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Non-destructive evaluation of mechanical properties of poly (vinyl) alcohol-hydroxyapatite nanocomposites

Suprabha Nayar · Sharmistha P. Sagar · Avijit Guha

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Abstract Hydroxyapatite-poly (vinyl) alcohol nanocomposite powder was synthesized using varying poly (vinyl) alcohol concentrations. The dried powder was compacted into micro-porous disks at a load of 4 tons. The disks were sintered at 1200°C to evolve porous nanocomposites. Size and shape of the pores observed in the scanning electron micrographs were quantified by using image processing software. Ultrasound velocity measurements were done to evaluate mechanical properties non-destructively.

1 Introduction

Synthetic calcium hydroxyapatite (HAp) is among the most commonly used materials in orthopedics and orthodontics. One of the main limitations of HAp is its inherent brittle nature. Emphasis these days is on a multidisciplinary approach for synthesis of HAp-synthetic/biopolymer composites that would simultaneously yield both porosity and load bearing capacity similar to natural bones and teeth. Conventional synthesis of porous ceramic structures using volatile organic salts often leads to an uncontrolled distribution of pore sizes and shapes, not interconnected and therefore, does not sinter even at high temperatures [1–4]. Hence, we have attempted to mimic 'biomineralization', a process that produces strong and tough porous HAp in bones and teeth from weak constituents at ambient conditions. This natural process is worth emulating because development of porous hydroxyapatite with inter-pore connectivity is ideal as bone substitutes [5]. Research shows that morphological sophistication is achieved by the intricate self-assembly of the nano-calcium hydroxyapatite particles synthesized in situ in the organic matrix at varying length scales [6–16]. While it is known that the mineral constituents of the bone matrix largely determine elasticity, the organic constituents have a role too; in patterning the inorganic particles within itself [17–19]. In the present manuscript, we report the synthesis of 10 g HAp using 0.0, 0.5, 1.0 and 2.0% poly (vinyl) alcohol (PVA) at ambient conditions, its compaction at 25°C using 4 ton load into disks and sintering at 1200°C for 1 h. PVA dependent porosity develops and these pores are either circular or elongated in the size range of 0.1–5.0 μm. The pore size and shape seems to have an effect on the mechanical properties as determined by image analysis of SEM micrographs and non-destructive ultrasound velocity measurements. The influence of the organic component on the elasticity in the synthesized HAp-PVA nanocomposite was explored by altering the PVA concentration. It is worth mentioning that a non-destructive measurement of the mechanical properties of materials using ultrasonics would be of considerable interest to the biomedical field.

2 Materials and methods

Freshly prepared alkaline calcium nitrate tetrahydrate solution of strength 0.4 M and 0.0, 0.5, 1.0 and 2.0% aqueous solution of PVA, respectively, (PVA obtained from Fluka, India, average molecular weight (1, 25000)) was mixed thoroughly to obtain a homogeneous solution, with the pH maintained at 11.0. The mixture was incubated at a temperature of 30 ± 2°C for 24 h. Stoichiometric amount of alkaline diammonium hydrogen phosphate

S. Nayar (✉) · S. P. Sagar · A. Guha
Materials Science and Technology Division,
National Metallurgical Laboratory, Jamshedpur, India
e-mail: nayar@nmlindia.org

solution was added gradually to the above-incubated mixture. Milky white coloration was observed almost instantaneously, the system was allowed to age for a week at a temperature of 30 ± 2°C and then washed thoroughly with double distilled water and oven dried at 60°C for 72 h. Oven dried HAp powder was compacted uni-directionally under a load of 4 Ton. The 20 mm diameter compacted disks were first heated to 600°C at a heating rate of 5°C/min and held for 1 h, temperature raised to 1200°C and held for another 1 h at the same heating rate.

2.1 Structural characterization

HAp disks were structurally characterized using scanning electron microscopy at 15 K eV (SEM, JSM-840 A, JEOL) and X-ray diffractometry (XRD PTS 3003, Seifert, using Co Kα as the radiation source, step size-0.3 s/step, and diffraction angle 2θ-20-80°). Micro hardness was determined using Leica VHMT Auto Vertical Microhardness tester at two different loads 50 and 100 g. Image processing of the micrographs was done offline using CLEMEX PE version 3.5.

2.2 Ultrasonic evaluation

Density of the PVA-HAp composites was measured using Archimedes principle. High power ultrasonic pulse echo technique was used to measure the longitudinal (V_l) as well as the shear wave (V_t) velocities. 5 MHz longitudinal and shear wave probes were used with vaseline as couplant. All measurements were carried out at a constant pressure and an average of ten measurements were taken from each specimen to determine the longitudinal and shear wave velocities and Poisson's ratio (μ) and modulus (E) were determined from the measured velocities using the equation.

$$\mu = \frac{V_l^2 - 2V_t^2}{2(V_l^2 - V_t^2)} \text{ and } E = \frac{\rho V_l^2(1+\mu)(1-2\mu)}{(1-\mu)}; \quad (1)$$

where ρ is the density of the material.

3 Results and discussion

For porous HAp applications, it is important to precisely control, not only the overall porosity, but also the pore size, shape and spatial distribution [16]. XRD patterns confirmed the synthesis of a single-phase HAp, no other reaction product was evident even after sintering at 1200°C for 1 h. Indexed diffraction patterns of sintered disks revealed the following peaks of hydroxyapatite (002), (210), (211), (112), (300), (002), (222) and (213), Fig. 1a, b, c and d.

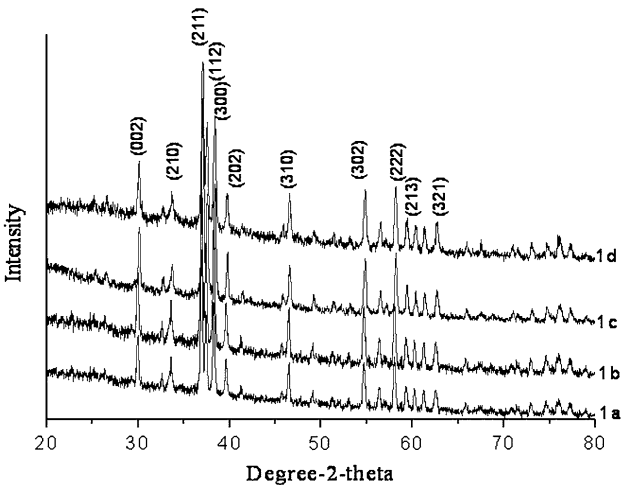

Fig. 1 XRD patterns of sintered HAp-PVA nanocomposites (*a*) 0.0% PVA, (*b*) 0.5% PVA, (*c*) 1.0% PVA and (*d*) 2.0% PVA

Figure 2a, b, c and d, depict a correlation between the SEM micrographs and the corresponding offline image processing data. Porosity, pore size and shape, dependent on the concentration of PVA used for the synthesis of the same total amount (i.e., 10 g) of HAp were obtained. While 0.0 and 0.5% PVA showed uniform round shaped pores, in the 1.0 and 2.0% PVA the number of pores increased but the size and shape of the pores were altered. It seems that there is increasing steric hindrance with increasing PVA concentration, and the strain thus introduced results in a distortion of the shape and size of the pores. There seems to be many small pores compared to few big ones i.e., the pore density increased. SEM results were correlated with non-destructive ultrasonic data such as the longitudinal velocity, shear velocity, Poisson's ratio and modulus of the sintered PVA-HAp samples Table 1. Poisson's effect is caused by slight movements between the stretching of molecular bands within the materials lattice to accommodate stress. The role of PVA was evident in the decreasing Poissons' ratio values. The modulus and pore density calculated by image analysis was plotted against concentration of PVA (Fig. 3).

The modulus as determined by ultrasonic technique for nanocrystalline HAp was 98 ± 5 GPa, close to the values reported by Ahn et.al [20]. The model of Phani and Neyogi considers the pore geometry and correlates modulus in porous material [21, 22], expressed as

$$E = E_0(1 - aP)^n \quad (2)$$

where E and E_0 are the elastic moduli at porosity P and zero, respectively, 'a' and 'n' are material constants. The value of 'n' depends on the grain morphology and pore geometry of the material. Hence the decrease in ultrasonic velocity as well as modulus in the measurements is probably due to the shape and size of the pores. There seems to be an optimum organic–inorganic ratio for the best

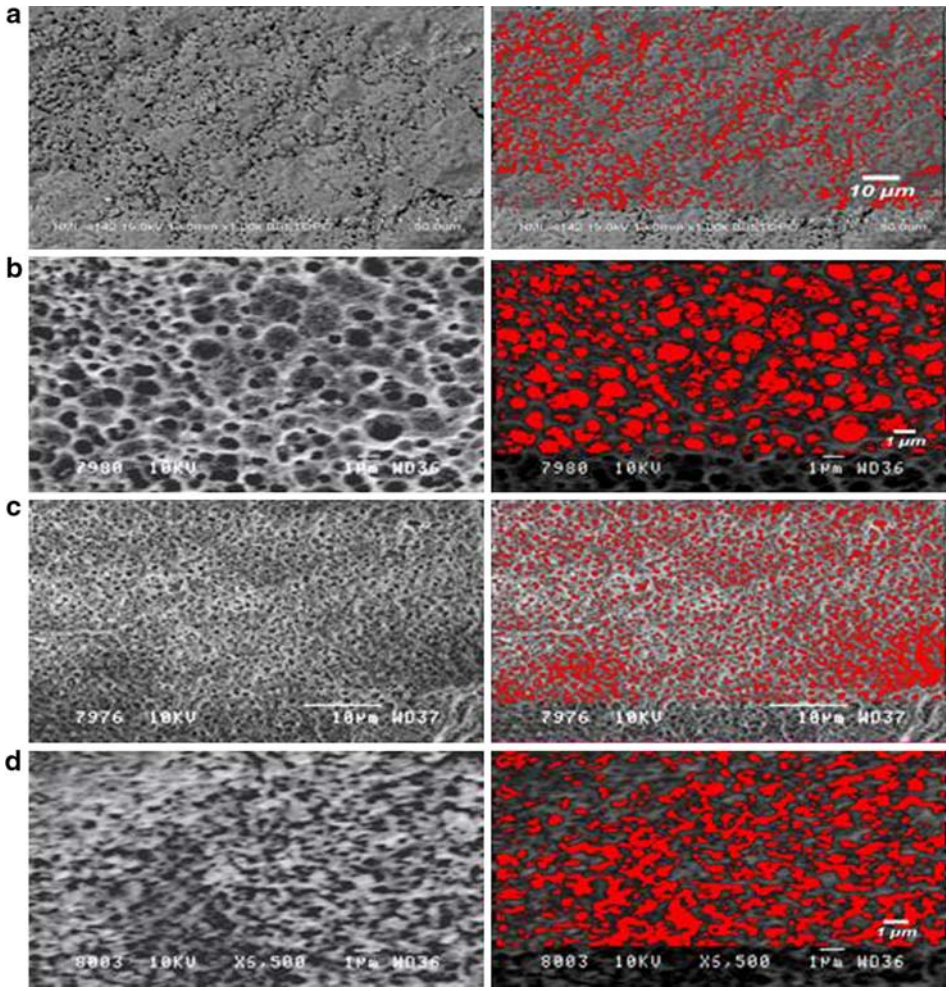

Fig. 2 SEM microstructures and processed images of sintered HAp-PVA nanocomposites (**a**) 0.0% PVA, (**b**) 0.5% PVA, (**c**) 1.0% PVA and (**d**) 2% PVA

Table 1 Longitudinal velocity, shear velocity, poisson's ratio and modulus of the sintered PVA-HAp samples as measured by ultrasonic technique

Sample	Longitudinal velocity (V_l) m/s	Shear velocity (V_t) m/s	Poisson's ratio μ	Young's modulus GPa
0% PVA	6500	3500	0.33	98 ± 5
0.5% PVA	7100	3600	0.33	88 ± 5
1.0% PVA	6174	3425	0.277	70 ± 5
2.0% PVA	5643	3288	0.243	62 ± 5

mechanical properties, over and above which the organic matrix just causes steric hindrance.

Micro hardness against PVA concentration showed that as PVA concentration is increased beyond 0.5%, the ability of the material to withstand the indent decreases considerably (Fig. 4).

The calcium ions in the PVA chains seem to form organised networks that results in a true nanocomposite, such that the porosity of the polymer conformation is not lost even after sintering of HAp-PVA nanocomposites.

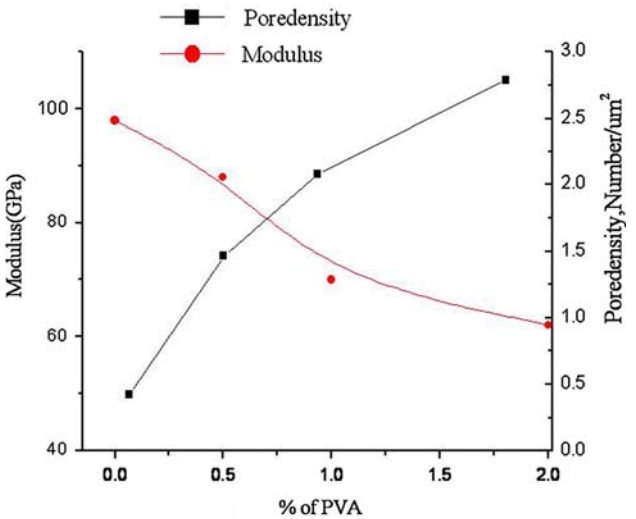

Fig. 3 Variation of modulus and pore density of the nanocomposites with different % of PVA

In nature, there is a strong dependence of self-assembly on the organic–inorganic ratio [23–25] of which the organic part is much lesser than the inorganic part.

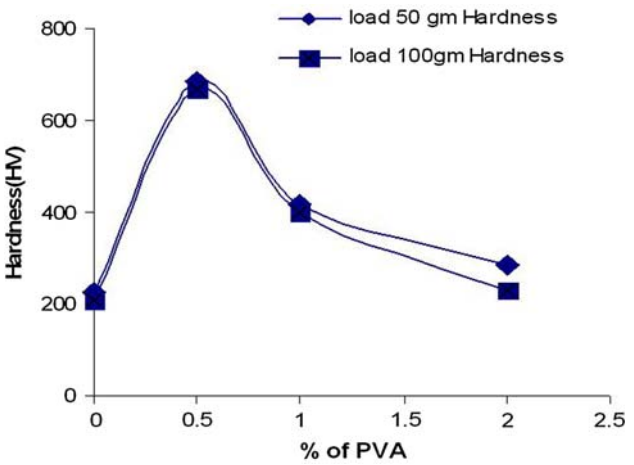

Fig. 4 Variation of Vicker's hardness using 50 and 100 g load with % of PVA

4 Summary

PVA dependent pore size, shape and number density, in different PVA-HAp nanocomposites has been determined by non-destructive ultrasonics and correlated with mechanical properties. A relatively new concept which will help in tailoring the HAp architecture to promote the growth of different tissue types in scaffolds and prosthesis. In addition, the use of non-destructive technique for evaluation of mechanical properties of the above is becoming increasingly important.

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