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Effect of vinyl acetate content on the sintering behavior of hydroxyapatite–ethylene vinyl acetate copolymer composites

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Ethylene vinyl acetate copolymer (EVA) alone could be used as a binder material for the fabrication of hydroxyapatite (HAP) into intricate shapes for various bone substitute applications. It was observed that as the vinyl acetate content in the polymer was increased from 12 to 28 wt % an increase in the sintered density of the HAP was observed. Retention of the shapes of HAP in the molded form was also observed.

1. Introduction

Bone substitutes are needed in the repair of segmental defects created upon removal of infected tissues or tumors of bone [1]. Hydroxyapatite (HAP) has been investigated as a bone-replacement for a long time since the material mimics the natural bone mineral [2, 3]. Hydroxyapatite is studied in cell cultures and has been found to possess good osteo-conductive properties [4–7]. As a result of more demanding applications of hydroxyapatite as hard tissue implants, where the quality and reliability of the materials are extremely important, many new methods of fabricating HAP are being sought.

Static and isostatic dry pressing of ceramic granulates are the molding methods widely used in ceramic technology [8]. Organic binders are normally added to these granulates to improve their pressing and processing qualities. A number of researchers have studied the effects of the addition of binder on the ceramic [9–13].

Hydroxyapatite is most frequently shaped by employing the process of cold or hot isostatic pressing, but advantageous method of mass producing accurate products of complex shapes is injection molding [14], where the principles of plastic forming techniques are employed [15]. The method involves mixing the ceramic powder with an organic binder in order to confer the system a suitable thermoplastic behavior. This binder must be removed prior to sintering to avoid cracking of the component. Hence the two dominant criteria for the selection the binder are that (i) it should meet the rheological characteristic of the feed and (ii) the extraction of the binder should not disrupt the ceramic body.

Since the material of our interest is intended for clinical applications it would be wise to select an organic binder, with good and easy burn-out schedule and that does not leave any toxic residues after the burn-out. Even though HAP reinforced polymer composites have been explored by many workers [16–20] not much interest has, however, been paid to use the polymer matrix as a binder for shaping the HAP into clinically significant shapes [14, 21].

Ethylene vinyl acetate copolymer has already been proved to be a candidate binder for the shaping of HAP into various forms without the use of any other liquid plasticizers by making use of the plastic forming techniques like extrusion [21]. The present study is designed to examine the effect of the vinyl acetate content in this particular copolymer on the processing as well as the sintering characteristics of HAP.

2. Experimental

2.1. Materials used

Hydroxyapatite for the preparation of the composite was synthesized by precipitation route involving ammoniated calcium nitrate and dihydrogen ammonium phosphate followed by freeze-drying technique [22]. The flow sheet for the preparation of the HAP powder is depicted in the Fig. 1. The particulate HAP powder, characterized using a Malvern Mastersizer 2000 particle size analyzer, exhibited monomodal size distribution, with average particle size of 48.5 μm (Fig. 2). The distribution peak is located at approximately 77.6 μm. SEM micrograph of HAP particles is shown in Fig. 3. The micrograph shows that the particles have an irregular morphology. The other characteristic features of the HAP powder used are given in Table I.

Three grades of thermoplastic binder, cryogenically ground ethylene vinyl acetate copolymer (EVA) powder, supplied by Shriswasan Chemicals (M) Pvt. Ltd.

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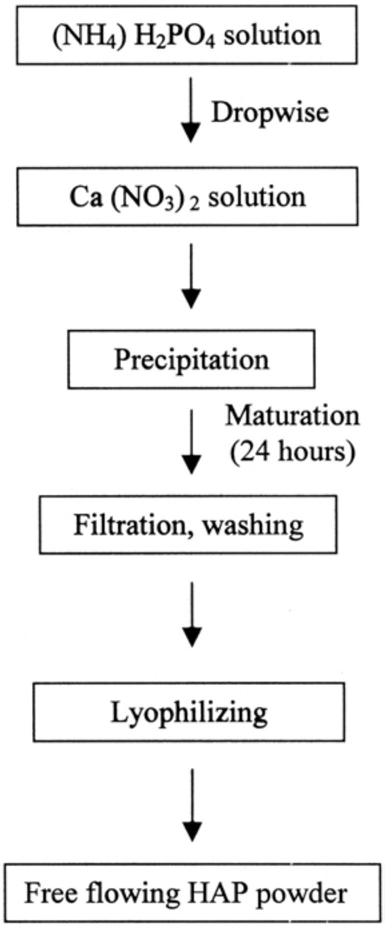

Figure 1 Preparation of hydroxyapatite.

Mumbai, were employed. The particle size of the powder was less than 300 µm. The vinyl acetate contents of the polymer used were 12, 18, and 28 wt % and are designated as EVA-12, EVA-18 and EVA-28 respectively.

2.2. Preparation of the composites

The HAP-EVA composites were prepared by varying the volume fraction in the range of 0.1–0.7. The composites were initially compounded by high speed mixing in a dry blender followed by hot-dry-static pressing in a cylindrical die, $\varnothing = 25$ mm, at a temperature of 120–150 °C and pressure varying from 30 to 70 MPa. The pressing time (pressure hold-up time) of 5 min was given in all the cases. Cylindrical blocks of approximately 6 mm height and 25 mm diameter were thus obtained.

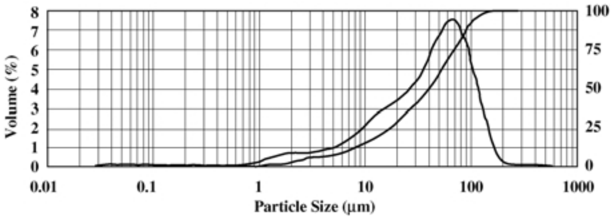

Figure 2 Size distribution of HAP particles ($d_{0.1} = 6.86$ µm, $d_{0.5} = 48.52$ µm, $d_{0.9} = 120.37$ µm).

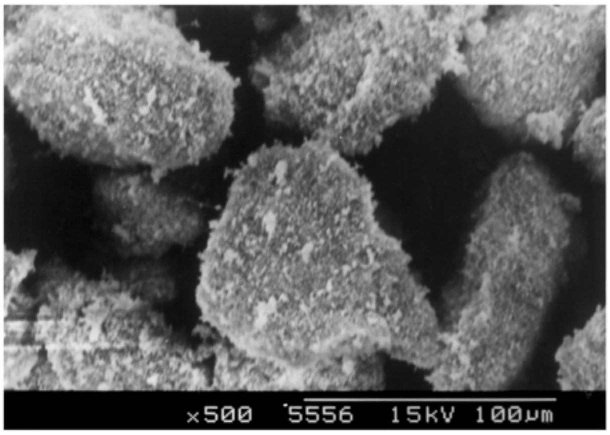

Figure 3 SEM micrograph showing the morphology of HAP particles.

2.3. Thermal debinding and sintering.

The hot pressed blocks were cooled in air to room temperature and then subjected to thermal debinding and subsequent sintering at elevated temperature to produce the final article. Thermal debinding was accomplished by heating the HAP–EVA composites in a raising hearth electric furnace (Baisakh and Company, India). The heating of the green bodies was programmed in such a manner that the rate of heating was kept 2 °C min^{-1} up to a temperature of 700 °C and held at this temperature for 2 h. The debinded composites were then heated to 1150 °C and sintering was carried out at this temperature for 3 h.

2.4. Density measurement

The density of the green as well as the sintered disk samples was measured from the weight and the dimensions of the samples.

2.5. Shrinkage

The percentage shrinkage of the HAP–EVA blocks was measured from the change in the dimensions of the blocks before and after the binder burn-out.

$$\%\ \text{Shrinkage} = [(D_0 - D_f)/D_0] \times 100$$

D_0 – dimension of the sample before sintering; D_f – dimension of the sample after sintering.

TABLE I Characteristics of hydroxyapatite powder

Parameter	Value
Particle density, g cm^{-3}	3.16
Specific surface area, m^{2}g^{-1}	0.45
Ca : P	1.67 : 1
Shape	Irregular
Trace element, ppm	As < 0.1 Cd < 0.01 Pb < 0.1 Hg < 0.1

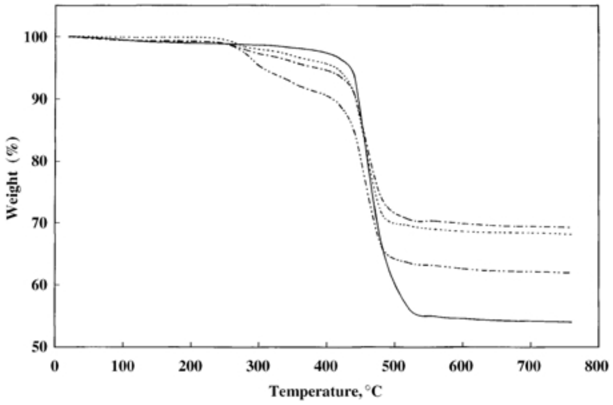

Figure 4 Thermal decomposition behavior of HAP–EVA composites with the various binders. LDPE(—), EVA-12(· · ·), EVA-18 (– • –) and EVA-28(– • • –).

2.6. Thermogravimetric analysis

Thermal analysis was conducted to study the degradation behavior of the composites on SDT 2960 simultaneous DTA–TGA analyzer. Here the weight percentage of the sample was measured continuously by heating the sample from room temperature to 800 °C at a constant rate of 10 °C min^{-1}.

2.7. Scanning electron microscopy

The surface and fracture morphology of the green as well as the sintered sample was observed in a scanning electron microscope (SEM Hitachi model S-2400) after gold sputtering.

3. Results

3.1. Thermogravimetric analysis

The weight loss versus the temperature curve of the HAP–EVA composites with varying vinyl acetate content is shown in Fig. 4. The thermal decomposition of all the different grades of EVA took place in the two identifiable steps. The first step of decomposition is in 240–400 °C range and the second in the 400–500 °C range. The details of the weight loss of the HAP–EVA composites with the temperature are given in Table II.

3.2. Sintering

The results of sintering are summarized in Table III. Irrespective of the EVA grades, densification was not observed for any of the samples containing 30 vol % of HAP. The samples fabricated using EVA-12 collapsed at lower HAP content, that is, at 30, 40, and 50 vol % as they did not have ample handling strength after the binder burn-out. However, retention of shapes was found after sintering for the samples with 60 and 70 vol % of HAP with EVA-12 as the binder material. The HAP samples fabricated using EVA-18 and the ones fabricated using EVA-28 as the binder material showed a better densification with the retention of shapes after the binder burn-out and sintering. A sintered density of 2.89 g cm^{-3} could be obtained with HAP–EVA-28 composites with 70-vol % of HAP, which was found to be the maximum value with the composites studied.

3.3. Shrinkage

The results of the percentage shrinkage of the various samples are given in Table IV. The percentage shrinkage of samples with 30 vol % of HAP could not be determined as they collapsed upon the binder burn out and subsequent sintering for all the binder material used. The other samples, which retained their shapes, showed a diametrical shrinkage in the range 15.6–18% and a lateral shrinkage in the range 12.8–17.5%.

TABLE II Weight loss (%) of the HAP-based composites with various binders from the thermogravimetric analysis

Binder	Weight loss (%)	
	First decomposition	Second decomposition
LDPE	44.4	—
EVA-12	4.6	29.1
EVA-18	6.3	29.9
EVA-28	9.7	35.9

TABLE III Sintering results with various contents of binder

Description	HAP content vol %	Relative density%	
		Green	Sintered
HAP–EVA-12	30	40.4 ± 0.02	Collapsed
	40	41.4 ± 0.02	Collapsed
	50	43.9 ± 0.11	Collapsed
	60	50 ± 0.12	74.6 ± 0.12
	70	56.8 ± 0.11	85.8 ± 0.1
HAP–EVA-18	30	45.3 ± 0.02	Collapsed
	40	48.4 ± 0.09	54.4 ± 0.23
	50	49.3 ± 0.02	62.1 ± 0.05
	60	50 ± 0.02	79.4 ± 0.05
	70	58.5 ± 0.05	85.2 ± 0.03
HAP–EVA-28	30	43.9 ± 0.02	Collapsed
	40	46.2 ± 0.02	67.1 ± 0.04
	50	48.4 ± 0.03	62.1 ± 0.04
	60	49.8 ± 0.03	80.6 ± 0.08
	70	59.2 ± 0.02	91.4 ± 0.03

TABLE IV Percentage shrinkage of the HAP–EVA samples with different binder materials

Description	Vol % of HAP	Diametrical shrinkage (%)	Lateral shrinkage (%)
HAP–EVA-12	60	17.1 ± 0.33	16.8 ± 0.74
	70	17.4 ± 0.24	16.8 ± 0.54
HAP–EVA-18	40	16.9 ± 0.27	16.1 ± 0.03
	50	17.1 ± 0.68	17.3 ± 0.25
	60	18 ± 0.74	17.2 ± 0.54
	70	17.8 ± 0.68	17.5 ± 0.76
HAP–EVA-28	40	15.63 ± 1.2	12.8 ± 0.76
	50	16.8 ± 0.76	15.5 ± 0.57
	60	16.1 ± 1.3	15.1 ± 2.4
	70	17.1 ± 0.25	16.8 ± 0.76

3.4. Microstructure

The SEM photomicrographs of the green and the sintered samples with 70-volume percentage of HAP are shown in Figs. 5–8. Figs. 5 and 6 show the green samples of hydroxyapatite fabricated using the binders, EVA-12 and EVA-28, respectively. The examination of the micrographs revealed no distinct differences between the two composite types during the powder compaction and consolidation using the different binders. The composite fabricated using EVA-18 also showed a similar appearance. It could also be observed that the HAP particles were exposed and distributed homogenously in the polymer matrix.

Fig. 7 shows the fracture surface of HAP fabricated using EVA-12 and Fig. 8 shows the one fabricated with EVA-28. The fracture surface of the former shows both micro as well as macroporosities. Large voids are also observed in the macrostructure. The microstructure of the latter is more uniform. Intergranular porosities with size comparable to sintered grain size of approximately 2 μm could also be observed.

4. Discussion

4.1. Thermogravimetric analysis

Following consolidation and prior to sintering it is necessary to remove various processing aids from the consolidated green body. Though many approaches are being sought for the removal of the processing aids from the ceramic body, thermal methods are often preferred

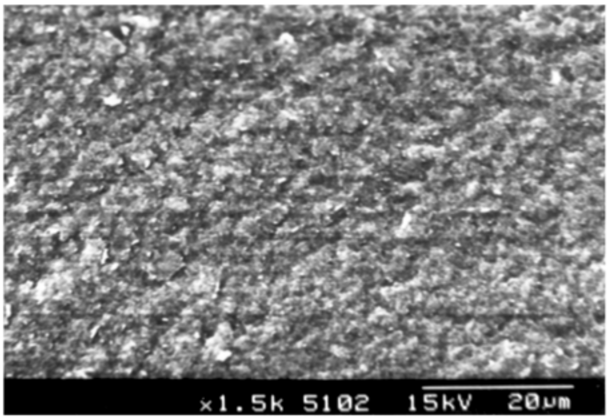

Figure 5 Fracture surface of green HAP–EVA-12 block with 70 vol % of HAP.

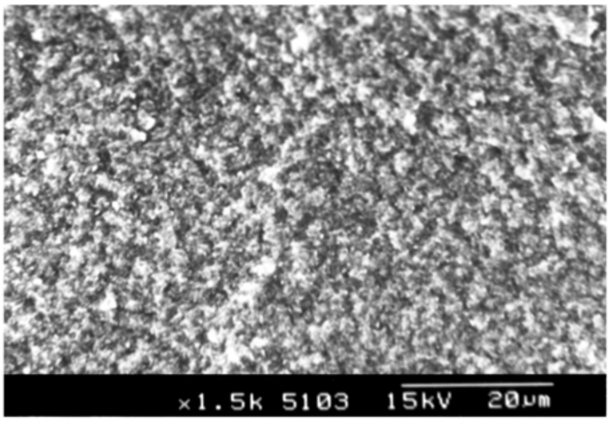

Figure 6 Fracture surface of green HAP–EVA-28 block with 70 vol % of HAP.

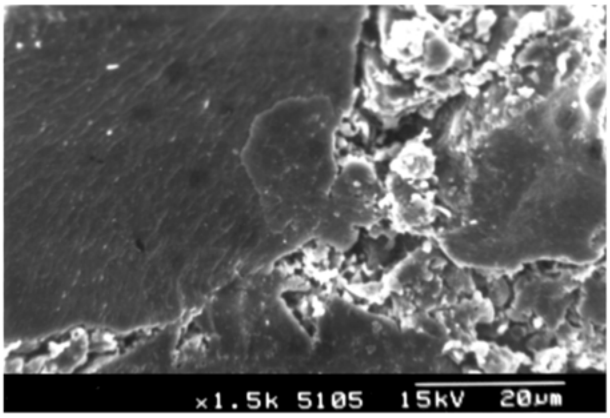

Figure 7 Fracture surface of sintered HAP–EVA-12 block with 70 vol % of HAP.

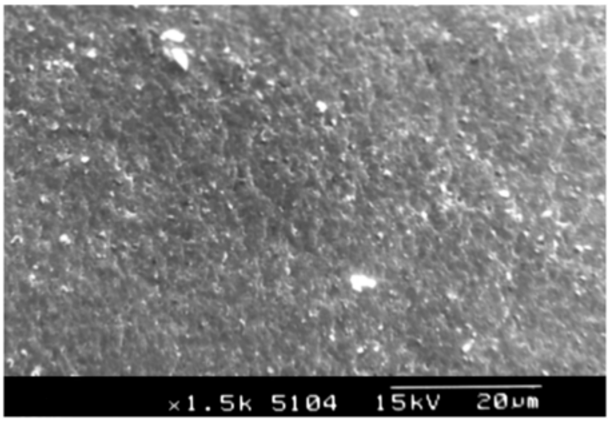

Figure 8 Fracture surface of sintered HAP–EVA-28 block with 70 vol % of HAP.

[23]. Degradation of polymers by thermal and oxidative mechanisms is well documented in the literature [24–27]. Thermal degradation may take place either by (a) depolymerization, where the backbone of the polymer is broken, ''unzipping'' the polymer or (b) removal of polymer side groups by substitution or rearrangement of the processes. Whatever be the mechanism involved in the degradation, the two important factors to the debinding of consolidated ceramic compacts are the rate at which the polymer is broken into fragments and the size of the resulting fragments.

In the present study, the thermal degradation of the three binders with varying vinyl acetate content are best analyzed from the thermograms obtained (Fig. 4) at a heating rate of $10\,^{\circ}\mathrm{C\,min^{-1}}$ under nitrogen atmosphere. A comparison with the decomposition behavior of low density polyethylene (LDPE) is also made in order to obtain a better insight into the debinding and sintering mechanism of these three binders.

From the figure it could be inferred that the thermogram of LDPE exhibits only a single decomposition stage. On heating polyethylene in the absence of oxygen, it is found to be stable at temperatures up to 290 °C. Above this temperature, decomposition was initiated and at about 390 °C the material starts degrading with a sudden loss in weight with the formation of many low molecular weight products [25]. Studies have shown that the generation of many low molecular weight products may result in increased gas pressure and thus burn-out related cracking [28]. This could be the possible reason for the rupture in the shapes of the composite fabricated with polyethylene as the binder material, as reported previously [21].

In the case of EVA, the degradation takes place at two distinct stages. The weight losses over the two distinctive temperature ranges indicate the selective volatilization of the functional groups. The first decomposition step involves loss of acetic acid and the second decomposition step involves the cleavage of C–H bonds. The acetic acid liberated leaves behind a network of pores through which the decomposition products of EVA could be easily removed, thus lowering the risk of disruption of the ceramic profiles, after the binder burn-out. Retention of the shapes of the ceramic bodies was also absent in the case of EVA with 12-wt % of vinyl content at lower volume fraction of HAP. However, at higher HAP loading, retention of the formed shapes was observed with EVA-12 also.

4.2. Sintering

Sintering is the process of the removal of pores between starting particles accompanied by shrinkage of the component combined with growth and formation of strong bonds between adjacent particles, leading to the densification of the component. The driving force for the sintering is the reduction in surface free energy of the system consisting of mass of consolidated particle [29].

Densification did not take place in samples with 30 vol % of HAP probably because of the absence of a proper particle to particle contact, which could not be achieved during the binder burn-out and subsequent sintering. The maximum relative density value obtained is about 91% of the theoretical density of HAP ($3.16\,\mathrm{g\,cm^{-3}}$), which was got by the fabrication of HAP with EVA-28 as the binder material. However, a relative density value of 95% of the theoretical density of HAP was obtained with extruded sample of HAP–EVA-28 composite with 40 vol % of HAP [30].

4.3. Microstructure

The micrograph of the sintered fracture surface of the composite fabricated with EVA-12 as the binder material (Fig. 7) showed large voids and cracks, probably because of the various inhomogenities that might have resulted from the unfavorable burn-out schedule of the polymer, whereas the micrograph of the ceramic profile fabricated with EVA-28 as the binder material under the same processing conditions showed less microstructural inhomogenities. But there are intergranular porosities present which could have prevented the maximum densification of the sintered composites.

5. Conclusion

The present study designed to understand the effect of vinyl acetate content on the processing and sintering behavior of HAP–EVA composites reveals that the weight percentage of vinyl acetate in the EVA do have an effect on the processing characteristics as well as the sintering characteristics of the composites. The study showed that EVA with vinyl acetate content of 28 wt % could act as a better binder material among the three grades of the copolymers compared. The relative density values of sintered HAP obtained showed that EVA-28 could give a better and uniformly densified sample under the experimental conditions employed for the study. Thus a judicious selection of the vinyl acetate content coupled with optimization of the processing conditions can make EVA an excellent binder material for the fabrication of intricately shaped bone substitute materials.

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