CONDITIONED POWDERS OF HYDROXIAPATITE USED IN SLS (SELECTIVE LASER SINTERING)

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Abstract: Selective laser sintering can be used in medicine to obtain the prothesis in orthopedy. The biomaterials used in medicine are the Ti powder (Ti-6Al-4V) and the hydroxiapatite powder. The hydroxiapatite powder is a new material used in medicine because is more identically with the bone structure. The hydroxiapatite contain collagen like the structure of bone and make be more easy adopted like prothesis by human body. The conditionated powders used in SLS are necessary for the process and for the final properties of prothesis.

1. INTRODUCTION

In orthopedy prothesis used frequently the Ti powder (alloy Ti-6Al-4V), but now a new material more identically and more biocompatible are developed, this is the hydroxiapatite powder.

The hydroxiapatite contain collagen like the structure of bone and make be more easy adopted like prothesis by human body.

The selective laser sintering station use the hydroxiapatite powders to obtain the prothesis in orthopedy, the hip prothesis, the knee prothesis, the shoulder prothesis.

2. HYDROXIAPATITE POWDER

All the structures bones have in common the principal protein component: the collagen and a little amount of organics phases and a component inorganic hydroxiapatite $Ca_{10}(PO_4)_6(OH)_2$.

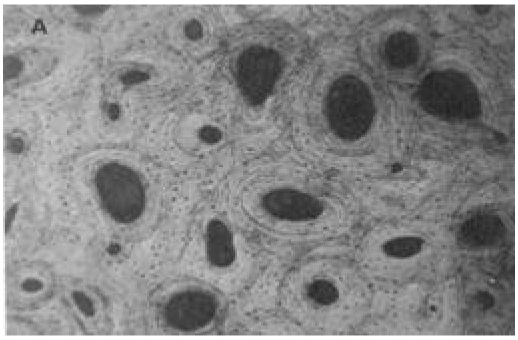

Fig.1. The human structure of bone

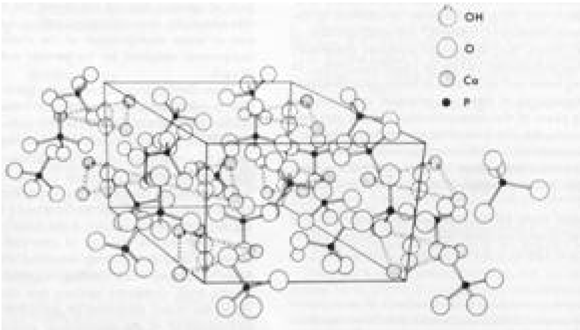

Fig.2. The hexagonal structure of hydroxiapatite

The structure of hydroxiapatite is hexagonal a=9.880Å and c=6.418Å. (fig.2)

The collagen contribute to hierarchical structure of bone. The collagen and the hydroxiapatite are arrange to make the compound to molecular level.

The arrangement can be compromise in the same cases, because of the alteration structure of collagen in the same diseases of bones and who conduct to physical properties very affects. In fig.1 is present a lamellar structure approximately circular, who form the secondary osteons who find in the humans adults bones.

The hydroxiapatite is a complex material and his properties are very complex. The hydroxiapatite present a good elasticity, because the bone contain collagen, the adhesion of prothesis to bone is quickly. The hydroxiapatite is a anisotropic and nehomogeneousness material and present viscoelastic properties like the other biologicals tissues. We remark a hard connection between the properties of material and the bones microstructure. The bone have an elastic, anisotropic and simetric structure, hexagonal isotropic inverse.

The hydroxiapatite have a porous structure, identically with the bone and this way can realise a better connection between prothesis and the environment tissues, because this tissues can developed in interior of pores.

The viscoelastic properties of hydroxiapatite are good. Recently, we remark the bone is a nonlinear material and thermorheologically is complex. The deformation to elongation is like the rheological model of Kelvin-Voigth. The tensile deformation is like the rheological model of Maxwell.

The hydroxiapatite is a natural tissue identically like the bones, it is easy to use in prothesis and it is easy to fit in the human body and for this thing the hydroxiapatite is use in orthopaedic applications.

3. CONDITIONATED POWDERS OF HYDROXIAPATITE

The orthopaedic prothesis are obtain by the process of SLS and the powder must be coat with an thermoplastic polymer. In time of process of SLS the thermoplastic polymer of two particles in contact must weld, for complete the resistance bridges of weld hydroxiapatite-hydroxiapatite.

The optimal form of particles is irregular with the marks vertex. The particles must have after condition, the parts coat with polymer. The presintering compacts realise by SLS must have a good mechanical stability to pass to final sintering. The thickness of the bridges hydroxiapatite-hydroxiapatite must assure a good mechanical stability in the phase of elimination of the bonding material.

A lower sintering of the particles of hydroxiapatite can compromise the final form of the compact, if the bridges of weld metal-metal surrender before to realise the necks hydroxiapatite-hydroxiapatite. The adhesion hydroxiapatite-polymer coat must be good to assure the mechanical resistance of the precompact.

We use to conditioned the powder of hydroxiapatite the polymer PMMA. PMMA is an polymer with amorph structure, transparent, hard, rigid, weldable, have a good adhesion.

PMMA present a tensile strength of 55-85MPa, the flexure is 80-130MPa, the elongation 4-5%, the elastic modulus 2400-3300MPa, the resilience is 1.5-3KJ/m^2, the hardness is 190MPa. Resist in poorly acids and alkalis, oils. We use PMMA (Premacril) for stomatologically applications.

The powder of hydroxiapatite is mixed with the powder of polymer PMMA. We realise an advanced homogeneousness and then we add the liquid component. We mix it at cold 15 minutes and then we make the polymerisation at 60^{0}C, 3 hours.

The composite result after polymerisation are in compacts and agglomerates forms with irregulars forms. Because of fragility of PMMA, the grinding to obtain the fine powder is very easy to realise. Result a integral powder coat with a transparent film of PMMA. (fig.3)

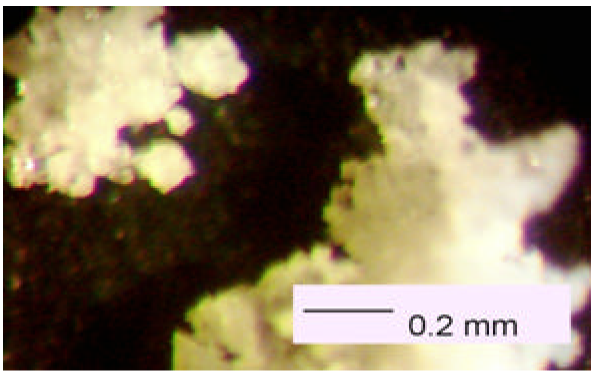

Fig.3. The composite powder HA-PMMA

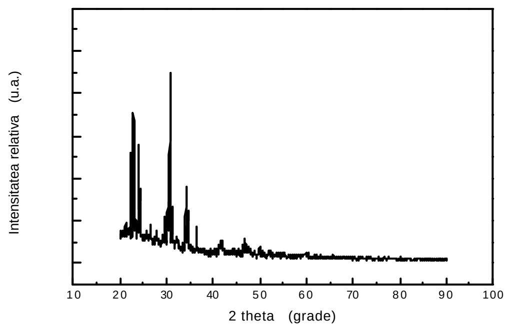

Fig.4. Ray-X diffraction

The crystals of hydroxiapatite can be obtain of aqueous solution of $Ca(NO_3)_2$ and NaH_2PO_4 in differents methods. In all cases, the precipitate filtered and seared to obtain a powder with the fines particles. In this conditions the burning, the operation to prolonged sintering of the compound to evaporate the volatiles components to follow realisation of the crystallization, after that the powder is press and sintering to high temperature, between 1050^0C and 1450^0C.

After 1250^0C, in hydroxiapatite can produced longways of boundary between grains, the precipitate of a secondary compound.

We prepare hydroxiapatite by method sol-gel. The reactives used are $Ca(NO_3)_2*4H_2O$ and $(NH_4)_2HPO_4$. After dissolving in water, $Ca(NO_3)_2*4H_2O$, through warming to 90^0C and $(NH_4)_2HPO_4$, to 20^0C, the solutions results are make in same receptacle.

The suspension result was laved in water many times and filtered. For evaporate the water, the gel was insert and keep in drying over time of 2 hours at 110^0C. The proves support a thermal treatment, 3 hours at 900^0C, and then was cold slowly in oven.

The following thermal treatment is make at 1150^0C, 1 hour, after then the proves are cold slowly (in same time with the oven) to 650^0C and then are extract to 20^0C.

The X-ray diffraction analysis make in evidence the crystalline character of the thermal treatment prouves. (fig.4)

The analysis was make on a diffractometer Bruker.

The method of thermal differential analysis permit to remark the modifications of structural nature product in a solid phase by warming.

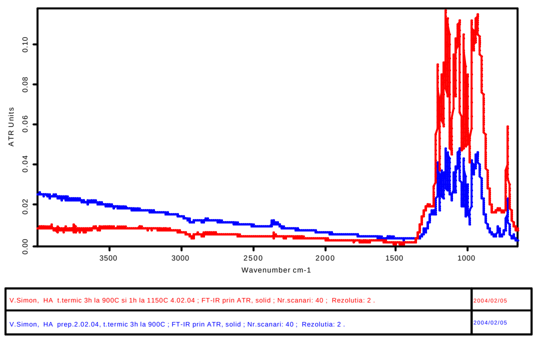

Fig.5. FT-IR spectrum by reflexion registers in domain 600-4000 cm^{-1}

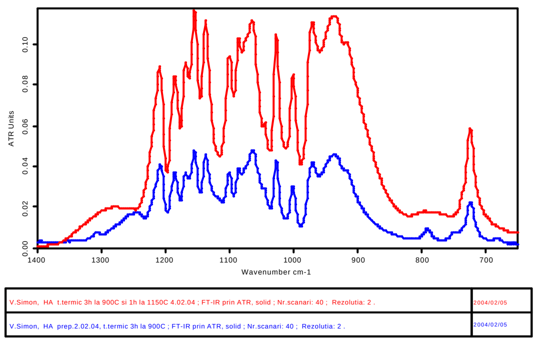

Fig.6. FT-IR spectrum by reflexion registers in domain 600-1400 cm^{-1} for HA

The curves TG, DTG, DTA make in evidence the great stability of the proves result by method sol-gel. The differential thermal analysis was realize with a derivatograf MOM, to 1000^0C, with the speed of temperature of 10^0C/min.

The spectrum IR was register with a spectrometer Bruker, with the transformate Fourier. (fig.5)
The important domain can be good remark in fig.6.
The position of bands for HA with heat treatment 3h at 900^0C and 1 h at 1500^0C is remark in fig.7 and the position of bands for HA with heat treatment 3h at 900^0C is remark in fig.8.

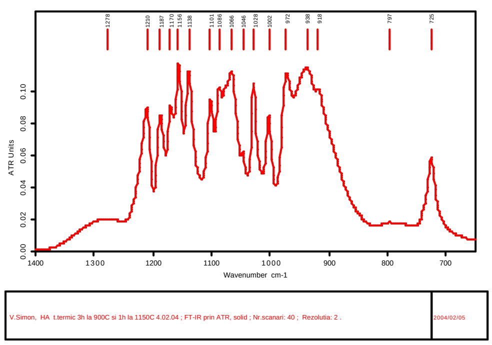

Fig.7. The position of bands for HA with heat treatment 3h at 900^0C and 1 h at 1500^0C

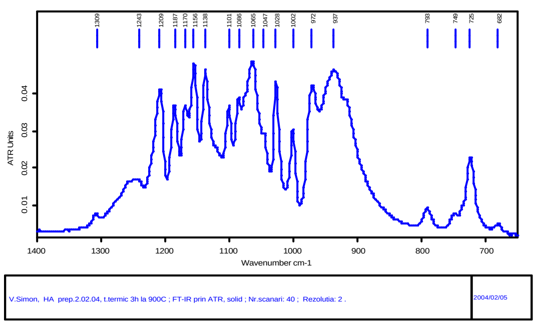

Fig.8. The position of bands for HA with heat treatment 3h at 900^0C

We prepare the proves of hydroxiapatite with the method sol-gel, where we insert Ag_2O, who have an antiseptic effect. The curves of thermal analysis for the proves with a variable content of Ag_2O (0.25%mol and 20%mol) are present fig.9 and fig.10.

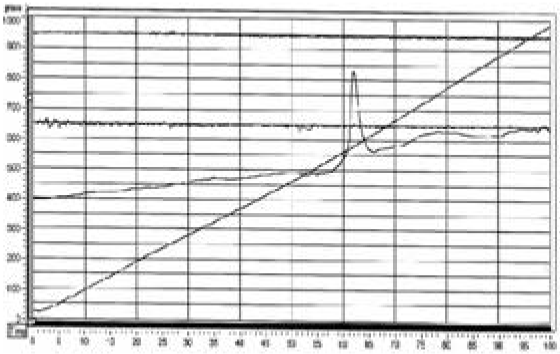

Fig.9. The thermal analysis for the powder HA with 0.25% mol Ag_2O

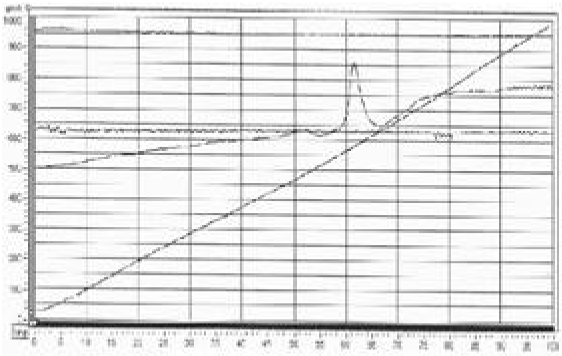

Fig.10. The thermal analysis for the powder HA with 20% mol Ag_2O

4. CONCLUSIONS

The orthopaedic prothesis are obtain by the process of SLS and the powder must be coat with an thermoplastic polymer.

The orthopaedic prothesis can be made of powder of Ti (Ti-6Al-4V) or powder of hydroxiapatite. The powder of hydroxiapatite is better like the powder of titan, because it have a structure same like the structure of bone and can be very fast integrate in human body. It have a very good biocompatibility, it isn't toxic for human body. The prothesis of powder of Ti aged and must to change the prothesis and the resistance of fatigue is not very good.

The hydroxiapatite contain collagen like the bone structure so the adhesion of prothesis to bone is quickly.

The hydroxiapatite have a porous structure, identically with the bone and this way can realise a better connection between prothesis and the environment tissues, because this tissues can developed in interior of pores.

The conditioned powder of hydroxiapatite the polymer PMMA is necessary for the manufacturing of prothesis by SLS method.

5. BIBLIOGRAPHY

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