synthesized a number of dymethacrylates with carboxyl groups AdO-1, AdO-2, and AdP-1, introduced by difunctional specific derivates, able to participate in polyaddition reactions.

18. Structural purity of synthesized monomers and oligomers was highlighted by spectral methods: IR spectroscopy and nuclear magnetic resonance (^{1}H-RMN) and high performance liquid chromatography (HPLC).

19. FTIR spectra of urethane dimethacrylate AdO-1 shows specific absorption bands at 3350 cm^{-1} ($\nu_{(N\text{-}H)}$ uretane), 2850 - 2950 cm^{-1} ($\nu_{(-CH2)}$ and 1720 cm^{-1} vibration of carbonyl group valence ($\nu_{(C=O)}$) of structure of urethane and ester and acid groups. Cetonic unsaturated group C=O appears at 1630 cm^{-1}, amide II - (($\delta_{(NH)}$) to 1540 cm^{-1} and C-O-C at 1100 - 1250 cm^{-1}. Following integrals unsaturated protons, the protons from PEG and the protons of 1,3,3-trimethylciclohexan (izoforon) could appreciate correct the AdO-1 urethane dimethacrylate structure.

20. Starting from the concept of directed modification of the resins properties, was taken in study the esterification reaction of HEMA with polyphosphoric acid (PA) to establish appropriate conditions that lead to unsaturated ester by phosphate type, avoiding unwanted complications related to polymerization of acrylic function.Thus was obtained methacryloyloxyethyl phosphate AdP-1.

21. AdP-1 was characterized by FTIR and ^{1}H-RMN spectrometry. In the IR spectrum of AdP-1, were observed specific absorption bands of carbonyl group (1705 cm^{-1}) and unsaturated group (1640 cm^{-1}). Other absorption bands defining formation of unsaturated ester are those appearing at 1200 cm^{-1} and 1025 cm^{-1}which is due to bond vibrations ties P=O şi P-O-CH_2-. The NMR spectrum of AdP-1 is observed peaks assigned to protons from hydroxyl groups of phosphoric ester at 7.88 ppm, unsaturated protons trans / cis at 6.02 and 5.62 ppm, methylene protons of ester group at 4.29 ppm, methylene protons of phosphonate group at 4.1 ppm, methyl protons at 1.83, similary to the proposed structure.

22. In order to obtain composite materials and adhesives, has achieved the synthesis of Bis-GMA superior oligomers. The $(\text{Bis-GMA})_{0\text{-}2}$, superior oligomers was synthesized by reaction of an epoxy resin with low molecular weight, composed of 84 % monomer (diglycidyl ether bisphenol A), 1% 15 % dimer and trimer (molar %) and methacrylic acid in the presence of an alkaline catalyst. In this synthesis, we studied the influence of the nature and amount of catalyst, reaction temperature, and reaction time and the nature and amount of inhibition of conversion of methacrylic acid.

23. Reaction product $(\text{Bis-GMA})_{0\text{-}2}$, was analyzed by IR spectroscopy and High Performance Liquid Chromatography. IR spectroscopy demonstrated the total transformation of epoxy resin oligomers by disappearance of bands at 770 cm^{-1} and 916 cm^{-1} respectively corresponding deformation vibration of ring epoxy group from terminal positions.

24. Separation of three oligomers $\text{Bis-GMA}_{0\text{-}2}$, was realized by reversed phase HPLC with gradient elution. The calculation of mixture of oligomers composition on the basis of chromatography, demonstrated the total transformation of each oligomers RE_n(n = 0, 1 ,2) in a oligomers $(\text{Bis-GMA})_{0\text{-}2}$. Normal phase HPLC technique with gradient elution was highlighted isomers of iso-Bis-GMA type in each hand.

25. An organic component was prepared (L1 and L2) of composite biomaterials based on monomers / oligomers synthesized, of Bis-GMA and TEGDMA. To initiate the photochemical polymerisation was introduced into the mixture of monomers an initiate polymerization system consisting of: photochemical initiation – camphorquinone (CQ), polymerization acceleration - dimethylaminoethyl methacrylate (DMAEM) and polymerization inhibitor 2,6-ditertbutyl-4-methylphenol (BHT).

26. In order to determine the properties of composite materials we formulated 15 composite with photochemical initiation in monopaste system consisting of liquid organic component and hybrid inorganic fillers silanizated consisting of radiopaque barium and strontium glasses, colloidal silica, nanofillers and quartz.

27. Properties and performance of dental composites are determined by three basic components of the composite material: the resin matrix, inorganic filler and coupling agent. In the adhesive systems an important characteristic is their adherence to dental hard tissues to achieve a lasting restoration. Laboratory testing of composite materials and adhesive properties is an essential step before their clinical use.

28. Studies of water absorption and solubility were made according to ISO 4049. Largest amount of water absorbed by the composites increase in the first seven days, after which it drops to 28 days, when we made the last determination. Noteworthy is the fact that composites C1 and C6 have low water absorption, and therefore will have greater stability over time. Water absorption values are higher in case of composite materials (C8 and C12) which have in composition Ad-O1 monomer.

29. Solubility of investigated composites have values between 0.14 to 0.64 $\mu g/mm^3$, values measured after seven days storage in water of the samples. These values increase after 28 days, falling within the range 0.1 to 0.87 $\mu g/mm^3$. The best values are recorded for composites C3, C6, C13 and Restacril.

30. The results reveald that samples kept in artificial saliva present higher values of absorption and solubility comparedwith those kept in water. The presence of hydroxyl and carboxyl groups in the monomers structure lead to the adhesive systems more hydrophilic and more predisposed to absorb a higher amount of water. Values lower of water absorption were recorded for A4 and A5 adhesives stoked in artificial saliva which have in composition AdO-1 and AdO-2 monomers and hydroxyapatite. The best values were recorded for A5, A6, A7 and A8 adhesive systems in two steps.

31. Hydrolytic degradation of C1, C6, C13 and C14 experimental composite materials based on urethane monomers / oligomers was studied after 33 days of immersion in water, artificial saliva and 50 % alcohol solution (ethilic alcohol) and was investigated by FTIR spectroscopy. In all spectra we observe bands at 1608 cm^{-1} due to stretching vibrations $\nu(C{=}C)_{as}$ aliphatic, at 1583 cm^{-1} due to stretching vibrations $\nu(C = C)_s$ aliphatic and 1508 cm^{-1} correspond to valence vibrations $\nu(C{=}C)$ of benzene rings disubstituite. It highlights the characteristic bands for Si-O-Si and Si-O-CH_2 bonds in the 1190 -1140 cm^{-1} domain.

32. FT-IR spectra recorded on samples made of the composites immersed in water, artificial saliva and alcohol solution, revealed in the majority of them the reduce of intensity of bond characteristic peaks Si-O-Si, less for the composite C6immersed in artificial saliva at the peak intensity remains unchanged.

33. In the study to determine the wear materials were chosen 4 composite with different inorganic composition in filling degree between 75-80 % and we used different wear discs. Wear differences between the composites investigated are not large, indicating that slight variation in filler particle size and chemical composition differences of the fillers does not affect in vitro wear of these composite materials. There was a reduction in the height of samples, after polishing with six discs. Minimum mass loss was observed in C6 composite polymerized with two lamps (Optilux 501 and Bluephase G2) and finished with fine granulation polypanth. All composites tested showed similar degrees of wear after polymerization with Optilux 501.

34. We prepared 14 dentin adhesives with nanofillers in three, two and one step application. We determined the pH, viscosity and surrounding light sensitivity of the 14 experimental materials.

35. Were determined residual doubles by IR spectroscopy for four of the 14 experimental adhesive systems and cured for 10 seconds with two different dental lamp (LED lamp Bluephase G2 and Optilux 501). The results obtained reveald a small percentage of residual double bonds and a high conversion of 61.37 % for experimental adhesive A5 in two steps of application based on urethane monomer AdO-1 and light cured with LED dental lamp, respectively 59.69 % for the same adhesive light cured with Optilux lamp.

36. Adhesion to dentin was tested using 11 systems with an experimentally composite C6 by resistance to shear bond strength. Values obtained are relevant for this type of testing, and the best value was obtained for adhesive A5.

37. SEM images obtained from dental hard tissue - experimental composites interface using experimental adhesives, revealed a good infiltration of adhesives in dental tubules. On microscopy images was observed that the adhesive film has a thickness of less than 10 microns, making it possible to use adhesive in indirect restorations. It was noted also the high degree of homogeneity of nanoadhesive polymerized layer.

38. The study of evaluatio to the marginal microinfiltration at the enamel and cement level in class II cavities used four experimental adhesive systems with inorganic filler based on hydroxyapatite and HA-SiO_2. Adhesive systems in three steps, involving etching and washing are a statistically significant difference in the tightness of the closure of marginal enamel against cement. Etching and washing systems offer better marginal sealing at the enamel to adhesive systems in two steps.

39. In vitro test results of physico-chemical and mechanical properties of composites and adhesives experimented led to the selection of hybrid composites C1, C6, C13, C14 and adhesives that A5, A8, A10, A13 for clinical testing. Adhesives with the best behavior in vitro are adhesives formulated for application in two and three steps.

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