Studies Regarding the Architectural Design of Various Composites and Nanofibres Used in Dental Medicine

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The aim of this study was represented by the definition and testing of a new formulation strategy and the functionality of composite materials, while ensuring the optimization of the relevant properties for the dental restoration processes through the use of precise techniques of characterization, the modification and functionality of the components in view of obtaining results that are characterized by an optimum biomechanical and bioactive relation, in full agreement with the particularities of the dental structure that requires restoration. In view of obtaining new resistant composite structures we made a number of 10 samples including extracted teeth with various losses of dental substance and the structural modifications included 3 types of composites, whose structure was improved by the introduction of inorganic fillings based on hydroxyapatite and silver nanoparticles. All these structures were reinforced with two types of fibers, Reforpost fiber glass kit (Angelus) and Fiber post Schulzer Pre-silanized; With regard to the use of composite structures improved by HA addition, we notice a slight lacunary structure on the SEM images due to the properties of HA, an aspect present at much smaller dimensions in the silver – HA mix. The size of the grains associated with their continuous uniformity and adherence for the fibrillar structure stands out at the samples with hydroxyapatite, the first place as uniformity and adherence going to the composite of the nanofiller technology category.

Key words: composite structures, hydroxyapatite . silver nanoparticles, nanofiller technology, fibers

In the contemporary dental medicine, reconstructive techniques hold a special territory, the most used materials being the composite materials, due to certain advantageous properties with a deep clinical impact, which include, among others, superior mechanical properties (stress resistance, resistance to impact and erosion, proper elasticity), thermal conductivity, water retention and reduced expansion coefficient, adherence, esthetic look, texture and surface properties that are adequate for the dental structure [1,2].

The remarkable evolution of the improvement of these systems, on the one hand through the optimization of the polymerization processes and superior adaptation to the requirements of restorative dental medicine, diversifying the various formulas of the inorganic filling, the large range of experimental design techniques and processing of composite materials have led to the elaboration of specific preparation, processing, analysis, optimization and application procedures for these materials [3,4].

In agreement with all these evolutionary aspects of the structure of reconstructive biomaterials, the diversity of clinical cases, the localization of dental substance losses that require reconstruction, the various archetypes of static and dynamic occlusion are very important premises that stand at the basis of elaborating new structural and functional characteristics, materializing into new complex research directions in the whole world, in view of obtaining the ideal biomaterials, individualized to the variety of clinical situations [5-7].

The various solutions aim at optimizing the applicative performance that are characteristic to dental composite, which require a thorough analysis of each structural component (polymerizable resin, filling, additives) of the interfaces made both between them and with the surrounding biological tissue, as well as of the potential interactions with the biological environment of insertion (local and systemic) as well as with a series of external factors[8,9]. The use of various reinforcing structures, based on fiber glass, constitutes feasible ways to increase the resistance of the various types of dental reconstructions [10,11].

Experimental part

The purpose of this study was represented by the definition and testing of a new formulation strategy and the functionality of composite materials, while ensuring the optimization of the relevant properties for the dental restoration processes through the use of precise techniques of characterization, the modification and functionality of the components and, in particular, of the inorganic filling, in view of obtaining results that are characterized by an optimum biomechanical and bioactive relation, in full agreement with the particularities of the dental structure that requires restoration. We thus aimed at making relevant contributions in the research directions for efficient solutions to formulate and apply restorative dental materials.

In view of obtaining new resistant composite structures we made a number of 10 samples including extracted

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teeth with various losses of dental substance and the structural modifications included 3 types of composites, whose structure was improved by the introduction of inorganic fillings based on hydroxyapatite and silver nanoparticles. All these structures were reinforced with two types of fibers, Reforpost fiber glass kit *(Angelus)* and Fiber post Schulzer Pre-silanized.The 3 types of composite materials were represented by: Nanocomposite (Gaenial Anterior)-GC,Nanocomposite Evetric-Ivoclar and Nanofiller Technology (Olirevo).

The working protocol was the same, in a first stage the cavities of extracted teeth were prepared, followed by the creation of the radicular lodges by means of specific drills in agreement with the diameter of the fiber glass used. At a later stage, demineralization with orthophosphoric acid was used for 1 minute, followed by the removal of the acid, the application of the universal adhesive, polymerized for 20s, and then the composite materials, in their initial form, as well as the new improved formulas by adding basic fillings of hydroxyapatite and silver, the latter being known for its antiseptic properties. In a first stage we selected for testing inorganic fillings of glass nanofibers, silica and HA whose compatibility in dental applications is well-known.Hydroxyapatite (HA) based nanocomposite fillings modified with silver nanoparticles (AgNP) in the presence of sodium lignosulphonate (NaLS) were obtained after the following protocol: suspended HA powder under energic shaking in deionized water is mixed with a watery solution of NaLS (2%), temperature is raised to 70^{0}C and $AgNO_3$ (0.1M) is added as drops (mass report HA: NaLS: $AgNO_3$ = 100: 40: 3.4). *p*H is maintained at 6-6.5 by means of a NaOH (0.1M) solution. After 2 h of reaction, the colloidal solution is subject to evaporation under vacuum at 60^{0}C until constant weight is reached. The organic component can be removed by calcination at 600^{0}C, for 3 h. HA and HA modified with AgNP were tested in *in vitro* by merging in a nanocomposite of the Evetric-Ivoclar type. Another strategy to cover and make HA compatible consisted in the use of a dendrimer of the poly (amidoamine) type in combination with polylactic acid (PLA).

The 10 samples reunited the following components :

Sample elaboration 1: used tooth: canine, mono-radicular;type of fibrillar structure: fiber post schulzer pre-silanized ;composite type: nanofiller technology (Olirevo) (fig.1);

Fig.1 Sample 1 elaboration

Sample elaboration 2: used tooth: premolar 2 superior, pluriradicular; type of fibrillar structure: Fiber post pre-silanized Schulzer;composite type; nanofiller technology (Olirevo)filling : HA+ Ag (fig.2).

Sample elaboration 3: used tooth: premolar 2 superior, pluriradicular type of fibrillar structure: Fiber post Schulzer pre-silanized;composite type: nanofiller technology (Olirevo);Filling : HA (fig.3).

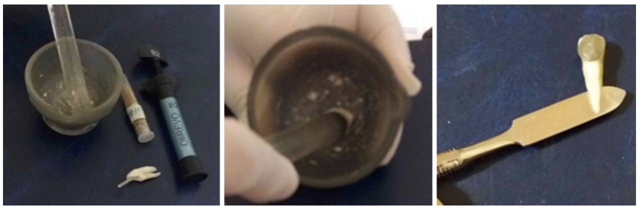

Fig.2 Sample 2 elaboration

Fig.3 Sample 3 elaboration

Sample elaboration 4: used tooth; premolar 1 inferior, monoradicular type of fibrillar structure: Referpost fiber glass kit(Angelus);composite type: nanocomposite (Gaenial anterior)-GC

Sample elaboration 5;used tooth; premolar 1 inferior, monoradicular; type of fibrillar structure: Referpost fiber glass kit(Angelus);composite type; nanocomposite (Gaenial anterior)-GC filling: HA; Sample elaboration 6: used tooth; premolar 1 inferior, monoradicular type of fibrillar structure: Referpost fiber glass kit(Angelus);composite type; nanocomposite (Gaenial anterior)-GC;filling: HA+Ag;Sample elaboration 7: used tooth:premolar 2 superior, pluriradicular;type of fibrillar structure: Fiber post Schulzer pre-silanized; composite type: nanocomposite Evetric-Ivoclar;Sample elaboration 8: used tooth; molar 2 inferior, pluriradicular

type of fibrillar structure: Fiber post Schulzer pre-silanized;composite type: nanocomposite Evetric – Ivoclar;filling: HA; Sample elaboration 9: used tooth; molar 3 superior, pluriradicular type of fibrillar structure: Fiber post Schulzer pre-silanized;composite type: nanocomposite evetric-ivoclar;filling: HA+Ag;

The elaborated samples were sectioned on the same sizes, width of 6 mm, height of 5mm, subsequently subjected to electronic microscopy with the elaboration of SEM images for each individual sample (fig.4).

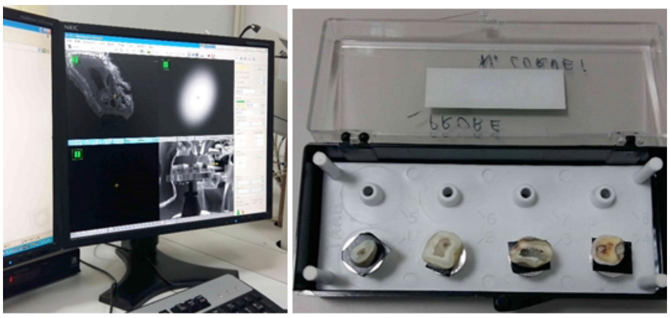

Fig.4 Aspects of electronic microscopy

Results and discussions

A major component of the research activity consisted in the selection, design and functionality of the nano-filling in dental systems which will be responsible for the biological activity and, therefore, for the new properties and applicative direction of the dental systems thus obtained (antimicrobial and osteointegration properties, restorative therapies, etc.)

With regard to the use of composite structures improved by HA addition, we notice a slight lacunary structure on the SEM images due to the properties of HA, an aspect present at much smaller dimensions in the silver - HA mix (fig.5).

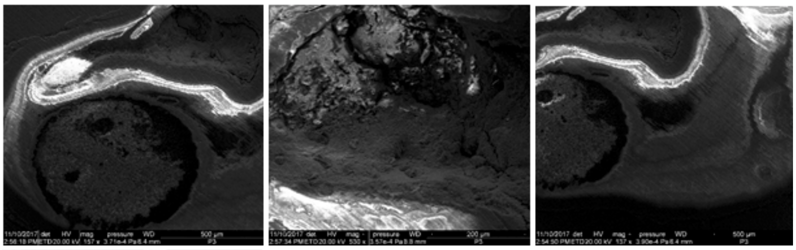

Fig. 5 The electronic microscopy images of the samples and nano-fibrillar structures optimized with HA fillings

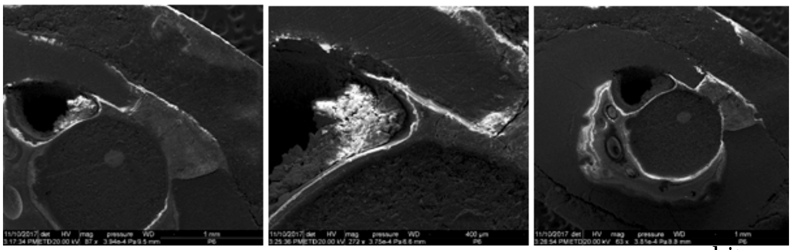

Fig.6 The electronic microscopy images of the samples and nano-fibrillar structures optimized with HA+Ag

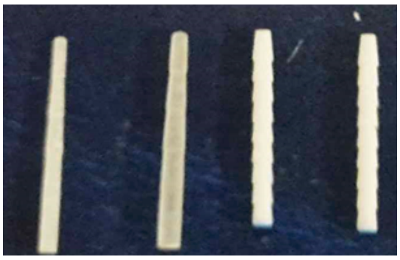

Fig. 7 Various types of fibers arhitecture

Nonetheless, the excellent biomimetic properties of HA (it represents 97% of the mass of dental enamel and 70% of the dentine; chemical and crystallographic composition similar to the bone tissue), correlated with other important advantages (biocompatibility *in vivo* in applications of implantology and prosthetics, bioactivity – facilitates osteogenesis, stability under physiological conditions of temperature, *p*H and composition of biological fluids, absence of toxicity and inflammatory processes) and with the limitations imposed by the projects were determining in its selection as a starting material in the conducted study [12,13]. We also took into account the fact that HA is already a common material in the dental technique, as filling for composite cements and resins for the restoration of bone cavities, in the dental surgery and in maxillofacial surgery endodontic treatments and obturation of mechanical perforations, in the restoration of periodontal defects, the formation of the apical barrier, the treatment of cavities and as de-sensitizing agent post - whitening . The modification potential of the HA surface in view of inducing supplementary properties, attractive from the applicative perspective, was investigated by means of AgNP and NaLS. AgNP was selected due to the special antimicrobial properties and their recent implementation in an increasing number of various applications in the field of dental medicine, such as the realization of dental implants (AgNP/TiO_2; reduces biofilm formation and bacterial colonization), maxillofacial prostheses (AgNP/silicones; reduces colonization with microorganisms and prevents fungal infections) and dental composite resins (AgNP/acrylates; improves resistance to bacterial colonization and viscous - elastic properties) in conditioning agents of periodontal tissues (AgNPs/zeolites; in stomatitis and plaque control) and anti-cavity agents (AgNPs/chitosan; extended cariostatic effect) [14-16]. It is also worth mentioning that the formation of AgNP and their deposition on the HA surfaces were made in conditions of the *green chemistry* type (water, NaLS non-toxic, catalytic concentrations of lactic acid, chloride and sodium hydroxide). Moreover, NaLS is a good compatibilizer of phases, surfactant, adhesive and absorptive cheap, available and can be completely removed by calcination at 600^0C [17-19] (fig.6).

Ensure an excellent esthetic, very good retention (due to the parallel, grooved form), high radio-opaqueness that allows radiographic visualization, similar elasticity to the dentin (low risk of root fracture), the cone shape means less tissue removed from the apical third of the radicular canal, the high percentage of fibers ensures excellent mechanical properties due to the longitudinal fibers it can be easily removed by the direct use (prefab) we save working time and reduce costs (fig.7).

At the same time, we assessed a need to diversify the architecture and fibrillar and nanocomposite structures, starting from the variety of clinical situations, as well as a relatively reduced adequacy of glass fibers to modifications and functionalities of the surface for the induction of bioactive effects (fig.8).

Preliminary studies on commercial products reinforced with glass nanofibers have confirmed, among others, that they confer excellent mechanical and esthetic properties, very good retention (due to the parallel, grooved form), high radio-opaqueness that allows radiographic visualization and a similar elasticity to the dentin (with a low risk of root fracture) (fig.9).

The first studies conducted on the HA consisted in the identification of practical solutions to improve its dispersion degree in the polymer systems used for bone reconstruction, a process known as generator of applicative problems .The selected strategy consisted in the introduction of a dendrimer of the poly (amidoamine) type with a role of compatibilizer between the HA powder and the hydrophobic organic phase of PLA .We assessed the formation of powerful physical connections between the dendrimer and the HA, accompanied by the insertion of the dendrimer in the interlamellar spaces of HA, the increase of dimension and area of the resulted particles surface. The SEM analysis reflects a relatively uniform

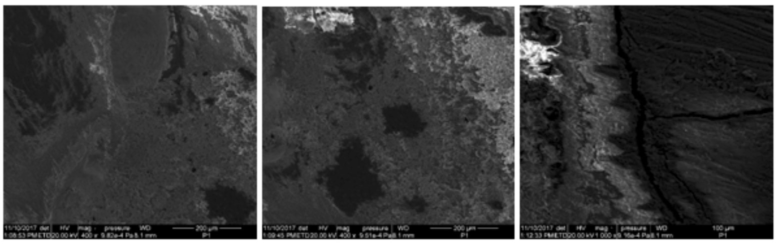

Fig.8. The electronic microscopy images of the samples and nano-fibrillar structures - Fiber post Schulzer pre-silanized

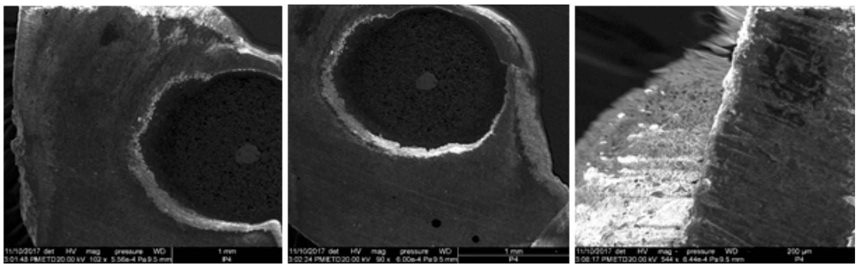

Fig.9. The electronic microscopy images of the samples and nano-fibrillar structures - Referpost fiber glass kit(Angelus)

crystalline morphology with various degrees of rugosity, formed of associations of nanocrystals with average dimensions of 5-6 nm .

Preliminary studies have indicated that the properties of the composite dental systems can be significantly modified and new characteristics can be introduced by a proper modification of the composition, morphology and surface of the traditionally inert filling. HA and AgNP were selected as a basis for the study due to biomimetic properties, namely antimicrobial bioactivity, as well as to the already established use in dental medicine.

Conclusions

We notice the superiority of the adherence of standardized composite structures to wrinkled fibrillar structures as opposed to a smooth surface, for the 2 types of fibers used: referpost fiber glass kit(Angelus) and fiber post kultzer pre-silanized ;

The size of the grains associated with their continuous uniformity and adherence for the fibrillar structure stands out at the samples with hydroxyapatite, the first place as uniformity and adherence going to the composite of the nanofiller technology category (Olirevo);

The presence of Ag in combination with HA doesn't interfere with the polymerization process, but as far as the density of the finite sample is concerned, one can notice hiatal areas where the Ag grains are concentrated;

Hydroxyapatite and silver nanoparticles were selected as a basis for the study due to biomimetic properties, namely antimicrobial bioactivity, as well as to the already established use in dental medicine;

We managed to completely avoid the use of potentially toxic supplementary additives in the preparation and modification of fillings;

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