Characterisation of hydroxyapatite powders and grain surface functionalisation using TEOS

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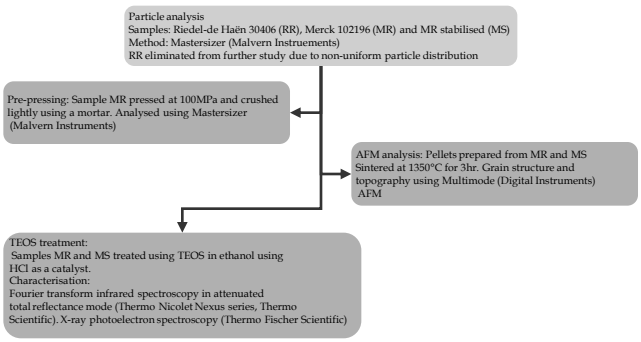
Abstract: Three samples of hydroxyapatite (HOAp) powders were studied. Particle size distribution was obtained and found that two out of the three samples were having better distribution and hence selected for further steps. A pre-pressing step was tried, in order to see if it can substitute the milling step during the stabilisation process. It was found that the pre-pressing done is equal to the milling process, in breaking the loosely bound particles. Further pellets were prepared from the two samples selected after particle analysis. The topography and phase imaging was obtained using an atomic force microscope. Further, these powders were functionalised using tetraethoxysilane (TEOS) to see the surface functionality. Functionalised powders were characterised using attenuated total reflectance Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. Although a physisorption was confirmed, more study has to be done in order to confirm the surface functionalisation on these powders.

Introduction

Hydroxyapatite (HOAp) is a promising material as bone implant material. The compound enters as the main inorganic phase in the bone tissue. It is used for various implant materials because of its better biocompatibility. Especially the polymer-inorganic hybrid implants are one of the applications where HOAp has the most usage. Composite materials of HOAp have been extensively studied in the pharmaceutical industry also, for applications like controlled delivery system for drug, protein, hormone, etc. The grain size and the surface state of the initial powder will play a role on the particle's morphology and hence on its biocompatibility. Therefore, the characterisation of commercially available hydroxyapatite powder is great necessity for further applications.

Materials and Methods

Three batches of HOAp powders were selected. Two were used as received from the manufacturer and the third sample was the pre-treated for stabilisation. This include a heat treatment at 1200°c and a subsequent milling to obtain the uniform particles size. A pre-pressing method was introduced as a substitution for the milling process in the stabilisation process. The pre-pressed and stabilised powders were again analysed to check the particle distribution. Further two of these powders were chosen for preparing pellets. Cylindrical pellets of 13mm was prepared for using the method shown in the flow chart diagram. These two powders were also tested for its possible functionalisation using TEOS. The resulting powder was analysed using FT-IR and XPS.



Results and Discussion

Particle Analysis: From Fig. 1 we can see that MS and MR powders are having better size distribution of particles, compared to powder RR. Number distributions is rather close in all the three cases ranging from 0.2 µm – 4 µm.

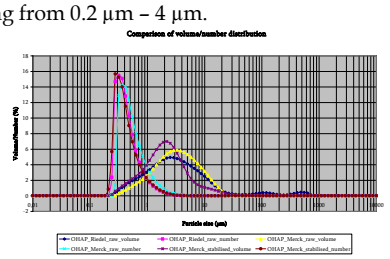


Fig. 1: Comparison of volume and number distribution of particles for the samples RR, MR and MS.

The result of pre-pressing showed the pre-pressed powder's volume distribution (Fig. 2) equal to that of MS which used the milling process for uniformity.

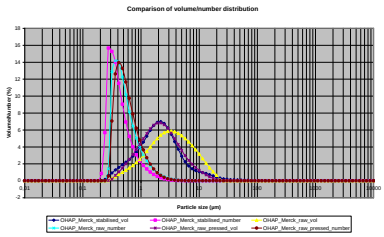
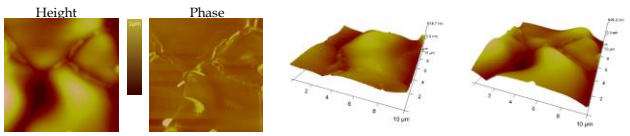


Fig. 2: Comparison of particle size distribution, showing the effect of the pre-pressing step.

AFM analysis: The phase image (Fig. 3a) showed the possibile contaminant accumulation at the grain boundaries. Fig. 3(b) shows the grain structure of the pellet. The morphology was similar in both the pellets. The RMS roughness values were 130nm, 158nm rescpectively for pellets perpared from MR and MS.



(a) (b)

Fig. 3: AFM micrograph showing contaminants at the grain boundary (a) and the 3D topography of the pellets prepared using MR and MS.

Silanisation: FT-IR spectra (Fig. 4) did not show significant characteristic peak for the confirmation of the functionaisation.

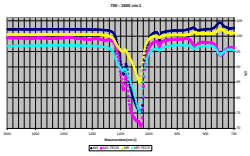


Fig.4: Comparison of FT-IR spectra for MR and MS samples and after the respective TEOS treatment. Zoomed at 700 – 1200cm^{-1}.

XPS elemental analysis (Table 1) result shows a possible physisorption happened on the surface. Further study has to be done in order to confirm the TEOS functionalisation.

Table 1: Result of XPS elemental analysis on TEOS treated hydroxyapatite powders

	MR	MS	MR-TEOS	MS-TEOS
	At. %			
C1s	15,18	35,39	14,02	24,3
Ca2p	19,98	15,26	20,11	9,94
Mg1s	0,98	1,39	0,85	1,98
Na1s	/	0,29	/	0,3
O1s	49,6	36,63	50,42	45,26
P2p	14,26	11,04	14,01	8,27
Si2p	/	/	0,6	9,96

Conclusion

Three batches of HOAp powder were selected for particle analysis. Two out of the three selected samples were having better particle size distribution and hence selected for the preparation of pellets. A pre-pressing was tried on the sample MR to check the possible elimination of the milling process during the stabilisation procedure. The pre-pressed samples of MR show that certain pressure is able to obtain similar results as milled powder during one hour. The pellets prepared were investigated using AFM and found to be similar in topography. The phase change found at the grain boundary, would come from probably the accumulation of contaminants in the grain boundaries during the grain formation. Further studies should be made in order to confirm their presence and would indicate the importance of the calcination process before the sintering step. The silanisation attempt was made on MR and MS powder. Further investigations have to be made in order to confirm the chemisorption of TEOS.